# Feasibility for Value Addition to Sucrose in South Africa through Conversion to Platform Chemicals

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# Executive Summary

The world sugar price is constantly changing in response to supply and demand and is currently very low as compared to the prices it is sold at domestically in South Africa. The drop in the worldwide price of sugar is due to its oversupply as yields of sugar production have increased in recent years and subsidies and protection measures in other producing countries. The low prices also mean imports are cheaper than local sugar. This pushes down the average sugar price and leads to a low profit margin. Further, sugar production in South Africa is facing a number of challenges. The industrialization of the sugar belt in KwaZulu-Natal has resulted in less plantations and challenging topography for these. Incentivisation of small, medium and micro-scale commercial operations has increased the number of smaller scaled operations, with less economy of scale and less capital backing. Climatic factors have impacted crop yields. Production costs have increased in accordance with South Africa's consumer price index whereas selling price has moved with the less inflationary global platform. Together, these have made the industry less economically viable. This has led to a need for value addition to sucrose and to eliminate the dependency on a single commodity. Re-positioning of sugar into value-added products has potential to boost the country's economy by introducing other sources of revenue. Moreover there is a worldwide need to find alternative means to produce petroleum-based fuels and chemicals and bio-based products are being targeted to meet some of this need. A review of the global status shows that there has been value addition in the sugar industry producing mostly ethanol and other commodity chemicals such as surfactants, organic acids and polyols. It is therefore imperative to find sustainable ways of generating value added platform chemicals from sucrose.

The quantitative and qualitative study of this project looks at determining the chemicals that should be considered as having the highest potential for value addition from sucrose in a South African context. The project was scoped to focus on chemicals and fuels that can be produced by biological conversions of sucrose. For the quantitative study, a set of 39 chemicals was selected from major studies performed globally on potential bio-based platform chemicals and these catalogued according to a set of criteria. The decision of the chemical/fuel to be studied was based on the gap in the chemical industry. This list comprised of chemicals that were selected in the US department of energy top 10 list in 2004 and 2010 and top 15 chemicals in the EU list in 2015. In addition to these, chemicals that are currently of interest (which were mostly chemicals that can be used as polymers and biofuels) were included to make up the list of 39 chemicals. The selected chemicals then went through a knock out selection where chemicals that cannot be produced with current technology from sugar or via a biological route were eliminated from the list. A quantitative analysis was then done on the remaining chemicals from the knock out stage. A weighting method which considered a series of factors was used to determine the top platform chemicals. The factors used were to identify platform chemicals that are at a high demand (both in South Africa and internationally), chemicals that showed great potential for profitability based on cost, technology readiness level and product yield. The quantitative analysis allowed seven chemicals to be selected. Finally a qualitative study based on interviews with experts in the field was done. Most of this information provided by the experts was supported by several literatures (Taylor, et al., 2015; Villadsen, et al., 2011; Choi, et al., 2015; Jansen & van Gulik, 2014). The qualitative study identified Succinic acid, Lactic acid and Citric acid as the top three chemicals.

A techno-economic study was done on succinic acid, one of the most promising platform chemicals identified. The reasons for its selection was because it has a higher performance and it generates less carbon footprint than petroleum based succinic acid, competiveness for niche market, multiple application via BDO and PBS and its overall favourable environmental process that uses up carbon dioxide from the environment. Firstly, the succinic acid process was designed to be produced using *Saccharomyces cerevisiae* in a dual phase fed batch fermentation process. The overall design for the succinic acid process was based on the design proposed by Efe, et al (2013). A cost evaluation was then done on the design for an economic analysis. The economic analysis was done on the process to ascertain that there is indeed value addition of sucrose to the platform chemicals chosen. This was done in the form of profitability analysis of the process. An economic analysis of the design shows that the plant is profitable after the first year of operation. The total investment on the plant is R 22.3 billion and the start-up expense is R 1.05 billion.

This project serves as a preliminary paper based overview of the general background for the selected platform chemicals that will be researched further in subsequent research.

Keywords: Platform chemical, value addition, Sucrose

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# Glossary

| | |
|---|---|
| Bio-based | Composed, in whole or in significant part of biological product, renewable domestic agricultural materials, forestry materials or an intermediate feedstock |
| Bioproducts | Materials, chemicals and energy that have been produced by using renewable raw materials |
| Biorefinery | Dedicated facilities that convert the sugar, oils and proteins derived from renewable biomass into marketable products (biofuels, chemicals and materials such as plastics and polymers) |
| Capnophilic microorganisms | Microorganisms that can grow in high concentration of carbon dioxide as long as there is a small amount of free oxygen present |
| Commodity | Raw materials, basic resources or agricultural products that can be bought or sold |
| Downstream | Last section of the processing line after the reactors that deals with extraction and concentrating the desired product |
| Freeboard | Space (clearance) kept between the top of the maximum water level and the bottom of the roof slab of a vessel |
| Heterotroph | Organism that ingest or absorb organic carbon in order to produce energy and synthesise compounds to maintain life |
| Metabolic engineering | Design, engineering and optimisation of a microorganism to optimise a production process for the production of chemicals for renewable resources |
| Osmophile | Microorganisms adapted to environments with high osmotic pressures, such as high sugar concentrations |
| Speciality chemicals | Materials that have unique molecules or mixtures of molecules known as formulations which are used on the basis of their performance or function |
| Sustainable development | Improvement of current systems in ways that does not infringe in the sustenance of the future generation |
| Platform chemicals | Building block compounds which can be used to produce a broad range of technologically relevant substances |

| | |
|---|---|
| Upstream | First section of the processing line from the feed to the reactors that deals with reactant processing and reaction to form desired products |

# Acronyms and Abbreviations

| | |
|---|---|
| BNDES | Brazilian Development Bank |
| DOE | US Department of Energy |
| EU | European Union |
| FCI | Fixed capital investment |
| FQD | Fuel and Quality Directive |
| GHG | Greenhouse Gas |
| GM | Genetically Modified |
| 5-HMF | Hydroxymethylfurfural |
| 3-HPA | 3-Hydroxypropionic acid |
| IP | Intellectual Property |
| LC | Low Carbon |
| LP | Low Pressure |
| PBS | Polybutylene succinate |
| PDO | Polydioxanone |
| PE | Poly-ethylene |
| PEF | Polyethylenefuranoate |
| PET | Polyethylene terephthalate |
| PHAs | Polyhydroxyalkanoates |
| PIP | Polyisoprene |
| PLA | Polylactic acid |
| PMMA | Poly(methyl methacrylate) |
| R&D | Research and development |
| RED | Renewable Energy Directive |
| SA | Succinic acid |
| SACU | Southern African Customs Union |
| TCI | Total capital investment |
| WCI | Working capital investment |

# 1 Introduction

## 1.1 Subject and background of study

The production of platform chemicals and fuels is an industry that has been traditionally dominated by fossil fuel production. Of recent, the transition from using raw materials from non-renewable fossil fuels to using renewable resources has been a very important subject of discussion. In light of alarming issues caused by global warming, environmental degradation and depleting natural resources, sustainable development through the low carbon economy is of paramount importance. Sustainable development was defined as “the development that meets the needs of the present without compromising the ability of future generations to meet their own needs” in the 1987 Report of the World Commission on Environment and Development (World Commission on Environment and Development, 1987). The two major aims of the bio-based chemical industry are to find innovative and sustainable ways of producing bio-based chemicals and liquid biofuels that are classically being produced from fossil fuels, both in the form of drop-in products and as products with new functional advantage, and produce these in an economically feasible manner with minimal environmental burden.

There has been a lot of work done worldwide on the value addition in the sugar industry to fuels (such as ethanol and butanol) and value added commodity chemicals (such as surfactants, organic acids, polyols and chemicals with primary use in food application). The South African sugar industry and ancillary industries relying on sugar or its by-products have long joined the rest of the world to be involved in value-added products mostly because of the fluctuating domestic and worldwide price of sugar.

There are a number of possible ways of converting sugar into biofuels and biochemicals. This includes chemical and biological routes. This study aims to investigate the value addition of producing platform chemicals and liquid biofuels using the renewable bio-based material sucrose as the sole carbon source. Biological conversion technologies will be the focus technology route. The top bio-based platform chemicals were assessed using a quantitative framework based on South Africa specific criteria. Bio-based production of these top platform chemicals has been investigated in the context of the South African industry. The chemicals considered were those with processes that are developed, ready for commercialisation or close to commercialisation (high technology readiness). Following selection of the three top platform chemical with good potential, a process flow sheet for an identified top chemical is proposed and analysed in terms of the potential for technoeconomic value generation in the process.

## 1.2 Problem statement

Pre-2016, South Africa produces more sucrose than can be used domestically, the remainder of which is exported. The low export price and limited profit margins even on local sugar are introducing limitations to sugar production in South Africa, leading to a shrinking resource and potential for severe job losses in the sector. **Error! Reference source not found.** shows sucrose imports and exports in outh Africa between 2010 and 2016. There is an average of 2.2 million tons of sugar produced per season with about 75% of the sugar marketed in the Southern African Customs Union (SACU) (South African Sugar Association, 2015). The remainder is exported to markets in Africa, Asia and USA. The export is sold either through a long term agreement or at world market prices. The world production of sucrose is currently experiencing an oversupply due to excellent growth conditions and high production yields (Reinbergr, 2015). This has resulted in the current low world sugar price compared to the domestic prices.

Value addition to sucrose through producing a variety of platform chemicals is imperative to diversify the country’s sources of revenue. Value addition could also potentially boost the economy of the country by generating higher revenues. In addition, there is an added advantage of finding sustainable ways of producing platform chemicals and fuels that are currently petroleum-based using sucrose.

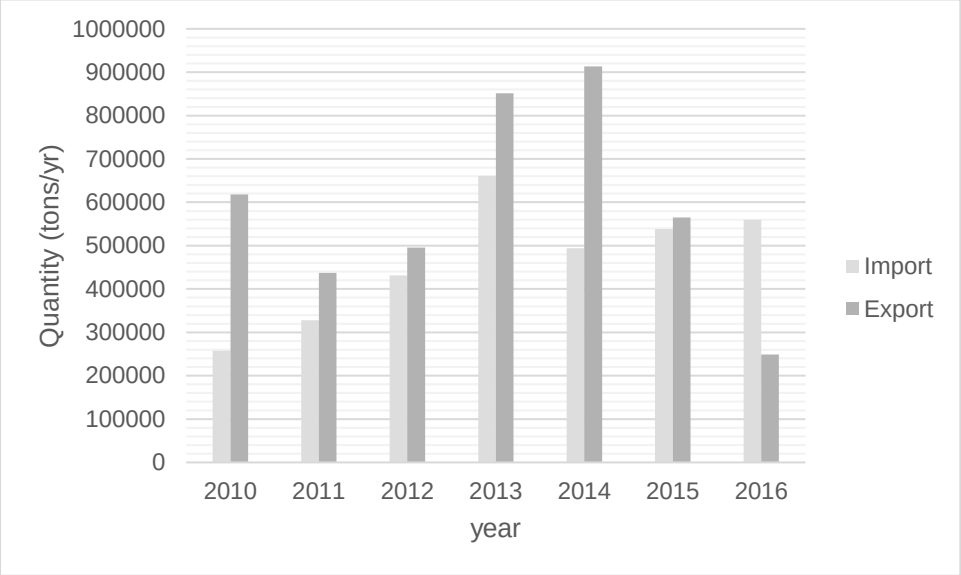


Figure 1-1 Sucrose imports and exports in South Africa between 2010 and 2016 (South African Department of Trade and Industry, 2016)

## 1.3 Overall objectives

This study looks at determining the feasibility of using biological alternative routes to produce platform chemicals. Numerous studies have focused on finding chemical and biological routes of producing these platform chemicals (Werpy, et al., 2004; Walford & Morel du Boil, 2006; Bozell & Petersen, 2010; Choi, et al., 2015).The focus here would be on proposing biochemicals that are ready for commercialisation in the near future. Therefore the biological routes of producing the platform chemicals that have already been industrialised or close to industrialisation will be looked at. Although most of the studies done have been majorly focused on the use of glucose as the carbon source (Lee, et al., 2011; Dhamankar, et al., 2014; van Dam, et al., 2005; Bozell & Petersen, 2010; Werpy, et al., 2004; Holladay, et al., 2007), this study will be based on the use of sucrose as the sole carbon source. The chemicals that will be chosen will also be looked at in the context of the South African industry. There are many chemicals that have been identified that meet the above criteria. The chemical that will be proposed by this study will be obtained by firstly narrowing down the list of chemicals through a quantitative study to find the highest ranked platform chemicals. A qualitative study will then be done to decide on the chemicals for techno-economic studies. Both the qualitative and the quantitative study aim to identify the gaps in the South African market and categorising the chemicals that can fill these gaps.

The overall objectives of this report are listed as follows:

- Determine the top platform chemicals that are currently in high demand in industry or that show a high potential for commercialisation
- Out of these chemicals, choose chemicals that can be produced via a biological route by using sucrose as a carbon source
- Using a series of factors to determine the weightings, rank the platform chemicals that meet the above criteria by using a quantitative study based on the weightings
- Investigate the opportunities for value addition of sucrose by producing the pre-determined building block chemicals by doing a qualitative study
- Based on the quantitative and qualitative analysis done, select a chemical for a techno-economic study
- Do a techno-economic study on the top chemical selected

# 2 Review of platform chemicals

The use of fossil-based resources has been the main focus in producing platform chemicals for the chemical and pharmaceutical industries (Jenkins, et al., 2011). These chemicals can be used as a precursor for the production of a variety of consumer goods such as plastics, healthcare and drug products, agrochemicals, and fertilizers (Jenkins, et al., 2011). Oil and gas have provided crucial inputs to the modern world. There is however a need to find alternative sources of production for current platform chemicals that uses fossil resources (Choi, et al., 2015).

## 2.1 Factors that motivate consideration of alternative resources for platform chemicals production

### 2.1.1 Diminishing oil reserves

Because of the finite nature of oil reserves, there is a need to diversify the sources from which platform chemicals are produced. Petroleum will run scarce in the future (Villadsen, et al., 2011). The problem of diminishing oil reserves is constantly worsening because of the rapidly increasing world population and increasing living standards. The use of renewable energy sources is core to the development of sustainable industrial chemistry in the 21st century in order to curb the depletion of fossil resources (Hermann, et al., 2007). This is because renewable sources such as sugar[R13]cane[WU4] is sufficiently robust and can grow without facing supply and demand disruption.

### 2.1.2 Environmental considerations

Large scale production of chemicals using fossil feedstocks has associated impacts on climate change, causing severe environmental effects. With the increasing demand of these chemicals, there is large amounts of greenhouse gases emission anticipated from their production. The areas where petroleum are obtained are usually located in environmentally sensitive places such as off-shore oil rigs. The introduction of bio-based production of chemicals allows for manufacturing processes that are often cleaner and better for the environment (Erickson, et al., 2012). The production of biomass photosynthetically and autotrophically actually consumes carbon dioxide which results in a decrease in greenhouse gas emissions and reduces global warming. Biological processes are particularly attractive because microorganisms tend to produce fewer toxic compounds and also by using renewable feedstocks.

### 2.1.3 Socio-Economical justifications

The political stability of the countries where the oil reserves are located is a major concern. This causes rapid price changes of petroleum. Isolated countries such as Iceland cannot easily access chemical components and additives from these countries because they are not within a reasonably close geographical region (de Jong, et al., 2012b). There is therefore a massive political interest to find alternative substitutes for petroleum based sources for platform chemicals to reduce the price vulnerability and to ensure greater security of production. A comparison between bio-based materials and petrochemical shows that it is more profitable to convert petroleum to oil and gas rather than using it in the chemical industry (Villadsen, et al., 2011). It was therefore suggested that fuel should be made from petroleum while alternative source of production should be investigated for platform chemical production. With the increase of oil prices, bio-production of platform chemicals has received increased interest (Erickson, et al., 2012). In recent years, establishing a bio-based economy is one of the key subject that has been studied greatly in order to achieve sustainable development (van Dam, et al., 2005).

## 2.2 Bio-based production of value added platform chemicals for bio-refinery development

Biorefineries are being developed with the aim to create bio-based production of chemicals and fuel as an alternative route to petroleum based production. This is targeted to be achieved at a competitive price to traditional petroleum-based production. Recently, work has been done on biofuels such as ethanol, biodiesel and butanol (Bozell & Petersen, 2010), with the development of bio-based products following this rapidly. According to de Jong (2012b), the production of bio-based products (excluding biofuels) was estimated to be close to 50 million tonnes, valued at US$10-15 billion of revenue in the global economy. The market conditions of bulk chemicals is predicted to increase by about 26 million tonnes in a less favourable market and 113 million tonnes under more favourable market conditions by 2050 (de Jong, et al., 2012a). With a compounded annual growth rate of 22.8 % in 2015, this is a lucrative field worth investigating.

### 2.2.1 Production of platform chemicals using biomass

Sources such as municipal solid waste, forestry products or residue, agricultural residue, bio-energy crops, sugar crops and oil crops can be used for bio-based production of petrochemicals (van Dam, et al., 2005). There are, however, large fractions of these biomass products that are not readily convertible to platform chemical. These include large amounts of water and unfermentable carbohydrates, phenols, lignin and protein. Several steps of refining and extraction will then be required to attain a specified product quality.

### 2.2.2 Sucrose as a source of producing platform chemicals

Sucrose (α-D-glucopyranosyl-(1→2)-β-D-fructofuranose) is a C12 disaccharide sugar containing two hexose sugar units. Sucrose consists of two monosaccharides, glucose and fructose. The two compounds are joined together by a α1-4-glyosidic bond. It is most commonly produced from sugarcane and sugar beet (Eggleston, 2008). Among all the disaccharides, it is one that reaches the status of commodity as it is a cheap industrial raw material (Eggleston, 2008). Commercial sucrose has a very high purity (>99.9%), making it one of the purest compounds produced on an industrial scale (Eggleston, 2008). It is used as a feedstock for many value-added products. This is supported by its chemical composition. This is due to the eight hydroxyl groups present on the molecule. Three of the hydroxyl group are in the primary position while the other five are in secondary positions. The groups in the primary positions have high reactivity and are therefore difficult to react individually (Eggleston, 2008).

Theoretically there are an enormous number of sucrose derivatives possible from the replacement of one hydroxyl group type being able to form 255 different compounds (Eggleston, 2008). Sucrose reactivity is, however, considered difficult because selectively introducing other functional groups into the molecule will require non-aqueous solvents or cost-intensive protective group chemistry; the sucrose group will also be in danger of degradation.

Modes of sucrose degradation to less complex molecules are by the addition of acids, oxidizing agents, alkalis catalytic hydrogen and catabolic metabolism in every microbe. Sucrose also acts as a donor molecule for enzymatic transfer reactions to form oligosaccharides and polysaccharides.

Sucrose is expected to develop to be as significant as petroleum in the near future as it is a superior feedstock in the production of platform chemicals (Eggleston, 2010). It is also one of the abundant chemicals found in nature. Furthermore, there is a promising potential for sucrose because it generates less by-products. In addition, this would make use of the large excess sugar produced by South Africa that currently exceeds its demand (Walford & Morel du Boil, 2006) and this would result in the creation of job opportunities.

## 2.3 Different processing routes that can be used to produce platform chemicals from sucrose

### 2.3.1 Biological routes used in value addition to sucrose

There are several modes by which the efficiency of the sucrose biorefinery can be improved. This includes Physiological Engineering, Metabolic Engineering, Synthetic Biology and Systems Biology (Villadsen, et al., 2011). These are currently areas of great research. For the resultant processes to be competitive, cost effective and sustainable compared to petrochemical production, the processes must be highly efficient, produce minimal waste and allow high recovery. Recent goals of the biorefinery are to produce platform chemicals that are commonly produced from oil and gas via "green" and sustainable routes. This is done by using microorganisms or enzymes produced from the microorganisms (Villadsen, et al., 2011).

In biological processes, biomass is digested using simple chemical processes and enzymes to convert carbon to useful products using microbial fermentation (Jenkins, et al., 2011). Advantages of fermentation (whole-cell or enzymatic) over traditional chemical synthesis include low energy costs, higher yields, product specificity and environmental friendliness (Choi, et al., 2015). Another advantage is that in biochemistry, reactions happen in water without the need for expensive protecting group chemistry (Erickson, et al., 2012). Biological production can be divided into extracellular and intracellular bioprocesses. The products that are produced extracellularly are mainly organic acids, simple gases, alcohols, diols, alkenes and alkanes while the products that are produced intracellularly are for example lipids and PHAs (Taylor, et al., 2015).

#### *2.3.1.1 Systems Biology*

Systems biology makes use of science and engineering to synthesize novel biological functions and systems. In the case where microorganisms are re-engineered, the biological organisms are designed to perform specific functions. The systematic re-engineering would involve developing the microorganisms to produce novel products or biosensor-signalling pathways (Jenkins, et al., 2011). These microorganisms can then be used to produce platform chemicals or precursors that could be converted to value-added speciality chemicals. The use of biotechnology gives high potential for producing special functionalities such as biodegradability, biocompatibility and non-toxicity which is becoming highly important in the emerging bio-economy (Walford & Morel du Boil, 2006). The demand in industry will drive the innovation of engineering these microorganisms.

#### *2.3.1.2 Metabolic engineering*

This is the area of engineering that is directed to improving product formation or cellular properties by modification of the specific biochemical pathways or by introducing new pathways using recombinant DNA technology (Villadsen, et al., 2011). Different strains have been engineered to improve the productivity of the desired product. Organisms have also been extended to use cheaper and more efficient substrates (Andersson, et al., 2007). Metabolic engineering is also done to introduce pathways that lead to the formation of new products. This is done by extending existing pathways from other organisms (Villadsen, et al., 2011). Completely new pathways can be developed for the production of new products by gene shuffling and other methods of directed evolution.

### 2.3.2 Chemical routes used in value addition of sucrose

Research has been done on the production of platform chemicals by chemical routes. Chemical routes includes chemical-enzymatic transformation such as chemical & catalytic processing and biotransformation (Werpy, et al., 2004). These are processes such as the hydrogenation of glucose to sorbitol, oxidation of glucose to gluconic and saccharic acid and acid dehydration of xylose to furfural. In general, chemical routes use aqueous phase reforming and dehydration hydrogenation to produce sugar alcohols, furans and organic acids. The top chemicals selected by DOE using chemical processes are furans, levulinic acid, glycerol, sorbitol, xylitol, glucaric acid and 3-hydroxybutyrolactone (Choi, et al., 2015). The top chemicals produced commercially by chemical routes proposed by the European Commission are sorbitol, xylitol, furfural, ethylene and ethylene glycol (Taylor, et al., 2015). Mostly,

these are not formed from sucrose. The production of platform chemicals by chemical routes is not the focus in this study.

## 2.4 The reaction process in microbial transformations

The criteria for designing a fermentative process differ, depending on the product that it is being designed for. The design of a high volume/low value-added product will be different from the design of a low volume/high value-added product.

The three most important parameters in the design of a reaction process are (Villadsen, et al., 2011):

- Yield of the desired process (g product per g substrate)
- Productivity (g product per L reactor per hour)
- Final titre (g product per L reactor volume)

For high volume/low cost products, the yield is very important since the raw material accounts for most of the total cost of production. This should be put into deliberation when deciding on the process to be developed.

Productivity is a good indicator of how efficiently the production capacity has been used. It is important to increase the productivity of a process in order for overall production to increase. Improvement in productivity reduces the capital and operating costs of the reaction process.

The final titre is important for the purification of the product downstream of the production process. For low concentration of final titre, the purification cost to the final product at a good yield may be very expensive (Villadsen, et al., 2011).

For the above-mentioned parameters to be maximised, appropriate microorganisms, reactor and medium must be used. This is as discussed in the succeeding sub-sections.

### 2.4.1 Microorganisms considered

Early studies on microbial transformations had focused on improving the performance of organisms that naturally produced target chemicals by random mutagenesis and by optimising the fermentation and downstream processes (Lee, et al., 2011). With the advancement of metabolic engineering, numerous work is being done on the engineering of cellular pathways by modification of the genome of microorganisms (mainly *Escherichia coli*) to optimise the production of the specific product. Some bacteria (typically *E. coli*) and the yeast *Saccharomyces cerevisiae* are mostly used in industrial fermentation (Villadsen, et al., 2011). This is because they are able to grow in both aerobic and anaerobic conditions. This is of great advantage because both aerobic and anaerobic conditions can be screened to determine the best production organism (Villadsen, et al., 2011). Table 2-1 shows further pros and cons of the different production organisms that can be used to produce platform chemicals.

Table 2-1: Pros and cons of Bacteria (E. coli) and Yeast (Saccharomyces cerevisiae) production organisms (Villadsen, et al., 2011)

| Host | Advantages | Disadvantages |
|---|---|---|
| Bacteria (E. coli) | • Wide choice of cloning vectors<br>• Gene expression easy to control<br>• Large yields possible | • Post-translational modifications lacking endotoxin content<br>• High endotoxin content<br>• Subject to bacteriophage |
| Yeast (Saccharomyces cerevisiae) | • Generally regarded as safe<br>• Large scale production established<br>• Low pH fermentation is possible<br>• Reduces gypsum formation caused by acid treatment during downstream purification processes<br>• Some post-translational modifications are possible | • Less cloning vectors available<br>• Genetic base is still less solid than is in the case for E. coli<br>• Low yields and productivity |

The type of microorganism used will determine the biochemical pathway that will be taken to obtain the desired product (Villadsen, et al., 2011). This is imperative because the biochemical path of production will determine the yield and also the productivity of the desired product.

### 2.4.2 Growth and production medium required

The proper functioning of microorganisms requires five basic groups of nutrients (Villadsen, et al., 2011). These are:

- Carbon source
- Energy source
- Nitrogen source
- Minerals
- Vitamins

The energy source is needed for the supply of Gibbs free energy for cell growth. In heterotrophic processes, this is usually identical to the carbon source. This could be fructose, glucose, sucrose etc. Fructose is more expensive than glucose with sucrose being the cheapest of the three. Also some organisms can only utilize certain carbon sources. Nitrogen is needed as a nutrient to promote the growth of biomass, without which growth will cease. For commercialisation, the target would be to run using minimal nutrients. Examples of these nutrients are yeast extracts and biotin. The nutrients needed and the sources from which these nutrients are obtained depend on the microorganism used or whether the fermentative process is aerobic or anaerobic. Cheap sources are desired for a cost effective production. By-products from the agricultural sector are commonly used as a source of obtaining nutrients.

It is essential that all the nutrients needed for the production of the desired product are available for high productivity to occur. This should be a consistent quality that must be available at all times (Villadsen, et al., 2011). It should also be ensured that these nutrients do not cause operational problems in the fermentation such as foaming and reduction in mass transfer from the gas phase (Villadsen, et al., 2011). Problems that may be caused downstream must also be avoided if possible.

### 2.4.3 Favourable reactors

An efficient fermentation reactor is required for the design of high performance processes. The dual phase fermenter has been recommended to overcome growth inhibition for the processes where *E. coli*

is used as the microorganism of choice and the product being formed is toxic to the microorganism (products such as organic acids and alcohols) (Choi, et al., 2015). This fermenter consists of the aerobic and the anaerobic phase. The cells are grown in the aerobic phase. When the desired cell concentration is reached, the fermentation is switched to the anaerobic phase where the cells consumes sugar to produce a mixture of organic acids with a higher selectivity of the desired organic acid depending on the microorganism that is used.

