Thermodynamic evaluation of the gasification of municipal solid waste

A thesis submitted to the Faculty of Engineering and the Built Environment for the award of the Degree of Master of Science in Sustainable Energy Engineering

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Abstract

The dependency on energy use is unavoidable in modern civilization. The burning of fossil fuels for energy use is regarded as one of the human activities that has a harmful environmental impact. Waste to energy is slowly becoming an evident argument that energy can be obtained from waste at a level that is enough to meet energy demands. Waste is viewed as a renewable source of energy and can lower emissions from the greenhouse gas (GHG) and mitigate climate change. The exploitation of municipal solid waste (MSW) can be implemented using various routes, either through thermal or biological conversion. The thermal conversion can be achieved through combustion, gasification, or pyrolysis.

This study aimed to evaluate the gasification of municipal solid waste. The investigation focused on the effects the selected operating parameters have on the syngas composition, H_2/CO ratio, and calorific value. The selection of the modelling approach focused on the problem statement. It was necessary to use a model that did not have a lot of limitations or relied on the geometry of the gasifier. A mathematical model that could analyse the selected operating parameters of the gasification process was utilized. A step-by-step procedure of the thermodynamic equilibrium model was implemented using MATLAB. The model was validated by comparing the predicted results of this study and empirical data in published literature.

The results showed that operating parameters affected the amount of syngas quality, calorific value, and H_2/CO ratio. The amount of carbon monoxide and nitrogen reduced with an increase in moisture content, and the amount of carbon dioxide increased with increased moisture content. A small amount of methane was recorded, with increased moisture content. Enhanced temperature brought about increased hydrogen while the amount of nitrogen remained constant. With high temperature, carbon dioxide composition reduced, and just over 1% of methane was recorded. The increased (ER) from 0.2 to 0.6 showed that ER has a notable impact on nitrogen. A sharp increase in nitrogen was noted when the ER increased while the amount of hydrogen and carbon monoxide decreased. Results showed acceptable agreement between the modelled data from this investigation and the experimental values reported in the literature.

The overall conclusion is that the thermodynamic model gives accurate prediction results of the gasification process. Additionally, when the investigated operating parameters were adjusted, syngas composition, H_2/CO ratio and calorific value were all affected (they either increased or reduced). Furthermore, it is concluded that the ER ratio is the most influential parameter in the gasification process.

Acknowledgements

I would like; to express my deepest appreciation to my supervisor Dr Amos Madhlopa for his admirable patience, time, and exceptional way of teaching. Thank you for the enthusiasm, motivation, and the immerse knowledge you shared continuously throughout this research project. Without your patience, this work would not have been possible may the good Lord continue to bless you. Thank you for the financial opportunities that you always alerted me to, the NRF grant nomination that gave me a head start. Thank you for the academic references and reports you sent out when I was applying for financial assistance. I doubt words can ever be enough to explain how grateful I am for the support you gave me. Thank you.

I would also like to thank Professor Tunde Ochende-Bello for his insightful comments.

Thank you to my dear friend, Dr Deepti Charitar; for the constant and continued emotional support, patience, time, and kind words. Thank you also for assisting with the learning of the MATLAB program.

I would also like to express my sincere gratitude to my partner Selaelo Masoga and son Neo Masoga for their patience, support, and love; and to my mother, Ledile Sebothoma for, being my pillar of strength throughout my life.

My friends, Zelda Lebelo, Likho Sikutshwa and Dipolelo Thobane: thank you for your support and words of encouragement during my research.

I would also like to thank the following organisations for financial support, the National Research Foundation, Masakh'iSizwe bursary, and the Heinrich Boell Foundation through Professor Winkler.

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List of Acronyms

ANN	Artificial Neural Network
CV	Calorific value
CGE	Cold gas efficiency
e	Equivalent
EPJ	Equi Plasma Jet
ESP	Electrostatic precipitators
ER	Equivalence ratio
FT	Fischer-Tropsch
GDP	Gross domestic product
Gt	Giga tonnes
GHG	Greenhouse gas
HFCs	Hydrofluorocarbons
IC	Internal combustion
IGCC	Integrated gasification combined cycle
IPCC	International Panel on Climate Change
ISWA	The International Solid Waste Association

kWe	Kilowatt-electric
LCA	Life cycle assessment
MFNN	Multilayer feedforward neural network
MBE	Mean bias error
MC	Moisture content
MSW	Municipal solid waste
Ni	Nickel
N-R	Newton-Raphson
TDP	Thermal design power
RMSE	Root mean square error
SNG	Synthetic natural gas
SOEC	Solid oxide electrolyzer cell
WGS	Water -gas shift
WtE	Waste to energy
PFCs	Perfluorocarbons
PPMV	Parts per million by volume
RPM	Random pore model
SCM	Shrinking core model
VM	Volumetric model

Nomenclature

Symbol quantity SI UNIT

a	Number of atoms of hydrogen per number atom of carbon (H/C)	
b	Number of atoms of oxygen per number atom of carbon (O/C)	
c	Number of atoms of nitrogen per number atom of carbon (N/C)	
C	Mass of carbon	
CH_4	Methane	
CO_2	Carbon dioxide	
C_w	The specific heat of water	J/kg° C
C_p	Specific heat of the gas	kJ/kg°K
cSt	Kinematic viscosity	Centistokes
$\bar{C}p$	Specific heat at constant pressure	kJ/kmol K
EJ	The exajoule	(EJ) is equal to 10^{18}
E	Activation energy	kJ/mol
$Ex_{feedstock}$	Exergy of the feedstock	kJ/kmol
Ex_{prod}	Exergy of the producer gas	kJ/kmol
$GtCO_2$	Gigatons of equivalent carbon dioxide	$GtCO_2e$
h_f^o	Enthalpy of formation	kJ/kmol
H	Mass fraction of hydrogen	
H	Enthalpy	J
HHV	Higher Heating Value	MJ/kg
H_2	Hydrogen gas	
H_2O	Water	
H_2S	Hydrogen sulfide	

H_g	Heating value of the gas	kJ/m^3
H_s	Lower heating value of gasifier fuel	kJ/kg
K	Equilibrium Constant	Dimensionless
l	Referred to water in liquid phase	m^3
$\dot{I}$	The total irreversibility flow rate	
$\bar{b}$	The mole specific exergy	
log	logarithm the inverse function to exponentiation	Dimensionless
LHV	Lower Heating Value	MJ/kg
m	Kmol of oxygen per kmol of feed stock	
$\mathrm{M_{wet}}$	The moisture fraction on a wet basis	
M_s	Gasifier solid fuel combustion	kg/s
mm	Unit of length	Milli meters
m/s	Unit for speed/ velocity	meters per second
mWh	Measure the output of a power plant	Megawatt hour
Mg/y	Unit of mass or weight per year	Milligram/year
Nm^3/h	Unit used to measure gas flow rate	Normal meter cubed per hour
N	Mass fraction of nitrogen	
NO_2	Nitrogen dioxide	
O	Mass fraction of oxygen	
P	Pressure	Pascal (Pa)
S	Mass fraction of sulfur	
Q_g	Volume flow of gas	m^3/s

Q_c	Heat absorbed per cycle from higher temperature	J
Q_h	Heat rejected per cycle to lower temperature	J
T	Temperature	K /°C
TWh	Unit of energy, to outputting one trillion watts for one hour	Tera watt hour
R	Universal constant of ideal gases	J/mol K
R_3	Boudouard reaction	
R_4	Water-gas heterogeneous reaction	
R_5	Methane formation reaction	
R_6	Water-gas shift homogeneous reaction.	
R_{11}	Methane reforming reaction	
μm	Measure for length	
V_g	Volume flow rate of the syngas	Nm^3/s
w	Molar quantity of water per mol of feedstock	
W	Work carried out per cycle	J
x	Mole fraction	

Greek symbols

∂	Partial derivative
Σ	Sum of multiple terms
Δ	Delta change in
ρ_g	Density of the gas (kg/m^3)
$ɧ_m$	Mechanical efficiency
η_{exp}	Exergy efficiency

$\oint$	Contour integral
δ	Inexact differential
θ	Thermal constant
$\int$	Integral

Chapter 1

INTRODUCTION

Chapter 1 introduces municipal solid waste management, waste to energy, gasification technology, and thermodynamic analysis of municipal solid waste. This chapter also contains the aim and scope of this study, problem statement, and organisation of the thesis.

1.1. Municipal solid waste management

Mismanaged landfills and dumping areas present several threats to the environment. These threats include groundwater contamination and air pollution. It is important to have dedicated efforts to avoid sending solid waste to landfills. This can reduce and prevent soil and groundwater pollution. Issues associated with ground water and soil pollution threaten the environment and can harm our health. Additionally, sending solid waste to landfills creates a need to design and build more landfills. The construction of landfills takes up space that could have been used in other developments. Municipal solid wastes can include grass, leaves, food, and paper.

Economic development, population growth, and urbanization have given rise to adjusted resource patterns and resulted in a quick increase in waste volumes and types. Simatele, Dlamini & Kubaza (2017) notes that urbanization is instrumental in waste generation, urban environmental degradation, caused health hazards as a result of unscientific waste treatment. In their study Ramachandra et al. (2018) states that in developing countries, municipal solid waste consists of about >70 of degradable materials, which have a significant role in greenhouse gas (GHG). The composition of the GHGs detailed by Jha et al. (2008) reports that around 40% of carbon dioxide (CO_2) and 60% of methane (CH_4) with other trace gases are generated from the decomposition of MSW in landfills. Despite ongoing initiatives to reduce and control solid waste by recycling and management through different policy regulations, illegal dumping, littering, lack of awareness, poor solid waste management systems, and other factors continue to hinder these efforts.

A strong connection has been found between waste generation and greenhouse gas (GHG) emissions (Hoornweg & Bhada-Tata, 2012). GHGs contain gases such as carbon dioxide (CO_2), hydrofluorocarbons (HFCs), methane (CH_4), nitrous oxide(N_2O), and perfluorocarbons (PFCs). More than half of these gases account for a total of the greenhouse impact (Liu, Guo & Xiao, 2019). According to the collected information from The World Bank Group (2018), the annual CO_2 emissions around the world increased from 22.15 Gt in 1990 to 36.14 Gt in 2014 and CH_4 emissions increased from 6.67 to 8.01 Gt carbon dioxide equivalence. Liu, Guo & Xiao (2019) further suggest that analysis of main factors that drive worldwide differences of CO_2, CH_4, and N_2O are important. Waste is a fundamental and unavoidable feature of humankind; the process of living utilizes consumer products whose production and use generate waste. Different regions have waste characteristics; they also apply unique waste management strategies, policies, and incentives. In developing countries, solid waste management is a problem, particularly in the cities. Municipalities have difficulties because of increased waste generation and the financial constraints associated with waste management (Guerrero, Maas & Hogland, 2013). Insufficient knowledge on different circumstances that influence stages of waste management and links required for handling the functioning of the system could be an issue.

Waste management systems often reflect their desirability, the priority is waste prevention; that means not producing waste. If waste must be produced, it must be reduced. The next important step is to increase reuse, followed by recycling and recovery (Harrison, 2014). The International Solid Waste Association (ISWA) indicates that globally landfilling remains the main disposal method of municipal solid waste. Developing countries are unable to manage their waste and are still dependent on fossil fuels for energy conversion systems and landfills for waste disposal (Munawar & Fellner, 2013). Similar reports are made by The World Bank (2018) that collection rates vary largely by income levels, high and upper-middle-class income level provide a nearly universal collection of waste. Moreover, waste around the world is expected to increase to 3.4 billion tons by 2050. High-income countries generate about 34% or 683 million tons of the world’s waste. It is also reported that waste generated in a day by individuals varies from

0.11 to 4.54 kilograms (Hoornweg & Bhada-Tata, 2012). The reported data on projected waste generation is presented in Figure 1.1 which shows the amount of waste generated in a year by regions.

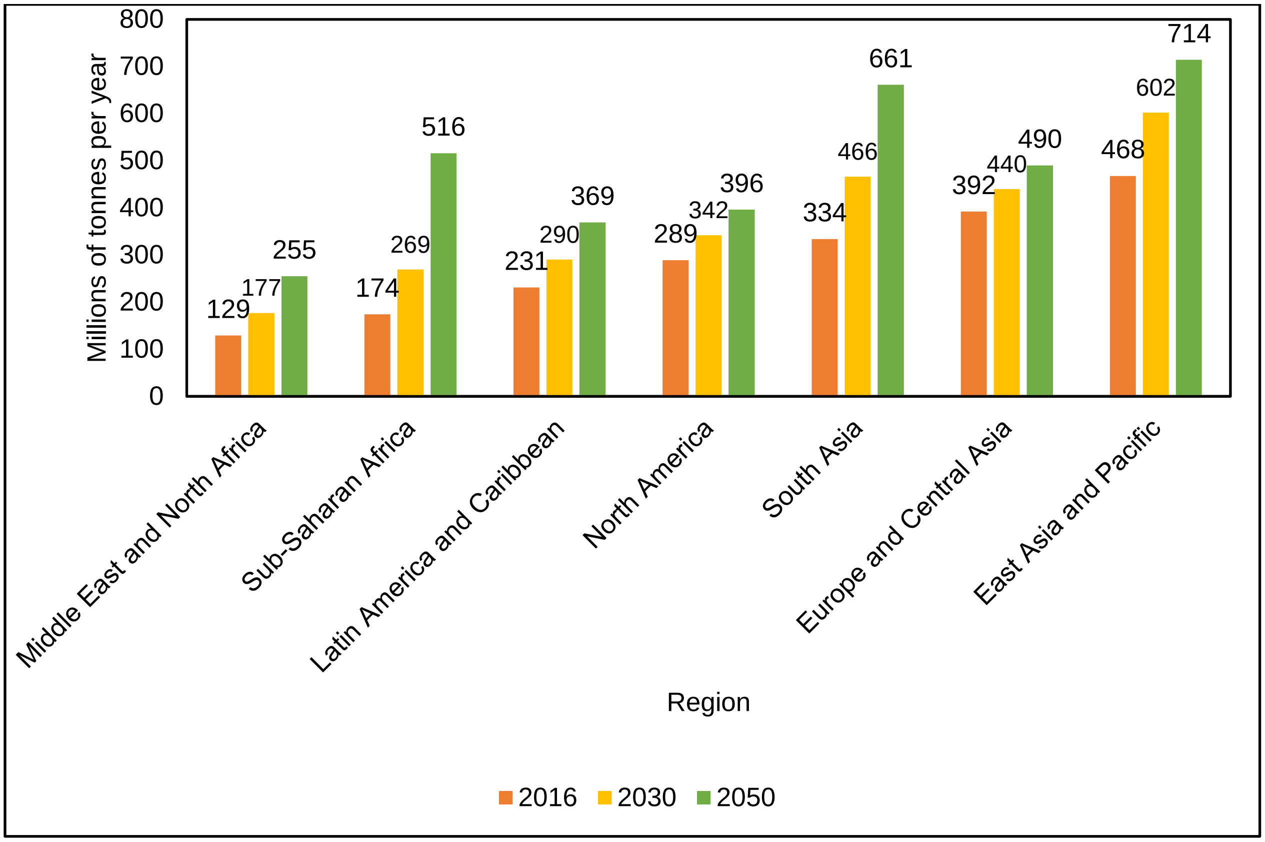


Figure 1.1: Projected waste generation by region: Source (The World Bank, 2018)

Drivers affecting waste composition include economic growth, population growth, urbanization, and varied resource patterns (Department of environmental affairs, 2018). According to The World Bank (2018), high-income countries generate small amount of green and food waste, at 32 % of the global-total waste. Middle and low-income countries generate 53% and 57% food and green waste respectively, and organic waste increases as economic development levels increase. In Figure 1.2, data compiled by The World Bank (2018) shows waste composition around the world. It is observed that waste composition differs across income levels and this leads to varied patterns of consumption, the figure shows the composition and types of waste that is produced globally.

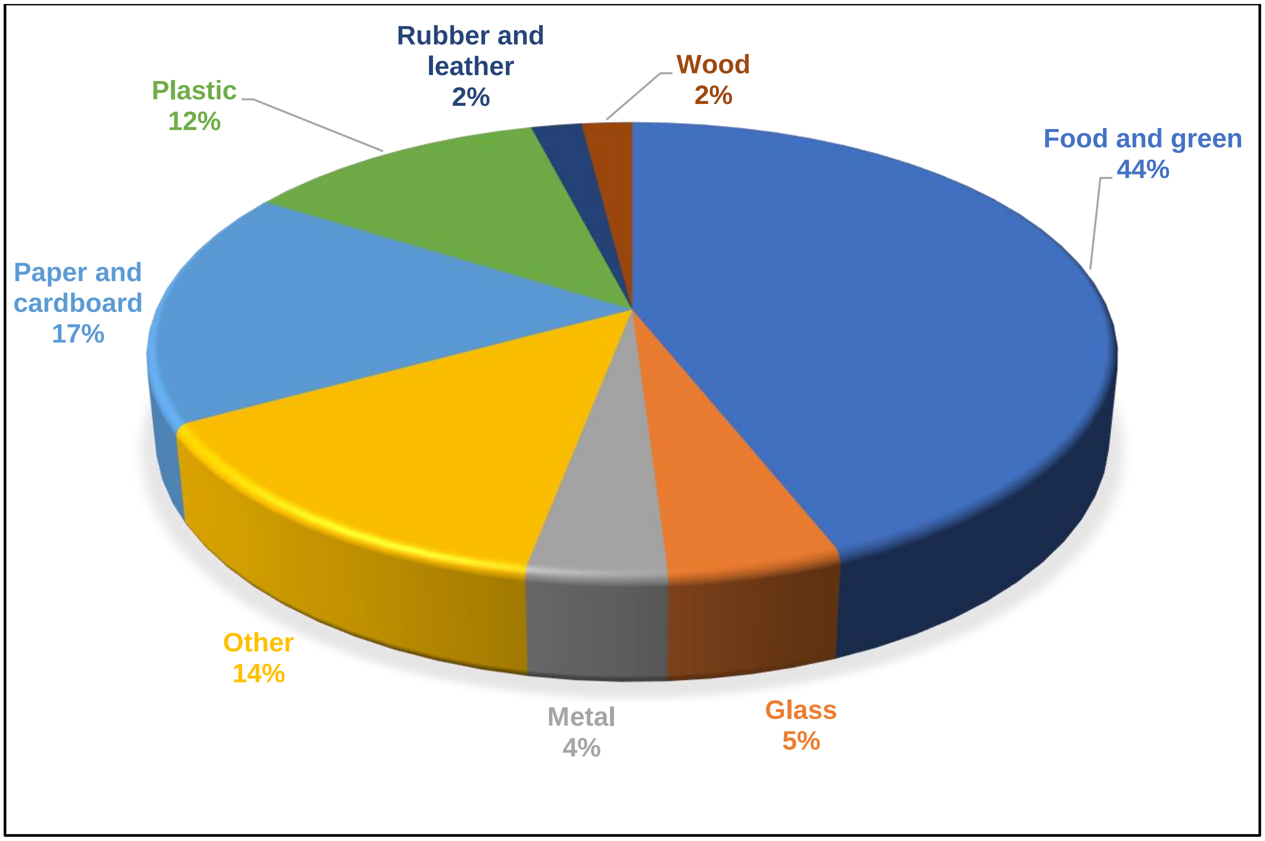


Figure 1.2: Global waste composition: Source (The World Bank, 2018)

1.2. Waste to energy

One of the methods that can be added to the initiatives of solid waste management is the conversion of Waste-to-Energy (WtE). Wastes and energy are closely connected, and it is necessary to address issues with both waste management and energy conversion. The increased energy consumption around the world over the years due to population growth and urbanization has caused a great deal of worry relating to the environmental impact of energy conversion systems. Climate change and global warming are considered the main human societal threats and are largely associated with energy consumption. The residential sector, accounting for 27% of global energy consumptions and 17% of CO_2 emissions, this sector has the most responsibility to mitigate global climate change (Nejat et al., 2015).

Sustainable methods are necessary to alleviate concerns associated with climate change resulting from energy consumption and the dependence on fossil fuels. Resources that are non-renewable, like gas, coal, and petroleum, may be scarce or nonexistent in the future and this would result in energy insecurity. Also, the protracted use of fossil fuel continues to create harmful environmental issues, like air pollution and global warming (Martins et al., 2019). Moreover, fossil fuels are unevenly distributed. It is estimated that by 2050, approximately 14% of oil reserves, 18% of gas and 72 % of coal proven reserves will remain in Europe (Martins et al., 2019). It is important to avoid the manifestation of energy insecurity because of the depletion of fossil fuels because the energy sector is sensitive and linked to economic development.

Waste to energy (WtE) is one of the ways that can assist in converting municipal solid waste (MSW) into desirable energy. The argument that energy can be obtained from waste at a level that is enough to meet energy demand is quite apparent from several studies. In Europe, about 40 million tons of MSW is incinerated a year for thermal and electrical generation, and 130 million tons of MSW is combusted annually worldwide (Nickolas, 2003). Waste to energy continues to establish itself and has been recognised by the International Panel on Climate Change (IPCC) as the key greenhouse gas emission technology (Rogoff & Screve, 2011). This idea is attractive because it carries environmental benefits like reducing environmental pollution and providing a renewable source of energy.

The main technologies associated with waste to energy are anaerobic digestion, combustion, pyrolysis, and gasification (Harrison, 2014). A natural procedure in which bacteria breaks down organic matter in the absence of oxygen into biogas is known as anaerobic digestion. Biogas comprises mainly of CH_4 (55e 75%) and CO_2 (25e 45%); a higher CH_4 concentration means a higher quality of biogas. Refined biogas can be used as fuel in households and vehicles (Meier et al., 2019). Combustion or incineration is the complete, rapid exothermic oxidation of the waste organic fraction when there is adequate oxygen to produce heat, steam, and electricity. Hot flue gas containing fully oxidized products are produced, and hydrocarbons content of waste gets converted to carbon dioxide and steam. Other fuel components, such as ash and gaseous pollutants may be formed and require emission control equipment (Arena, 2011). Pyrolysis is the thermal degradation of solid waste; it occurs between 400 and 800°C, in a total absence of any oxidant or with a limited supply that does not permit gasification to an appreciable extent. It is one of the several reaction steps or zones observed in a gasifier (Basu, 2018). Gasification is the thermochemical conversion of liquid or solid carbon-based material into a combustible gaseous product combustible gas by the supply of a gasification agent (Belgiorno et al., 2003). Gasification and pyrolysis have similarities in operation, except that less oxygen is fed into the combustor in the gasification process (Harrison, 2014). A number of products can be produced from the application of these technologies.

1.3. Gasification process

Gasification is a process that was initially used for the conversion of coal into fuels, thermal energy, and electricity. It has been greatly used since the 18th century. The growth of the gas and oil industry in the 20th century demoted the technology (Higman & van der Burgt, 2008). Different scenarios have made the technology gain popularity in the 21st century. The increase of fossil fuel prices, the decrease of oil reserves, and the proven negative impact of fossil fuels on the environment have led to an interest in gasification as part of the mix in the energy generation process (Brown, 2011). It is necessary to develop gasification technology and make it more appealing either in the private sector or in government institutions. This can be done by improving the process with efficient operating conditions, and this can encourage sectors to subsidize or commercialize the technology.

Gasification has three steps: the first step is devolatilization of feedstock to produce fuel gas for the second step. The second step is combustion, this step produces the required heat.; The final step is called the reduction step. The reduction step is the slowest phase in the gasification process and controls the complete gasification reaction rate (Park, Roy & Kim, 2018). Gasification steps are outlined in Figure 1.3. The steps are part of the process that converts feedstock into synthesis gas and other gaseous products. A gasifier is the main component of a gasification plant, and it is where gasification takes place. Gasifiers are generally classified into three groups, namely the fixed bed, fluidized bed, and entrained flow gasifier. These gasifiers are discussed further in Chapter 2.

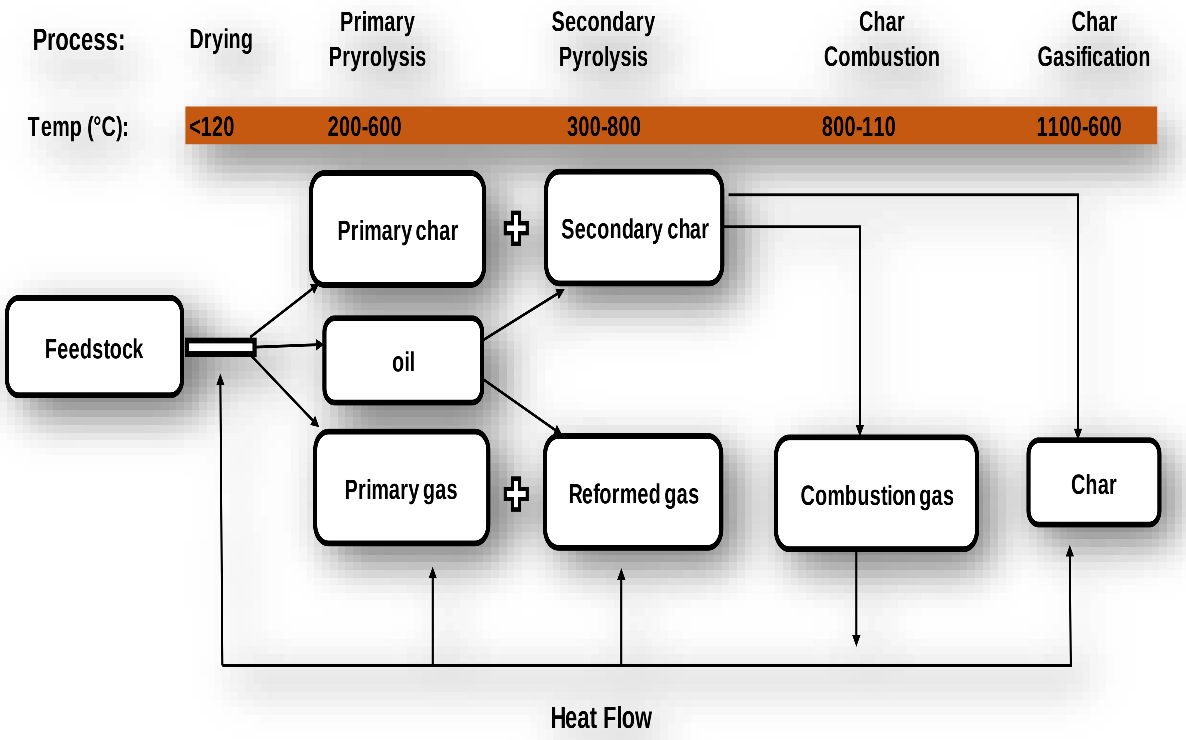


Figure 1.3 The gasification process steps: Adapted from (Reed, 1981).

The negative environmental impact of solid waste requires sustainable, scientific solid-waste management solutions. Heat for electricity generation and fuels can be derived from municipal solid waste, using gasification technology. Mathematical models are useful tools in the presentation of the gasification process; models aid in recognizing the sensitivity of the gasifier performance to different operating parameters or design characteristics (La Villetta, Costa & Massarotti, 2017). Gasification models are developed to study the thermochemical processes occurring during the gasification process and to evaluate the influence of the operating parameters. The focus in this work is on the thermodynamic equilibrium model. This model predicts the composition of the syngas based on the assumption that the reactant reacts in a fully mixed condition for an infinite period.

Thermodynamic equilibrium models are categorised as stoichiometric and non-stoichiometric models. Stoichiometric models are based on equilibrium constants. To predict maximum yield that can be achieved by a reagent system equilibrium models are useful; they produce ideal gasification performance. Other modelling approaches are discussed in Chapter 2 and results from different studies. To find out the gasification performance of municipal solid-waste, thermodynamic analysis is utilized. Couto, Silva & Rouboa (2016) mention that analysis of MSW gasification assists in improving energy efficiency, enhancing mathematical algorithms, and understanding the thermochemical transformation process Thermodynamic analysis of municipal solid waste can help determine the effects of gasification parameters in achieving an optimal operating point.

It is necessary to have a variety of robust validated mathematical models on thermodynamic analysis of the gasification of municipal solid waste. This can assist in getting beneficial results of operating parameters. Operating parameters of a gasifier have a strong effect on the composition quality and final application of the syngas. Parameters that were observed in this study are moisture content, temperature, and equivalence ratio. Moisture content may be present in different forms in a feedstock.; the heating value of the syngas produced by any kind of gasifier partly relies on the feedstock's moisture content (Speight, 2014).

Feedstock containing high moisture content lowers the reactor temperature and slows down definite endothermic reactions. High moisture materials require to be fed at lower feed rates to maintain reactor bed conditions, such as fluidization state and temperature profile (Motta et al., 2018). Gasification temperature affects the syngas composition and properties. Temperature affects devolatilization, it also modifies the macro products (La Villetta, Costa & Massarotti, 2017). Increased temperature results in higher syngas production and reduction of the composition of tar (Narváez et al., 1996). The Le Chatelier's principle suggests that high temperatures shifts the chemical equilibrium to the side of the reactant with exothermic reactions, and in the case of endothermic reactions to the side of the products (Motta et al., 2019).

The equivalence ratio (ER) is the ratio of the actual fuel/air ratio to the stoichiometric fuel/air ratio. ER is the most influential operating parameter affecting gasification, when the value of ER is equal to zero, there is no oxidation in the system (La Villetta, Costa & Massarotti, 2017). Equivalence ratio has more noticeable effects on the reactor temperature and gas yield (Xiao et al., 2007). Various studies conducted on thermodynamic analysis of gasification have maintained the typical equivalence ratio range between 0.2-0.4. In experimental work by Lv et al. (2004), ER was varied from 0.19 to 0.27, the optimal ER for that study was 0.23. Sharma & Sheth (2016) concluded in their experiment that the optimum ER is 0.24. In the thermodynamic evaluation of MSW in Portugal, ER was between 0.15-0.35 (Couto, Silva & Rouboa, 2016). To investigate the effect ER has on the gasification process, this present study found it important to increase the equivalence ratio from 0.2 to 0.6 and to obverse the sensitivity of the model. ER is regarded as an important parameter and its adjustment can affect other operating parameters.

A theoretical investigation on plasma gasification and utilizing municipal solid waste as feedstock concluded that in general, lower ER values prevent syngas dilution, and that leads to a more H_2 enriched product (Tavares, Ramos & Rouboa, 2019). Khosasaeng & Suntivarakorn (2017) investigated the effect of equivalence ratio on a single throat downdraft gasifier, with ER tested at a range of 0.15-0.5. Their study concludes that for maximum outcome and stability, gasification should be operated with ER of 0.35. In a study by Tanigaki, Manako & Osada (2012), material recovery and the co-gasification of municipal solid waste was investigated. The effects of the equivalence ratio evaluated showed that when ER increased, carbon monoxide concentration decreased, while carbon dioxide and the syngas temperature increased. To analyze the sensitivity of the model, it was necessary to investigate the impact a slightly adjusted equivalence ratio can have on the model and the gasification process.

1.4. Scope of study

This study investigated the relationship between the operating parameters and syngas quality and explored the most influencing parameter in gasification. Moreover, a thermodynamic equilibrium modelling method was used to determine the amount of syngas derived from the municipal solid waste. MATLAB software was used to simulate gasification parameters, moisture content, temperature, and equivalence ratio at various operating conditions. The study was mainly theoretical, but numerical results were compared with empirical data from the public domain to validate the mathematical model.

1.5. Research objectives

The aim of this study was to evaluate the gasification of municipal solid waste (MSW), with the following objectives:

- To develop a thermodynamic mathematical model of a gasifier.
- To simulate the gasifier.
- To validate the model using empirical data.
- To perform a sensitivity analysis.

1.6. Thesis organization

This thesis consists of 5 Chapters. In Chapter 1, municipal solid waste management and waste to energy concepts are introduced and discussed. Chapter 1 further discusses the gasification process, thermodynamic analysis of municipal solid waste, the problem statement, the scope of the study, research objectives, chapter summary, and thesis organisation. In Chapter 2, the literature review gives a background on energy sources, energy conversions, municipal waste management and waste to energy. Also, Chapter 2 covers the gasification process, gasification applications, gasification models, gasifier designs, and thermodynamic analysis of gasification. In Chapter 3, the methodology used for the mathematical thermodynamic model and simulation of a gasifier using MATLAB is discussed. The results obtained are presented and discussed in Chapter 4, and conclusions and recommendations based on the results are covered in Chapter 5.

1.7. Chapter summary

This Chapter gave an overview of the study and focused on municipal solid waste management and waste to energy. The gasification process and thermodynamic analysis of MSW were defined and discussed. Furthermore, the Chapter highlighted the need for scientific management of MSW. Waste to energy is one of the ways that can be used to avoid landfilling of MSW. Chapter 1 also identified that gasification is a promising waste to energy technology, and the thermodynamic analysis of the gasification of MSW is necessary to assist in determining the effects of gasification parameters. These can provide an understanding of the chemical and physical mechanisms of the gasification of MSW.

Chapter 2

LITERATURE REVIEW

In Chapter 2, sustainable energy, municipal solid waste management, and climate change are discussed. The analysis of sources of energy, and factors affecting the environment are also covered. The Chapter also covers waste to energy and the theory of gasification. Moreover, there is a detailed analysis of waste to energy technologies, types of gasifiers, and gasification operating parameters. Finally, thermodynamic theory, types of feedstock, and feedstock characteristics are discussed.

