Assessment of Pre-treatment Technologies for Bio-ethanol Production Using Multi-objective Optimisation

Joanne Crimes

Supervisors: Dr. Adeniyi Isafiade and Prof. Duncan Fraser

Thesis submitted for the degree

MASTER OF SCIENCE

Department of Chemical Engineering

February 2015

Acknowledgements

I would like to thank my supervisors, Niyi and Duncan, for their support and encouragement throughout this thesis.

Mike, thank you for always helping to put thing into perspective to quell my worrying.

To my Mom, Dad and Steve, thanks for forcing me to take holidays.

To Nerine and Dave, my other parents, thanks for Sunday braais to make the weekends longer.

Thanks to CTBE in Brazil for their Aspen simulations without which this work would not have been possible.

Carlos, Jonathon, Héctor, Yvonne and Ángela in Manizales for making me feel so welcome in Colombia.

Thanks to the NRF and UCT for their financial support.

Declaration

I, Joanne Crimes hereby declare that the work on which this thesis is based is my original work (except where acknowledgements indicate otherwise) and that neither the whole work nor any part of it has been, is being, or is to be submitted for another degree in this or any other university. I authorise the University to reproduce for the purpose of research either the whole or any portion of the contents in any manner whatsoever.

Signed by candidate

.....

.....

Abstract

South Africa's liquid fuels have a large carbon footprint due to coal-to-liquid fuels however, this could be reduced by blending bio-ethanol in the fuel. It is estimated that 3.3 Mt/year of sugarcane bagasse, a non-food biomass, could be available for biofuel production in South Africa if steam generation from bagasse at the sugarcane mills was more efficient (Lynd et al., 2003). Bagasse comprises lignocellulose which does not contain free sugars, but requires pre-treatment so as to promote access to polysaccharides for hydrolysis to sugars prior to fermentation to ethanol. Lignin present in bagasse prevents access to cellulose, thus lignin is often solubilised in a basic solution prior to hydrolysis. A variety of methods exist for pre-treating bagasse which require different raw materials and have different operating conditions, and thus have different costs and environmental impacts associated with them. In order to determine an optimal pre-treatment network of sugarcane bagasse for the production of bio-ethanol, a systematic procedure which considers economics and environmental impact as objectives should be employed.

This thesis uses a systematic approach to develop mixed integer non-linear programs (MINLPs) of pre-treatment options for sugarcane bagasse. The superstructure of pre-treatment options is aimed at embedding the key pre-treatment alternatives, and the optimisation of each of these alternatives is performed using GAMS (General Algebraic Modelling System). The superstructure incorporates the following pre-treatment options: acid pre-treatment and steam explosion (acid-catalysed and un-catalysed), and both acid and enzymatic hydrolysis. The use of delignification using sodium hydroxide prior to hydrolysis was investigated. The benefits of producing methane from the xylose-rich liquid leaving the pre-treatment unit was also included.

The superstructure which embeds the aforementioned pre-treatment options was developed using insights obtained from detailed modelling and simulation of some key aspects of individual unit operations involved in possible pre-treatment flowsheets. The acid pre-treatment unit was developed in Matlab using reaction kinetic data to generate 13 sets of black box data at differing acid weight percentages and temperatures. The two steam explosion methods and the enzymatic hydrolysis unit, used black box data obtained from Aspen Plus simulations from CTBE (Brazilian Bio-ethanol Science and Technology Laboratory) (Bonomi, Dayan, Jesus, Cunha, & Mantelatto, 2011). Kinetic equations describing the acid hydrolysis of cellulose were included directly in the GAMS model for acid hydrolysis. Linear relationships describing the solubilisation of solid components with sodium hydroxide weight percentage during delignification were used in the delignification model. The superstructure was decomposed into fixed flowsheets which involved all possible combinations of these models. The optimal pre-treatment flowsheet was then chosen based on both economic and environmental objectives by evaluating the solution space.

It was found that recycling of sodium hydroxide is needed for profitability in the delignification flowsheets. A recycle cost of 25% of the total annual sodium hydroxide cost with no recycling was used in the flowsheets although the recovery process could possibly be more efficient. However, adding delignification reduced the profitability of all flowsheets except steam explosion with enzymatic hydrolysis. Acid-catalysed steam explosion with acid hydrolysis was one of the most profitable flowsheets and had the lowest environmental impact, however the glucose flowrate produced by this flowsheet was low. Acid-catalysed steam explosion followed by enzymatic hydrolysis produces more glucose and was more profitable however the environmental impact of this method may be very large due to the use of enzymes. Enzymes (excluding transportation) can contribute significantly to environmental impact if the production method is energy intensive and the energy production method is carbon-intensive method. More research into the environmental impact of enzymes should be conducted to determine which hydrolysis method should be chosen.

Table of Contents

List of Figures

List of Tables

Nomenclature

Abbreviations

AA	-	acid pre-hydrolysis and acid hydrolysis
ADA	-	acid pre-hydrolysis, delignification and acid hydrolysis
ADE	-	acid pre-hydrolysis, delignification and enzymatic hydrolysis
AE	-	acid pre-hydrolysis and enzymatic hydrolysis
AFEX	-	ammonia fibre explosion
ARP	-	ammonia recycle percolation
ASL	-	acid soluble lignin
CBP	-	consolidated bioprocessing
CEPCI	-	Chemical Engineering Plant Cost Index
CNG	-	compressed natural gas
CO_2	-	carbon dioxide
CSTR	-	continuously stirred tank reactor
CTBE	-	Brazilian Bio-ethanol Science and Technology Laboratory
CTL	-	coal-to-liquid
EI	-	environmental impact
EMSO	-	Environment for Modelling Simulation and Optimisation
FAME	-	fatty acid methyl esters
GAMS	-	General Algebraic Modelling System
GHG	-	greenhouse gas
HMF	-	5-hydroxymethyl furfural
ILs	-	ionic liquids
LCA	-	Life Cycle Analysis
LCI	-	life cycle inventory
LCIA	-	life cycle impact assessment
LHW	-	liquid hot water pre-treatment
MILP	-	mixed-integer linear program
MINLP	-	mixed-integer non-linear program
MipSyn	-	Mixed-Integer Process Synthesizer
MIP	-	mixed-integer program
NLP	-	non-linear program
OA	-	Outer-Approximation
PCE	-	purchased cost of equipment
PEI	-	potential environmental impact
PHB	-	poly-3-hydroxybutyrate
PSO	-	Particle Swarm Optimisation
SA	-	steam explosion and acid hydrolysis
SDA	-	steam explosion, delignification and acid hydrolysis
SDE	-	steam explosion, delignification and enzymatic hydrolysis
SE	-	steam explosion and enzymatic hydrolysis
SHF	-	separate hydrolysis and fermentation
SPORL	-	sulphite pre-treatment to overcome the recalcitrance of lignocellulose
SSCF	-	simultaneous saccharification and co-fermentation
SSF	-	simultaneous saccharification and fermentation
WAR	-	Waste Reduction Algorithm

Variables

Please note that variables relating to the GAMS model equations in *Section 3* are presented at the beginning in *Section 3.1.1.*

α	continuous	Mass ratio between different types of polymer [kg of easy to hydrolyse polymer/total kg polymer]
τ	continuous	Residence time of the reactor [s]
ϕ	continuous	Ratio of solid bagasse to liquid [g/g]
$Ax = a$	linear	Material and energy balances and design equations
$By^K + Cx \leq d$	logical	Constraint to ensure that the selected flowsheet is within the superstructure
c_i	continuous	Mass concentration of species *i* [kg/m^3]
c^T	nonlinear	Represents the variable costs such as revenue, operating costs and costs
$Ey^K \leq e$	logical	Constraint to ensure that the selected flowsheet is within the superstructure
F_i	continuous	Mass flowrate of species *i* [kg/s]
$f(x)$	nonlinear	Represents the variable costs such as revenue, operating costs and costs involving vessel size
$g(x)$	nonlinear	Process specifications
$h(x)$	nonlinear	Material and energy balances and design equations
k_1	continuous	Reaction rate constant for reaction 1 [s^{-1}]
L_0	continuous	Initial lignin concentration in bagasse [0.235 g/g solid]
L_{ASL}	continuous	Final concentration of acid soluble lignin [g/g solid]
M_i	continuous	Mass of component *i* [g]
R_i	continuous	Reaction rate of species *i* [kg.m^{-3}.s^{-1}]
t	continuous	Time [s]
V	continuous	Reactor volume [m^3]
$\dot{V}$	continuous	Volumetric flowrate [m^3/s]
x	continuous	Continuous variables such as stream variables such as flowrates, pressures, temperatures as well as vessel sizes
x_L	continuous	Lower bound on *x*
x_U	continuous	Upper bound on *x*
y^K	binary	Binary variables that represent the existence of process units at the *Kth* iteration of the program

1. Introduction

1.1. Background

Combustion of fossil fuels produces carbon dioxide, CO_2, which is a greenhouse gas, GHG. Consequently, the use of fossil fuels contributes significantly to global warming. The environmental impact associated with the mining of coal and drilling of oil are also significant. As oil, coal and natural gas are non-renewable resources, fossil fuel use is not sustainable.

Plants combine CO_2 and water while using energy from the sun to produce glucose and oxygen in a process called photosynthesis. The glucose produced can then be used by the plant as an energy source and can be used to form polysaccharides such as cellulose and hemicelluloses which are components of the cell wall and necessary for growth. These polysaccharides can be broken down into sugars and fermented to produce bio-ethanol which can be used as a fuel. Although combustion of biofuels does produce CO_2, the impact is reduced when checked using a cradle to grave approach, since the process of growing the plants consumes CO_2. As a result of this, biofuels are regarded as potentially carbon neutral, however this neutrality may be undermined when the CO_2 produced in the manufacture of the fertilizer used to grow the plants, and the CO_2 emitted during the transportation of the biomass to the processing facility are considered (von Blottnitz & Curran, 2007) . In spite of this, biofuels are a renewable fuel source and thus are generally more sustainable than fossil fuels.

Biofuels are referred to as either **first or second generation**. **First generation biofuels** are characterised by the use of food crops to produce biofuels. These food crops include: oil seeds, such as soy and rape seed; starch-rich grains, such as corn; and sugar-rich plants, such as sugarcane and sugarbeet (von Blottnitz & Chakraborty, n.d.). Commercial processes used to produce first generation biofuels are mature and 50 billion litres are produced annually (Naik et al. 2010:579). There are several shortcomings associated with first generation biofuels such as: competition with food crops which leads to increased food prices, reduced biodiversity associated with land use, large subsidies which are needed to ensure economic feasibility and small GHG reduction (Naik et al., 2010; Sims et al., 2008; von Blottnitz & Chakraborty, n.d.). Using plant wastes associated with food production, such as leaves and husks, to produce biofuels eliminates competition with food crops and requires no additional land use. Biofuels produced from plant wastes are termed **second generation biofuels**. Biofuels produced from crops such as switchgrass and short rotation trees are also second generation biofuels (von Blottnitz & Chakraborty, n.d.).

Biofuels can be produced from both **thermochemical and biochemical routes**. Thermochemical routes include combustion, gasification and pyrolysis (Damartzis & Zabaniotou, 2011). These methods will not be discussed further as this thesis focuses on biochemical processes. There are three types of biofuels produced from a biochemical route: biodiesel (also called fatty acid methyl esters, FAME), bio-ethanol and biogas. This project focuses on the production of bio-ethanol using biochemical routes.

Bio-ethanol is produced from the fermentation of sugars. The product of the fermentation is a dilute ethanol stream which requires concentrating using separations. Water and ethanol form an azeotrope and thus further more complex separation methods are required after distillation to produce a high purity ethanol stream. Bio-ethanol is often produced from sugarcane and other sugar-rich plants. Starches such as corn are also commonly used. More recently, lignocellulosic materials such as sugarcane bagasse are being investigated as feedstocks for bio-ethanol production. However these materials require extensive processing prior to fermentation to produce sugars for fermentation.

1.1.1. Biofuels in a South African Context

South Africa is one of the top 20 GHG emitters in the world and the largest emitter in Africa (South African Government, 2010). As fossil fuels provide 94% of South Africa's primary energy, it is not surprising that the energy sector is the largest contributor of GHG emissions which accounted for 78.9% (344 106 Gg CO_2 eq) of the country's total GHG emissions in 2000 (Lynd et al., 2003; Department of Environmental Affairs and Tourism, 2009). This represented an increase of 15.6% from the GHG emissions of 1994 (Department of Environmental Affairs and Tourism, 2009). **Renewable energy** provided only 5% of South Africa's primary energy in 2000 (Department of Environmental Affairs and Tourism, 2009).

South Africa has large **coal** reserves and as a result coal provides 82% of South Africa's energy supply (Lynd et al., 2003). Sasol uses the Fischer-Tropsch process at its plant in Secunda to produce liquid fuels from coal. In 2007, the plant was producing 150 000 barrels/day and by installing a new reactor Sasol plans to increase this to 180 000 barrels/day by 2015 (Sasol, 2007). Sasol's Secunda plant is the largest coal-to-liquid (CTL) fuels plant in the world and also the largest point-source of CO_2 in the world (Kintisch, 2008). CTL fuels and chemicals in South Africa provide 290 PJ/year which is the largest non-petroleum hydrocarbon processing industry in the world; larger than bio-ethanol from sugarcane in Brazil (280 PJ) and bio-ethanol from maize in the United States of America (179 PJ) (Lynd et al., 2003). CTL fuels provide 28% of South Africa's annual fuel requirements (Schutze, n.d.). However petrol produced in this manner emits roughly double the amount of CO_2 as petrol produced from crude oil (Schutze, n.d.). As a result of this, GHG emissions from petrol in South Africa are higher than if crude oil was used exclusively for petrol production. By blending bio-ethanol in fuel these emissions could be reduced.

The government set a target of 2% biofuels in the national liquid fuel supply by 2013 (Department of Minerals and Energy, 2007). However, this target was not met and the deadline has been shifted to October 2015 (SouthAfrica.info, 2013). The 2% blend amounts to 400 million litres of bio-ethanol per annum and excludes the use of maize for biofuel production in order to prevent compromising food security (Department of Minerals and Energy, 2007). In order to help realise this target, tax exemptions and subsidies have been granted for bio-ethanol and biodiesel production. Bio-ethanol receives a 100% petrol tax exemption (equivalent to R 1.21 per litre) as well as a subsidy of R 0.273 per litre up to a maximum of R 20 million (Department of Minerals and Energy, 2007). The main goals of this strategy are to promote farming in areas previously neglected under the apartheid regime, which amounts to 3 million hectares of land, and to create jobs (Department of Minerals and Energy, 2007). The 2% biofuels blend can create 25 000 jobs, primarily in rural areas, which results in a 0.6% decrease in unemployment; increases economic growth by 0.05%; as well as decreasing greenhouse gas emissions and improving the country's energy security (Department of Minerals and Energy, 2007). The jobs-to-investment ratio for biofuels is 100 times higher than for crude oil refineries which shows that a thriving biofuels industry will stimulate the country's economy (Department of Minerals and Energy, 2007).

Meeting the biofuels target requires 1.4% of the country's arable land which is far less than the 14% of arable land that is classified as underutilised (Department of Minerals and Energy, 2007). However, studies have suggested that this land is used extensively and so more research should be conducted to determine the extent to which this land is used (von Malititz & Brent, 2008).

Sugarcane bagasse is an underutilised resource that can potentially be used to reduce the environmental impact of South Africa's fuel without threatening food security and with no additional

land use (Melamu & von Blottnitz, 2011). This project aims to provide insight into how this feedstock can be processed to produce bio-ethanol in a sustainable manner.

1.1.2. Sugarcane Bagasse as an Energy Feedstock in South Africa

The South African climate is well suited for sugarcane production. The bagasse produced by sugar production is used to produce steam for use in the sugar refining process (Lynd et al., 2003). If this steam was produced more efficiently, there would be excess bagasse which could be used for bio-ethanol production (Lynd et al., 2003). Lynd et al. (2003) estimated that 3.3 Mt/year of sugarcane bagasse could be available for energy production in South Africa.

A biofuels industry in South Africa would boost the economy, create jobs and reduce the environmental impact associated with the fuel industry. Using a non-food biomass, such as sugarcane bagasse, is important to prevent an increase in food prices. Sugarcane bagasse is used to produce steam in sugar mills but, as this is done inefficiently, excess bagasse can be available for bio-ethanol production.

1.1.3. Modelling and Optimisation

Sugarcane bagasse is a fibrous material that does not contain free sugars for fermentation to bio-ethanol. This fibrous material, lignocellulose, requires processing to break it into sugars which can be fermented. This is called pre-treatment. Many different methods are available for pre-treating bagasse and often these require a hydrolysis step aimed at breaking cellulose into glucose after pre-treatment. Delignification can also be included prior to hydrolysis as the removal of lignin can improve the efficiency of hydrolysis. Since many pre-treatment, delignification and hydrolysis methods are available, as well as many combinations of these methods, determining the optimal flowsheet for processing sugarcane bagasse is a complicated task. Computer modelling can be used to help understand these interactions and make more informed decisions. By using optimisation software in combination with these models the process flowsheet can be optimised in terms of unit choices and flowrates. More than one objective can be investigated, such as an economic and an environmental objective, to solve the problem from a more holistic view.

1.2. Objectives and Scope

This thesis aims to determine an optimal pre-treatment sequence for the production of bio-ethanol from sugarcane bagasse. This sequence includes all units prior to the fermentation section, such as pre-treatment, delignification and hydrolysis. The fermentation and separation sections will be discussed briefly in *Section 2.1* of the literature review, however, they will not be included in the model development. Only fermentation of glucose for bio-ethanol production will be considered. Other biochemical production methods and thermochemical production methods will not be discussed. Only sugarcane bagasse will be considered as the feedstock and first generation feedstocks and other second generation feedstocks will not be included in this study. Bio-ethanol is the main product considered in this work. Additionally, the liquid stream produced by pre-treatment can be digested to produce methane. Fermentation of xylose to ethanol is not a mature technology thus methane production was investigated instead. The production of methane was not modelled in detail but conversion factors were used.

Determining the environmental impact in this project is for the purpose of screening technologies and the evaluation is not as explicit as is required to draw strict conclusions. However, this study lays the groundwork for a more detailed environmental impact study to be performed.

This project serves to investigate the economic and environmental implications of producing bio-ethanol from sugarcane bagasse in South Africa with a particular focus on the pre-treatment needed prior to fermentation. A biofuels industry will create jobs and serve to reduce the carbon footprint of liquid fuels in a country with a coal-driven economy. *Chapter 2* of this thesis contains the literature review which provides an overview of bio-ethanol production but focusses on methods of pre-treatment, delignification and hydrolysis as these are the processes pertinent to this work. Modelling and optimisation as well as multi-objective optimisation are also discussed. The methodology for developing the models used in this project is discussed in *Chapter 3.* This includes the pre-treatment, delignification and hydrolysis models, as well as the costing and environmental impact modelling, and the overall research approach used to combine the models and generate the results. The results produced from the modelling are discussed in *Chapter 4* with regards to both an economic and environmental perspective. Sensitivity analyses that were performed are also described and discussed in this section. The conclusions of this thesis can be found in *Chapter 5* and recommendations for future work can be found in *Chapter 6.*

2. Literature Review

2.1. Overview of Bio-ethanol Production

Bio-ethanol production from lignocellulosic biomass can be broken down into a few process steps: pre-treatment, hydrolysis, fermentation and separation. *Figure 2.1:* below shows a block flow diagram of a bio-ethanol plant.

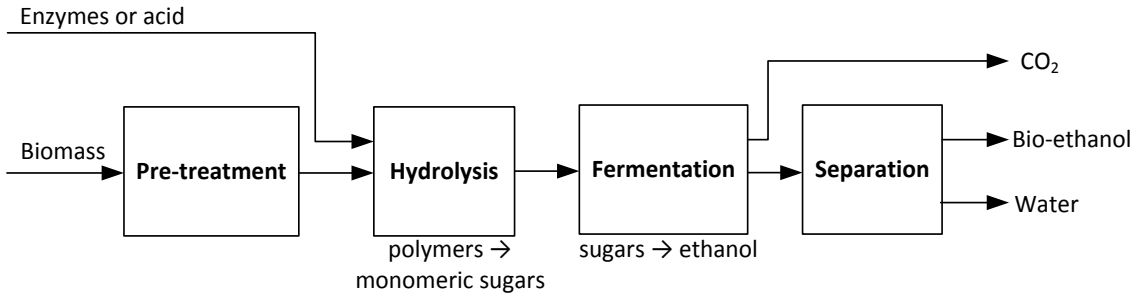


Figure 2.1: Block flow diagram of bio-ethanol plant
Adapted from Naik et al., (2010); Galbe & Zacchi, (2007)

Pre-treatment breaks up the structure of the lignocellulosic biomass in order to enable effective hydrolysis. Lignocellulosic biomass is comprised of three main components: lignin, cellulose and hemicellulose, in a matrix as is shown in *Figure 2.2* below. Lignin is an aromatic polymer which is hydrophobic (Sarkar et al., 2012). Cellulose is a straight chain glucose polymer but is structurally different from starches (Demirbas, 2005) which forms both crystalline fibres and amorphous chains (Menon & Rao, 2012). Hemicellulose is a branched glucose polymer that also contains sugars such as xylose, mannose, galactose and arabinose (Menon & Rao, 2012). The presence of lignin and the way in which molecules in crystalline cellulose are so tightly packed makes enzymatic attack difficult (Menon & Rao, 2012). Pre-treatment is a crucial step in bio-ethanol production as it reduces cellulose crystallinity to facilitate hydrolysis (Mosier et al., 2005). Pre-treatment is discussed in more detail in *Section2.2.*.

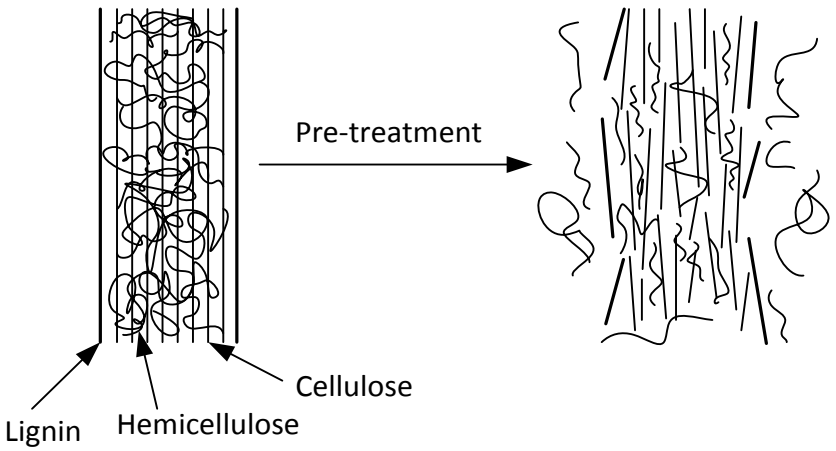


Figure 2.2: Effects of Pre-treatment on lignocellulosic biomass
Adapted from Mosier et al. (2005)

Delignification is sometimes included prior to hydrolysis. Alkalis are used to solubilise lignin which increases access to cellulose for hydrolysis. More information on delignification can be found in *Section 2.4.*

Hydrolysis, often also called saccharification, refers to the process of breaking the glycosidic bonds that link the monomers in cellulose and hemicellulose. This process is crucial as it produces the hexose and pentose sugars necessary for fermentation. Some pre-treatment methods hydrolyse the biomass to such an extent that a subsequent hydrolysis step is not required. Hydrolysis is discussed in more detail in *Section 2.3.*

Depending on the pre-treatment used, **detoxification** is sometimes necessary prior to fermentation to remove inhibitors to fermentation such as furfural, 5-hydroxymethyl furfural (HMF), acetic acid and other aliphatic acids and phenolic compounds which are produced by the degradation of sugars, lignin and acetyl groups (Cardona et al., 2010). These degradation products are more likely to form when the pre-treatment used is at a high temperature or utilises acid (Cardona et al., 2010). Detoxification is discussed in more detail in *Section 2.4.*

Fermentation uses microorganisms, such as yeast, bacteria or fungi, to convert the sugars produced by hydrolysis into ethanol under anaerobic or aerobic conditions (Hamelinck et al., 2005). The equations below show the fermentation reactions for glucose and xylose respectively (Hamelinck et al., 2005). $C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2\ CO_2$

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2\ CO_2$$

$$3C_5H_{10}O_5 \rightarrow 5C_2H_5OH + 5\ CO_2$$

Genetically modified organisms are capable of performing both glucose and xylose fermentations simultaneously and this is known as **co-fermentation** (Mosier et al., 2005). When hydrolysis and fermentation occur in separate vessels it is known as **separate hydrolysis and fermentation (SHF)** (Menon & Rao, 2012). SHF ensures that both hydrolysis and fermentation can operate at optimal process conditions (Menon & Rao, 2012). However, hydrolysis and fermentation can be performed simultaneously in a single vessel and is referred to as **simultaneous saccharification and fermentation (SSF)** (Mosier et al., 2005). SSF ensures that hydrolysis is not inhibited by the products formed as these are quickly reacted to produce ethanol (Menon & Rao, 2012). However, as hydrolysis and fermentation require different operating conditions, optimisation of conditions is difficult (Cardona et al., 2010). When both hemicellulose and cellulose are hydrolysed, and xylose and glucose are fermented, in the same vessel it is called **simultaneous saccharification and co-fermentation (SSCF)** (Mosier et al., 2005). Both SSF and SSCF reduce capital cost as fewer units are required (Mosier et al., 2005). When the enzymes required for hydrolysis are produced in the same vessel as the hydrolysis and the fermentation it is referred to as **consolidated bioprocessing (CBP)** (Menon & Rao, 2012). CBP would provide obvious capital cost reductions however microorganisms capable of CBP had not yet been developed in 2005 (Hamelinck et al., 2005). *Figure 2.3* on the following page shows a block flow diagram of a bio-ethanol plant that shows the differences between these different hydrolysis and fermentation routes. Detoxification and delignification have been excluded from the diagram for simplification.

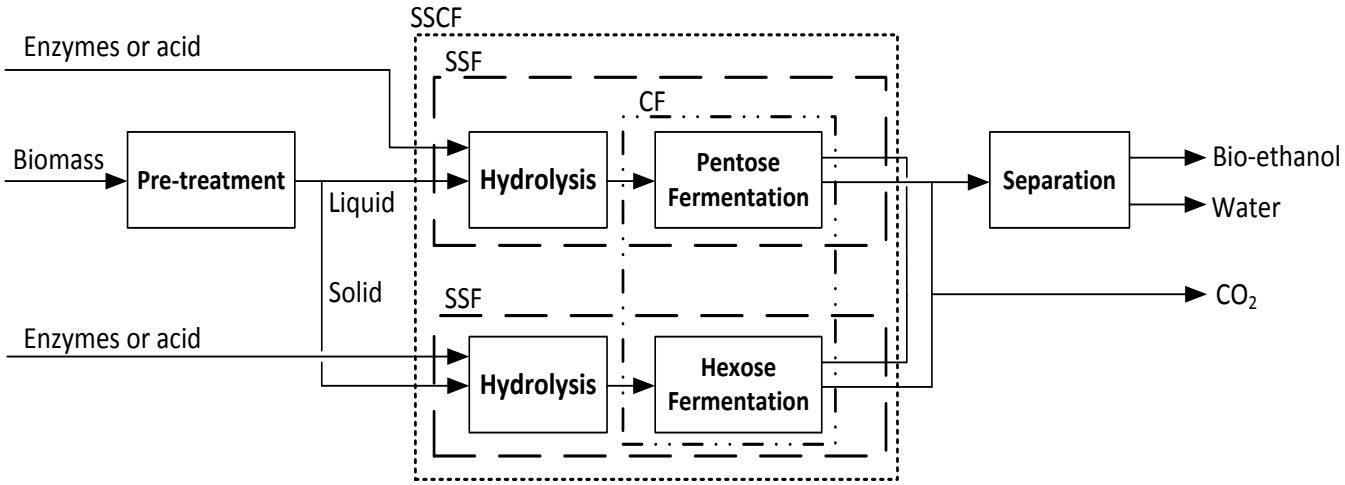


Figure 2.3: Block Flow Diagram of Different Fermentation Types
Adapted from Cardona et al., (2010); Galbe & Zacchi, (2007)

Fermentation produces a dilute ethanol stream (usually 5-12 wt% ethanol) and **separation** is used to purify the ethanol (Huang et al., 2008). Separation is an energy intensive process as the mixture forms an azeotrope which makes effective separation difficult (Huang et al., 2008). Distillation is often used to bring the mixture close to the azeotropic composition, approximately 92.4 wt%, following this, more rigorous separation methods such as azeotropic distillation, extractive distillation, liquid-liquid extraction, adsorption or hybrid separation methods are used to increase the purity (Huang et al., 2008).

In the following sections methods of pre-treatment, hydrolysis, delignification and detoxification will be discussed in more detail.

2.2. Pre-treatment

Pre-treatment is a crucial step in the processing of lignocellulosic biomass as it has a significant influence on the efficacy of the downstream processes such as hydrolysis and fermentation.

Lignocellulose consists of a matrix of cellulose and lignin connected by hemicelluloses chains (Sarkar et al., 2012:20). Lignin is covalently associated with hemicellulose (Cardona et al., 2010:4755) and thus prevents enzymes from accessing their substrate (cellulose or hemicellulose) (Menon & Rao, 2012:10). Lignin also binds irreversibly with enzymes (Menon & Rao, 2012:10) reducing the amount of enzyme available for hydrolysis. The presence of lignin thus prevents enzymes from accessing the cellulose and reduces hydrolysis rate.

By removing lignin, the efficiency of hydrolysis is improved. Lignin can be removed from the solid by solubilising hemicellulose (Galbe & Zacchi, 2007:48). Lignin can be burnt to produce steam and generate electricity or it can be used to produce value added products such as such as carbon fibres, resins, adhesives and low-molecular weight aromatic and phenolic compounds such as benzene, toluene, xylene aliphatic acids and polyesters (Yuan et al., 2013).

Cellulose crystallinity prevents hydrolysis as the fibres are tightly packed reducing access to the cellulose (Menon & Rao, 2012:4). Pre-treatment can disrupt the crystalline cellulose which increases the amount of amorphous cellulose which is more susceptible to attack (Sarkar et al., 2012:20). This makes cellulose hydrolysis more effective.

Both lignin and monomeric sugars formed in pre-treatment can degrade to produce compounds which inhibit microbial growth and thus reduce the effectiveness of fermentation (Cardona et al., 2010:4756). Methods of pre-treatment that produce large concentrations of inhibitors require detoxification before fermentation. Although not all pre-treatment methods produce significant quantities of inhibitors.

Pre-treatment methods with low energy requirements or that can utilise heat integration to balance the impact of energy inputs are preferred (Galbe & Zacchi, 2007:44). Low capital and operating costs are also desirable (Galbe & Zacchi, 2007:44).

The type of pre-treatment used is influenced by the feedstock as the fraction of lignin, hemicellulose and cellulose vary with each source of biomass. The choice of fermentation also influences the type of pre-treatment used.

Pre-treatment methods can be classified as biological, physical, chemical and physicochemical. Some pre-treatment methods are difficult to classify as they use a combination of aspects to treat the biomass.

2.2.1. Biological Pre-treatment

Microorganisms such as fungi and bacteria can be used to degrade lignin and hemicelluloses (Sarkar et al., 2012). Brown rot fungi attacks cellulose which is not desirable, while white and soft rot fungi attack both cellulose and lignin (Sun & Cheng, 2002). Mutants have been developed that lack enzymes that hydrolyse cellulose and thus do not attack cellulose but degrade lignin (Sarkar et al., 2012). Biological pre-treatment requires no chemicals, requires very little mechanical input and operates at mild conditions. However, reaction rates are slow with low yields, and well controlled conditions and a large space is required (Menon & Rao, 2012:8; Sarkar et al., 2012:22). As a result, biological pre-treatment is not seen as commercially viable (Menon & Rao, 2012:8).

2.2.2. Physical Pre-treatment

Methods of physical pre-treatment can include mechanical size reduction, pyrolysis and irradiation. Physical pre-treatment methods are energy intensive and as a result, the energy consumed is often greater than the theoretical energy content of the biomass (Menon & Rao, 2012:5). This results in these methods being expensive and not commercially viable (Galbe & Zacchi, 2007:48). However, mechanical size reduction is sometimes used to a certain extent in combination with other pre-treatment methods.

2.2.3. Physicochemical Pre-treatment

These pre-treatment methods combine both a physical and a chemical aspect. Physicochemical methods include steam explosion, liquid hot water method, ammonia fibre explosion, ammonia recycle percolation and carbon dioxide explosion. Microwave irradiation catalysed with acid or alkali is also a physicochemical pre-treatment.

2.2.3.1. Steam Explosion

Steam explosion is a mature technology that has been used to hydrolyse hemicellulose in the manufacture of fibreboard and other products by the Masonite process (Mosier et al., 2005). High pressure steam usually 20-50 bar (corresponding to 210-290°C) is used to rapidly heat biomass (Hamelinck et al., 2005). The biomass is maintained at this temperature for a few minutes to facilitate hemicellulose hydrolysis (Menon & Rao, 2012). This is usually either at a high temperature with a short residence time (270°C, 1 minute) or low temperature with a longer residence time (190°C, 10 minutes) (Sun & Cheng, 2002). After this, the pressure is quickly reduced to atmospheric pressure which results in an explosive decompression of the biomass (Hamelinck et al., 2005).

Steam explosion yields high xylose recoveries and increased surface area however, lignin solubility is low (Sarkar et al., 2012; Hamelinck et al., 2005). The use of steam to heat the biomass prevents excessive dilution of the sugars (Mosier et al., 2005). Sugarcane bagasse has been separated into cellulose, hemicellulose and lignin using steam explosion (Menon & Rao, 2012). It requires a low capital cost, has low environmental impact and requires 70% less energy than conventional physical pre-treatment methods (Menon & Rao, 2012; Sun & Cheng, 2002). However, as a result of the high temperatures, inhibitors are formed and some of the xylose is degraded (Sun & Cheng, 2002).

Steam explosion can be catalysed using an acid which reduces inhibitor formation as milder reactions temperatures can be used and increases hydrolysis of hemicellulose and cellulose (Sun & Cheng, 2002; Galbe & Zacchi, 2007).

2.2.3.2. Liquid Hot Water Method

Liquid hot water pre-treatment (LHW) is performed at pressures above the saturation point of water to maintain the liquid phase at high temperatures (Sarkar et al., 2012). Typical operating conditions are 200-230°C at 5 MPa for up to 15 minutes (Mosier et al., 2005; Sarkar et al., 2012). At 200°C the pH of water is 5 which causes the hemicellulose to be solubilised and results in the production of acetic acid and other organic acids from hemicellulose (Mosier et al., 2005). These acids promote oligosaccharide formation however, they also lead to the degradation of the monomers which results in inhibitor formation (Mosier et al., 2005) and acetic acid is itself an inhibitor to fermentation. Co-current, counter-current and flow-through reactor configurations can be used (Mosier et al., 2005).

LHW results in high hemicellulose hydrolysis and increased access to cellulose for efficient hydrolysis (Mosier et al., 2005).

The sugar solution produced by LHW is dilute which increases the energy intensity of downstream processes (Galbe & Zacchi, 2007). Size reduction is not required prior to LHW (Menon & Rao 2012). A base is required to prevent the pH from decreasing below 4 in order to minimise monomer formation and thus reduce the amount of inhibitors formed (Mosier et al., 2005).

2.2.3.3. Ammonia Fibre Explosion

In ammonia fibre explosion, AFEX, the biomass is treated with liquid ammonia for 10–60 minutes at temperatures below 100°C and elevated pressure, typically above 3 MPa (Galbe & Zacchi, 2007:48). This is followed by a rapid decrease in pressure as in steam explosion (Sarkar et al., 2012). AFEX requires 1–2 kg of ammonia/kg of dry biomass (Menon & Rao, 2012).

AFEX results in a small degree of solubilisation but the structure of the biomass is changed which increases the digestibility of the material (Galbe & Zacchi, 2007:48). AFEX is particularly effective for herbaceous and agricultural residues and over 90% cellulose and hemicellulose conversion by hydrolysis has been achieved for bagasse with low enzyme loading (Mosier et al., 2005; Menon & Rao, 2012). AFEX does not produce inhibitors and does not require small particle sizes (Sun & Cheng, 2002). The cost of both ammonia and its recovery significantly influence the profitability of this pre-treatment (Mosier et al., 2005).

2.2.3.4. Ammonia Recycle Percolation

In ammonia recycle percolation, ARP, a 10–15 wt% aqueous ammonia solution flows through a column reactor packed with biomass at temperatures of 150–170°C with a fluid velocity of 1 cm/min and a residence time of 14 minutes (Galbe & Zacchi, 2007; Menon & Rao, 2012; Mosier et al., 2005). ARP affects the lignin in biomass and causes lignin depolymerisation and breaks lignin-carbohydrate linkages (Mosier et al., 2005). Inhibitors are not formed in ARP and, as with AFEX, economics are dependent on ammonia cost and recovery efficiency (Menon & Rao, 2012).

2.2.3.5. Carbon Dioxide Explosion

Carbon dioxide, CO_2, can be used as an alternative to steam and ammonia in an explosion method. The use of CO_2 is more cost effective than ammonia and less inhibitors are formed than in steam explosion (Sarkar et al., 2012; Sun & Cheng, 2002; Hamelinck et al., 2005). Glucose yields from subsequent hydrolysis are lower for CO_2 explosion than steam explosion or AFEX (Sun & Cheng, 2002; Hamelinck et al., 2005).

2.2.4. Chemical Pre-treatment

Pre-treatment methods using acids, alkalis, ionic liquids and other chemicals can be termed chemical pre-treatment. Chemicals have been used extensively in the paper industry to remove lignin from cellulosic materials (Menon & Rao, 2012) however, these methods tend to preserve the cellulose crystallinity (Sims et al., 2008). Chemical pre-treatment is attractive due to its high yields for short reaction times and easy operation however the cost of chemicals and required material strength of process units is sometimes not cost effective (Sarkar et al., 2012). The following sections discuss a variety of chemical pre-treatment methods.

2.2.4.1. Acid Pre-treatment

Pre-treatment with acid causes the biomass to hydrolyse. Often two stages of acid treatment are used, a pre-treatment stage that reacts hemicellulose and a hydrolysis stage that hydrolyses cellulose. Both dilute and concentrated acids can be used to pre-treat biomass. The hydrolysis reactions are discussed in more detail in *Section 2.3*. Acid pre-treatments require expensive materials of construction due to the corrosive nature of acids and are also toxic and hazardous substances which pose a health and safety issues (Sun & Cheng, 2002).

2.2.4.1.1. Dilute Acid Pre-treatment

Dilute sulphuric acid is used commercially to manufacture furfural from hemicellulose (Menon & Rao, 2012). Hemicellulose is easier to hydrolyse than cellulose and thus, to prevent the degradation of hemicellulose monomers, cellulose hydrolysis is often performed in a subsequent step using either acid or enzymes (Demirbas, 2005; Mosier et al., 2005). The solubilisation of hemicellulose also increases the digestibility of the solids which contain the cellulose (Mosier et al., 2005).

Dilute acid pre-treatment at temperatures greater than 160°C has high reaction rates which enables it to be used in continuous processes (Sun & Cheng, 2002; Demirbas, 2005). Various reactor configurations, such as co-current, counter-current and flow-through, can be used for dilute acid pre-treatment as well as acid-catalysed steam explosion (Mosier et al., 2005). Two-stage flow-through reactor configurations are sometimes used (Mosier et al., 2005). The first reactor operates at a lower temperature and hydrolyses the more reactive hemicellulose (Mosier et al., 2005). The residual solids progress to a second reactor which operates at a higher temperature to hydrolyse the cellulose (Balat, 2011). Although this configuration has produced high conversion of hemicellulose, a large amount of energy is required (Mosier et al., 2005). The biomass also requires size reduction before dilute acid pre-treatment which increases the amount of energy required (Balat, 2011).

The sugar solution produced by dilute acid pre-treatment requires neutralisation before fermentation which leads to the formation of salts that can be costly to dispose of (Mosier et al., 2005). Detoxification is often required to remove inhibitors before fermentation (Sarkar et al., 2012). The hydrolysate may also need to be concentrated before fermentation (Cardona et al., 2010).

2.2.4.1.2. Sulphite Pre-treatment to Overcome Recalcitrance of Lignocellulose (SPORL)

This method is similar to dilute acid pre-treatment and uses either a sulphite or bisulphite catalyst (Zhu et al., 2010). Sulphite pre-treatment to overcome recalcitrance of lignocellulose (SPORL) operates at temperatures of 160-190°C for 10–30 minutes and is a batch process (Zhu et al., 2010). The catalyst lowers the pH and significantly reduces the formation of inhibitors compared to dilute acid pre-treatment (Zhu et al., 2010). The interaction of the catalyst with lignin forms lignosulphonate which weakens the lignin-enzyme interactions and thus improves hydrolysis efficiency (Zhu et al., 2010).

Lignosulphonate can also be sold and thus increases the process revenue (Zhu et al., 2010). SPORL is based on the sulphite piping process which is used on a commercial scale and thus should be easy to scale-up (Zhu et al., 2010).

2.2.4.1.3. Concentrated Acid Pre-treatment

Concentrated acid hydrolysis involves two stages. The first stage uses either concentrated or dilute acid to hydrolyse hemicellulose (Balat, 2011). Following this, the biomass is dried and concentrated acid is added (Balat, 2011). Both hemicellulose and cellulose can be effectively hydrolysed by concentrated acids with little degradation of the sugars formed (Demirbas, 2005). These processes require mild temperatures and ambient pressures however reaction times are longer than for dilute acid pre-treatment (Demirbas, 2005). Concentrated acids are expensive and thus acid recovery is key to the process economics (Sims et al., 2008). The drying stage also requires additional energy input.

2.2.4.1.4. Types of Acids Used

Sulphuric acid is the most common for acid pre-treatment (Sarkar et al., 2012). Environmental issues and the highly corrosive nature of hydrochloric acid have limited its use (Cardona et al., 2010). An advantage of using phosphoric acid is that neutralisation with sodium hydroxide forms sodium phosphate which can be used as a growth nutrient for the microorganisms (Cardona et al., 2010). This results in less nutrients being purchased for fermentation, avoids salt disposal costs and has a positive environmental impact (Cardona et al., 2010). Nitric acid has also been used (Cardona et al., 2010).

2.2.4.2. Alkaline Pre-treatment

Bases can be used to pre-treat lignocellulosic biomass. Hydroxides of sodium, potassium, calcium and ammonium are commonly used (Sarkar et al., 2012). Of these bases, lime, calcium hydroxide, is the least expensive by far (Menon & Rao, 2012). Sodium hydroxide (NaOH) is by far the most effective alkali for degrading lignin (Rezende et al., 2011). Alkaline pre-treatment requires less severe processing conditions than many other pre-treatments but has long reaction times, which may last for hours or even days (Mosier et al., 2005).

Biomass is soaked in the alkaline solution and is heated to a target temperature (Menon & Rao, 2012). This temperature is maintained with constant mixing for a specific amount of time (Menon & Rao, 2012). Lastly, neutralisation is required to remove lignin and inhibitors (Menon & Rao, 2012). Lime can be neutralised using CO_2 to produce calcium carbonate which can be converted back to lime using a kiln (Mosier et al., 2005).

Alkaline pre-treatment causes the biomass to swell which causes an increase in surface area, decreased cellulose crystallinity, the degree of polymerisation to be reduced, the bonds between lignin and hemicellulose to break, and disruption of the lignin structure (Sun & Cheng, 2002). Lignin can be separated effectively from the biomass as it is soluble in the alkaline solution (Sarkar et al., 2012). This enables hydrolysis to be effective.

2.2.4.3. Wet Oxidation

Wet oxidation is most suited to biomass with low lignin content (Galbe & Zacchi, 2007). Biomass is treated with water, typically 1 litre of water per 6 g of biomass, and air or oxygen at temperatures greater than 120°C (Sarkar et al., 2012). An alkali catalyst can be used to reduce the inhibitors formed

(Cardona et al., 2010). Wet oxidation is effective in solubilising lignin and hemicellulose and thus increases the digestibility of the cellulose (Cardona et al., 2010). However, hemicellulose is not hydrolysed into monomers but rather oligomers which can be hydrolysed further (Cardona et al., 2010).

2.2.4.4. Ionic Liquid Solvents

The ionic species consists of an unsymmetrical cation and one or both of the ions are large (Menon & Rao, 2012). This results in a reduced lattice energy which lowers the melting point making the species liquid at room temperature (Menon & Rao, 2012). Ionic liquids (ILs) can be developed to suit specific process requirements and have often been called designer solvents (Menon & Rao, 2012). Pre-treatment with ILs results in increased cellulose porosity and a higher fraction of amorphous cellulose which increases hydrolysis efficiency (Menon & Rao, 2012). These processes tend to be less energy intensive and easy to operate (Menon & Rao, 2012). However, there are still many challenges to be overcome. The high cost of ILs means that efficient recovery techniques are required which increases the energy requirements (Menon & Rao, 2012). Very little is known about how the ILs react with hemicellulose and lignin. ILs do generate inhibitors and very little is known about the toxicity of ILs (Menon & Rao, 2012). Extensive research and development of ILs is required before commercialisation (Menon & Rao, 2012).

2.2.4.5. Organosolv

Organic or organic-aqueous solvents can be used to remove lignin from biomass (Sarkar et al., 2012). Some examples of solvents are ethanol, methanol, acetone, ethylene glycol, phenol, acetic acid and performic acid (Galbe & Zacchi, 2007; Sarkar et al., 2012). Supercritical CO_2 can be used to reduce the amount of solvent required and enable lignin recovery by decreasing the pressure (Cardona et al., 2010). Organosolv pre-treatments produce high purity lignin which can be used to produce adhesives and biodegradable polymers (Zhu et al., 2010).

Acids can be used as catalysts to help break the lignin-hemicellulose linkage and increase the xylose yield (Sun & Cheng, 2002). At temperatures higher than 185°C acids are generally not required (Sun & Cheng, 2002).

Many solvents act as inhibitors of hydrolysis and fermentation and thus must be effectively removed (Galbe & Zacchi, 2007:44). Solvent recovery is important to improve the process economics however, this usually requires an energy-intensive distillation step (Sun & Cheng, 2002; Zhu et al., 2010). Many solvents are explosive and/or flammable and thus present handling and safety concerns (Galbe & Zacchi, 2007:44).

2.2.4.6. Oxidative Delignification

Hydrogen peroxide in combination with the peroxidise enzyme can be used to degrade lignin and improve the hydrolysis of biomass (Sun & Cheng, 2002). This process solubilises most of the hemicellulose and a large amount of the lignin using 2% hydrogen peroxide at 30°C for 8 hours (Sun & Cheng, 2002).

2.2.4.7. Ozonolysis

Ozone can be used as to remove lignin effectively at ambient conditions without producing inhibitors (Sun & Cheng, 2002). However the process is expensive as large amounts of ozone are required (Sun & Cheng, 2002) and also poses an obvious environmental concern.

2.3. Hydrolysis

Lignocellulose does not contain free sugars but rather polysaccharides of pentose and hexose sugars. These polysaccharides must be broken down into monomers before fermentation can occur. The process of breaking the glycosidic bonds that link the monomers is called hydrolysis or saccharification. The equation below shows how cellulose is broken down into glucose using water. The hydrolysis of hemicellulose is more complicated as a range of pentose sugars are formed.

$$(C_6H_{10}O_5)_n + nH_2O \rightarrow n(C_6H_{12}O_6)$$

(Hamelinck et al., 2005).

Hydrolysis can be catalysed using enzymes or chemicals such as acids. These methods are discussed below. Combinations of these methods can also be used where acids are used to hydrolyse hemicellulose followed by enzymatic hydrolysis of cellulose.

2.3.1. Enzymatic Hydrolysis

Enzymes can be used to hydrolyse cellulose and hemicellulose. Processes typically operate at a pH of 4.8, atmospheric pressure and a temperature of 45-50°C (Balat, 2011). Pre-treatment is required before enzymatic hydrolysis to improve access to cellulose. The cellulose hydrolysis rate is affected by: the surface area, crystallinity of cellulose, amount of swelling of the cellulose fibres, the amount of lignin present and the molecular structure of cellulose (Balat, 2011). As a result of this, physical pre-treatment methods are not usually effective enough for enzymatic hydrolysis (Hamelinck et al., 2005). Effective pre-treatment reduces the required enzyme loading which has a significant influence on process economics as enzymes are expensive (Sarkar et al., 2012). Depending on the pre-treatment method used, neutralisation or detoxification may be required before enzymatic hydrolysis (Hamelinck et al., 2005).

2.3.2. Chemical Hydrolysis

Chemical hydrolysis can use either dilute or concentrated acids. These methods have already been discussed in *Section 2.2.4.1.1* and *Section 2.2.4.1.3* above.

2.3.3. Hydrolysis using Supercritical Fluids

A supercritical fluid is a fluid at a temperature and pressure above the critical point and thus the fluid is neither liquid nor gas (Sandler, 2006). For water the critical point is 644 K and 22 MPa and for CO_2 it is 304 K and 7.4 MPa (Sandler, 2006). At high temperatures (523–573 K) or supercritical conditions water separates into acidic H^+ and basic OH^- ions which break up the polymers into monomers and oligomers (Naik et al., 2010). SO_2 can be used to further catalyse the hydrolysis and increase the yield of monomers (Cardona et al., 2010).

2.4. Detoxification and Delignification

Hydrolysis of hemicellulose produces xylose, mannose, acetic acid, galactose and glucose (Balat, 2011). Xylose can degrade to produce water, methanol, formic acid, acetic acid, propionic acid, hydroxy-1-propanone, hydroxyl-1-butanone and 2-furfuraldehyde (Balat, 2011). Further degradation of xylose can produce furfural (Balat, 2011). Cellulose hydrolysis yields glucose which can degrade to form 5-hydroxymethyl furfural, HMF, (Balat, 2011). Degradation products are more likely to form when high temperatures or acids are used in pre-treatment (Cardona et al., 2010). Many of these degradation products reduce enzymatic hydrolysis and fermentation efficiency and should be removed to enable more effective processes (Cardona et al., 2010; Hamelinck et al., 2005).

Alkalis can be used to remove lignin from solid biomass, delignification, and to remove inhibitors to fermentation from liquid hydrolysate, detoxification. The principles of delignification and detoxification using alkalis are the same as alkaline pre-treatment, which was discussed in *Section 2.2.4.2.*

For detoxification, first pre-treated biomass is separated into a solid and liquid fraction (Hamelinck et al., 2005). The solid fraction is washed using water and the wash water is added to the liquid fraction (Cardona et al., 2010). The liquid fraction is then detoxified. Common methods of detoxification include: neutralisation, overliming, adsorption, ion exchange, the use of enzymes and electrodialysis (Cardona et al., 2010). Sometimes these methods need to be used in combination to effectively remove all inhibitors (Cardona et al., 2010). The need for detoxification and the extent of detoxification required depends on the pre-treatment and hydrolysis method used as well as the tolerance of the microorganism used in fermentation.

2.5. Modelling and Optimisation

Computer modelling can be used to investigate the interactions between competing factors in a simultaneous way. This enables a greater understanding of complex problems and a wide variety of solutions to be generated and evaluated. Determining the optimal pre-treatment configuration for production of bio-ethanol from sugar-cane bagasse is no trivial task. The problem is open-ended and there are many factors which interact with each other in very complex ways. In order to take these interactions and the trade-offs associated with them into account, a simultaneous approach is required to optimise the system. Mathematical modelling can be used to simulate the various pre-treatment units. These units can then be set up in a superstructure, which is explained in *Section 2.5.2*, and optimisation software, GAMS (General Algebraic Modelling System) or MipSyn (Mixed-Integer Process Synthesizer), can be used to determine the optimal pre-treatment configuration.

2.5.1. Process Synthesis Problem Formulation

Process synthesis problems may be formulated as mixed-integer non-linear programs (MINLPs) which have the following general structure:

$$z(y^K) = \min_x c^T y^K + f(x)$$

Such that:

$$g(x) \leq 0$$

$$h(x) = 0$$

$$A\,x = a$$

$$B\,y^K + C\,x \leq d$$

$$x \in X = \{x | x \in R^n, x_L \leq x \leq x_U\}$$

$$y^K \in Y = \{y^K | y^K \in \{0,1\}^m, Ey^K \leq e\}$$

From (Kocis & Grossmann, 1987).

In this formulation, *x* represents continuous variables such as stream variables (for example flowrates, pressures, temperatures as well as vessel sizes). These factors are bounded by upper and lower values, x_U and x_L. The binary y^K variables represent the existence of process units at the *Kth* iteration of the program and are subject to the logical constraints $Ey^K \leq e$. Non-linear equations are represented by *f(x)*, *g(x)* and *h(x)*. In the objective function, represents the fixed costs and *f(x)* represents the variable costs such as revenue, operating costs and costs involving vessel size. Process specifications are incorporated in *g(x).* Material and energy balances and design equations are included using *h(x)* and *Ax = a.* Logical constraints, $By^K + Cx \leq d$ and $Ey^K \leq e$, are used to ensure that the selected flowsheet is within the superstructure. (Kocis & Grossmann, 1987).

The problem formulation shown above is a mixed-integer non-linear program (MINLP) as it contains both binary variables and nonlinear equations. Non-linear equations are difficult to optimise due to the presence of local maxima and minima and they introduce non-convexities adding to the complexity of the problem. Binary variables cause discontinuities and require intelligent formulation of equations to avoid mathematical errors.

Some of the algorithms that have been used to solve MINLP problems are Branch and Bound, Generalised Benders Decomposition and Outer-Approximation (OA) methods (Kocis & Grossmann, 1987). MipSyn uses a modified version of the OA method that includes equality relaxation and

modelling and decomposition strategy (Kravanja, 2010). This aims to reduce the problems associated with non-convexities and binary variables.

2.5.2. Superstructures for Continuous Optimisation

Superstructures are representations of various processing options embedded in one structure. *Figure 2.4* below shows an example of a simple superstructure where product *c* is being produced. *c* can be produced directly from *b* or by reacting *a* to form *b* and then reacting *b* to form *c*. Possible processing routes include: reactor 1 followed by reactor 3, reactor 2 followed by reactor 3, or reactor 3 on its own. The superstructure in *Figure 2.4* incorporates all 3 possible processing routes and uses binary variables, *y*, to denote the existence of each process unit. If *y* is 1, the unit exists and if *y* is 0 the unit does not exist. These binary variables can then be used to ensure the flowrates into and out of the existing units are non-zero and are zero for the non-existing units. By using a superstructure the program can evaluate all possible processing routes by switching units on and off and thus determine which processing route is optimal.

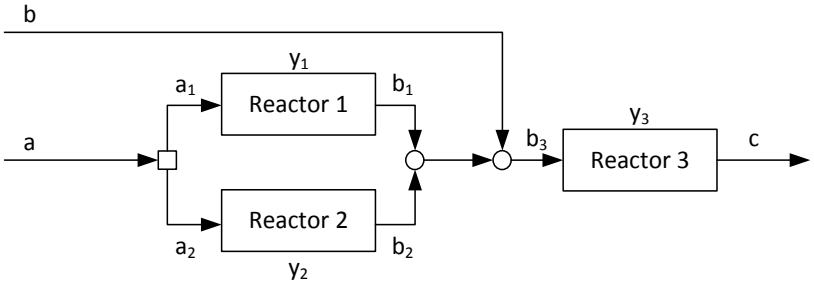


Figure 2.4: Example of a simple superstructure
Adapted from Kocis & Grossmann, (1987, 1989)

Superstructures have been used in the simultaneous optimisation of heat and mass exchange networks and other process synthesis problems using such MINLP formulations (Yee & Grossmann, 1990; Yee, Grossmann & Kravanja, 1990; Papalexandri & Pistikopoulos, 1994; Szitkai et al., 2006). MINLPs can be used to describe many problems in chemical engineering, such as reactor networks synthesis and separator networks synthesis (Kravanja, 2010), mechanical engineering, such as design of gate structures and steel frame structures (Kravanja, 2010), economics, mathematics, and determining optimal distribution networks in scheduling operations. These problems can then be optimised by using GAMS or, for larger applications, a combination of GAMS and MipSyn.

2.5.3. Optimisation Models using Sugarcane Bagasse

Moncada, Matallana and Cardona (2013) modelled a sugarcane bagasse bio-refinery to produce ethanol, poly-3-hydroxybutyrate (PHB) and electricity. Their model used dilute acid pre-treatment and choose between acid or enzymatic hydrolysis. Both pentose and hexose fermentation were modelled. In the work of Moncada, Matallana and Cardona (2013), kinetics data were used in Matlab to determine conversion and energy use factors and these were then used in GAMS to determine the optimal flowrate distribution. The problem formulation formed a mixed-integer program (MIP). The optimised flowsheet was then simulated with heat integration as well as a scenario with pure cogeneration and a no cogeneration scenario and economic and environmental analyses were performed. The WAR GUI which uses the Waste Reduction Algorithm, (United States Environmental Protection Agency, n.d.), was used to determine the potential environmental impact (PEI) of the optimal flowsheet.

Furlan et al. (2012) modelled a distillery which produces ethanol from sugarcane juice and determines the amount of bagasse available for ethanol production whilst keeping the plant energetically self-sufficient. Organosolv was used for pre-treatment followed by enzymatic hydrolysis. Scenarios with pentose and/or hexose fermentation were modelled. EMSO (Environment for Modelling Simulation and Optimisation), (Soares & Secchi, n.d.),with PSO (Particle Swarm Optimisation) algorithm, (Eberhart & Kennedy, 1995), was used to maximise the profit for these scenarios by optimising flowrate splits. It was found that ethanol production from bagasse increases the thermal demands of the plant by 25% and, as a result, less electricity is produced.

2.5.4. Other Optimisation Models

Zondervan et al. (2011) modelled a bio-refinery system from lignocellulosic biomass. The model involved 72 processing steps, including a large variety of pre-treatment methods, and was more focussed on process flowsheet optimisation than the other models discussed so far. GAMS was used with an MINLP model using conversion factors. Ethanol, butanol, succinic acid and gasoline blends were produced. Different process flowsheets were chosen for different scenarios. The objective function was economic incorporating product yields, cost of feedstock, cost of chemicals, waste production and the fixed cost of equipment. The superstructure was optimised for four different goals: maximise yield, minimise operating costs, minimise waste and minimise fixed costs. Different flowsheets were generated for each of the goal and this was used to provide a more well-rounded evaluation of possible processing options.

The model of Martin and Grossmann (2012) also used GAMS with an MINLP model which optimised a process flowsheet to produce ethanol from switchgrass minimising energy input. Two pre-treatment options were considered, acid pre-treatment and ammonia fibre explosion, which was followed by enzymatic hydrolysis, fermentation and a number of separation options were considered for the dehydration of ethanol. Flowsheets were optimised in terms of an economic objective.

2.6. Multi-objective Optimisation

If two or more objectives are to be optimised they need to be optimised simultaneously in order to account for synergistic effects. This can be represented using a Pareto curve, *Figure 2.5* below is an example of a Pareto curve. In order to construct a Pareto curve, both objective functions need to be defined, for example annual profit as an economic objective and environmental impact as an environmental objective. Then the optimum solution when considering each objective separately is determined. In this case, for point A (as shown in *Figure 2.5)*, the minimum environmental impact (EI) is zero and this occurs when production is zero, in other words no plant is built. On the other hand, the environmental impact for maximum profit can be taken as the maximum environmental impact, i.e. point C in *Figure 2.5*. The Pareto curve is then obtained by varying the EI between this upper and lower limit and maximising the profit or, by varying the profit between the upper and lower limit and minimising the EI. A Pareto curve can then be plotted that shows the relationship between annual profit and EI. Each point on the curve represents an optimal solution and a choice needs to be made to decide on the actual plant configuration by choosing a compromise between the two objectives. In the study of Santibanez-Aguilar et al., (2011) which involves the optimsation of a bio-refinery in Mexico, Point B in *Figure 2.5* below was chosen as the optimal configuration as EI is 25% of the maximum EI and profit is 75% of the maximum possible profit.

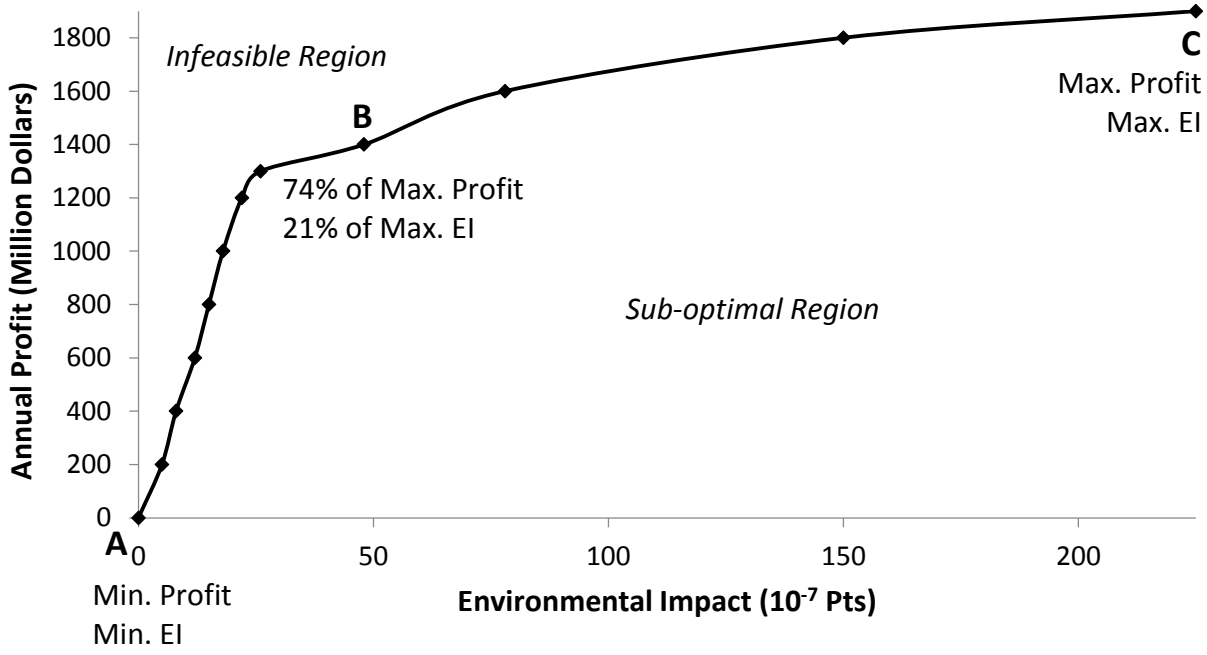


Figure 2.5: Example of a Pareto Curve
Adapted from Santibanez-Aguilar et al. (2011)

The use of Life Cycle Analysis (LCA) in combination with process design can help engineers design and optimise sustainable processes. Because LCA uses a cradle to grave approach it prevents impacts from being shifted to another stage in the product life cycle when reducing the environmental impact of the plant (Azapagic, 1999).

A common method for Life Cycle Impact Assessment (LCIA) is the EDIP/UMIP method (Stranddorf et al., 2005) which has the following eleven impact categories:

- Climate change
- Stratospheric ozone depletion
- Photochemical ozone formation
- Acidification
- Nutrient enrichment
- Human toxicity vis air
- Human toxicity via water
- Human toxicity via soil
- Ecotoxicity, water, acute
- Ecotoxicity, water, chronic
- Ecotoxicity, soil, chronic

  (Stranddorf et al., 2005)

The scores from each impact category can be normalised to scale the magnitude of each category so that each category's effect on the overall environmental impact can be determined (Product Ecology Consultants, 2010). Once normalised, all categories have the same unit and can therefore be weighted and added to get a final score. The normalisation and weighting factors used in this study are discussed in *Section 3.8.*

The following section, *Chapter 3*, describes the methodology used in constructing these models, and the formulation of the economic and environmental objective functions.

3. Methodology

This chapter describes the methodology used in this thesis. *Section 3.1* shows the nomenclature used in the equations and describes how the bagasse flowrate was determined for the models. Modelling and optimisation tools were used to investigate the economic and environmental feasibility of the pre-treatement network for producing bio-ethanol from sugarcane bagasse shown in *Figure 3.1* below. A more detailed process flow diagram of the superstructure can be seen in *Figure 3.2*. Fermentation of xylose is not widely used on an industrial scale and thus in this work the only hexose fermentation was considered for bio-ethanol production. However, the liquid stream produced by pre-treatment should be utilised. This work considered using the liquid stream to produce methane using bio-digestion.

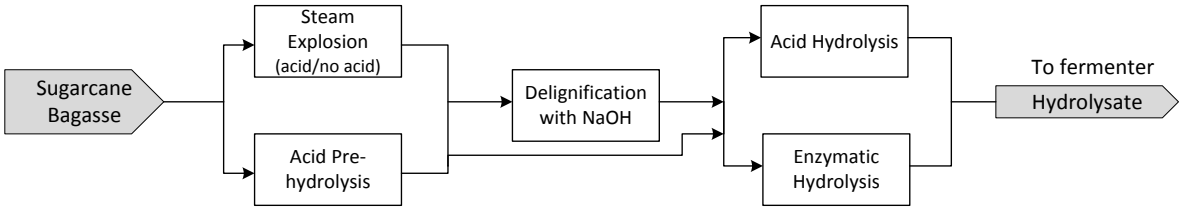


Figure 3.1: Block flow diagram superstructure for pre-treatment of sugarcane bagasse.

A variety of methods are available for treating sugarcane bagasse to produce a liquid stream that can be fermented to produce bio-ethanol. Pre-treatment and hydrolysis are required to break the lignocellulose into glucose. Delignification can improve hydrolysis yields by improving the access to cellulose.

Of the physicochemical processes described in *Section 2.2.3*, steam explosion provides good glucose yields, does not necessarily require any chemicals and does not produce a dilute sugar stream. For these reasons, steam explosion was chosen to be modelled. Acid-catalysed steam explosion was also modelled to investigate the effect of increasing the yield of free sugars and reducing inhibitors in steam explosion. *Section 3.2* describes in detail how the steam explosion model was constructed.

Based on the review of chemical pre-treatment methods in *Section 2.2.4*, it can be seen that acid and alkaline pre-treatments are the most common methods used industrially. Also, the acid and alkaline methods have readily available data (Lavarack, Griffin & Rodman, 2002; Zhao, Zhou & Liu, 2012; Aguilar et al. 2002; Rezende et al., 2011), hence they were chosen as part of the options of pre-treatment methods modelled in this study. The acid and alkaline pre-treatment models used in this study are described in *Sections 3.3* and *3.4* respectively. In this study, delignification has been modelled for use prior to hydrolysis however only the solubilisation of solids and not the detoxifying effect was modelled. The delignification model is described in *Section 3.4.*

Both acid and enzymatic hydrolysis are used in industrial processes and are well studied in literature (Saeman, 1945; Xiang, Kim & Lee, 2003; Gurgel & Marabezi, 2012; Kadam, 2000; Pushpa et al., 2010; Carvalho, Jr & Suarez, 2013). This project includes models of both acid and enzymatic hydrolysis and the modelling procedure for acid and enzymatic hydrolysis is described in *Section 3.5* and *3.6* respectively.

It is worth mentioning that the papers discussed in *Section2.5.3* that used sugarcane bagasse as the raw material (Moncada, Matallana and Cardona, 2013; Furlan et al., 2012) only considered one pre-treatment option. Although Zondervan et al. (2011) and Martin and Grossmann (2012) modelled more than one pre-treatment option, their models had a different lignocellulosic raw material. This work

uses sugarcane bagasse as the raw material and evaluates a variety of pre-treatment and hydrolysis options as well as the option of including delignification prior to hydrolysis. Further, all the models discussed above except Moncada, Matallana and Cardona (2013) were only optimised in terms of one objective i.e. economics. However, when biofuels are considered the environmental analysis is as important as the economics. Both these aspects should be considered when determining the optimal flowsheet and this work considers both economic and environmental perspectives to decide the optimal solution.

In order to perform a true simultaneous optimisation of the pre-treatment flowsheet the superstructure shown in *Figure 3.2* on the following page needs to be programmed in GAMS so that all possible options can be compared simultaneously in terms of both economic and environmental objectives. For a network involving many choices of unit operations, and thus many binary variables, a sophisticated optimisation procedure, such as MipSyn (Kravanja, 2010), is needed. To use this approach, GAMS models with fixed topologies would be solved individually as MINLPs and used to initialise the overall superstructure MINLP which would then be solved using MipSyn. However, solving the initial fixed flowsheets was a time consuming task and the overall superstructure in MipSyn could not be completed. As a result of this, a more sequential approach was used for the pre-treatment flowsheet optimisation.

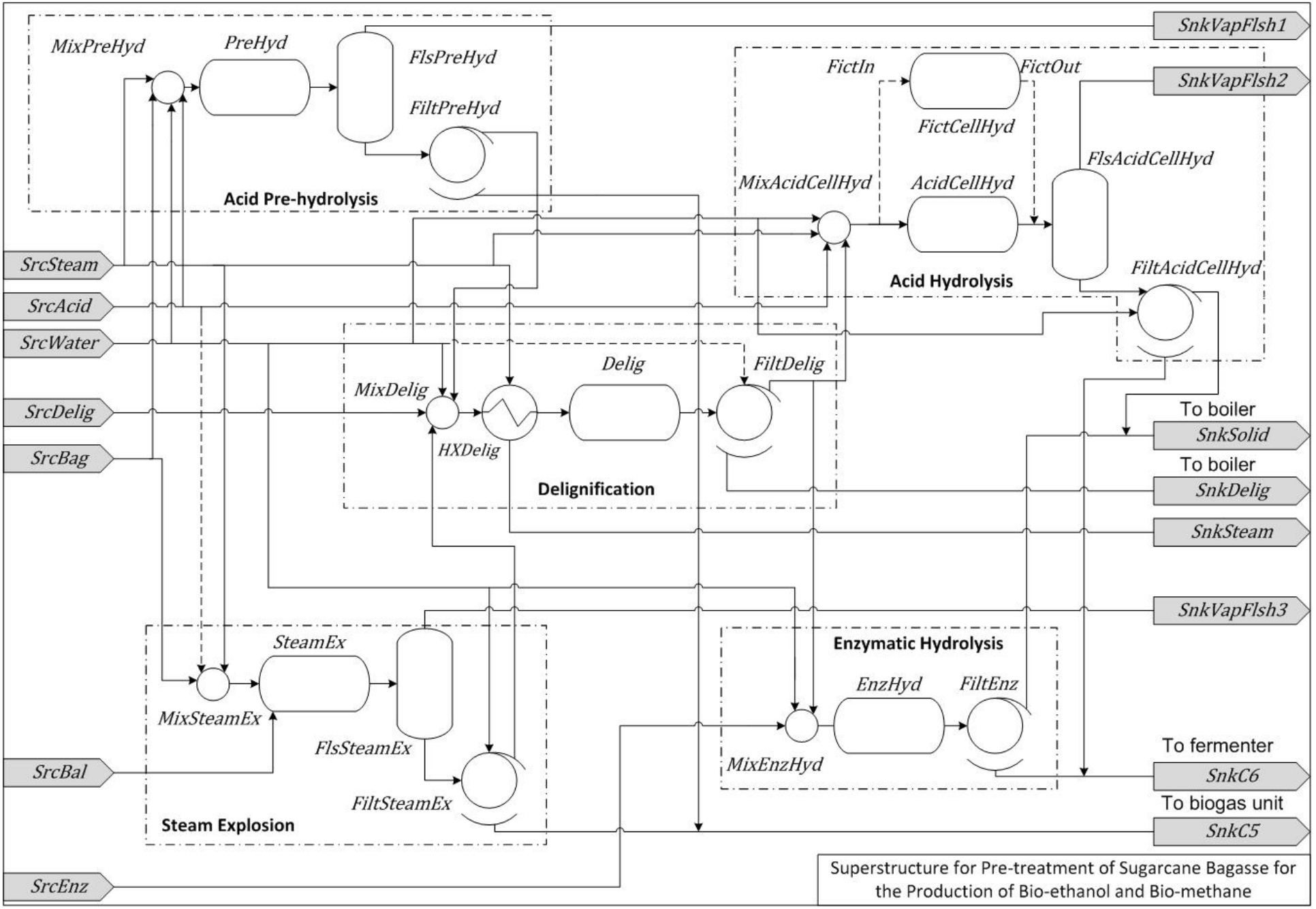


Figure 3.2: Superstructure for pre-treatment of sugarcane bagasse

A sequential method used in this work involves decomposing the superstructure of *Figure 3.1* and *Figure 3.2* into fixed flowsheets. These fixed flowsheets can then be optimised separately. *Figure 3.3* below shows how the superstructure can be decomposed into the eight separate flowsheets.

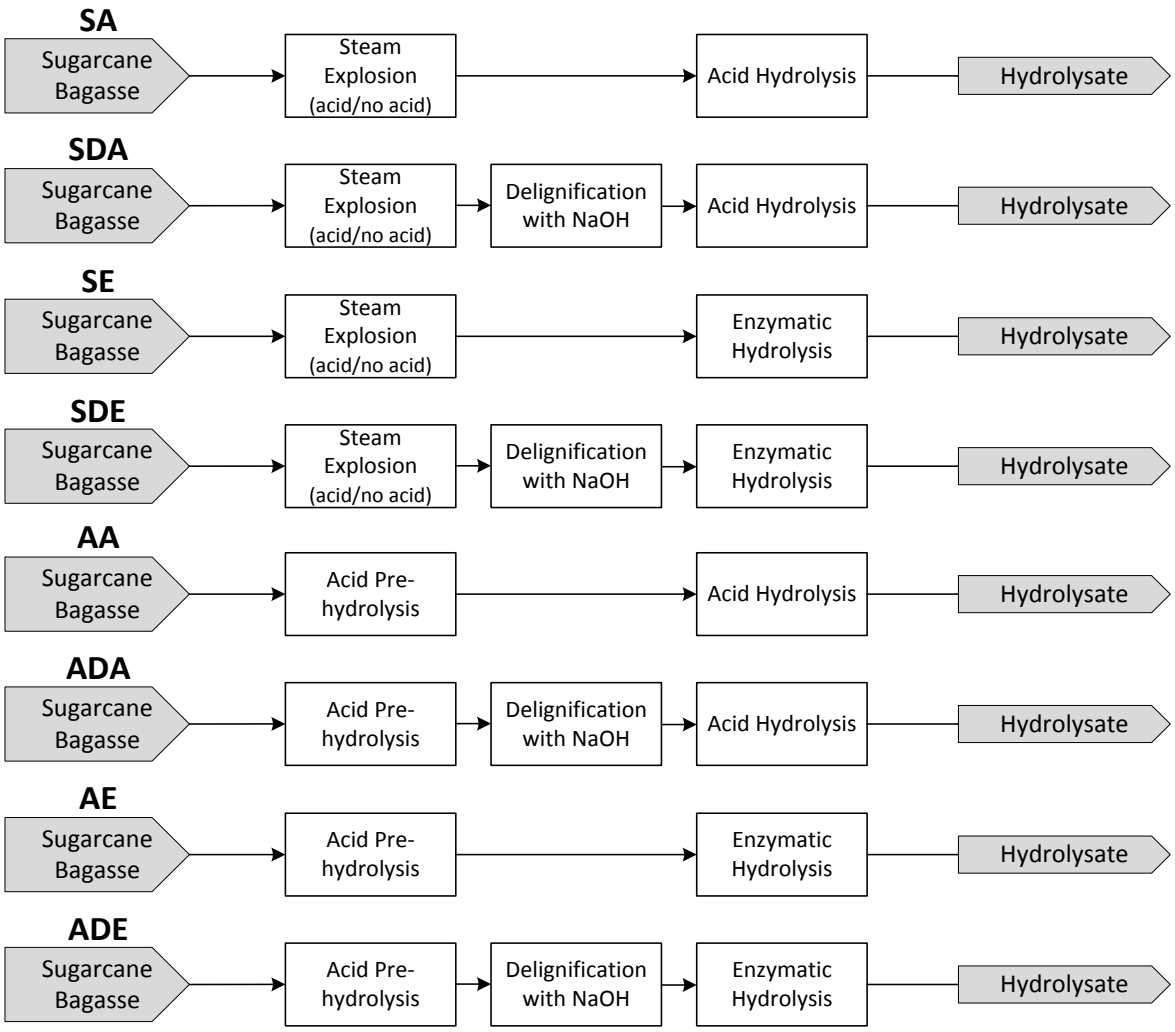


Figure 3.3: Decomposed superstructure for pre-treatment of sugarcane bagasse

The eight flowsheets shown in *Figure 3.3* above are:

steam explosion with acid hydrolysis (SA);

steam explosion, delignification and acid hydrolysis (SDA);

steam explosion with enzymatic hydrolysis (SE);

steam explosion, delignification and enzymatic hydrolysis (SDE);

acid pre-hydrolysis with acid hydrolysis (AA);

acid pre-hydrolysis, delignification and acid hydrolysis (ADA);

acid pre-hydrolysis with enzymatic hydrolysis (AE);

acid pre-hydrolysis, delignification and enzymatic hydrolysis (ADE).

Each of these flowsheets is a possible pre-treatment route for producing bio-ethanol from sugarcane bagasse. Flowsheets including steam explosion, acid pre-hydrolysis or acid hydrolysis contain binary variables and thus all the eight flowsheets are MINLPs rather than NLPs. In the steam explosion models, the binary variables select whether the steam explosion is acid-catalysed or not. The acid pre-hydrolysis model contains 13 datasets which represent the unit operation with different acid weight percentages and different temperatures and residence times. Binary variables are used to select a specific dataset (see *Section 3.3* for more information). The binary variables in the acid hydrolysis model select which steam level is used to heat the reactor. Both the economic and environmental implications of each possible flowsheet were determined. *Section 3.7* provides details on the costing and the economic objective function. The environmental impacts and objective function are discussed in *Section 3.8.* The following methodology was used in this thesis:

1. The set of eight flowsheets shown in *Figure 3.3* were solved as MINLP models to maximise total profit. The environmental impact associated with the total profit obtained was then calculated for each flowsheet.
2. From this analysis it was discovered that all flowsheets involving delignification were unprofitable and the possibility of recycling sodium hydroxide was investigated. A sensitivity analysis with regards to the amount of sodium hydroxide purged was also performed and can be seen in *Section 4.3* (see *Appendix B.1* for code). A sodium hydroxide recycle of 75% seemed feasible from literature (discussed in *Section 4.3)* and this was used for further investigations.
3. A sensitivity analysis was also performed with regards to the amount of lignin solubilised by acid in hydrolysis. This was found to have a very small effect on the overall solution and thus no changes were made regarding the acid soluble lignin constant. *Section 4.2* provides more details of this analysis.
4. After this, step 1 was repeated with a fixed sodium hydroxide purge of 25%.
5. Each fixed flowsheet MINLP was then solved to minimise the total environmental impact. The profit associated with the total environmental impact was then calculated.

Profit and environmental impacts from steps 4 and 5 were then plotted on a graph. This was the procedure for generating the overall solution space seen in *Figure 4.6* in *Section 4.8.*The models were programmed in **GAMS V24.2.1** and the MINLP solver used was **Dicopt, Conopt** was used as the NLP solver and **Cplex** was the MIP solver. The model statistics can be seen in *Table 3.1* below. On average the models had 2 293 variables and 2 774 equations and the largest model was ADA which had 3 183 equations and 3 573 variables. These models are fairly large and complex so rigorous initialisations and bounds were needed to aid the solvers.

Table 3.1: Model Statistics

Model	Number of Equations	Number of Variables
SE	1 552	2 107
SA	1 888	2 389
AE	1 727	2 126
AA	1 622	1 922
SDE	2 610	3 253
SDA	2 959	3 559
ADE	2 803	3 265
ADA	3 183	3 573
Average	2 293	2 774

3.1. Nomenclature Used in Model Equations and Bagasse Flowrate

This section shows the nomenclature used in the model equations and these are divided into sets, parameters, scalars, variables and binary variables. A fixed bagasse flowrate was used in all the models and this section describes how this bagasse flowrate was determined.

3.1.1. Nomenclature Used in Model Equations

Sets

c	Environmental impacts categories in EDIP/UMIP	
	GW	Global warming (GWP 100)
	OD	Ozone depletion
	Ac	Acidification
	Eu	Eutrophication
	PS	Photochemical smog
	EWC	Ecotoxicity water chronic
	EWA	Ecotoxicity water acute
	ESC	Ecotoxicity soil chronic
	HTA	Human toxicity air
	HTW	Human toxicity water
	HTS	Human toxicity soil
	BW	Bulk waste
	HW	Hazardous waste
	RW	Radioactive waste
	Sas	Slags/ashes
	Res	Resources (all)
J	Set of components used in models	
	$AceA$	Acetic acid
	$Acetyl$	Acetyl groups in bagasse
	$Acid$	Acid used for acid pre-treatment, acid hydrolysis and acid-catalysed steam explosion (H_2SO_4)
	ASL	Acid soluble lignin
	$Balance$	A component used to resolve the mass balance on the steam explosion unit
	$Cellulose$	Cellulose
	Enz	Enzyme mix used for enzymatic hydrolysis
	$Furf$	Furfural
	$Gluc$	Glucose
	$Glucolig$	Glucose oligomers formed in steam explosion unit
	$GluSol$	Glucose solubilised in delignification
	$Hemi$	Hemicellulose
	HMF	5-hydroxymethyl furfural
	$Lignin$	Lignin
	Min	Minerals from soil
	$NaOH$	Sodium hydroxide for delignification
	$NaSulp$	Sodium sulphate precipitated due to presence of acid in delignification unit
	$OrgAc$	Organic acids from soil
	$Phos$	Phosphates from soil
	$Salts$	Salts from soil
	$Soil$	Soil
	$Sucrose$	Sucrose
	$Water$	Water

Xylo	Xylose
Xylolig	Xylose oligomers formed in steam explosion unit
XylSol	Xylose solubilised in delignification

d(J) Components that are inert in the delignification unit
AceA, Acetyl, Acid, Balance, Enz, Furf, Gluc, Glucolig, HMF, Min, OrgAc, Phos, Salts, Soil, Sucrose, Xylo, Xylolig

e(J) Components that are inert in the enzymatic hydrolysis unit
ASL, Balance, Enz, Furf, GluSol, HMF, Lignin, NaOH, NaSulp, Sucrose, XylSol

h(J) Components that are inert in the acid hydrolysis unit
Balance, Enz, GluSol, NaOH, NaSulp, XylSol

i(J) Components that are inert everywhere except where precipitation occurs
Acid, Min, OrgAc, Phos, Salts, Soil

L(J) Liquid components used in filters
AceA, Acid, ASL, Balance, Furf, Gluc, Glucolig, GluSol, HMF, Min, NaOH, OrgAc, Phos, Salts, Sucrose, Water, Xylo, Xylolig, XylSol

Ll(J) Liquid components that are vapourised in the acid hydrolysis flash
Acid, Gluc, Glucolig, Xylo, Xylolig

NoPPT(J) Inert components in precipitation reactions
AceA, Acetyl, ASL, Balance, Cellulose, Enz, Furf, Gluc, Glucolig, GluSol, Hemi, HMF, Lignin, Min, OrgAc, Phos, Salts, Soil, Sucrose, Xylo, Xylolig, XylSol

p(J) Inert components in acid pre-hydrolysis unit
Balance, Enz

Ppt(J) Components involved in precipitation reactions
Acid, NaOH, NaSulp, Water

S(J) Solid components used in filters
Acetyl, Cellulose, Enz, Hemi, Lignin, NaSulp, Soil

si(J) Components that are inert in the steam explosion unit
Enz, NaOH

n Number of elements in a set of binary variables (see *binary variables* below)

st Set of steam levels used in models

LPS	Low pressure steam
MPS1	Medium pressure steam 1
MPS2	Medium pressure steam 2
HPS1	High pressure steam 1
HPS2	High pressure steam 2
CTBE1	Steam used in CTBE (Brazilian Bio-ethanol Science and Technology Laboratory) acid-catalysed steam explosion reactor (low pressure)
CTBE2	Steam used in CTBE steam explosion reactor (medium pressure)

g		Components involved in environmental impact calculations *AceA, Acid, AcidFl, Bag, CH4, CTBE1, CTBE2, Enz, Eth, Furf, HPS1, HPS2, LPS, MPS1, MPS2, NaOH, Water* Where: *AcidFl* is the acid in the flash vapour, *CH4* is the methane produced, *Eth* is the ethanol produced.
unit		Set of processing units used in models
	AcidCellHyd	Acid hydrolysis unit
	Delig	Delignification unit
	EnzHyd	Enzymatic hydrolysis unit
	FictCell	Fictitious acid hydrolysis unit
	FictIN	Input to fictitious acid hydrolysis unit
	FictOUT	Output from fictitious acid hydrolysis unit
	FiltCellHyd	Filter following acid hydrolysis unit
	FiltDelig	Filter following delignification unit
	FiltEnz	Filter following enzymatic hydrolysis unit
	FiltPreHyd	Filter following acid pre-treatment unit
	FiltSteamEx	Filter following steam explosion unit
	FlsAcidCellHyd	Flash following acid hydrolysis unit
	FlsPreHyd	Flash following acid pre-treatment unit
	FlsSteamEx	Flash following steam explosion unit
	HXDelig	Heat exchanger after delignification mixer and before delignification unit
	MixAcidCellHyd	Mixer of components for acid hydrolysis
	MixDelig	Mixer of components for delignification
	MixEnzHyd	Mixer of components for enzymatic hydrolysis
	MixPreHyd	Mixer of components for acid pre-treatment
	MixSteamEx	Mixer of components for steam explosion
	PreHyd	Acid pre-treatment unit
	SnkC5	Sink for liquid stream rich in pentose sugars
	SnkC6	Sink for liquid stream rich in hexose sugars
	SnkCW	Sink for cooling water out of HX1 heat exchanger
	SnkDelig	Liquid sink from delignification unit (contains Na_2SO_4)
	SnkSolid	Sink for solids remaining after hydrolysis
	SnkSteam	Sink for steam out of HXDelig heat exchanger
	SnkVapFlsh1	Vapour sink from acid pre-treatment flash
	SnkVapFlsh2	Vapour sink from acid hydrolysis flash
	SnkVapFlsh3	Vapour sink from steam explosion flash
	SrcAcid	Source of acid (98 wt% H_2SO_4, 2% water)
	SrcBag	Source of sugarcane bagasse
	SrcBal	Source of component balance, used to fix steam explosion mass balance
	SrcDelig	Source of NaOH used in delignification (98 wt% NaOH, 2 wt% water)
	SrcEnz	Source of enzymes (98 wt% enzymes, 2 wt% water)
	SrcSteam	Source of steam used for heating
	SrcWater	Source of water used for dilution and cooling
	SteamEx	Steam explosion unit

Parameters		Value
B_J	Variable costs of raw materials and products	See *Table 3.7.1.* kg/t
$CEPCI_{2004}$	CEPCI (Chemical Engineering Plant Cost Index) for 2004	444.2
$CEPCI_{2005}$	CEPCI for 2005	468.2
$CEPCI_{2014}$	CEPCI for 2014	577
$C_{P,J}$	Individual component heat capacities	See *Table A.1.1* $kJ.kg^{-1}.K^{-1}$
E_{EnzHyd}	Mass fraction of enzymes in the mixed stream entering the enzymatic hydrolysis reactor	0.000487805
$F_{HXDelig}$	Heat exchanger F_T correction factor	0.9
Fls	Linear parameters for determining the fraction of liquid vapourised in the flash following acid hydrolysis ($X_{CellHydVap,L(J),n}$)	See *Appendix A.3.2*
H	Acid hydrolysis Arrhenius data sets	See *Table A.3.3*
$Lang$	Lang factor for solid-fluid operations	4.41
MF_{unit}	Material factor of reactors	See *Table 3.7.3*
MW_J	Molar mass of components	See *Table A.1.1* kg/kmol
P	Acid pre-hydrolysis data sets	See *Appendix A.2.3.1*
PF_{unit}	Pressure factor of reactors	See *Table 3.7.3*
R_{Acid}	Mass ratio of acid in steam explosion relative to bagasse flowrate	0.0025
$R_{ASL,AcidCellHyd}$	Mass ratio of lignin solubilised in acid hydrolysis unit per grams of solid	mg/g solid
$R_{SteamEx}$	Mass ratio of steam in steam explosion relative to bagasse flowrate (un-catalysed)	0.254
$R_{SteamExAcid}$	Mass ratio of steam in steam explosion relative to bagasse flowrate (acid-catalysed)	0.183
$Temp_{SteamEx}$	Temperature of steam explosion unit (un-catalysed) in K	463.15
$Temp_{SteamExAcid}$	Temperature of steam explosion unit (acid-catalysed) in K	423.15
$T_{SteamSupply,st}$	Steam *st* supply temperature	See *Table 3.7.2*
$T_{SteamTarget,st}$	Steam *st* target temperature	See *Table 3.7.2*
$U_{HXDelig}$	Overall heat transfer co-efficient	1845 $W.m^{-2}.K^{-1}$
$W_{AcidCellHyd}$	Water to solids mass ratio in the acid cellulose hydrolysis unit	kg water/ kg solids
W_{Delig}	Water to solids mass ratio in the delignification unit	kg water/ kg solids
W_{EnzHyd}	Mass fraction of water in the mixed stream entering the enzymatic hydrolysis reactor	0.887380069
W_{PreHyd}	Water to solids mass ratio in the acid pre-hydrolysis unit	kg water/ kg solids
$X_{EnzHyd,r}$	Conversion of reference component in reaction r in enzymatic hydrolysis unit	See *Table 3.6.1*
$X_{FlsSteamEx,L(J)}$	Mass percentage vapourised of liquid components in flash after steam explosion	See *Table 3.2.2*
$X_{FlsSteamExAcid,L(J)}$	Mass percentage vapourised of liquid components in flash after acid-catalysed steam explosion	See *Table 3.2.2*
$X_{Hemi,AcidCellHyd}$	Conversion of hemicellulose to xylose in acid cellulose hydrolysis unit	0.99
$X_{PreHydVap,L(J),n}$	Fraction vapourised of liquids in the flash following acid pre-hydrolysis	See *Appendix A.2.3.2*
$x_{SCB,J}$	Mass fraction of component J in sugarcane bagasse	See *Table A.1.1*

$X_{SteamEx,r}$	Conversion of reference component in reaction r in steam explosion unit	See *Table 3.2.1*
$X_{SteamExAcid,r}$	Conversion of reference component in reaction r in acid-catalysed steam explosion unit	See *Table 3.2.1*
$X_{XylFurf,AcidCellHyd}$	Conversion of xylose to furfural in acid cellulose hydrolysis unit	0.8
$y_{FiltSol}$	Mass fraction of solid components exiting the filter in the solids slurry	0.995
$\Delta H_{rxn,ppt}$	Precipitation heat of reaction	kJ/kmol
$\Delta H_{vap,steam}$	Steam heat of vapourisation	kJ/kg
ΔT_{min}	Minimum approach temperature	5 K
ρ_J	Density of component	See *Table A.1.1* kg/m^3
τ_{Delig}	Residence time of the delignification unit	40 min
τ_{EnzHyd}	Residence time of the enzymatic hydrolysis unit	4320 min
$\tau_{SteamEx}$	Residence time of the steam explosion unit	15 min

Scalars		Value
$Temp_{Amb}$	Ambient temperature	303.15 K
$Temp_{CTBEFlsh}$	Temperature of flash following steam explosion unit (un-catalysed)	374.01 K
$Temp_{Delig}$	Delignification unit temperature	393.15 K
$Temp_{EnzHyd}$	Enzymatic hydrolysis temperature	323.15 K
$Temp_{Max}$	Maximum stream temperature	573.15 K
$Temp_{Max,AcidHyd}$	Upper temperature for acid hydrolysis unit	503.15 K
$Temp_{Max,PreHyd}$	Upper temperature for acid pre-hydrolysis unit	401.15 K
$Temp_{Min,\ PreHyd}$	Lower temperature for acid pre-hydrolysis unit	373.15 K
$Temp_{Min,AcidHyd}$	Lower temperature for acid hydrolysis unit	453.15 K
$Temp_{SteamEx}$	Temperature of steam explosion unit (un-catalysed)	463.15 K
$Temp_{SteamExAcid}$	Temperature of steam explosion unit (acid-catalysed)	423.15 K

Some of these scalars appear in equations particularly when a binary variable determines the unit temperature, for example: the temperature of the steam explosion unit. Other scalars were used as part of the initialisations: to fix certain reactor temperatures, for example: the delignification unit; while some were used to bound reactor temperatures, for example: the acid hydrolysis unit.

Variables		Units
$Area_{Filt}$	Surface area of filter	m^2
$Area_{HXDelig}$	Heat exchanger area	m^2
A_{unit}	Acid weight percent	%
$C_{b,HXDelig}$	Base cost of heat exchanger	$ in 2005
C_{Rem}	Fraction of cellulose remaining after acid cellulose hydrolysis	%
D_{unit}	Diameter of unit	m
$EI_{c,e}$	Environmental impact of component *e* in category *c*	$year^{-1}$
$f_{J,unit,unit1}$	Mass flowrate of component J between unit and unit1	kg/s
$F_{unit,unit1}$	Total flowrate between unit and unit1	kg/s
$LMTD_{HXDelig}$	Log mean temperature difference	K
L_{unit}	Length or height of unit	m
$MF_{HXDelig}$	Material factor of $HXDelig$	-
N_{Delig}	Sodium hydroxide percent entering the delignification unit	w/v %
$newX_{EnzHyd,r}$	New conversion of reference component in reaction r in enzymatic hydrolysis unit	-
$n_{J,unit,unit1}$	Molar flowrate of component J between unit and unit1	kmol/s
PCE_{unit}	Purchased cost of equipment	$ in 2014
$Profit$	Annualised profit, used in economic objective function	R1 000 000 /year
$Q_{HXDelig}$	Heat added by steam in the delignification heat exchanger	kJ
Rev_{CH4}	Methane revenue from xylose stream, *SnkC5*	R1 000 000 /year
$R_{L/D}$	Ratio of vessel length over diameter	-
$S_{unitFiltSplit}$	Mass split fraction of each liquid component exiting the filter in the solids slurry	-
$S_{unitLiqFrac}$	Total mass fraction of liquid components in the solids slurry exiting the filter	-
$TotEI$	Total environmental impact, used in environmental objective function	$year^{-1}$
V_{unit}	Volume of unit	m^3
$X_{CellHydVap,L(J),n}$	Fraction of liquids vapourised in the flash following acid hydrolysis	-
$x_{J,unit,unit1}$	Mass fraction of component J between unit and unit1	-
Y_{Decr}	Decrease in glucose yield between the fictitious and real acid cellulose hydrolysis reactors	%
Y_{Fict}	Percentage yield of glucose in fictitious acid cellulose hydrolysis reactor	%
$Y_{Inc,EnzHyd}$	Change in conversion for the reactions involving cellulose in the enzymatic hydrolysis unit	%
Y_{Real}	Percentage yield of glucose in real acid cellulose hydrolysis reactor	%
$\tau_{CellHyd}$	Residence time of the acid hydrolysis unit	min
τ_{PreHyd}	Residence time of the acid pre-hydrolysis unit	min
$\dot{V}_{unit,unit1}$	Volumetric flowrate of component J between unit and unit1	m^3/s
Binary variables		*n*
$z_{AcidCellHyd,n}$	Choice of acid weight percent in acid cellulose hydrolysis unit	3
$z_{PreHyd,n}$	Choice between data sets for acid pre-hydrolysis	13
$z_{SteamCellHyd,st}$	Choice between steam pressures in acid cellulose hydrolysis unit	7
$z_{SteamEx,n}$	Choice between acid-catalysed or un-catalysed steam explosion	2
$z_{unit,n}$		

3.1.2. Determination of Bagasse Flowrate

The data shown in *Table 3.2* below gives the capacities of South Africa sugarcane mills (The Sugar Engineers, n.d.). These capacities were converted to a flowrate of bagasse as follows for Amatikulu mill:

$$2069760\frac{t\ cane}{year} \times 240\frac{kg\ SCB}{t\ cane} \times \frac{1}{365 \times 24 \times 60 \times 60} = 15.8\ kg\ SCB/s$$

Where: 240 is the amount of bagasse with 50% humidity per ton of sugarcane (Dias et al., 2009).