## 2.5 Challenges envisaged from production of platform chemicals from renewable sources

### 2.5.1 Sustainable production

Sustainability is one of the issues faced by the newly developing chemical industries that are diverting from the use of fossil feedstocks as the carbon source for the production of platform chemicals. Sustainable productivity of platform chemicals by innovative environmentally friendly processes is a factor that is of great concern (Eggleston, 2010). Important aspects such as competition of food with biomass resources, water use and quality of water disposed, soil degradation and impact on biodiversity should be considered (de Jong, et al., 2012a). For sustainable development to be achieved, these issues must be balanced out with the interdependent pillars of society and the economy (Eggleston, 2010). The three aforementioned factors (ecology, society and economy) that contribute to sustainable development are interlinked as a tripod that serve as a pillar to sustainable development. Although processes that make use of renewable sources often have the advantage of having low energy, more improvements still need to be made on the reduction of waste produced.

### 2.5.2 Accumulation of undesired products and waste water

As mentioned previously, one of the challenges met with the production of platform chemicals from renewable sources is the accumulation of undesired products. Many biological conversions experience very low yields which result in the production of a large proportion of undesired products. It is very often difficult to separate these undesired products from the actual desired product. This limits the efficiency of production of the useful chemicals. This is especially a problem in the production of alcohols (such as ethanol) and organic acids (such as Succinic acid) where there is low concentration of end-products in the fermentation broth due to toxicity effects of the end products on the microorganism. It is important to choose a processing route that has high yields. If this is achieved, downstream processing becomes less complicated and there is a considerable reduction in energy demand and consequently less environmental impact and reduced operational cost. Obtaining a favourable production with high yields is achieved through metabolic engineering. New improvement of microbial strains are reported frequently. A review of the case study of the metabolic engineering of different strains towards the commercialisation of succinic acid and 3-hydroxypropionic acids is discussed by Choi et al (2015). Process integration also helps in reducing waste generation. This is done by producing multiple products and value streams, creating closed loop industrial systems that eliminate wastes. Microbial fermentation actively needs water because fermentation occurs in fluid. The large amount of waste water streams must be recycled as input for new process streams to minimise waste and to promote economic competitiveness (Choi, et al., 2015; Erickson, et al., 2012). Deciding on the method that is used to purify the product from the by-products is also imperative. This should be an inexpensive purification obtaining high recovery of the desired product.

### 2.5.3 Competing with pre-existing methods in industry

Most of the processes diverging from using fossil feedstocks as the carbon source for the production of platform chemicals are still in their initial phase of development and are yet to be optimised. They will be competing with chemicals produced from the oil refinery that cost only about 20-30% of the raw material cost for biobased feedstock (Villadsen, et al., 2011). Biofuels such as butanol, ethanol and biodiesel are low value products. As a result, their return on investment is a significant factor that hinders achieving their economic goals. The commercialisation of novel bio-based processes using renewable energy sources will depend heavily on government intervention to be able to establish their base in industry. Such interventions include initiatives and policies such as green purchasing requirements,

emission taxes, regulations and tax credits for research and investments in renewable processes and products. Integrated biorefinery development is still in its infancy, but shows great potential for optimal production. A few methods of improving biological production of platform chemicals that are currently being studied include improving lignocellulosic biomass fractionation, increasing the efficiency of energy utilised during product separation, reducing biological inhibition, improving chemical selectivity and monomer purity and improving the overall whole process chain integration. These novel developments however still remain promising hypothetical scenarios with no existing commercial technology.

## 2.6 The development of the biochemical industry undertaken by several countries

Much innovative research, demonstration and commercialisation of high value platform chemicals and biofuels by biological conversions has been done (Taylor, et al., 2015; Erickson, et al., 2012; Meynial-Salles, et al., 2008), (http://www.myriant.com; http://www.bio-amber.com). Discussions of different levels of technological development of platform chemicals is discussed in the fourth chapter. This is mainly based on what has been done in the EU and USA. The USA focused on the production of value-added products such as fuel and speciality chemicals that will replace the conventional petroleum based production. This idea was introduced with the vision of the Biomass research and development Technical Advisory Committee established by the Biomass R&D Act of 2000 (Biomass research and development initiative, 2006). Cuba has majorly focused on research on the production of pharmaceuticals while Brazil's main focus is on the production of ethanol and ethanol derived products (Taylor, et al., 2015). The plants in India use bagasse, molasses and filter cake to produce a wide variety of chemicals such as yeast, citric acid, and lactic acid. The US and Brazil are in the forefront of the industrial development of biochemicals because they have more attractive feedstock and investment conditions (Taylor, et al., 2015).

The main regions that focused on research of top chemicals are the USA and the EU. China focussed on the commercialisation of known processes (mainly from research done by the EU) while Brazil's main focus was on the development of its biofuel industry (manufacturing). Table 2-2 shows the top chemicals identified by the research done by the US Department of Energy (in 2004 and 2010) and the European Commission (in 2015). This approach was done to target pre-identified chemicals as opposed to a broad technology development.

Table 2-2: Top platform chemicals identified for development in the USA and EU

| Chemical | DOE (2004) | DOE (2010) | EU (2015) |
|---|---|---|---|
| Adipic acid | | | ✔ |
| 1,4 – Butanediol (BDO) | | | ✔ |
| 3-Hydroxypropionic/aldehyde (acrylic acid) | ✔ | ✔ | ✔ |
| 3-Hydroxybutyrolactone (3-HBL) | ✔ | | |
| Aspartic acid | ✔ | | |
| Biohydrocarbons (Isoprene) | | ✔ | |
| Ethanol | | ✔ | |
| Farnesene | | | ✔ |
| Fumaric acid (1,4-Dicarboxilic acid) | ✔ | | |
| 2,5 furan-dicarboxylic acid (FDCA) (Furan) | ✔ | ✔ | ✔ |
| Furfural (Furan) | | ✔ | ✔ |
| Hydroxymethylfurfural (Furan) | | | ✔ |
| Glucaric acid | ✔ | | |
| Glutamic acid | ✔ | | |
| Glycerol and derivatives | ✔ | ✔ | |
| Isobutene | | | ✔ |
| Itaconic acid | ✔ | | |
| Lactic acid (Polylactic acid) | | ✔ | ✔ |
| Levulinic Acid | ✔ | ✔ | |
| Malic Acid (1,4-Dicarboxilic acid) | ✔ | | |
| Sorbitol | ✔ | ✔ | |
| Succinic acid (1,4-Dicarboxilic acid) | ✔ | ✔ | ✔ |
| Poly-ethylene (PE) | | | ✔ |
| Poly-hydroxy-alkanoates (PHAs) | | | ✔ |
| Xylitol/arabinitol | ✔ | ✔ | |

### 2.6.1 The development of the biochemical industry undertaken by the EU

The EU majorly focused on downstream processes such as polymerisation, rather than building block. There is currently an addition of downstream bio-based polymer pathways (PLA, PET, PBS, PEF, PE, PMMA, PIP) added to the selected 25 products for further research to evaluate their opportunities and production barriers and to investigate potential mitigation activities. There has been a ban on single-use, non-biodegradable plastic bags since 2006 (Hermann, et al., 2011). Public perception and consumer demand of bioproducts are very high. The EU has an advanced biochemical research industry (consequently most R&D labs and pilot plant are located in Europe and North America) owing to the fact that governments have incentivised this work, a lot of money has been dedicated to it and there is a surplus of qualified professionals.

The EU has not concentrated on mandates to improve their bio-industry like USA, Brazil and China (Carus, et al., 2011). Although considerable amount of work has been done with regards to biofuels, not much has been done to incentivise the development of bio-chemical commercial plants. The policies that are in place for biofuels are not long term stable mandates such as sustainability requirements for fuels (Taylor, et al., 2015). It is also lacking manufacturers and provisions of funding for developers. It is for these reasons that industrialisation of chemicals and the overall level of commercial activity of the EU bio-industry is relatively low. Another drawback for the development of commercial production of

biochemicals is due to the high labour and energy costs. This results in high operational costs. The most common and cheap feedstock is wheat which is at a high cost compared to feedstock in USA, Brazil and China (OECD-FAO Agricultural Outlook, 2014).

### 2.6.2 The development of the biochemical industry undertaken by the USA

USA has developed a lot of incentives and policies to boost the growth of commercial biochemicals and biofuels (Biomass research and development initiative, 2006; Taylor, et al., 2015),There are provisions made by the DOE and BNDES to give loans for bio-industry investment in the US. There is also a vast amount of research that has been carried out (and is ongoing) by the DOE to develop the biorefinery industry. The country's public perception of bio-based products is very positive and there is therefore a high consumer demand for these products. The feedstock commonly produced and used in the US is maize (OECD-FAO Agricultural Outlook, 2014). This is produced at a more competitive price than in the UK. The US has the highest activity in their bio-industry compared to EU, Brazil, China and India (when comparing research, demonstration and manufacturing altogether) (Taylor, et al., 2015). The level of research in the US (and also in EU) is also very high with the amount of research resources compared to India, China and Brazil. Although the country's energy cost is relatively low, the operating cost is slightly higher because of high average wages. US is the leading country in terms of biofuel/chemical demonstration facilities (Taylor, et al., 2015).

### 2.6.3 The development of the biochemical industry undertaken by Brazil

Brazil, the leading country in biofuel production focuses on the production of ethanol and the cultivation of feedstock (Taylor, et al., 2015). The most produced feedstock is sugarcane (OECD-FAO Agricultural Outlook, 2014). Because of the years of experience that Brazil has in producing these feedstock, there is an increasingly cheap bagasse available. In boosting the growth of its bio-industry, Brazil developed mandates for bioethanol and its products. This has resulted in the increase in flexible fuel cars which now represent almost 90% of the cars used (Taylor, et al., 2015). The DOE and the BNDES also provides loans for the Brazilian bio-industry (Schroeder, 2014). Brazil now has a few new commercial plants. The major challenges that Brazil's bio-industry is facing are high capital investment and energy costs. The country's high capital cost is due to government deficits, however the low interest loans provided by BNDES guarantees ease of the financial barriers that developers may face.

### 2.6.4 The development of the biochemical industry undertaken by China

China's main focus is on manufacturing (Taylor, et al., 2015). It has one of the largest bio-chemical production industries. China benefits from the fact that it has a low capital cost due to its high reserves, controlled currency and low interest rates. Low operating costs also served as a push for the growth of its commercial biochemical production. The low operating costs is due to a relatively low wages (pwc, 2013). They also have a low electricity cost compared to the EU and Brazil (Taylor, et al., 2015).The most important feedstock used is maize and wheat (OECD-FAO Agricultural Outlook, 2014). The country has a potential for cheap feedstock but improvements must be done on residue collection.

Of recent, China has been trying to develop its research and development of the bio-industry. This is being done by investing in the research of many scientific papers. China has published many papers focused on bioprocesses in the last decade (Taylor, et al., 2015). There have also been mandates in place for the promotion of bioethanol and bio-products development. Their renewable energy five year plan (2011-2015) was focused on producing 3.5-4 million tonnes of bio-ethanol with the use of marginal land, avoidance of environmental damage and competition with food and feed (Yue, 2013)

### 2.6.5 Criteria for selecting platform chemicals as discussed by the US Department of Energy

For more conceivable research to be applied in industry, the top building block chemicals that showed potential growth in industry were determined by US Department of Energy (DOE) in 2004. This was done by screening about 300 substances (Werpy, et al., 2004). From the 300 chemicals, 30 potential candidates were shortlisted. The selection process was based on petrochemical model of building blocks, chemical data, market size, economics, properties and performance of potential candidates and known processes. Out of the 30 selected compounds, 12 compounds were selected as the top sugar

derived chemicals. This was done by examining the size of the markets for the platform chemicals, their derivatives and the technical complexity of the synthesis pathways.

The chemicals chosen in 2004 were reviewed and chemicals that no longer showed potential for industrial use were removed in 2010 with more commercially promising chemicals added to the list. Although the criteria for selecting chemicals in 2004 and 2010 were similar, additional conditions were used in 2010. The criteria for the selections of the top chemicals in 2010, as discussed by Bozell & Petersen (2010), are listed below:

1. There is a significant amount of research done on the compound and the technological structure is available in literature.
2. The platform compound shows a wide range of application for multiple products.
3. The technology offers direct substitution of existing production of compounds from petroleum.
4. The technology can be used for high volume products.
5. The compound has a strong potential to be a platform chemical.
6. The scale up of the product or technology to pilot, demo or full scale is underway.
7. The bio-based product is an existing commercial product prepared at intermediate or commodity level.
8. The compound may serve as a primary building block of the biorefinery.
9. The commercial production of the chemical by a renewable carbon source is well established.

The criteria listed are in order of importance. Adjacent criteria are not significantly different from each other. Table 2-2 shows a review of the top platform chemicals in 2004 and 2010 that can be produced via biological routes suggested by DOE as explained by Choi et al (2015).

### 2.6.6 Deciding on the top platform chemicals as undertaken by the European Commission

The European Commission identified top platform chemicals driven by the Renewable Energy Directive (RED) and the Fuel and Quality Directive (FQD). These chemicals were categorised as chemicals that are in the research stage, pilot stage, demonstration stage and commercialisation stage. The chemicals that were already commercialised and produced by biological routes are low carbon (LC) ethanol, succinic acid, lactic acid, acetic acid, n-butanol, iso-butanol, PDO and itaconic acid (Taylor, et al., 2015). Bioethanol is said to be the most dominant sugar platform product followed by n-butanol, acetic acid and lactic acid. The platform chemicals with the smallest market demand are those in the earliest stage of production such as 3-HPA, acrylic acid, isoprene, adipic acid and 5-HMF.

The criteria for selection of the top 10 platform chemicals as discussed by Taylor et al (2015) are:

- The technologies involved have at least been tested at large scale prototype in the intended environment for production. This is to ensure that the pathway has commercial potential relevant within the next 10 years
- An existing market place and interested companies willing to take on the exploration of the chemical exist
- At least one EU company is involved in the development of the technology along the pathway
- Notable market size, economic value, and GHG (Green House Gas) emissions savings are expected
- Selecting product pathways begins at biomass feedstock and ends at a final material (fuel, chemical or polymer). Whole pathways were analysed rather than terminating at platform chemicals with significant potential for downstream processing

### 2.6.7 Deciding on the platform chemical to be studied by South Africa

South African industries are looking to identify more sustainable production of platform chemicals using renewable raw materials. A case study of the routes taken by other countries to develop their biorefinery

that has been discussed in the preceding sections. This can be used as a guideline for South Africa. Important factors to be put into consideration are the market position, proprietary access to a specialised feedstock, specific IP, experience in the field and existing infrastructures. Table 2-2 is a good starting point for identifying promising platform chemicals.

#### *2.6.7.1 Market strategy for type of platform chemical to be produced: Drop-in chemicals vs. novel chemicals*

The market strategy for chemical production can be divided into producing drop-in or novel bio-based chemicals (Taylor, et al., 2015). Drop-in chemicals are chemicals that have existing methods of production by using fossil fuels and bio-based chemicals are direct substitutes of these chemicals. This strategy ensures that there is an existing substantial market for the platform chemicals which reduces the risks and makes it more accessible to market. It also gives the added advantage of offsetting petroleum based production of chemicals. Drop-in biofuels were also identified by the research done by IEA Bioenergy to be the most desired type of biofuel production because it can be easily mixed and used as a blend with existing fossil fuels (Jungmeier, et al., 2013). Because this method of production is limited to replacing petrochemicals, it is restricted by cost competitiveness and environmental footprint comparisons of existing petrochemical production.

A “market push” is however not a sufficient driving force for deciding on the type of platform chemical to be produced. Producing novel bio-chemicals such as producing custom-engineered products that are based on chiral compounds are easy to produce by a biological route as opposed to much more expensive petroleum based conversions. Previous studies that had focused on the development of novel bio-chemicals and had not considered bio-based routes of producing existing chemicals have had little impacts (Choi, et al., 2015). The reason why this research has failed is that the scientists did not fully consider the market (Eggleston, 2010). This method introduces a higher marketing risk than the production of drop-in chemicals because there is no existing market for the produced chemical; however, there may be substantial functional advantage. For these chemicals, product and market development is necessary. The market demands should be matched in terms of product type, pricing, quality and quantity (van Dam, et al., 2005). In addition to “market push” (producing “drop-in product”), there has to be a substantial technology development of the chemical/fuel to be selected. The chemical selection done by the US and the EU shown in Table 2-2 had resorted to the strategy of producing drop-in chemicals that have inherent properties suited for biomass production (Erickson, et al., 2012). If industrial considerations are in place when the ideas are conceptualised, the scientific development would have more impact.

#### *2.6.7.2 Considerations of existing technologies available for the production of platform chemicals*

Because of South Africa’s poor financial standing compared to the developed countries that have commenced initiatives for the growth of their bio-industry, it is recommended that South Africa focuses its resources to the application of existing known processes as opposed to doing research for potential novel chemicals. The previous studies of top platform chemicals done by the US and the EC should then be used to determine the chemicals that are most suitable for commercialisation in South Africa. These would be chemicals that have undergone rigorous studies and have been developed to a stage where they can be commercialised. This is to ensure the viability of the processes developed and to eliminate complications that might arise from scaling up. The chemicals to be chosen are those with known processes of production by biological conversions from sugar.

# 3 Research approach

The steps undertaken for the design of the processes proposed in this study for converting sucrose into platform chemicals that are of high demand in the South African industry context are discussed in this section.

This review analysis was started using a list of 39 chemicals compiled from the top chemicals by the US Department of Energy (DOE) in 2004 (Werpy, et al., 2004) and 2010 (Bozell & Petersen, 2010) and the European Commission (2015) (Taylor, et al., 2015). These are shown in Table 2-2. In addition to these chemicals, chemicals that are currently of high interest were added to the list of chemicals that were screened. Emphasis was placed on platform (building block) chemicals. Unless in the categories aforementioned, polymers and chemicals that are produced from platform chemicals were not looked at. There has been a variation in the top chemicals identified over the years, apart from 3-hydroxypropionic acid, 2,5 furan-dicarboxylic acid and succinic acid which have constantly remained among the top chemicals. The new chemicals that are currently of interest are chemicals that can be used for making polymers.

As discussed in Section 2.6.7, two approaches can be undertaken on deciding the top platform chemicals/fuels. The technology-based approach (previously referred to as the production of novel chemicals) focuses on developing chemicals with favourable properties and novel functionalities that are more easily made using bioprocess technologies available for the manufacture from renewable bio-based raw material. This is however a high risk approach that offers no guarantee for the market of these manufactured products, hence rigorous market research is essential. Potential reward is also large. The second approach which is the target based approach (previously referred to as producing “drop-in” chemicals”) looks for the opportunities and needs in the market and fills these gaps by developing bioprocesses for the manufacture of these products that are in high demand from renewable bio-based raw materials. This is generally limited to chemicals that are currently being produced by the petrochemical industry. Although this approach has a lower risk as it can enter the market easily, the challenge is in solving the technical hurdles of developing a commercially feasible process. These two approaches were both considered in determining the top platform chemicals. This was also done in the development of top 10 chemicals by the US Department of Energy as discussed in the previous chapter.

Essentially, the ideal chemical would be one with an established technology and market. The quantitative study uses a series of criteria or factors to rank chemicals by using weightings of these factors. The factors used to determine if the chemical has an established market are the chemical yield (theoretical and actual), technology readiness level and the selling price. The factors used to gauge the market opportunity of the chemicals is market size (world market size, South African imports and exports) of the chemical.

Following the quantitative study considering the above mentioned factors, the qualitative study was done. The qualitative study incorporated factors that cannot necessarily be quantified into deciding the top platform chemicals. These factors are as follows:

- Number (diversity) of products that can be manufactured from the platform chemical
- Platform chemicals that can act as a substitute for existing chemical products
- Relevance to South Africa
- Chemicals that can be promoted by the introduction of government policy
- Obtaining expert opinions from industrial personnel and experienced academic researchers

Both the quantitative and the qualitative study of the top chemicals were used to determine the top chemical to be selected for a techno-economic study. The remainder of the reaction process was then designed. This included deciding on the fermentation medium, the most suitable reactor and the optimal process conditions. After this was done, a techno-economic study was done.

# 4 Quantitative and qualitative study

## 4.1 Quantitative study

### 4.1.1 Selection of chemicals to be screened

In this section, the screening carried out on the initial chemicals selected is reported. The criteria for the first elimination step was to select chemicals that can be produced from sugar and can be produced by a biological route.

Table 4-1shows the catalogued chemicals and an indication of possible production of these chemicals from sugar. Chemicals that cannot be primarily produced from sugar but require a chemical derivative of sugar as a raw material were not considered to have a production from sugar (as a carbon source). The type of carbon sources listed may not necessarily be the conventional sources used in industry. Furthermore, these listed sources omit fossil sources that may be the conventional source used in industry.

Table 4-1 Chemicals selected to be screened showing carbon sources and route of production

| Number | Chemical | Type of Carbon source | Route of production | Reference |
|---|---|---|---|---|
| **1** | **Acetic acid** | Fructose | Biological | (Huang, et al., 1998; Ren, et al., 2010) |
| **2** | **Adipic acid** (hexanedioic acid or 1,4-butanedicarboxylic acid) | Glucose | Biological or Chemical | (Anbarasan, et al., 2012) |
| **3** | **Algal lipids** | Sugars or $CO_2$ | Biological (Intracellular) | (Taylor, et al., 2015) |
| **4** | **Aspartic acid** | Fumaric acid | Biological | (Scott, et al., 2007; Chinthapalli & Smith, 2010) |
| **5** | **1,4–Butanediol (BDO)** | Succinic acid | Biological | (Chinthapalli & Smith, 2010; de Jong, et al., 2012a) |
| **6** | **Citric acid** | Glucose | Biological | (Paul, et al., 1999; Max, et al., 2010) |
| **7** | **Ethanol** | Glucose, Sucrose, Carbohydrates | Biological | (Lin & Tanaka, 2006; Liu, et al., 2012) |
| **8** | **Ethyl acetate** | Ethanol | Chemical | (Chinthapalli & Smith, 2010) |
| **9** | **Ethylene** | Ethanol | Chemical | (Chinthapalli & Smith, 2010) |

| | | | | |
|---|---|---|---|---|
| **10** | **Ethylene glycol (MEG)** | Ethanol | Chemical | (India glycols limited, 2015) |
| **11** | **Farnesene (Biohydrocarbon)** | Sucrose, Xylose | Biological | (De guzman, 2013; Taylor, et al., 2015) |
| **12** | **Fumaric acid (1,4-Dicarboxilic acid)** | Glucose | Biological | (Ling & Thomas, 1989) |
| **13** | **2,5 furan-dicarboxylic acid (FDCA)** | Glucose, Fructose, Manose | Chemical | (European union, 2012) |
| **14** | **Furfural (Furfuraldehyde) (Chemical group Furan)** | Xylose | Chemical | (Taylor, et al., 2015) |
| **15** | **Glucaric acid (Saccharic acid)** | Glucose | Chemical | (Moon, et al., 2010) |
| **16** | **Gluconic acid** | Glucose | Chemical | (Chinthapalli & Smith, 2010; Werpy, et al., 2004) |
| **17** | **Glutamic acid** | Sugars (Sucrose, fructose, glucose) | Biological | (Patel, et al., 2006; Xu, et al., 2013) |
| **18** | **Glycerol and derivatives** | From oil/lipids | Chemical | (Bridgwater, et al., 2010; Werpy, et al., 2004) |
| **19** | **3-Hydroxybutyrolactone (3-HBL)** | Malic acid, Glucose | Biological or Chemical | (Dhamankar, et al., 2014; Choi, et al., 2015; Kumar, et al., 2013) |
| **20** | **5-Hydroxymethyl furfural (5-HMF)** | Glucose and fructose | Chemical | (Taylor, et al., 2015; Voegele, 2014) |
| **21** | **3-Hydroxypropionic acid** | Glucose, Sucrose, Fructose, Dextrose, Lactose, Glycerol | Biological | (Bozell & Petersen, 2010; Lynch, et al., 2014) |
| **22** | **Iso-butanol** | Glucose | Biological | (Atsumi, et al., 2008) |
| **23** | **Isobutene (Isobutylene, 2-methylpropene)** | Iso-butanol | Biological | (Taylor, et al., 2015) |
| **24** | **Isoprene (Biohydrocarbons)** | Xylose or glucose | Biological | (Cervin, et al., 2014) |

| | | | | |
|---|---|---|---|---|
| **25** | **Itaconic acid (methylene succinic acid or 2-methylidenebutanedioc acid)** | Molasses, Glucose, Sucrose, Corn starch | Biological | (Mondala, 2015; Okabe, et al., 2009) |
| **26** | **Lactic acid** | Corn starch, Tapioca, sugar cane, sugar beet and glucose | Biological | (Thongchul, 2013) |
| **27** | **Levulinic Acid** | Starch, lignocellulostic biomass, xylose, arabinose, glucose, sucrose | Chemical | (Bozell & Petersen, 2010; Girisuta, et al., 2006; Ramli & Amin, 2016) |
| **28** | **Malic Acid (1,4-Dicarboxilic acid)** | Glucose | Biological | (Zhang, et al., 2013) |
| **29** | **n-Butanol (ABE process)** | Glucose, Sucrose, Lactose | Biological | (Zhao, et al., 2013; Ren, et al., 2010) |
| **30** | **Para-xylene** | Wood waste, corn, stover, sugar cane, baggase, glucose | Thermo-chemical | (de Jong, et al., 2012a) |
| **31** | **Poly-ethylene (PE)** | Ethanol | Chemical | (de Jong, et al., 2012b) |
| **32** | **Poly-hydroxy-alkanoates (PHAs)(i.e. PHB and PHBV)** | Glucose, Starch, Sucrose, levulinic acid | Biological (intracellular) | (de Jong, et al., 2012b; Yu, 2013; Reis, et al., 2003) |
| **33** | **Polylactic acid (PLA)** | Corn starch, tapioca, sugarcane, sugar beets, glucose | Biological | (de Jong, et al., 2012b; Thongchul, 2013) |
| **34** | **1,3-propanediol (PDO)** | Glucose, glycerol | Biological or chemical | (Um & Kim, 2013; de Jong, et al., 2012a) |
| **35** | **Propylene** | Ethanol, butanol, propane, vegetable oil, methanol, glycerol | Chemical | (de Jong, et al., 2012b; de Jong, et al., 2012a) |
| **36** | **Propylene glycol (1-2 propanediol)** | Glycerol | Chemical | (de Jong, et al., 2012a) |
| **37** | **Sorbitol (D-glucitol)** | Glucose, fructose | Biological | (de Jong, et al., 2012b) |

| | | | | |
|---|---|---|---|---|
| **38** | **Succinic acid (1,4-Decarboxilic acid)** | Glucose, fructose, sucrose, lactose, soluble starches, corn syrups | Biological | (de Jong, et al., 2012a; de Jong, et al., 2012b) |
| **39** | **Xylitol/arabinitol** | Xylose and glucose, xylose and glycerol | Chemical | (de Jong, et al., 2012b; Choi, et al., 2015) |

The pre-selection of chemicals was done as follows:

- Identify the carbon sources that chemicals can be produced from
    - Check if chemical can be produced from sugar. If it can be produced from sugar, what type of carbon sources have been documented?
    - Chemicals that cannot be primarily produced from sucrose but require a chemical derivative of sugar (i.e. ethane) as a raw material were not considered to have a production from sugar
    - This analysis allowed the list to be cut down to 28 chemicals
- Look at the mode of production
    - These are either biological (intracellular or extracellular) or chemical routes
    - The pre-selected chemicals based on biological routes was reduced to 21 chemicals

The pre-selected 21 chemicals are listed below in no particular order of prominence:

- Alcohols
    - Ethanol
    - Isobutanol
    - N-butanol (ABE process)
- Biopolymers
    - Poly-hydroxyalkanoates (PHAs)(i.e. PHB and PHBV)
    - Polylactic acid (PLA)
- Carboxylic acids
    - Acetic acid
    - Adipic acid (hexanedioic acid or 1,4-butanedicarboxylic acid)
    - Citric acid
    - Fumaric acid (1,4-Dicarboxilic acid)
    - Glutamic acid
    - Itaconic acid (methylene succinic acid or 2-methylidenebutanedioc acid)
    - Lactic acid
    - Malic acid
- Hydrocarbons
    - Farnesene (Biohydrocarbon)
    - Isoprene (Biohydrocarbons)
- Speciality chemicals
    - Algal lipids
    - 3-Hydroxybutyrolactone
    - 3-Hydropropionic acid
    - 1,3-Propanediol (PDO)
-
    - Sorbitol (D-glucitol)
    - Succinic acid (1,4-Dicarboxylic acid)

### 4.1.2 Collection of data to be used for categorising of chemicals and fuel

The 21 chemicals that were selected were categorised by using a system of weightings. This was done by collecting several types of information of the chemicals and applying weightings to the different factors to determine the top chemicals. The information used included:

- Product yield (theoretical and actual yield)
- Technology readiness level (TRL)
- Market size (world market size, SA imports and SA exports)
- Selling price
-

#### *4.1.2.1 Product yield*

The product theoretical yield was calculated from balanced chemical equations obtained from Deloitte (2014) shown in Table A3 in the appendix. The equations in terms of glucose were adjusted to sucrose (which is the carbon source of focus in this study). Table 4-2 shows the theoretical (maximum) yields of the selected chemicals.