2.1 Sustainable energy and municipal solid waste

The concept of sustainability is an important objective for policymakers and industries. Sustainable development is described as a development that satisfies the needs of the current generation and not compromising the ability to meet the needs of the future generations (World Commission on Environment and Development 1987). In terms of energy options sustainability entails, the ability to provide energy that is reliable, for a long period using a method that is environmentally friendly, viable, and safe without depriving the future generation (Brook et al., 2014). Limited fossil resources have compelled the development of sustainable technologies. In managing the increased energy demands because of the growing global industries and population, there is a need to increase energy production and avoid increasing CO_2 emissions or negatively affecting the environment (Kim et al., 2019). Developing countries face an increased energy demand-supply gap, and this could also be extended globally. Evaluation of alternative energy strategies are required, and scientific approaches are necessary when conducting these evaluations (Solangi et al., 2019).

Solid waste management is an essential sector in the environmental management system, and handling waste disposal provides an example of how closely waste management is related to sustainability (Das et al., 2019). There are solid-waste management plans to investigate waste to energy technologies, such as identifying roles of life cycle assessment (LCA), and other feasible approaches for sustainable solid-waste management solutions (Das et al., 2019). In the quest for global sustainability, both the energy and waste sectors have the potential of working together.

2.1.1 Sustainable energy

A transition towards renewable and sustainable energy requires changes in consumer behaviour and technological solutions (Geels et al., 2015). Recognising energy transitions is a highly complex and uncertain process that involves multiple sectors and societal domains (Rutherford & Coutard, 2014). The demand for commodities and services in urban area has placed pressure on natural resources and the environment and contributes to countless social and environmental concerns like energy security, air pollution, climate change, and the depletion of natural resources (O'Neill et al., 2018). Energy systems and human activities have proven to have adverse environmental impacts (Ginley & Cahen, 2012). Moving away from energy supply alternatives with high GHG emissions is a required component of sustainable global energy systems. According to (Ginley & Cahen, 2012) scaling down GHG emissions can reduce emissions of harmful air pollutants and provide improved energy security by enhancing the diversification of energy supply and energy efficiency.

2.1.1.1Sources of energy

Life depends on energy in some way or the other, the earth's energy a great amount of it comes from the sun and travels in rays or waves to the earth (Zito & Ardebili, 2019). The sun's energy is also stored in coal, wood, oil, and gas, in addition it used to produce food and adjust matter. Figure 2.1 shows how the world's primary energy supply is shared. It can be seen from the data that fossil fuels have the majority share. In scientific and economic literature, general primary energy sources of energy that are conventional, include biomass, fossil fuels, geothermal energy, nuclear energy, solar energy, and tidal energy (Zito & Ardebili, 2019). These sources of energy are classified into two categories, non-renewable and renewable source.

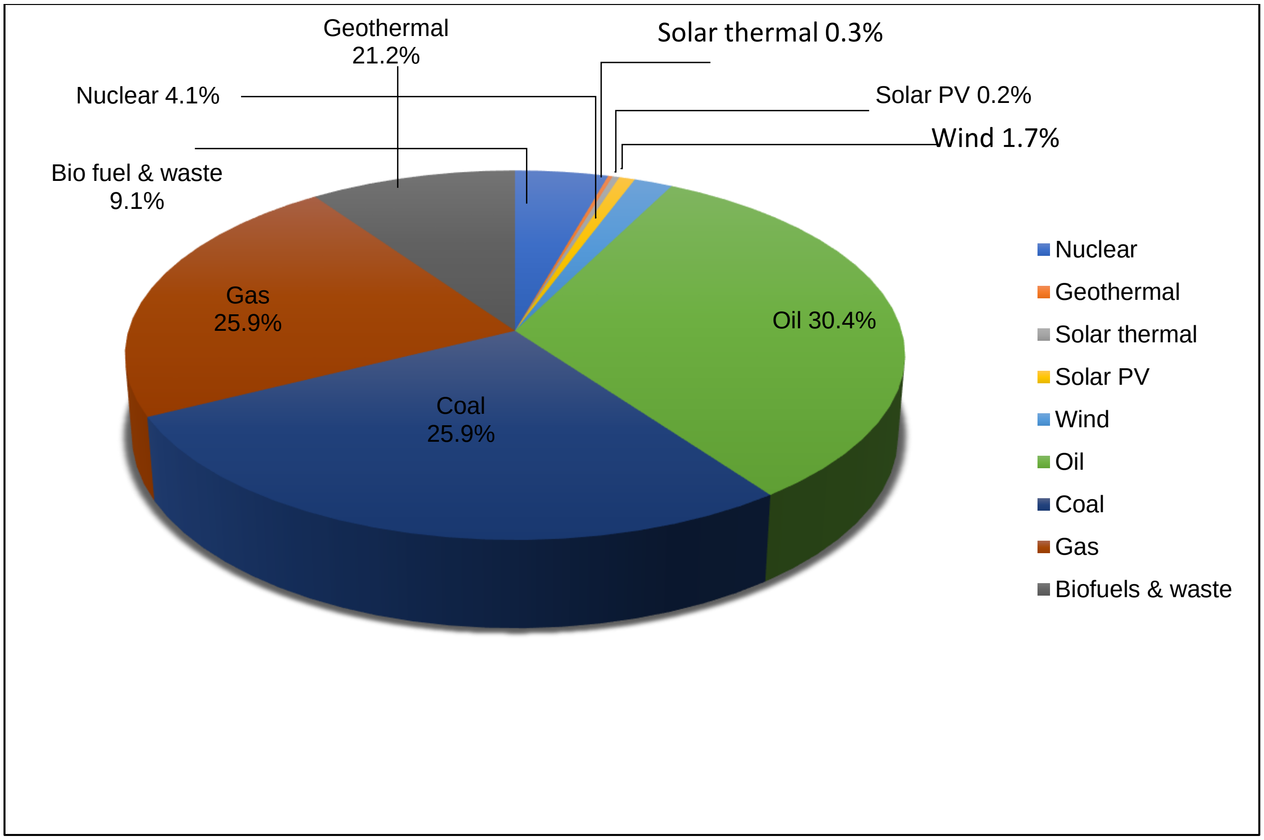


Figure 2.1: World energy supply: Source of data: (World energy data organization, 2019).

2.1.1.1.1 Non-renewable sources of energy

Most industries depend on non-renewable sources of energy for power and day to day operations. These sources will eventually run out and in addition they have been associated with undesirable environmental impact. Below is a discussion of some of the non-renewable energy resources.

(a) Fossil fuels

Fossil fuels are formed from the fossilized remains and have high carbon content. They include coal, crude oil, and natural gases. Fossil power plants have a system of devices that convert fossil energy to electrical energy or mechanical work, the main systems include the steam cycle and gas turbines (Cleveland, Cutler & Morris, 2009). Fossil fuels share in the energy mix is debatable because 80% or more of all the energy consumed comes from fossil fuels. Coal is used to generate roughly 28% of the world's total electricity. Oil records roughly 39% of the energy consumption globally and followed by natural gas with a 22% share (NS Energy, 2015). Fossil fuels like coal, oil and gas are good and convenient source of energy, and they meet the energy demands of society very effectively. However, there is a major problem with fossil fuels they are not renewable and could be limited (Basu, 2010). Fossil fuels are also associated with global inequality, environmental degradation, and injustice, they are also a threat to health (Perera, 2017).

(b) Nuclear energy

Nuclear energy is renewable energy, but the material used in nuclear power plants is not renewable (Brook et al., 2014). Nuclear power plants use a rare type of uranium U-235, and it is a nonrenewable resource (Kalogirou, 2014). Nuclear power plants are complex to build and run. Their design and operation include the control of nuclear fission to produce electricity. The powerful energy in the nucleus or core of an atom is harvested in nuclear energy. Through nuclear fission energy is released and that is when the nucleus of an atom splits (Kalogirou, 2014). Nuclear power plants are the most efficient energy sources, but due to international disasters associated with them, they have a stigma. Nuclear energy; is non-polluting but has potential danger during the production stage. The operation of nuclear plants results in radioactive waste. The waste cannot be reused or recycled; it is stored in a special landfill or some cases, incineration and super-compaction are used (Kalogirou, 2014).

2.1.1.1.2 Renewable energy

Renewable energy (RE) comes from renewable resources that can be replenished and used as much as possible without them running out. They are regarded as environmentally more friendly than fossil fuels. Renewable energy is considered as an essential choice in the cutting down of greenhouse gas emissions and as a possible solution to reducing the use of fossil fuels (Kuriqi et al., 2019). Consumption of renewable energy intensively could guarantee energy security, reduce foreign energy sources dependence, and improve sustainable development of economies. As a result, evaluating the sustainability of renewable energy is important for the renewable energy sustainability. It is also necessary for the sustainability of energy, economy, environment, and society (Wang & Zhan, 2019).

(a) Solar energy

Solar energy is defined as the radiation from the sun that can efficiently produce heat, cause chemical reactions, or generate electricity. In a year, the solar energy absorbed by the earth's atmosphere, ocean, and land masses is about 3 850 000 EJ (Huang et al., 2020). Photosynthesis captures roughly 3000 EJ per year in biomass (Huang et al., 2020). A range of solar evolving technologies are explored to exploit solar energy, heat from the sun and radiant light. Technologies like solar PV, solar thermal electricity, solar heating, solar architecture, and artificial photosynthesis. Solar technologies are described as active or passive solar relying on the pattern of solar energy capture, conversion, and distribution (Huang et al., 2020). Passive solar techniques involve the selection of materials with light-dispersing properties and good thermal mass to build eco-system in a building. Active solar techniques energy is harnessed by using PV panels and solar collectors. It is suggested that the solar market is one of the fastest growing renewable markets in the world.

(b) Wind energy

Wind power is the exploitation of wind, when the wind blows the turbine blades spin capturing energy. Useful form of energy can be derived from wind energy, the conversion produces wind power using wind turbines to generate electrical power, wind pumps for pumping water, and windmills for mechanical power. Communal facilities such as streetlight can get electricity from small domestic wind turbines (Huang et al., 2020). The main shaft of the wind turbine is triggered, and it is linked to a gear box with a nacelle that spins. The gearbox transfers the energy to the generator; and the generator converts the energy to electricity. The electricity is transmitted to the transformer and voltage levels are adjusted to correspond with the grid. Huang et al. (2020) mention that ordinarily wind turbines are built close to each other in high numbers, and are called wind farms, these farms can function as single power plants and send electricity to the grid.

(c) Geothermal energy

The earth ‘s interior is a lot hotter than its surface, the continuous energy flows from the hot interior up to the surface, is called the terrestrial heat-flow (Bassam, Maegaard & Schlichting, 2013). In the high temperature of the earth ‘s crust, mantle and core, there is geothermal energy (Toth & Bobok, 2017). This energy can be recovered by means of suitable energy bearing medium. Currently geothermal production is generally achieved from hot water and steam production through deep boreholes. Toth & Bobok (2017) mention that another popular production technology involves exploiting energy contentment near surface regions by using shallow borehole heat exchanger and heat pumps.

(d) Tidal energy

Tidal energy is the gravitational pull from the moon and the sun. The earth ‘s rotational and gravitational power pulls water down and creates high and low tides. The change in tides is a natural form of kinetic energy (Jones, 2014). The tidal energy extraction methods are barrage and the hydrokinetic method. The barrage is also called the tidal range, and it utilizes the potential energy generated by the variation in sea level between the high and low tides. The hydrokinetic approach is the tidal stream, which captures the kinetic energy from the horizontal flow of tidal currents (Jones, 2014).

(e) Biomass energy

In comparison to other renewable technologies like wind or solar, biomass has limited energy storage issues, theoretically, biomass is stored energy, and it is an adaptable fuel that can produce biogas, electricity, and liquid fuels (Heinz, 2007). Biomass comes from living organisms, and it is generally defined to be the fraction of biodegradable products waste and residue that come from plants and animals. Through the application of direct or indirect methods, these organisms can be converted into useable energy. Heat is created when biomass is burned directly and converted into electricity; biomass can also be processed into biofuels indirectly (Doty & Turner, 2013). Biomass is regarded as a great renewable energy source and has a variety of applications when it comes to fuel sources. The uses involve biofuels for transportation, direct use, or combined heat and power industry. Energy crops that are cultivated for transportation fuels include grain to produce ethanol. Doty & Turner (2013) report that in a conventional sustainability window of 100 years, using biofuels is sustainable.

Energy crops yields can come from different types of woody, and non-woody crops, creating economic energy from wood is an effective logistical system. For harvesting;

recovery, transportation, and compacting storage is needed (Golušin & Dodi, 2013). These requirements can have an impact on the cost and energy balance. Golušin & Dodi (2013) further suggest that energy crops do not need the best land, or water they also do not require the best care what is essential with these crops is the quantity than quality. Arent et al. (2011) mention that the growth of the biomass industry depends on the traditional fuel prices, potential instability of existing fossil fuel resources, and distribution.

2.1.2 Municipal solid waste

Municipal solid waste generation is a concern around the world, especially in urban areas. The challenges associated with solid waste generation in developing countries are environmental pollution issues caused by the large amount of solid waste that is generated (Al-Khatib et al., 2010). Municipal solid waste sources and origins vary according to human activities. It is reported that 50-80% of MSW generated from developing countries is generally from household and 10-30% is from the commercial industry (Al-Khatib et al., 2010). Generally, solid waste is heterogeneous in nature, depending on its original source, it has variable physical and chemical characteristics (Nabegu, 2010).

The composition of MSW differs considerably from one municipality to another, and from country to country the difference depends mainly on lifestyle, economic situation waste management regulations, and industrial structure (Nabegu, 2010). It is necessary to have the information on the composition and quantity of the municipal solid waste. Also, knowing the calorific value and elemental compositions can assist in deciding the utility of MSW as a fuel in converting waste to energy (Abdel-Shafy & Mansour, 2018). It is important to continuously come up with more research that improves the information that is currently available on the composition of MSW.

2.1.2.1Sustainable solid waste management

Technological advancement and economic development occurring at increased rates have affected the continued generation of unsustainable amounts of solid waste increase around the world, and this continues to cause concern. The culture of throwaway and disposable mentality led to a crisis in the field of waste production and waste management (O'Brien, 2013). However, Pereira & Fernandino, (2019) argue that O'Brien, (2013) did not find any evidence that the throwaway culture was different from the practices of our predecessor. The type and amount of waste has changed and has led to several socio-environmental problems (Pereira & Fernandino, 2019). Solid waste requires special attention because of its complexity, increased volume, diverse composition, and that it originates from different sources (Aleluia & Ferrão, 2016).

Several solid waste management (SWM) options have been explored to curb the unceasing increase of solid waste (Pujara et al., 2019). To adapt to new requirements, society must have new behavioural patterns and reduce solid waste generation (da Silva, Pedro & Pavan, 2019). However, it should be accepted that it will take a considerable amount of time to reduce solid waste generation, waste to energy as a treatment technology is an important method, that is feasible and sustainable as a treatment option (da Silva, Pedro & Pavan, 2019). To manage solid waste, the integration between different phases of management collection, sorting, transport, and destination is important (de Souza et al., 2017). Some several techniques and tools that are utilized to evaluate this integration and the quality of solid waste. Some of the analyses are applied when data on waste management is available because they are based on a mathematical tests or life cycle evaluation methodologies (Coelho & Lange, 2018). Sustainability indicators can also be used and can be calculated by public managers and municipal employees in the waste sector, not only by scientists and researchers (Pereira & Fernandino, 2019).

2.2 Climate change

The world is going through climate change; for the most part, it is due to human actions (van der Linden, Leiserowitz & Maibach, 2019). According to Nriagu (2011) climate change refers to the increase in mean air and ocean temperatures, the predicted increased frequency and severity of related events, such as droughts and floods. Climate change is anticipated to intensify environmental issues such as pollution, and cause disturbance on human health and wellbeing (Brusseau et al., 2019). Climate change is a measurable reality, and the impact will be felt across various sectors; people will be affected more irrespective of their contribution to causing it (Mishra, Singh & Jain, 2010). The impacts of climate change can be controlled; through interventions that can sustain social, economic, and environmental resilience.

Intergovernmental Panel on Climate Change (2014) reports that greenhouse gases from human activities contribute largely to climate change. Gas that absorbs and emits infrared radiation, is greenhouse gas. The main greenhouse gases in the atmosphere are carbon dioxide, vapor, methane, nitrous oxide, and water (Easterbrook, 2016). If a greenhouse gas like carbon dioxide; continues to increase in the atmosphere, the infrared opacity of air also increases and enhances the absorption of longwave in the atmosphere (Manabe, 2019). The direct driving force indicators of GHG emissions are the energy intensity of the gross domestic product (GDP) (Zheng et al., 2019). The main force indirectly driving GHG emissions is the carbon intensity of the final energy supply; relying on the mix of electricity generation and gross energy-supply, and the share of renewables in the final energy consumption (Zheng et al., 2019).

A study by Liu, Guo & Xiao (2019) indicates that by improving energy efficiency and technology, innovation can contribute significantly to reducing GHG emissions reduction and emission intensity. Energy use is an unavoidable part of modern civilization; human wellbeing, economic development, and security depend on abundant and affordable energy supplies (Ginley & Cahen, 2012). In 2010, 25% of GHG emissions were reported in the heat and electricity production sector as a result of burning coal, natural gas, and oil for heat (Intergovernmental Panel on Climate, 2015).

Waste related GHG emissions are also contributors to climate change (Yang et al., 2018). Globally, GHG emissions emanating from the waste sector were roughly 1.3 Gt CO2e and contributed about 2.8% of total emissions (Yaman, 2020). The waste management system connects and works with other systems and the quantification of GHG must be looked at in a wider range and context (Das et al., 2019). Other processes in the waste management system include waste collection, waste transportation, and ignoring emissions from these processes that may undermine the efforts of GHG reductions in the integrated waste management system (Das et al., 2019). Emission factors for the waste management process are essential, and data is required for a detailed GHG accounting process (Friedrich & Trois, 2013). The increase in solid waste generation is associated with greenhouse gases and the system of reporting and quantifying of GHG from waste management is done in most large municipalities. When waste data that is recorded, landfills are generally targeted for emissions (Friedrich & Trois, 2013). The clean development mechanism (CDM) requirement is not applied in the whole waste management system (Friedrich & Trois, 2013). In South Africa, according to the greenhouse gas inventory, the energy sector contributed 75.1% to the total greenhouse gas inventory in the year 2000 and further increased to 78.7% in 2010, and the waste sector also had increased emissions (Department of Environmental Affairs, 2014). To reduce the adverse effect of waste management and energy; it is necessary to intensify the research and investment in waste to energy.

2.3 Waste to energy

To control and manage waste; the waste management industry has an identified hierarchy to prevent, reuse, recycle, recover, and dispose, but prevention is somewhat unavoidable. By 2025 the annual global MSW production is anticipated to reach 2.2 billion tons (Hoornweg & Bhada-Tata, 2012). In South Africa, it is estimated that 53.1 million tons of waste end up at landfills and 10% of the waste is recycled (Dlamini, Simatele & Nzalalemba, 2019). Whatever success is achieved in reducing waste and separating material for recycling, some waste will always remain. To achieve waste reduction, a technology component is required, and it has become clear that it is possible to obtain energy from waste. The concept of waste to energy (WtE); is being accepted; it has environmental benefits like reducing environmental pollution, providing a renewable source of energy, greenhouse gas (GHG) mitigation, and improved quality of life (Prasad, 2016). The author further mentions that the idea of obtaining products from waste is convincing and will become more serious with the growing urgency of tackling the twin problems of energy demand and climate change.

Waste-management and energy-supply (generation and distribution) are often treated separately in decision and policymaking. Research is currently proving that waste management and energy supply are increasingly becoming more interconnected (Malinauskaite et al., 2017). Every recovery by WtE plants is an example of a direct connection between energy and waste management (Malinauskaite et al., 2017). Waste to energy is perceived as an influential tool that can be used to prohibit greenhouse gas emissions and to mitigate climate change (Rogoff & Screve, 2011). The average efficiency of a WtE plant is about 18% for electricity generation and 63% for heat production (Leme et al., 2014). The heating value is set particularly from the available carbon content and hydrogen and in the fuel that provides heat from combustion and results in by-products of carbon dioxide and water. Contrary, the heating value is lowered by the level of non-combustible materials remaining in the waste. Glass, metal, and dirt are the most significant factors to the non-combustible portion of the waste stream (Cleveland, 2004). The low heating value (LHV) of the major part of MSW incineration in EU was recorded at 10 GJ/Mg in 2001 to 10.3 to GJ/Mg in 2010, on a dry basis (Lombardi, Carnevale & Corti, 2012). Other waste streams such as stabilized sewage sludge may range from 7-23GJ/Mg. Commercial and industrial waste have an average LHV of 9.47GJ/Mg, and mixed plastic has LHV of 31.7-40.2GJ/Mg (Arena, 2011). Other industrial waste, such as scrap wood, has a LHV of 16GJ/Mg, sugarcane bagasse 18.6GJ/Mg, and plastic scrap 32.8GJ/Mg (Tsai, 2010). Also, Lombardi, Carnevale & Corti (2012) indicate that when the water content is reduced; to 10%, pulper residue has LHV of 21GJ/Mg.

2.3.1 Waste to energy technologies

The technology of waste to energy has been associated with incineration. The term is more comprehensive and supports different waste treatment processes generating energy in the form of electricity, heat, or producing fuel derived from waste (Malinauskaite et al., 2017). WtE can occur through anaerobic digestion, landfill gas recovery, combustion, incineration, pyrolysis, and gasification the classification is illustrated in Figure 2.2. Waste to energy technology has been getting a lot of attention recently; however, (Dastjerdi et al., 2019) suggest that other than incineration systematic assessment of different WtE technologies is still not enough. WtE method is a suitable approach for treating undesired end products that would remain after recycling (Eboh, Andersson & Richards, 2019). The energy efficiency for heat generation is approximately 80%, and for electricity generation, it is estimated between 20 and 30% (Dastjerdi et al., 2019). The advantage of WtE technologies when applied to MSW is their design; they are flexible and can operate in small-scale units (Panepinto et al., 2015).

2.3.1.1Classification of WtE technologies

To select a WtE technology it is important to identify and evaluate different waste to energy technologies based on requirements and projects. The criteria that can be used to select a WtE technology include scale and degree of experience in operation, energy, cost to the agency, reliability to dispose of municipal solid waste, material market compatibility, and environmental acceptance (Rogoff & Screve, 2019). Waste to energy technologies is discussed in section 2.3.2.1, and Figure 2.2 illustrates waste to energy classification.

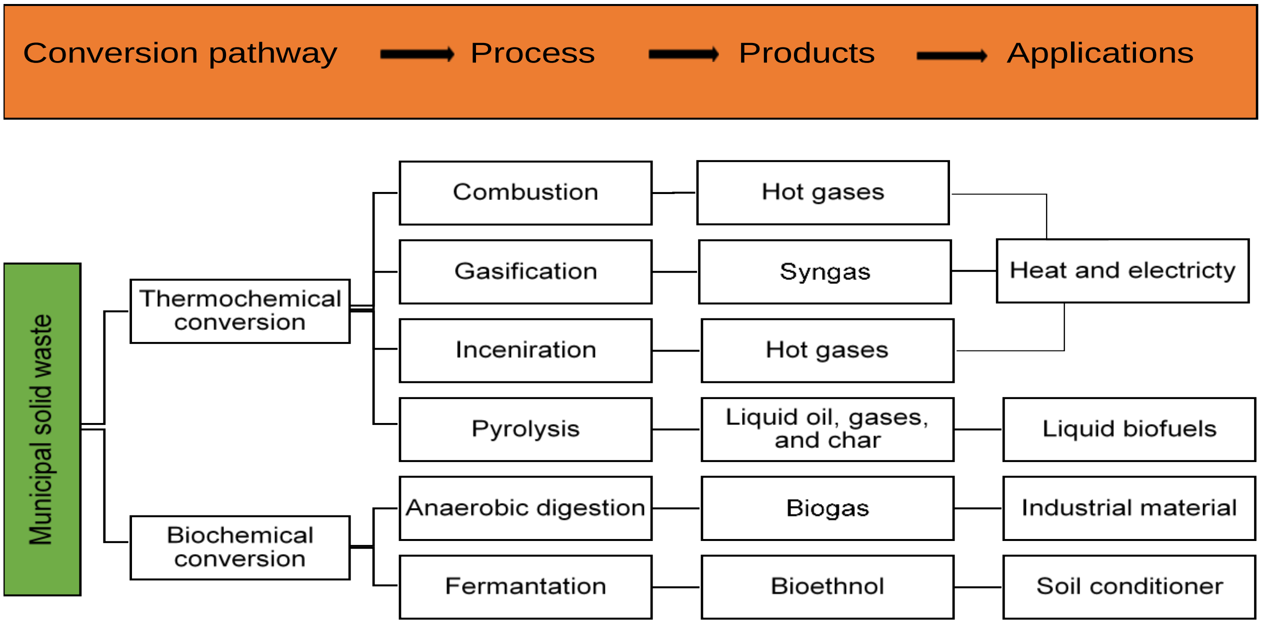


Figure 2.2: Waste to energy classification: Source (Malinauskaite et al., 2017)

2.3.1.1.1 Anaerobic digestion

One of the oldest technologies is the anaerobic digestion (AD) process, introduced in 1870 through the development of the septic tank system (Obulisamy et al., 2018) .The first AD plant, for treating an organic fraction of MSW was constructed in 1939 in the USA, and other improved AD plants constructed over time (Obulisamy et al., 2018). Anaerobic digestion is defined as a series of complex biological treatment of organic substance, the process is carried out by mixed anaerobic culture, and it has four-phases (a) hydrolysis,

(b) acidogenesis, (c) acetogenesis, and (d) methanogenesis (Basile & Dalena, 2019). In hydrolysis, the complex is broken down; into simple monomeric form this breakdown is carried out; by hydrolase enzyme. In the acidogenic phase, monomers developed in hydrolysis are turned into alcohols, carbon dioxide, organic acids, and hydrogen. The CO_2 and H_2 produced in the acidogenic phase are reduced to form acetic acid in the acetogenic phase, and the alcohols and organic acids are converted to acetate (Chandra et al., 2012). This acetate acts as a substrate for methanogenic bacteria in the methanogenesis phase, and the formation of (CH_4) along with CO_2 and H_2O occurs (Chandra et al., 2012). The technology is used for the treatment of organic waste and wastewater (Pramanik et al., 2019). Anaerobic digestion is a sustainable bio-conversion technology, it produces renewable gaseous fuel biogas and reduces the volume of waste. In the integrated waste management system, AD reduces GHG emissions (Chandra et al., 2012). Biogas is generally used for electricity production and as a fuel for heating purposes, and advanced technologies such as solid oxide cells and proton exchange membrane fuel cells and used to generate electricity from biogas (Kumar & Samadder, 2020). Moreover, there is conversion efficiency of 56%, it is almost 20% higher than the conventional system.

2.3.1.1.2 Landfill gas recovery

Landfill gas (LFG) contains approximately 50% methane, which can be used for energy purposes (Speight, 2011). LFG must be collected, from landfills. The collection process consists of vertical extraction well gas pipeline, blower units, and a flare to burn off the gases safely (Speight, 2011). It is estimated; that half of the GHG emissions in the waste and waste management sector come from LFG emissions from landfills (Bogner et al., 2008). A review on methodologies for measuring fugitive methane emission from landfills by Mønster, Kjeldsen & Scheutz (2019) suggested that accurate CH_4 emission quantification downwind of the landfill should be measured using methods like differential absorption and gas dispersion. The collection of LFG has a strong impact on GHG emissions of landfills; Niskanen et al (2013); further stated that when the methane generations get too low for gas utilization, the landfilled material could be incinerated. The heating value of landfill gas is high enough to be utilized in the combustion process (Gewald et al., 2012). Electricity generation from LFG can be achieved by using technologies such as internal and external combustion engines, and turbines (Speight, 2011). In Mauritius, a study that evaluated the potential for energy to be recovered using landfill gas found that the methane generation potential was about 129.94m^3/ton MSW, and the calculated volume of the landfill gas generated was 259.88m^3 LFG/ton MSW. The total power produced was estimated to be 55.75GWh and expected a peak of 67GW (Purmessur & Surroop, 2019). In Delhi, landfill sites that were not engineered were used to estimate methane emissions and it was found that the emissions had enough potential to supply electricity to nearby areas (Ghosh et al., 2019).

2.3.1.1.3 Combustion

Waste combustion incinerators started as simple incinerators, with only wet scrubbers gas clean technology and not capable of recovering any energy the practice reduced the quantity of waste that would have ended up in landfills by 75-85% (Cleveland, 2004). It is also reported that the incinerators were small, waste is introduced into the furnace and the process was considered mass burn in starved air, multi staged incinerators. With improved technology the processed focused on waste to energy, this is accomplished by using heat engines. Combustion engines are heat engines; their operation include converting chemical energy into mechanical energy the conversion is done through the combustion process in which energy is released (Basshuysen & Schäfer, 2016). The engine concept is generally affected by many factors, such as the working cycles and the working process but the most important principle for an engine is its purpose and the requirements it must produce (Basshuysen & Schäfer, 2016).

Combustion engines are open machines that are supplied with oxidizer and fuel and discharge exhaust gases (Feidt, 2017). In combustion engines, fuel, and oxidizer usually air or oxygen are reacted and combusted in a closed combustion chamber (Mokhtari et al., 2017). Combustion engines are either an external or internal combustion engine. In external combustion engines, the heat to drive the engine cycle is provided from outside the engine, and they generate energy from various sources (Okubo & Kuwahara, 2020). External combustion engines separate the combustion process from the working gas (Harrison, 2011). Internal combustion engines are the primary transportation mover in today's society (Naber & Johnson, 2014). The internal combustion engine converts the chemical energy available in the fuel through combustion to thermal energy and the expansion of the working fluid (Naber & Johnson, 2014). Internal combustion engines are classified in to two main types: (a) the spark ignition engines and (b) the diesel or compression-ignition engine. Each of these engines are defined by how fuel is admitted into the cylinder of the engine and how ignition of the air-fuel mixture is initiated. The internal combustion engine can be further be subdivided according to the engine cycle they use. The common cycles; are the two stroke and four stroke cycle. In a two-stroke engine, intake and exhaust strokes are not separate instead, fuel is forced into the piston chamber. Breeze (2014) indicates that the four-stroke cycle is identified by the movement of the piston in the chamber, two of expansion and two of compression.

Modern combustion engines are utilized for electricity generation; it is necessary to know the thermodynamic process used in power plants. The power turbine cycle and the steam boiler principle are used throughout the world to generate electricity. To generate heat fuel is burned in a furnace; in a power boiler steam is generated a and the boiler drives a power turbine to generate electricity this process involves the power cycle (Rankine cycle) (Cleveland, 2004). The Rankine cycle is used in combined power plants, in Figure 2.3 the principle of the Rankine cycle is illustrated. Starting from point A, the source of the heat is applied to expand the medium at constant pressure at point B the adiabatic expansion occurs until the medium reaches a point C, the medium is reduced until it reaches point D and compressed back to its initial condition (Lindsley, Grist & Parker, 2018).

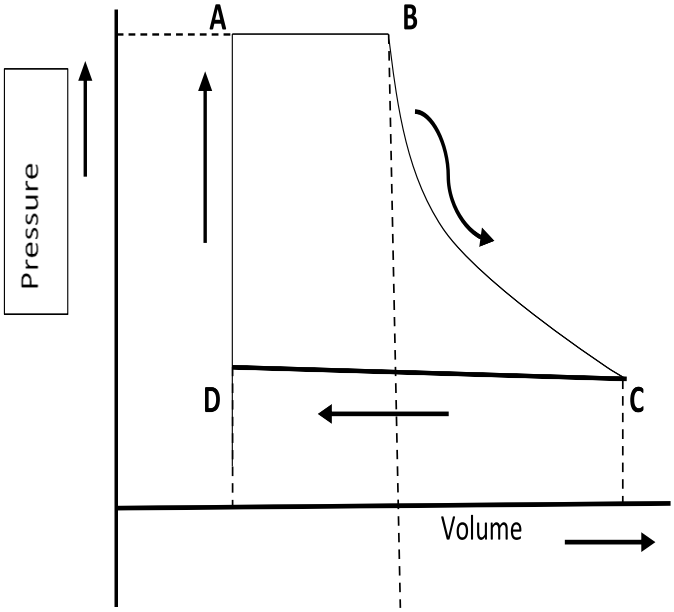


Figure 2.3: The Rankine cycle: Adapted from (Lindsley, Grist & Parker, 2018).

It is reported that a typical Rankine cycle can deliver a gross generation of 25 500kW, and approximately 40 Thermal design power (TDP) per megawatt (TDP/MW) of incoming municipal waste to power generation (Cleveland, 2004). The efficiency of a power plant is measured by its effectiveness in converting fuel into electrical energy, or process heat this assist to determine the revenue that will be earned by the plant (Lindsley, Grist & Parker, 2018). Prior to combustion, pre-processing of the feedstock is required including size reduction and possibly drying (Klass, 1998).