The average mill size was found to be 13 kg/s however a flowrate of 15 kg/s was used in the models as bio-ethanol production is more likely to be implemented on the larger plants. This is still smaller than a large capacity Brazilian plant which would produce about 26.3 kg/s of sugarcane bagasse as is shown in the calculation below:

$$493\frac{t\ cane}{hour} \times 240\frac{kg\ SCB}{t\ cane} \times 0.8 \div 3600 = 26.3\ kg\ SCB/s$$

Where: 0.8 is the percentage of sugarcane that is used for ethanol production (Dias et al., 2009).

Table 3.2: South African sugarcane mill capacities (The Sugar Engineers, n.d.)

Mill	Crushing Capacity 10^3 t/year	Bagasse Produced kg/s
Amatikulu	2 070	15.8
Darnall	1 640	12.5
Eston	1 400	10.7
Felixton	2 500	19.0
Gledhow	1 510	11.5
Komati	2 500	19.0
Maidstone	2 340	18.0
Malelani	1 830	13.9
Noodsberg	1 340	10.2
Pongola	1 400	10.7
Sezela	2 500	19.0
UCL	775	5.90
Umfolozi	1 200	9.13
Umzikulu	1 400	10.7

3.2. Steam Explosion Model

Many studies have been performed using steam explosion on lignocellulosic materials (Garrote, Dominguez & Parajo, 1999; Laser et al., 2002; Martín, Marcet & Thomsen, 2008; Carrasco et al., 2010) however, it was difficult to adapt data from these papers into a rigorous mass balance as not all the required components were measured. The model used in this study was based on an Aspen simulation for steam explosion for bagasse pre-treatment developed by CTBE (Brazilian Bio-ethanol Science and Technology Laboratory) (Bonomi et al., 2011). The CTBE model was based on a paper by Rocha et al. (2012). Both un-catalysed and acid-catalysed steam explosions were modelled in this study. *Figure 3.4* below (which is also delineated as '**Steam Explosion**' in the overall superstructure of *Figure 3.2*) shows a block flow diagram of the units in the model (as used in this study) with their GAMS unit names shown. In the actual process, the mixer, flash and the steam explosion unit are one physical unit but they were modelled as three separate units in this study so that flowrates through each separate operation could be seen and checked.

The GAMS code for the steam explosion model can be found in *Appendix B.1*. The model is a mixed-integer non-linear program as there is a binary choice between acid-catalysed or un-catalysed steam explosion, and some capital costing equations in the economic objective function are non-linear. This GAMS model is used in the SA, SDA, SE and SDE flowsheets shown in *Figure 3.3*.

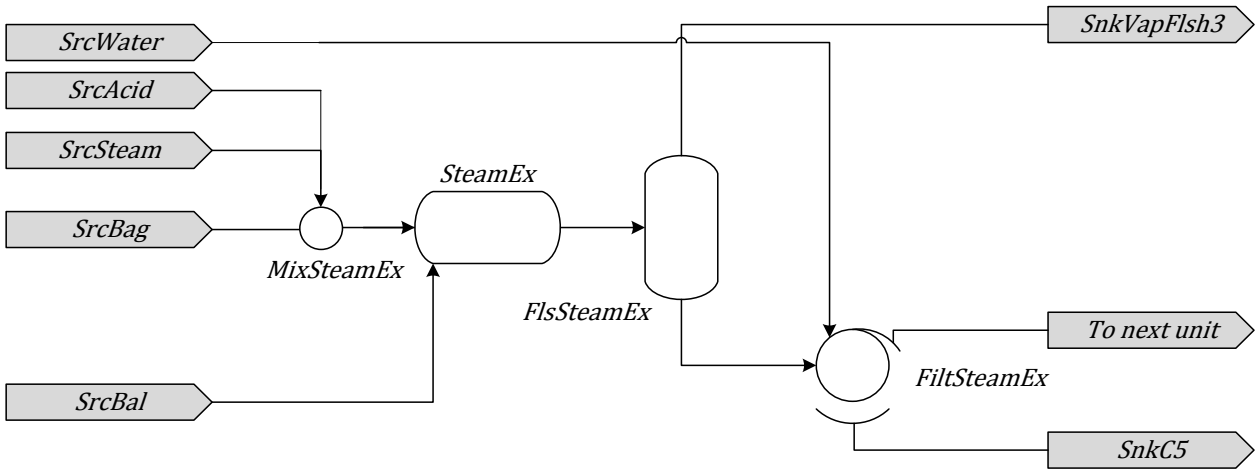


Figure 3.4: Block flow diagram for steam explosion model

3.2.1. Steam Explosion Mixer Equations ($MixSteamEx$)

All the components required in the reactor, $SteamEx$, are first mixed in the mixer, $MixSteamEx$. In reality the mixer may not exist but it was easier to include this unit to set up the model equations. The flowrate of sugarcane bagasse from $SrcBag$ is fixed. Steam and acid are added based on mass ratios, R_{Acid}, $R_{SteamEx}$ and $R_{SteamExAcid}$.

Setting the component mass fractions in the sugarcane bagasse stream based on parameter $x_{SCB,J}$:

$$x_{J,SrcBag,MixSteamEx} = x_{SCB,J}$$

Binary variables, $z_{SteamEx,n}$, are used to choose between the un-catalysed and the acid-catalysed steam explosion reactor. The following logical condition on the sum of binary variables is necessary:

$$\sum_{n} z_{SteamEx,n} = 1$$

Where: $z_{SteamEx,1}$ represents the un-catalysed reactor and $z_{SteamEx,2}$ represents the acid-catalysed reactor.

Calculating the acid flowrate into the steam explosion mixer based on a mass ratio of acid to bagasse, R_{Acid}:

$$f_{Acid,SrcAcid,MixSteamEx} = F_{SrcBag,MixSteamEx}\left[R_{Acid} \cdot z_{SteamEx,2}\right]$$

Where: F represents total mass flowrates [kg/s] and f represents component mass flowrates [kg/s].

Calculating the steam flowrate into the steam explosion mixer based on a mass ratio to bagasse, $R_{SteamEx}$ and $R_{SteamExAcid}$:

$$F_{SrcSteam,MixSteamEx} = F_{SrcBag,MixSteamEx}\left[R_{SteamEx} \cdot z_{SteamEx,1} + R_{SteamExAcid} \cdot z_{SteamEx,2}\right]$$

Component mass balance over steam explosion mixer:

$$f_{J,MixSteamEx,SteamEx} = f_{J,SrcBag,MixSteamEx} + f_{J,SrcSteam,MixSteamEx} + f_{J,SrcAcid,MixSteamEx}$$

Component mole balance over steam explosion mixer:

$$n_{J,MixSteamEx,SteamEx} = n_{J,SrcBag,MixSteamEx} + n_{J,SrcSteam,MixSteamEx} + n_{J,SrcAcid,MixSteamEx}$$

Where: n represents the component molar flowrate [kmol/s].

Setting the exit temperature of the mixer using parameters, $Temp$:

$$T_{MixSteamEx,SteamEx} = Temp_{SteamEx} \cdot z_{SteamEx,1} + Temp_{SteamExAcid} \cdot z_{SteamEx,2}$$

Setting the temperature of the mixed stream to the steam temperature:

$$T_{MixSteamEx,SteamEx} = T_{SrcSteam,MixSteamEx}$$

3.2.2. Steam Explosion Reactor Equations ($SteamEx$)

The reactor, $SteamEx$, is where the lignocellulose is converted to sugars and degradation products. *Table 3.3* below shows the reactions used in the steam explosion reactor and the conversions of these reactions for un-catalysed and acid-catalysed steam explosion. The overall mass balance and component mass balances are shown below.

Table 3.3: Reactions and conversions for steam explosion reactor

r	Reaction	Reference Component (Ref. Cmpnt)	Conversion of Ref. Cmpnt $X_{SteamEx,r}$	Conversion of Ref. Cmpnt With Acid $X_{SteamExAcid,r}$
1	Water + Cellulose → Glucose	Cellulose	0.005	0.050
2	Cellulose → Glucose Oligomers	Cellulose	0.030	0.020
3	Cellulose → 2 Water + HMF	Cellulose	0.015	0.015
4	Water + Hemicellulose → Xylose	Hemicellulose	0.300	0.650
5	Hemicellulose → Xylose Oligomers	Hemicellulose	0.300	0.050
6	Hemicellulose → Furfural + 2 Water	Hemicellulose	0.100	0.100
7	Lignin → Soluble Lignin	Lignin	0.100	0.150
8	Acetyl → Acetic acid	Acetyl	0.700	0.800
9	Water + Sucrose → 2 Glucose	Sucrose	0.500	0.500
10	Sucrose → 5 Water + 2 HMF	Sucrose	0.500	0.500

The reactor overall mass balance:

$$F_{MixSteamEx,SteamEx} = F_{SteamEx,FlsSteamEx}$$

Mole balance for cellulose:

$$\begin{aligned} n_{Cellulose,SteamEx,FlsSteamEx} &= n_{Cellulose,MixSteamEx,SteamEx}\{1 - \left[X_{SteamEx,1}.z_{SteamEx,1} + X_{SteamExAcid,1}.z_{SteamEx,2}\right] \\ &\quad -\left[X_{SteamEx,2}.z_{SteamEx,1} + X_{SteamExAcid,2}.z_{SteamEx,2}\right] \\ &\quad -\left[X_{SteamEx,3}.z_{SteamEx,1} + X_{SteamExAcid,3}.z_{SteamEx,2}\right]\} \end{aligned}$$

Mole balance for glucose:

$$\begin{aligned} n_{Gluc,SteamEx,FlsSteamEx} &= n_{Cellulose,MixSteamEx,SteamEx}\left[X_{SteamEx,1}.z_{SteamEx,1} + X_{SteamExAcid,1}.z_{SteamEx,2}\right] \\ &\quad + 2n_{Sucrose,MixSteamEx,SteamEx}\left[X_{SteamEx,9}.z_{SteamEx,1} + X_{SteamExAcid,9}.z_{SteamEx,2}\right] \end{aligned}$$

Mole balance for glucose oligomers:

$$\begin{aligned} n_{GlucOlig,SteamEx,FlsSteamEx} &= n_{Cellulose,MixSteamEx,SteamEx}\left[X_{SteamEx,2}.z_{SteamEx,1} + X_{SteamExAcid,2}.z_{SteamEx,2}\right] \end{aligned}$$

Mole balance for HMF:

$$\begin{aligned} n_{HMF,SteamEx,FlsSteamEx} &= n_{Cellulose,MixSteamEx,SteamEx}\left[X_{SteamEx,3}.z_{SteamEx,1} + X_{SteamExAcid,3}.z_{SteamEx,2}\right] \\ &\quad + 2n_{Sucrose,MixSteamEx,SteamEx}\left[X_{SteamEx,10}.z_{SteamEx,1} + X_{SteamExAcid,10}.z_{SteamEx,2}\right] \end{aligned}$$

Mole balance for hemicellulose:

$$n_{Hemi,SteamEx,FlsSteamEx} = n_{Hemi,MixSteamEx,SteamEx}\{1 - [X_{SteamEx,4}.z_{SteamEx,1} + X_{SteamExAcid,4}.z_{SteamEx,2}] - [X_{SteamEx,5}.z_{SteamEx,1} + X_{SteamExAcid,5}.z_{SteamEx,2}] - [X_{SteamEx,6}.z_{SteamEx,1} + X_{SteamExAcid,6}.z_{SteamEx,2}]\}$$

Mole balance for xylose:

$$n_{Xylo,SteamEx,FlsSteamEx} = n_{Hemi,MixSteamEx,SteamEx}[X_{SteamEx,4}.z_{SteamEx,1} + X_{SteamExAcid,4}.z_{SteamEx,2}]$$

Mole balance for xylose oligomers:

$$n_{XylOlig,SteamEx,FlsSteamEx} = n_{Hemi,MixSteamEx,SteamEx}[X_{SteamEx,5}.z_{SteamEx,1} + X_{SteamExAcid,5}.z_{SteamEx,2}]$$

Mole balance for furfural:

$$n_{Furf,SteamEx,FlsSteamEx} = n_{Hemi,MixSteamEx,SteamEx}[X_{SteamEx,6}.z_{SteamEx,1} + X_{SteamExAcid,6}.z_{SteamEx,2}]$$

Mole balance for lignin:

$$n_{Lignin,SteamEx,FlsSteamEx} = n_{Lignin,MixSteamEx,SteamEx}\{1 - [X_{SteamEx,7}.z_{SteamEx,1} + X_{SteamExAcid,7}.z_{SteamEx,2}]\}$$

Mole balance for soluble lignin:

$$n_{ASL,SteamEx,FlsSteamEx} = n_{Lignin,MixSteamEx,SteamEx}[X_{SteamEx,7}.z_{SteamEx,1} + X_{SteamExAcid,7}.z_{SteamEx,2}]$$

Mole balance for acetyl:

$$n_{Acetyl,SteamEx,FlsSteamEx} = n_{Cellulose,MixSteamEx,SteamEx}\{1 - [X_{SteamEx,8}.z_{SteamEx,1} + X_{SteamExAcid,8}.z_{SteamEx,2}]\}$$

Mole balance for acetic acid:

$$n_{AceA,SteamEx,FlsSteamEx} = n_{Acetyl,MixSteamEx,SteamEx}[X_{SteamEx,8}.z_{SteamEx,1} + X_{SteamExAcid,8}.z_{SteamEx,2}]$$

Mole balance for sucrose:

$$n_{Sucrose,SteamEx,FlsSteamEx} = n_{Sucrose,MixSteamEx,SteamEx}\{1 - [X_{SteamEx,9}.z_{SteamEx,1} + X_{SteamExAcid,9}.z_{SteamEx,2}] - [X_{SteamEx,10}.z_{SteamEx,1} + X_{SteamExAcid,10}.z_{SteamEx,2}]\}$$

Mole balance for water:

$$
\begin{aligned}
n_{Water,SteamEx,FlsSteamEx} &= n_{Water,MixSteamEx,SteamEx} \\
&- n_{Cellulose,MixSteamEx,SteamEx}\{[X_{SteamEx,1}.z_{SteamEx,1} + X_{SteamExAcid,1}.z_{SteamEx,2}] \\
&\quad - 2[X_{SteamEx,3}.z_{SteamEx,1} + X_{SteamExAcid,3}.z_{SteamEx,2}]\} \\
&- n_{Hemi,MixSteamEx,SteamEx}\{[X_{SteamEx,4}.z_{SteamEx,1} + X_{SteamExAcid,4}.z_{SteamEx,2}] \\
&\quad - 2[X_{SteamEx,6}.z_{SteamEx,1} + X_{SteamExAcid,6}.z_{SteamEx,2}]\} \\
&- n_{Hemi,MixSteamEx,SteamEx}\{[X_{SteamEx,4}.z_{SteamEx,1} + X_{SteamExAcid,4}.z_{SteamEx,2}] \\
&\quad - 2[X_{SteamEx,6}.z_{SteamEx,1} + X_{SteamExAcid,6}.z_{SteamEx,2}]\} \\
&+ n_{Sucrose,MixSteamEx,SteamEx}\{-[X_{SteamEx,9}.z_{SteamEx,1} + X_{SteamExAcid,9}.z_{SteamEx,2}] \\
&\quad + 5[X_{SteamEx,10}.z_{SteamEx,1} + X_{SteamExAcid,10}.z_{SteamEx,2}]\}
\end{aligned}
$$

Mass balance for components that are inert in the process $(Acid, Min, OrgAc, Phos, Salts, Soil)$:

$$f_{i(J),MixSteamEx,SteamEx} = f_{i(J),SteamEx,FlsSteamEx}$$

Mass balance for components that are inert in the steam explosion unit $(Enz, NaOH)$:

$$f_{si(J),MixSteamEx,SteamEx} = f_{si(J),SteamEx,FlsSteamEx}$$

The overall mass balance over the unit was found to be out by a small amount. This is possibly due to slight inaccuracies in the molar masses. As this is problematic in GAMS a fictitious component called $Balance$ was added into the reactor to fix the mass balance.

Mass balance for component $Balance$:

$$f_{Balance,SrcBal,SteamEx} = f_{Balance,SteamEx,FlsSteamEx}$$

3.2.3. Steam Explosion Flash Equations *(FlsSteamEx)*

The steam explosion reactor performs an explosion decompression which breaks the sugarcane bagasse apart and causes some of the liquid components to vapourise. This was modelled as a flash unit, $FlsSteamEx$, with mass percentage vaporised of liquid components, $X_{FlsSteamEx,L(J)}$ and $X_{FlsSteamExAcid,L(J)}$.

Setting the flash temperature using parameter $Temp_{CTBEFlsh}$:

$$T_{SteamEx,FlsSteamEx} = Temp_{CTBEFlsh}$$

Setting the temperature of the flash exit streams:

$$T_{FlsSteamEx,SnkVapFlsh3} = T_{SteamEx,FlsSteamEx}$$

$$T_{FiltSteamEx,SnkC5} = T_{SteamEx,FlsSteamEx}$$

Overall component mass balance:

$$f_{J,SteamEx,FlsSteamEx} = f_{J,FlsSteamEx,FiltSteamEx} + f_{J,FlsSteamEx,SnkVapFlsh3}$$

It was assumed that all solid components end up in the liquid stream.

Mass flowrate of solid components in exiting liquid stream, $FlsSteamEx$:

$$f_{S(J),FlsSteamEx,FiltSteamEx} = f_{S(J),SteamEx,FlsSteamEx}$$

Flash equations using Antoine coefficients are non-linear which cause difficulties for the solvers. Instead a linear conversion percentage approach was used to model the flash. These conversion factors were based on the CTBE Aspen simulation (Bonomi et al., 2011). *Table 3.4* below shows the percentage vapourised for the liquid components in the flash, $X_{FlsSteamEx,L(J)}$ and $X_{FlsSteamExAcid,L(J)}$.

Table 3.4: Percentage vapourised for liquid components in flash following the steam explosion reactor

Component	**Steam Explosion Flash** $X_{FlsSteamEx,L(J)}$	**Acid-Catalysed Steam Explosion Flash** $X_{FlsSteamExAcid,L(J)}$
Acetic Acid	0.0630	0.0319
Acid Soluble Lignin	0	0
Balance	0	0
Furfural	0.627	0.438
Glucose	6.2×10^{-9}	3.0×10^{-9}
Glucose Oligomers	6.2×10^{-9}	3.0×10^{-9}
H_2SO_4	0	1.49×10^{-5}
HMF	4.05×10^{-4}	1.99×10^{-4}
Organic Acid	7.71×10^{-6}	3.78×10^{-6}
Sucrose	0	0
Water	0.235	0.131
Xylose	3.17×10^{-6}	1.55×10^{-6}
Xylose Oligomers	3.17×10^{-6}	1.55×10^{-6}

Using these percentages the mass flowrates of each liquid component exiting the flash in the liquid and vapour streams were calculated.

Mass flowrate of liquid components in exiting liquid stream:

$$f_{L(J),FlsSteamEx,FiltSteamEx} = f_{L(J),SteamEx,FlsSteamEx}\left\{1 - \left[X_{FlsSteamEx,L(J)} \cdot z_{SteamEx,1} + X_{FlsSteamExAcid,L(J)} \cdot z_{SteamEx,2}\right]\right\}$$

Mass flowrate of liquid components in exiting vapour stream:

$$f_{L(J),FlsSteamEx,SnkVapFlsh3} = f_{L(J),SteamEx,FlsSteamEx}\left[X_{FlsSteamEx,L(J)} \cdot z_{SteamEx,1} + X_{FlsSteamExAcid,L(J)} \cdot z_{SteamEx,2}\right]$$

3.2.4. Steam Explosion Filter Equations ($FiltSteamEx$)

All the solid-liquid filters were modelled in the same way. The liquid stream exiting the filter must have a liquid mass fraction between 0.5 and 0.6 to enable it to be pumped. In some filters this requires the addition of water using stream, $F_{SrcWater,FilterUnit}$, however it was possible for this flowrate to be zero in cases where the liquid content was already sufficient for pumping.

Overall flowrate mass balance over steam explosion filter unit:

$$F_{FlsSteamEx,FiltSteamEx} + F_{SrcWater,FiltSteamEx} = F_{FiltSteamEx,HX1} + F_{FiltSteamEx,SnkC5}$$

Component mass balances over steam explosion filter unit:

$$f_{J,FlsSteamEx,FiltSteamEx} + f_{J,SrcWater,FiltSteamEx} = f_{J,FiltSteamEx,HX1} + f_{J,FiltSteamEx,SnkC5}$$

Overall energy balance for the filter to determine temperature changes if water is added:

$$\sum_J \left(f_{J,FlsSteamEx,FiltSteamEx}.C_{P,J}.T_{FlsSteamEx,FiltSteamEx}\right) + \sum_J \left(f_{SrcWater,FiltSteamEx}.C_{P,J}.T_{SrcWater,FiltSteamEx}\right) = \sum_J \left(f_{FiltSteamEx,HX1}C_{P,J}.T_{FiltSteamEx,HX1}\right) + \sum_J \left(f_{FiltSteamEx,SnkC5}.C_{P,J}.T_{FiltSteamEx,SnkC5}\right)$$

Equation to ensure the temperature of the two exiting streams is the same:

$$T_{FiltSteamEx,HX1} = T_{FiltSteamEx,SnkC5}$$

Mass flowrate of solid components in the filter cake:

$$f_{S(J),FiltSteamEx,HX1} = f_{S(J),FlsSteamEx,FiltSteamEx}.y_{FiltSol}$$

Where: the parameter $y_{FiltSol}$ is the mass fraction of solid components exiting the filter in the solids slurry.

Mass flowrate of liquid components in the filter cake:

$$f_{L(J),FiltSteamEx,HX1} = \left(f_{L(J),FlsSteamEx,FiltSteamEx} + f_{L(J),SrcWater,FiltSteamEx}\right).S_{SteamExFiltSplit}$$

Where: the variable $S_{SteamExFiltSplit}$ is the mass split fraction of each liquid component exiting the filter in the solids slurry. This value is the same for each component and this is bounded between 0.05 and 0.3 to represent typical filter operation.

The definition of the variable $S_{SteamExLiqFrac}$ is shown in the equation below:

$$S_{SteamExLiqFrac} = \sum_{L(J)} \left(\frac{f_{L(J),FiltSteamEx,HX1}}{F_{FiltSteamEx,HX1}}\right)$$

Where: $S_{SteamExLiqFrac}$ is the total mass fraction of liquid components in the solids slurry exiting the filter. This is bounded between 0.5 and 0.6 to ensure the slurry can be pumped.

Water is added using $F_{SrcWater,FiltSteamEx}$, if necessary, to ensure $S_{SteamExLiqFrac}$ meets the limits described above. The following equation was used to initialise the water flowrate:

$$F_{SrcWater,FiltSteamEx} \geq 1.5 \sum_{S(J)} f_{S(J)FiltSteamEx,HX1}$$

In some filters ($FiltEnz$ and $FiltDelig$) where the stream entering the filter already has a high liquid fraction and less or possibly no water is needed, the parameters, $F_{SrcWater,FiltSteamEx}$ and $f_{S(J)FiltSteamEx,HX1}$, in this equation are related to one another using 'less than' rather than 'greater than'.

An upper limit was placed on the mass fraction of water in the $SnkC5$ stream to prevent this stream from becoming too dilute:

$$x_{Water,FiltSteamEx,SnkC5} \leq 0.93$$

The component $Balance$ was used to fix inaccuracies in the mass balance that occurred from using a different number of decimal places for the molar masses in GAMS than in the Aspen simulation. $Balance$ is not required by the downstream units and so the following equation ensures all $Balance$ exits the system in the liquid stream, $SnkC5$.

Mass flowrate of component $Balance$ over the filter:

$$f_{Balance,FiltSteamEx,SnkC5} = f_{Balance,FlsSteamEx,FiltSteamEx}$$

This section summarised the model equations used in the steam explosion unit. The choice of reactor can be un-catalysed or acid-catalysed and this is selected using a binary variable, $z_{SteamEx,n}$. There is very little flexibility in the model as steam and acid are added based on mass ratios and temperature, while residence time and conversions are fixed for both acid-catalysed and un-catalysed scenarios.

3.3. Acid Pre-hydrolysis of Sugarcane Bagasse

Sulphuric acid is the most common acid used industrially for acid pre-hydrolysis of sugarcane bagasse (Sarkar et al., 2012; Moreno, Andersen & Díaz, 2013) and was chosen for use in this study due to the availability of kinetic data in the literature. Although many authors investigated the kinetics of xylose formation by sulphuric acid during pre-treatment of sugarcane bagasse (Lavarack, Griffin & Rodman, 2002; Zhao, Zhou & Liu, 2012) none of these determined kinetic parameters for the formation of acetic acid. Furfural, HMF and acetic acid inhibit fermentation and thus it is important to know the quantities of these inhibitors formed in pre-treatment. Aguilar et al. (2002) determined kinetic parameters for the formation of all these inhibitors at different temperatures and acid concentrations and thus was chosen for the GAMS models developed in this study. *Section 3.3.1* describes how reaction kinetics from literature were modelled using Matlab in order to generate datasets for the conversion and concentration of key components at specific temperatures and using fixed acid weight percentages for use in the GAMS model. The equations describing how these datasets were used in the GAMS model is then presented in *Section 3.3.2.*

3.3.1. Kinetics and Matlab Modelling of Acid Pre-hydrolysis

Aguilar et al. (2002) made use of the Saeman model (1945) which uses the reaction scheme shown below:

$$A \overset{k_1}{\rightarrow} B \overset{k_2}{\rightarrow} C$$

Where: k_1 is the rate constant of the generation reaction (min^{-1}) and k_2 is the decomposition rate constant (min^{-1}).

When used for cellulose, the reaction scheme has the following equation:

$$Cellulose \overset{k_1}{\rightarrow} Glucose \overset{k_2}{\rightarrow} Decomposition\ products$$

This can be generalised to the following form:

$$Polymers \overset{k_1}{\rightarrow} Monomers \overset{k_2}{\rightarrow} Decomposition\ products$$

The Saeman model (1945) has also been used to model the hydrolysis of hemicellulose and the reaction scheme is shown below:

$$Hemicellulose \overset{k_1}{\rightarrow} Xylose \overset{k_2}{\rightarrow} Decomposition\ products$$

The rate equations for each species, assuming the reactions are first order, are shown below:

$$R_A = \frac{dc_A}{dt} = -\alpha k_1 c_A$$

$$R_B = \frac{dc_B}{dt} = \alpha k_1 c_A - k_2 c_B$$

$$R_C = \frac{dc_C}{dt} = k_2 c_B$$

It is important to note that the concentrations, c_A, c_B and c_C, are all mass concentrations [kg/m^3]. Aguilar et al. (2002) introduced the α parameter as the model was inaccurate and a bad fit for the

data without α. The use of α is a common modification to the Saeman model (1945) (Rodríguez-Chong et al., 2004; Gámez et al., 2006; Lenihan et al., 2010). This modification assumes the existence of two types of polymer, one that is easy to hydrolyse and one that is difficult to hydrolyse. The α parameter represents the mass ratio between these different types of polymer [kg of easy to hydrolyse polymer/total kg polymer]. This α parameter is not measured but is determined using data regression analysis of experimental results and is a function of temperature and acid strength.

Aguilar et al. (2002) determined k and α values experimentally using the measured concentration of the *B* components for glucose and xylose. *Tables A.2.1* and *A.2.2* in *Appendix A.2.1* show the kinetic parameters for cellulose and hemicellulose as generated by Aguilar et al. (2002). In this study, Matlab models were developed using this data to generate concentration profiles for the various components in a continuously stirred tank reactor (CSTR). The general CSTR mass balance is shown below:

$$In - Out = Accumulation - Generation$$

For steady state operation it is assumed that there is no accumulation and thus the mass balance simplifies to the following equation:

$$In - Out = Generation$$

For a species, i, the following can be written and simplified:

$$F_{i,in} - F_{i,out} = -VR_i$$

$$\dot{V}(c_{i,in} - c_{i,out}) + VR_i = 0$$

$$1/\tau\,(c_{i,in} - c_{i,out}) + R_i = 0$$

Where: F_i is the mass flowrate [kg/s], V is the reactor volume [m^3], R_i is the reaction rate [kg.m^{-3}.s^{-1}], $\dot{V}$ is the volumetric flowrate [m^3/s], c_i is the mass concentration [kg/m^3] and τ is the residence time of the reactor [s].

The following equation for τ was used in the above simplification:

$$\tau = \frac{V}{\dot{V}}$$

Mass balances for components *A*, *B* and *C* can be written by substituting in the rate equations written above:

For A:

$$1/\tau\,(c_{A,in} - c_{A,out}) - \alpha k_1 c_{A,out} = 0$$

For B:

$$1/\tau\,(-c_{B,out}) + \alpha k_1 c_A - k_2 c_{B,out} = 0$$

For C:

$$1/\tau\,(-c_{C,out}) + k_2 c_{B,out} = 0$$

These mass balances were used in Matlab with the values for k and α to model the concentration profiles of xylose and glucose (B components), hemicellulose and cellulose (A components) and 5-hydroxymethyl furfural (C component).

Aguilar et al. (2002) also measured and modelled the formation rate of acetic acid and furfural as these components are inhibitors to fermentation. Kinetic models were developed for these components using the following reaction scheme and reaction rates:

$$D \xrightarrow{k} E$$

$$R_D = \frac{dc_D}{dt} = -kc_D$$

$$R_E = \frac{dc_E}{dt} = kc_E$$

The mass balances are derived in the same way as described above and these are shown below:

For D:

$$^1/_\tau\,(c_{D,in} - c_{D,out}) - kc_{D,out} = 0$$

For E:

$$^1/_\tau\,(-c_{E,out}) + kc_{D,out} = 0$$

In the above equations, $c_{D,in}$ is a regression parameter related to the stoichiometric amount of E that can be produced from D. As a result of this, $c_{D,in}$ is not actually the concentration of D. The kinetic parameters as presented by Aguiler et al. (2002) for furfural and acetic acid can be found in *Tables A.2.3* and *A.2.4* in *Appendix A.2.1.*

The Matlab code titled *ppalTablesIntArrAcetyl*, shown in *Appendix A.2.2,* is the principal code used in this study which plots the concentration profiles. This code calls the function *tablefuncFixSimpleAcetyl* which includes all the species balances. The principal code, *ppalTablesIntArrAcetyl*, also calls functions (*xylTableIntConcTempArr, glucTableIntConcTemp, aceticTableIntConcTemp* and *furfTableIntConcTemp*) which are used to select the appropriate k and α values from the tables of the kinetic parameters determined by Aguilar et al. (2002). These functions are also capable of performing linear interpolations to predict the change in the kinetic parameters with change in temperature and acid concentration. However the interpolation values were found to be inaccurate as the relationship is non-linear. Only specific values of acid concentration and temperature for which experimental values of k and α were present were used.

Arrhenius parameters were only provided for the k_1 parameter of hemicellulose by Aguilar et al. (2002) and as a result the temperature was not a free variable in the GAMS model of this study, but was restricted to discrete values. The Matlab code was run with each combination of temperatures (100°C, 122°C and 128°C) and acid concentration (2%, 4% and 6%). The graphs and data tables were used to choose the reactor residence time for each temperature and acid concentration combination of which there are nine. In some cases the concentration of hemicellulose decreased sharply therefore two residence times were chosen, one with a small residence time and one with a larger residence time, to include the option of removing more hemicellulose. For A components (hemicellulose and cellulose) and D components (acetyl, potential furfural) the conversion was calculated for the data tables. For B components (xylose and glucose) and E components (acetic acid and furfural) mass concentrations were used. These $P_{J,n}$ data tables can be seen in *Appendix A.2.3.1*. The subscript J represents the component and n is the number corresponding to the binary variable chosen. There were nine temperature and acid concentration combinations and the final number of data sets was thirteen as additional sets with larger residence times were taken for four combinations.

Lignin is partially soluble in acid, however Aguilar et al. (2002) neglected to determine the degree to which lignin is solubilised by acid pre-treatment. Lavarack et al. (2002) did investigate this and found that the following reaction scheme fits the data best:

$$Lignin\ (s) \xrightarrow{k_1} ASL\ (aq) \underset{k_3}{\overset{k_2}{\rightleftarrows}} Decomposition\ Products$$

Where the kinetic rate constants (k_1, k_2 and k_3) obey the Arrhenius equation shown below:

$$k_i = c_A^n\ A_i\ e^{-E_i/RT}$$

Where: A_i is the pre-exponential constant for reaction i [s^{-1}], c_A is the sulphuric acid concentration [wt%], E_i is the activation energy for reaction i [J/mol], n is the order of reaction which is dependent on acid concentration, T is the temperature [K] and R is the ideal gas constant [$J.mol^{-1}K^{-1}$].

Table 3.5 below shows the values for the required constants:

Table 3.5: Data for Arrhenius Equation for solubilisation of lignin in acid (Lavarack et al., 2002)

Kinetic Parameter	$\boldsymbol{A_i}$ [s^{-1}]	$\boldsymbol{E_i}$ [kJ/mol]	$\boldsymbol{n}$ [-]
$\boldsymbol{k_1}$	2.16×10^6	85.2	0.39
$\boldsymbol{k_2}$	1.23×10^9	95.7	0.39
$\boldsymbol{k_3}$	4.54×10^4	64.4	0.39

The following equation (Lavarack et al., 2002) can be used to determine the concentration of acid soluble lignin:

$$L_{ASL} = L_0\left[\frac{k_1-\phi k_3}{\phi k_3+\phi k_2-k_1}\ e^{-k_1 t} - \left(\frac{k_3}{k_2+k_3}+\frac{k_1-\phi k_3}{\phi k_3+\phi k_2-k_1}\right)e^{-\phi t(k_2+k_3)} + \frac{k_3}{k_2+k_3}\right]$$

Where: L_{ASL} is the final concentration of acid soluble lignin [g/g solid], L_0 is the initial lignin concentration in bagasse [0.235 g/g solid], t is the reaction time [s] and ϕ is the ratio of solid bagasse to liquid [g/g]. Acid pre-treatment has a water to solids ratio of 10 which is equivalent to ϕ of 0.1 and acid hydrolysis has a water to solids ratio of 20 which is equivalent to ϕ of 0.05.

The equation above is highly non-linear and would create difficulties for the solvers in the GAMS models. Instead, this equation was modelled in Matlab (see *Appendix A.2.2.* for code) and used to determine a fixed acid soluble lignin concentration for each acid pre-treatment dataset (the $P_{J,n}$ datasets in *Appendix A.2.3.1)* in the GAMS model. This was used to calculate the flowrate of solubilised lignin, component *ASL*, exiting the reactor.

The Matlab modelling was used to get datasets for the conversion and concentrations of the key components at specific temperatures and with specific acid concentrations for use in the GAMS model. The following section describes how these datasets were used in the GAMS model.

3.3.2. GAMS Modelling of Acid Pre-hydrolysis

The diagram below, *Figure 3.5* (which is the delineated section labelled '**Acid Pre-hydrolysis**' in *Figure 3.2*), illustrates the structure that was modelled in GAMS as a mixed-integer non-linear program due to binary choices among datasets generated through Matlab modelling in *Section 3.3.1* and non-linear capital cost equations in the economic objective function. In reality, the mixer, reactor and flash are one unit but they were separated in this study (as shown in *Figure 3.5*) so as to ensure clarity in the model and ensure the flowrates could be checked easily. According to Dias et al., (2009), the reactor acts as a flash to keep the reactor isothermal.

The GAMS code for the acid pre-hydrolysis model can be found in *Appendix B.2*. This code is used in the AA, ADA, AE and ADE flowsheets shown in *Figure 3.3*.

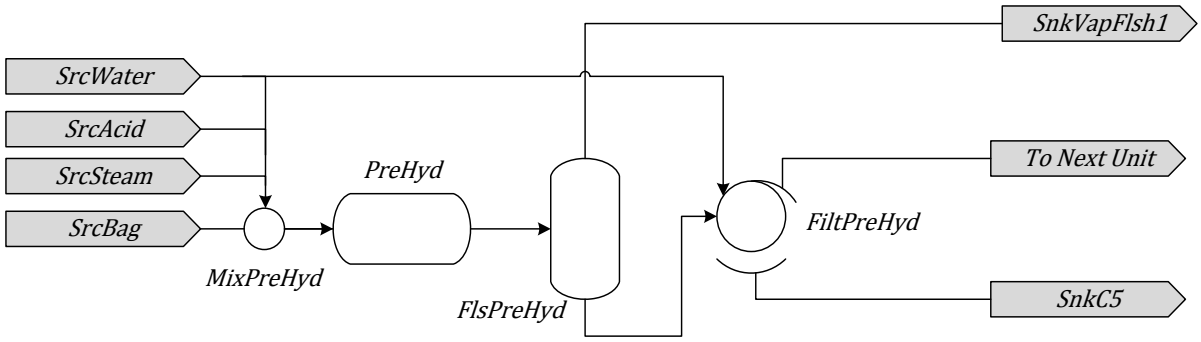


Figure 3.5: Diagram for acid pre-hydrolysis model

3.3.2.1. Acid Pre-hydrolysis Mixer Equations ($MixPreHyd$)

The components required in the reactor are mixed in the mixer. The amount of acid added depends on the acid weight percent, A_{PreHyd}, which depends on the $P_{J,n}$ dataset chosen. The amount of water and steam added must ensure that the water to solids ratio, W_{PreHyd}, is met. Steam is added to satisfy the energy balance and the temperature of this steam is fixed as low pressure steam (LPS) which provides enough heat to satisfy the reactor temperature (100°C, 122°C or 128°C).

Setting the component mass fractions in the sugarcane bagasse stream based on parameter, $x_{SCB,J}$:

$$x_{J,SrcBagasse,MixSteamEx} = x_{SCB,J}$$

Setting the acid mass fraction in the acid pre-hydrolysis unit using the acid weight percent, A_{PreHyd}:

$$x_{Acid,MixPreHyd,AcidCellHyd} = \frac{A_{PreHyd}}{100}$$

Water mass balance in the pre-hydrolysis mixer:

$$F_{SrcWater,MixPreHyd} + F_{SrcSteam,MixPreHyd} + f_{Water,SrcBag,MixPreHyd} + f_{Water,SrcAcid,MixPreHyd} = W_{PreHyd} \sum_{s(J)} f_{s(J),SrcBag,MixPreHyd}$$

This equation ensures that the water to solids mass ratio, W_{PreHyd}, is met.

Overall component mass balance in the pre-hydrolysis mixer:

$$f_{J,MixPreHyd,PreHyd} = f_{J,SrcWater,MixPreHyd} + f_{J,SrcSteam,MixPreHyd} + f_{J,SrcBag,MixPreHyd} + f_{J,SrcAcid,MixPreHyd}$$

Mixer energy balance:

$$\sum_J \left(f_{J,SrcBag,MixPreHyd} . C_{P,J} . T_{SrcBag,MixPreHyd}\right) + \sum_J \left(f_{SrcAcid,MixPreHyd} . C_{P,J} . T_{SrcAcid,FiltSteamEx}\right) + \sum_J \left(f_{SrcWater,MixPreHyd} . C_{P,J} . T_{SrcWater,FiltSteamEx}\right) + \sum_J \left(f_{SrcSteam,MixPreHyd} . C_{P,J} . T_{SrcSteam,FiltSteamEx}\right) + \sum_J \left(f_{SrcSteam,MixPreHyd} . \Delta H_{vap,LPS}\right) = \sum_J \left(f_{MixPreHyd,PreHyd} C_{P,J} . T_{MixPreHyd,PreHyd}\right)$$

3.3.2.2. Acid Pre-hydrolysis Reactor Equations ($PreHyd$)

In the reactor, the $P_{J,n}$ datasets are used extensively to calculate the flowrates of the components exiting the reactor. The explanation of how these datasets were determined is described in *Section 3.3.1.*

Overall mass balance for pre-hydrolysis unit:

$$F_{PreHyd,FlsPreHyd} = F_{MixPreHyd,PreHyd}$$

The mass balance of reacting components in the pre-hydrolysis unit use the datasets, $P_{J,n}$, calculated from using kinetic data from Aguilar et al. (2002) as described above in *Section 3.3.1*. It should be known that the form in which the $P_{J,n}$ is used is such that for reacting components (hemicellulose, cellulose and acetate) $P_{J,n}$ represents a conversion but for products (xylose, furfural, glucose, HMF and acetic acid), it represents the concentration [kg/m^3]. The data tables for $P_{J,n}$ can be seen in *Appendix A.2.3.1*.

It was assumed that none of the following components are present in the bagasse stream: glucose, HMF, xylose, furfural, acid soluble lignin, acetic acid. It was assumed that all sucrose, glucose oligomers and xylose oligomers react in the pre-hydrolysis reactor.

A set of n binary variables, $z_{PreHyd,n}$, is used to ensure that only one of the $P_{J,n}$ datasets, and thus one set of reactor conditions, may be used at any time. In the pre-hydrolysis model n is thirteen as this is the number of $P_{J,n}$ datasets and J refers to the component. The set of binary variables is subject to the following logical constraint to ensure that only one dataset is chosen:

$$\sum_n z_{PreHyd,n} = 1$$

Mass balance on cellulose in acid pre-hydrolysis:

$$f_{Cellulose,PreHyd,FlsPreHyd} = f_{Cellulose,MixPreHyd,PreHyd}\left\{1 - \sum_n \left[P_{Cellulose,n} z_{PreHyd,n}\right]\right\}$$

Mass balance on glucose in acid pre-hydrolysis:

$$f_{Gluc,PreHyd,FlsPreHyd} = f_{Gluc,MixPreHyd,PreHyd} + f_{Glucolig,MixPreHyd,PreHyd} + 2.f_{Sucrose,MixPreHyd,PreHyd} + \frac{F_{PreHyd,FlsPreHyd}}{1000}\sum_n \left[P_{Gluc,n} z_{PreHyd,n}\right]$$

Ensuring all sucrose is consumed in the pre-hydrolysis reactor:

$$f_{Sucrose,PreHyd,FlsPreHyd} = 0$$

Ensuring all glucose oligomers are consumed in the pre-hydrolysis reactor:

$$f_{Glucolig,PreHyd,FlsPreHyd} = 0$$

Mass balance on HMF in acid pre-hydrolysis:

$$f_{HMF\ ,PreHyd,FlsPreHyd} = \frac{F_{PreHyd,FlsPreHyd}}{1000}\sum_n \left[P_{HMF\ ,n} z_{PreHyd,n}\right]$$

Mass balance on hemicellulose in acid pre-hydrolysis:

$$f_{Hemi,PreHyd,FlsPreHyd} = f_{Hemi,MixPreHyd,PreHyd}\left\{1 - \sum_n \left[P_{Hemi,n} z_{PreHyd,n}\right]\right\}$$

Mass balance on xylose in acid pre-hydrolysis:

$$f_{Xylo,PreHyd,FlsPreHyd} = f_{Xylolig,MixPreHyd,PreHyd} + \frac{F_{PreHyd,FlsPreHyd}}{1000}\sum_n \left[P_{Xyl,n} z_{PreHyd,n}\right]$$

Mass balance on xylose oligomers in acid pre-hydrolysis:

$$f_{Xylolig,PreHyd,FlsPreHyd} = 0$$

Mass balance on furfural in acid pre-hydrolysis:

$$f_{Furf,PreHyd,FlsPreHyd} = \frac{F_{PreHyd,FlsPreHyd}}{1000}\sum_n \left[P_{Furf,n} z_{PreHyd,n}\right]$$

Mass balance on lignin in acid pre-hydrolysis:

$$f_{Lignin\ ,PreHyd,FlsPreHyd} = f_{Lignin\ ,MixPreHyd,PreHyd} - f_{ASL\ ,PreHyd,FlsPreHyd}$$

Mass balance on acid soluble lignin in acid pre-hydrolysis:

$$f_{ASL\ ,PreHyd,FlsPreHyd} = F_{SrcBag,MixPreHyd}\sum_n \left[P_{ASL\ ,n} z_{PreHyd,n}\right]$$

Mass balance on acetyl in acid pre-hydrolysis:

$$f_{Acetyl,PreHyd,FlsPreHyd} = f_{Acetyl,MixPreHyd,PreHyd}\left\{1 - \sum_{n}\left[P_{Acetyl,n}z_{PreHyd,n}\right]\right\}$$

Mass balance on acetic acid in acid pre-hydrolysis:

$$f_{\mathrm{AceA},PreHyd,FlsPreHyd} = \frac{F_{PreHyd,FlsPreHyd}}{1000}\sum_{n}\left[P_{\mathrm{AceA},n}z_{PreHyd,n}\right]$$

Component mass balance for inerts in the process $(Acid, Min, OrgAc, Phos, Salts, Soil)$:

$$f_{i(J),MixPreHyd,PreHyd} = f_{i(J),PreHyd,FlsPreHyd}$$

Component mass balance for other inerts in acid pre-hydrolysis reactor $(Balance, Enz)$:

$$f_{p(J),MixPreHyd,PreHyd} = f_{p(J),PreHyd,FlsPreHyd}$$

It is important to note that a component mass balance for water has not been included. Water is necessary for hydrolysis reactions and is consumed during hydrolysis. Water is also produced by the production of HMF and furfural. Attempts to calculate the exiting water flowrate using stoichiometry resulted in imbalances in the overall mass balance. For this reason, the exiting water flowrate was not calculated explicitly using stoichiometry but was rather used to balance the overall mass balance. Overall water was consumed in the pre-hydrolysis reactor which was expected.

Setting the acid weight percent, A_{PreHyd}, from the data table:

$$A_{PreHyd} = \sum_{n}\left[P_{C_A,n}z_{PreHyd,n}\right]$$

Acid pre-hydrolysis reactor temperature from the data table:

$$T_{MixPreHyd,PreHyd} = \sum_{n}\left[P_{T,n}z_{PreHyd,n}\right]$$

Ensuring the reactor is isothermal:

$$T_{MixPreHyd,PreHyd} = T_{PreHyd,FlsPreHyd}$$

Acid pre-hydrolysis reactor residence time from the data table:

$$\tau_{PreHyd} = \sum_{n}\left[P_{Tau,n}z_{PreHyd,n}\right]$$

Volumetric flowrate entering the acid pre-hydrolysis reactor:

$$\dot{V}_{MixPreHydPreHyd} = \sum_{J}\frac{f_{J,MixPreHydPreHyd}}{\rho_J}$$

3.3.2.3. Acid Pre-hydrolysis Flash Equations ($FlsPreHyd$)

The pre-hydrolysis reactor flash was modelled in Aspen using the CTBE database (Bonomi et al., 2011). The GAMS model for the acid pre-hydrolysis mixer and reactor was run with each binary variable set to '1' and the exiting stream compositions and flowrates were recorded in an Excel spreadsheet. These streams were used as the input to a flash unit in Aspen. The exiting flowrates of the flash were then copied into the spreadsheet and the fraction vaporised of each component was calculated as follows:

$$X_{PreHydVap,L(J),n} = \frac{f_{L(J),flashVapour}}{f_{L(J),PreHyd,FlsPreHyd}}$$

The values for $X_{PreHydVap,L(J),n}$ can be seen in *Appendix A.2.3.2*.

The $X_{PreHydVap,L(J),n}$ of xylose and glucose oligomers was assumed to be the same as that of xylose and glucose respectively. It was assumed that the following components did not vapourise at all as the vapour flowrates were very small in the simulation: solubilsed lignin, organic acid, minerals and salts. Sucrose was ignored as all sucrose reacts in the acid pre-hydrolysis unit. The following components were ignored as their flowrates entering the acid pre-hydrolysis unit are zero: balance, sodium hydroxide, solubilised glucose and solubilised xylose.

In three cases, $z_{PreHyd,10}$, $z_{PreHyd,11}$ and $z_{PreHyd,13}$, the GAMS models were infeasible and thus the flash data tables could not be generated. However, these three cases all used the same temperature and acid weight percent as another dataset, $z_{PreHyd,3}$, $z_{PreHyd,6}$ and $z_{PreHyd,4}$ respectively, but had different residence times. In these cases, the flash table for the corresponding dataset with the same temperature and acid weight percent was used.

Component mass balance for over acid pre-hydrolysis flash:

$$f_{J,PreHyd,FlsPreHyd} = f_{J,FlsPreHyd,SnkVapFlsh1} + f_{J,FlsPreHyd,FiltPreHyd}$$

Mass flowrate of liquid components in exiting vapour stream:

$$f_{L(J),FlsPreHyd,SnkVapFlsh1} = f_{L(J),PreHyd,FlsPreHyd} \sum_{n} \left[X_{PreHydVap,L(J),n} z_{PreHyd,n}\right]$$

Mass flowrate of liquid components in exiting liquid stream:

$$f_{L(J),FlsPreHyd,FiltPreHyd} = f_{L(J),PreHyd,FlsPreHyd} \sum_{n} \left[\left(1 - X_{PreHydVap,L(J),n}\right). z_{PreHyd,n}\right]$$

Mass flowrate of solid components in exiting liquid stream:

$$f_{S(J),FlsPreHyd,FiltPreHyd} = f_{S(J),PreHyd,FlsPreHyd}$$

3.3.2.4. Acid Pre-hydrolysis Filter Equations ($FiltPreHyd$)

The equations describing the filter have already been described in the steam explosion section (*Section 3.2.4*).

3.4. Delignification

Delignification was used to remove lignin before hydrolysis to enable better access to the cellulose and increase hydrolysis yields. Sodium hydroxide was used in the models developed in this study for delignification as it is the most effective base for degrading lignin (Rezende et al., 2011) and thus has shorter reaction times than other bases (Mosier et al., 2005). The structure can be seen in the delineated section of Figure 3.2 labelled '*Delignification*'. Cellulose and hemicellulose are also solubilised during delignification. The derivation of this relationship is discussed in *Section 1.3.4.1. Section 1.3.4.2* describes the equations used in the GAMS models for delignification.

3.4.1. Solubilisation of Solids

During delignification some of the solids are dissolved. Rezende et al. (2011) investigated the amounts of these components removed from bagasse and published a figure showing the fraction of each component remaining after various treatments. The data shown in *Table 3.6* below was read from the figure in Rezende et al. (2011). Increasing the sodium hydroxide, NaOH, weight percent above 1 wt% has little increase in percentage of the component removed and so this was used as the maximum NaOH wt% in this work.

Table 3.6: Percentage of component remaining after delignification relative to amount in original bagasse (from Figure 1 in Rezende et al. (2011))

Component	**Treatment Used**			
	Acid 1 wt%	NaOH 0.25 wt%	NaOH 0.5 wt%	NaOH 1 wt%
Cellulose	94	90	85	73
Hemicellulose	20	12	10	4
Lignin	85	60	46	16

In order to use this data in the models, it was necessary to derive a relationship between the weight percent of NaOH and the amount of lignin removed. To do this the amount of each component in the original bagasse is needed. This is shown in *Table 3.7* below as taken from Rezende et al. (2011). The sum of the percentages in the original data was larger than 100%. These percentages were adjusted by subtracting half the error, provided in the paper, for cellulose, hemicellulose and lignin. For ash, 2% was subtracted. The adjusted mass percentages are also shown in below.

Table 3.7: Composition of sugarcane bagasse for delignification calculations (using Table 1 in Rezende et al. (2011))

Component	**Composition [wt %]**	
	Untreated Bagasse	Adjusted Composition
Cellulose	35.2 ± 0.9	34.75
Hemicellulose	24.5 ± 0.6	24.2
Lignin	22.2 ± 0.1	22.15
Ash	20.9 ± 4.3	18.9
Total	**102.8**	**100**

Using a basis of 100 g of bagasse the mass of each component in the initial bagasse was calculated using the adjusted percentages shown in on the previous page. Based on this mass and the percentage removed shown in *Table 3.6* above, the mass of each component remaining was calculated and these values are shown in *Table 3.8* below.

Table 3.8: Remaining mass of each component after treatment

Component	**Mass of Components [g]**				
	Bagasse $M_{Bagassse}$	Acid 1% M_{Acid}	NaOH 0.25%	NaOH 0.5% M_{NaOH}	NaOH 1%
Cellulose	34.75	32.7	31.3	29.5	25.4
Hemicellulose	24.2	4.84	2.90	2.42	0.968
Lignin	22.15	18.8	13.3	10.2	3.54

The percentage values in *Table 3.6* which was presented by Rezende et al. (2011) for the NaOH treatments include an acid pre-treatment step. In order to use these values in the models, it was necessary to determine the percentage of lignin removed in only the delignification unit. This was achieved by calculating the difference between the mass in the Acid 1% column and in the delignification step (the different NaOH columns in *Table 3.8*). This difference was then used to calculate the percentage relative to the mass of each component in the initial bagasse using the equation below. These values are shown in *Table 3.9*.

$$\%\ lignin\ removed\ by\ NaOH = \frac{M_{Acid} - M_{NaOH}}{M_{Bagassse}}.100$$

Table 3.9: Percentage of each component removed by delignification relative to original bagasse

Component	**Percentage Removed by Delignification**		
	NaOH 0.25 wt%	NaOH 0.5 wt%	NaOH 1 wt%
Cellulose	4	9	21
Hemicellulose	8	10	16
Lignin	25	39	69

It was observed that the relationship between the percentage of each component removed and the NaOH percentage follow a fairly linear relationship. This is useful when modelling the delignification in GAMS. Excel was used to plot this relationship, shown in *Figure 3.6* on the following page, and determine the equations of the straight lines. R^2 values were all greater than 0.99 which shows that the model fits the data reasonable well which is to be expected with only three data points. This linear relationship may not be a very accurate representation however it is not possible to tell without more data.

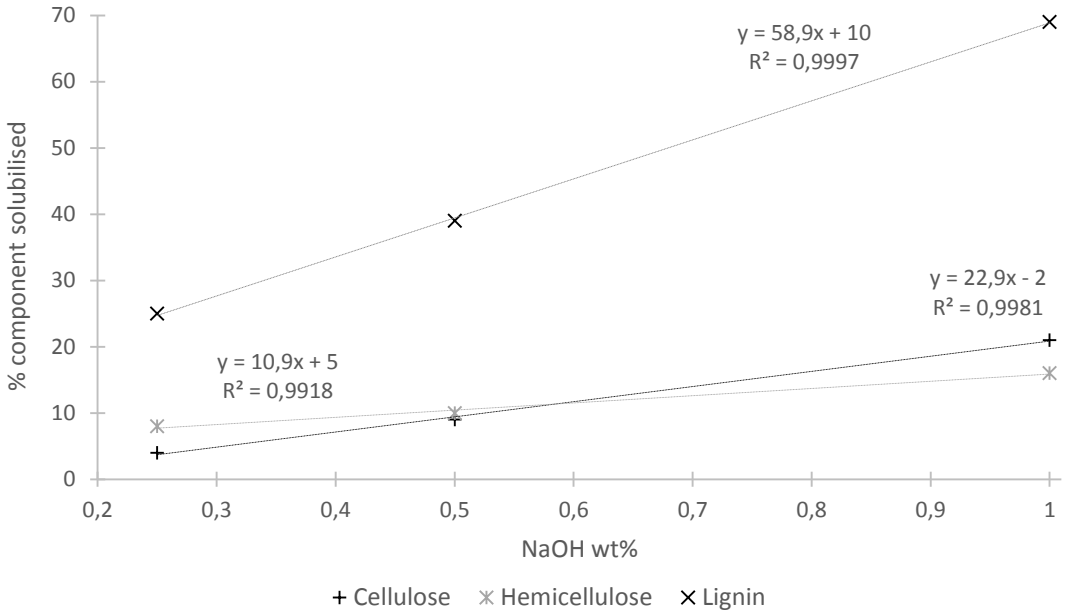


Figure 3.6: Percentage of solids solubilised by delignification with different sodium hydroxide concentrations

It is important to note that the above relationship was determined using acid pre-treated sugarcane bagasse at 120°C for 40 minutes using 1 vol% H_2SO_4 (2 wt%). These conditions are similar to some of the acid pre-treatment models used in this work (2-6 wt% acid and 100°C, 122°C and 128°C). However, this relationship may not be applicable to steam exploded bagasse. The relationship was used in any case as there was no other option available.

3.4.2. GAMS Modelling of Delignification

Figure 3.7 below shows a diagram of the delignification model in GAMS (which is also delineated as '**Delignification**' in the overall superstructure of *Figure 3.2*). The GAMS code for this model can be found in *Appendix B.1*. This code is used in the ADA, ADE, SDA and ADE flowsheets in *Figure 3.2*. A precipitate is formed when acid was used in the pre-treatment. In the model all the precipitate is formed in the heat exchanger, $HXDelig$, as this is an exothermic reaction and the required flowrate of steam used in the heat exchanger is adjusted based on this.

In some scenarios, recycling of NaOH was considered. This did not change the following equations but was incorporated in the costing and environmental impact analysis. The recycling of NaOH is discussed in more detail in *Section 4.2.* The recycling of NaOH was not modelled explicitly and is thus not shown on the diagram.

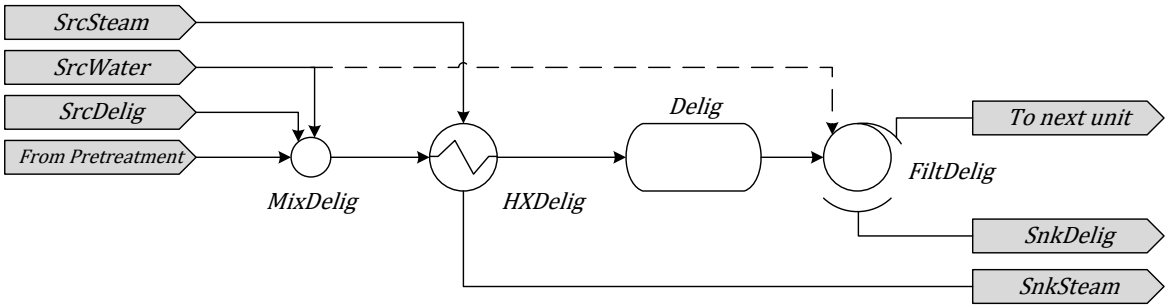


Figure 3.7: Diagram for delignification model

3.4.2.1. Delignification Mixer ($MixDelig$)

The mixer is used to mix sodium hydroxide and water with the solid stream from the pre-treatment unit and calculate the mixed stream temperature. The possibility of a precipitate forming from any acid entrained in the solid is ignored in this unit and is calculated in the following unit, $HXDelig$.

Component mass balance over the mixer:

$$f_{J,MixDelig,HXDelig} = f_{J,SrcDelig,MixDelig} + f_{J,SrcWater,MixDelig} + f_{J,Previous,MixDelig}$$

Where: the subscript $Previous$ is the relevant preceding unit ($FiltPreHyd$ or $FiltSteamEx$).

Using the water to solids ratio, W_{Delig}, to calculate the water flowrate:

$$F_{SrcWater,MixDelig} = W_{Delig} \sum_{S(J)} f_{S(J),MixDelig,HXDelig} - f_{Water,SrcDelig,MixDelig} - f_{Water,Previous,MixDelig}$$

Energy balance over the mixer:

$$\sum_{J} \left(f_{J,MixDelig,HXDelig} . C_{P,J} . T_{MixDelig,HXDelig} \right)$$

$$= \sum_{J} \left(f_{J,Previous,MixDelig} . C_{P,J} . T_{Previous,MixDelig} + f_{J,SrcDelig,MixDelig} . C_{P,J} . T_{SrcDelig,MixDelig} + f_{J,SrcWater,MixDelig} . C_{P,J} . T_{SrcWater,MixDelig} \right)$$

Setting a temperature bound on the mixed stream temperature:

$$T_{MixDelig,HXDelig} \leq T_{Previous,MixDelig}$$

3.4.2.2. Delignification Heat Exchanger ($HXDelig$)

Low pressure steam is used to heat the mixture to the temperature of the delignification unit (120°C).The precipitate forms in the heat exchanger unit. It was assumed that only the sulphuric acid reacts and other acids such as acetic acid, phosphoric acid and organic acids were ignored.

Mass balance on components not involved in precipitate reactions $(AceA, Acetyl, ASL, Balance, Cellulose, Enz, Furf, Gluc, Glucolig, GluSol, Hemi, HMF, Lignin, Min, OrgAc, Phos, Salts, Soil, Sucrose, Xylo, Xylolig, XylSol)$:

$$f_{NoPpt(J),HXDelig,Delig} = f_{NoPpt(J),MixDelig,HXDelig}$$

It was assumed that all sulphuric acid reacts to form the precipitate and this was then the limiting reagent.

Setting the acid exit flowrate to zero:

$$f_{Acid,HXDelig,Delig} = 0$$

The precipitation reaction is shown below:

$$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$$

Component molar balance on sodium sulphate based on stoichiometry:

$$n_{NaSulp,HXDelig,Delig} = n_{Acid,MixDelig,HXDelig}$$

Component molar balance on water based on stoichiometry:

$$n_{Water,HXDelig,Delig} = n_{Water,MixDelig,HXDelig} + 2n_{NaSulp,HXDelig,Delig}$$

Component molar balance on sodium hydroxide based on stoichiometry:

$$n_{NaOH,HXDelig,Delig} = n_{NaOH,MixDelig,HXDelig} - 2n_{NaSulp,HXDelig,Delig}$$

Energy balance over the delignification heat exchanger:

$$\sum_J \left(f_{J,HXDelig,Delig} . C_{P,J} . T_{HXDelig,Delig}\right) = \sum_J \left(f_{J,MixDelig,HXDelig} . C_{P,J} . T_{MixDelig,HXDelig}\right) + F_{SrcSteam,HXDelig} . \Delta H_{vap,LPS} + n_{NaSulp,HXDelig,Delig} . \Delta H_{rxn,ppt}$$

Calculating the amount of heat added in the heat exchanger by the steam:

$$Q_{HXDelig} = F_{SrcSteam,HXDelig} . \Delta H_{vap,LPS}$$

Overall component mass balance on steam:

$$f_{J,SrcSteam,HXDelig} = f_{J,HXDelig,SnkSteam}$$

3.4.2.3. Delignification Unit ($Delig$)

The solubilisation equations derived in *Section 3.4.1* were used in the delignification unit to calculate the amount of cellulose, hemicellulose and lignin that are solubilised. Furans, such as furfural and HMF, also react under alkaline conditions but these reactions were ignored as the majority of these components remain in the liquid phase which is not used in the hydrolysis reactor but is in $SnkDelig$.

Volumetric flowrate entering the delignification unit:

$$\dot{V}_{HXDelig,Delig} = \sum_{J} \frac{f_{J,HXDelig,Delig}}{\rho_J}$$

The amount of sodium hydroxide entering the delignification unit is related to the weight percent of sodium hydroxide, N_{Delig}, by the following equation:

$$N_{Delig}.100 = \frac{f_{NaOH,HXDelig,Delig}}{\dot{V}_{HXDelig,Delig} - \frac{f_{NaOH,HXDelig,Delig}}{\rho_{NaOH}}}$$

The relationships describing the solubilisation of the solids, which were discussed in *Section 3.4.1,* are used in the following equations for cellulose, hemicellulose and lignin.

Mass balance on cellulose in the delignification unit:

$$f_{Cellulose,Delig,FiltDelig} = f_{Cellulose,HXDelig,Delig} - f_{Cellulose,SrcBag,MixPreHyd}.\frac{22.857.N_{Delig} - 2}{100}$$

Where: $MixPre$ is the appropriate pre-hydrolysis mixer *(*$MixPreHyd$ or $MixSteamEx$*).*

Mass balance on hemicellulose in the delignification unit:

$$f_{Hemi,Delig,FiltDelig} = f_{Hemi,HXDelig,Delig} - f_{Hemi,SrcBag,MixPreHyd}.\frac{10.857.N_{Delig} + 5}{100}$$

Mass balance on lignin in the delignification unit:

$$f_{Lignin,Delig,FiltDelig} = f_{Lignin,HXDelig,Delig} - f_{Lignin,SrcBag,MixPreHyd}.\frac{58.857.N_{Delig} + 10}{100}$$

Calculating the amount of cellulose solubilised in the delignification unit:

$$f_{GluSol,Delig,FiltDelig} = f_{Cellulose,HXDelig,Delig} - f_{Cellulose,Delig,FiltDelig}$$

Calculating the amount of hemicellulose solubilised in the delignification unit:

$$f_{XylSol,Delig,FiltDelig} = f_{Hemi,HXDelig,Delig} - f_{Hemi,Delig,FiltDelig}$$

Calculating the amount of lignin solubilised in the delignification unit:

$$f_{ASL,Delig,FiltDelig} = f_{Lignin,HXDelig,Delig} - f_{Lignin,Delig,FiltDelig} + f_{ASL,HXDelig,Delig}$$

Component balance on other components that are inert in the delignification unit ($AceA, Acetyl, Acid, Balance, Enz, Furf, Gluc, Glucolig, HMF, Min, OrgAc, Phos, Salts, Soil, Sucrose, Xylo, Xylolig$):

$$f_{d(J),Delig,FiltDelig} = f_{d(J),HXDelig,Delig}$$

Component balance on the components involved in precipitation reactions which are inert in the delignification unit as the precipitation occurred in the heat exchanger unit $(Acid, NaOH, NaSulp, Water)$:

$$f_{Ppt(J),Delig,FiltDelig} = f_{Ppt(J),HXDelig,Delig}$$

Setting the exit temperature of the delignification unit:

$$T_{Delig,FiltDelig} = T_{HXDelig,Delig}$$

3.4.2.4. Delignification Filter ($FiltDelig$)

The equations describing the filter have already been described in the steam explosion section (*Section 3.2.4*). In this filter, the flowrate of water added could be zero if the solid stream already contains sufficient liquid.

3.5. Acid Hydrolysis

Although many authors have investigated the kinetics of cellulose hydrolysis of lignocellulosic biomass (Saeman, 1945; Xiang, Kim & Lee, 2003) few studies have been conducted with sugarcane bagasse. In this work, the kinetics of Gurgel & Marabezi (2012) were used as they utilised sugarcane bagasse as a feedstock and provided a large amount of data which is useful for constructing optimisation models in GAMS.

3.5.1. Kinetics of Acid Hydrolysis

The kinetics of Gurgel & Marabezi (2012) also used the Saeman Model (1945) which was used by Aguilar et al. (2002) for the pre-hydrolysis model described in *Section 3.3.1.* However, an α parameter, which assumes the presence of two types of cellulose, one that is easy to hydrolyse and one that is difficult to hydrolyse (see *Section 3.3*), was not necessary. The reaction scheme is shown below:

$$A \overset{k_1}{\rightarrow} B \overset{k_2}{\rightarrow} C$$

$$Cellulose \overset{k_1}{\rightarrow} Glucose \overset{k_2}{\rightarrow} HMF$$

Where: HMF is 5-hydroxymethyl furfural, a degradation product of glucose.

The reaction rates and simplified CSTR balances, derived in *Section 3.3.1,* for each component are shown below:

For cellulose:

$$R_{Cellulose} = \frac{dc_{Cellulose}}{dt} = -k_1 c_{Cellulose}$$

$$1/\tau \, (c_{Cellulose,in} - c_{Cellulose,out}) - k_1 c_{Cellulose,out} = 0$$

For glucose:

$$R_{Gluc} = \frac{dc_{Gluc}}{dt} = k_1 c_{Cellulose} - k_2 c_{Gluc}$$

$$1/\tau \, (c_{Gluc,in} - c_{Gluc,out}) + k_1 c_{Cellulose} - k_2 c_{Gluc,out} = 0$$

For acid hydrolysis any glucose oligomers and sucrose need to be included in the reaction as is shown below. It was assumed that all glucose oligomers and sucrose react to form glucose.

$$1/\tau \, (c_{Gluc,in} - c_{Gluc,out} + c_{Glucolig,in} + 2\, c_{Sucrose,in}) + k_1 c_{Cellulose} - k_2 c_{Gluc,out} = 0$$

For HMF:

$$R_{HMF} = \frac{dc_{HMF}}{dt} = k_2 c_{Gluc}$$

$$1/\tau \, (c_{HMF,in} - c_{HMF,out}) + k_2 c_{Gluc,out} = 0$$

The parameters for the Eyring Equation given in Gurgel & Marabezi (2012) for both the observed and calculated k values were unable to calculate k with temperature reliably. Errors in this calculation

ranged from 4% to 97%. As a result of these large errors, an Arrhenius model for the effect of temperature on k was derived using the values given for k at different temperatures in the paper (Gurgel & Marabezi, 2012). Details of the derivation can be found in *Appendix A.3.1*. These Arrhenius parameters were then used in the optimisation model and are shown in *Table 3.10* below.

Table 3.10: Calculated kinetic parameters (Gurgel & Marabezi, 2012) and determined Arrhenius constants

Acid weight [%]	k_i [min^{-1}]	Temperature [°C] 190	200	210	E_i [J]	A_i [min^{-1}]	R^2 [-]
0.07	k_1	0.0065	0.0189	0.0396	168 284	6.51E+16	0.9915
	k_2	0.0229	0.0418	0.0717	106 195	2.17E+10	0.9996
0.14	k_1	0.0143	0.0342	0.0954	176 415	1.09E+18	0.9965
	k_2	0.0322	0.0509	0.0927	98 255	3.78E+09	0.9920
0.28	k_1	0.0291	0.0808	0.2033	180 863	7.36E+18	0.9997
	k_2	0.0423	0.0757	0.1330	106 561	4.41E+10	1.0000

$k_i$values are for the calculated k_i values in Gurgel & Marabezi (2012) where k_1 was in *Table 2* and k_2 was in *Table 5*.

3.5.2. Modelling Other Components

The kinetics of **hemicellulose** in sugarcane bagasse using low acid percentages and at high temperatures are not well documented. Usually, hemicellulose is reacted using higher acid weight percentages and lower temperatures such as those in the pre-hydrolysis unit (Bustos et al., 2003; Gámez et al., 2006; Taherzadeh & Karimi, 2007). According to Wyman et al. (2005) 85-90% of hemicellulose can be reacted at 160°C using 0.7% acid for 10 minutes. Dias et al. (2009) assumed a conversion of hemicellulose of 99% using 0.07 wt% sulphuric acid at 205°C and an 80% decomposition of xylose to furfural. The conditions in the acid hydrolysis reactor used in this model (180-230°C and acid of 0.07-0.28 wt%), were more similar to those of Dias et al. (2009) so the same conversion factors were used. The conversion of hemicellulose in the acid hydrolysis reactor is not very important to the overall economic and environmental impact of the model as revenue of the product stream, $SnkC6$, only depends on the amount of glucose present. The environmental impact of $SnkC6$ is not included in the calculation of the overall environmental impact as this stream is fed into the fermenter and is not an exit of the overall process. Furfural in $SnkC6$ can be a problem for the downstream fermentation and so it was decided to rather overestimate the possible amount of furfural than underestimate it.

Acetic acid can form under mild hydrolysis conditions as it is formed from the acetyl groups on the hemicellulose and hemicellulose is more reactive than cellulose (Taherzadeh & Karimi, 2007). It is likely that acetic acid will form in the hydrolysis unit, however little information was available for the reaction conditions specific to this study. The conversion of acetyl groups was excluded from the hydrolysis model, however in the Aspen simulations of the flash unit carried out in this study, and which is discussed in more detail in *Section 3.5.5.4,* 98% of the acetic acid is vapourised by the reactor thus removing it from the glucose liquor.

The amount of **lignin** solubilised by acid hydrolysis was investigated using the kinetics of Lavarack, Griffin & Rodman (2002). The methodology used has already been described in *Section 3.3.1* and the Matlab code can be found in *Appendix A.2.2.* Lavarack, Griffin & Rodman (2002) investigated a wide range of experimental conditions (temperature: 180-200°C; mass ratio of solid to liquid: 1:5-1:20; acid concentration: 0.25-8 wt%; reaction time of 10-2000 min) and stated that the maximum ASL concentration achieved was 47 mg/g solids. However when ASL concentrations were investigated at

200°C the maximum ASL concentration reached with 0.28 wt% acid and a ratio of solid bagasse to liquid (g/g) of 0.05 was 62 mg/g solids at a residence time of 25 minutes. This value is greater than the maximum determined by Lavarack, Griffin & Rodman (2002) even though it is within the range of all the experimental parameters. This caused some doubt as to the accuracy of the model especially at higher temperatures and low acid concentrations such as the conditions of the acid hydrolysis unit.

As both temperature and residence time are variables in the model, the most accurate way of determining the ASL concentration would be to use the equation of Lavarack, Griffin & Rodman (2002) to calculate the ASL concentration in the GAMS model. However this equation is highly non-linear which will increase the complexity of the model and may cause difficulties for the optimisation solvers. For these models a fixed ASL concentration was assumed as the overall effect on glucose production is small. A sensitivity analysis was performed to check whether this assumption was valid (see *Section 4.2*). The value chosen for the ASL concentration was 4 mg/g solid as this was the average of the ASL concentrations at 128°C used in the pre-hydrolysis models.

A binary dataset was used to provide a choice among seven levels of **steam**. This was done in an attempt to give some flexibility to the model with regards to optimising energy consumption and environmental impact. However, in retrospect it may have been better to simplify the steam selection option as this would reduce the complexity of the model and make it easier for the solvers to find the global optimum. One of the following two approaches could be used to simplify the steam choice. The first approach may involve only giving one option of steam to the model however this would remove the flexibility for energy optimisation. The second approach entails deriving a series of linear relationships to describe how the steam properties, costs and environmental impacts change with temperature. The conversion of acetyl to acetic acid or lignin solubilisation.

3.5.3. Effects of Delignification on Acid Hydrolysis Conversions

The kinetics' of Gurgel & Marabezi (2012) were derived for bagasse that has been pre-treated in the following way: depithed, acid hydrolysed to remove hemicellulose and delignified. To ensure an accurate model, the effect of the extent of delignification should affect the yields of acid hydrolysis model. Xiang et al. (2003) describe how the yield of glucose produced from SCB by dilute acid hydrolysis (0.07 wt% acid at 220°C) changes depending on the amount of lignin removed. *Table 3.11* below shows the percentage of lignin removed by various treatments and the glucose yield as a percentage of the maximum glucose possible from the cellulose. This data was taken from Xiang et al. (2003). For the model in this study, a relationship was needed that described how the glucose yield decreased if less lignin is removed than the kinetics were derived for (85% lignin removed).

Table 3.11: Effect of delignification on glucose yield
From Xiang et al. (2003)

Treatment	**Lignin removed** [%]	**Glucose yield** [%]	**Change in glucose yield*** [%]
Untreated SCB	0	52.6	31.2
Treated, 1% H_2O_2 at 170°C	50	61.3	19.9
10% aqueous ammonia	85	76.5	0.00

*relative to 10% aqueous ammonia treatment

The percentage decrease in glucose yield was then plotted with the percentage of lignin removed and a straight line was fitted to the data, *Figure 3.8*. The R^2 value was 0.9353. Although this value is not very high the relationship was used in the model as more data could not be found in literature and a

relationship was needed to describe the decrease in glucose yield if less than 85% of the lignin is removed in the optimisation models.

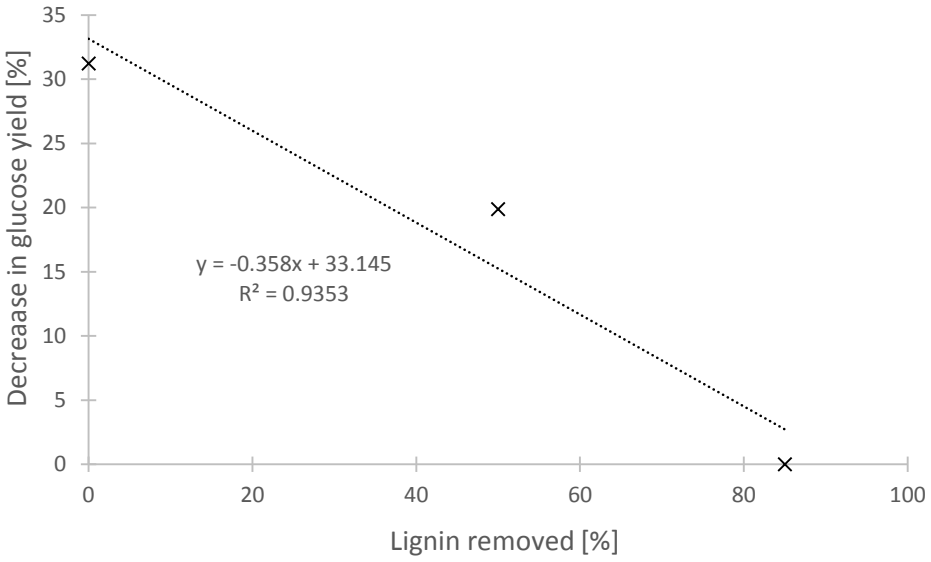


Figure 3.8: Decrease in glucose yield [%] with amount of lignin removed [%]

3.5.4. Implementing Effects of Delignification in GAMS

Incorporating the yield changes due to the extent of delignification in GAMS requires the definition of a fictitious reactor in parallel with the real reactor, see *Figure 3.9* on the following page. The fictitious reactor and the real reactor have the same input stream, residence time and the same conversion of all components except for those based on Gurgel & Marabezi's (2012) kinetic equations (cellulose, glucose and HMF). In the fictitious reactor, the flowrates and concentrations of cellulose, hemicellulose and glucose are calculated using Gurgel & Marabezi's (2012) kinetic equations which assume that 85% of the total lignin in bagasse has been removed and the yield of the fictitious reactor is calculated. The amount of lignin removed prior to the real reactor may be less than 85% and thus the conversion of cellulose need to be adjusted accordingly. The yield in the real reactor is the yield in the fictitious reactor decreased by the amount calculated using the relationship in *Figure 3.8* above which depends on the amount of lignin removed prior to hydrolysis which can be easily calculated. The concentration of glucose exiting the real reactor can then be calculated from the yield of the real reactor.

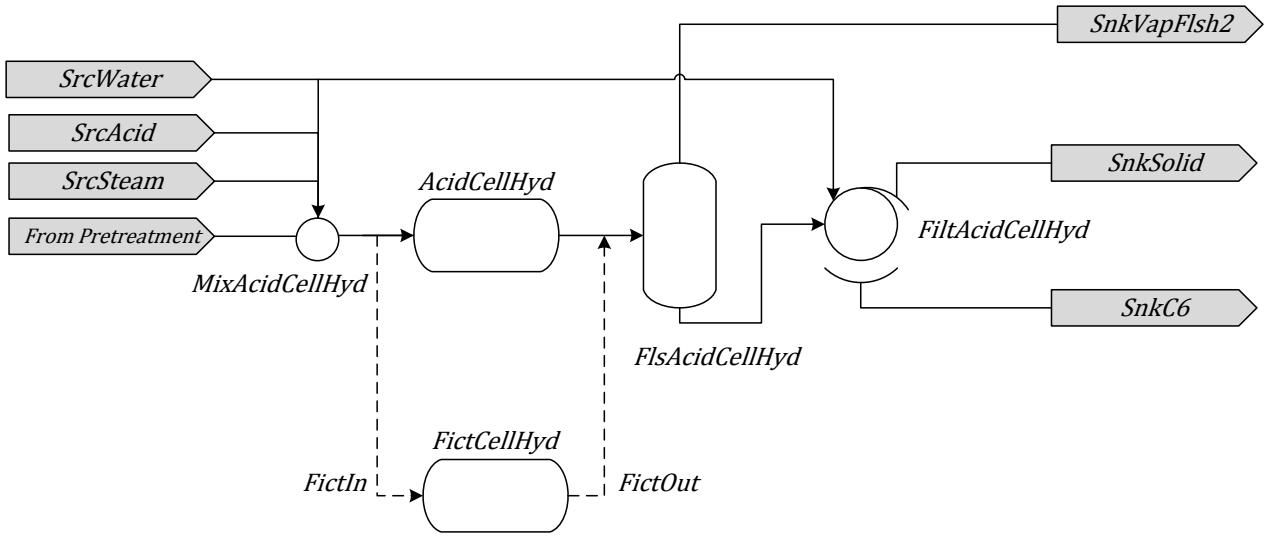


Figure 3.9: GAMS model of acid hydrolysis of cellulose

The percentage of lignin removed was calculated as follows:

$$\%\ lignin\ removed = \frac{f_{Lignin,bagasse} - f_{Lignin,in}}{f_{Lignin,bagasse}}$$

Where: $f_{Lignin,in}$is the mass flowrate of lignin into the reactor [kg/s] and $f_{Lignin,bagasse}$is the mass flowrate of lignin in bagasse [kg/s].

The equation below was used to calculate the yield of glucose in the fictitious reactor and in the real reactor.

$$Yield = \frac{c_{Glucose,out} - c_{Glucose,in}}{48.3\left(1 - {}^{c_{Cellulose,out}}/_{c_{Cellulose,in}}\right)} \times 100$$

Where: 48.3 g/l is the initial concentration of cellulose in bagasse.

The percentage by which the yield is required to decrease in the real reactor was calculated using the linear relationship obtained in *Figure 3.8*, as is shown below:

$$YieldDecr = 33.145 - 0.358\left(\frac{f_{Lignin,bagasse} - f_{Lignin,in}}{f_{Lignin,bagasse}} \times 100\right)$$

The calculated yield decrease is used to constrain the glucose yield in the real reactor using the yield decrease as shown in the equation below:

$$Yield_{Real} = Yield_{Fictitious}\left(1 - {}^{YieldDecr}/_{100}\right)$$

As both the fictitious and real reactor have the same kinetic parameters and tau, the use of Gurgel & Marabezi's (2012) kinetic equations to calculate the exit concentration of cellulose in the real reactor would simply produce the same concentration as in the fictitious reactor. The increase in mass flowrate of cellulose out of the real reactor is however, related to the difference of mass flowrate of glucose in the fictitious and real reactors as shown in the equation below.

$$f_{Cellulose,out,real} = f_{Cellulose,out,fictitious} + f_{Glucose,out,fictitious} - f_{Glucose,out,real}$$

This flowrate can then be used to calculate the concentration on cellulose out of the real reactor.

Gurgel & Marabezi's (2012) kinetic equation for the concentration of glucose depends on the concentration of cellulose out of the reactor. In the real reactor, the concentration of cellulose out has increased as there is less access to cellulose due to less lignin having been removed and so less cellulose has reacted. Thus, if the concentration of glucose out of the real reactor was calculated using the kinetic equation shown above, which is based on the concentration of cellulose out, the concentration of glucose out of the real reactor would be larger than that of the fictitious reactor which is not correct. The yield relationship can be used to calculate the glucose concentration out of the real reactor as the concentration of cellulose in and out of the real reactor are known.

Gurgel & Marabezi's (2012) kinetic equation can be used to calculate the concentration of HMF in the real reactor as this is only based on the concentration of glucose out of the real reactor.

3.5.5. GAMS Modelling of Acid Hydrolysis

The diagram shown previously, *Figure 3.9* on page 62*,* shows the GAMS model for acid hydrolysis and the unit names (which is also delineated as '**Acid Hydrolysis**' in the overall superstructure of *Figure 3.2*). This model is used in the AA, ADA, SA and SDA flowsheets shown in *Figure 3.3*. The mixer, reactor and flash would in reality be one unit but they were separated to ensure clarity in the model. If this stage is preceded by delignification, the addition of acid in the mixer causes a precipitate to form. As in acid pre-hydrolysis, the reactor acts as a flash to keep the reactor isothermal (Dias et al., 2009).

The GAMS code for the acid hydrolysis model can be found in *Appendix B.2*.

3.5.5.1. Acid Hydrolysis Mixer Equations ($MixAcidCellHyd$)

When delignification is followed by acid hydrolysis the acid added will react with any NaOH entrained in the solids leaving the delignification unit. As a result of this, more acid will need to be added. Precipitation reactions are similar to those described in *Section 3.4.2.2,* however the limiting reagent is NaOH rather than acid. The following equations are added in the acid hydrolysis mixer in the ADA and SDA models.

Assume all sodium hydroxide reacts to form a precipitate in the acid cellulose hydrolysis mixer:

$$f_{NaOH,MixAcidCellHyd,AcidCellHyd} = 0$$

Component molar balance for sodium sulphate:

$$\begin{aligned} n_{NaSulp,MixAcidCellHyd,AcidCellHyd} - (&n_{NaSulp,FiltDelig,MixAcidCellHyd} + n_{NaSulp,SrcAcid,MixAcidCellHyd} \\ &+ n_{NaSulp,SrcSteam,MixAcidCellHyd} + n_{NaSulp,SrcWater,MixAcidCellHyd}) \\ = \ 2(&n_{NaOH,FiltDelig,MixAcidCellHyd} + n_{NaOH,SrcAcid,MixAcidCellHyd} \\ &+ n_{NaOH,SrcSteam,MixAcidCellHyd} + n_{NaOH,SrcWater,MixAcidCellHyd}) \end{aligned}$$

Component molar balance for water:

$$n_{Water,MixAcidCellHyd,AcidCellHyd} - (n_{Water,FiltDelig,MixAcidCellHyd} + n_{Water,SrcAcid,MixAcidCellHyd} + n_{Water,SrcSteam,MixAcidCellHyd} + n_{Water,SrcWater,MixAcidCellHyd}) = (n_{NaOH,FiltDelig,MixAcidCellHyd} + n_{NaOH,SrcAcid,MixAcidCellHyd} + n_{NaOH,SrcSteam,MixAcidCellHyd} + n_{NaOH,SrcWater,MixAcidCellHyd})$$

Component molar balance for acid:

$$n_{Acid,MixAcidCellHyd,AcidCellHyd} - (n_{Acid,FiltDelig,MixAcidCellHyd} + n_{Acid,SrcAcid,MixAcidCellHyd} + n_{Acid,SrcSteam,MixAcidCellHyd} + n_{Acid,SrcWater,MixAcidCellHyd}) = -2(n_{NaOH,FiltDelig,MixAcidCellHyd} + n_{NaOH,SrcAcid,MixAcidCellHyd} + n_{NaOH,SrcSteam,MixAcidCellHyd} + n_{NaOH,SrcWater,MixAcidCellHyd})$$

Setting the acid weight percent in the acid cellulose hydrolysis unit:

$$x_{Acid,MixAcidCellHyd,AcidCellHyd} = \frac{A_{AcidCellHyd}}{100}$$

Determining the mass flowrate of $SrcWater$:

$$F_{SrcAcid,MixAcidCellHyd} + F_{SrcSteam,MixAcidCellHyd} + F_{SrcWater,MixAcidCellHyd} + f_{Water,Previous,MixAcidCellHyd} = \sum_{S(J)} f_{S(J),FiltSteamEx,MixAcidCellHyd} . W_{AcidCellHyd}$$

Where: $Previous$ refers to the preceding unit and $W_{AcidCellHyd}$ is the mass ratio of water to solids required in the acid hydrolysis unit.

Component mass balance over the mixer:

$$f_{J,MixAcidCellHyd,AcidCellHyd} = f_{J,SrcAcid,MixAcidCellHyd} + f_{J,SrcSteam,MixAcidCellHyd} + f_{J,SrcWater,MixAcidCellHyd} + f_{J,Previous,MixAcidCellHyd}$$

When delignification precedes the acid hydrolysis the above equation is only applied to the components that are not involved in the precipitation reactions, $NoPPT(J)$ $(AceA, Acetyl, ASL, Balance, Cellulose, Enz, Furf, Gluc, Glucolig, GluSol, Hemi, HMF, Lignin, Min, OrgAc, Phos, Salts, Soil, Sucrose, Xylo, Xylolig, XylSol)$.

Mixer energy balance to determine the temperature of the mixed stream:

$$\sum_J (f_{J,MixAcidCellHyd,AcidCellHyd} . C_{P,J} . T_{MixAcidCellHyd,AcidCellHyd}) + \Delta H_{rxn,ppt}(n_{NaSulp,MixAcidCellHyd,AcidCellHyd} - n_{NaSulp,Previous,MixAcidCellHyd}) = \sum_J (f_{J,Previous,MixAcidCellHyd} . C_{P,J} . T_{Previous,MixAcidCellHyd}) + \sum_J (f_{J,SrcAcid,MixAcidCellHyd} . C_{P,J} . T_{SrcAcid,MixAcidCellHyd}) + \sum_J (f_{J,SrcWater,MixAcidCellHyd} . C_{P,J} . T_{SrcWater,MixAcidCellHyd}) + \sum_{J,st} \left(z_{SteamCellHyd,st} . f_{J,SrcSteam,MixAcidCellHyd} . (C_{P,J} . T_{SteamSupply,st} + \Delta H_{vap,n})\right)$$

Setting the steam temperature:

$$T_{SrcSteam,MixAcidCellHyd} = \sum_{st} z_{SteamCellHyd,st} T_{SteamSupply,st}$$

The model was given a choice of steam levels (LPS, MPS1, MPS2, HPS1, HPS2, CTBE1, CTBE2) that could be used to heat the reactor. This choice was incorporated in the model with a binary variable, $z_{SteamCellHyd,st}$, which has the following condition to ensure that only one steam level is selected.

Steam selection constraint:

$$\sum_{st} z_{SteamCellHyd,st} = 1$$

The temperature of the selected steam is set using the following logical condition:

$$T_{MixAcidCellHyd,AcidCellHyd} \leq \sum_{st} z_{SteamCellHyd,st} T_{SteamSupply,st} - \Delta T_{min}$$

3.5.5.2. Acid Hydrolysis Reactor Equations ($AcidCellHyd$)

The reactor equations for the reactions involving cellulose were based on the kinetics of Gurgel & Marabezi (2012) which have been described in *Section 3.5.1.* The H dataset is used to describe the Arrhenius temperature dependence of the kinetic parameters and these can be seen in *Table A.3.3* in *Appendix A.3.1*.

Determining k_1 and k_2 for acid cellulose hydrolysis kinetics:

$$k_1 = \sum_{n} z_{AcidCellHyd,n} \cdot \left(H_{n,k1,A} . 10^{H_{n,k1,Aexp}} . e^{-H_{n,k1,E} / RT_{MixAcidCellHyd,AcidCellHyd}} \right)$$

$$k_2 = \sum_{n} z_{AcidCellHyd,n} \cdot \left(H_{n,k2,A} . 10^{H_{n,k2,Aexp}} . e^{-H_{n,k2,E} / RT_{MixAcidCellHyd,AcidCellHyd}} \right)$$

Setting the acid weight percent:

$$A_{AcidCellHyd} = \sum_{n} z_{AcidCellHyd,n} . H_{n,c_A}$$

Constraint on acid binary variables:

$$\sum_{n} z_{AcidCellHyd,n} = 1$$

The reactor acts as a flash to keep the reactor isothermal (Dias et al., 2009):

$$T_{MixAcidCellHyd,AcidCellHyd} = T_{AcidCellHyd,FlsAcidCellHyd}$$

Overall mass balance over acid cellulose hydrolysis unit:

$$F_{MixAcidCellHyd,AcidCellHyd} = F_{AcidCellHyd,FlsAcidCellHyd}$$

Overall volumetric flowrate balance over acid cellulose hydrolysis unit:

$$\dot{V}_{MixAcidCellHyd,AcidCellHyd} = \dot{V}_{AcidCellHyd,FlsAcidCellHyd}$$

Calculating the mass concentration of each component entering the reactor:

$$c_{J,MixAcidCellHyd,AcidCellHyd} = \frac{f_{J,MixAcidCellHyd,AcidCellHyd}}{\dot{V}_{MixAcidCellHyd,AcidCellHyd}}$$

Calculating the mass concentration of each component leaving the reactor:

$$c_{J,AcidCellHyd,FlsAcidCellHyd} = \frac{f_{J,AcidCellHyd,FlsAcidCellHyd}}{\dot{V}_{AcidCellHyd,FlsAcidCellHyd}}$$

Mass balance on components that are calculated using conversion factors and not kinetics:
Hemicellulose:

$$f_{Hemi,AcidCellHyd,FlsAcidCellHyd} = f_{Hemi,MixAcidCellHyd,AcidCellHyd}\,(1 - X_{Hemi,AcidCellHyd})$$

Xylose:

$$f_{Xylo,AcidCellHyd,FlsAcidCellHyd} = (f_{Hemi,MixAcidCellHyd,AcidCellHyd} \cdot X_{Hemi,AcidCellHyd} + f_{Xylo,MixAcidCellHyd,AcidCellHyd} + f_{Xylolig,MixAcidCellHyd,AcidCellHyd}) \cdot (1 - X_{XylFurf,AcidCellHyd})$$

Assuming all xylose oligomers present in the feed react to form xylose.
Xylose oligomers:

$$f_{Xylolig,AcidCellHyd,FlsAcidCellHyd} = 0$$

Furfural:

$$f_{Furf,AcidCellHyd,FlsAcidCellHyd} = (f_{Hemi,MixAcidCellHyd,AcidCellHyd} \cdot X_{Hemi,AcidCellHyd} + f_{Xylo,MixAcidCellHyd,AcidCellHyd} + f_{Xylolig,MixAcidCellHyd,AcidCellHyd}) \cdot X_{XylFurf,AcidCellHyd} + f_{Furf,MixAcidCellHyd,AcidCellHyd}$$

All glucose oligomers and sucrose react fully in the acid cellulose hydrolysis reactor:

$$f_{Glucolig,AcidCellHyd,FlsAcidCellHyd} = 0$$

$$f_{Sucrose,AcidCellHyd,FlsAcidCellHyd} = 0$$

Mass flowrate of lignin solubilised during acid hydrolysis:

$$f_{ASL,AcidCellHyd,FlsAcidCellHyd} - f_{ASL,MixAcidCellHyd,AcidCellHyd} = \sum_{s(J)} f_{S(J),previous,MixAcidCellHyd} \cdot R_{ASL,AcidCellHyd}$$

Mass flowrate of lignin exiting acid hydrolysis reactor:

$$f_{Lignin,AcidCellHyd,FlsAcidCellHyd} = f_{Lignin,MixAcidCellHyd,AcidCellHyd} - (f_{ASL,AcidCellHyd,FlsAcidCellHyd} - f_{ASL,MixAcidCellHyd,AcidCellHyd})$$

Component mass balance for inert species $i\ (Acid, Min, OrgAc, Phos, Salts, Soil)$:

$$f_{i(J),AcidCellHyd,FlsAcidCellHyd} = f_{i(J),MixAcidCellHyd,AcidCellHyd}$$

Component mass balance for inert species $h\ (Balance, Enz, GluSol, NaOH, NaSulp, XylSol)$:

$$f_{h(J),AcidCellHyd,FlsAcidCellHyd} = f_{h(J),MixAcidCellHyd,AcidCellHyd}$$

Component mass balance on other components that are assumed to be inert in the acid cellulose hydrolysis unit $(Acetyl, AceA)$:

$$f_{Acetyl,AcidCellHyd,FlsAcidCellHyd} = f_{Acetyl,MixAcidCellHyd,AcidCellHyd}$$

$$f_{AceA,AcidCellHyd,FlsAcidCellHyd} = f_{AceA,MixAcidCellHyd,AcidCellHyd}$$

The amount of HMF reacting only depends on the concentration of glucose and can be calculated outside of the fictitious unit.
Overall component mass balance for HMF:

$$^{1}/_{\tau_{AcidCellHyd}} \left(c_{HMF,MixAcidCellHyd,AcidCellHyd} - c_{HMF,AcidCellHyd,FlsAcidCellHyd}\right) + k_2 c_{Gluc,AcidCellHyd,FlsAcidCellHyd} \frac{MW_{HMF}}{MW_{Gluc}} = 0$$

3.5.5.3. Fictitious Acid Hydrolysis Reactor Equations ($FictCell$)

The fictitious reactor was used to calculate the flowrates of cellulose and glucose using Gurgel & Marabezi's (2012) kinetic equations. These flowrates were then scaled based on the amount of lignin removed from bagasse using the equations derived in *Section 3.5.3* using the relationship derived by Xiang et al. (2003).