Table 4-2 Theoretical (maximum) and actual yields of selected platform chemicals

| Chemical/fuel Name | Molar mass (g/mol) | Sucrose coefficient | Product coefficient | Theoretical yield (g/g) | Actual yield (g/g) |
|---|---|---|---|---|---|
| **Acetic acid** | **60** | **1** | **4** | **0.70** | **0.90 (Huang, et al., 1998)** |
| **Adipic acid** | **146** | **7** | **6** | **0.37** | **0.18 (Niu, et al., 2002)** |
| **Algal lipids** | **Dependent on the structural formula of the lipid** | | | | |
| **Citric acid** | **192** | **1** | **2** | **1.12** | **0.70 (Max, et al., 2010)** |
| **Ethanol** | **46** | **1** | **4** | **0.54** | **0.50 (Lin & Tanaka, 2006)** |
| **Farnesene** | **204** | **7** | **4** | **0.34** | **0.15 (Lane, 2013)** |
| **Fumaric acid** | **116** | **1** | **3** | **1.02** | **1.00 (Ling & Thomas, 1989)** |
| **Glutamic acid** | **147** | **5** | **12** | **1.03** | **0.41 (Shi, et al., 2006)** |
| **3-Hydroxybutyrolactone** | **86** | **2** | **6** | **0.75** | **0.031 (Dhamankar , et al., 2014)** |
| **3-Hydroxypropionic acid** | **90** | **1** | **4** | **1.05** | **1.02 (Huang, et al., 2012)** |
| **Iso-butanol** | **74** | **1** | **2** | **0.43** | **0.34 (Atsumi, et al., 2008)** |
| **Isoprene** | **68** | **7** | **24** | **0.68** | **0.11 (Cervin, et al., 2009)** |
| **Itaconic acid** | **130** | **5** | **12** | **0.91** | **0.52 (Liao & Chang, 2010)** |
| **Lactic acid** | **90** | **1** | **4** | **1.05** | **0.99 (Zhu, et al., 2007)** |
| **Malic acid** | **134** | **1** | **4** | **1.57** | **1.04 (Jantama, et al., 2008)** |
| **n-Butanol** | **74** | **1** | **2** | **0.43** | **0.21 (Jiang, et al., 2014)** |
| **PHAs** | **Dependent on the structure of the PHA** | | | | |
| **Polylactic acid** | **From theoretical yield of lactic acid from sucrose and the theoretical yield of PLA from lactic acid** | | | | |
| **1,3-propanediol** | **76.09** | **1** | **3** | **0.67** | **0.51 (Kaur, et al., 2012)** |
| **Sorbitol** | **182** | **1** | **2** | **1.06** | |

| | | | | | |
|---|---|---|---|---|---|
| **Succinic acid** | **118** | **7** | **24** | **1.18** | **0.41 (Ma, et al., 2014)** |

The actual yields were obtained from experimental results from literature and from website of companies. Some actual yields were reported in terms of glucose yields where sucrose yields could not be found.

#### *4.1.2.2 Technology readiness level (TRL)*

The TRL is a ranking that is used to specify the scope of activities and level of technology development for bio-products. This is according to the report from the EU framework programme for research and innovation (Schild, 2013). Table 4-3 shows the TRL explanation used in ranking selected chemicals. The TRL value allocated for each chemical is the highest documented value that is known to have been achieved. The TRL indicates the technological and economic feasibility of developing a particular product.

Table 4-3 Technology readiness levels and description of selected Bio-Products (Schild, 2013)

| TRL | Description | Explanation | Bio-Product |
|---|---|---|---|
| 0 | Idea | Unproven concept, no test has been performed | |
| 1 | Basic research | Principles postulated and observed but no experimental proof available | |
| 2 | Technology formulation | Concept and application have been formulated | |
| 3 | Applied research | First laboratory tests completed; proof of concept | |
| 4 | Small scale prototype | Built in a laboratory environment ("ugly" prototype) | Fumaric acid<br>Malic acid |
| 5 | Large scale prototype | Tested in intended environment | Adipic acid<br>3-Hydroxypropionic acid<br>Isoprene |
| 6 | Prototype system | Tested in intended environment close to expected performance | Farnesene |
| 7 | Demonstration system | Operating in operational environment at pre-commercial scale | 3-Hydroxybutyrolactone<br>Poly-hydroxy-alkanoates |
| 8 | First of a kind commercial system | Manufacturing issues solved | Algal lipids<br>Iso-butanol<br>Polylactic acid<br>Succinic acid |
| 9 | Full commercial application | Technology available for consumers | Acetic acid<br>Citric acid<br>Ethanol<br>Glutamic acid<br>Itaconic acid<br>Lactic acid<br>n-butanol<br>1,3-propanediol<br>Sorbitol |

#### *4.1.2.3 Market size*

The South African import and export values for each chemical were obtained from the Department of Trade and Industry (DTI) website (South African Department of Trade and Industry, 2016). Several of the chemicals and fuels have both import and export values. The world market size in Table 4-4 was obtained from literature. The world market size of 3-hydroxybutyrolactone is unknown because the studies done on it are in their preliminary stages and it is yet to reach market.

Table 4-4 Market size for selected chemicals to be screened

| HS # | Name of Chemical or Fuel | SA Import (tonne/yr) | SA Export (tonne/yr) | World Market (tonne/yr) |
|---|---|---|---|---|
| H29152100 | Acetic acid | 6797 | 8045 | 13 570 000 |
| H291712 | Adipic acid | 1564 | 8.4 | 3 019 000 |
| | Algal lipids | - | - | 122 000 |
| H291814 | Citric acid | 21513 | 2846 | 1 600 000 |
| H2207 | Ethanol | 21967 | 183310 | 76 677 000 |
| | Farnesene (Biohydrocarbon) | - | - | 12 200 |
| H29171935 | Fumaric acid (1,4-Dicarboxilic acid) | 49.4 | 74.6 | 90 000* |
| H292242/H29224200 | Glutamic acid | 13214 | 81.0 | 2 300 000 |
| | 3-Hydroxybutyrolactone (3-HBL) | - | - | Unknown |
| | 3-Hydroxypropionic acid | - | - | 40 |
| H290514 | Iso-butanol | 30.9 | 6523 | 500 000 |
| H400260 | Isoprene (Biohydrocarbons) | 2119 | 627 | 850 000 |
| | Itaconic acid (methylene succinic acid or 2-methylidenebutanedioc acid) | - | - | 41 400 |
| H291811 | Lactic acid | 2767 | 413 | 472 000 |
| H29181910 | Malic Acid (1,4-Dicarboxilic acid) | 322 | 5838 | 200 000* |
| H290513 | n-butanol (ABE process) | 161 | 132125 | 3 000 000 |
| | Poly-hydroxy-alkanoates (PHAs)(i.e. PHB and PHBV) | - | - | 54 000 |
| H390770 | Polylactic acid (PLA) | 0.083 | 11.8 | 472 000 |
| | 1,3-propanediol (PDO) | - | - | 128 000 |
| H290544 | Sorbitol (D-glucitol) | 3919 | 109 | 164 000 |
| | Succinic acid (1,4-Decarboxilic acid) | - | - | 76 000 |

The world market values were obtained from Taylor et al (2015). The world market values marked with * was obtained from Yang & Yu (2013) & Zhang et al (2013), while ** was obtained from Bridgewater et al (2010) and *** was obtained from Choi (2015). The South African market size (import and export) were obtained from the South African trade date website (South African Department of Trade and Industry, 2016)

#### *4.1.2.4 Selling price*

The world market price was obtained as explained on Table 4-5. The lower value of the range reported in literature or on company websites was used. The exchange rate used to convert the world market value to South African rand was 15 R/USD (exchange rate from 2015). An attempt was made to report the SA import and export selling prices. The import and export selling prices were obtained by dividing the total annual revenue of product by the product volume. The values that were obtained were

incompatible with available world prices and were therefore not reported. The discrepancy is assumed to be a result of the inaccuracy of the data on the DTI website.

Table 4-5 Selling price for selected chemicals

| HS # | Chemical/Fuel Name | Selling price (ZAR/ton) |
|---|---|---|
| H29152100 | Acetic acid | 9260 |
| H291712 | Adipic acid | 27800 |
| | Algal lipids | 15000 |
| H291814 | Citric acid | 10500* |
| H2207 | Ethanol | 12300 |
| | Farnesene (Biohydrocarbon) | 83700 |
| H29171935 | Fumaric acid (1,4-Dicarboxilic acid) | 22500* |
| H292242/H2922 4200 | Glutamic acid | 30000* |
| | 3-Hydroxybutyrolactone (3-HBL) | - |
| | 3-Hydroxypropionic acid | 16500 |
| H290514 | Iso-butanol | 25800 |
| H400260 | Isoprene (Biohydrocarbons) | 30000 |
| | Itaconic acid | 28500 |
| H291811 | Lactic acid | 21800 |
| H29181910 | Malic Acid (1,4-Dicarboxilic acid) | 15000* |
| H290513 | n-butanol (ABE process) | 18800 |
| | Poly-hydroxy-alkanoates (PHAs)(i.e. PHB and PHBV) | 97500 |
| H390770 | Polylactic acid (PLA) | 54000* |
| | 1,3-propanediol (PDO) | 26400 |
| H290544 | Sorbitol (D-glucitol) | 9750 |
| | Succinic acid (1,4-Decarboxilic acid) | 37500 |

The world market value were obtained from Taylor et al (2015) except the values marked with * which were obtained from Alibaba group (2016)

### 4.1.3 Categorising selected chemicals using weightings

The different categories that were used in the ranking of the chemicals were as follows:

- Actual yield (g/g)
- Theoretical (maximum) yield (g/g)
- Import amounts (tonne/yr)
- Export amounts (tonne/yr)
- World market size (tonne/yr)
- World price (R/tonne)
- TRL

To normalise scores for each chemical in each category, the highest value was allocated 100% such that the remaining values were linearly scaled from a value of 0 to 100% as they ranged from 0 to the highest value. For sections with no known information, a value of zero was allocated to the segment. For example, the chemical with the highest value for a particular category will have a score of 100%

while the chemical with no information (NI) for a particular category will have a score of zero for that category. The values for different percentages across categories are displayed on Table 4-6.

Table 4-6: Listing different value of the categories as a percentage

| Category | Percentage | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 0 | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 100 |
| World price (R/tonne) | NI | 9 750 | 19 500 | 29 300 | 39 000 | 48 700 | 58 500 | 68 200 | 78 000 | 87 800 | 97 500 |
| Actual yield | NI | 0.104 | 0.208 | 0.312 | 0.416 | 0.520 | 0.624 | 0.728 | 0.832 | 0.936 | 1.04 |
| Theoretical yield | NI | 0.157 | 0.314 | 0.471 | 0.628 | 0.785 | 0.942 | 1.09 | 1.26 | 1.41 | 1.57 |
| TRL | NI | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| Imports (tonnes/yr) | NI | 2 200 | 4 390 | 6 590 | 8 790 | 11 000 | 13 200 | 15 400 | 17 600 | 19 800 | 22 000 |
| Exports (tonnes/yr) | NI | 18 300 | 36 700 | 55 000 | 73 300 | 91 700 | 110 000 | 128 000 | 147 000 | 165 000 | 183 000 |
| World demand (tonnes/yr) | NI | 7 670 000 | 15 300 000 | 23 000 000 | 30 700 000 | 38 300 000 | 46 000 000 | 54 700 000 | 61 300 000 | 69 000 000 | 76 700 000 |

After scoring was done, the compounds were ranked using different weighting for each criterion. The weighting is a way of summing up all the scores across different categories for a particular chemical or fuel. The weighting was done by allocating a value of 0.25 for a low weight and a value of 0.75 for a high weight. The scores for each category was then multiplied by the weighting on the particular category and summed up for all the categories to determine the overall score of each chemical. Different weightings were used to look at five scenarios.

The five scenarios looked at were:

- High rating on yields (theoretical and actual)
- High rating on imports/exports
- High rating on world demand
- High rating on TRL
- High rating on market value

Table 4-7: Different weightings done

| Category | Weighting | | | | |
|---|---|---|---|---|---|
| | **High yields** | **High Imports/Exports** | **High world demand** | **High TRL** | **High market value** |
| **World price (R/tonne)** | 0.25 | 0.25 | 0.25 | 0.25 | 0.75 |
| **Actual yield** | 0.75 | 0.25 | 0.25 | 0.25 | 0.25 |
| **Theoretical yield** | 0.75 | 0.25 | 0.25 | 0.25 | 0.25 |
| **TRL** | 0.25 | 0.25 | 0.25 | 0.75 | 0.25 |
| **Imports (tonnes/yr)** | 0.25 | 0.75 | 0.25 | 0.25 | 0.25 |
| **Exports (tonnes/yr)** | 0.25 | 0.75 | 0.25 | 0.25 | 0.25 |
| **World demand (tonnes/yr)** | 0.25 | 0.25 | 0.75 | 0.25 | 0.25 |

For each scenario, the factor that was considered high was given a weighting of 0.75 while the other factors were given a weighting of 0.25. This is as shown on Table 4-7. Table 4-8 shows the top ten chemicals ranked from the chemical that obtained the highest score to the chemical that obtained the least score. The chemicals highlighted in green, yellow, red and purple are chemicals that appear on 5, 4, 3, and 1 group respectively. For values of the scoring and the different weightings of individual chemicals, refer to **Error! Reference source not found.** in the Appendix.

Table 4-8: Top 10 chemicals for five different weighting scenarios

| High yields | High Imports/Exports | High world demand | High TRL | High market value |
|---|---|---|---|---|
| Malic acid | Ethanol | Ethanol | Ethanol | Ethanol |
| Ethanol | Citric acid | Citric acid | Citric acid | PHAs |
| Citric acid | Glutamic acid | Acetic acid | Glutamic acid | Farnesene |
| Lactic acid | n-butanol | Glutamic acid | Lactic acid | Citric acid |
| 3-HPA | Acetic acid | Lactic acid | Acetic acid | Glutamic acid |
| Fumaric acid | Lactic acid | Malic acid | n-butanol | Lactic acid |
| Acetic acid | Malic acid | n-butanol | Itaconic acid | Succinic acid |
| Glutamic acid | Succinic acid | Succinic acid | Succinic acid | Acetic acid |
| Succinic acid | 3-HPA | 3-HPA | PDO | Malic acid |
| Itaconic acid | Itaconic acid | Itaconic acid | Sorbitol | Itaconic acid |

The list of top ten chemicals is a very robust list with seven of the chemicals identified in all the categories. The top chemicals do not change significantly, except for the order that the chemicals are listed. In total, there are 15 different top chemicals across all the categories looked at. Because a value of zero was allocated to segments where there were no available information, some chemicals drop in ranking because there were no available information for these chemicals. These unavailable information were assumed to be non-existent or insignificant. For example, there are no South African trade data for chemicals such as Farnesene, 3-Hydrybutyrolactone and 3-Hydropropionic acid. These

are relatively new speciality chemicals with a currently small world market as can be seen in their values on Table 4-4. It can therefore be assumed that the South African market is non-existent. Chemicals such as Algal lipids do not have biological yields (from sugar) documented yet. Chemicals such as PHAs and PLAs with data constraints (i.e. yields cannot be defined) will have a lower apparent score than actual score.

## 4.2 Qualitative study

The quantitative study identified seven platform chemicals which were in the top ten platform chemicals across the five scenarios considered. These are citric acid, ethanol, lactic acid, succinic acid, acetic acid, glutamic acid and itaconic acid. These chemicals underwent a qualitative study to determine the top three chemicals from which a single chemical was selected for a techno-economic study.

### 4.2.1 Citric acid

Citric acid is an approved flavouring and preservative used in foods and beverages. It is also used as a buffering agent in household cleaners and pharmaceuticals (Taylor, et al., 2015).

Citric acid has a long history of bio-based production and is a well-established industry with many notable actors, one of which is Jungbunslauer AG. Citric acid production is dominated by China with a contribution of about 40% of the total world production (Zhang, et al., 2013). Although citric acid has been commercialised, several issues such as perfecting the mechanism of citric acid production and controlling cell morphology for acid production have still not yet been completely addressed.

Citric acid could potentially be a competitive chemical to produce in South Africa. South Africa currently imports a significant amount more citric acid than it exports. This indicates both a large demand for the chemical and also an inherent manufacturing capability. The trade volumes of this chemical in South Africa are large, amounting to ZAR 411 million in import and ZAR 38 million in export in 2015.

### 4.2.2 Ethanol

Although ethanol was not selected by the US DOE as one of the top chemicals for research and development in 2004, bioethanol production has been almost exclusively the main focus of the biorefining industry in recent years (Holladay, et al., 2007). This is because it has become the most widely used biofuel worldwide. Although bioethanol is mostly used to make fuels, about 18% of bioethanol is being used for non-fuel applications (Harmsen, et al., 2014). It can be used to make ethylene, one of the chemicals with the largest market size (Choi, et al., 2015). Chemical bioethanol is however not of the same grade as fuel ethanol. Bioethanol is mostly being produced from lignocellulosic biomass to avoid competition with food crops and reduction in greenhouse gas emissions. With the reduction in sugarcane price and the increasing cost of crude oil, the bio-based production of ethanol is now becoming more favourable.

Related alcohols such as propanol and butanol are also now of interest as precursors to corresponding olefins (Bozell & Petersen, 2010). In addition to bioethanol, current top biofuels that have been identified by IEA Bioenergy are biodiesel (FAME – fatty acid methyl ester), Fischer-Tropsch (FT)-biofuels and bio-methane from upgraded biogas and synthetic natural gas (SNG) (Jungmeier, et al., 2013). The combined production of bioethanol and biodiesel industries was more than 102 billion litres in 2010 generating a wholesale value of $56.4 billion (Erickson, et al., 2012).

### 4.2.3 Lactic acid

Lactic acid can be produced via fermentation or chemical synthesis. Although the chemical route produces high quality product, it is less favourable because of the use of hazardous raw materials (hydrogen cyanide, acetaldehyde), the use of high energy intensive distillation (triple distillation) and an overall high manufacturing cost (Taylor, et al., 2015). The chemical route also cannot make L-lactic acid and D-lactic acid stereoisomers independently; these can be produced exclusively via fermentation. Sucrose, molasses and corn syrup have been the historically preferred raw materials, however most recent fermentations are now based on corn syrup as the substrate of choice.

The top actors of lactic acid are Chongquing Bofei Biochemical Products Co. Ltd, Corbion Purac, Galactic, Henan Jindan, HiSun and Wuhan Sanjiang Space Gude Biotech. The companies are based in UK, US and Asia. Companies like Plaxica are seeking for potential licensees and partners for expansion. Lactic acid main application is in the food industry but currently, about 40% of lactic acid is used to make polylactic acid (PLA) (Bozell & Petersen, 2010). This is used mostly for packaging, insulation, automotive and fibres (Taylor, et al., 2015). PLA has an advantage over other polymers in that it is durable, degradable, easily composted and it does not contain any potentially harmful chemical building block (Harmsen, et al., 2014; Taylor, et al., 2015). Countries such as Taiwan, France and Italy have already restricted the use of non-biodegradable plastics which is favouring the increase in the demand for PLA (Taylor, et al., 2015). If the South African government follow suit, the demand for PLA could have an extensive increase. In the absence of this, PLA would be largely for the export market.

Lactic acid in combination with an alcohol could also be converted cheaply to lactate esters, a very valuable group of chemicals used to make a whole family of products within the industrial, food and cosmetic sector. Lactate esters are currently also made from maize by NatureWorks, Cargill – USA.

### 4.2.4 Succinic acid

Succinic acid is a 4 carbon dicarboxylic acid that has a wide range of applications from high-value niche applications (personal care products and in food and beverage industry) to large volume applications (plasticizers, polyurethanes, resins and coatings). Succinic acid can also be used as a monomer for the production of several bio-based polymers (Choi, et al., 2015). Succinic acid was found as one of the five most promising bio-based platform chemicals by the US DOE both in 2004 and 2010.

Petroleum based succinic acid is currently manufactured through oxidation of n-butane or benzene followed by hydrolysis and finally dehydrogenation. This requires heavy metal catalysts, organic solvents, high temperatures and high pressures. This makes the production not ecologically friendly. Bio-based succinic acid is mostly produced through fermentation of sugar by bacteria or by yeast at low pH. It can also be produced from glycerol. The cost of production compared to petroleum derived succinic acid have been equal as of 2013 (Taylor, et al., 2015). Due to increased production costs, bio-based succinic acid is mainly being used only in niche markets. Bio based production shows a reduction in GHG emission and in energy use. Succinic acid is currently mostly being produced by Myriant, Reverdia, Succinity and BioAmber (Choi, et al., 2015; Taylor, et al., 2015)

### 4.2.5 Acetic acid

Acetic acid is a C2 compound that is used as a food ingredient and as a cleaning agent. It is also used in the production of plastics such as PVA (Harmsen, et al., 2014). It was previously not a targeted top chemical worldwide because it was considered to have lower potential than higher carbon number chemicals. There are also unresolved production issues such as pH drop and expensive recovery. Acetic acid was not in any of the list of top chemicals (US2004, US2010 & EU2015) because of the aforementioned reasons. The major players of acetic acid are Jubilant Lifescience, Sekab, Songyuan Ji'an Biochemical (Taylor, et al., 2015).

Total world acetic acid production amounts to 13.6 million tonnes per year, with the majority of acetic acid supply (70 %) coming from Asia and with a corresponding demand (68 %) from this region alone (Methanol Market Services Asia Pte Ltd, 2016). South Africa imports 6 700 tons per year and exports only 500 tons per year (South African Department of Trade and Industry, 2016). There is a demand for acetic acid in South Africa but in order to have a competitive edge, concentration on the derivatives of acetic acid towards biopolymers such Polyvinyl Alcohol as shown in Table 4-9 could position the country in a niche market with less barriers and competition in the market sector.

Table 4-9: Major acetic acid derivatives and their uses, adapted from (Methanol Market Services Asia Pte Ltd, 2016)

| Primary Derivative | Secondary Derivative | Tertiary Derivative | End Use Applications |
|---|---|---|---|
| Vinyl acetate | Polyvinyl acetate | polyvinyl alcohol | Paints, adhesives, textiles, paper |
| Acetic anhydride | Cellulose acetate (filter tow) | EVA | Barrier and other films Cigarette filters, acetate fibres, paracetamol/aspirin and preservatives |
| Terephthalic acid | Polyesters (polyethylene terephthalate) | | Fibres, film, plastic bottles |
| Acetate esters | | | Automotive paints, printing inks |

### 4.2.6 Glutamic acid

Glutamic acid is a five carbon amino acid that was considered as one of the top platform chemicals in the list made by the US DOE in 2004 (Werpy, et al., 2004). Like malic acid, it also has been removed from the list because it was almost exclusively used in the form of monosodium glutamate (used as a flavour enhancer) (Bozell & Petersen, 2010; Choi, et al., 2015). Although the market for glutamic acid is very large (2.3 million tons/yr), there are many technical challenges that has to be resolved in order to attain a profitable operation via a biological route. These technical barriers include improving microbial biocatalyst, reducing other coproducts, increasing yield and productivity, lowering recovery costs, and resolving scaling up and integration issues. The building block and derivatives of glutamic acid have a potential of building similar polymers as is currently been produced by maleic anhydride but with new functionality. This include polyesters and polyamides (Werpy, et al., 2004). The top producers of glutamic acid are Fufeng, Juhua, Meihua and Veden. These producers are mainly located in China.

Glutamic acid features in the top 7 chemicals for the South African climate because of its high readiness in technology and also has a large import demand into South Africa. Careful consideration needs to be applied if considering manufacturing capacity for glutamic acid as there will be stiff competition from dominant producers in Asia.

### 4.2.7 Itaconic acid

Itaconic acid was selected as one of the top building block chemicals in 2004, but was excluded in 2010 because the market size did not expand as expected. This was mainly because the polymerisation process remained a challenge. Some studies claim that the demand will increase to about 410 000 ton/yr in 2020 through its application in diverse value added products (Choi, et al., 2015). The current production of itaconic acid is mainly in China (Zhang, et al., 2013).

## 4.3 Conclusion

Table 4-11[WU5] shows an overview of the top platform chemicals/fuels after a quantitative study. It can be seen that the main challenges faced by the bio-based industry is lack (or underdevelopment) of conversion technology and competing with an existing established petroleum industry for market. There is therefore a need for improved conversion technologies.

From qualitative study, the potential bio-based products identified are:

- Succinic acid
- Lactic acid

- Citric acid

Table 4-10 is a summary of justification of the rationale for the selection of the three chemicals as the top chemicals for a techno-economic study.

Table 4-10 Summary of justifications for or against selected chemicals

| Platform chemical | Products | Upside | Downside |
|---|---|---|---|
| Citric acid | **Flavouring and preservative used in food and beverages<br>Buffering agent in household cleaners and for pharmaceutical production** | **High SA demand<br>Well established technology** | **Well established industry with many notable players therefore very competitive market<br>Dominated by production in China (40% of world citric acid is produced from China) (Zhang, et al., 2013)** |
| Lactic acid | **Polylactic acid<br>Acrylic acid<br>Propylene glycol<br>Pyruvic acid<br>Acetaldehyde<br>2,3-pentanedione<br>Pentanol** | **Less hazardous raw materials used in biological route<br>High world demand for PLA production** | **Highly dependent on its use to produce polylactic acid (Choi, et al., 2015)** |
| Acetic acid | **Cleaning agent<br>Production of plastics such as PVA** | **High SA demand** | **Unresolved production issues (pH drops and expensive recovery)** |
| Ethanol | **Production of bioPET, biofuels, solvent** | **Major use envisioned as fuel<br>Limited building block** | **Well established industry with many notable players** |
| Glutamic acid | **Monosodium glutamate<br>Glutaminol<br>Pyroglutamic acid<br>14Prolinol<br>Pyroglutaminol** | **Its building blocks have the potential for polymers including polyesters and polyamides (Werpy, et al., 2004)<br>Large import demand in South Africa** | **Dominated by Asian market<br>Almost exclusively used to produce monosodium glutamine<br>Minimum current research being done on it<br>Technical challenges that remain unresolved (Improving purity, improving purity, increasing yields and productivity, lowering recovery costs, and resolving scaling up and integration issues) (Kumar, et al., 2013)** |
| Succinic acid | **1,4-butanediol<br>Gamma-butyrolactone<br>Tetrahydrofuran<br>N-methylpyrrolidone<br>1,4-diaminobutane** | **Higher performance and generates less carbon footprint than petroleum based succinic acid (Erickson, et al., 2012)<br>Multiple application via BDO and PBS<br>Competitive for niche application<br>Overall favourable environmental process that uses up carbon dioxide from the environment** | **Many of its derivatives can be produced by petroleum based technologies (Choi, et al., 2015)** |
| Itaconic acid | **Acrylamide-co-itaconic acid<br>Methyl methacrylate** | **Application in producing diverse value added products** | **Polymerisation process remains a challenge<br>Small world market<br>No SA market** |

As have been seen earlier, current goals in the biorefinery industry focuses majorly on the development of products that can be used for energy such as ethanol, biodiesel and advanced biofuel (butanol, algal biodiesel, etc.) for sustainable energy generation (Erickson, et al., 2012). The technologies required for these fuels are generally more established than biochemicals. Although these fuels have high volumes, they are low value products. They remain a long term opportunity for developers to be able find additional sources of revenue streams to increase the value of production of the bio-fuels. High value low volume products such as citric acid and lactic acid, on the other hand, offer higher return on investment and are therefore attractive for commercial development. There are however technological

hurdles that needs to be overcome as the technology development of many of these bio-chemical products are still behind compared to the conventional petrochemical route of producing them.