2.3.1.1.4 Incineration

Combusting of materials is described as incineration; an incinerator is a furnace that is utilized to incinerate waste-organic materials until only ash remains. The process is an effective method of reducing the volume of MSW and recover energy as a co-benefit (Ashraf, Ghouleh & Shao, 2019). In addition, incineration has an important role in sustainable development and in a regional circular economy (Liu et al., 2019). Incineration uses temperature from 1100 to 1300°C (Schaschke, 2014). MSW incineration for power generation plays an important role in municipal solid waste management in countries like

China (Yao et al., 2019). Compared to the landfill, it is suggested that MSW incineration for power generation can control the GHG emissions by avoiding the release of methane from landfills (Cheng & Hu, 2010). Incineration is feasible for power generation in a carbon-constrained world (Havukainen et al., 2017). It is popular because it can reduce the volume of MSW that would have been sent to the landfill it is also highlighted that it can reduce the dependence on fossil fuel and GHG emissions (Cheng & Hu, 2010). It is reported that in 2015, 255 million tons of MSW were incinerated annually, in 1180 MSW incineration plants around the world (Gu et al., 2019). It is further, suggested that soon, eco-cement could be produced within MSW incineration using incineration residue (Ashraf, Ghouleh & Shao, 2019). In a model that analyzed a hybrid solar concentrating system, Sadi & Arabkoohsar (2019) suggested that a bed for increasing the solar share of thermal power can bring more waste incinerators to the electricity market and prevent 8000 tons of carbon dioxide emissions per month.

2.3.1.1.5 Cogeneration

Cogeneration is defined as the generation of work, and useful heat simultaneously, from the same primary energy source (Frangopoulos, 2017). Waste cogeneration is generally a combination of waste associated with the electricity generation and heating process where a plant is based (Rosen & Koohi-Fayegh, 2016). Cogeneration focuses on that the bulk of the heat released during the convention of fuel energy into mechanical or electrical energy, and energy is not wasted or lost, the heat is economically used (Frangopoulos, 2017). A cogeneration system can use renewable sources such as wood, waste products, and methane gas from landfills (Hordeski, 2011). An environmental assessment of MSW waste to energy plants considered different sizes that operated in various methods from power only to full production (Lombardi & Carnevale, 2018). Values for climate change were negative with cogeneration; the fossil fuel depletion indicator benefited from the increase of both the plant sizes. While the residual MSW burning with energy recovery provided savings of primary energy (Lombardi & Carnevale, 2018). The exhaust gas of solid power plant as a heat source and the output of the study was that the net power output of the actual power plant improved by almost 20% when adapting a suitable heat recovery model as an alternative (Tozlu, Abusoglu & Ozahi, 2018).

2.3.1.1.6 Pyrolysis

Pyrolysis is defined as a thermochemical decomposition process or cracking of feedstock into a different useful product. The process occurs with limited supply or total absence of oxidizing agents and does not allow gasification to occur to an appreciable extend (Basu, 2018). The temperature and time spent in the reactor determines the range of products than can be produced. At a lower temperature with a short residence time more oils and tars are produced, and longer residence time results in more residue (Breeze, 2011). The process is regarded as a sustainable approach for the valorization of feedstocks into energy as well as carbon capture and sequestration (Kwon, Kim & Lee, 2019). Thermal pyrolysis of municipal solid waste using a thermogravimetric approach investigated components such as yard waste, food waste, textile, rubber, and paper. For pyrolysis, individual compounds the pyrolytic range of compound was 170-490°C with E/log to A ranges between 10.54 and 13.9 (Chhabra, Bhattacharya & Shastri, 2019).

A pyrolysis process was done on plastic waste to obtain liquid fuel, the investigation found that on different liquid fuels under different conditions it was concluded that the properties of the fuel studied were very similar to those of commercial fuels except for the viscosity (Quesada et al., 2019). In a fluidized reactor pyrolyzed municipal solid waste obtained a pyrolytic oil yield of 38.4–56.5wt% liquid products and separated into soluble water and organic phases. The high carbon content and low oxygen content of the organic phase made the heating value of 27.5 – 32.1 MJ/kg and quality higher than bio-oils (Ding et al., 2016), this work suggested that pyrolysis is an effective method of producing pyrolytic oils by pyrolysis using mixture of municipal solid waste as feedstock.

2.3.1.1.7 Gasification

Gasification is defined in Chapter 1. Gasification has a few potential advantages over the conventional combustion of solid waste (Arena, 2012). The benefits generally relate to the possibility of combining the operating conditions specifically, temperature and equivalence ratio. Arena (2012) further highlights that gasification has a feature that allows the utilization of a specific reactor that is suitable for different applications. The syngas obtained from gasification can be combusted in a traditional burner connected to a boiler and steam turbine and used on gas reciprocating engine or gas turbine (Young

& Young, 2010). Temperature is an important parameter in gasification; a temperature of 800°C or higher is essential for high carbon conversion (Pandey et al., 2015). Analysis of technological aspects of municipal waste solid gasification by Arena, (2012); found that the technology is promising also, the gasification of MSW can reduce landfills significantly and meet emission requirements. Municipal solid waste gasified with switchgrass on a 100kg/h commercial-scale downdraft gasifier showed that co-gasification of up to 40% MSW is satisfactory (Bhoi et al., 2018).

2.4 Theory of the gasification process and applications

Gasification is a process that was initially used for the conversion of coal into fuels, thermal energy, and electricity. It has been greatly used since the 18th century. The growth of the gas and oil industry in the 20th century demoted the technology, different scenarios have made the technology to gain popularity in the 21st century (Brown, 2011). The increase of fossil fuel prices, the decrease of oil reserves, and the proven negative impact fossil fuels have on the environment have led to an interest in gasification as part of the mix in the energy generation process (Brown, 2011).

2.4.1 Theory of gasification

The gasification process has a sequence of reaction steps the feedstock is converted into synthesis gas such as carbon monoxide (CO), hydrogen (H_2), and other gaseous products. The standard conversion is achieved by introducing a gasifying agent like air, oxygen, or steam into a reactor that contains the feedstock; the temperature, pressure, and flow pattern in the reactor are controlled (Speight, 2014). In Figure 2.4 steps of a typical gasification process are illustrated the preheating, thermal decomposition, char gasification and combustion.

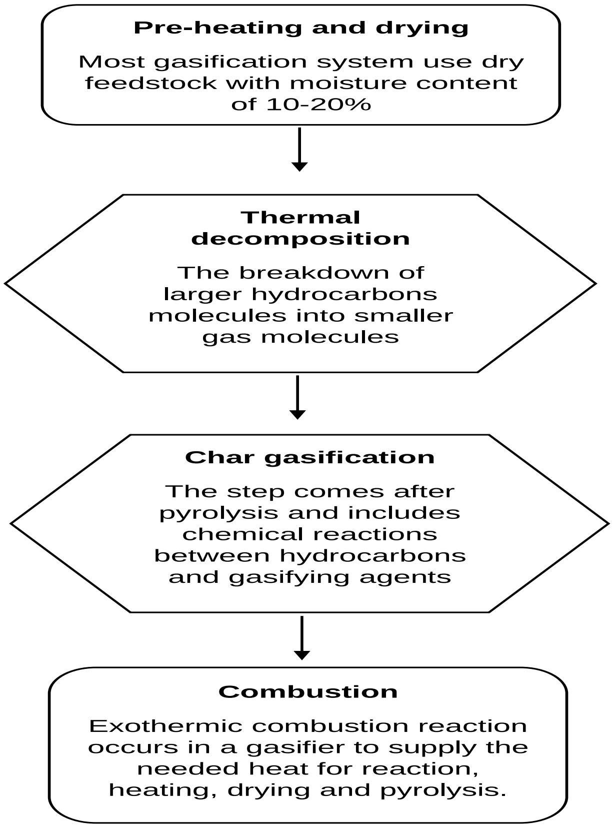


Figure 2.4: Steps of a typical gasification process: Adapted from (Basu, 2010)

Gasification process routes have different syngas specification requirements. Syngas must go through the cleaning and condition steps. The steps include the removing unwanted impurities from the gas mixtures. These impurities include particulate matter, ammonia (NH3), hydrogen cyanide (HCN), hydrogen sulfide (H_2S), and other gases that have Nitrogen (N_2) or sulfur dioxide (SO_2) with different molecular weights and ash (Chianese, Musmarra & Molino, 2016). The gaseous products apart from carbon monoxide (CO), hydrogen (H_2) and the proportions of these products gases like carbon dioxide (CO_2), sulfur dioxide (SO2), methane (CH_4), hydrogen sulfide (H_2S) and water vapor, rely on the following: (a). type of feedstock and chemical composition of the feedstock, (b). gasifying agents, and (c). chemistry and thermodynamics of the gasification reactions determined the process operating parameters (Speight, 2014).

The main chemical reactions of char gasification can be divided into homogeneous and heterogeneous, and they are summarized in Table 2.1. The oxidation of volatiles takes place, and the reactions are represented by equations (2.1) and (2.2).

$$\mathrm{C} + \mathrm{O_2} === \mathrm{CO_2} \tag{2.1}$$

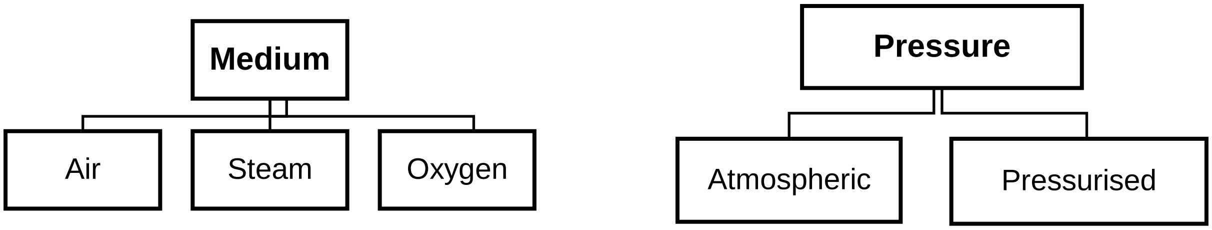
$$\mathrm{Volatiles} + \mathrm{O_2} === \mathrm{CO_2} + \mathrm{H_2O} \tag{2.2}$$

Table 2.1: Main gasification reactions (Acevedo et al., 2018).

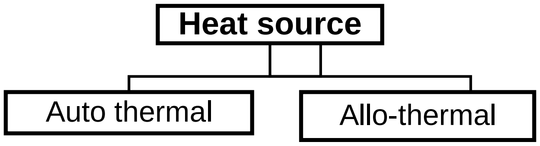
Heterogeneous reactions	**Chemical reaction process**	**Reaction**
$CO+O_2 \rightarrow CO_2$+394kJ/mol	Complete combustion	R1
$C+0.5O_2 \rightarrow CO$+111kJ/mol	Partial combustion	R2
$C+CO_2 \rightarrow 2CO$-172kJ/mol	Boudouard	R3
$C+H_2O \rightarrow CO+H_2$-131kJ/mol	Water-gas	R4
$C+2H_2 \rightarrow CH_4$+75kJ/mol	Methanation	R5
Homogeneous reactions		
$CO+0.5O_2 \rightarrow CO$+283kJ/mol	Co-partial combustion H_2 combustion	R6
$H_2+0.5O_2 \rightarrow H_2O$+242kJ/mol	H_2 combustion	R7
$CO+H_2O \rightarrow CO_2+H_2$+41kJ/mol	Water -gas shift (WGS)	R8
$CH_4+H_2O \rightarrow CO+3H_2$-206kJ/mol	Reforming	R9
H_2S and NH_3 formation reactions		
$H_2+S \rightarrow H_2S$	H_2S formation	R10
$3H_2+N_2 \rightarrow 2NH_3$	NH_3 formation	R11

2.4.1.1Gasification technology

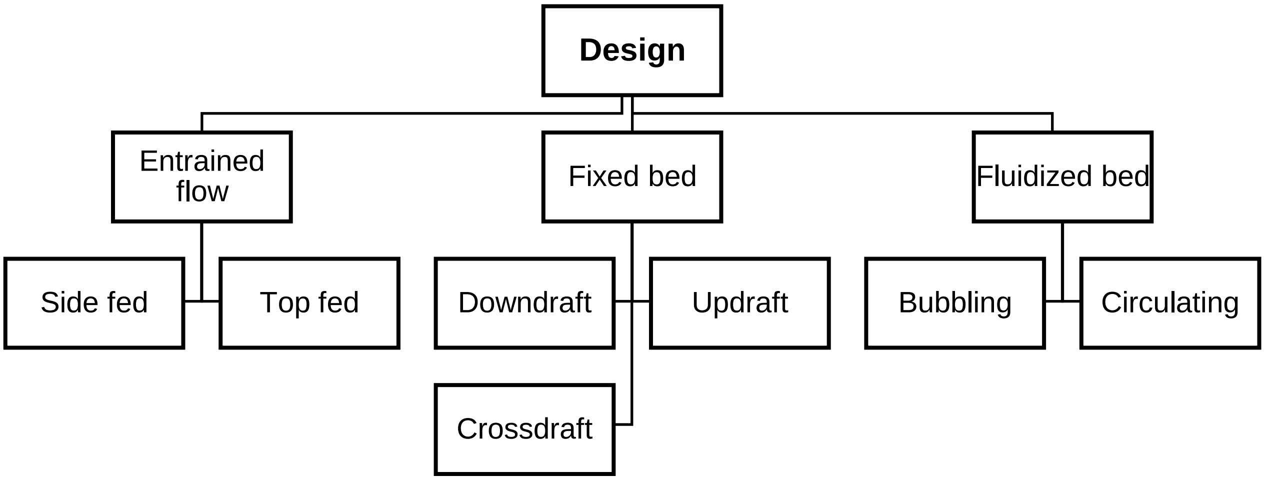
Gasification technology is a mature technology. The reactors used for gasification have been available for decades (Luque, 2016). Around 1850; the gasification industry was already established, the siemens gasifier (1861), the Winkler gasifier (1926) produced fuel gas, and in (1938) the Koppers Totzek entrained gasifier came into commercial use (Luque, Campelo & Clark, 2011). In Figure 2.5 the classification of gasification is illustrated.



(a) Gasifying medium (b) Pressurized method



(c) Heat source



(d) Gasifier types/design

Figure 2.5: Gasification technology classification (La Villetta, Costa & Massarotti, 2017)

The main objectives of gasification are: (a). to convert all the non-ash fraction of the feedstock into gas. (b). to produce gasses that preserve heat combustion of the feedstock as much as possible (Bell, Towler & Fan, 2011). The process has four stages: drying, devolatilization, oxidation, and reduction. Considering the type of gasifier used, stages can overlap Luque, (2016), the steps are illustrated in Figure 2.4. The type of gasifier used, operating conditions, for instance, temperature, and particle size, contribute to the composition of the syngas (Singh & Chaudhary, 2019). To generate heat and electricity using internal combustion engines and gas turbines syngas can be used (Demirbas, 2010). Depending on how the syngas is applied, it must be cleaned of contaminants, or upgraded to meet the requirements of the application (Singh & Chaudhary, 2019). The contaminants and removal techniques limits are presented in Table 2.2.

Table 2.2: Contaminants limits and removal techniques (Singh & Chaudhary, 2019; Sikarwar et al., 2016)

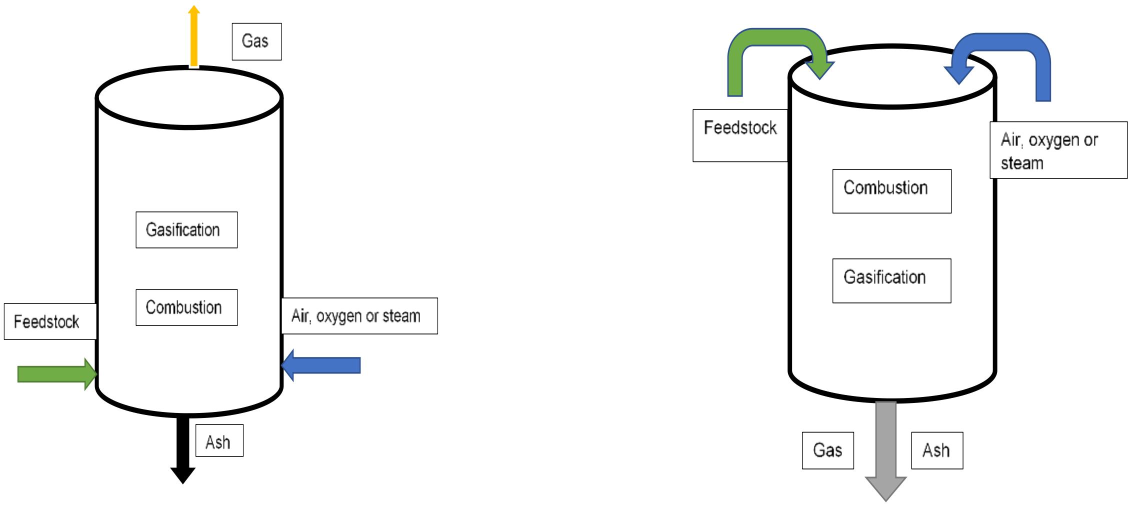
Contaminants	**Downstream application**				**Removal techniques**
	Gas turbine	IC engine	Methanol synthesis	FT synthesis	
Particulates (mg/m^3) (ash, char)	< 30	<50	<0.02	<0.1	Cyclone, barriers filter, wet scrubber, electrostatic precipitators (ESP).
Tar (mg/Nm^3)	<5	<100	<0.1	<0.1-1	Chemical, physical, and catalytic methods
Sulphur contaminants (H_2S, COS) (ppmv)	<20	-	<1	<0.01	Absorber tower and scrubbing
Nitrogen contaminants (NH_3, HCN) (ppmv),	<50	-	<0.1	0.02	Catalyst and wet scrubber
Alkali(ppmv)	<0.02	-	-	0.01	Gas cooler and barrier filters
Halides (ppmv)	<1	-	<0.1	0.01	Wet scrubber

2.4.1.2 Types of gasifiers

A gasifier is regarded as the main component of a gasification plant, it has an obligation of keeping syngas production as steady as possible (Zhang et al., 2019). The gasifier is where the feedstock and the gasifying agent are mixed to a particular degree, in some case together with other inert materials, catalyst or additives, and where the reaction in the gasification takes place (Ruiz et al., 2013). Figure 2.5 illustrates how gasifiers are classified, gasifiers are also separated as single stage unit or multistage unit and the multistage are further subcategorized into single line operation or double line operation. This is how gasifiers are categorised: (a). methods of introducing feedstock into the gasifier, on top or into the side of the gasifier (b). the use of an oxidant such as oxygen, air, or steam, (c). the temperature ranges, (d). the pressure at which the gasifier is operated, and (e). heat supply method for the gasifier directly or indirectly (Speight, 2014).

2.4.1.2.1 Entrained flow gasifier

Operational temperature of an entrained bed gasifier is generally high at a range of 1200-1500°C, at a pressure of 20-70 bar and feedstock with fine particle size less than 1mm (Singh & Chaudhary, 2019). Entrained bed gasifier is classified into two types, the top-fed-downflow utilized by GE energy and Siemens, and the side fed up-flow used by Shell and Koppers-Totzek (Basu, 2018). This gasifier at high operating pressure it can supply syngas at high pressure to the integrated gasification combined cycle (IGCC) system without additional compression (Luque, Campelo & Clark, 2011). The majority of entrained flow gasifiers are designed to use oxygen rather than air, and they operate above the slagging temperature of the feedstock mineral matter (Arena, 2012). Entrained flow gasifiers are categorized according to how and where the fuel is injected into the reactor, in Figure 2.6 schematics of entrained flow gasifiers are shown.



(a) Side fed (b) Top fed

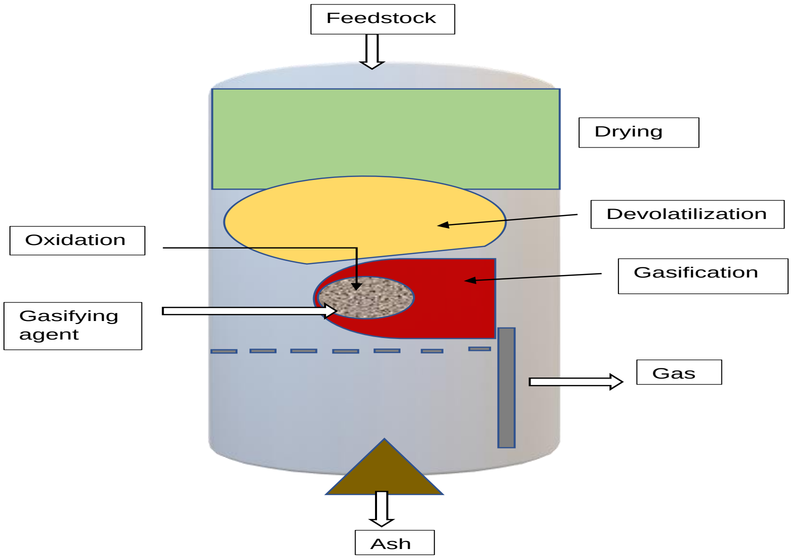
Figure 2.6: Illustration of entrained gasifiers (a). Side fed entrained gasifier and (b). Top fed gasifier: Adapted from (Basu, 2018).

Entrained flow gasifiers can produce high-quality syngas with low tar content (0.01g/Nm3), Singh & Chaudhary (2019) entrained flow gasifiers are also favorable in destroying high tar composition in biomass; however, it can be a problem in gasification (Basu, 2018). In gasification technology, entrained gasifiers are generally utilized in large scales and considered to be effective; owing to their large commercial scale availability and high efficiency to produce syngas (Hernández, Aranda-Almansa & Bula, 2010). Entrained flow gasifiers are generally inappropriate for biomass gasification because of the following reasons: (a). short residence time in a reactor, fine fuel is necessary, and it is hard to grind fibrous biomass into fine particles, and (b), the ash melting point is high for biomass with calcium oxide (CaO) and without alkali, and consequently have higher oxygen need (Basu, 2018).

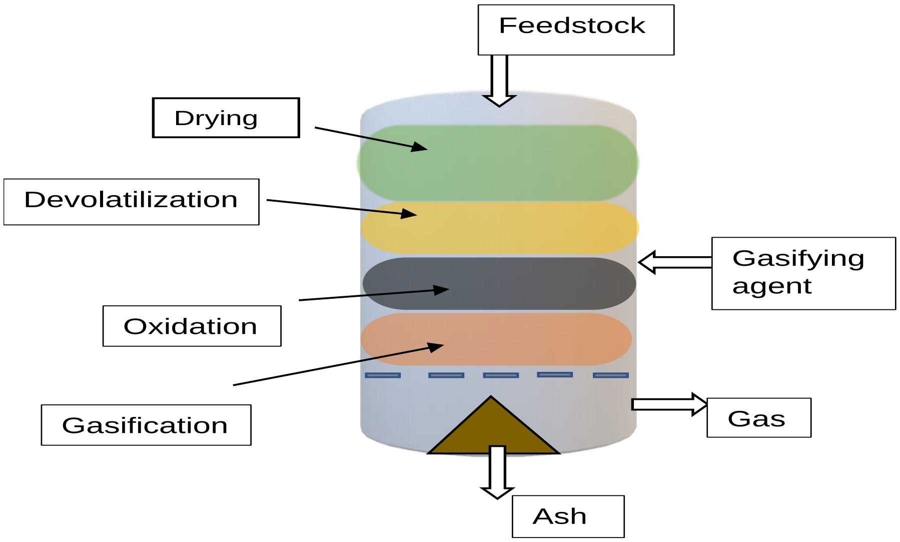
2.4.1.2.2 Fixed bed gasifier

A fixed bed gasifier generally operates with high carbon conversion and the design is not complicated; the gasifier can also provide low gas velocity, long solid residence time, and low ash carryover (Speight, 2014). Cleaning system and gas cooling are part of the fixed bed gasification system, this gasifier system contains a bed of solid fuel particle and the gasifying agent passes through either up or down. This gasifier generally has a cylindrical space for fuel, gasifying media with a fuel feeding unit, an ash removal unit, and gas exit (Chopra & Jain, 2007). Benefits of fixed bed gasifiers include high production rate and calorific value gas production, preferable gas-solid reaction with heat and mass transfer, and improved char conversion (Al-Salem, 2019).

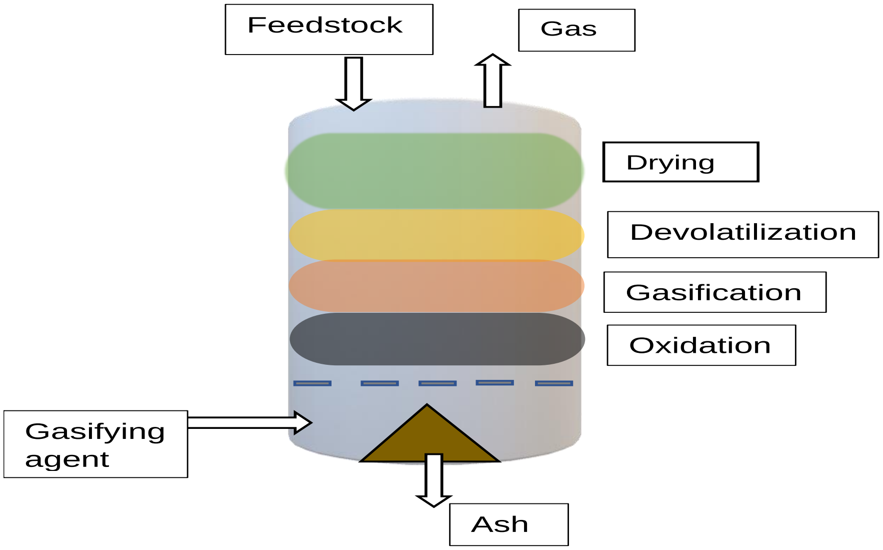
Removing tar is a substantial issue with fixed bed gasifiers, although latest improvements in thermal and catalytic conversion gives options that are reliable, and the heat exchange is effective (Chopra & Jain, 2007). Fixed bed gasifiers typically have a lower heat and mass transfer and often generate higher amounts of tar and char (Heidenreich & Foscolo, 2015). The design of fixed bed should be non-caking and have high mechanical strength especially when coal is used as a co-gasification feedstock to form a permeable bed (Speight, 2014). In a fixed bed gasifier, the feedstock is reduced to small shreds and combustion gases pass through the supported feedstock after which the hot product gases exit from the top of the reactor (Speight, 2014). There are three types of fixed bed gasifiers, cross draft, downdraft, and updraft gasifiers they are illustrated in Figure 2.7.



(a). Cross draft gasifier



(b). Downdraft gasifier



(c) Updraft gasifier

Figure 2.7: Schematic of fixed bed gasifiers (a) Cross draft gasifier, (b) Downdraft gasifier, and (c) Updraft gasifier: Adapted from (Pang, 2016).

2.4.1.2.2.1 Cross draft gasifier

The feed enters from the top, and the gasifying agent enters on the side of the cross-draft gasifier. The advantages of the cross-draft gasifier are the fast response against the load, flexible gas producer, small startup time, compatibility with a dry air blast, and short design height (Pandey et al., 2019). The gas exit is close to the entrance, the combustion is close to the entrance of the air while the devolatilization and pyrolysis zones are higher than the exit (Pandey et al., 2015). For charcoal gasification cross draft gasifiers are generally used. Although the temperature could reach 1500°C during the process, this can result in material problems (Luque, Campelo & Clark, 2011). Cross draft gasifier's disadvantage is that for small feed particles and high tar content it is not desirable (Pandey et al., 2019). The gasifiers have few applications because the fuel gas is produced at high temperatures, and the reduction in carbon dioxide is insufficient.

2.4.1.2.2.2 Downdraft fixed bed gasifier

Downdraft fixed gasifiers are categorised by a concurrent flow of feedstock and gasification agent, they both move downwards through the gasification reactor hence it is regarded as the co-current gasifier (Bermudez & Fidalgo, 2016). The downdraft gasifiers are most common Kumar & Anand (2019), they are easy to control and have an outlet temperature of 800°C and an operating temperature of 800 to 1200°C (Prasad, 2016). The gasifier has four zones (a) the upper zone, (b) upper -middle pyrolysis section, (c) the lower oxidation zone, and (d) the lower reduction zone (Richardson et al., 2015). Figure 2.7 shows a diagram of a downdraft gasifier; this gasifier syngas with low tar content of (0.1 wt%) is produced and it is equivalent to 0.015-3g/Nm^3 (Fabry et al., 2013). However, Singh & Chaudhary (2019) mention that limitations with this gasifier are that the required particle size range is 4-10mm, and the moisture content must be lower than 25%.

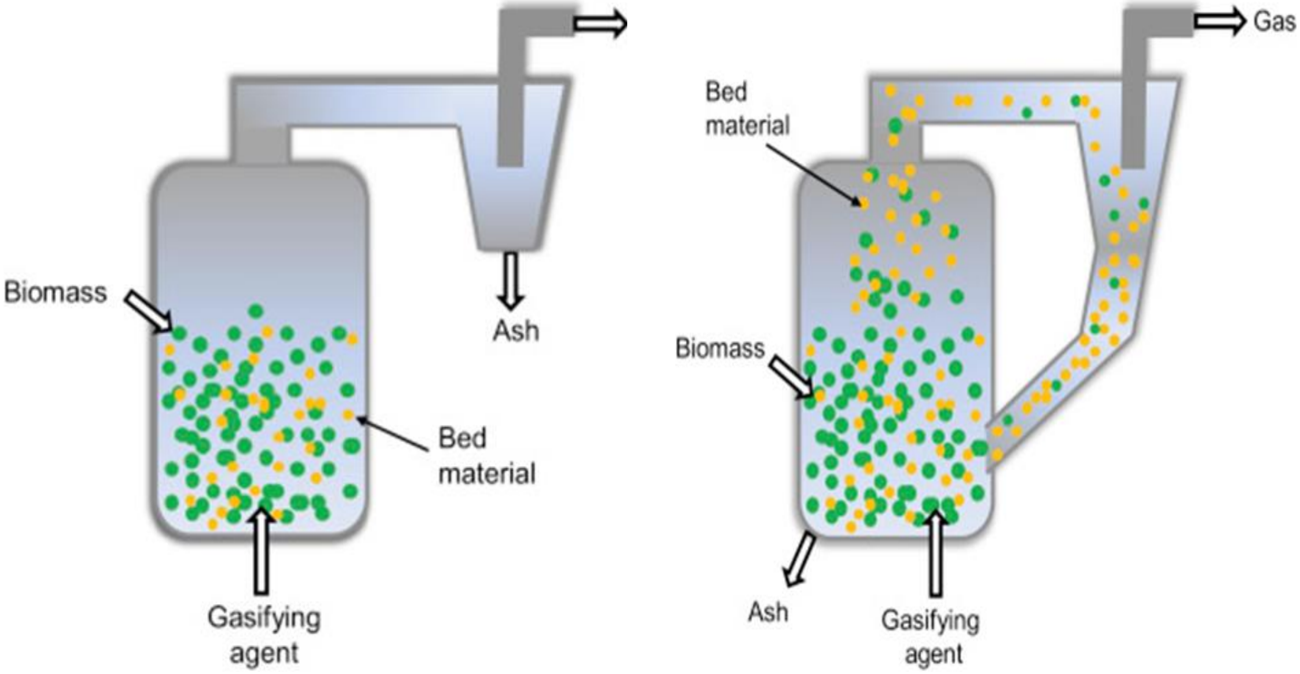
2.4.1.2.2.3 Updraft gasifier

In the updraft fixed bed gasifier, the gasifying medium enters at the bottom and the feedstock is already in the reduction zone, the direction of the gases is in the counter current site for this reason it can also be referred to as countercurrent gasifier (Pandey et al., 2019). Updraft gasifiers are mostly used because they can take feedstock with high moisture content, and because of low exit temperature, they have high efficiency (Watson et al., 2018). Updraft gasifier are sensitive to tar production, and low production of syngas and this can be a problem (Pandey et al., 2019). With an updraft gasifier, the tar of the content of the syngas is high, as a result, it is not suitable for direct engine applications. Also, the pyrolysis zones lie above the combustion zone, the formed tar does not pass through the combustion zone and results to high tar content in the syngas (Luque, Campelo & Clark, 2011). In the drying zone, the steam released is taken away with the syngas and possibly take in biomass with high ash content (Luque, Campelo & Clark, 2011). The updraft gasifier is beneficial because of its simple design and the efficient internal heat exchange, consequently, gives energy efficiency (Luque, Campelo & Clark, 2011).

2.4.1.2.3 Fluidized bed gasifier

Fresh solid fuel particles touch a hotbed of solids, in fluidized bed gasifiers, the solids rapidly heat the particles to the bed temperature, particle then go through quick drying and pyrolysis, char and gases also get produced (Basu, 2010). Even when the bed solids are mixed well, the fluidizing gas stays in plug flow mode, enters at the bottom, and exits from the top (Basu, 2010). Fluidized beds are the most used gasifier types due to advantages such as feeding flexibility, scalability, good mixing capacity, high heat, mass transfer rates, and conversions (Anukam et al., 2016). Fluidized bed gasifiers can work at low temperatures within 800-900°C, this directly affects NOx emissions reduction (Al-Salem, 2019). In addition, efficiency in process carbon dioxide capture and improved fuel flexibility are few of the benefits of this kind of gasifier (Luque, Campelo & Clark, 2011).