The fictitious reactor has the same dimensions and entering flowrate as the real reactor. These equations below set the volumetric flowrate, temperature and residence time of the fictitious unit to that of the acid cellulose hydrolysis unit:

$$\dot{V}_{FictIn,FictCell} = \dot{V}_{MixAcidCellHyd,AcidCellHyd}$$

$$T_{FictIn,FictCell} = T_{MixAcidCellHyd,AcidCellHyd}$$

$$\tau_{FictCell} = \tau_{AcidCellHyd}$$

Ensuring the fictitious unit is isothermal and has a constant volumetric flowrate:

$$T_{FictIn,FictCell} = T_{FictCell,FictOut}$$

$$\dot{V}_{FictIn,FictCell} = \dot{V}_{FictCell,FictOut}$$

Setting the component mass flowrates into the fictitious unit to the mass flowrates entering the acid cellulose hydrolysis unit:

$$f_{J,FictIn,FictCell} = f_{J,MixAcidCellHyd,AcidCellHyd}$$

Overall mass balance over fictitious unit:

$$F_{FictIn,FictCell} = F_{FictCell,FictOut}$$

Setting the flowrates of components exiting the fictitious unit for components determined in the acid cellulose hydrolysis unit:

Inerts i $(Acid, Min, OrgAc, Phos, Salts, Soil)$:

$$f_{i(J),FictCell,FictOut} = f_{i(J),AcidCellHyd,FlsAcidCellHyd}$$

Inerts $h\ (Balance, Enz, GluSol, NaOH, NaSulp, XylSol)$:

$$f_{h(J),FictCell,FictOut} = f_{h(J),AcidCellHyd,FlsAcidCellHyd}$$

Hemicellulose:

$$f_{Hemi,FictCell,FictOut} = f_{Hemi,AcidCellHyd,FlsAcidCellHyd}$$

Xylose:

$$f_{Xylo,FictCell,FictOut} = f_{Xylo,AcidCellHyd,FlsAcidCellHyd}$$

Furfural:

$$f_{Furf,FictCell,FictOut} = f_{Furf,AcidCellHyd,FlsAcidCellHyd}$$

Acetyl:

$$f_{Acetyl,FictCell,FictOut} = f_{Acetyl,AcidCellHyd,FlsAcidCellHyd}$$

Acetic acid:

$$f_{AceA,FictCell,FictOut} = f_{AceA,AcidCellHyd,FlsAcidCellHyd}$$

Acid soluble lignin:

$$f_{ASL,FictCell,FictOut} = f_{ASL,AcidCellHyd,FlsAcidCellHyd}$$

Lignin:

$$f_{Lignin,FictCell,FictOut} = f_{Lignin,AcidCellHyd,FlsAcidCellHyd}$$

Setting oligomers and sucrose flowrates exiting the fictitious unit to zero:

$$f_{Xylolig,FictCell,FictOut} = 0$$

$$f_{Glucolig,FictCell,FictOut} = 0$$

$$f_{Sucrose,FictCell,FictOut} = 0$$

The CSTR equations are based on concentrations which were calculated as follows:

$$c_{J,FictIn,FictCell} = \frac{f_{J,FictIn,FictCell}}{\dot{V}_{FictIn,FictCell}}$$

$$c_{J,FictCell,FictOut} = \frac{f_{J,FictCell,FictOut}}{\dot{V}_{FictCell,FictOut}}$$

Using kinetics in the component mass balances to calculate the flowrates exiting the fictitious reactor, for cellulose:

$$1/\tau_{FictCell}\,(c_{Cellulose,FictIn,FictCell} - c_{Cellulose,FictCell,FictOut}) - k_1 c_{Cellulose,FictCell,FictOut} = 0$$

Fictitious reactor mass balance for glucose:

$$1/\tau_{FictCell}\,(c_{Gluc,FictIn,FictCell} + c_{Glucolig,FictIn,FictCell} + 2.c_{Sucrose,FictIn,FictCell} - c_{Gluc,FictCell,FictOut}) + k_1 c_{Cellulose,FictCell,FictOut}\frac{MW_{Gluc}}{MW_{Cellulose}} - k_2 c_{Gluc,FictCell,FictOut} = 0$$

Fictitious reactor mass balance for HMF:

$$^{1}/_{\tau_{FictCell}}\left(c_{HMF,FictIn,FictCell}-c_{HMF,FictCell,FictOut}\right)+k_2 c_{Gluc,FictCell,FictOut}\frac{MW_{HMF}}{MW_{Gluc}}=0$$

Using relationships developed by Xiang et al. (2003), described in *Section 3.5.3,* to alter the yield of glucose based on the amount of lignin left in the bagasse after previous stages:

The yield of glucose in the real acid cellulose hydrolysis reactor:

$$Y_{Real}=\frac{\left(c_{Gluc,AcidCellHyd,FlsAcidCellHyd}-c_{Gluc,MixAcidCellHyd,AcidCellHyd}\right)}{48.3\left(1-\frac{C_{Rem,Real}}{100}\right)}.100$$

The yield of glucose in the fictitious acid cellulose hydrolysis reactor:

$$Y_{Fict}=\frac{\left(c_{Gluc,FictCell,FictOut}-c_{Gluc,FictIn,FictCell}\right)}{48.3\left(1-\frac{C_{Rem,Fict}}{100}\right)}.100$$

Both yields are based on the amount of cellulose remaining, C_{Rem}, which is calculated as follows for the fictitious and real reactors:

$$C_{Rem,Fict}=\frac{f_{Cellulose,FictCell,FictOut}}{f_{Cellulose,FictIn,FictCell}}.100$$

$$C_{Rem,Real}=\frac{f_{Cellulose,AcidCellHyd,FlsAcidCellHyd}}{f_{Cellulose,MixAcidCellHyd,AcidCellHyd}}.100$$

The flowrate of cellulose exiting the real reactor can be calculated using the flowrate of cellulose exiting the fictitious reactor and the difference in exiting glucose flowrates between the fictitious and real reactors and the molar mass ratio of cellulose to glucose:

$$f_{Cellulose,AcidCellHyd,FlsAcidCellHyd}=f_{Cellulose,FictCell,FictOut}$$
$$+\left(f_{Glucose,FictCell,FictOut}-f_{Glucose,AcidCellHyd,FlsAcidCellHyd}\right).\frac{MW_{Cellulose}}{MW_{Gluc}}$$

The real and fictitious yields are related by the following equation:

$$Y_{Real}=Y_{Fict}\left(1-\frac{Y_{Decr}}{100}\right)$$

Where the yield decrease is calculated as is shown below:

$$Y_{Decr}=33.145-0.358\left(\frac{f_{Lignin,SrcBag,MixPre}-f_{Lignin,MixAcidCellHyd,AcidCellHyd}}{f_{Lignin,SrcBag,MixPre}}.100\right)$$

Where: $MixPre$ is the appropriate pre-hydrolysis mixer *(*$MixPreHyd$ or $MixSteamEx$*)*.

3.5.5.4. Acid Hydrolysis Flash Equations ($FlsAcidCellHyd$)

The hydrolysis reactor flash was modelled in Aspen using the CTBE database (Bonomi et al., 2011). The GAMS model for the acid hydrolysis mixer and reactor was run for each acid weight percent over a range of temperatures (180-230°C) and the exiting stream compositions and flowrates were recorded in an Excel spreadsheet. These streams were used as the input to a flash model in Aspen. The exiting flowrates of the flash were then copied into the spreadsheet and the fraction vaporised of each component was calculated as follows:

$$X_{CellHydVap,L(J),c_A,T} = \frac{f_{L(J),flashVapour}}{f_{L(J),AcidCellHyd,FlsAcidCellHyd}}$$

The values for $X_{CellHydVap,L(J),c_A,T}$ can be seen in *Tables A.3.4, A.3.6* and *A.3.8* in *Appendix A.3.2*.

The fraction vapourised of minerals and salts was very small (around 10^{-76}) so the fraction vapourised for these component was set to zero in the GAMS model.

For some components (furfural, HMF and water) the fraction vapourised was reasonably constant regardless of the temperature and acid weight percent. For these components, a constant value was used in the models which can be seen in *Table A.3.10* in *Appendix A.3.2*.

For liquid components that were not present in the hydrolysis reactor effluent (sucrose, balance and sodium hydroxide) the fraction vapourised was set to zero in the GAMS model.

Flowrates of organic acid, phosphoric acid and acid soluble lignin entering the flash are very low and for these components the fraction vapourised was set to zero in the GAMS model.

In the pre-hydrolysis flash models (see *Appendix A.2.3.2*) an average of 97% of the acetic acid was vapourised at 128°C. The amount of acetic acid vapourised increased with temperature and decreased with an increase in acid concentration. The acid cellulose hydrolysis models are at a higher temperature (180-230°C) and use a lower acid weight percent (0.07-0.28 wt %) than the pre-hydrolysis models and so for the flash the amount of acetic acid vapourised was fixed at 98% however this may underestimate the amount of acetic acid vapourised.

For the rest of the liquid components (xylose, xylose oligomers, glucose, glucose oligomers and sulphuric acid) the fraction vapourised varied with temperature and acid weight percent. For these components a linear relationship between the fraction vapourised and the temperature was determined for each acid weight percent. These linear relationships was then used in the GAMS code as is shown in the following equation:

$$X_{CellHydVap,Ll(J)} = \sum_n Fls_{m,Ll(J)} \cdot z_{AcidCellHyd,n} \cdot (T_{MixAcidCellHyd,AcidCellHyd} - 273.15) + \sum_n Fls_{c,Ll(J)} \cdot z_{AcidCellHyd,n}$$

Tables A.3.4, A.3.6 and A.3.8 in *Appendix A.3.2* show the data used to generate these linear relationships. The parameters used for Fls can be found in *Tables A.3.5, A.3.7 and A.3.9* in *Appendix A.3.2*. The R^2 values for these relationships was above 0.9 which is reasonable.

Isothermal flash equation:

$$T_{J,AcidCellHyd,FlsAcidCellHyd} = T_{J,FlsAcidCellHyd,FiltCellHyd}$$

Overall component mass balance:

$$f_{J,AcidCellHyd,FlsAcidCellHyd} = f_{J,FlsAcidCellHyd,FiltCellHyd} + f_{J,FlsAcidCellHyd,SnkVapFlsh2}$$

Mass flowrate of liquid components in exiting vapour stream:

$$f_{L(J),FlsAcidCellHydHyd,SnkVapFlsh2} = f_{L(J),AcidCellHyd,FlsAcidCellHyd} X_{CellHydVap,L(J)}$$

Mass flowrate of liquid components in exiting liquid stream:

$$f_{L(J),FlsAcidCellHydHyd,FiltCellHyd} = f_{L(J),AcidCellHyd,FlsAcidCellHyd}\left(1 - X_{CellHydVap,L(J)}\right)$$

Mass flowrate of solid components in exiting liquid stream:

$$f_{S(J),FlsAcidCellHydHyd,FiltCellHyd} = f_{S(J),AcidCellHyd,FlsAcidCellHyd}$$

3.5.5.5. Acid Hydrolysis Filter Equations ($FiltCellHyd$)

The equations describing the filter have already been described in the steam explosion section (*Section 3.2.4*).

3.6. Enzymatic Hydrolysis Model

Although many studies have been conducted on enzymatic hydrolysis of sugarcane bagasse (Kadam, 2000; Pushpa et al., 2010; Carvalho, Jr & Suarez, 2013) the enzyme mixtures that are investigated are bought from a company and the composition of these mixtures is a trade secret. Whether or not these enzymes have been successfully used on an industrial scale is often not known. For this study, the final model was based on an Aspen simulation from CTBE (Bonomi et al., 2011) as this model is based on industrial processing of sugarcane bagasse for bio-ethanol production in Brazil. *Figure 3.10* below shows the units in the model with their GAMS unit names indicated (which is also delineated as '**Enzymatic Hydrolysis** in the overall superstructure of *Figure 3.2*). In the actual process, the mixer and hydrolysis reactor unit are one physical unit but they were modelled as two separate units in this study so that flowrates through each separate operation could be seen and checked.

The GAMS code for the enzymatic hydrolysis model can be found in *Appendix B.1*. This code is used in the AE, ADE, SE and SDE flowsheets shown in *Figure 3.3*.

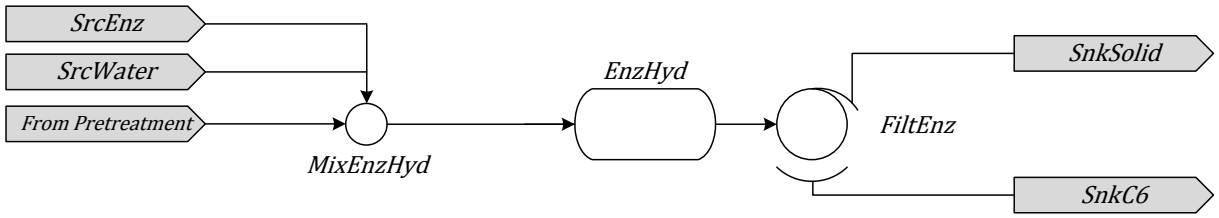


Figure 3.10: Diagram for enzymatic hydrolysis model

The pre-treatment temperature is usually greater than the enzymatic hydrolysis temperature. The temperature after the steam explosion flash is typically 374 K and the temperature exiting the acid pre-hydrolysis reactor ranges between 373 K and 401 K. Delignification occurs at 393 K. The enzymatic hydrolysis reactor operates at 323 K. Initially, a heat exchanger was included prior to the mixer, $MixEnzHyd$, to cool the pre-treatment stream, however, it was found that sufficient water is added in the mixer to reduce the temperature and that in most cases heating would be required rather than cooling.

Ideally it would be useful to include this heat exchanger in the model and allow it to be used as either a heater, using low pressure steam, or a cooler, using cooling water. However, including logical programming and decision making in GAMS is no trivial task and requires the use of disjunctive programming. As the utility usage of this heat exchanger and the cost associated with it would be minor in comparison to the cost of the enzymes and the reactor the heat exchanger was excluded and instead the reactor inlet temperature was bounded to a lower limit of 303 K and an upper limit of 328 K.

3.6.1. Enzymatic Hydrolysis Mixer Equations *(MixEnzHyd)*

The mixer combines the solids stream from the previous unit *(FiltPreHyd, FiltSteamEx* or *FiltDelig)* with enzymes and water. These are added based on fixed mass ratios.

Mass balance for enzymatic hydrolysis mixer:

$$F_{SrcEnz,MixEnzHyd} + F_{SrcWater,MixEnzHyd} + F_{Previous,MixEnzHyd} = F_{MixEnzHyd,EnzHyd}$$

Where: $Previous$ is the preceding unit *(FiltPreHyd, FiltSteamEx* or *FiltDelig)*.

Component mass balance for enzymatic hydrolysis mixer:

$$f_{J,SrcEnz,MixEnzHyd} + f_{J,SrcWater,MixEnzHyd} + f_{J,Previous,MixEnzHyd} = f_{J,MixEnzHyd,EnzHyd}$$

Setting the mass fraction of water in the stream exiting the mixer to the fixed mass fraction value, W_{EnzHyd}:

$$x_{Water,MixEnzHyd,EnzHyd} = W_{EnzHyd}$$

Fixing mass fraction of enzymes exiting the mixer:

$$x_{Enz,MixEnzHyd,EnzHyd} = E_{EnzHyd}$$

3.6.2. Enzymatic Hydrolysis Reactor Equations *(EnzHyd)*

The operation of the enzymatic hydrolysis reactor is based on the Aspen simulation of CTBE (Bonomi et al., 2011). These conversions are influenced by the amount of lignin removed using a relationship developed from Rezende et al. (2011) which is shown later in this section.

Overall mass balance for enzymatic hydrolysis reactor:

$$F_{EnzHyd,FiltEnz} = F_{MixEnzHyd,EnzHyd}$$

Volumetric flowrate exiting the enzymatic hydrolysis reactor:

$$\dot{V}_{EnzHyd,FiltEnzHyd} = \sum_{J} \frac{f_{J,EnzHyd,FiltEnzHyd}}{\rho_J}$$

Table 3.12 below shows the reactions used in the enzymatic hydrolysis reactor and the conversions of these reactions.

Table 3.12: Reactions and conversions for enzymatic hydrolysis reactor

r	Reaction	Reference Component (Ref. Cmpnt)	Conversion of Ref. Cmpnt $XEnzHyd,r$
1	Water + Cellulose → Glucose	Cellulose	0.50
2	Cellulose → Glucose Oligomers	Cellulose	0.01
3	Water + Xylan → Xylose	Xylan	0.25
4	Xylan → Xylose Oligomers	Xylan	0.00
5	Acetate → Acetic acid	Acetate	0.25

The conversion of the enzymatic hydrolysis reactions are strongly affected by the degree of delignification (Rocha et al., 2012; Rezende et al., 2011; Pushpa et al., 2010). Data presented by Rezende et al. (2011) was used to determine a linear relationship between the percentage of lignin removed and the increase in the released glucose concentration. The full details of this analysis are presented in *Appendix A.4.1*. Reactions 3 to 5 were not modified as data for this analysis was unavailable. These reactions are less significant in the overall model performance as they do not effect the formation of glucose.

The following equations were added into the enzymatic hydrolysis model to modify the conversion of cellulose based on the amount of lignin removed prior to hydrolysis:

$$Y_{Inc,EnzHyd} = \frac{162}{180}(3.9815)\left(\frac{f_{Lignin,SrcBag,MixPre} - f_{Lignin,MixEnzHyd,EnzHyd}}{f_{Lignin,SrcBag,MixPre}}.100 - 10\right)$$

Where: $MixPre$ is the pre-hydrolysis mixer unit ($MixPreHyd$ or $MixSteamEx$), $Y_{Inc,EnzHyd}$ is the change in the percentage change in the conversion, $\frac{162}{180}$ is the molar mass ratio of cellulose over glucose, 3.9815 is the gradient of the curve in *Figure A.4.1* in *Appendix A.4*. The bracketed term subtracts 10 in order to account for the fact that the conversions used, $X_{EnzHyd,r}$, are based on a case where 10% of the lignin was removed in steam explosion prior to the enzymatic hydrolysis.

The conversions of reaction 1 and 2 are modified using $Y_{Inc,EnzHyd}$ in the following way:

$$newX_{EnzHyd,1} = X_{EnzHyd,1} + X_{EnzHyd,1}\frac{Y_{Inc,EnzHyd}}{100}$$

$$newX_{EnzHyd,2} = X_{EnzHyd,2} + X_{EnzHyd,2}\frac{Y_{Inc,EnzHyd}}{100}$$

The individual component mass balances are shown below.

Mole balance for cellulose exiting enzymatic hydrolysis reactor:

$$n_{Cellulose,EnzHyd,FiltEnz} = n_{Cellulose,MixEnzHyd,EnzHyd}.\left(1 - newX_{EnzHyd,1} - newX_{EnzHyd,2}\right)$$

Mole balance for glucose exiting enzymatic hydrolysis reactor:

$$n_{Gluc,EnzHyd,FiltEnz} = n_{Cellulose,MixEnzHyd,EnzHyd}.newX_{EnzHyd,1} + n_{Gluc,MixEnzHyd,EnzHyd} + n_{Glucolig,MixEnzHyd,EnzHyd}$$

Assuming all glucose oligomers entering the reactor react to form glucose.

Mole balance for glucose oligomers exiting enzymatic hydrolysis reactor:

$$n_{Glucolig,EnzHyd,FiltEnz} = n_{Cellulose,MixEnzHyd,EnzHyd}.newX_{EnzHyd,2}$$

Mole balance for hemicellulose exiting enzymatic hydrolysis reactor:

$$n_{Hemi,EnzHyd,FiltEnz} = n_{Hemi,MixEnzHyd,EnzHyd}.\left(1 - X_{EnzHyd,3}\right)$$

Mole balance for xylose exiting enzymatic hydrolysis reactor:

$$n_{Xylo,EnzHyd,FiltEnz} = n_{Hemi,MixEnzHyd,EnzHyd}.X_{EnzHyd,3} + n_{Xylo,MixEnzHyd,EnzHyd} + n_{Xylolig,MixEnzHyd,EnzHyd}$$

Assuming all xylose oligomers entering the reactor react to form xylose.

Component balance for xylose oligomers in enzymatic hydrolysis reactor:

$$f_{Xylolig,EnzHyd,FiltEnz} = 0$$

Mole balance for acetate exiting enzymatic hydrolysis reactor:

$$n_{Acetyl,EnzHyd,FiltEnz} = n_{Acetyl,MixEnzHyd,EnzHyd} . \left(1 - X_{EnzHyd,5}\right)$$

Mole balance for acetic acid exiting enzymatic hydrolysis reactor:

$$n_{AceA,EnzHyd,FiltEnz} = n_{Acetyl,MixEnzHyd,EnzHyd} . X_{EnzHyd,5} + n_{AceA,MixEnzHyd,EnzHyd}$$

Component mass balance for inerts, i, in enzymatic hydrolysis reactor $(Acid, Min, OrgAc, Phos, Salts, Soil)$:

$$f_{i(J),EnzHyd,FiltEnz} = f_{i(J),MixEnzHyd,EnzHyd}$$

Component mass balance for other inerts, e, in enzymatic hydrolysis reactor $(ASL, Balance, Enz, Furf, GluSol, HMF, Lignin, NaOH, NaSulp, Sucrose, XylSol)$:

$$f_{e(J),EnzHyd,FiltEnz} = f_{e(J),MixEnzHyd,EnzHyd}$$

3.6.3. Enzymatic Hydrolysis Filter Equations ($FiltEnz$)

The equations describing the filter have already been described in the steam explosion section (*Section 3.2.4*). The enzymatic hydrolysis filter has no water added.

3.7. Costing

Both variable and fixed costs were included in the models. The details of the parameters used in the models can be found in the following sections.

3.7.1. Variable Costs

Table 3.13: below shows a summary of the variable costs used in the model.

Table 3.13: Variable costs for GAMS model

Component	Cost, ***B*** [R/t]
Glucose	5510
Methane	14000
Enzymes[*]	1384
Sodium hydroxide	6000
Sugarcane bagasse	0
Sulphuric acid	2560
Water	0.027

[*] per ton of glucose

3.7.1.1. Revenues

Glucose

The stream exiting the process, $SnkC6$, is not a product in itself but requires further processing to be reacted to ethanol. However, some revenue needs to be associated with the glucose in the exit stream in order to effectively screen technologies. The revenue associated with glucose, B_{Gluc}, was calculated as follows:

$$B_{Gluc} = \frac{1.05 \times 4.6 \times 0.9}{\rho_{Eth}} \times 1000 \times 1000 = R5510/ton$$

Where: 1.05 is the cost of ethanol [R$/l] (Bonomi et al., 2011), 4.6 is the R/R$ exchange rate, 0.9 is the conversion of glucose to ethanol [kg ethanol/kg glucose] (Bonomi et al., 2011), ρ_{Eth} is the density of ethanol [789 kg/m^3] and 1000 are conversion factors for converting from l to m^3 and from kg to ton so that B_{Gluc} is in [R/ton].

Methane

The retail price of compressed natural gas (CNG) in South Africa is R10/l (Lamprecht, 2014) which can be converted to a price per kg (R23.67/kg) using the density of CNG (422.36 kg/m^3). The cost of producing methane from xylose needs to be subtracted from this price to incorporate the cost of producing bio-methane from xylose into the model. The equation below shows how the price of methane was determined:

$$B_{CH_4} = 23.67 - (0.7 \times 13.83) = R14/kg$$

Where: 23.67 is the CNG price in South Africa [R/kg], 0.7 is the cost of producing bio-methane in Europe [€/kg] (BioNett, n.d.) and 13.83 is the R/€ exchange rate.

The revenue generated from methane produced by bio-digestion of the xylose:

$$Rev_{CH_4} = f_{Xylo,PreFilt,SnkC5}.X_{XylCH_4}.B_{CH_4}.\frac{3600 \times 24 \times 365 \times 0.8}{1000 \times 10^6}$$

Where: 0.8 is the fraction of annual operating hours, $3600 \times 24 \times 365$ is used to convert from s^{-1} to $year^{-1}$, 1000 converts from kg to ton and 10^6 is used to make Rev_{CH_4} in millions of Rand.

An Aspen simulation from CTBE (Bonomi et al., 2011) was used to determine the conversion of xylose to methane as a mass ratio as shown in the following equation:

$$X_{XylCH_4} = \frac{F_{Methane}}{F_{Xylose}} = \frac{642}{1783} = 0.36$$

Where: the mass flowrates, F, are in kg/h.

In the CTBE Aspen simulation 67% of the glucose and glucose oligomers were also used to produce the methane so this xylose conversion may lead to an overestimate of the actual amount of methane produced. In the CTBE simulation 8 times more xylose is converted to methane than glucose by mass so xylose is the main contributor to methane production. The mass ratio of xylose to glucose in the CTBE simulation is 5.3. In the GAMS models in this work, the stream which is used to produce methane also contains glucose with a mass ratio of xylose to glucose of 1.5 for acid pre-treatment models and 3.4 for acid-catalysed steam explosion models.

3.7.1.2. Raw Materials

Enzymes

The cost of enzymes was taken from Dias et al. (2012) as \$0.11/l of cellulosic ethanol and was converted as follows:

$$B_{Enzymes} = \frac{0.11 \times 11.03 \times 0.9}{\rho_{Eth}} \times 1000 \times 1000 = R1384/ton\ of\ glucose\ produced$$

Where: 0.11 is the price of cellulosic ethanol Dias et al. (2012) [\$/l], 11.03 is the R/\$ exchange rate, 0.9 is the conversion of glucose to ethanol [kg ethanol/kg glucose] (Bonomi et al., 2011), $\rho_{Eth}$is the density of ethanol [789 kg/m^3], and 1000 are conversion factors for converting from l to m^3 and from kg to ton so that $B_{Enzymes}$ is in [R/ton].

Sodium hydroxide

Sodium hydroxide was taken to be R6000/ton (Norceline Chemicals, n.d.; Shield Technology, n.d.).

Sugarcane Bagasse

It was assumed that sugarcane bagasse is a waste stream and thus does not have any costs associated with it.

Sulphuric Acid

Sulphuric acid was taken to be R2.56/kg (Alibaba, n.d.; Ec21, n.d.; Norceline Chemicals, n.d.).

3.7.1.3. Utilities

Water

The cost of water was taken as an average of the regional costs for domestic and industrial for 2013/2014 (Department of Water Affairs, 2014) which was found to be R0.0272/m^3 however this value is possibly too low.

Steam

The cost of each steam level was calculated using the work of Smith & Varbanov (2005) by interpolating or, in the case of HPS2, extrapolating the data for actual steam turbines that have been optimised. In Smith & Varbanov (2005) the cost of low pressure steam was found to be negative \$0.55/t. The value for LPS in this study which was calculated using the relationship in Smith & Varbanov (2005) was found to be negative \$0.28/ton. However, the value used for the LPS cost in the GAMS models used in this study it was zero instead as it was undesirable to have revenue from the LPS as this may overinflate the actual profit of the models. *Table 3.14* below shows the pressure, temperature, heat of vapourisation and cost of each steam level.

Table 3.14: Data used for steam in GAMS model

Steam ***st***	**Pressure** [barg]	**Supply Temperature** [K]	**Heat of vapourisation** $\Delta H_{vap,steam}$ [kJ/kg]	**Cost,** B_{st} Derived from Smith & Varbanov (2005) [2005 \$/t]
LPS	3	417.15	2133.8	0.00
MPS1	10	459.15	2000.4	1.56
MPS2	46	533.15	1662.5	5.58
HPS1	85	573.15	1404.9	7.28
HPS2	186	633.15	720.5	11.67
CTBE1	5	431.15	2086.3	0.24
CTBE2	11	463.28	1986.2	1.82

The target temperature of steam was assumed to be 0.01 K lower than the supply temperature to prevent computational difficulties in the model with temperature differences of zero.

The amount of steam required to heat the enzymatic hydrolysis unit was not accounted for in the utility costs however low pressure steam is used for this and there was no cost associated with low pressure steam in this model.

Pumping and other motor costs were excluded from the models as it was assumed that these would be similar for all models.

3.7.2. Fixed Costs

The volume of a vessel is calculated as follows:

$$V_{Unit} = \frac{\pi}{4} D_{Unit}^2 . L_{Unit}$$

The L over D ratio is calculated as shown:

$$R_{L/D} = \frac{L_{Unit}}{D_{Unit}}$$

Storage Vessels

According to heuristics (Walas, 1988) storage vessels should be large enough to hold a month's supply of materials. In cases where the volume of this unit was larger than 8000 m^3 the volume would be for a week or two weeks and the purchased cost of equipment, PCE, of this vessel would be multiplied by '2' or '4' so as to increase the number of vessels to allow a month's supply to be kept on site.

Volume of storage units for a month's supply $(SrcEnz, SrcAcid, SrcDelig)$:

$$V_{Unit} = 1.1 \times \frac{F_{Src,Next} \times 3600 \times 24 \times 30}{\sum_J \left(x_{J,Src,Next} . \rho_J \right)}$$

Where: 1.1 is an overdesign factor.

The purchased cost of equipment for cone roof storage vessels was calculated using the following equation from Coulson and Richardson Volume 6 (Sinnott, 2005):

$$PCE_{Unit} = \frac{CEPCI_{2014}}{CEPCI_{2004}} \times MF \times \ 2300 \times V_{Unit}^{0.55}$$

The material factor, MF, is 2 in cases where stainless steel is required ($SrcAcid$) and the MF is 1 in other cases.

Reactors

Volume of the reactors $(PreHyd, SteamEx, Delig, EnzHyd, AcidCellHyd)$ was calculated using the residence time, τ, and the volumetric flowrate, $\dot{V}$:

$$V_{Unit} = 1.1 \times \dot{V}_{Unit,Next} . \tau_{Unit} \times 60$$

The equation needed to be multiplied by 60 to convert the residence time from minutes to seconds.

The purchased cost of equipment for vertical pressure vessels was calculated using the following equation from Coulson and Richardson Volume 6 (Sinnott, 2005):

$$PCE_{Unit} = \frac{CEPCI_{2014}}{CEPCI_{2004}} . MF . PF \times \ 5000 \times L_{Unit}$$

Material factors, MF, and pressure factors, PF, *are* shown in *Table 3.15.* and *Table 3.16* on the following page (Sinnott, 2005). Specific unit MF and PF values are shown in *Table 3.17* on the following page.

Table 3.15: Material factors from Sinnott (2005)

Material of Construction	MF
CS	1.0
SS	2.0
Monel	3.4
SS clad	1.5
Monel Clad	2.1

Table 3.16: Pressure factors from Sinnott (2005)

Pressure [bara]	PF [-]
1-5	1.0
5-10	1.1
10-20	1.2
20-30	1.4
30-40	1.6
40-50	1.8
50-60	2.2

Table 3.17: Specific material factors and pressure factors used in GAMS models

Reactor	Material Factor MF	Pressure [bara]	Pressure Factor PF
$Delig$	2	11	1.2
$EnzHyd$	1	1	1.0
$PreHyd$	1	1	1.0
$SteamEx,$ acid-catalysed	2	4	1.0
$SteamEx,$ un-catalysed	2	5	1.1
$Delig$	1	12	1.2

The pressure of the $AcidCellHyd$ and $PreHyd$ reactors depends on the steam used to heat the reactor. $PreHyd$ uses only low pressure steam which is at 3 barg. $AcidCellHyd$ has a choice between all steam levels but medium pressure steam 1, which is at 10 barg, was chosen most often in the solutions obtained in this study.

Heat Exchangers

To determine the area of a heat exchanger the log mean temperature difference is needed. Careful bounding of the variables involved in this equation was used to prevent infeasibilities of the model.

$$LMTD_{HXDelig} = \frac{\left(T_{HXDelig,SnkSteam} - T_{MixDelig,HXDelig}\right) - \left(T_{SrcSteam,HXDelig} - T_{HXDelig,Delig}\right)}{log\frac{\left(T_{HXDelig,SnkSteam} - T_{MixDelig,HXDelig}\right)}{\left(T_{SrcSteam,HXDelig} - T_{HXDelig,Delig}\right)}}$$

The area can be calculated using the following equation:

$$Area_{HXDelig} = \frac{Q_{HXDelig} \times 1000}{U_{HXDelig}.F_{HXDelig}.LMTD_{HXDelig}}$$

Where: $U_{HXDelig}$ is the overall heat transfer co-efficient, 1845 W.m^{-2}.K^{-1}, $F_{HXDelig}$ is the heat exchanger correction factor, 0.9, and 1000 is used to convert $Q_{HXDelig}$ from kJ to J.

$U_{HXDelig}$ was taken as the midpoint in the range for condensing steam and water which is 250-400 Btu.°F^{-1}.ft^{-2}.h^{-h} or 1420-2271 W.m^{-2}.K^{-1} (Green & Perry, 2007).

The base cost of a fixed head heat exchanger, C_b, in $ in 2005 can then be calculated using this relationship from Seider et al. (2010):

$$C_{b,HXDelig} = e^{11.0545-0.9228\times log\left(Area_{HXDelig}\times 10.76391\right)+0.09861\times\left(log\left(Area_{HXDelig}\times 10.76391\right)\right)^2}$$

Since the above equation is based on an area in ft^2, the conversion factor 10.76391 above is needed to convert the area to ft^2 from m^2. This equation is for a maximum area of 12000 ft^2 or 1115 m^2 which is large enough for the heat exchangers in the models.

The material cost for a carbon steel shell and stainless steel tubes is calculated using the equation below (Seider et al., 2010):

$$MF_{HXDelig} = 1.75 + \left(\frac{Area_{HXDelig} \times 10.76391}{100}\right)^{0.13}$$

The purchased cost of the heat exchanger in 2014 can then be calculated as follows:

$$PCE_{HXDelig} = \frac{CEPCI_{2014}}{500} C_{b,HXDelig} MF_{HXDelig}$$

Filters

Surface area of filter:

$$Area_{Filt} = \pi D_{Filt} L_{Filt}$$

Where: D_{Filt} represents the diameter of the filter in m and L_{Filt} is the width of the filter in m.

The maximum filtration rate for coarse solids is 6000 lb/(ft^2.day) (Walas, 1988) and this was used to determine the filtration area required:

$$1.1 \times F_{Filt.Next} \times 3600 \times 24 \leq Area_{Filt} \times 6000 \times 0.453592 \times 10.76391$$

Where: 1.1 is an overdesign factor and conversion factors have been used to convert the maximum filtration rate to kg/(m^2.day) and the flowrate to kg/day.

The purchased cost of vacuum drum filters (Sinnott, 2005) was determined as follows:

$$PCE_{Filt} = \frac{CEPCI_{2014}}{CEPCI_{2004}} \times 34000 \times Area_{Filt}^{0.6}$$

This equation is applicable up to a size of 10 m^2, however some of the filters in the models were up to 100 m^2. Filters of this size are available industrially however costing equations were not available so this equation was used even though it may not be an accurate cost estimation.

3.7.3. Economic Objective Function

The economic objective function below calculates the annual profit [millions of R/year] based on the revenues from glucose and methane, the annualised capital costs and the raw material costs.

$$Profit = [Revenue] - \{Purchased\ Cost\ of\ Equipment\} - (Cost\ of\ Raw\ Materials)$$

$$\begin{aligned} Profit = {} & [Revenue\ from\ Glucose + Revenue\ from\ Methane] \\ & - \{Purchased\ Cost\ of\ Units + \ Purchased\ Cost\ of\ Heat\ Exchangers\} \\ & - (Cost\ of\ Water + \ Cost\ of\ Acid + Cost\ of\ NaOH + Cost\ of\ Enzymes \\ & + Cost\ of\ Steam) \end{aligned}$$

$$\begin{aligned} Profit = {} & \left[B_{Gluc} f_{Gluc,unit,SnkC6} \times \frac{3600 \times 24 \times 365 \times 0.8 \times 10^{-6}}{1000} + Rev_{CH_4}\right] \\ & - \left\{\sum_{unit} \frac{PCE_{unit} \times 11.03 \times Lang}{10} \times 10^{-6} + \sum_{HX} \frac{PCE_{HX} \times 11.03 \times Lang}{5} \times 10^{-6}\right\} \\ & - \left(\sum_{unit} F_{SrcWater,unit}\, B_{Water} + \sum_{unit} F_{SrcAcid,unit}\, B_{Acid} + \sum_{unit} F_{SrcNaOH,unit}\, B_{NaOH}\right. \\ & + \sum_{unit} f_{Gluc,EnzHyd,FiltEnz}\, B_{Enz} + \sum_{unit,st} z_{unit,st} F_{SrcSrcSteam,unit}\, B_{st} \frac{CEPCI_{2014}}{CEPCI_{2005}} \\ & \left. \times 11.03\right) \frac{3600 \times 24 \times 365 \times 0.8 \times 10^{-6}}{1000} \end{aligned}$$

Where: B are costs or revenues [R/ton except Bst which is $ in 2005/ton], flowrates are divided by 1000 to convert from kg to t, unit conversions are also done to convert from s^{-1} to $year^{-1}$ and to millions of R, 0.8 is the fraction of annual operating time, 11.03 is the R/$ exchange rate, $Lang$ is a Lang factor used to convert from purchased cost of equipment to fixed cost of equipment, 10 is the lifetime of major units, 5 is the lifetime of heat exchangers and a ratio of CEPCI is used to convert the steam cost from Smith & Varbanov (2005) from 2005 to 2014.

The objective function is non-linear as some of the equations for purchased cost of equipment are non-linear. In some models, those with steam explosion or acid hydrolysis, the objective function contains binary variables associated with steam choice ($z_{unit,st}$). The following section describes the calculations of the environmental impact and shows the environmental objective function.

3.8. Environmental Impacts

Environmental impacts were determined using **SimaPro V7.3.3** by Product Ecology Consultants (PRé Consultants) using **EDIP/UMIP 97 V2.05** with World normalisation factors and the **Ecoinvent V2.2** database. Some components were taken from the South African Liquid Fuels Database developed by the University of Cape Town and The Green House. The weighting factors used were the global values, while the EU-15 values were used when global values were not available. Weighting factors were taken from Stranddorf et al. (2005) and can be found in *Appendix A.5.2*.

3.8.1. Calculation of Environmental Impacts Using SimaPro

Life Cycle Assessment (LCA) consists of the following four steps (Product Ecology Consultants, 2010):

1. Goal and scope definition.
2. Conducting a life cycle inventory (LCI) to determine the environmental inputs and outputs of the life cycle.
3. Determining the environmental impacts of the inputs and outputs referred to as the life cycle impact assessment (LCIA) phase.
4. Interpretation of the LCA.

3.8.1.1. Step 1

The goal and scope of this study have been discussed in *Section 1.2.* This study is concerned with determining the environmental impact of various pre-treatment, delignification and hydrolysis flowsheets for the production of bio-ethanol and bio-methane as a co-product from sugarcane bagasse. It should be noted that the main purpose of this study is to screen technologies based on economic and environmental factors. As a result of this, the environmental impact is not necessarily representative of a full cradle-to-grave approach. However, this work provides a good starting point for a more rigorous environmental study to be conducted.

The **functional unit** is the flowrate of sugarcane bagasse which was fixed at 15 kg/s in all the models. Details of how this flowrate was determined are discussed in *Section 3.1.*

Each model produces different amounts of methane and glucose from the same amount of sugarcane bagasse. Producing methane and ethanol from sugarcane bagasse displaces fossil fuels and the system boundaries of the study should be expanded to incorporate the benefits of reducing fossil fuel consumption.

3.8.1.2. Step 2

Inputs to the process are: sugarcane bagasse, sulphuric acid, sodium hydroxide, water, steam and enzymes.

Outputs from the process are: the methane produced from xylose, glucose that will be used to produce ethanol, and the exit gas from the flash streams which contains acetic acid, furfural and sulphuric acid.

Steps 2 and 3 are incorporated in the GAMS model.

3.8.1.3. Step 3

In SimaPro the required processes were selected and the impacts were calculated using the 'Analyze' tool. The normalised impacts were copied into an Excel spreadsheet and the data was arranged in tables that were input into GAMS. The data tables used for the environmental analysis can be found in *Table A.5.1, Table A.5.2* and *Table A.5.3* in *Appendix A.5.1.*

Inputs

The sugarcane **bagasse** component in the database did not include the carbon dioxide used by the sugarcane to grow which would produce a negative impact on global warming. This was calculated using the general formula for bagasse of $CH_{1.61}O_{0.7}$ (Pellegrini & De Oliveira, 2007). The mass of carbon per kg of bagasse was calculated (0.484 kg C) and it was assumed that all of this carbon was produced using CO_2. The corresponding mass of CO_2 used to produce this carbon was found to be 1.77 kg CO_2/kg bagasse. The environmental impact of CO_2 was then calculated and subtracted from the global warming potential of the bagasse component in the database. This resulted in bagasse having a negative global warming potential as can be seen in *Table A.5.1* in *Appendix A.5.1.*

Sulphuric acid, sodium hydroxide and **water** were taken from the Ecoinvent database. The impacts of these components can be found in *Table A.5.1* in *Appendix A.5.1.*

In many cases (Bonomi et al., 2011; Moncada, Matallana & Cardona, 2013) some bagasse is used for **steam** and electricity production to ensure that the plant is energetically self-sufficient. It was assumed that the steam used on the plant would be produced using the solid by-product from the pre-treatment and bagasse when necessary. The database component, electricity from bagasse, was modified to determine the environmental impact of the different levels of steam, $EI_{c,s}$, based on their heat of vapourisation using the following equation:

$$EI_{c,s} = \frac{EI_{c,electricity\ from\ bagasse}}{0.7 \times 1000 \times \Delta H_{vap,s}}$$

Where: $EI_{c,electricity\ from\ bagasse}$ is the normalised environmental impact of electricity produced from bagasse from SimaPro [Normalised EI/MJ^{-1}], 0.7 is the isentropic efficiency ratio of a steam turbine producing electricity from bagasse (Dias et al., 2011), 1000 is used to convert from MJ to kJ and $\Delta H_{vap,s}$ is the heat of vapourisation of steam *s* [kJ/kg].

The environmental impact of the different steam levels can be found in *Table A.5.2* in *Appendix A.5.1.*

Enzymes are not included in Ecoinvent V2.2 however it was important to include enzymes in the environmental impact analysis. Few studies have been conducted concerning the environmental impact of enzymes other than those conducted by the company producing the enzymes (Nielsen, Oxenbøll & Wenzel, 2007; Skals et al., 2008). These studies also used different methodologies (Eco-Indicator 95 V2.1) and could not be adapted for use in this study. The work of Harding (2008) was used to develop a process in SimaPro. Full details of this can be found in *Appendix A.5.3*. Although the error of some of the impact categories was as large as 95%, the model was still used because for most categories the model underestimated the environmental impact when compared to the values calculated by Harding (2008) (see *Appendix A.5.3*) and it is important to get an idea of the contribution of enzymes to the overall environmental impact.

When compared with the results of Harding (2008) in *Appendix A.5.3*, he EDIP/UMIP 97 category where this work may overestimate EI of enzymes- is global warming. Underestimation of the enzyme environmental impact may occur in the following categories: ozone depletion, human toxicity and soil ecotoxicity. EDIP/UMIP 97 does not differentiate between fresh water and marine ecotoxicity and as a result it is not possible to know if the water ecotoxicity will be overestimated or underestimated.

Results showed that the environmental impact of enzymes was large even when transport of the enzymes was excluded (91.3% to 114%, see *Section 4.4.1.3*). As a result of this, the possible environmental impacts associated with transportation of enzymes was excluded. If enzymatic hydrolysis is used it would be environmentally beneficial to have on-site enzyme production.

Outputs

The Ecoinvent database has the environmental impact for 1 kg of 96 vol% **methane** produced from a mix of biomass raw materials. This includes the environmental impact of cleaning and upgrading the bio-methane.

The environmental impact of the downstream processing of glucose to **ethanol** was excluded in this work.

In order to include the reduction in environmental impact due to using biofuels rather than fossil fuels a **system expansion** was performed. This analysis was performed for both methane and ethanol. For **methane**, it was assumed that the bio-methane produced would replace methane from natural gas. The environmental impact for natural gas from offshore sources per m^3 was found in the Ecoinvent database and converted to an impact per kg by using the density at normal temperature and pressure (20°C and 1 atm) which was 0.668 kg/m^3 and multiplied by negative one to cause a reduction in environmental impact. The values obtained can be seen in *Table A.5.4* in *Appendix A.5.1.*

The system expansion for **ethanol** was based on ethanol replacing an energy equivalent amount of petrol. In South Africa, 70% of petrol is produced from crude oil and 30% from coal-to-liquid fuels. In SimaPro the environmental impact of petrol from crude was taken from the Ecoinvent database. The petrol produced by coal-to-liquid fuels was taken from the South African Liquid Fuels Database developed by the University of Cape Town and The Green House. These components were then added in the proportions above to get the EI of 1 kg of South African petrol. Ethanol and petrol have different higher heating values (29 700 kJ/kg for ethanol and 48 000 kJ/kg for petrol), the ratio of these was used to determine the energy equivalent mass ratio for the two fuels (0.619 kg petrol/kg ethanol). This was used to convert the calculated EI from mass of petrol to mass of ethanol. The EI values for this can be found in *Table A.5.4* in *Appendix A.5.1.*

It was assumed that the bio-methane produced by the plant and the fossil methane have the same use and thus the same EI associated with their use. The bio-methane in this process includes upgrading so that both the bio-methane and fossil methane have a similar energy content. Desulphurisation of bio-methane is included which results in cleaner burning methane than the fossil methane which contains hydrogen sulphide. The reduction of EI based on the cleaner burning nature of bio-methane was not included in this analysis.

The amount of CO_2 produced from combusting ethanol and petrol was calculated assuming complete combustion. *Table A.5.5* in *Appendix A.5.1* shows this comparison. It was found that combusting energy equivalent amounts of petrol and ethanol produces the same amount of CO_2 and thus it was not necessary to include the combustion in the analysis. Petrol produced from coal contains impurities

such as sulphur and nitrogen which produce environmentally damaging oxides when combusted. Ethanol, however, does not contain these impurities and is thus cleaner burning. The reduction in the EI of ethanol as a result of its cleaner burning nature has not been included in this analysis.

Sulphuric acid exiting in the **flash vapour** had to be described as an equal mix of SO_2 and SO_x in order to be included in the analysis using EDIP/UMIP 97. Furfural in the flash vapour had no environmental impact as **furfural** is not included in the EDIP/UMIP 97 calculations.

Weighting Factors

In order to construct Pareto curves, a single score is needed for the environmental impact. The normalised environmental impacts for each category need to be multiplied by weighting factors before they can be added to get a single score. The weighting factors used were the global values and the EU-15 values when global values were not available. Weighting factors were taken from Stranddorf et al. (2005) and can be found in *Table A.5.6* in *Appendix A.5.2*.

3.8.1.4. Step 4

Step 4 is discussed in *Section 4*.

3.8.2. Environmental Objectives in GAMS

The environmental impact of each component involved in the environmental analysis, *g*, can be calculated in each impact category, *c*, as follows:

$$EI_{c,g} = EIData_{c,g} \times F_g \times 3600 \times 24 \times 365 \times 0.8$$

Where: $EIData_{c,g}$ is the normalised environmental impact data for 1 kg of each component in the tables in *Appendix A.5.1,* F_g is the flowrate of the component *g* [kg/s] which is converted to [kg/year] using the numbers shown, where 0.8 is the percentage operating time in a year. Steam components will be multiplied by the appropriate binary variable to ensure that the impact is only calculated if that utility is selected.

$EI_{c,g}$ is then be multiplied by a weighting factor, WF_c (see *Table A.5.6* in *Appendix A.5.2*), and summed over the impact categories *c* and components *g* to get the total environmental impact per year which is used as the **environmental objective function**:

$$TotEI = \sum_g \left(\sum_c WF_c . EI_{c,g} \right)$$

4. Results and Discussion

The results of the modelling are presented and discussed in this chapter. Two sets of investigations were conducted. In the first, it was assumed that no sodium hydroxide was recycled and in the second set the amount of sodium hydroxide recycled was fixed. The results of the models with no sodium hydroxide recycling are discussed in *Section 4.1*. A sensitivity analysis to determine whether the fixed value of the acid soluble lignin concentration has a large effect on the overall model when acid hydrolysis was used is presented in *Section 4.2.* From the analysis in *Section 4.1* it was found that in order for delignification to be profitable, sodium hydroxide would need to be recycled. A sensitivity analysis was performed to examine how the amount of sodium hydroxide recycled affects the objective functions and this analysis can be found in *Section 4.3.* Results with a fixed recycle of sodium hydroxide of 75% are then presented in *Section 4.4.* In *Section 4.5,* the effect of adding delignification to the models is discussed. *Section 4.6* discusses the possibility of recycling enzymes to reduce the environmental impact associated with them. In *Section 4.7* the concentration of inhibitors formed in the models is shown and evaluated. *Section 4.8* compares the models with regards to both objectives and presents a graphical representation of the solution space.

4.1. Economic Objective with No Recycling

Initially the models were run without including recycling of sodium hydroxide. *Figure 4.1* below shows the results when the models are optimised in terms of an economic objective. In this figure, revenues are shown above the axis as these are positive and costs are shown below the axis as these reduce profit. The overall profit is shown above each bar and this is the sum of revenues added to the sum of expenses which are negative.

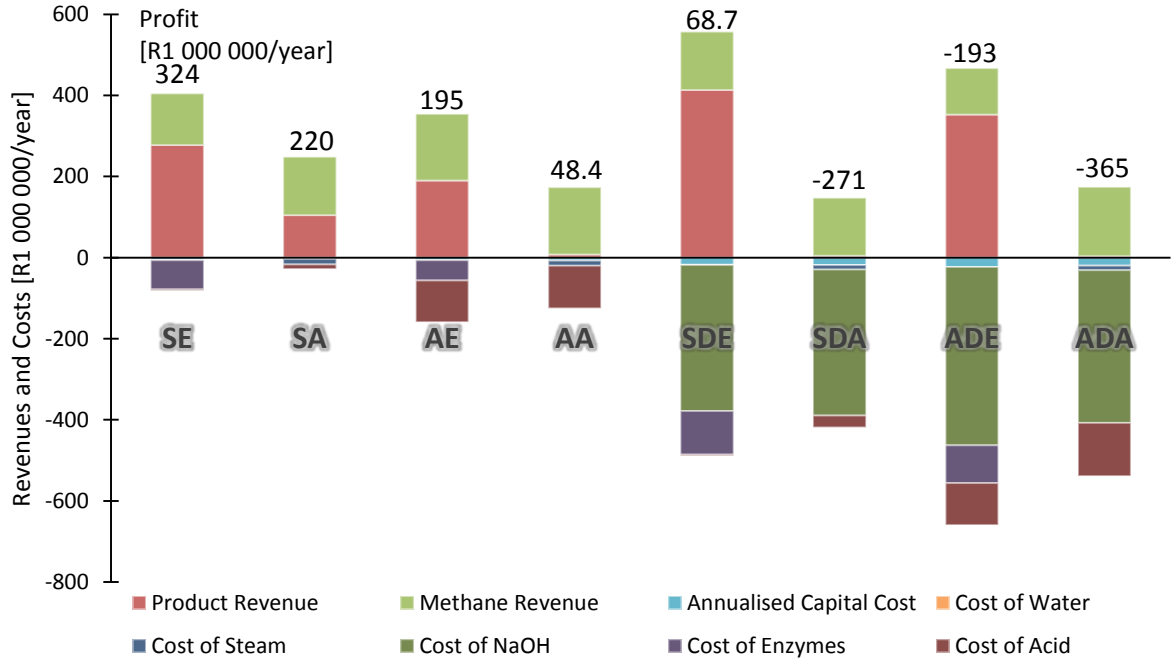


Figure 4.1: Revenues and costs for models with no sodium hydroxide recycle

Reminder of acronyms: steam explosion with acid hydrolysis (SA); steam explosion, delignification and acid hydrolysis (SDA); steam explosion with enzymatic hydrolysis (SE); steam explosion, delignification and enzymatic hydrolysis (SDE); acid pre-hydrolysis with acid hydrolysis (AA); acid pre-hydrolysis, delignification and acid hydrolysis (ADA); acid pre-hydrolysis with enzymatic hydrolysis (AE); acid pre-hydrolysis, delignification and enzymatic hydrolysis (ADE).

This analysis showed delignification to be expensive and only one scenario involving delignification had a positive annualised profit as can be seen in *Table 4.1* below. This was a result of the large cost of sodium hydroxide as it was assumed that sodium hydroxide was not recycled in the plants. The average sodium hydroxide cost was R384 000 000/year and the ADE model had the largest sodium hydroxide cost (R440 000 000/year in *Table 4.1*) while SDA and SDE had the lowest sodium hydroxide cost (R360 000 000/year in *Table 4.1*). This result leads to a sensitivity analysis regarding the recycling of sodium hydroxide which is discussed in *Section 4.3.*

Table 4.1: Change in profit and environmental impact with amount of lignin solubilised

Model	Revenues and Expenses [R1 000 000/year]					Raw Material Costs [R1 000 000/year]				
	Profit	*Glucose Revenue*	*Methane Revenue*	*Annualised Capital Cost*	*Raw Material Cost*	*NaOH*	*Acid*	*Enzymes*	*Steam*	*Water*
SE	324	277	128	6.11	91.4	0	2.47	71.8	0.226	0.0329
SA	220	105	143	3.59	24.4	0	11.6	0	12.8	0.0658
AE	195	190	164	6.68	164	0	103	49.2	0	0.0941
AA	48.4	7.79	166	7.12	118	0	105	0	13	0.127
SDE	68.7	414	143	18	496	360	2.47	107	0.226	0.101
SDA	-271	4.07	143	18.1	401	360	29.5	0	11.0	0.124
ADE	-193	353	114	23	659	440	103	93.5	0	0.126
ADA	-365	3.53	171	19.9	519	377	131	0	11.2	0.187

Adding delignification into the models results in solubilisation of cellulose which can result in a decrease in the concentration of glucose, although the yield of glucose may have increased due to improved access to cellulose resulting from the removal of lignin. This is a consequence of the large sodium hydroxide cost. All the models that included delignification in this scenario, chose a sodium hydroxide weight percent of 0.25 in order to reduce the cost of sodium hydroxide. At this sodium hydroxide weight percent, 4% of the cellulose is solubilised and 25% of the lignin is solubilised. However, the gradient of the solubilisation curves (*Figure 3.6* in *Section 3.4*) is steeper for lignin than for cellulose (58.9 and 22.9 respectively). This indicates that as the sodium hydroxide weight percentage increases, the increase in the amount of lignin solubilised increases more significantly than the amount of cellulose solubilised. Since the amount of lignin solubilised influences the conversion of cellulose to glucose, delignification will provide greater increases to cellulose conversion when higher sodium hydroxide weight percentages are used.

Delignification also increases the amount of acid that must be used in acid hydrolysis as sodium hydroxide entrained in the solids forms a precipitate when acid is added. The amount of acid added in the hydrolysis unit in SDA increased to 0.419 kg/s from 0.141 kg/s in SA, and for ADA 0.428 kg/s was needed compared to 0.0222 kg/s in AA. In AA the amount of acid added in hydrolysis is very low as the stream already contains acid from the acid pre-hydrolysis. If acid has been used in pre-treatment the amount of sodium hydroxide required increases as some of the sodium hydroxide forms a precipitate with the residual acid. In the steam explosion models, SDE and SDA, 2.43 kg/s of sodium hydroxide was required for 0.25 wt% sodium hydroxide but 2.96 kg/s was required in ADE and 2.54 kg/s in ADA for the same sodium hydroxide mass percentage.

4.2. Sensitivity to Acid Soluble Lignin (ASL) Concentration in Acid Hydrolysis

As described in *Section 3.5.2*, a fixed value of 4 mg/g solid was used for the amount of lignin solubilised by acid in the hydrolysis unit. A sensitivity analysis was conducted to investigate the effect the amount of lignin solubilised in acid hydrolysis has on the objective functions of profit and environmental impact.

Lavarack, Griffin & Rodman (2002) stated that the maximum acid soluble lignin (ASL) concentration achieved was 47 mg/g solids for the investigated experimental conditions (temperature: 180-200°C; mass ratio of solid to liquid: 1:5-1:20; acid concentration: 0.25-8 wt%; reaction time of 10-2000 min). However, when a Matlab model using the kinetics of Lavarack, Griffin & Rodman (2002) was used to investigate the concentration of ASL at the conditions used in the GAMS models, higher values of ASL concentration were achieved. For this reason, a higher maximum concentration was used in the sensitivity analysis.

A sensitivity analysis was conducted where $ASLconc$ was varied between 4 mg/g solid and 70 mg/g solid. The results of this sensitivity analysis can be seen in *Table 4.2* below. The amount of lignin solubilised by acid in the hydrolysis unit had very little effect on the profit (maximum percentage difference of 1.90%) or the environmental impact (maximum percentage difference of 1.16%). This shows that it is not necessary to include a complicated non-linear equation to describe this relationship in the GAMS for acid hydrolysis model, instead a fixed acid soluble lignin concentration of 4 mg/g solid was used.

Table 4.2: Change in profit and environmental impact with amount of lignin solubilised

Model	Profit		Environmental Impact	
	Difference [R1 000 000/year]	Percentage Difference	Difference [year $^{-1}$]	Percentage Difference
AA	0.073	0.160	451	0.0192
SA	0.992	0.534	8 560	1.160
ADA	0.105	0.133	1 080	0.0333
SDA	0.047	1.90	255	0.0119

4.3. Sensitivity to Recycling Sodium Hydroxide

A variable, $NaOHRecycCost$, was added into the models to investigate the sensitivity of the models to the recycling of sodium hydroxide. The cost of sodium hydroxide and the environmental impact (EI) of sodium hydroxide was multiplied by $NaOHRecycCost$ such that when $NaOHRecycCost$ is zero, there would be no costs and environmental impact associated with sodium hydroxide. When $NaOHRecycCost$ is one, the full cost and environmental impact is included in the model as in *Section 4.1* above. This sensitivity analysis essentially determines the profitability of the flowsheet with respects to the cost of recycling sodium hydroxide.

The results of the sensitivity analysis can be seen in *Figure 4.2* on the following page. The SDE flowsheet was profitable for all values of $NaOHRecycCost$ as was expected from the results in *Section 4.1*. For ADE however the flowsheet is only profitable when $NaOHRecycCost$ is less than 0.57 (*Figure 4.2*). This means that if the annual recovery cost of sodium hydroxide (including annualised capital costs, energy costs and sodium hydroxide make-up costs) is less than 57% of the total cost per annum of sodium hydroxide required by the plant with no recycling, the plant will be profitable. For SDA this crucial $NaOHRecycCost$ value was lower, 0.26 (*Figure 4.2*). For ADA the profit was negative for all values of $NaOHRecycCost$ below 0.052 (*Figure 4.2*) so this flowsheet is not profitable unless there is almost no cost involved with recycling sodium hydroxide.

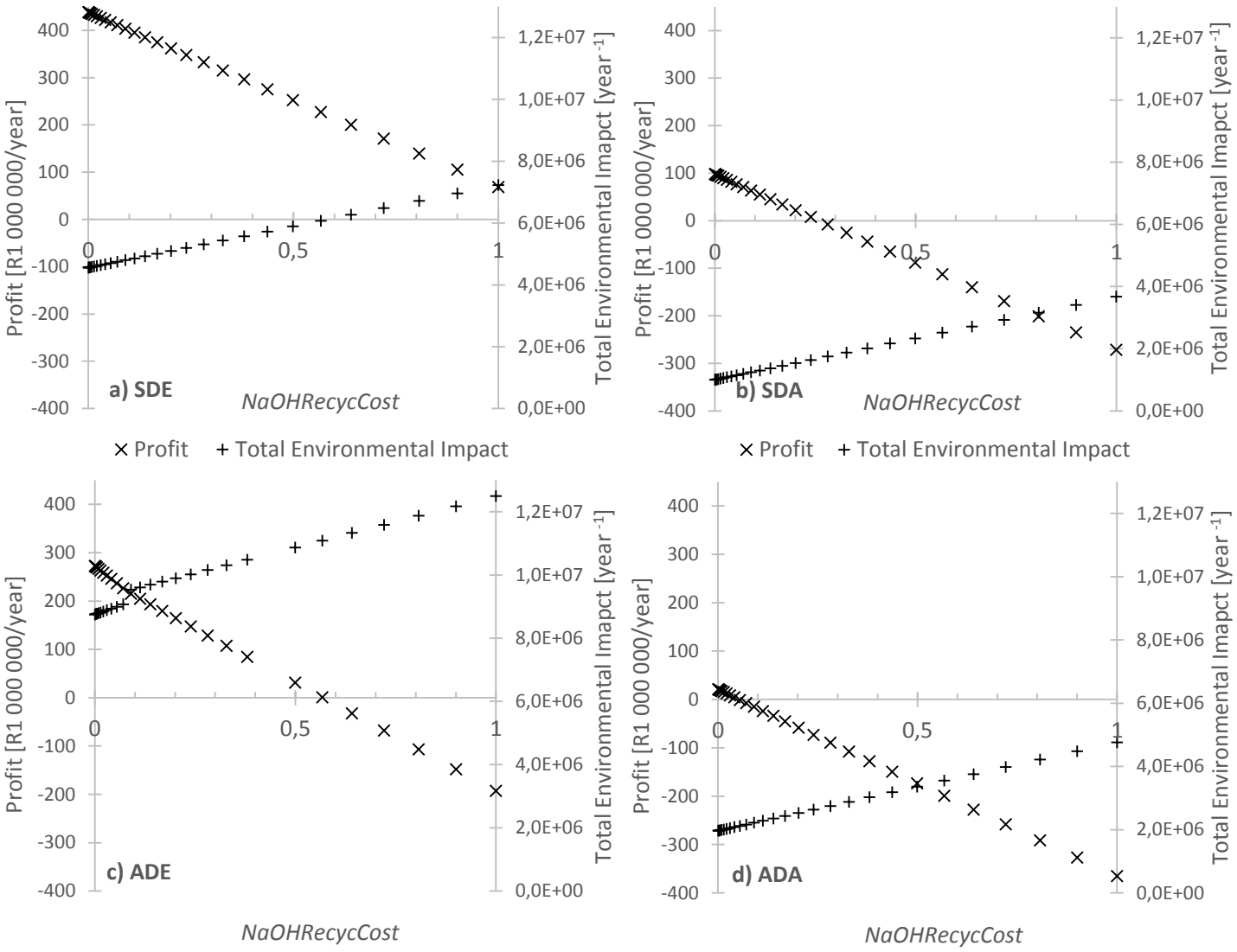


Figure 4.2: Sensitivity analysis to sodium hydroxide recycle cost

4.4. Results with 25% $NaOHRecycCost$

Delignification using sodium hydroxide is similar to the Kraft Process that has been used in the paper industry since 1885 (Ragauskas, n.d.). The Kraft Process has a high recovery of chemicals, about 97% (Tran & Vakkilainnen, 2012). Little information is available for the recycling of sodium hydroxide when herbaceous biomass such as sugarcane bagasse is used. However it is likely that a lower recovery will be possible as minerals, such as silicon, in biomass may impede the recovery and require purging.

In this study the $NaOHRecycCost$ value, described in *Section 4.3* above, was set to 0.25 which implies that the cost and environmental impact associated with sodium hydroxide recycling is equivalent to 25% of the total annual cost of sodium hydroxide without recycling. This value attempts to account for the capital costs, operating costs and the cost of make-up of sodium hydroxide associated with the recovery process. Although the recovery process includes a boiler which can be used to produce steam and electricity, the process also requires a kiln which requires a large energy input and may contribute significantly to the operating costs. The recycle process was not explicitly modelled and further investigation into the economics of this recovery process is recommended.

Results for both an economic and an environmental optimisation of the various flowsheet options with a $NaOHRecycCost$ value of 0.25 are presented below.

4.4.1. Economic Optimisation

When only 25% of the total sodium hydroxide cost is included in the models almost all the scenarios become profitable and only ADA is unprofitable. *Figure 4.3* below shows the revenues and costs for these models. In this figure, revenues are shown above the axis as these are positive and costs are shown below the axis as these reduce profit. The overall profit is shown above each bar and this is the sum of revenues added to the sum of expenses which are negative. SDA is barely profitable and ADA is not profitable which implies that delignification should only be considered for SDE and ADE. Adding delignification causes the profitability of SE to increase from R324 000 000 per year for SE to R344 000 000 per year for SDE. However the profitability of AE is reduced from R195 000 000 per year for AE to R143 000 000 per year for ADE.

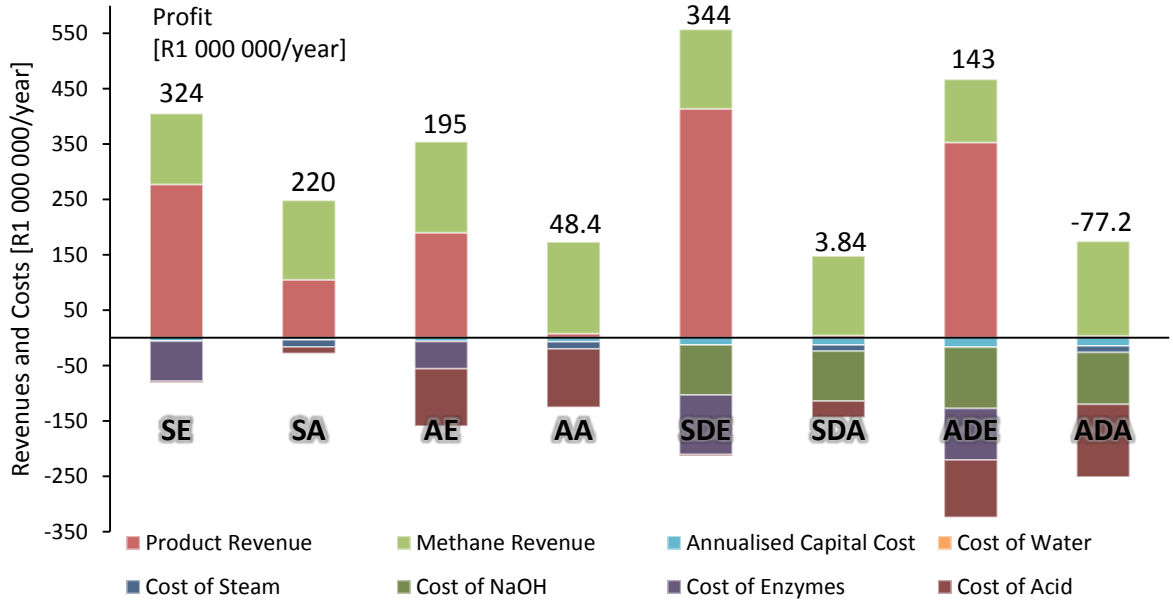


Figure 4.3: Revenues and costs for models with 25% sodium hydroxide recycle cost

Table 4.3 below summarises the economic results of each model as shown in *Figure 4.3* on the previous page. The results from this table are discussed in terms of revenue in *Section 4.4.1.1* and costs in *Section 4.4.1.2.* The environmental impact of the models are presented in *Section 4.4.1.3*.

Table 4.3: Economic results of models using economic objective function

Model	Revenues and Expenses [R1 000 000/year]					Raw Material Costs [R1 000 000/year]				
	Profit	*Glucose Revenue*	*Methane Revenue*	*Annualised Capital Cost*	*Raw Material Cost*	*NaOH*	*Acid*	*Enzymes*	*Steam*	*Water*
SE	324	277	128	6.11	91.4	0	2.47	71.8	0.226	0.033
SA	220	105	143	3.59	24.4	0	11.6	0	12.8	0.066
AE	195	190	164	6.68	164	0	103	49.2	0	0.094
AA	48.4	7.79	166	7.12	118	0	105	0	13.0	0.127
SDE	344	414	143	12.9	225	90.0	2.47	107	0.226	0.101
SDA	3.84	4.07	143	13.0	131	90.0	29.5	0	11.0	0.124
ADE	143	353	114	17.2	329	110	103	93.5	0	0.126
ADA	-77.2	3.53	171	14.7	237	94.2	131	0	11.2	0.187
Avg.	150	169	147	10.2	165	96.0*	61.1	80.5*	6.06	0.107

*Average calculated using non-zero cost values.

4.4.1.1. Revenue Based

In all the models where acid hydrolysis was used (SA, AA, SDA and ADA) the revenue from methane was much greater than the revenue from glucose. The methane revenue accounted for 24.4-97.9% of the total revenue. This highlights the importance of a bio-refinery approach rather than a single product plant. Especially as the production of methane does not compete with glucose production because methane is produced from the xylose resulting from hemicellulose hydrolysis which exits the pre-treatment unit in stream $SnkC5$, and glucose is produced by the hydrolysis of cellulose in the hydrolysis unit and exits in stream $SnkC6$.

Using acid in pre-treatment causes more hemicellulose to react and thus increases methane revenue. AE and ADE produced large amounts of methane but ADE was able to produce more glucose than AE as a result of increased enzymatic hydrolysis yields caused by delignification. The other scenarios where enzymatic hydrolysis was used had larger glucose revenues than methane revenues (SE, SDE and ADE).

4.4.1.2. Cost Based

Figure 4.4 on the following page, shows the average contribution of the different costs in all the models with 25% sodium hydroxide recycle cost. From this graph it can be seen that raw material costs are more significant than capital costs.

Capital costs were annualised over ten years except for heat exchangers which were annualised over five years. CTBE annualise over twenty five years (Bonomi et al., 2011) however this is probably unrealistic for South Africa where the bio-ethanol industry is only starting up. Capital costs were less significant than raw material costs and the average annualised capital cost for the models was 6.13% of the total costs which can be seen in *Figure 4.4*. Annualised capital costs ranged from R3 590 000 per year for the SA model to R17 200 000 per year for the ADE model as can be seen in *Table 4.3*. Delignification models had higher capital costs as these involve additional units ($HXDelig$, $Delig$ and $FiltDelig$).

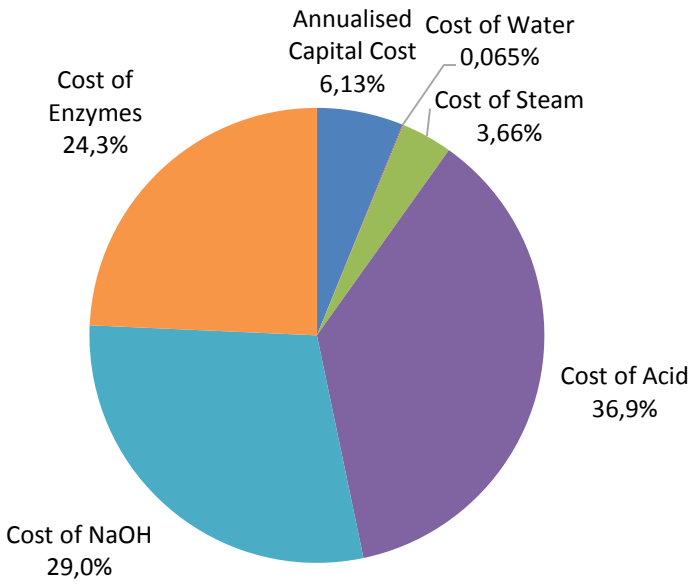


Figure 4.4: Average contribution of costs for models with 25% sodium hydroxide recycle cost

Acid costs were the largest overall contributor to costs and average 36.9% of the total costs (*Figure 4.4*.). There were no models where the acid cost was zero as all the steam explosion models selected the binary variable for acid-catalysed steam explosion. Acid pre-treatment uses higher concentrations of acid (2-6 wt%) than acid hydrolysis (0.07-0.28 wt%) which causes models involving acid pre-treatment to have a much larger acid cost. The acid cost increases when delignification is added to the models which is as a result of the precipitation of acid in the hydrolysis unit which requires that larger amounts of acid be added to the hydrolysis reactor to achieve the same acid mass percent. In order to reduce costs, the models involving delignification reduced the wt% of acid used in hydrolysis from 0.14 wt% to 0.07 wt% however, the acid cost still increased.

Sodium hydroxide costs were still large, R96 000 000 on average (see *Table 4.3*) in the delignification models, and contributed an average of 29.0% of the total costs (*Figure 4.4*.). Even with the lower sodium hydroxide costs, the lowest weight percent of sodium hydroxide (0.25 wt%) was used in all the delignification models.

Enzyme costs were on average R80 500 000 per year (see *Table 4.3*) which contributed between 28.8% (ADE) and 89.0% (SE) of the total costs. The largest enzyme cost was in the SDE model and was R107 000 000 per year (see *Table 4.3*).

The steam cost is greatest in models involving acid hydrolysis as these reactors are at higher temperatures (180-230°C) than all the other units and require steam at higher pressures for heating. The cost of low pressure steam was zero (see *Section 3.7.1.3*) which resulted in some models (AE and ADE) having zero steam cost (see *Table 4.3*) even though steam was used for heating. The AA and SA models had the highest steam cost of R13 000 000 per year and R12 800 000 per year respectively (see *Table 4.3*). On average, steam contributed 3.66% of the total costs as can be seen in *Figure 4.4*. The energy generation section of the plant should be modelled to check that enough steam will be produced and that the cost of low pressure steam is not underestimated significantly.

The cost of water was low for all models and was on average R107 000 per year (see *Table 4.3*). The cost of water was greatest for the ADA model which was R187 000 (see *Table 4.3*). On average, water contributed 0.065% of the total costs (*Figure 4.4*.).

4.4.1.3. Environmental Impact

The environmental results in this study were not verified as it was difficult to source literature that had studied the environmental impacts of similar systems and used the same environmental impact methodology. The environmental impact (EI) of enzymes was far greater than any other raw material or product. Although enzymatic hydrolysis requires milder operating conditions than acid hydrolysis this does very little to reduce the large environmental impact associated with enzyme production. In the models involving enzymatic hydrolysis, the enzymes accounted for 92.8% to 119% of the total environmental impact. As some of the impacts were negative (for example, ethanol) it was possible for the percentage to be greater than 100%. The average environmental impact of enzymes in the enzymatic hydrolysis models was 7 380 000/year which accounted for 67.8% of the average total environmental impact of the models (*Figure 4.5* on the following page). This impact was calculated assuming the enzymes would be produced on site as the environmental impact was large. If enzymes have to be imported for use in South Africa the environmental impact will increase further.

From the comparison with Harding (2008), a possible category in which the environmental impact may have been overestimated in this work was global warming potential (see *Section 3.8.1.3* and *Appendix A.5.3* for more detail). In the work of Harding (2008) the global warming potential is negative as the production of wood chips consumes carbon dioxide which results in the overall global warming potential of enzymes being negative. However, the global warming potential of all wood chips in the **EcoInvent V2.2** database have a positive environmental impact caused by the use of the machinery to harvest and process the wood. As a result, the global warming potential of enzymes in this work is positive. However as global warming potential contributes 2.75% of the enzyme environmental impact it is more likely that one of the other categories have been overestimated.

The method used by Harding (2008), **CML baseline 2000 V2.03 / World, 1990**, differentiated between fresh water and marine ecotoxicity. When the environmental impact of enzymes developed in this work was compared to that of Harding (2008) using the same method, the environmental impact of the enzymes in this work was overestimated for 'fresh water aquatic toxicity' and underestimated for 'marine aquatic ecotoxicity' (see *Section 3.8.1.3* and *Appendix A.5.3* for more detail). The **EDIP/UMIP 97** method used in this work does not have separate categories for 'fresh water' and 'marine ecotoxicity' so it was unclear whether the 'water ecotoxicity' would be overestimated or underestimated. The environmental impact of 'ecotoxicity water chronic' and 'acute' combined make up 69.3% of the total environmental impact of enzymes in this work which suggests that the 'water ecotoxicity' may be overestimated.

Electricity contributes 93.6% of both ecotoxicity categories and is the major contributor to the total EI score for enzymes. The mass balance of Harding (2008) for extracellular, aerobic production of cellulase in a batch reactor requires 183.1 MJ of electricity to produce 1 kg of cellulase enzymes. However, methods that require less energy are also available such as solid state cultivation which requires 6.5 MJ of electricity per kg of cellulase (Harding, 2008).

Possible categories where the EI of enzymes may have been underestimated when compared to Harding (2008) were 'ozone depletion' which contributes an average of 0.004% of the total EI of enzymes, 'human toxicity' (15.2% contribution) and 'soil ecotoxicity' (0.03% contribution).

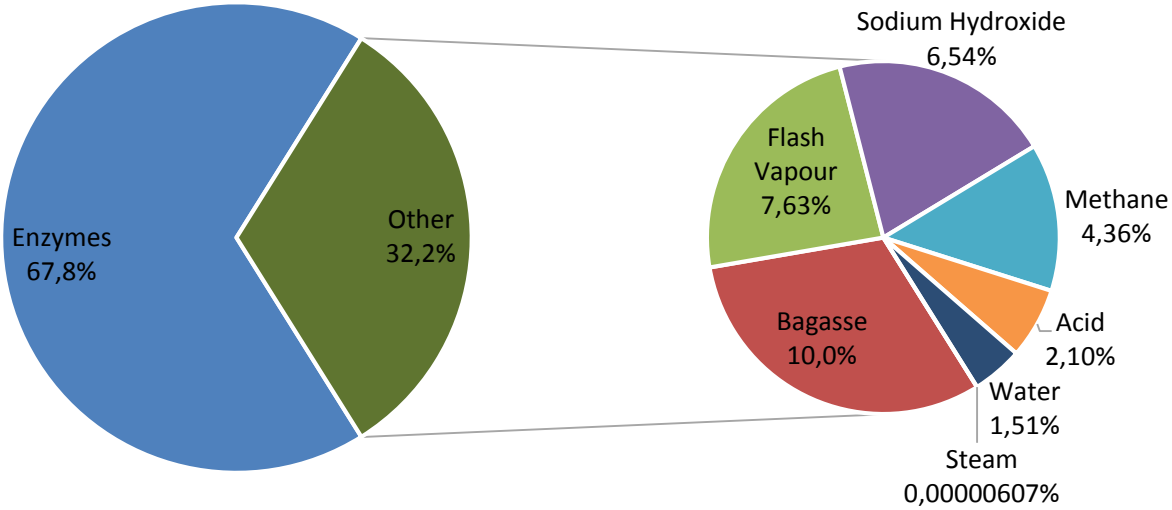


Figure 4.5: Average environmental impacts for models with 25% NaOH recycle cost

The sugarcane bagasse accounted for the second largest environmental impact and was an average of 10.0% of the total environmental impact *(Figure 4.5)*. The main contributor to the impact of sugarcane bagasse was human toxicity in soil which accounted for 104% of the bagasse impact. This percentage is greater than 100% as the global warming potential of bagasse is negative as CO_2 is consumed when the sugarcane grows. As bagasse is the raw material of the process this impact is unavoidable. Bagasse is also a waste product from the sugar industry and this impact is more of a consequence of sugar production than an impact of the bio-refinery plant.

The environmental impact of sodium hydroxide in the delignification models was on average 712 000/year which accounted for 6.54% of the total EI. However, this assumes that the cost of recycling sodium hydroxide is 25% of the total annual sodium hydroxide cost with no recycling. It is possible that this impact can be reduced if more of the sodium hydroxide is recycled.

The vapour emissions resulting from the flashes in acid pre-hydrolysis, acid hydrolysis and steam explosion account for a total of 7.63% of the total EI (*Figure 4.5*). The average magnitude of the environmental impact is 72 300/year and 759 000/year for steam explosion models and acid pre-treatment models respectively. Models with steam explosion had lower environmental impacts than those with acid pre-treatment and models with steam explosion and enzymatic hydrolysis had the lowest in this category. In reality a scrubber would probably be installed to prevent the release of acidic chemicals into the environment so these impacts could be greatly reduced.

Methane which is produced from the xylose rich stream that exits the pre-treatment accounts for 4.36% of the total EI (*Figure 4.5*). The average EI of methane in all models was 237 000/year. This impact is overestimated as the impact associated with producing the feedstock for methane production is included in the impact calculation however these impacts have already been taken into account in the impact of the bagasse.

Sulphuric acid contributes 2.10% of the total EI (*Figure 4.5*). The average acid EI was 108 000/year and models that used acid pre-treatment had the largest acid impact as pre-treatment consumes more acid than other units.

Water was accounted for an average of 82 000/year. In enzymatic hydrolysis models, water accounted for 1.51% of the total environmental impact (*Figure 4.5*).

The environmental impact of steam was the lowest of all components and was 0.183/year on average which accounted for only 0.00000607% of the total EI (*Figure 4.5*). It was assumed that sugarcane trash, leaves and residual solids from pre-treatment would be burnt to produce steam and electricity. Some of the sugarcane bagasse could also be burnt to ensure the plant is energetically self-sufficient. The steam needed to heat the enzymatic hydrolysis unit was not included in the model as low pressure steam would be required and this was a free utility thus the cost was not included in the model. However, this means that the environmental impact of steam has been underestimated in enzymatic hydrolysis models but the impact of enzymes is so large that this oversight is not significant.

The categories that contribute the most to the environmental impact of models using enzymatic hydrolysis are: 'ecotoxicity water chronic' and 'acute', 30.1% and 33.2% of the total EI respectively. In acid hydrolysis models, 'human toxicity soil' is the largest contributor (36.0%) but 'ecotoxicity water chronic' and 'acute' are the next greatest contributors to the total EI (17.9% and 14.7% respectively).

4.4.2. Environmental Optimisation

Table 4.4 below shows the profit and environmental impact (EI) for each model when the objective is to maximise profit, and when the objective is to minimise environmental impact.

Table 4.4: Comparison of results for economic and environmental objective functions

Model	Economic Objective Function		Environmental Objective Function		Percentage Difference	
	Profit [10^6 R/year]	**EI** [10^6/year]	**Profit** [10^6 R/year]	**EI** [10^6/year]	**Profit** [%]	**EI** [%]
SE	324	7.07	324	7.07	0.00	3.02×10^{-13}
SA	220	0.400	141	0.270	36.2	32.5
AE	195	8.42	195	8.42	2.56×10^{-11}	-6.33×10^{-14}
AA	48.4	1.90	-93.4	1.31	293	31.4
SDE	344	5.23	315	5.20	8.54	0.419
SDA	3.84	1.64	-26.1	1.59	781	3.09
ADE	143	7.89	130	7.62	9.22	3.48
ADA	-77.2	2.64	-272	2.15	253	18.7

The SE and AE models were unable to reduce the EI by a significant amount. As enzymes are responsible for the majority of the EI, the only way these models can reduce the EI is by decreasing the amount of enzymes. In these model combinations the enzyme flowrate could not be reduced substantially. The amount of enzymes required depends on the total stream flowrate entering the enzymatic hydrolysis unit and in all the models the bagasse flowrate is fixed. In the AE model, of the stream entering $MixEnzHyd$, 46% of the total mass is water, 30% is cellulose and 17% is lignin. The water to solids ratio in acid pre-treatment is fixed and very little cellulose and lignin react in the acid hydrolysis unit. This means that there is very little flexibility in the total stream flowrate and thus the enzyme flowrate and thus EI cannot be decreased substantially.

In both SE optimisations the steam explosion model was acid-catalysed. When the environmental objective function is used nothing significant can be done to the steam explosion unit to change the EI as the bagasse flowrate is fixed and the steam and acid flowrates are related to the bagasse flowrate and thus also fixed. This causes the stream entering $MixEnzHyd$ and thus determining the enzyme flowrate to be fixed resulting in little flexibility with regards to the environmental impact.

The SDE and ADE models have the same lack of flexibility as the SE and AE models, however adding delignification gives the model a small amount of flexibility and enables a small decrease in the environmental impact of 0.419% and 3.48% respectively. The small difference in the SDE model results from the stream leaving $FiltDelig$ containing less liquids entrained in the solid thus reducing the total stream flowrate. This in turn reduces the amount of enzymes added in the mixer, $MixEnzHyd$, however this is only a minor reduction in EI but also reduces the profit by 8.54%. In the ADE model, the sodium hydroxide weight percent used in delignification has increased from 0.25 wt% to 0.365 wt%. This caused the amount of solids entering the mixer, $MixEnzHyd$, to decrease which reduces the amount of enzymes added and thus decreases the EI.

In the SA and SDA models, the amount of methane produced has been decreased to result in a 32.5% and 3.09% decrease in the EI respectively. In the SA model this decrease was caused by using acid-catalysed steam explosion in the economically optimal model and un-catalysed steam explosion in the environmentally optimal model. In the SDA model, the decrease in EI is caused by increasing the

amount of liquid entrained in the solids exiting $FiltSteamEx$ by increasing $S_{SteamExFiltSplit}$ from 0.124 to 0.300. This causes less methane to be produced as less xylose is in the $SnkC5$ stream. This small change in the filter results in a 3.09% decrease in the environmental impact but also reduces the profit by 781%.

In the AA model a 31.4% reduction in EI was achieved which was the second largest percentage reduction in EI, however this made the model unprofitable with an annual loss of R93 400 000. The reduction in EI was achieved by reducing the amount of acetic acid in the flash gas and the methane produced. These accounted for 34.3% and 14.1% respectively of the total EI in the economically optimised AA model. The other main contributor to EI was bagasse (28.7%) but this flowrate is fixed. By changing the *P* dataset used in acid pre-hydrolysis from 13 to 1, the acetic acid concentration is reduced from 3.55 kg/m^3 to 0.74 kg/m^3 and the xylose concentration decreases from 18.2 kg/m^3 to 3.1 kg/m^3 (see *Appendix A.2.3.1*). Another consequence of reducing the methane production was that no additional acid needed to be added in the hydrolysis unit as enough acid was entrained in the solids and so even though a higher acid concentration was used in hydrolysis (0.28 wt% for EI optimisation and 0.14% for economic optimisation) the total acid added decreased.

In the economically optimised ADA model, 47.1% of the total EI is caused by bagasse and sodium hydroxide. The bagasse flowrate is fixed and thus cannot be used to decrease the EI. The sodium hydroxide weight percent in the economically optimised model is already the minimum (0.25 wt%). The acid weight percent used in pre-treatment also influences the amount of sodium hydroxide added and this is also already at the minimum (2 wt%) in the economically optimised model. As a result of this, there is little that can be done to significantly reduce the EI in the ADA model. The same change in *P* dataset is observed as in the AA model, however this has less of an effect on change in EI because sodium hydroxide accounts for a large percentage of the EI.

4.5. Effect of Adding Delignification

This section discusses how the models change when delignification is included between pre-treatment and hydrolysis. *Section 4.5.1* discusses the economic changes in the models and *Section 4.5.2* explains the environmental changes observed in the models.

4.5.1. Economic Changes

In all models except SE, adding delignification reduced the profitability of the model. This was mostly due to an increase in raw material costs which was largely due to the cost of sodium hydroxide. *Table 4.5* below presents a summary of the economic changes in the models. These are discussed in more detail below.

Table 4.5: Effects of delignification on revenues and costs

Model	Percentage Change [%]					Contribution to Raw Material Change [%]				
	Profit	Glucose Revenue	Methane Revenue	Annualised Capital Cost	Raw Material Cost	NaOH	Enzymes	Acid	Water	Steam
SDE	6.02	49.2	12.3	110	147	67.2	26.6	0	0.051	0
SDA	-98.3	-96.1	0.00	262	435	84.7	0	16.9	0.055	-1.69
ADE	-26.6	85.8	-30.5	158	100	66.8	26.9	0[1]	0.019	0
ADA	-259	-54.6	2.96	106	101	79.3	0	22.1	0.051	-1.48
Avg.	**-95**			**159**	**196**	**74.5**	**26.7[2]**	**19.5[2]**	**0.044**	**-1.58[2]**

[1] 8.63×10^{-15}; [2] Average for models with non-zero flowrates of the specific raw material.

4.5.1.1. Revenue Based

Since delignification results in the solubilisation of cellulose, as was discussed in *Section 3.4.1*, the glucose revenue for models using enzymatic hydrolysis after delignification increased by 49.2% for SDE and 85.8% for ADE (*Table 4.5*). This is as a result of the increase in conversion of cellulose to glucose and glucose oligomers ($newX_{EnzHyd,1}$ and $newX_{EnzHyd,2}$ respectively) as a result of increased access to cellulose for the enzymes caused by the removal of lignin. Full details of this relationship and how it was implemented in the GAMS models can be found in *Section 3.6.2*. *Table 4.6* below shows the cellulose flowrate into the reactor ($f_{Cellulose,MixEnzHyd,EnzHyd}$) and the new conversions ($newX_{EnzHyd,1}$ and $newX_{EnzHyd,2}$) for each model. The original conversions ($X_{EnzHyd,1}$ and $X_{EnzHyd,2}$) are shown in brackets in the table heading. When delignification is added the conversions increase substantially. The conversion of reaction 1 increased by an average of 87.4% when delignification is included in the models and reaction 2 by 94%. This corresponds to a 56.7% increase in the amount of cellulose reacting in SDE and a 101% increase for ADE which increases the glucose revenue by 49.2% for SDE and 85.8% for ADE (*Table 4.5*).

Table 4.6: Effects of delignification on cellulose conversions for enzymatic hydrolysis models

Model	$f_{Cellulose,MixEnzHyd,EnzHyd}$ [kg/s]	$newX_{EnzHyd,1}$ (0.5)	$newX_{EnzHyd,2}$ (0.01)	Cellulose Reacting [kg/s]
SE	2.96	0.597	0.012	1.80
SDE	2.83	0.979	0.021	2.83
AE	2.93	0.406	0.008	1.21
ADE	2.80	0.856	0.017	2.44

In both acid hydrolysis models, SDA and ADA, the glucose revenue decreases when delignification is included by 96.1% in SDA and 54.6% in ADA (*Table 4.5*). The concentration of acid used in the

hydrolysis unit decreases when delignification is added in order to reduce costs (from 0.14 wt% in SA and AA, to 0.07 wt% in SDA and ADA). However, in the ADA model 19 times more acid is needed in the acid hydrolysis unit even though the acid concentration in hydrolysis has decreased. For SDA, 3 times mores acid is needed.

The methane revenue depends on the pre-hydrolysis unit, steam explosion or acid pre-hydrolysis. There is no clear trend in the change in methane revenue when delignification is added. For the acid pre-hydrolysis models, methane revenue in ADE decreases by 30.5% and increases by 2.96% for ADA (*Table 4.5*). Both these models are using pre-hydrolysis dataset 13 as are AE and AA. The methane change in these models is related entirely to the filter split. In the steam explosion models, the filter split is also responsible for the change in methane revenue as the xylose flowrate out of $FlsSteamEx$ is the same from SE to SDE and from SA to SDA.

4.5.1.2. Cost Based

Adding delignification increases annualised capital costs by an average of 159% (*Table 4.5*) due to the additional reactor $(Delig)$, filter $(FiltDelig)$, and storage unit $(SrcDelig)$. However, the increase in capital costs only contributed on average 6.24% of the total increase in costs.

Raw material costs accounted for on average 95.3% of the increase in costs associated with adding delignification. The smallest percentage increase in raw material costs was in ADE, 100%, and the largest was in SDA, 435%, (*Table 4.5*). The main contributor to the increase in raw material costs was sodium hydroxide which contributed an average of 74.5% of the increase in raw materials (*Table 4.5*).

In enzymatic hydrolysis models, enzyme costs contributed an average of 33.0% of the raw material costs in SDE and ADE (*Table 4.5*). The cost of enzymes is calculated based on the glucose flowrate so this increase in enzyme cost is as a result of the increased glucose production. In the enzymatic hydrolysis models, glucose revenues increased by an average of R100 000 000/year while enzymes costs increased by an average of R49 300 000/year. Adding delignification to the models increases the access of the enzymes to the cellulose, thus that the cost of enzymes should possibly stay the same or even decrease when delignification is added even though more glucose is produced.

The cost of acid in acid hydrolysis models contributed an average of 19.5% of the increase in raw material costs (*Table 4.5*). More acid is required in the hydrolysis step when delignification is included as the sodium hydroxide entrained in the solids will react with the acid to form a precipitate. In the ADA model 19 times more acid is needed due to delignification even though the acid concentration in hydrolysis has decreased from 0.14 acid wt% in AA to 0.07 wt% in ADA. For SDA, 3 times mores acid is needed and the same decrease in acid wt% for hydrolysis was observed.

Water usage increases by an average of 94.2% in the models however, this contributes very little to the increase in raw material costs, an average of 0.044% for all models (*Table 4.5*).

Steam use remained the same in SDE and ADE however steam cost was reduced in SDA and ADA. The steam cost decreased by R1 480 000 (ADA) to R1 690 000 (SDA) (*Table 4.5*) when delignification was added as delignification requires heating using LPS which is free and this reduces the amount of heating required with more expensive steam in the acid hydrolysis unit. This implies that steam costs could possibly be reduced in acid hydrolysis models by using some LPS to preheat the stream before the higher pressure steam is used.

The only model in which both methane and glucose revenues increased was SDE. Steam explosion, although acid-catalysed, has lower acid flowrates than acid pre-hydrolysis which causes less NaOH to be required for the same weight percentage of delignification. This also reduces the total flowrate to

the delignification unit which also reduces the capital cost of the delignification unit compared with acid pre-hydrolysis models. All these factors combined result in SDE being more profitable than SE when the cost of recycling the NaOH is 25% of the NaOH cost with no recycling.

4.5.2. Environmental Changes

Adding delignification to the models increased the environmental impact of all models with acid hydrolysis (SDA and ADA). *Table 4.*7 below summarises the changes in environmental impact when delignification is added to the models by showing the magnitude and percentage change in the environmental impact between the model without delignification and the model with delignification, and the percentage that each component contributes to this change in EI. The EI of some components decreased when delignification was added which enables some components to have large contributions which can theoretically be greater than 100%.