Succinic acid is not only a high value product but a high volume product as it can be used as a biological replacement for chemically produced maleic anhydride. **Error! Reference source not found.**2 shows hat there is a South African market for maleic anhydride. In addition to this, market age of bio-succinic acid in SA is an emerging stage and increasing. Revenues are projected to increase in the coming years, with potential growth rates of 1.8 % per annum. The degree of competition is relatively low in SA. Succinic acid also has a wide range of products that can be produced from it. Because of the high score in the quantitative study and the above mentioned justifications, succinic acid was selected as the platform chemical for a techno-economic study

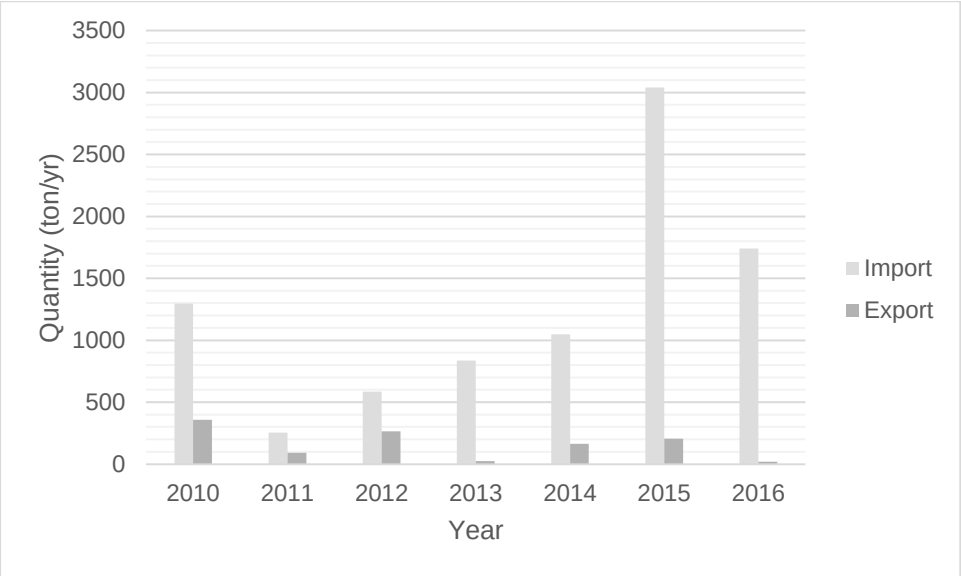


Figure 4-1 South African Imports and Exports of Maleic anhydride between 2010 and 2016 (South African Department of Trade and Industry, 2016)

Table 4-11: Overview of top seven bio-based chemicals/fuels

| Number | Bio-based product | Feedstock | Actors | Key markets & value proposition | TRL (complexity of development) & barriers | Notes |
|---|---|---|---|---|---|---|
| 1 | Citric acid | C6, C5 sugars | Jungbunslauer | Used in beverages and soft drinks, food processing, pharmaceuticals, technical applications (foaming, cleaning, softening, decalcifying and derusting agent) (Zhang, et al., 2013) | Well established technology (Taylor, et al., 2015) | China produces about 40% of worldwide output<br>Produced by large scale production of filamentous fungi (Zhang, et al., 2013) |
| 2 | Glutamic acid | Sugars (unspecified) | Fufeng, Juhua, Meihua, Veden | Monosodium glutamate (used as a flavour enhancer), glutaminol, pyroglutamic acid, prolinol & pyroglutaminol (Werpy, et al., 2004) | Research activity on product is minimal (Bozell & Petersen, 2010)<br>Easily made (Werpy, et al., 2004) | Biodegradable and soluble (Werpy, et al., 2004)<br>Dominated by Asian market. |
| 3 | Succinic acid | C6 & C5 sugars, glycerol | main actors in Europe:<br>Reverdia: (a joint venture of DSM and Ronquette)<br>Succinity: (a joint venture of BASF and Purac)<br>Globally<br>BioAmber: A joint venture of DNP Green Technology and ARD<br>Myriant | Drop-in replacement for fossil succinic acid and a near-drop-in for fossil adipic acid in resins, plasticisers, and polyester polyols, for which it can provide improved performance (Choi, et al., 2015).<br>Multiple application via BDO and PBS. | Low production costs need to be achieved by improving strains for yields and productivity (Taylor, et al., 2015). | Fermentation by genetically modified microorganisms<br>Competitive in niche application (Taylor, et al., 2015). |
| 4 | Ethanol | LC sugars, C5 & C6 sugars | INEOS | Production of bioPET, biofuels, solvent (Holladay, et al., 2007; Harmsen, et al., 2014) | High cost and energy use in product separation.<br>Strains developed are not stable enough (Erickson, et al., 2012). | Process efficiently utilises sugars giving high yields<br>Chemical production via Fisher-Tropsch synthesis (syngas)<br>Not a large variety of applications as n-butanol but a significantly more established technology (Bozell & Petersen, 2010). |
| 5 | Lactic acid | C6, C5 sugars | Chongquing Bofei Biochemical Products, Corbion Purac, Galactic, Henan Jindan, HiSun, Wuhan Sanjiang Space Gude Biotech | Production of PLA and other applications (Bozell & Petersen, 2010; Taylor, et al., 2015) | Investigations still have to be undertaken to extend the application area.<br>Fermentation of lignocellulostic streams under development. | Produced by fermentation of bacterial strains. High yields of product (Harmsen, et al., 2014) |

| Number | Bio-based product | Feedstock | Actors | Key markets & value proposition | TRL (complexity of development) & barriers | Notes |
|---|---|---|---|---|---|---|
| | | | | | Broth separation needs improving (Taylor, et al., 2015). | |
| 6 | Acetic acid | C6, C5 sugars | Jubilant Lifescience, Sekab, Songyuan Ji'an Biochemical | Used as a food ingredient and as a cleaning agent. Used in the production of plastics i.e. PVA (Harmsen, et al., 2014). | pH drops Low concentration of product (Choi, et al., 2015; Harmsen, et al., 2014) | Produced by fermentation of bacteria strains (Taylor, et al., 2015) It is a limited building block Large commodity scale is from syngas Interesting for niche application (Harmsen, et al., 2014). |
| 7 | Itaconic acid | | Alpha Chemika, Jinan Huaming Biochemistry, Qingdao Kehai Biochemistry Co, Zhejiang Guoguang Biochemistry | Bioactive compounds in agriculture and medicine; polymer intermediate; coating, plasticizer (Choi, et al., 2015). | Market size did not expand as expected Polymerisation process remains a challenge (Zhang, et al., 2013). | Produced by large scale production of filamentous fungi (Zhang, et al., 2013) |

# 5 Techno-economic study

## 5.1 Introduction

Succinic acid (also known as amber acid or butanedioic acid) has been postulated as a potentially large volume commodity produced at a scale of 30 000-50 000 tons per year (Jansen & van Gulik, 2014). Succinic acid (SA) is mostly produced from petrochemicals by catalytic hydrogenation of maleic acid or maleic anhydride. It can also serve as a direct substitute for chemically produced maleic acid because of their very similar chemical behaviour (Cukalovic & Stevens, 2008). Biologically produced succinic acid is derived from fermentation of agricultural carbohydrates. In recent years biologically produced succinic acid has shown great potential, especially in the production of a wide range of bio-based polymers (Bechthold, et al., 2008). Succinic acid has a specialty chemical market in industries producing food and pharmaceutical products, surfactants and detergents, green solvents and biodegradable plastics, and ingredients to stimulate animal and plant growth. It can also be used for the production of industrial chemicals such as 1,4-butanediol (BDO; a precursor to biodegradable plastics), tetrahydrofuran, γ-butyrolactone, adipic acid (a nylon precursor), n-methylpyrrolidone and linear aliphatic esters (Zeikus, et al., 1999). About a third of bio-based succinic acid produced worldwide is expected to be used as an intermediate for the production of 1,4-butanediol (BDO) and tetrahydrofuran (THF) by 2020 (Cavani, et al., 2016). There are several other derivatives from succinic acid that have been identified for use in various industrial branches (Cukalovic & Stevens, 2008). Economic feasibility has been shown for the use of succinic acid to produce high value-added products that do not require very cheap feedstock (Beauprez, et al., 2010). The worldwide bio-based market of succinic acid production is about 38 000 t/yr (Taylor, et al., 2015). Table 5-1 outlines the advantages and disadvantages of biological production of SA in comparison to its chemical production.

Table 5-1: Advantages and disadvantages of biological production of succinic acid in comparison to its chemical production

| | Advantages | Disadvantages |
|---|---|---|
| Biological SA | Can be used in specialty chemical market in industries producing food and pharmaceutical products, surfactants and detergents, green solvents and biodegradable plastics (Zeikus, et al., 1999)<br><br>Saving of 30-40% of energy and carbon dioxide is used up during fermentation therefore the 'green' label given to the process (Kidwell, 2008)<br><br>Much milder operating conditions<br><br>Increased interest improving currently applied routes and innovations | High feedstock and nutrient price<br><br>Sensitivity of microorganisms<br><br>Requires large capacity (due mostly to high dilution of substrates and products)<br><br>Much longer reaction time<br><br>Routes and technologies are under constant improvement (Sensitivity of microorganisms, nutrient requirements, complicated product recovery, large amount of waste) |

## 5.2 Review of commercial processes

### 5.2.1 Succinic acid overproducers

Several overproducers for succinic acid have been identified. This includes both natural and metabolically engineered microorganisms. Natural succinate overproducers include *Actinobacillus succinogenes*, *Anaerobiospirillum succiniciproducens*, and *Mannheimia succiniproducens* (Cheng, et al., 2013). All of the above mentioned are capnophilic microorganisms isolated in the rumen of

ruminants (Beauprez, et al., 2010). Although natural producers have a tendency of producing succinic acid without manipulation, they are faced with limitations such as slow growth, high nutrient requirements, sensitivity to environmental and atmospheric conditions of production and low production rates and yields (Cukalovic & Stevens, 2008; Becker & Wittmann, 2015). Metabolic engineered overproducers of succinic acid are *Escherichia coli*, *Corynebacterium glutamicum*, and *Saccharomyces cerevisiae*. These microorganisms have been modified to be more resilient and adapted to produce the desired product. They are generally chosen on the bases of their genetic accessibility. Table 5-2 shows the substrate, reactor type, yield, productivity and final concentration of different microorganisms that can be used for succinic acid production. From Table 5-2, it can be seen that optimum performance (yield, productivity and final titre) are obtained from *Escherichia coli* (AFP111), *Corynebacterium glutamicum* and *Actinobacillus succinogenes*. The reactor type and substrate used also play a major role in succinic acid production efficiency. *Saccharomyces cerevsiae* and *Escherichia coli are* however the most widely used microorganisms as can be seen on Table 5-4 .

Table 5-2 Substrate, reactor type, yields, productivity and final concentration of different microorganisms that can be used for succinic acid production

| **Organism** | **Substrate** | **Reactor type** | **Yield (g/g)** | **Productivity (g/l/h)** | **Final SA concentration (g/L)** | **Reference** |
|---|---|---|---|---|---|---|
| Saccharomyces cerevisiae (hypothetical) | Sucrose | Dual phase fermenter | 0.5 | 1.3 | 7.07 | (Efe, et al., 2013) |
| Saccharomyces cerevsiae | Glucose | Aerobic batch | 0.015 | 0.005 | 2.32 | (Arikawa, et al., 1999) |
| Saccharomyces cerevsiae | Glucose | Aerobic batch | 0.072 | 0.022 | 3.62 | (Raab, et al., 2010) |
| Escherichia coli (AFP111) | Glucose | Dual phase fermenter | 1.1 | 1.3 | 99.2 | (Cheng, et al., 2012) |
| Corynebacterium glutamicum | Glucose | Dual phase fermenter | 0.92 | 3.17 | 146 | (Okino, et al., 2008) |
| Mannheimia succiniciproducens | Glucose | Fed-batch | 0.76 | 1.80 | 52.4 | (Lee, et al., 2006) |
| Basfia succiniciproducens | Glucose | batch | 0.71 | 1.50 | 31.7 | (Becker, et al., 2015) |
| Actinobacilus succinogenes | Glucose | batch | 0.8 | 1.34 | 106 | (Becker, et al., 2015) |

Table 5-3 shows the advantages of different microorganisms for the production of succinic acid. The classical microorganisms mostly used in industry are *Escherichia coli* and *Saccharomyces cerevisiae*. *Escherichia coli* is the most resilient to withstand the desired low pH required for succinic acid production. It is also generally the easiest to manipulate as it is the microorganism with the most established understanding of its metabolism. *Saccharomyces cerevisiae* is however often preferred practically as it is suited to produce the desired quality of succinic acid as will be discussed in Section 5.5.1.

Table 5-3 Advantages of different microorganisms that can be used for succinic acid production

| Organism | Advantages |
|---|---|
| Saccharomyces cerevsiae | Awarded GRAS status for use in human consumables<br>Grows well at low pH which significantly minimizes purification and acidification costs associated with organic acid production<br>Suited to produce more of the desired quality of succinic acid consequently simplifying downstream processing<br>Can utilize diverse carbon substrates in chemically defined medium |
| Escherichia coli | High productivity (up to 3 g/l/h) obtained by dual phase fermentation<br>Susceptibility to various manipulations<br>Fast growth rate<br>Standardized cultivation techniques<br>Cheap media |
| Corynebacterium glutamicum | Promising productivity and yield (see Table 5-2) |
| Mannheimia succiniciproducens | Little or no formation of acetic, formic or lactic acid byproducts |
| Actinobacilus succinogenes | Moderate osmophile<br>High tolerance to succinate salts<br>Can ferment a broad spectrum of carbon sources(cane molasses, whey and wheat hydrolysates) |
| Anaerobiospirillum succiniciproducens | High tolerance to succinate salts<br>Can ferment a broad spectrum of carbon sources(Whey and wood hydrolysates) |

Table 5-4 Companies that produce succinic acid

| Company/source | Country | Initial year | Capacity Kt p.a. | Product expansion Kt p.a. | Strain |
|---|---|---|---|---|---|
| **BioAmber** | France | 2009 | 2 | - | Escherichia coli |
| **BioAmber** | Canada | 2013 | 7 | 34 | Escherichia coli, Saccharomyces cerevisiae |
| **Myriant** | USA | 2013 | 13.6 | 25 | Escherichia coli |
| **Reverdia (DSM-Roquett)** | Italy | 2014 | 10 | - | Saccharomyces cerevisiae |
| **Succinity (BASF-Corbion Purac joint venture)** | Spain | 2014 | 10 | 50 | Basfia Succiniproducer |

### 5.2.2 Succinic acid reactor type and ideal process conditions

The production of succinic acid is very sensitive to pH. At a high pH, the dissociated succinic salt produced is not of the quality required for industry. A further conversion using electrodialysis is required to convert the dissociated succinic acid to undissociated succinic acid. This is a very expensive step. The desired undissociated succinic acid is produced at low pH (3-4). The production of undissociated

succinic acid eliminates the need for electrodialysis thus making downstream processing less complicated and cheaper.

Purification and downstream processing of succinic acid after fermentation is the largest cost contributor to the succinic acid production process (Taylor, et al., 2015; Cukalovic & Stevens, 2008). This is because it involves the removal of cells, by-products and contaminating proteins and it also involves the conversion of succinic salts into succinic acid. The desired undissociated form of succinic acid is harmful for biomass formation and substrate consumption. Succinate itself harms the microorganisms in the same way that other weak acids do (Cheng, et al., 2013). The pH value needs to be maintained near neutral for the benefit of the producing micro-organism (E coli) (Zeikus, et al., 1999).

For a succinic acid production process that operates at low pH to produce undissociated succinic acid, the dual phase fermentation method is increasingly becoming a more preferred fermentation method compared to the conventional single phase aerobic fermentation because it allows for the required low fermentation pH for succinate production while preventing the microbial growth from being compromised (Ahn, et al., 2016; Ma, et al., 2014; Efe, et al., 2013; Lu, et al., 2009; Vemuri, et al., 2002). In a dual phase process, cell growth is followed by succinate production. The dual phase fermenter is preferred because it prevents inhibition of the microorganism growth which would have been caused by the succinic acid produced during fermentation. Dual phase fermentation has the advantage of uncoupling growth from production and thus unique operational conditions can be applied to each phase. High cell density is produced in the first fermentation phase while product with high yield and productivity is attained in the second phase. Because the cell growth and product formation are completely separate, this fermentation method is capable of producing succinic acid at a concentration 10 times higher than the conventional fermentation method (100 g/l as opposed to the aerobic fermentation's concentration of 6.7 g/l) ( (Lu, et al., 2009).

### 5.2.3 Downstream processing

Table 5-5 shows several succinic acid purification methods shown in literature. As mentioned earlier, recovery and purification is the major cost contributor to the overall succinic acid production process (and organic acids in general). A key problem faced with many of the downstream purification processes suggested in literature is the complexity involved in applying the separation technology to large-scale industrial processes in a cost and time effective manner that increases productivity and yield (Kurzrock & Weuster-Botz, 2010; Cheng, et al., 2012). Many of these suggested downstream processing methods such as precipitation, electrodialysis have issues such as industrial relevance, competing with existing processes or serious problems with scaling up to an industrial scale.

Simultaneous fermentation and precipitation of calcium or ammonium succinate uses $Ca(OH)_2$ or CaO followed by subsequent re-acidification using sulphuric acid. In membrane separation, a combination of microfiltration, ultrafiltration and nanofiltration are used. Classical liquid-liquid extraction method used more popularly for citric acid extraction has been explored but there is no known application on an industrial scale for succinic acid. Direct esterification is done by acidifying dried succinate salts in ethanol using $H_2SO_4$, forming both esters and free succinic acid (Orjuela, et al., 2011). In chromatography, adsorption is done on resins such as high silica ZSM-5 Zeolite. Succinic acid fermentation with a simultaneous crystallisation process followed by electrolysis to avoid large amounts of waste has also been suggested. In order to separate the residual cationic, anionic and amino acids, cation and anion exchange resins were integrated.

Table 5-5: Several succinic acid recovery and purification methods

| Method | Advantage | Disadvantage | Reference |
|---|---|---|---|
| Simultaneous fermentation and precipitation of Calcium or ammonium succinate | **Easily scalable<br>Robust** | **High cost of acids and bases<br>Large amount of waste salts generated during the process** | **(Datta, et al.,; Data 1992; Berglund et al. 1991)** |
| Membrane separation | **Can give high yield and purity<br>Mature for commercial application** | **Membrane pollution can be very serious<br>Equipment cost is high** | **(Cheng, et al., 2012)** |

| | | | |
|---|---|---|---|
| Liquid-liquid extraction | **Well and extensively used method in industry<br>Easily scalable<br>Robust<br>The separation yield is high** | **Only citric acid extraction from the fermentation broth has been carried out on an industrial scale (Baniel & Eyal, 1995). Shows unfavourable distribution coefficients for organic acids** | **(Cukalovic & Stevens, 2008; Kurzrock & Weuster-Botz, 2010)** |
| Direct crystallization | **Few unit operations** | **Large amounts of waste are only partly avoided in combination with electrodialysis<br>Low yields and purity<br>Large amounts of energy consumption from evaporation and distillation<br>Immature for commercial application** | **(Cheng, et al., 2012; Cukalovic & Stevens, 2008)** |
| Esterification | **Easily scalable** | **Raw materials (EtOH, $H_2SO_4$) comprises 85% of overall production cost** | **(Orjuela, et al., 2011; Orjuela, et al., 2013)** |
| Electrodialysis combined with ion-exchange columns | **Environmentally friendly<br>Separation yields are very high (final succinic acid purity 80%)<br>High potential for commercialisation** | **High energy cost<br>High cost of material for membranes<br>Low selectivity for succinic acid<br>Fouling<br>Only functional at high pH (7) where succinic acid is completely dissociated** | **(Zeikus, et al., 1999; Kurzrock & Weuster-Botz, 2010)** |
| Precipitation + Filtration + Ion exchange | **Separation yields are very high<br>Recycling of used reagent is possible<br>Low technical barrier and risk<br>Expensive process<br>Produces low volume of waste** | **The dosage of chemicals are very large<br>High energy consumption and equipment damage caused by high temperature in recycle of used reagent and low pH** | **(Datta, et al., 1992; Kurzrock & Weuster-Botz, 2010)** |
| Extraction of succinic acid with an amine-based extractant (tri-n-octylamine and 1-Octanol as diluent) | **Requires less energy<br>Produces less waste<br>99.8% purity<br>73.1% yield** | **Possible toxic or inhibitory effects of extractant and solvent for the microorganisms<br>Includes addition steps such as vacuum distillation and crystallization for high purity succinic acid production** | **(Huh, et al., 2006)** |
| Chromatography | **Clean<br>Reduction in the amount of additional chemicals, acids or bases needed<br>Regeneration of catalyst does not require pH shifting agents<br>Purity> 99.5%** | **High price of adsorbents<br>pH of the fermentation broth not ideal for adsorption materials<br>co-adsorption of other molecules present in the fermentation media** | **(Efe, et al., 2011; Davison, et al., 2004)** |

### 5.2.4 Conclusion

Bio-production of succinic acid has been known to have challenges with operating at the required low pH that will allow the efficient production of the desired product which will reduce the complexity of the downstream processing for a more efficient and economically feasible process (Song & Lee, 2006; Efe, et al., 2013; Debabov, 2015). The overall succinic acid production process cost estimation comprises of 10-15% feedstock cost, 20-25% fermentation cost with the bulk cost of 60-70% allocated to purification (Bechthold, et al., 2008; Kurzrock & Weuster-Botz, 2010; Morales, et al., 2016). Over the years, several companies in industry have taken up this challenge and have improved the succinic acid production process by developing new strains of microorganism, using specialised reactor systems and optimized process conditions, exploitation of new and cheaper raw materials, and the development of new purification processes.

There is currently no standard technology for succinic acid production. For example, the choice for a specific host organism determines to a large extent the process configuration of succinic acid

production. Different companies use different microorganism as presented on Table 5-4 (adapted from Debabov (2015)). It can be seen that the rapid commercialisation of bio-succinate results in different processes because of the reliance on different microorganisms. Unfortunately most of the improvements made by industry are not available for researchers to analyse. The specifics of the conditions for which the production of succinic acid is achieved by these companies are not available. This is a major setback for projects such as this that try to determine the feasibility of commercialising succinic acid. An extra layer of difficulty is furthermore added because this project is solely paper based and there are no lab experiments done to obtain very important parameters such as yield, fermentation time and process flow configuration of the proposed design. A lot of postulation made in this design can only be supported by engineering judgment, chemistry, and literature values but no experiments were carried out by the author.

## 5.3 Process development

This is a conceptual design of the succinic acid production process. The primary aim is not to investigate the feasibility of the individual unit operations but to estimate the succinic acid production cost using the proposed process, so that the future research targets for this process can be evaluated. Average plant sizes range from 2 000 – 10 000 tonnes/yr with potential future expansion capacity of up to 50 000 tonnes/yr as presented on Table 5-4 (Debabov, 2015) . A commercial-scale facility to produce about 40 000 tonnes/yr of succinic acid from sucrose is developed using a combination of continuous and batch processing. ASPEN and Microsoft excel was used to model the process developed by Efe et al (2013). The process was designed to produce a purity of 99.5 Wt% to meet the current industrial requirement. In the techno-economic study, a simplifying assumption is made that there is only one main product. This simplification will make possible the comparison of different chemicals thus allowing for an overview of the techno-economic potential of the different chemicals to be individually identified.

## 5.4 Process modelling

The primary aim of this design is to present a conceptual design for succinic acid production and to evaluate the feasibility of the overall process. This is to aid the identification of future research targets. The feasibility of individual unit operations will not be looked at and is thus recommended for investigation in subsequent studies. Alternative process routes will also not be assessed.

Table 5-6 Justification of major unit operations used in ASPEN or excel modelling

| Unit | Modelled as | Justification |
|---|---|---|
| **Reactors (growth and production reactors)** | Stoichiometric Batch Reactor modelled on excel | Since there is no fermentation data, metabolic modelling was used |
| **Centrifuge** | Continuous Separator modelled on excel | Simple separation with ratio of separation of the different components and energy required obtained from literature |
| **Adsorption column** | Continuous Separator + heat exchanger on excel | No model available. Only reported literature parameters for a high silica ZSM-5 Zeolite adsorbtion unit |
| **Flash** | Continuous Flash modelled on ASPEN | In-built thermodynamic properties (phase and chemical equilibrium) to accurately describe the mass and energy balance in the unit |
| **Evaporator** | Continuous Evaporator modelled on ASPEN | In-built thermodynamic properties (phase and chemical equilibrium) to accurately describe the mass and energy balance in the unit |
| **Crystallizer** | Continuous Scraper surface heat exchanger design on excel | Suitable when there is crystallisation occurring because there is a rotating element that has spring-loaded scraper blades which wipe the inside surface of the tube |
| **Rotary Filter** | Continuous Separator on excel | Simple separation with ratio of separation of the different components and energy required obtained from literature |
| **Rotary Drier** | Continuous Separator on excel | Simple separation with ratio of separation of the different components and energy required obtained from literature |

### 5.4.1 Feed Sterilisation

For sterilisation, the stream is heated from 20 ºC to 134 ºC and then cooled. To reduce the heating and cooling requirement, a heat exchanger is introduced to preheat the feed to the steriliser while also cooling the sterilised feed. The streams are arranged in a counter-current fashion such that the heat used to heat the incoming stream from 20 ºC to 134 ºC is obtained from the heat removed from cooling the hot heated stream from 134 ºC to 30 ºC. This arrangement is done for both the incoming sucrose and nutrient feed separately. The reason for the separation of the nutrient and the carbon source will be explained further by examining the reactions that occurs in the different reactors.

### 5.4.2 Air sterilisation and compression

The compressed air into the reactor is sterilised by filtration for the aerobic process in the growth and production reactors. Air is sent to the reactor via a single stage isentropic reciprocating piston compressor. The air comes in at 1 atm and enters both the growth and production reactors at 2 atm.