The fluidized bed gasifier has no reaction zone, as the reactor is mixed and so close to isothermal, at the bottom of the reactor the fuel particles are injected and can be incorporated with the bed material and be readily heated up to the bed temperature (Prasad, 2016). This results in very fast pyrolysis, in the gas phase the reactions that occur are gasification, and tar conversion (Prasad, 2016). Fluidized bed gasifiers may differ in design configurations and in ash conditions, for improved char utilization. To ensure that temperature does not exceed the ash softening point, the temperature is controlled (Miller, 2011). The most popular fluidized bed gasifier, on a commercial scale, is the Winkler gasifier, which was developed in the 1920s (Schobert, 2013). The Winkler design started as an air blown atmospheric pressure gasifier, it operates at about 950°C, with a residence time of up to three hours. It is suggested that it is difficult to handle caking coal with fluidized gasifiers and the relatively low temperature also makes it hard to run coals of low reactivity (Schobert, 2013). It is pointed out that biomass gasification in fluidized beds receives much attention either academically or industrially (Motta et al., 2018). Depending on the inflow speed, the fluidized bed gasifier can be categorized into two types of the bubbling fluidized bed (BFB) and circulating fluidized bed (CFB) gasifiers. The types of fluidized bed gasifiers are illustrated in Figure 2.8.



(a) Bubbling fluidized bed gasifier (b) Circulating fluidized bed gasifier

Figure 2.8: Schematic of types of fluidized gasifiers (a). Bubbling fluidized bed gasifier (b). Circulating fluidized bed gasifier: Adapted from (Pang, 2016).

2.4.1.2.3.1 Bubbling fluidized bed (BFB)

The bubbling fluidized bed (BFB) gasifier is usually set at a lower velocity (2-2.5 m/s) to make sure that particles do not leave the reactor (Luque, Campelo & Clark, 2011). The upward feedstock diameter of 6mm is fed into a fluidized bed and heated by the hot inert solid making up the bed (Kutz, 2015). The BFB gasifier is characterized by moderate fluidization velocities. Also, the fluid mechanic behavior is dominated by gas bubbles that go up in the gasifier and are responsible for the good mixing behavior in the reactor (Materazzi & Foscolo, 2019). The bed temperature is regulated at 700-900°C, and the temperature is maintained by controlling the air/feedstock ratio (Pandey et al., 2015). The major disadvantage of the BFB gasifier is that satisfactory solids conversion is not reached because of the formation of oxidation and back mixing because of slow oxygen (Bermudez & Fidalgo, 2016).

2.4.1.2.3.2 Circulating bed (CFB)

A circulating fluidized bed (CFB) gasifier is distinctive for biomass gasification since it can provide long gas residence time and works at a higher velocity of 3-m/s (Luque, Campelo & Clark, 2011). Moreover, CFB is also effective for fuels with high volatile; it has a cyclone, a riser, and a solid recycle device (Luque, Campelo & Clark, 2011). In a CFB gasifier, the gasifying agent is introduced upward at fast velocity to move the bed material throughout a circulating loop, and full mixing is achieved because of the long residence time (Bermudez & Fidalgo, 2016). Feedstock with small particle size (<400 μm) can be processed by CFB and achieve wider particle size distribution without losing entrainment, CFB gasifiers are also good for a variety of feedstock (Bermudez & Fidalgo, 2016).

In a CFB gasifier, solids are spread on top of the tall riser; this permits a long residence time for the gas and the fine particles. A large scale of solids moves out of the CFB riser, they are contained and constantly returned to the riser base (Luque, Campelo & Clark, 2011). The fluidization velocity and the rate at which the solids are recycled in the riser; are enough to keep the riser in a hydrodynamic condition recognized as a fast fluidized bed (Luque, Campelo & Clark, 2011). Based on the application and fuel, the riser function at a temperature of 800 –1000°C (Luque, Campelo & Clark, 2011).

According to La Villetta, Costa & Massarotti (2017) the design and variety of gasifiers have been investigated and researched for over a century. A summary of gasifiers is presented in Table 2.3 based on configuration or size.

Table 2.3: Summary of characteristics of various commercial gasifiers (Basu, 2018).

Parameter	**Entrained bed**	**Fixed bed**	**Fluidized bed**
Feed size	<0.15mm	<51mm	<6mm
Tolerance for fines	Excellent	Limited	Good
Tolerance for course	Poor	Very good	Good
Exit gas temperature	>1260°C	450-650 °C	800-1000°C
Reaction zone Temperature	1990°C	1090°C	800-000°C
Feedstock tolerance	Any coal, but unsuitable for biomass	Low rank coal	Low rank coal and excellent for biomass
Oxidant requirements	High	Low	Moderate
Requirement of Steam	Low	High	Moderate
Ash characteristics	Slagging	Dry	Dry
Cold gas efficiency	80%	80%	89%
Application	Large in size	Small capacities	Medium capacities
Disadvantages	Raw gas cooling	Production of tar	Carbon conversion

2.4.1.3 Types of gasification processes

Gasification process differs from the types of gasifiers, when selecting gasification type for syngas generation factors such as fuel type, plant size, and reactivity of fuel are taken into consideration.

2.4.1.3.1 Air gasification

The most popular, easy, and affordable kind of gasification process is the air gasification, the gasifying agent for this process notwithstanding heat is air (Zainal et al., 2001). Air contains 79% by volume of nitrogen, which does not react with the biomass (Zainal et al., 2001). When air is utilized as the gasifying agent, the nitrogen dilutes the gas produced and consequently lowers its heating value to about 4-5MJ/m3. Even though the gas produced is capable of operating boilers or engines; it is overly diluted to cost effectively transport in pipelines over a long distance (Zainal et al., 2001). A clear trend is observed, in an experiment and modelling analysis of air and CO2 biomass gasification (Antolini et al., 2019). Some parameters are functions of the equivalence ratio, increasing ER the fraction of methane, and char composition reduced. In air gasification, the range of measurements, hydrogen, and carbon monoxide showed similar trends, and increased with the increase of the equivalence ratio. The use of air and CO_2 increases the conversation of carbon (Antolini et al., 2019).

2.4.1.3.2 Oxygen gasification

Using oxygen as a gasifying agent rather than air, approximately 8 MJ/m^3 of medium energy gas will be produced, and it is suitable for limited pipeline distribution (Zainal et al., 2001). The gas can be utilized for industrial process heat or as synthesis gas to make gasoline, methanol, ammonia, hydrogen, or methane (Zainal et al., 2001). Oxygen can partially replace air or used completely as the oxidant. Oxygen has the advantages that at a higher reaction temperature which leads to lower tar levels, lower gas volumes, efficient use of gas, and improved heating value of gas (Archer & Barber, 2004). Procurement and other additional measures required to reduce the hazards associated with using oxygen have added energy and financial cost (Archer & Barber, 2004).

2.4.1.3.3 Steam gasification

Steam gasification is the reaction of steam with solid carbonaceous feedstock such as biomass, coal, coke, or carbon-containing waste to produce syngas (Blasi et al., 2014). Steam gasification offers high stoichiometric yield of hydrogen, and it is an effective and efficient technique for generating hydrogen from biomass. Few factors have an impact on the hydrogen yield. The general factors that influence the yield include biomass feed, biomass type, reaction temperature, steam, and particle size (Parthasarathy & Narayanan, 2014). Occasionally steam is added with air as gasifying agent to enhance the quality of the produced gas and lower the reaction heat (Parthasarathy & Narayanan, 2014). Having a small amount of steam contribute to the production of methane, from the drying process of biomass steam is also generated (Zainal et al., 2001). Steam gasification is used to produce H_2 from bio-oil/char slurry, char as a byproduct of the fast pyrolysis process is mixed with bio-oil/char slurry, and high density is observed. The first general procedure of steam gasification occurs, followed by methanation, and shifts the equilibrium to improve the H_2 yields. The reverse boudouard reaction may also take place based on these conditions. If there is no solid carbon formation, the maximum stoichiometric yield of H_2 could be achieved (Blasi et al., 2014).

2.4.1.3.4 Plasma gasification

Plasma gasification is the thermal breakdown of carbonaceous material in an oxygen-starved environment into pieces of compounds (Basu, 2010). Plasma gasification, produces high energy content, has high enthalpy, and shows high temperature. Plasma gasification has high energy content therefore the process can be attained with no oxidizing media (Hlina et al., 2014). It is necessary to include oxygen, air, H_2O, and CO_2 or it will cause insufficient carbon conversion, Hlina et al (2014) further mention that gas composition of plasma gasification has to be stable and simple due to the quenching and short residence time. The operating center of the process is a plasma gun, in a closed vessel that has two electrodes spaced apart, and the intense electric arc is created, and the inert gas is passed (Basu, 2010).

2.4.1.4Gasification Application

The gasification process can generate fuel gas that is effective for few applications, this is controlled by the type of gasifier and other operating conditions (Speight, 2014). For the purpose of electric power generation gasification allows the use of technology that is regular and acceptable in modern gas-fired power plants. The rate char is generated in gasification is longer than the rate at which char is generated during the pyrolysis of the biomass (Speight, 2014).

2.4.1.4.1 Gasifier efficiency

A significant factor determining whether a gasifier is sensible economically and the actual operation is the gasification efficiency (FAO, 1986). Based on the gasifier design and characteristics of the gasification fuel efficiency can range between 60 and 75%, and the thermal application may be 93% high (FAO, 1986). The efficiency of a gasifier can be described by its capacity to convert the solid material and its energy content into gas (La Villetta, Costa & Massarotti, 2017). Equation (2.3) describes gasification efficiency when the gas is for engine applications (FAO, 1986).

$$\eta_m = \frac{H_g \text{ x } Q_g}{H_s \text{ x } M_s} \text{ x } 100\ (\%) \qquad (2.3)$$

where:

η_m = gasification efficiency (%) mechanical

H_s= lower heating value of gasifier fuel (kJ/kg)

H_g = heating value of the gas (KJ/m^3)

M_s= gasifier solid fuel combustion (kg/s)

Q_g=volume flow of gas (m^3/s)

When the gas is utilized for direct burning gasification efficiency is defined by equation (2.4).

$$\eta_{th} = \frac{(H_g \text{ x } Q_g) + (Q_g \text{ x } \rho_g \text{ x } C_p \text{ x } \Delta T)}{H_s \text{ x } M_s} \text{ x } 100\ \% \qquad (2.4)$$

Where:

C_p= specific heat of the gas (kJ/kg°K)

η_{th}= gasification efficiency (%) thermal

ρ_g= density of the gas (kg/m^3)

ΔT= change in temperature between the gas at the burner inlet and the fuel entering the gasifier (°K).

2.4.1.4.2 Design and operating parameters of a gasifier

The hub of the gasification process is the gasifier, it is designed to consistently process fuel in different ways (Speight, 2011). The application range of the gasifier is influenced by the gasifier design, fixed bed gasifiers are suitable for smaller units of 10-10 000 kW, fluidized bed gasifiers are appropriate for medium-sized units of 5-100mW, and entrained flow gasifier are for large units above 50mW (Guangul, Sulaiman & Ramli, 2012). For any design specifications are important; gasification medium, syngas and the specification of the fuel are part of the inputs (Basu, 2018).

2.4.1.4.3 Gasifier process design

In a standard design process of a gasifier a mass balance precedes the energy balance around the gasifier (Basu, 2018). The standard mass and energy balance are general to all kinds of gasifiers and require calculations of fuel feed rate and products gas flow.

2.4.1.4.3.1 Mass balance

The required thermal output $\mathrm{Q}\ (\mathrm{MW_{th}})$ syngas flow rate is significant input parameter of a gasifier. The volume flow rate of the syngas $\mathrm{V_g}(\mathrm{Nm^3}/s)$ with the desired heating value, $\mathrm{LHV_g}(\mathrm{MJ/Nm^3})$ is found by equation (2.5).

$$\mathrm{V_g} = \frac{\mathrm{Q}}{\mathrm{LHV_g}} \mathrm{N.m^3/s} \qquad (2.5)$$

From its composition the net heating value of syngas can be calculated, to predict the composition the equilibrium calculation may be used. Out of a comparable gasification condition in published data a sensible prediction can be made. To find the fuel feed rate, $\mathrm{M_f}$, the required output is divided by the LHV of the feedstock $\mathrm{LHV_f}$, and by the gasifier efficiency, η_{gef}., and it is expressed in equation (2.6).

$$M_f = \frac{Q}{LHV_f \eta_{\mathrm{gef}}} \qquad (2.6)$$

The lower heating value on wet basis $\mathrm{LHV_f}$, could be linked to the higher heating value $(\mathrm{HHV_d})$ on dry basis and its hydrogen $\mathrm{H_d}$ fraction on wet basis and moisture fraction M on wet basis.

2.4.1.4.4 Energy balance

Gasification reactions are endothermic, for these reactions to occur at an acceptable temperature heat should be allocated to the gasifier. The heat requirement of the endothermic reactions and the gasification temperature influence the external heat amount that is supplied to the gasifier (Basu, 2018). In a study by Wan et al. (2013), the energy balance results showed that 50-59% of wood heating value was converted to the producer gas while 10-12% of heating value was dissipated.

The energy conversion rate from wood to syngas can be calculated using equation (2.7).

Energy conversion rate:

$$= \frac{\mathrm{LHV}_{\mathrm{syngas}} * \mathrm{Volume}_{\mathrm{syngas}}}{\mathrm{LHV}_{\mathrm{feedstock}} * \mathrm{Weight}_{\mathrm{feedstock}}} \mathrm{\ x\ } 100\% \qquad (2.7)$$

Wan et al. (2013), calculated the entrapped heat energy in the producer gas from the gasifier and it was calculated according to the gas composition, heat capacities and gas temperature when getting in the heat exchanger ($\mathrm{T}_{\mathrm{hex\ in}}$). The calculation procedure of the mass and energy balance is further detailed in Chapter 3. Carbon conversion and cold-gas efficiency are performance parameters of a gasifier. The design of the gasifier can be affected by gasification parameter as follows: (a). heating value, the desired heating value of a syngas dictates the choice of gasification medium, (b). steam can maximize hydrogen (c). air cannot be chosen if nitrogen is not acceptable in the product, (d). capital cost is lower for air, followed by steam, and (e). equivalence ratio has crucial effect on carbon conversion efficiency (Basu, 2018). The output process design includes the geometry of the gasifier and operating performance parameters. The geometry includes (hardware design) the size, height, cross sectional area, and gasifier configuration (Basu, 2018). The significant parameters are: (a). amount of steam/feedstock ratio in relation to the proportion of the gasifying medium (b). reactor and preheat temperature, and (c). steam, air, or oxygen (Basu, 2018).

2.4.1.5 Operating parameters

A general understanding of the operating and control of gasification is important for the identification of the input parameters which affect the gas quality more than the other. In this section, the effects of some of the main operating conditions are briefly discussed. The parameters include moisture content, equivalence ratio, particle size, gasifying agents, temperature, pressure addition of a catalyst, and superficial velocity. Research shows that the operating conditions of a gasifier have considerable influence on the composition and quality and final application of the producer gas (Hernández, Aranda-Almansa & Bula, 2010). The significance of an input parameter is described according to the number of times it shows an important impact on the output parameters (Mirmoshtaghi et al., 2016).

2.4.1.5.1 Moisture Content

Moisture in a feedstock may be present in different forms, as water molecules, unbound liquid, and as water vapor (Pandey et al., 2015). Moisture content can be decided on a dry basis as well as on a wet basis (Doran, 2009). Moisture content is expressed by equation (2.8).

$$\mathrm{MC_{dry}} = \frac{\text{wet weight}-\text{dry weight}}{\text{dry weight}} \text{ x } 100\% \qquad (2.8)$$

Feedstock with low moisture content is beneficial, however with high moisture content increased energy to evaporate liquid forms of moisture is needed (Luque, Campelo & Clark, 2011). When moisture moves in a material its enthalpy is carried with and consequently contributes to the heat transfer. Moisture flows enthalpy is higher in the vapor phase than in the liquid phase in the phase changes, energy is released and absorbed (Trechsel & Bomberg, 2009). The effects of moisture content on heat transfer, is divided into three components. (a). Effect I: heat flux $\mathrm{q_I}$,heat flow caused by the temperature gradient in a condition of moisture equilibrium, there is no moisture transfer, (b). Effect II: heat flux $\mathrm{q_{II}}$, heat transfer by moisture flow, particular enthalpies of water vapor and the water are carried with. The latent heat of evaporation is used to distinguish the enthalpy of water vapor from the enthalpy of water (c). Effect III: heat flux $\mathrm{q_{III}}$, heat transfer due to phase changes (Trechsel & Bomberg, 2009). Feedstock properties with lower moisture content generate high combustible gas yield (Ku et al., 2019).

2.4.1.5.2 Equivalence ratio

The equivalence ratio (ER) represents the ratio between the biomass in and masses air gasification under the actual operating conditions to the same ratio under stoichiometric conditions (Basu, 2010). The equivalence ratio is regarded as the main operating parameter affecting gasification; when ER is equal to zero, there is no oxidation in the system (Basu, 2010). Excessive equivalence ratio is not necessary, when increasing ER, more air is introduced in the gasifier, the oxidation reaction is better with a higher rate than that of cracking and reforming reaction (Al-Salem, 2019). Moreover, these improves the formation of CO_2, H_2O, and N_2. A high equivalence ratio leads to adsorption and cracking of the tar, and high ER supports a high working temperature, this promotes increased production of H_2 (Kim et al., 2011). Standard ER values are between 0.2 and 0.4; when ER is equal to one it represents stoichiometric combustion; combustion in fuel-lean conditions takes place when ER is greater than one, and fuel-rich combustion occurs when ER is below one (La Villetta, Costa & Massarotti, 2017).

The equivalence ratio is possibly the most significant parameter for developing the quality of gas yield in air gasification of plastic (Narváez et al., 1996). Equivalence ratio has significant impact on the gas yield and reactor temperature in the gasification of plastic than fluidization velocity and bed height (Xiao et al., 2007). ER has a great impact on the gasification process, it regulates the system’s temperature and calorific value of the fuel system, it further has an effect on the composition of the syngas and also depends on other considerations like steam to biomass ratio and temperature (Kumar, Jones & Hanna, 2009). In an investigation that aimed to find the effects of furnace temperature, steam to biomass, and equivalence ratio on gas composition, carbon conversion, and energy, it was reported that an increase in ER from 0.07 to 0.25 led to an increase in gas yields, carbon conversions and energy efficiencies (Kumar et al., 2009). With increased freeboard temperature in the fluidized bed system, reduced ER can be balanced and a high amount of gas produced with increased temperature and high ER; such cases occur during the pyrolysis stage of gasification (Al-Salem, 2019).

2.4.1.5.3 Particle size

Particle size is another key parameter for solid feedstock in gasification (Burgt & Higman, 2008). In detailed work on a downdraft fixed bed gasifier by Reed & Das (1988) it is suggested that the shape and fuel particle size could regulate the fuel feeding and behavior inside the reactor. Feedstock that has a smaller particle size can lead to an increase in gas yield and a decrease in char and tar yields in the pyrolysis step (Wei et al., 2006). Experiment work of air-steam gasification in a fluidized bed, it was concluded that smaller particle size causes a higher carbon conversion and calorific value (Lv et al., 2004). To obtain maximum efficiency in the biomass burning rate, smaller particle sizes have to be utilized (Tinaut et al.,2008). Gasification in a fixed bed reactor study concluded that both smaller fuel particle size resulted in higher gas yield (Chen et al., 2003). In a study that looked at steam gasification of almond shells in a fluidized bed reactor, Rapagnà & Latif, (1997) found similar results in a fluidized bed and reported that the gasification process is generally regulated by the reaction kinetics for smaller particles. Smaller particle size leads to more CH_4 and tar yield however carbon conversion is reduced and less content of CO_2 in the syngas, smaller particles have more surface area (Mirmoshtaghi et al., 2016).

2.4.1.5.4 Gasifying Agent

Air, oxygen, and steam are generally the main gasifying agents utilized for gasification. The producer gas composition and heating values are influenced by the gasifying agents (Basu, 2010). Air gasification generates producer gas with a low heating value (LHV_{syngas}) owing to the high nitrogen content, and for small scale applications the technology is considerably economical (La Villetta, Costa & Massarotti, 2017). Oxygen is essentially utilized for the combustion step and it is a favored gasifying agent, it can be allocated to a gasifier through air or in pure form (Basu, 2010). Due to nitrogen removal oxygen gasification increases the LHV, and it is an alternative for producing high carbon sequestration and storage, and increases operating cost and difficulty because of the need of an air separation unit and the storage and distribution system (Narváez et al., 1996). Steam is an important parameter when adjusting the syngas H_2/CO ratio, steam-methane reforming reactions are promoted by it. Steam entering the gasifier is superheated or saturated, meaning it carries heat, when steam is the only gasifying agent the gasifier will be directly heated (Motta et al., 2019). Syngas with high quality is produced by steam gasification, and it is carried out with steam/oxygen mixtures (Gil et al., 1999). Table 2.4 gives a summary of the different gasifying agents compared, their advantages, disadvantages, and the syngas.

Table 2.4: Gasifying agents compared (Al-Salem, 2019).

Gasifying agent	Advantages	Disadvantages	Syngas
Air	Simple and affordable	Diluted syngas, low CV, formation of NOx	Notable N_2 in the syngas.
Oxygen	High calorific value, increased combustion reaction in gasification and low preheating cost	Generates pure O_2 and it is energy intensive.	Increased combustible gases and low amount of N_2 in the syngas
Steam	Increased heating value and gas quality. Better water gas shift reaction and reforming.	High tar formation than oxygen and air.	Enhanced CO and H_2 concentration in the syngas

2.4.1.5.5 Temperature

The selection of gasification temperature should be done with caution because when temperature is higher than 1000°C, ash melting and sintering can occur, and they are not suitable for a stable gasifier (Motta et al., 2019). The Le Chatelier principle suggests that higher temperatures shift the chemical equilibrium to the side of the reactant in the case of exothermic reactions, and to the side of the products in the case of endothermic reactions (Motta et al., 2019). Gasification temperature influences the syngas composition and properties. Temperature affects devolatilization and modifies the macro products (La Villetta, Costa & Massarotti, 2017). The increased temperature results in higher syngas production and reduction of tar content (Narváez et al., 1996). A study that looked at sugarcane bagasse gasification by Motta et al. (2019) also concluded that temperature is the only parameter when raised led to higher CO, and lower CO_2 concentrations. At a laboratory scale temperature is an operating parameter, it is a function of the equivalence ratio, gas and solid flow-rates, and thermal dispersions (La Villetta, Costa & Massarotti, 2017).

2.4.1.5.6 Pressure

Working pressure is ordinarily set on conditional requirements, downstream or upstream of the gasifier. The compression energy is saved by high processing pressure and the size of the equipment is reduced (Burgt & Higman, 2008). Operating pressure controls product yields and distribution the amount of CO_2 and CH_4 in the fuel gas increase with pressure; at the same time, the amount of syngas and light hydrocarbons decrease (Luque, Campelo & Clark, 2011). Additionally, tar yields decrease with great pressure because of the destruction of the volatile release from the fuel particles by the physical effect of the external pressure (Luque, Campelo & Clark, 2011). Applications with high-pressure such as power generation gas turbines could regard syngas from pressurized gasifiers as useful (Al-Salem, 2019).

2.4.1.5.7 Addition of catalyst

In the thermochemical conversion of biomass, the use of a catalyst could be insignificant; but it could assist in other conditions (Basu, 2010). The incentives for catalyst use are tar removal, and reduction in methane content (Basu, 2010). Some of the impurities in the producer gas is tar, and it is the main issue for researchers. Catalysts greatly influence acquired products in the gasification process (Luque, Campelo & Clark, 2011). Also, the role of the water-gas shift reaction influences the heating value of the gas obtained, and catalysts increase H_2 concentration and customize the production of CO and CO_2 (Luque, Campelo & Clark, 2011). The use of a catalyst in biomass gasification can be classified into two well-defined groups considering the position of the catalytic reactor relative to the gasifier. The first group of catalysts, known as the primary catalysts, is added to the biomass directly to reduce tar content (Pandey et al., 2015). The effect of these catalysts is very small on the conversion of methane and C_{2-3} hydrocarbons in the syngas (Pandey et al., 2015).

Most primary catalysts are non-renewable and have similar operating conditions as the gasifier, these catalysts usually have cheap disposable material. The second group of catalyst is put in a secondary reactor downstream from the gasifier. These catalysts are active in reforming hydrocarbons and methane. The three distinct groups of catalyst materials for biomass gasification are: (a). dolomite catalyst, (b). nickel and other catalysts, and (c). alkali metal and other catalysts (Pandey et al., 2015). A dolomite catalyst is a magnesium ore with the general formula $MgCO_3CaCO_3$, and it could be utilized as the main catalyst; commonly referred to as a guard bed; it is a dry mixture with biomass in a downstream reactor (Pandey et al., 2015). Nickel catalysts are often utilized during biomass gasification process for hot gas cleaning, nickel catalysts contain an active component, nickel (Ni), a dopant or promoter as a second added component and a support phase. Higher nickel contents generally result in lower tar yield and higher H_2 and CO yields (Pandey et al., 2015). According to Bartholomew, Weathebee & Jarvi, (1980), the amount of nickel in the catalyst has the most effect on the catalyst deactivation by coking. Alkali metal catalysts generally can be directly added to the biomass by dry mixing or wet impregnation, this makes recovering of the catalyst difficult, and not worthwhile all the time for the gasification process. In addition, it increases the remaining ash content after char gasification and makes the disposal a problem for the technology (Pandey et al., 2015). As investigated by Mudge et al. (1985), small amount or no carbon was observed in the used catalyst. These alkali metals may impact the pyrolysis process significantly, form a reactive char that intensify gasification.

The development of a catalyst creates challenges for tar removal and syngas conditioning (Pandey et al., 2015). A standard selection of catalyst for tar removal (a). strong resistant to deactivation by carbon fouling and sintering, and (b). effective resistance to attrition (Basu, 2010). In methane reduction, Basu (2010) mentions that the catalyst must be effective in reforming methane and provide the required CO/H_2 ratio for the syngas process. The utilization of an active and stable catalyst allows the gasification of biomass at reduced temperature. Close to the thermodynamic equilibrium operation, catalytic steam gasification of biomass assists in tar reforming and eliminates high-cost downstream processing. In addition, tar conversion adds value to the syngas with increased H_2 and CO yields. Consequently, catalytic biomass steam gasification yields high energy efficiency process, and produces high quality and tar-free synthesis gas (Mazumder & de Lasa, 2016). The successful application of syngas relies not only on the quality of tar but also on the combustion of tar components and properties (Anis & Zainal, 2011). As a result, tar treatment to selectively convert or remove tar is a challenge for future research in the application of syngas.

2.4.1.5.8 Superficial Velocity

Superficial Velocity (SV) is the ratio of air to the cross-sectional area of the gasifier, that takes away the influence of the gasifier dimension by normalization (Kumar, Jones & Hanna, 2009). With a high value of SV, very fast pyrolysis occurs and reduces the amount of char and high-temperature gases in the flaming zone are high (Kumar, Jones & Hanna, 2009). Superficial velocity notably decreases the syngas residence time in the gasifier and results in lower efficiencies in the tar cracking process (La Villetta, Costa & Massarotti, 2017). Superficial velocity is higher in a circulating fluidized bed gasifier than in a bubbling fluidized bed gasifier, high velocity combined with good mixing allows a CFB to have large throughputs of biomass (Basu, 2010). Increasing air superficial velocity solid yield decreases, this was concluded in a study by Chen et al. (2013), the authors found that, in coconut and oil palm fiber, surface oxidation dominates torrefaction. Moreover, an upper limit of air-superficial velocity in the reduction of solid-yield, and that biomass degradation is not controlled by surface oxidation anymore, instead internal mass transport directs it.

2.5 Thermodynamic theory and application in gasification

Thermodynamics deals with the relationships between properties of matter such as heat, work, temperature, and transfer of energy between matter and its surroundings that make changes (Schaschke, 2014). The changes can either be chemical and physical. The four laws of thermodynamics define the relationships in terms of energy, entropy, and temperature (Schaschke, 2014). The gasification reaction process produces a gaseous fuel-rich product and a small amount of char and ash; the process occurs when it reacts with an oxidizer (Luque, 2016). The process occurs at high temperatures and involves several reactions that occur, at the same time (Luque, 2016). According to Klass (1998), gasification reactions are endothermic in general and to thermally balance the exothermic and endothermic reactions; the design can be adjusted.

2.5.1 Laws of thermodynamics

Four fundamental laws govern thermodynamics: zeroth law, first, second, and third law of thermodynamics. Atkins & de Paula (2016), these laws were developed and discovered on observation and experimental research.

2.5.1.1 Zeroth law

Zeroth law is a property of a system based on the equilibrium concept. If systems A and B are in equilibrium with each other, and systems B and C are also in equilibrium with each other we can conclude that systems A and C are also in equilibrium (Tabatabaian & Rajput, 2018). Monitored experiments confirm the statement, A ⇔C and B⇔ C, then A, B, C share the same temperature (Tabatabaian & Rajput, 2018). “If two systems are in thermal equilibrium with each other and, there is a physical property that is common to the two systems this common property is the temperature” (Tiwari & Mishra, 2012). The physical systems of zeroth law are represented in Figure 2.9.

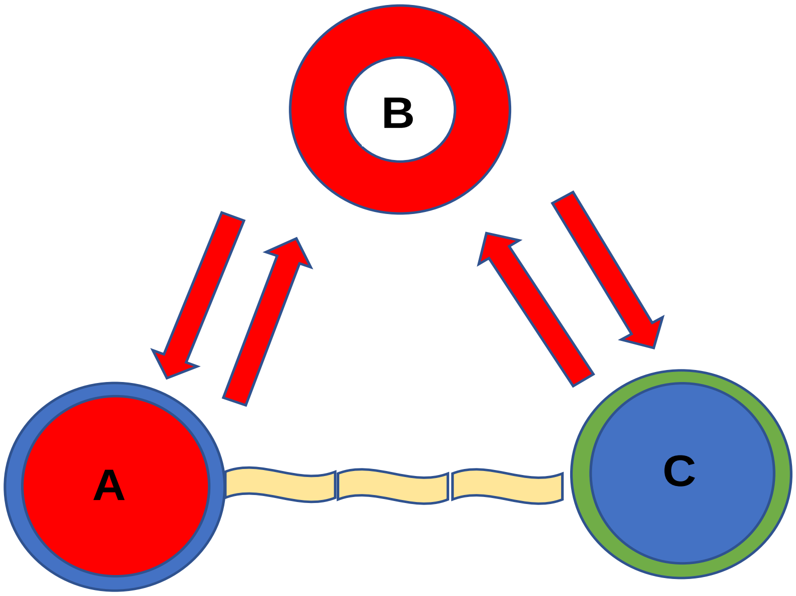


Figure 2.9: Illustration of Zeroth law of thermodynamics: Adapted from (Bera et al., 2017)

2.5.1.2First law of thermodynamics

The first law of thermodynamics is based on the principle of energy conservation, and it is stated as “energy can neither be created nor destroyed but can be transformed from one form to another”. The first law defines the state of energy of a system based on the principle of conservation of the total energy generally concentrating on internal energy (Khan, 2015). It is the convention that when work is done by a system the amount of work done is positive (Basu & Debnath, 2019). When work is done on the system the amount of work transfer is considered negative, this is expressed by equation (2.9).

$$\mathrm{dE} = \partial \mathrm{Q} - \partial \mathrm{W} \qquad (2.9)$$

There is a property of a system called energy E, in order to change in its value, the algebraic sum of the heat supplied and the work done during any change in state (Basu & Debnath, 2019). This is also described as a corollary of the first law of thermodynamics, energy E, and may include kinetic and potential energy. In a thermodynamic system these values are negligible only the energy due to change in temperature is considered and this energy is called the internal energy and it is denoted by U. A thermodynamic process occurs in the absence of heat transfer from or to an external source it is defined as the adiabatic process, that is whenever the change of state takes place without any heat transfer the processes can be expressed by equation (2.10) (Basu & Debnath, 2019).

$$\Delta \mathrm{U} = \mathrm{W}_{\mathrm{ad}} \qquad (2.10)$$

W_{ad} is the adiabatic work done?

When the change of state takes place without any heat transfer, it is called the adiabatic process, and the change in internal energy $\Delta \mathrm{U}$ is independent of the process path.

2.5.1.3 Second law of thermodynamics

The second law of thermodynamics defines entropy changes as a state property of a system based on the principles of Carnot, Clausius, Kelvin, and Caratheodory (Çengel &

Boles, 2014). **Carnot principle:** The efficiency of an irreversible heat engine is always less than the efficiency of a reversible one operating between the same two reservoirs. The efficiencies of all reversible heat engines operating between the same two reservoirs are the same. **Clausius' principle**: Heat cannot to move by itself from low temperature to high temperature, for heat transfer to occur it has to be in the direction of where temperature is decreasing (Dincer & Rosen 2013). Equation (2.11) shows the principle.

$$\oint \left(\frac{\delta \mathrm{Q}}{\mathrm{T}}\right) \leq 0 \qquad (2.11)$$

Equation (2.11) can be expressed without the inequality as:

$$\mathrm{S}_{\mathrm{gen}} = - \oint \left(\frac{\delta \mathrm{Q}}{\mathrm{T}}\right) \qquad (2.12)$$

Where:

$$\mathrm{S}_{\mathrm{gen}} = \Delta \mathrm{S}_{\mathrm{total}} = \Delta \mathrm{S}_{\mathrm{sys}} + \Delta \mathrm{S}_{\mathrm{surr}} \qquad (2.13)$$

The quantity of S_{gen} is the entropy generation linked with a process because of irreversibility, the following are cases for values of $\mathrm{S}_{\mathrm{gen}}$.