Table 4.7: Effects of delignification on environmental impact

Model	Change in EI		Contribution to Environmental Impact Change [%]							
	[%]	[10^6/year]	NaOH	Water	Acid	Steam	Methane	Acid Flash	Acetic Acid Flash	Enzymes
SDE	-26.1	-1.84	36.3	2.81	0	$1.12x10^{-5}$	1.38	0	0	-95
SDA	311	1.24	53.7	3.60	2.56	$1.31x10^{-5}$	0[2]	-6.52	-3.15	0
ADE	-6.24	-0.525	44.3	1.31	0[1]	$3.93x10^{-5}$	-4.40	0	0	-15.4
ADA	39.0	0.742	94.1	6.19	6.26	$2.14x10^{-5}$	1.07	-10.94	-0.192	0
Avg.	**79.4**	**-0.0955**	**57.1**	**3.48**	**4.41***	**$2.12x10^{-5}$**	**-0.65***	**-8.73***	**-1.67***	**-55.2***

[1] $1.58x10^{-15}$; [2] $4.68x10^{-15}$; *Average for models with non-zero flowrates of the specific component.

Acid hydrolysis models had a larger percentage change (311% for SDA and 39.0% for ADA in *Table 4.*7*)* because no enzymes are used in these models and, as was discussed in *Section 4.4.2*, enzymes have a significantly larger environmental impact than all other components.

SDE showed an overall decrease in EI of 26.1% *(Table 4.*7*)* which was caused by a decrease in enzyme flowrate of 0.259 kg/s and caused the EI of enzymes to reduce by 21.9% and contributed 95% to the change in EI *(Table 4.*7*).* The amount of enzymes and water added to the mixer, $MixEnzHyd$, before hydrolysis depends on the total stream flowrate entering the hydrolysis unit as water and enzymes have specified mass fractions after the mixer. Adding delignification solubilises cellulose, hemicellulose and lignin which reduces the total flowrate of solids exiting the filter and also decreases the amount of liquids entrained in the solids after the filter. This results in a decrease in the total stream flowrate entering the mixer, $MixEnzHyd$, and thus the amount of enzymes that needs to be added to achieve the specified mass fraction also decreases.

The enzyme flowrate was also decreased in the ADE model by 0.042 kg/s which caused the EI of enzymes to decrease by 3.63% which contributed 15.4% of the 6.24% decrease in the EI *(Table 4.*7*).* More of the solids are reacted in acid pre-hydrolysis than in steam explosion. Because of this, more solids are available to be solubilised in the delignification unit after steam explosion and thus delignification has a greater effect on the EI of enzymes in the SDE model than the ADE model.

The EI of enzymes is related to the flowrate of enzymes but the cost of enzymes is related to the flowrate of glucose produced. This makes it possible for the EI of enzymes to decrease although the cost of enzymes has increased in *Section 4.5.1.2*.

The main contributor to increasing the environmental impact of the models was sodium hydroxide which on average accounted for 57.1% of the change in environmental impact *(Table 4.7).* Water is added to the delignification unit which caused the environmental impact of water to increase and cause an average contribution of 3.48% of the change in EI *(Table 4.7).*

Models involving acid hydrolysis required an increase in the acid flowrate due to the formation of a precipitate with sodium hydroxide. The amount of acid added in acid hydrolysis increases in the models including delignification even though the acid concentration used has decreased from 0.14 wt% to 0.07 wt%. This caused the EI of acid to increase by an average of 4.41% of the change in EI for SDA and ADA *(Table 4.7)*. The environmental impact of the flash gas containing acid and acetic acid decreases with the addition of delignification in the SDA and ADA models due to the decrease in the acid concentration used in hydrolysis. The flash gas contributed a 10.4% decrease of the EI in the acid hydrolysis models *(Table 4.7)*. The environmental impact of steam increased in all models as steam is required for heating the delignification unit however this was a minor contribution (2.12×10^{-5}%) as the EI of steam is very small *(Table 4.7)*.

Section 4.5.1.1 discussed the changes in methane revenue. The EI of methane had the same trend as the methane revenue where EI of SDA remained the same, ADE decreased (-4.40%) and ADA increased (1.07%) *(Table 4.7)*. The methane EI of SDE increased (1.38%) which was different to the trend observed for the revenue in *Section 4.5.1.1* which remained the same.

4.6. Immobilisation of Enzymes

Studies have been conducted to determine the feasibility of recycling enzymes in an effort to reduce costs (Lu, Yang & Gregg, 2002; Weiss et al., 2013; Jordan & Theegala, 2014). Enzymes can be recycled by separating the supernatant liquid using ultrafiltration (Lu, Yang & Gregg, 2002) however this option is not cost effective on an industrial scale. Methods for recycling enzymes on an industrial scale include immobilisation (Jordan & Theegala, 2014) or recycling all the solids (Weiss et al., 2013). Although enzyme dosage can be reduced by 30% when all solids are recycled (Weiss et al., 2013) this would require a significant increase in reactor size and capital cost as well as the associated operating costs. Immobilisation of enzymes can enable six recycles of the enzymes and immobilised enzymes have a higher activity stability when recycled than free enzymes (Jordan & Theegala, 2014). However immobilisation of enzymes is a relatively new development and may not be ready for industrial scale operations.

4.7. Inhibitors

Sugar degradation products and other undesired components which act as inhibitors to fermentation can be formed in pre-treatment. When assessing a pre-treatment the concentration of inhibitors should also be considered. The maximum tolerable concentration of each inhibitor depends on the fermentation conditions and the microbe used. *Table 4.8* below shows the concentrations of inhibitors in the models.

Sugar degradation products that inhibit fermentation are furfural and HMF. Furfural concentrations less than 0.25 g/l do not inhibit fermentation (Mussatto & Roberto, 2004). SE and SA have a concentration higher than this, 0.348 kg/m^3 and 0.481 kg/m^3 respectively, so the fermentation may be inhibited in these models. It is possible that this concentration was overestimated in SA by the conversion factors used for the hemicellulose reactions. The furfural concentration could be reduced by including delignification, or detoxification after hydrolysis, if necessary. HMF is considered less toxic than furfural but concentrations of 0.5 g/l can affect fermentation (Mussatto & Roberto, 2004). HMF in SE and SA may inhibit fermentation and delignification or detoxification may be necessary to prevent this. Furfural and HMF can also have a synergistic effect and can inhibit fermentation if their combined concentration is 0.9 g/l (Mussatto & Roberto, 2004). Again, this is only applicable to the SE and SA models.

Acetic acid is formed from the acetyl groups in the lignocellulose structure. According to (Purwadi, Niklasson & Taherzadeh, 2004), acetic acid concentrations greater than 3 g/l are harmful. The highest acetic acid concentration in the models was SE with 0.873 kg/m^3, *Table 4.8*, and thus none of the models should cause inhibition of the fermentation as a result of acetic acid. Models with acid hydrolysis may underestimate the acetic acid concentration and this should be investigated further before implementing acid hydrolysis models to ensure the acetic acid concentration is not greater than 3 g/l.

Alkalis can be used to convert furans to less toxic compounds (Tran & Vakkilainnen, 2012). In this work the effect of sodium hydroxide on HMF and furfural was not included. The neutralisation of acetic acid by sodium hydroxide was also not included. As a result of this, all the delignification models may overestimate inhibitor concentrations. However, all inhibitor concentrations in the delignification models are below the limits and should not cause inhibition of fermentation.

SE and SA may cause inhibition of fermentation due to high concentrations of inhibitors. However, this depends on the microorganism used in the fermentation. An alkali could be used to detoxify the liquid prior to fermentation.

Table 4.8: Concentration of inhibitors formed in pre-treatment models

Model	**Concentration** [kg/m^3]		
	Furfural	*HMF*	*Acetic Acid*
SE	0.348	0.746	0.873
SA	0.481	0.708	0.393
AE	0.00141	0.00345	0.0425
AA	0.0404	0.132	0.00144
SDE	0.00691	0.0148	0.244
SDA	0.0241	0.0832	0.00145
ADE	0.000283	0.00069	0.0276
ADA	0.0227	0.0747	3.77×10^{-5}

4.8. Multi-objective Evaluation

The profit and environmental impacts determined using each objective function, in *Table 4.4,* can be plotted on a set of axes to graphically compare each model in terms of both objectives as is shown in *Figure 4.6* below. This is not strictly a Pareto curve as it was not constructed from a simultaneous approach. All delignification models include 25% of the total sodium hydroxide cost and environmental impact. In some cases, models with complete recycle of sodium hydroxide were included on the graph as SDE-R. Cases where only methane was produced from steam explosion or acid pre-hydrolysis, shown as S or A respectively, were also included on *Figure 4.6*.

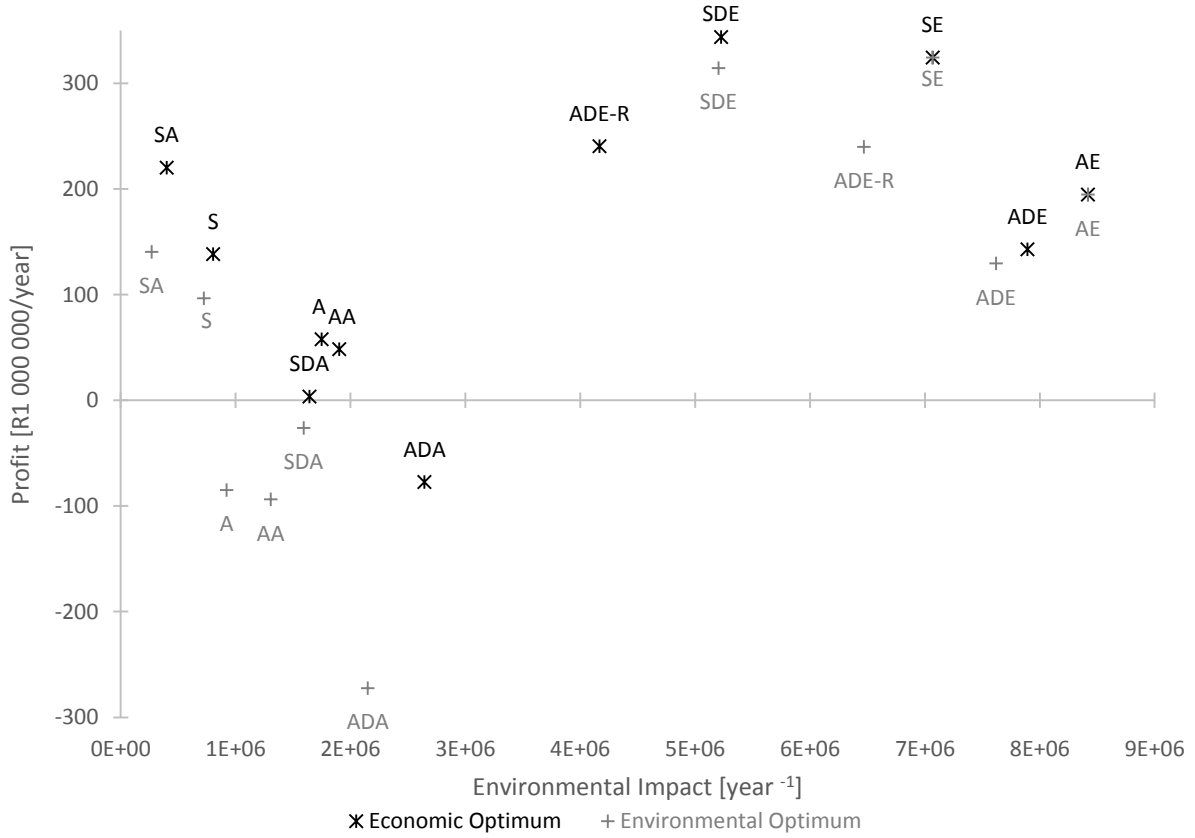


Figure 4.6: Solution space for pre-treatment flowsheets

The graphical representation of the optimum solutions in *Figure 4.6* above highlights how much larger the environmental impact of models using enzymatic hydrolysis is even though on-site enzyme production was used in the models. For enzymatic hydrolysis models, AE and SE, the two optimum points are very close together because the enzyme flowrate cannot be reduced significantly as was discussed in *Section 4.4.2* above. When delignification is added to the enzymatic models, ADE and SDE, the increase in flexibility discussed in *Section 4.4.2* above is seen as an increase in separation of the optimal points. From an environmental perspective, the use of enzymes is not recommended. However, if the main aim of the pre-treatment is to produce glucose, enzymatic models produce more glucose than acid hydrolysis models and SE has a larger profit and lower EI than AE.

In acid hydrolysis models, ADA and SDA, adding delignification reduced the profit and increased the environmental impact, the optimum points move down and right on *Figure 4.6.* In enzymatic hydrolysis models, SDE and ADE however, the environmental impact of the model was decreased by adding delignification due to a decrease in the total enzyme flowrate. The effect of delignification on the models is discussed in detail in *Section 4.5* above. Delignification should only be considered if efficient recycling of sodium hydroxide is possible. From the results that were obtained when 25% of

the cost and EI associated with sodium hydroxide was used, adding delignification reduced the profit of all the models except SE where SDE increased the profit. Further studies need to be conducted to determine the feasibility of recycling sodium hydroxide. If recycle costs and EI are lower than 25% of the total annual sodium hydroxide cost it may be worth implementing in other models such as AE. The models that can benefit from adding delignification are SE and AE, as SDE and AE have lower the environmental impacts. With full recycling, ADE-R on *Figure 4.6,* the profit of ADE is greater than that of AE. The SE flowsheet is most likely to benefit from the addition of delignification.

Figure 4.7 below shows the section of the Pareto curve where acid hydrolysis models are clustered in *Figure 4.6* above. Adding delignification to acid hydrolysis models SA and AA decreases the profit and increases the environmental impact. When no cost or EI is associated with sodium hydroxide recycling as is shown by SDA-R and ADA-R in *Figure 4.7,* the profit is less than the models with no delignification, SA and AA, and for SDA-R the EI is still greater than SA. ADA-R however was able to reduce the EI of AA however this model was not profitable. Delignification is not recommended for acid hydrolysis models.

For comparison, steam explosion and acid pre-hydrolysis without any subsequent hydrolysis were included on *Figure 4.6* and *Figure 4.7* as points S and A respectively. S and A have no revenue from glucose but only produce methane and have no subsequent hydrolysis step. Adding acid hydrolysis (AA) to acid pre-treatment (A) causes an increase in environmental impact and a decrease in profit. If acid pre-treatment is used for glucose production, it should be in combination with enzymatic hydrolysis rather than acid hydrolysis. The S model is preferable to the A model for a methane only scenario as the EI is less and profit is greater. When both EI and profit are considered, the SA model has a low EI and reasonable profit and is recommended for the production of methane and glucose.

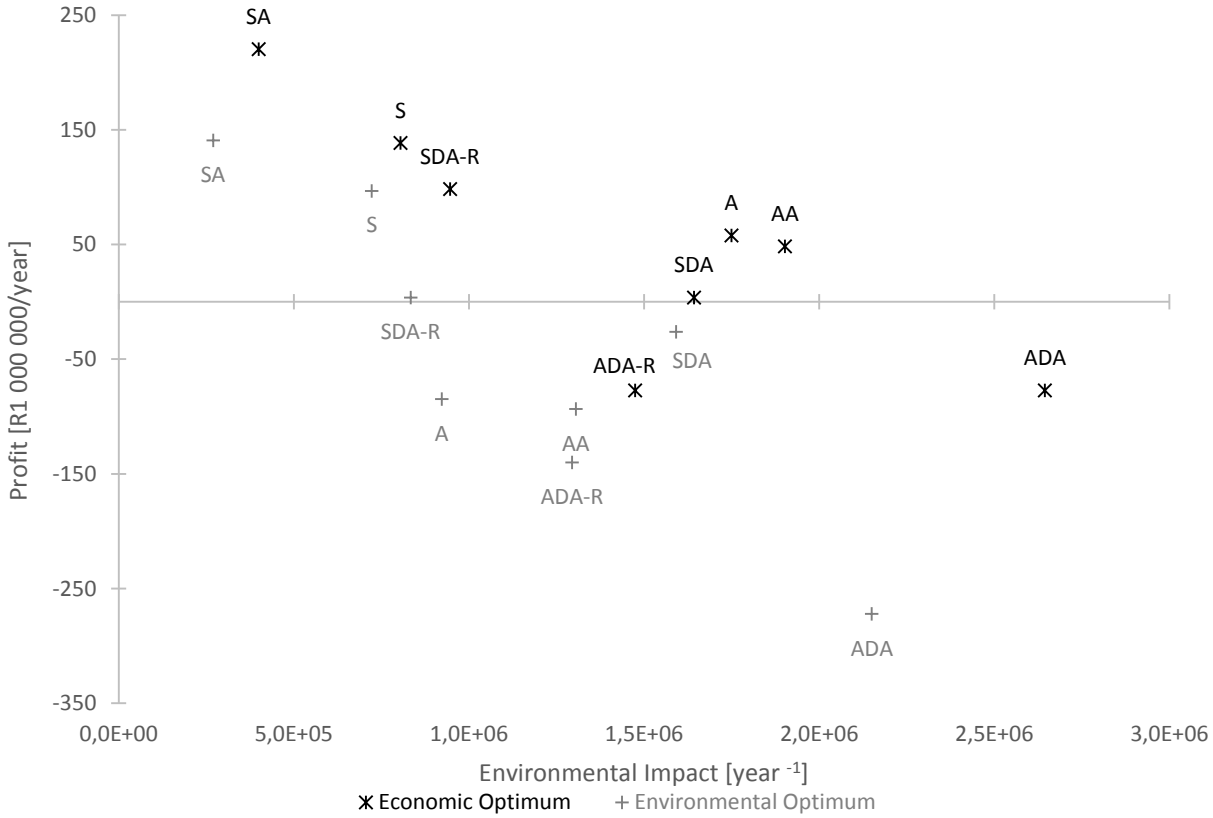


Figure 4.7: Solution space for acid hydrolysis pre-treatment flowsheets

4.8.1. Environmental Impact of Enzymes

As the environmental impact of enzymes was so large as to make enzymatic hydrolysis uncompetitive with acid hydrolysis, further investigation was conducted into the environmental impact of enzymes. The environmental impact of enzymes that was described in *Section 3.8.1.3* and *Appendix A.5.3* was based on the work of Harding (2008) who investigated mass balances for three different methods of cellulase production: submerged aerobic fermentation, submerged anaerobic fermentation and anaerobic solid state fermentation. For each production method, three flowsheets were developed, one which was strictly based on literature, and two which were less strictly based on literature. In the results sections above, the enzyme modelling was based on the submerged aerobic fermentation of Harding (2008) which was strictly based on the work of Heinzle, Biwer & Cooney (2006), scenario H1 in Harding (2008).

The electricity requirement in the work of Heinzle, Biwer & Cooney (2006) was 139 MJ/kg cellulase however this assumed 100% oxygen utilisation during microbial growth and product formation which, according to Harding (2008), is unrealistic. Scenario H1 of Harding (2008) had a higher energy use (183 MJ/kg cellulase) than Heinzle, Biwer & Cooney (2006) due to the use of a different aeration rate.

As the electricity was the major contributor to the environmental impact of enzymes, other scenarios from Harding (2008) which had lower energy use than scenario H1 were also modelled in SimaPro. The scenarios chosen were: scenario H2 and scenario SSC1. Scenario H2 was similar to scenario H1 as it is also aerobic submerged fermentation based on Heinzle, Biwer & Cooney (2006), however this scenario was less strictly based on Heinzle, Biwer & Cooney (2006) than scenario H1 as approximately 45% of the parameters were based on Heinzle, Biwer & Cooney (2006) (Harding, 2008). Scenario SSC1 was based on the work of Zhuang & Marchant (2007) and is an anaerobic solid state fermentation. This was the scenario of Harding (2008) that was strictly based on the literature of Zhuang & Marchant (2007). An anaerobic submerged fermentation was excluded from this analysis as the electricity requirements were much larger than the original scenario H1 (1402-4032 MJ/kg cellulase) (Harding, 2008). The mass balances for the three cellulose production scenarios chosen for this investigation are shown in *Table A.5.9* in *Appendix A.5.4*. In all scenarios, the electricity used in SimaPro was for a South African electricity mix taken from the South African Liquid Fuels Database developed by the University of Cape Town and The Green House.

The new scenarios (H2 and SSC1) were constructed as processes in SimaPro using the same methodology as described in *Appendix A.5.3.* A graphical comparison of these three scenarios can be seen in *Figure 4.8* on the following page and the table of this data can be found in *Table A.5.10* in *Appendix A.5.4*. Scenario H1 has a larger environmental impact than the other two scenarios in almost all categories and this is significantly larger in the two ecotoxicity water categories (chronic and acute, EWC and EWA).

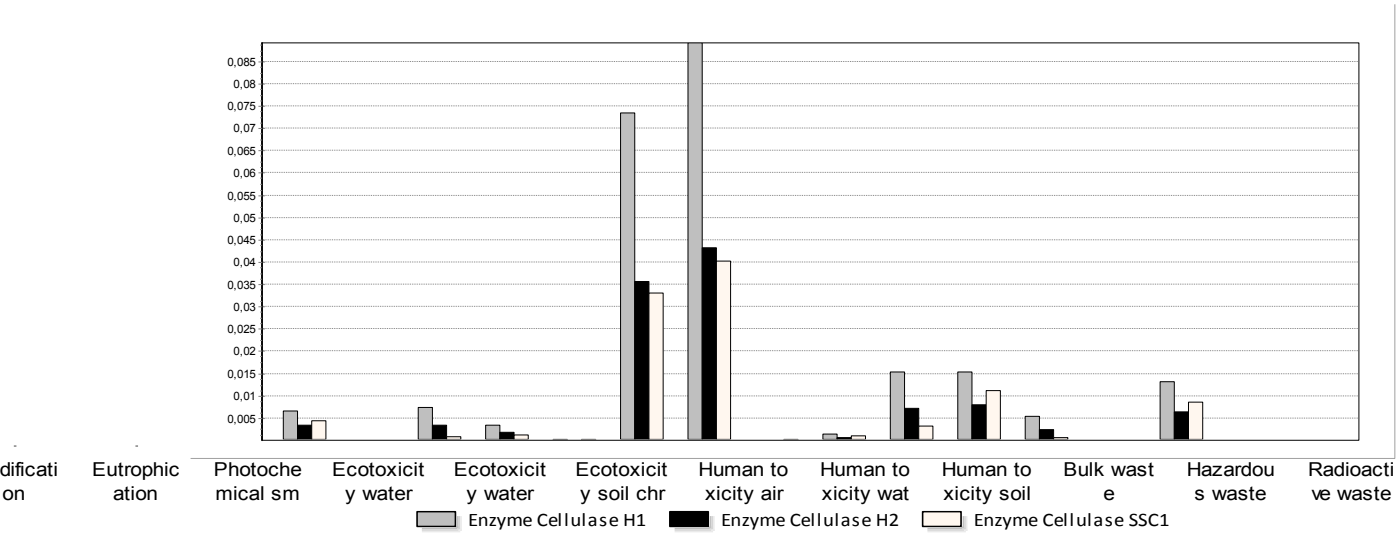


Figure 4.8: Comparison of normalised environmental impacts for three methods of enzyme production

For comparison with the previous results, scenario H2 was used as the EI for enzymes and the models were run. The EI of enzymes decreased by a large amount and enabled the enzymatic hydrolysis models to be competitive with the acid hydrolysis models from an environmental perspective. *Figure 4.9* below shows how the EI of the enzymatic hydrolysis models decreases when enzyme production requires less electricity. The enzymatic hydrolysis models are now much more competitive with the acid hydrolysis models from an environmental perspective. The same trends as were discussed above in *Section 4.8* were observed.

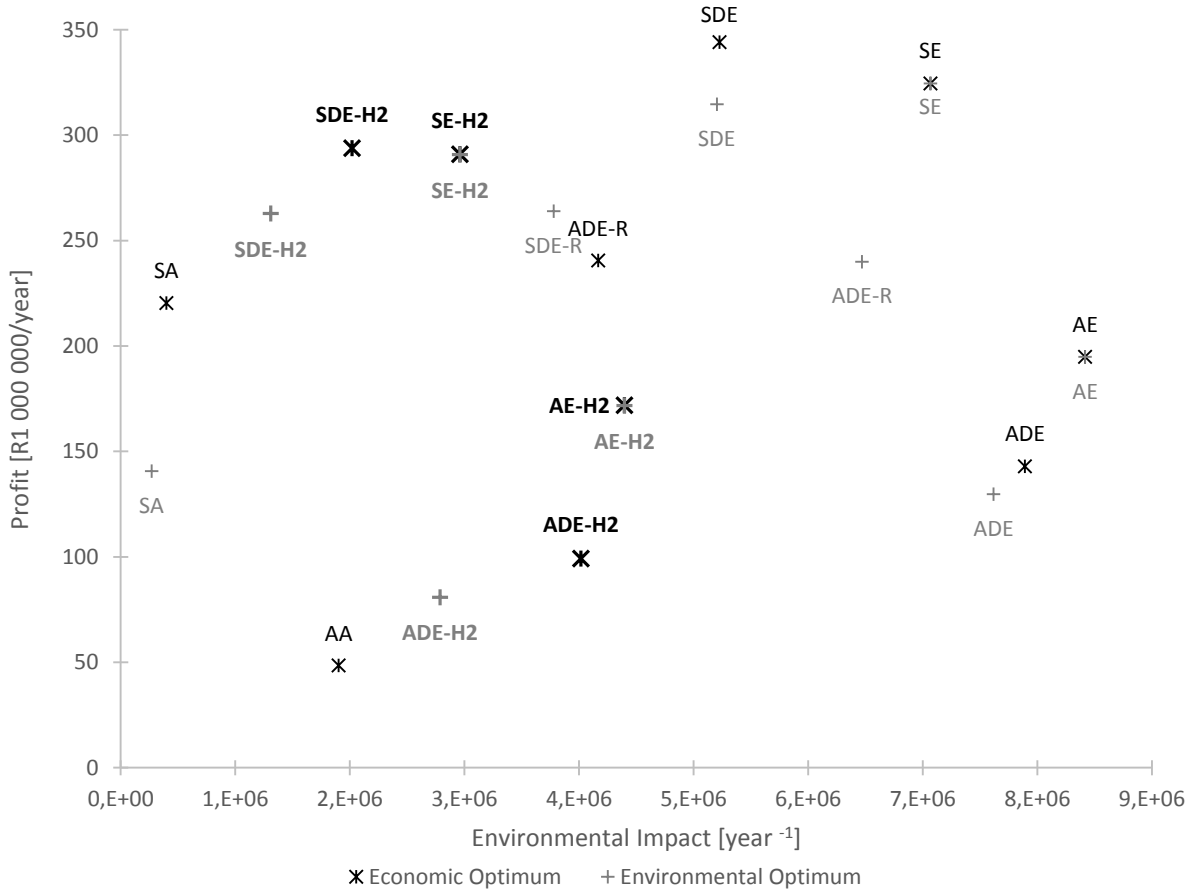


Figure 4.9: Solution space for pre-treatment flowsheets including scenario H2 enzymes

Novozymes, one of the leading producers of enzymes, has worked to reduce the environmental impact of enzymes. Their one plant in Kalundborg in Denmark uses excess steam from a nearby combined heat and power plant (Nielsen, Oxenbøll & Wenzel, 2007). Novozymes have also managed to significantly reduce electricity consumption and increase enzyme output by using genetically modified microorganisms (Nielsen, Oxenbøll & Wenzel, 2007). The use of highly optimised genetically modified microorganisms would reduce the environmental impact of enzymes and may result in an impact even lower than scenario H2.

4.9. Difficulties and Shortcomings of the Models

This section discusses some of the difficulties that were encountered in solving the MINLPs as well as some of the shortcomings of the models.

Solving the flowsheets separately rather than in a superstructure is a sequential approach rather than a simultaneous approach, even though some of the individual flowsheet were solved as MINLP models. It is possible that a more optimal solution could be found using a simultaneous approach especially if more sophisticated software is used that provides better initialisations for solving the overall superstructure.

The optimisation models which are non-linear, required initialisations and specific bounding of many of the variables so as to find a feasible and good solution. These bounds had to be tested to allow a solution to be obtained with each binary variable. Although testing was done to check whether feasible solutions could be obtained for each variable, in some cases the selection of some binary variables resulted in infeasible solutions. Binary variables also cause difficulties for the solvers in finding a globally optimal solution.

It was difficult to account for the effects of pre-treatment and delignification on hydrolysis conversions and kinetics. Hydrolysis experiments are usually performed on bagasse that has been pre-treated in a specific way which may be similar to one flowsheet option but will not be similar to all possible flowsheets. It was not possible to use different kinetics or conversion depending on the pre-treatment used in the model, however the kinetics and yields were adjusted based on the amount of lignin that had been removed. Physical effects, such as the explosive rupturing of bagasse in steam explosion, are especially hard to quantify or incorporate in subsequent models.

Experiments have very specific conditions which often caused the flexibility in models to be reduced as it was not possible to accurately adjust parameters to different conditions.

Filters can affect the profitability of a model by a fair amount as the filter determines how much of the product components remain entrained in the solids. Units downstream of filters are also affected by the amount of acid or sodium hydroxide that remains in the solids.

5. Conclusions

Using modelling and optimisation this work aimed to determine the optimal pre-treatment flowsheet for sugarcane bagasse by evaluating both economic and environmental objectives. This was performed through kinetic modelling and the use of conversion factors. The superstructure included steam explosion (un-catalysed and acid-catalysed) or acid pre-treatment followed by an optional delignification step before enzymatic or acid hydrolysis. Xylose and glucose are produced by the pre-treatment and were the products of this project. Revenue was calculated from xylose produced in the pre-treatment phase based on possible yields from bio-digestion to produce bio-methane. Glucose exiting the hydrolysis unit was given a revenue based on its conversion to ethanol. The problem was solved using a more sequential approach and the solution space was plotted on a graph for evaluation. From this investigation the following conclusions have been drawn.

The environmental impact of enzymes with on-site production was much greater than any other raw material or product when scenario H1, a submerged aerobic fermentation method, was used. However, these models became more competitive when enzyme production used less electricity such as in scenario H2 which was also submerged aerobic fermentation. Without specific information about enzyme production method used industrially it is difficult to say whether flowsheets that use enzymatic hydrolysis are environmentally feasible. Immobilisation of enzymes could be used to facilitate enzyme recycling and thus reduce the environmental impact associated with enzymes. The use of specialised genetically modified micro-organisms could significantly reduce the energy consumption of enzyme production.

Adding delignification prior to hydrolysis increased the cost of all models except steam explosion with enzymatic hydrolysis (SE), and increased the environmental impact for all acid hydrolysis models. In order for delignification to be a viable option, cost effective recycling of sodium hydroxide is needed. Delignification should only be considered for SE as it has the potential to increase the profit beyond that of SE while decreasing the environmental impact.

Furfural and HMF may cause inhibition in SE and SA however this depends on the microorganism used for the fermentation. An alkali could be used to degrade these components prior to fermentation.

The bagasse could be used to produce bio-methane using steam explosion (S). This has a low environmental impact (805 000/year) and is profitable (R138 000 000/year). Using steam explosion followed by acid hydrolysis (SA) could be used to produce both bio-methane and glucose for bio-ethanol production and is more profitable than bio-methane only scenario (R220 000 000/year) and has a lower EI (400 000/year). If the focus is to produce high glucose flowrates, steam explosion with enzymatic hydrolysis (SE) would be recommended. The model is profitable (R324 000 000/year) however the environmental impact could be quite large (7 070 000/year) if a lot of electricity is used in enzyme production. The environmental impact of this method may be lower (2 960 000/year) if the enzymes are produced in a more energy efficient manner however this is still larger than steam explosion with acid hydrolysis. Adding delignification to the enzymatic hydrolysis models can reduce the EI by 4% to 68%, depending on the efficiency of sodium hydroxide recycling, and can also increase the glucose flowrate by 49% to 107%. The acid hydrolysis model with the highest glucose flowrate is steam explosion with acid hydrolysis (SA) however the glucose flowrate is 62% lower than in steam explosion with enzymatic hydrolysis.

6. Recommendations

This work was primarily aimed on selecting pre-treatment technologies for the production of bio-ethanol from sugarcane bagasse. It would be beneficial to program the superstructure in MipSyn so that simultaneous optimisation of the flowsheet could be performed and Pareto curves could be generated. To determine the overall profitability and environmental impact of bio-ethanol production the downstream processes such as fermentation and separation should also be modelled and combined with pre-treatment methods. Constraints could be added to prevent inhibitor concentrations from reaching undesirable levels or to add in a detoxification unit to reduce the concentration to tolerable levels for the fermentation. A minimum glucose concentration could also be added to the models to ensure a specific ethanol output.

The energy generation section of the plant could be included in the modelling to determine the actual cost and environmental impact of steam. The bagasse flowrate to pre-treatment could also be a variable so that some bagasse could be diverted straight to the furnace to enable the plant to be energetically self-sufficient. Modelling of this section could also determine the environmental impact and profitability of this section by itself and in combination with biogas production to decide whether bio-ethanol should be the desired product. Sugarcane is a seasonable feedstock and so a multi-period approach that considers the use of other feedstocks depending on seasonable availability would be useful.

More detailed modelling of the bio-methane unit would be useful as this provided on average 65.6% of the total revenue in the economically optimised models.

The profitability of including delignification in the pre-treatment of sugarcane bagasse depends greatly on the efficacy of the recycling of the sodium hydroxide. Although the paper industry manages to achieve recoveries of around 97% in the Kraft Process (Tran & Vakkilainnen, 2012), minerals present in sugarcane bagasse may reduce the efficiency of the recovery loop. Further work should be done to determine the efficiency of sodium hydroxide recovery in order to determine whether including delignification is feasible.

Other alkalis, such as calcium hydroxide, have been used for delignification however these are not as efficient as sodium hydroxide. In the interest of reducing cost, further investigation could be done to quantify the economics and EI of other alkalis.

The viability of recycling enzymes should be quantified so that the environmental impact of enzymes can be reduced. Enzymes should be produced on site to prevent an increase in environmental impact and this would also grow the local economy.

Development of more flexible steam explosion and enzymatic hydrolysis models would be useful in order to evaluate a wider range of operating conditions.

Acetic acid formation should be included in the acid hydrolysis model as this can impede fermentation.

The filters can make a large difference to the downstream units. For example, the pre-treatment filter determines how much of the xylose can be used to produce biogas and how much acid remains in the solid stream effecting the amount of acid to be added in acid hydrolysis or sodium hydroxide in delignification. Further work should be done to make these filters more realistic and optimise the amount of washing.

The binary variables for steam choice in the acid hydrolysis model could be removed as these add complexity and make it difficult for the solvers to determine the optimal solution. The economically

optimal models all chose medium pressure steam 1, however this steam is not hot enough to heat the acid hydrolysis reactor to the maximum temperature. A single level of steam, such as medium pressure steam 2, could be used for the small temperature range (180-230°C) or the binary variables could be reduced from seven to two or three. If possible, a series of linear equations that describe how temperature, enthalpy and cost change with steam pressure could be used instead of binary variables. Reducing the binary variables would enable more complexity to be included in the model such as a kinetic equation for hemicellulosic reactions or the formation of acetic acid.

Allowing a mix of steam sources to be used in a reactor could reduce the cost of models however this is unlikely to have a large impact as steam cost contributes on average 3.46% of the costs.

The bagasse flowrate in the models could be made a variable rather than a fixed value to investigate the effect of plant size on profitability.

References

Aguilar, R., Ramırez, J., Garrote, G. & Vazquez, M. 2002. Kinetic study of the acid hydrolysis of sugar cane bagasse. Journal of Food Engineering. 55:309–318. Available: http://www.sciencedirect.com/science/article/pii/S0260877402001061 [2013, May 21].

Alibaba. n.d. Sulfuic Acid. Available: http://www.alibaba.com/showroom/sulfuric-acid-98%25.html [2014, November 05].

Azapagic, A. 1999. Life cycle assessment and its application to process selection, design and optimisation. Chemical engineering journal. 73(1385):1–21. Available: http://www.sciencedirect.com/science/article/pii/S138589479900042X [2013, March 06].

Balat, M. 2011. Production of bioethanol from lignocellulosic materials via the biochemical pathway: A review. Energy Conversion and Management. 52(2):858–875. DOI: 10.1016/j.enconman.2010.08.013.

BioNett. n.d. Bio-Methane Fact Sheet. Available: http://www.sts-technology.com/docs/Biomethane-Fact-Sheet-Final.pdf.

Bonomi, A., Dayan, C., Jesus, F. De, Cunha, M.P. & Mantelatto, P.E. 2011. Technological Assessment Program (PAT): The Virtual Sugarcane Biorefinery (VSB) - 2011 Report.

Bustos, G., Ramírez, J.A., Garrote, G. & Vázquez, M. 2003. Modeling of the hydrolysis of sugar cane bagasse with hydrochloric acid. Applied biochemistry and biotechnology. 104(1):51–68. Available: http://www.ncbi.nlm.nih.gov/pubmed/12495205.

Cardona, C.A., Quintero, J.A. & Paz, I.C. 2010. Production of bioethanol from sugarcane bagasse: Status and perspectives. Bioresource technology. 101(13):4754–66. DOI: 10.1016/j.biortech.2009.10.097.

Carrasco, C., Baudel, H.M., Sendelius, J., Modig, T., Roslander, C., Galbe, M., Hahn-Hägerdal, B., Zacchi, G., et al. 2010. SO2-catalyzed steam pre-treatment and fermentation of enzymatically hydrolyzed sugarcane bagasse. Enzyme and Microbial Technology. 46(2):64–73. Available: http://www.sciencedirect.com/science/article/pii/S0141022909002531 [2013, October 17].

Carvalho, M.L., Jr, R.S. & Suarez, C.A.G. 2013. Kinetic Study of the Enzymatic Hydrolysis of Sugarcane Bagasse. 30(03):437–447.

Damartzis, T. & Zabaniotou, a. 2011. Thermochemical conversion of biomass to second generation biofuels through integrated process design—A review. Renewable and Sustainable Energy Reviews. 15(1):366–378. DOI: 10.1016/j.rser.2010.08.003.

Demirbas, A. 2005. Bioethanol from Cellulosic Materials: A Renewable Motor Fuel from Biomass. Energy Sources. 27(4):327–337. DOI: 10.1080/00908310390266643.

Department of Environmental Affairs and Tourism. 2009. Greenhouse Gas Inventory South Africa.

Department of Minerals and Energy. 2007. Biofuels Industrial Strategy of the Republic of South Africa.

Department of Water Affairs. 2014. Water Management Areas Charges - Approved Water Charges for 2013/2014 Financial Year. Available: http://www.dwaf.gov.za/Projects/WARMS/Revenue/WRM2013.pdf.

Dias, M.O.S., Ensinas, A. V., Nebra, S. a., Maciel Filho, R., Rossell, C.E.V. & Maciel, M.R.W. 2009. Production of bioethanol and other bio-based materials from sugarcane bagasse: Integration to conventional bioethanol production process. Chemical Engineering Research and Design. 87(9):1206–1216. DOI: 10.1016/j.cherd.2009.06.020.

Dias, M.O.S., Pereira, M., Jesus, C.D.F. & Rossell, C.E. V. 2011. Simulation of integrated first and second generation bioethanol production from sugarcane : comparison between different biomass pretreatment methods. 955–966. DOI: 10.1007/s10295-010-0867-6.

Dias, M.O.S., Junqueira, T.L., Cavalett, O., Cunha, M.P., Jesus, C.D.F., Rossell, C.E. V, Maciel, R. & Bonomi, A. 2012. Bioresource Technology Integrated versus stand-alone second generation ethanol production from sugarcane bagasse and trash. Bioresource Technology. 103(1):152–161. DOI: 10.1016/j.biortech.2011.09.120.

Eberhart, R. & Kennedy, J. 1995. A new optimizer using particle swarm theory. *MHS'95. Proceedings of the Sixth International Symposium on Micro Machine and Human Science*. 39–43. DOI: 10.1109/MHS.1995.494215.

Ec21. n.d. Sulfuric Acid. Available: http://za.countrysearch.ec21.com/sulfuric-acid.html [2014, November 05].

Galbe, M. & Zacchi, G. 2007. Pre-treatment of Lignocellulosic Materials for Efficient Bioethanol Production. Advances in Biochemical Engineering/Biotechnology. 108(July):41–65. DOI: 10.1007/10.

Gámez, S., González-Cabriales, J.J., Ramírez, J.A., Garrote, G. & Vázquez, M. 2006. Study of the hydrolysis of sugar cane bagasse using phosphoric acid. Journal of Food Engineering. 74(1):78–88. DOI: 10.1016/j.jfoodeng.2005.02.005.

Garrote, G., Dominguez, H. & Parajo, J.C. 1999. Hydrothermal processing of lignocellulosic materials. 57:191–202.

Green, D. & Perry, R. 2007. *Perry's Chemical Engineers' Handbook*. 8th ed. McGraw Hill Professional.

Gurgel, L. & Marabezi, K. 2012. Dilute acid hydrolysis of sugar cane bagasse at high temperatures: A kinetic study of cellulose saccharification and glucose decomposition. Part I: sulfuric acid as the catalyst. Industrial & Engineering Chemistry Research. 51:1173–1185. DOI: dx.doi.org/10.1021/ie2025739.

Hamelinck, C.N., Hooijdonk, G. Van & Faaij, A.P. 2005. Ethanol from lignocellulosic biomass: techno-economic performance in short-, middle- and long-term. Biomass and Bioenergy. 28(4):384–410. DOI: 10.1016/j.biombioe.2004.09.002.

Harding, K. 2008. A Generic Approach to Environmental Assessment of Microbial Bioprocesses through Life Cycle Assessment (LCA). University of Cape Town.

Huang, H.-J., Ramaswamy, S., Tschirner, U.W. & Ramarao, B.V. 2008. A review of separation technologies in current and future biorefineries. Separation and Purification Technology. 62(1):1–21. DOI: 10.1016/j.seppur.2007.12.011.

Jordan, J. & Theegala, C. 2014. Probing the limitations for recycling cellulase enzymes immobilized on iron oxide (Fe3O4) nanoparticles. Biomass Conversion and Biorefinery. 4(1):25–33. DOI: 10.1007/s13399-013-0089-z.

Kadam, K.L. 2000. Environmental Life Cycle Implications of Using Bagasse- Derived Ethanol as a Gasoline Oxygenate in Mumbai (Bombay) Environmental Life Cycle Implications of Using Bagasse- Derived Ethanol as a Gasoline Oxygenate in Mumbai (Bombay). (November).

Kintisch, E. 2008. The Greening of Synfuels. SCIENCE Volume 320. (April):306–308. Available: http://www.atmos.washington.edu/2008Q2/111/Readings/Kintisch2008_Green_Synfuels.pdf.

Kocis, G.R. & Grossmann, I.E. 1987. Relaxation Strategy for the Structural Optimization of Process Flow Sheets. Industrial & Engineering Chemistry Research. 26(205):1869–1880.

Kocis, G.R. & Grossmann, I.E. 1989. A Modelling and Decomposition Strategy for the MINLP Optimization of Process Flowsheets. Computers & chemical engineering. 13(7):797–819. Available: http://www.sciencedirect.com/science/article/pii/0098135489850537 [2012, November 02].

Kravanja, Z. 2010. Challenges in sustainable integrated process synthesis and the capabilities of an MINLP process synthesizer MipSyn. Computers & Chemical Engineering. 34(11):1831–1848. DOI: 10.1016/j.compchemeng.2010.04.017.

Lamprecht, I. 2014. An alternative to rising petrol prices? Available: http://www.moneyweb.co.za/moneyweb-south-africa/an-alternative-to-rising-petrol-prices [2014, November 05].

Lavarack, B.P., Griffin, G.J. & Rodman, D. 2002. The acid hydrolysis of sugarcane bagasse hemicellulose to produce xylose, arabinose, glucose and other products. Biomass and Bioenergy. 23:367–380.

Laser, M., Schulman, D., Allen, S.G., Lichwa, J., Antal, M.J. & Lynd, L.R. 2002. A comparison of liquid hot water and steam pre-treatments of sugar cane bagasse for bioconversion to ethanol. Bioresource technology. 81(1):33–44. Available: http://www.ncbi.nlm.nih.gov/pubmed/11708754.

Lenihan, P., Orozco, a., O'Neill, E., Ahmad, M.N.M., Rooney, D.W. & Walker, G.M. 2010. Dilute acid hydrolysis of lignocellulosic biomass. Chemical Engineering Journal. 156(2):395–403. DOI: 10.1016/j.cej.2009.10.061.

Lu, Y., Yang, B. & Gregg, D. 2002. Cellulase adsorption and an evaluation of enzyme recycle during hydrolysis of steam-exploded softwood residues. Applied biochemistry and …. 98-100:641–654. Available: http://link.springer.com/article/10.1385/ABAB:98-100:1-9:641 [2014, November 10].

Lynd, L.R., von Blottnitz, H., Tait, B., de Beer, J., Pretorius, I.S., Rumbold, K. & van Zyl, W.H. 2003. Converting plant biomass to fuels and commodity chemicals in South Africa: a third chapter? South African Journal of Science. 99(November/December):499–507.

Martín, C., Marcet, M. & Thomsen, A.B. 2008. Comparison between wet oxidation and steam explosion as pre-treatment methods for enzymatic hydrolysis of sugarcane bagasse. BioResources. 3(3):670–683.

Melamu, R. & von Blottnitz, H. 2011. 2nd Generation biofuels a sure bet? A life cycle assessment of how things could go wrong. *Journal of Cleaner Production*. 19(2-3):138–144. DOI: 10.1016/j.jclepro.2010.08.021.

Menon, V. & Rao, M. 2012. Trends in bioconversion of lignocellulose: Biofuels, platform chemicals & biorefinery concept. Progress in Energy and Combustion Science. (March). DOI: 10.1016/j.pecs.2012.02.002.

Moncada, J., Matallana, L. & Cardona, C. 2013. Selection of Process Pathways for Biorefineries Design using Optimization Tools: A Colombian Case for Conversion of Sugarcane Bagasse to Ethanol, Poly-3-hydroxybutyrate (PHB), and Energy. Industrial & Engineering Chemistry Research. Available: http://pubs.acs.org/doi/abs/10.1021/ie3019214 [2013, April 05].

Moreno, M.S., Andersen, F.E. & Díaz, M.S. 2013. Dynamic Modeling and Parameter Estimation for Unit Operations in Lignocellulosic Bioethanol Production. Industrial & Engineering Chemistry Research. 52(11):4146–4160. DOI: 10.1021/ie302358e.

Mosier, N., Wyman, C., Dale, B., Elander, R., Lee, Y.Y., Holtzapple, M. & Ladisch, M. 2005. Features of promising technologies for pre-treatment of lignocellulosic biomass. Bioresource technology. 96(6):673–86. DOI: 10.1016/j.biortech.2004.06.025.

Mussatto, S.I. & Roberto, I.C. 2004. Alternatives for detoxification of diluted-acid lignocellulosic hydrolyzates for use in fermentative processes: a review. Bioresource technology. 93(1):1–10. DOI: 10.1016/j.biortech.2003.10.005.

Naik, S.N., Goud, V. V., Rout, P.K. & Dalai, A.K. 2010. Production of first and second generation biofuels: A comprehensive review. Renewable and Sustainable Energy Reviews. 14(2):578–597. DOI: 10.1016/j.rser.2009.10.003.

Nielsen, P.H., Oxenbøll, K.M. & Wenzel, H. 2007. LCA Case Studies Cradle-to-Gate Environmental Assessment of Enzyme Products Produced Industrially in Denmark by Novozymes A / S. 12(2006):432–438.

Norceline Chemicals. n.d. Price List One - Chemicals Suppliers in Southern Africa and Beyond. Available: http://norcelinechemicals.webs.com/pricelistone.htm [2014, November 05].

Papalexandri, K.P. & Pistikopoulos, E.N. 1994. A multiperiod MINLP model for the synthesis of flexible heat and mass exchange networks. *Computers & chemical engineering*. (11-12):1125–1139. DOI: 10.1016/0098-1354(94)E0022-F.

Pellegrini, L. & De Oliveira, S. 2007. Exergy analysis of sugarcane bagasse gasification. Energy. 32(4):314–327. DOI: 10.1016/j.energy.2006.07.028.

Product Ecology Consultants. 2010. SimaPro 7 - Introduction to LCA.

Purwadi, R., Niklasson, C. & Taherzadeh, M.J. 2004. Kinetic study of detoxification of dilute-acid hydrolyzates by Ca(OH)2. Journal of biotechnology. 114(1-2):187–98. DOI: 10.1016/j.jbiotec.2004.07.006.

Pushpa, S., Tiwari, P., Arya, N., Suman, A., Rai, R., Kumar, R. & Shrivastava, A.K. 2010. Cellulose digestibility and monomeric sugar yields in acid pre-treated sugarcane bagasse. Indian Journal of Sugarcane Technology. 25:66–76.

Ragauskas, A.J. n.d. Basics of Kraft Pulping & Recovery Process. Available: http://ipst.gatech.edu/faculty/ragauskas_art/technical_reviews/Kraft Pulping and Recovery Process basics.pdf [2014, November 10].

Rezende, C.A., Lima, M.A. De, Maziero, P. & Ribeiro, E. 2011. Chemical and morphological characterization of sugarcane bagasse submitted to a delignification process for enhanced enzymatic digestibility. 54(November).

Rocha, G.J.M., Martín, C., Vinícius, F.N., Gómez, E.O. & Gonçalves, A.R. 2012. Mass balance of pilot-scale pretreatment of sugarcane bagasse by steam explosion followed by alkaline delignification. Bioresource Technology. 111:447–452. DOI: 10.1016/j.biortech.2012.02.005.

Rodríguez-Chong, A., Alberto Ramírez, J., Garrote, G. & Vázquez, M. 2004. Hydrolysis of sugar cane bagasse using nitric acid: a kinetic assessment. Journal of Food Engineering. 61(2):143–152. DOI: 10.1016/S0260-8774(03)00080-3.

Saeman, J. 1945. Kinetics of wood saccharification-hydrolysis of cellulose and decomposition of sugars in dilute acid at high temperature. Industrial & Engineering Chemistry. (9). Available: http://pubs.acs.org/doi/pdf/10.1021/ie50421a009 [2013, October 21].

Sandler, S.I. 2006. Chemical, Biochemical, and Engineering Thermodynamics. 4th ed. John Wiley & Sons.

Santibanez-Aguilar, J.E., González-Campos, J.B., Ponce-Ortega, J.M., Serna-González, M. & El-Halwagi, M.M. 2011. Optimal planning of a biomass conversion system considering economic and environmental aspects. Industrial & Engineering Chemistry Research. 8558–8570. Available: http://pubs.acs.org/doi/abs/10.1021/ie102195g [2013, April 23].

Sarkar, N., Ghosh, S.K., Bannerjee, S. & Aikat, K. 2012. Bioethanol production from agricultural wastes: An overview. Renewable Energy. 37(1):19–27. DOI: 10.1016/j.renene.2011.06.045.

Schutze, E. n.d. *Liquid Fuel from Coal.* Available: http://www.mediaclubsouthafrica.com/index.php?option=com_content&view=article&catid=38:innovation_bg&id=123:liquid-fuel-from-coal [2012, September 25]

Seider, W.D., Seader, J.D., Lewin, D.R. & Widagdo, S. 2010. Product and Process Design Principles. Third ed. John Wiley & Sons.

Shield Technology. n.d. Shield Technologies. Available: http://core.i4africa.com/index.php?siteid=153&pageid=94 [2014, November 05].

Sims, R., Taylor, M. & Saddler, J. 2008. From 1st to 2nd Generation Biofuel Technologies. Available: http://www.iea.org/papers/2008/2nd_Biofuel_Gen.pdf.

Sinnott, R.K. 2005. Coulson and Richardson's Chemical Engineering Volume 6 - Chemical Engineering Design. 4th ed. Elsevier.

Skals, P.B., Krabek, A., Nielsen, P.H. & Wenzel, H. 2008. LCA Case Studies Environmental Assessment of Enzyme Assisted Processing in Pulp and Paper Industry *. 13(2):124–132.

Soares, R. de P. & Secchi, A.R. n.d. *EMSO Environment for Modeling Simulation and Optimization*. Available: http://vrtech.com.br/rps/emso.html [2005, March 20].

Smith, R. & Varbanov, P. 2005. What's the price of steam? Chemical engineering progress. (July):29–33. Available: http://www.cheric.org/research/tech/periodicals/view.php?seq=508738 [2014, August 18].

South African Government. 2010. South Africa Yearbook 2010/11 - Energy. Available: http://www.gcis.gov.za/sites/default/files/docs/resourcecentre/yearbook/chapter8.pdf.

SouthAfrica.info. 2013. SA to blend biofuels from 2015. Available: http://www.southafrica.info/business/trends/newbusiness/biofuels-011013.htm#.VIaPEDGUdWp [2014, December 09].

Statistics South Africa. 2012. Statistical Release Quarterly Labour Force Survey.

Stranddorf, H.K., Hoffmann, L., Schmidt, A. & FORCE Technology. 2005. Impact categories, normalisation and weighting in LCA.

Sun, Y. & Cheng, J. 2002. Hydrolysis of lignocellulosic materials for ethanol production: a review. Bioresource technology. 83(1):1–11. Available: http://www.ncbi.nlm.nih.gov/pubmed/12058826.

Szitkai, Z., Farkas, T., Lelkes, Z., Rev, E., Fonyo, Z. & Kravanja, Z. 2006. Fairly Linear Mixed Integer Nonlinear Programming Model for the Synthesis of Mass Exchange Networks. Industrial & Engineering Chemistry Research. 45(1):236–244. DOI: 10.1021/ie050453i.

Taherzadeh, M.J. & Karimi, K. 2007. Acid-based hydrolysis processes for ethanol from lignocellulosic materials: a review. BioResources. 2(3):472–499.

The Sugar Engineers. n.d. Sugar Factories of South Africa. Available: http://www.sugartech.co.za/factories/list.php?cid=238&submit2=go [2014, November 21].

Tran, H. & Vakkilainnen, E.K. 2012. The Kraft Chemical Recovery Process. Available: http://www.tappi.org/content/events/08kros/manuscripts/1-1.pdf.

United States Environmental Protection Agency. n.d. *Chemical Process Simulation for Waste Reduction: WAR Algorithm*. Available: http://www.epa.gov/nrmrl/std/war/sim_war.htm.

Von Blottnitz, H. & Chakraborty, A. n.d. 2nd Generation Bio-energy Technology: Thoughts about Getting the Best New Developments to Work for Africa, Chemical Engineering Department, University of Cape Town (Unpublished).

Von Malititz, G.P. & Brent, A. 2008. Assessing the biofuel options for southern Africa. Available: http://researchspace.csir.co.za/dspace/handle/10204/2579 [2012, October 31].

Walas, S.M. 1988. Chemical Process Equipment: Selection and Design. Elsevier.

Weiss, N., Börjesson, J., Pedersen, L.S. & Meyer, A.S. 2013. Enzymatic lignocellulose hydrolysis: Improved cellulase productivity by insoluble solids recycling. Biotechnology for biofuels. 6(1):1–14. DOI: 10.1186/1754-6834-6-5.

Wyman, C.E., Decker, S.R., Himmel, M.E., Brady, J.W. & Skopec, C.E. 2005. Hydrolysis of Cellulose and Hemicellulose.

Xiang, Q., Kim, J.S. & Lee, Y.Y. 2003. A Comprehensove kinetic Model for Dilute-Acid Hydrolysis of Cellulose. Applied Biochemistry and Biotechnology. 105-108(1):337–352.

Yee, T. & Grossmann, I. 1990. Simultaneous Optimization Models for Heat Integration—II. Heat Exchanger Network Synthesis. Computers & Chemical Engineering. 14(10):1165–1184. Available: http://www.sciencedirect.com/science/article/pii/0098135490850108 [2012, November 08].

Yee, T., Grossmann, I.E. & Kravanja, Z. 1990. Simultaneous Optimization Models for Heat Integration - I. Area and Energy Targeting and Modeling of Multi-stream Exchangers. Computers & chemical engineering. 14(10):1151–1164.

Yuan, T.-Q., Xu, F. & Sun, R.-C. 2013. Role of lignin in a biorefinery: separation characterization and valorization. Journal of Chemical Technology & Biotechnology. 88(3):346–352. DOI: 10.1002/jctb.3996.

Zhao, X., Zhou, Y. & Liu, D. 2012. Kinetic model for glycan hydrolysis and formation of monosaccharides during dilute acid hydrolysis of sugarcane bagasse. Bioresource technology. 105:160–8. DOI: 10.1016/j.biortech.2011.11.075.

Zhu, J.Y., Pan, X. & Zalesny, R.S. 2010. Pre-treatment of woody biomass for biofuel production: energy efficiency, technologies, and recalcitrance. Applied microbiology and biotechnology. 87(3):847–57. DOI: 10.1007/s00253-010-2654-8.

Zhuang, J. & Marchant, M. 2007. Economic analysis of cellulase production methods for bio-ethanol. Applied Engineering in Agriculture. 23(5):679–687. Available: http://www.eng.buffalo.edu/~jzhuang/Papers/Zhuang_AEA_2007.pdf [2014, December 17].

Appendix

A Data Used in GAMS Models

This section shows data that was to develop models, Matlab code that was used to determine parameters, and parameters used in the GAMS models. *Appendix A.1* shows physical property data for the components. *Appendix A.2* provides more information regarding the acid pre-hydrolysis model such as, the data which was used to develop the Matlab models, the Matlab code and the parameters obtained from the Matlab modelling which were used in the GAMS code. More information regarding the acid hydrolysis model can be found in *Appendix A.3.* This includes: an explanation of how the Arrhenius parameters used in the GAMS model were determined and a more detailed explanation of the Aspen model used to develop the acid hydrolysis flash model. *Appendix A.4* expands on how the effects of delignification on glucose conversion were incorporated in the enzymatic hydrolysis model. *Appendix A.5* incudes the environmental impact data. The raw data from SimaPro, weighting factors used and a more detailed explanation of how the environmental impact of enzymes was determined can be found in this section.

A.1 Component Physical Property Data

Table A.1.1 below shows data used for parameters of set *J* in the GAMS model. This includes physical property data, such as the heat capacity, molecular weight and density; the cost of raw materials and products, B_J, (see *Section 3.7.1*); and the mass fractions of components *J* in sugarcane bagasse were taken from the CTBE Aspen simulation (Bonomi et al., 2011). Physical property data was taken from Aspen Plus v7.3 using the CTBE database (Bonomi et al., 2011) which incorporates the NREL database (Wooley, Putsche & NREL, 1996). The bagasse mass fractions, $x_{SCB,J}$, were taken from the CTBE Aspen simulation (Bonomi et al., 2011). Some components have zero costs as they are waste products with no value associated with them.

Table A.1.1: Physical property data, cost data and mass fractions of sugarcane bagasse

Component (J)	B_J *R/t*	$C_{P,J}$ kJ.kg^{-1}.K^{-1}	MW_J *kg/kmol*	$x_{SCB,J}$ *Mass fraction*	ρ_J kg/m^3
AceA	0	2.74	60.1	0	1054
Acetyl	0	1.97	60.1	0.0119	1054
Acid	2560	1.66	98.1	0	1840
ASL	0	1.02	194	0	1820
Balance	0	0	18.0	0	999
Cellulose	0	1.68	162	0.217	1530
Enz	1708	1.48	24.0	0	1580
Furf	0	2.02	96.1	0	1164
Gluc	3682	1.15	180.158	0.000892	1181
Glucolig	0	1.15	162	0	1063
GluSol	0	1.15	162	0	1063
Hemi	0	1.68	132	0.116	1529
HMF	0	2.05	126	0	2221
Lignin	0	1.02	194	0.116	2377
Min	0	1.14	94.2	0.00154	315
NaOH	6000	2.21	40.0	0	133
NaSulp	0	3.40	119	0	2700
OrgAc	0	2.74	174	0.00227	2895
Phos	0	1.86	98.0	0.000122	1877
Salts	0	0.987	74.6	0.0122	248
Soil	0	1.43	60.1	0.000956	3924
Sucrose	0	8.49	342	0.0208	903
Water	0.0272	4.31	18.0	0.500	999
Xylo	2509	1.15	150	0	1826
Xylolig	0	1.15	132	0	16067
XylSol	0	1.15	132	0	1607

A.2 Acid Pre-hydrolysis of Sugarcane Bagasse

Kinetic parameters from Aguilar et al. (2002) are shown in *Appendix A.2.1*. These parmaters were used in this study in the Matlab code in *Appendix A.2.2* to generate the data tables of the reactor products used in the GAMS models as the $P_{J,n}$ datasets which are shown in *Appendix A.2.3.1* The explantation of this methodology can be found in *Section 3.3.1. Appendix A.2.3.2* shows the fraction vaporised of each component in the flash unit. This data was obtained using an Aspen simulation with the CTBE database (Bonomi et al., 2011). The methodology describing how the simulation was performed can be found in *Section 3.3.2.3.*

A.2.1 Data Used in Matlab Models

The kinetic parameters for hemicellulose, cellulose, furfural and acetic acid from Aguilar et al. (2002) are shown in the following tables. This data was used in the Matlab code in *Appendix A.2.2*.

Table A.2.1: Kinetic parameters for hemicellulose (Aguilar et al., 2002)

	α	k_1	k_2	R^2
2% at 100°C	0.554	0.0246	0	0.997
4% at 100°C	0.821	0.0188	0	0.997
6% at 100°C	0.827	0.0775	0	0.986
2% at 122°C	0.973	0.1885	0.0021	0.996
4% at 122°C	0.998	0.1581	0.0033	0.998
6% at 122°C	0.933	0.2271	0.004	0.986
2% at 128°C	0.742	0.2162	0.003	0.998
4% at 128°C	0.672	0.421	0.0036	0.998
6% at 128°C	0.69	0.8226	0.0089	0.982

Table A.2.2: Kinetic parameters for cellulose (Aguilar et al., 2002)

	α	$k_1 \times 10^3$	$k_2 \times 10^3$	R^2
2% at 100°C	0.055	8.62	0	0.963
4% at 100°C	0.116	7.57	0	0.998
6% at 100°C	0.13	2.56	0	0.994
2% at 122°C	0.121	35.7	0.29	0.979
4% at 122°C	0.146	84.2	0.42	0.997
6% at 122°C	0.182	74.1	0	0.995
2% at 128°C	0.367	6.31	7.95	0.910
4% at 128°C	0.432	6.05	5.49	0.976
6% at 128°C	0.512	5.97	5.97	0.927

Table A.2.3: Kinetic parameters for furfural (Aguilar et al., 2002)

	$C_{Furfural,0}$	k_1	R^2
2% at 100°C	0.74	0.0293	0.85
4% at 100°C	1.28	0.0158	0.89
6% at 100°C	1.8	0.0134	0.91
2% at 122°C	2.96	0.0080	0.96
4% at 122°C	4.14	0.0118	0.94
6% at 122°C	4.51	0.0172	0.99
2% at 128°C	3.63	0.0112	0.97
4% at 128°C	4.86	0.0185	0.98
6% at 128°C	5.59	0.0255	0.98

Table A.2.4: Kinetic parameters for acetic acid (Aguilar et al., 2002)

	$C_{Acetic,0}$	k_1	R^2
2% at 100°C	2.64	0.0356	0.991
4% at 100°C	3.66	0.0368	0.960
6% at 100°C	3.79	0.0700	0.959
2% at 122°C	3.65	1.55	0.930
4% at 122°C	4.06	0.914	0.918
6% at 122°C	4.53	0.851	0.949
2% at 128°C	2.67	0.0599	0.919
4% at 128°C	2.88	0.0504	0.964
6% at 128°C	3.42	0.0472	0.989

A.2.2 Matlab Code

Section 3.3.1 describes how the Matlab code, shown in the following pages, was constructed from the kinetics of Aguilar et al. (2002) and Lavarack, Griffin & Rodman (2002). The code was used to generater the $P_{J,n}$ datasets which can be found in *Appendix A.2.3.1.* Part of *Section 3.3.1* is repeated below to give context to the code.

The Matlab code titled *ppalTablesIntArrAcetyl*, shown in *Appendix A.2.2,* is the principal code used in this study which plots the concentration profiles. This code calls the function *tablefuncFixSimpleAcetyl* which includes all the species balances. The principal code, *ppalTablesIntArrAcetyl*, also calls functions (*xylTableIntConcTempArr, glucTableIntConcTemp, aceticTableIntConcTemp* and *furfTableIntConcTemp*) which are used to select the appropriate k and α values from the tables of the kinetic parameters determined by Aguilar et al. (2002). These functions are also capable of performing linear interpolations to predict the change in the kinetic parameters with change in temperature and acid concentration. However the interpolation values were found to be inaccurate as the relationship is non-linear. Only specific values of acid concentration and temperature for which experimental values of k and α were present were used.

ppalTablesIntArrAcetyl

```
clc, clear all, close all
% Parameters
tau=0.01:0.5:30;%residence time in minutes
D=1./tau;
Ca=2;%concentration of acid in % w/w
T=128+273.15;%temperature in K

%calls the methods that interpolate between Aguilar data tables
xyl=xylTableIntConcTempArr(Ca,T);
gluc=glucTableIntConcTemp(Ca,T);
acetic=aceticTableIntConcTemp(Ca,T);
furf=furfTableIntConcTemp(Ca,T);

double Cf;
Cf(1)=23.4;%initial hemicellulose concentration g/L
Cf(2)=0; %initial xylose concentration g/L
%Cf(3)=0;%initial acetic acid concentration g/L
%Cf(4)=0;%initial furfural concentration g/L
Cf(5)=43.2;%initial cellulose concentration g/L
Cf(6)=0;%initial glucose concentration g/L
Cf(7)=0;%initial HMF concentration g/L
Cf(8)=acetic(1);%acetic acid Ac0 parameter used in Aguilar equations
Cf(9)=furf(1);%furfural F0 parameter used in Aguilar equations

Co=[5    0.01     30    0.5   36   3   0 0 0];%initial guess for final
concentrations
for i=1: length(D)
    Cesp(i,:)=fsolve(@(C)
tablefuncFixSimpleAcetyl(C,D(i),Cf,T,Ca,xyl,gluc,acetic,furf),Co);
end

rend=max(Cesp(:,2))/Cf(1)

%renaming output for display and graph purposes
Hemi=Cesp(end,1);
Xyl=Cesp(end,2);
```

```
Fur=Cesp(end,3);
Acetic=Cesp(end,4);
Glucan=Cesp(end,5);
Glucose=Cesp(end,6);
HMF=Cesp(end,7);
Acet=Cesp(end,8);
Xyfur=Cesp(end,9);
%res=[Hemi;Xyl; Fur; Acetic;Glucan;Glucose;HMF]
disp([tau',Cesp])
disp([num2str(Ca),  '  ',  num2str(T-273.15)]);
xyl;
gluc;
acetic;
furf;

%graph plotting
figure1 = figure('Color',[1 1 1]);
plot(tau(:),Cesp,'LineWidth',2)
title('CSTR',...
    'FontWeight','bold',...
    'FontSize',16,...
    'FontName','Calibri');
xlabel('tau [min]','FontWeight','bold','FontSize',12,'FontName','Calibri');
ylabel('C [g/L]','FontWeight','bold','FontSize',12,'FontName','Calibri');
legend('Hemicellulose','Xylose','Furfural','Acetic','Cellulose','Glucose','
HMF')
grid on

figure2 = figure('Color',[1 1 1]);
plot(tau(:),Cesp(:,[3:4,7:9]),'LineWidth',2)
title('CSTR smaller components',...
    'FontWeight','bold',...
    'FontSize',16,...
    'FontName','Calibri');
xlabel('tau [min]','FontWeight','bold','FontSize',12,'FontName','Calibri');
ylabel('C [g/L]','FontWeight','bold','FontSize',12,'FontName','Calibri');
legend('Furfural','Acetic','HMF','Acetyl','FurfInit')
grid on
```

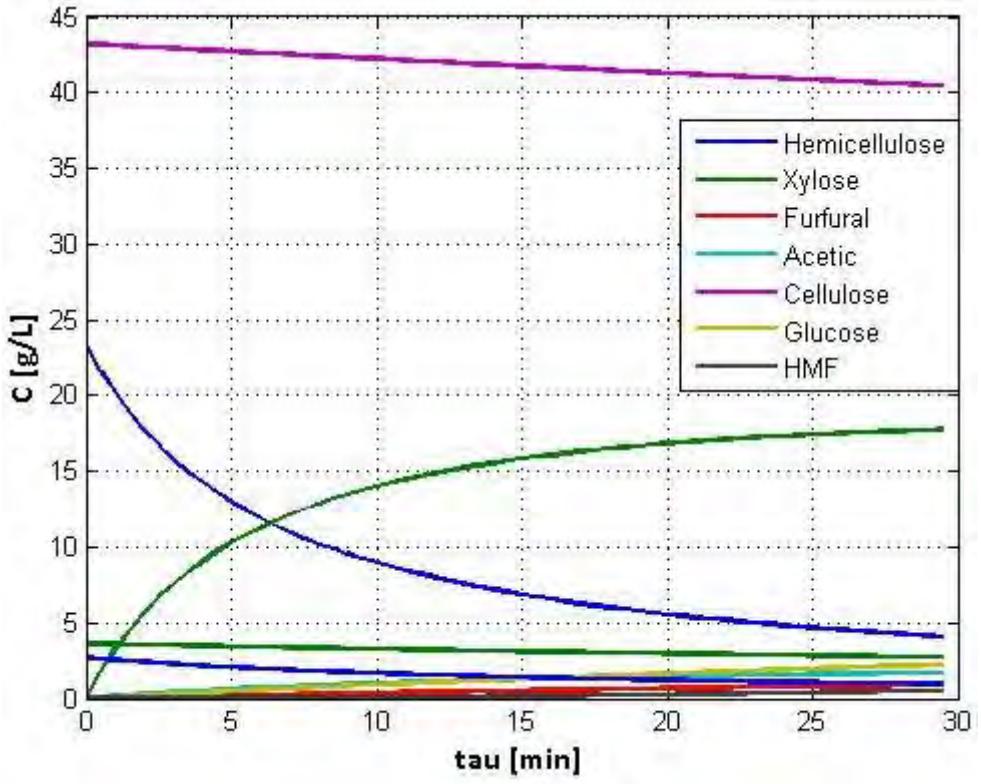


Figure A.2.1: Example of graph from Matlab code for pre-hydrolysis kinetics at 128°C using 2 wt% acid

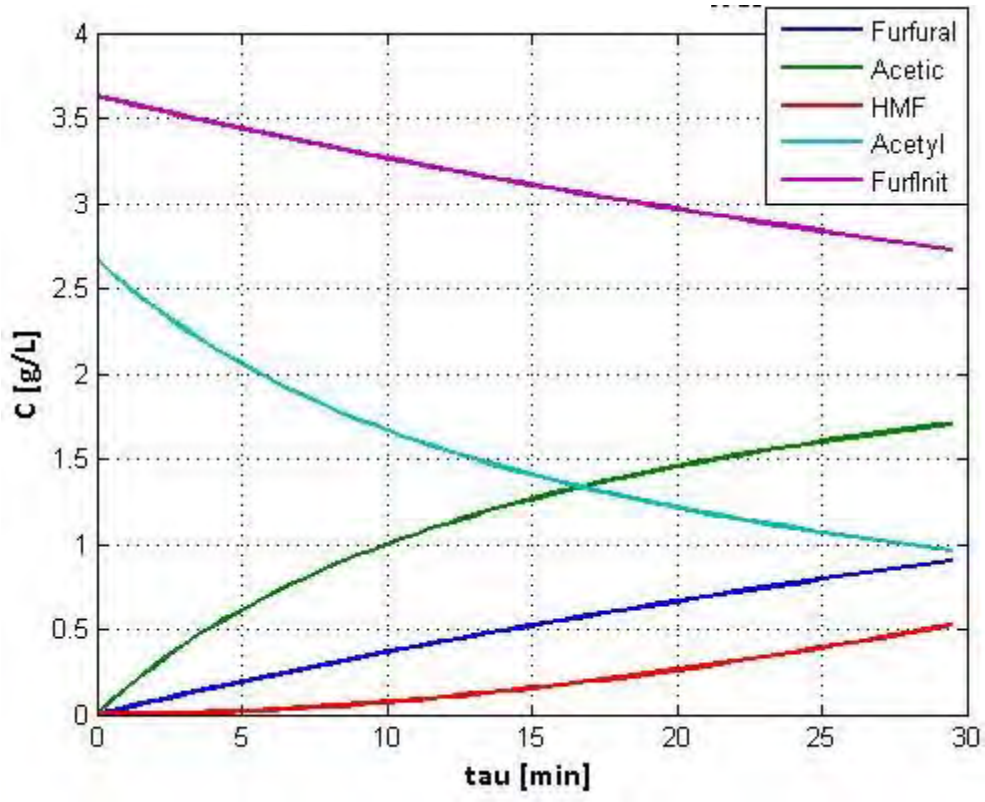


Figure A.2.2: Example of graph from Matlab code of components with smaller concentrations for pre-hydrolysis kinetics at 128°C using 2 wt% acid

tablefuncFixSimpleAcetyl

```
function[Fob]=tablefuncFixSimpleAcetyl(C,D,Cf,T,Ca,xyl,gluc,acetic,furf)

Chemi=C(1);
Cxy=C(2);
Cfur=C(3);
Cacetic=C(4);
Cglucan=C(5);
Cglucose=C(6);
CHMF=C(7);
Cacet=C(8);
Cxyfur=C(9);

Chemif=Cf(1); %initial hemicellulose concentration g/L
Cxyf=Cf(2);%initial xylose concentration g/L
%Cfurf=Cf(3);%initial furfural concentration g/L
%Caceticf=Cf(4);%initial acetic acid concentration g/L
Cglucanf=Cf(5);%initial cellulose concentration g/L
Cglucosef=Cf(6);%initial glucose concentration g/L
CHMFf=Cf(7);%initial HMF concentration g/L
%Cacetf=Cf(4);%acetic acid Ac0 parameter used in Aguilar equations
%Cxyfurf=Cf(3);%furfural F0 parameter used in Aguilar equations

%renaming parameters
alphax=xyl(1);
k1x=xyl(2);
k2x=xyl(3);

alphag=gluc(1);
k1g=gluc(2);
k2g=gluc(3);

Caceticf=0;
Cacetf=acetic(1);
k1a=acetic(2);
Cfurf=0;
Cxyfurf=furf(1);
k1f=furf(2);

R=8.3145;% J/mol.K
stoichx=150/132;
stoichg=180/162;

tau=1./D;

%Rate equations
RChemi=-k1x.*alphax*Chemi;
RCxy=k1x.*alphax*Chemi-k2x*Cxy;
RCglucan=-k1g.*alphag*Cglucan;
RCglucose=k1g.*alphag*Cglucan - k2g.*Cglucose;
RCHMF=k2g.*Cglucose;
RCacetic=k1a.*Cacet;    %CSTR
RCacet=-k1a.*Cacet;    %CSTR
RCfur=k1f.*Cxyfur;          %CSTR
RCxyfur=-k1f.*Cxyfur;          %CSTR

%Objective functions - molar balances for each species
Fob(1)=D*(Chemif-Chemi)+RChemi; %hemicellulose
```

```
Fob(2)=D*(Cxyf-Cxy)+RCxy;%xylose
Fob(3)=D*(-Cfur)+RCfur;%furfural       %%PFR has no D
Fob(4)=D*(-Cacetic)+RCacetic;%acetic acid  %%PFR has no D
Fob(5)=D*(Cglucanf-Cglucan)+RCglucan;%cellulose
Fob(6)=D*(Cglucosef-Cglucose)+RCglucose;%glucose
Fob(7)=D*(CHMFf-CHMF)+RCHMF;%HMF
Fob(8)=D*(Cacetf-Cacet)+RCacet;%acetyl
Fob(9)=D*(Cxyfurf-Cxyfur)+RCxyfur;%xylose that reacts to furfural

Fob=Fob(:);
```

xylTableIntConcTempArr

```
function [xylParams] = xylTableIntConcTempArr (Ca,T)

XylData = {'','Ca','T','Alpha','k1','k2';
           '2% at 100',2,100,0.554,0.0246,0;
           '4% at 100',4,100,0.821,0.0188,0;
           '6% at 100',6,100,0.827,0.0775,0;
           '2% at 122',2,122,0.973,0.1885,2.1*10^-3;
           '4% at 122',4,122,0.998,0.1581,3.3*10^-3;
           '6% at 122',6,122,0.933,0.2271,4*10^-3;
           '2% at 128',2,128,0.742,0.2162,3*10^-3;
           '4% at 128',4,128,0.672,0.4210,3.6*10^-3;
           '6% at 128',6,128,0.690,0.8226,8.9*10^-3;};%data from Aguilar
paper

double TC;%temperature in degrees celcius
TC=T-273.15;
int row;
int col;
row=size(XylData,1);%number of rows in data
col=size(XylData,2);%number of columns in data

double alpha;
double k1;
double k2;
xylParams=[1  1  1];

int found;%used to test if data has been found
found=0;%initialised to zero
first=[1 1 1 1];%arrays used to store current data for interpolation
second=[1 1 1 1];%arrays used to store current data for interpolation
ParamsC1=[1 1];
ParamsC2=[1 1];

 for i=1:row
if (Ca == XylData{i,2})
    if (TC == XylData{i,3})
    disp(['Nothing to interpolate, Ca:',num2str(Ca),' T:',num2str(TC)]);
    found=1;
    XylData{i,:};
    xylParams(1)=XylData{i,4};
    xylParams(2)=XylData{i,5};
    xylParams(3)=XylData{i,6};
    i=row;
    end
end
 %end
 end

 if found == 0
    xylParams(2)=exp(30.7).*Ca.^(0.734).*exp(-13080./(T)); % min^-1

         %Something needs to be interpolated
     if(Ca == 2 || Ca == 4 || Ca == 6)
         %Ca is fine so interpolate T
     if(TC>128)
        disp(['T too high: T = ',  num2str(TC)]);
     elseif(TC<100)
```

```
    disp(['T too low: T = ',  num2str(TC)]);
    elseif(TC ~= 100 && TC ~= 122 && TC ~= 128)
    disp(['Time to interpolate, T = ',  num2str(TC)]);
       if(TC>100 && TC<122)
           for(i=2:4)
               if (Ca == XylData{i,2})
                  first(1)=XylData{i,2};
                  first(2)=XylData{i,3};
                  first(3)=XylData{i,4};
                  %first(4)=XylData{i,5};
                  first(5)=XylData{i,6}

                  second(1)=XylData{i+3,2};
                  second(2)=XylData{i+3,3};
                  second(3)=XylData{i+3,4};
                  %second(4)=XylData{i+3,5};
                  second(5)=XylData{i+3,6}

                  found=1;
                   disp(['Interpolating 100 < T < 122 at constant Ca =
',num2str(Ca)]);
                  xylParams(1)=XylData{i,4}+(((TC-
XylData{i,3})/(XylData{i+3,3}-XylData{i,3}))*(XylData{i+3,4}-
XylData{i,4}));
                  xylParams(3)=XylData{i,6}+(((TC-
XylData{i,3})/(XylData{i+3,3}-XylData{i,3}))*(XylData{i+3,6}-
XylData{i,6}));
               end
           end
       else
           for(i=5:7)
               if (Ca == XylData{i,2})
                  first(1)=XylData{i,2};
                  first(2)=XylData{i,3};
                  first(3)=XylData{i,4};
                  first(5)=XylData{i,6}

                  second(1)=XylData{i+3,2};
                  second(2)=XylData{i+3,3};
                  second(3)=XylData{i+3,4};
                  second(5)=XylData{i+3,6}
                  found=1;
                   disp(['Interpolating 122 < T < 128 at constant Ca
=',num2str(Ca)]);

                  xylParams(1)=XylData{i,4}+(((TC-
XylData{i,3})/(XylData{i+3,3}-XylData{i,3}))*(XylData{i+3,4}-
XylData{i,4}));
                  xylParams(3)=XylData{i,6}+(((TC-
XylData{i,3})/(XylData{i+3,3}-XylData{i,3}))*(XylData{i+3,6}-
XylData{i,6}));
               end
           end
       end

    end
    else
       if(Ca>6)
           disp(['Ca too high: Ca = ',  num2str(Ca)]);
       elseif(Ca<2)
```

```
            disp(['Ca too low: Ca = ',  num2str(Ca)]);
        elseif(Ca ~= 2 && Ca ~= 4 && Ca ~= 6)
            disp(['Time to interpolate, Ca = ',  num2str(Ca),' T = ',
num2str(TC)]);
             if(TC>128)
               disp(['T too high: T = ',  num2str(TC)]);
             elseif(TC<100)
               disp(['T too low: T = ',  num2str(TC)]);

             elseif(Ca>2 && Ca<4)

               for(i=2:3:8)
               if (TC == XylData{i,3})
                   disp('Interpolating 2 < Ca < 4 at constant T ');
                  first(1)=XylData{i,2};
                  first(2)=XylData{i,3};
                  first(3)=XylData{i,4};
                  first(5)=XylData{i,6}

                  second(1)=XylData{i+1,2};
                  second(2)=XylData{i+1,3};
                  second(3)=XylData{i+1,4};
                  second(5)=XylData{i+1,6}

                  found=1;
                  xylParams(1)=XylData{i,4}+(((Ca-
XylData{i,2})/(XylData{i+1,2}-XylData{i,2}))*(XylData{i+1,4}-
XylData{i,4}));
                  xylParams(3)=XylData{i,6}+(((Ca-
XylData{i,2})/(XylData{i+1,2}-XylData{i,2}))*(XylData{i+1,6}-
XylData{i,6}));
               end
               end
                   if(found==0)
                       disp('Interpolating both, 2 < Ca < 4');
                                          for(i=2:3:8)
                                            if (TC > XylData{i,3} && TC
< XylData{i+3,3})

                                            firstC1(1)=XylData{i,2};
                                            firstC1(2)=XylData{i,3};
                                            firstC1(3)=XylData{i,4};
                                            firstC1(5)=XylData{i,6}

                                            secondC1(1)=XylData{i+1,2};
                                            secondC1(2)=XylData{i+1,3};
                                            secondC1(3)=XylData{i+1,4};
                                            secondC1(5)=XylData{i+1,6}

                                            firstC2(1)=XylData{i+3,2};
                                            firstC2(2)=XylData{i+3,3};
                                            firstC2(3)=XylData{i+3,4};
                                            firstC2(5)=XylData{i+3,6}

                                            secondC2(1)=XylData{i+4,2};
                                            secondC2(2)=XylData{i+4,3};
                                            secondC2(3)=XylData{i+4,4};
                                            secondC2(5)=XylData{i+4,6}
```

```
                                                found=1;


ParamsC1(1)=firstC1(3)+(((Ca-XylData{i,2})/(XylData{i+1,2}-
XylData{i,2}))*(secondC1(3)-firstC1(3)));

ParamsC1(3)=firstC1(5)+(((Ca-XylData{i,2})/(XylData{i+1,2}-
XylData{i,2}))*(secondC1(5)-firstC1(5)))

ParamsC2(1)=firstC2(3)+(((Ca-XylData{i,2})/(XylData{i+1,2}-
XylData{i,2}))*(secondC2(3)-firstC2(3)));

ParamsC2(3)=firstC2(5)+(((Ca-XylData{i,2})/(XylData{i+1,2}-
XylData{i,2}))*(secondC2(5)-firstC2(5)))


xylParams(1)=ParamsC1(1)+(((TC-XylData{i,3})/(XylData{i+3,3}-
XylData{i,3}))*(ParamsC2(1)-ParamsC1(1)));

xylParams(3)=ParamsC1(3)+(((TC-XylData{i,3})/(XylData{i+3,3}-
XylData{i,3}))*(ParamsC2(3)-ParamsC1(3)));
                                                  end
                                               end
                    end
                elseif(Ca>4 && Ca<6)
                 for(i=3:3:9)
                 if (TC == XylData{i,3})
                    disp('Interpolating 4 < Ca < 6 at constant T ');
                    first(1)=XylData{i,2};
                    first(2)=XylData{i,3};
                    first(3)=XylData{i,4};
                    first(5)=XylData{i,6}

                    second(1)=XylData{i+1,2};
                    second(2)=XylData{i+1,3};
                    second(3)=XylData{i+1,4};
                    second(5)=XylData{i+1,6}

                    found=1;
                    xylParams(1)=XylData{i,4}+(((Ca-
XylData{i,2})/(XylData{i+1,2}-XylData{i,2}))*(XylData{i+1,4}-
XylData{i,4}));
                    xylParams(3)=XylData{i,6}+(((Ca-
XylData{i,2})/(XylData{i+1,2}-XylData{i,2}))*(XylData{i+1,6}-
XylData{i,6}));
                end
            end
                        if(found==0)
                            disp('Interpolating both, 4 < Ca < 6');
                                          for(i=3:3:9)
                                             if (TC > XylData{i,3} && TC
< XylData{i+3,3})
                                             firstC1(1)=XylData{i,2};
                                             firstC1(2)=XylData{i,3};
                                             firstC1(3)=XylData{i,4};
                                             firstC1(5)=XylData{i,6}

                                             secondC1(1)=XylData{i+1,2};
                                             secondC1(2)=XylData{i+1,3};
                                             secondC1(3)=XylData{i+1,4};
```

```
                                                secondC1(5)=XylData{i+1,6}

                                                firstC2(1)=XylData{i+3,2};
                                                firstC2(2)=XylData{i+3,3};
                                                firstC2(3)=XylData{i+3,4};
                                                firstC2(5)=XylData{i+3,6}

                                                secondC2(1)=XylData{i+4,2};
                                                secondC2(2)=XylData{i+4,3};
                                                secondC2(3)=XylData{i+4,4};
                                                secondC2(5)=XylData{i+4,6}

                                                found=1;


ParamsC1(1)=firstC1(3)+(((Ca-XylData{i,2})/(XylData{i+1,2}-
XylData{i,2}))*(secondC1(3)-firstC1(3)));

ParamsC1(3)=firstC1(5)+(((Ca-XylData{i,2})/(XylData{i+1,2}-
XylData{i,2}))*(secondC1(5)-firstC1(5)))

ParamsC2(1)=firstC2(3)+(((Ca-XylData{i,2})/(XylData{i+1,2}-
XylData{i,2}))*(secondC2(3)-firstC2(3)));

ParamsC2(3)=firstC2(5)+(((Ca-XylData{i,2})/(XylData{i+1,2}-
XylData{i,2}))*(secondC2(5)-firstC2(5)))

xylParams(1)=ParamsC1(1)+(((TC-XylData{i,3})/(XylData{i+3,3}-
XylData{i,3}))*(ParamsC2(1)-ParamsC1(1)));

xylParams(3)=ParamsC1(3)+(((TC-XylData{i,3})/(XylData{i+3,3}-
XylData{i,3}))*(ParamsC2(3)-ParamsC1(3)));
                                                   end
                                               end
                          end
        end
        end
    end
 end
 xylParams=xylParams(:);
```

glucTableIntConcTemp

```
function [glucParams] = glucTableIntConcTemp (Ca,T)

glucData = {'','Ca','T','Alpha','k1','k2';
           '2% at 100',2,100,0.055,8.62*10^-3,0;
           '4% at 100',4,100,0.116,7.57*10^-3,0;
           '6% at 100',6,100,0.130,2.56*10^-3,0;
           '2% at 122',2,122,0.121,35.7*10^-3,0.29*10^-3;
           '4% at 122',4,122,0.146,84.2*10^-3,0.42*10^-3;
           '6% at 122',6,122,0.182,74.1*10^-3,0;
           '2% at 128',2,128,0.367,6.31*10^-3,7.95*10^-3;
           '4% at 128',4,128,0.432,6.05*10^-3,5.49*10^-3;
           '6% at 128',6,128,0.512,5.97*10^-3,5.97*10^-3;};%data from
Aguilar paper

double TC;%temperature in degrees celcius
TC=T-273.15;
int row;
int col;
row=size(glucData,1);%number of rows in data
col=size(glucData,2);%number of columns in data

double alpha;
double k1;
double k2;
glucParams=[1  1  1];

int found;%used to test if data has been found
found=0;%initialised to zero
first=[1 1 1 1 1];%arrays used to store current data for interpolation
second=[1 1 1 1 1];%arrays used to store current data for interpolation
ParamsC1=[1 1 1];
ParamsC2=[1 1 1];

 for i=1:row
if (Ca == glucData{i,2})
    if (TC == glucData{i,3})
                disp(['Nothing to interpolate, Ca:',num2str(Ca),'
T:',num2str(TC)]);
    glucData{i,:};
    glucParams(1)=glucData{i,4};
    glucParams(2)=glucData{i,5};
    glucParams(3)=glucData{i,6};
    found=1;
    i=row;
    end
end
end

if(found==0)
     %Something needs to be interpolated
     if(Ca == 2 || Ca == 4 || Ca == 6)
         %Ca is fine so interpolate T
     if(TC>128)
        disp(['T too high: T = ',  num2str(TC)]);
     elseif(TC<100)
     disp(['T too low: T = ',  num2str(TC)]);
     elseif(TC ~= 100 && TC ~= 122 && TC ~= 128)
     disp(['Time to interpolate, T = ',  num2str(TC)]);
```

```
        if(TC>100 && TC<122)
            for(i=2:4)
                if (Ca == glucData{i,2})
                   first(1)=glucData{i,2};
                   first(2)=glucData{i,3};
                   first(3)=glucData{i,4};
                   first(4)=glucData{i,5};
                   first(5)=glucData{i,6}

                   second(1)=glucData{i+3,2};
                   second(2)=glucData{i+3,3};
                   second(3)=glucData{i+3,4};
                   second(4)=glucData{i+3,5};
                   second(5)=glucData{i+3,6}

                   found=1;
                    disp(['Interpolating 100 < T < 122 at constant Ca =
',num2str(Ca)]);
                    test1=TC-glucData{i,3};
                    test2=(glucData{i+3,3}-glucData{i,3});
                    test3=(glucData{i+3,4}-glucData{i,4});
                   glucParams(1)=glucData{i,4}+(((TC-
glucData{i,3})/(glucData{i+3,3}-glucData{i,3}))*(glucData{i+3,4}-
glucData{i,4}));
                   glucParams(2)=glucData{i,5}+(((TC-
glucData{i,3})/(glucData{i+3,3}-glucData{i,3}))*(glucData{i+3,5}-
glucData{i,5}));
                   glucParams(3)=glucData{i,6}+(((TC-
glucData{i,3})/(glucData{i+3,3}-glucData{i,3}))*(glucData{i+3,6}-
glucData{i,6}));
                end
            end
        else
            for(i=5:7)
               % disp(['For i: ', num2str(i)]);
                if (Ca == glucData{i,2})
                   first(1)=glucData{i,2};
                   first(2)=glucData{i,3};
                   first(3)=glucData{i,4};
                   first(4)=glucData{i,5};
                   first(5)=glucData{i,6}

                   second(1)=glucData{i+3,2};
                   second(2)=glucData{i+3,3};
                   second(3)=glucData{i+3,4};
                   second(4)=glucData{i+3,5};
                   second(5)=glucData{i+3,6}
                   found=1;
                    disp(['Interpolating 122 < T < 128 at constant Ca
=',num2str(Ca)]);

                   glucParams(1)=glucData{i,4}+(((TC-
glucData{i,3})/(glucData{i+3,3}-glucData{i,3}))*(glucData{i+3,4}-
glucData{i,4}));
                   glucParams(2)=glucData{i,5}+(((TC-
glucData{i,3})/(glucData{i+3,3}-glucData{i,3}))*(glucData{i+3,5}-
glucData{i,5}));
                   glucParams(3)=glucData{i,6}+(((TC-
glucData{i,3})/(glucData{i+3,3}-glucData{i,3}))*(glucData{i+3,6}-
glucData{i,6}));
```

```
                end
            end
        end

    end
    else
        %Ca is not fine so interpolate that
        if(Ca>6)
            disp(['Ca too high: Ca = ',  num2str(Ca)]);
        elseif(Ca<2)
            disp(['Ca too low: Ca = ',  num2str(Ca)]);
        elseif(Ca ~= 2 && Ca ~= 4 && Ca ~= 6)
            disp(['Time to interpolate, Ca = ',  num2str(Ca),' T = ',
num2str(TC)]);
             if(TC>128)
               disp(['T too high: T = ',  num2str(TC)]);
             elseif(TC<100)
               disp(['T too low: T = ',  num2str(TC)]);
             elseif(Ca>2 && Ca<4)
               for(i=2:3:8)
               if (TC == glucData{i,3})
                   disp('Interpolating 2 < Ca < 4 at constant T ');
                  first(1)=glucData{i,2};
                  first(2)=glucData{i,3};
                  first(3)=glucData{i,4};
                  first(4)=glucData{i,5};
                  first(5)=glucData{i,6}

                  second(1)=glucData{i+1,2};
                  second(2)=glucData{i+1,3};
                  second(3)=glucData{i+1,4};
                  second(4)=glucData{i+1,5};
                  second(5)=glucData{i+1,6}

                  found=1;
                  glucParams(1)=glucData{i,4}+(((Ca-
glucData{i,2})/(glucData{i+1,2}-glucData{i,2}))*(glucData{i+1,4}-
glucData{i,4}));
                  glucParams(2)=glucData{i,5}+(((Ca-
glucData{i,2})/(glucData{i+1,2}-glucData{i,2}))*(glucData{i+1,5}-
glucData{i,5}));
                  glucParams(3)=glucData{i,6}+(((Ca-
glucData{i,2})/(glucData{i+1,2}-glucData{i,2}))*(glucData{i+1,6}-
glucData{i,6}));
               end
               end
                   if(found==0)
                       disp('Interpolating both, 2 < Ca < 4');
                                       for(i=2:3:8)
                                         if (TC > glucData{i,3} && TC
< glucData{i+3,3})

                                         firstC1(1)=glucData{i,2};
                                         firstC1(2)=glucData{i,3};
                                         firstC1(3)=glucData{i,4};
                                         firstC1(4)=glucData{i,5};
                                         firstC1(5)=glucData{i,6}

                                         secondC1(1)=glucData{i+1,2};
                                         secondC1(2)=glucData{i+1,3};
```

```
                                                secondC1(3)=glucData{i+1,4};
                                                secondC1(4)=glucData{i+1,5};
                                                secondC1(5)=glucData{i+1,6}

                                                firstC2(1)=glucData{i+3,2};
                                                firstC2(2)=glucData{i+3,3};
                                                firstC2(3)=glucData{i+3,4};
                                                firstC2(4)=glucData{i+3,5};
                                                firstC2(5)=glucData{i+3,6}

                                                secondC2(1)=glucData{i+4,2};
                                                secondC2(2)=glucData{i+4,3};
                                                secondC2(3)=glucData{i+4,4};
                                                secondC2(4)=glucData{i+4,5};
                                                secondC2(5)=glucData{i+4,6}

                                                found=1;


ParamsC1(1)=firstC1(3)+(((Ca-glucData{i,2})/(glucData{i+1,2}-
glucData{i,2}))*(secondC1(3)-firstC1(3)));

ParamsC1(2)=firstC1(4)+(((Ca-glucData{i,2})/(glucData{i+1,2}-
glucData{i,2}))*(secondC1(4)-firstC1(4)));

ParamsC1(3)=firstC1(5)+(((Ca-glucData{i,2})/(glucData{i+1,2}-
glucData{i,2}))*(secondC1(5)-firstC1(5)))


ParamsC2(1)=firstC2(3)+(((Ca-glucData{i,2})/(glucData{i+1,2}-
glucData{i,2}))*(secondC2(3)-firstC2(3)));

ParamsC2(2)=firstC2(4)+(((Ca-glucData{i,2})/(glucData{i+1,2}-
glucData{i,2}))*(secondC2(4)-firstC2(4)));

ParamsC2(3)=firstC2(5)+(((Ca-glucData{i,2})/(glucData{i+1,2}-
glucData{i,2}))*(secondC2(5)-firstC2(5)))


glucParams(1)=ParamsC1(1)+(((TC-glucData{i,3})/(glucData{i+3,3}-
glucData{i,3}))*(ParamsC2(1)-ParamsC1(1)));

glucParams(2)=ParamsC1(2)+(((TC-glucData{i,3})/(glucData{i+3,3}-
glucData{i,3}))*(ParamsC2(2)-ParamsC1(2)));

glucParams(3)=ParamsC1(3)+(((TC-glucData{i,3})/(glucData{i+3,3}-
glucData{i,3}))*(ParamsC2(3)-ParamsC1(3)));
                                                  end
                                               end
                    end
                elseif(Ca>4 && Ca<6)
                 for(i=3:3:9)
                 if (TC == glucData{i,3})
                    disp('Interpolating 4 < Ca < 6 at constant T ');
                    first(1)=glucData{i,2};
                    first(2)=glucData{i,3};
                    first(3)=glucData{i,4};
                    first(4)=glucData{i,5};
                    first(5)=glucData{i,6}
```

```
                    second(1)=glucData{i+1,2};
                    second(2)=glucData{i+1,3};
                    second(3)=glucData{i+1,4};
                    second(4)=glucData{i+1,5};
                    second(5)=glucData{i+1,6}

                    found=1;
                    glucParams(1)=glucData{i,4}+(((Ca-
glucData{i,2})/(glucData{i+1,2}-glucData{i,2}))*(glucData{i+1,4}-
glucData{i,4}));
                    glucParams(2)=glucData{i,5}+(((Ca-
glucData{i,2})/(glucData{i+1,2}-glucData{i,2}))*(glucData{i+1,5}-
glucData{i,5}));
                    glucParams(3)=glucData{i,6}+(((Ca-
glucData{i,2})/(glucData{i+1,2}-glucData{i,2}))*(glucData{i+1,6}-
glucData{i,6}));
                end
            end
                        if(found==0)
                            disp('Interpolating both, 4 < Ca < 6');
                                        for(i=3:3:9)
                                            if (TC > glucData{i,3} && TC
< glucData{i+3,3})

                                            firstC1(1)=glucData{i,2};
                                            firstC1(2)=glucData{i,3};
                                            firstC1(3)=glucData{i,4};
                                            firstC1(4)=glucData{i,5};
                                            firstC1(5)=glucData{i,6}

                                            secondC1(1)=glucData{i+1,2};
                                            secondC1(2)=glucData{i+1,3};
                                            secondC1(3)=glucData{i+1,4};
                                            secondC1(4)=glucData{i+1,5};
                                            secondC1(5)=glucData{i+1,6}

                                            firstC2(1)=glucData{i+3,2};
                                            firstC2(2)=glucData{i+3,3};
                                            firstC2(3)=glucData{i+3,4};
                                            firstC2(4)=glucData{i+3,5};
                                            firstC2(5)=glucData{i+3,6}

                                            secondC2(1)=glucData{i+4,2};
                                            secondC2(2)=glucData{i+4,3};
                                            secondC2(3)=glucData{i+4,4};
                                            secondC2(4)=glucData{i+4,5};
                                            secondC2(5)=glucData{i+4,6}

                                            found=1;


ParamsC1(1)=firstC1(3)+(((Ca-glucData{i,2})/(glucData{i+1,2}-
glucData{i,2}))*(secondC1(3)-firstC1(3)));

ParamsC1(2)=firstC1(4)+(((Ca-glucData{i,2})/(glucData{i+1,2}-
glucData{i,2}))*(secondC1(4)-firstC1(4)));

ParamsC1(3)=firstC1(5)+(((Ca-glucData{i,2})/(glucData{i+1,2}-
glucData{i,2}))*(secondC1(5)-firstC1(5)))
```

```
ParamsC2(1)=firstC2(3)+(((Ca-glucData{i,2})/(glucData{i+1,2}-
glucData{i,2}))*(secondC2(3)-firstC2(3)));

ParamsC2(2)=firstC2(4)+(((Ca-glucData{i,2})/(glucData{i+1,2}-
glucData{i,2}))*(secondC2(4)-firstC2(4)));

ParamsC2(3)=firstC2(5)+(((Ca-glucData{i,2})/(glucData{i+1,2}-
glucData{i,2}))*(secondC2(5)-firstC2(5)))


glucParams(1)=ParamsC1(1)+(((TC-glucData{i,3})/(glucData{i+3,3}-
glucData{i,3}))*(ParamsC2(1)-ParamsC1(1)));

glucParams(2)=ParamsC1(2)+(((TC-glucData{i,3})/(glucData{i+3,3}-
glucData{i,3}))*(ParamsC2(2)-ParamsC1(2)));

glucParams(3)=ParamsC1(3)+(((TC-glucData{i,3})/(glucData{i+3,3}-
glucData{i,3}))*(ParamsC2(3)-ParamsC1(3)));
                                                  end
                                                end
                        end
        end
        end
     end
     end
glucParams=glucParams(:);
```