### 5.4.3 Reactor and Microorganism

The microorganism used in this study is a hypothetical *Saccharomyces cerevisiae* strain discussed by Efe et al (2013). Recent studies have shown that it is more economically feasible to produce succinic acid using *Saccharomyces cerevisiae* (Cavani, et al., 2016) (Efe, et al., 2013). This was selected because it has been developed to produce succinic acid at low pH (pH 3.5-5.5) fermentations so that

succinic acid will be present in its undissociated form, which is preferred (Efe, et al., 2013; Yun & Jens, 2016). Jansen & van Gulik (2014) states that it is theoretically possible to produce succinic acid at a pH less than 3 and Reverdia has reportedly achieved this by using highly modified *Saccharomyces cerevisiae* (Ahn, et al., 2016; Cavani, et al., 2016). The process that achieves the claimed target has not been publicly disclosed (Cavani, et al., 2016). Operation below the $pK_a$ of succinic acid (4.2) increases the proportion of succinic acid to succinate salt produced. The advantages of this are the reduction of the likelihood of contamination, cost reduction in pH titration and in cost reduction in downstream processing. Moreover, less succinic acid in the dissociated form allows for direct crystallization and is therefore more attractive from an environmental prospective compared to other fermentation routes and petrochemical processes (Cok, et al., 2014). *Saccharomyces cerevisiae* has been selected as the microorganism of choice because of its clear economic and environmental benefits and because there is also an established technical knowledge and know-how of the production process. In addition, *Saccharomyces cerevisiae* is regarded as safe, robust, scalable (1L to 100000L) industrial production, capable of growth on diverse carbon sources, chemically defined medium, both aerobic and anaerobic, with a wide pH operating range (3-0-6.0) (Otero, et al., 2013). The schematics highlighting the advantages for the selection of *Saccharomyces cerevisiae* is presented in Figure 5-1.

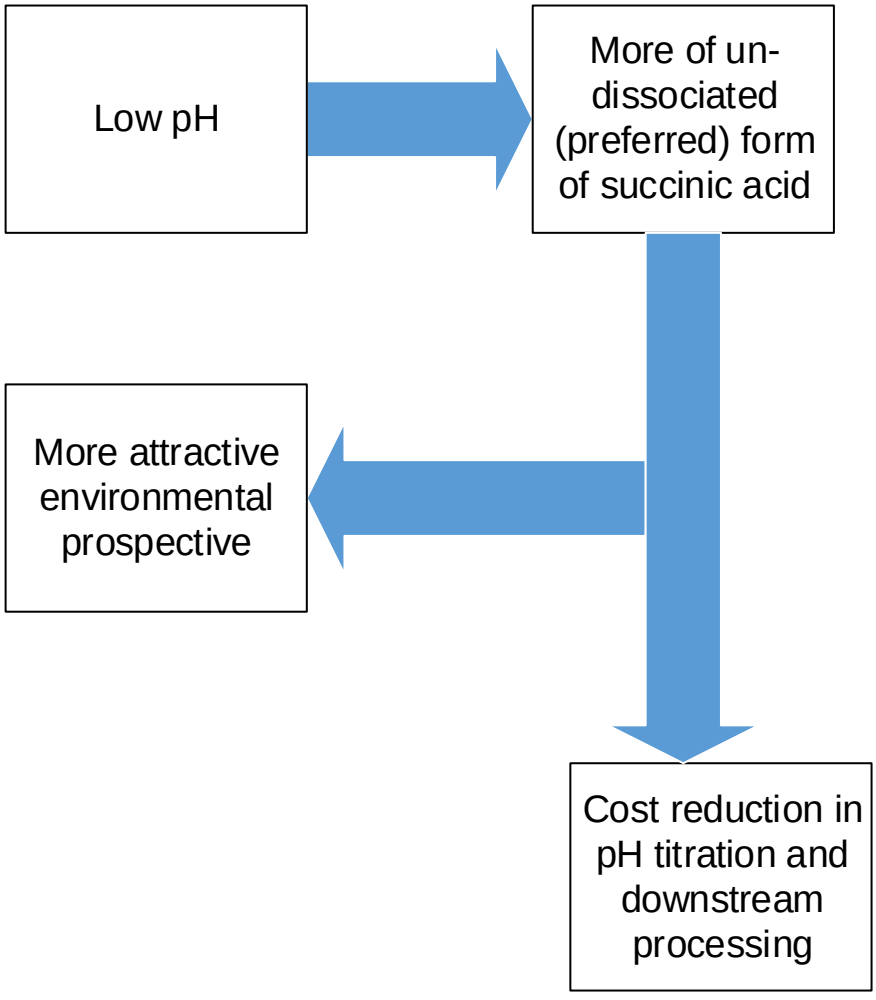


Figure 5-1: Schematic describing significance of low pH succinic acid fermentation

The aerobic growth of yeast cells and the production of succinic acid is operated in a fed-batch dual phase fermentation. The dual phase fermenter was modelled in two different reactors for simplicity. In the first reactor, the yeast is grown aerobically on sucrose at a pH of 7 from a cell density of about 4 g/L to 40 g/L (Efe, et al., 2013).

The cells are then transferred to the second part of the dual phase reactor which operates at a pH of 4 where succinic acid is produced from sucrose. A low pH is favourable for downstream processing to

reduce the amount of acid and base consumption and salt generation (Efe, et al., 2010). This is a feature that requires sensitivity analysis because within a pH range of 4-4.5, there is between 30 and 60% undissociated succinic acid as a ratio of total succinate (Efe, et al., 2011). In this second part of fermentation, cells do not grow substantially because of low pH and nitrogen limitation. The final succinic acid concentration and productivity are 13.7 g/L and 1.3 g/L/hr respectively where 52% by mass of the total succinic acid is undissociated (Efe, et al., 2013).

Metabolic modelling was used to determine the reaction stoichiometry. The lumped reactions that were used for maintenance and succinic acid production as shown in Efe et al (2013) are presented in Equations (5-1) and (5-2) respectively. The coefficients of these equations are mass relations (g/g). The rate of maintenance is twice the succinic acid production rate. The production reaction shows carbon dioxide production instead of consumption. This may be as a result of an uncoupling effect (maintenance requirement for the cells) meditated by weak acid that is due to the low pH production. This explains why the oxidative succinic acid pathway is very dominant which results in a beneficial effect when oxygen is added to the fermentation (Jansen & van Gulik, 2014).

$$C_{12}H_{22}O_{11} + 4.125\ O_2 + 1.5\ NH_3 \rightarrow 7.5\ CH_{1.8}O_{0.5}N_{0.2} + 4.5\ CO_2 + 6.5\ H_2O \quad (5\text{-}1)$$

$$C_{12}H_{22}O_{11} + 3.72\ O_2 \rightarrow 2.112\ Succ + 0.024\ Pyr + 0.024\ Acet + 0.12\ EtOH + 0.12\ Gly + 2.832\ CO_2 + 3.728\ H_2O \quad (5\text{-}2)$$

Several postulations were made to develop the model for the reactors in this design. The actual rates of the reaction can however only be obtained in the laboratory. The residence times needed in the reactor and other major parameters such as productivity and optimum titres must be found from a pilot plant.

### 5.4.4 Centrifugation

Here, cells are removed from the effluent culture stream and recycled back into the reactor. During centrifugation 80% (by mass) of the cells that are removed from the effluent are recycled back into the reactor. This is done in a batch nozzle type centrifuge that can handle a solid concentration up to 20-30% by volume. A value of 20% was used from the recommended range (20-30%) by Efe et al (2013). The maximum throughput is 96 $m^3h^{-1}$ for a bowl diameter of 0.69 m at a maximum rotation frequency of 70 Hz, with a typical engine power of 93 kW (Perry & Green, 1997).

### 5.4.5 Adsorption unit

After centrifugation, the supernatant is sent to the adsorption unit where adsorption is done on a high-silica ZSM-5 zeolite. This is the main recovery step. It allows succinic acid to be separated from its salts without use of additional chemicals such as acids or bases (Efe, et al., 2011). This type of adsorption unit cannot be used for feed containing spent lignocellulosic material or molasses because of the high concentrations of impurities in them. These impurities interfere with the adsorption operation (Efe, et al., 2013).

Recovery is focused on removing undissociated succinic acid. Here, succinic acid is adsorbed whereas dissociated succinate salts are eluted from the column. Compared to hydrophobic zeolites used in previous studies, the ZSM-5 zeolite is cost effective while maintaining relatively the same extent of separation (Efe, et al., 2011). The adsorption unit consists of two adsorption units working parallel to each other. While one column is being loaded, the already loaded column is being regenerated using hot water desorption. While undissociated succinate is captured (60% of the total succinate mass) with some of the organic acids, the remaining succinate salts and volatile organic acids that are eluted out of the adsorption column are sent to a bio-digester. This is discussed further in the subsequent sections.

Solvent selection was done by considering the following criteria: “toxicity and safety, solubility, distribution coefficient (solvent in water and succinic acid in solvent), stability of solvents at operation conditions, affinity to zeolite toward solvent, volatility, and stability of zeolite in solvent” (Efe, et al., 2010). Desorption using water is selected and performed using hot water at 150ºC instead of a base to

ensure that all the succinic acid is converted into succinate (Efe, et al., 2011). Desorption using organic solvent would leave some organic solvent on the zeolite thus causing a high temperature desorption step (Efe, et al., 2011). After every three cycles, the column is exposed to hot air from a fired heater to remove the fouling components (Efe, et al., 2013).

### 5.4.6 Flash and evaporation

The stream coming into the flash at 150 ºC is flashed off at 100ºC and atmospheric pressure (0.99 atm) after which the supernatant is sent off to the storage tank (to facilitate a continuous operation further downstream). More water is then evaporated (at 104 ºC) in a horizontal tube evaporator. In these units, volatile organics are also removed. The flash drum and the evaporator are modelled with the Flash2 on ASPEN. The Flash2 models two stream outlet systems of several units such as flash drums and evaporators using rigorous vapour-liquid and vapour-liquid-liquid equilibrium. In the flash drum, the operating temperature and pressure were specified while the operating temperature and duty were specified in the evaporator. The NRTL-RK property method was used as it is suitable in measuring non-ideal interactions and this is the most readily used in industry (Bibolet, et al., 2011). This is a relatively simple separation aimed at concentrating succinic acid salt by removing excess water. The stream leaving the evaporation unit is concentrated to 300 g/kg of succinic acid before entering the crystallisation unit (Efe, et al., 2013). To achieve this, the duty in the evaporator was manipulated until the desired outlet concentration of succinic acid leaving the evaporator was achieved.

### 5.4.7 Crystallization

The scraped-surface heat exchanger is used because the process fluid will crystallise. This type of heat exchanger is suitable when there is crystallisation occurring because there is a rotating element that has spring-loaded scraper blades which wipe the inside surface of the tube which may typically be 0.15 m in diameter (Coulson & Richardson, 1999). The heat transfer in this type of exchanger ranges from 15 to 90 $W/m^2/K$. A guesstimate value of 30 $W/m^2/K$ was used. A heat exchanger design was used to design the crystalliser. The temperature of the crystallizer is maintained at 27ºC and atmospheric pressure to allow for 3 g/kg supersaturation of succinic acid (Efe, et al., 2013). Aluminium, which is the most suitable material of construction was used (Chong, 2001). Because the crystallizer is continuous, there has to be a storage tank before it to facilitate the continuous system. These storage tanks however are not part of the scope of this work.

### 5.4.8 Rotary Filter and Dryer

Separation of crystals from the saturated solution are carried out by rotary vacuum filter. This type of filter is both versatile and has a relatively low cost when compared to centrifugation equipment (Efe, et al., 2013). Typical flux values and filter areas are in the range 200-500 L $m^{-2}h^{-1}$ and 1-80 $m^2$ respectively with a power consumption of 0.8 $kWm^{-2}$ filter area (Hugot, 1972).

Succinic acid crystals are dried by counter current hot air in inclined horizontal rotary dryers. The initial water content of the wet crystal is assumed to be 50 g/kg (Efe, et al., 2013).

### 5.4.9 Storage vessels

Two storage vessels are needed in the process. They are designed for the sucrose raw material, and for the final succinic acid product. The heuristics used were obtained from Turton et al (1998) and Walas (1988). These were used to determine the tank freeboard, residence time, size of each tank, L/D ratios, orientation, temperature and pressure of the tank. The volumetric flow into the storage tanks were calculated by assuming a density of 1000 $kg/m^3$ for the incoming streams into the storage vessels. The residence time for the sucrose feed was assumed to be 7 hours, the cycle time for the process. The storage time for the product was set as 3 days. The storage tanks are designed with a freeboard capacity of 10% as suggested in Walas (1988). The number of vessels were obtained by specifying a unit storage tank as 100 $m^3$ and 38 $m^3$ for the feed and production storage tanks respectively. The L/D ratio (between 2.5 and 5) is taken to be 3.Both tanks are vertical tanks on concrete pads.

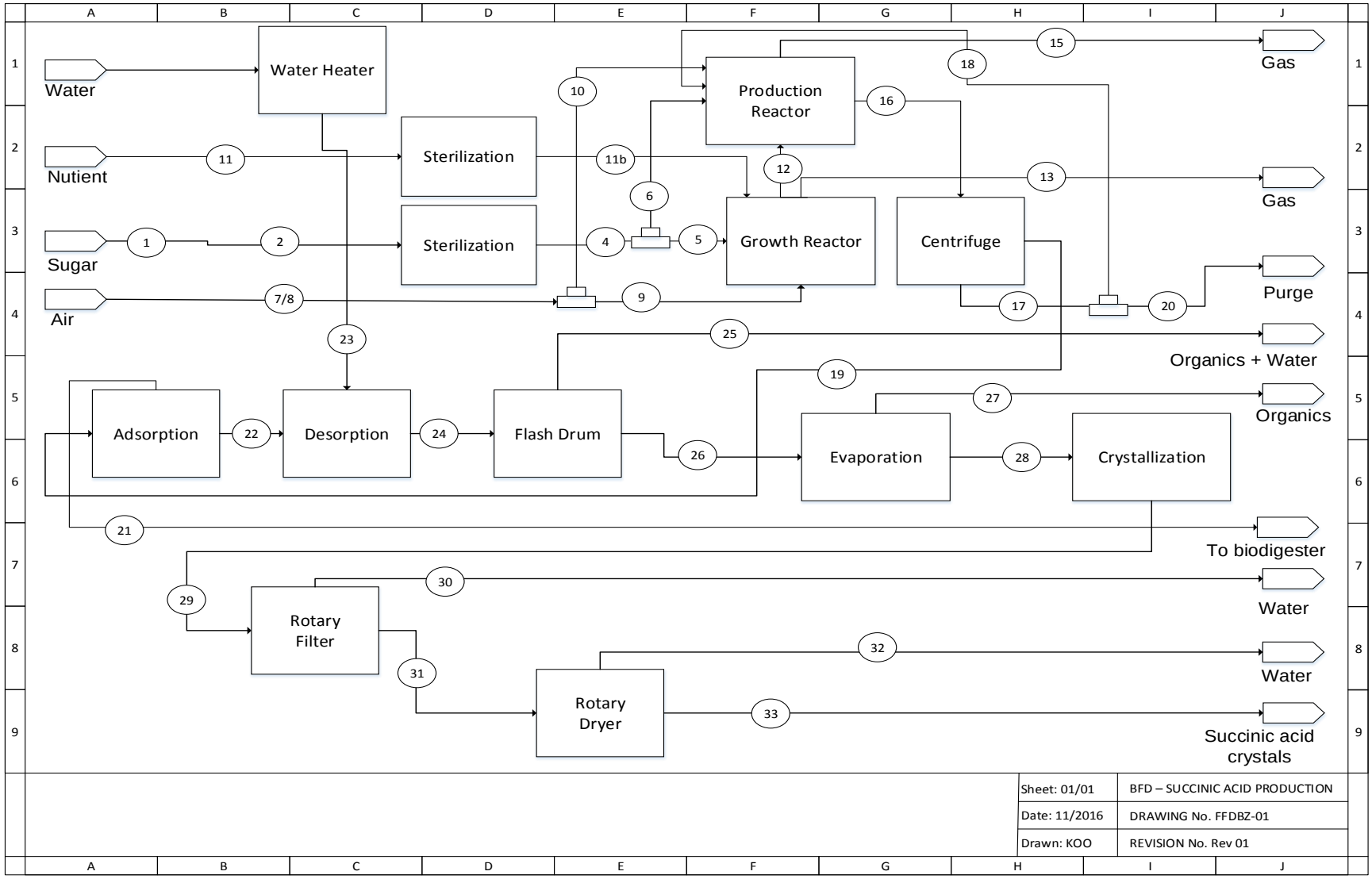


Figure 5-2: Succinic acid production using Saccharomyces cerevsiae as discussed in this study (Efe, et al., 2013)

## 5.5 Mass and energy balance

Table 5-7 shows a summary of the development of the succinic acid process

Table 5-7 Development of the succinic acid process

| Objective | Unit | Modelled as |
|---|---|---|
| Feed sterilization | Sterilizer and cooler | Heater and cooler |
| Fermentation | Dual phase fermenter | Growth + Production reactor |
| Cell mass removal + recycle | Centrifuges | Separator |
| Adsorption of succinic acid | ZSM-5 zeolite column | Separator |
| Desorption of succinic acid | Hot water heater | Heat exchanger |
| Removal of excess heat | Flash | Flash |
| Removal of water | Evaporator | Evaporator |
| Crystallization of succinic acid | Crystallizer | Heat exchanger |
| Removal of crystals | Rotary vacuum filter | Separator |
| Drying of crystals | Rotary dryer | Separator |

### 5.5.1 Mass balance

Reaction 1 occurred in the growth reactor according to Equation *(*5-1*)* while reaction 2 occurred in the production reactor according to equation *(*5-2*)*. The mass balances across the reactors were done with sucrose as the limiting reagent. Table 5-8 shows the parameters that were used for mass balance. Some of the parameters were specified while some were obtained from literature.

Table 5-8 Information used for mass balance calculations[R16][WU7]

| *From Literature* (Efe, et al., 2013) | | | *Specified value* | | |
|---|---|---|---|---|---|
| ***Parameter*** | ***Value*** | ***Unit*** | ***Parameter*** | ***Value*** | ***Unit*** |
| ***Ratio of SA recycled from the adsorber to inflow*** | ***0.4*** | ***g/g*** | ***Sucrose in fresh feed*** | ***0.10*** | ***g/g*** |
| ***Fraction of SA in stream to dryer*** | ***0.5*** | ***g/g*** | ***Ammonia feed*** | ***10000*** | ***kg/h*** |
| ***Final product purity*** | ***0.995*** | ***g/g*** | ***Reactor purge fraction*** | ***0.2*** | ***-*** |
| ***Fraction of SA in stream to crystallizer*** | ***0.3*** | ***g/g*** | ***Fraction of water recycled back to the adsorber*** | ***0.05*** | ***-*** |
| ***Mole fraction of SA out adsorption unit*** | ***0.125*** | ***mol/ mol*** | ***Sucrose split ratio R1/total*** | ***0.2*** | ***-*** |
| ***Concentration of the desorption effluent*** | ***638.4*** | ***mmo l/L*** | | | |

Table 5-9: Step by step stream calculations

| Stream # | Stream name | Calculation |
|---|---|---|
| 1 | Fresh sucrose | |
| 2 | Sucrose MixOut | $M_2 = M_1 + M_{21}$ |
| 3 | OutSter | $M_3 = M_2$ |
| 4 | Out Cooler | $M_4 = M_3$ |
| 5 | Sucrose SpR1 | $M_5 = 0.2M_4$ |
| 6 | Sucrose SpR2 | $M_6 = (1 - 0.2)M_4$ |
| 7 | Oxy in Comp | $M_7 = M_8$ |
| 8 | Oxy out Comp | $M_8 = M_9 + M_{10}$ |
| 9 | Oxy Sp R1 | $n_{total} = \frac{Oxygen\ required \times \%Excess}{0.21} = \frac{n_{glucose} \times Stoic\ coefficient\ O_2 \times 1.5}{0.21}$ |
| 10 | Oxy Sp R2 | $n_{total} = \frac{Oxygen\ required \times \%Excess}{0.21} = \frac{n_{glucose} \times Stoic\ coefficient\ O_2 \times 1.5}{0.21}$ |
| 11 | Ammonia in R1 | $M_{Ammonia} = n_{glucose} \times Stoic\ coefficient NH_3 \times Molar\ mass NH_3$ |
| 12 | Out R1 non gas | $n_{component} = n_{into\ R1} + Amount\ created/used$ |
| 13 | R1 gas | $n_{component} = n_{into\ R1} + Amount\ created/used$ |
| 14 | Out R2 gas | $n_{component} = n_{into\ R2} + Amount\ created/used$ |
| 15 | R2 gas out | $M_{15} = M_{14}$ |
| 16 | R2 non gas | $M_{16} = M_{14}$ |
| 17 | ReactorCent | $M_{Biomass,17} = M_{Biomass,16}$ , $X_{Biomass,17} = 0.2\ g/g$ |
| 18 | CentRecycle | $M_{18} = M_{Biomass,16}$ , $Recycle\ ratio \times M_{17} = 0.8M_{16}$ |
| 19 | CentAdsorb | $M_{19} = M_{16} - M_{17}$ |
| 20 | CentrifugePurge | $M_{20} = (1 - Recycle\ ratio)M_{17} = (1 - 0.8)M_{17}$ |
| 21 | Adsorb Recy | $M_{21} = M_{19} - M_{22}$ |
| 22 | AdsorbDesorp | $M_{SA,22} = (1 - fraction\ dissociated)M_{SA,19}$, $x_{SA,22} = 0.125\ mol/mol$ |
| 23 | DesorpWater | $C_{total,24} = 638.4 mmol/l$ |
| 24 | DesorpFlash | $M_{24} = M_{22} + M_{23}$ |
| 25 | FlashOut | Aspen |
| 26 | FlashEvap | Aspen |
| 27 | EvapOut | Aspen |
| 28 | EvapCrys | Aspen |
| 29 | CrysFilter | $M_{29} = M_{28}$ |
| 30 | FilterOut | $M_{30} = M_{29} - M_{31}$ |

| | | |
|---|---|---|
| 31 | FilterDry | $X_{SA,31} = 0.5\ g/g$ |
| 32 | Dryer Out | $M_{32} = M_{31} - M_{33}$ |
| 33 | Product | $X_{SA,33} = 0.995\ g/g$ |

#### *5.5.1.1 Reactor feed streams*

The sucrose fed in the fresh feed is 100 g/kg[R18][WU9] (Vaswani, 2010). This is a typical concentration of substrate for batch fermentation. Continuous fermentation on the other hand can operate at a lower concentration ranging from as little as 0.5g/L/hr to 4.0 g/L/hr of substrate (Vaswani, 2010). The incoming fresh feed is sterilised before entering the reactors.

The incoming flow of ammonia into the growth reactor is provided at an exact stoichiometric amount into the growth reactor i.e. it is a limiting reagent. This is done so that no excess ammonia flows out of the growth reactor into the production reactor to prevent biomass growth in the production vessels so that nutrients can be maximised for succinic acid production.

Sodium hydroxide is a base used to maintain the growth reactor at a pH of 7 and the production reactor at a pH at 4. This is the same base used in the succinic acid plants of BioAmber and Mitsui (Jansen & van Gulik, 2014). The sodium hydroxide base reacts with the dissociated succinic acid to form succinate as the sodium salt and water. The Henderson-Hasselbalch equation below is the equation used to calculate the amount of base needed for a given amount of acid. The reactions in the reactors are complex and therefore it is difficult to calculate the base required using the Henderson-Hasselbalch equation. The complexity is due to the fact that the acid present in the reactors can only be approximated. The amount of base required in the reactor is also dependent on the type of microorganism (Soares & Seynaeve, 2000). The amount of base (sodium hydroxide) required in the reactors will be determined by an approximation from the reported value by Efe et al (2013). According to Efe et al (2013), the concentration of sodium hydroxide required in the broth is 57.6 mmol/L. This will be used to calculate the amount of sodium hydroxide required in the production reactors.

$$\boldsymbol{pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)} \qquad (5\text{-}3)$$

The air is supplied into both the growth and production reactors to meet the stoichiometric requirement of the reactors in excess of 50%. Complete combustion was assumed because the air was fed in excess.

$$O_{2,\,R1} = 4.5\ Sucrose_{R1} \times Excess_{\%} \qquad (5\text{-}4)$$

$$O_{2,\,R2} = 4.5\ (Sucrose_{R1,exit} + Sucrose_{Recycle} + Sucrose_{Split,R2}) \times Excess_{\%} \qquad (5\text{-}5)$$

#### *5.5.1.2 Reactor recycle and cell recovery*

The first design (configuration A – Figure 5.3) of the succinic acid process considered recycling biomass after it has been filtered out in the centrifuge. This was done to ensure that all the cells centrifuged are sent back to the production reactors. This also reduces the volume of effluent coming back into the reactor by introducing a concentrated stream back into the production reactors. To prevent accumulation of aged biomass, a purge stream was added leaving the production reactors. 20% of the non-gas stream leaving the production reactors were purged out.

After consideration of the succinic acid product that was going to be lost due to the purge stream at the production reactors, it was suggested that the waste stream should be removed at the centrifuge. The recycle of the biomass was then done at the production reactors where 80% of the product in the

production reactor is being recycled back into the reactors (Configuration B). This modification allows for the overall reduction of the amount of succinic acid lost in the process. The pitfall of this approach is that not all the cells centrifuged are recycled back into the production reactors. Figure 5-3 shows configuration (A) and configuration (B) of the reactor and centrifuge.

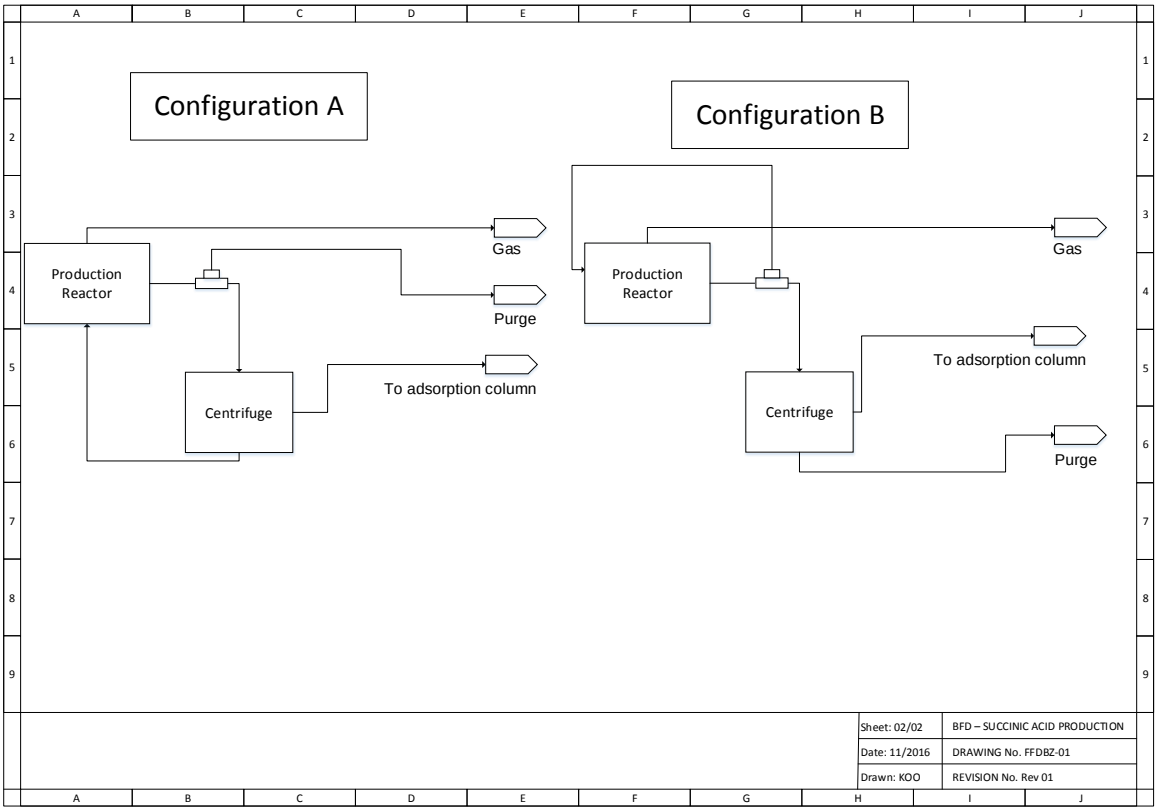


Figure 5-3: Older configurations of the production reactor and centrifuge

After considering the pitfalls of configuration A and B, configuration C was developed. This is presented in Figure 5-4. This configuration uses the idea of configuration A of recycling the biomass after centrifugation to reduce the overall volume recycled while keeping the concentration of the desired biomass high. Instead of having a purge stream at the production reactor (as in configuration A), the purge stream was introduced at the centrifuge to reduce the amount of succinic acid product lost in the process. Configuration C was used in the process design.