$\mathrm{S}_{\mathrm{gen}} < 0$ for no process

$\mathrm{S}_{\mathrm{gen}} > 0$ for an irreversible process

$\mathrm{S}_{\mathrm{gen}} = 0$ for a reversible process

A reversible process can be presented as:

$\Delta S_{sys} = \left(\frac{Q}{T}\right), and\ \Delta S_{surr} = -\left(\frac{Q}{T}\right) rev$ for irreversible process $\Delta \mathrm{S}_{\mathrm{sys}} > (\frac{\mathrm{Q}}{\mathrm{T}})$

Due to the entropy generation within the system resulting from internal irreversibility. The entropy change is balanced with temperature-scaled heat exchanges in reversible cycles, when compared to irreversible cycles it does not balance out (Tiwari & Mishra, 2012).

Kelvin's principle: A cyclic process does not exists if it does not produce any other effect than the extraction of heat from a body and its converts it into an equivalent amount of work (Tiwari & Mishra, 2012). In heat engines and refrigeration or a system that converts heat into work the efficiency of the system is presented as equation (2.14) (Boljanovic, 2016).

$$\eta = \frac{W}{Q_h} = 1 - Q_c/Q_h \tag{2.14}$$

Where:

Q_c =heat absorbed per cycle from higher temperature (J)

Q_h =heat rejected per cycle to lower temperature (J)

W= Work carried out per cycle (J)

Caratheodory's principle: States of a system with minute difference from a given state, which is not reachable from that state by any quasistatic adiabatic process (Tiwari & Mishra, 2012).

2.5.1.4 Third law of thermodynamics

In the third law of thermodynamics, it is declared that "while absolute zero can be approached to an arbitrary degree, it can never be reached" (Howell, 2017). This law of thermodynamics enables the measure of the entropy of a substance at temperature (T). Entropy range between T_1 and T_2 , and set the lower temperature at absolute zero that is $T_1 = 0K$, and set the higher temperature T_2, (Chang & Thoman, 2014). Entropy change (ΔS) can be presented by equation (2.15).

$$\Delta S = S_T - S_0 = \frac{C_p}{T} dT \tag{2.15}$$

The entropy of a substance at any temperature T is equal to the sum of the contribution from 0 K to the specified temperature (Chang & Thoman, 2014).

2.5.2 Selected thermodynamics properties and processes

Selected thermodynamic properties that affect this present study are work and heat. In thermodynamics, essential systems are interactions and properties. Heat and work are interactions between a system and its surroundings (de Souza-Santos, 2010). There are similarities between heat and work; heat interactions occur between a system and its surroundings, and temperature difference exists between the surroundings only in the absence of adiabatic walls. Work is an interaction that occurs along a system and its surroundings if the only effect could be represented by the resisted descent of weight in the environment (Winterbone & Turan, 2015).

2.5.2.1 Thermodynamic properties

Some of the properties of a system include enthalpy, temperature, entropy pressure, volume, Gibbs free energy, specific heat, and exergy (de Souza-Santos, 2010). In terms of the laws of thermodynamics, the temperature is not dependent on the properties of the body measured. Temperature is generally expressed using the Kelvin scale, and it is not measured directly, but it is usually inferred from measurements with a gas thermometer (Schaschke, 2014). Pressure as a thermodynamic property is a concept that can only exist if molecules are present. Lack of molecules is a perfect vacuum; the pressure for a perfect vacuum is defined at 0 (Bar-Cohen, 2013). The Ideal Gas Law provides a thermodynamic equation of state for ideal gases. The expression provides a relationship between temperature, pressure, and density, the relationship is expressed using equation (2.16) (Bar-Cohen, 2013).

$$\mathrm{P} = \rho \mathrm{RT} \tag{2.16}$$

Pressure measurements are therefore able to establish the thermodynamic state of a gas, such as air (Bar-Cohen, 2013). In a system of a constant volume, the volume of a system is constant, and work done is zero when adding heat to the system there would be an increase in internal energy and vice versa. In a constant pressure system, the system is maintained at constant pressure and any heat transfer would result in work done by the system or on the system (Basu & Debnath, 2019). Enthalpy H is the meaure of the combination of internal energy E and the product of pressure P and Volume V of a system

(Basu & Debnath, 2019). Enthalpy can be presented by equation (2.17). The enthalpies of gasification reactions are presented in Table 2.5.

$$\mathrm{H = E + PV} \tag{2.17}$$

Table 2.5: Gasification reactions enthalpies (Cleveland, 2004)

Reaction	Enthalpy of reactions (kJ/mol)
$C+CO_2=2CO$ (Boudouard)	159.7
$C+2H_2O=CO+H_2$(Water -gas)	118.7
$C+2H_2=CH_4$(Methanation)	-87.4

Entropy is a measure of the disorder of a system Reichle (2020), the reversible part of heat generation is directly related to absolute temperature of a system and it is connected to the entropy (Ziebert et al., 2017). The entropy change (ΔS) and enthalpy change $(\Delta \mathrm{H})$ describe the change in the Gibbs free energy $(\Delta \mathrm{G})$. An important thermodynamic function is Gibbs free energy G and it is expressed by equation (2.18).

$$\Delta \mathrm{G} = \Delta \mathrm{H} - \mathrm{T}\Delta S \tag{2.18}$$

Gibbs free energy of chemical reactions as expressed in equation (2.18) is the part of the heat reaction which can be converted into useful work. The product $T\Delta S$, or the or the entropy part, is the heat which dissipates into the environment where T is the absolute temperature and entropy ΔS, is a measure of the number of certain methods in which a thermodynamic system could be ordered. Specific heat is an indication of heat capacity of a substance, it is the amount of heat to be supplied or taken out of the unit mass of a system to increase or reduce its temperature by one degree (Feidt, 2017). Moisture and temperature affect specific heat of feedstock, the effect of moisture on specific heat is expressed by equation (2.19).

$$\mathrm{C_P = M_{wet}C_w + (1 - M_{wet})C_{p\theta}} \tag{2.19}$$

Where:

$\mathrm{C}_{\mathrm{p}\theta}$ is the specific heat of the feedstock,

C_{w} is the specific heat of water and $\mathrm{M}_{\mathrm{wet}}$ is the moisture fraction on a wet basis (Basu, 2018).

The thermodynamic technique based on the second law of thermodynamics is called exergy analysis, it provides an alternative of assessing and comparing process and systems rationally (Dincer & Rosen, 2013). A functional method of using the second law of thermodynamics is through exergy analysis (La Villetta, Costa & Massarotti, 2017). Exergy analysis produces efficiencies that give an accurate measure of how close to an actual performance approaches the ideal (Dincer & Rosen, 2013). Exergy efficiencies are functions of mass transfer and heat and parameters (Dincer & Rosen, 2007). In gasification, the ratio between useful exergy outputs from the gasifier to the necessary exergy input to the gasifier is the exergetic efficiency (La Villetta, Costa & Massarotti, 2017). When considering the gasification process under stationary conditions of flow, where mass, energy and exergy continuously flow the total irreversibly flow rate/ destroyed exergy flow rate is given by equation (2.20).

$$\dot{\mathrm{I}} = \mathrm{n}_{\mathrm{f}\overline{\mathrm{b}_{\mathrm{f}}}} + \dot{\sum}_{\imath=1} \mathrm{n}\, \mathrm{n}_{\mathrm{a\imath r},\imath}\overline{\mathrm{b}_{\mathrm{a\imath r},\imath}} - \dot{\sum}_{\imath=1} \mathrm{n}\, \overline{\mathrm{n}_{\mathrm{pg},\imath}} - \mathrm{n}_{\mathrm{sp}}\dot{\overline{\mathrm{b}_{\mathrm{sp}}}} \qquad (2.20)$$

$\dot{\mathrm{I}}$ is the total irreversibility flow rate and $\bar{b}$ is the mole specific exergy Katia (2015), exergy efficiency is expressed by equation (2.21).

$$\eta_{\mathrm{exp}} = \frac{\mathrm{Ex}_{\mathrm{prod}}}{\mathrm{Ex}_{\mathrm{feedstock}} + \mathrm{Ex}_{\mathrm{medium}}} \qquad (2.21)$$

Where:

$\mathrm{Ex}_{\mathrm{prod}}$ and $\mathrm{Ex}_{\mathrm{feedstock}}$ are exergies of the producer gas and feedstock and $\mathrm{Ex}_{\mathrm{medium}}$ is the exergy of the gasifying medium. With the second law of thermodynamics equation (2.22) is generated (Katia, 2015).

$$\sum_{i=reactant} Ex - \sum_{j=products} Ex = I_{rr} \quad (2.22)$$

Where:

$\mathrm{I_{rr}}$ is irreversibility and represents the internal exergy lost.

2.5.2.2 Thermodynamic process

In a closed system, the exact energy balance between the variation of the total energy is established through the application of first law of thermodynamics. The transformation during reversible or irreversible and total work and the quantities of heat absorbed by the system and can be expressed by equation (2.23) (Vidal, 2003).

$$\Delta E = \Delta\left(E_{pot} + E_{kin} + U\right) = W + W' + Q \quad (2.23)$$

The work done by pressure and the thermal exchanges are expressed by equation (2.24).

$$\Delta U = W + Q \quad (2.24)$$

For a closed system, idealized interaction with the surroundings can be of different types; the ideal processes are: (a). isothermal, (b). isobaric, and (c). isochoric process (Constales, Yablonsky & D'hooge, 2016). The isothermal process occurs when the temperature within the surrounding is not exchanged and continues to stay constant. The temperature of the system continues at a constant value by adding or removing heat at the same rate it is produced or removed (Schaschke, 2014). The isothermal mode in reactor design is rarely used; unless the process is very slow, like fermentation or for a small reactor where the surface area is large to maintain the reactor thermostat (Schmidt, 2004). The isobaric process is the compressing of air under constant pressure, and isochoric is the compressing of air under constant volume (Cleveland, Cutler & Morris, 2009). Adiabatic is not difficult to reach in large reactors and will be achieved if heat removal stops, for endothermic reactions the reactor shuts itself as it cools. For exothermic reaction, it is more complex this type of operation is for fast oxidation reactions because heat release is too fast (Schmidt, 2004).

2.5.2.3 Thermodynamics of gasification

In thermodynamics, gasification process must comply with both first and second laws of thermodynamics (La Villetta, Costa & Massarotti, 2017). The gasification process occurs at a temperature range of 800–1800°C, the properties of the feedstock determine the temperature (Burgt & Higman, 2008). At thermodynamic equilibrium condition gasification reactions occur, in the system there is no heat loss the process is entirely adiabatic (Xu, Jin & Cheng, 2017). Equilibrium constants or minimization of the Gibbs free energy controls the chemical equilibrium theory, and this is used in the gasification process (Klass, 1998). In thermodynamics the equilibrium for an isolated system is achieved when the Gibbs function reaches a minimum. At equilibrium state the forward reaction rate is equal to the reverse reaction (a). the concentration in the products and reactants does not change, (b). minimum Gibbs energy of the system, and (c). maximum entropy of the system (Basu, 2018). When considering the reaction, it is expressed by equation (2.25).

$$\mathrm{nA + mB \overset{for}{\rightarrow} pC + qD} \tag{2.25}$$

Where n, m, p, and q are stoichiometric coefficients, the rate of the reaction, $\mathrm{r_1}$ depends on $\mathrm{C_A}$ and $\mathrm{C_B}$ the concentration of the reactants A and B are represented as equation (2.26).

$$\mathrm{r_1 = \ k_{for}C_A^nC_B^mA} \tag{2.26}$$

The reaction can move in the opposite direction and expressed by equation (2.27).

$$\mathrm{pC + q \xrightarrow{back} nA + mB} \tag{2.27}$$

The rate of the reverse reaction $\mathrm{r_2}$ is similarly expressed in terms of $\mathrm{C_c}$ and $\mathrm{C_D}$

$$\mathrm{r_2 = \ k_{back}C_c^pC_B^qD} \tag{2.28}$$

When reaction rate begins the concentration of the reactants A and B is higher than that of the product C and D, and the rate $\mathrm{r_1}$ of forward reaction equation (2.26) is initially higher than $\mathrm{r_2}$, the reverse reaction that means the reaction is not in equilibrium because $\mathrm{r_1} > \mathrm{r_2}$ (Basu, 2018). As the reaction continues the forward reaction increases the buildup of products C and D that increases the reverse reaction, eventually the two rates will be equal $\mathrm{r}_2 = \mathrm{r}_2$ and equilibrium state is achieved (Basu, 2018).

Constant reaction

In a constant reaction constant k_i depend on the reaction temperature but not on the concentration of reactants (Basu, 2018).

$$\mathrm{k} = \mathrm{A}_0 \exp\left(-\frac{\mathrm{E}}{\mathrm{RT}}\right) \tag{2.29}$$

Where A_0 is the preexponential constant, R is the universal gas constant and E is the activation energy for the reaction. The ratio rate constants for the forward and reverse reaction are the equilibrium constant as shown on equation (2.30).

$$\mathrm{K}_\mathrm{e} = \frac{\mathrm{k}_\mathrm{for}}{\mathrm{k}_\mathrm{back}} = \frac{\mathrm{C}_\mathrm{c}\mathrm{C}_\mathrm{D}}{\mathrm{C}_\mathrm{A}^\mathrm{n}\mathrm{C}_\mathrm{B}^\mathrm{m}} \tag{2.30}$$

Equilibrium constant K_e depends on temperature and not on pressure.

2.6 Feedstocks

A feedstock is a renewable biological material that may be utilized as a fuel, feedstock can also be converted into an energy product (Kataki et al., 2015). The common criteria for selecting a suitable feedstock in gasification, generally, are limited to the feedstock's abundance and availability (Vaezi et al., 2012). Feedstock parameters have influence on the performance of a gasifier, and it is necessary to know the volatility a feedstock, elemental analysis, and heat content (Ptasinski, 2008). The purpose of gasification is not only energy conversion, production of chemical feedstock is also important, gasification's feedstock includes coal, biomass, liquid, gases to produce more useful fuels, and solid waste (Basu, 2018).

2.6.1 Types of feedstock and characteristics

Promising feedstocks are used in regions based on their climatic conditions, the feedstocks can be classified into first and second generations (Basile & Dalena, 2019). This categorisation could be beneficial in predicting the distribution and quality of the product in the thermochemical conversion process (Pandey et al., 2015). Moreover, taking into consideration the characteristics and composition of feedstocks, it is practical to design essential pre-treatment processes.

2.6.1.1. Coal

Coal is a black or brownish-black solid combustible substance formed by the incomplete decomposition of vegetable matter in the absence of air (Chambers & Kerr, 1996). Coal is a chemically and physically heterogeneous combustible sedimentary rock, it consists of organic and inorganic material; coal consists primarily of carbon, hydrogen, oxygen, and lesser amounts of sulfur and nitrogen (Miller, 2011). Coal is classified in terms of its rank, the classification of coal is by rank for ash, and moisture-free (Burgt & Higman, 2008). The rank of coal which includes anthracite, bituminous coal, sub-bituminous coal, and lignite is based on fixed carbon, volatile matter, and heating values (Chambers & Kerr, 1996). The classification of coal is presented in Table 2.6.

Table 2.6: Classification of coals (Burgt & Higman, 2008).

Class	Volatile matter (wt%)	Fixed Carbon (wt%)	Heating Value (mJ/KG)
Anthracite	<8	>92	36-37
Bituminous	8-22	78-92	32-36
Sub-bituminous	22-27	73-78	28-32
Brown-coal (lignite)	27-35	65-73	26-28

Coal gasification is a process where coal is converted to low grade gas, in many ways it can be regarded as fuel rich combustion (Smoot & Baxter, 2003). Coal gasification may also be on seams that are still in place, with the coal being converted to gaseous fuel in the absence of intermediate mining operation, this process is regarded as in situ or underground gasification (Ward, 2013). The situ gasification process is illustrated in Figure 2.10.

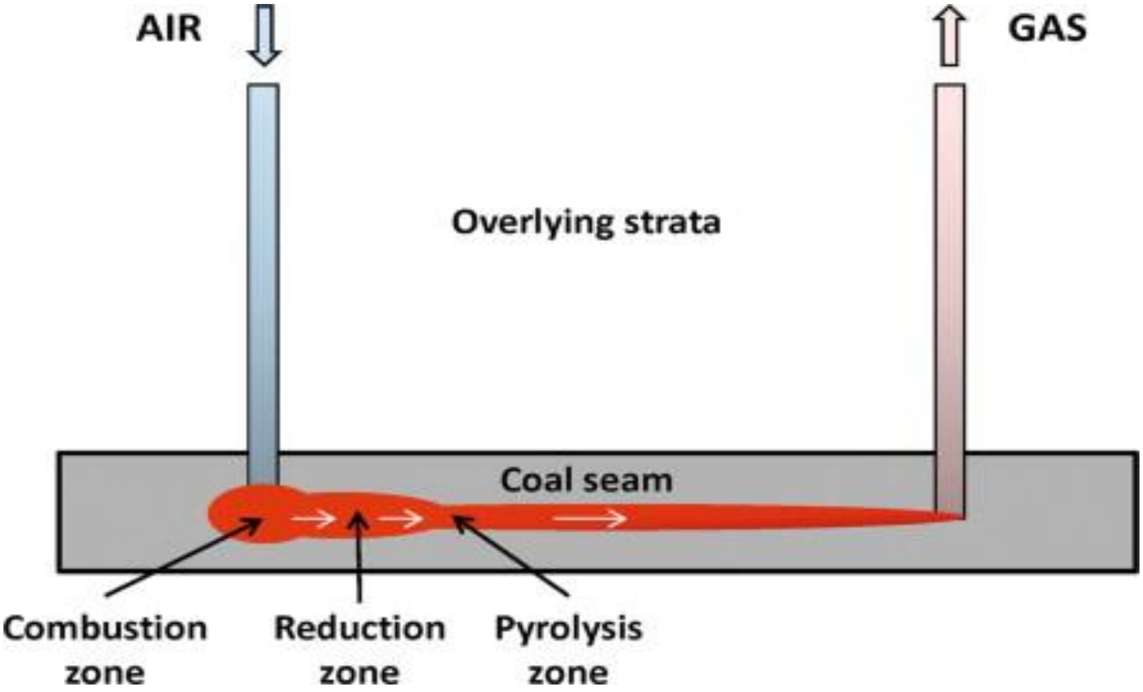


Figure 2.10: Schematic illustration of in situ gasification process: Source (Ward, 2013)

2.6.1.2 Biomass

Biomass is a carbohydrate; it is a renewable source with mostly defined properties, biomass is any organic matter which is obtained from plants. Biomass is a plant material like wood, crops, seaweed, waste from agricultural and forestry process, organic industrial human, and animal waste (Saidur et al., 2011). Biomass has been the main source of energy for a very long time and contributes 10% more to the world’s energy supply (Saidur et al., 2011). Biomass, as a feedstock, can be used in the same area where it is generated and can reduce cost associated with storage and transportation (Lapuerta et al., 2008). Exploitation of biomass may be done in various routes in energy conversion, biomass conversion into energy can be divided into biological and thermochemical process (Widjaya et al., 2018). The biological process includes fermentation into ethanol and anaerobic digestion into methane gas combustion, pyrolysis, and gasification are the main thermochemical conversion methods. In this current study the focus is on the gasification process, the thermochemical method is the most applied technique in biomass conversion contribution of biomass to commercial energy needs. Biomass may be classified into valuable first-generation feedstock to produce biodiesel and feedstocks that are regarded as second-generation are non-edible and comprise of raw materials extracted from lignocellulosic biomass Gupta (2011), in Figure 2.11 the classification of biomass is illustrated.

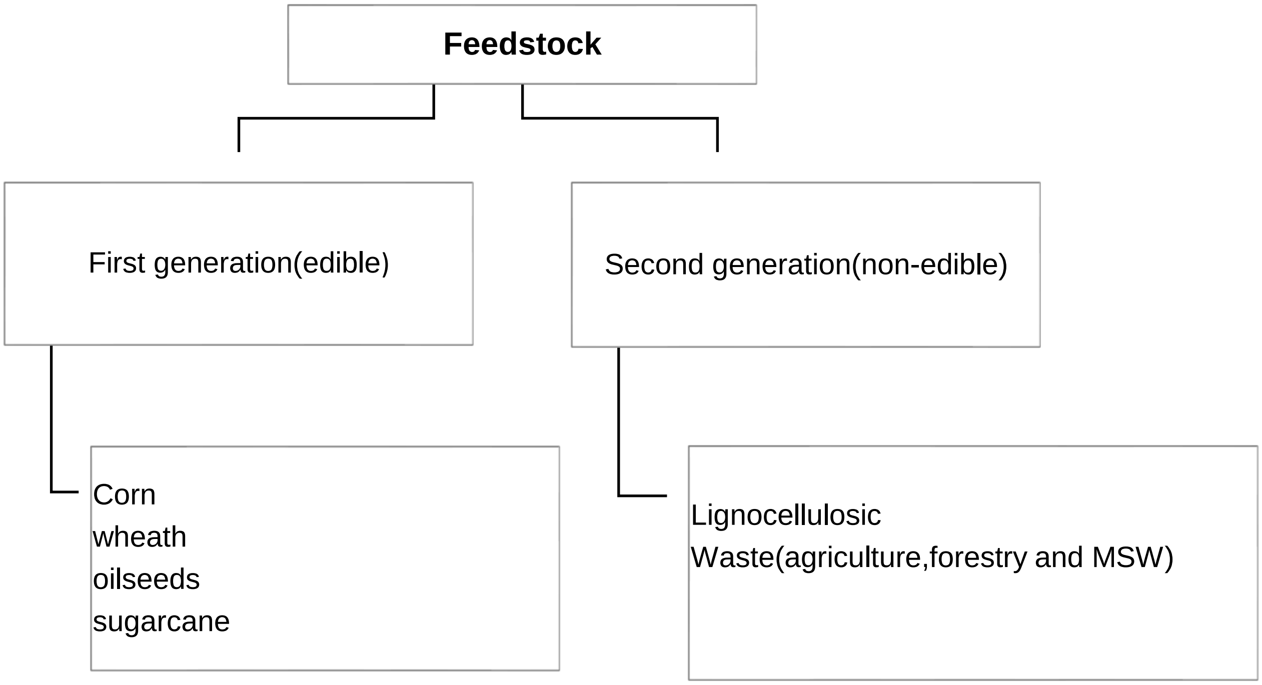


Figure 2.11: Classification of feedstock (Nigam & Singh, 2011).

A better understanding of biomass, and its role in energy conversion is required to further improve the quality in its contribution to commercial energy needs. A study by Bousdia et al. (2014) on the comparison between the concentration fixed carbon and of volatile matter for different kinds of biomass is detailed in Table 2.7.

Table 2.7: Concentrations of volatile matter and fixed carbon for different types of biomasses (Bousdia et al. 2014)

Types of Biomasses	FC %			VM %		
	Mean	Minimum	Maximum	Mean	Minimum	Maximum
Wood	18.5	12.3	26.3	78	69.5	86.3
Agricultural Residue	19.1	12.4	37.9	75.2	59.3	85.5
Straw	17.1	13.6	19.5	74.3	64.3	80.5
Variety of Biomass	9.4	0.5	17.3	72.01	48.0	84.2
Animal Biomass	13.6	_	_	55.5	_	_

Biomass fractionation and more mainly, biomass pretreatments include many different processes and the optimum conditions. They are strictly controlled by the characteristics of each raw material as well as the final purpose. If the main purpose of the fractionation or pretreatment is to exploit (hemi) cellulose fraction it should increase the accessibility and the reactivity of the cellulose (Aresta, Dibenedetto & Dumeignil, 2012). It should also break down the semi-crystalline and hemicellulose, without significant degradation of polysaccharides.

A functional pretreatment should meet the following requirements Aresta, Dibenedetto & Dumeignil, (2012):(a). get over lignocellulosic biomass recalcitrance, (b). give highly digestible pre-treated solid, (c). avoid sugar degradation, (d). evade formation of inhibitory toxic by-products, (e). permit lignin use and recovery to offer co-products that are valuable, and (f). be cost effective, low waste amounts and low energy requirements. Even though utilization of biomass as an energy sources offers several advantages, there are also restrictions (Crocker, 2011).The low density and high-water content of biomass makes shipping cost prohibitive and, in many cases yet most sub-sequent purifying process require centralized facilities. Crocker (2011) further suggests that large scale operations can largely improve process efficiencies and economics. Moreover, most harvested biomass contains significant amounts of moisture adsorbed physically, around 50% by weight short of considerable drying, the biomass feed per unit in energy content is even smaller. In a study that looked at biomass gasification under various operating conditions, Gu et al (2019) suggest that the overall conversion of biomass strongly relies on other factors like biomass composition, biomass properties and conversion methods.

2.6.1.3 Liquid and gaseous feedstock

Residue from petroleum refining are regular liquid feedstocks, and they have low ash content and high sulfur content that lead to fouling of syngas coolers (Branan, 2005). With fuel oil feedstock the effluent discharged contains suspended carbon, ammonia, and metals like vanadium, nickel, and iron (Cheremisinoff, 1995). When a CO rich syngas is required natural gas is applied as a feedstock gasifier (Branan, 2005). Compared with different aspects when dealing with liquid feedstocks, natural gas is relatively simple, and the principle issues to be considered are more of an economic rather than technical nature (Burgt & Higman, 2008). Applications for gasification of liquid and gaseous feedstocks on multiproduct facilities are summarised in Table 2.8.

Table 2.8: Application of liquid and gaseous feedstock (Burgt & Higman, 2008).

Chemical constituent	**Liquid feedstock (MM Nm^3/d)**	**Gaseous feedstock (MM Nm^3/d)**	**Total syngas (MM Nm^3/d)**
Ammonia	50.5	0.8	51.3
Methanol	15.3	6.3	21.7
Hydrogen	7.1	2.0	9
Synfuel	-	7.6	7.

2.6.1.4 Solid waste

Solid waste may be municipal solid waste or commercial waste for an efficient and accurate gasification process; a homogeneous carbon-based material is a requirement, and not all waste can be gasified (Belgiorno et al., 2003). Waste like paper mills waste, agricultural and forest residue, can be directly gasified (Belgiorno et al., 2003). The volume of these wastes generated has increased with population growth and economic development (Basile & Dalena, 2019). The organic fraction of these wastes has the potential to produce about 170-486 L of bioethanol per ton (Hoornweg & Bhada-Tata, 2012). Solid waste is available various forms and quantities with mixed contents of inorganics and moisture (Ouadi et al., 2017). Furthermore, this mixture results in limited and excessive costs associated with disposal, but the materials are available in large quantities with energy contents that can be compared to coal (Ouadi et al., 2017). For fuel synthesis, solid waste is enticing; the energy inside can be converted successfully into a homogenous form that is suitable for energy generating devices like boilers, engines, combustors, fuel cells, or turbines (Ouadi et al., 2017).

Products produced from residual MSW using the thermo-catalytic reforming (TCR) process Ouadi et al. (2017); the authors suggest that the highly variable composition of solid waste requires several pre-treatment steps. Moreover, the bio-oil produced had a high energy content of (38.2 MJ/kg), low oxygen content (6.7 wt.%), a total acid number of (2.9 mg KOH/g), and kinematic viscosity of 6.5 cSt. A study by Sudibyo et al. (2017); focused on the technological evaluation of municipal solid waste management system in Indonesia. The authors suggested that using a thermal-based process in the waste management system in Indonesia could promise good economic feasibility, and plasma gasification can consume MSW for producing electricity to get profit. There are significant differences among the chemical compositions of solid wastes; plastics have a high content of cellulose (65 wt%) while cattle manure has a low content of cellulose 2.7wt% (Pandey et al., 2019).

Solid waste such as wastewater sludge, animal manure, and fish waste are rich in moisture or water; the high moisture content may be higher than 80% and makes the solid waste to have low energy content. As a result, this makes it difficult to treat or convert them through certain technologies, however, the high moisture content allows easy handling through other technologies such as digestion and extraction (Pandey et al., 2019). Proximate analysis of some solid waste is presented in Table 2.9, and shows the moisture content on wet basis, and both fixed carbon content and volatile content on a dry basis.

Table 2.9: Proximate analysis of solid waste (Xu, Jin & Cheng 2017)

Waste type	Moisture content	Fixed carbon content (%)	Volatile content (%)	HHV (mJ/kg)
Food	69.85	12.23	66.79	15.39
Green waste	42.95	17.29	75.87	19.46
Paper	13.15	11.6	76.14	15.89
Textile	13.75	13.75	82.69	20.16
Rubber	0.89	19.67	64.74	43.45

Chapter 3

METHODOLOGY

Studies of energy, including thermodynamic analysis that allows the performance and efficiency of engineering systems, have been conducted widely. Thermodynamic analysis of gasification has been carried out in various studies. The renewed interest is given to gasification technology in the municipal solid waste treatment because it has the potential to reduce GHGs emissions. Studies conducted on the thermodynamic analysis of the gasification of municipal solid waste using various thermodynamic methodologies include (Xu, Jin & Cheng, 2017; Couto, Silva & Rouboa, 2016). It is observed from their conclusions that more robust thermodynamic analysis of MSW is necessary.

In Chapter 2, different studies on thermodynamic analysis of gasification have been discussed. The selection of the modelling approach focused on the problem statement. It was necessary to use a model that did not have a lot of limitations or relied on the geometry of the gasifier. A mathematical model that could analyze various parameters of the gasification process was utilized. In this chapter, the methodology used in the present study is presented and discussed. A thermodynamic model was developed and validated using empirical data.

3.1. Gasification mathematical models

Transformation of chemical energy of the feedstock or other solid fuels into the necessary gas is determined by the proper sizing, configuration, and selection of operating conditions of a gasifier (Basu, 2010). Mathematical modelling of a gasifier may not give very accurate predictions of its performance. However, it can produce qualitative guidance on the effect of the design and feedstock operation parameters (Basu, 2010). Gasification models are developed to study the thermochemical processes that occur during the gasification process. Also, these models evaluate the influence of the operating parameters. Operating parameters that influence the gasification process include a gasifying agent, equivalence ratio, pressure, temperature, and residence time. The categories of gasification models are artificial neural networks (ANN), thermodynamic equilibrium, and kinetic models (Safarian, Unnþórsson & Richter, 2019).

In a survey of gasification modelling, it is reported that gasification simulation models are roughly 66% of equilibrium and 34% of kinetic models (Safarian, Unnþórsson & Richter, 2019). Mathematical models are practical tools in the presentation of the gasification process. A model can produce the actual operation with an admissible degree of deviation (de Souza-Santos, 2004).

3.1.1. Characteristics of a good mathematical model

Running numerous experiments can be avoided, for improved gasification parameters, an alternative and effective option with minimized resources is to develop mathematical models that simulate operational conditions and predict syngas quality and yield (Ramos, Monteiro & Rouboa, 2019). Mathematical model analysis can assist in determining the effects of a parameter in a system and help evaluate optimal operating points. Characteristics of a good model are outlined below (Basu, 2018):

- They find perfect operating conditions.
- Identify potential hazard in operation.
- Give details of exceptional operating conditions (high pressure or temperature)
- Supply comprehensive information of conditions as opposed to experiments.
- Improved interpretation of experimental results and analyse irregular behaviour of a gasifier.
- Aid scale-up a successful gasifier operating size to another and from one feedstock to another.

3.1.2. Classification of gasification models

Gasification is adaptable in terms of both feedstock type and fuel production or energy generation and this consequently contributes to research expansion. The implementation of gasification and research development are advanced by modelling work (Safarian, Unnþórsson & Richter, 2019). In practice, modelling always has a role both in applied gasification research and development. Applied work models are validated through experiments to reliably predict a gasifier performance as a function of feedstock and give qualitative and quantitative information for practical operations (Patra & Sheth, 2015). The interest in gasification modelling has advanced over the years.

There are several review articles about these models. Ahmed et al. (2012) analysed several models based on artificial neural network, kinetics, and thermodynamic equilibrium. Some of the models are discussed in Section 3.1.2.1. Modelling is helpful in optimizing the operation of an existing gasifier, exploring operational limits, and getting insight into the link between operational limits, and explaining trends in the data (Basu, 2010).

3.1.2.1. Kinetic models

Kinetic models are used to study reaction progress in the reactor, allowing the product composition at a various positions throughout the gasifier, considering the geometry and fluid dynamics (La Villetta, Costa & Massarotti, 2017). Kinetic-based models present accurate and comprehensive results but contain high computational cost (Puig-Arnavat, Bruno & Coronas, 2010; Ahmed et al., 2012). In kinetic modeling, there are two components: reaction kinetics and reactor hydrodynamics. Kinetic models give the gas yield and product composition a gasifier achieves after a finite time (Basu, 2010). The models involve parameters such as reaction rate, residence time of particles, and reactor hydrodynamics (Basu, 2010). Reaction kinetics are solved simultaneously with bed hydrodynamics and mass and energy balance to obtain the yields of gas, tar, and char at given operating conditions (Basu, 2010). Reactor hydrodynamics includes the understanding of the physical mixing process (Baruah & Baruah, 2014).

A kinetic model is effective and reliable at relatively low operating temperatures (Altafini, Wander & Barreto, 2003). He et al. (2009) investigated the catalytic steam gasification of municipal solid waste by using a kinetic model. The authors concluded that the model revealed good agreement between experimental and modelled results. The kinetic study of food waste char in isothermal CO_2 gasification was conducted by Izaharuddin et al. (2020). Three various kinetic models namely: shrinking core model (SCM), random pore model (RPM), and the volumetric model (VM), were developed, and their effectiveness was investigated. The models were compared to the experimental results. SCM showed a high regression at 850°C while RPM showed a high regression at 900 and 950°C. Thakare & Nandi (2016) investigated the potential of gasification technology for municipal waste in Pune city. They concluded that gasification technology is efficient to treat most solid waste. The authors further suggested that irrespective of the sources, material present can be gasified directly.

