Feasibility study for maize as a feedstock for liquid fuels production based on a simulation developed in Aspen Plus®

MSc Research Dissertation

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EXECUTIVE SUMMARY

South Africa's energy sector is vital to the development of its economy. Instability in the form of disruption in supply affects production costs, investments, and social and economic growth. Domestic sources are no longer able to meet the country's demands. South Africa must find a local alternative fuel source in order to reclaim stability and encourage social and economic development.

Biomass is one of the most abundant renewable energy sources, and has great potential as a fuel source. Currently biomass contributes 12% of the world's energy supply, while in some developing countries it is responsible for up to 50% of the energy supply. South Africa is the highest maize producer on the African continent. Many studies carried out indicated that maize, and its residue contain valuable materials, and has the highest lower heating value in comparison to other agricultural crops. This indicates that maize can be a potential biomass for renewable energy generation in South Africa.

A means for energy conversion for biomass, is the process of gasification. Gasification results in gaseous products H_2, CO and CO_2. Since the process of biomass gasification involves a series of complex chemical reactions involving a number of parameters, which include flow, heat transfer and mass transfer, it is very difficult to study the process of gasification by relying on experimentation only. Numerical simulation was used to provide further insight on this process, and accelerate development and application of maize gasification in a cost effective and efficient manner. The objective of this study was therefore, to verify and evaluate the feasibility of maize gasification and liquid fuels production in South Africa from an economic and energy perspective.

The simulation model was developed in Aspen Plus® based on two thermodynamic models specified as Soave – Redlich – Kwong and the Peng Robinson equation of state. All binary parameters required for this simulation were available in Aspen Plus®. The gasification unit was modelled based on a modified Gibbs free energy minimization model.

Gasification of maize and downstream processing in the form of Fischer-Tropsch (FT) synthesis and gas to liquids (GTL) processing for liquid fuels production was modelled in Aspen Plus®. Sensitivity analyses were carried out on the process variables: equivalence ratio (ER), steam to biomass ratio (SBR), temperature and pressure, to obtain the optimum gasification conditions. The optimum reactor conditions, which maximized syngas volume and quality was found to be an ER of 0.22 and SBR of 0.2 at a temperature of 611°C. An increase in pressure was found to have a negative effect; therefore atmospheric conditions of 101.325 kPa were chosen, in order to maximize CO and H_2 molar volumes. Based on these conditions the produced syngas consisted of 35% H_2, 16% CO, 24% CO_2 and 3%CH_4.

The results obtained from gasification, based on a modified Gibbs free energy model, show a closer agreement with experimental data, than other simulations based on the assumption that equilibrium is reached and no tar is formed. However, these results were still idealistic as it under predicted the formation of CO and CH_4. Although tar was accounted for as 5.5% of the total product from the gasifier (Barman *et al.*, 2012), it may have been an insufficient estimation resulting in the discrepancy in CO and CH_4.

The feasibility of maize as a feed for gasification was examined based on quality of syngas produced in relation to the requirements for FT synthesis. A H_2/CO ratio of 2.20 was found, which is within range of 2.1 – 2.56 found to support greater conversions of CO with deactivation of the FT catalyst (Lillebo *et al.*, 2017). The syngas produced from maize was found to have a higher H_2/CO ratio than conventional fossil fuel feeds; implying that maize can result in a syngas feed which is both renewable and richer in CO and H_2 molar volumes. Liquid fuels generation was modelled based on experimental production distributions obtained from literature for FT synthesis and hydrocracking. The liquid fuel production for 1000 kg/hr maize feed, was found to be 152 kg/hr LPG, 517 kg/hr petrol and 155 kg/hr diesel. The simulation of liquid fuels production via the Fischer-Tropsch synthesis and hydrocracking process showed fair agreement with literature. Where significant deviations were found, they could be reasonably explained and supported. This simulation was found to be a suitable means to predict liquid fuels production from maize gasification and downstream processing.

The feasibility of liquid fuels production from maize in South Africa was examined based on the country's resource capacity to support additional maize generation. It was found that based on 450 000 hectares of underutilized land found in the Homelands, an additional 1.216 billion litre/annum of synthetic fuels in the form of diesel and petrol could be produced. This has the potential to supplement South African liquid fuels demand by 6% using a renewable fuel source. This fuel generation from maize will not impact food security due to the use of underutilized arable land for maize cultivation, or impact water supply as maize does not require irrigation. In addition, fuel generation in this manner supports the Biofuels Industry Strategy (2007) by targeting the use of underutilized land, ensuring minimal impact on food security, and exceeds its primary objective of achieving a 2% blending rate from renewable sources.