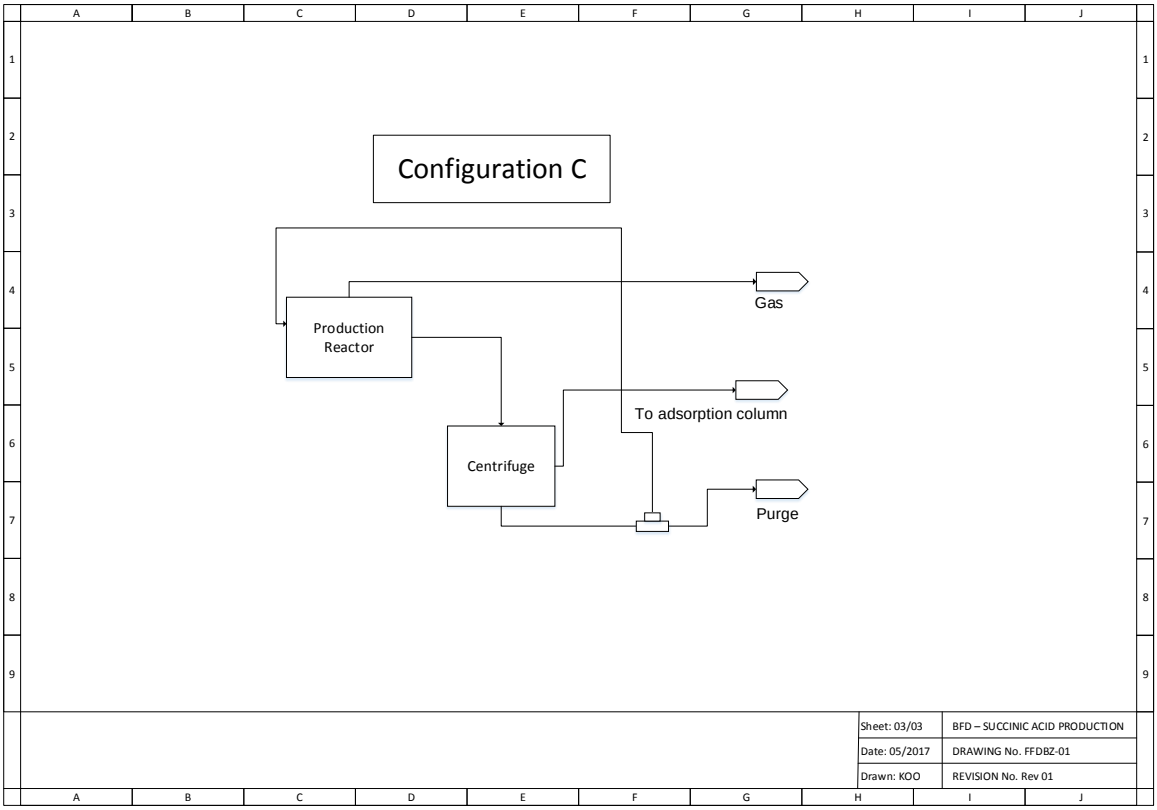


Figure 5-4: The new configuration setup of the production reactor and centrifuge

#### *5.5.1.3 Adsorption of succinic acid*

The adsorption process is based on the hydrophobic character of succinic acid and the high silica MFI type zeolites in the adsorption unit (Efe, et al., 2010). There is lower adsorption for other components that may be present in the stream such as water, acetic acid, ethanol and salts.

Figure 5-5 shows the effect of pH on the dissociation level of succinic acid. At very low pH (pH less than 2, only the undissociated succinic acid ($H_2SA$) is formed. At a fermentation of a pH higher than 2, both dissociated succinate salt ($SA^{2-}$) and succinic acid ($HAS^-$) is formed. Succinic acid formation increases rapidly until it reaches its peak at a pH of about 4.8 after which it experiences a steep decrease until it reaches a percentage of zero at a pH of about 8. Undissociated succinic acid and succinate salt formation experience an inverse relation as pH increases as presented on Figure 5-5. Bacterial formation of succinic acid at high pH (5.5-7.5) results in the formation of dissociated succinate salt which results in a complicated recovery (Bechthold, et al., 2008; Zeikus, et al., 1999; Kurzrock & Weuster-Botz, 2010; Beauprez, et al., 2010).

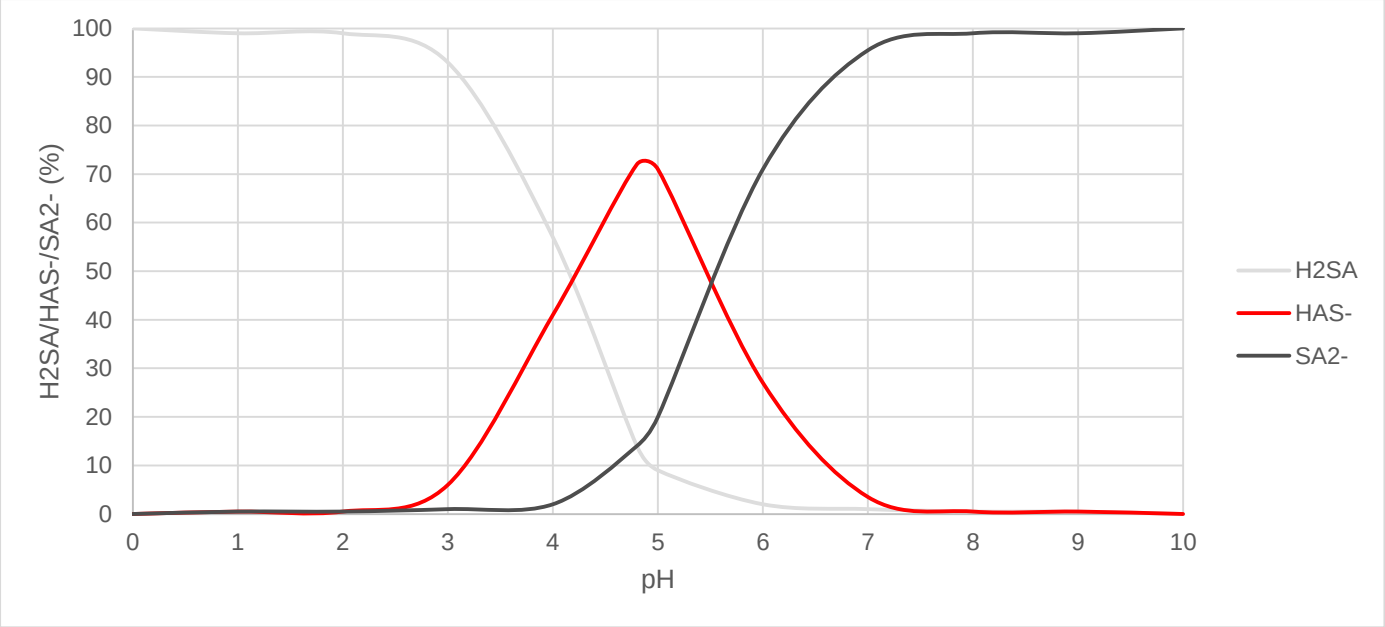


Figure 5-5: Effect of pH on the dissociation level of succinic acid (Jansen & van Gulik, 2014)

At the operational pH of 4, undissociated succinic acid is about 60% of the total succinate mass. This is presented on Figure 5-5. The mole fraction of succinic acid adsorbed is 0.125 (Efe, et al., 2010). Undissociated succinic acid is captured, while the remaining unadsorbed succinate salts that are eluted from the column and discharged. According to Cok et al (2014), the large fraction of the unadsorbed stream leaving the adsorption unit can be digested to produce biogas which can be used to generate energy for the process. The design of the bio-digester is however not included in the current economic analysis.

The unabsorbed succinic acid from the adsorption unit can also be recycled back into the fermenters, allowing the dissociated succinic acid to act as a buffer in the fermenter producing a culture with a high cellular viability. In an experiment done, the pH value of the medium with the succinic acid buffer only decreased from 5.9 to 4 (Soares & Seynaeve, 2000). The pH value of the medium without the succinic acid buffer had a low buffer capacity which caused a pH decrease from 5.3 to 2.2 (Soares & Seynaeve, 2000).

Because of the large size of the unadsorbed stream, the stream cannot be recycled back into the fresh feed. The current design therefore sends off the unadsorbed stream to a bio-digester. In addition to a major reduction in the size of reaction vessels and the maintenance of the concentration of sucrose in the fresh feed, this also ensures that there is no accumulation of non-adsorbing succinate salt in the system and also contamination reduction in the production reactors.

The optimum concentration of undissociated succinic acid leaving the desorption unit is 638.4mmol/l (Efe, et al., 2013). This is the highest concentration of undissociated succinic acid that can be achieved with the lowest water flowrate into the desorption unit. This concentration was used to determine the amount of hot water needed to be sent into the desorption unit.

#### *5.5.1.4 Filter and Drier*

Concentrated succinic acid stream of 300g/kg from the Crystallizer enters the filter. This stream is further concentration to 500g/kg (Efe, et al., 2013). The wet succinic acid from the filter is then finally dried in the drier to a final purity of 99.5% (on a mass basis).

#### *5.5.1.5 Mass balance assumptions*

Ammonia (nitrogen source) is not present in the production reactors to limit growth of the microorganism

All gasses in the production reactors are separated in an ideal manner

All the undissociated succinic acid are adsorbed and all succinate salts are not adsorbed and thus eluted from the column and sent back to the biodigester.

All succinic acid crystallises out with no impurities in the crystal

100% recovery of all masses through the units

### 5.5.2 Energy balance

The incoming process stream is required to be sterilised by heating it with high pressure steam from 20°C to 134°C after which it is cooled by using cooling water (at 20°C) to 30°C before sending it to the reactor. The heat duties required by each stream was calculated using equation *(*5-6*)*:

$$\boldsymbol{Q = mC_p(T_{out} - T_{in})} \quad \textit{(5-6)}$$

Q is the energy required or generated (kW), m is the mass flow of the media to be heated/cooled (kg/s), $C_p$ is the heat capacity of the stream ($kJkg^{-1}°C^{-1}$), $T_{out}$ and $T_{in}$ are the exit and inlet temperatures of the stream (°C). The $C_p$ used for all streams is the $C_p$ of water which is a value of 4.21 $kJkg^{-1}°C^{-1}$. For air, a $C_p$ value of 1.009 $kJkg^{-1}°C^{-1}$ was used. The area of the heat exchanger required is then calculated by equation *(*5-7*)*:

$$\boldsymbol{A = \frac{Q}{UF(LMTD)}} \quad \textit{(5-7)}$$

U is the overall heat transfer coefficient. This value for the feed sterilizer is 1500-4000 $Wm^{-2}°C^{-1}$ and that of the feed cooler and feed heat exchanger is 800-1500 $Wm^{-2}°C^{-1}$ (Sinnott, 2005). The overall heat transfer coefficients that were used are 2000 and 850 $Wm^{-2}°C^{-1}$ respectively. F is given a value of 1 for cases where one stream is at constant temperature or a value of 0.90 for a more conservative value for all other cases (except for the steriliser where F is assumed to be 1). The log mean temperature difference (LMTD) for a counter current flow (in °C) was calculated according to Equation *(*5-8*)*:

$$\boldsymbol{LMTD = \frac{(T_{hot,in} - T_{cold,out}) - (T_{hot,out} - T_{cold,in})}{ln\left[\frac{T_{hot,in} - T_{cold,out}}{T_{hot,out} - T_{cold,in}}\right]}} \quad \textit{(5-8)}$$

Table 5-10 Services available in the plant battery limit

| **Service** | **Cost** (University of Cape Town, 2014) |
|---|---|
| **Electricity – purchased from grid** | *ZAR 0.80/kWh* |
| **Municipal water (7barg)** | *ZAR 15/m³* |
| **Cooling water (20 ºC, 10 barg)** | *ZAR 0.60/m³* |
| **Low pressure (LP) steam (5 bar)** | *ZAR 60/tonne* |
| **Intermediate pressure (IP) steam (15 bara)** | *ZAR 80/tonne* |
| **High pressure (HP) steam (40 bara, 250ºC)** | *ZAR 100/tonne* |

The utilities used are electricity, high pressure (HP) steam, hot air and cooling water. A minimum approach temperature of 10 ºC was adhered to for all utility fluids. For cooling water, an outlet temperature of 45 ºC was used. This is the maximum allowable outlet temperature (Franklin, 2014). The amount for the cost of steam on Table 5-10 indicates the cost that will be required to produce steam in the plant, this does not mean steam will be purchased for use. Steam boilers are used to produce the steam required in the plant.

#### *5.5.2.1 Reactors*

According to Perry et al (1997), the power input to a homogenous reactor stirred tank is 0.6-2 $kW/m^3$. The maximum value of 2 $kW/m^3$ was used. This gives a power input of 800 kW for each 400$m^3$ reactor

used. The total power input required for the growth reactors is 1600 kW and the total power input for the production reactors was calculated to be 3200 kW.

#### *5.5.2.2 Flash drum and Evaporator*

Horizontal tube evaporators were selected. The energy requirement for both the evaporators and the flash drums were obtained from ASPEN.

#### *5.5.2.3 Rotary Filter and dryer*

The power consumption of the rotary filter (for filter areas in the range 1-80 $m^2$) is 0.8 $kWm^{-2}$ (Efe, et al., 2013).

The heat load ($Q_{Evaporation}$) in kJ and the minimum air requirement ($W_A$) in the dryer in kg/hr are calculated using equation (5-9) and (5-10) respectively. These equations were obtained from Efe et al (2013). $W_S$ is the mass of crystals to be dried (kg/h), h is the moisture fraction in crystals, $L_W$ is the latent heat of water at dryer operating conditions in kJ/kg and H0 and H1 are the mass of water vapour contained in saturated air at inlet and outlet temperatures respectively (kg/kg air) .

$$\boldsymbol{Q_{Evaporation} = 0.98 W_S h L_W} \quad (5\text{-}9)$$

$$\boldsymbol{W_A = \frac{W_S h}{H_1 - H_0}} \quad (5\text{-}10)$$

The initial moisture fraction of the crystal is assumed to be 500g/kg (Efe, et al., 2013). The entry temperature of the air into the dryer is 85°C which corresponds to a moisture content 20.28 g/kg saturated air while the outlet temperature out of the dryer is 40°C which corresponds to a moisture content 55.8 g/kg saturated air.

From the energy balance, Table 5-11 was generated for the utility usage of the different units. All utilities were calculated in 10% excess as suggested by Turton et al (1998) and adjusted to 2015 as the base year.

Table 5-11 Utility usage of different unit/equipment

| Unit/equipment | $Q_{Electricity}$ [kW] | $F_{Utility}$ [kg/yr] | Amount/unit [ZAR/unit] | Unit of costing | Total amount [ZAR] |
|---|---|---|---|---|---|
| Growth reactor | 1 600 | | 500 | ZAR/MWh | 3 660 000 |
| Production reactor | 3 200 | | 500 | ZAR/MWh | 12 600 000 |
| Sterilizer | | 3 220 | 100 | ZAR/tonne | 2 540 000 |
| Cooler | | 104 000 | 0.6 | ZAR/$m^3$ | 492 000 |
| Compressor | 2 490 | | 500 | ZAR/MWh | 9 850 000 |
| Centrifuge | 93 | | 500 | ZAR/MWh | 368 000 |
| Flash | | 89 700 | 100 | ZAR/tonne | 71 100 000 |
| Evaporator | | 69 300 | 100 | ZAR/tonne | 54 900 000 |
| Crystallizer | | 57 100 | 0.6 | ZAR/$m^3$ | 271 452 |
| Rotary filter | 33.5 | | 500 | ZAR/MWh | 133 000 |
| Rotary dryer (Hot air furnace) | 1 504 | | 500 | ZAR/MWh | 16 000 000 |
| Adsorption unit water heater | | 20 200 | 100 | ZAR/tonne | 181 000 000 |

## 5.6 Financial Assessment

The cost estimates are based on equipment sizing and basic simulation. This is usually done for the objective of getting a preliminary estimate or budget authorisation. According to the Association for the Advancement of Cost Engineering (AACE) International, the accuracy level of this cost estimate is about 30% (Association for the Advancement of Cost Engineering International, 2011). The method used to conduct financial analysis follow closely those prescribed by Sinnott (2005), Turton (1998) and EL-Halwagi (2012). Table 5-12 shows the parameters that were used for economic analysis.

Table 5-12 Parameters for economic analysis

| Parameter | Value | Unit |
|---|---|---|
| **Base year** | *2015* | |
| **Exchange rate $ to ZAR (Feb 2016)** | *16.03* | *Zar/$* |
| **Location index** | *1.09* | *SA/US* |
| **Inflation rate** | *8* | *%* |
| **Tax rate** | *28* | *%* |
| **Discount rate** | *20* | *%* |
| **Construction time (from start of construction)** | *1* | *year* |
| **Plant life** | *10* | *years* |
| **Plant capacity** | *40 000* | *ton/yr* |
| **Price of succinic acid** | *3* | *$/kg* |
| **Working time** | *7920* | *hrs* |
| **Cost index 1998** | *389.5* | *-* |
| **Cost index 2004** | *444.2* | *-* |
| **Cost index 2015** | *513.1* | *-* |
| **Lang factor** | *3.9* | *-* |
| **Depreciation** | *10* | *Years* |

### 5.6.1 Capital and Operating cost

The delivered equipment cost (DEC) in $ is calculated using equation (5-11) as well as equation (5-12) (for shell and tube heat exchangers) as given by Sinnott (2005) where C is the cost constant, S is the characteristic size parameter and n is the index for that type of equipment in the unit given on Table 5-13. The cost of equipment has a cost basis from mid-2004. The location index and exchange rate were also accounted for in the calculations.

$$DEC = CS^n \quad (5\text{-}11)$$

$$DEC = (bare\ cost\ from\ fiqure) \times Type\ factor \times Pressure\ factor \quad (5\text{-}12)$$

Table 5-13 Delivered equipment cost, cost factors for use in equation (5-14)

| Equipment | Size unit, S | Size range | Constant C,$ | Index n | Comment |
|---|---|---|---|---|---|
| Agitators Propeller Turbine | Driver power, kW | 5-75 | 1900 | 0.5 | |
| Boilers packaged up to 10 bar | kg/h steam | $(5-50)\times 10^3$ | 120 | 0.8 | Oil or gas fired |

| | | | | | |
|---|---|---|---|---|---|
| Boilers packaged 10 to 60 bar | kg/h steam | $(5-50)\times10^3$ | 100 | 0.8 | Oil or gas fired |
| Centrifuges (Horizontal baskets) | Diameter (m) | 0.5-1.0 | 58 000 | 1.3 | Carbon steel x 1.7 for SS |
| Centrifuges (Vertical baskets) | Diameter (m) | 0.5-1.0 | 58 000 | 1.0 | Carbon steel x 1.7 for SS |
| Compressors (centrifugal) | Driver power, kW | 20-500 | 1920 | 0.8 | Electric, max pressure 50 bar |
| Compressors (Reciprocating) | Driver power, kW | 20-500 | 2700 | 0.8 | Electric, max pressure 50 bar |
| Dryers (Rotary) | Area, $m^2$ | 5-30 | 35 000 | 0.35 | |
| Evaporators (Vertical tube) | Area, $m^2$ | 10-100 | 20 000 | 0.53 | Carbon steel |
| Filters (plate and frame) | Area, $m^2$ | 5-50 | 8 800 | 0.6 | Cast iron |
| Filters (Vacuum and drum) | Area, $m^2$ | 1-10 | 34 000 | 0.6 | Carbon steel |
| Furnaces (process cylindrical) | Heat abs, kW | $10^3$-$10^4$ | 540 | 0.77 | Carbon steel x 2.0 SS |
| Furnaces (box) | Heat abs, kW | $10^3$-$10^5$ | 560 | 0.77 | Carbon steel x 2.0 SS |
| Reactors (jacketed, agitated) | Capacity $m^3$ | 3-30 | 15 000 | 0.40 | Carbon steel |
| Reactors (jacketed, agitated) | Capacity $m^3$ | 3-30 | 31 000 | 0.45 | Glass lined |
| Tanks (Process, vertical) | Capacity $m^3$ | 1-50 | 2 400 | 0.6 | Atmospheric pressure, carbon steel. X 2 SS |
| Tanks (Process, horizontal) | Capacity $m^3$ | 10-100 | 2 900 | 0.6 | Atmospheric pressure, carbon steel. X 2 SS |
| Tanks (Storage, floating roof) | Capacity $m^3$ | 50-8 000 | 4 350 | 0.55 | Atmospheric pressure, carbon steel. X 2 SS |
| Tanks (Storage, cone roof | Capacity $m^3$ | 50-8 000 | 2 300 | 0.55 | Atmospheric pressure, carbon steel. X 2 SS |

Table 5-14 presents the major equipment capital cost for the process. A brief explanation of justification for the cost is also shown. The equipment cost were calculated using cost indices as presented in equation (5-13). These indices are used to adjust for the different location and year of the available cost information that is used. The Chemical Engineering Plant Cost index is used to adjust the difference in years while for the correction of location, the Cost Data Online (2008) was used.

$$C_{Present} = C_{Past} \times \left(\frac{Index_{Present}}{Index_{Past}}\right) \quad (5\text{-}13)$$

Together with the plant lifespan (of 10 years), the equipment life of each unit was accounted for as recommended by the South African revenue services (South African Revenue Service, 2009). These two information were used to determine the total number of each unit that will be required.

Table 5-14 Capital cost of equipment and justification thereof

| Unit/equipment | Capital Cost (ZAR) | Comment |
|---|---|---|
| Sterilizer heat exchanger (sucrose) | 66 100 000 | Modelled as a heat exchanger. As reported by Efe et al (2013), U is taken as 2000 W/$m^2$/°C |
| Sterilizer heat exchanger (nutrient) | 9 450 000 | Modelled as a heat exchanger. As reported by Efe et al (2013), U is taken as 2000 W/$m^2$/°C |
| Sterilizers | 9 450 000 | Modelled as a heat exchanger |

| | | |
|---|---|---|
| **Cooler** | **18 900 000** | **Modelled as a heat exchanger** |
| **Compressor** | **153 000 000** | **Based on the capacity of air and the outlet pressure, a reciprocating compressor was selected (Sinnott, 2005). This type of compressor is can be used over a wide range of capacities and pressure and they are used extensively in industrial operations.** |
| **Growth Reactor** | **72 300 000** | **The capacity of the growth reactor was determined by assuming 12 hours residence time. The size of each Growth Reactor was assumed to be 400 $m^3$ which is the largest achievable volume for aerated fermenters.** |
| **Production Reactor** | **145 000 000** | **The capacity was determined by using a productivity for *E. coli* of 1.2 g/l/h (89g/kg/h) reported by Cheng et al (2012) was used. This value is the lowest productivity reported for a fed batch dual phase fermentation and it was used because there is currently no known productivity for dual phase fermentation of Saccharomyces cerevisiae.<br>The size of each Production Reactor was assumed to be 400 $m^3$ which is the largest achievable volume for aerated fermenters.** |
| **Centrifuge** | **2 820 000** | **For a centrifuge with a diameter of 0.69 and a capacity of about 80 $m^3$/h, the engine power is reported to be about 93 kW (Efe, et al., 2013)** |
| **Adsorption column** | **31 600 000** | **The dimensions of the adsorption column were varied to find the optimum column dimension to be 1.5 diameter and 10.7 length (Efe, et al., 2013). The cost of catalyst is incorporated** |
| **Flash** | **7 870 000** | **Cost as a shell and tube heat exchanger** |
| **Evaporator** | **141 000 000** | **Cost of a vertical tube evaporator** |
| **Crystallizer** | **236 000 000** | **Modelled as a heat exchanger** |
| **Rotary filter** | **6 510 000** | **A flux value of 400 $Lm^{-2}h^{-1}$ was used (ranges from 200-500). The power consumption was reported as 0.8 $KWm^{-2}$.** |
| **Rotary dryer** | **10 000 000** | **Inclined horizontal rotary dryers are used** |
| **Hot air furnace** | **11 900 000** | **The radiant rate of a fired heater is 37.6kW/$m^2$ (Walas, 1988)** |
| **Adsorption water heater** | **9 450** | **Hot water enough to make the mole fraction of the succinic acid out of the adsorption unit 0.125 is heated from 20 to 150°C** |
| **Reactant storage tank** | **15 100 000** | **Cost calculation for a cone roof storage tank was used (Sinnott, 2005)** |
| **Product storage tank** | **14 400 000** | **Cost calculation for a cone roof storage tank was used (Sinnott, 2005)** |
| **Total** | **952 000 000** | |

The equations used to calculate the fixed, working and total capital cost/investment are presented in equations (5-14); (5-15) and (5-16) where FC is the Fixed Capital, DEC is the delivered equipment cost, N is the total Number of equipment in the process, q is the equipment delivered to the site, LF is the Lang Factor, WC is the Working Capital and TCI is the Total Capital Investment. The Lang factor of a solid-fluid plant type of 4.55 (Sinnott, 2005). This factor incorporates the cost of major equipment, equipment erection, piping, instrumentation, electrical, buildings and process, utilities, storages, site development and ancillary buildings. Because the costing of utilities and storage have been done separately, these components were removed from the total Lang factor which then reduced the Lang factor to 3.9. A Lang factor of 3.9 was then used.

$$FCI = \mathrm{LF} \times \sum_{q=1}^{N_{Equipment}} DEC_q \quad (5\text{-}14)$$

$$WCI = 0.15 \times FCI \quad (5\text{-}15)$$

$$TCI = FCI + WCI \quad (5\text{-}16)$$

The FCI is the money required to pay for the “processing equipment and the ancillary units, acquiring and preparation of land, civil structures, facilities and control systems” (EL-Halwagi, 2012). The fixed capital is the summation of the manufacturing (or direct) and nonmanufacturing investment. The manufacturing FCI are the cost items that are directly associated with production such as “process equipment, installation, piping/compression, process instrumentation, process utility facilities and distribution, process waste treatment systems, and all the civil work associated with the production units” (EL-Halwagi, 2012). The nonmanufacturing FCI includes fixed cost items that are not directly linked to production such as “land, analytical laboratories, storage areas and waste treatment, engineering centers, research and development laboratories, administrative offices, cafeterias and restaurants and recreational facilities”.

The WCI is the money needed to start up the plant and finance the first few months of operation, to pay salaries, raw material inventories etc. before production (typically for one to two months of raw materials are stockpiled prior to production). The WCI ranges between 10 to 25% of the FCI.

The TCI is the money needed to purchase and install the plant and all its ancillaries to start the operation of the process. This is a summation of both the FCI and the WCI.

### 5.6.2 Financial Basis

#### *5.6.2.1 Operating cost*

The operating cost is the continuous expenses needed to run the plant once the plant is in production mode. This includes the fixed operating costs that do not vary significantly with production rate and the variable operating cost that are only incurred when the plant operates. The fixed operating costs are the operating labour, depreciation, property tax insurance, rent and plant overheads (Medical services, safety, holiday allowance, restaurant facilities and employee benefits). The variable costs are raw materials and utilities.