3.1.2.2. Artificial neural network models

An artificial neural network is a computational model that has processing elements that deliver outputs and receive inputs according to the predefined activation functions (La Villetta, Costa & Massarotti, 2017). This modelling approach usually combines partial first principle models that describe characteristics of the simulated process. They involve a multilayer feedforward neural network (MFNN) and serve as an estimator of unmeasured process parameters that are difficult to model from the first principle (Guo et al., 2001). The authors further concluded that the significance of this kind of application lies not only in process modelling itself but also in that it has the potential to find the unseen process structure. This technique has been used with credible success to predict gas yield and composition from the gasification of bagasse, cotton stem, pine sawdust, poplar, and municipal waste in fluidized beds (Guo et al., 1997).

Artificial neural network model is utilized as a new approach to studying biomass gasification. It is a possible substitute to the sophisticated modelling of the gasification process (Baruah & Baruah, 2014). An ANN prediction model was used to look at characteristics MSW when gasified (Xiao et al., 2009). It was concluded that gasification characteristics of MSW could be estimated by the ANN method. Pandey et al. (2016) also conducted a study on ANN-based modelling of municipal solid waste gasification in a fluidized bed reactor. Simulation results showed that the ANN-based method is a feasible alternative that can predict the performance of a fluidized bed gasifier.

3.1.2.3. Thermodynamic equilibrium models

Thermodynamic equilibrium modelling is a proven method of analysis. It is a numerical application method that estimates the capabilities of a gasifier. Thermodynamic equilibrium cannot be reached but the results of a thermodynamic model illustrate possible maximum efficiency in an ideal system for a given feedstock (Silva et al., 2019). Gasification reactions inside the gasifier are the basis of thermodynamic equilibrium models, with the assumption that a state of equilibrium can be reached by the system (Silva et al., 2019). Equilibrium models allow a practical illustration of the gasification process (Basu 2010). In a study by Pan et al. (2019), a thermodynamic equilibrium model was used, and the result demonstrated potential in the application of the synthetic natural gas (SNG) production by combining MSW gasifier and solid oxide electrolyzer cell (SOEC). To achieve total recovery of the carbon in waste with high efficiency, Pan et al. (2019) suggest that the production of SNG derived through the gasification of solid waste is an attractive option.

Brachi et al. (2018) investigated a thermodynamic equilibrium model to simulate oxygen–steam gasification of low-value agricultural waste in a high temperature entrained flow gasifier; and recommended that more studies on the influence other kinds of non-woody biomass have should be investigated. To model Tehran's WtE plant, which is the only MSW based power plant in Iran, Behzadi et al. (2018) used an equilibrium model to model the gasifier. The study aimed to investigate a multicriteria optimization and comparative performance analysis of a power plant fed by municipal solid waste using a gasifier and a digester. Behzadi et al. (2018) 's results showed that the combustion chamber and the gasifier had the highest exergy destruction in the model. Baruah & Baruah (2014) found that a thermodynamic equilibrium model emphasized the thermodynamic limits and relations between different gasification parameters and the composition of the gas flowing out.

Thermodynamic equilibrium models are used to predict the composition of the syngas, based on the assumption that the reactants react in a fully mixed condition for an infinite period. In a study that looked at the reduction reactions for a downdraft gasifier applying equilibrium modelling, Sharma (2008) considered reactions R3, R4, R5, R6, and R11. It was reported that the calorific value (CV) of the gas improved with the increase in moisture content range of 0 to 10% with a maximum CV value of 4738kJ/m^3. Sharma, (2008) further reported that the gas efficiency showed similar trends and peaked close to 20% in moisture content when char gets consumed. Moreover, percentage of CO and H_2 decreased when the pressure increases and, CH_4, CO_2, N_2, and unconverted char increased with increasing pressure.

In a study by Jarungthammachote & Dutta (2007), to predict the composition of the producer gas in a downdraft waste gasifier; a thermodynamic equilibrium model was used, based on the equilibrium constant. It was found that the when the moisture content increased the reaction temperature, the calorific value, and the second law efficiency decreased. The authors further concluded that solar drying and separation of waste is important for the gasification of MSW. In the thermodynamic analysis of plasma gasification technology by Mountouris, Voutsas & Tassios (2006), the prediction of the produced gas composition, energy, and exergy the calculations focused on R4, R6, and R11. It was reported that gas composition as a function of the oxygen amount showed that an increase of the airflow decreases H_2 and CO while CO_2, N_2, and H_2O increases. Also, it was observed that CO and H_2O concentration increased with gasification temperature while H_2 and CO_2 concentration decreased.

3.2. Gasification reaction process

A combination of chemical reactions illustrates gasification, the reactions that are divided into four stages: (a). drying (endothermic), (b). pyrolysis (endothermic), (c). oxidation (exothermic), and (d). reduction (endothermic stage). Stages can take place at the same time and region in a fluidized gasifier, while with fixed bed gasifiers, they occur in different regions of the gasifier (Silva et al., 2019). In the drying stage, the feedstock is fed in the gasifier and preheated, and the drying process occurs, where the feedstock moisture is converted to water vapor at a temperature range of 100-200°C (Basu, 2010).

Feedstock with high moisture content needs increased heat for drying (Susastriawan, Saptoadi & Purnomo, 2017). In the pyrolysis stage, feedstock molecules are thermally decomposed into volatile gases (CO, CO_2, H_2, CH_4, and H_2O) and light hydrocarbons (La Villetta, Costa & Massarotti, 2017). In the oxidation stage, partial and total oxidation of the products of pyrolysis occurs, other reactions involved in the process get heat from the combustion reactions. If there is oxygen present in substoichiometric quantities, the oxidation of char results in the formation of CO_2 and CO (Silva et al., 2019). In the reduction stage, endothermic and exothermic reactions occur (Molino, Chianese, & Musmarra, 2016). The main gasification reactions are presented as: (Safarian, Unnþórsson & Richter, 2019; Mountouris, Voutsas & Tassios, 2006).

$C + CO_2 \Longrightarrow 2CO$ (Boudouard equilibrium reaction–endothermic)

$C + H_2O \Longrightarrow CO + H_2$ (Heterogeneous water gas shift reaction–endothermic)

$C + 2H_2 \Longrightarrow CH_4$ (Hydrogenating reaction–exothermic)

$CO + H_2O \Longleftrightarrow CO_2 + H_2$ (Water gas shift reaction–exothermic)

Gasification reactions that are considered in this study are:

$$C + CO_2 = 2CO \tag{3.1}$$

$$C + H_2O = CO + H_2 \tag{3.2}$$

In the reduction zone of the gasifier, hydrogen is reduced to methane by the carbon.

$$C + 2H_2 = CH_4 \tag{3.3}$$

Equations (3.1) and (3.2) can be combined to give the shift reaction.

$$CO + H_2O = CO_2 + H_2 \tag{3.4}$$

The equilibrium constant for methane formation equation (3.3) can be presented as equation (3.5)

$$K_1 = \frac{PCH_4}{(PH_2)^2} \tag{3.5}$$

And the equilibrium constant for the shift reaction is represented by equation (3.6)

$$K_2 = \frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}} \tag{3.6}$$

The typical chemical formula for a material, based on a single atom of carbon is:

$C_nH_aO_b$

The formation of $\mathrm{CH_{1.44}O_{0.66}}$ is based on the following reaction

$$\mathrm{C + O_2 \Rightarrow CO_2} \qquad \Delta \mathrm{H_c} = -393\ 509 \tag{3.7}$$

$$\mathrm{0.72H_2 + 0.36O_2 \rightarrow 0.72H_2O} \qquad \Delta \mathrm{H_c} = 0.72(-285\ 830) \tag{3.8}$$

$$\mathrm{CO_2 + 0.72H_2O \rightarrow CH_{1.44}O_{0.66} + 2.06O_2} \qquad \Delta \mathrm{H_c} = 433\ 034 \tag{3.9}$$

$$\text{Heat of formation of municipal solid waste} = \Delta \mathrm{H_c} + \Delta \mathrm{H_c} + \Delta \mathrm{H_c} \tag{3.10}$$

$$\text{Heat of formation of municipal solid waste} = 433\ 034 - 393\ 509 + 0.72(-245\ 830)$$

$$\mathrm{C + 0.72H_2 + 0.33O_2 \rightarrow CH_{1.44}O_{0.66}} \qquad \Delta \mathrm{H_f} = -137\ 472.6\ \mathrm{kJ/kmol} \tag{3.11}$$

Therefore, the heat of formation MSW is assumed to be -137 427.6 kJ/kmol, in this work the heat of formation of liquid water is used according to the HHV definition as explained by (Mountouris, Voutsas & Tassios, 2006). The ultimate analyses and the heating values for municipal solid waste is shown in Table 3.1.

Table 3.1: Analysis for municipal solid waste (dry basis, weight percentage) (Perry & Green, 1998).

Material	C	H	N	S	O	Ash	HHV (kJ/kmol)
Municipal waste	47.6	6.0	1.2	0.3	32.9	12.0	433 034

At constant pressure, the specific heat can be written as

$$\mathrm{C_p} = \left(\frac{\partial \mathrm{H}}{\partial \mathrm{T}}\right) \tag{3.12}$$

$$\mathrm{dH} = \mathrm{C_p dT} \tag{3.13}$$

$$\Delta \mathrm{H} = \int_{\mathrm{T_1}}^{\mathrm{T_2}} \mathrm{C_p dT} \tag{3.14}$$

H is the enthalpy, T is the temperature, as shown in equation (3.15)

$$\Delta H = C_{pmh}(T_{2-}T_1) \quad (3.15)$$

and the average specific heat over the temperature change is written as equation (3.16)

$$C_{pmh} \equiv \frac{\int_{T_2}^{T_2} C_p dT}{(T_2 - T_1)} \quad (3.16)$$

The dependence of specific heat on temperature is derived by Perry & Green, (1998) is simplified to equation (3.17).

$$C_{pmh=}R\left(A + T_{am} + C/3(T_{am} - T_1T_2) + \frac{D}{T_1T_2}\right) \quad (3.17)$$

Starting with the analysis of the biomass and the mass fraction of the carbon, hydrogen, and oxygen.

The substitution formula can be calculated assuming $n = 1$

$a = \frac{H}{C}$, $b = \frac{O}{C}$ determined from the ultimate analysis of the biomass.

The global gasification formula can be written as equation (3.18) (Silva et al., 2019; Zainal et al., 2001)

$$CH_aO_bN_c + wH_2O + m(O_2 + 3.76N_2) = x_1H_2 + x_2CO + x_3CO_2 + x_4 H_2O +$$

$$x_5CH_4 + 3.76m\, N_2 \quad (3.18)$$

Where a, b and c are the number of atoms of hydrogen, oxygen, and nitrogen per number of atoms of carbon in the feedstock respectively, m is the amount of oxygen per kmol of feedstock, w is the amount of moisture per kmol of feedstock, and $x_{1,}x_{2,}x_{3,}x_4$ and x_5 are number of the moles of the products that are unknown.

3.3. Gasification Modelling

The thermodynamic modelling approach of this study was based on the methodology reported by (Zainal et al., 2001). This work focused on the equilibrium reaction equation (3.1), water gas shift reactions equation (3.2) and methane formation reaction equation (3.3). The model was developed based on the following assumptions (La Villetta, Costa & Massarotti, 2017; Zainal et al., 2001).

- At the thermodynamic equilibrium condition the gasification process occurs.
- The process is adiabatic without heat loss.
- There is no reactor temperature; the amount of the gasifying agent(s) based on the energy balance determines the temperature.
- The required input is the elemental composition of the feed.

3.3.1. Moisture Content

There may be moisture in the feedstock in different forms. Absorbed water molecules onto the hydroxyl functionalities of cellulose and hemicellulose through hydrogen bonds and removal of this bound water require a drying temperature of up to 160°C (Pandey et al., 2015). Inside the pores, and voids of biomass particles, unbound liquid water may also be present. If the water contents exceed the fiber saturation point, water vapor may also be present in the gas phase, occupying the voids within the biomass (Pandey et al., 2015). Quality of water per kmol of feedstock can be written as:

$$\mathrm{MC} = \frac{\text{Mass of water}}{\text{Mass of wet biomass}}\ \mathrm{X}\ 100\% \Rightarrow \mathrm{MC} = \frac{18\mathrm{w}}{24+18\mathrm{w}}\ \mathrm{X}\ 100\% \qquad (3.19)$$

And $$\mathrm{W} = \frac{24\mathrm{MC}}{18(1-\mathrm{MC})} \qquad (3.20)$$

Where: MC is moisture content and w is amount of water per kmol.

In this study, maximum moisture content of up to 40% was selected and it is in the range reported by Veksha et al. (2019) and, it is suggested by the authors that 40% moisture content is close to the 38.5 % content found in the raw MSW for their study. The value of w becomes a constant when the moisture content is known.

From the global reaction in equation (3.18), there are six unknowns $x_{1,}\ x_{2,}\ x_{3,}\ x_4$ and x_5 and m, and six equations are therefore required.

3.3.2. Equivalence ratio

To estimate equivalence ratio a generic formula for feedstock is assumed to be $C_nH_aO_b$ and it is considered as a model for the composition of the biomass ratio between the actual oxygen molar quantity and the stoichiometric amount of oxygen necessary for complete oxidation (Azzone, Morini & Pinelli, 2012). Equation (3.21) shows how the equivalence ratio is calculated.

$$ER = \frac{m}{(1+\frac{a}{4}-\frac{b}{2})} \qquad (3.21)$$

3.3.3. Calorific value

The calorific value and the quality of the syngas ratio of H_2/CO are influenced by the equilibrium reactions equations (3.1), (3.2), and (3.4). These reactions are the homogeneous reactions in the reduction zone (Ratnadhariya & Channiwala, 2009; Puig-Arnavat, Bruno & Coronas, 2010). Gasification temperature is a significant parameter in the gasification processes. Equilibrium is not achieved when the gasification temperature is below 800°C. To achieve equilibrium and satisfy the assumption that the feedstock would burn completely without waste; this study investigated the gasification temperature range from 800°C to 1200°C. Komilis et al. (2012) investigated the elemental composition and the calorific value of the organic fraction of municipal waste, and suggested that based on their empirical model statistically carbon, hydrogen and oxygen are the sole and notable predictors of calorific value.

3.3.4. Mass and energy balance

The purpose of heat and mass balance, it is to check a good match between fuel/air consumption and flow rate of the producer gas, and to calculate the efficiency of the gasification process, and how much of the energy from the feedstock is converted into chemically bound energy in the producer gas (Chern, Walawender & Fan, 1989). When finding the species of the syngas some equations are needed those equations are generated, using equilibrium constant and mass balance and relationships.

Carbon balance:

$$1 = x_2 + x_3 + x_5 \qquad (3.22)$$

Hydrogen Balance:

$$2w + a = 2x_1 + 2x_4 + 4x_5 \Rightarrow w + a = x_1 + x_4 + 2x_5 \qquad (3.23)$$

Oxygen balance:

$$w + b + 2m = x_2 + 2x_3 + x_4 \qquad (3.24)$$

The mass and energy balances are verified by (Vaezi et al., 2008; Jarungthammachote & Dutta, 2007; Zainal et al., 2001). For all chemical reactions in the gasification zone, the thermodynamic equilibrium is assumed. All reactions form a pressure at 1 atm all gases are assumed to be ideal. Therefore, the equilibrium constants, which are functions of temperature, are represented by equations (3.25) and (3.26).

The equilibrium constant for methane reaction from equation (3.5), can be expressed as:

$$K_1 = \frac{x_5}{x_1^2} \qquad (3.25)$$

From equation (3.6) the equilibrium constant for water- gas shift reaction.

$$K_2 = \frac{x_1 x_3}{x_2 x_4} \qquad (3.26)$$

The gasification process is assumed to be adiabatic, the equation for the heat balance for the process is presented in equation (3.27).

$$H_f^O(\text{feedstock}) + w\left(H_f^O H_2O(1) + H_{(vap)}\right) + mH_f^O O_2 + 3.76mH_f^O N_2 = x_1 H_f^O H_2 + x_2 H_f^O CO$$

$$+x_3CO_2 + x_4\, H_f^O H_{2(vap)} + x_5 H_f^O CH_4 + \Delta T(x_1 C_{P_{H_2}} + x_2 C_{PCO} + x_3 C_{PO_2} + x_4 C_{P_{H_2O}}$$

$+x_5C_{PCH_4} + 3.76mC_{PN_2}$ (3.27)

$H_f^O H_{2,}$ $H_f^O N_2$ and $H_f^O O_2$ are zero at ambient temperature and equation (3.27) is reduced to equation (3.28).

$$H_f^O(\text{feedstock}) + w\left(H_f^O H_2O(l) + H_{(vap)}\right)$$
$$= x_2H_f^O CO + x_3H_f^O CO_2 + x_4H_f^O H_2O(vap) + x_5H_f^O CH_4$$

$$+\Delta T(x_1C_{PH_2} + x_2C_{PCO} + x_3C_{PCO_2} + x_4 C_{PH_20} + x_5C_{PCH_4} + 3.76mC_{PN_2}) \quad (3.28)$$

Where $H_f^O(\text{feedstock})$ is the heat of formation of the selected feedstock, $H_f^O H_2O(l)$ is the heat of formation of water, $H_{(vap)}$ is the heat of vaporization of water, $H_f^0 H_2O(vap)$ is the total heat of formation of water vapor, $H_f^O CO$, $H_f^O CO_2$, $H_f^O CH_4$ are heats of formation of the gaseous products, $C_{PH_2}, C_{PCO}, C_{PCO_2}, C_{PH_2O}, C_{PCH_4}, C_{PN_2}$ are specific heats of the gaseous products. Under the gasification temperature at the reduction zone ($T1$) and the ambient temperature at the reduction zone, equation (3.27) can be simplified to equation (3.29).

$$dH_{(feedstock)} + wdH_{H_2O(l)} = x_1dH_{H_2} + x_2dH_{CO} + x_3dH_{CO_2} + x_4dH_{H_2o(vap)} + x_5dH_{CH_4} + 3.76mdH_{N_2} \quad (3.29)$$

Where $dH(\text{of any gas})$ is the heat formation + enthalpy change, represented in equation (3.30).

$$dH(\text{of any gas}) = H_f^O + \Delta H, = \Delta T(C_{p(g)} \quad (3.30)$$

$$H_2O(l) = H_{f_{H_2O(l)}}^O + H_{(vap)}$$

$dH(MSW) = H_{f_{(feedstock)}}^0$ and $\Delta T = T_2 - T_1$

There are six unknowns from equations (3.22) to (3.26) and (3.29), and two of the equations (3.25) and (3.26) are nonlinear equations while the rest are linear.

From equation (3.22)

$$x_5 = 1 - x_2 - x_3 \tag{3.31}$$

From equation (3.23)

$$x_4 = w + \frac{a}{2} - x_1 - 2x_5 \tag{3.32}$$

Substituting of equation (3.31) into equation (3.32) gives:

$$x_4 = w + \frac{a}{2} - x_1 - 2(1 - x_2 - x_3)$$

$$x_4 = 2x_3 - 2x_2 - x_1 + w + \frac{a}{2} - 2 \tag{3.33}$$

From equation (3.24)

$$m = \frac{1}{2}\ (x_2 + 2x_3 + x_4 - w - b) \tag{3.34}$$

substituting equation (3.32) into equation (3.34)

$$m = \frac{1}{2}\ (x_2 + 2x_3 + (2x_3 + 2x_2 - x_1 + w + \frac{a}{2} - 2) - w - b)$$

$$m = \frac{1}{2}\ (4x_3 - x_2 - x_1 + \frac{a}{2} - b)$$

$$m = \frac{1}{2}\ (-x_1 + 3x_2 + 4x_3 - 1.94) \tag{3.35}$$

From equation (3.25)

$$x_5 = x_1^2 K_1 \tag{3.36}$$

Substituting equation (3.21) into equation (3.36)

$$1 - x_2 - x_3 = x_1^2 K_1$$

$$x_1^2K_1 + x_2 + x_3 - 1 = 0 \tag{3.37}$$

From equation (3.26)

$$x_1x_3 = x_2x_4K_2 \tag{3.38}$$

Substituting equation (3.32) into equation (3.38)

$$x_1x_3 = x_2(2x_3 - 2x_2 + w + \frac{a}{2} - 2)K_2$$

$$K_2x_2\left(2x_3 - 2x_2 + w + \frac{a}{2} - 2\right) - x_1x_3 = 0 \tag{3.39}$$

$$2K_2x_2x_3 - 2K_2x_2^2 + K_2x_2w + \frac{K_2x_2a}{2} - 2K_2x_2 - x_1x_3 = 0 \tag{3.40}$$

Substitution of equation (3.31), (3.33) and (3.35) into equation (3.29) gives equation (3.41)

$$dH_{(feedstock)} + wdH_{H_2O(l)} = x_1dH_{H_2} + x_2dH_{CO} + x_3dH_{CO_2} + \left(2x_3 - 2x_2 - x_1 + w + \frac{a}{2} - 2\right)dH_{H_2O(g)} + (1 - x_2 - x_3)dH_{CH_4} + 3.76 * \frac{1}{2}(-x_1 + 3x_2 + 4x_3 - 1.94) * dH_{N_2} \tag{3.41}$$

$$\left(dH_{H_2} - dH_{H_2O(g)} - 1.88dH_{N_2}\right)x_1 + \left(dH_{CO} - 2dH_{H_2O(g)} - dH_{CH_4} + 5.64dH_{N_2}\right)x_2 + \left(dH_{CO_2} + 2dH_{H_2O(g)} - dH_{CH_4} + 7.52dH_{N_2}\right)x_3 + (dH_{H_2O(g)} - wdH_{H_2O(l)})_w + (dH_{CH_4} + \left(\frac{a}{2} - 2\right)dH_{H_2O(g)} - 3.6472dH_{N_2} - dH_{(feedstock)} = 0 \tag{3.42}$$

To simplify equation (3.42) the known constants are simplified as follows

$$A = dH_{H_2} - dH_{H_2O(g)}$$

$$B = dH_{CO} - 2dH_{H_2O(g)} - -dH_{CH_4} + 5.64dH_{N_2}$$

$$C = dH_{CO_2} + 2dH_{H_2O(g)} - dH_{CH_4} + 7.52dH_{N_2}$$

$D = dH_{H_2O(g)} - dH_{H_2O(l)}$

$E = dH_{CH_4} + \left(\frac{a}{2} - 2\right) dH_{H_2O(g)} - 3.6472 dH_{N_2} - dH_{(feedstock)}$

Therefore equation (3.42) is simplified to equation (3.42)

$$Ax_1 + Bx_2 + Cx_3 + D_w + E = 0 \quad (3.42)$$

The system of the remaining equations comprises two nonlinear equation (3.37) and (3.39) while one linear equation (3.42). The Newton-Raphson method was used to analyze the system of equations; and a general chemical formula of solid biomass based on a single atom carbon as described by (Zainal et al., 2001):

$CH_{1.44}O_{0.66}$

From equation (3.18) the global gasification reaction can be written as follows:

$$CH_{1.44}O_{0.66} + wH_2O + mO_2 + 3.76mN_2 = x_1H_2 + x_2CO + x_3CO_2 + x_4H_2O + x_5CH_4 + 3.76mN_2 \quad (3.43)$$

Where:

m is the amount of oxygen per kmol of feedstock.

w is the amount of water per kmol of feedstock.

x_1, x_2, x_3, x_4 and x_5 the coefficients of constituents of the products

From the global reaction, there are six unknowns of the products: coefficients and the amount of oxygen per kmol. The from equation (3.27) the heat balance for the gasification process is assumed to be adiabatic. Table 3.2 to 3.4 shows the heat capacities contants, standard Gibbs function of formation, and heats of formation. Since $H_f^o(H_2)$, $H_f^o(N_2)$ are zero at ambient temperature equation (3.28) reduces to equation (3.44).

$$\mathrm{H_f^o(feedstock) + w\left(H_f^o H_{H_2O(\mathit{l})} + H_{(\mathit{vap})}\right) = x_2 H_f^o CO + x_3 H_f^o CO_2 \ + x_4 H_f^o H_2O(g) + x_5 H_f^o CH_4 + \Delta T((x_1 C_{pH_2} + x_2 C_{pCO} + x_3 C_{pCO_2} + x_4 C_{pH_2O} + x_5 C_{pCH_4} + 3.76mC_{pN_2}} \qquad (3.44)$$

Table 3.2: Heat capacities contants (A,B,C and D) (Perry & Green, 1998).

Chemical species	**Formula**	**T_{max}**	**A**	**B 10^3**	**C 10^6)**	**D 10^{-5})**
Water	$H_2O_{(g)}$	2000	3.470	1.450	-	0.121
Carbon dioxide	$CO_{2(g)}$	2000	5.457	1.047	-	-1.157
Carbon monoxide	$CO_{(g)}$	2500	3.376	0.557	-	-0.031
Methane	$CH_{4(g)}$	1500	1.702	9.081	-2.164	-
Hydrogen	$H_{2(g)}$	3000	0.422	-	-	0.083
Nitrogen	$N_{2(g)}$	2000	3.280	0.593	-	0.040
Carbon	$C_{(s)}$	2000	1.771	0.771	-	-0.867

Table 3.3: Standards Gibbs function of formation at 298.15K (kJ/kmol) (Perry & Green, 1998).

Chemical species	**Formula**	$\mathbf{\Delta GH_{f298}^o}$
Water	$H_2O_{(g)}$	-228 572
Water	$H_2O_{(l)}$	-237 129
Carbon dioxide	$CO_{2(g)}$	-394 359
Carbon monoxide	$CO_{(g)}$	-137 169
Methane	$CH_{4(g)}$	-50 460
Hydrogen	$H_{2(g)}$	0
Oxygen	$O_{2(g)}$	0
Nitrogen	$N_{2(g)}$	0
Carbon	$C_{(s)}$	-

Table 3.4: Heats of formation at 25 °C (kJ/kmol) (Perry & Green, 1998).

Chemical species	Formula	ΔH^{o}_{f298} (kJ/kmol)
Water	$H_2O_{(g)}$	-241 818
Water	$H_2O_{(l)}$	-285 830
Carbon dioxide	$CO_{2(g)}$	-393 509
Carbon monoxide	$CO_{(g)}$	-110 525
Methane	$CH_{4(g)}$	-74 520
Hydrogen	$H_{2(g)}$	0
Oxygen	$O_{2(g)}$	0
Nitrogen	$N_{2(g)}$	0
Carbon	$C_{(s)}$	0

3.3.5. Temperature

The syngas composition depends on the operating temperature, the chemical reactions are temperature dependent. The dependence of specific heat on temperature is simplified by equation (4.45).

$$C_{pmh=}R\left(A + T_{am} + \frac{C}{3}(T_{am} - T_1T_2) + \frac{D}{T_1T_2}\right) \qquad (3.45)$$

With $(T_{am} = T_1 + T_2)$ is the mean arithmetic mean temperature and $A, B, C, \text{and } D$ are constants for the properties of the gases concerned the values are in Table 3.2 and R is the universal gas constant (8.314J/molK). The gasification temperature of the gas increases from $T_1 = 298°C$ to $T_2 = 1073°C$, and the enthalpy change ΔH can be determined and expreesed by equation (3.46).

$$\Delta H = C_{pmh}(T_2 - T_1) \qquad (3.46)$$

The term $dH_{(\text{of any gas})}$ in equation(3.30) can be achieved from the value of the enthalpy change $\Delta H°$ of the gases. The equilibrium constant K is a function of temperature represented by equation (3.47) (Zainal et al., 2001).

$$-RT\ln K = \Delta G° \qquad (3.47)$$

The standard Gibbs function of formation $\Delta G°$ and the heat of formation $\Delta H°$ with the values for the included gases are in Table 3.3 and in Table 3.4 respectively. The dependence of $\Delta G°$ on temperature T is presented by equation(3.49) (Zainal et al., 2001).

$$\frac{d\ln K}{dT} = \frac{\Delta H°}{RT^2} \tag{3.49}$$

The effect of temperature on the equilibrium constant is given by equation (3.49) if it is negative; the reaction is exothermic. With increased temperature the equilibrium constant K decreases and for an endothermic reaction K will increase with T. The heat of formation is a function of T, and equation (3.49) can be integrated to equation (3.50).

$$\ln K = \int \frac{\Delta H°}{RT^2 dT} + I \tag{3.50}$$

Where I is the constant of intergration $\Delta H°$ is given in the following equation:

$$\frac{\Delta H°}{R} = \frac{J}{R} + (\Delta A)T + \frac{\Delta B}{2}T^2 + \frac{\Delta C}{6}T^3 \frac{\Delta D}{T} \tag{3.51}$$

Where J is a constant and $(\Delta A), (\Delta B), (\Delta C), (\Delta C)$ are the coofiecients for determining specific heat. Subtituiting equation (3.51) into equation (3.50) and intergrating can be expressed as equation (3.52).

$$\ln K = -\frac{J}{RT} + (\Delta A)\ln T + \frac{\Delta B}{2} + \frac{\Delta C}{6T^2} + \frac{\Delta D}{2T^2} + I \tag{3.52}$$

From equation (3.47), $\Delta G° = -RT\ln K$, and multiplying with equation (3.52) with $-RT$ gives:

$$\Delta G° = J - RT(\Delta A\ln T + \frac{\Delta B}{2} + \frac{\Delta C}{6T^2} + \frac{\Delta A}{2T^2} + I) \tag{3.53}$$

Equations (3.48) - (3.50) are used to determine the equilibrium constants for any reaction temperature T, and to determine the constant J and K, knowlegge about the specific heat is sufficient. The constant J can be found using equation (3.52) or (3.53) when the values of $\ln K$ or $\Delta G°$ are known, generally at a temperature of 298.15 K as shown in Table 3.3. Two equilibrium equations are required to determine the equilibrium contant K_1 and K_2. The equilibrium constant (K_1) is for the reaction of equation (3.3) and is solved as $\Delta A, \Delta B, \Delta C, \Delta D$ and can be obtained from the data of heat capacity for the reaction from equation (3.3).

$$\mathrm{C + 2H_2 = CH_4} \tag{3.54}$$

$$\mathrm{\Delta A = CH_4 - C - 2H_2} \tag{3.55}$$

The equations to determine the values of $\mathrm{\Delta A, \Delta B, \Delta C, and\ \Delta D}$ are written as:

$$\mathrm{\Delta A = ACH_4 - AC - 2AH_2}$$

$$\mathrm{\Delta B = BCH_4 - BC - 2BH_2}$$

$$\mathrm{\Delta C = CCH_4 - CC - 2CH_2}$$

$$\mathrm{\Delta D = DCH_4 - DC - 2DH_2}$$

The values of $\mathrm{A, B, C, and\ D}$ are from the heat capacity in Table 3.2.

Calculation of the constants J and I for equation (3.51) and (3.53) at 298.15K requires the values for $\mathrm{\Delta H^o_{298}}$ and $\Delta G°_{298}$.

$$\mathrm{\Delta H^o_{298} = (\Delta H^o_{298})CH_4 - (\Delta H^o_{298})C - 2(\Delta H^o_{298})H_2;}$$

$$\mathrm{\Delta H^o_{298} = -74520 - 0 - 2(0) = -\frac{74520J}{mol};}$$

$$\mathrm{\Delta G^o_{298} = (\Delta G^o_{298})CH_4 - (\Delta G^o_{298})C - 2(\Delta G^o_{298})H_2;}$$

$$\mathrm{\Delta G^{\circ}_{298} = -50460 - 0 - 0 = 50460;}$$

Substituting the known values into equation (3.50) for $\mathrm{T = 298.15\ K}$ gives $\mathrm{\frac{J}{R} = -7052.848}$.

Substituting the known values into equation (3.53) for $\mathrm{T = 298.15\ K}$ gives $\mathrm{I = 32.541}$.

The standard equation for $\mathrm{lnK_1}$ using equation (3.52) as reported by (Zainal et al., 2001) is represented in equation (3 56).

$$\mathrm{lnK_1 = \frac{7082.848}{T} + (-6.567)lnT + \frac{70466\ x10^{-3}}{2}T + \frac{-2.164x10^{-6}}{6}T^2 + \frac{0.701x10^{-5}}{2(T)^2}}$$
$$\mathrm{+32.541} \tag{3.56}$$

The equilibrium constant $\mathrm{K_1}$ for any temperature can be obtained by substituting the temperature T into equation (3.56). Similarly for the reaction of equation (3.6) the value of K_2 can be determined. The equations to obtain $\Delta A, \Delta B, \Delta C$ and ΔD values can be expressed as:

$$\Delta A = A_{CO} + A_{H_2O} - A_{CO_2} - A_{H_2}$$

$$\Delta B = B_{CO} + B_{H_2o} - B_{CO_2} - B_{H_2}$$

$$\Delta C = C_{CO} + C_{H_2O} - C_{CO_2} - C_{H_2}$$

$$\Delta D = D_{CO} + D_{H_2O} - D_{CO_2} - D_{H_2}$$

After the calculation steps the standard equation $\ln K_2$ is represented by equation (3.57).

$$\ln K_2 = \frac{5870.53}{T} + 1.86\ln T + 2.7x10^{-4}T + + \frac{58200}{T^2} + 18.007 \quad (3.57)$$

Equilibrium constant K_2 for any temperature can be determined with the substitution of the temperature T into equation (3.57).