The economic feasibility of liquid fuels derived from maize was determined based on current economic conditions in 2016. Based on these conditions of 49 $/bbl Brent Crude, 40 $/MT coal and 6.5 $/mmBTU of natural gas at a R/$ exchange rate of R14.06 per U.S. dollar, it was found that coal, natural gas and oil processing are more economically viable feeds for fuel generation relative to maize. However, based on projected market conditions for South Africa, the R/$ exchange rate is expected to weaken further, the coal supply is expected to diminish and supply of natural gas is expected to be a continued issue for South Africa. Based on this, maize should be considered as a feed for fuel generation to reduce the dependency on non-renewable fossil fuel sources.

The energy feasibility of liquid fuels produced from maize was only evaluated from a thermal energy perspective. It was found that maize gasification and FT processing requires 0.91 kg steam/kg feed. This 0.91kg of steam accounts for the raw material feed, distillation and heating required for every 1kg of maize processed. It was found that 2.56 kg steam/kg feed was generated from the reactor units. This was assumed to be in the form of 10 bar steam, as in this form it can be sent to steam turbines for electricity generation to assist with overall energy efficiency for this process. In addition, the amount of CO_2 (kg/kg feed) produced, was examined for maize processing in comparison to fossil fuel feeds: natural gas and coal. The CO_2 production from liquid fuels processing based on a maize feed, was found to be the highest at 0.66 kg/kg feed. However, a coal feed has higher ash and fix carbon content indicating greater solid waste generation in the gasifer. While dry reforming of natural gas is a net consumer of CO_2, but had significantly higher steam requirements in order to achieve the same H_2/CO ratio as maize. This indicates that although maize results in more CO_2/kg feed, it is 88% more energy efficient than dry methane reforming.

Additional experimental work on FT processing using syngas derived from maize is recommended. This will assist in further verification of liquid fuels quantity, quality and process energy requirements.

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I would like to thank my supervisor Dr Kevin Harding for his patience, understanding and support during this process.

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Finally, I owe the continued determination, resilience and motivation required in completing this report to my family. The inspiration of my mother’s academic success has undoubtedly led to the pursuit and completion of this dissertation. Support from my partner Byron Butka and my nunu’s Captain and Mayo; has been invaluable to my morale and overall mental, physical and psychological wellbeing. I owe them everything.

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NOMENCLATURE

Symbol	**Description**
W_n	Weight fraction of a product consisting of n carbons
α	Chain growth probability factor
n	Number of carbons in product
R_x	Reactivity for x% of carbon conversion
$x\ \%$	Percentage of carbon conversion
m_o	Initial carbon content
m	Carbon converted into gaseous products
t_x	Time required to achieve carbon conversion of x%
G_T	total Gibbs free energy in system
n_i	Number of moles in species i
μ_i	Chemical potential of species i
R	Universal gas constant 8.314 $\frac{\mathrm{J}}{\mathrm{mol\ K}}$
T	Absolute temperature of the system
f_i	Fugacity of species i
${f_i}^o$	Standard fugacity of species i
Φ	Fugacity coefficient
P_i	Pressure of species i in the system
${P_i}^o$	Standard pressure of species i
y_i	Mole fraction of gas species i

$\Delta {G_{fi}}^{o}$	Standard Gibbs free energy of formation
a_{ij}	Number of atoms of the jth element in a mole of species i
a_j	Total number of atoms of jth element in a reaction mixture
δ_c	Function of equivalence ratio
ε	Number of hydrogens per carbon atom in biomass molecule
b	Number of oxygens per carbon atom in biomass molecule
ρ	The nitrogen to oxygen molar ratio in the oxidizing agent
$x_{H2}\ x_{H2O}, x_{CO2}, x_{CO}$ $and\, x_{CH4}$	The molar gas ratios of these components within the specific biomass

1 CHAPTER 1: INTRODUCTION

1.1 Background

South Africa’s energy sector is vital to the wellbeing of its economy. Any form of instability or disruption in supply affects production costs, investments, retail and purchasing power of private and corporate consumers. Local sources and available substitutes such as coal, natural gas and crude oil processing, are no longer able to meet the country’s demand (Nkomo, 2009). As a result, in 2007 South Africa experienced a crisis in its energy sector due to increasing demand. This has resulted in continued forced load shedding and a significant increase in liquid fuels imports. (Department of Energy, 2015)

Research indicates that South Africa has limited oil and natural gas reserves; therefore the country makes use of its large coal deposits to meet its energy needs. South Africa mines approximately 2.2 million tons of coal per year (Africa Mining, 2015). 21% of this coal is exported, 21% is used to supply local industries and the rest is deemed not saleable and discarded. Of the 21% used locally; 62% is used for electricity generation and 23 % is used for liquid fuels production. This accounts for only 30% of the total domestic petrol and diesel needs (World Coal Institute, 2006). The balance of liquid fuels demand is met by crude oil imports. This level of dependence on imported oils exposes the economy to interrupted supply and fluctuations in liquid fuels prices which undermines economic growth. In addition, due to this heavy dependence on fossil fuels: coal and crude oil; South Africa is one of the highest carbon dioxide emitters in the world (Inglesi-Lotz & Blignaut, 2011).