Table 5-15 Estimation of operating cost

| Cost | Estimate | Amount [ZAR/yr] | Source |
|---|---|---|---|
| Variable operating cost | | | |
| Sucrose | - | 232 000 000 | 3550 ZAR/tonne (Taylor, et al., 2015) |
| Ammonia | - | 62 800 000 | 3210 ZAR/tonne (Jones, 2016) |
| Sodium hydroxide | - | 6 297 | 2000 ZAR/tonne (Markestad, 2010) |
| Utilities | - | 181 000 000 | Calculated (see section 5.5.2) |
| Labor | From manning estimates | 10 800 000 | www.statssa.gov.za/ |
| Maintenance | $\frac{10}{100} \times FC$ | 9 520 000 | This cost is considered to be divided evenly between labour and material (Sinnott, 2005) |
| Miscellaneous materials (plant supplies) | $\frac{10}{100} \times Maintenance$ | 950 000 | (Sinnott, 2005) |
| Administration | $\frac{2}{139} \times FC$ | 10 800 000 | Guess |
| Plant overheads | $Labour\ cost$ | 10 800 000 | (Sinnott, 2005) |
| Depreciation | Calculated | 95 200 000 | (South African Revenue Service, 2009) |
| Property tax | 28% of profit | 395 000 000 | South African tax rate |
| Marketing, distribution and selling | $\frac{5}{100} \times Variable\ cost$ | 23 800 000 | Guess |
| Fixed operating cost | | | |
| Insurance | $\frac{1}{100} \times TC$ | 952 000 | (Sinnott, 2005) |
| Legal expenses | $\frac{1}{100} \times FC$ | 952 000 | (Sinnott, 2005) |

Table 5-16 shows the breakdown of the operating cost for this process. The labour cost was obtained from www.statssa.gov.za/ . The salaries were for 2010 and therefore the highest values in the ranges were used. The plant is designed to be a 24 hour running plant. There are four major units namely, pre-treatment, reaction, recovery/extraction and purification/concentration. There are three shifts that run for the shift foreman and the general foreman and one shift allocated for the assistant manager and the manager. This makes the total number of shifts for the shift foreman, general foreman, assistant manager and manager to be 12, 12, 1 and 1 respectively. The shift foreman was categorised as a top 10% technician with a monthly salary of R 15 500 while the general foreman was categorised as a top 5% technician with a monthly salary of R19 250. The assistant manager and manager were categorised as top 10% and top 5% manager respectively. This corresponds to a salary of R 31 000 and R 48 000. This is presented on Table 5-16. The yearly cost for labour is R 10 800 000/yr.

Table 5-16 Monthly operating salary allocation

| Employee | Number/shift | Shifts | Units | Total employee | Salary [ZAR/month] | Total salary [ZAR/month] |
|---|---|---|---|---|---|---|
| Shift foreman | 2 | 3 | 4 | 24 | 15 500 | 360 000 |
| General foreman | 2 | 3 | 4 | 24 | 19 250 | 462 000 |
| Assistant manager | 1 | 1 | - | 1 | 31 000 | 31 000 |
| Manager | 1 | 1 | - | 1 | 48 000 | 48 000 |
| Total | 901 000 | | | | | |

#### *5.6.2.2 Revenue Choice*

The revenue is attained solely from the sale of succinic acid. The revenue for a particular year *i* was calculated by using equation *(*5-17*)*.

$$\boldsymbol{Revenue_{year\ i}} = \mathbf{Revenue} \times (\mathbf{1} + \boldsymbol{Inflation\ rate})^{\boldsymbol{year\ i}} \quad (5\text{-}17)$$

The selling price used is 3 $/kg (converted to rand using the exchange rate of 16.03 R/$). This value was a roundup of the selling price of 2 940 $/t for bio-based market and 2 500 $/t for total market (bio+fossil) (Taylor, et al., 2015). Efe et al (2013) also reported succinic acid selling price to be about 3 $/kg (2.26 $/kg) but warns that the price has a potential to drop to a value as low as 1 $/kg.

#### *Expenses*

The total expenses was calculated as the sum of all the operating costs. This included fixed and variable operating costs and other operating costs. The expenses for a particular year was calculated by using equation *(*5-18*)*.

$$\boldsymbol{Expenses_{year\ i}} = \mathbf{Expenses} \times (\mathbf{1} + \boldsymbol{Inflation\ rate})^{\boldsymbol{year\ i}} \quad (5\text{-}18)$$

#### *5.6.2.3 Escalation Rate*

Escalation rate or inflation rate is the rate at which the average prices of goods and services reduce in value. This is the 2015 value of 8%.

#### *5.6.2.4 Gross profit*

The gross profit for each year is the difference between the revenue and the expenses for each year.

#### *5.6.2.5 Depreciation Type and Rates*

Depreciation is the annual income tax deduction that is intended to allow the company to recover from the cost of an asset over a period of time. There are several methods of calculating depreciation. In this project, the straight line approach was used. This is the most commonly used method that measures annual depreciation, the initial value of property, the recovery period over which the depreciation is made in years, and the salvage(scrap) value which corresponds to the worth of the property at the end of the recovery period. Equation *(*5-19 was used to calculate depreciation. A value of 10 years was used for the process units. In the calculations, the scrap value was assumed to be zero.

$$\boldsymbol{DEPRECIATION} = \frac{\boldsymbol{INITIAL\ VALUE - SCRAP\ VALUE}}{\boldsymbol{RECOVERY\ PERIOD}} \quad (5\text{-}19)$$

Depreciation rates depends on government policy, and on the accounting practices of the company. In this financial analysis, a high depreciation rate was used to reduce tax.

***Net profit***

The net profit is calculated by using

$$\boldsymbol{Net\ profit} = (\mathbf{Gross\ profit} - \mathbf{Depreciation}) \times (\mathbf{1} - \boldsymbol{Tax\ rate}) \quad (5\text{-}20)$$

#### *5.6.2.6 Level of Taxation*

Company tax in South Africa is currently 28% of all profit from the business for businesses that make income greater than R300 000. The profit on which tax is paid is the income less expenses less depreciation.

## 5.7 Profitability Analysis

### 5.7.1 Income statement

Table 5-17 Income statement of the project on the 1th operational year

| Succinic acid plant income statement | |
|---|---|
| For the end of the 1th operational year | |
| Parameter | Value [million ZAR] |
| Revenue (cost of succinic acid sold) | 2 080 |
| Gross profit | 1 500 |
| Expenses | |
| Variable operating cost | 476 |
| Fixed operating cost | 2.06 |
| General expenses | 576 |
| Total expenses | (577) |
| Earnings before interest, taxes, depreciation and amortization (EBITDA) | 1 500 |
| Depreciation | 95.2 |
| Taxable income | 1 409 |
| Tax | 395 |
| Net profit | 1 014 |

### 5.7.2 Cash Flow indicators

#### *5.7.2.1 Break Even*

This is used to determine the amount of throughput that will make the total production cost equal to the total income (revenue).

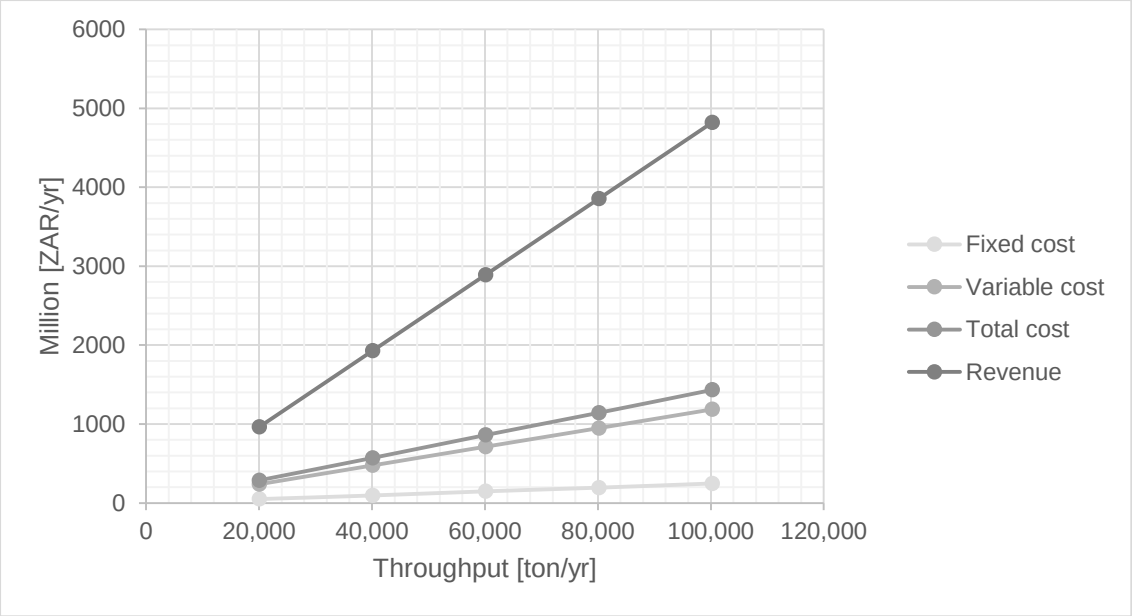


Figure 5-6: Throughput against cost to determine the breakeven point

Figure 5-6 shows that the revenue gradient is always steeper than that of the total operating cost. At the current selling price ($3/kg), the plant is profitable. Efe et al (2013) however reported that the price of succinic acid has been known to be fluctuating therefore the sensitivity of the price of succinic acid on the overall profitability of the process will be analysed under the sensitivity analysis.

At any given throughput, breakeven has been exceeded as presented on Figure 5-6. The profitability margin increases as the throughput increases. The plant will therefore benefit from economies of scale and obtain greater savings as the throughput increases.

A throughput of 40 000 ton/yr of succinic acid was selected. This was based on the average succinic acid plant sizes reported in literature. Vaswani el al (2010) designed a plant with a capacity of 37 500 t/yr. In 2012, Reverdia opened a plant in Cassano Spinola, Italy with a capacity of 10 000 t/yr (Reverdia, 2014). In 2015, BioAmber reported that they have opened a plant with a capacity of 30 000 ton/yr (www.bio-amber.com). Efe et al (2013) hypothetical plant was designed to operate with a 30 000 ton/yr production. The throughput choice was therefore not based on maximizing economics but on the feasibility of operation as discussed by the aforementioned references.

#### *5.7.2.2 Cumulative cash flow analysis*

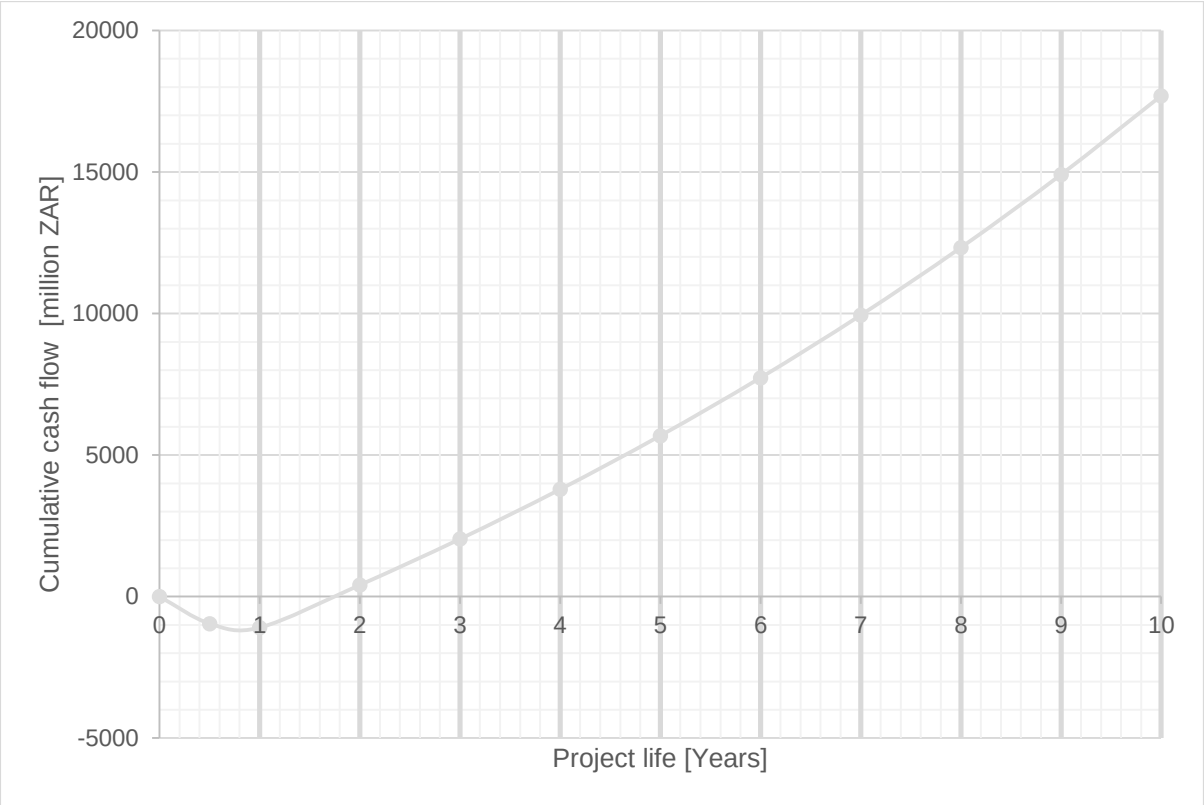


Figure 5-7: Project cash-flow diagram

Figure 5-7 shows the project cash flow diagram. Given that it take one year for the construction of the plant, the plant will begin to make profit during the 1st year of operation. This is a relatively short period of time. The profit potential of this venture is therefore high.

In analysing the cumulative cash flow, the project life is considered as an isolated system, and taxes on profits and the effect of depreciation are not considered.

### 5.7.3 Profitability indicators

#### *5.7.3.1 Payback Period (PBP)*

This is the payout period indicating how fast the depreciable FCI can be recovered. The payback period of the project is 1 year. This means that it takes 1 year to pay back the fixed capital investment. This makes the project a low risk venture.

#### *5.7.3.2 Net Present Value (NPV)*

This value is referred to as annual cost when the NPV of the project is positive and annual revenue when the NPV of the project is negative. For this project at a discount rate of 20%, the NPV is 9.85 billion annual revenue at the end of 10 years. This indicates a profitable project. A discount rate of 20% was used which was significantly higher than the weighted average Cost of Capital (which is 10.7%) of various firms in the chemical industry because the biobased plant has a higher risk than an average chemical plant (Bibolet, et al., 2011).

#### *5.7.3.3 Internal rate of return*

This value shows how well the capital investment is being used. It is the value of the discounted rate that will result in a net present value of zero. The internal rate of return for this project is 108%. This is significantly higher than the discounted rate of the project. From the IRR of value, it can be deduced that the project is therefore worth investing in.

## 5.8 Sensitivity Analysis

### 5.8.1 Optimisation of major units

The design used follow closely the prescribed design by Efe et al (2013). The reactor conditions were optimised in terms of microorganism optimum temperature and pH. The adsorption column was optimised by Efe et al (2011). The optimum dimensions of the adsorption unit was investigated and the size determined was used in this design. The optimum concentration of the stream leaving desorption unit determined by Efe was also used in this design. The crystalliser was operated at a temperature of 27°C. This corresponds to a solubility of about 96 $kg^{-1}$ (Attane & Doumani, 1949). These optimum parameters were used in this design.

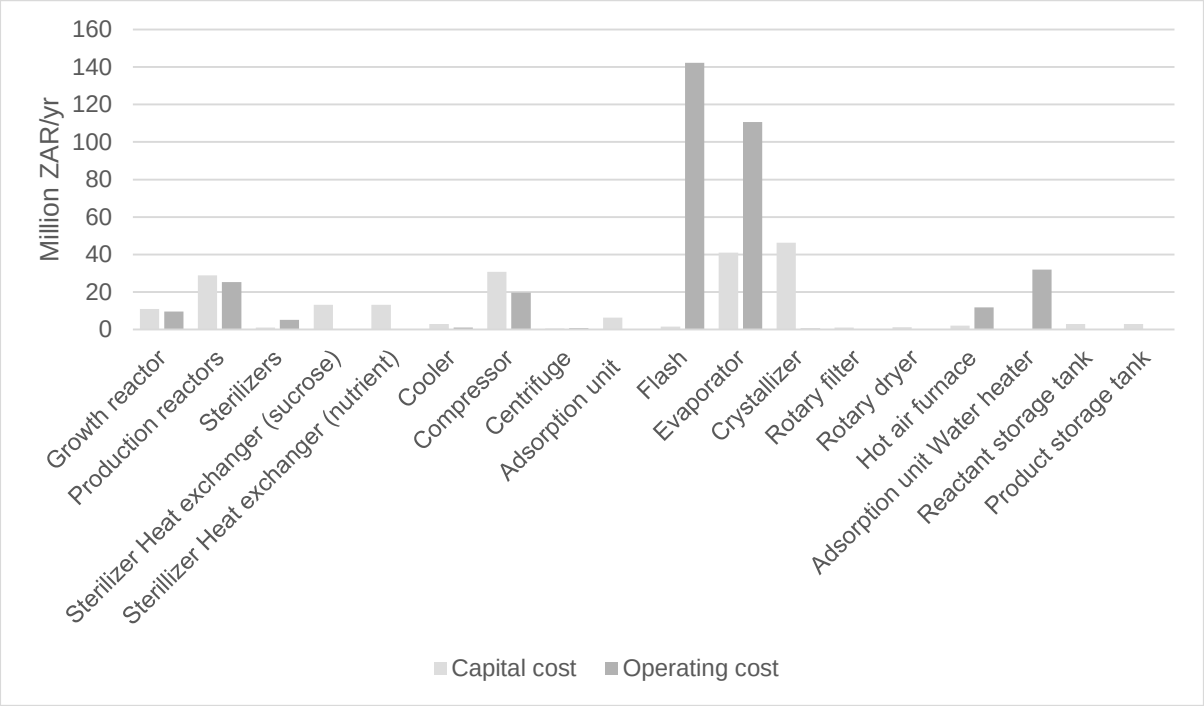


Figure 5-8: Comparison of Capital and Operating costs of major units

Figure 5-8 shows a comparison between the capital and operating costs between major units. For the capital cost to be compared with the operating cost, the capital cost was presented in a yearly basis by dividing the capital cost with the operational lifespan of the plant (10 years).

From Figure 5-8, it can be seen that the flash and evaporator have the highest operating costs. A lot of energy is required to concentrate succinic acid to the final product required. Energy is very expensive which explains the proportion contributions of these units to the total operating cost. The operating cost of the production reactor and the adsorption unit water heater are also significantly high because of the energy requirement of the blades that are used to keep the reactor broth homogenous and heating up solvent water for the adsorption unit. Although a lot of cooling water is required for the crystalliser because the minimum approach temperature between the cooling water and the final crystallisation is quite low (7°C), the crystalliser operating cost does not contribute significantly to the operating cost because the price of cooling water is relatively cheap.

The crystallisers, evaporator, compressor and the production reactor contribute high proportions toward the capital costs. The justification for the high capital cost of the crystalliser is due to very large surface area required to cool down the evaporator effluent from 104°C to the crystallisation temperature of 27°C. There temperature interval of the cooling is very high. The evaporator is quite expensive (Sinnott, 2005). The compressor and the production reactor high costs are due to very high volumes of capacity needed upstream of the succinic acid process.

The steriliser operating cost were able to be reduced by the introduction of heat integration for these units. The economic payoffs are great because the heat exchangers introduced to achieve this (although have large areas) are very cheap.

There are no available models for the major units (reactors and adsorption unit). These units were designed by using specific optimised values. These models are not flexible enough to investigate effect that varying local variables will have on the global process. A sensitivity analysis on individual units can therefore not be done in this study. From Figure 5-8, the major units that require optimisation and sensitivity analysis in subsequent studies can be seen as discussed earlier.

### 5.8.2 Sensitivity of the amount of biomass recycled on succinic acid production

The significance of the effect of different amounts of biomass recycled into the reactor on the production of succinic acid in the production reactor is of great interest. The growth and production reactor metabolic equations are however completely independent. The regulatory role that biomass plays in the production reactor is not captured by the metabolic engineering model. Although this is a very significant sensitivity analysis, the role that biomass has on succinic acid production cannot be investigated.

### 5.8.3 Sensitivity analysis on raw material prices

The sucrose price of R3.55/kg used was obtained from Taylor et al (2015). This value is quite close to the South African 2015 export price which is R3.6/kg (South African Department of Trade and Industry, 2016).. This was the lowest price of sucrose recorded within the six years looked at. The value of sucrose (H1701) export has generally increased from R4.33/kg in 2010 to R8.25/kg in 2016. Sucrose import has also generally increased from 6.48 R/kg to 8.04 R/kg from 2010 to 2016 respectively (South African Department of Trade and Industry, 2016). Figure 5-9 shows the price of sucrose from 2010 to 2016.

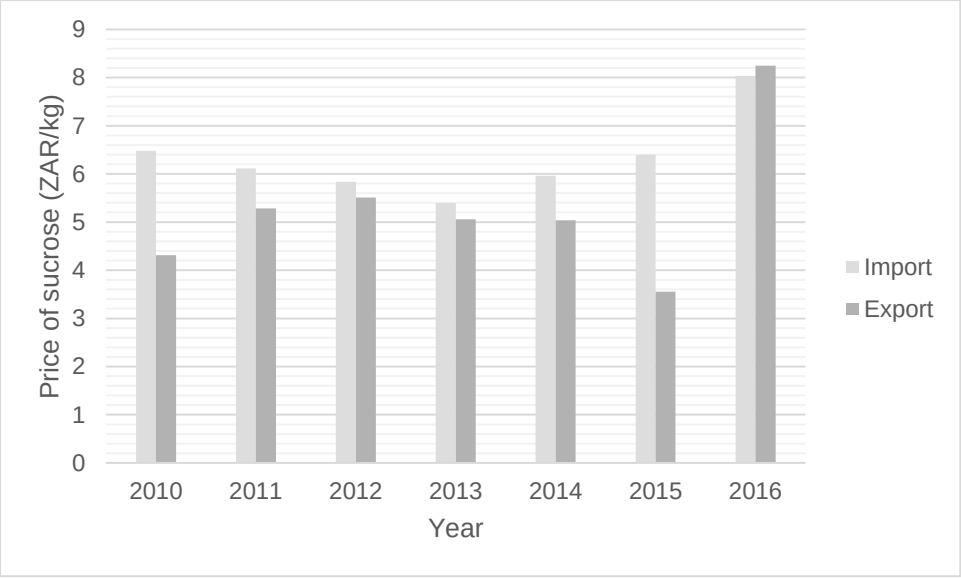


Figure 5-9: Price of sucrose import and exports from 2010 to 2016 (South African Department of Trade and Industry, 2016)

A sensitivity analysis was done on the proportion of sucrose cost in the overall operating cost ranging from 2 to 10 R/kg.

Table 5-18 Sensitivity of sucrose price on process profitability

| Cost [ZAR/kg | Percentage of operating cost [%] | ROI [%] | PBP [YRS] | NPV [million ZAR] | IRR [%] |
|---|---|---|---|---|---|
| 4 | 51.8 | 134 | 1.62 | 4760 | 72 |
| 5 | 57.3 | 127 | 1.71 | 4480 | 68 |
| 6 | 61.7 | 120 | 1.80 | 4190 | 64 |
| 7 | 65.3 | 113 | 1.91 | 3900 | 60 |
| 8 | 68.2 | 106 | 2.02 | 3610 | 56 |
| 9 | 70.7 | 98.6 | 2.16 | 3320 | 52 |
| 10 | 72.9 | 91.6 | 2.31 | 3030 | 48 |

***5.8.3.1***

The succinic acid process shows a profitable process from a sucrose cost of R4/kg to the high sucrose cost of R10/kg as presented on Table 5-18. The proportion contribution of sucrose cost to the total operating cost shows a gradual increase from 51.8% to 72.9% as the sucrose price increases from R4/kg to R10/kg.

### 5.8.4 Sensitivity analysis on product prices

The 2015 selling price of succinic acid was reported as $3/kg (R48 000/ton) (Taylor, et al., 2015). Maleic anhydride is the chemical alternative of succinic acid. As described previously, succinic acid can act as a direct substitute for Maleic anhydride. The South African import of Maleic anhydride varied from R13 300 000 in 2013 to R25 400 000 in 2016. The import volumes for these years were 837 tonnes and 1 740 tonnes in 2013 and 2016 respectively. These results in price of R15 900/tonne and R14 600/ton import prices. The South African export of maleic anhydride earned R1 260 000 in 2013 and R1 470 000 in 2016 with export volumes of 24.3 tonnes and 18.9 tonnes respectively which results in selling price of R51 900/ton and R77 800/ton.

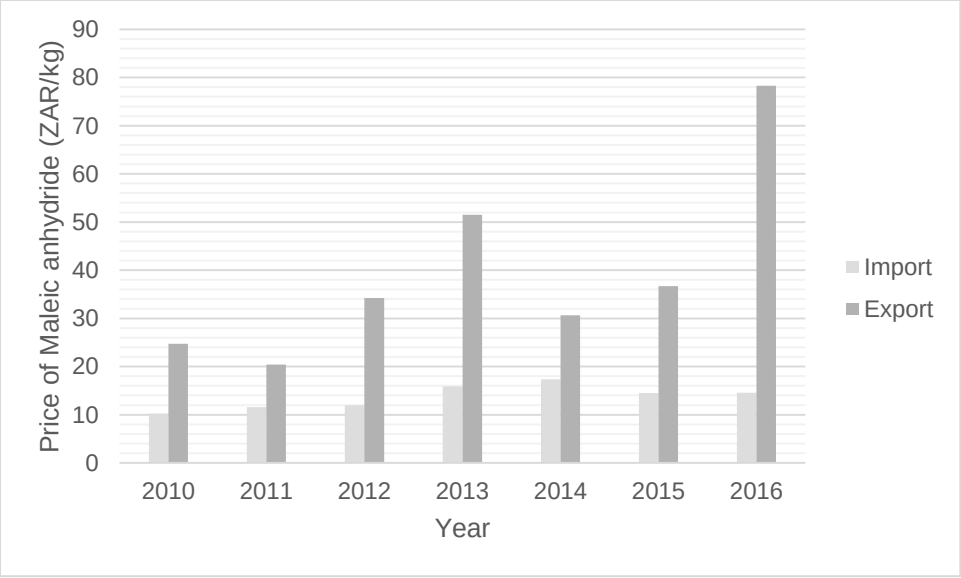


Figure 5-10: Price of Maleic anhydride imports and exports from 2010 to 2016 (South African Department of Trade and Industry, 2016)

From the prices presented on Figure 5-10, it was decided to vary the succinic acid price between R14/kg to R80/kg and observe the effect on the profitability indicators of the entire process.

Table 5-19 Sensitivity of succinic acid price on process profitability

| Cost [ZAR/kg] | ROI [%] | PBP [YRS] | NPV [million ZAR] | IRR [%] |
|---|---|---|---|---|
| 14 | -3.54 | 42.6 | -872 | -25.0 |
| 20 | 21.2 | 7.68 | 144 | 3.00 |
| 40 | 104 | 2.06 | 3530 | 55.0 |
| 60 | 186 | 1.19 | 9610 | 103 |
| 80 | 269 | 0.836 | 10300 | 150 |

Table 5-19 shows that at a succinic acid price of R14 000/ton, the process is very unprofitable. R20 000/ton shows a slight profitability. The profitability of the succinic acid process increases sharply as the cost of succinic acid increases with an extremely high profitable process at a succinic acid price of R80 000/ton. From the above sensitivity analysis using the selling price of Maleic anhydride which is the petrochemical alternative of succinic acid, it can be deduced that biological production route of succinic acid is compatible with the petrochemical production route.