aceticTableIntConcTemp

```
function [aceticParams] = aceticTableIntConcTemp (Ca,T)

aceticData = {'','Ca','T','Ac0','k1';
           '2% at 100',2,100,2.64,0.0356;
           '4% at 100',4,100,3.66,0.0368;
           '6% at 100',6,100,3.79,0.0700;
           '2% at 122',2,122,3.65,1.55;
           '4% at 122',4,122,4.06,0.914;
           '6% at 122',6,122,4.53,0.851;
           '2% at 128',2,128,2.67,0.0599;
           '4% at 128',4,128,2.88,0.0504;
           '6% at 128',6,128,3.42,0.0472;};%data from Aguilar paper

double TC;%temperature in degrees celcius
TC=T-273.15;
int row;
int col;
row=size(aceticData,1);%number of rows in data
col=size(aceticData,2);%number of columns in data

double alpha;
double k1;
double k2;

int found;%used to test if data has been found
found=0;%initialised to zero
first=[1 1 1 1];%arrays used to store current data for interpolation
second=[1 1 1 1];%arrays used to store current data for interpolation
ParamsC1=[1 1];
ParamsC2=[1 1];

aceticParams=[1  1];
 for i=1:row
        if (Ca == aceticData{i,2})
            if (TC == aceticData{i,3})
            aceticData{i,:};
            disp(['Nothing to interpolate, Ca:',num2str(Ca),'
T:',num2str(TC)]);
            found=1;
            aceticParams(1)=aceticData{i,4};
            aceticParams(2)=aceticData{i,5};
            i=row;
            end
        end
 end

if(found==0)
     %Something needs to be interpolated
     if(Ca == 2 || Ca == 4 || Ca == 6)
         %Ca is fine so interpolate T
     if(TC>128)
        disp(['T too high: T = ',  num2str(TC)]);
     elseif(TC<100)
     disp(['T too low: T = ',  num2str(TC)]);
     elseif(TC ~= 100 && TC ~= 122 && TC ~= 128)
     disp(['Time to interpolate, T = ',  num2str(TC)]);
        if(TC>100 && TC<122)
            for(i=2:4)
```

```
                if (Ca == aceticData{i,2})
                   first(1)=aceticData{i,2};
                   first(2)=aceticData{i,3};
                   first(3)=aceticData{i,4};
                   first(4)=aceticData{i,5}

                   second(1)=aceticData{i+3,2};
                   second(2)=aceticData{i+3,3};
                   second(3)=aceticData{i+3,4};
                   second(4)=aceticData{i+3,5}

                   found=1;
                    disp(['Interpolating 100 < T < 122 at constant Ca =
',num2str(Ca)]);
                   aceticParams(1)=aceticData{i,4}+(((TC-
aceticData{i,3})/(aceticData{i+3,3}-aceticData{i,3}))*(aceticData{i+3,4}-
aceticData{i,4}));
                   aceticParams(2)=aceticData{i,5}+(((TC-
aceticData{i,3})/(aceticData{i+3,3}-aceticData{i,3}))*(aceticData{i+3,5}-
aceticData{i,5}));

                end
            end
        else
            for(i=5:7)
                if (Ca == aceticData{i,2})
                   first(1)=aceticData{i,2};
                   first(2)=aceticData{i,3};
                   first(3)=aceticData{i,4};
                   first(4)=aceticData{i,5}

                   second(1)=aceticData{i+3,2};
                   second(2)=aceticData{i+3,3};
                   second(3)=aceticData{i+3,4};
                   second(4)=aceticData{i+3,5}
                   found=1;
                    disp(['Interpolating 122 < T < 128 at constant Ca
=',num2str(Ca)]);

                   aceticParams(1)=aceticData{i,4}+(((TC-
aceticData{i,3})/(aceticData{i+3,3}-aceticData{i,3}))*(aceticData{i+3,4}-
aceticData{i,4}));
                   aceticParams(2)=aceticData{i,5}+(((TC-
aceticData{i,3})/(aceticData{i+3,3}-aceticData{i,3}))*(aceticData{i+3,5}-
aceticData{i,5}));
                end
            end
        end

    end
    else
       %Ca is not fine so interpolate that
       if(Ca>6)
           disp(['Ca too high: Ca = ',  num2str(Ca)]);
       elseif(Ca<2)
           disp(['Ca too low: Ca = ',  num2str(Ca)]);
       elseif(Ca ~= 2 && Ca ~= 4 && Ca ~= 6)
           disp(['Time to interpolate, Ca = ',  num2str(Ca),' T = ',
num2str(TC)]);
             if(TC>128)
```

```
                disp(['T too high: T = ',  num2str(TC)]);
              elseif(TC<100)
                disp(['T too low: T = ',  num2str(TC)]);
              elseif(Ca>2 && Ca<4)
                for(i=2:3:8)
                if (TC == aceticData{i,3})
                    disp('Interpolating 2 < Ca < 4 at constant T ');
                   first(1)=aceticData{i,2};
                   first(2)=aceticData{i,3};
                   first(3)=aceticData{i,4};
                   first(4)=aceticData{i,5}

                   second(1)=aceticData{i+1,2};
                   second(2)=aceticData{i+1,3};
                   second(3)=aceticData{i+1,4};
                   second(4)=aceticData{i+1,5}

                   found=1;
                   aceticParams(1)=aceticData{i,4}+(((Ca-
aceticData{i,2})/(aceticData{i+1,2}-aceticData{i,2}))*(aceticData{i+1,4}-
aceticData{i,4}));
                   aceticParams(2)=aceticData{i,5}+(((Ca-
aceticData{i,2})/(aceticData{i+1,2}-aceticData{i,2}))*(aceticData{i+1,5}-
aceticData{i,5}));
                end
                end
                    if(found==0)
                        disp('Interpolating both, 2 < Ca < 4');
                                          for(i=2:3:8)
                                            if (TC > aceticData{i,3} &&
TC < aceticData{i+3,3})

                                            firstC1(1)=aceticData{i,2};
                                            firstC1(2)=aceticData{i,3};
                                            firstC1(3)=aceticData{i,4};
                                            firstC1(4)=aceticData{i,5}


secondC1(1)=aceticData{i+1,2};

secondC1(2)=aceticData{i+1,3};

secondC1(3)=aceticData{i+1,4};

secondC1(4)=aceticData{i+1,5}


firstC2(1)=aceticData{i+3,2};

firstC2(2)=aceticData{i+3,3};

firstC2(3)=aceticData{i+3,4};
                                            firstC2(4)=aceticData{i+3,5}


secondC2(1)=aceticData{i+4,2};

secondC2(2)=aceticData{i+4,3};

secondC2(3)=aceticData{i+4,4};
```

```
secondC2(4)=aceticData{i+4,5}

                                                found=1;


ParamsC1(1)=firstC1(3)+(((Ca-aceticData{i,2})/(aceticData{i+1,2}-
aceticData{i,2}))*(secondC1(3)-firstC1(3)));

ParamsC1(2)=firstC1(4)+(((Ca-aceticData{i,2})/(aceticData{i+1,2}-
aceticData{i,2}))*(secondC1(4)-firstC1(4)))


ParamsC2(1)=firstC2(3)+(((Ca-aceticData{i,2})/(aceticData{i+1,2}-
aceticData{i,2}))*(secondC2(3)-firstC2(3)));

ParamsC2(2)=firstC2(4)+(((Ca-aceticData{i,2})/(aceticData{i+1,2}-
aceticData{i,2}))*(secondC2(4)-firstC2(4)))


aceticParams(1)=ParamsC1(1)+(((TC-aceticData{i,3})/(aceticData{i+3,3}-
aceticData{i,3}))*(ParamsC2(1)-ParamsC1(1)));

aceticParams(2)=ParamsC1(2)+(((TC-aceticData{i,3})/(aceticData{i+3,3}-
aceticData{i,3}))*(ParamsC2(2)-ParamsC1(2)));
                                             end
                                            end
                    end
                elseif(Ca>4 && Ca<6)
                 for(i=3:3:9)
                 if (TC == aceticData{i,3})
                    disp('Interpolating 4 < Ca < 6 at constant T ');
                    first(1)=aceticData{i,2};
                    first(2)=aceticData{i,3};
                    first(3)=aceticData{i,4};
                    first(4)=aceticData{i,5}

                    second(1)=aceticData{i+1,2};
                    second(2)=aceticData{i+1,3};
                    second(3)=aceticData{i+1,4};
                    second(4)=aceticData{i+1,5}

                    found=1;
                    aceticParams(1)=aceticData{i,4}+(((Ca-
aceticData{i,2})/(aceticData{i+1,2}-aceticData{i,2}))*(aceticData{i+1,4}-
aceticData{i,4}));
                    aceticParams(2)=aceticData{i,5}+(((Ca-
aceticData{i,2})/(aceticData{i+1,2}-aceticData{i,2}))*(aceticData{i+1,5}-
aceticData{i,5}));
                end
            end
                        if(found==0)
                            disp('Interpolating both, 4 < Ca < 6');
                                        for(i=3:3:9)
                                           if (TC > aceticData{i,3} &&
TC < aceticData{i+3,3})
                                           firstC1(1)=aceticData{i,2};
                                           firstC1(2)=aceticData{i,3};
                                           firstC1(3)=aceticData{i,4};
                                           firstC1(4)=aceticData{i,5}
```

```
secondC1(1)=aceticData{i+1,2};

secondC1(2)=aceticData{i+1,3};

secondC1(3)=aceticData{i+1,4};

secondC1(4)=aceticData{i+1,5}


firstC2(1)=aceticData{i+3,2};

firstC2(2)=aceticData{i+3,3};

firstC2(3)=aceticData{i+3,4};
                                                    firstC2(4)=aceticData{i+3,5}


secondC2(1)=aceticData{i+4,2};

secondC2(2)=aceticData{i+4,3};

secondC2(3)=aceticData{i+4,4};

secondC2(4)=aceticData{i+4,5}

                                                    found=1;


ParamsC1(1)=firstC1(3)+(((Ca-aceticData{i,2})/(aceticData{i+1,2}-
aceticData{i,2}))*(secondC1(3)-firstC1(3)));

ParamsC1(2)=firstC1(4)+(((Ca-aceticData{i,2})/(aceticData{i+1,2}-
aceticData{i,2}))*(secondC1(4)-firstC1(4)))


ParamsC2(1)=firstC2(3)+(((Ca-aceticData{i,2})/(aceticData{i+1,2}-
aceticData{i,2}))*(secondC2(3)-firstC2(3)));

ParamsC2(2)=firstC2(4)+(((Ca-aceticData{i,2})/(aceticData{i+1,2}-
aceticData{i,2}))*(secondC2(4)-firstC2(4)))


aceticParams(1)=ParamsC1(1)+(((TC-aceticData{i,3})/(aceticData{i+3,3}-
aceticData{i,3}))*(ParamsC2(1)-ParamsC1(1)));

aceticParams(2)=ParamsC1(2)+(((TC-aceticData{i,3})/(aceticData{i+3,3}-
aceticData{i,3}))*(ParamsC2(2)-ParamsC1(2)));
                                                       end
                                                   end
                          end
        end
        end
     end
     end
aceticParams=aceticParams(:);
```

furfTableIntConcTemp

```
function [furfParams] = furfTableIntConcTemp (Ca,T)

furfData = {'','Ca','T','F0','k1';
           '2% at 100',2,100,0.74,0.0293;
           '4% at 100',4,100,1.28,0.0158;
           '6% at 100',6,100,1.80,0.0134;
           '2% at 122',2,122,2.96,0.0080;
           '4% at 122',4,122,4.14,0.0118;
           '6% at 122',6,122,4.51,0.0172;
           '2% at 128',2,128,3.63,0.0112;
           '4% at 128',4,128,4.86,0.0185;
           '6% at 128',6,128,5.59,0.0255;};%data from Aguilar paper

double TC;%temperature in degrees celcius
TC=T-273.15;
int row;
int col;
row=size(furfData,1);%number of rows in data
col=size(furfData,2);%number of columns in data

double alpha;
double k1;
double k2;

int found;%used to test if data has been found
found=0;%initialised to zero
first=[1 1 1 1];%arrays used to store current data for interpolation
second=[1 1 1 1];%arrays used to store current data for interpolation
ParamsC1=[1 1];
ParamsC2=[1 1];
furfParams=[1  1];

 for i=1:row
if (Ca == furfData{i,2})
    if (TC == furfData{i,3})
    disp(['Nothing to interpolate, Ca:',num2str(Ca),' T:',num2str(TC)]);
    found=1;
    furfData{i,:};
    furfParams(1)=furfData{i,4};
    furfParams(2)=furfData{i,5};
    i=row;
    end
end
 end

 if(found==0)
     %Something needs to be interpolated
     if(Ca == 2 || Ca == 4 || Ca == 6)
         %Ca is fine so interpolate T
     if(TC>128)
        disp(['T too high: T = ',  num2str(TC)]);
     elseif(TC<100)
     disp(['T too low: T = ',  num2str(TC)]);
     elseif(TC ~= 100 && TC ~= 122 && TC ~= 128)
     disp(['Time to interpolate, T = ',  num2str(TC)]);
        if(TC>100 && TC<122)
            for(i=2:4)
                if (Ca == furfData{i,2})
```

```
                    first(1)=furfData{i,2};
                    first(2)=furfData{i,3};
                    first(3)=furfData{i,4};
                    first(4)=furfData{i,5}

                    second(1)=furfData{i+3,2};
                    second(2)=furfData{i+3,3};
                    second(3)=furfData{i+3,4};
                    second(4)=furfData{i+3,5}

                    found=1;
                     disp(['Interpolating 100 < T < 122 at constant Ca =
',num2str(Ca)]);
                    furfParams(1)=furfData{i,4}+(((TC-
furfData{i,3})/(furfData{i+3,3}-furfData{i,3}))*(furfData{i+3,4}-
furfData{i,4}));
                    furfParams(2)=furfData{i,5}+(((TC-
furfData{i,3})/(furfData{i+3,3}-furfData{i,3}))*(furfData{i+3,5}-
furfData{i,5}));

                end
            end
        else
            for(i=5:7)
                if (Ca == furfData{i,2})
                    first(1)=furfData{i,2};
                    first(2)=furfData{i,3};
                    first(3)=furfData{i,4};
                    first(4)=furfData{i,5}

                    second(1)=furfData{i+3,2};
                    second(2)=furfData{i+3,3};
                    second(3)=furfData{i+3,4};
                    second(4)=furfData{i+3,5}
                    found=1;
                     disp(['Interpolating 122 < T < 128 at constant Ca
=',num2str(Ca)]);

                    furfParams(1)=furfData{i,4}+(((TC-
furfData{i,3})/(furfData{i+3,3}-furfData{i,3}))*(furfData{i+3,4}-
furfData{i,4}));
                    furfParams(2)=furfData{i,5}+(((TC-
furfData{i,3})/(furfData{i+3,3}-furfData{i,3}))*(furfData{i+3,5}-
furfData{i,5}));
                end
            end
        end
    end
    else
        %Ca is not fine so interpolate that
        if(Ca>6)
            disp(['Ca too high: Ca = ',  num2str(Ca)]);
        elseif(Ca<2)
            disp(['Ca too low: Ca = ',  num2str(Ca)]);
        elseif(Ca ~= 2 && Ca ~= 4 && Ca ~= 6)
            disp(['Time to interpolate, Ca = ',  num2str(Ca),' T = ',
num2str(TC)]);
              if(TC>128)
                disp(['T too high: T = ',  num2str(TC)]);
              elseif(TC<100)
```

```
                disp(['T too low: T = ',  num2str(TC)]);
              elseif(Ca>2 && Ca<4)
                for(i=2:3:8)
                if (TC == furfData{i,3})
                    disp('Interpolating 2 < Ca < 4 at constant T ');
                   first(1)=furfData{i,2};
                   first(2)=furfData{i,3};
                   first(3)=furfData{i,4};
                   first(4)=furfData{i,5}

                   second(1)=furfData{i+1,2};
                   second(2)=furfData{i+1,3};
                   second(3)=furfData{i+1,4};
                   second(4)=furfData{i+1,5}

                   found=1;
                   furfParams(1)=furfData{i,4}+(((Ca-
furfData{i,2})/(furfData{i+1,2}-furfData{i,2}))*(furfData{i+1,4}-
furfData{i,4}));
                   furfParams(2)=furfData{i,5}+(((Ca-
furfData{i,2})/(furfData{i+1,2}-furfData{i,2}))*(furfData{i+1,5}-
furfData{i,5}));
                end
                end
                    if(found==0)
                        disp('Interpolating both, 2 < Ca < 4');
                                        for(i=2:3:8)
                                          if (TC > furfData{i,3} && TC
< furfData{i+3,3})

                                          firstC1(1)=furfData{i,2};
                                          firstC1(2)=furfData{i,3};
                                          firstC1(3)=furfData{i,4};
                                          firstC1(4)=furfData{i,5}

                                          secondC1(1)=furfData{i+1,2};
                                          secondC1(2)=furfData{i+1,3};
                                          secondC1(3)=furfData{i+1,4};
                                          secondC1(4)=furfData{i+1,5}

                                          firstC2(1)=furfData{i+3,2};
                                          firstC2(2)=furfData{i+3,3};
                                          firstC2(3)=furfData{i+3,4};
                                          firstC2(4)=furfData{i+3,5}

                                          secondC2(1)=furfData{i+4,2};
                                          secondC2(2)=furfData{i+4,3};
                                          secondC2(3)=furfData{i+4,4};
                                          secondC2(4)=furfData{i+4,5}

                                          found=1;


ParamsC1(1)=firstC1(3)+(((Ca-furfData{i,2})/(furfData{i+1,2}-
furfData{i,2}))*(secondC1(3)-firstC1(3)));

ParamsC1(2)=firstC1(4)+(((Ca-furfData{i,2})/(furfData{i+1,2}-
furfData{i,2}))*(secondC1(4)-firstC1(4)))
```

```
ParamsC2(1)=firstC2(3)+(((Ca-furfData{i,2})/(furfData{i+1,2}-
furfData{i,2}))*(secondC2(3)-firstC2(3)));

ParamsC2(2)=firstC2(4)+(((Ca-furfData{i,2})/(furfData{i+1,2}-
furfData{i,2}))*(secondC2(4)-firstC2(4)))


furfParams(1)=ParamsC1(1)+(((TC-furfData{i,3})/(furfData{i+3,3}-
furfData{i,3}))*(ParamsC2(1)-ParamsC1(1)));

furfParams(2)=ParamsC1(2)+(((TC-furfData{i,3})/(furfData{i+3,3}-
furfData{i,3}))*(ParamsC2(2)-ParamsC1(2)));
                                              end
                                            end
                    end
                elseif(Ca>4 && Ca<6)
                 for(i=3:3:9)
                 if (TC == furfData{i,3})
                    disp('Interpolating 4 < Ca < 6 at constant T ');
                    first(1)=furfData{i,2};
                    first(2)=furfData{i,3};
                    first(3)=furfData{i,4};
                    first(4)=furfData{i,5}

                    second(1)=furfData{i+1,2};
                    second(2)=furfData{i+1,3};
                    second(3)=furfData{i+1,4};
                    second(4)=furfData{i+1,5}

                    found=1;
                    furfParams(1)=furfData{i,4}+(((Ca-
furfData{i,2})/(furfData{i+1,2}-furfData{i,2}))*(furfData{i+1,4}-
furfData{i,4}));
                    furfParams(2)=furfData{i,5}+(((Ca-
furfData{i,2})/(furfData{i+1,2}-furfData{i,2}))*(furfData{i+1,5}-
furfData{i,5}));
                 end
             end
                        if(found==0)
                            disp('Interpolating both, 4 < Ca < 6');
                                          for(i=3:3:9)
                                             if (TC > furfData{i,3} && TC
< furfData{i+3,3})

                                             firstC1(1)=furfData{i,2};
                                             firstC1(2)=furfData{i,3};
                                             firstC1(3)=furfData{i,4};
                                             firstC1(4)=furfData{i,5}

                                             secondC1(1)=furfData{i+1,2};
                                             secondC1(2)=furfData{i+1,3};
                                             secondC1(3)=furfData{i+1,4};
                                             secondC1(4)=furfData{i+1,5}

                                             firstC2(1)=furfData{i+3,2};
                                             firstC2(2)=furfData{i+3,3};
                                             firstC2(3)=furfData{i+3,4};
                                             firstC2(4)=furfData{i+3,5}
```

```
                                                secondC2(1)=furfData{i+4,2};
                                                secondC2(2)=furfData{i+4,3};
                                                secondC2(3)=furfData{i+4,4};
                                                secondC2(4)=furfData{i+4,5}

                                                found=1;


ParamsC1(1)=firstC1(3)+(((Ca-furfData{i,2})/(furfData{i+1,2}-
furfData{i,2}))*(secondC1(3)-firstC1(3)));

ParamsC1(2)=firstC1(4)+(((Ca-furfData{i,2})/(furfData{i+1,2}-
furfData{i,2}))*(secondC1(4)-firstC1(4)))


ParamsC2(1)=firstC2(3)+(((Ca-furfData{i,2})/(furfData{i+1,2}-
furfData{i,2}))*(secondC2(3)-firstC2(3)));

ParamsC2(2)=firstC2(4)+(((Ca-furfData{i,2})/(furfData{i+1,2}-
furfData{i,2}))*(secondC2(4)-firstC2(4)))


furfParams(1)=ParamsC1(1)+(((TC-furfData{i,3})/(furfData{i+3,3}-
furfData{i,3}))*(ParamsC2(1)-ParamsC1(1)));

furfParams(2)=ParamsC1(2)+(((TC-furfData{i,3})/(furfData{i+3,3}-
furfData{i,3}))*(ParamsC2(2)-ParamsC1(2)));
                                                   end
                                               end
                          end
        end
        end
     end
     end
furfParams=furfParams(:);
```

ASL for hemicellulose

This code was used to determine that acid soluble lignin concentration for each $P_{J,n}$ dataset. The methodology of this code is described in *Section 3.3.1* and the $P_{J,n}$ datasets can be found in *Appendix A.2.3.1.*

```
clc, clear all, close all

CL0=0.235;
Ca=2;%acid concentration in % w/w
T=122+273.15;%temperature
phi=0.1;

tao=0.01:0.5:25;%residence time
D=1./tao;
%parameters
R=8.3145;% J/mol.K

%parameters for bagasse
Ea1=85.2;% kJ·mol-1
Ea2=95.7;% kJ·mol-1
Ea3=64.4;% kJ·mol-1
A1=2.16*10^6;% s-1
A2=1.23*10^9;% s-1
A3=45400;% s-1
n=0.39;

k1r=A1.*(Ca.^n).*exp(-Ea1*1000./(R.*T)) % s^-1
k2r=A2.*(Ca.^n).*exp(-Ea2*1000./(R.*T)) % s^-1
k3r=A3.*(Ca.^n).*exp(-Ea3*1000./(R.*T)) % s^-1

for i=1: length(tao)
    CL(i)=CL0*(((k1r-phi*k3r)/(phi*k3r+phi*k2r-k1r))*exp(-k1r*tao(i)*60)-
((k3r/(k2r+k3r))+((k1r-phi*k3r)/(phi*k3r+phi*k2r-k1r)))*exp(-
phi*(k2r+k3r)*tao(i)*60)+(k3r/(k2r+k3r)));
end

%parameters for bagacillo
Ea12=77.2;% kJ·mol-1
Ea22=20.57;% kJ·mol-1
Ea32=73.4;% kJ·mol-1
A12=115.5*10^3;% s-1
A22=0.574;% s-1
A32=2.41*10^5;% s-1
n2=0.85;

k1r2=A12.*(Ca.^n2).*exp(-Ea12*1000./(R.*T)) % s^-1
k2r2=A22.*(Ca.^n2).*exp(-Ea22*1000./(R.*T)) % s^-1
k3r2=A32.*(Ca.^n2).*exp(-Ea32*1000./(R.*T)) % s^-1

for i=1: length(tao)
    CL2(i)=CL0*((k1r2-phi*k3r2)/(phi*k3r2+phi*k2r2-k1r2)*exp(-
k1r2*tao(i)*60)-(k3r2/(k2r2+k3r2)+(k1r2-phi*k3r2)/(phi*k3r2+phi*k2r2-
k1r2))*exp(-phi*(k2r2+k3r2)*tao(i)*60)+k3r2/(k2r2+k3r2));
end

CL;

figure1 = figure('Color',[1 1 1]);
```

```
plot(tao(:),[CL*1000;CL2*1000],'LineWidth',2)
title('CSTR',...
    'FontWeight','bold',...
    'FontSize',16,...
    'FontName','Calibri');
xlabel('Tau [min]','FontWeight','bold','FontSize',12,'FontName','Calibri');
ylabel('C [mg/g
solid]','FontWeight','bold','FontSize',12,'FontName','Calibri');
legend('Bagasse','Bagacillo')
grid on
```

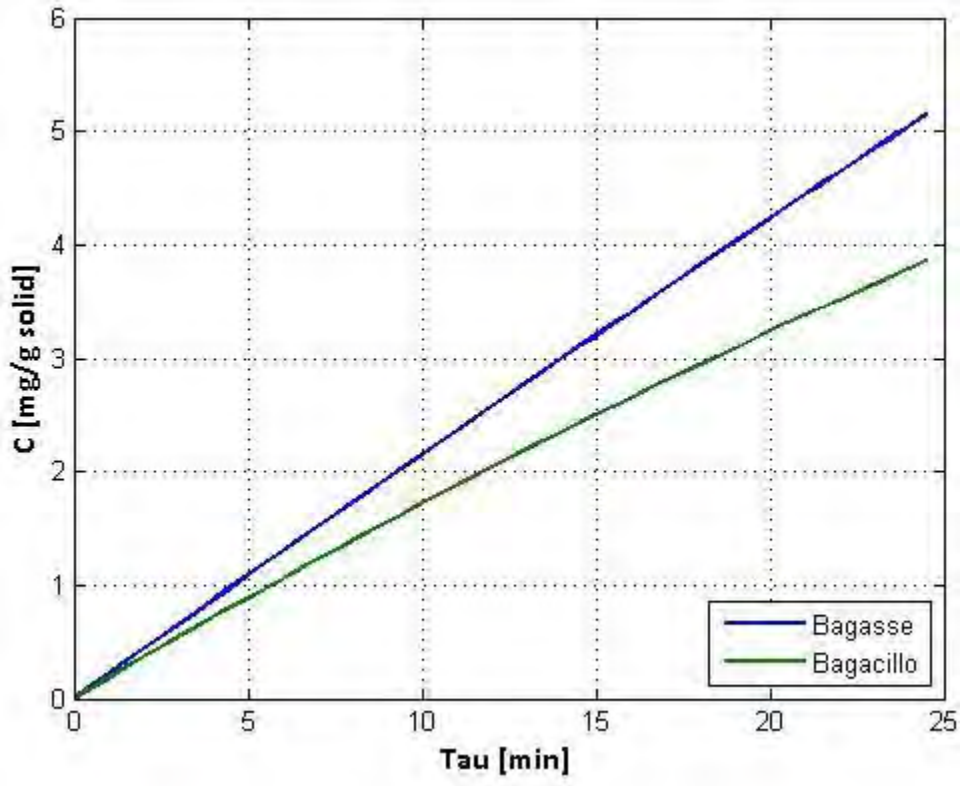


Figure A.2.3: Example of graph from Matlab code describing lignin solubilisation in acid

A.2.3 Data Used in GAMS Models

The Matlab code shown in the previous section, *Appendix A.2.2*, was used to generate the $P_{J,n}$ datasets used in the GAMS models which are shown in *Appendix A.2.3.1*. The datasets describing the fraction of each component vapourised in the acid pre-hydrolysis flash, $X_{PreHydVap,L(J),n}$, are shown in *Appendix A.2.3.2.*

A.2.3.1 $P_{J,n}$ tables

These tables show the P datasets. These describe the reactor operation using either conversions or concentrations and the residence time, temperature and acid concentration used. *Section 3.3.1* in the main report explains the methodology used to obtain these datasets.

Table A.2.5: $P_{J,n}$ datasets for acid pre-hydrolysis reactions at 100°C

Dataset		$P_{J,1}$	$P_{J,2}$	$P_{J,3}$	$P_{J,10}$
Temperature	[°C]	**100**			
Acid Weight	[%]	2	4	6	
Residence Time	[min]	11.01	10.01	12.01	28.01
Hemicellulose Conversion	[-]	0.13047009	0.13382479	0.43494872	0.39082479
Xylose Concentration	[kg.m^{-3}]	3.053	3.1315	10.1778	15.0286
Furfural Concentration	[kg.m^{-3}]	0.1805	0.1748	0.2495	0.4912
Cellulose Conversion	[-]	0.00519213	0.00871296	0.00398148	0.00331944
Glucose Concentration	[kg.m^{-3}]	0.2243	0.3764	0.172	0.399
HMF Concentration	[kg.m^{-3}]	0	0	0	0
Acetyl Conversion	[-]	0.28159091	0.26920765	0.45672823	0.66224274
Acetic Concentration	[kg.m^{-3}]	0.7434	0.9853	1.731	2.5099
ASL Concentration	[kg/kg solids]	0.0005	0.00062	0.00082	0.002

Table A.2.6: $P_{J,n}$ datasets for acid pre-hydrolysis reactions at 122°C

Dataset		$P_{J,4}$	$P_{J,13}$	$P_{J,5}$	$P_{J,6}$	$P_{J,11}$
Temperature	[°C]	**122**				
Acid Weight	[%]	2		4	6	
Residence Time	[min]	10.51	24.01	10.51	10.51	16.51
Hemicellulose Conversion	[-]	0.65842735	0.81494017	0.62382051	0.69010684	0.777688034
Xylose Concentration	[kg.m^{-3}]	15.0745	18.1543	14.1081	15.497	17.0706
Furfural Concentration	[kg.m^{-3}]	0.2296	0.4769	0.4568	0.6905	0.9975
Cellulose Conversion	[-]	0.04342824	0.09396991	0.11441898	0.12414352	0.182108796
Glucose Concentration	[kg.m^{-3}]	1.8704	4.0314	4.9212	5.363	7.8671
HMF Concentration	[kg.m^{-3}]	0.0057	0.0281	0.0217	0	0
Acetyl Conversion	[-]	0.94216438	0.97383562	0.90571429	0.89942605	0.933554084
Acetic Concentration	[kg.m^{-3}]	3.4389	3.5545	3.6772	4.0744	4.229
ASL Concentration	[kg/kg solids]	0.00225	0.005	0.0028	0.0034	0.0052

Table A.2.7: $P_{J,n}$ datasets for acid pre-hydrolysis reactions at 128°C

Dataset		$\boldsymbol{P_{J,7}}$	$\boldsymbol{P_{J,8}}$	$\boldsymbol{P_{J,9}}$	$\boldsymbol{P_{J,12}}$
Temperature	[°C]	**128**			
Acid Weight	[%]	2	4	6	
Residence Time	[min]	10.01	11.01	5.01	11.01
Hemicellulose Conversion	[-]	0.61624359	0.75697863	0.73982906	0.86205556
Xylose Concentration	[kg.m^{-3}]	13.9997	17.038	16.5731	18.3718
Furfural Concentration	[kg.m^{-3}]	0.3659	0.8224	0.6332	1.2254
Cellulose Conversion	[-]	0.02265509	0.02796991	0.01508333	0.03255787
Glucose Concentration	[kg.m^{-3}]	0.9066	1.1395	0.6327	1.3198
HMF Concentration	[kg.m^{-3}]	0.0721	0.0689	0.0189	0.0867
Acetyl Conversion	[-]	0.37483146	0.356875	0.19125731	0.34195906
Acetic Concentration	[kg.m^{-3}]	1.0008	1.0278	0.6541	1.1695
ASL Concentration	[kg/kg solids]	0.0032	0.0043	0.0025	0.0053

A.2.3.2 $\boldsymbol{X_{PreHydVap,L(J),n}}$ Tables

The datasets for $X_{PreHydVap,L(J),n}$ which are used to describe the fraction of each component vapourised in the acid pre-hydrolysis flash are in the following tables. *Section 3.3.2.3* describes the methodology used to generate these tables.

Table A.2.8: $X_{PreHydVap,L(J),n}$ datasets for acid pre-hydrolysis flash unit at 100°C

Dataset		$\boldsymbol{P_{J,1}}$	$\boldsymbol{P_{J,2}}$	$\boldsymbol{P_{J,3}, P_{J,10}}$
Temperature	[°C]	**100**		
Acid Weight	[%]	2	4	6
Xylose	[-]	0.000318156	0.000116906	7.60585E-05
Furfural	[-]	0.984210078	0.968070089	0.951692378
Glucose	[-]	0.001500944	0.000565986	0.000368289
HMF	[-]	0.037156169	0.014185910	0.009274925
Acetic Acid	[-]	0.855752323	0.693091341	0.595434086
Sulphuric Acid	[-]	0.003045513	0.001119059	0.000728312
Water	[-]	0.963967543	0.910871575	0.869263457
Phos	[-]	0.000452111	0.000166989	0.000108652

Table A.2.9: $X_{PreHydVap,L(J),n}$ datasets for acid pre-hydrolysis flash unit at 122°C

Dataset		$\boldsymbol{P_{J,4}, P_{J,13}}$	$\boldsymbol{P_{J,5}}$	$\boldsymbol{P_{J,6}, P_{J,11}}$
Temperature	[°C]		**122**	
Acid Weight	[%]	2	4	6
Xylose	[-]	0.003471174	0.002089916	0.001465735
Furfural	[-]	0.981789179	0.970062703	0.957809518
Glucose	[-]	0.010989372	0.006636526	0.004660846
HMF	[-]	0.246375324	0.164268499	0.121084842
Acetic Acid	[-]	0.972835811	0.955639245	0.937929065
Sulphuric Acid	[-]	0.033375256	0.020337343	0.014341654
Water	[-]	0.993346333	0.988983585	0.984359150
Phos	[-]	0.004516156	0.002720877	0.001908864

Table A.2.10: $X_{PreHydVap,L(J),n}$ datasets for acid pre-hydrolysis flash unit at 128°C

Dataset	[-]	$\boldsymbol{P_{J,7}}$	$\boldsymbol{P_{J,8}}$	$\boldsymbol{P_{J,9}}$	$\boldsymbol{P_{J,12}}$
Temperature	[°C]		**128**		
Acid Weight	[%]	2	4	6	
Xylose	[-]	0.006291684	0.003649760	0.002624165	0.002564924
Furfural	[-]	0.984454929	0.973423078	0.963386637	0.962552795
Glucose	[-]	0.017825332	0.010391256	0.007485521	0.007317467
HMF	[-]	0.354133922	0.240827554	0.185566505	0.182131586
Acetic Acid	[-]	0.981719911	0.968820900	0.957094178	0.956173758
Sulphuric Acid	[-]	0.059673068	0.035414763	0.025693255	0.025126324
Water	[-]	0.995461567	0.992183614	0.989149539	0.988905059
Phos	[-]	0.007947698	0.004614897	0.003319166	0.003244738

A.3 Acid Hydrolysis

This appendix relates to the acid hydrolysis model discussed in *Section 3.5* of the main report. The first section, *Appendix A.3.1*, describes how the Arrhenius parameters used in the acid hydrolysis model were derived. The details of how the linear equations used in the acid hydrolysis flash were derived are shown in *Appendix A.3.2.*

A.3.1 Determination of Arrhenius Parameters

In Gurgel & Marabezi (2012) the Eyring equation was used to describe the change in the kinetic parameters, k, with temperature. However, when these parameters were used, large errors (sometimes as large as 97%) occurred in the k values calculated. As a result of this, an Arrhenius relationship was derived for use in the GAMS models. This section describes how that relationship was derived.

There were two sets of k values in Gurgel & Marabezi (2012), observed and calculated k values. The calculated k values in Gurgel & Marabezi (2012) were used in this analysis as more data was available. These values are shown below in *Table A.3.1*.

Table A.3.1: Calculated kinetic parameters (Gurgel & Marabezi, 2012) and determined Arrhenius constants

Acid weight [%]	k_i [min^{-1}]	Temperature [°C]			E_i [J]	A_i [min^{-1}]	R^2 [-]
		190	200	210			
0.07	$\boldsymbol{k_1}$	0.0065	0.0189	0.0396	168284	6.51E+16	0.9915
	$\boldsymbol{k_2}$	0.0229	0.0418	0.0717	106195	2.17E+10	0.9996
0.14	$\boldsymbol{k_1}$	0.0143	0.0342	0.0954	176415	1.09E+18	0.9965
	$\boldsymbol{k_2}$	0.0322	0.0509	0.0927	98255	3.78E+09	0.9920
0.28	$\boldsymbol{k_1}$	0.0291	0.0808	0.2033	180863	7.36E+18	0.9997
	$\boldsymbol{k_2}$	0.0423	0.0757	0.1330	106561	4.41E+10	1.0000

$\boldsymbol{k_i}$values are for the calculated $\boldsymbol{k_i}$ values in Gurgel & Marabezi (2012) where $\boldsymbol{k_1}$ was in *Table 2* and $\boldsymbol{k_2}$ was in *Table 5*.

The Arrhenius Equation can be rearranged as shown below so that a graph of $\ln k_i$ versus $\frac{1}{T}$, *Figure A.3.1* below, can be used to determine the activation energy (E_i) and pre-exponential factor (A_i). This graph was plotted for each given acid weight percent (0.07, 0.14 and 0.28%). The values determined for activation energy and pre-exponential factor are shown in *Table A.3.1* above.

The Arrhenius Equation:

$$k_i = A_i\, e^{-E_i/RT}$$

Linearised Arrhenius Equation:

$\ln k_i = \ln A_i - \frac{E_i}{R}\frac{1}{T}$ Intercept of $\ln A_i$ and slope of $\frac{E_i}{R}$.

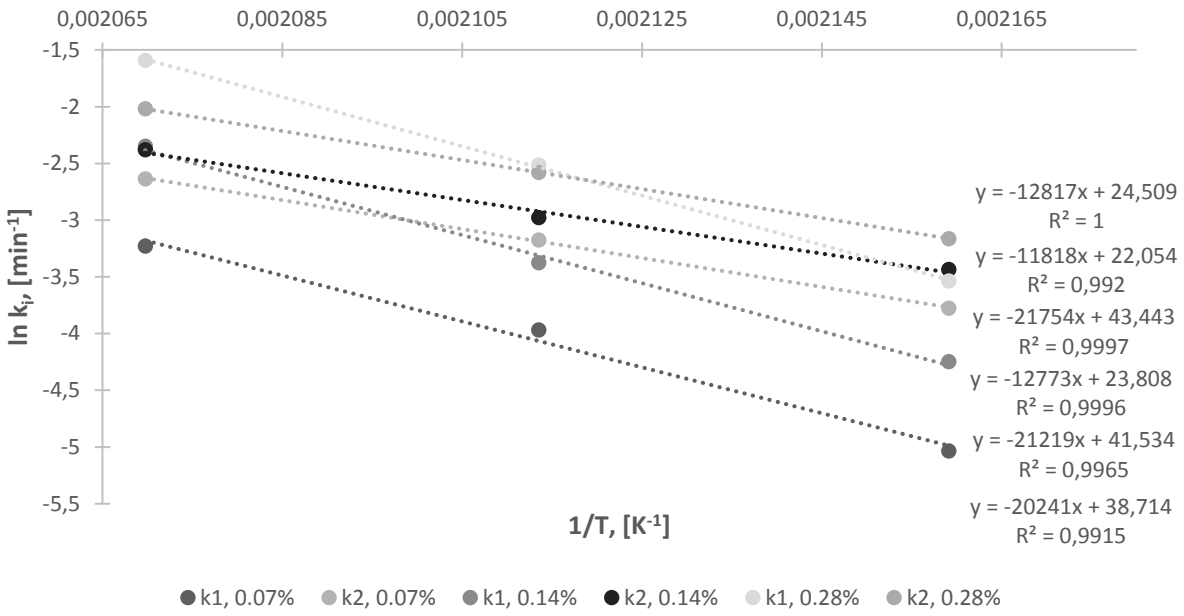


Figure A.3.1: Arrhenius relationship for acid cellulose hydrolysis derived using Gurgel & Marabezi (2012)

The R^2 values in *Table A.3.1* were greater than 0.9915 which implies that the model is a good fit. Further confirmation of this is shown in *Table A.3.2* below. The calculated activation energy and pre-exponential factor, shown in *Table A.3.3*, values were used to calculate k_1 and k_2 and the average absolute error was 2.78% and the maximum error was 9.21%

Table A.3.2: Error in the $\boldsymbol{k_i}$ values calculated using the derived Arrhenius parameters

Acid weight [%]	$\boldsymbol{k_i}$ [min^{-1}]	**Temperature** [°C]			**Error in $\boldsymbol{k_i}$** [%]		
		190	**200**	**210**			
0.07	$\boldsymbol{k_1}$	0.006813	0.017159	0.041593	4.82	-9.21	5.03
	$\boldsymbol{k_2}$	0.023040	0.041268	0.072156	0.61	-1.27	0.64
0.14	$\boldsymbol{k_1}$	0.013835	0.036434	0.092178	-3.25	6.53	-3.38
	$\boldsymbol{k_2}$	0.031349	0.053757	0.090147	-2.64	5.61	-2.75
0.28	$\boldsymbol{k_1}$	0.029403	0.079344	0.205491	1.04	-1.80	1.08
	$\boldsymbol{k_2}$	0.042234	0.075800	0.132789	-0.16	0.13	-0.16

Table A.3.3: Arrhenius parameters, H, used in GAMS model

Acid weight [%]	$\boldsymbol{k_i}$ [min^{-1}]	$\boldsymbol{A_i}$ [min^{-1}]	**A exponent** [-]	$\boldsymbol{E_i}$ [J]
0.07	$\boldsymbol{k_1}$	6.50544	16	168284
	$\boldsymbol{k_2}$	2.18617	10	106195
0.14	$\boldsymbol{k_1}$	1.09141	18	176415
	$\boldsymbol{k_2}$	3.78382	9	98255
0.28	$\boldsymbol{k_1}$	7.36301	18	180863
	$\boldsymbol{k_2}$	4.40680	10	106561

A.3.2 Determination of Flash Fraction Vapourised

An Aspen model was developed using the database used in CTBE's models (Bonomi et al., 2011) for the flash after the acid hydrolysis reactor. The inputs to this flash were taken from GAMS models of the acid hydrolysis reactor. The full details of the methodology used can be found in *Section 3.5.5.4* of the main report. This analysis was done for each acid weight percent used and a range of temperatures.

0.07 weight % acid

Table A.3.4 below shows the fraction vapourised, $X_{CellHydVap,L(J),c_A,T}$, of each component in the flash for 0.07 wt% acid at a range of temperatures. This data was used to plot the graph, *Figure A.3.2* on the following page, from which the linear parameters were determined and are shown in *Table A.3.4.* The same analysis was repeated for an acid weight percent of 0.14 and 0.28 and the tables are shown later.

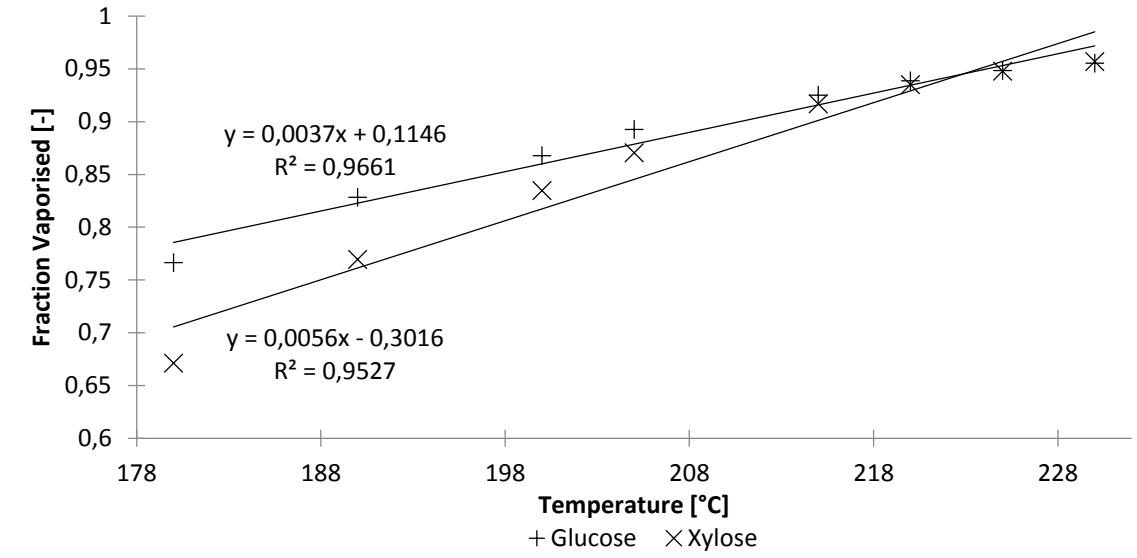
Table A.3.4: Fraction vapourised, $X_{CellHydVap,L(J),c_A,T}$, from Aspen simulation for acid 0.07 weight percent acid

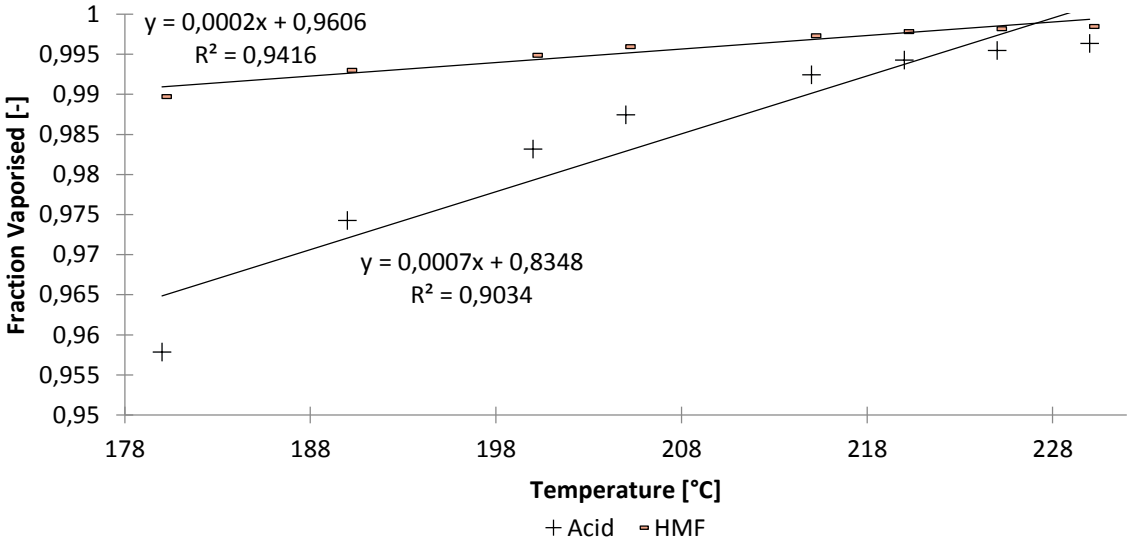
Component	Temperature [°C]							
	180	**190**	**200**	**205**	**215**	**220**	**225**	**230**
Xylose	0.6712	0.7695	0.8346	0.8706	0.917	0.9351	0.9479	0.957
Furfural	0.9996	0.9997	0.9997	0.9997	0.9998	0.9998	0.9998	0.9999
Glucose	0.7664	0.8283	0.8679	0.8927	0.9251	0.9387	0.9485	0.9554
HMF	0.9897	0.993	0.9949	0.996	0.9973	0.9978	0.9982	0.9985
Sulphuric Acid	0.9579	0.9743	0.9832	0.9875	0.9925	0.9943	0.9955	0.9963
Water	0.99993	0.99994	0.99995	0.99996	0.99997	0.99997	0.99997	0.99998
Minerals	2.23×10^{-76}	2.22×10^{-76}	2.09×10^{-76}	2.21×10^{-76}	2.31×10^{-76}	2.43×10^{-76}	2.48×10^{-76}	2.46×10^{-76}
Salts	2.39×10^{-76}	2.36×10^{-76}	2.20×10^{-76}	2.32×10^{-76}	2.42×10^{-76}	2.54×10^{-76}	2.59×10^{-76}	2.56×10^{-76}

Table A.3.5: Linear parameters, Fls, for determining fraction vapourised, $X_{CellHydVap,L(J),c_A,T}$, in GAMS (0.07 weight % acid)

Component	Parameter		R^2
	Fls_m	Fls_c	
Xylose	0.0056	- 0.3016	0.9527
Furfural	0.000006	0.9986	0.9881
Glucose	0.0037	0.1146	0.9661
HMF	0.0002	0.9606	0.9416
Sulphuric Acid	0.0007	0.8348	0.9034
Water	0.000001	0.9998	0.9851

Only the relationships for xylose, glucose and sulphuric acid were used in the GAMS models. Other components had constant values which can be seen in *Table A.3.10.* Xylose and glucose oligomers were assumed to vapourise in the same way as xylose and glucose and used the same relationship.





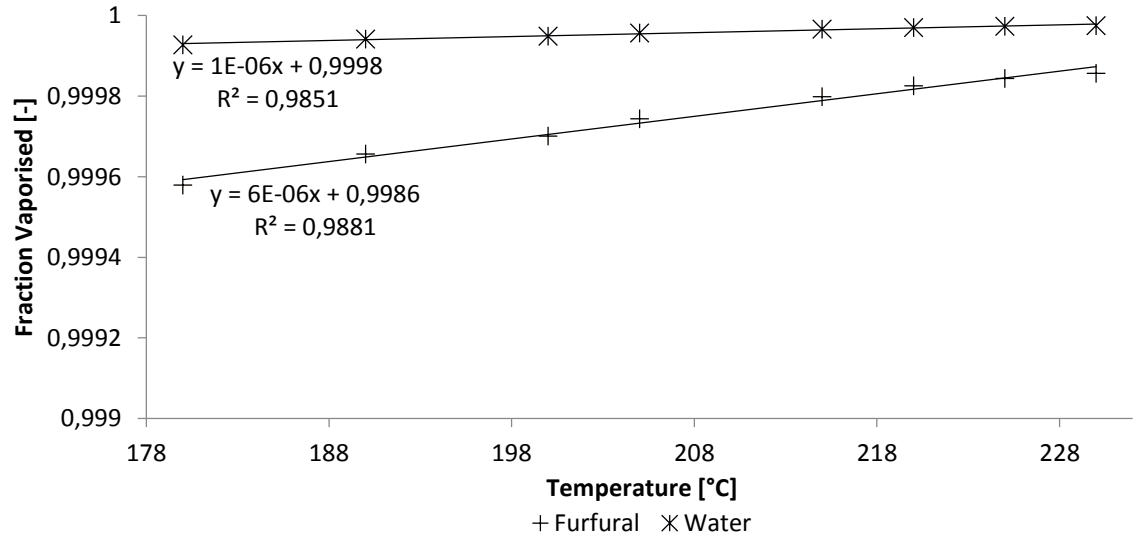


Figure A.3.2: Linear relationships for the fraction of each component vaporised in the acid hydrolysis flash with temperature for 0.07 wt% acid

0.14 weight % acid

Table A.3.6: Fraction vapourised, $X_{CellHydVap,L(J),c_A,T}$, from Aspen simulation (0.14 weight % acid)

Component	Temperature [°C]					
	180	**190**	**205**	**220**	**225**	**230**
Xylose	0.6133	0.7278	0.8443	0.8767	0.9465	0.9561
Furfural	0.9995	0.9996	0.9997	0.9996	0.9998	0.9999
Glucose	0.7183	0.7945	0.8703	0.8834	0.9471	0.9545
HMF	0.9868	0.9913	0.995	0.9956	0.9982	0.9984
Sulphuric Acid	0.9464	0.9681	0.9845	0.9885	0.9954	0.9963
Water	0.99991	0.99993	0.99995	0.99994	0.99997	0.99997
Minerals	1.74×10^{-76}	1.78×10^{-76}	1.78×10^{-76}	1.21×10^{-76}	2.41×10^{-76}	2.41×10^{-76}
Salts	1.86×10^{-76}	1.89×10^{-76}	1.87×10^{-76}	1.26×10^{-76}	2.51×10^{-76}	2.51×10^{-76}

Table A.3.7: Linear parameters, Fls, for determining fraction vapourised, $X_{CellHydVap,L(J),c_A,T}$, in GAMS (0.14 weight % acid)

Component	Parameter		R^2
	Fls_m	Fls_c	
Xylose	0.0065	- 0.5236	0.9582
Furfural	0.000007	0.9982	0.8551
Glucose	0.0044	- 0.0563	0.9493
HMF	0.0002	0.9497	0.9339
Sulphuric Acid	0.0009	0.7891	0.9158
Water	0.000001	0.9997	0.8574

0.28 weight % acid

Table A.3.8: Fraction vapourised, $X_{CellHydVap,L(J),c_A,T}$, from Aspen simulation for acid 0.28 weight percent acid

Component	Temperature [°C]						
	180	**190**	**200**	**205**	**215**	**225**	**230**
Xylose	0.6606	0.7714	0.7903	0.8272	0.8687	0.9438	0.9547
Furfural	0.9996	0.9997	0.9996	0.9996	0.9997	0.9998	0.9998
Glucose	0.7578	0.8299	0.8308	0.8556	0.881	0.9444	0.953
HMF	0.9892	0.9931	0.9932	0.9943	0.9955	0.9981	0.9984
Sulphuric Acid	0.9559	0.9746	0.9776	0.9824	0.9875	0.9951	0.9961
Water	0.99992	0.99994	0.99993	0.99994	0.99994	0.99997	0.99997
Minerals	2.13×10^{-76}	2.25×10^{-76}	1.56×10^{-76}	1.58×10^{-76}	1.40×10^{-76}	2.29×10^{-76}	2.33×10^{-76}
Salts	2.28×10^{-76}	2.39×10^{-76}	1.65×10^{-76}	1.65×10^{-76}	1.46×10^{-76}	2.39×10^{-76}	2.43×10^{-76}

Table A.3.9: Linear parameters, Fls, for determining fraction vapourised, $X_{CellHydVap,L(J),c_A,T}$, in GAMS (0.28 weight % acid)

Component	Parameter		R^2
	Fls_m	Fls_c	
Xylose	0.0056	- 0.3210	0.9710
Furfural	0.000005	0.9986	0.7817
Glucose	0.0037	0.1025	0.9564
HMF	0.0002	0.9595	0.9510
Sulphuric Acid	0.0007	0.8292	0.9339
Water	0.0000009	0.9998	0.7917

Table A.3.10: Constant fraction vapourised, $X_{CellHydVap,L(J),c_A,T}$, used in GAMS

Component	$X_{CellHydVap,L(J),c_A,T}$
Water	0.9999
Furfural	0.999
HMF	0.99
Sucrose	0
Balance	0
Minerals	0
Salts	0
Acetic Acid	0.98
Organic Acid	0
Phosphoric Acid	0
Acid Soluble Lignin	0
Sodium Hydroxide	0

A.4 Enzymatic Hydrolysis

The removal of lignin by delignification effects the conversion in the enzymatic hydrolysis reactor. *Appendix A.4.1* explains how this relationship was derived so that this effect could be included in the GAMS model which is described in *Section 3.6.2*.

A.4.1 Effects of Delignification on Glucose Conversion

The total hydrolysis yield (*HY*) was read from the graph (Figure 11 in Rezende et al., (2011)) and is shown in *Table A.4.1*. The equation below relates the *HY* to the released glucose concentration (*RG*):

$$HY = \frac{RG}{25.C(1.1)}.100$$

Where: HY is the total hydrolysis yield [%], RG is the concentration of released glucose [g/l], C is the cellulose mass percentage in bagasse [%] and 25 is the biomass concentration and 1.1 is a correction factor related to the addition of water during hydrolysis (Rezende et al., 2011).

The above equation can be rearranged in terms of released glucose as shown below:

$$RG = \frac{HY.25(35.2)(1.1)}{100}$$

Where: 35.2 is the cellulose mass percentage in sugarcane bagasse.

The released glucose was calculated and this was used to calculate the percentage increase in glucose yield using the following equation:

$$RG\ increase = \frac{RG - RG_{UntreatedSCB}}{RG_{UntreatedSCB}}.100$$

A graph of the increase in RG versus the percentage of lignin removed was plotted for a residence time of 72 hours and is shown in *Figure A.4.1* on the following page. The data used in this analysis is shown in *Table A.4.1below*.

Table A.4.1: Data used to derive the relationship between lignin removed and increase in released glucose for enzymatic hydrolysis

NaOH [%]	Total HY [%]	RG [g/l]	Lignin removed [%]	RG increase [%]
Untreated bagasse	19	1.839	0	0
0.25	39	3.775	25	105
0.5	57	5.518	39	200
1	66	6.389	69	247

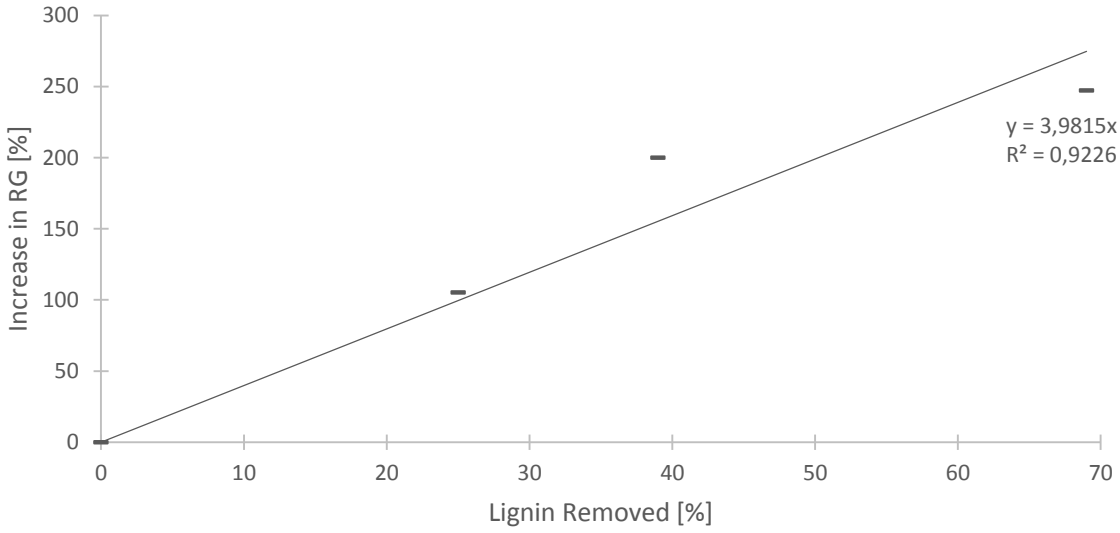


Figure A.4.1: Increase in released glucose with change in lignin removed

The R^2 value of the curve is low (0.9226) however the relationship was used as there was nothing better available. The equation of the straight line in *Figure A.4.1* was used to scale the conversions from the Aspen simulation of CTBE depending on the amount of lignin removed. The equations describing this are found in *Section 3.6.2* but are repeated below:

$$Y_{Inc,EnzHyd} = \frac{162}{180}(3.9815)\left(\frac{f_{Lignin,SrcBag,MixPre} - f_{Lignin,MixEnzHyd,EnzHyd}}{f_{Lignin,SrcBag,MixPre}}.100 - 10\right)$$

Where: $MixPre$ is the pre-hydrolysis mixer unit ($MixPreHyd$ or $MixSteamEx$), $Y_{Inc,EnzHyd}$ is the change in the percentage change in the conversion, $\frac{162}{180}$ is the molar mass ratio of cellulose over glucose, 3.9815 is the gradient of the curve in *Figure A.4.1*. The bracketed term subtracts 10 in order to account for the fact that the conversions used, $X_{EnzHyd,r}$, are based on a case where 10% of the lignin was removed in steam explosion prior to the enzymatic hydrolysis.

The conversions of reaction 1 and 2 are modified using $Y_{Inc,EnzHyd}$ in the following way:

$$newX_{EnzHyd,1} = X_{EnzHyd,1} + X_{EnzHyd,1}\frac{Y_{Inc,EnzHyd}}{100}$$

$$newX_{EnzHyd,2} = X_{EnzHyd,2} + X_{EnzHyd,2}\frac{Y_{Inc,EnzHyd}}{100}$$

A.5 Environmental Impact Data

This section provides data and more information for the environmental impact methodology in *Section 3.8* of the main report. *Appendix A.5.1* includes data that was generated using SimaPro which was used to calculate the environmental impact of each component in the GAMS models as well as the data used for the system expansion. The weighting factors used in the GAMS models are shown in *Appendix A.5.2.* The method used to determine the environmental impact of enzymes using the work of Harding (2008) is described in *Appendix A.5.3.*

A.5.1 Data from SimaPro

The following tables show the data generated using SimaPro for the environmental impacts of the components. Details of the system expansion and the comparison of combustion of ethanol and octane are also included.

Inputs

Table A.5.1: Normalised environmental impacts for input components used in GAMS models

Impact Category *c*	**Component, *e*** [Normalised EI/ton of component]				
	H_2SO_4	**NaOH**	**Enzyme**	**Bagasse**	**Water**
Global warming (GWP 100)	1.43E-05	1.26E-04	6.59E-03	-2.03E-04	7.51E-07
Ozone depletion	1.21E-07	6.59E-07	2.16E-06	1.42E-08	6.22E-09
Acidification	1.82E-04	6.82E-05	7.42E-03	2.29E-06	2.57E-07
Eutrophication	2.88E-05	3.22E-04	3.34E-03	4.44E-06	1.67E-07
Photochemical smog	1.31E-06	5.32E-06	1.20E-04	1.57E-05	2.11E-08
Ecotoxicity water chronic	1.37E-03	1.37E-02	7.35E-02	4.05E-05	7.22E-07
Ecotoxicity water acute	1.67E-03	1.65E-02	8.91E-02	6.31E-05	8.51E-07
Ecotoxicity soil chronic	9.54E-06	3.09E-05	7.37E-05	2.41E-06	2.15E-08
Human toxicity air	2.35E-05	6.86E-05	1.39E-03	7.18E-06	1.31E-07
Human toxicity water	1.57E-04	2.49E-03	1.53E-02	6.73E-06	4.19E-07
Human toxicity soil	3.04E-04	1.86E-03	1.54E-02	1.22E-03	8.35E-07
Bulk waste	2.85E-05	1.05E-04	5.41E-03	3.29E-06	1.18E-05
Hazardous waste	2.28E-07	5.62E-06	2.99E-06	1.08E-08	0
Radioactive waste	1.23E-04	3.30E-03	1.31E-02	4.20E-06	2.58E-06
Slags/ashes	1.54E-07	5.85E-07	1.21E-06	1.87E-07	3.47E-09
Resources (all)	0	0	0	0	0

Table A.5.2: Normalised environmental impacts for steam used in GAMS models

Impact Category ***c***	**Component, *e*** [Normalised EI/ton of component] **Steam Pressure** [barg]						
	LPS	**CTBE1**	**MPS1**	**CTBE2**	**MPS2**	**HPS1**	**HPS2**
	3	**5**	**10**	**11**	**46**	**85**	**186**
Global warming (GWP 100)	3.71E-13	3.79E-13	3.87E-13	4.04E-13	4.07E-13	4.86E-13	5.75E-13
Ozone depletion	4.00E-15	4.09E-15	4.18E-15	4.36E-15	4.39E-15	5.24E-15	6.20E-15
Acidification	6.44E-13	6.58E-13	6.73E-13	7.02E-13	7.07E-13	8.45E-13	1.00E-12
Eutrophication	1.25E-12	1.28E-12	1.30E-12	1.36E-12	1.37E-12	1.64E-12	1.94E-12
Photochemical smog	4.41E-12	4.51E-12	4.62E-12	4.81E-12	4.85E-12	5.79E-12	6.86E-12
Ecotoxicity water chronic	1.14E-11	1.17E-11	1.19E-11	1.24E-11	1.25E-11	1.50E-11	1.77E-11
Ecotoxicity water acute	1.78E-11	1.82E-11	1.86E-11	1.94E-11	1.95E-11	2.33E-11	2.76E-11
Ecotoxicity soil chronic	6.78E-13	6.93E-13	7.09E-13	7.39E-13	7.45E-13	8.90E-13	1.05E-12
Human toxicity air	2.02E-12	2.06E-12	2.11E-12	2.20E-12	2.22E-12	2.65E-12	3.13E-12
Human toxicity water	1.89E-12	1.94E-12	1.98E-12	2.07E-12	2.08E-12	2.49E-12	2.94E-12
Human toxicity soil	3.43E-10	3.51E-10	3.59E-10	3.74E-10	3.77E-10	4.50E-10	5.32E-10
Bulk waste	9.26E-13	9.46E-13	9.68E-13	1.01E-12	1.02E-12	1.21E-12	1.44E-12
Hazardous waste	3.04E-15	3.11E-15	3.18E-15	3.32E-15	3.34E-15	3.99E-15	4.72E-15
Radioactive waste	1.18E-12	1.21E-12	1.24E-12	1.29E-12	1.30E-12	1.55E-12	1.83E-12
Slags/ashes	5.26E-14	5.38E-14	5.50E-14	5.74E-14	5.78E-14	6.90E-14	8.17E-14
Resources (all)	0	0	0	0	0	0	0

Outputs

Table A.5.3: Normalised environmental impacts for output components used in GAMS models

Impact Category ***c***	**Component, *e*** [Normalised EI/ton of component]			
	Methane	**Flash Gas**		
		Acetic acid	**Sulphuric Acid**	**Furfural**
Global warming (GWP 100)	2.34E-04	4.09E-02	1.78E-02	0
Ozone depletion	6.58E-07	2.53E-04	0	0
Acidification	7.10E-05	0	0	0
Eutrophication	1.06E-04	0	1.76E-02	0
Photochemical smog	2.34E-05	0	0	0
Ecotoxicity water chronic	5.66E-03	2.08E-02	0	0
Ecotoxicity water acute	6.88E-03	2.73E-04	0	0
Ecotoxicity soil chronic	2.22E-05	0	0	0
Human toxicity air	3.36E-04	8.22E-04	0	0
Human toxicity water	5.54E-04	3.60E-03	2.34E-04	0
Human toxicity soil	2.59E-03	8.24E-04	0	0
Bulk waste	1.38E-04	1.51E-02	0	0
Hazardous waste	8.96E-07	0	0	0
Radioactive waste	3.34E-03	0	0	0
Slags/ashes	1.71E-05	0	0	0
Resources (all)	0	0	0	0

System Expansion

A system expansion was performed to reduce the environmental impacts of ethanol and methane product from sugarcane bagasse by the amount of environmental impact that would be produced by fossil fuel alternatives. The system expansion methodology is explained in *Section 3.8.1.* The environmental impacts for methane and ethanol as a result of the system expansion are shown in *Table A.5.4* below.

Table A.5.4: Normalised environmental impacts for system expansion used in GAMS models

Impact Category *c*	**Component, *e*** [Normalised EI/ton of component]	
	Methane	**Ethanol**
Global warming (GWP 100)	-1.33E-06	-2.69E-04
Ozone depletion	-5.25E-08	-6.02E-06
Acidification	-1.43E-06	-2.52E-04
Eutrophication	-1.72E-06	-1.26E-04
Photochemical smog	-3.94E-07	-5.86E-05
Ecotoxicity water chronic	-1.13E-04	-7.78E-03
Ecotoxicity water acute	-1.81E-04	-9.41E-03
Ecotoxicity soil chronic	-7.42E-08	-5.74E-06
Human toxicity air	-9.01E-07	-6.50E-04
Human toxicity water	-1.63E-05	-6.46E-04
Human toxicity soil	-1.79E-05	-6.06E-03
Bulk waste	-7.87E-07	-2.01E-04
Hazardous waste	-5.22E-08	-1.05E-06
Radioactive waste	-4.47E-06	-4.59E-04
Slags/ashes	-7.71E-09	-2.99E-07
Resources (all)	0	0

The end use of methane was assumed to be the same for both the biomethane and the fossil methane.

The combustion of ethanol and petrol was compared to determine if the amount of CO_2 produced was different. It was assumed that petrol is comprised of only octane. For both cases, only complete combustion was examined and it was assumed that all of the fuel reacted. ***Error! Not a valid bookmark self-reference.*** below shows the details of this comparison.

Table A.5.5: Comparison of combustion of ethanol and petrol

Ethanol Combustion

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$$

Component	**Molar Mass** [kg/kmol]	**Stoichiometric Constant** [-]	**Mass** [kg]	**Moles** [kmol]
Ethanol	46	1	1.00	0.0217
Oxygen	32	3	2.08	0.0651
CO_2	44	2	1.91	0.0434
Water	18	3	1.17	0.0651

Petrol Combustion

$$2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O$$

Component	**Molar Mass** [kg/kmol]	**Stoichiometric Constant** [-]	**Mass** [kg]	**Moles** [kmol]
Octane	114	2	1.00	0.00877
Oxygen	32	25	3.51	0.110
CO_2	44	16	3.09	0.0702
Water	18	18	1.42	0.0789

Energy Equivalent Comparison

1	kg ethanol	produces 1.91 kg CO_2
0.612	kg petrol	produces 1.91 kg CO_2

A.5.2 Weighting Factors Used

Global weighting factors were used when available. The EU-15 values when global values were not available. Weighting factors were taken from Stranddorf et al. (2005) and can be seen in *Table A.5.6* below.

Table A.5.6: Weighting factors used in GAMS models
From Stranddorf et al. (2005)

Impact Category *c*		**Weighting Factor**
Global warming (GWP 100)	Global	1.12
Ozone depletion	Global – developing	4.40
Acidification	EU-15	1.27
Eutrophication	EU-15	1.22
Photochemical smog	Global	1.00
Ecotoxicity water chronic	EU-15	1.18
Ecotoxicity water acute	EU-15	1.11
Ecotoxicity soil chronic	EU-15	1.00
Human toxicity air	EU-15	1.40
Human toxicity water	EU-15	1.30
Human toxicity soil	EU-15	1.23
Bulk waste	EU-15	1.10
Hazardous waste	EU-15	1.10
Radioactive waste	EU-15	1.10
Slags/ashes	EU-15	1.10

A.5.3 Determining the Environmental Impact of Enzymes

The **Ecoinvent V2.2** Database does not have any enzymes or cellulases and so a process had to be created in SimaPro to ensure the environmental impact of the cellulases could be included.

Although Novozymes has published papers describing the environmental impact of enzymes using a cradle to gate framework one of these did not include cellulases (Nielsen, Oxenbøll & Wenzel, 2007) and the other did not include details of the cellulase production (Skals et al., 2008). For these reasons it was not possible to create a process in SimaPro based on data from Novozymes.

Harding (2008) determined the environmental impact of cellulases produced in three different ways and provided detailed mass and energy balances associated with these processes. Data was unavailable as to how Novozymes produces cellulases but aerobic fermentation using *Trichoderma reesei* is a common method (Harding, 2008). The mass balances used in Harding (2008) for aerobic fermentation using *Trichoderma reesei* were based on the work of Heinzle, Biwer & Cooney (2006) and Scenario H1 was found to be the most accurate thus the mass balance from Scenario H1 was used in this work.

The mass balances used can be seen in *Table A.5.7*. Some components (nutrients and *Trichoderma reesei*) were excluded from the process in SimaPro because there was no suitable process in the database. Oxygen was also ignored as it was assumed that this came from air and thus has a negligible environmental impact. Since according to Harding (2008) electricity, cellulose and corn liquor were the greatest contributors to the environmental impact this should not cause the environmental impact to be inaccurate.

Table A.5.7: Mass and energy balance used to develop EI for enzymes in SimaPro (Harding, 2008)

Component	**Unit**	**In**	**Out**
Ammonia	[kg]	0.10	0
Carbon Dioxide	[kg]	-	4.00
Cellulase Waste	[kg]	-	0.02
Cellulose	[kg]	3.78	0.28
Corn Liquor	[kg]	0.77	0.16
Enzyme	[kg]	-	16.4
Nutrients	[kg]	0.52	0.10
Oxygen	[kg]	3.21	-
Trichoderma reesei	[kg]	0.07	1.22
Water	[kg]	78.9	65.2
Energy			
Component	Unit		
Electricity	[MJ]	183	
Steam (152°C, 3 bar)	[kg]	2.65	
Chilled water	[kg]	1.60	
Cooling water	[kg]	-	

The process constructed for cellulases in SimaPro was analysed using **CML baseline 2000 V2.05/World 1990** with **Ecoinvent v2.2** in order to compare the environmental impact with that of Harding (2008) who used **CML baseline 2000 V2.03 / World, 1990** with **Ecoinvent v1.3**. The results of this comparison can be seen in *Table A.5.8*. The errors ranged from 2.89% to 105%. In most categories, the impacts of this model were less than those of Harding (2008). The model overestimated the impact for acidification, eutrophication and fresh water aquatic ecotoxicity.

Table A.5.8: Comparison of environmental impact for cellulases of (Harding, 2008) and this work using CML Baseline

Impact Category	Unit	Harding (2008)	This Work	Error [%]
Abiotic Depletion	[kg Sb eq]	0.500	0.474	-5.26
Acidification	[kg SO2 eq]	0.510	0.579	13.5
Eutrophication	[kg PO4--- eq]	0.034	0.039	13.3
Global Warming (Gwp100)	[kg CO2 eq]	-1240	57.0	95
Ozone Layer Depletion (Odp)	[kg CFC-11 eq]	2.28	0.00	-100
Human Toxicity	[kg 1,4-DB eq]	23.9	9.02	-62.2
Fresh Water Aquatic Ecotoxicity	[kg 1,4-DB eq]	6.26	10.10	61.3
Marine Aquatic Ecotoxicity	[kg 1,4-DB eq]	38300	19078	-50.2
Terrestrial Ecotoxicity	[kg 1,4-DB eq]	0.110	0.041	-62.6
Photochemical Oxidation	[kg C2H4 eq]	0.020	0.019	-2.89

The errors are most likely a result of differences in the components used in SimaPro and could also be attributed to changes in the Ecoinvent database and CML methodology. The most likely sources of error are the electricity, cellulose and corn liquor as these are the biggest contributors to the environmental impact. For the required electricity, a South African medium voltage electricity process was used which was taken from the South African Liquid Fuels Database developed by the University of Cape Town and The Green House. This should be similar to the coal-based South African electricity mix that was used by Harding (2008).

The difference in global warming results from the cellulose which was wood chips. The wood chips used by Harding (2008) had a negative global warming potential due to the carbon dioxide used by the tree during its lifetime. However, all the various wood chips available for use in this work had a positive global warming potential.

The categories in which the biggest overestimations of the environmental impacts were made were: global warming and fresh water aquatic ecotoxicity. The categories in which the biggest underestimations of the environmental impacts were made were: ozone layer depletion, human toxicity, marine aquatic ecotoxicity and terrestrial ecotoxicity. The EDIP/UMIP 97 where overestimation may occur is global warming. Underestimation of the enzyme environmental impact may occur in the following categories: ozone depletion, human toxicity and soil ecotoxicity. EDIP/UMIP 97 does not differentiate between fresh water and marine ecotoxicity and as a result it is not possible to know if the water ecotoxicity will be overestimated or underestimated.

This process was used in the GAMS model in spite of the inaccuracies as it was important to include enzymes in the environmental impact calculations. Transportation of enzymes was excluded although this could significantly increase the environmental impact of enzymes as if the demand for enzymes caused by this plant is large it may be beneficial to produce enzymes on-site.

A.5.4 Comparison of Enzymatic Production Methods

Other possible methods of enzyme production were investigated to determine the environmental impact of less energy intensive methods of production. *Section 4.8.1* discusses the different scenarios for enzyme production that were chosen. *Table A.5.9* below shows the mass balances for the three enzyme production scenarios which was taken from Harding (2008). These mass balances were modelled in SimaPro as processes using the methodology described in *Section A.5.3*. The normalised environmental impacts for these different enzyme production scenarios can be seen in

Table A.5.10 on the following page.

Table A.5.9: Mass balances for different cellulase production scenarios (Harding, 2008)

Component	Unit	Scenario H1		Scenario H2		Scenario SSC1	
		In	Out	In	Out	In	Out
Ammonia	[kg]	0.10	0	0.10	0	-	-
Carbon Dioxide	[kg]	-	4.00	-	4.00	-	24.0
Cellulase Waste	[kg]	-	0.02	-	0.02	-	-
Cellulose	[kg]	3.78	0.28	3.47	0.28	89.5	0
Clostridium thermocellum	[kg]	-	-	-	-	0.01	0
Corn Liquor	[kg]	0.77	0.16	0.77	0.16	-	-
Enzyme	[kg]	-	16.4	-	14.9	-	313.9
Hydrogen	[kg]	-	-	-	-	-	0.3
Nutrients	[kg]	0.52	0.10	0.52	0.10	-	-
Oxygen	[kg]	3.21	-	3.21	-	-	-
Trichoderma reesei	[kg]	0.07	1.22	0.07	1.22	-	-
Urea	[kg]	-	-	-	-	0.79	0
Water	[kg]	78.9	65.2	71.8	59.1	244.3	0
Yeast extract	[kg]	-	-	-	-	3.18	0
Energy							
Component	**Unit**	**Scenario H1**		**Scenario H2**		**Scenario SSC1**	
Electricity	[MJ]	183		82.4		6.5	
Steam (152°C, 3 bar)	[kg]	2.65		2.40		17.4	
Chilled water	[kg]	1.60		1.60		-	
Cooling water	[kg]	-		-		5.8	

Table A.5.10: Normalised environmental impacts for enzymes using different production scenarios

Impact Category ***c***	**Component, *Enz*** [Normalised EI/ton of component]		
	Scenario H1	**Scenario H2**	**Scenario SSC1**
Global warming (GWP 100)	6.59E-03	3.32E-03	4.30E-03
Ozone depletion	2.16E-06	1.69E-06	1.37E-05
Acidification	7.42E-03	3.39E-03	8.62E-04
Eutrophication	3.34E-03	1.83E-03	1.10E-03
Photochemical smog	1.20E-04	6.13E-05	1.89E-04
Ecotoxicity water chronic	7.35E-02	3.56E-02	3.31E-02
Ecotoxicity water acute	8.91E-02	4.32E-02	4.01E-02
Ecotoxicity soil chronic	7.37E-05	6.79E-05	2.11E-04
Human toxicity air	1.39E-03	6.67E-04	1.06E-03
Human toxicity water	1.53E-02	7.23E-03	3.12E-03
Human toxicity soil	1.54E-02	7.97E-03	1.12E-02
Bulk waste	5.41E-03	2.46E-03	6.28E-04
Hazardous waste	2.99E-06	2.12E-06	9.65E-06
Radioactive waste	1.31E-02	6.27E-03	8.52E-03
Slags/ashes	1.21E-06	1.09E-06	5.47E-06
Resources (all)	0	0	0

B GAMS Code

The GAMS code for two of the models has been included in this section. *Appendix B.1* contains the code for steam explosion followed by delignification and enzymatic hydrolysis. This code also includes the sodium hydroxide sensitivity analysis. The GAMS code for acid pre-treatment followed by acid hydrolysis is shown in *Appendix B.2.*

A CD ROM has been provided with this thesis which contains all the following GAMS files.

B.1 GAMS code for SDE with NaOH Sensitivity Analysis

Please note: this code still includes HX1, the heat exchanger discussed in Section 3.6 in the main report, however, the equations for this unit make it an inert unit (both temperature and flowrates are constant over the unit). The removal of this heat exchanger was a late modification to the code and it is easier and far less time consuming to keep the unit and make it inert than to restructure all the code.