South Africa must find a local alternative fuel source in order to reclaim stability and encourage social and economic development. This report proposes gasification of maize to produce liquid fuels as a renewable and environmentally friendly alternative.

South Africa has taken the initial steps in solving this energy problem by enhancing energy efficiency in production facilities and promoting renewable energy fuel sources, but overall there is a failure of any large scale efforts. The two greatest barriers to investments in renewable energy technology arise from a restricted South African energy innovation system and the high costs associated with renewable energy technologies. The restriction on the innovation system and lack of innovation results from dominance by state owned companies, Eskom and Sasol, which have their core strengths in fossil fuel technologies. In addition, developments in renewable energy is lacking in research due to cost and risk to investment planning. As a result, renewable energies contribute less than 1% of South Africa's total energy needs (Pagels, 2009).

Although local reserves are low, natural gas is currently being implemented as an alternative to fossil fuels for energy production. In 2004, Sasol opened an 865 km natural gas pipeline from Mozambique to the Mpumalanga synthetic fuels plant known as Secunda Coal to Liquids (Sasol, 2015). The gas is used by Sasol to substitute some of the coal used at its plants to make chemicals and diesel to supply industry in Gauteng. In addition, the state owned gas to liquids plant, PetroSA, located in Mossel Bay is also responsible for converting natural gas into a variety of liquid fuels for domestic and commercial use. Both the Sasol and Mossel Bay synthetic fuels plants have a combined capacity of over 200 thousand barrels/day (Eskom, 2014; Department of Energy, 2015), yet natural gas contributes only 3% of South Africa's total energy demands. Beside the above mentioned obstacles to alternate fuels, the use of natural gas as a primary fuel source for South Africa is limited by the difficulty and cost associated with importation and transportation of natural gas.

This report proposes that the gasification of maize to form synthesis gas (syngas) can be used as an alternative to the natural gas feed required by the synthetic fuels plants. Biomass makes up the fourth largest energy source after fossil fuels and is the only renewable source of carbon that can be converted to gas, liquid and solid products through biological and thermochemical processes (Brown, 2003). Based on this, biomass has been recognized as the possible solution to the world's energy demand (Ni *et al.*, 2006). Sources of biomass include the residue obtained from maize, sugarcane and other agricultural crops, as well as other carbonaceous waste such as municipal solids and animal manure.

As reported by the South African agricultural sector, maize is cultivated on 3.3 million hectares of the available 14.7 million hectares of arable land; making South Africa the second largest producer of maize in Africa. The world's maize production is approximately 500 million metric tons, of which 1.7 % is produced in South Africa (Mavukwana *et al.*, 2013). Due to the vast availability of maize, it is a good potential fuel source and can provide a sustainable and renewable source of energy which can improve the energy and economic state of South Africa.

The most widely applied biomass conversion process is still direct combustion, which involves the combustion of biomass in the presence of excess oxygen to produce steam for electricity or heat generation. This however, is a highly inefficient process as it requires excess air for complete oxidation, which facilitates the production of toxic emissions (Che *et al.*, 2012). An alternative and better conversion process is gasification as it offers a higher relative conversion efficiency. It also assists with remediation of the environment, as it converts waste materials into clean sources of energy.

The process of biomass gasification involves a series of complex chemical reactions involving a number of parameters which include flow, heat transfer and mass transfer. Thus it is very difficult to study the process of gasification by relying on experimentation only. Numerical simulation can be used as a supplementary tool to provide further insight on the process as well as accelerate the development and application of biomass gasification in a cost effective and efficient manner. Computational simulation is a method which can model natural phenomena and physical problems through numerical calculations and image display. In comparison with traditional experimentation methods, computational simulation has been widely applied in many aspects of mechanical and chemical processes, as it is efficient and cost effective. This increased efficiency of a numerical simulation arises, as the experimental results can be predicted by simulating the process of the reaction through appropriate software (Che *et al.*, 2012).

Since computational simulations for maize have been limited to the simulation of the gasifer (Mavukwana *et al.*, 2013), the objective of this study is to verify and evaluate the process of maize gasification and downstream processing through the numerical simulation program: Aspen Plus®. This will involve extensive modelling of the gasification of maize which will be validated through comparison with experimental data obtained from literature. Thereafter the quality of the synthesis gas produced will be assessed with respect to Fischer-Tropsch synthesis. Further modelling of downstream processing will then be done in order to evaluate the feasibility of maize biomass supplementing the feed of fossil fuels in the production of liquid fuels.