# 6 Conclusion and recommendations

## 6.1 Conclusion

Quantitative and qualitative analysis was done on an initial 39 chemicals for this study. The preliminary selection identified 21 chemicals that can be produced from sucrose via a biological route. The list of chemicals contained alcohols, biopolymers, carboxylic acids, hydrocarbons and speciality chemicals. This was then followed by a quantitative study that allowed the selection of 7 chemicals. The factors that were considered in identifying the top 7 chemicals were chemical product yield (theoretical and actual yield), TRL, market size (world market size, SA imports and SA export) and selling price. The 7 chemicals selected from the quantitative study are citric acid, ethanol, lactic acid, succinic acid, acetic acid, glutamic acid and itaconic acid. Quantitative study was then followed by a qualitative analysis. The qualitative analysis was majorly based on opinions of experts and were supported by several literature reports. The major factors that were used in selecting the top three chemicals are how established and competitive the markets are and if the chemicals of interest have multiple uses. The qualitative study identified succinic acid, lactic acid and citric acid as the top 3 chemicals. Succinic acid was then selected for a techno-economic study because it has a higher performance (in terms of yield and productivity) and generates less carbon footprint than the petroleum based succinic acid, it has multiple application via BDO and PBS, competiveness for niche application and its overall favourable environmental process that uses up carbon dioxide from the environment.

It is important to note that the list of proposed chemicals for a techno-economic study is subjective in that it is based on a selected set of criteria. The data used also is constantly changing. Because technology is constantly changing, technological advances will introduce new compounds or change the order of the compounds proposed. There is no correct answer to the question, what chemical is best to look at in the context of South African industry. The case studies looked at have shown that the financial and skill investment in a particular chemical/fuel is the driver of industry. The question is not which direction is industry going but which gap has been identified in industry to make a conscious focus on the development in that direction.

The succinic acid process was designed as suggested by Efe et al (2013). Here succinic acid is produced in a dual phase reactor system to allow for optimal growth of *Saccharomyces cerevsiae* (at a pH of 6-7) and production of succinic acid (at a pH of 3-4). The low production pH allows for the desired production of undissociated succinic acid. The production of undissociated succinic acid eliminates the need of converting dissociated succinic acid (produced at a high pH) to the desired undissociated succinic acid using electrodialysis which would have made downstream processing more complicated and expensive.

The succinic acid process designed shows high profitability. The main contribution to the operating cost is sucrose. This, however, does not change the profitability of the process significantly with varying sucrose price because the overall cost consists mostly of the capital cost. The second main contributor to the operating cost is the energy cost. This is comprised mostly of the flash and evaporator operating cost. The highest contributors to the capital cost are also the flash unit and the evaporators. It is strongly recommended that these units are subjected to optimisation. With increased concentration of final titre upstream, a bulk of this cost can be curbed. The third contributor to the operating cost is the cost of the production reactors. This can be reduced by increasing the productivity of the succinic acid production process.

The process is very sensitive to the price of succinic acid. Profitability of the process is seen with succinic acid prices higher than R14 000/ton. With a raw material of sucrose and one product (succinic acid), the profit potential of the venture is very high. Bio-succinic acid is a relatively new product in the chemical industry. Specialisation provides room for succinic acid to gain more economic advantage. Since the succinic acid process is not fully investigated and optimised, there is a cost reduction potential for the process.

Although the succinic acid process shows potential for future development, it does not fare well in terms of IP considerations. The current established technologies developed for the production of succinic acid are not accessible for academics to be developed.

## 6.2 Recommendations

This study has been done considering several factors that are crucial in determining the chemicals and fuels that South Africa should consider producing; however, availability of relevant data for the South African industry was very limited. Cost and production information of platform chemicals and fuels that are specific to South Africa would give a more suitable prediction.

A major recommendation includes the experimental investigation of the feasibility of the metabolic engineering of *Saccharomyces cerevisiae* strain, of the fermentation parameters and the adsorption unit. The metabolic model can also then be compared to experimental results. In addition, experimental work will provide more information for sensitivity analysis, allowing the overall process to be more robust. The major factors that affect the adsorption unit analysed experimentally by Efe et al (2010) that should be incorporated in a model are:

- The pH in the reactor, which affects the percentage of undissociated succinic acid (that will not be adsorbed). This is a feature that requires further analysis because within a pH range of 4-4.5, there is between 30-60% undissociated succinic acid as a ratio of total succinate
- Concentration ratio of acetic acid to succinic acid affects the adsorption capacity. The amount produced will depend on the bacteria/yeast strain
- Concentration of ethanol in the solution. Succinic acid has a low solubility in ethanol compared to in an aqueous solution
- Effect of temperature on the adsorption capacity
- Catalyst used

Other units that need further investigation are the desorption unit and crystallization unit. It is necessary for a pilot plant to be developed in order to attain valuable information on material and energy balance, process conditions and other design variables. The most important units for optimisation however are the production reactors, the flash unit and the evaporators as they constitute a large fraction of the capital and operating costs. The process was developed using very little experimental data. For a more reliable data, this design should be forwarded for pilot scale analysis. The project would be more relevant and reliable if academia work in collaboration with an existing succinic acid company.

The bulk of the operating cost was the cost of sucrose and the cost of the utility used. To reduce the raw material cost, a study on cheaper (and more effective) carbon sources such as lignocellulose and molasses can be looked at. To cut down on utility cost, heat optimisation and integration of the process should be looked at.

Improving the value of succinic acid by producing 1,4-Butanediol is one of the many chemicals that have been looked at in literature. This should be done in conjunction with other chemical engineering units as further subsequent steps of value addition of succinic acid are not biological processes. Future research targets should involve collaboration of several chemical engineering units to obtain the required expertise. It has been suggested that instead of purifying the succinic acid, the platform chemical be used for formation of another product such as 1,4-Butanediol i.e. one of the ways of cutting down cost would be to eliminate the need for succinic acid isolation by performing the production of 1,4-Butanediol conversion in the fermentation medium (Cukalovic & Stevens, 2008)

Integrated biorefinery is an area that is still in its infancy but should be considered to increase the economic benefit of processes. Instead of looking at the feasibility of individual chemicals and fuels, a study on the production of several chemicals combined in one plant should be researched. A process focused on the production of succinic acid and ethanol for example may be beneficial. This will allow the carbon dioxide waste produced in ethanol production to be used in succinic acid production. Another alternative for cost reduction would be developing an integrated sugar-succinic acid plant that directly utilises the juice from sugarcane crushing. A techno-economic study can then be based on several of these integrated processes.

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# Appendix A:

Table. A-1 Stream table for the Succinic acid production process

| Stream number | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **MASS [kg/hr]** | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Sucrose | 16500 | 16500 | 16500 | 16500 | 3300 | 13200 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Oxygen | 0 | 0 | 0 | 0 | 0 | 0 | 65900 | 65900 | 14300 | 51600 | 0 | 0 | 681 | 2460 | 2460 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Ammonia | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 4950 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Bug | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 24800 | 0 | 124000 | 0 | 124000 | 124000 | 99000 | 0 | 24800 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| CO2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 14900 | 37400 | 37400 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Water | 149000 | 149000 | 149000 | 149000 | 29700 | 119000 | 0 | 0 | 0 | 0 | 0 | 51200 | 0 | 565000 | 0 | 565000 | 432000 | 346000 | 133000 | 86500 | 109000 | 24100 | 99700 | 124000 | 5560 | 118000 | 95800 | 22400 | 22400 | 11200 | 11100 | 56.3 |
| SA | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 71900 | 0 | 71900 | 55000 | 44000 | 16900 | 11000 | 6750 | 10100 | 0 | 10100 | 0.285 | 10100 | 1.4 | 10100 | 10100 | 0 | 10100 | 0 | 10100 |
| Pyruvate | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 817 | 0 | 817 | 625 | 500 | 192 | 125 | 157 | 34.9 | 0 | 34.9 | 0.153 | 34.7 | 10.8 | 24 | 24 | 12 | 12 | 11.9 | 0.0602 |
| Acetic | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 817 | 0 | 817 | 625 | 500 | 192 | 125 | 157 | 34.9 | 0 | 34.9 | 0.853 | 34 | 24 | 10 | 10 | 5 | 5 | 4.97 | 0.0251 |
| Ethanol | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 4080 | 0 | 4080 | 3130 | 2500 | 959 | 625 | 785 | 174 | 0 | 174 | 62.5 | 112 | 109 | 2.52 | 2.52 | 1.26 | 1.26 | 1.25 | 0.00633 |
| Glycerol | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 4080 | 0 | 4080 | 3130 | 2500 | 959 | 625 | 785 | 174 | 0 | 174 | 0.263 | 174 | 0.2 | 174 | 174 | 86.9 | 86.9 | 86.5 | 0.437 |
| Nitrogen | 0 | 0 | 0 | 0 | 0 | 0 | 217000 | 217000 | 47000 | 170000 | 0 | 0 | 47000 | 170000 | 170000 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Total | 165000 | 165000 | 165000 | 165000 | 33000 | 132000 | 283000 | 283000 | 61300 | 221000 | 4950 | 75900 | 62600 | 980000 | 210000 | 771000 | 619000 | 495000 | 152000 | 124000 | 117000 | 34700 | 99700 | 134000 | 5620 | 129000 | 95900 | 32700 | 32700 | 11300 | 21400 | 11300 | 10200 |
| **MASS FRACTION [-]** | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Sucrose | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Oxygen | 0 | 0 | 0 | 0 | 0 | 0 | 0.233 | 0.233 | 0.233 | 0.233 | 0 | 0 | 0.0109 | 0.0025 | 0.0117 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Ammonia | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Bug | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.326 | 0 | 0.126 | 0 | 0.161 | 0.2 | 0.2 | 0 | 0.2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| CO2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.237 | 0.0381 | 0.178 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Water | 0.9 | 0.9 | 0.9 | 0.9 | 0.9 | 0.9 | 0 | 0 | 0 | 0 | 0 | 0.674 | 0 | 0.577 | 0 | 0.733 | 0.699 | 0.699 | 0.874 | 0.699 | 0.926 | 0.696 | 1 | 0.921 | 0.989 | 0.919 | 0.998 | 0.684 | 0.684 | 0.991 | 0.523 | 0.991 | 0.00553 |
| SA | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.0733 | 0 | 0.0933 | 0.0889 | 0.0889 | 0.111 | 0.0889 | 0.0576 | 0.292 | 0 | 0.0754 | 0 | 0.0787 | 0 | 0.309 | 0.309 | 0 | 0.472 | 0 | 0.994 |
| Pyruvate | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.00106 | 0.00101 | 0.00101 | 0.00126 | 0.00101 | 0.00134 | 0.00101 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.00106 | 0 | 0.00106 | 0 |
| Acetic | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.00106 | 0.00101 | 0.00101 | 0.00126 | 0.00101 | 0.00134 | 0.00101 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Ethanol | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.00417 | 0 | 0.0053 | 0.00505 | 0.00505 | 0.00631 | 0.00505 | 0.0067 | 0.00503 | 0 | 0.0013 | 0.0111 | 0 | 0.00114 | 0 | 0 | 0 | 0 | 0 | 0 |
| Glycerol | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.00417 | 0 | 0.0053 | 0.00505 | 0.00505 | 0.00631 | 0.00505 | 0.0067 | 0.00503 | 0 | 0.0013 | 0 | 0.00135 | 0 | 0.00531 | 0.00531 | 0.00769 | 0.00405 | 0.00769 | 0 |
| Nitrogen | 0 | 0 | 0 | 0 | 0 | 0 | 0.767 | 0.767 | 0.767 | 0.767 | 0 | 0 | 0.752 | 0.173 | 0.81 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Total | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| **MOLES [Kmol/hr]** | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Sucrose | 48.2 | 48.2 | 48.2 | 48.2 | 9.64 | 38.6 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Oxygen | 0 | 0 | 0 | 0 | 0 | 0 | 2060 | 2060 | 447 | 1610 | 0 | 0 | 21.3 | 76.7 | 76.7 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Ammonia | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 291 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Bug | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1050 | 0 | 5270 | 0 | 5270 | 5270 | 4210 | 0 | 1050 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| CO2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 337 | 849 | 849 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Water | 8240 | 8240 | 8240 | 8240 | 1650 | 6590 | 0 | 0 | 0 | 0 | 0 | 2840 | 0 | 31400 | 0 | 31400 | 24000 | 19200 | 7360 | 4800 | 6030 | 1340 | 5530 | 6870 | 309 | 6560 | 5320 | 1240 | 1240 | 622 | 622 | 619 | 3.12 |
| SA | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 609 | 0 | 609 | 466 | 373 | 143 | 93.2 | 57.2 | 85.7 | 0 | 85.7 | 0.00241 | 85.7 | 0.0119 | 85.7 | 85.7 | 0 | 85.7 | 0 | 85.7 |
| Pyruvate | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 9.28 | 0 | 9.28 | 7.1 | 5.68 | 2.18 | 1.42 | 1.78 | 0.396 | 0 | 0.396 | 0.00173 | 0.394 | 0.122 | 0.272 | 0.272 | 0.136 | 0.136 | 0.135 | 0 |
| Acetic | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 13.6 | 0 | 13.6 | 10.4 | 8.33 | 3.19 | 2.08 | 2.61 | 0.58 | 0 | 0.58 | 0.0142 | 0.566 | 0.4 | 0.167 | 0.167 | 0.0833 | 0.0833 | 0.0828 | 0 |
| Ethanol | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 88.7 | 0 | 88.7 | 67.9 | 54.3 | 20.8 | 13.6 | 17 | 3.78 | 0 | 3.78 | 1.36 | 2.43 | 2.37 | 0.0547 | 0.0547 | 0.0274 | 0.0274 | 0.0272 | 0 |
| Glycerol | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 44.4 | 0 | 44.4 | 33.9 | 27.2 | 10.4 | 6.79 | 8.52 | 1.89 | 0 | 1.89 | 0.00285 | 1.89 | 0.00217 | 1.89 | 1.89 | 0.944 | 0.944 | 0.939 | 0.00474 |
| Nitrogen | 0 | 0 | 0 | 0 | 0 | 0 | 7740 | 7740 | 1680 | 6060 | 0 | 0 | 1680 | 6060 | 6060 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Total | 8290 | 8290 | 8290 | 8290 | 1660 | 6630 | 9800 | 9800 | 2130 | 7670 | 291 | 3890 | 2040 | 44400 | 6990 | 37400 | 29900 | 23900 | 7540 | 5970 | 6110 | 1430 | 5530 | 6960 | 310 | 6650 | 5320 | 1330 | 1330 | 623 | 709 | 620 | 88.9 |
| **MOLE FRACTION [-]** | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Sucrose | 0.00581 | 0.00581 | 0.00581 | 0.00581 | 0.00581 | 0.00581 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Oxygen | 0 | 0 | 0 | 0 | 0 | 0 | 0.21 | 0.21 | 0.21 | 0.21 | 0 | 0 | 0.0104 | 0.00173 | 0.011 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Ammonia | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Bug | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.271 | 0 | 0.119 | 0 | 0.156 | 0.156 | 0.156 | 0 | 0.194 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| CO2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.165 | 0.0454 | 0.0827 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Water | 0.994 | 0.994 | 0.994 | 0.994 | 0.994 | 0.994 | 0 | 0 | 0 | 0 | 0 | 0.729 | 0 | 0.361 | 0 | 0.8 | 0.8 | 0.8 | 0.948 | 0.764 | 0.968 | 0.865 | 1 | 0.987 | 0.979 | 0.986 | 0.999 | 0.934 | 0.934 | 0.998 | 0.877 | 0.998 | 0.0352 |
| SA | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.0158 | 0 | 0.035 | 0.035 | 0.035 | 0.0415 | 0.0334 | 0.0207 | 0.125 | 0 | 0.0123 | 0.0179 | 0.0129 | 0 | 0.0644 | 0.0644 | 0 | 0.121 | 0 | 0.965 |
| Pyruvate | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Acetic | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Ethanol | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.0023 | 0 | 0.0051 | 0.0051 | 0.0051 | 0.00604 | 0.00487 | 0.00617 | 0.00551 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Glycerol | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.00115 | 0 | 0.00255 | 0.00255 | 0.00255 | 0.00302 | 0.00244 | 0.00309 | 0.00276 | 0 | 0 | 0 | 0 | 0 | 0.00142 | 0.00142 | 0.00151 | 0.00133 | 0.00151 | 0 |
| Nitrogen | 0 | 0 | 0 | 0 | 0 | 0 | 0.79 | 0.79 | 0.79 | 0.79 | 0 | 0 | 0.824 | 0.463 | 0.843 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Total | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1.01 | 0.936 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 0.996 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| **TEMPERATURE [°C]** | 20 | 20 | 134 | 30 | 30 | 30 | 20 | 24.4 | 24.4 | 24.4 | 30 | 30 | 0 | 30 | 30 | 30 | 0 | 30 | 30 | 0 | 30 | 30 | 150 | 150 | 100 | 100 | 104 | 104 | 27 | 0 | 0 | 30 | 0 |
| **PRESSURE [atm]** | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 2 | 2 | 2 | 1 | 2 | 0 | 2 | 2 | 2 | 0 | 2 | 2 | 0 | 2 | 0 | 0 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |

Table. A-2 Scoring and different weightings done for pre-selected 21 chemicals

| | | | | | | | | | | | | | | | | Weightings | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Number | Name | Sucrose Yield(g/g) | Score | Max yield | Score | Import (to | Score | Export (to | Score | World ma | Score | World pric | score | Max TRL | Score | Yield | Import/exp | World demand | TRL | Market value |
| 1 | Acetic acid | 0.9 | 86.5 | 0.7 | 44.6 | 6800 | 30.9 | 8050 | 4.39 | 13600000 | 17.7 | 9260 | 9.49 | 9 | 100 | 139 | 91.1 | 82.3 | 123 | 78.2 |
| 2 | Adipic acid (hexanedioic acid or 1,4-buta | 0.18 | 17.3 | 0.37 | 23.6 | 1560 | 7.12 | 8.4 | 0.00458 | 3020000 | 3.94 | 27800 | 28.5 | 5 | 60 | 55.5 | 38.7 | 37.1 | 65.1 | 49.3 |
| 3 | Algal lipids | UNKNOWN | 0 | N/A | NA | 0 | 0 | 0 | 0 | 122000 | 0.159 | 15000 | 15.4 | 8 | 90 | 26.4 | 26.4 | 26.5 | 71.4 | 34.1 |
| 4 | Citric acid | 0.7 | 67.3 | 1.12 | 71.3 | 21500 | 97.9 | 2850 | 1.55 | 1600000 | 2.09 | 10500 | 10.8 | 9 | 100 | 157 | 137 | 88.8 | 138 | 93.1 |
| 5 | Ethanol | 0.5 | 48.1 | 0.54 | 34.4 | 22000 | 100 | 183000 | 100 | 76700000 | 100 | 12300 | 12.7 | 9 | 100 | 165 | 224 | 174 | 174 | 130 |
| 6 | Farnesene (Biohydrocarbon) | 0.15 | 14.4 | 0.34 | 21.7 | 0 | 0 | 0 | 0 | 12200 | 0.0159 | 83700 | 85.9 | 7 | 80 | 68.5 | 50.5 | 50.5 | 90.5 | 93.4 |
| 7 | Fumaric acid (1,4-Dicarboxilic acid) | 1 | 96.2 | 1.02 | 65 | 49.4 | 0.225 | 74.6 | 0.0407 | 90000 | 0.117 | 22500 | 23.1 | 4 | 50 | 139 | 58.8 | 58.7 | 83.6 | 70.2 |
| 8 | Glutamic acid | 0.41 | 39.4 | 1.03 | 65.6 | 13200 | 60.2 | 81 | 0.0442 | 2300000 | 3 | 30000 | 30.8 | 9 | 100 | 127 | 105 | 76.2 | 125 | 90.1 |
| 9 | 3-Hydroxybutyrolactone | 0.031 | 2.98 | 0.75 | 47.8 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 7 | 80 | 58.1 | 32.7 | 32.7 | 72.7 | 32.7 |
| 10 | 3-Hydroxypropionic acid | 1.02 | 98.1 | 1.05 | 66.9 | 0 | 0 | 0 | 0 | 40 | 0 | 16500 | 16.9 | 5 | 60 | 143 | 60.5 | 60.5 | 90.5 | 68.9 |
| 11 | Iso-butanol | 0.34 | 32.7 | 0.43 | 27.4 | 30.9 | 0.141 | 6520 | 3.56 | 500000 | 0.652 | 25800 | 26.5 | 8 | 90 | 75.3 | 47.1 | 45.6 | 90.2 | 58.5 |
| 12 | Isoprene (Biohydrocarbons) | 0.11 | 10.6 | 0.68 | 43.3 | 2120 | 9.65 | 627 | 0.342 | 850000 | 1.11 | 30000 | 30.8 | 5 | 60 | 65.9 | 43.9 | 39.5 | 68.9 | 54.3 |
| 13 | Itaconic acid (methylene succinic acid or | 0.52 | 50 | 0.91 | 58 | 0 | 0 | 0 | 0 | 41400 | 0.054 | 28500 | 29.2 | 9 | 100 | 113 | 59.3 | 59.3 | 109 | 73.9 |
| 14 | Lactic acid | 0.99 | 95.2 | 1.05 | 66.9 | 2770 | 12.6 | 413 | 0.225 | 472000 | 0.616 | 21800 | 22.3 | 9 | 100 | 155 | 80.9 | 74.8 | 124 | 85.6 |
| 15 | Malic acid | 1.04 | 100 | 1.57 | 100 | 322 | 1.47 | 5840 | 3.18 | 200000 | 0.261 | 15000 | 15.4 | 4 | 50 | 168 | 69.9 | 67.7 | 92.6 | 75.3 |
| 16 | n-butanol (ABE process) (butyl alcohol) | 0.21 | 20.2 | 0.43 | 27.4 | 161 | 0.733 | 132000 | 72.1 | 3000000 | 3.91 | 18800 | 19.2 | 9 | 100 | 84.7 | 97.3 | 62.8 | 111 | 70.5 |
| 17 | Poly-hydroxy-alkanoates (PHAs)(i.e. PHE | 0.36 | 34.6 | NA | NA | 0 | 0 | 0 | 0 | 54000 | 0.0704 | 97500 | 100 | 7 | 80 | 71 | 53.7 | 53.7 | 93.7 | 104 |
| 18 | Polylactic acid (PLA) | 0 | 0 | NA | NA | 0.083 | 0 | 11.8 | 0.00644 | 472000 | 0.616 | 54000 | 55.4 | 8 | 90 | 36.5 | 36.5 | 36.8 | 81.5 | 64.2 |
| 19 | 1,3-propanediol (PDO) | 0.51 | 49 | 0.67 | 42.7 | 0 | 0 | 0 | 0 | 128000 | 0.167 | 26400 | 27.1 | 9 | 100 | 101 | 54.7 | 54.8 | 105 | 68.3 |
| 20 | Sorbitol (D-glucitol) | UNKNOWN | 0 | 1.06 | 67.5 | 3920 | 17.8 | 109 | 0.0595 | 164000 | 0.214 | 9750 | 10 | 9 | 100 | 82.7 | 57.9 | 49 | 98.9 | 53.9 |
| 21 | Succinic acid (1,4-Dicarboxylic acid) | 0.41 | 39.4 | 1.18 | 75.2 | 0 | 0 | 0 | 0 | 76000 | 0.0991 | 37500 | 38.5 | 8 | 90 | 118 | 60.8 | 60.8 | 106 | 80 |

Table. A-3 Table of Chemical Formulae

| Chemical/fuel Name | Stoichiometric reaction equation | Molar mass (g/mol) | Sucrose coefficient | Product coefficient | Theoretical yield (g/g) |
|---|---|---|---|---|---|
| Acetic acid | $C_{12}H_{22}O_{11} + 5\ H_2O \rightarrow 4\ C_2H_4O_2 + 8\ H_2 + 4\ CO_2$ | 60 | 1 | 4 | 0.70 |
| Adipic acid | $7\ C_{12}H_{22}O_{11} + 51\ O_2 + 12\ H_2 \rightarrow 6\ C_6H_{10}O_4 + 59\ H_2O + 48\ CO_2$ | 146 | 7 | 6 | 0.37 |
| Algal lipids | Dependant on the structural formula of the lipid | Dependent on the structural formula of the lipid | | | |
| Citric acid | $C_{12}H_{22}O_{11} + 3\ O_2 \rightarrow 2\ C_6H_8O_7 + 3\ H_2O$ | 192 | 1 | 2 | 1.12 |
| Ethanol | $C_{12}H_{22}O_{11} + H_2O \rightarrow 4\ C_2H_6O + 4\ CO_2$ | 46 | 1 | 4 | 0.54 |
| Farnesene | $7\ C_{12}H_{22}O_{11} + 7\ H_2O \rightarrow 4\ C_{15}H_{24} + 24\ CO_2 + 36\ H_2O$ | 204 | 7 | 4 | 0.34 |
| Fumaric acid | $C_{12}H_{22}O_{11} + 4\ CO_2 \rightarrow 4\ C_4H_4O_4 + 3\ H_2O$ | 116 | 1 | 3[R110][WU11] | 1.02 |
| Glutamic acid | $5\ C_{12}H_{22}O_{11} + 6\ O_2 + 12\ NH_3 \rightarrow 12\ C_5H_9NO_4 + 19\ H_2O$ | 147 | 5 | 12 | 1.03 |
| 3-Hydroxybutyrolactone | $2\ C_{12}H_{22}O_{11} + 2\ H_2O \rightarrow 6\ C_4H_6O_2 + 6\ H_2O + 3\ O_2$ | 86 | 2 | 6 | 0.75 |
| 3-Hydroxypropionic acid | $C_{12}H_{22}O_{11} + H_2O \rightarrow 4\ C_3H_6O_3$ | 90 | 1 | 4 | 1.05 |
| Iso-butanol | $C_{12}H_{22}O_{11} \rightarrow 2\ C_4H_{10}O + 4\ CO_2 + H_2O$ | 74 | 1 | 2 | 0.43 |
| Isoprene | $7\ C_{12}H_{22}O_{11} \rightarrow 12\ C_5H_8 + 24\ CO_2 + 29\ H_2O$ | 68 | 7 | 24 | 0.68 |
| Itaconic acid | $5\ C_{12}H_{22}O_{11} + 6\ O_2 \rightarrow 12\ C_5H_6O_4 + 19\ H_2O$ | 130 | 5 | 12 | 0.91 |
| Lactic acid | $C_{12}H_{22}O_{11} + H_2O \rightarrow 4\ C_3H_6O_3$ | 90 | 1 | 4 | 1.05 |
| Malic acid | $C_{12}H_{22}O_{11} + 4\ CO_2 + H_2O \rightarrow 4\ C_4H_6O_5$ | 134 | 1 | 4 | 1.57 |
| n-Butanol | $C_{12}H_{22}O_{11} \rightarrow 2\ C_4H_{10}O + 4\ CO_2 + H_2O$ | 74 | 1 | 2 | 0.43 |
| PHAs | Dependent on the structure of the PHA | Dependent on the structure of the PHA | | | |
| Polylactic acid | This can be determined from the theoretical yield of lactic acid from sucrose and the theoretical yield of PLA from lactic acid | From theoretical yield of lactic acid from sucrose and the theoretical yield of PLA from lactic acid | | | |
| 1,3-propanediol | $C_{12}H_{22}O_{11} + H_20 \rightarrow 3\ C_3H_8O_2 + 3\ CO_2$ | 76.09 | 1 | 3 | 0.67 |
| Sorbitol | $C_{12}H_{22}O_{11} + 2\ H_2 + H_20 \rightarrow 2\ C_6H_{14}O_6$ | 182 | 1 | 2 | 1.06 |
| Succinic acid | $7\ C_{12}H_{22}O_{11} + 12\ CO_2 \rightarrow 24\ C_4H_6O_4 + 5\ H_2O$ | 118 | 7 | 24 | 1.18 |
| Sucrose | | 342.3 | | | |