Sensitivity analyses were performed using a solve statement in a while loop. The key variable investigated ($NaOHPurge$ which was called $NaOHRecycCost$ in the main report to avoid confusion as this value is not really a purge) was changed for each iteration of the loop to determine the value of the objective function at each value of the key variable. A certain range of the key variable was investigated which for the recycle scenarios was between '0' and '1', which stands for 'full recycle' and 'no recycle' respectively. Certain variables were printed to a 'Comma Separated Value' file for each loop iteration so that graphs could be plotted.

```
Set
      unit   units
     /SrcBag,SrcSteam,SrcEnz, SrcBal,SrcAcid,SrcWater,FlsSteamEx, MixSteamEx,
SteamEx,SnkC5,SnkVapFlsh3,MixEnzHyd, FiltSteamEx,
       EnzHyd, SnkC6, FiltEnz,SnkSolid,HX1,
SnkCW,MixDelig,HXDelig,Delig,FiltDelig,SnkDelig,SnkSteam,SrcDelig/

      Src(unit) sources
      /SrcBag,SrcSteam,SrcBal,SrcAcid,SrcWater,SrcEnz,SrcDelig/

      Snk(unit) sinks
      /SnkC5,SnkVapFlsh3,SnkC6,SnkSolid,SnkCW,SnkDelig,SnkSteam/

      Mix(unit) mixers
      /MixSteamEx,MixEnzHyd,MixDelig/

      HX(unit) heat exchangers
      /HXDelig  /

      Filt(unit) filters
      /FiltSteamEx, FiltEnz,FiltDelig/

      J     components
      /Cellulose, Hemi, Lignin, Acetyl, Phos, Xylo,Xylolig, Gluc,Glucolig, Sucrose, Furf, HMF,
      AceA,  Water, Acid, ASL, Min, OrgAc, Salts, Soil, Balance, Enz,NaOH, GluSol, XylSol,NaSulp/

      liquids(J)
      /Xylo,Xylolig, Gluc,Glucolig,Sucrose, Furf, HMF, AceA,  Water, Acid, ASL, OrgAc,Balance,Phos, Min,
Salts,NaOH, GluSol, XylSol  /
      solids(J)
```

```
        /Cellulose, Hemi, Lignin, Acetyl, Soil,Enz,NaSulp/

        filtSol(J)
        /Cellulose, Hemi, Lignin, Acetyl, Soil, Enz,NaSulp/

        filtLiq(J)
        /Xylo,Xylolig, Gluc,Glucolig,Sucrose, Furf, HMF, AceA,  Water, Acid, ASL, OrgAc,Min,  Salts,Phos,NaOH,
GluSol, XylSol /

        i(J) inerts
        /Phos,  Acid, Min, OrgAc, Salts, Soil/

        Deligi(J) delig inerts
        /Acetyl,Phos, Min, OrgAc, Salts, Soil,Enz, Xylo, Xylolig, Gluc, Glucolig,Sucrose, Furf, HMF,
        AceA, Balance/
        NoPPT(J)
        /Cellulose, Hemi, Lignin, Acetyl, Phos, Xylo, Xylolig, Gluc, Glucolig, Sucrose, Furf, HMF,
        AceA, ASL, Min, OrgAc, Salts, Soil,Balance,Enz, GluSol, XylSol/
        ppt(J)
        /Water, Acid,NaOH,NaSulp/

        SteamExi(J)      inerts in steam explosion
        /Enz,NaOH,GluSol, XylSol,NaSulp/

        Enzi (J) inerts in Enzymatic Hydrolysis
        /Balance, ASL,  Enz, Sucrose,Furf, HMF,Lignin,NaOH,GluSol, XylSol,NaSulp/

        U      utilities
        /CW, LPS,MPS1,MPS2,HPS1,HPS2,CTBE1,CTBE2/
        UtilData/ CostMon, TSupply, TTarget, CpVap, Cost /
        HXData/U, F/

Alias(unit, unit1)

Parameters
        x_SCB(J)
        /Cellulose   0.21685935
         Hemi    0.116241708
         Lignin   0.116213417
         Acetyl   0.011918937
         Phos    0.000121522
         Xylo     0
         Xylolig  0
         Gluc     0.000892313
         Glucolig 0
         Sucrose  0.020820644
         Furf     0
         HMF      0
         AceA     0
         Water    0.499962619
         Acid     0
         ASL      0
         Min      0.00154437
         OrgAc    0.002268413
         Salts    0.01220052
         Soil     0.000956187
         Balance  0
```

```
      Enz       0
      NaOH      0
      NaSulp    0
      GluSol    0
      XylSol    0   /

*     Cost or price   Rand per ton
      worth(J)
      /Cellulose  0
      Hemi   0
      Lignin  0
      Acetyl  0
      Phos   0
      Xylo    0
      Gluc    3682
      Furf    0
      HMF     0
      AceA    0
      Water   0.027205
      Acid    2560
      ASL     0
      Min     0
      OrgAc   0
      Salts   0
      Soil    0
      Enz     1708
      NaOH    6000/

*     individual liquid heat capacity of a component (average in a range 20 C - 100 C)
*     in kJ/(kg*C), assume: constant heat capacities
      cp_ind(J)
      /Cellulose  1.681734096
      Hemi      1.680623519
      Lignin    1.02130151
      Acetyl    1.968
      Phos      1.864396721
      Xylo      1.151371399
      Xylolig   1.151371399
      Xylsol    1.151371399
      Gluc      1.15138583
      Glucolig  1.15138583
      GluSol    1.15138583
      Sucrose   8.492681297
      Furf      2.024476785
      HMF       2.049797796
      AceA      2.742778034
      Water     4.310177683
      Acid      1.659065815
      ASL       1.02130151
      NaOH      2.213041274
      NaSulp    3.394772877
      Min       1.135929339
      OrgAc     2.742778034
      Salts     0.987197493
      Soil      1.427527657
      Balance   0
      Enz       1.47957994/
```

```
MW(J)
/Cellulose 162.1436
 Hemi     132.117
 Lignin   194.197
 Acetyl   60.053
 Phos     97.9952
 Xylo     150.131
 Xylolig  132.116
 Xylsol   132.116
 Gluc     180.158
 Glucolig 162.142
 GluSol   162.142
 Sucrose  342.3
 Furf     96.086
 HMF      126.11
 AceA     60.05
 Water    18.015
 Acid     98.079
 ASL      194.197
 NaOH     39.997
 Min      94.196
 OrgAc    174.110
 Salts    74.551
 Soil     60.0843
 Enz      24.0156
 Balance  18.015
 NaSulp   119.0524/

dens(J)
/Cellulose  1529.7
 Hemi      1529.1
 Lignin    2376.9
 Acetyl    1054.4
 Phos      1877.0
 Xylo      1826.1
 Xylolig   1606.9
 Xylsol    1606.9
 Gluc      1180.5
 Glucolig  1062.5
 GluSol    1062.5
 Sucrose   902.6
 Furf      1163.5
 HMF       2220.7
 AceA      1054.4
 Water     999.0
 Acid      1840
 ASL       1820.3
 Min       315.1
 OrgAc     2894.8
 Salts     247.8
 Soil      3923.6
 Balance   999
 Enz       1580.0
NaOH       132.7
 NaSulp    2700/
```

```
Parameter   FlashVapCTBE(liquids)/
*100 degrees
      Xylo      0.00000317
      Xylolig   0.00000317
      Gluc      0.0000000062
      Glucolig  0.0000000062
      Sucrose   0
      Furf      0.627485508
      HMF       0.000404736
      AceA      0.062985149
      Water     0.234672924
      Acid      0
      ASL       0
      OrgAc     0.00000771
      Balance   0 /

Parameter   FlashVapCTBEAcid(liquids)/
*100 degrees
      Xylo      0.0000015523
      Xylolig   0.0000015523
      Gluc      0.0000000030
      Glucolig  0.0000000030
      Sucrose   0
      Furf      0.437958791
      HMF       0.0001982407
      AceA      0.031869208
      Water     0.1308381152
      Acid      0.0000148985
      ASL       0
      OrgAc     0.0000037781
      Balance   0     /
set AcidCat /1*2/
Parameter SteamRatio /0.254/
Parameter SteamRatioAcid /0.183/
Parameter AcidRatio     /0.0025/
Parameter pureAcid   /0.98/
      pureNaOH/0.98/
Parameter SteamCost   /1.82/
Parameter SteamCostAcid  /0.24/

*++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
++++++++
*Filter
Parameter SteamFiltWatRatio/0.488/
Parameter SteamFiltLiq     /0.364/
Parameter SteamFiltLiqDRY  /0.0789/
Parameter SteamFiltSol     /0.995/
*++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
++++++++++++++++++++++++++++++++++
*EnzHyd
Parameter MassFracEnz mass fraction of enzyme in solution   /0.02/
Parameter FracEnzMix Mass fraction of enzymes in mixed stream   /0.000487805/
Parameter FracWatMix Mass fraction of water in mixed stream     /0.887380069/

parameter  XEnzHyd
/react1   0.5
```

```
react2  0.01
react3  0.25
react4  0
react5  0.25/;

Table   HXprops (HX,HXData)
        U     F
*HX1        850    0.9
HXDelig     1845   0.9    ;

Set numSteam/1*7/;
Table       utilProps(U, UtilData)
       CostMon  TSupply  TTarget    CpVap   Cost
CW      0.44     303.15   318.15     4.184  0.44
LPS     1.57     417.15   417.14     2133.8  0
MPS1    3.28     459.15   459.14     2000.4  1.557
MPS2    8.52     533.15   533.14     1662.5  5.5768
HPS1    9.41     573.15   573.14     1404.9  7.2767
HPS2    11.65    633.15   633.14     720.5   11.674
*CTBE1  1.203    400.15   400.14     2181.5  0
CTBE1   2.060    431.15   431.14     2086.3  0.24
CTBE2   3.53     463.28   463.27     1986.2  1.82   ;

Set cats /GW, OD, Ac, Eu, PS, EWC, EWA, ESC, HTA, HTW, HTS, BW, HW, RW, Sas, Res/;
Set Cmpnts /Acid,NaOH,Enz,Bag,Water,CTBE1,LPS,CTBE2,MPS1,MPS2,HPS1,HPS2,AceA, Furf, AcidFl, CH4, WF,
Eth/;
Set Expan /ExpBag, ExpCH4, ExpEth/;
Table Enviro(cats, Cmpnts)
         Acid          NaOH          Enz           Bag             Water         CTBE2         LPS          CTBE1
MPS1          MPS2          HPS1          HPS2          AceA          Furf     AcidFl          CH4        WF
GW       1.42881E-05       0.000126412       6.59E-03          1.31724E-06       7.50593E-07       4.069791E-07
3.78827E-7       3.87452E-7       4.0409E-7       4.86221E-7       5.75373E-7       1.12192E-6       0.040854722
0       0.017783805      2.34E-04       1.12
OD       1.21112E-07       6.5887E-07       2.16184E-06       1.42041E-08       6.21598E-09       4.388709E-09
4.08513E-9       4.17814E-9       4.35756E-9       5.24322E-9       6.20461E-9       1.20983E-8       0.000253          0
0            6.58E-07       4.4
Ac       0.000181646       6.82024E-05       0.007421255       2.28843E-06       2.5697E-07       7.069978E-07
6.58093E-7       6.73076E-7       7.01979E-7       8.44655E-7       9.9953E-7       1.94898E-6       0             0
0            7.10E-05       1.27
Eu       2.87518E-05       0.00032239       0.003340917       4.43608E-06       1.67478E-07       1.370500E-06
1.2757E-6       1.30474E-6       1.36077E-6       1.63735E-6       1.93757E-6       3.77805E-6       0             0
0.01755          1.06E-04       1.22
PS       1.30511E-06       5.31969E-06       0.000120227       1.56948E-05       2.1126E-08       4.848772E-06
4.51337E-6       4.61613E-6       4.81435E-6       5.79286E-6       6.85503E-6       1.33666E-5       0             0
0            2.34E-05       1
EWC      0.001368795       0.013656376       0.073468838       4.05229E-05       7.21621E-07       1.251921E-05
1.16532E-5       1.19185E-5       1.24303E-5       1.49568E-5       1.76992E-5       3.45117E-5       0.0208          0
0            5.66E-03       1.18
EWA      0.001666648       0.016525167       0.089146148       6.3139E-05       8.51281E-07       1.950553E-05
1.81563E-5       1.85697E-5       1.93671E-5       2.33034E-5       2.75763E-5       5.37708E-5       0.00027264
0       0            6.88E-03       1.11
ESC      9.53987E-06       3.09275E-05       7.36685E-05       2.41007E-06       2.14699E-08       7.445831E-07
6.93078E-7       7.08858E-7       7.39298E-7       8.89558E-7       1.05267E-6       2.05259E-6       0             0
0            2.22E-05       1
HTA      2.34807E-05       6.85574E-05       0.001392699       7.17546E-06       1.30666E-07       2.216683E-06
2.06335E-6       2.11033E-6       2.20095E-6       2.64829E-6       3.13387E-6       6.11072E-6       0.0008216
0       0            3.36E-04       1.4
```

```
HTW      0.000156748      0.002489761      0.015346475      6.73479E-06      4.19291E-07      2.080685E-06
1.93676E-6      1.98085E-6      2.06592E-6      2.48581E-6      2.9416E-6      5.73582E-6      0.003597      0
0.000233805      5.54E-04      1.3
HTS      0.000303801      0.001861645      0.015398899      0.001219034      8.34879E-07      3.766350E-04
3.50582E-4      3.58564E-4      3.73961E-4      4.49968E-4      5.32474E-4      1.03827E-3      0.00082368
0      0      2.59E-03      1.23
BW      2.8521E-05      0.000104754      0.00541214      3.29075E-06      1.18069E-05      1.016731E-06
9.46402E-7      9.67949E-7      1.00951E-7      1.2147E-6      1.43742E-6      2.80282E-6      0.0151104      0
0      1.38E-04      1.10
HW      2.27744E-07      5.61968E-06      2.98755E-06      1.0813E-08      0      3.340724E-09
3.10964E-9      3.18044E-9      3.31701E-9      3.99119E-9      4.723E-9      9.20936E-9      0      0      0
8.96E-07      1.10
RW      0.000122592      0.003298263      0.013137083      4.20091E-06      2.58223E-06      1.297896E-06
1.20812E-6      1.23562E-6      1.28868E-6      1.5506E-6      1.83492E-6      3.5779E-6      0      0      0
3.34E-03      1.10
Sas      1.5399E-07      5.85146E-07      1.20575E-06      1.87091E-07      3.46914E-09      5.779027E-08
5.37928E-8      5.50175E-8      5.738E-8      6.90424E-8      8.17019E-8      1.5931E-8      0      0      0
1.71E-05      1.10
Res      0      0      0      0      0      0      0      0      0
0      0      0      0      0      0      0.00E+00      0    ;

Table SysExp(cats, Expan)
        ExpBag          ExpCH4        ExpEth
GW       0.00020395       1.33E-06       2.69E-04
OD       0              5.25E-08       6.02E-06
Ac       0              1.43E-06       2.52E-04
Eu       0              1.72E-06       1.26E-04
PS       0              3.94E-07       5.86E-05
EWC      0              1.13E-04       7.78E-03
EWA      0              1.81E-04       9.41E-03
ESC      0              7.42E-08       5.74E-06
HTA      0              9.01E-07       6.50E-04
HTW      0              1.63E-05       6.46E-04
HTS      0              1.79E-05       6.06E-03
BW       0              7.87E-07       2.01E-04
HW       0              5.22E-08       1.05E-06
RW       0              4.47E-06       4.59E-04
Sas      0              7.71E-09       2.99E-07
Res      0              0.00E+00       0.00E+00    ;
*++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
++++++++++++++++++++++++++++++++++++

SET     Arc(unit,unit1) stream matrix;
*setting entries in stream matrix
Arc(unit, unit1)=No;

*Define all existing streams Arc('1','2') is stream from unit 1 to unit 2
*PreHydrolysis
Arc('SrcBag','MixSteamEx')=Yes;
Arc('SrcSteam','MixSteamEx')=Yes;
Arc('SrcAcid','MixSteamEx')=Yes;
Arc('SrcBal','SteamEx')=Yes;
Arc('MixSteamEx','SteamEx')=Yes;
Arc('SteamEx','FlsSteamEx')=Yes;
Arc('FlsSteamEx','SnkVapFlsh3')=Yes;
Arc('FlsSteamEx','FiltSteamEx')=Yes;
Arc('SrcWater','FiltSteamEx')=Yes;
```

```
Arc('FiltSteamEx','SnkC5')=Yes;
Arc('FiltSteamEx','MixDelig')=Yes;

*Delig
Arc('SrcDelig','MixDelig')=Yes;
Arc('SrcWater','MixDelig')=Yes;
Arc('MixDelig','HXDelig')=Yes;
Arc('SrcSteam','HXDelig')=Yes;
Arc('HXDelig','Delig')=Yes;
Arc('HXDelig','SnkSteam')=Yes;
Arc('SrcWater','FiltDelig')=Yes;
Arc('Delig','FiltDelig')=Yes;
Arc('FiltDelig','HX1')=Yes;
Arc('FiltDelig','SnkDelig')=Yes;
*EnzHyd
Arc('SrcWater','HX1')=Yes;
Arc('HX1','SnkCW')=Yes;
Arc('HX1','MixEnzHyd')=Yes;
Arc('SrcEnz','MixEnzHyd')=Yes;
Arc('SrcWater','MixEnzHyd')=Yes;
Arc('MixEnzHyd','EnzHyd')=Yes;
Arc('SrcWater','FiltEnz')=Yes;
Arc('EnzHyd','FiltEnz')=Yes;
Arc('FiltEnz','SnkC6')=Yes;
Arc('FiltEnz','SnkSolid')=Yes;

Positive Variables
*       streams and mass fractions: all in kg/s
        F(unit,unit1)           total streams in kg s^-1
        fc(J,unit,unit1)        individual components streams in kg s^-1
        x(J,unit,unit1)         mass fraction of comp J in stream
        fcmol(J,unit,unit1)     component molar flowrate in kmol s^-1

        V(unit,unit1)           Volumetric flow between units in m^3 s^-1
        Tau(unit)               residence time in min
        Volume(unit)    Volume of unit in m3
        LDrat(unit)     L over D ratio
        Diameter(unit)      Diameter of unit in m
        Length(unit)            Length of unit in m
        thick(unit)             Thickness of unit in mm
        weight(unit)            Weight of unit in lbs of carbon steel unit
        SA(filt)                surface area in m^2 for filters
        Cp(unit)                purchase cost for equipment in $

        NaOHWt                  NaOH wt per V%
        NaOHPurge               Fraction of NaOH purged
        WSRDelig                    water solid ratio (g water per g solid)

        newXEnzHyd      new conversions - increased based on delignification
        newX2EnzHyd       new conversions - increased based on delignification
        YieldInc                percentage by which enzymatic hydrolysis conversion increases
        StExFiltSplit           liquid split ratio in filter after steam explosion
        StExLiqFrac             liquid fraction in the solid stream exiting the filter after steam explosion
        DeligFiltSplit          liquid split ratio in filter after delignification
        DeligLiqFrac            liquid fraction in the solid stream exiting the filter after delig
        EnzFiltSplit            liquid split ratio in filter after enzymatic hydrolysis
        EnzLiqFrac              liquid fraction in the solid stream exiting the filter after enzymatic hydrolysis
```

```
      T(unit,unit1)        temperature of stream in C
      LMTD(HX)          log mean temperature difference using Chen 2 for HX sizing
      Area(HX)          area of HX m2
      Cb(HX)            heat exchanger cost from curve in $
      Fm(HX)               heat exchanger material of construction factor
      W(Unit)              power consumption of unit in kW (efficiency included);

Variable
*       heat
      Q(Unit)       heat produced or consumed in unit in kW (efficiency included)
      z             objective variable;
Binary variable    steamExpChoice(AcidCat);
*Global relationships
Equations
      Rel_1, Rel_2,Rel_3,VolFlow1,VolFlow2;

*relationship between F, fc and x
Rel_1(J,unit,unit1)$Arc(unit,unit1)..
      fc(J,unit,unit1) =E= F(unit,unit1)*x(J,unit,unit1);

Rel_2(unit,unit1)$Arc(unit,unit1)..
      Sum(J,fc(J,unit,unit1)) =E= F(unit,unit1);

Rel_3(J,unit,unit1)$Arc(unit,unit1)..
       fcmol(J,unit,unit1)*MW(J) =e= fc(J,unit,unit1);
VolFlow1..
      V('MixSteamEx', 'SteamEx') =E= sum(J, fc(J,'MixSteamEx','SteamEx')/dens(J));
VolFlow2..
      V('MixEnzHyd', 'EnzHyd')    =E= sum(J, fc(J,'MixEnzHyd','EnzHyd')/dens(J));

*Total flowrate bounds
F.lo(unit,unit1)$Arc(unit,unit1)=0;
F.up(unit,unit1)$Arc(unit,unit1)=500;

F.lo('MixSteamEx','SteamEx')=8;
F.l('MixSteamEx','SteamEx')=41;
F.lo('SteamEx','FlsSteamEx')=8;
*Component flowrate bounds
fc.lo(J,unit,unit1)$Arc(unit,unit1)=0;
fc.up(J,unit,unit1)$Arc(unit,unit1)=50;
fcmol.lo(J,unit,unit1)$Arc(unit,unit1)=0;
fcmol.up(J,unit,unit1)$Arc(unit,unit1)=10;

V.lo(unit,unit1)$Arc(unit,unit1) = 0;
V.up(unit,unit1)$Arc(unit,unit1) = 10;

fc.up('Water',unit,unit1)$Arc(unit,unit1)=400;
fcmol.up('Water',unit,unit1)$Arc(unit,unit1)=25;
*Setting flowrates to zero for non-exisitng units
F.up(unit,unit1)$(not Arc(unit,unit1)) = 0;
fc.up(J,unit,unit1)$(not Arc(unit,unit1)) = 0;

fc.l('Cellulose','SrcBag','MixSteamEx')=   6;
fc.l('Hemi','SrcBag','MixSteamEx')=   3;
fc.l('Lignin','SrcBag','MixSteamEx')=   3;
fc.l('Acetyl','SrcBag','MixSteamEx')=   0.5;
*fc.l('Phos','SrcBag','MixSteamEx')=   1;
```

```
fc.l('Xylo','SrcBag','MixSteamEx')=  0;
fc.l('Xylolig','SrcBag','MixSteamEx')=  0;
fc.l('Gluc','SrcBag','MixSteamEx')=  0;
fc.l('Glucolig','SrcBag','MixSteamEx')=  0;
fc.l('Sucrose','SrcBag','MixSteamEx')=  0;
fc.l('Furf','SrcBag','MixSteamEx')=  0;
fc.l('HMF','SrcBag','MixSteamEx')=  0;
fc.l('AceA','SrcBag','MixSteamEx')=  0;
fc.l('Water','SrcBag','MixSteamEx')=  17;
fc.l('Acid','SrcBag','MixSteamEx')=  0;
fc.l('ASL','SrcBag','MixSteamEx')=  0;
fc.l('Min','SrcBag','MixSteamEx')=  0.01;
fc.l('OrgAc','SrcBag','MixSteamEx')=  0.01;
fc.l('Salts','SrcBag','MixSteamEx')=  0.3;
fc.l('Soil','SrcBag','MixSteamEx')=  0.01;
fc.l('Balance','SrcBag','MixSteamEx')=  0;

fc.lo('Cellulose','SrcBag','MixSteamEx')=  0.1;
fc.lo('Hemi','SrcBag','MixSteamEx')=  0.1;
fc.lo('Lignin','SrcBag','MixSteamEx')=  0.1;
fc.lo('Acetyl','SrcBag','MixSteamEx')=  0.1;
*fc.lo('Phos','SrcBag','MixSteamEx')=  0.1;
fc.lo('Xylo','SrcBag','MixSteamEx')=  0;
fc.lo('Xylolig','SrcBag','MixSteamEx')=  0;
fc.lo('Gluc','SrcBag','MixSteamEx')=  0;
fc.lo('Glucolig','SrcBag','MixSteamEx')=  0;
fc.lo('Sucrose','SrcBag','MixSteamEx')=  0;
fc.lo('Furf','SrcBag','MixSteamEx')=  0;
fc.lo('HMF','SrcBag','MixSteamEx')=  0;
fc.lo('AceA','SrcBag','MixSteamEx')=  0;
fc.lo('Water','SrcBag','MixSteamEx')=  2;
fc.lo('Acid','SrcBag','MixSteamEx')=  0;
fc.lo('ASL','SrcBag','MixSteamEx')=  0;
fc.lo('Min','SrcBag','MixSteamEx')=  0.001;
fc.lo('OrgAc','SrcBag','MixSteamEx')=  0.001;
fc.lo('Salts','SrcBag','MixSteamEx')=  0.03;
fc.lo('Soil','SrcBag','MixSteamEx')=  0.001;
fc.lo('Balance','SrcBag','MixSteamEx')=  0;

fc.fx('Cellulose','SrcSteam','MixSteamEx')=  0;
fc.fx('Hemi','SrcSteam','MixSteamEx')=  0;
fc.fx('Lignin','SrcSteam','MixSteamEx')=  0;
fc.fx('Acetyl','SrcSteam','MixSteamEx')=  0;
fc.fx('Phos','SrcSteam','MixSteamEx')=  0;
fc.fx('Xylo','SrcSteam','MixSteamEx')=  0;
fc.fx('Xylolig','SrcSteam','MixSteamEx')=  0;
fc.fx('Gluc','SrcSteam','MixSteamEx')=  0;
fc.fx('Glucolig','SrcSteam','MixSteamEx')=  0;
fc.fx('Sucrose','SrcSteam','MixSteamEx')=  0;
fc.fx('Furf','SrcSteam','MixSteamEx')=  0;
fc.fx('HMF','SrcSteam','MixSteamEx')=  0;
fc.fx('AceA','SrcSteam','MixSteamEx')=  0;
*fc.fx('Water','SrcSteam','MixSteamEx')=  0;
fc.fx('Acid','SrcSteam','MixSteamEx')=  0;
fc.fx('ASL','SrcSteam','MixSteamEx')=  0;
fc.fx('Min','SrcSteam','MixSteamEx')=  0;
fc.fx('OrgAc','SrcSteam','MixSteamEx')=  0;
```

```
fc.fx('Salts','SrcSteam','MixSteamEx')=   0;
fc.fx('Soil','SrcSteam','MixSteamEx')=   0;
fc.fx('Balance','SrcSteam','MixSteamEx')=   0;
fc.fx('Enz','SrcSteam','MixSteamEx')=   0;
fc.fx('NaOH','SrcSteam','MixSteamEx')=   0;
fc.fx('NaSulp','SrcSteam','MixSteamEx')=   0;
fc.fx('GluSol','SrcSteam','MixSteamEx')=   0;
fc.fx('XylSol','SrcSteam','MixSteamEx')=   0;

fc.fx('Cellulose','SrcAcid','MixSteamEx')=   0;
fc.fx('Hemi','SrcAcid','MixSteamEx')=       0;
fc.fx('Lignin','SrcAcid','MixSteamEx')=  0;
fc.fx('Acetyl','SrcAcid','MixSteamEx')=   0;
fc.fx('Phos','SrcAcid','MixSteamEx')=   0;
fc.fx('Xylo','SrcAcid','MixSteamEx')=   0;
fc.fx('Xylolig','SrcAcid','MixSteamEx')=   0;
fc.fx('Gluc','SrcAcid','MixSteamEx')=   0;
fc.fx('Glucolig','SrcAcid','MixSteamEx')=   0;
fc.fx('Sucrose','SrcAcid','MixSteamEx')=   0;
fc.fx('Furf','SrcAcid','MixSteamEx')=   0;
fc.fx('HMF','SrcAcid','MixSteamEx')=   0;
fc.fx('AceA','SrcAcid','MixSteamEx')=   0;
*fc.fx('Water','SrcAcid','MixSteamEx')=  0;
*fc.fx('Acid','SrcAcid','MixSteamEx')=   0;
fc.fx('ASL','SrcAcid','MixSteamEx')=   0;
fc.fx('Min','SrcAcid','MixSteamEx')=   0;
fc.fx('OrgAc','SrcAcid','MixSteamEx')=   0;
fc.fx('Salts','SrcAcid','MixSteamEx')=   0;
fc.fx('Soil','SrcAcid','MixSteamEx')=   0;
fc.fx('Balance','SrcAcid','MixSteamEx')=   0;
fc.fx('Enz','SrcAcid','MixSteamEx')=   0;
fc.fx('NaOH','SrcAcid','MixSteamEx')=   0;
fc.fx('NaSulp','SrcAcid','MixSteamEx')=   0;
fc.fx('GluSol','SrcAcid','MixSteamEx')=   0;
fc.fx('XylSol','SrcAcid','MixSteamEx')=   0;

fc.fx('Cellulose','SrcBal','SteamEx')=   0;
fc.fx('Hemi','SrcBal','SteamEx')=       0;
fc.fx('Lignin','SrcBal','SteamEx')=  0;
fc.fx('Acetyl','SrcBal','SteamEx')=   0;
fc.fx('Phos','SrcBal','SteamEx')=   0;
fc.fx('Xylo','SrcBal','SteamEx')=   0;
fc.fx('Xylolig','SrcBal','SteamEx')=   0;
fc.fx('Gluc','SrcBal','SteamEx')=   0;
fc.fx('Glucolig','SrcBal','SteamEx')=   0;
fc.fx('Sucrose','SrcBal','SteamEx')=   0;
fc.fx('Furf','SrcBal','SteamEx')=   0;
fc.fx('HMF','SrcBal','SteamEx')=   0;
fc.fx('AceA','SrcBal','SteamEx')=   0;
fc.fx('Water','SrcBal','SteamEx')=  0;
fc.fx('Acid','SrcBal','SteamEx')=   0;
fc.fx('ASL','SrcBal','SteamEx')=   0;
fc.fx('Min','SrcBal','SteamEx')=   0;
fc.fx('OrgAc','SrcBal','SteamEx')=   0;
fc.fx('Salts','SrcBal','SteamEx')=   0;
fc.fx('Soil','SrcBal','SteamEx')=   0;
*fc.fx('Balance','SrcBal','SteamEx')=   0;
```

```
fc.fx('Enz','SrcBal','SteamEx')=  0;
fc.fx('NaOH','SrcBal','SteamEx')=  0;
fc.fx('NaSulp','SrcBal','SteamEx')=  0;
fc.fx('GluSol','SrcBal','SteamEx')=  0;
fc.fx('XylSol','SrcBal','SteamEx')=  0;

fc.fx('Cellulose','SrcWater','HX1')=  0;
fc.fx('Hemi','SrcWater','HX1')=  0;
fc.fx('Lignin','SrcWater','HX1')=  0;
fc.fx('Acetyl','SrcWater','HX1')=  0;
fc.fx('Phos','SrcWater','HX1')=  0;
fc.fx('Xylo','SrcWater','HX1')=  0;
fc.fx('Xylolig','SrcWater','HX1')=  0;
fc.fx('Gluc','SrcWater','HX1')=  0;
fc.fx('Glucolig','SrcWater','HX1')=  0;
fc.fx('Sucrose','SrcWater','HX1')=  0;
fc.fx('Furf','SrcWater','HX1')=  0;
fc.fx('HMF','SrcWater','HX1')=  0;
fc.fx('AceA','SrcWater','HX1')=  0;
*fc.fx('Water','SrcWater','HX1')=  0;
fc.fx('Acid','SrcWater','HX1')=  0;
fc.fx('ASL','SrcWater','HX1')=  0;
fc.fx('Min','SrcWater','HX1')=  0;
fc.fx('OrgAc','SrcWater','HX1')=  0;
fc.fx('Salts','SrcWater','HX1')=  0;
fc.fx('Soil','SrcWater','HX1')=  0;
fc.fx('Balance','SrcWater','HX1')=  0;
fc.fx('Enz','SrcWater','HX1')=  0;
fc.fx('NaOH','SrcWater','HX1')=  0;
fc.fx('NaSulp','SrcWater','HX1')=  0;
fc.fx('GluSol','SrcWater','HX1')=  0;
fc.fx('XylSol','SrcWater','HX1')=  0;

fc.fx('Cellulose','SrcWater','FiltSteamEx')=  0;
fc.fx('Hemi','SrcWater','FiltSteamEx')=  0;
fc.fx('Lignin','SrcWater','FiltSteamEx')=  0;
fc.fx('Acetyl','SrcWater','FiltSteamEx')=  0;
fc.fx('Phos','SrcWater','FiltSteamEx')=  0;
fc.fx('Xylo','SrcWater','FiltSteamEx')=  0;
fc.fx('Xylolig','SrcWater','FiltSteamEx')=  0;
fc.fx('Gluc','SrcWater','FiltSteamEx')=  0;
fc.fx('Glucolig','SrcWater','FiltSteamEx')=  0;
fc.fx('Sucrose','SrcWater','FiltSteamEx')=  0;
fc.fx('Furf','SrcWater','FiltSteamEx')=  0;
fc.fx('HMF','SrcWater','FiltSteamEx')=  0;
fc.fx('AceA','SrcWater','FiltSteamEx')=  0;
*fc.fx('Water','SrcWater','FiltSteamEx')=  0;
fc.fx('Acid','SrcWater','FiltSteamEx')=  0;
fc.fx('ASL','SrcWater','FiltSteamEx')=  0;
fc.fx('Min','SrcWater','FiltSteamEx')=  0;
fc.fx('OrgAc','SrcWater','FiltSteamEx')=  0;
fc.fx('Salts','SrcWater','FiltSteamEx')=  0;
fc.fx('Soil','SrcWater','FiltSteamEx')=  0;
fc.fx('Balance','SrcWater','FiltSteamEx')=  0;
fc.fx('Enz','SrcWater','FiltSteamEx')=  0;
fc.fx('NaOH','SrcWater','FiltSteamEx')=  0;
fc.fx('NaSulp','SrcWater','FiltSteamEx')=  0;
```

```
fc.fx('GluSol','SrcWater','FiltSteamEx')=   0;
fc.fx('XylSol','SrcWater','FiltSteamEx')=   0;

fc.fx('Cellulose','SrcWater','FiltDelig')=   0;
fc.fx('Hemi','SrcWater','FiltDelig')=        0;
fc.fx('Lignin','SrcWater','FiltDelig')=  0;
fc.fx('Acetyl','SrcWater','FiltDelig')=   0;
fc.fx('Phos','SrcWater','FiltDelig')=   0;
fc.fx('Xylo','SrcWater','FiltDelig')=   0;
fc.fx('Xylolig','SrcWater','FiltDelig')=   0;
fc.fx('Gluc','SrcWater','FiltDelig')=   0;
fc.fx('Glucolig','SrcWater','FiltDelig')=   0;
fc.fx('Sucrose','SrcWater','FiltDelig')=   0;
fc.fx('Furf','SrcWater','FiltDelig')=   0;
fc.fx('HMF','SrcWater','FiltDelig')=   0;
fc.fx('AceA','SrcWater','FiltDelig')=   0;
*fc.fx('Water','SrcWater','FiltDelig')=  0;
fc.fx('Acid','SrcWater','FiltDelig')=   0;
fc.fx('ASL','SrcWater','FiltDelig')=   0;
fc.fx('Min','SrcWater','FiltDelig')=   0;
fc.fx('OrgAc','SrcWater','FiltDelig')=   0;
fc.fx('Salts','SrcWater','FiltDelig')=   0;
fc.fx('Soil','SrcWater','FiltDelig')=   0;
fc.fx('Balance','SrcWater','FiltDelig')=   0;
fc.fx('Enz','SrcWater','FiltDelig')=   0;
fc.fx('NaOH','SrcWater','FiltDelig')=   0;
fc.fx('NaSulp','SrcWater','FiltDelig')=   0;
fc.fx('GluSol','SrcWater','FiltDelig')=   0;
fc.fx('XylSol','SrcWater','FiltDelig')=   0;

fc.fx('Cellulose','SrcWater','FiltEnz')=   0;
fc.fx('Hemi','SrcWater','FiltEnz')=        0;
fc.fx('Lignin','SrcWater','FiltEnz')=  0;
fc.fx('Acetyl','SrcWater','FiltEnz')=   0;
fc.fx('Phos','SrcWater','FiltEnz')=   0;
fc.fx('Xylo','SrcWater','FiltEnz')=   0;
fc.fx('Xylolig','SrcWater','FiltEnz')=   0;
fc.fx('Gluc','SrcWater','FiltEnz')=   0;
fc.fx('Glucolig','SrcWater','FiltEnz')=   0;
fc.fx('Sucrose','SrcWater','FiltEnz')=   0;
fc.fx('Furf','SrcWater','FiltEnz')=   0;
fc.fx('HMF','SrcWater','FiltEnz')=   0;
fc.fx('AceA','SrcWater','FiltEnz')=   0;
*fc.fx('Water','SrcWater','FiltEnz')=  0;
fc.fx('Acid','SrcWater','FiltEnz')=   0;
fc.fx('ASL','SrcWater','FiltEnz')=   0;
fc.fx('Min','SrcWater','FiltEnz')=   0;
fc.fx('OrgAc','SrcWater','FiltEnz')=   0;
fc.fx('Salts','SrcWater','FiltEnz')=   0;
fc.fx('Soil','SrcWater','FiltEnz')=   0;
fc.fx('Balance','SrcWater','FiltEnz')=   0;
fc.fx('Enz','SrcWater','FiltEnz')=   0;
fc.fx('NaOH','SrcWater','FiltEnz')=   0;
fc.fx('NaSulp','SrcWater','FiltEnz')=   0;
fc.fx('GluSol','SrcWater','FiltEnz')=   0;
fc.fx('XylSol','SrcWater','FiltEnz')=   0;
```

```
fc.fx('Cellulose','HX1','SnkCW')=  0;
fc.fx('Hemi','HX1','SnkCW')=       0;
fc.fx('Lignin','HX1','SnkCW')=  0;
fc.fx('Acetyl','HX1','SnkCW')=  0;
fc.fx('Phos','HX1','SnkCW')=  0;
fc.fx('Xylo','HX1','SnkCW')=  0;
fc.fx('Xylolig','HX1','SnkCW')=  0;
fc.fx('Gluc','HX1','SnkCW')=  0;
fc.fx('Glucolig','HX1','SnkCW')=  0;
fc.fx('Sucrose','HX1','SnkCW')=  0;
fc.fx('Furf','HX1','SnkCW')=  0;
fc.fx('HMF','HX1','SnkCW')=  0;
fc.fx('AceA','HX1','SnkCW')=  0;
*fc.fx('Water','HX1','SnkCW')=  0;
fc.fx('Acid','HX1','SnkCW')=  0;
fc.fx('ASL','HX1','SnkCW')=  0;
fc.fx('Min','HX1','SnkCW')=  0;
fc.fx('OrgAc','HX1','SnkCW')=  0;
fc.fx('Salts','HX1','SnkCW')=  0;
fc.fx('Soil','HX1','SnkCW')=  0;
fc.fx('Balance','HX1','SnkCW')=  0;
fc.fx('Enz','HX1','SnkCW')=  0;
fc.fx('NaOH','HX1','SnkCW')=  0;
fc.fx('NaSulp','HX1','SnkCW')=  0;
fc.fx('GluSol','HX1','SnkCW')=  0;
fc.fx('XylSol','HX1','SnkCW')=  0;

fc.fx('Cellulose','SrcEnz','MixEnzHyd')=  0;
fc.fx('Hemi','SrcEnz','MixEnzHyd')=  0;
fc.fx('Lignin','SrcEnz','MixEnzHyd')=  0;
fc.fx('Acetyl','SrcEnz','MixEnzHyd')=  0;
fc.fx('Phos','SrcEnz','MixEnzHyd')=  0;
fc.fx('Xylo','SrcEnz','MixEnzHyd')=  0;
fc.fx('Xylolig','SrcEnz','MixEnzHyd')=  0;
fc.fx('Gluc','SrcEnz','MixEnzHyd')=  0;
fc.fx('Glucolig','SrcEnz','MixEnzHyd')=  0;
fc.fx('Sucrose','SrcEnz','MixEnzHyd')=  0;
fc.fx('Furf','SrcEnz','MixEnzHyd')=  0;
fc.fx('HMF','SrcEnz','MixEnzHyd')=  0;
fc.fx('AceA','SrcEnz','MixEnzHyd')=  0;
*fc.fx('Water','SrcEnz','MixEnzHyd')=  0;
fc.fx('Acid','SrcEnz','MixEnzHyd')=  0;
fc.fx('ASL','SrcEnz','MixEnzHyd')=  0;
fc.fx('Min','SrcEnz','MixEnzHyd')=  0;
fc.fx('OrgAc','SrcEnz','MixEnzHyd')=  0;
fc.fx('Salts','SrcEnz','MixEnzHyd')=  0;
fc.fx('Soil','SrcEnz','MixEnzHyd')=  0;
fc.fx('Balance','SrcEnz','MixEnzHyd')=  0;
*fc.fx('Enz','SrcEnz','MixEnzHyd')=  0;
fc.fx('NaOH','SrcEnz','MixEnzHyd')=  0;
fc.fx('NaSulp','SrcEnz','MixEnzHyd')=  0;
fc.fx('GluSol','SrcEnz','MixEnzHyd')=  0;
fc.fx('XylSol','SrcEnz','MixEnzHyd')=  0;

fc.fx('Cellulose','SrcWater','MixEnzHyd')=  0;
fc.fx('Hemi','SrcWater','MixEnzHyd')=  0;
fc.fx('Lignin','SrcWater','MixEnzHyd')=  0;
```

```
fc.fx('Acetyl','SrcWater','MixEnzHyd')=  0;
fc.fx('Phos','SrcWater','MixEnzHyd')=  0;
fc.fx('Xylo','SrcWater','MixEnzHyd')=  0;
fc.fx('Xylolig','SrcWater','MixEnzHyd')=  0;
fc.fx('Gluc','SrcWater','MixEnzHyd')=  0;
fc.fx('Glucolig','SrcWater','MixEnzHyd')=  0;
fc.fx('Sucrose','SrcWater','MixEnzHyd')=  0;
fc.fx('Furf','SrcWater','MixEnzHyd')=  0;
fc.fx('HMF','SrcWater','MixEnzHyd')=  0;
fc.fx('AceA','SrcWater','MixEnzHyd')=  0;
*fc.fx('Water','SrcWater','MixEnzHyd')=  0;
fc.fx('Acid','SrcWater','MixEnzHyd')=  0;
fc.fx('ASL','SrcWater','MixEnzHyd')=  0;
fc.fx('Min','SrcWater','MixEnzHyd')=  0;
fc.fx('OrgAc','SrcWater','MixEnzHyd')=  0;
fc.fx('Salts','SrcWater','MixEnzHyd')=  0;
fc.fx('Soil','SrcWater','MixEnzHyd')=  0;
fc.fx('Balance','SrcWater','MixEnzHyd')=  0;
fc.fx('Enz','SrcWater','MixEnzHyd')=  0;
fc.fx('NaOH','SrcWater','MixEnzHyd')=  0;
fc.fx('NaSulp','SrcWater','MixEnzHyd')=  0;
fc.fx('GluSol','SrcWater','MixEnzHyd')=  0;
fc.fx('XylSol','SrcWater','MixEnzHyd')=  0;

Parameter MinMolFlowEnz /0.000001/ ;
fcmol.lo('Cellulose','SrcBag','MixSteamEx')=  MinMolFlowEnz  ;
fcmol.lo('Hemi','SrcBag','MixSteamEx')=  MinMolFlowEnz  ;
fcmol.lo('Lignin','SrcBag','MixSteamEx')=  MinMolFlowEnz  ;
fcmol.lo('Acetyl','SrcBag','MixSteamEx')=  MinMolFlowEnz  ;
*fcmol.lo('Phos','SrcBag','MixSteamEx')=  MinMolFlowEnz  ;
fcmol.lo('Xylo','SrcBag','MixSteamEx')=  0;
fcmol.lo('Xylolig','SrcBag','MixSteamEx')=  0;
fcmol.lo('Gluc','SrcBag','MixSteamEx')=  0;
fcmol.lo('Glucolig','SrcBag','MixSteamEx')=  0;
fcmol.lo('Sucrose','SrcBag','MixSteamEx')=  0;
fcmol.lo('Furf','SrcBag','MixSteamEx')=  0;
fcmol.lo('HMF','SrcBag','MixSteamEx')=  0;
fcmol.lo('AceA','SrcBag','MixSteamEx')=  0;
fcmol.lo('Water','SrcBag','MixSteamEx')= MinMolFlowEnz ;
fcmol.lo('Acid','SrcBag','MixSteamEx')=  0;
fcmol.lo('ASL','SrcBag','MixSteamEx')=  0;
fcmol.lo('Min','SrcBag','MixSteamEx')=  MinMolFlowEnz ;
fcmol.lo('OrgAc','SrcBag','MixSteamEx')=  MinMolFlowEnz  ;
fcmol.lo('Salts','SrcBag','MixSteamEx')=  MinMolFlowEnz  ;
fcmol.lo('Soil','SrcBag','MixSteamEx')=  MinMolFlowEnz  ;
fcmol.lo('Balance','SrcBag','MixSteamEx')=  0;
*++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
++++++++++++++++++++++++++++++++++
fc.lo('Water','SrcSteam','MixSteamEx')=  0.1;

fc.lo('Cellulose','MixSteamEx','SteamEx')=  0.1;
fc.lo('Hemi','MixSteamEx','SteamEx')=  0.1;
fc.lo('Lignin','MixSteamEx','SteamEx')=  0.1;
fc.lo('Acetyl','MixSteamEx','SteamEx')=  0.01;
*fc.lo('Phos','MixSteamEx','SteamEx')=  0.1;
fc.lo('Xylo','MixSteamEx','SteamEx')=  0;
fc.lo('Xylolig','MixSteamEx','SteamEx')=  0;
```

```
fc.lo('Gluc','MixSteamEx','SteamEx')=  0;
fc.lo('Glucolig','MixSteamEx','SteamEx')=  0;
fc.lo('Sucrose','MixSteamEx','SteamEx')=  0;
fc.lo('Furf','MixSteamEx','SteamEx')=  0;
fc.lo('HMF','MixSteamEx','SteamEx')=  0;
fc.lo('AceA','MixSteamEx','SteamEx')=  0;
fc.lo('Water','MixSteamEx','SteamEx')=  0.05;
fc.lo('Acid','MixSteamEx','SteamEx')=  0;
fc.lo('ASL','MixSteamEx','SteamEx')=  0;
fc.lo('Min','MixSteamEx','SteamEx')=  0.001;
fc.lo('OrgAc','MixSteamEx','SteamEx')=  0.001;
fc.lo('Salts','MixSteamEx','SteamEx')=  0.03;
fc.lo('Soil','MixSteamEx','SteamEx')=  0.001;
fc.lo('Balance','MixSteamEx','SteamEx')=  0;

fc.lo('Cellulose','SteamEx','FlsSteamEx')=  0.01;
fc.lo('Hemi','SteamEx','FlsSteamEx')=  0.01;
fc.lo('Lignin','SteamEx','FlsSteamEx')=  0.01;
fc.lo('Acetyl','SteamEx','FlsSteamEx')=  0.001;
*fc.lo('Phos','SteamEx','FlsSteamEx')=  0.1;
fc.lo('Xylo','SteamEx','FlsSteamEx')=  0.01;
fc.lo('Xylolig','SteamEx','FlsSteamEx')=  0.01;
fc.lo('Gluc','SteamEx','FlsSteamEx')=  0.01;
fc.lo('Glucolig','SteamEx','FlsSteamEx')=  0.001;
fc.lo('Sucrose','SteamEx','FlsSteamEx')=  0;
fc.lo('Furf','SteamEx','FlsSteamEx')=  0.01;
fc.lo('HMF','SteamEx','FlsSteamEx')=  0.01;
fc.lo('AceA','SteamEx','FlsSteamEx')=  0.01;
fc.lo('Water','SteamEx','FlsSteamEx')=  0.005;
fc.lo('Acid','SteamEx','FlsSteamEx')=  0;
fc.lo('ASL','SteamEx','FlsSteamEx')=  0.001;
fc.lo('Min','SteamEx','FlsSteamEx')=  0.001;
fc.lo('OrgAc','SteamEx','FlsSteamEx')=  0.001;
fc.lo('Salts','SteamEx','FlsSteamEx')=  0.03;
fc.lo('Soil','SteamEx','FlsSteamEx')=  0.001;
fc.lo('Balance','SteamEx','FlsSteamEx')=  0;

fc.lo('Cellulose','FlsSteamEx','SnkVapFlsh3')=  0;
fc.lo('Hemi','FlsSteamEx','SnkVapFlsh3')=  0;
fc.lo('Lignin','FlsSteamEx','SnkVapFlsh3')=  0;
fc.lo('Acetyl','FlsSteamEx','SnkVapFlsh3')=  0;
*fc.lo('Phos','FlsSteamEx','SnkVapFlsh3')=  0;
fc.lo('Xylo','FlsSteamEx','SnkVapFlsh3')=  0.0000001;
fc.lo('Xylolig','FlsSteamEx','SnkVapFlsh3')=  0.0000001;
fc.lo('Gluc','FlsSteamEx','SnkVapFlsh3')=  0;
fc.lo('Glucolig','FlsSteamEx','SnkVapFlsh3')=  0;
fc.lo('Sucrose','FlsSteamEx','SnkVapFlsh3')=  0;
fc.lo('Furf','FlsSteamEx','SnkVapFlsh3')=  0.0000001;
fc.lo('HMF','FlsSteamEx','SnkVapFlsh3')=  0.0000001;
fc.lo('AceA','FlsSteamEx','SnkVapFlsh3')=  0.0000001;
fc.lo('Water','FlsSteamEx','SnkVapFlsh3')= 0.1;
fc.lo('Acid','FlsSteamEx','SnkVapFlsh3')=  0;
fc.lo('ASL','FlsSteamEx','SnkVapFlsh3')=  0;
fc.lo('Min','FlsSteamEx','SnkVapFlsh3')=  0;
fc.lo('OrgAc','FlsSteamEx','SnkVapFlsh3')=  0.0000001;
fc.lo('Salts','FlsSteamEx','SnkVapFlsh3')=  0;
fc.lo('Soil','FlsSteamEx','SnkVapFlsh3')=  0;
```

```
fc.lo('Balance','FlsSteamEx','SnkVapFlsh3')=   0;

fc.lo('Cellulose','FlsSteamEx','FiltSteamEx')=   0.01;
fc.lo('Hemi','FlsSteamEx','FiltSteamEx')=    0.01;
*fc.lo('Lignin','FlsSteamEx','FiltSteamEx')=   0.01;
*fc.lo('Acetyl','FlsSteamEx','FiltSteamEx')=   0.0001;
*fc.lo('Phos','FlsSteamEx','FiltSteamEx')=   0.01;
fc.lo('Xylo','FlsSteamEx','FiltSteamEx')=   0.01;
fc.lo('Xylolig','FlsSteamEx','FiltSteamEx')=  0.01;
fc.lo('Gluc','FlsSteamEx','FiltSteamEx')=   0.01;
fc.lo('Glucolig','FlsSteamEx','FiltSteamEx')=  0.001;
fc.lo('Sucrose','FlsSteamEx','FiltSteamEx')=   0;
fc.lo('Furf','FlsSteamEx','FiltSteamEx')=   0.001;
fc.lo('HMF','FlsSteamEx','FiltSteamEx')= 0.01;
fc.lo('AceA','FlsSteamEx','FiltSteamEx')=   0.01;
fc.lo('Water','FlsSteamEx','FiltSteamEx')=0.01;
fc.lo('Acid','FlsSteamEx','FiltSteamEx')=   0;
fc.lo('ASL','FlsSteamEx','FiltSteamEx')=  0.001;
fc.lo('Min','FlsSteamEx','FiltSteamEx')=    0.001;
fc.lo('OrgAc','FlsSteamEx','FiltSteamEx')=  0.001;
fc.lo('Salts','FlsSteamEx','FiltSteamEx')=    0.01;
*fc.lo('Soil','FlsSteamEx','FiltSteamEx')=   0.0001;
fc.lo('Balance','FlsSteamEx','FiltSteamEx')=   0;

fc.lo('Cellulose','FiltSteamEx','SnkC5')=    0.0001;
fc.lo('Hemi','FiltSteamEx','SnkC5')=    0.0001;
fc.lo('Lignin','FiltSteamEx','SnkC5')=    0.0001;
fc.lo('Acetyl','FiltSteamEx','SnkC5')=     0.00001;
*fc.lo('Phos','FiltSteamEx','SnkC5')=    0.0001;
fc.lo('Xylo','FiltSteamEx','SnkC5')=   0.001;
fc.lo('Xylolig','FiltSteamEx','SnkC5')= 0.001;
fc.lo('Gluc','FiltSteamEx','SnkC5')=   0.001;
fc.lo('Glucolig','FiltSteamEx','SnkC5')= 0.001;
fc.lo('Sucrose','FiltSteamEx','SnkC5')=   0;
fc.lo('Furf','FiltSteamEx','SnkC5')=   0.0001;
fc.lo('HMF','FiltSteamEx','SnkC5')=  0.0001;
fc.lo('AceA','FiltSteamEx','SnkC5')=  0.0001;
fc.lo('Water','FiltSteamEx','SnkC5')= 0.1;
fc.lo('Acid','FiltSteamEx','SnkC5')=   0;
fc.lo('ASL','FiltSteamEx','SnkC5')=   0.001;
fc.lo('Min','FiltSteamEx','SnkC5')=   0.0001;
fc.lo('OrgAc','FiltSteamEx','SnkC5')=   0.00001;
fc.lo('Salts','FiltSteamEx','SnkC5')=    0.0001;
fc.lo('Soil','FiltSteamEx','SnkC5')=    0.000001;
fc.lo('Balance','FiltSteamEx','SnkC5')=   0;

fc.lo('Cellulose','FiltSteamEx','MixDelig')=   0.01;
fc.lo('Hemi','FiltSteamEx','MixDelig')=    0.01;
fc.lo('Lignin','FiltSteamEx','MixDelig')=    0.01;
fc.lo('Acetyl','FiltSteamEx','MixDelig')=     0.0001;
*fc.lo('Phos','FiltSteamEx','MixDelig')=   0.1;
fc.lo('Xylo','FiltSteamEx','MixDelig')=   0.001;
fc.lo('Xylolig','FiltSteamEx','MixDelig')= 0;
fc.lo('Gluc','FiltSteamEx','MixDelig')=   0.001;
fc.lo('Glucolig','FiltSteamEx','MixDelig')= 0;
fc.lo('Sucrose','FiltSteamEx','MixDelig')=   0;
fc.lo('Furf','FiltSteamEx','MixDelig')=  0.001;
```

```
fc.lo('HMF','FiltSteamEx','MixDelig')=  0.001;
fc.lo('AceA','FiltSteamEx','MixDelig')= 0.001;
fc.lo('Water','FiltSteamEx','MixDelig')= 0.001;
fc.lo('Acid','FiltSteamEx','MixDelig')=   0;
fc.lo('ASL','FiltSteamEx','MixDelig')=   0.0001;
fc.lo('Min','FiltSteamEx','MixDelig')=    0.0001;
fc.lo('OrgAc','FiltSteamEx','MixDelig')=   0.001;
fc.lo('Salts','FiltSteamEx','MixDelig')=    0.001;
fc.lo('Soil','FiltSteamEx','MixDelig')=    0.001;
fc.lo('Balance','FiltSteamEx','MixDelig')=   0;
*+++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
fcmol.lo('Water','SrcSteam','MixSteamEx')=  MinMolFlowEnz  ;

fcmol.lo('Cellulose','MixSteamEx','SteamEx')=  MinMolFlowEnz  ;
fcmol.lo('Hemi','MixSteamEx','SteamEx')=   MinMolFlowEnz ;
fcmol.lo('Lignin','MixSteamEx','SteamEx')=   MinMolFlowEnz;
fcmol.lo('Acetyl','MixSteamEx','SteamEx')=   MinMolFlowEnz;
*fcmol.lo('Phos','MixSteamEx','SteamEx')=   MinMolFlowEnz;
fcmol.lo('Xylo','MixSteamEx','SteamEx')=   0;
fcmol.lo('Xylolig','MixSteamEx','SteamEx')=   0;
fcmol.lo('Gluc','MixSteamEx','SteamEx')=   0;
fcmol.lo('Glucolig','MixSteamEx','SteamEx')=   0;
fcmol.lo('Sucrose','MixSteamEx','SteamEx')=   0;
fcmol.lo('Furf','MixSteamEx','SteamEx')=   0;
fcmol.lo('HMF','MixSteamEx','SteamEx')=   0;
fcmol.lo('AceA','MixSteamEx','SteamEx')=   0;
fcmol.lo('Water','MixSteamEx','SteamEx')= MinMolFlowEnz;
fcmol.lo('Acid','MixSteamEx','SteamEx')=   0;
fcmol.lo('ASL','MixSteamEx','SteamEx')=   0;
fcmol.lo('Min','MixSteamEx','SteamEx')=   MinMolFlowEnz;
fcmol.lo('OrgAc','MixSteamEx','SteamEx')=  MinMolFlowEnz;
fcmol.lo('Salts','MixSteamEx','SteamEx')= MinMolFlowEnz;
fcmol.lo('Soil','MixSteamEx','SteamEx')=   MinMolFlowEnz;
fcmol.lo('Balance','MixSteamEx','SteamEx')=   0;

fcmol.lo('Cellulose','SteamEx','FlsSteamEx')=  MinMolFlowEnz;
fcmol.lo('Hemi','SteamEx','FlsSteamEx')=  MinMolFlowEnz;
fcmol.lo('Lignin','SteamEx','FlsSteamEx')=  MinMolFlowEnz;
fcmol.lo('Acetyl','SteamEx','FlsSteamEx')=   MinMolFlowEnz;
*fcmol.lo('Phos','SteamEx','FlsSteamEx')=  MinMolFlowEnz;
fcmol.lo('Xylo','SteamEx','FlsSteamEx')=   MinMolFlowEnz;
fcmol.lo('Xylolig','SteamEx','FlsSteamEx')=   MinMolFlowEnz;
fcmol.lo('Gluc','SteamEx','FlsSteamEx')=   MinMolFlowEnz;
fcmol.lo('Glucolig','SteamEx','FlsSteamEx')=  MinMolFlowEnz;
fcmol.lo('Sucrose','SteamEx','FlsSteamEx')=   0;
fcmol.lo('Furf','SteamEx','FlsSteamEx')=   MinMolFlowEnz;
fcmol.lo('HMF','SteamEx','FlsSteamEx')=MinMolFlowEnz;
fcmol.lo('AceA','SteamEx','FlsSteamEx')=  MinMolFlowEnz;
fcmol.lo('Water','SteamEx','FlsSteamEx')= MinMolFlowEnz;
fcmol.lo('Acid','SteamEx','FlsSteamEx')=   0;
fcmol.lo('ASL','SteamEx','FlsSteamEx')=   MinMolFlowEnz;
fcmol.lo('Min','SteamEx','FlsSteamEx')= MinMolFlowEnz;
fcmol.lo('OrgAc','SteamEx','FlsSteamEx')=   MinMolFlowEnz;
fcmol.lo('Salts','SteamEx','FlsSteamEx')=  MinMolFlowEnz;
fcmol.lo('Soil','SteamEx','FlsSteamEx')=  MinMolFlowEnz;
fcmol.lo('Balance','SteamEx','FlsSteamEx')=   0;
```

```
fcmol.lo('Cellulose','FlsSteamEx','SnkVapFlsh3')=   0;
fcmol.lo('Hemi','FlsSteamEx','SnkVapFlsh3')=    0;
fcmol.lo('Lignin','FlsSteamEx','SnkVapFlsh3')=    0;
fcmol.lo('Acetyl','FlsSteamEx','SnkVapFlsh3')=    0;
*fcmol.lo('Phos','FlsSteamEx','SnkVapFlsh3')=   0;
*fcmol.lo('Xylo','FlsSteamEx','SnkVapFlsh3')=  0.0000000001;
*fcmol.lo('Xylolig','FlsSteamEx','SnkVapFlsh3')= 0.00000000001;
fcmol.lo('Gluc','FlsSteamEx','SnkVapFlsh3')=   0;
fcmol.lo('Glucolig','FlsSteamEx','SnkVapFlsh3')=  0;
fcmol.lo('Sucrose','FlsSteamEx','SnkVapFlsh3')=   0;
fcmol.lo('Furf','FlsSteamEx','SnkVapFlsh3')=  MinMolFlowEnz;
fcmol.lo('HMF','FlsSteamEx','SnkVapFlsh3')=  0.0000000001;
*$ontext
fcmol.lo('AceA','FlsSteamEx','SnkVapFlsh3')=  MinMolFlowEnz;
fcmol.lo('Water','FlsSteamEx','SnkVapFlsh3')= MinMolFlowEnz;
fcmol.lo('Acid','FlsSteamEx','SnkVapFlsh3')=   0;
fcmol.lo('ASL','FlsSteamEx','SnkVapFlsh3')=   0;
fcmol.lo('Min','FlsSteamEx','SnkVapFlsh3')=    0;
fcmol.lo('OrgAc','FlsSteamEx','SnkVapFlsh3')=    0;
fcmol.lo('Salts','FlsSteamEx','SnkVapFlsh3')=    0;
fcmol.lo('Soil','FlsSteamEx','SnkVapFlsh3')=    0;
fcmol.lo('Balance','FlsSteamEx','SnkVapFlsh3')=   0;

fcmol.lo('Cellulose','FlsSteamEx','FiltSteamEx')=  MinMolFlowEnz;
fcmol.lo('Hemi','FlsSteamEx','FiltSteamEx')=   MinMolFlowEnz;
fcmol.lo('Lignin','FlsSteamEx','FiltSteamEx')=  MinMolFlowEnz;
fcmol.lo('Acetyl','FlsSteamEx','FiltSteamEx')=  MinMolFlowEnz;
*fcmol.lo('Phos','FlsSteamEx','FiltSteamEx')=  MinMolFlowEnz;
fcmol.lo('Xylo','FlsSteamEx','FiltSteamEx')=   MinMolFlowEnz;
fcmol.lo('Xylolig','FlsSteamEx','FiltSteamEx')=  MinMolFlowEnz;
fcmol.lo('Gluc','FlsSteamEx','FiltSteamEx')=  MinMolFlowEnz;
fcmol.lo('Glucolig','FlsSteamEx','FiltSteamEx')=  MinMolFlowEnz;
fcmol.lo('Sucrose','FlsSteamEx','FiltSteamEx')=   0;
fcmol.lo('Furf','FlsSteamEx','FiltSteamEx')=   MinMolFlowEnz;
fcmol.lo('HMF','FlsSteamEx','FiltSteamEx')= MinMolFlowEnz;
fcmol.lo('AceA','FlsSteamEx','FiltSteamEx')=  MinMolFlowEnz;
fcmol.lo('Water','FlsSteamEx','FiltSteamEx')=MinMolFlowEnz;
fcmol.lo('Acid','FlsSteamEx','FiltSteamEx')=   0;
fcmol.lo('ASL','FlsSteamEx','FiltSteamEx')=  MinMolFlowEnz;
fcmol.lo('Min','FlsSteamEx','FiltSteamEx')=    MinMolFlowEnz;
fcmol.lo('OrgAc','FlsSteamEx','FiltSteamEx')=  MinMolFlowEnz;
fcmol.lo('Salts','FlsSteamEx','FiltSteamEx')=   MinMolFlowEnz;
fcmol.lo('Soil','FlsSteamEx','FiltSteamEx')=  MinMolFlowEnz;
fcmol.lo('Balance','FlsSteamEx','FiltSteamEx')=   0;

fcmol.lo('Cellulose','FiltSteamEx','SnkC5')=    0.000001   ;
fcmol.lo('Hemi','FiltSteamEx','SnkC5')=     0.000001 ;
fcmol.lo('Lignin','FiltSteamEx','SnkC5')=   0.000001   ;
fcmol.lo('Acetyl','FiltSteamEx','SnkC5')=    0.000001   ;
*fcmol.lo('Phos','FiltSteamEx','SnkC5')=    0.000001   ;
fcmol.lo('Xylo','FiltSteamEx','SnkC5')=    MinMolFlowEnz;
fcmol.lo('Xylolig','FiltSteamEx','SnkC5')=  MinMolFlowEnz;
fcmol.lo('Gluc','FiltSteamEx','SnkC5')=    MinMolFlowEnz;
fcmol.lo('Glucolig','FiltSteamEx','SnkC5')= MinMolFlowEnz;
fcmol.lo('Sucrose','FiltSteamEx','SnkC5')=   0;
fcmol.lo('Furf','FiltSteamEx','SnkC5')=    MinMolFlowEnz;
fcmol.lo('HMF','FiltSteamEx','SnkC5')=   MinMolFlowEnz;
```

```
fcmol.lo('AceA','FiltSteamEx','SnkC5')=   MinMolFlowEnz;
fcmol.lo('Water','FiltSteamEx','SnkC5')=  MinMolFlowEnz;
fcmol.lo('Acid','FiltSteamEx','SnkC5')=   0;
fcmol.lo('ASL','FiltSteamEx','SnkC5')=    MinMolFlowEnz;
fcmol.lo('Min','FiltSteamEx','SnkC5')=   MinMolFlowEnz;
fcmol.lo('OrgAc','FiltSteamEx','SnkC5')=   MinMolFlowEnz;
fcmol.lo('Salts','FiltSteamEx','SnkC5')=    MinMolFlowEnz;
*fcmol.lo('Soil','FiltSteamEx','SnkC5')=   MinMolFlowEnz;
fcmol.lo('Balance','FiltSteamEx','SnkC5')=   0;

fcmol.lo('Cellulose','FiltSteamEx','MixDelig')=   MinMolFlowEnz;
fcmol.lo('Hemi','FiltSteamEx','MixDelig')=    MinMolFlowEnz;
fcmol.lo('Lignin','FiltSteamEx','MixDelig')=    MinMolFlowEnz;
fcmol.lo('Acetyl','FiltSteamEx','MixDelig')=     MinMolFlowEnz;
*fcmol.lo('Phos','FiltSteamEx','MixDelig')=    MinMolFlowEnz;
fcmol.lo('Xylo','FiltSteamEx','MixDelig')=    MinMolFlowEnz;
fcmol.lo('Xylolig','FiltSteamEx','MixDelig')=  MinMolFlowEnz;
fcmol.lo('Gluc','FiltSteamEx','MixDelig')=    MinMolFlowEnz;
fcmol.lo('Glucolig','FiltSteamEx','MixDelig')=  MinMolFlowEnz;
fcmol.lo('Sucrose','FiltSteamEx','MixDelig')=   0;
fcmol.lo('Furf','FiltSteamEx','MixDelig')=   MinMolFlowEnz;
fcmol.lo('HMF','FiltSteamEx','MixDelig')=  MinMolFlowEnz;
fcmol.lo('AceA','FiltSteamEx','MixDelig')= MinMolFlowEnz;
fcmol.lo('Water','FiltSteamEx','MixDelig')= MinMolFlowEnz;
fcmol.lo('Acid','FiltSteamEx','MixDelig')=   0;
fcmol.lo('ASL','FiltSteamEx','MixDelig')=   MinMolFlowEnz;
fcmol.lo('Min','FiltSteamEx','MixDelig')=    MinMolFlowEnz;
fcmol.lo('OrgAc','FiltSteamEx','MixDelig')=    MinMolFlowEnz;
fcmol.lo('Salts','FiltSteamEx','MixDelig')=   MinMolFlowEnz;
fcmol.lo('Soil','FiltSteamEx','MixDelig')=    MinMolFlowEnz;
fcmol.lo('Balance','FiltSteamEx','MixDelig')=   0;

F.up('SrcBal','SteamEx')=   0.05;
F.lo('SrcSteam','MixSteamEx')=   0.05;
*-------------------------------------------------------------------------------------------------------------------
*Delig
fc.lo('Water','SrcWater','MixDelig')=  1;
fc.lo('Water','SrcSteam','MixDelig')=  0.001;
fc.lo('Water','SrcDelig','MixDelig')=  0;

fc.lo('NaOH','SrcDelig','MixDelig')= 0.1;
fc.lo('NaOH','MixDelig','HXDelig')=  0.1;
fc.lo('NaOH','HXDelig','Delig')=  0.1;
fc.lo('NaOH','Delig','FiltDelig')=  0.1;
*fc.lo('NaOH','FiltDelig','SnkDelig')=  1;

fc.fx('Cellulose','SrcDelig','MixDelig')=   0;
fc.fx('Hemi','SrcDelig','MixDelig')=  0;
fc.fx('Lignin','SrcDelig','MixDelig')=  0;
fc.fx('Acetyl','SrcDelig','MixDelig')=   0;
fc.fx('Phos','SrcDelig','MixDelig')=  0;
fc.fx('Xylo','SrcDelig','MixDelig')=   0;
fc.fx('Xylolig','SrcDelig','MixDelig')=   0;
fc.fx('Gluc','SrcDelig','MixDelig')=   0;
fc.fx('Glucolig','SrcDelig','MixDelig')=   0;
fc.fx('Sucrose','SrcDelig','MixDelig')=  0;
fc.fx('Furf','SrcDelig','MixDelig')=   0;
```

```
fc.fx('HMF','SrcDelig','MixDelig')=  0;
fc.fx('AceA','SrcDelig','MixDelig')=  0;
*fc.fx('Water','SrcDelig','MixDelig')=  5;
fc.fx('Acid','SrcDelig','MixDelig')=  0;
fc.fx('ASL','SrcDelig','MixDelig')=  0;
fc.fx('Min','SrcDelig','MixDelig')=  0;
fc.fx('OrgAc','SrcDelig','MixDelig')=  0;
fc.fx('Salts','SrcDelig','MixDelig')=  0;
fc.fx('Soil','SrcDelig','MixDelig')=  0;
fc.fx('Balance','SrcDelig','MixDelig')=  0;
fc.fx('Enz','SrcDelig','MixDelig')=  0;
fc.fx('NaSulp','SrcDelig','MixDelig')=  0;
fc.fx('GluSol','SrcDelig','MixDelig')=  0;
fc.fx('XylSol','SrcDelig','MixDelig')=  0;

fc.fx('Cellulose','SrcSteam','HXDelig')=  0;
fc.fx('Hemi','SrcSteam','HXDelig')=  0;
fc.fx('Lignin','SrcSteam','HXDelig')=  0;
fc.fx('Acetyl','SrcSteam','HXDelig')=  0;
fc.fx('Phos','SrcSteam','HXDelig')=  0;
fc.fx('Xylo','SrcSteam','HXDelig')=  0;
fc.fx('Xylolig','SrcSteam','HXDelig')=  0;
fc.fx('Gluc','SrcSteam','HXDelig')=  0;
fc.fx('Glucolig','SrcSteam','HXDelig')=  0;
fc.fx('Sucrose','SrcSteam','HXDelig')=  0;
fc.fx('Furf','SrcSteam','HXDelig')=  0;
fc.fx('HMF','SrcSteam','HXDelig')=  0;
fc.fx('AceA','SrcSteam','HXDelig')=  0;
*fc.fx('Water','SrcSteam','HXDelig')=  5;
fc.fx('Acid','SrcSteam','HXDelig')=  0;
fc.fx('ASL','SrcSteam','HXDelig')=  0;
fc.fx('Min','SrcSteam','HXDelig')=  0;
fc.fx('OrgAc','SrcSteam','HXDelig')=  0;
fc.fx('Salts','SrcSteam','HXDelig')=  0;
fc.fx('Soil','SrcSteam','HXDelig')=  0;
fc.fx('Balance','SrcSteam','HXDelig')=  0;
fc.fx('Enz','SrcSteam','HXDelig')=  0;
fc.fx('NaSulp','SrcSteam','HXDelig')=  0;
fc.fx('GluSol','SrcSteam','HXDelig')=  0;
fc.fx('XylSol','SrcSteam','HXDelig')=  0;
fc.fx('NaOH','SrcSteam','HXDelig')=  0;

fc.fx('Cellulose','HXDelig','SnkSteam')=  0;
fc.fx('Hemi','HXDelig','SnkSteam')=  0;
fc.fx('Lignin','HXDelig','SnkSteam')=  0;
fc.fx('Acetyl','HXDelig','SnkSteam')=  0;
fc.fx('Phos','HXDelig','SnkSteam')=  0;
fc.fx('Xylo','HXDelig','SnkSteam')=  0;
fc.fx('Xylolig','HXDelig','SnkSteam')=  0;
fc.fx('Gluc','HXDelig','SnkSteam')=  0;
fc.fx('Glucolig','HXDelig','SnkSteam')=  0;
fc.fx('Sucrose','HXDelig','SnkSteam')=  0;
fc.fx('Furf','HXDelig','SnkSteam')=  0;
fc.fx('HMF','HXDelig','SnkSteam')=  0;
fc.fx('AceA','HXDelig','SnkSteam')=  0;
*fc.fx('Water','HXDelig','SnkSteam')=  5;
fc.fx('Acid','HXDelig','SnkSteam')=  0;
```

```
fc.fx('ASL','HXDelig','SnkSteam')=   0;
fc.fx('Min','HXDelig','SnkSteam')=   0;
fc.fx('OrgAc','HXDelig','SnkSteam')=  0;
fc.fx('Salts','HXDelig','SnkSteam')=   0;
fc.fx('Soil','HXDelig','SnkSteam')=  0;
fc.fx('Balance','HXDelig','SnkSteam')=   0;
fc.fx('Enz','HXDelig','SnkSteam')=   0;
fc.fx('NaSulp','HXDelig','SnkSteam')=   0;
fc.fx('GluSol','HXDelig','SnkSteam')=   0;
fc.fx('XylSol','HXDelig','SnkSteam')=   0;
fc.fx('NaOH','HXDelig','SnkSteam')=   0;

fc.lo('Cellulose','MixDelig','HXDelig')=   0.01;
fc.lo('Hemi','MixDelig','HXDelig')=   0.01;
fc.lo('Lignin','MixDelig','HXDelig')=   0.01;
fc.lo('Acetyl','MixDelig','HXDelig')=   0.001;
fc.lo('Phos','MixDelig','HXDelig')=   0.00001;
fc.lo('Xylo','MixDelig','HXDelig')=   0.0001;
fc.lo('Xylolig','MixDelig','HXDelig')=   0;
fc.lo('Gluc','MixDelig','HXDelig')=    0.0001;
fc.lo('Glucolig','MixDelig','HXDelig')=   0;
fc.lo('Sucrose','MixDelig','HXDelig')=   0;
fc.lo('Furf','MixDelig','HXDelig')=    0.00001;
fc.lo('HMF','MixDelig','HXDelig')=    0.00001;
fc.lo('AceA','MixDelig','HXDelig')=     0.0001;
fc.lo('Water','MixDelig','HXDelig')=  0.001;
fc.lo('Acid','MixDelig','HXDelig')=    0;
fc.lo('ASL','MixDelig','HXDelig')=    0.0001;
fc.lo('Min','MixDelig','HXDelig')=   0.0001;
fc.lo('OrgAc','MixDelig','HXDelig')=    0.0001;
fc.lo('Salts','MixDelig','HXDelig')=   0.003;
fc.lo('Soil','MixDelig','HXDelig')=   0.0001;
fc.lo('Balance','MixDelig','HXDelig')=   0;
fc.lo('Enz','MixDelig','HXDelig')=   0;

fc.lo('Cellulose','HXDelig','Delig')=   0.01;
fc.lo('Hemi','HXDelig','Delig')=   0.01;
fc.lo('Lignin','HXDelig','Delig')=   0.01;
fc.lo('Acetyl','HXDelig','Delig')=   0.001;
fc.lo('Phos','HXDelig','Delig')=   0.00001;
fc.lo('Xylo','HXDelig','Delig')=   0.0001;
fc.lo('Xylolig','HXDelig','Delig')=   0;
fc.lo('Gluc','HXDelig','Delig')=    0.0001;
fc.lo('Glucolig','HXDelig','Delig')=   0;
fc.lo('Sucrose','HXDelig','Delig')=   0;
fc.lo('Furf','HXDelig','Delig')=    0.00001;
fc.lo('HMF','HXDelig','Delig')=    0.00001;
fc.lo('AceA','HXDelig','Delig')=     0.0001;
fc.lo('Water','HXDelig','Delig')=  0.001;
fc.lo('Acid','HXDelig','Delig')=     0;
fc.lo('ASL','HXDelig','Delig')=    0.0001;
fc.lo('Min','HXDelig','Delig')=   0.0001;
fc.lo('OrgAc','HXDelig','Delig')=    0.0001;
fc.lo('Salts','HXDelig','Delig')=   0.003;
fc.lo('Soil','HXDelig','Delig')=   0.0001;
fc.lo('Balance','HXDelig','Delig')=   0;
fc.lo('Enz','HXDelig','Delig')=   0;
```

```
fc.lo('Cellulose','Delig','FiltDelig')=   0.5;
fc.lo('Hemi','Delig','FiltDelig')=   0.01;
fc.lo('Lignin','Delig','FiltDelig')=   0.01;
fc.lo('Acetyl','Delig','FiltDelig')=   0.0001;
fc.lo('Phos','Delig','FiltDelig')=   0.00001;
fc.lo('Xylo','Delig','FiltDelig')=   0.0001;
fc.lo('Xylolig','Delig','FiltDelig')=   0;
fc.lo('Gluc','Delig','FiltDelig')=    0.00001;
fc.lo('Glucolig','Delig','FiltDelig')=   0;
fc.lo('Sucrose','Delig','FiltDelig')=   0;
fc.lo('Furf','Delig','FiltDelig')=    0.00001;
fc.lo('HMF','Delig','FiltDelig')=    0.00001;
fc.lo('AceA','Delig','FiltDelig')=    0.0001;
fc.lo('Water','Delig','FiltDelig')=  0.001;
fc.lo('Acid','Delig','FiltDelig')=    0;
fc.lo('ASL','Delig','FiltDelig')=    0.0001;
fc.lo('Min','Delig','FiltDelig')=   0.0001;
fc.lo('OrgAc','Delig','FiltDelig')=    0.0001;
fc.lo('Salts','Delig','FiltDelig')=   0.003;
fc.lo('Soil','Delig','FiltDelig')=   0.0001;
fc.lo('Balance','Delig','FiltDelig')=   0;
fc.lo('Enz','Delig','FiltDelig')=   0;
fc.lo('XylSol','Delig','FiltDelig')=   0.01;
fc.lo('GluSol','Delig','FiltDelig')=   0.01;

fc.lo('Cellulose','FiltDelig','HX1')=   0.5;
fc.lo('Hemi','FiltDelig','HX1')=   0.01;
fc.lo('Lignin','FiltDelig','HX1')=   0.01;
fc.lo('Acetyl','FiltDelig','HX1')=   0.0001;
*fc.lo('Phos','FiltDelig','SnkDelig')=   0.0001;
fc.lo('Xylo','FiltDelig','SnkDelig')=   0.0001;
fc.lo('Xylolig','FiltDelig','SnkDelig')=   0;
fc.lo('Gluc','FiltDelig','SnkDelig')=    0.00001;
fc.lo('Glucolig','FiltDelig','SnkDelig')=   0;
fc.lo('Sucrose','FiltDelig','SnkDelig')=   0;
fc.lo('Furf','FiltDelig','SnkDelig')=    0.00001;
fc.lo('HMF','FiltDelig','SnkDelig')=    0.00001;
fc.lo('AceA','FiltDelig','SnkDelig')=    0.0001;
fc.lo('Water','FiltDelig','SnkDelig')=  0.001;
fc.lo('Acid','FiltDelig','SnkDelig')=    0;
fc.lo('ASL','FiltDelig','SnkDelig')=    0.0001;
*fc.lo('Min','FiltDelig','HX1')=   0.0001;
fc.lo('OrgAc','FiltDelig','SnkDelig')=    0.0001;
*fc.lo('Salts','FiltDelig','HX1')=   0.003;
*fc.lo('Soil','FiltDelig','HX1')=   0.0001;
fc.lo('Balance','FiltDelig','SnkDelig')=   0;
fc.lo('Enz','FiltDelig','SnkDelig')=   0;
fc.lo('XylSol','FiltDelig','SnkDelig')=   0.01;
fc.lo('GluSol','FiltDelig','SnkDelig')=   0.01;
*-------------------------------------------------------------------------------------------------------------------
*EnzHyd
F.fx('SteamEx','MixEnzHyd') = 16.39166;
F.lo('SrcEnz','MixEnzHyd') = 0.001;
F.lo('SrcWater','MixEnzHyd') = 0.001;
F.lo('MixEnzHyd','EnzHyd') = 1;
F.lo('EnzHyd','FiltEnz') = 1;
```

```
F.l('SrcWater','MixEnzHyd') = 50;
F.l('SrcEnz','MixEnzHyd') = 1;
F.l('MixEnzHyd','EnzHyd') = 70;
F.l('EnzHyd','FiltEnz') = 70;

fc.lo('Water','SrcWater','MixEnzHyd')=  0.00001;
fc.lo('Water','SrcEnz','MixEnzHyd')=  0.00001;
fc.lo('Enz','SrcEnz','MixEnzHyd')=  0.0001;
fc.lo('Enz','MixEnzHyd','EnzHyd')=  0.0001;


*fc.lo('Cellulose','MixEnzHyd','EnzHyd')=   0.1;
*fc.lo('Hemi','MixEnzHyd','EnzHyd')=   0.1;
*fc.lo('Lignin','MixEnzHyd','EnzHyd')=   0.1;
*fc.lo('Acetyl','MixEnzHyd','EnzHyd')=   0.01;
*fc.lo('Phos','MixEnzHyd','EnzHyd')=   0.1;
*fc.lo('Xylo','MixEnzHyd','EnzHyd')=  0.0001;
*fc.lo('Xylolig','MixEnzHyd','EnzHyd')=   0.001;
*fc.lo('Gluc','MixEnzHyd','EnzHyd')=   0.001;
*fc.lo('Glucolig','MixEnzHyd','EnzHyd')=   0.001;
fc.lo('Sucrose','MixEnzHyd','EnzHyd')=   0;
*fc.lo('Furf','MixEnzHyd','EnzHyd')=   0.01;
*fc.lo('HMF','MixEnzHyd','EnzHyd')=   0.01;
*fc.lo('AceA','MixEnzHyd','EnzHyd')=   0.1;
fc.lo('Water','MixEnzHyd','EnzHyd')=  2;
fc.lo('Acid','MixEnzHyd','EnzHyd')=   0;
*fc.lo('ASL','MixEnzHyd','EnzHyd')=   0.01;
*fc.lo('Min','MixEnzHyd','EnzHyd')=   0.0001;
*fc.lo('OrgAc','MixEnzHyd','EnzHyd')=   0.0001;
*fc.lo('Salts','MixEnzHyd','EnzHyd')=   0.03;
*fc.lo('Soil','MixEnzHyd','EnzHyd')=   0.0001;
fc.lo('Balance','MixEnzHyd','EnzHyd')=   0;
fc.lo('Enz','MixEnzHyd','EnzHyd')=   0.0001;


*$ontext
*fc.lo('Cellulose','EnzHyd','FiltEnz')=   0.1;
*fc.lo('Hemi','EnzHyd','FiltEnz')=   0.1;
*fc.lo('Lignin','EnzHyd','FiltEnz')=   0.01;
*fc.lo('Acetyl','EnzHyd','FiltEnz')=   0.01;
*fc.lo('Phos','EnzHyd','FiltEnz')=   0.1;
*fc.lo('Xylo','EnzHyd','FiltEnz')=  0.01;
fc.lo('Xylolig','EnzHyd','FiltEnz')=   0;
*fc.lo('Gluc','EnzHyd','FiltEnz')=   0.1;
*fc.lo('Glucolig','EnzHyd','FiltEnz')=   0.0000001;
fc.lo('Sucrose','EnzHyd','FiltEnz')=   0;
*fc.lo('Furf','EnzHyd','FiltEnz')=   0.01;
*fc.lo('HMF','EnzHyd','FiltEnz')=   0.01;
*fc.lo('AceA','EnzHyd','FiltEnz')=   0.1;
fc.lo('Water','EnzHyd','FiltEnz')=  2;
fc.lo('Acid','EnzHyd','FiltEnz')=   0;
*fc.lo('ASL','EnzHyd','FiltEnz')=   0.01;
*fc.lo('Min','EnzHyd','FiltEnz')=   0.0001;
*fc.lo('OrgAc','EnzHyd','FiltEnz')=   0.0001;
*fc.lo('Salts','EnzHyd','FiltEnz')=   0.03;
*fc.lo('Soil','EnzHyd','FiltEnz')=   0.0001;
```

```
fc.lo('Balance','EnzHyd','FiltEnz')=   0;
fc.lo('Enz','EnzHyd','FiltEnz')=   0.0001;

fcmol.lo('Water','SrcWater','MixEnzHyd')=  MinMolFlowEnz;
fcmol.lo('Water','SrcEnz','MixEnzHyd')=  MinMolFlowEnz;
fcmol.lo('Enz','SrcEnz','MixEnzHyd')= MinMolFlowEnz;
fcmol.lo('Enz','MixEnzHyd','EnzHyd')=  MinMolFlowEnz;

*---------------------------------------------------------------------------------------------------------------------
*FIXING
*mass fractions
x.lo(J,unit,unit1)$Arc(unit,unit1)=0;
x.UP(J,unit,unit1)$Arc(unit,unit1)=1;
x.fx('Water','SrcSteam','MixSteamEx') = 1;
x.fx('Balance','SrcBal','SteamEx') = 1;
x.fx('Acid','SrcAcid','MixSteamEx')=pureAcid;
x.fx('Water','SrcAcid','MixSteamEx')=1-pureAcid;
x.fx('Water','SrcWater','FiltSteamEx')=1;

F.fx('SrcBag','MixSteamEx')= 15;

Tau.fx('SteamEx')=15;

x.fx('NaOH','SrcDelig','MixDelig')=pureNaOH  ;
x.fx('Water','SrcDelig','MixDelig')=1-pureNaOH    ;
x.fx('Water','SrcSteam','HXDelig')=1  ;
x.fx('Water','SrcWater','MixDelig')=1  ;
Tau.fx('Delig')=40;
WSRDelig.fx = 19;
NaOHWt.lo=0.25;
NaOHWt.up=1;

NaOHPurge.lo = 0;
NaOHPurge.up = 1;

x.fx('Water','SrcWater','MixEnzHyd')=1;
x.fx('Enz','SrcEnz','MixEnzHyd')=MassFracEnz;
x.fx('Water','SrcEnz','MixEnzHyd')=1-MassFracEnz;

*EnzHyd
Tau.fx('EnzHyd')=4320;

*Specifying heat consumption of certain units
Q.Fx(Mix)=0;
Q.Fx(Src)=0;
Q.Fx(Snk)=0;

*Specify power consumption for cerain units
W.fx('SteamEx')=0;
W.Fx(Mix)=0;
W.Fx(Src)=0;
W.Fx(Snk)=0;

newXEnzHyd.lo=0;
newXEnzHyd.up=1;

newX2EnzHyd.lo=0;
```

```
newX2EnzHyd.up=1;

YieldInc.lo=0;

EnzFiltSplit.lo=0.03;
EnzFiltSplit.up=0.3;

*-------------------------------------------------------------------------------------------------------------------------
*Temperature settings
Scalars
*Define temperatures in K
      T_amb         ambient temperature /303.15/
      dT_min        EMAT /5/
      T_steam_max   max steam temperature /573.15/
      T_SteamEx     Steam explosion temperature /463.15/
      T_SteamExAcid  Acid catalysed steam explosion temperature /423.15/
      T_CTBEFlshAcid  CTBE acid catalysed steam explosion flash temperature /374.005/
      T_delig       delignification temperature /393.15/
      T_EnzHyd      CTBE enzymatic hydrolysis temperature /323.15/   ;

*global temperature bounds
T.LO(unit,unit1)=T_amb;
T.UP(unit,unit1)=T_steam_max;

*Specifying temperatures
*Pretreatment
T.fx('SrcBag','MixSteamEx')=T_amb ;
T.fx('SteamEx','FlsSteamEx')= T_CTBEFlshAcid;
T.fx('FlsSteamEx','FiltSteamEx') = T_CTBEFlshAcid;
T.fx('FlsSteamEx','SnkVapFlsh3')= T_CTBEFlshAcid;
T.fx('SrcWater','FiltSteamEx')=T_amb ;
*Delig
T.fx('SrcWater','MixDelig')=T_amb;
T.fx('SrcDelig','MixDelig')=T_amb;
T.l('Delig','FiltDelig')=T_delig;
T.fx('HXDelig','Delig')=T_delig;
T.up('MixDelig','HXDelig')=T_delig;
T.fx('SrcWater','FiltDelig')=T_amb ;
*EnzHyd
T.fx('SrcWater','HX1')=T_amb ;
T.lo('HX1','MixEnzHyd')=T_amb+1 ;
T.up('HX1','MixEnzHyd')=T_delig ;
T.l('MixEnzHyd','EnzHyd')=T_EnzHyd ;
T.lo('MixEnzHyd','EnzHyd')=T_EnzHyd-15 ;
T.up('MixEnzHyd','EnzHyd')=T_EnzHyd-5 ;
T.fx('SrcWater','MixEnzHyd')=T_amb ;
T.fx('SrcEnz','MixEnzHyd')=T_amb ;
T.fx('EnzHyd','FiltEnz')=T_EnzHyd ;
T.fx('SrcWater','FiltEnz')=T_amb ;


*MixSteamEx
Equations
      MixSteamEx_1, MixSteamEx_2      ;

MixSteamEx_1(J)..
```

```
      fc(J,'MixSteamEx','SteamEx') =E=
fc(J,'SrcBag','MixSteamEx')+fc(J,'SrcSteam','MixSteamEx')+fc(J,'SrcAcid','MixSteamEx');

MixSteamEx_2(J)..
      fcmol(J,'MixSteamEx','SteamEx') =E=
fcmol(J,'SrcBag','MixSteamEx')+fcmol(J,'SrcSteam','MixSteamEx')+fcmol(J,'SrcAcid','MixSteamEx');

Equations BagIn, AcidIn,SteamIn,SteamBin,
      TSteamEx1,TSteamEx2;

BagIn(J)..
      x(J,'SrcBag','MixSteamEx') =E= x_SCB(J);
AcidIn..
      fc('Acid','SrcAcid','MixSteamEx')  =E=
F('SrcBag','MixSteamEx')*(0*steamExpChoice('1')+AcidRatio*steamExpChoice('2'));

SteamIn..
      F('SrcSteam','MixSteamEx') =E=
F('SrcBag','MixSteamEx')*(SteamRatio*steamExpChoice('1')+SteamRatioAcid*steamExpChoice('2'));
SteamBin..
       steamExpChoice('1')+ steamExpChoice('2')  =E= 1;

TSteamEx1..
      T('MixSteamEx','SteamEx')=e=T_SteamEx*steamExpChoice('1')+T_SteamExAcid*steamExpChoice('2');

TSteamEx2..
      T('MixSteamEx','SteamEx')=e=T('SrcSteam','MixSteamEx');

*=====================================================================================
*Steam Explosion unit as done in the VSB for 2nd gen Ind_Fut LCM
*=====================================================================================
*fractional conversion of key components
parameter  XsteamEx
/react1   0.005
 react2   0.03
 react3   0.015
 react4   0.3
 react5   0.3
 react6   0.1
 react7   0.1
 react8   0.7
 react9   0.5
 react10  0.5/;
parameter  XsteamExAcid
/react1   0.05
 react2   0.02
 react3   0.015
 react4   0.65
 react5   0.05
 react6   0.1
 react7   0.15
 react8   0.8
 react9   0.5
 react10  0.5/;

equations
       SteamExpMassBal mass balance,
```

```
        SteamExpInerts inerts,
        SteamExpInerts2,
        SteamExpBal,
        SteamExp1 cellulose* (solid) + H2O --> Glucose,
        SteamExp11 water overall balance,
        SteamExp12 cellulose overall balance,
        SteamExp2 cellulose* (solid) --> Glucolig,
        SteamExp3 cellulose* (solid)  --> HMF + 2H2O,
        SteamExp4 Hemi* (solid)+H2O --> Xylose ,
        SteamExp41 Hemi balance ,
        SteamExp5 Hemi* --> Xylolig,
        SteamExp6 Hemi* (solid) --> furfural+2H2O,
        SteamExp7 Lignan* (solid) --> ASL,
        SteamExp71 lignan balance,
        SteamExp8 Acetyl*  (solid) --> Acet-Ac,
        SteamExp81 Acetyl balance,
        SteamExp9 sucrose* +H2O --> 2 Glucose;

SteamExpMassBal.. F('MixSteamEx','SteamEx')=e=F('SteamEx','FlsSteamEx');

SteamExpBal..   fc('Balance','SrcBal','SteamEx')=e=fc('Balance','SteamEx','FlsSteamEx');

SteamExpInerts(i)..  fc(i,'MixSteamEx','SteamEx')=e=fc(i,'SteamEx','FlsSteamEx');
SteamExpInerts2(SteamExi)..  fc(SteamExi,'MixSteamEx','SteamEx')=e=fc(SteamExi,'SteamEx','FlsSteamEx');

SteamExp1..
fcmol('Cellulose','MixSteamEx','SteamEx')*(XsteamEx('react1')*steamExpChoice('1')+XsteamExAcid('react1')*st
eamExpChoice('2'))+

2*fcmol('sucrose','MixSteamEx','SteamEx')*(XsteamEx('react9')*steamExpChoice('1')+XsteamExAcid('react9')*
steamExpChoice('2'))
                =e= fcmol('Gluc','SteamEx','FlsSteamEx');

SteamExp11..fcmol('water','MixSteamEx','SteamEx')-
fcmol('Cellulose','MixSteamEx','SteamEx')*((XsteamEx('react1')*steamExpChoice('1')+XsteamExAcid('react1')*s
teamExpChoice('2'))
                                                -
(2*(XsteamEx('react3')*steamExpChoice('1')+XsteamExAcid('react3')*steamExpChoice('2'))))
                                -
fcmol('Hemi','MixSteamEx','SteamEx')*((XsteamEx('react4')*steamExpChoice('1')+XsteamExAcid('react4')*steam
ExpChoice('2'))
                                                -
(2*(XsteamEx('react6')*steamExpChoice('1')+XsteamExAcid('react6')*steamExpChoice('2'))))
                                -
fcmol('sucrose','MixSteamEx','SteamEx')*(XsteamEx('react9')*steamExpChoice('1')+XsteamExAcid('react9')*ste
amExpChoice('2'))

+(5*fcmol('sucrose','MixSteamEx','SteamEx')*(XsteamEx('react10')*steamExpChoice('1')+XsteamExAcid('react1
0')*steamExpChoice('2')))
        =e= fcmol('water','SteamEx','FlsSteamEx');

SteamExp12.. fcmol('Cellulose','MixSteamEx','SteamEx')*(1-
(XsteamEx('react1')*steamExpChoice('1')+XsteamExAcid('react1')*steamExpChoice('2'))
                                -
(XsteamEx('react3')*steamExpChoice('1')+XsteamExAcid('react3')*steamExpChoice('2'))
                                -
(XsteamEx('react2')*steamExpChoice('1')+XsteamExAcid('react2')*steamExpChoice('2')))
```

```
                =e= fcmol('Cellulose','SteamEx','FlsSteamEx');

SteamExp2..
fcmol('Cellulose','MixSteamEx','SteamEx')*(XsteamEx('react2')*steamExpChoice('1')+XsteamExAcid('react2')*st
eamExpChoice('2'))
                                =e= fcmol('glucolig','SteamEx','FlsSteamEx');

SteamExp3..
fcmol('Cellulose','MixSteamEx','SteamEx')*(XsteamEx('react3')*steamExpChoice('1')+XsteamExAcid('react3')*st
eamExpChoice('2'))

+(2*fcmol('sucrose','MixSteamEx','SteamEx')*(XsteamEx('react10')*steamExpChoice('1')+XsteamExAcid('react1
0')*steamExpChoice('2')))
                 =e= fcmol('hmf','SteamEx','FlsSteamEx');

SteamExp4..
fcmol('Hemi','MixSteamEx','SteamEx')*(XsteamEx('react4')*steamExpChoice('1')+XsteamExAcid('react4')*stea
mExpChoice('2'))
                =e= fcmol('Xylo','SteamEx','FlsSteamEx');

SteamExp41.. fcmol('Hemi','MixSteamEx','SteamEx')*(1-
(XsteamEx('react4')*steamExpChoice('1')+XsteamExAcid('react4')*steamExpChoice('2'))
                                -
(XsteamEx('react5')*steamExpChoice('1')+XsteamExAcid('react5')*steamExpChoice('2'))
                                -
(XsteamEx('react6')*steamExpChoice('1')+XsteamExAcid('react6')*steamExpChoice('2')))
          =e= fcmol('Hemi','SteamEx','FlsSteamEx');

SteamExp5..
fcmol('Hemi','MixSteamEx','SteamEx')*(XsteamEx('react5')*steamExpChoice('1')+XsteamExAcid('react5')*stea
mExpChoice('2'))
                             =e= fcmol('xylolig','SteamEx','FlsSteamEx');

SteamExp6..
fcmol('Hemi','MixSteamEx','SteamEx')*(XsteamEx('react6')*steamExpChoice('1')+XsteamExAcid('react6')*stea
mExpChoice('2'))
                             =e= fcmol('Furf','SteamEx','FlsSteamEx');

SteamExp7..
fcmol('lignin','MixSteamEx','SteamEx')*(XsteamEx('react7')*steamExpChoice('1')+XsteamExAcid('react7')*stea
mExpChoice('2'))
                            =e= fcmol('ASL','SteamEx','FlsSteamEx');

SteamExp71.. fcmol('lignin','MixSteamEx','SteamEx')*(1-
(XsteamEx('react7')*steamExpChoice('1')+XsteamExAcid('react7')*steamExpChoice('2')))
                            =e= fcmol('lignin','SteamEx','FlsSteamEx');

SteamExp8..
fcmol('Acetyl','MixSteamEx','SteamEx')*(XsteamEx('react8')*steamExpChoice('1')+XsteamExAcid('react8')*stea
mExpChoice('2'))
                            =e= fcmol('AceA','SteamEx','FlsSteamEx');

SteamExp81.. fcmol('Acetyl','MixSteamEx','SteamEx')*(1-
(XsteamEx('react8')*steamExpChoice('1')+XsteamExAcid('react8')*steamExpChoice('2')))
                            =e= fcmol('Acetyl','SteamEx','FlsSteamEx');
```

```
SteamExp9..fcmol('sucrose','MixSteamEx','SteamEx')*(1-
(XsteamEx('react9')*steamExpChoice('1')+XsteamExAcid('react9')*steamExpChoice('2'))
                                    -
(XsteamEx('react10')*steamExpChoice('1')+XsteamExAcid('react10')*steamExpChoice('2')))
                              =e= fcmol('sucrose','SteamEx','FlsSteamEx');


fcmol.l('water','SteamEx','FlsSteamEx')=1;
fcmol.l('Cellulose','SteamEx','FlsSteamEx')=0.04;
fcmol.l('Hemi','SteamEx','FlsSteamEx')=0.0089;
fcmol.l('lignin','SteamEx','FlsSteamEx')=0.01;
fcmol.l('Acetyl','SteamEx','FlsSteamEx')=0.0018;
fcmol.l('xylolig','SteamEx','FlsSteamEx')=0.0089;
fcmol.l('sucrose','SteamEx','FlsSteamEx')=0;
fcmol.l('hmf','SteamEx','FlsSteamEx')=0.002;
fcmol.l('Furf','SteamEx','FlsSteamEx')=0.003;
fcmol.l('glucolig','SteamEx','FlsSteamEx')=0.001;
fcmol.l('AceA','SteamEx','FlsSteamEx')=0.006;
fcmol.l('ASL','SteamEx','FlsSteamEx')=0.002;
fcmol.l('xylo','SteamEx','FlsSteamEx')=0.009;
fcmol.l('gluc','SteamEx','FlsSteamEx')=0.002;

f.lo('MixSteamEx','SteamEx')=10;
f.lo('SteamEx','FlsSteamEx')=10;

fc.l('Xylo','SteamEx','FlsSteamEx')=1.39;
fc.l('Cellulose','SteamEx','FlsSteamEx')=7.1;
fc.l('Water','SteamEx','FlsSteamEx')=26.2;
fc.l('Acetyl','SteamEx','FlsSteamEx')=0.12;

fc.l('Balance','SrcBal','SteamEx')=0.00005;
F.l('SrcBal','SteamEx')=0.00005;
*+++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
*Steam Ex Flash
Equation Flsh1SteamEx, Flsh2SteamEx,Flsh3SteamEx,Flsh4SteamEx;
Flsh1SteamEx(J)..
     fc(J,'SteamEx','FlsSteamEx') =E= fc(J,'FlsSteamEx','FiltSteamEx') + fc(J,'FlsSteamEx','SnkVapFlsh3');
*SnkC5 is liquid, MixEnzHyd is vapour
Flsh2SteamEx(liquids)..
     fc(liquids,'FlsSteamEx','FiltSteamEx') =E= fc(liquids,'SteamEx','FlsSteamEx')*(1-
(FlashVapCTBE(liquids)*steamExpChoice('1')+FlashVapCTBEAcid(liquids)*steamExpChoice('2')));
Flsh3SteamEx(solids)..
     fc(solids,'FlsSteamEx','FiltSteamEx') =E= fc(solids,'SteamEx','FlsSteamEx');

Flsh4SteamEx(liquids)..
     fc(liquids,'FlsSteamEx','SnkVapFlsh3') =E=
fc(liquids,'SteamEx','FlsSteamEx')*(FlashVapCTBE(liquids)*steamExpChoice('1')+FlashVapCTBEAcid(liquids)*ste
amExpChoice('2'));

F.lo('FlsSteamEx','FiltSteamEx')=0.001;
F.lo('FlsSteamEx','SnkVapFlsh3')=0.001;

F.l('FlsSteamEx','FiltSteamEx')=30;
F.l('FlsSteamEx','SnkVapFlsh3')=4;
*+++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
*FILTER
Equation Filt1SteamEx,Filt1aSteamEx,Filt1bSteamEx,Filt2SteamEx,Filt3SteamEx,Filt4SteamEx,FiltSteamExT1,
```

```
      FiltSteamExT2,FiltWaterSteamEx, FiltWaterSteamEx2    ;

Filt1SteamEx(filtSol)..
      fc(filtSol, 'FlsSteamEx','FiltSteamEx')*SteamFiltSol =E= fc(filtSol, 'FiltSteamEx','MixDelig');

Filt1aSteamEx(filtLiq)..
      (fc(filtLiq, 'FlsSteamEx','FiltSteamEx')+fc(filtLiq, 'SrcWater','FiltSteamEx'))*StExFiltSplit =E= fc(filtLiq,
'FiltSteamEx','MixDelig');

Filt1bSteamEx..
      fc('Balance', 'FlsSteamEx','FiltSteamEx') =E= fc('Balance', 'FiltSteamEx','SnkC5');

Filt2SteamEx..
      F('FlsSteamEx','FiltSteamEx')+F('SrcWater','FiltSteamEx') =E=
F('FiltSteamEx','MixDelig')+F('FiltSteamEx','SnkC5');

Filt3SteamEx(J)..
      fc(J,'FlsSteamEx','FiltSteamEx')+fc(J,'SrcWater','FiltSteamEx') =E=
fc(J,'FiltSteamEx','MixDelig')+fc(J,'FiltSteamEx','SnkC5');

Filt4SteamEx..
      sum(filtLiq, fc(filtLiq, 'FiltSteamEx','MixDelig'))/F('FiltSteamEx','MixDelig') =e= StExLiqFrac;

FiltSteamExT1..
      sum(J,fc(J,'FlsSteamEx','FiltSteamEx')*cp_ind(J))*T('FlsSteamEx','FiltSteamEx')
      +sum(J,fc(J,'SrcWater','FiltSteamEx')*cp_ind(J))*T('SrcWater','FiltSteamEx')
      =E= sum(J,fc(J,'FiltSteamEx','MixDelig')*cp_ind(J))*T('FiltSteamEx','MixDelig')
      + sum(J,fc(J,'FiltSteamEx','SnkC5')*cp_ind(J))*T('FiltSteamEx','SnkC5');

FiltSteamExT2..
      T('FiltSteamEx','MixDelig')=E=T('FiltSteamEx','SnkC5');

FiltWaterSteamEx..
      F('SrcWater','FiltSteamEx') =g= 1.5*sum(filtSol, fc(filtSol,'FiltSteamEx','MixDelig'));

FiltWaterSteamEx2..
      x('Water','FiltSteamEx','SnkC5') =l= 0.93;


F.lo('FiltSteamEx','MixDelig') = 1;
F.up('FiltSteamEx','MixDelig') = 100;
F.lo('SrcWater','FiltSteamEx') = 0.1;
F.up('SrcWater','FiltSteamEx') = 400;
F.l('SrcWater','FiltSteamEx') = 19;
F.lo('FiltSteamEx','SnkC5') = 0.01;

StExLiqFrac.up = 0.55;
StExLiqFrac.lo = 0.5;
StExFiltSplit.lo = 0.03;
StExFiltSplit.up = 0.3;
*-------------------------------------------------------------------------------------------------------------------------
*Delig unit
Equations  VolFlowDelig1,
       DeligMixer1,DeligMixer1a,DeligMixer2,  DeligMixerT,
       DeligHX1,DeligHX2,
       SrcNeuteqn,
       DeligConstTemp,
```

```
            Delig1,Delig2,Delig3,Delig4,Delig5,Delig6,Delig7,  Delig7d,
Delig7a,
      Delig8,Delig9,
Delig10,Delig11,
DeligHX3,DeligHXQ;

VolFlowDelig1..
       V('HXDelig','Delig') =E= (sum(J, fc(J,'HXDelig','Delig')/dens(J)));

DeligMixer1(J)..
      fc(J,'MixDelig','HXDelig') =E=
fc(J,'SrcDelig','MixDelig')+fc(J,'FiltSteamEx','MixDelig')+fc(J,'SrcWater','MixDelig');
DeligMixer1a(J)..
      WSRDelig*(sum(solids,fc(solids,'MixDelig','HXDelig'))) -fc('Water','SrcDelig','MixDelig')-
fc('Water','FiltSteamEx','MixDelig') =E= F('SrcWater','MixDelig');
DeligMixer2..
      sum(J,fc(J,'SrcDelig','MixDelig')*cp_ind(J))*T('SrcDelig','MixDelig')
      +sum(J,fc(J,'FiltSteamEx','MixDelig')*cp_ind(J))*T('FiltSteamEx','MixDelig')
      +sum(J,fc(J,'SrcWater','MixDelig')*cp_ind(J))*T('SrcWater','MixDelig')
      =E= sum(J,fc(J,'MixDelig','HXDelig')*cp_ind(J))*T('MixDelig','HXDelig');

DeligMixerT..
         T('MixDelig','HXDelig') =l=  T('FiltSteamEx','MixDelig');
DeligHX1(NoPPT(J))..
*(J)..
*(NoPPT(J))..
      fc(J,'HXDelig','Delig') =E= fc(J,'MixDelig','HXDelig');

DeligHX2..
      sum(J,fc(J,'MixDelig','HXDelig')*cp_ind(J))*T('MixDelig','HXDelig')
      +197830*fcmol('NaSulp','HXDelig','Delig')
      +F('SrcSteam','HXDelig')*utilProps('LPS','CpVap')
      =E= sum(J,fc(J,'HXDelig','Delig')*cp_ind(J))*T('HXDelig','Delig')  ;
DeligHX3(J)..
      fc(J,'SrcSteam','HXDelig') =e= fc(J,'HXDelig','SnkSteam');
DeligHXQ..
      Q('HXDelig') =E=   F('SrcSteam','HXDelig')*utilProps('LPS','CpVap') ;

      T.fx('SrcSteam','HXDelig')=utilProps('LPS','Tsupply');

      T.fx('HXDelig','SnkSteam')= utilProps('LPS','TTarget');
F.lo('SrcSteam','HXDelig')=0.01;
F.lo('HXDelig','SnkSteam')=0.01;

SrcNeuteqn..
            NaOHWt *100         =E= fc('NaOH','HXDelig','Delig')/(V('HXDelig','Delig')-
(fc('NaOH','HXDelig','Delig')/dens('NaOH')));
V.lo('HXDelig','Delig')=0.0000001;

Delig1..
      fc('Cellulose','HXDelig','Delig')-(fc('Cellulose','SrcBag','MixSteamEx')*(22.857*NaOHWt-2)/100) =E=
fc('Cellulose','Delig','FiltDelig');

Delig2..
      fc('Hemi','HXDelig','Delig')-(fc('Hemi','SrcBag','MixSteamEx')*(10.857*NaOHWt+5)/100) =E=
fc('Hemi','Delig','FiltDelig');
Delig3..
```

```
      fc('Lignin','HXDelig','Delig')-(fc('Lignin','SrcBag','MixSteamEx')*(58.857*NaOHWt+10)/100) =E=
fc('Lignin','Delig','FiltDelig');

Delig4..
      fc('Cellulose','HXDelig','Delig')-fc('Cellulose','Delig','FiltDelig') =E= fc('GluSol','Delig','FiltDelig');

Delig5..
      fc('Hemi','HXDelig','Delig')-fc('Hemi','Delig','FiltDelig') =E= fc('XylSol','Delig','FiltDelig');
Delig6..
      fc('Lignin','HXDelig','Delig')-fc('Lignin','Delig','FiltDelig') +fc('ASL','HXDelig','Delig')=E=
fc('ASL','Delig','FiltDelig');

Delig7(Deligi(J))..
      fc(J,'HXDelig','Delig') =E= fc(J,'Delig','FiltDelig');
Delig8..
      fcmol('NaSulp','HXDelig','Delig') =E=  fcmol('Acid','MixDelig','HXDelig')   ;
Delig9..
      fc('Acid','HXDelig','Delig')   =e= 0  ;
Delig10..
      fcmol('Water','HXDelig','Delig')  =E= fcmol('Water','MixDelig','HXDelig') +
2*fcmol('NaSulp','HXDelig','Delig')    ;

Delig11..
      fcmol('NaOH','HXDelig','Delig')  =E= fcmol('NaOH','MixDelig','HXDelig') - 2*fcmol('NaSulp','HXDelig','Delig')
;
Delig7a(ppt(J))..
      fc(ppt,'HXDelig','Delig') =E= fc(ppt,'Delig','FiltDelig');

Delig7d..
      fcmol('NaSulp','HXDelig','Delig') =E= fcmol('NaSulp','Delig','FiltDelig');

DeligConstTemp..
         T('Delig','FiltDelig') =E=  T('HXDelig','Delig') ;
*-------------------------------------------------------------------------------------------------------------------------------
Equation Filt1Delig,Filt1aDelig,Filt2Delig,Filt3Delig,Filt4Delig,
      FiltWaterDelig,FiltDeligT1,FiltDeligT2;

Filt1Delig(filtSol)..
      fc(filtSol, 'Delig','FiltDelig')*SteamFiltSol =E= fc(filtSol, 'FiltDelig','HX1');

Filt1aDelig(filtLiq)..
      (fc(filtLiq, 'Delig','FiltDelig')+fc(filtLiq, 'SrcWater','FiltDelig'))*DeligFiltSplit =E= fc(filtLiq, 'FiltDelig','HX1');

Filt2Delig..
      F('Delig','FiltDelig') +F('SrcWater','FiltDelig') =E= F('FiltDelig','HX1')+F('FiltDelig','SnkDelig');

Filt3Delig(J)..
      fc(J,'Delig','FiltDelig') +fc(J,'SrcWater','FiltDelig')=E= fc(J,'FiltDelig','HX1')+fc(J,'FiltDelig','SnkDelig');

Filt4Delig..
      sum(filtLiq, fc(filtLiq, 'FiltDelig','HX1'))/F('FiltDelig','HX1') =e= DeligLiqFrac;

FiltWaterDelig..
      F('SrcWater','FiltDelig') =l= 1.5*sum(filtSol, fc(filtSol,'FiltDelig','HX1'));

FiltDeligT1..
      sum(J,fc(J,'Delig','FiltDelig')*cp_ind(J))*T('Delig','FiltDelig')
```

```
        +sum(J,fc(J,'SrcWater','FiltDelig')*cp_ind(J))*T('SrcWater','FiltDelig')
        =E= sum(J,fc(J,'FiltDelig','HX1')*cp_ind(J))*T('FiltDelig','HX1')
        + sum(J,fc(J,'FiltDelig','SnkDelig')*cp_ind(J))*T('FiltDelig','SnkDelig');

FiltDeligT2..
        T('FiltDelig','HX1')=E=T('FiltDelig','SnkDelig');

F.lo('FiltDelig','SnkDelig') = 0.01;
F.lo('SrcWater','FiltDelig') = 0;
F.up('SrcWater','FiltDelig') = 100;
F.lo('FiltDelig','HX1') = 0.01;

DeligLiqFrac.up = 0.55;
DeligLiqFrac.lo = 0.4;
DeligFiltSplit.lo=0.03;
DeligFiltSplit.up=0.3;
*-------------------------------------------------------------------------------------------------------------------------------
*HX1
Equations  HX1_1,HX1_1a,HX1_2,HX1_3,HX1_4,HX1_4a;

*Outlet temperature of mixer
HX1_1(J)..
        fc(J,'FiltDelig','HX1') =E= fc(J,'HX1','MixEnzHyd');

HX1_1a..
        F('FiltDelig','HX1') =E= F('HX1','MixEnzHyd');

HX1_2..  T('HX1','SnkCW')=E= T('SrcWater','HX1');

HX1_3..
        T('HX1','MixEnzHyd') =E=  T('FiltDelig','HX1');
HX1_4(J)..
        fc(J,'HX1','SnkCW') =E= fc(J,'SrcWater','HX1');

HX1_4a..
        F('HX1','SnkCW') =E= F('SrcWater','HX1');

F.lo('SrcWater','HX1')=1;
F.up('SrcWater','HX1')=500;
*++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
*EnzHyd Mixer
Equation MixEnzHyd1,MixEnzHyd2,  MixEnzHydEB,
        EnzSrcWaterEqn,EnzSrcEnzEqn;

MixEnzHyd1..
        F('SrcEnz','MixEnzHyd')+ F('SrcWater','MixEnzHyd') +F('HX1','MixEnzHyd') =E=  F('MixEnzHyd','EnzHyd');
MixEnzHyd2(J)..
        fc(J,'SrcEnz','MixEnzHyd')+ fc(J,'SrcWater','MixEnzHyd') +fc(J,'HX1','MixEnzHyd') =E=
fc(J,'MixEnzHyd','EnzHyd');
MixEnzHydEB..
        sum(J, fc(J,'SrcEnz','MixEnzHyd')*cp_ind(J))*T('SrcEnz','MixEnzHyd')+ sum(J,
fc(J,'SrcWater','MixEnzHyd')*cp_ind(J))*T('SrcWater','MixEnzHyd')
        +sum(J, fc(J,'HX1','MixEnzHyd')*cp_ind(J))*T('HX1','MixEnzHyd') =E=  sum(J,
fc(J,'MixEnzHyd','EnzHyd')*cp_ind(J))*T('MixEnzHyd','EnzHyd')    ;

EnzSrcWaterEqn..
         x('Water','MixEnzHyd','EnzHyd') =E= FracWatMix;
```

```
EnzSrcEnzEqn..
        x('Enz','MixEnzHyd','EnzHyd') =E= FracEnzMix;

Equations DeligPerc, newX, newX2;

DeligPerc..
       YieldInc =E= (MW('Cellulose')/MW('Gluc'))*3.9815*(((fc('Lignin', 'SrcBag', 'MixSteamEx')-fc('Lignin',
'MixEnzHyd','EnzHyd'))/fc('Lignin', 'SrcBag', 'MixSteamEx'))*100 -10);

newX..
         newXEnzHyd =l=  XEnzHyd('react1')+XEnzHyd('react1')*(YieldInc)/100;
newXEnzHyd.lo= XEnzHyd('react1');

newX2..
        newX2EnzHyd =e=  XEnzHyd('react2')+XEnzHyd('react2')*(YieldInc)/100;
newX2EnzHyd.lo= XEnzHyd('react2');

Equations
        EnzHyd1   cellulose* (solid) + H2O --> Glucose,
        EnzHyd2   cellulose* (solid) --> Glucolig,
        EnzHyd3   Hemi* (solid)+H2O --> Xylose ,
        EnzHyd5    Acetyl*  (solid) --> Acet-Ac,
        EnzHydCell Cellulose overall balance,
        EnzHydHemi Hemi overall balance,
        EnzHydAcetyl Acetyl overall balance,
        EnzHydMB    Overall MB,
        EnzHydInerts  Inerts MB,
        EnzHydInerts2,
        EnzHydXylolig,
        EnzHydVolFlow2;


EnzHyd1.. fcmol('Cellulose','MixEnzHyd','EnzHyd')*newXEnzHyd + fcmol('Gluc','MixEnzHyd','EnzHyd')  +
fcmol('Glucolig','MixEnzHyd','EnzHyd')
                                    =e= fcmol('Gluc','EnzHyd','FiltEnz');

EnzHyd2.. fcmol('Cellulose','MixEnzHyd','EnzHyd')*newX2EnzHyd
                                  =e= fcmol('Glucolig','EnzHyd','FiltEnz');

EnzHyd3.. fcmol('Hemi','MixEnzHyd','EnzHyd')*XEnzHyd('react3') +
fcmol('Xylo','MixEnzHyd','EnzHyd')+fcmol('Xylolig','MixEnzHyd','EnzHyd')
                =e= fcmol('Xylo','EnzHyd','FiltEnz');

EnzHyd5.. fcmol('Acetyl','MixEnzHyd','EnzHyd')*XEnzHyd('react5') + fcmol('AceA','MixEnzHyd','EnzHyd')
                              =e= fcmol('AceA','EnzHyd','FiltEnz');

EnzHydCell.. fcmol('Cellulose','MixEnzHyd','EnzHyd')*(1-newXEnzHyd-newX2EnzHyd)
                =e= fcmol('Cellulose','EnzHyd','FiltEnz');

EnzHydHemi.. fcmol('Hemi','MixEnzHyd','EnzHyd')*(1-XEnzHyd('react3'))
                =e= fcmol('Hemi','EnzHyd','FiltEnz');

EnzHydAcetyl.. fcmol('Acetyl','MixEnzHyd','EnzHyd')*(1-XEnzHyd('react5'))
                =e= fcmol('Acetyl','EnzHyd','FiltEnz');

EnzHydMB.. F('MixEnzHyd','EnzHyd') =E= F('EnzHyd','FiltEnz');
```

```
EnzHydInerts(i).. fc(i,'MixEnzHyd','EnzHyd') =E= fc(i,'EnzHyd','FiltEnz');

EnzHydInerts2(Enzi).. fc(Enzi,'MixEnzHyd','EnzHyd') =E= fc(Enzi,'EnzHyd','FiltEnz');

EnzHydXylolig..  fc('Xylolig','EnzHyd','FiltEnz') =E= 0;

EnzHydVolFlow2..
       sum(J, fc(J,'EnzHyd','FiltEnz')/dens(J)) =e= V('EnzHyd','FiltEnz');
*+++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
*FILTER
Equation Filt1Enz,Filt1aEnz,Filt2Enz,Filt3Enz,
      Filt4Enz,FiltEnzT1,FiltEnzT2,FiltWaterEnz;

Filt1Enz(filtSol)..
      fc(filtSol, 'EnzHyd','FiltEnz')*SteamFiltSol =E= fc(filtSol, 'FiltEnz','SnkSolid');

Filt1aEnz(filtLiq)..
      (fc(filtLiq, 'EnzHyd','FiltEnz')+fc(filtLiq, 'SrcWater','FiltEnz'))*EnzFiltSplit =E= fc(filtLiq, 'FiltEnz','SnkSolid');


Filt2Enz..
      F('EnzHyd','FiltEnz')+F('SrcWater','FiltEnz') =E= F('FiltEnz','SnkSolid')+F('FiltEnz','SnkC6');

Filt3Enz(J)..
      fc(J,'EnzHyd','FiltEnz')+fc(J, 'SrcWater','FiltEnz') =E= fc(J,'FiltEnz','SnkSolid')+fc(J,'FiltEnz','SnkC6');

Filt4Enz..
      sum(filtLiq, fc(filtLiq, 'FiltEnz','SnkSolid'))/F('FiltEnz','SnkSolid') =e= EnzLiqFrac;

FiltEnzT1..
      sum(J,fc(J,'EnzHyd','FiltEnz')*cp_ind(J))*T('EnzHyd','FiltEnz')
      +sum(J,fc(J,'SrcWater','FiltEnz')*cp_ind(J))*T('SrcWater','FiltEnz')
      =E= sum(J,fc(J,'FiltEnz','SnkSolid')*cp_ind(J))*T('FiltEnz','SnkSolid')
      + sum(J,fc(J,'FiltEnz','SnkC6')*cp_ind(J))*T('FiltEnz','SnkC6');

FiltEnzT2..
      T('FiltEnz','SnkSolid')=E=T('FiltEnz','SnkC6');

FiltWaterEnz..
      F('SrcWater','FiltEnz') =l=1.5*sum(filtSol, fc(filtSol,'FiltEnz','SnkSolid'));


F.lo('FiltEnz','SnkC6') = 0.01;
F.lo('FiltEnz','SnkSolid') = 0.01;
x.fx('Water','SrcWater','FiltEnz')=1;
EnzLiqFrac.up = 0.55;
EnzLiqFrac.lo = 0.5;
EnzFiltSplit.lo=0.03;
EnzFiltSplit.up=0.3;
*+++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
***Capital costing calculations
Parameters
      opHours Percentage operating time /0.8/
      convFt Convert m to ft /3.28084/
      rohCS density of carbon steel/490/
      FmSS316 Material factor for SS316  /2.1/
```

```
      PlantLife Plant lifetime /10/
      plantLifeSml plant lifetime for short term units (HX) /5/
      RandDollar Rand to Dollar exchange rate /11.03/
      CEPCI  CEPCI for 2014   /577/
      overDesFact over design factor /1.1/
      lang     lang factor for fluids-solids /4.41/
      CEPCIsteam      CEPCI for 2005 /468.2/;

Equation    CpSrcEnz,  VolSrcEnz ,
         CpSrcAcid,    VolSrcAcid,
        VolEnzHyd, CpEnzHyd   ;

VolEnzHyd..
      Volume('EnzHyd')   =E=  overDesFact*V('MixEnzHyd', 'EnzHyd')*Tau('EnzHyd')*60;
CpEnzHyd ..
     Cp('EnzHyd') =E= (CEPCI/444.2)*(5000*Length('EnzHyd'));
*MF of 2, PF of 1

VolSrcEnz..
      Volume('SrcEnz') =E=
overDesFact*(F('SrcEnz','MixEnzHyd'))*3600*24*30/(x('Enz','SrcEnz','MixEnzHyd')*dens('Enz')+x('Water','SrcEn
z','MixEnzHyd')*dens('Water'));
*Closed storage tank
CpSrcEnz..
*C&R
       Cp('SrcEnz') =E= (CEPCI/444.2)*2300*Volume('SrcEnz')**0.55;
VolSrcAcid..
      Volume('SrcAcid') =E=
overDesFact*(F('SrcAcid','MixSteamEx'))*3600*24*30/(x('Acid','SrcAcid','MixSteamEx')*dens('Acid')+x('Water','
SrcAcid','MixSteamEx')*dens('Water'));
*Closed storage tank
CpSrcAcid..
*C&R
       Cp('SrcAcid') =E= (CEPCI/444.2)*2300*2*Volume('SrcAcid')**0.55;
*MF of 2
*+++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
Equation  VolDelig,CpDelig,
VolSrcDelig,  CpSrcDelig  ;
VolDelig..
      Volume('Delig')   =E=  overDesFact*V('HXDelig', 'Delig')*Tau('Delig')*60;

VolSrcDelig..
      Volume('SrcDelig') =E=
overDesFact*NaOHPurge*(F('SrcDelig','MixDelig'))*3600*24*7/(x('NaOH','SrcDelig','MixDelig')*dens('NaOH')+x
('Water','SrcDelig','MixDelig')*dens('Water'));
*Closed storage tank
CpSrcDelig..
*C&R
       Cp('SrcDelig') =E= 4*((CEPCI/444.2)*2300*Volume('SrcDelig')**0.55);
CpDelig ..
     Cp('Delig') =E= (CEPCI/444.2)*(5000*Length('Delig'));
*MF of 2, PF of 1
*$offtext
*+++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
***Capital costing calculations
Equation  VolEqn,LDratEqn,CpSteamEx,VolSteamEx;
```

```
VolEqn(unit)..
       Volume(unit)   =E=PI/4*Diameter(unit)**2*Length(unit);

LDratEqn(unit)..
        LDrat(unit) =E=   Length(unit)/Diameter(unit);

**SteamEx
VolSteamEx..
       Volume('SteamEx')   =E=  overDesFact*V('MixSteamEx', 'SteamEx')*Tau('SteamEx')*60;

CpSteamEx ..
      Cp('SteamEx') =E=
(CEPCI/444.2)*(5000*Length('SteamEx'))*(steamExpChoice('1')*1.2+2*steamExpChoice('2')*1.1);
*MF of 2, PF of 1.1 (acid) or 1.2
*+++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
Diameter.lo('Delig')= 1;
Diameter.lo('SteamEx')= 1;
Diameter.lo('EnzHyd')= 1;
Diameter.up('SteamEx')= 4;
Diameter.up('EnzHyd')= 100;
Diameter.up('Delig')= 9;
Length.lo(unit)= 0 ;
Length.up(unit)= 50;
Length.up('EnzHyd')= 100;
Length.up('SrcDelig')= 100;

Volume.lo(unit)=0.0001;
Volume.lo('SrcAcid')=0;
Volume.up(unit)=10000;
Volume.up('EnzHyd')=3000000;
Volume.up('Delig')=1000;
Volume.up('SrcDelig')=1000000;

Cp.lo(unit)=0;
Cp.up(unit)=100000000;

LDrat.lo(unit)=2.5;
LDrat.lo('SrcAcid')=0;
LDrat.up(unit)=5;
Diameter.lo(unit)= 0.3 ;
*+++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
*Filters
*Max of 6000 lb/(sq ft.day)
*Length is width
Parameter  maxMassFlow   lb per (sq ft day) /6000/
        convLb  kg per lb              /0.453592/
        convSqFt  sq m per sq ft        /0.092903/    ;

Equation      filt1,filt2,filt2a,filt2b,filt3;
*calc surface area
filt1(filt)..
     SA(filt) =E= pi*Diameter(filt)*Length(filt);
*compare to max flowrate
filt2..
     overDesFact*(F('FiltSteamEx','MixDelig'))*3600*24 =L= SA('FiltSteamEx')*maxMassFlow*convLb/convSqFt;

filt2a..
```

```
     overDesFact*(F('FiltEnz','SnkSolid'))*3600*24 =L= SA('FiltEnz')*maxMassFlow*convLb/convSqFt;
filt2b..
     overDesFact*(F('FiltDelig','HX1'))*3600*24 =L= SA('FiltDelig')*maxMassFlow*convLb/convSqFt;

filt3(filt)..
       Cp(filt) =E=  34000*SA(filt)**0.6*CEPCI/444.2;

Diameter.lo(filt)=0.1;
Diameter.up(filt)=100;
Length.lo(filt)=0.01;
Length.up(filt)=100;
SA.lo(filt)=0.001;
SA.up(filt)=5000;
*-------------------------------------------------------------------------------------------------------------------------------
*HX for costing
Equations          HX1_ch2a,HX1_Area,HX1_Cb,HX1_Fm,HX1_Cp;

HX1_ch2a..
       LMTD('HXDelig') =E= ((T('HXDelig','SnkSteam')-T('MixDelig','HXDelig'))-(T('SrcSteam','HXDelig')-
T('HXDelig','Delig')))
            /log((T('HXDelig','SnkSteam')-T('MixDelig','HXDelig'))/(T('SrcSteam','HXDelig')-T('HXDelig','Delig')));

LMTD.lo('HXDelig')=-500;
LMTD.up('HXDelig')=500;
Area.lo('HXDelig')=0.1;
Area.up('HXDelig')=1000;

HX1_Area('HXDelig')..
      Area('HXDelig')*(HXprops('HXDelig','U')*HXprops('HXDelig','F')*LMTD('HXDelig')) =E=Q('HXDelig')*1000;
HX1_Cb(HX)..
      Cb('HXDelig') =E=exp(11.0545-
0.9228*log(Area('HXDelig')*convFt*convFt)+0.09861*log(Area('HXDelig')*convFt*convFt)*log(Area('HXDelig')*
convFt*convFt));
*for a fixed heat HX
HX1_Fm(HX)..
       Fm('HXDelig') =E= 1.75+(Area('HXDelig')*convFt*convFt/100)**0.13;
*CS shell and SS tubes
HX1_Cp(HX)..
       Cp('HXDelig') =E=(CEPCI/500)*Cb('HXDelig')*Fm('HXDelig');

*+++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
*Other revenues
Parameter XylToCH4       mass ratio of methane to xylose /0.360006877/,
       CH4Worth       price of methane R per ton /14000/;
Variable CH4Rev   Revenue from methane in millions of R per annum;
Equation CH4Eqn1   ;
CH4Eqn1..
       CH4Rev =E=  fc('Xylo','FiltSteamEx','SnkC5')*XylToCH4*CH4Worth/1000*3600*24*365*opHours/10**6;
*+++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
Equation  Obj;
Obj.. z =E= worth('Gluc')*fc('Gluc','FiltEnz','SnkC6')/1000*3600*24*365*opHours/10**6
            +CH4Rev
        -
(F('SrcSteam','MixSteamEx')*(SteamCost*steamExpChoice('1')+SteamCostAcid*steamExpChoice('2')))*CEPCI/C
EPCIsteam*RandDollar/1000*3600*24*365*opHours/10**6
       -worth('Acid')*F('SrcAcid','MixSteamEx')/1000*3600*24*365*opHours/10**6
```

```
        -
worth('Water')*(F('SrcWater','FiltSteamEx')+F('SrcWater','MixEnzHyd')+F('SrcWater','HX1')+F('SrcWater','MixD
elig')
            +F('SrcWater','FiltEnz')+F('SrcWater','FiltDelig'))/1000*3600*24*365*opHours/10**6
        -worth('Enz')*fc('Gluc','EnzHyd','FiltEnz')/1000*3600*24*365*opHours/10**6
        -worth('NaOH')*NaOHPurge*fc('NaOH','SrcDelig','MixDelig')/1000*3600*24*365*opHours/10**6
            - (Cp('SrcAcid')*RandDollar/plantLife/10**6
            + Cp('SrcEnz')*RandDollar/plantLife/10**6
            + Cp('SteamEx')*RandDollar/plantLife/10**6
             + Cp('EnzHyd')*RandDollar/plantLife/10**6
            + Cp('HX1')*RandDollar/plantLifeSml/10**6
            + Cp('FiltEnz')*RandDollar/plantLife/10**6
            + Cp('FiltSteamEx')*RandDollar/plantLife/10**6
            + Cp('FiltDelig')*RandDollar/plantLife/10**6
            + Cp('Delig')*RandDollar/plantLife/10**6
            + Cp('SrcDelig')*RandDollar/plantLife/10**6
            + Cp('HXDelig')*RandDollar/plantLifeSml/10**6   )*Lang
        -
F('SrcSteam','HXDelig')*CEPCI/CEPCIsteam/1000*RandDollar*3600*24*365*opHours/10**6*utilProps('LPS','C
ost')   ;

Variable
        EIRM(cats, Cmpnts),
        EIProd(cats, Cmpnts),
        TotEIRM(Cmpnts),TotEIProd(Cmpnts),TotEIcat(cats),
        DUAL;
Variable   TotEI;

Equation EIAcid, EIEnz, EIBag, EINaOH, EIWater, EILPS, EICTBE1, EICTBE2, EIEth,
        EICh4,EITotCat,EITotRM,EITotProd, TotEICalc,EIAceA, EIFurf,EIAcidFl ;
EIAcid(cats)..
        EIRM(cats,'Acid') =E= Enviro(cats, 'WF')*Enviro(cats,
'Acid')*F('SrcAcid','MixSteamEx')*3600*24*365*opHours ;
EINaOH(cats)..
        EIRM(cats,'NaOH') =E= Enviro(cats, 'WF')*Enviro(cats,
'NaOH')*NaOHPurge*fc('NaOH','SrcDelig','MixDelig')*3600*24*365*opHours ;
EIEnz(cats)..
        EIRM(cats,'Enz') =E= Enviro(cats, 'WF')*Enviro(cats, 'Enz')*F('SrcEnz','MixEnzHyd')*3600*24*365*opHours
;
EIBag(cats)..
        EIRM(cats,'Bag') =E= Enviro(cats, 'WF')*(Enviro(cats, 'Bag')-SysExp(cats,
'ExpBag'))*F('SrcBag','MixSteamEx')*3600*24*365*opHours;
EIWater(cats)..
        EIRM(cats,'Water') =E= Enviro(cats, 'WF')*Enviro(cats,
'Water')*(F('SrcWater','FiltSteamEx')+F('SrcWater','MixEnzHyd')+F('SrcWater','MixDelig')+F('SrcWater','FiltDelig
')
        +F('SrcWater','FiltEnz'))*3600*24*365*opHours ;
EILPS(cats)..
        EIRM(cats,'LPS') =E= Enviro(cats, 'WF')*Enviro(cats,
'LPS')*(F('SrcSteam','HX1')+F('SrcSteam','HXDelig'))*3600*24*365*opHours ;

EICTBE1(cats)..
        EIRM(cats,'CTBE1') =E= Enviro(cats, 'WF')*Enviro(cats,
'CTBE1')*steamExpChoice('2')*F('SrcSteam','MixSteamEx')*3600*24*365*opHours ;

EICTBE2(cats)..
```

```
      EIRM(cats,'CTBE2') =E= Enviro(cats, 'WF')*Enviro(cats,
'CTBE2')*(steamExpChoice('1')*F('SrcSteam','MixSteamEx'))*3600*24*365*opHours;

EIAceA(cats)..
      EIProd(cats,'AceA') =E= Enviro(cats,'WF')*Enviro(cats,
'AceA')*(fc('AceA','FlsSteamEx','SnkVapFlsh3'))*3600*24*365*opHours ;
EIFurf(cats)..
      EIProd(cats,'Furf') =E= Enviro(cats,'WF')*Enviro(cats,
'Furf')*(fc('Furf','FlsSteamEx','SnkVapFlsh3'))*3600*24*365*opHours;
EIAcidFl(cats)..
      EIProd(cats,'AcidFl') =E= Enviro(cats,'WF')*Enviro(cats,
'AcidFl')*(fc('Acid','FlsSteamEx','SnkVapFlsh3'))*3600*24*365*opHours;
EICh4(cats)..
      EIProd(cats,'CH4') =E= Enviro(cats, 'WF')*(Enviro(cats, 'CH4')-SysExp(cats,
'ExpCH4'))*fc('Xylo','FiltSteamEx','SnkC5')*XylToCH4*3600*24*365*opHours;
EIEth(cats)..
      EIProd(cats,'Eth') =E= Enviro(cats, 'WF')*(-SysExp(cats,
'ExpEth'))*fc('Gluc','FiltEnz','SnkC6')/0.9*3600*24*365*opHours;

EITotCat(cats)..
      TotEIcat(cats)=E=sum(Cmpnts,(EIRM(cats,Cmpnts)+EIProd(cats,Cmpnts)));
EITotRM(Cmpnts)..
      TotEIRM(Cmpnts)=E=sum(cats,EIRM(cats,Cmpnts));
EITotProd(Cmpnts)..
      TotEIProd(Cmpnts)=E=sum(cats,EIProd(cats,Cmpnts));
TotEICalc..
      TotEI=E= sum(cats, TotEIcat(cats));

TotEIRM.lo('Acid')=0;
TotEIRM.lo('NaOH')=0;
TotEIRM.lo('Enz')=0;
TotEIRM.lo('Bag')=0;
TotEIRM.lo('Water')=0;
TotEIRM.lo('CTBE1')=0;
TotEIRM.lo('CTBE2')=0;
TotEIRM.lo('LPS')=0;
TotEIRM.lo('MPS1')=0;
TotEIRM.lo('MPS2')=0;
TotEIRM.lo('HPS1')=0;
TotEIRM.lo('HPS2')=0;
TotEIRM.lo('AceA')=0;
TotEIRM.lo('Furf')=0;
TotEIRM.lo('AcidFl')=0;
TotEIRM.lo('CH4')=0;
TotEIRM.lo('WF')=0;
TotEIRM.lo('Eth')=0;
*Acid,NaOH,Enz,Bag,Water,CTBE1,LPS,CTBE2,MPS1,MPS2,HPS1,HPS2,AceA, Furf, AcidFl, CH4, WF, Eth
TotEIProd.lo('Acid')=0;
TotEIProd.lo('NaOH')=0;
TotEIProd.lo('Enz')=0;
TotEIProd.lo('Bag')=0;
TotEIProd.lo('Water')=0;
TotEIProd.lo('CTBE1')=0;
TotEIProd.lo('CTBE2')=0;
TotEIProd.lo('LPS')=0;
TotEIProd.lo('MPS1')=0;
TotEIProd.lo('MPS2')=0;
```

```
TotEIProd.lo('HPS1')=0;
TotEIProd.lo('HPS2')=0;
TotEIProd.lo('AceA')=0;
TotEIProd.lo('Furf')=0;
TotEIProd.lo('AcidFl')=0;
TotEIProd.lo('CH4')=0;
TotEIProd.lo('WF')=0;
*TotEIProd.lo(cats,'Eth')=0;

PARAMETER
BEST Best values for objectives
WORST Worst values for objectives
DRatio Weighting for TAC in dual objective function /0/
CRatio Scaling of EI constraint /0/  ;

WORST('EI') = 1 ;
BEST('EI') = 0;

Equation CONSTRAINT_OBJECTIVE;
CONSTRAINT_OBJECTIVE..
      NaOHPurge =E= CRatio;
Model PreHydrolysis /ALL/;
Solve PreHydrolysis Using MINLP Maximising z;
*Solve PreHydrolysis Using MINLP minimising TotEI;
Parameter Overall,BalCheck,
       MoleFrac(unit, unit1);
Overall =
F.l('SrcBag','MixSteamEx')+F.l('SrcSteam','MixSteamEx')+F.l('SrcAcid','MixSteamEx')+F.l('SrcBal','SteamEx')-
F.l('SteamEx','FlsSteamEx');
BalCheck =
F.l('SrcBag','MixSteamEx')+F.l('SrcSteam','MixSteamEx')+F.l('SrcAcid','MixSteamEx')+F.l('SrcBal','SteamEx')-
F.l('SteamEx','FlsSteamEx')+ fc.l('Balance','SteamEx','FlsSteamEx');
MoleFrac(unit,unit1)=sum(J,x.l(J,unit,unit1));
option decimals = 5 ;

Parameter RMCost,ProdCost, AnnualCapCost,sumnegs,AcidCost,WaterCost, SteamCost,EnzCost, DeligCost;

ProdCost= worth('Gluc')*fc.l('Gluc','FiltEnz','SnkC6')/1000*3600*24*365*opHours/10**6 ;
AnnualCapCost=   ( Cp.l('SteamEx')*RandDollar/plantLife/10**6
             + Cp.l('EnzHyd')*RandDollar/plantLife/10**6
            + Cp.l('HX1')*RandDollar/plantLifeSml/10**6
            + Cp.l('FiltEnz')*RandDollar/plantLife/10**6
            + Cp.l('FiltSteamEx')*RandDollar/plantLife/10**6
            + Cp.l('SrcAcid')*RandDollar/plantLife/10**6
            + Cp.l('SrcEnz')*RandDollar/plantLife/10**6
            + Cp.l('FiltDelig')*RandDollar/plantLife/10**6
            + Cp.l('Delig')*RandDollar/plantLife/10**6
            + Cp.l('SrcDelig')*RandDollar/plantLife/10**6
            + Cp.l('HXDelig')*RandDollar/plantLifeSml/10**6 )*Lang   ;
EnzCost =  worth('Enz')*fc.l('Gluc','EnzHyd','FiltEnz')/1000*3600*24*365*opHours/10**6  ;
DeligCost =
worth('NaOH')*NaOHPurge.l*fc.l('NaOH','SrcDelig','MixDelig')/1000*3600*24*365*opHours/10**6;
AcidCost=  worth('Acid')*F.l('SrcAcid','MixSteamEx')/1000*3600*24*365*opHours/10**6 ;
WaterCost=
worth('Water')*(F.l('SrcWater','FiltSteamEx')+F.l('SrcWater','MixEnzHyd')+F.l('SrcWater','HX1')+F.l('SrcWater','
MixDelig')
      +F.l('SrcWater','FiltDelig')+F.l('SrcWater','FiltEnz'))/1000*3600*24*365*opHours/10**6   ;
```

```
SteamCost=
(F.l('SrcSteam','MixSteamEx')*(SteamCost*steamExpChoice.l('1')+SteamCostAcid*steamExpChoice.l('2')))*CEP
CI/CEPCIsteam/1000*3600*24*365*opHours*RandDollar/10**6

+F.l('SrcSteam','HXDelig')*utilProps('LPS','Cost')*CEPCI/CEPCIsteam/1000*RandDollar*3600*24*365*opHours/
10**6   ;
RMCost= AcidCost+WaterCost+SteamCost+EnzCost+DeligCost;
sumnegs= RMCost+  AnnualCapCost;

Parameter dt1,dt2,lmtdtest;
dt1=-T.l('HX1','SnkCW')+T.l('FiltSteamEx','MixDelig') ;
dt2=-T.l('SrcWater','HX1')+T.l('HX1','MixEnzHyd') ;
lmtdtest= (dt1-dt2)/log(dt1/dt2);

Parameter filtTest1,filtTest2;
filtTest1=sum(filtLiq, fc.l(filtLiq,'EnzHyd','FiltEnz'))/F.l('EnzHyd','FiltEnz');
filtTest2=sum(filtLiq, fc.l(filtLiq,'FiltEnz','SnkSolid'))/F.l('FiltEnz','SnkSolid');

Parameter maxWaterEnzFilt, maxWaterStExFilt,maxWaterDeligFilt;
maxWaterEnzFilt=1.5*sum(filtSol, fc.l(filtSol,'FiltEnz','SnkSolid'))  ;
maxWaterStExFilt=1.5*sum(filtSol, fc.l(filtSol,'FiltSteamEx','MixDelig'))  ;
maxWaterDeligFilt=1.5*sum(filtSol, fc.l(filtSol,'FiltDelig','HX1'))  ;

Parameter  percLigRem, newXCheck;
percLigRem=(fc.l('Lignin', 'SrcBag', 'MixSteamEx')-fc.l('Lignin', 'MixEnzHyd','EnzHyd'))/fc.l('Lignin', 'SrcBag',
'MixSteamEx')*100;
newXCheck =  XEnzHyd('react1')+XEnzHyd('react1')*(YieldInc.l)/100;

display F.l, fc.l, fcmol.l,dt1,dt2,lmtdtest ;
*,rohoverall;
display x.l, T.l, Q.l, z.l,  Overall, MoleFrac,BalCheck, Volume.l,Cp.l;
display RMCost,ProdCost, AnnualCapCost,sumnegs,AcidCost,WaterCost,EnzCost,DeligCost, SteamCost,
      EIRM.l,EIProd.l,TotEIRM.l,TotEIProd.l,TotEIcat.l,TotEI.l,
      filtTest1,filtTest2,maxWaterStExFilt,maxWaterDeligFilt,maxWaterEnzFilt,percLigRem,newXCheck;
*$ontext
file sensitivity /SDE Sensitivity to NaOH.csv/;
put sensitivity;
sensitivity.pc=5;
sensitivity.nd=8;
put 'Sensitivity Curve Data'/;
put 'Steam, delignification, Enzymatic'/;
put 'i', 'CRatio', 'NaOHPurge', 'TAC', 'TotEI','SteamExp Choice Acid',  'NaOH Wt%'/;
option CRatio:5;
set a indexing /1*30/;
parameter report(*,*) "Sensitivity curve data";
scalar
count counter /1/
EILimit The EI constraint set;
while(count <= card(a),
 CRatio = ((count-1)/(card(a)-1))**3;
Solve PreHydrolysis Using MINLP Maximising z;
 EILimit = BEST('EI')+CRatio*(WORST('EI')-BEST('EI'));
 report(a,'CRatio') = CRatio;
 report(a,'TAC') = z.L;
 report(a,'NaOHPurge') = NaOHPurge.L;
 report(a,'TotEI') = TotEI.l;
 report(a,'SteamExp Choice Acid') = steamExpChoice.l('2');
```

```
 report(a,'NaOH Wt%') = NaOHWt.l;
 put count, CRatio, NaOHPurge.L, z.L, TotEI.l,steamExpChoice.l('2'),NaOHWt.l/;
 count = count + 1;
);
display report ;
*$offtext
```