3.4. Procedure for numerical solution

Step by step structure of the equilibrium model to solve the system of equations using Newton-Raphson theory in MATLAB. The first stage of gasifier simulation starts from the mass fractions of carbon, hydrogen, oxygen, and nitrogen in the biomass, and the relative mass of the moisture content, the molar water content, and the total enthalpy of the reactants is calculated. In the second stage it is the gasifier simulation, the syngas composition is estimated, and minimizing the Gibbs free energy for calculation of the equilibrium constant and a Newton-Raphson (N-R) algorithm was implemented. The Newton -Raphson method is based on sequential linearization of the nonlinear equation using Taylor's theorem (Radosavljević, 2018). The (N-R) method involves a computational algorithm to solve non-linear algebraic equations using derivative information (Upreti, 2017). Depending on the initial sensitivity, with good initial values the Newton Raphson method can convergence fast (Wu Minglu, 2011).

The (N-R) method has the following algorithm, and it is described in the following steps (Radosavljević, 2018).

1. Make an initial guess of x, x^0
2. Represent $f(x)$ by a Taylor series about $x^{(k)}$

$$f(x) = f\left(x^{(k)}\right) + \frac{df(x)}{dx}\bigg|_{x^{(k)}}.\ (x - x^{(k)} + \frac{1}{2}\frac{d^2f(x)}{dx^2}\bigg|_{x^{(k)}}.\ (x - x^{(k)})^2 + \text{higher order numbers} \tag{3.58}$$

Where $k = 0,1,2, \ldots$

3. Approximate $f(x)$ by neglecting all terms except the first two:

$$f(x) = f\left(x^{(k)}\right) + \frac{df(x)}{dx}\left|x^{(k)}.\left(x - x^{(k)}\right) = 0\right. \tag{3.59}$$

4. Using this linear approximation to determine $\Delta x^{(k)} = x - x^{(k)}$

$$\Delta x^{(k)} = -\left[\frac{df(x)}{dx}\left|x^{(k)}\right.\right]^{-1} f\left(x^{(k)}\right) \tag{3.60}$$

5. Compute the value of x at iteration $(k + 1)$:

$$x^{(k+1)} = x^{(k)} + \Delta x^{(k)} \tag{3.61}$$

6. The process is repeated until the error $\Delta f = \left|f\left(x^{(k+1)}\right) - f(x^{(k)})\right|$ is less than a specified tolerance, this procedure can be generalised for set of nonlinear equations with n unknowns. For this study, equations (3.62), (3.63), and 3.64) were solved.

$$f_1(x_1, x_2, x_3) = 0 \tag{3.62}$$

$$f_2(x_1, x_2, x_3) = 0 \tag{3.63}$$

$$f_3(x_1, x_2, x_3) = 0 \tag{3.64}$$

The set of equations can be represented in matrix form:

$\mathrm{f(x)} = 0$

The Newton-Raphson iterative procedure for calculating the unknowns is:

$$\Delta \mathrm{x}^{(\mathrm{k})} = -\left[\mathrm{J}(\mathrm{x}^{(\mathrm{k})}\right]^{-1}.\,\mathrm{f}(\mathrm{x}^{(\mathrm{k})}) \tag{3.65}$$

$$\mathrm{X}^{(\mathrm{k}+1)} = \mathrm{X}^{(\mathrm{k})} + \Delta \mathrm{X}^{(\mathrm{k})} \tag{3.66}$$

Where: $\mathrm{x} = \left[\mathrm{x}_{1,}\mathrm{x}_{2,}\ \mathrm{x}_3 \ldots .\mathrm{x}_\mathrm{n}\right]^{\mathrm{T}}$, and $\mathrm{f(x)} = [\mathrm{f}_1(\mathrm{x}), \mathrm{f}_2(\mathrm{x}), \mathrm{f}_3(\mathrm{x}) \ldots .\mathrm{f}_\mathrm{n}(\mathrm{x})]^{\mathrm{T}}$. The transcript T denotes the transposition operator J is the Jacobian matrix $\mathrm{J}(\mathrm{x}^{(\mathrm{k})})$, and it is defined by equation (3.67).

$$\mathrm{J}(\mathrm{x}^{(\mathrm{k})}) = \begin{pmatrix} \frac{\partial \mathrm{f}_1(\mathrm{x})}{\partial \mathrm{x}_1} & \frac{\partial \mathrm{f}_1(\mathrm{x})}{\partial \mathrm{x}_2} & \frac{\partial \mathrm{f}_1(\mathrm{x})}{\partial \mathrm{x}_3} \\ \frac{\partial \mathrm{f}_2(\mathrm{x})}{\partial \mathrm{x}_1} & \frac{\partial \mathrm{f}_2(\mathrm{x})}{\partial \mathrm{x}_2} & \frac{\partial \mathrm{f}_2(\mathrm{x})}{\partial \mathrm{x}_3} \\ \frac{\partial \mathrm{f}_3(\mathrm{x})}{\partial \mathrm{x}_1} & \frac{\partial \mathrm{f}_3(\mathrm{x})}{\partial \mathrm{x}_2} & \frac{\partial \mathrm{f}_3(\mathrm{x})}{\partial \mathrm{x}_3} \end{pmatrix} \tag{3.67}$$

Figure 3.1 illustrates how the system of equations were solved using Newton-Raphson algorithm, and how the syngas composition was calculated. The chart also shows the sequential order of the code.

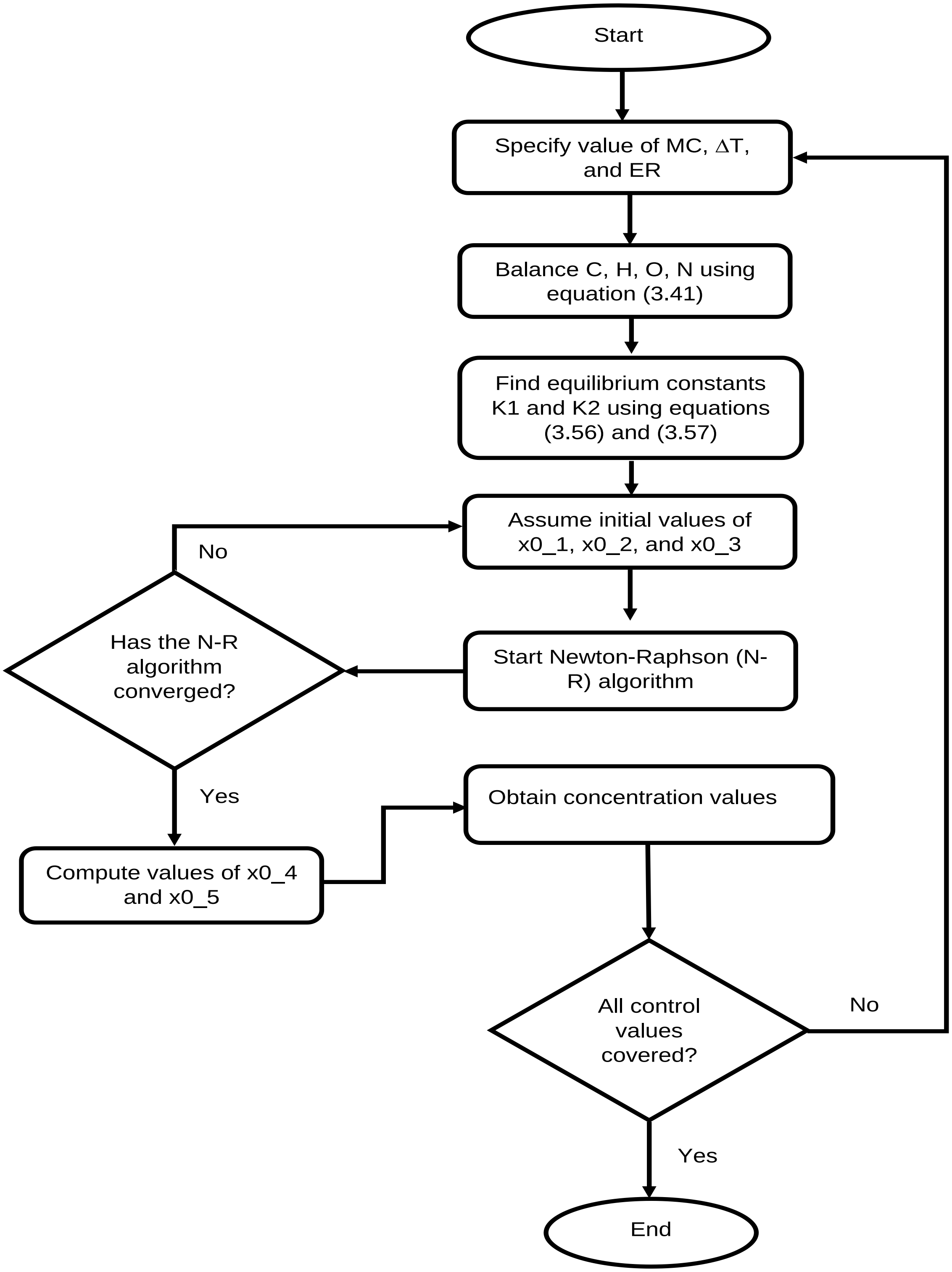


Figure 3.1: A flowchart of the procedure for solving the system of equations using the Newton-Raphson theory in MATLAB.

3.5. Model validation

To validate this equilibrium gasification model; results of an experiment by Zainal et al. (2001) were compared with predicted results in this work. This study focused on moisture content, temperature, and equilibrium ratio as operating parameters. To validate and get a sensible estimate value of the ER, equation (3.21) was used based on empirical data reported by (Zainal et al., 2001). The amount of oxygen per kmol of feedstock m is presented by equation (3.19). The RMSE gives information on the brief performance of a model by recognizing a term-by-term comparison of the actual difference. The MBE supplies information on the prolonged performance of a model (Stone, 1993). For statistical validation, the root mean square error (RMSE) and mean bias error (MBE) of deviation were calculated using equations (3.68) and (3.69) (Stone, 1993).

$$\mathrm{RMSE} = \left(\frac{1}{\mathrm{n}}\sum_{\mathrm{i}=1}^{\mathrm{n}} \mathrm{d}_{\mathrm{i}}^{2}\right)^{\frac{1}{2}} \qquad (3.68)$$

$$\mathrm{MBE} = \frac{1}{\mathrm{n}}\sum_{\mathrm{i}=1}^{\mathrm{n}} \mathrm{d}_{\mathrm{i}} \qquad 3.69)$$

Where n is the number of data pairs and $\mathrm{d_i}$ is the difference between $\mathrm{i^{th}}$ estimate and $\mathrm{i^{th}}$ measured values (Stone, 1993).

3.6. Sensitivity analysis

After model validation, conducting a sensitivity analysis is essential, which provides the relative effects of the uncertain input parameters (Hong et al., 2019). Sensitivity analysis aims to determine the parameter or a set of parameters that influence the output of the model (Dündar & Yelten, 2020; Dietterich, 1998). As a result of the assumptions made in developing mathematical models for a complex process such as gasification, performing a sensitivity analysis is necessary (Pérez, Benjumea & Melgar, 2015). The sensitivity analysis was estimated by varying the values of one parameter, while other parameters were constant. The default values assumed for each parameter are reported in the experiment. In Table 3.5 the summary of sensitivity analysis of this study is illustrated, in a specified parameter range comparison between the default values and the studied range was done, and the percentage of the syngas was observed.

Table 3.5: Sensitivity analysis summary

Parameter	Unit	Default value	Studied range
Temperature	°C	800	800 – 1200
Moisture content	%	20	0 – 40
Equivalence ratio	Dimensionless	0.4	0.2 – 0.6

Chapter 4

RESULTS AND DISCUSSION

This study investigated the effects of operating conditions moisture content, temperature, and equivalence ratio (ER) on the gasification of MSW using a thermodynamic equilibrium model. The analysis assumes that the gasification reactions occur at thermodynamic equilibrium, and the calculations are independent of the type of gasifier or design. Moreover, all proposed reactions are perfect reactions, and the effect of humidity inside the feedstock is not considered. This work ignored the impurities within the feedstock and assumed that all the feedstocks would totally burn without waste. Results are presented and discussed in this chapter.

4.1. Gasifier simulation

To show the overall gasification process and to adjust various gasification parameters, the simulation considered a thermodynamic equilibrium model. It was observed that by minimizing the Gibbs Free Energy for calculation of the equilibrium constant, the results compared relatively well with published literature. The simulation approach can be applied to various models and literature indicates that using the minimization of Gibbs Energy is a reliable approach. In Table 4.1 the modelled values are presented and a comparison between the experimental data from Zainal et al. (2001) and the modelled values from this study is shown. In this study the heat of formation of liquid water was used.

4.2. Model validation

A strong agreement was observed between experimental data in literature and predicted values in this study. The model represented an ideal gasification process. The modelled results were compared with experimental data from (Zainal et al. 2001). The gasification temperature, moisture content and equivalence ratio were the considered gasification parameters in the developed model, and they gave accurate and valid results. The equivalence ratio indicates the biggest influence on the gasification process as it affected the syngas composition, calorific value, and the H_2/CO ratio. Table 4.1 shows the compared experimental data and the modelled values.

Table 4.1: Comparison between experimental results from Zainal et al. (2001) and modelled results obtained from this study

Gaseous product	Experimental values (%)	Modelled values (%)	
		Zainal et al. (2001)	Present study
H_2	15.23	21.06	24.34
CO	23.04	19.61	12.85
CO_2	16.42	12.01	14.37
CH_4	1.58	0.64	0.96
N_2	42.31	46.68	43.63
CV	4.85	4.72	4.35

The errors found between the modelled and experimental values are presented in Table 4.2. Acceptable errors, MBE and RMSE of -0.486% and 6.215%, respectively, were calculated. The observed values of MBE and RMSE suggest that the model can predict accurate data. In a paired t-test in this present study, a p-value of 0.883 was recorded. The p-value in the experiment and modelled values of Zainal et al. (2001) was 0.897. The paired test was used to find any significant difference between the models and to determine if the present modelled results occurred by chance. A p-value ranges from 0% to 100% and a low p-value shows that the data did not occur by chance (Cho et al., 2019). Since the analyzed p-value is low in this study, this suggests that the model is valid, and the results did not occur by chance.

Table 4.2: Statistical performance of models

Models	MBE (%)	RMSE (%)	P - value
Zainal et al. (2001)	0.284	4.127	0.897
Present study	-0.486	6.215	0.883

4.3. Model sensitivity

The effects of the selected gasification parameters were investigated on the syngas composition, calorific value, and H_2/CO ratio. It was observed that moisture content, temperature, and ER have an influence on the syngas composition, calorific value, and H_2/CO ratio. Justifiable results were observed when the selected parameters were modified, and the results are acceptable when compared to the literature. The observed results of the effect of moisture content, temperature, and equivalence ratio on the syngas composition, calorific value, and H_2/CO are discussed in Section 4.3.1 to 4.3.4, and further illustrated in Figures 4.1 - 4.6.

4.3.1. Effect of operating parameters on the syngas composition

The content and composition of syngas vary, depending on the feedstock, gasifier type, and operating parameters. In Sections 4.3.1.1 – 4.3.1.3 the variation of the syngas composition observed in this study are discussed.

4.3.1.1. Effect of moisture content on the syngas composition

In Figure 4.1 results show that with increased moisture content, carbon monoxide is reduced. It is also observed that the increase in moisture content leads to a reduced nitrogen composition, because of the water gas shift reaction where carbon monoxide and water vapor react together and CO_2 and H_2 are produced (Samadi, Ghobadian & Nosrati, 2020). Hydrogen and carbon dioxide increase with moisture content. A small amount of methane is recorded and increased to just over 1% when the moisture content increases. The methanation and water-gas shift reactions explain the increase of hydrogen and carbon dioxide (Samadi, Ghobadian & Nosrati, 2020).

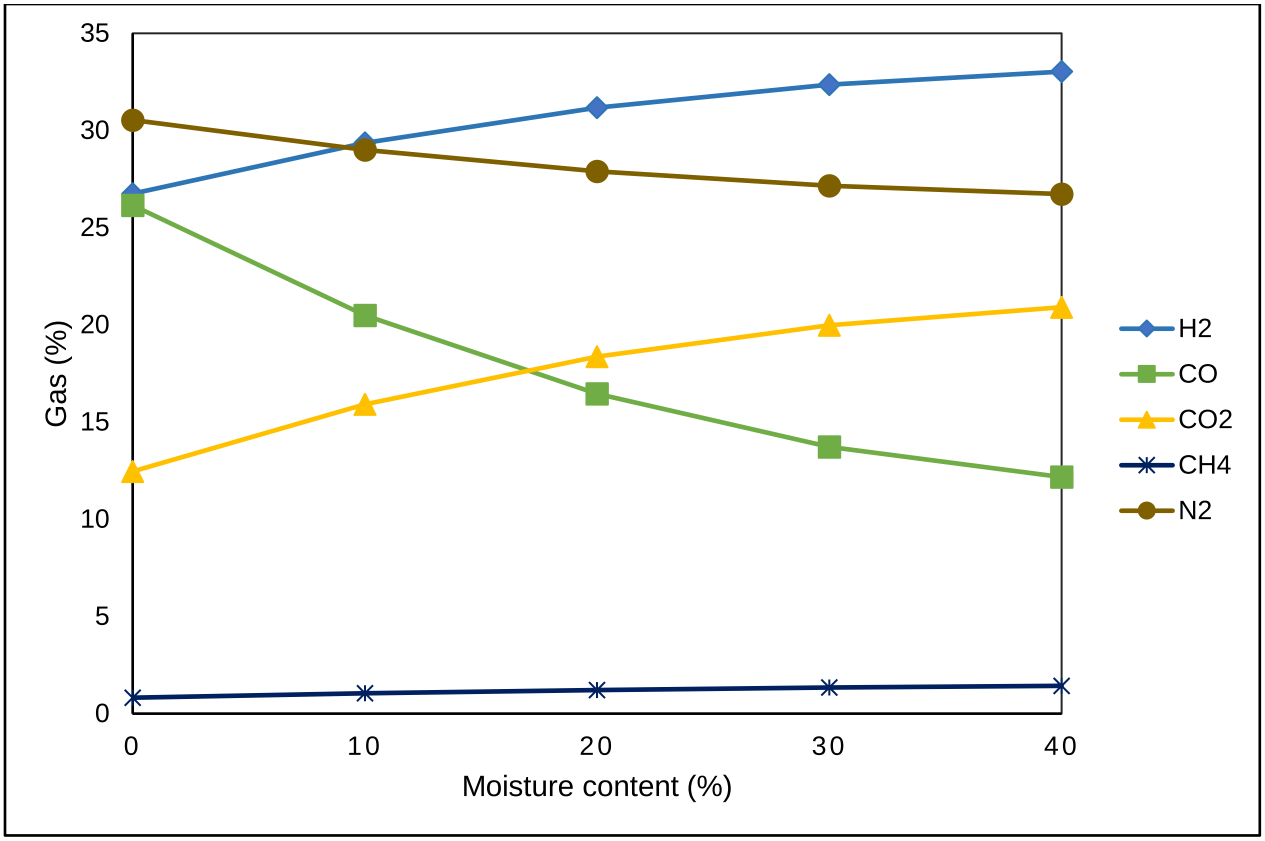


Figure 4.1: Effect of moisture content on syngas composition

4.3.1.1.1. Summary of the effect of moisture content on the syngas composition

There are notable changes when the moisture content exceeds 10%, and a sharp decrease in carbon monoxide is observed. At a maximum moisture content of 40%, a maximum hydrogen composition is recorded, with the gas increasing from 26.75 – 33.03%. The increase in hydrogen is a result of the water-gas shift reaction. Carbon monoxide decreased from 26.15 to 12.17% when moisture content increased. The summarized trend is shown in Table 4.3.

Table 4.3: Summary of effects of moisture content on the syngas composition

Gas	Low MC 0 – 10%	Moderate MC 10 – 20%	High MC 30 – 40%	Observed results
H_2	Increase	Increase	Increase	With increased MC H_2 continues to increase
CO	Decrease	Decrease	Considerable decrease	Results show considerable decreased amount of CO with increased MC
CO_2	Increase	Increase	Increase	CO_2 is affected by the increase of MC; the amount of CO2 reduces
CH_4	Increase	Increase	Increase	Results show consistent increase of CH_4 with increased MC.
N_2	Decrease	Decrease	Decrease	Nitrogen amount decreases with increased MC

4.3.1.2. Effect of temperature on syngas composition

Results in Figure 4.2 show that the increase of gasification temperature led to increased hydrogen (H_2), while nitrogen (N_2) remained almost constant. It was also observed that carbon dioxide (CO_2) is slightly reduced with the increase in temperature and then remains constant from 1000°C. Similarly, with carbon monoxide (CO), the marginal changes are noticed at 1000°C. With the increase in temperature, CO increases slightly and remains almost constant. Moreover, the increased temperature resulted in a small amount of methane of just over 1%, and with a further increase in temperature methane was almost 0%. Similar results were reported by Lau Sze Yii et al. (2019) that the production of the syngas increases as temperature increases. At a higher temperature, thermal cracking is complete, and gasification is improved. Moreover, at a temperature higher than 800°C, H_2, CO, and CO_2 increase, because of the Boudouard reaction and water-gas shift reactions. These reactions are influential and lead to the production of CO and H_2. The increased H_2 is due to cracking and steam reforming reactions explained in equation (3.8) and equation (3.9) (Franco et al., 2003; Lau Sze Yii et al., 2019). According to Xu, Jin & Cheng (2017), the reactor temperature is controlled by the energy balance, and more energy is driven into the system when the steam temperature is higher. The authors further mentioned that with the increase of temperature, CH_4 gets converted to CO_2, and the water-gas shift reaction takes place, the composition of CO_2 and H_2 is reduced, while a slight increase of CO is observed.

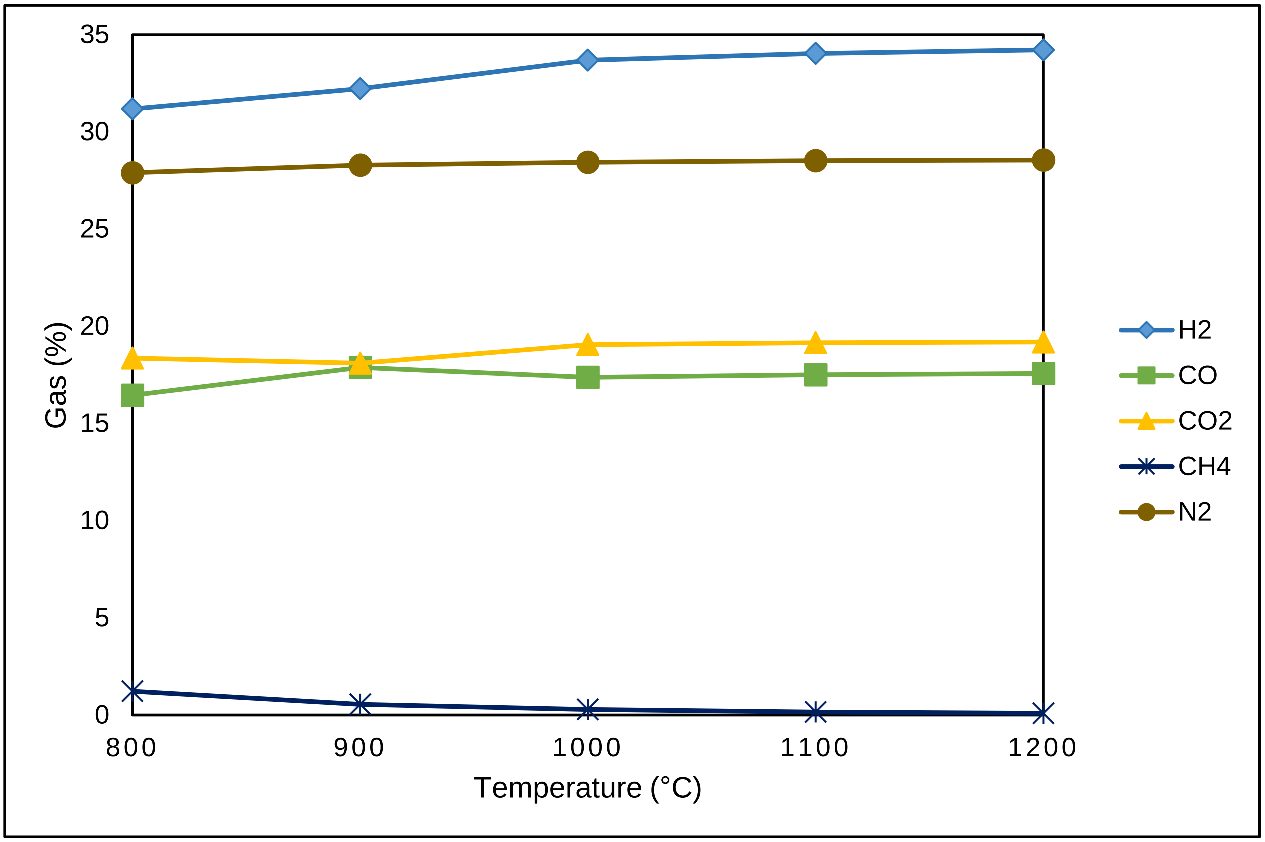


Figure 4.2: Effect of temperature on syngas composition

4.3.1.2.1. Summary of the effect of temperature on the syngas composition

The increase in temperature has varying effects on the syngas. The summarized trend is shown in Table 4.4 indicating that from 900°C changes are noticed. At a maximum temperature of 1200°C, a hydrogen composition of 34.22% and the lowest amount of methane 0.09% are recorded. CO_2 slightly increases from 18.36% at 800°C to 19.19% at maximum temperature. CO and N_2 also increase and they both remain constant with increased temperature.

Table 4.4: Summary of effects of temperature on the syngas composition

Gas	Moderate temperature 800– 900°C	High temperature 1000 – 1200°C	Observed results
H_2	Increase	Increase	Increased temperature results in increased H_2
CO	Increase	Constant	CO increases with increased temperatures and remains constant
CO_2	Constant	Increase	CO_2 increases slightly with increased temperature
CH_4	Decrease	Decrease	There is notable decrease in methane with increased temperature
N_2	Increase	Constant	N_2 increases with increased temperatures and remains constant

4.3.1.3. Effect of equivalence ratio on syngas composition

In Figure 4.3 the effect of ER is shown. It is observed that the increase of ER has an impact on nitrogen and hydrogen. When the ER increased, there is an increase in nitrogen. Hydrogen decreased with the increase in ER. Moreover, there is also a constant reduction in carbon dioxide and carbon monoxide when the ER increased. A small amount of methane is recorded which continuously reduced with the increase of ER. Similar results were recorded by (Lau Sze Yii et al., 2019). When the ER is high, the oxidation reaction is promoted (Kumar, Jones & Hanna, 2009). The authors further mentioned that with the increased ER, CO_2 is produced, while H_2 and CO decreased. A study by Tanigaki, Manako & Osada, (2012) reported similar results and indicated that CO decreases with increased ER. The authors suggest that the decrease in CO indicates chemical energy that is represented by a low heating value of the syngas, and that with increased ER, the carbon monoxide and carbon dioxide concentration is decreased.

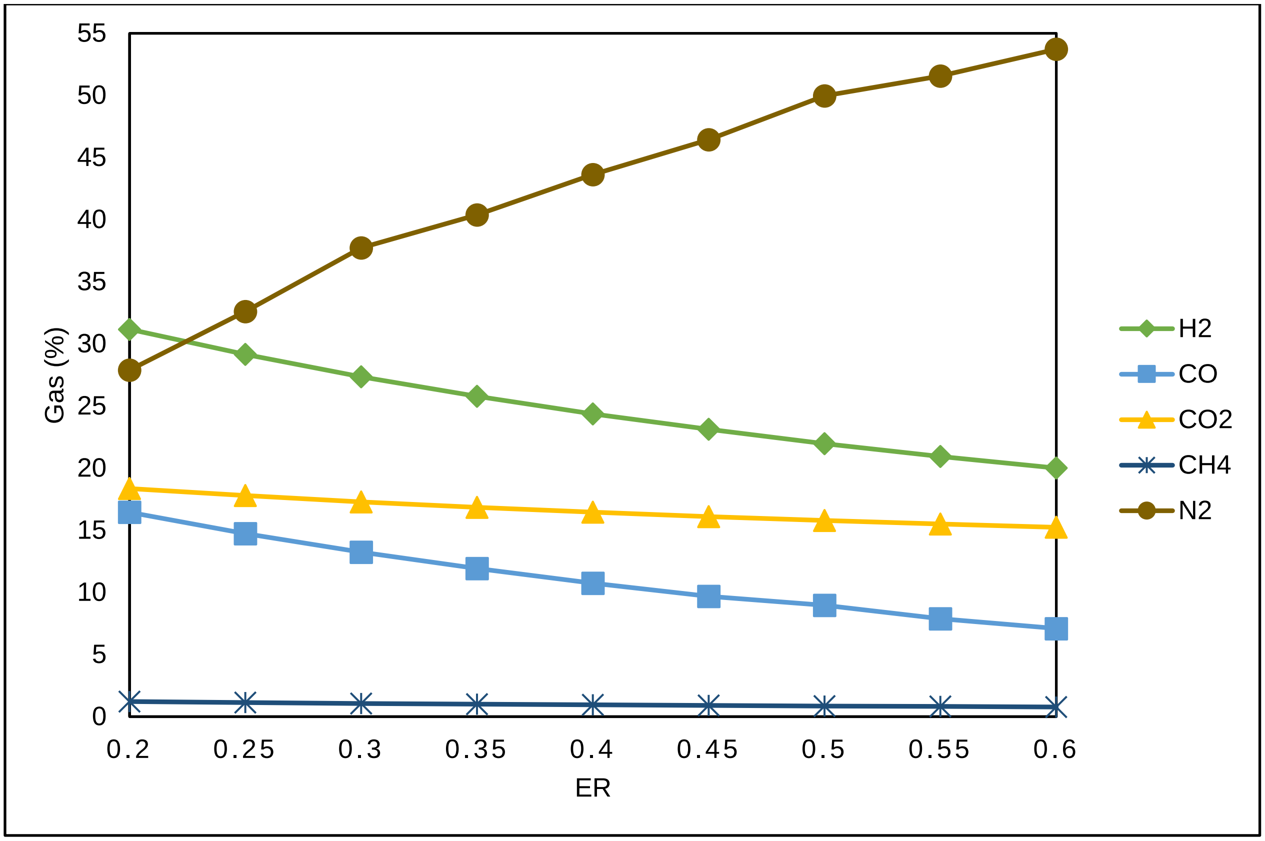


Figure 4.3: Effect of equivalence ratio (ER) on the syngas composition

4.3.1.3.1. Summary of the effect of equivalence ratio on the syngas composition

Table 4.5 summarizes the effects ER has on syngas composition. The increase of ER led to reduced syngas composition. The lowest H_2 was recorded with increased ER, H_2 decreased from 31.18 to 20.01% and the highest N_2 was recorded with increased ER.

Table 4.5: Summary of effects of equivalence ratio on the syngas compositio

Gas	Low ER (0.2 – 0.3)	Moderate ER (0.3-0.4)	High ER (0.4- 0.6)	Observed results
H_2	Decrease	Decrease	Decrease	Increased ER, led to low amount of H_2
CO	Decrease	Decrease	Decrease	High ER, led to reduced CO amount
CO_2	Decrease	Decrease	Decrease	CO_2 decreased with increased ER
CH_4	Decrease	Decrease	Decrease	With increased ER, the amount of CH_4 continued to decrease
N_2	Increase	Increase	Considerable increase	Increasing ER led to a substantial and continuous increase in N_2

4.3.2. Effect of operating parameters on the calorific value

The calorific value is an essential factor in selecting feedstock, and the observed results show that adjusting the operating parameters has an impact on the calorific value.

4.3.2.1. Effect of moisture content on calorific value of the gasification of MSW

Figure 4.4 shows a notable decrease in the calorific value of the syngas when moisture content increased. It is reported that this is due to the decrease of CO (Veksha et al., 2019). The observed effects are comparable to those reported by Veksha et al. (2019) and Couto et al. (2016) in their studies that researched the gasification of solid waste. Koroneos & Lykidou (2011) reported similar results of the calorific value of the syngas that decreases with the increase in moisture content.

The effect of moisture content on caloric value was also studied by Szymajda & Łaska (2019) and they confirmed that the calorific value of solid biofuel increases with decreasing moisture. Zainal et al. (2001) mentioned that the calorific value of the syngas reduced when the moisture content in the feedstock increased. The increase of moisture content has a notable effect on the calorific value. Results by Atnaw, Sulaiman & Yusup

(2014) showed that with high moisture content, oxidation temperature remained low during the experiment. These authors indicated that to produce syngas that has acceptable heating value and have the advantage of the production of high calorific value, initial drying of feedstock is necessary.