B.2 GAMS code for AA Pareto Code

```
Options LimRow = 70, LimCol = 0;
*Global settings
Set
      unit    units
     /SrcBag, SrcAcid, SrcSteam, SrcWater, MixPreHyd,  PreHyd, SnkVapFlsh1,SnkC5,
      MixAcidCellHyd, FlsPreHyd,FiltPreHyd, AcidCellHyd, SnkC6,
      SnkSolid, SnkVapFlsh2, FlsAcidCellHyd, FictIN, FictOUT, FictCell, FiltCellHyd/

      Mix(unit) mixers
     /MixPreHyd,MixAcidCellHyd/

      Src(unit) sources
      /SrcBag, SrcAcid, SrcSteam, SrcWater/

      Snk(unit) sinks
      /SnkVapFlsh1,SnkC5,SnkVapFlsh2,SnkSolid/

      Flash(unit) flash
      /FlsPreHyd,FlsAcidCellHyd/

      Filt(unit) filters
      /FiltPreHyd, FiltCellHyd/

*     Define components
      J      components
      /Cellulose, Hemi, Lignin, Acetyl, Phos, Xylo, Xylolig, Gluc, Glucolig, Sucrose, Furf, HMF,
      AceA,  Water, Acid, ASL, Min, OrgAc, Salts, Soil,Balance,Enz/

      liquids(J)
      /Xylo, Xylolig, Gluc, Glucolig,  Sucrose, Furf, HMF, AceA,  Min,  Salts, Water, Acid, ASL,
OrgAc,Balance,Phos/

      ll(liquids)
      /Xylo, Xylolig, Gluc, Glucolig, Acid, ASL/

      solids(J)
      /Cellulose, Hemi, Lignin, Acetyl,Enz,  Soil/

      i(J) inerts
      /Phos,  Acid, Min, OrgAc, Salts, Soil,Balance,Enz/

      filtSol(J)
      /Cellulose, Hemi, Lignin, Acetyl,Soil,Enz/

      filtLiq(J)
      /Xylo, Xylolig, Gluc, Glucolig, Sucrose, Furf, HMF, AceA,  Water, Acid, ASL, OrgAc,Min,  Salts, Phos/

      react
      /Hemi_react,
      Xylo_Furf/

      PreHydComps/TPreHyd,CA,Tau,Hemi,Xyl,Fur,Acetic,Cellulose,Glucose,HMF,Acetyl,
      Xyfur, AcidLig/

      U      utilities
```

```
      /CW, LPS,MPS1,MPS2,HPS1,HPS2,CTBE1,CTBE2/

      UtilData/ CostMon, TSupply, TTarget, CpVap, Cost /
      HXData/U, F/

Alias(unit, unit1)
Parameter PreHyd2122(PreHydComps)/
TPreHyd       395.15
CA          2
Tau          10.51
Hemi          0.65842735
Xyl          15.0745
Fur          0.2296
Acetic        3.4389
Cellulose      0.043428241
Glucose        1.8704
HMF          0.0057
Acetyl        0.942164384
Xyfur         0.077567568
AcidLig       0.00225  /
*lig soln   2.25 mg/g solid

Parameter PreHyd4122(PreHydComps) /
TPreHyd       395.15
CA          4
Tau          10.51
Hemi          0.623820513
Xyl          14.1081
Fur          0.4568
Acetic        3.6772
Cellulose      0.114418981
Glucose        4.9212
HMF          0.0217
Acetyl        0.905714286
Xyfur         0.110338164
AcidLig       0.0028     /
*lig soln   2.8 mg/g solid

Parameter PreHyd6122(PreHydComps)/
TPreHyd       395.15
CA          6
Tau          10.51
Hemi          0.690106838
Xyl          15.497
Fur          0.6905
Acetic        4.0744
Cellulose      0.124143519
Glucose        5.363
HMF          0
Acetyl        0.899426049
Xyfur         0.153104213
AcidLig       0.0034     /
*lig soln   3.4 mg/g solid

Parameter PreHyd2128(PreHydComps)    /
TPreHyd       401.15
CA          2
```

Tau 10.01
Hemi 0.61624359
Xyl 13.9997
Fur 0.3659
Acetic 1.0008
Cellulose 0.022655093
Glucose 0.9066
HMF 0.0721
Acetyl 0.374831461
Xyfur 0.100798898
AcidLig 0.0032 /
*lig soln 3.2 mg/g solid

Parameter PreHyd4128(PreHydComps) /
TPreHyd 401.15
CA 4
Tau 11.01
Hemi 0.756978632
Xyl 17.038
Fur 0.8224
Acetic 1.0278
Cellulose 0.027969907
Glucose 1.1395
HMF 0.0689
Acetyl 0.356875
Xyfur 0.169218107
AcidLig 0.0043 /
*lig soln 4.3 mg/g solid

Parameter PreHyd6128(PreHydComps) /
TPreHyd 401.15
CA 6
Tau 5.01
Hemi 0.73982906
Xyl 16.5731
Fur 0.6332
Acetic 0.6541
Cellulose 0.015083333
Glucose 0.6327
HMF 0.0189
Acetyl 0.19125731
Xyfur 0.113273703
AcidLig 0.0025 /
*lig soln 2.5 mg/g solid

Parameter PreHyd2100(PreHydComps) /
TPreHyd 373.15
CA 2
Tau 11.01
Hemi 0.130470085
Xyl 3.053
Fur 0.1805
Acetic 0.7434
Cellulose 0.00519213
Glucose 0.2243
HMF 0
Acetyl 0.281590909

```
Xyfur         0.243918919
AcidLig       0.0005     /
*lig soln   0.5 mg/g solid

Parameter PreHyd4100(PreHydComps)     /
TPreHyd       373.15
CA          4
Tau          10.01
Hemi         0.133824786
Xyl         3.1315
Fur         0.1748
Acetic       0.9853
Cellulose     0.008712963
Glucose       0.3764
HMF          0
Acetyl       0.26920765
Xyfur        0.1365625
AcidLig       0.00062     /
*lig soln   0.62 mg/g solid

Parameter PreHyd6100(PreHydComps)     /
TPreHyd       373.15
CA          6
Tau          12.01
Hemi         0.434948718
Xyl         10.1778
Fur         0.2495
Acetic       1.731
Cellulose     0.003981481
Glucose       0.172
HMF          0
Acetyl       0.456728232
Xyfur        0.138611111
AcidLig       0.00082     /
*lig soln   0.82 mg/g solid

Parameter PreHyd61002(PreHydComps)     /
TPreHyd       373.15
CA          6
Tau          28.01
Hemi         0.390824786
Xyl         15.0286
Fur         0.4912
Acetic       2.5099
Cellulose     0.003319444
Glucose       0.399
HMF          0
Acetyl       0.662242744
Xyfur        0.272888889
AcidLig       0.002     /
*lig soln   2 mg/g solid

Parameter PreHyd61222(PreHydComps)     /
TPreHyd       395.15
CA          6
Tau          16.51
Hemi         0.777688034
```

```
Xyl          17.0706
Fur          0.9975
Acetic       4.229
Cellulose    0.182108796
Glucose      7.8671
HMF          0
Acetyl       0.933554084
Xyfur        0.221175166
AcidLig      0.0052    /
*lig soln   5.2 mg/g solid

Parameter PreHyd61282(PreHydComps)    /
TPreHyd      401.15
CA           6
Tau          11.01
Hemi         0.862055556
Xyl          18.3718
Fur          1.2254
Acetic       1.1695
Cellulose    0.03255787
Glucose      1.3198
HMF          0.0867
Acetyl       0.341959064
Xyfur        0.21921288
AcidLig      0.0053    /
*lig soln   5.3 mg/g solid

Parameter PreHyd21222(PreHydComps)    /
TPreHyd      395.15
CA           2
Tau          24.01
Hemi         0.814940171
Xyl          18.1543
Fur          0.4769
Acetic       3.5545
Cellulose    0.093969907
Glucose      4.0314
HMF          0.0281
Acetyl       0.973835616
Xyfur        0.161047297
AcidLig      0.005     /
*lig soln   5 mg/g solid

set numSets /1*13/;

Parameter   FlashVap21001(liquids)/
*2%, 104 degrees, PreHyd 1
      Xylo      0.000318156
      Gluc      0.001500944
      Xylolig   0.000318156
      Glucolig  0.001500944
      Sucrose   0
      Furf      0.984210078
      HMF       0.037156169
      AceA      0.855752323
      Water     0.963967543
      Acid      0.003045513
```

```
      ASL       0
      Phos      0.000452111
      OrgAc     0
      Balance   0    /

Parameter   FlashVap41002(liquids)/
*4%, 104 degrees, PreHyd 2
      Xylo      0.000116906
      Gluc      0.000565986
      Xylolig   0.000116906
      Glucolig  0.000565986
      Sucrose   0
      Furf      0.968070089
      HMF       0.01418591
      AceA      0.693091341
      Water     0.910871575
      Acid      0.001119059
      ASL       0
      Phos      0.000166989
      OrgAc     0
      Balance   0  /

Parameter   FlashVap61003(liquids)/
*6%, 104 degrees, PreHyd 3
      Xylo      0.0000760585
      Gluc      0.000368289
      Xylolig   0.0000760585
      Glucolig  0.000368289
      Sucrose   0
      Furf      0.951692378
      HMF       0.009274925
      AceA      0.595434086
      Water     0.869263457
      Acid      0.000728312
      ASL       0
      Phos      0.000108652
      OrgAc     0
      Balance   0  /

Parameter   FlashVap21287(liquids)/
*2%, 128 degrees, PreHyd 7
      Xylo      0.006291684
      Gluc      0.017825332
      Xylolig   0.006291684
      Glucolig  0.017825332
      Sucrose   0
      Furf      0.984454929
      HMF       0.354133922
      AceA      0.981719911
      Water     0.995461567
      Acid      0.059673068
      ASL       0
      Phos      0.007947698
      OrgAc     0
      Balance   0 /

Parameter   FlashVap21224(liquids)/
```

*2%, 122 degrees, PreHyd 4
Xylo 0.003471174
Gluc 0.010989372
Xylolig 0.003471174
Glucolig 0.010989372
Sucrose 0
Furf 0.981789179
HMF 0.246375324
AceA 0.972835811
Water 0.993346333
Acid 0.033375256
ASL 0
Phos 0.004516156
OrgAc 0.008059282
Balance 0 /

Parameter FlashVap41225(liquids)/
*4%, 122 degrees, PreHyd 5
Xylo 0.002089916
Gluc 0.006636526
Xylolig 0.002089916
Glucolig 0.006636526
Sucrose 0
Furf 0.970062703
HMF 0.164268499
AceA 0.955639245
Water 0.988983585
Acid 0.020337343
ASL 0
Phos 0.002720877
OrgAc 0.004861228
Balance 0 /

Parameter FlashVap61226(liquids)/
*6%, 122 degrees, PreHyd 6
Xylo 0.001465735
Gluc 0.004660846
Xylolig 0.001465735
Glucolig 0.004660846
Sucrose 0
Furf 0.957809518
HMF 0.121084842
AceA 0.937929065
Water 0.98435915
Acid 0.014341654
ASL 0
Phos 0.001908864
OrgAc 0.003412186
Balance 0 /

Parameter FlashVap41288(liquids)/
*4%, 128 degrees, PreHyd 8
Xylo 0.00364976
Gluc 0.010391256
Xylolig 0.00364976
Glucolig 0.010391256
Sucrose 0

```
      Furf      0.973423078
      HMF       0.240827554
      AceA      0.9688209
      Water     0.992183614
      Acid      0.035414763
      ASL       0
      Phos      0.004614897
      OrgAc     0.008387147
      Balance   0  /

Parameter   FlashVap61289(liquids)/
*6%, 128 degrees, PreHyd 9
      Xylo      0.002624165
      Gluc      0.007485521
      Xylolig   0.002624165
      Glucolig  0.007485521
      Sucrose   0
      Furf      0.963386637
      HMF       0.185566505
      AceA      0.957094178
      Water     0.989149539
      Acid      0.025693255
      ASL       0
      Phos      0.003319166
      OrgAc     0.006038407
      Balance   0 /

Parameter   FlashVap612812(liquids)/
*6%, 128 degrees, PreHyd 12
      Xylo      0.002564924
      Gluc      0.007317467
      Xylolig   0.002564924
      Glucolig  0.007317467
      Sucrose   0
      Furf      0.962552795
      HMF       0.182131586
      AceA      0.956173758
      Water     0.988905059
      Acid      0.025126324
      ASL       0
      Phos      0.003244738
      OrgAc     0.005902534
      Balance   0  /
*-------------------------------------------------------------------------------------------------------------------------------------------------
--------
*Acid cellulose hydrolysis data
Set setAcid /a, b, c/
ArrDatak1  /CA, A, AExp, Ea/
ArrDatak2  /CA, A, AExp, Ea/
numAcid/1*3/
FlshData  /CA,m,c/;

Parameter R /8.3145/

Table       Arrheniusk1(setAcid, ArrDatak1)
   CA     A         AExp         Ea
a   0.07   6.50544      16        168283.7
```

```
b   0.14   1.09141      18        176414.8
c   0.28   7.36301      18        180862.8          ;

Table        Arrheniusk2(setAcid, ArrDatak2)
    CA      A          AExp         Ea
a   0.07   2.18617      10         106194.7
b   0.14   3.78382       9         98254.85
c   0.28   4.40680      10         106560.5          ;

Table        FlshCell1(liquids, FlshData)
        CA         m              c
Xylo     0.07        0.0056       - 0.3016
Gluc     0.07        0.0037         0.1146
Xylolig  0.07        0.0056       - 0.3016
Glucolig 0.07        0.0037         0.1146
Furf     0.07        0.000006       0.9986
HMF      0.07        0.0002         0.9606
AceA     0.07        0              0
Water    0.07        0.000001       0.9998
Acid     0.07        0.0007         0.8348
ASL      0.07        0              0
OrgAc    0.07        0              0
Balance    0         0              0
Sucrose    0         0              0  ;
Table        FlshCell2(liquids, FlshData)
        CA         m              c
Xylo     0.14        0.0065       - 0.5236
Gluc     0.14        0.0044       - 0.0563
Xylolig  0.14        0.0065       - 0.5236
Glucolig 0.14        0.0044       - 0.0563
Furf     0.14        0.000007       0.9982
HMF      0.14        0.0002         0.9497
AceA     0.14        0              0
Water    0.14        0.000001       0.9997
Acid     0.14        0.0009         0.7891
ASL      0.14        0              0
OrgAc    0.14        0              0
Balance    0         0              0
Sucrose    0         0              0   ;
Table        FlshCell3(liquids, FlshData)
        CA         m              c
Xylo     0.28        0.0056       - 0.321
Gluc     0.28        0.0037         0.1025
Xylolig  0.28        0.0056       - 0.321
Glucolig 0.28        0.0037         0.1025
Furf     0.28        0.000005       0.9986
HMF      0.28        0.0002         0.9595
AceA     0.28        0              0
Water    0.28        0.0000009      0.9998
Acid     0.28        0.0007         0.8292
ASL      0.28        0              0
OrgAc    0.28        0              0
Balance    0         0              0
Sucrose    0         0              0  ;

parameter ASLconc /0.004/
```

```
*       conversion of the individual reactions
        conv(react)
     /  Hemi_react       0.99
        Xylo_Furf        0.8  /
*-------------------------------------------------------------------------------------------------------------------------------
*Data
Parameters
        x_SCB(J)
        /Cellulose   0.21685935
         Hemi        0.116241708
         Lignin      0.116213417
         Acetyl      0.011918937
         Phos        0.000121522
         Xylo        0
         Xylolig     0
         Gluc        0.000892313
         Glucolig    0
         Sucrose     0.020820644
         Furf        0
         HMF         0
         AceA        0
         Water       0.499962619
         Acid        0
         ASL         0
         Min         0.00154437
         OrgAc       0.002268413
         Salts       0.01220052
         Soil        0.000956187
         Balance     0
         Enz         0/

*Concentrated acid wt%
pureAcid/0.98/
*       Stoichiometric ratio for xylose
        stoichXyl /1.136363636/

*       individual liquid heat capacity of a component (average in a range 20 C - 100 C)
*       in kJ/(kg*C), assume: constant heat capacities
        cp_ind(J)
        /Cellulose   1.681734096
         Hemi        1.680623519
         Lignin      1.02130151
         Acetyl      1.968
         Phos        1.864396721
         Xylo        1.151371399
         Xylolig     1.151371399
         Gluc        1.15138583
         Glucolig    1.15138583
         Sucrose     8.492681297
         Furf        2.024476785
         HMF         2.049797796
         AceA        2.742778034
         Water       4.310177683
         Acid        1.659065815
         ASL         1.02130151
         Min         1.135929339
         OrgAc       2.742778034
```

Salts 0.987197493
Soil 1.427527657
Balance 0
Enz 1.47957994/

* Densities of componenets kg/m3
dens(J)
/Cellulose 1529.7
Hemi 1529.1
Lignin 2376.9
Acetyl 1054.4
Phos 1877.0
Xylo 1826.1
Xylolig 1606.9
Gluc 1180.5
Glucolig 1062.5
Sucrose 902.6
Furf 1163.5
HMF 2220.7
AceA 1054.4
Water 999.0
Acid 1840
ASL 1820.3
Min 315.1
OrgAc 2894.8
Salts 247.8
Soil 3923.6
Balance 999
Enz 1580.0 /

* Molar mass in g/mol
MW(J)
/Cellulose 162.1436
Hemi 132.117
Lignin 194.197
Acetyl 60.053
Phos 97.9952
Xylo 150.131
Xylolig 132.116
Gluc 180.158
Glucolig 162.142
Sucrose 342.3
Furf 96.086
HMF 126.11
AceA 60.05
Water 18.015
Acid 98.079
ASL 194.197
Min 94.196
OrgAc 174.110
Salts 74.551
Soil 60.0843
Enz 24.0156
Balance 18.015/

* Cost or sale price

```
*       Rand per ton
       worth(J)
       /Cellulose   0
        Hemi       0
        Lignin     0
        Acetyl     0
        Phos       0
        Xylo       0
        Gluc     3682
        Furf       0
        HMF        0
        AceA       0
        Water      0.027205
        Acid     2560
        ASL        0
        Min        0
        OrgAc      0
        Salts      0
        Soil       0
        Enz      1708/

Set numSteam/1*7/;
Table       utilProps(U, UtilData)
         TSupply   TTarget     CpVap      Cost
CW         303.15    318.15         4.184   0.44
LPS        417.15    417.14     2133.8      0
MPS1       459.15    459.14     2000.4      1.557
MPS2       533.15    533.14     1662.5      5.5768
HPS1       573.15    573.14     1404.9      7.2767
HPS2       633.15    633.14      720.5     11.674
CTBE1      431.15    431.14     2086.3      0.24
CTBE2      463.28    463.27     1986.2      1.82    ;
*LPS at 3 barg
*for steam, CP is delta H vap in kJ/kg
*cost in $/ton for steam
*       R/ton for CW
                ;
Set cats /GW, OD, Ac, Eu, PS, EWC, EWA, ESC, HTA, HTW, HTS, BW, HW, RW, Sas, Res/;
Set Cmpnts /Acid,NaOH,Enz,Bag,Water,CTBE1,LPS,CTBE2,MPS1,MPS2,HPS1,HPS2,AceA, Furf, AcidFl, CH4, WF,
Eth/;
Set Expan /ExpBag, ExpCH4, ExpEth/;
Table Enviro(cats, Cmpnts)
          Acid           NaOH          Enz           Bag              Water         CTBE2          LPS          CTBE1
MPS1          MPS2          HPS1          HPS2          AceA          Furf     AcidFl          CH4         WF
GW       1.42881E-05       0.000126412       6.59E-03          1.31724E-06       7.50593E-07       4.069791E-07
3.78827E-7       3.87452E-7       4.0409E-7       4.86221E-7       5.75373E-7       1.12192E-6       0.040854722
0       0.017783805      2.34E-04       1.12
OD       1.21112E-07       6.5887E-07       2.16184E-06       1.42041E-08       6.21598E-09       4.388709E-09
4.08513E-9       4.17814E-9       4.35756E-9       5.24322E-9       6.20461E-9       1.20983E-8       0.000253          0
0            6.58E-07       4.4
Ac       0.000181646       6.82024E-05       0.007421255       2.28843E-06       2.5697E-07       7.069978E-07
6.58093E-7       6.73076E-7       7.01979E-7       8.44655E-7       9.9953E-7       1.94898E-6       0              0
0            7.10E-05       1.27
Eu       2.87518E-05       0.00032239       0.003340917       4.43608E-06       1.67478E-07       1.370500E-06
1.2757E-6       1.30474E-6       1.36077E-6       1.63735E-6       1.93757E-6       3.77805E-6       0              0
0.01755          1.06E-04       1.22
```

PS 1.30511E-06 5.31969E-06 0.000120227 1.56948E-05 2.1126E-08 4.848772E-06
4.51337E-6 4.61613E-6 4.81435E-6 5.79286E-6 6.85503E-6 1.33666E-5 0 0
0 2.34E-05 1
EWC 0.001368795 0.013656376 0.073468838 4.05229E-05 7.21621E-07 1.251921E-05
1.16532E-5 1.19185E-5 1.24303E-5 1.49568E-5 1.76992E-5 3.45117E-5 0.0208 0
0 5.66E-03 1.18
EWA 0.001666648 0.016525167 0.089146148 6.3139E-05 8.51281E-07 1.950553E-05
1.81563E-5 1.85697E-5 1.93671E-5 2.33034E-5 2.75763E-5 5.37708E-5 0.00027264
0 0 6.88E-03 1.11
ESC 9.53987E-06 3.09275E-05 7.36685E-05 2.41007E-06 2.14699E-08 7.445831E-07
6.93078E-7 7.08858E-7 7.39298E-7 8.89558E-7 1.05267E-6 2.05259E-6 0 0
0 2.22E-05 1
HTA 2.34807E-05 6.85574E-05 0.001392699 7.17546E-06 1.30666E-07 2.216683E-06
2.06335E-6 2.11033E-6 2.20095E-6 2.64829E-6 3.13387E-6 6.11072E-6 0.0008216
0 0 3.36E-04 1.4
HTW 0.000156748 0.002489761 0.015346475 6.73479E-06 4.19291E-07 2.080685E-06
1.93676E-6 1.98085E-6 2.06592E-6 2.48581E-6 2.9416E-6 5.73582E-6 0.003597 0
0.000233805 5.54E-04 1.3
HTS 0.000303801 0.001861645 0.015398899 0.001219034 8.34879E-07 3.766350E-04
3.50582E-4 3.58564E-4 3.73961E-4 4.49968E-4 5.32474E-4 1.03827E-3 0.00082368
0 0 2.59E-03 1.23
BW 2.8521E-05 0.000104754 0.00541214 3.29075E-06 1.18069E-05 1.016731E-06
9.46402E-7 9.67949E-7 1.00951E-7 1.2147E-6 1.43742E-6 2.80282E-6 0.0151104 0
0 1.38E-04 1.10
HW 2.27744E-07 5.61968E-06 2.98755E-06 1.0813E-08 0 3.340724E-09
3.10964E-9 3.18044E-9 3.31701E-9 3.99119E-9 4.723E-9 9.20936E-9 0 0 0
8.96E-07 1.10
RW 0.000122592 0.003298263 0.013137083 4.20091E-06 2.58223E-06 1.297896E-06
1.20812E-6 1.23562E-6 1.28868E-6 1.5506E-6 1.83492E-6 3.5779E-6 0 0 0
3.34E-03 1.10
Sas 1.5399E-07 5.85146E-07 1.20575E-06 1.87091E-07 3.46914E-09 5.779027E-08
5.37928E-8 5.50175E-8 5.738E-8 6.90424E-8 8.17019E-8 1.5931E-8 0 0 0
1.71E-05 1.10
Res 0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0.00E+00 0 ;

Table SysExp(cats, Expan)
ExpBag ExpCH4 ExpEth
GW 0.00020395 1.33E-06 2.69E-04
OD 0 5.25E-08 6.02E-06
Ac 0 1.43E-06 2.52E-04
Eu 0 1.72E-06 1.26E-04
PS 0 3.94E-07 5.86E-05
EWC 0 1.13E-04 7.78E-03
EWA 0 1.81E-04 9.41E-03
ESC 0 7.42E-08 5.74E-06
HTA 0 9.01E-07 6.50E-04
HTW 0 1.63E-05 6.46E-04
HTS 0 1.79E-05 6.06E-03
BW 0 7.87E-07 2.01E-04
HW 0 5.22E-08 1.05E-06
RW 0 4.47E-06 4.59E-04
Sas 0 7.71E-09 2.99E-07
Res 0 0.00E+00 0.00E+00 ;
Parameter SteamFiltSol /0.995/

SET Arc(unit,unit1) stream matrix;

```
*setting entries in stream matrix
Arc(unit, unit1)=No;
*Define all existing streams Arc('1','2') is stream from unit 1 to unit 2
*PreHydrolysis
Arc('SrcBag','MixPreHyd')=Yes;
Arc('SrcAcid','MixPreHyd')=Yes;
Arc('SrcSteam','MixPreHyd')=Yes;
Arc('SrcWater','MixPreHyd')=Yes;
Arc('MixPreHyd','PreHyd')=Yes;
Arc('PreHyd','FlsPreHyd')=Yes;
Arc('FlsPreHyd','SnkVapFlsh1')=Yes;
Arc('FlsPreHyd','FiltPreHyd')=Yes;
Arc('SrcWater','FiltPreHyd')=Yes;
Arc('FiltPreHyd','SnkC5')=Yes;
Arc('FiltPreHyd','MixAcidCellHyd')=Yes;

*Acid cellulose hydrolysis
Arc('SrcAcid','MixAcidCellHyd')=Yes;
Arc('SrcSteam','MixAcidCellHyd')=Yes;
Arc('SrcWater','MixAcidCellHyd')=Yes;
Arc('MixAcidCellHyd','AcidCellHyd')=Yes;
Arc('AcidCellHyd','FlsAcidCellHyd')=Yes;
Arc('FlsAcidCellHyd','FiltCellHyd')=Yes;
Arc('FlsAcidCellHyd','SnkVapFlsh2')=Yes;
Arc('SrcWater','FiltCellHyd')=Yes;
Arc('FiltCellHyd','SnkSolid')=Yes;
Arc('FiltCellHyd','SnkC6')=Yes;
Arc('FictIN','FictCell')=Yes;
Arc('FictCell','FictOUT')=Yes;

Positive Variables
      WSRPre              water solid ratio (g water per g bagasse)
      WSRCell             water solid ratio (g water per g bagasse)
      F(unit,unit1)       total streams in kg s^-1
      fc(J,unit,unit1)    individual components streams
      x(J,unit,unit1)     mass fraction of comp J in stream
      FU(U,unit)          utility flowrates in kg s^-1
      V(unit, unit1)      total stream in m3 per s
      conc(J,unit,unit1)    mass concentration of components in kg per m3
      Volume(unit)        Volume of unit in m3
      LDrat(unit)         L over D ratio
      Diameter(unit)      Diameter of unit in m
      Length(unit)        Length of unit in m
      thick(unit)         Thickness of unit in mm
      weight(unit)        Weight of unit in lbs of carbon steel unit
      SA(filt)            surface area of filters in m^2
      Cv(unit)            Vessel cost in $
      Cpl(unit)           Cost for platforms and ladders in $
      Cp(unit)            purchase cost for equipment in $
      acidWtPre           dilute acid wt%
      acidWtCell          dilute acid wt%
      PreHydFiltSplit     liquid split ratio in filter after prehydrolysis
      PreHydLiqFrac       liquid fraction in the solid stream exiting the filter after prehydrolysis
      CellHydFiltSplit    liquid split ratio in filter after cellulose hydrolysis
      CellLiqFrac         liquid fraction in the solid stream exiting the filter after cellulose hydrolysis
      k1Gluc              rate constant for glucose production in min^-1
      k2Gluc              rate constant for glucose consumpion in min^-1
```

```
      Tau(unit)            residence time of unit in minutes
      FlshVapFrac(liquids)    weight percent of component vapourised in the flash, T dependent
      YieldDecr            % by which the yield in CellAcidHyd is decreased based on delignification
      fictGYield           glucose yield %
      fictcellRem           cellulose remaining %
      GYield               glucose yield %
      cellRem              cellulose remaining %
      T(unit,unit1)         temperature of stream in C
      W(Unit)              power consumption of unit in kW (efficiency included);

Variable
      Q(Unit)       heat produced or consumed in unit in kJ (efficiency included)
      z            overall profit in millions of Rand per year;

Binary Variable PreHydBin(numSets),acidChoice(numAcid),steamChoice(numSteam);
*Global relationships
Equations
      Rel_1, Rel_2,VolFlow1,VolFlow2,VolFlow3,VolFlow4,VolFlow5,VolFlow6;
*relationship between F, fc and x
Rel_1(J,unit,unit1)$Arc(unit,unit1)..
      fc(J,unit,unit1) =E= F(unit,unit1)*x(J,unit,unit1);

Rel_2(unit,unit1)$Arc(unit,unit1)..
      Sum(J,fc(J,unit,unit1)) =E= F(unit,unit1);

VolFlow1..
       V('SrcAcid','MixAcidCellHyd') =E= sum(J, fc(J,'SrcAcid','MixAcidCellHyd')/dens(J));

VolFlow2..
       V('SrcSteam','MixAcidCellHyd') =E= sum(J, fc(J,'SrcSteam','MixAcidCellHyd')/dens(J));

VolFlow3..
       V('SrcWater','MixAcidCellHyd') =E= sum(J, fc(J,'SrcWater','MixAcidCellHyd')/dens(J));

VolFlow4..
       V('FiltPreHyd','MixAcidCellHyd') =E= sum(J, fc(J,'FiltPreHyd','MixAcidCellHyd')/dens(J));

VolFlow5..
       V('MixAcidCellHyd','AcidCellHyd') =E= sum(J, fc(J,'MixAcidCellHyd','AcidCellHyd')/dens(J));

VolFlow6..
       V('MixPreHyd','PreHyd') =E= sum(J, fc(J,'MixPreHyd','PreHyd')/dens(J));

*Define global bounds and fix specific variables
*WSRPre is fixed at 10.
WSRPre.fx = 10;
*mass fractions
x.UP(J,unit,unit1)$Arc(unit,unit1)=1;
x.lo(J,unit,unit1)$Arc(unit,unit1)=0;
*Total streams
F.lo(unit,unit1)$Arc(unit,unit1)=0;
F.UP(unit,unit1)$Arc(unit,unit1)=3000;
*Component streams
fc.UP(J,unit,unit1)$Arc(unit,unit1)=500;
fc.UP('Water',unit,unit1)$Arc(unit,unit1)=1200;

F.up(unit,unit1)$(not Arc(unit,unit1)) = 0;
```

```
fc.up(J,unit,unit1)$(not Arc(unit,unit1)) = 0;

V.lo(unit,unit1) = 0.0000001;
V.lo('SrcAcid','MixAcidCellHyd') = 0;
V.up(unit,unit1) = 20;

conc.lo(J,unit,unit1)$Arc(unit,unit1)=0;
conc.UP(J,unit,unit1)$Arc(unit,unit1)=700;
conc.UP('Water',unit,unit1)$Arc(unit,unit1)=2000;

fc.lo('Cellulose','SrcBag','MixPreHyd')=  0.1;
fc.lo('Hemi','SrcBag','MixPreHyd')=  0.01;
fc.lo('Lignin','SrcBag','MixPreHyd')=  0.1;
fc.lo('Acetyl','SrcBag','MixPreHyd')=  0.01;
fc.lo('Phos','SrcBag','MixPreHyd')=  0.00001;
fc.lo('Xylo','SrcBag','MixPreHyd')=  0;
*fc.lo('Xylolig','SrcBag','MixPreHyd')=  0.01;
fc.lo('Gluc','SrcBag','MixPreHyd')=  0;
*fc.lo('Glucolig','SrcBag','MixPreHyd')=  0.01;
*fc.lo('Sucrose','SrcBag','MixPreHyd')=  0;
fc.lo('Furf','SrcBag','MixPreHyd')=  0;
fc.lo('HMF','SrcBag','MixPreHyd')=  0;
fc.lo('AceA','SrcBag','MixPreHyd')=  0;
fc.lo('Water','SrcBag','MixPreHyd')=  0.2;
fc.lo('Acid','SrcBag','MixPreHyd')=  0;
fc.lo('ASL','SrcBag','MixPreHyd')=  0;
fc.lo('Min','SrcBag','MixPreHyd')=  0.0001;
fc.lo('OrgAc','SrcBag','MixPreHyd')=  0.0001;
fc.lo('Salts','SrcBag','MixPreHyd')=  0.003;
fc.lo('Soil','SrcBag','MixPreHyd')=  0.0001;
fc.lo('Balance','SrcBag','MixPreHyd')=  0;
fc.lo('Enz','SrcBag','MixPreHyd')=  0;

fc.lo('Water','SrcSteam','MixPreHyd')=  0.1;
fc.lo('Water','SrcWater','MixPreHyd')=  0.1;
fc.lo('Water','SrcAcid','MixPreHyd')=  0.001;
fc.lo('Acid','SrcAcid','MixPreHyd')=  0.001;
fc.lo('Water','SrcWater','FiltPreHyd')=  0;

fc.lo('Cellulose','MixPreHyd','PreHyd')=  0.1;
fc.lo('Hemi','MixPreHyd','PreHyd')=  0.01;
fc.lo('Lignin','MixPreHyd','PreHyd')=  0.1;
fc.lo('Acetyl','MixPreHyd','PreHyd')=  0.001;
fc.lo('Phos','MixPreHyd','PreHyd')=  0.00001;
fc.lo('Xylo','MixPreHyd','PreHyd')=  0;
*fc.lo('Xylolig','MixPreHyd','PreHyd')=  0.01;
fc.lo('Gluc','MixPreHyd','PreHyd')=  0;
*fc.lo('Glucolig','MixPreHyd','PreHyd')=  0.01;
*fc.lo('Sucrose','MixPreHyd','PreHyd')=  0;
fc.lo('Furf','MixPreHyd','PreHyd')=  0;
fc.lo('HMF','MixPreHyd','PreHyd')=  0;
fc.lo('AceA','MixPreHyd','PreHyd')=  0;
fc.lo('Water','MixPreHyd','PreHyd')=  0.2;
fc.lo('Acid','MixPreHyd','PreHyd')=  0.01;
fc.lo('ASL','MixPreHyd','PreHyd')=  0;
fc.lo('Min','MixPreHyd','PreHyd')=  0.0001;
fc.lo('OrgAc','MixPreHyd','PreHyd')=  0.0001;
```

```
fc.lo('Salts','MixPreHyd','PreHyd')=  0.003;
fc.lo('Soil','MixPreHyd','PreHyd')=  0.0001;
fc.lo('Balance','MixPreHyd','PreHyd')=  0;
fc.lo('Enz','MixPreHyd','PreHyd')=  0;

fc.lo('Cellulose','PreHyd','FlsPreHyd')=  0.1;
fc.lo('Hemi','PreHyd','FlsPreHyd')=  0.01;
fc.lo('Lignin','PreHyd','FlsPreHyd')=  0.1;
fc.lo('Acetyl','PreHyd','FlsPreHyd')=  0.001;
fc.lo('Phos','PreHyd','FlsPreHyd')=  0.00001;
fc.lo('Xylo','PreHyd','FlsPreHyd')=  0.01;
*fc.lo('Xylolig','PreHyd','FlsPreHyd')=  0.01;
fc.lo('Gluc','PreHyd','FlsPreHyd')=  0.01;
*fc.lo('Glucolig','PreHyd','FlsPreHyd')=  0.01;
*fc.lo('Sucrose','PreHyd','FlsPreHyd')=  0;
fc.lo('Furf','PreHyd','FlsPreHyd')=  0.0001;
fc.lo('HMF','PreHyd','FlsPreHyd')=  0;
fc.lo('AceA','PreHyd','FlsPreHyd')=  0.001;
fc.lo('Water','PreHyd','FlsPreHyd')=  0.2;
fc.lo('Acid','PreHyd','FlsPreHyd')=  0.001;
fc.lo('ASL','PreHyd','FlsPreHyd')=  0.001;
fc.lo('Min','PreHyd','FlsPreHyd')=  0.0001;
fc.lo('OrgAc','PreHyd','FlsPreHyd')=  0.0001;
fc.lo('Salts','PreHyd','FlsPreHyd')=  0.003;
fc.lo('Soil','PreHyd','FlsPreHyd')=  0.0001;
fc.lo('Balance','PreHyd','FlsPreHyd')=  0;
fc.lo('Enz','PreHyd','FlsPreHyd')=  0;

*fc.lo('Cellulose','PreHyd','FlsPreHyd')=  0.1;
*fc.lo('Hemi','PreHyd','FlsPreHyd')=  0.1;
*fc.lo('Lignin','PreHyd','FlsPreHyd')=  0.1;
*fc.lo('Acetyl','PreHyd','FlsPreHyd')=  0.01;
*fc.lo('Phos','PreHyd','FlsPreHyd')=  0.1;
fc.lo('Xylo','FlsPreHyd','SnkVapFlsh1')=  0.000000001;
*fc.lo('Xylolig','FlsPreHyd','SnkVapFlsh1')=  0.01;
*fc.lo('Gluc','FlsPreHyd','SnkVapFlsh1')=  0.000000001;
*fc.lo('Glucolig','FlsPreHyd','SnkVapFlsh1')=  0.01;
*fc.lo('Sucrose','FlsPreHyd','SnkVapFlsh1')=  0;
fc.lo('Furf','FlsPreHyd','SnkVapFlsh1')=  0.0000000001;
fc.lo('HMF','FlsPreHyd','SnkVapFlsh1')=  0;
fc.lo('AceA','FlsPreHyd','SnkVapFlsh1')=  0.000000001;
fc.lo('Water','FlsPreHyd','SnkVapFlsh1')=  1;
fc.lo('Acid','FlsPreHyd','SnkVapFlsh1')=  0.000000001;
*fc.lo('ASL','PreHyd','FlsPreHyd')=  0.001;
*fc.lo('Min','PreHyd','FlsPreHyd')=  0.001;
*fc.lo('OrgAc','PreHyd','FlsPreHyd')=  0.001;
*fc.lo('Salts','PreHyd','FlsPreHyd')=  0.03;
*fc.lo('Soil','PreHyd','FlsPreHyd')=  0.001;
*fc.lo('Balance','PreHyd','FlsPreHyd')=  0;
*fc.lo('Enz','PreHyd','FlsPreHyd')=  0;

*fc.lo('Cellulose','PreHyd','FlsPreHyd')=  0.1;
*fc.lo('Hemi','PreHyd','FlsPreHyd')=  0.1;
*fc.lo('Lignin','PreHyd','FlsPreHyd')=  0.1;
*fc.lo('Acetyl','PreHyd','FlsPreHyd')=  0.01;
fc.lo('Phos','PreHyd','FlsPreHyd')=  0.00001;
fc.lo('Xylo','FlsPreHyd','FiltPreHyd')=  0.001;
```

```
*fc.lo('Xylolig','FlsPreHyd','SnkC5')=   0.01;
fc.lo('Gluc','FlsPreHyd','FiltPreHyd')=    0.001;
*fc.lo('Glucolig','FlsPreHyd','SnkC5')=   0.01;
*fc.lo('Sucrose','FlsPreHyd','SnkC5')=   0;
fc.lo('Furf','FlsPreHyd','FiltPreHyd')=    0.00001;
fc.lo('HMF','FlsPreHyd','FiltPreHyd')=   0;
fc.lo('AceA','FlsPreHyd','FiltPreHyd')=    0.0001;
fc.lo('Water','FlsPreHyd','FiltPreHyd')=  0.01;
fc.lo('Acid','FlsPreHyd','FiltPreHyd')=    0.001;
fc.lo('ASL','FlsPreHyd','FiltPreHyd')=    0.001;
*fc.lo('Min','PreHyd','FlsPreHyd')=   0.001;
fc.lo('OrgAc','FlsPreHyd','FiltPreHyd')=    0.0001;
*fc.lo('Salts','PreHyd','FlsPreHyd')=   0.03;
*fc.lo('Soil','PreHyd','FlsPreHyd')=   0.001;
*fc.lo('Balance','PreHyd','FlsPreHyd')=   0;
*fc.lo('Enz','PreHyd','FlsPreHyd')=   0;

fc.lo('Cellulose','FlsPreHyd','FiltPreHyd')=   0.1;
fc.lo('Hemi','FlsPreHyd','FiltPreHyd')=   0.01;
fc.lo('Lignin','FlsPreHyd','FiltPreHyd')=   0.1;
fc.lo('Acetyl','FlsPreHyd','FiltPreHyd')=   0.001;
fc.lo('Phos','FlsPreHyd','FiltPreHyd')=    0.00001;
*fc.lo('Xylo','FlsPreHyd','MixAcidCellHyd')=   0.001;
*fc.lo('Xylolig','FlsPreHyd','MixAcidCellHyd')=   0.01;
*fc.lo('Gluc','FlsPreHyd','MixAcidCellHyd')=    0.001;
*fc.lo('Glucolig','FlsPreHyd','MixAcidCellHyd')=   0.01;
*fc.lo('Sucrose','FlsPreHyd','MixAcidCellHyd')=   0;
*fc.lo('Furf','FlsPreHyd','MixAcidCellHyd')=    0.001;
*fc.lo('HMF','FlsPreHyd','MixAcidCellHyd')=   0.001;
*fc.lo('AceA','FlsPreHyd','MixAcidCellHyd')=    0.001;
*fc.lo('Water','FlsPreHyd','MixAcidCellHyd')=  0.01;
*fc.lo('Acid','FlsPreHyd','MixAcidCellHyd')=    0.001;
*fc.lo('ASL','FlsPreHyd','MixAcidCellHyd')=    0.001;
fc.lo('Min','FlsPreHyd','FiltPreHyd')=   0.0001;
*fc.lo('OrgAc','FlsPreHyd','MixAcidCellHyd')=    0.001;
fc.lo('Salts','FlsPreHyd','FiltPreHyd')=   0.003;
fc.lo('Soil','FlsPreHyd','FiltPreHyd')=   0.0001;
*fc.lo('Balance','FlsPreHyd','MixAcidCellHyd')=   0;
*fc.lo('Enz','FlsPreHyd','MixAcidCellHyd')=   0;


fc.lo('Cellulose','FiltPreHyd','SnkC5')=   0.0001;
fc.lo('Hemi','FiltPreHyd','SnkC5')=   0.00001;
fc.lo('Lignin','FiltPreHyd','SnkC5')=   0.0001;
fc.lo('Acetyl','FiltPreHyd','SnkC5')=   0.000001;
fc.lo('Phos','FiltPreHyd','SnkC5')=    0.000001;
fc.lo('Xylo','FiltPreHyd','SnkC5')=   0.0001;
*fc.lo('Xylolig','FlsPreHyd','SnkC5')=   0.01;
fc.lo('Gluc','FiltPreHyd','SnkC5')=    0.0001;
*fc.lo('Glucolig','FlsPreHyd','SnkC5')=   0.01;
*fc.lo('Sucrose','FlsPreHyd','SnkC5')=   0;
fc.lo('Furf','FiltPreHyd','SnkC5')=    0.000001;
fc.lo('HMF','FiltPreHyd','SnkC5')=   0;
fc.lo('AceA','FiltPreHyd','SnkC5')=    0.00001;
fc.lo('Water','FiltPreHyd','SnkC5')=  0.001;
fc.lo('Acid','FiltPreHyd','SnkC5')=    0.0001;
fc.lo('ASL','FiltPreHyd','SnkC5')=    0.0001;
```

```
fc.lo('Min','FiltPreHyd','SnkC5')=   0.00001;
fc.lo('OrgAc','FiltPreHyd','SnkC5')=    0.0001;
fc.lo('Salts','FiltPreHyd','SnkC5')=    0.00001;
fc.lo('Soil','FiltPreHyd','SnkC5')=    0.000001;
*fc.lo('Balance','PreHyd','FlsPreHyd')=   0;
*fc.lo('Enz','PreHyd','FlsPreHyd')=   0;

fc.lo('Cellulose','FiltPreHyd','MixAcidCellHyd')=   0.1;
fc.lo('Hemi','FiltPreHyd','MixAcidCellHyd')=   0.01;
fc.lo('Lignin','FiltPreHyd','MixAcidCellHyd')=   0.1;
fc.lo('Acetyl','FiltPreHyd','MixAcidCellHyd')=   0.001;
fc.lo('Phos','FiltPreHyd','MixAcidCellHyd')=     0.00001;
fc.lo('Xylo','FiltPreHyd','MixAcidCellHyd')=   0.001;
*fc.lo('Xylolig','FiltPreHyd','MixAcidCellHyd')=   0.01;
fc.lo('Gluc','FiltPreHyd','MixAcidCellHyd')=    0.001;
*fc.lo('Glucolig','FiltPreHyd','MixAcidCellHyd')=   0.01;
*fc.lo('Sucrose','FiltPreHyd','MixAcidCellHyd')=   0;
*fc.lo('Furf','FiltPreHyd','MixAcidCellHyd')=    0.0001;
fc.lo('HMF','FiltPreHyd','MixAcidCellHyd')=   0;
*fc.lo('AceA','FiltPreHyd','MixAcidCellHyd')=     0.001;
*fc.lo('Water','FiltPreHyd','MixAcidCellHyd')=  0.01;
fc.lo('Acid','FiltPreHyd','MixAcidCellHyd')=     0.001;
fc.lo('ASL','FiltPreHyd','MixAcidCellHyd')=    0.0001;
fc.lo('Min','FiltPreHyd','MixAcidCellHyd')=   0.00001;
fc.lo('OrgAc','FiltPreHyd','MixAcidCellHyd')=    0.00001;
fc.lo('Salts','FiltPreHyd','MixAcidCellHyd')=   0.0003;
fc.lo('Soil','FiltPreHyd','MixAcidCellHyd')=   0.00001;
fc.lo('Balance','FiltPreHyd','MixAcidCellHyd')=   0;
fc.lo('Enz','FiltPreHyd','MixAcidCellHyd')=   0;
*-------------------------------------------------------------------------------------------------------------------------------------------------
---
F.l('SrcSteam','MixAcidCellHyd')= 82;
F.l('SrcWater','MixAcidCellHyd')= 138;
F.l('MixAcidCellHyd','AcidCellHyd')= 230;

F.l('FictIN','FictCell')= 230;

FlshVapFrac.lo(liquids)=0;
FlshVapFrac.up(liquids)=1;
FlshVapFrac.fx('ASL')=0;

fc.lo('Water','SrcWater','MixAcidCellHyd')= 0.001;
fc.lo('Water','SrcSteam','MixAcidCellHyd')= 0.01;

fc.fx('Cellulose','SrcWater','MixAcidCellHyd')=   0;
fc.fx('Hemi','SrcWater','MixAcidCellHyd')=    0;
fc.fx('Lignin','SrcWater','MixAcidCellHyd')=   0;
fc.fx('Acetyl','SrcWater','MixAcidCellHyd')=   0;
fc.fx('Phos','SrcWater','MixAcidCellHyd')=     0;
fc.fx('Xylo','SrcWater','MixAcidCellHyd')=     0;
fc.fx('Xylolig','SrcWater','MixAcidCellHyd')=  0;
fc.fx('Gluc','SrcWater','MixAcidCellHyd')=     0;
fc.fx('Glucolig','SrcWater','MixAcidCellHyd')=   0;
fc.fx('Sucrose','SrcWater','MixAcidCellHyd')=  0;
fc.fx('Furf','SrcWater','MixAcidCellHyd')=   0;
fc.fx('HMF','SrcWater','MixAcidCellHyd')=   0;
fc.fx('AceA','SrcWater','MixAcidCellHyd')=   0;
```

```
fc.lo('Water','SrcWater','MixAcidCellHyd')=  0.001;
fc.fx('Acid','SrcWater','MixAcidCellHyd')=  0;
fc.fx('ASL','SrcWater','MixAcidCellHyd')=  0;
fc.fx('Min','SrcWater','MixAcidCellHyd')=  0;
fc.fx('OrgAc','SrcWater','MixAcidCellHyd')=  0;
fc.fx('Salts','SrcWater','MixAcidCellHyd')=  0;
fc.fx('Soil','SrcWater','MixAcidCellHyd')=  0;
fc.fx('Balance','SrcWater','MixAcidCellHyd')=  0;

fc.fx('Cellulose','SrcSteam','MixAcidCellHyd')=  0;
fc.fx('Hemi','SrcSteam','MixAcidCellHyd')=  0;
fc.fx('Lignin','SrcSteam','MixAcidCellHyd')=  0;
fc.fx('Acetyl','SrcSteam','MixAcidCellHyd')=  0;
fc.fx('Phos','SrcSteam','MixAcidCellHyd')=  0;
fc.fx('Xylo','SrcSteam','MixAcidCellHyd')=  0;
fc.fx('Xylolig','SrcSteam','MixAcidCellHyd')=  0;
fc.fx('Gluc','SrcSteam','MixAcidCellHyd')=  0;
fc.fx('Glucolig','SrcSteam','MixAcidCellHyd')=  0;
fc.fx('Sucrose','SrcSteam','MixAcidCellHyd')=  0;
fc.fx('Furf','SrcSteam','MixAcidCellHyd')=  0;
fc.fx('HMF','SrcSteam','MixAcidCellHyd')=  0;
fc.fx('AceA','SrcSteam','MixAcidCellHyd')=  0;
*fc.lo('Water','SrcSteam','MixAcidCellHyd')=  0.001;
fc.fx('Acid','SrcSteam','MixAcidCellHyd')=  0;
fc.fx('ASL','SrcSteam','MixAcidCellHyd')=  0;
fc.fx('Min','SrcSteam','MixAcidCellHyd')=  0;
fc.fx('OrgAc','SrcSteam','MixAcidCellHyd')=  0;
fc.fx('Salts','SrcSteam','MixAcidCellHyd')=  0;
fc.fx('Soil','SrcSteam','MixAcidCellHyd')=  0;
fc.fx('Balance','SrcSteam','MixAcidCellHyd')=  0;
fc.fx('Enz','SrcSteam','MixAcidCellHyd')=  0;

fc.fx('Cellulose','SrcAcid','MixAcidCellHyd')=  0;
fc.fx('Hemi','SrcAcid','MixAcidCellHyd')=  0;
fc.fx('Lignin','SrcAcid','MixAcidCellHyd')=  0;
fc.fx('Acetyl','SrcAcid','MixAcidCellHyd')=  0;
fc.fx('Phos','SrcAcid','MixAcidCellHyd')=  0;
fc.fx('Xylo','SrcAcid','MixAcidCellHyd')=  0;
fc.fx('Xylolig','SrcAcid','MixAcidCellHyd')=  0;
fc.fx('Gluc','SrcAcid','MixAcidCellHyd')=  0;
fc.fx('Glucolig','SrcAcid','MixAcidCellHyd')=  0;
fc.fx('Sucrose','SrcAcid','MixAcidCellHyd')=  0;
fc.fx('Furf','SrcAcid','MixAcidCellHyd')=  0;
fc.fx('HMF','SrcAcid','MixAcidCellHyd')=  0;
fc.fx('AceA','SrcAcid','MixAcidCellHyd')=  0;
*fc.lo('Water','SrcAcid','MixAcidCellHyd')=  0.001;
*fc.fx('Acid','SrcAcid','MixAcidCellHyd')=  0;
fc.fx('ASL','SrcAcid','MixAcidCellHyd')=  0;
fc.fx('Min','SrcAcid','MixAcidCellHyd')=  0;
fc.fx('OrgAc','SrcAcid','MixAcidCellHyd')=  0;
fc.fx('Salts','SrcAcid','MixAcidCellHyd')=  0;
fc.fx('Soil','SrcAcid','MixAcidCellHyd')=  0;
fc.fx('Balance','SrcAcid','MixAcidCellHyd')=  0;
fc.fx('Enz','SrcAcid','MixAcidCellHyd')=  0;

*fc.fx('Cellulose','SrcBag','MixPreHyd')=  1;
*fc.fx('Hemi','SrcBag','MixPreHyd')=  1;
```

```
*fc.fx('Lignin','SrcBag','MixPreHyd')=   1;
*fc.fx('Acetyl','SrcBag','MixPreHyd')=    0.01;
*fc.fx('Phos','SrcBag','MixPreHyd')=   0.0001;
fc.fx('Xylo','SrcBag','MixPreHyd')=   0;
fc.fx('Xylolig','SrcBag','MixPreHyd')=   0;
*fc.fx('Gluc','SrcBag','MixPreHyd')=   0.001;
fc.fx('Glucolig','SrcBag','MixPreHyd')=   0;
*fc.fx('Sucrose','SrcBag','MixPreHyd')=   0.001;
fc.fx('Furf','SrcBag','MixPreHyd')=   0;
fc.fx('HMF','SrcBag','MixPreHyd')=   0;
fc.fx('AceA','SrcBag','MixPreHyd')=   0;
*fc.fx('Water','SrcBag','MixPreHyd')=   5;
fc.fx('Acid','SrcBag','MixPreHyd')=   0;
fc.fx('ASL','SrcBag','MixPreHyd')=   0;
*fc.fx('Min','SrcBag','MixPreHyd')=   0.001;
*fc.fx('OrgAc','SrcBag','MixPreHyd')=   0.001;
*fc.fx('Salts','SrcBag','MixPreHyd')=   0.03;
*fc.fx('Soil','SrcBag','MixPreHyd')=   0.001;
fc.fx('Balance','SrcBag','MixPreHyd')=   0;
fc.fx('Enz','SrcBag','MixPreHyd')=   0;

fc.fx('Cellulose','SrcAcid','MixPreHyd')=   0;
fc.fx('Hemi','SrcAcid','MixPreHyd')=       0;
fc.fx('Lignin','SrcAcid','MixPreHyd')=  0;
fc.fx('Acetyl','SrcAcid','MixPreHyd')=    0;
fc.fx('Phos','SrcAcid','MixPreHyd')=   0;
fc.fx('Xylo','SrcAcid','MixPreHyd')=   0;
fc.fx('Xylolig','SrcAcid','MixPreHyd')=   0;
fc.fx('Gluc','SrcAcid','MixPreHyd')=   0;
fc.fx('Glucolig','SrcAcid','MixPreHyd')=   0;
fc.fx('Sucrose','SrcAcid','MixPreHyd')=    0;
fc.fx('Furf','SrcAcid','MixPreHyd')=   0;
fc.fx('HMF','SrcAcid','MixPreHyd')=   0;
fc.fx('AceA','SrcAcid','MixPreHyd')=   0;
*fc.fx('Water','SrcAcid','MixPreHyd')=   5;
*fc.fx('Acid','SrcAcid','MixPreHyd')=   0;
fc.fx('ASL','SrcAcid','MixPreHyd')=   0;
fc.fx('Min','SrcAcid','MixPreHyd')=   0;
fc.fx('OrgAc','SrcAcid','MixPreHyd')=   0;
fc.fx('Salts','SrcAcid','MixPreHyd')=   0;
fc.fx('Soil','SrcAcid','MixPreHyd')=   0;
fc.fx('Balance','SrcAcid','MixPreHyd')=   0;
fc.fx('Enz','SrcAcid','MixPreHyd')=   0;

fc.fx('Cellulose','SrcSteam','MixPreHyd')=   0;
fc.fx('Hemi','SrcSteam','MixPreHyd')=       0;
fc.fx('Lignin','SrcSteam','MixPreHyd')=  0;
fc.fx('Acetyl','SrcSteam','MixPreHyd')=    0;
fc.fx('Phos','SrcSteam','MixPreHyd')=   0;
fc.fx('Xylo','SrcSteam','MixPreHyd')=   0;
fc.fx('Xylolig','SrcSteam','MixPreHyd')=   0;
fc.fx('Gluc','SrcSteam','MixPreHyd')=   0;
fc.fx('Glucolig','SrcSteam','MixPreHyd')=   0;
fc.fx('Sucrose','SrcSteam','MixPreHyd')=    0;
fc.fx('Furf','SrcSteam','MixPreHyd')=   0;
fc.fx('HMF','SrcSteam','MixPreHyd')=   0;
fc.fx('AceA','SrcSteam','MixPreHyd')=   0;
```

```
*fc.fx('Water','SrcSteam','MixPreHyd')=  5;
*fc.fx('Acid','SrcSteam','MixPreHyd')=  0;
fc.fx('ASL','SrcSteam','MixPreHyd')=  0;
fc.fx('Min','SrcSteam','MixPreHyd')=  0;
fc.fx('OrgAc','SrcSteam','MixPreHyd')=  0;
fc.fx('Salts','SrcSteam','MixPreHyd')=  0;
fc.fx('Soil','SrcSteam','MixPreHyd')=  0;
fc.fx('Balance','SrcSteam','MixPreHyd')=  0;
fc.fx('Enz','SrcSteam','MixPreHyd')=  0;

fc.fx('Cellulose','SrcWater','MixPreHyd')=  0;
fc.fx('Hemi','SrcWater','MixPreHyd')=  0;
fc.fx('Lignin','SrcWater','MixPreHyd')=  0;
fc.fx('Acetyl','SrcWater','MixPreHyd')=  0;
fc.fx('Phos','SrcWater','MixPreHyd')=  0;
fc.fx('Xylo','SrcWater','MixPreHyd')=  0;
fc.fx('Xylolig','SrcWater','MixPreHyd')=  0;
fc.fx('Gluc','SrcWater','MixPreHyd')=  0;
fc.fx('Glucolig','SrcWater','MixPreHyd')=  0;
fc.fx('Sucrose','SrcWater','MixPreHyd')=  0;
fc.fx('Furf','SrcWater','MixPreHyd')=  0;
fc.fx('HMF','SrcWater','MixPreHyd')=  0;
fc.fx('AceA','SrcWater','MixPreHyd')=  0;
*fc.fx('Water','SrcWater','MixPreHyd')=  5;
fc.fx('Acid','SrcWater','MixPreHyd')=  0;
fc.fx('ASL','SrcWater','MixPreHyd')=  0;
fc.fx('Min','SrcWater','MixPreHyd')=  0;
fc.fx('OrgAc','SrcWater','MixPreHyd')=  0;
fc.fx('Salts','SrcWater','MixPreHyd')=  0;
fc.fx('Soil','SrcWater','MixPreHyd')=  0;
fc.fx('Balance','SrcWater','MixPreHyd')=  0;
fc.fx('Enz','SrcWater','MixPreHyd')=  0;

fc.fx('Cellulose','SrcWater','FiltPreHyd')=  0;
fc.fx('Hemi','SrcWater','FiltPreHyd')=  0;
fc.fx('Lignin','SrcWater','FiltPreHyd')=  0;
fc.fx('Acetyl','SrcWater','FiltPreHyd')=  0;
fc.fx('Phos','SrcWater','FiltPreHyd')=  0;
fc.fx('Xylo','SrcWater','FiltPreHyd')=  0;
fc.fx('Xylolig','SrcWater','FiltPreHyd')=  0;
fc.fx('Gluc','SrcWater','FiltPreHyd')=  0;
fc.fx('Glucolig','SrcWater','FiltPreHyd')=  0;
fc.fx('Sucrose','SrcWater','FiltPreHyd')=  0;
fc.fx('Furf','SrcWater','FiltPreHyd')=  0;
fc.fx('HMF','SrcWater','FiltPreHyd')=  0;
fc.fx('AceA','SrcWater','FiltPreHyd')=  0;
*fc.fx('Water','SrcWater','FiltPreHyd')=  5;
fc.fx('Acid','SrcWater','FiltPreHyd')=  0;
fc.fx('ASL','SrcWater','FiltPreHyd')=  0;
fc.fx('Min','SrcWater','FiltPreHyd')=  0;
fc.fx('OrgAc','SrcWater','FiltPreHyd')=  0;
fc.fx('Salts','SrcWater','FiltPreHyd')=  0;
fc.fx('Soil','SrcWater','FiltPreHyd')=  0;
fc.fx('Balance','SrcWater','FiltPreHyd')=  0;
fc.fx('Enz','SrcWater','FiltPreHyd')=  0;

fc.fx('Cellulose','SrcWater','MixAcidCellHyd')=  0;
```

```
fc.fx('Hemi','SrcWater','MixAcidCellHyd')=       0;
fc.fx('Lignin','SrcWater','MixAcidCellHyd')=  0;
fc.fx('Acetyl','SrcWater','MixAcidCellHyd')=    0;
fc.fx('Phos','SrcWater','MixAcidCellHyd')=   0;
fc.fx('Xylo','SrcWater','MixAcidCellHyd')=   0;
fc.fx('Xylolig','SrcWater','MixAcidCellHyd')=   0;
fc.fx('Gluc','SrcWater','MixAcidCellHyd')=   0;
fc.fx('Glucolig','SrcWater','MixAcidCellHyd')=   0;
fc.fx('Sucrose','SrcWater','MixAcidCellHyd')=    0;
fc.fx('Furf','SrcWater','MixAcidCellHyd')=   0;
fc.fx('HMF','SrcWater','MixAcidCellHyd')=   0;
fc.fx('AceA','SrcWater','MixAcidCellHyd')=   0;
*fc.fx('Water','SrcWater','MixAcidCellHyd')=   5;
fc.fx('Acid','SrcWater','MixAcidCellHyd')=   0;
fc.fx('ASL','SrcWater','MixAcidCellHyd')=   0;
fc.fx('Min','SrcWater','MixAcidCellHyd')=   0;
fc.fx('OrgAc','SrcWater','MixAcidCellHyd')=   0;
fc.fx('Salts','SrcWater','MixAcidCellHyd')=   0;
fc.fx('Soil','SrcWater','MixAcidCellHyd')=   0;
fc.fx('Balance','SrcWater','MixAcidCellHyd')=   0;
fc.fx('Enz','SrcWater','MixAcidCellHyd')=   0;

fc.lo('Cellulose','MixAcidCellHyd','AcidCellHyd')=   0.1;
fc.lo('Hemi','MixAcidCellHyd','AcidCellHyd')=   0.01;
fc.lo('Lignin','MixAcidCellHyd','AcidCellHyd')=   0.1;
fc.lo('Acetyl','MixAcidCellHyd','AcidCellHyd')=   0.001;
fc.lo('Phos','MixAcidCellHyd','AcidCellHyd')=   0.00001;
fc.lo('Xylo','MixAcidCellHyd','AcidCellHyd')=   0.01;
fc.lo('Xylolig','MixAcidCellHyd','AcidCellHyd')=   0;
fc.lo('Gluc','MixAcidCellHyd','AcidCellHyd')=   0.01;
fc.lo('Glucolig','MixAcidCellHyd','AcidCellHyd')=   0;
fc.lo('Sucrose','MixAcidCellHyd','AcidCellHyd')=   0;
fc.lo('Furf','MixAcidCellHyd','AcidCellHyd')=  0.00001;
*fc.lo('HMF','MixAcidCellHyd','AcidCellHyd')=   0.0001;
fc.lo('AceA','MixAcidCellHyd','AcidCellHyd')=    0.0001;
fc.lo('Water','MixAcidCellHyd','AcidCellHyd')=   1;
fc.lo('Acid','MixAcidCellHyd','AcidCellHyd')=   0.01;
fc.lo('ASL','MixAcidCellHyd','AcidCellHyd')=   0.001;
fc.lo('Min','MixAcidCellHyd','AcidCellHyd')=   0.00001;
fc.lo('OrgAc','MixAcidCellHyd','AcidCellHyd')=    0.00001;
fc.lo('Salts','MixAcidCellHyd','AcidCellHyd')=  0.0003;
fc.lo('Soil','MixAcidCellHyd','AcidCellHyd')=   0.00001;
fc.lo('Balance','MixAcidCellHyd','AcidCellHyd')=   0;

fc.lo('Cellulose','AcidCellHyd','FlsAcidCellHyd')=   0.01;
fc.lo('Hemi','AcidCellHyd','FlsAcidCellHyd')=   0.0001;
fc.lo('Lignin','AcidCellHyd','FlsAcidCellHyd')=   0.1;
fc.lo('Acetyl','AcidCellHyd','FlsAcidCellHyd')=   0.001;
fc.lo('Phos','AcidCellHyd','FlsAcidCellHyd')=   0.00001;
fc.lo('Xylo','AcidCellHyd','FlsAcidCellHyd')=   0.01;
fc.lo('Xylolig','AcidCellHyd','FlsAcidCellHyd')=   0;
fc.lo('Gluc','AcidCellHyd','FlsAcidCellHyd')=   0.01;
fc.lo('Glucolig','AcidCellHyd','FlsAcidCellHyd')=   0;
fc.lo('Sucrose','AcidCellHyd','FlsAcidCellHyd')=   0;
fc.lo('Furf','AcidCellHyd','FlsAcidCellHyd')=   0.01;
fc.lo('HMF','AcidCellHyd','FlsAcidCellHyd')=  0.0001;
fc.lo('AceA','AcidCellHyd','FlsAcidCellHyd')=   0.0001;
```

```
fc.lo('Water','AcidCellHyd','FlsAcidCellHyd')=  0.5;
fc.lo('Acid','AcidCellHyd','FlsAcidCellHyd')=  0.0001;
*fc.lo('ASL','AcidCellHyd','FlsAcidCellHyd')=  0.001;
fc.lo('Min','AcidCellHyd','FlsAcidCellHyd')=  0.00001;
fc.lo('OrgAc','AcidCellHyd','FlsAcidCellHyd')=  0.00001;
fc.lo('Salts','AcidCellHyd','FlsAcidCellHyd')=  0.0003;
fc.lo('Soil','AcidCellHyd','FlsAcidCellHyd')=  0.00001;
fc.lo('Balance','AcidCellHyd','FlsAcidCellHyd')=  0;

fc.lo('Cellulose','FlsAcidCellHyd','FiltCellHyd')=  0.5;
fc.lo('Hemi','FlsAcidCellHyd','FiltCellHyd')=  0.0001;
fc.lo('Lignin','FlsAcidCellHyd','FiltCellHyd')=  0.1;
fc.lo('Acetyl','FlsAcidCellHyd','FiltCellHyd')=  0.001;
*fc.lo('Phos','FlsAcidCellHyd','SnkVapFlsh2')=  0.0001;
fc.lo('Xylo','FlsAcidCellHyd','SnkVapFlsh2')=  0.01;
*fc.lo('Xylolig','FlsAcidCellHyd','SnkVapFlsh2')=  0;
fc.lo('Gluc','FlsAcidCellHyd','SnkVapFlsh2')=  0.01;
*fc.lo('Glucolig','FlsAcidCellHyd','SnkVapFlsh2')=  0;
*fc.lo('Sucrose','FlsAcidCellHyd','SnkVapFlsh2')=  0;
fc.lo('Furf','FlsAcidCellHyd','SnkVapFlsh2')=  0.01;
fc.lo('HMF','FlsAcidCellHyd','SnkVapFlsh2')=  0.0001;
*fc.lo('AceA','FlsAcidCellHyd','SnkVapFlsh2')=  0.0001;
fc.lo('Water','FlsAcidCellHyd','SnkVapFlsh2')=  1;
fc.lo('Acid','FlsAcidCellHyd','SnkVapFlsh2')=  0.1;
*fc.lo('ASL','FlsAcidCellHyd','SnkVapFlsh2')=  0;
fc.lo('Min','FlsAcidCellHyd','FiltCellHyd')=  0.00001;
*fc.lo('OrgAc','FlsAcidCellHyd','SnkSolid')=  0.0001;
fc.lo('Salts','FlsAcidCellHyd','FiltCellHyd')=  0.0003;
fc.lo('Soil','FlsAcidCellHyd','FiltCellHyd')=  0.00001;
fc.lo('Balance','FlsAcidCellHyd','FiltCellHyd')=  0;

fc.fx('Cellulose','SrcWater','FiltCellHyd')=  0;
fc.fx('Hemi','SrcWater','FiltCellHyd')=  0;
fc.fx('Lignin','SrcWater','FiltCellHyd')=  0;
fc.fx('Acetyl','SrcWater','FiltCellHyd')=  0;
fc.fx('Phos','SrcWater','FiltCellHyd')=  0;
fc.fx('Xylo','SrcWater','FiltCellHyd')=  0;
fc.fx('Xylolig','SrcWater','FiltCellHyd')=  0;
fc.fx('Gluc','SrcWater','FiltCellHyd')=  0;
fc.fx('Glucolig','SrcWater','FiltCellHyd')=  0;
fc.fx('Sucrose','SrcWater','FiltCellHyd')=  0;
fc.fx('Furf','SrcWater','FiltCellHyd')=  0;
fc.fx('HMF','SrcWater','FiltCellHyd')=  0;
fc.fx('AceA','SrcWater','FiltCellHyd')=  0;
fc.lo('Water','SrcWater','FiltCellHyd')=  0.001;
fc.fx('Acid','SrcWater','FiltCellHyd')=  0;
fc.fx('ASL','SrcWater','FiltCellHyd')=  0;
fc.fx('Min','SrcWater','FiltCellHyd')=  0;
fc.fx('OrgAc','SrcWater','FiltCellHyd')=  0;
fc.fx('Salts','SrcWater','FiltCellHyd')=  0;
fc.fx('Soil','SrcWater','FiltCellHyd')=  0;
fc.fx('Balance','SrcWater','FiltCellHyd')=  0;

fc.lo('Cellulose','FiltCellHyd','SnkSolid')=  0.5;
fc.lo('Hemi','FiltCellHyd','SnkSolid')=  0.0001;
fc.lo('Lignin','FiltCellHyd','SnkSolid')=  0.001;
fc.lo('Acetyl','FiltCellHyd','SnkSolid')=  0.001;
```

```
*fc.lo('Phos','FiltCellHyd','SnkVapFlsh2')=  0.0001;
*fc.lo('Xylo','FiltCellHyd','SnkVapFlsh2')=  0.01;
*fc.lo('Xylolig','FiltCellHyd','SnkVapFlsh2')=  0;
*fc.lo('Gluc','FlsAcidCellHyd','SnkVapFlsh2')=  0.01;
*fc.lo('Glucolig','FlsAcidCellHyd','SnkVapFlsh2')=  0;
*fc.lo('Sucrose','FlsAcidCellHyd','SnkVapFlsh2')=  0;
*fc.lo('Furf','FlsAcidCellHyd','SnkVapFlsh2')=  0.01;
*fc.lo('HMF','FlsAcidCellHyd','SnkVapFlsh2')=  0.0001;
*fc.lo('AceA','FlsAcidCellHyd','SnkVapFlsh2')=  0.0001;
*fc.lo('Water','FlsAcidCellHyd','SnkVapFlsh2')=  1;
*fc.lo('Acid','FlsAcidCellHyd','SnkVapFlsh2')=  0.1;
*fc.lo('ASL','FlsAcidCellHyd','SnkVapFlsh2')=  0;
fc.lo('Min','FiltCellHyd','SnkSolid')=  0.00000001;
*fc.lo('OrgAc','FlsAcidCellHyd','SnkSolid')=  0.0001;
fc.lo('Salts','FiltCellHyd','SnkSolid')=  0.000003;
fc.lo('Soil','FiltCellHyd','SnkSolid')=  0.00001;
fc.lo('Balance','FiltCellHyd','SnkSolid')=  0;

*fc.lo('Cellulose','FlsAcidCellHyd','SnkC6')=  0.5;
*fc.lo('Hemi','FlsAcidCellHyd','SnkC6')=  0.01;
*fc.lo('Lignin','FlsAcidCellHyd','SnkC6')=  1;
*fc.lo('Acetyl','FlsAcidCellHyd','SnkC6')=  0.001;
*fc.lo('Phos','FiltCellHyd','SnkC6')=  0.0001;
fc.lo('Xylo','FiltCellHyd','SnkC6')=  0.001;
*fc.lo('Xylolig','FlsAcidCellHyd','SnkC6')=  0;
fc.lo('Gluc','FiltCellHyd','SnkC6')=  0.01;
*fc.lo('Glucolig','FlsAcidCellHyd','SnkC6')=  0;
*fc.lo('Sucrose','FlsAcidCellHyd','SnkC6')=  0;
fc.lo('Furf','FiltCellHyd','SnkC6')=  0.00001;
fc.lo('HMF','FiltCellHyd','SnkC6')=  0.0000001;
*fc.lo('AceA','FiltCellHyd','SnkC6')=  0.0001;
fc.lo('Water','FiltCellHyd','SnkC6')=  0.001;
fc.lo('Acid','FiltCellHyd','SnkC6')=  0.0001;
*fc.lo('ASL','FiltCellHyd','SnkC6')=  0.001;
*fc.lo('Min','FlsAcidCellHyd','SnkC6')=  0.001;
fc.lo('OrgAc','FiltCellHyd','SnkC6')=  0.000001;
*fc.lo('Salts','FlsAcidCellHyd','SnkC6')=  0.03;
*fc.lo('Soil','FlsAcidCellHyd','SnkC6')=  0.001;
fc.lo('Balance','FiltCellHyd','SnkC6')=  0;

*fc.lo('Cellulose','FlsAcidCellHyd','SnkC6')=  0.5;
*fc.lo('Hemi','FlsAcidCellHyd','SnkC6')=  0.01;
*fc.lo('Lignin','FlsAcidCellHyd','SnkC6')=  1;
*fc.lo('Acetyl','FlsAcidCellHyd','SnkC6')=  0.001;
fc.lo('Phos','FlsAcidCellHyd','FiltCellHyd')=  0.00001;
fc.lo('Xylo','FlsAcidCellHyd','FiltCellHyd')=  0.01;
*fc.lo('Xylolig','FlsAcidCellHyd','SnkC6')=  0;
fc.lo('Gluc','FlsAcidCellHyd','FiltCellHyd')=  0.01;
*fc.lo('Glucolig','FlsAcidCellHyd','SnkC6')=  0;
*fc.lo('Sucrose','FlsAcidCellHyd','SnkC6')=  0;
fc.lo('Furf','FlsAcidCellHyd','FiltCellHyd')=  0.00001;
fc.lo('HMF','FlsAcidCellHyd','FiltCellHyd')=  0.0000001;
*fc.lo('AceA','FlsAcidCellHyd','FiltCellHyd')=  0.0001;
fc.lo('Water','FlsAcidCellHyd','FiltCellHyd')=  0.001;
fc.lo('Acid','FlsAcidCellHyd','FiltCellHyd')=  0.0001;
*fc.lo('ASL','FlsAcidCellHyd','FiltCellHyd')=  0.001;
*fc.lo('Min','FlsAcidCellHyd','SnkC6')=  0.001;
```

```
fc.lo('OrgAc','FlsAcidCellHyd','FiltCellHyd')=   0.00001;
*fc.lo('Salts','FlsAcidCellHyd','SnkC6')=   0.03;
*fc.lo('Soil','FlsAcidCellHyd','SnkC6')=   0.001;
fc.lo('Balance','FlsAcidCellHyd','FiltCellHyd')=   0;

fc.lo('Cellulose','FictIN','FictCell')=   0.1;
fc.lo('Hemi','FictIN','FictCell')=   0.01;
fc.lo('Lignin','FictIN','FictCell')=   0.1;
fc.lo('Acetyl','FictIN','FictCell')=   0.001;
fc.lo('Phos','FictIN','FictCell')=   0.00001;
fc.lo('Xylo','FictIN','FictCell')=   0.01;
fc.lo('Xylolig','FictIN','FictCell')=   0;
fc.lo('Gluc','FictIN','FictCell')=   0.01;
fc.lo('Glucolig','FictIN','FictCell')=   0;
fc.lo('Sucrose','FictIN','FictCell')=   0;
fc.lo('Furf','FictIN','FictCell')=  0.00001;
*fc.lo('HMF','FictIN','FictCell')=   0.0001;
fc.lo('AceA','FictIN','FictCell')=    0.0001;
fc.lo('Water','FictIN','FictCell')=   1;
fc.lo('Acid','FictIN','FictCell')=    0.01;
*fc.lo('ASL','FictIN','FictCell')=   0.0001;
fc.lo('Min','FictIN','FictCell')=   0.00001;
fc.lo('OrgAc','FictIN','FictCell')=   0.00001;
fc.lo('Salts','FictIN','FictCell')=   0.0003;
fc.lo('Soil','FictIN','FictCell')=   0.00001;
fc.lo('Balance','FictIN','FictCell')=   0;

fc.lo('Cellulose','FictCell','FictOUT')=   0.01;
fc.lo('Hemi','FictCell','FictOUT')=   0.0001;
fc.lo('Lignin','FictCell','FictOUT')=   0.1;
fc.lo('Acetyl','FictCell','FictOUT')=   0.001;
fc.lo('Phos','FictCell','FictOUT')=   0.00001;
fc.lo('Xylo','FictCell','FictOUT')=   0.01;
fc.lo('Xylolig','FictCell','FictOUT')=   0;
fc.lo('Gluc','FictCell','FictOUT')=   0.01;
fc.lo('Glucolig','FictCell','FictOUT')=   0;
fc.lo('Sucrose','FictCell','FictOUT')=   0;
fc.lo('Furf','FictCell','FictOUT')=   0.001;
fc.lo('HMF','FictCell','FictOUT')=  0.0001;
fc.lo('AceA','FictCell','FictOUT')=   0.0001;
fc.lo('Water','FictCell','FictOUT')=   0.5;
fc.lo('Acid','FictCell','FictOUT')=    0.0001;
*fc.lo('ASL','FictCell','FictOUT')=    0.001;
fc.lo('Min','FictCell','FictOUT')=   0.00001;
fc.lo('OrgAc','FictCell','FictOUT')=   0.00001;
fc.lo('Salts','FictCell','FictOUT')=   0.0003;
fc.lo('Soil','FictCell','FictOUT')=   0.00001;
fc.lo('Balance','FictCell','FictOUT')=   0;
*-------------------------------------------------------------------------------------------------------------------------------
WSRCell.fx = 20;

x.fx('Water','SrcWater','MixPreHyd')=1;
x.fx('Water','SrcSteam','MixPreHyd')=1;
x.fx('Acid','SrcAcid','MixPreHyd')=pureAcid;
x.fx('Water','SrcAcid','MixPreHyd')=1-pureAcid;
x.fx('Water','SrcWater','FiltPreHyd')=1;
x.fx('Water','SrcSteam','MixAcidCellHyd')=1;
```

```
x.fx('Water','SrcWater','MixAcidCellHyd')=1;
x.fx('Acid','SrcAcid','MixAcidCellHyd')=pureAcid;
x.fx('Water','SrcAcid','MixAcidCellHyd')=1-pureAcid;
x.fx('Water','SrcWater','FiltCellHyd')=1;

F.lo('SrcSteam','MixAcidCellHyd')= 0.1;
F.lo('SrcWater','MixAcidCellHyd')= 0.01;
F.lo('MixAcidCellHyd','AcidCellHyd')= 1;

F.fx('SrcBag','MixPreHyd')= 15;


*Specifying heat consumption of certain units
Q.Fx(Mix)=0;
Q.Fx(Src)=0;
Q.Fx(Snk)=0;

*Specify power consumption for cerain units
W.fx('PreHyd')=0;
W.fx('AcidCellHyd')=0;
W.Fx(Mix)=0;
W.Fx(Src)=0;
W.Fx(Snk)=0;

acidWtPre.lo=2;
acidWtPre.up=6;

acidWtCell.lo=0.07;
acidWtCell.up=0.28;

Tau.lo(unit)=1;
Tau.up(unit)=200;

k1Gluc.up=50;
k2Gluc.up=50;
*-------------------------------------------------------------------------------------------------------------------
*Temperature settings
Scalars
*Define temperatures in K
       T_amb          ambient temperature /303.15/
       T_cooldown     cool down temperature /298.15/
       dT_min         EMAT /5/
       T_max          max temperature for a process stream /423.15/
       T_steam_max    max steam temperature /573.15/;

*global temperature bounds - bounds get redefined for specific streams
T.LO(unit,unit1)=T_amb;
T.UP(unit,unit1)=T_steam_max;

*Specifying temperatures
*Pretreatment
T.fx('SrcBag','MixPreHyd')=T_amb;
T.fx('SrcAcid','MixPreHyd')=T_amb;
T.fx('SrcSteam','MixPreHyd')=utilProps('LPS','TSupply');
T.fx('SrcWater','MixPreHyd')=T_amb;
T.fx('SrcWater','FiltPreHyd')=T_amb;
T.LO('MixPreHyd','PreHyd')=373.15;
```

```
T.up('MixPreHyd','PreHyd')=401.15;
T.LO('PreHyd','FlsPreHyd')=373.15;
T.up('PreHyd','FlsPreHyd')=401.15;
*Acid Hydrolysis
T.fx('SrcAcid','MixAcidCellHyd')=T_amb;
T.lo('SrcSteam','MixAcidCellHyd')=utilProps('LPS','TSupply');
T.up('SrcSteam','MixAcidCellHyd')=utilProps('HPS2','TSupply');
T.fx('SrcWater','MixAcidCellHyd')=T_amb;
T.LO('MixAcidCellHyd','AcidCellHyd')=453.15;
T.up('MixAcidCellHyd','AcidCellHyd')=503.15;
T.fx('SrcWater','FiltCellHyd')=T_amb;

*++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
*PreHyd Equations
Equations
      SrcAcideqn,SrcSteameqn, MixPreHyd_1, MixPreHyd_2;
*Acid in SrcAcid
SrcAcideqn..
      x('Acid','MixPreHyd','PreHyd') =E=  acidWtPre/100;

SrcSteameqn..

F('SrcWater','MixPreHyd')+F('SrcSteam','MixPreHyd')+fc('Water','SrcBag','MixPreHyd')+fc('Water','SrcAcid','Mix
PreHyd')=E= sum(solids, fc(solids,'SrcBag','MixPreHyd'))*WSRPre;

*Mass balance to mix in CSTR
MixPreHyd_1(J)..
      fc(J,'MixPreHyd','PreHyd') =E=
fc(J,'SrcBag','MixPreHyd')+fc(J,'SrcAcid','MixPreHyd')+fc(J,'SrcSteam','MixPreHyd')+fc(J,'SrcWater','MixPreHyd');

MixPreHyd_2.. sum(J,fc(J,'SrcBag','MixPreHyd')*cp_ind(J))*T('SrcBag','MixPreHyd')
      +sum(J,fc(J,'SrcAcid','MixPreHyd')*cp_ind(J))*T('SrcAcid','MixPreHyd')

+sum(J,fc(J,'SrcSteam','MixPreHyd')*utilProps('LPS','CpVap'))+sum(J,fc(J,'SrcSteam','MixPreHyd')*cp_ind(J))*T('
SrcSteam','MixPreHyd')
      +sum(J,fc(J,'SrcWater','MixPreHyd')*cp_ind(J))*T('SrcWater','MixPreHyd')
      =E= sum(J,fc(J,'MixPreHyd','PreHyd')*cp_ind(J))*T('MixPreHyd','PreHyd');

Equations
      PreHyd_1, PreHyd_2, PreHyd_3,
      PreHyd_4, PreHyd_5, PreHyd_6,
      PreHyd_7, PreHyd_8, PreHyd_10,
      PreHyd_11, PreHyd_12,  PreHyd_13,
      PreHyd_14,PreHyd_15,PreHyd_16,PreHyd_17,
      PreHyd_binary,PreHyd_CA,PreHyd_T,PreHyd_Tau,PreHyd_isothermal;

*Individual flowrates of SrcBag
PreHyd_1(J)..
      x(J,'SrcBag','MixPreHyd') =E= x_SCB(J);
*Inerts in SnkVapFlsh1
PreHyd_3(I)..
      fc(I,'PreHyd','FlsPreHyd') =E= fc(I,'MixPreHyd','PreHyd');

*Exit flowrates based on conversions
PreHyd_4(J)..
      fc('Cellulose','PreHyd','FlsPreHyd') =E= fc('Cellulose','MixPreHyd','PreHyd')*(1-(
PreHydBin('1')*PreHyd2100('Cellulose')    +
```

```
                                        PreHydBin('2')*PreHyd4100('Cellulose')    +
                                        PreHydBin('3')*PreHyd6100('Cellulose')    +
                                        PreHydBin('4')*PreHyd2122('Cellulose')    +
                                        PreHydBin('5')*PreHyd4122('Cellulose')    +
                                        PreHydBin('6')*PreHyd6122('Cellulose')    +
                                        PreHydBin('7')*PreHyd2128('Cellulose')    +
                                        PreHydBin('8')*PreHyd4128('Cellulose')    +
                                        PreHydBin('9')*PreHyd6128('Cellulose')    +
                                        PreHydBin('10')*PreHyd61002('Cellulose')  +
                                        PreHydBin('11')*PreHyd61222('Cellulose')  +
                                        PreHydBin('12')*PreHyd61282('Cellulose')  +
                                        PreHydBin('13')*PreHyd21222('Cellulose')  )) ;

PreHyd_5(J)..
      fc('Hemi','PreHyd','FlsPreHyd') =E= fc('Hemi','MixPreHyd','PreHyd')*(1-(
PreHydBin('1')*PreHyd2100('Hemi')    +
                                        PreHydBin('2')*PreHyd4100('Hemi')    +
                                        PreHydBin('3')*PreHyd6100('Hemi')    +
                                        PreHydBin('4')*PreHyd2122('Hemi')    +
                                        PreHydBin('5')*PreHyd4122('Hemi')    +
                                        PreHydBin('6')*PreHyd6122('Hemi')    +
                                        PreHydBin('7')*PreHyd2128('Hemi')    +
                                        PreHydBin('8')*PreHyd4128('Hemi')    +
                                        PreHydBin('9')*PreHyd6128('Hemi')    +
                                        PreHydBin('10')*PreHyd61002('Hemi')  +
                                        PreHydBin('11')*PreHyd61222('Hemi')  +
                                        PreHydBin('12')*PreHyd61282('Hemi')  +
                                        PreHydBin('13')*PreHyd21222('Hemi')  )) ;

PreHyd_6(J)..
      fc('Acetyl','PreHyd','FlsPreHyd') =E= fc('Acetyl','MixPreHyd','PreHyd')*(1-(
PreHydBin('1')*PreHyd2100('Acetyl')    +
                                        PreHydBin('2')*PreHyd4100('Acetyl')    +
                                        PreHydBin('3')*PreHyd6100('Acetyl')    +
                                        PreHydBin('4')*PreHyd2122('Acetyl')    +
                                        PreHydBin('5')*PreHyd4122('Acetyl')    +
                                        PreHydBin('6')*PreHyd6122('Acetyl')    +
                                        PreHydBin('7')*PreHyd2128('Acetyl')    +
                                        PreHydBin('8')*PreHyd4128('Acetyl')    +
                                        PreHydBin('9')*PreHyd6128('Acetyl')    +
                                            PreHydBin('10')*PreHyd61002('Acetyl')    +
                                            PreHydBin('11')*PreHyd61222('Acetyl')    +
                                            PreHydBin('12')*PreHyd61282('Acetyl')  +
                                            PreHydBin('13')*PreHyd21222('Acetyl')  )) ;

PreHyd_7(J)..
      fc('Xylo','PreHyd','FlsPreHyd') =E= F('PreHyd','FlsPreHyd')*( PreHydBin('1')*PreHyd2100('Xyl') +
                                        PreHydBin('2')*PreHyd4100('Xyl')    +
                                        PreHydBin('3')*PreHyd6100('Xyl')    +
                                        PreHydBin('4')*PreHyd2122('Xyl')    +
                                        PreHydBin('5')*PreHyd4122('Xyl')    +
                                        PreHydBin('6')*PreHyd6122('Xyl')    +
                                        PreHydBin('7')*PreHyd2128('Xyl')    +
                                        PreHydBin('8')*PreHyd4128('Xyl')    +
                                        PreHydBin('9')*PreHyd6128('Xyl')   +
                                            PreHydBin('10')*PreHyd61002('Xyl')    +
                                            PreHydBin('11')*PreHyd61222('Xyl')    +
```

```
                                        PreHydBin('12')*PreHyd61282('Xyl')   +
                                        PreHydBin('13')*PreHyd21222('Xyl')   )/1000
                                        + fc('Xylolig','MixPreHyd','PreHyd');

PreHyd_8(J)..
      fc('Gluc','PreHyd','FlsPreHyd') =E=  F('PreHyd','FlsPreHyd')*( PreHydBin('1')*PreHyd2100('Glucose')    +
                                        PreHydBin('2')*PreHyd4100('Glucose')    +
                                        PreHydBin('3')*PreHyd6100('Glucose')    +
                                        PreHydBin('4')*PreHyd2122('Glucose')    +
                                        PreHydBin('5')*PreHyd4122('Glucose')    +
                                        PreHydBin('6')*PreHyd6122('Glucose')    +
                                        PreHydBin('7')*PreHyd2128('Glucose')    +
                                        PreHydBin('8')*PreHyd4128('Glucose')    +
                                        PreHydBin('9')*PreHyd6128('Glucose')   +
                                            PreHydBin('10')*PreHyd61002('Glucose')    +
                                            PreHydBin('11')*PreHyd61222('Glucose')    +
                                            PreHydBin('12')*PreHyd61282('Glucose')   +
                                            PreHydBin('13')*PreHyd21222('Glucose')   )/1000
                                    + fc('Gluc','MixPreHyd','PreHyd') + 2*fc('Sucrose','MixPreHyd','PreHyd')+
fc('Glucolig','MixPreHyd','PreHyd');

PreHyd_15..
      fc('Sucrose','PreHyd','FlsPreHyd') =e=0;

PreHyd_16..
      fc('Glucolig','PreHyd','FlsPreHyd') =e=0;

PreHyd_17..
      fc('Xylolig','PreHyd','FlsPreHyd') =e=0;

PreHyd_10(J)..
      fc('Furf','PreHyd','FlsPreHyd') =E= F('PreHyd','FlsPreHyd')*( PreHydBin('1')*PreHyd2100('Fur')    +
                                        PreHydBin('2')*PreHyd4100('Fur')    +
                                        PreHydBin('3')*PreHyd6100('Fur')    +
                                        PreHydBin('4')*PreHyd2122('Fur')    +
                                        PreHydBin('5')*PreHyd4122('Fur')    +
                                        PreHydBin('6')*PreHyd6122('Fur')    +
                                        PreHydBin('7')*PreHyd2128('Fur')    +
                                        PreHydBin('8')*PreHyd4128('Fur')    +
                                        PreHydBin('9')*PreHyd6128('Fur')   +
                                            PreHydBin('10')*PreHyd61002('Fur')    +
                                            PreHydBin('11')*PreHyd61222('Fur')    +
                                            PreHydBin('12')*PreHyd61282('Fur')   +
                                            PreHydBin('13')*PreHyd21222('Fur')   )/1000;
PreHyd_11(J)..
      fc('HMF','PreHyd','FlsPreHyd') =E=  F('PreHyd','FlsPreHyd')*( PreHydBin('1')*PreHyd2100('HMF')    +
                                        PreHydBin('2')*PreHyd4100('HMF')    +
                                        PreHydBin('3')*PreHyd6100('HMF')    +
                                        PreHydBin('4')*PreHyd2122('HMF')    +
                                        PreHydBin('5')*PreHyd4122('HMF')    +
                                        PreHydBin('6')*PreHyd6122('HMF')    +
                                        PreHydBin('7')*PreHyd2128('HMF')    +
                                        PreHydBin('8')*PreHyd4128('HMF')    +
                                        PreHydBin('9')*PreHyd6128('HMF')   +
                                            PreHydBin('10')*PreHyd61002('HMF')    +
                                            PreHydBin('11')*PreHyd61222('HMF')    +
                                            PreHydBin('12')*PreHyd61282('HMF')   +
```

```
                                        PreHydBin('13')*PreHyd21222('HMF')   )/1000;

PreHyd_12(J)..
      fc('AceA','PreHyd','FlsPreHyd') =E=  F('PreHyd','FlsPreHyd')*( PreHydBin('1')*PreHyd2100('Acetic')    +
                                        PreHydBin('2')*PreHyd4100('Acetic')    +
                                        PreHydBin('3')*PreHyd6100('Acetic')    +
                                        PreHydBin('4')*PreHyd2122('Acetic')    +
                                        PreHydBin('5')*PreHyd4122('Acetic')    +
                                        PreHydBin('6')*PreHyd6122('Acetic')    +
                                        PreHydBin('7')*PreHyd2128('Acetic')    +
                                        PreHydBin('8')*PreHyd4128('Acetic')    +
                                        PreHydBin('9')*PreHyd6128('Acetic')   +
                                            PreHydBin('10')*PreHyd61002('Acetic')    +
                                            PreHydBin('11')*PreHyd61222('Acetic')    +
                                            PreHydBin('12')*PreHyd61282('Acetic')  +
                                            PreHydBin('13')*PreHyd21222('Acetic')   )/1000;
PreHyd_13(J)..
      fc('ASL','PreHyd','FlsPreHyd') =E=  F('SrcBag','MixPreHyd')*( PreHydBin('1')*PreHyd2100('AcidLig')    +
                                        PreHydBin('2')*PreHyd4100('AcidLig')    +
                                        PreHydBin('3')*PreHyd6100('AcidLig')    +
                                        PreHydBin('4')*PreHyd2122('AcidLig')    +
                                        PreHydBin('5')*PreHyd4122('AcidLig')    +
                                        PreHydBin('6')*PreHyd6122('AcidLig')    +
                                        PreHydBin('7')*PreHyd2128('AcidLig')    +
                                        PreHydBin('8')*PreHyd4128('AcidLig')    +
                                        PreHydBin('9')*PreHyd6128('AcidLig')   +
                                            PreHydBin('10')*PreHyd61002('AcidLig')    +
                                            PreHydBin('11')*PreHyd61222('AcidLig')    +
                                            PreHydBin('12')*PreHyd61282('AcidLig')  +
                                            PreHydBin('13')*PreHyd21222('AcidLig')   );

PreHyd_14(J)..
      fc('Lignin','PreHyd','FlsPreHyd') =E=  fc('Lignin','MixPreHyd','PreHyd')-fc('ASL','PreHyd','FlsPreHyd');
PreHyd_binary..
         sum(numSets, PreHydBin(numSets)) =E= 1;
PreHyd_CA..
       acidWtPre =E= PreHydBin('1')*PreHyd2100('CA')    +
                PreHydBin('2')*PreHyd4100('CA')    +
                PreHydBin('3')*PreHyd6100('CA')    +
                PreHydBin('4')*PreHyd2122('CA')    +
                PreHydBin('5')*PreHyd4122('CA')    +
                PreHydBin('6')*PreHyd6122('CA')    +
                PreHydBin('7')*PreHyd2128('CA')    +
                PreHydBin('8')*PreHyd4128('CA')    +
                PreHydBin('9')*PreHyd6128('CA')    +
                PreHydBin('10')*PreHyd61002('CA')    +
                PreHydBin('11')*PreHyd61222('CA')    +
                PreHydBin('12')*PreHyd61282('CA')    +
                PreHydBin('13')*PreHyd21222('CA')    ;

PreHyd_T..
       T('MixPreHyd','PreHyd') =E= PreHydBin('1')*PreHyd2100('TPreHyd')    +
                PreHydBin('2')*PreHyd4100('TPreHyd')    +
                PreHydBin('3')*PreHyd6100('TPreHyd')    +
                PreHydBin('4')*PreHyd2122('TPreHyd')    +
                PreHydBin('5')*PreHyd4122('TPreHyd')    +
                PreHydBin('6')*PreHyd6122('TPreHyd')    +
```

```
                PreHydBin('7')*PreHyd2128('TPreHyd')    +
                PreHydBin('8')*PreHyd4128('TPreHyd')    +
                PreHydBin('9')*PreHyd6128('TPreHyd')    +
                PreHydBin('10')*PreHyd61002('TPreHyd')    +
                PreHydBin('11')*PreHyd61222('TPreHyd')    +
                PreHydBin('12')*PreHyd61282('TPreHyd')    +
                PreHydBin('13')*PreHyd21222('TPreHyd')    ;

PreHyd_Tau..
        Tau('PreHyd') =E= PreHydBin('1')*PreHyd2100('Tau')    +
                PreHydBin('2')*PreHyd4100('Tau')    +
                PreHydBin('3')*PreHyd6100('Tau')    +
                PreHydBin('4')*PreHyd2122('Tau')    +
                PreHydBin('5')*PreHyd4122('Tau')    +
                PreHydBin('6')*PreHyd6122('Tau')    +
                PreHydBin('7')*PreHyd2128('Tau')    +
                PreHydBin('8')*PreHyd4128('Tau')    +
                PreHydBin('9')*PreHyd6128('Tau')    +
                PreHydBin('10')*PreHyd61002('Tau')    +
                PreHydBin('11')*PreHyd61222('Tau')    +
                PreHydBin('12')*PreHyd61282('Tau')    +
                PreHydBin('13')*PreHyd21222('Tau')    ;

PreHyd_isothermal..
       T('MixPreHyd','PreHyd') =E= T('PreHyd','FlsPreHyd') ;
*Unit overall MB
PreHyd_2..
       F('PreHyd','FlsPreHyd') =E= F('MixPreHyd','PreHyd');
*+++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
*Flash equations
Equation Flsh1PreHyd, Flsh2PreHyd,Flsh3PreHyd,Flsh4PreHyd;
Flsh1PreHyd(J)..
     fc(J,'PreHyd','FlsPreHyd') =E= fc(J,'FlsPreHyd','SnkVapFlsh1')+ fc(J,'FlsPreHyd','FiltPreHyd');
*SnkVapFlsh1 is vapour, MixAcidCellHyd is solids, SnkC5 is liquids

Flsh2PreHyd(liquids)..
     fc(liquids,'FlsPreHyd','SnkVapFlsh1') =E=
fc(liquids,'PreHyd','FlsPreHyd')*FlashVap21224(liquids)*(PreHydBin('4'))+
                        fc(liquids,'PreHyd','FlsPreHyd')*FlashVap41225(liquids)*(PreHydBin('5'))+
                        fc(liquids,'PreHyd','FlsPreHyd')*FlashVap61226(liquids)*(PreHydBin('6'))+
                        fc(liquids,'PreHyd','FlsPreHyd')*FlashVap21287(liquids)*(PreHydBin('7'))+
                        fc(liquids,'PreHyd','FlsPreHyd')*FlashVap41288(liquids)*(PreHydBin('8'))+
                        fc(liquids,'PreHyd','FlsPreHyd')*FlashVap61289(liquids)*(PreHydBin('9'))+

                        fc(liquids,'PreHyd','FlsPreHyd')*FlashVap612812(liquids)*(PreHydBin('12'))+

                        fc(liquids,'PreHyd','FlsPreHyd')*FlashVap21001(liquids)*(PreHydBin('1')) +
                        fc(liquids,'PreHyd','FlsPreHyd')*FlashVap41002(liquids)*PreHydBin('2')+

fc(liquids,'PreHyd','FlsPreHyd')*FlashVap61003(liquids)*(PreHydBin('3')+PreHydBin('10'))+
                        fc(liquids,'PreHyd','FlsPreHyd')*FlashVap61226(liquids)*PreHydBin('11')+
                        fc(liquids,'PreHyd','FlsPreHyd')*FlashVap21224(liquids)*PreHydBin('13') ;

Flsh3PreHyd(solids)..
     fc(solids,'FlsPreHyd','FiltPreHyd') =E= fc(solids,'PreHyd','FlsPreHyd');

Flsh4PreHyd(liquids)..
```

```
    fc(liquids,'FlsPreHyd','FiltPreHyd') =E=  fc(liquids,'PreHyd','FlsPreHyd')*(1-
FlashVap21224(liquids))*(PreHydBin('4'))+
                        fc(liquids,'PreHyd','FlsPreHyd')*(1-FlashVap41225(liquids))*(PreHydBin('5'))+
                        fc(liquids,'PreHyd','FlsPreHyd')*(1-FlashVap61226(liquids))*(PreHydBin('6'))+
                        fc(liquids,'PreHyd','FlsPreHyd')*(1-FlashVap21287(liquids))*(PreHydBin('7'))+
                        fc(liquids,'PreHyd','FlsPreHyd')*(1-FlashVap41288(liquids))*(PreHydBin('8'))+
                        fc(liquids,'PreHyd','FlsPreHyd')*(1-FlashVap61289(liquids))*(PreHydBin('9'))+

                        fc(liquids,'PreHyd','FlsPreHyd')*(1-FlashVap612812(liquids))*(PreHydBin('12'))+

                        fc(liquids,'PreHyd','FlsPreHyd')*(1-FlashVap21001(liquids))*(PreHydBin('1')) +
                        fc(liquids,'PreHyd','FlsPreHyd')*(1-FlashVap41002(liquids))*PreHydBin('2')+
                        fc(liquids,'PreHyd','FlsPreHyd')*(1-
FlashVap61003(liquids))*(PreHydBin('3')+PreHydBin('10'))+
                        fc(liquids,'PreHyd','FlsPreHyd')*(1-FlashVap61226(liquids))*PreHydBin('11')+
                        fc(liquids,'PreHyd','FlsPreHyd')*(1-FlashVap21224(liquids))*PreHydBin('13') ;

*++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
*FILTER
Equation Filt1PreHyd,Filt1aPreHyd,Filt1bPreHyd,Filt2PreHyd,Filt3PreHyd,
      Filt4PreHyd,FiltPreHydT1,FiltPreHydT2,FiltWaterPreHyd,FiltWaterPreHyd2;

Filt1PreHyd(filtSol)..
      fc(filtSol, 'FlsPreHyd','FiltPreHyd')*SteamFiltSol =E= fc(filtSol, 'FiltPreHyd','MixAcidCellHyd');

Filt1aPreHyd(filtLiq)..
      (fc(filtLiq, 'FlsPreHyd','FiltPreHyd')+fc(filtLiq, 'SrcWater','FiltPreHyd'))*PreHydFiltSplit =E= fc(filtLiq,
'FiltPreHyd','MixAcidCellHyd');

Filt1bPreHyd..
      fc('Balance', 'FlsPreHyd','FiltPreHyd') =E= fc('Balance', 'FiltPreHyd','SnkC5');

Filt2PreHyd..
      F('FlsPreHyd','FiltPreHyd')+ F('SrcWater','FiltPreHyd') =E=
F('FiltPreHyd','MixAcidCellHyd')+F('FiltPreHyd','SnkC5');

Filt3PreHyd(J)..
      fc(J,'FlsPreHyd','FiltPreHyd')+fc(J, 'SrcWater','FiltPreHyd') =E=
fc(J,'FiltPreHyd','MixAcidCellHyd')+fc(J,'FiltPreHyd','SnkC5');

Filt4PreHyd..
      sum(filtLiq, fc(filtLiq, 'FiltPreHyd','MixAcidCellHyd'))/F('FiltPreHyd','MixAcidCellHyd') =e= PreHydLiqFrac;

FiltWaterPreHyd..
      F('SrcWater','FiltPreHyd') =g= 1.5*sum(filtSol, fc(filtSol,'FiltPreHyd','MixAcidCellHyd'));

FiltPreHydT1..
      sum(J,fc(J,'FlsPreHyd','FiltPreHyd')*cp_ind(J))*T('FlsPreHyd','FiltPreHyd')
      +sum(J,fc(J,'SrcWater','FiltPreHyd')*cp_ind(J))*T('SrcWater','FiltPreHyd')
      =E= sum(J,fc(J,'FiltPreHyd','MixAcidCellHyd')*cp_ind(J))*T('FiltPreHyd','MixAcidCellHyd')
      + sum(J,fc(J,'FiltPreHyd','SnkC5')*cp_ind(J))*T('FiltPreHyd','SnkC5');

FiltPreHydT2..
      T('FiltPreHyd','MixAcidCellHyd')=E=T('FiltPreHyd','SnkC5');

FiltWaterPreHyd2..
      x('Water','FiltPreHyd','SnkC5') =l= 0.93;
```

```
F.lo('FiltPreHyd','SnkC5') = 0.01;
F.lo('SrcWater','FiltPreHyd') = 0;
F.up('SrcWater','FiltPreHyd') = 100;
F.lo('FiltPreHyd','MixAcidCellHyd') = 0.01;

PreHydFiltSplit.lo=0.03;
PreHydFiltSplit.up=0.3;
PreHydLiqFrac.lo = 0.5;
PreHydLiqFrac.up = 0.55;
*++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
*Acid Hydrolysis Equations
*MixAcidCellHyd
Equations
      SrcAcideqnAcidCell,SrcWatereqn, MixAcidCellHyd_1,
MixAcidCellHyd_2,logSteamTemp,SteamTemp,binSteam  ;
*Acid in SrcSteam
SrcAcideqnAcidCell..
      x('Acid','MixAcidCellHyd','AcidCellHyd') =E=  acidWtCell/100;
*Water added to mixer
SrcWatereqn..

F('SrcAcid','MixAcidCellHyd')+F('SrcSteam','MixAcidCellHyd')+F('SrcWater','MixAcidCellHyd')+fc('Water','FiltPre
Hyd','MixAcidCellHyd') =E= sum(solids, fc(solids,'FiltPreHyd','MixAcidCellHyd'))*WSRCell;
*Mass balance to mix in CSTR
MixAcidCellHyd_1(J)..
      fc(J,'MixAcidCellHyd','AcidCellHyd') =E=
fc(J,'SrcAcid','MixAcidCellHyd')+fc(J,'SrcSteam','MixAcidCellHyd')+fc(J,'SrcWater','MixAcidCellHyd')+fc(J,'FiltPre
Hyd','MixAcidCellHyd');
*Mixer EB
MixAcidCellHyd_2.. sum(J,fc(J,'SrcAcid','MixAcidCellHyd')*cp_ind(J))*T('SrcAcid','MixAcidCellHyd')
      +sum(J,fc(J,'SrcWater','MixAcidCellHyd')*cp_ind(J))*T('SrcWater','MixAcidCellHyd')

+steamChoice('1')*(sum(J,fc(J,'SrcSteam','MixAcidCellHyd')*utilProps('LPS','CpVap'))+sum(J,fc(J,'SrcSteam','Mix
AcidCellHyd')*cp_ind(J))*utilProps('LPS','TSupply') )

+steamChoice('2')*(sum(J,fc(J,'SrcSteam','MixAcidCellHyd')*utilProps('MPS1','CpVap'))+sum(J,fc(J,'SrcSteam','
MixAcidCellHyd')*cp_ind(J))*utilProps('MPS1','TSupply') )

+steamChoice('3')*(sum(J,fc(J,'SrcSteam','MixAcidCellHyd')*utilProps('MPS2','CpVap'))+sum(J,fc(J,'SrcSteam','
MixAcidCellHyd')*cp_ind(J))*utilProps('MPS2','TSupply')  )

+steamChoice('4')*(sum(J,fc(J,'SrcSteam','MixAcidCellHyd')*utilProps('HPS1','CpVap'))+sum(J,fc(J,'SrcSteam','M
ixAcidCellHyd')*cp_ind(J))*utilProps('HPS1','TSupply')   )

+steamChoice('5')*(sum(J,fc(J,'SrcSteam','MixAcidCellHyd')*utilProps('HPS2','CpVap'))+sum(J,fc(J,'SrcSteam','M
ixAcidCellHyd')*cp_ind(J))*utilProps('HPS2','TSupply')    )

+steamChoice('6')*(sum(J,fc(J,'SrcSteam','MixAcidCellHyd')*utilProps('CTBE1','CpVap'))+sum(J,fc(J,'SrcSteam','
MixAcidCellHyd')*cp_ind(J))*utilProps('CTBE1','TSupply')    )

+steamChoice('7')*(sum(J,fc(J,'SrcSteam','MixAcidCellHyd')*utilProps('CTBE2','CpVap'))+sum(J,fc(J,'SrcSteam','
MixAcidCellHyd')*cp_ind(J))*utilProps('CTBE2','TSupply')    )
      +sum(J,fc(J,'FiltPreHyd','MixAcidCellHyd')*cp_ind(J))*T('FiltPreHyd','MixAcidCellHyd')
      =E= sum(J,fc(J,'MixAcidCellHyd','AcidCellHyd')*cp_ind(J))*T('MixAcidCellHyd','AcidCellHyd');
```

```
SteamTemp..
      T('SrcSteam','MixAcidCellHyd') =E=  (steamChoice('1')*utilProps('LPS','TSupply') +
                                          steamChoice('2')*utilProps('MPS1','TSupply') +
                                          steamChoice('3')*utilProps('MPS2','TSupply') +
                                          steamChoice('4')*utilProps('HPS1','TSupply') +
                                          steamChoice('5')*utilProps('HPS2','TSupply')  +
                                          steamChoice('6')*utilProps('CTBE1','TSupply') +
                                          steamChoice('7')*utilProps('CTBE2','TSupply')  ) ;
logSteamTemp..
        T('MixAcidCellHyd','AcidCellHyd')=L= (steamChoice('1')*utilProps('LPS','TSupply') +
                                          steamChoice('2')*utilProps('MPS1','TSupply') +
                                          steamChoice('3')*utilProps('MPS2','TSupply') +
                                          steamChoice('4')*utilProps('HPS1','TSupply') +
                                          steamChoice('5')*utilProps('HPS2','TSupply')  +
                                          steamChoice('6')*utilProps('CTBE1','TSupply') +
                                          steamChoice('7')*utilProps('CTBE2','TSupply')  )-dT_min;
binSteam..
       steamChoice('1')+steamChoice('2')+steamChoice('3') +steamChoice('4')
+steamChoice('5')+steamChoice('6')+steamChoice('7')   =E= 1;

Equations k1eqn, k2eqn,acidEqn, binAcid,ConstVolFlow,ConstTemp;
k1eqn..
      k1Gluc =E= acidChoice('1')*(Arrheniusk1('a', 'A')*10**Arrheniusk1('a', 'AExp')*exp(-Arrheniusk1('a',
'Ea')/(R*(T('MixAcidCellHyd','AcidCellHyd'))))  +
           acidChoice('2')*(Arrheniusk1('b', 'A')*10**Arrheniusk1('b', 'AExp')*exp(-Arrheniusk1('b',
'Ea')/(R*(T('MixAcidCellHyd','AcidCellHyd'))))  +
           acidChoice('3')*(Arrheniusk1('c', 'A')*10**Arrheniusk1('c', 'AExp')*exp(-Arrheniusk1('c',
'Ea')/(R*(T('MixAcidCellHyd','AcidCellHyd')))) ;

k2eqn..
      k2Gluc =E= acidChoice('1')*(Arrheniusk2('a', 'A')*10**Arrheniusk2('a', 'AExp')*exp(-Arrheniusk2('a',
'Ea')/(R*(T('MixAcidCellHyd','AcidCellHyd'))))  +
           acidChoice('2')*(Arrheniusk2('b', 'A')*10**Arrheniusk2('b', 'AExp')*exp(-Arrheniusk2('b',
'Ea')/(R*(T('MixAcidCellHyd','AcidCellHyd'))))  +
           acidChoice('3')*(Arrheniusk2('c', 'A')*10**Arrheniusk2('c', 'AExp')*exp(-Arrheniusk2('c',
'Ea')/(R*(T('MixAcidCellHyd','AcidCellHyd')))) ;

acidEqn..
     acidWtCell =E= acidChoice('1')*Arrheniusk1('a', 'CA')  +  acidChoice('2')*Arrheniusk1('b', 'CA')+
                acidChoice('3')*Arrheniusk1('c', 'CA');

binAcid..
      acidChoice('1')+acidChoice('2')+acidChoice('3') =E= 1;

ConstVolFlow..
        V('MixAcidCellHyd','AcidCellHyd') =E=  V('AcidCellHyd','FlsAcidCellHyd') ;
ConstTemp..
        T('MixAcidCellHyd','AcidCellHyd') =E=  T('AcidCellHyd','FlsAcidCellHyd') ;

Equations AcidCellHyd1,
      AcidCellHemi,AcidCellInerts, AcidCellHMF,    AcidCellSucrose,
      AcidCellXylo,AcidCellFurf,AcidCellAceA,     AcidCellXylolig,   AcidCellGlucolig,
      AcidCellAcetyl,concEqnIn,concEqnOut,AcidCellASL,AcidCellLignin;
*Overall MB
AcidCellHyd1..
        F('MixAcidCellHyd','AcidCellHyd') =E=  F('AcidCellHyd','FlsAcidCellHyd') ;
```

```
AcidCellHMF..
      1/Tau('AcidCellHyd')*(conc('HMF','MixAcidCellHyd','AcidCellHyd')-
conc('HMF','AcidCellHyd','FlsAcidCellHyd'))
    + k2Gluc*conc('Gluc','AcidCellHyd','FlsAcidCellHyd')*(MW('HMF')/MW('Gluc'))=E= 0;

concEqnIn(J,'MixAcidCellHyd','AcidCellHyd')..
       conc(J,'MixAcidCellHyd','AcidCellHyd')*V('MixAcidCellHyd', 'AcidCellHyd') =E= fc(J,'MixAcidCellHyd',
'AcidCellHyd');

concEqnOut(J,'AcidCellHyd', 'FlsAcidCellHyd')..
       conc(J,'AcidCellHyd','FlsAcidCellHyd')*V('AcidCellHyd', 'FlsAcidCellHyd') =E= fc(J,'AcidCellHyd',
'FlsAcidCellHyd');

AcidCellHemi..
      fc('Hemi','MixAcidCellHyd','AcidCellHyd')*(1-conv('Hemi_react'))=E=
fc('Hemi','AcidCellHyd','FlsAcidCellHyd');

AcidCellAcetyl..
      fc('Acetyl','MixAcidCellHyd','AcidCellHyd') =E= fc('Acetyl','AcidCellHyd','FlsAcidCellHyd');

AcidCellXylo..
      (fc('Hemi','MixAcidCellHyd','AcidCellHyd')*(conv('Hemi_react'))
+fc('Xylo','MixAcidCellHyd','AcidCellHyd')+fc('Xylolig','MixAcidCellHyd','AcidCellHyd'))*(1-conv('Xylo_furf'))
       =E= fc('Xylo','AcidCellHyd','FlsAcidCellHyd');
AcidCellFurf..

fc('Hemi','MixAcidCellHyd','AcidCellHyd')*(conv('Hemi_react'))*(conv('Xylo_furf'))+fc('Xylo','MixAcidCellHyd','A
cidCellHyd')*conv('Xylo_furf')

+fc('Xylolig','MixAcidCellHyd','AcidCellHyd')*conv('Xylo_furf')+fc('Furf','MixAcidCellHyd','AcidCellHyd')=E=fc('Fu
rf','AcidCellHyd','FlsAcidCellHyd')  ;

AcidCellXylolig..
       fc('Xylolig','AcidCellHyd','FlsAcidCellHyd') =E= 0;

AcidCellGlucolig..
       fc('Glucolig','AcidCellHyd','FlsAcidCellHyd') =E= 0;
AcidCellSucrose..
       fc('Sucrose','AcidCellHyd','FlsAcidCellHyd') =E= 0;

AcidCellAceA..
      fc('AceA','MixAcidCellHyd','AcidCellHyd') =E= fc('AceA','AcidCellHyd','FlsAcidCellHyd');

AcidCellASL..
       sum(solids(J), fc(solids,'FiltPreHyd','MixAcidCellHyd'))*ASLconc=E=
fc('ASL','AcidCellHyd','FlsAcidCellHyd')-fc('ASL','MixAcidCellHyd','AcidCellHyd');

AcidCellLignin..
      fc('Lignin','AcidCellHyd','FlsAcidCellHyd')=E=fc('Lignin','MixAcidCellHyd','AcidCellHyd')-
(fc('ASL','AcidCellHyd','FlsAcidCellHyd')-fc('ASL','MixAcidCellHyd','AcidCellHyd'));


AcidCellInerts(i)..
      fc(i,'MixAcidCellHyd','AcidCellHyd') =E= fc(i,'AcidCellHyd','FlsAcidCellHyd');
*++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
*Ficticious unit equations
Equation   BagIn,DeligPerc,
```

```
        FictInEqn,FictOutEqn,
        FictVol, FictT, FictConstVolFlow, FictConstTemp,
            FictTau  ,  FictAcidCellGlucolig,    FictAcidCellSucrose,
        FictAcidCellCellulose,FictAcidCellGluc, FictAcidCellHMF,  FictconcEqnIn,
FictconcEqnOut,FictAcidCellHemi,FictAcidCellAcetyl,
        FictAcidCellXylo,FictAcidCellXylolig, FictAcidCellFurf, FictAcidCellAceA,FictAcidCellASL,FictAcidCellLignin,
       FictAcidCellInerts,fictCellEqn,
concGlucose,
        YieldEqn, CellEqn,
       fictYieldEqn,fictCellEqn, cellRemEqn     ;

BagIn(J)..
       fc(J, 'SrcBag', 'MixPreHyd') =E= x_SCB(J)* F('SrcBag', 'MixPreHyd')    ;

DeligPerc..
       YieldDecr =E= 33.145-0.358*((fc('Lignin', 'SrcBag', 'MixPreHyd')-fc('Lignin', 'MixAcidCellHyd',
'AcidCellHyd'))/fc('Lignin', 'SrcBag', 'MixPreHyd'))*100   ;

FictOutEqn..
       F('FictCell', 'FictOUT') =E=  F('FictIN', 'FictCell');

FictVol..
      V('FictIN', 'FictCell') =E=  V('MixAcidCellHyd','AcidCellHyd') ;
FictT..
      T('FictIN', 'FictCell') =E=  T('MixAcidCellHyd','AcidCellHyd') ;
FictConstVolFlow..
          V('FictIN', 'FictCell') =E=  V('FictCell', 'FictOUT') ;
FictConstTemp..
          T('FictIN', 'FictCell') =E=  T('FictCell', 'FictOUT') ;

FictTau..
         Tau('FictCell') =E= Tau('AcidCellHyd');

FictAcidCellCellulose..
       1/Tau('FictCell')*(conc('Cellulose','FictIN', 'FictCell')-conc('Cellulose','FictCell', 'FictOUT'))
                          - k1Gluc*conc('Cellulose','FictCell', 'FictOUT') =E= 0;
*Tau and k are using min
FictAcidCellGluc..

1/Tau('FictCell')*(conc('Gluc','FictIN','FictCell')+conc('Glucolig','FictIN','FictCell')+2*conc('Sucrose','FictIN','FictC
ell')-conc('Gluc','FictCell', 'FictOUT'))
      + k1Gluc*conc('Cellulose','FictCell', 'FictOUT')*(MW('Gluc')/MW('Cellulose')) - k2Gluc*conc('Gluc','FictCell',
'FictOUT')=E= 0;
FictAcidCellHMF..
       1/Tau('FictCell')*(conc('HMF','FictIN','FictCell')-conc('HMF','FictCell','FictOUT'))
     + k2Gluc*conc('Gluc','FictCell','FictOUT')*(MW('HMF')/MW('Gluc'))=E= 0;

FictconcEqnIn(J,'FictIN','FictCell')..
        conc(J,'FictIN','FictCell')*V('FictIN', 'FictCell') =E= fc(J,'FictIN', 'FictCell');

FictconcEqnOut(J,'FictCell', 'FictOUT')..
        conc(J,'FictCell','FictOUT')*V('FictCell', 'FictOUT') =E= fc(J,'FictCell', 'FictOUT');

FictAcidCellHemi..
       fc('Hemi','FictCell','FictOUT') =E= fc('Hemi','AcidCellHyd','FlsAcidCellHyd');
FictAcidCellAcetyl..
       fc('Acetyl','FictCell','FictOUT') =E= fc('Acetyl','AcidCellHyd','FlsAcidCellHyd');
```

```
FictAcidCellXylo..
      fc('Xylo','FictCell','FictOUT') =E= fc('Xylo','AcidCellHyd','FlsAcidCellHyd');

FictAcidCellXylolig..
      fc('Xylolig','FictCell','FictOUT') =E= 0;

FictAcidCellGlucolig..
      fc('Glucolig','FictCell','FictOUT') =E= 0;

FictAcidCellSucrose..
      fc('Sucrose','FictCell','FictOUT') =E= 0;

FictAcidCellFurf..
      fc('Furf','FictCell','FictOUT') =E=fc('Furf','AcidCellHyd','FlsAcidCellHyd')  ;
FictAcidCellAceA..
      fc('AceA','FictCell','FictOUT') =E= fc('AceA','AcidCellHyd','FlsAcidCellHyd');

FictAcidCellASL..
       fc('ASL','FictCell','FictOUT') =E= fc('ASL','AcidCellHyd','FlsAcidCellHyd');
FictAcidCellLignin..
      fc('Lignin','FictCell','FictOUT') =E= fc('Lignin','AcidCellHyd','FlsAcidCellHyd');

FictAcidCellInerts(i)..
      fc(i,'FictIN', 'FictCell') =E= fc(i,'FictCell','FictOUT');

FictInEqn(J)..
      fc(J, 'FictIN', 'FictCell') =E=  fc(J, 'MixAcidCellHyd','AcidCellHyd');

fictYieldEqn..
      fictGYield =E=  (conc('Gluc','FictCell', 'FictOUT')-conc('Gluc','FictIn', 'FictCell')) /(48.3*(1-
fictcellRem/100))*100;

fictCellEqn..
      fictcellRem=E=(fc('Cellulose','FictCell', 'FictOUT')/fc('Cellulose','FictIN', 'FictCell'))*100;

YieldEqn..
      GYield =E=  (conc('Gluc','AcidCellHyd','FlsAcidCellHyd')-conc('Gluc','MixAcidCellHyd','AcidCellHyd'))
/(48.3*(1-cellRem/100))*100;
concGlucose..
      GYield =E=  fictGYield*(1-YieldDecr/100);
**Feed the change in yield to the real unit based on the decrease in the fictitious unit
*concGlucose..
*       conc('Gluc','AcidCellHyd','FlsAcidCellHyd') =E=   conc('Gluc','FictCell','FictOut')*(1-YieldDecr/100);

CellEqn..
cellRem=E=(fc('Cellulose','AcidCellHyd','FlsAcidCellHyd')/fc('Cellulose','MixAcidCellHyd','AcidCellHyd'))*100;

cellRemEqn..
      fc('Cellulose','AcidCellHyd','FlsAcidCellHyd') =e=  fc('Cellulose','FictCell', 'FictOUT')
     +(fc('Gluc','FictCell', 'FictOUT')-(fc('Gluc','AcidCellHyd','FlsAcidCellHyd')))*(MW('Cellulose')/MW('Gluc'))   ;
*+++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
YieldDecr.lo=0;
YieldDecr.up=100;
YieldDecr.l=26;
fc.lo('Lignin', 'SrcBag', 'MixPreHyd')   =0.01;
```

```
fc.lo('Cellulose','MixAcidCellHyd','AcidCellHyd')=0.0001;
fc.l('Cellulose','MixAcidCellHyd','AcidCellHyd')=5;
fc.lo('Cellulose','FictIN', 'FictCell')=0.0001;

GYield.lo=0.001;
GYield.up=99.9;
cellRem.lo=0.001;
cellRem.up=99.9;
fictGYield.lo=0.001;
fictGYield.up=99.9;
fictcellRem.lo=0.001;
fictcellRem.up=99.9;
*+++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
*Flash equations
Equation Flsh1AcidCell, Flsh2AcidCell,Flsh3AcidCell,Flsh4AcidCell,Flsh5AcidCell,   FlshVaps,FlshAcidCellT;
Flsh1AcidCell(J)..
     fc(J,'AcidCellHyd','FlsAcidCellHyd') =E= fc(J,'FlsAcidCellHyd','FiltCellHyd')+
fc(J,'FlsAcidCellHyd','SnkVapFlsh2');

Flsh2AcidCell(liquids)..
     fc(liquids,'FlsAcidCellHyd','FiltCellHyd') =E= fc(liquids,'AcidCellHyd','FlsAcidCellHyd')*(1-
FlshVapFrac(liquids));

Flsh3AcidCell(solids)..
     fc(solids,'FlsAcidCellHyd','FiltCellHyd') =E= fc(solids,'AcidCellHyd','FlsAcidCellHyd');

Flsh5AcidCell..
     fc('Lignin','FlsAcidCellHyd','FiltCellHyd') =E= fc('Lignin','AcidCellHyd','FlsAcidCellHyd');

Flsh4AcidCell(liquids)..
     fc(liquids,'FlsAcidCellHyd','SnkVapFlsh2') =E=
fc(liquids,'AcidCellHyd','FlsAcidCellHyd')*(FlshVapFrac(liquids));

FlshAcidCellT..
     T('FlsAcidCellHyd','FiltCellHyd') =E= T('AcidCellHyd','FlsAcidCellHyd');

FlshVaps(ll)..
      FlshVapFrac(ll) =E=
(FlshCell1(ll,'m')*acidChoice('1')+FlshCell2(ll,'m')*acidChoice('2')+FlshCell3(ll,'m')*acidChoice('3'))*(T('MixAcidC
ellHyd','AcidCellHyd')-273.15) +
                (FlshCell1(ll,'c')*acidChoice('1')+FlshCell2(ll,'c')*acidChoice('2')+FlshCell3(ll,'c')*acidChoice('3'))   ;

FlshVapFrac.fx('AceA')=0.98;
FlshVapFrac.fx('OrgAc')=0;
FlshVapFrac.fx('ASL')=0;
FlshVapFrac.fx('Sucrose')=0;

FlshVapFrac.fx('Water')=0.9999;
FlshVapFrac.fx('Furf')=0.999;
FlshVapFrac.fx('HMF')=0.99;

*+++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
*Hydrolysis Filter
Equation Filt1Cell,Filt1aCell,Filt2Cell,Filt3Cell, FiltWaterCell,
      Filt4Cell,FiltCellT1,FiltCellT2;
Filt1Cell(filtSol)..
      fc(filtSol, 'FlsAcidCellHyd','FiltCellHyd')*SteamFiltSol =E= fc(filtSol, 'FiltCellHyd','SnkSolid');
```

```
Filt1aCell(filtLiq)..
      (fc(filtLiq, 'FlsAcidCellHyd','FiltCellHyd')+fc(filtLiq, 'SrcWater','FiltCellHyd'))*CellHydFiltSplit =E= fc(filtLiq,
'FiltCellHyd','SnkSolid');

Filt2Cell..
      F('FlsAcidCellHyd','FiltCellHyd')+F('SrcWater','FiltCellHyd') =E=
F('FiltCellHyd','SnkSolid')+F('FiltCellHyd','SnkC6');

FiltWaterCell..
      F('SrcWater','FiltCellHyd') =l=1.5*sum(filtSol, fc(filtSol,'FiltCellHyd','SnkSolid'));

Filt3Cell(J)..
      fc(J,'FlsAcidCellHyd','FiltCellHyd')+ fc(J,'SrcWater','FiltCellHyd') =E=
fc(J,'FiltCellHyd','SnkSolid')+fc(J,'FiltCellHyd','SnkC6');

Filt4Cell..
      sum(filtLiq, fc(filtLiq, 'FiltCellHyd','SnkSolid'))/F('FiltCellHyd','SnkSolid') =e= CellLiqFrac;
FiltCellT1..
      sum(J,fc(J,'FlsAcidCellHyd','FiltCellHyd')*cp_ind(J))*T('FlsAcidCellHyd','FiltCellHyd')
      +sum(J,fc(J,'SrcWater','FiltCellHyd')*cp_ind(J))*T('SrcWater','FiltCellHyd')
      =E= sum(J,fc(J,'FiltCellHyd','SnkSolid')*cp_ind(J))*T('FiltCellHyd','SnkSolid')
      + sum(J,fc(J,'FiltCellHyd','SnkC6')*cp_ind(J))*T('FiltCellHyd','SnkC6');

FiltCellT2..
      T('FiltCellHyd','SnkSolid')=E=T('FiltCellHyd','SnkC6');

F.lo('FiltCellHyd','SnkC6') = 0.01;
F.lo('SrcWater','FiltCellHyd') = 0;
F.l('SrcWater','FiltCellHyd') = 10;
F.up('SrcWater','FiltCellHyd') = 50;
F.lo('FiltCellHyd','SnkSolid') = 0.01;

CellHydFiltSplit.lo=0.03;
CellHydFiltSplit.up=0.3;
CellLiqFrac.up = 0.55;
CellLiqFrac.lo = 0.1;
*+++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
*Capital costing calculations
Parameters
      opHours    Percentage operating time /0.8/
      convFt     Convert m to ft /3.28084/
      rohCS      density of carbon steel/490/
      FmSS316    Material factor for SS316  /2.1/
      PlantLife  Plant lifetime /10/
      RandDollar  Rand to Dollar exchange rate /11.03/
      CEPCI      CEPCI for 2014   /577/
      overDesFact over design factor /1.1/
      lang       lang factor for fluids-solids /4.41/
      CEPCIsteam  CEPCI for 2005 /468.2/;

Equation  VolAcidCell,CpCellHyd,VolStorage,
            CpSrcAcid;
VolAcidCell..
       Volume('AcidCellHyd')   =E=  overDesFact*V('MixAcidCellHyd', 'AcidCellHyd')*Tau('AcidCellHyd')*60;
***Tau is 20
VolStorage..
```

```
        Volume('SrcAcid') =E=
overDesFact*(F('SrcAcid','MixAcidCellHyd')+F('SrcAcid','MixPreHyd'))*3600*24*30/(x('Acid','SrcAcid','MixAcidC
ellHyd')*dens('Acid')+x('Water','SrcAcid','MixAcidCellHyd')*dens('Water'));
*Closed storage tank
CpSrcAcid..
*C&R
         Cp('SrcAcid') =E= (CEPCI/444.2)*2*2300*Volume('SrcAcid')**0.55;
CpCellHyd ..
        Cp('AcidCellHyd') =E= (CEPCI/444.2)*(5000*Length('AcidCellHyd'))*2*1.2;
*MF of 2, PF of 1.2
*+++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
*Capital costing calculations
Equation  VolEqn,LDratEqn,CpPreHyd,VolPreHyd;

VolEqn(unit)..
        Volume(unit)   =E=PI/4*Diameter(unit)**2*Length(unit);

LDratEqn(unit)..
         LDrat(unit) =E=   Length(unit)/Diameter(unit);

VolPreHyd..
        Volume('PreHyd')   =E=  overDesFact*V('MixPreHyd', 'PreHyd')*Tau('PreHyd')*60;

CpPreHyd ..
        Cp('PreHyd') =E= (CEPCI/444.2)*(5000*Length('PreHyd'))*2;
*MF of 2, PF of 1
*+++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
Diameter.lo('PreHyd')= 1;
Diameter.lo('AcidCellHyd')= 1;
Diameter.up('PreHyd')= 4;
Diameter.up('AcidCellHyd')= 4;
Length.lo(unit)= 0 ;
Length.up(unit)= 50;

Volume.lo(unit)=0.0001;
Volume.up(unit)=300;
Volume.up('SrcAcid')=10000;

Cp.lo(unit)=0;
Cp.up(unit)=100000000;

LDrat.lo(unit)=2.5;
LDrat.up(unit)=5;
Diameter.lo(unit)= 0.3 ;
*+++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
*Filters
*Max of 6000 lb/(sq ft.day)
*Length is width
Parameter  maxMassFlow   lb per (sq ft day) /6000/
         convLb  kg per lb              /0.453592/
         convSqFt  sq m per sq ft        /0.092903/     ;

Equation       filt1,filt2,filt2a,filt3;
*calc surface area
filt1(filt)..
     SA(filt) =E= pi*Diameter(filt)*Length(filt);
*compare to max flowrate
```

```
filt2..
     overDesFact*(F('FiltPreHyd','MixAcidCellHyd'))*3600*24 =L=
SA('FiltPreHyd')*maxMassFlow*convLb/convSqFt;
filt2a..
     overDesFact*(F('FiltCellHyd','SnkSolid'))*3600*24 =L= SA('FiltCellHyd')*maxMassFlow*convLb/convSqFt;
filt3(filt)..
       Cp(filt) =E=  34000*SA(filt)**0.6*CEPCI/444.2;

Diameter.lo(filt)=0.1;
Diameter.up(filt)=100;
Length.lo(filt)=0.01;
Length.up(filt)=100;
SA.lo(filt)=0.001;
SA.up(filt)=5000;
*+++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
*Other revenues
Parameter XylToCH4      mass ratio of methane to xylose /0.360006877/,
        CH4Worth       price of methane R per ton /14000/,
        RSolEnergy     ratio of energy out of turbine to energy in solids /-0.076401695/
        ElecCost       Rand per kWh /0.8/
        ElecSalePrice  Rand per kWh /0.56/;
Variable  CH4Rev       Revenue from methane in millions of R per annum,
        SolEn    Energy inherent in the solids in kW,
        TurEn    Energy produced by the turbine in kW,
        EnUsed   Energy used in plant in kWh per annum,
        EnRev;
Equation CH4Eqn1;
CH4Eqn1..
        CH4Rev =E=  fc('Xylo','FiltPreHyd','SnkC5')*XylToCH4*CH4Worth/1000*3600*24*365*opHours/10**6;
*+++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
Equation  Obj;
*in million R per year - need to add in hours factor (20% downtime)
Obj.. z =E= worth('Gluc')*fc('Gluc','FiltCellHyd','SnkC6')/1000*3600*24*365*opHours/10**6
         +CH4Rev
            - (Cp('PreHyd')*RandDollar/plantLife/10**6
             + Cp('SrcAcid')*RandDollar/plantLife/10**6
             + Cp('AcidCellHyd')*RandDollar/plantLife/10**6
        + Cp('FiltPreHyd')*RandDollar/plantLife/10**6
        + Cp('FiltCellHyd')*RandDollar/plantLife/10**6    )*Lang
          -
worth('Acid')*(F('SrcAcid','MixPreHyd')+F('SrcAcid','MixAcidCellHyd'))/1000*3600*24*365*opHours/10**6
        -
worth('Water')*(F('SrcWater','FiltPreHyd')+F('SrcWater','MixPreHyd')+F('SrcWater','MixAcidCellHyd')+F('SrcWa
ter','FiltCellHyd'))/1000*3600*24*365*opHours/10**6
         - (steamChoice('1')*F('SrcSteam','MixAcidCellHyd')*utilProps('LPS','Cost')
        +steamChoice('2')*F('SrcSteam','MixAcidCellHyd')*utilProps('MPS1','Cost')
        +steamChoice('3')*F('SrcSteam','MixAcidCellHyd')*utilProps('MPS2','Cost')
        +steamChoice('4')*F('SrcSteam','MixAcidCellHyd')*utilProps('HPS1','Cost')
        +steamChoice('5')*F('SrcSteam','MixAcidCellHyd')*utilProps('HPS2','Cost')
        +steamChoice('6')*F('SrcSteam','MixAcidCellHyd')*utilProps('CTBE1','Cost')
        +steamChoice('7')*F('SrcSteam','MixAcidCellHyd')*utilProps('CTBE2','Cost'))
*CEPCI/CEPCIsteam/1000*3600*24*365*opHours*RandDollar/10**6
        -
F('SrcSteam','MixPreHyd')*utilProps('LPS','Cost')*CEPCI/CEPCIsteam/1000*3600*24*365*opHours*RandDollar
/10**6    ;

Variable   EIRM(cats, Cmpnts),
```

```
      EIProd(cats, Cmpnts) ,
      TotEIRM(Cmpnts),TotEIProd(Cmpnts),TotEIcat(cats),
      DUAL;
Variable   TotEI;


Equation EIAcid, EIBag, EIWater,
            EILPS,   EIMPS1, EIMPS2, EIHPS1, EIHPS2 ,EICTBE1,  EICTBE2,
            EICh4, EIAceA, EIFurf,   EIAcidFl, EITotCat, EITotRM, EITotProd, TotEICalc,EIEth;
EIAcid(cats)..
      EIRM(cats,'Acid') =E= Enviro(cats,'WF')*Enviro(cats,
'Acid')*(F('SrcAcid','MixPreHyd')+F('SrcAcid','MixAcidCellHyd'))*3600*24*365*opHours ;
EIBag(cats)..
      EIRM(cats,'Bag') =E= Enviro(cats,'WF')*(Enviro(cats, 'Bag')-SysExp(cats,
'ExpBag'))*F('SrcBag','MixPreHyd')*3600*24*365*opHours;
EIWater(cats)..
      EIRM(cats,'Water') =E= Enviro(cats,'WF')*Enviro(cats,
'Water')*(F('SrcWater','FiltPreHyd')+F('SrcWater','MixPreHyd')+F('SrcWater','MixAcidCellHyd')
            +F('SrcWater','FiltCellHyd'))*3600*24*365*opHours ;
EILPS(cats)..
      EIRM(cats,'LPS') =E= Enviro(cats,'WF')*Enviro(cats,
'LPS')*(steamChoice('1')*F('SrcSteam','MixAcidCellHyd')+F('SrcSteam','MixPreHyd'))*3600*24*365*opHours ;
EIMPS1(cats)..
      EIRM(cats,'MPS1') =E= Enviro(cats,'WF')*Enviro(cats,
'MPS1')*(steamChoice('2')*F('SrcSteam','MixAcidCellHyd'))*3600*24*365*opHours;
EIMPS2(cats)..
      EIRM(cats,'MPS2') =E= Enviro(cats,'WF')*Enviro(cats,
'MPS2')*steamChoice('3')*F('SrcSteam','MixAcidCellHyd')*3600*24*365*opHours;
EIHPS1(cats)..
      EIRM(cats,'HPS1') =E= Enviro(cats,'WF')*Enviro(cats,
'HPS1')*steamChoice('4')*F('SrcSteam','MixAcidCellHyd')*3600*24*365*opHours ;
EIHPS2(cats)..
      EIRM(cats,'HPS2') =E= Enviro(cats,'WF')*Enviro(cats,
'HPS2')*steamChoice('5')*F('SrcSteam','MixAcidCellHyd')*3600*24*365*opHours;
EICTBE1(cats)..
      EIRM(cats,'CTBE1') =E= Enviro(cats,'WF')*Enviro(cats,
'CTBE1')*steamChoice('6')*F('SrcSteam','MixAcidCellHyd')*3600*24*365*opHours;
EICTBE2(cats)..
      EIRM(cats,'CTBE2') =E= Enviro(cats,'WF')*Enviro(cats,
'CTBE2')*(steamChoice('7')*F('SrcSteam','MixAcidCellHyd'))*3600*24*365*opHours;
EIAceA(cats)..
      EIProd(cats,'AceA') =E= Enviro(cats,'WF')*Enviro(cats,
'AceA')*(fc('AceA','FlsPreHyd','SnkVapFlsh1')+fc('AceA','FlsAcidCellHyd','SnkVapFlsh2'))*3600*24*365*opHour
s ;
EIFurf(cats)..
      EIProd(cats,'Furf') =E= Enviro(cats,'WF')*Enviro(cats,
'Furf')*(fc('Furf','FlsPreHyd','SnkVapFlsh1')+fc('Furf','FlsAcidCellHyd','SnkVapFlsh2'))*3600*24*365*opHours;
EIAcidFl(cats)..
      EIProd(cats,'AcidFl') =E= Enviro(cats,'WF')*Enviro(cats,
'AcidFl')*(fc('Acid','FlsPreHyd','SnkVapFlsh1')+fc('Acid','FlsAcidCellHyd','SnkVapFlsh2'))*3600*24*365*opHours;
EICh4(cats)..
      EIProd(cats,'CH4') =E= Enviro(cats,'WF')*(Enviro(cats, 'CH4')-SysExp(cats,
'ExpCH4'))*fc('Xylo','FiltPreHyd','SnkC5')*XylToCH4*3600*24*365*opHours;
EIEth(cats)..
      EIProd(cats,'Eth') =E= Enviro(cats, 'WF')*(-SysExp(cats,
'ExpEth'))*fc('Gluc','FiltCellHyd','SnkC6')/0.9*3600*24*365*opHours;
EITotCat(cats)..
```

```
      TotEIcat(cats)=E=sum(Cmpnts,(EIRM(cats,Cmpnts)+EIProd(cats,Cmpnts)));
EITotRM(Cmpnts)..
      TotEIRM(Cmpnts)=E=sum(cats,EIRM(cats,Cmpnts));
EITotProd(Cmpnts)..
      TotEIProd(Cmpnts)=E=sum(cats,EIProd(cats,Cmpnts));
TotEICalc..
      TotEI=E= sum(cats, TotEIcat(cats));

TotEIRM.lo('Acid')=0;
TotEIRM.lo('NaOH')=0;
TotEIRM.lo('Enz')=0;
TotEIRM.lo('Bag')=0;
TotEIRM.lo('Water')=0;
TotEIRM.lo('CTBE1')=0;
TotEIRM.lo('CTBE2')=0;
TotEIRM.lo('LPS')=0;
TotEIRM.lo('MPS1')=0;
TotEIRM.lo('MPS2')=0;
TotEIRM.lo('HPS1')=0;
TotEIRM.lo('HPS2')=0;
TotEIRM.lo('AceA')=0;
TotEIRM.lo('Furf')=0;
TotEIRM.lo('AcidFl')=0;
TotEIRM.lo('CH4')=0;
TotEIRM.lo('WF')=0;
TotEIRM.lo('Eth')=0;

TotEIProd.lo('Acid')=0;
TotEIProd.lo('NaOH')=0;
TotEIProd.lo('Enz')=0;
TotEIProd.lo('Bag')=0;
TotEIProd.lo('Water')=0;
TotEIProd.lo('CTBE1')=0;
TotEIProd.lo('CTBE2')=0;
TotEIProd.lo('LPS')=0;
TotEIProd.lo('MPS1')=0;
TotEIProd.lo('MPS2')=0;
TotEIProd.lo('HPS1')=0;
TotEIProd.lo('HPS2')=0;
TotEIProd.lo('AceA')=0;
TotEIProd.lo('Furf')=0;
TotEIProd.lo('AcidFl')=0;
TotEIProd.lo('CH4')=0;
TotEIProd.lo('WF')=0;

PARAMETER
BEST Best values for objectives
WORST Worst values for objectives
DRatio Weighting for TAC in dual objective function /0/
CRatio Scaling of EI constraint /0/  ;

BEST('TAC')  = 46;
WORST('EI')  = 2487934;
BEST('EI')   = 1967442;
WORST('TAC') = -99 ;
*AA       46       2487934       -99       1967442
```

```
Equation    DUAL_OBJECTIVE,   CONSTRAINT_OBJECTIVE;
DUAL_OBJECTIVE..
      DUAL =E= DRatio*z/BEST('TAC')+(1-DRatio)*TotEI/BEST('EI');
CONSTRAINT_OBJECTIVE..
*       TotEI =L= BEST('EI')+CRatio*(WORST('EI')-BEST('EI'));
*       z =L= BEST('TAC')+CRatio*(WORST('TAC')-BEST('TAC'));
*       TotEI =g= WORST('EI')-CRatio*(WORST('EI')-BEST('EI'));
      z =g= WORST('TAC')-CRatio*(WORST('TAC')-BEST('TAC'));

Model SteamExplosion /ALL/;

*Solve SteamExplosion Using MINLP Maximising z;
Solve SteamExplosion Using MINLP minimsing TotEI;

Parameter Balance(J)
       Overall
       MoleFrac(unit, unit1),
      test1, test2, test3,test4;


Overall = F.l('SrcBag','MixPreHyd')+F.l('SrcAcid','MixPreHyd')- F.l('PreHyd','FlsPreHyd');

MoleFrac(unit,unit1)=sum(J,x.l(J,unit,unit1));

Parameter RMCost,ProdCost, AnnualCapCost,sumnegs,AcidCost,WaterCost, SteamCost;

ProdCost= worth('Gluc')*fc.l('Gluc','FiltCellHyd','SnkC6')/1000*3600*24*365*opHours/10**6 ;
AnnualCapCost=   (Cp.l('PreHyd')*RandDollar/plantLife/10**6
            +Cp.l('SrcAcid')*RandDollar/plantLife/10**6
            + Cp.l('FiltPreHyd')*RandDollar/plantLife/10**6
            + Cp.l('FiltCellHyd')*RandDollar/plantLife/10**6
            + Cp.l('AcidCellHyd')*RandDollar/plantLife/10**6)*Lang   ;

AcidCost=
worth('Acid')*(F.l('SrcAcid','MixPreHyd')+F.l('SrcAcid','MixAcidCellHyd'))/1000*3600*24*365*opHours/10**6 ;
WaterCost=
worth('Water')*(F.l('SrcWater','FiltPreHyd')+F.l('SrcWater','MixPreHyd')+F.l('SrcWater','MixAcidCellHyd')+F.l('Sr
cWater','FiltCellHyd'))/1000*3600*24*365*opHours/10**6 ;
SteamCost= (steamChoice.l('1')*F.l('SrcSteam','MixAcidCellHyd')*utilProps('LPS','Cost')
      +steamChoice.l('2')*F.l('SrcSteam','MixAcidCellHyd')*utilProps('MPS1','Cost')
      +steamChoice.l('3')*F.l('SrcSteam','MixAcidCellHyd')*utilProps('MPS2','Cost')
      +steamChoice.l('4')*F.l('SrcSteam','MixAcidCellHyd')*utilProps('HPS1','Cost')
      +steamChoice.l('5')*F.l('SrcSteam','MixAcidCellHyd')*utilProps('HPS2','Cost')
      +steamChoice.l('6')*F.l('SrcSteam','MixAcidCellHyd')*utilProps('CTBE1','Cost')
      +steamChoice.l('7')*F.l('SrcSteam','MixAcidCellHyd')*utilProps('CTBE2','Cost'))
*CEPCI/CEPCIsteam/1000*3600*24*365*opHours*RandDollar/10**6

+F.l('SrcSteam','MixPreHyd')*utilProps('LPS','Cost')*CEPCI/CEPCIsteam/1000*3600*24*365*opHours*RandDol
lar/10**6   ;
RMCost= AcidCost+WaterCost+SteamCost;
sumnegs= RMCost+  AnnualCapCost;

Parameter filtTest1,filtTest2;
filtTest1=sum(filtLiq, fc.l(filtLiq,'FlsAcidCellHyd','FiltCellHyd'))/F.l('FlsAcidCellHyd','FiltCellHyd');
filtTest2=sum(filtLiq, fc.l(filtLiq,'FiltCellHyd','SnkSolid'))/F.l('FiltCellHyd','SnkSolid');

Parameter maxWaterCellFilt, maxWaterPreFilt;
```

```
maxWaterPreFilt=1.5*sum(filtSol, fc.l(filtSol,'FiltPreHyd','MixAcidCellHyd'))  ;
maxWaterCellFilt=1.5*sum(filtSol, fc.l(filtSol,'FiltCellHyd','SnkSolid'))  ;

option decimals = 5;
display F.l, fc.l, V.l;
display x.l, conc.l, z.l, Overall, MoleFrac, T.l, Q.l;
display PreHydBin.l, acidWtPre.l,diameter.l,length.l,LDrat.l,Volume.l,cp.l;
display RMCost,ProdCost, AnnualCapCost,sumnegs,AcidCost,WaterCost, SteamCost,
        EIRM.l,EIProd.l,TotEIRM.l,TotEIProd.l,TotEIcat.l,TotEI.l, filtTest1,filtTest2,
         maxWaterPreFilt, maxWaterCellFilt;

Parameter  PreSteam,HydSteam;
HydSteam= (steamChoice.l('1')*F.l('SrcSteam','MixAcidCellHyd')*utilProps('LPS','Cost')
       +steamChoice.l('2')*F.l('SrcSteam','MixAcidCellHyd')*utilProps('MPS1','Cost')
       +steamChoice.l('3')*F.l('SrcSteam','MixAcidCellHyd')*utilProps('MPS2','Cost')
       +steamChoice.l('4')*F.l('SrcSteam','MixAcidCellHyd')*utilProps('HPS1','Cost')
       +steamChoice.l('5')*F.l('SrcSteam','MixAcidCellHyd')*utilProps('HPS2','Cost')
       +steamChoice.l('6')*F.l('SrcSteam','MixAcidCellHyd')*utilProps('CTBE1','Cost')
       +steamChoice.l('7')*F.l('SrcSteam','MixAcidCellHyd')*utilProps('CTBE2','Cost'))
*CEPCI/CEPCIsteam/1000*3600*24*365*opHours/10**6    ;
PreSteam =
F.l('SrcSteam','MixPreHyd')*utilProps('LPS','Cost')*CEPCI/CEPCIsteam/1000*3600*24*365*opHours/10**6   ;
display  PreSteam,HydSteam;

*$ontext
file pareto /AA Pareto.csv/;
put pareto;
pareto.pc=5;
pareto.nd=8;
put 'Pareto Curve Data'/;
put 'Acid and Acid'/;
put 'i', 'CRatio', 'EI', 'TAC', 'EI Limit', 'DUAL', 'DRatio','acidWtPre','acidWtCell'/;
option CRatio:5;
set a indexing /1*30/;
parameter report(*,*) "Pareto curve data";
scalar
count counter /1/
EILimit The EI constraint set;
while(count <= card(a),
 CRatio = ((count-1)/(card(a)-1))**3;
Solve SteamExplosion Using MINLP minimsing TotEI;
*Solve SteamExplosion Using MINLP Maximising z;
EILimit =  WORST('TAC')-CRatio*(WORST('TAC')-BEST('TAC'));
*BEST('EI')+CRatio*(WORST('EI')-BEST('EI'));
 report(a,'CRatio') = CRatio;
 report(a,'TAC') = z.L;
 report(a,'EI') = TotEI.L;
 report(a,'EI Limit') = EILimit;
 report(a,'DUAL') = DUAL.L;
 report(a,'DRatio') = DRatio;
 report(a,'acidWtPre') = acidWtPre.l;
 report(a,'acidWtCell') = acidWtCell.L;
 put count, CRatio, TotEI.L, z.L, EILimit, DUAL.L, DRatio,acidWtPre.l,acidWtCell.L/;
 count = count + 1;
);
display report ;
*$offtext
```

References

Aguilar, R., Ramırez, J., Garrote, G. & Vazquez, M. 2002. Kinetic study of the acid hydrolysis of sugar cane bagasse. *Journal of Food Engineering*. 55:309–318. Available: http://www.sciencedirect.com/science/article/pii/S0260877402001061 [2013, May 21].

Bonomi, A., Dayan, C., Jesus, F. De, Cunha, M.P. & Mantelatto, P.E. 2011. Technological Assessment Program (PAT): The Virtual Sugarcane Biorefinery (VSB) - 2011 Report.

Gurgel, L. & Marabezi, K. 2012. Dilute acid hydrolysis of sugar cane bagasse at high temperatures: A kinetic study of cellulose saccharification and glucose decomposition. Part I: sulfuric acid as the catalyst. *Industrial & Engineering Chemistry Research,* 51:1173–1185. DOI: dx.doi.org/10.1021/ie2025739.

Harding, K. 2008. A Generic Approach to Environmental Assessment of Microbial Bioprocesses through Life Cycle Assessment (LCA). University of Cape Town.

Heinzle, E., Biwer, A. & Cooney, C. 2006. Modelling and Simulation of Bioprocesses. In *Development of Sustainable Bioprocesses: Modelling and Assessment*. John Wiley & Sons. 61–80.

Lavarack, B.P., Griffin, G.J. & Rodman, D. 2002. The acid hydrolysis of sugarcane bagasse hemicellulose to produce xylose , arabinose , glucose and other products. *Biomass and Bioenergy*. 23:367–380.

Nielsen, P.H., Oxenbøll, K.M. & Wenzel, H. 2007. LCA Case Studies Cradle-to-Gate Environmental Assessment of Enzyme Products Produced Industrially in Denmark by Novozymes A / S. 12(2006):432–438.

Rezende, C.A., Lima, M.A. De, Maziero, P. & Ribeiro, E. 2011. Chemical and morphological characterization of sugarcane bagasse submitted to a delignification process for enhanced enzymatic digestibility. 54(November).

Skals, P.B., Krabek, A., Nielsen, P.H. & Wenzel, H. 2008. LCA Case Studies Environmental Assessment of Enzyme Assisted Processing in Pulp and Paper Industry *. 13(2):124–132.

Stranddorf, H.K., Hoffmann, L., Schmidt, A. & FORCE Technology. 2005. *Impact categories, normalisation and weighting in LCA.*

Wooley, R.J., Putsche, V. & NREL. 1996. *Development of an ASPEN PLUS Physical Property Database for Biofuels Components*.