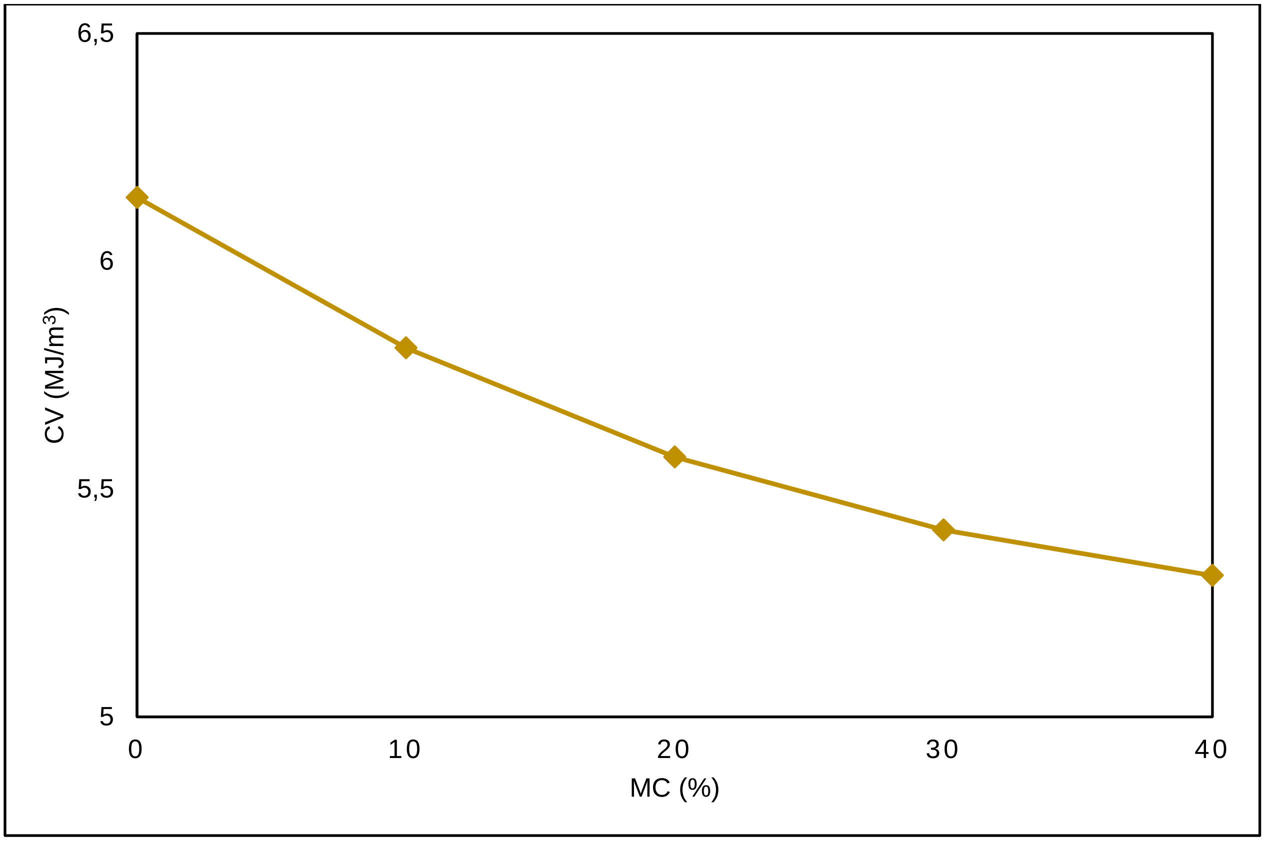


Figure 4.4: Effect of moisture content on the calorific value (CV)

4.3.2.2. Effect of temperature on calorific value of

The results in Figure 4.5 show that when the temperature is the operational parameter, there is an almost constant calorific value. The calorific value remains constant from 800 – 1200°C. At a higher temperature, there are complete gasification reactions, and a greater amount of H_2 and CO, as well as higher H_2 and CO caloric values (Franco et al., 2003). The recorded amount of H_2 in this study (31.18%) agrees closely with the explanation given by (Franco et al., 2003). As a result of the high calorific value of the syngas, the cold gas efficiency of the gasification process increases with temperature (Shayan, Zare & Mirzaee, 2018; Torres, Pansare & Goodwin, 2007).

The influence of temperature on the calorific value of gases was investigated by Klejnowska et al. (2020). Observed results indicated that at a higher temperature, there were increased amounts of syngas, and the calorific value of the gas was higher at maximum temperature. Similar results reported on experimental work by Lau Sze Yii et al. (2019) and Zainal et al. (2001). These studies reported that the calorific value of the syngas decreased when the temperature increased. The present study found that the calorific value in the gasification of MSW increased slightly and then remained constant with the increase in temperature. At a temperature of 900 °C slight changes were noted, higher H_2 and lower CH_4 were recorded with increased gasification temperature. Similar results were observed by Cortazar et al. (2018) and Franco et al. (2003).

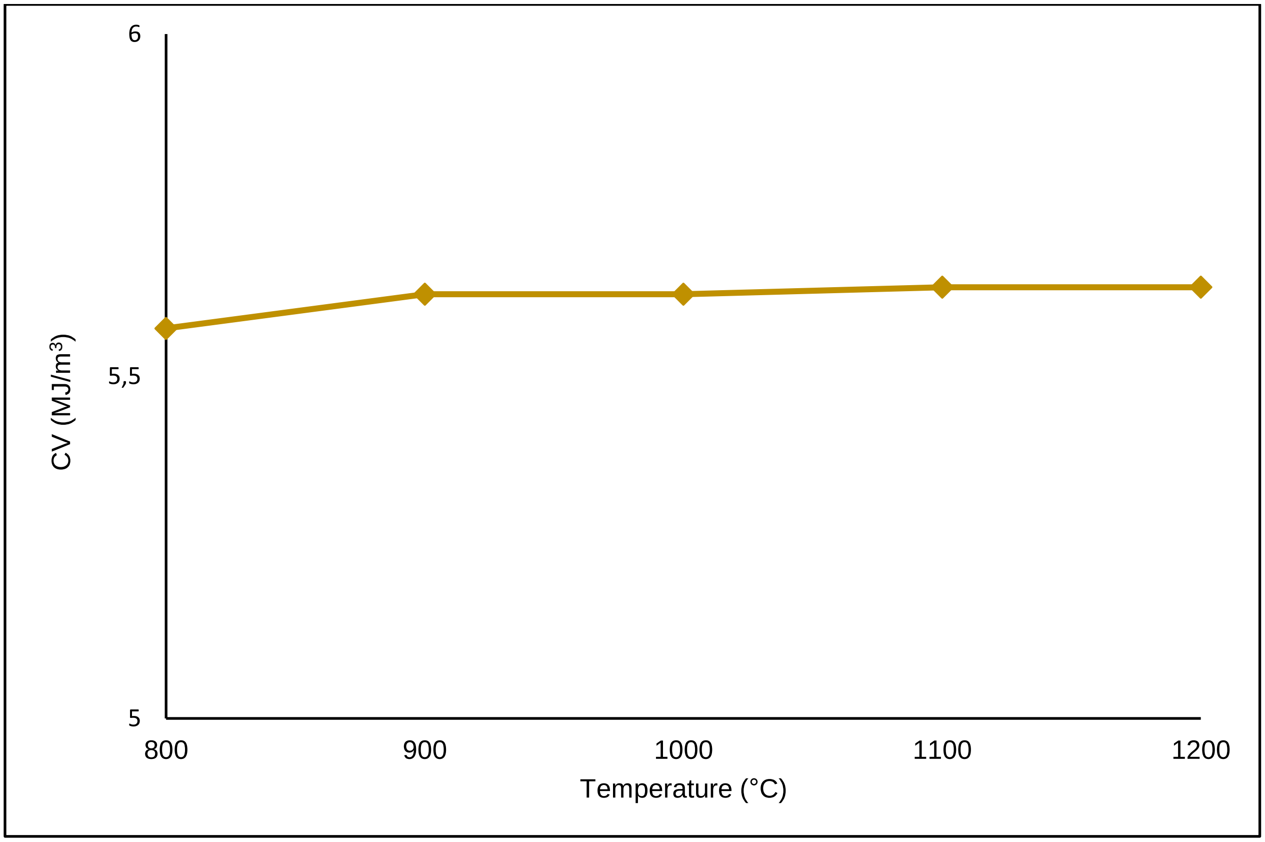


Figure 4.5: Effect of temperature on calorific value (CV)

4.3.2.3. Effect of ER on caloric value

It is observed that calorific value is effected by the increase of equivalence ratio, as shown in Figure 4.6. Increased ER produces lower H_2 and CO yields. Moreover, the increased ER enhances the quality of CO_2, and this reduces the calorific value of the syngas. An increased ER can assist in the tar formation, when there is oxygen available to react with the volatile species (Vaish et al., 2017). An analysis based on the effect of equivalence ratio on calorific value by Dillibabu (2014), suggests that increased hydrogen in the gas mixture improves the heating value. The author mentions that it is because hydrogen has a calorific value of 141.79MJ/m^3. Increasing ER, the total amount of H_2, CO, and CH_4 is reduced, and the calorific value of the product gas decreased (Chen, 2015).

A parametric study on the effects of equivalence ratio by Vaezi et al.(2011) concluded that with the gasification of heavy fuels oil at a low ER of 0.3, it is possible to produce syngas with a considerable caloric value of about 15MJ/m^3. In experimental work by Guo et al. (2014), it is mentioned that due to stronger combustion reactions, the increase of ER leads to higher temperature in the gasifier. This is as a result of an oxidation reaction. The authors further highlight that at a higher ER value, more CH_4 burns with O_2 and the formation of CH_4 is inhibited at a higher temperature.

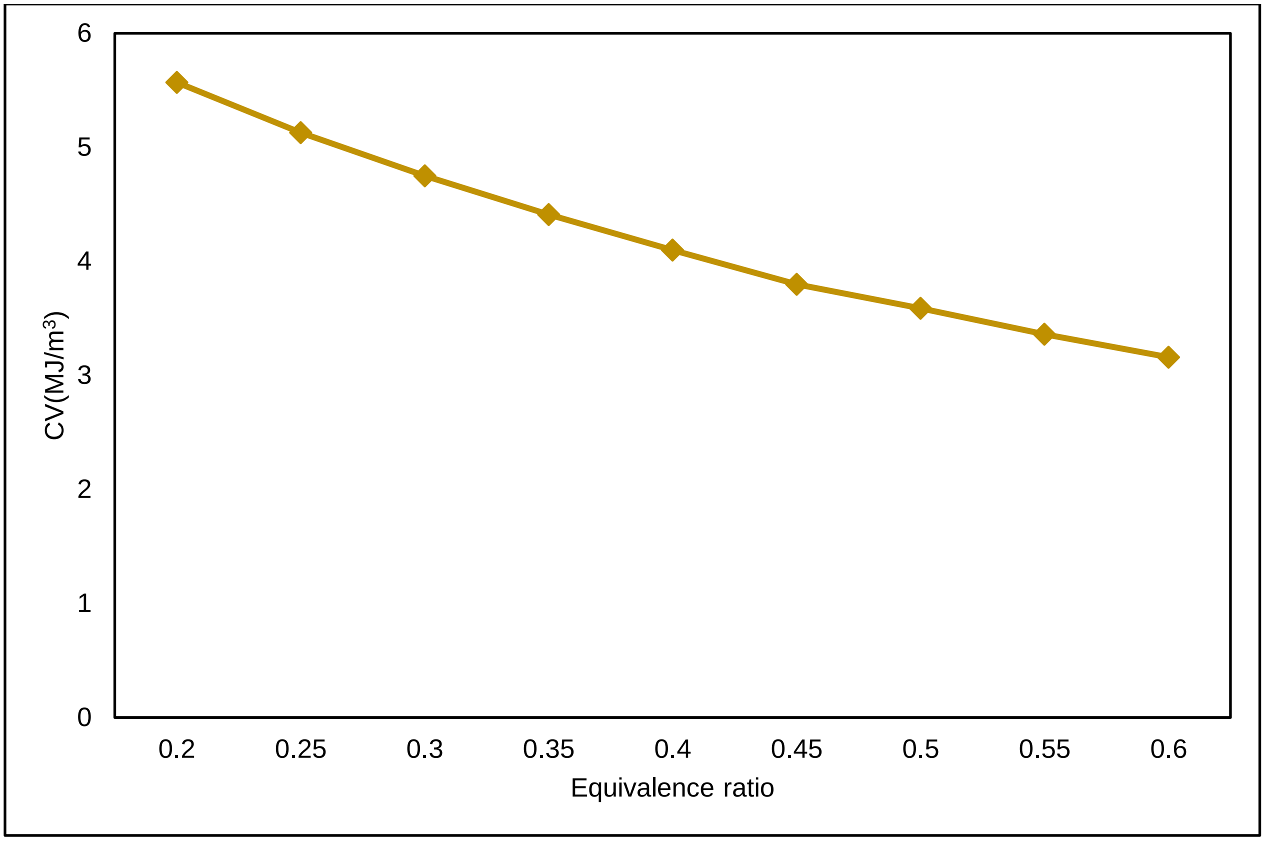


Figure 4.6: Effect of ER on calorific value

4.3.3. Effect of operating parameters on the hydrogen to carbon monoxide (H_2/CO) ratio

Gas products of gasification contain moisture, carbon dioxide, carbon monoxide, hydrogen sulphide, and methane, and from this mixture hydrogen and carbon monoxide must be separated to produce syngas (Basu, 2018). To produce various gaseous and liquid hydrocarbons, a definite ratio of CO and H_2 is necessary. The molar ratio is found through the shift reaction that converts excess carbon monoxide into hydrogen. In Figure 4.7 – 4.9, the H_2/CO ratio at various gasification parameters is shown and further discussed.

4.3.3.1. Effect of moisture content on H_2/CO ratio of the gasification of MSW

Figure 4.7 shows that increased moisture content has an effect on the H_2/CO ratio. When moisture content increased from 0 to 40%, the H_2/CO ratio increased from 0.92 to 2.24. The oxidation synthesis process requires syngas with an H_2/CO molar ratio of 1, and for the production of Fischer Tropsch synthesis, fuels ratio close to 2 is needed (Im-orb, Simasatitkul & Arpornwichanop, 2016). The results observed in this study are relatively acceptable and agree with literature.

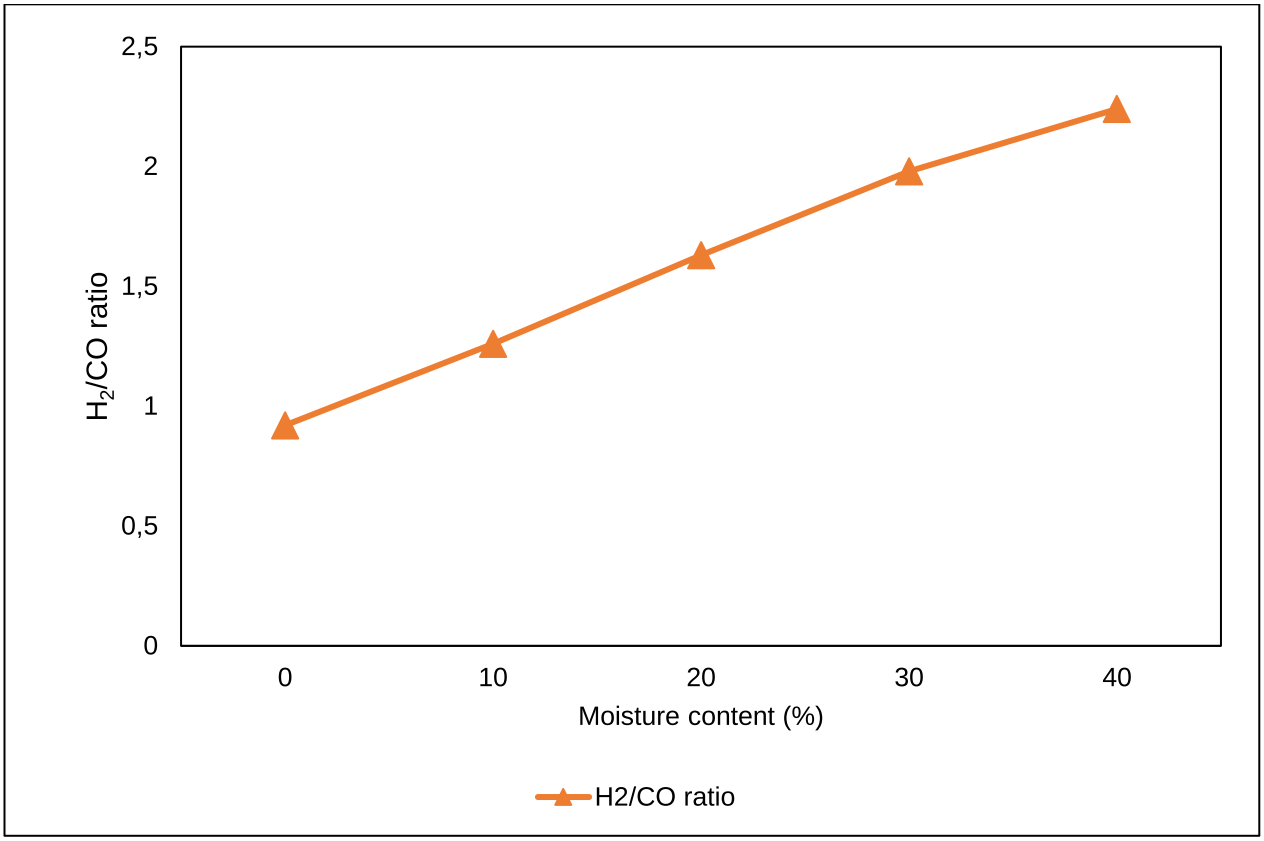


Figure 4.7: Effect of the increase in moisture content on the H_2/CO ratio

4.3.3.2. Effect of temperature on H2/CO ratio

It is observed that the H_2/CO ratio increases, and then it remains constant with increased temperature as shown in Figure 4.8. The H_2/CO ratio increased from 1.89 to 1.94. Rahmat & Rasid (2017) suggest that at a higher temperature, moisture content decreases and that reduces the production of H_2 from the gasification process. Ammar et al. 's (2016) model showed that with increased temperature, hydrogen to carbon monoxide ratio increased. The authors also mention that the rise in the H_2/CO ratio is because of increased temperature steam that reforms for biomass char and methane is intensified, and these reactions are endothermic. Similar results were reported by Liu et al. (2019). The authors aimed to explore the high H_2/CO ratio syngas production from chemical looping co-gasification of biomass and polyethylene, with CaO/Fe2O3 oxygen carrier. Their results showed that with increased temperature, the H_2/CO ratio increased. The results of this current study are satisfactory and agree with literature.

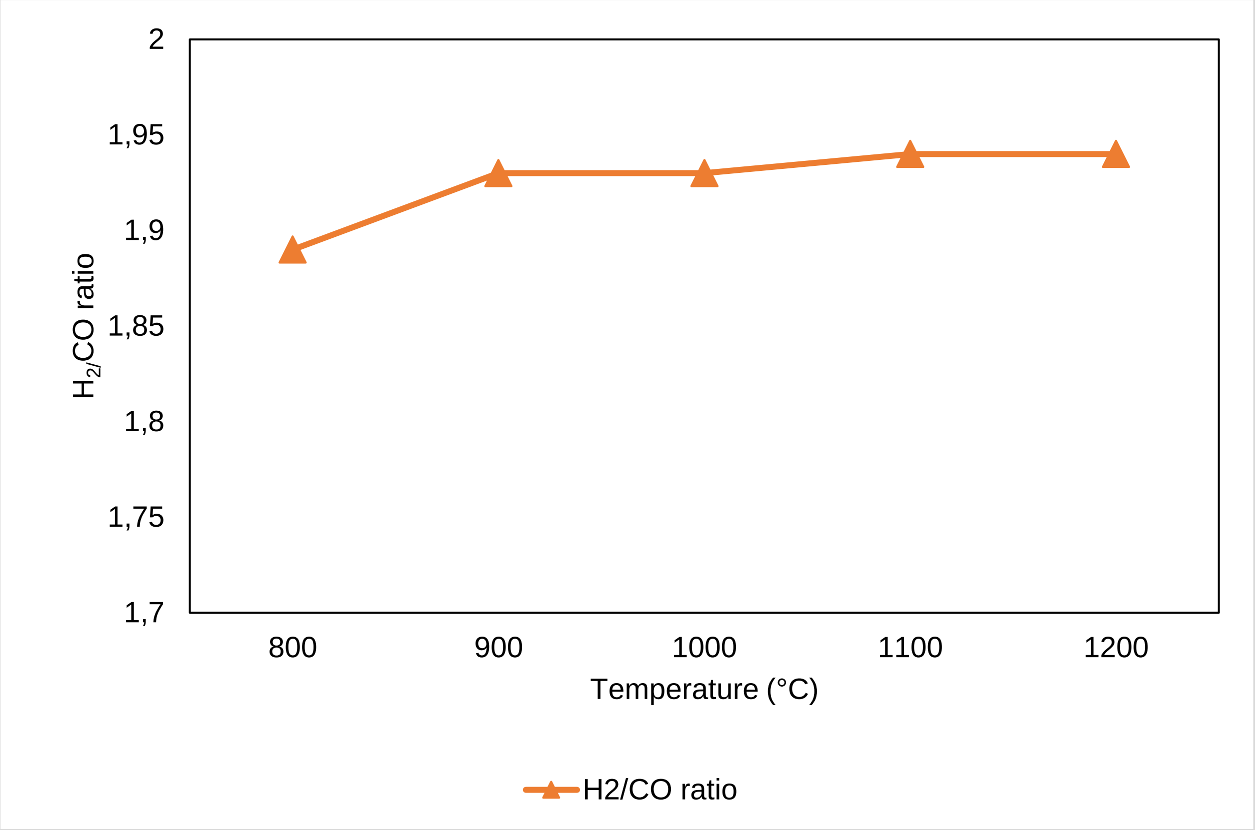


Figure 4.8: Effect of temperature on H_2/CO ratio

4.3.3.3. Effect of ER on H_2/CO ratio

Figure 4.9 shows that with increased ER, the hydrogen to carbon monoxide ratio increased. The increase in ER led to a satisfactory H_2/CO ratio. The H_2/CO ratio increased from 1.89 to 2.72 – at ER (0.6) the H_2/CO ratio was predicted to be maximum.

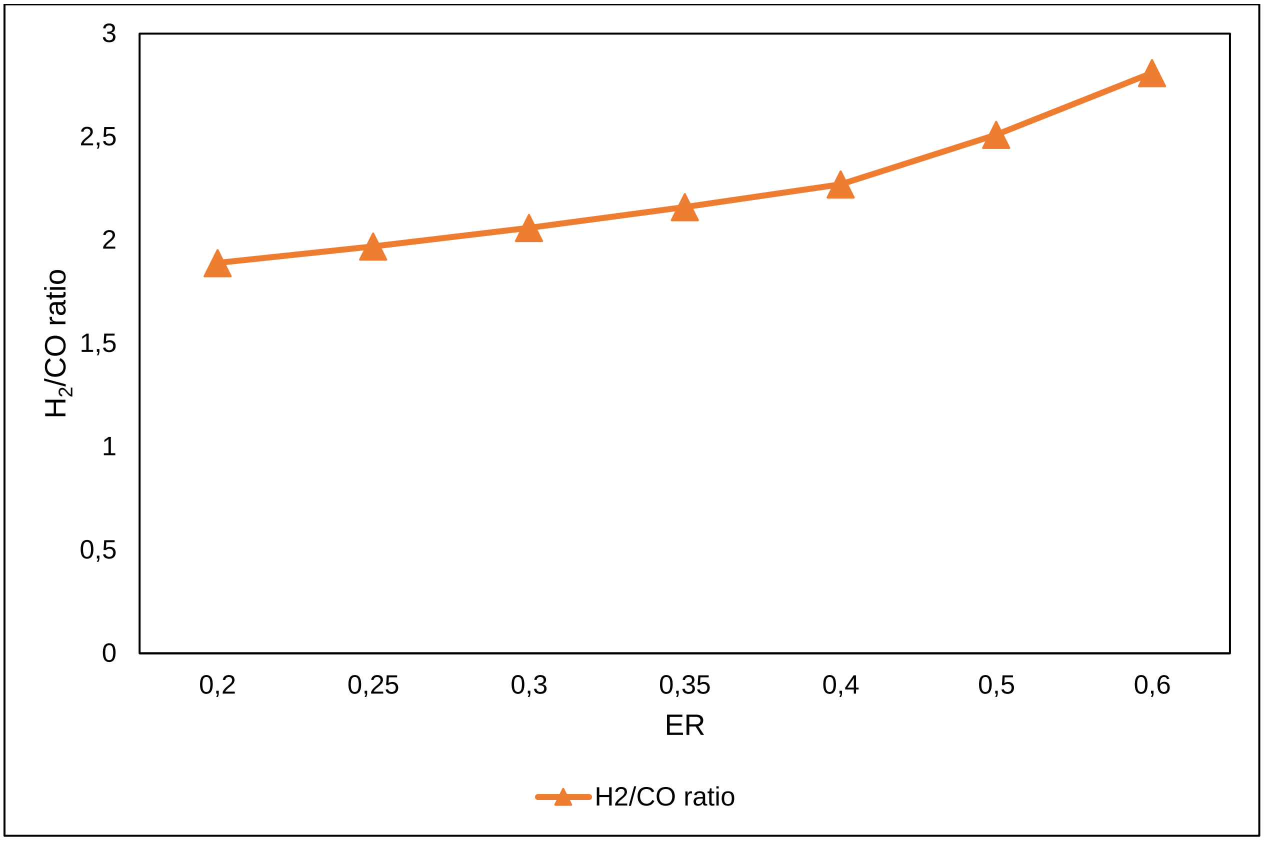


Figure 4.9: Effect of ER on H_2/CO ratio

Chapter 5

CONCLUSIONS AND RECOMMENDATIONS

This study aimed to evaluate the gasification of municipal solid waste. To achieve this aim, the following objectives were set: (a) to develop a thermodynamic mathematical model of a gasifier; (b) to simulate the gasifier; (c) to validate the model using empirical data; (d) to perform a sensitivity analysis. The evaluation of the gasification of municipal solid waste was conducted while controlling gasification parameters. The gasification of municipal solid waste was discussed in Chapter 1. A literature review is presented in Chapter 2, while the research methodology is discussed In Chapter 3. In Chapter 4 the observed results are analysed and discussed, and in Chapter 5 the conclusions and recommendations are presented.

5.1 Conclusions

5.1.1 Model validation

The RMSE, MBE and p-value were 6.215%, -0.486% and 0.883, respectively. Therefore, the developed mathematical model gives accurate predictions.

5.1.2 Model Sensitivity

A sensitivity analysis was performed by modifying the values of one parameter at a given time. This analysis provided the effects of the moisture content, temperature, and equivalent ratio (ER).

5.1.2.1 Effect of moisture content on the syngas composition

The increase in moisture content influenced the syngas composition, and there are notable changes in the syngas composition when the moisture content passes 10%. There is a considerable decrease in CO, while H_2, CO2, and CH4 increased, and the caloric value also reduced. A small amount of methane was recorded with the increase of moisture content. Moreover, the H_2/CO ratio increased from 0.92 to 2.24 with increased moisture content. It is an acceptable H_2/CO ratio; therefore, it is concluded that increased moisture content affects syngas.

5.1.2.2 Effect of temperature on the syngas composition

The increase of gasification temperature led to increased concentrations of hydrogen (H_2), nitrogen (N_2) remained constant, while carbon dioxide (CO_2) reduced. From 1000 °C carbon monoxide (CO) increased slightly, and then remained almost constant. The increased temperature also resulted in a small amount of methane of just over 1%, which then reduced to almost 0%. Calorific value remains almost constant when the temperature varies. Furthermore, increased temperature resulted in a moderate increase in the H_2/CO ratio. Therefore, it is concluded that temperature has an impact on the syngas, but not on the calorific value.

5.1.2.3 Effect of equivalence ratio on the syngas composition gasification of MSW

Increasing the ER showed an increase in nitrogen, while hydrogen decreased. There is also a constant reduction in carbon dioxide and carbon monoxide, with increased ER and a small amount of methane. Increasing ER produces lower H_2 and CO yields, while increased ER improves the amount of CO_2, and this reduces the calorific value of the syngas. Increased ER showed an acceptable H_2/CO ratio of 2.72, which is the highest H_2/CO ratio recorded, when compared to other gasification parameters at ER=0.6. Therefore, this study concludes that the ER is the most influential parameter of the gasification process.

5.2 Recommendations

5.2.1 Gasification modelling

In this study a mathematical model was developed for the thermodynamic analysis of the gasification process. Satisfactory syngas, calorific value, and H_2/CO ratio results were obtained and compared to the published experimental values. This study focused on thermodynamic equilibrium models. Even though equilibrium models give accurate results, they are not for a specific gasifier, therefore there is a need to develop a model based on the applicable gasifier design.

5.2.2 Thermodynamic analysis of the gasification of MSW

The model developed in this study can be utilised and compared to other thermodynamic equilibrium models. However, more robust models would be a worthwhile venture for more improved results in the gasification of municipal solid waste.

5.2.3 Incorporation of the gasification of MSW in the waste management industry

The effectiveness of waste as an energy source relies on the composition or heating value. The composition of municipal solid waste varies from one place to another. Therefore, it is recommended that further investigation should be conducted by using empirical data that is more specific to the South African climate, lifestyle, and economy.

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APPENDICES

Appendix A

Algorithm for solving system of equations using MATLAB

The sequence of MATLAB files was saved as thermodynamic analysis.m for repeated use. The green comments are used as reminders, they explain the code and refer to commands that do not have to run.

Gasification process simulation

Thermodynamic equilibrium calculation is independent of a gasifier design, the following code is used to simulate the gasification process

```
a=1.44.                 %a=mole fraction ratios of (H/C) is (determined from the ultimate
analysis of biomass
b=0.66.                 %b=mole fraction ratios of (O/C) is (determined from the ultimate
analysis of biomass
ER=0.2.                 %ER is the equivalence ratio
MM=ER*(1+(a/4-(b/2))).
%MM=0.42.
mc=0.2.                 %mc is the moisture content
w=24*mc/18*(1-mc)           %is the amount of water per kmol
%T is temperature in Kelvin
% At T=1073.15
%LN= Natural logarithm
%K1=(7082.848/(T)) +(-6.567*LN(T))+((7.466*10^-3)/2)*(T)+(((-2.164*10^-
6)/6)*((T^2)))+((0.701*10^-5)/(2*(T^2)))+32.541
%K2=(5870.53/(T)) +(1.86*LN(T)) +((2.7*10^-4) *(T)) +((58200/(T^2))) +18.007
%
K1= 0.045271086.
K2=9.56987E+15.
%
dHCO2=46256.0-393509.
```

```
dHCO=24608.0-110525.
dHCH4=-66937.0-74520.
dHN2=25237.0.
dHH2=18644.0.
dHH2Oliquid=61710.0-285830.
dHH2Ogas=-241818.
dHfeedstock=-137472.6.
%
A=dHH2-dHH2Ogas.
B=dHCO+2*dHH2Ogas-dHCH4.
C=dHCO2+2*dHH2Ogas-dHCH4.
D=dHH2Ogas-dHH2Oliquid.
E=dHCH4-1.28*dHH2Ogas+3.76*MM*dHN2-dHwood.
%
```

Newton Raphson algorithm

```
x0_1= 0.6782.
x0_2=0.7215.
x0_3=0.2575.
%
count = 0.
while 1
%
f1=(x0_1) ^2*K1+x0_2+x0_3-1;
f2=-K2*x0_1*x0_2+K2*w*x0_2-1.28*K2*x0_2+2*K2*(x0_2) ^2-
x0_1*x0_3+2*K2*x0_2*x0_3;
f3=A*x0_1+B*x0_2+C*x0_3+D*w+E.
%
F= ([f1; f2; f3]);
A0= ([x0_1; x0_2; x0_3]);
%
dF1_dx0_1=2*x0_1*K1.
```

```
dF1_dx0_2=1.
dF1_dx0_3=1.
dF2_dx0_1=0.
dF2_dx0_2=w*K2-1.28*K2+4*K2*x0_2.
dF2_dx0_3=0.
dF3_dx0_1=A.
dF3_dx0_2=B.
dF3_dx0_3=C.
%
Jac=([[dF1_dx0_1, dF1_dx0_2,dF1_dx0_3];[dF2_dx0_1,
dF2_dx0_2,dF2_dx0_3];[dF3_dx0_1,dF3_dx0_2,dF3_dx0_3]]);
J_inv=inv (Jac);
A1=A0-J_inv*F.
%
xn_1=A1(1,1).
xn_2=A1(2,1).
xn_3=A1(3,1).
%
residual=abs(A1-A0).
count=count+1.
x0_1=xn_1.
x0_2=xn_2.
x0_3=xn_3.
if all(residual<=0.00001)
   break
end
Table1(count, :) = {count xn_1}.
fprintf ('%d xn_1 %d\n',Table1{count,:});
Table2(count, :) = {count xn_2}.
fprintf ('%d xn_2 %d\n’, Table2{count:});
Table3(count, :) = {count xn_3}.
```

```
fprintf (‘%d xn_3 %d\n’, Table3{count:});
end
An= ([xn_1; xn_2; xn_3])
xn_5=1-xn_2-xn_3.
xn_4=w+0.72-xn_1+2*xn_5.
```

Syngas composition

```
JUM=(xn_1+xn_2+xn_3+xn_4+xn_5) +(3.76*MM).
H2=(xn_1/JUM) *100.
CO=(xn_2/JUM) *100.
CO2=(xn_3/JUM) *100.
H2O=(xn_4/JUM) *100.
CH4=(xn_5/JUM) *100.
N2=(3.76*MM/JUM) *100.
per=H2+CO+CO2+CH4+N2
CV=CO * 0.01 * 11.97 + H2 * 0.01 * 10.22 + CH4 *0.01 * 33.95
```