1.2 Research questions

The research questions of this study are:

- Can Aspen Plus® be used to simulate maize gasification?
- Is maize feasible for synthetic gas production?
- Is it economically viable to produce liquid fuels from maize gasification on a commercial scale?

1.3 Research objectives

The objectives of this study are to:

- Validate the Aspen Plus® simulation for maize gasification with experimental data obtained from literature in terms of product gas composition;
- Determine (based on the Aspen Plus® simulation) the optimum reactor conditions (equivalence ratio, steam to biomass ratio, temperature and pressure) and configuration which yields the highest quality syngas production in comparison to literature;
- Determine the feasibility of maize as a feed for syngas and liquid fuels production in South Africa and;
- Evaluate the viability of maize gasification to produce liquid fuels on a commercial scale from an economic and energy perspective.

1.4 Hypothesis

Based on the elemental and proximate analysis of maize, gasification of this agricultural crop to produce synthetic fuels will be a viable option; able to supplement the synthetic fuels industry in South Africa.

1.5 Structure

The first section of this report includes the executive summary, table of contents, lists of figures, tables, and nomenclature. The executive summary provides a broad overview, which summarizes the research problem, main results, conclusion, and how this dissertation advances knowledge in the field of chemical engineering.

<ins>Chapter 1</ins> briefly outlines the energy challenges South Africa is facing, which provides the context and background for this dissertation. It also provides a brief overview of the project, and how it can contribute to solving existing problems in society. This leads to the outline of the main research questions, and objectives that will be covered in this report.

<ins>Chapter 2</ins> is a survey of literature, which is relevant to maize gasification as a potential supplement to liquid fuels via syngas conversion. It examines the background and current energy state in South Africa in terms of liquid fuels, electricity, natural gas and renewable energies. It also describes the current environmental impact of these energy sources. This leads to the definition and background of syngas; a brief overview of the traditional Fischer-Tropsch process and the steps required for gas to liquids processing.

Chapter 3 presents a short summary of the available methods for modelling the gasification of maize and downstream processing for liquid fuels production. It also indicates the reasoning behind using Aspen Plus® for this application, and provides a detailed report of how the model was developed, optimized and used for simulation.

Chapter 4 is a validation of the developed Aspen Plus® model. It provides an evaluation of the data obtained from the developed simulation, against other studies involving simulations and experimental data of biomass gasification. This chapter indicates how the model was optimized by conducting sensitivity analyses on the following process variables: steam, air, temperature and pressure in order to maximize and, optimize syngas and liquid fuels quality and volume.

Chapter 5 is a critical evaluation was carried out which assessed maize as a feed for liquid fuels production based on the Aspen Plus® simulation in relation to conventional fossil fuels. The evaluation was done based on resource availability, conversion, quality, volumes and practicality. Further assessment of maize gasification and FT processing from an economic and energy perspective was then carried out to assess the specific viability of this process in South Africa.

Chapter 6 is a summation of this report based on the research questions indicated in chapter 1. The conclusions drawn in this chapter are based on the Aspen Plus® simulation of maize gasification and liquid fuels production developed and optimized in chapters 3 and 4. Chapter 5 provides the conclusion on the feasibility of maize biomass for liquid fuels production in South Africa in terms of cost, available resources, quality, volumes and energy. It also indicates a number of recommendations which require further investigation in order to further the knowledge in using gasification of maize for liquid fuels production in South Africa.

2 CHAPTER 2: LITERATURE REVIEW

2.1 South Africa's current energy state

2.1.1 Background

The South African fuel industry is fundamentally based on crude oil imports, coal mining and natural gas imports. Figure 2-1 indicates the country's energy consumption for 2012. South Africa's coal reserves were estimated at 28 billion tons, accounting for 95% of the total African coal reserves and almost 4% of total world reserves. (BP Statistical Review of Energy, 2012). Most of the oil consumed in the country is obtained from the Middle East and West African producers, and refined locally for use in the transportation sector. Oil refineries such as Enref, Chevref, Sapref and Natref are responsible for refining crude oil into liquid fuels and chemicals while Sasol and Mossgas convert natural gas to synthetic liquid fuels to assist with liquid fuels demands. Figure 2-1 indicates the major liquid fuels producers and their production capacities. Since crude oil processing is small (22%), the synthetic fuels industry accounts for almost all of the country's domestically produced petroleum and diesel **(**Department of Energy, 2015).

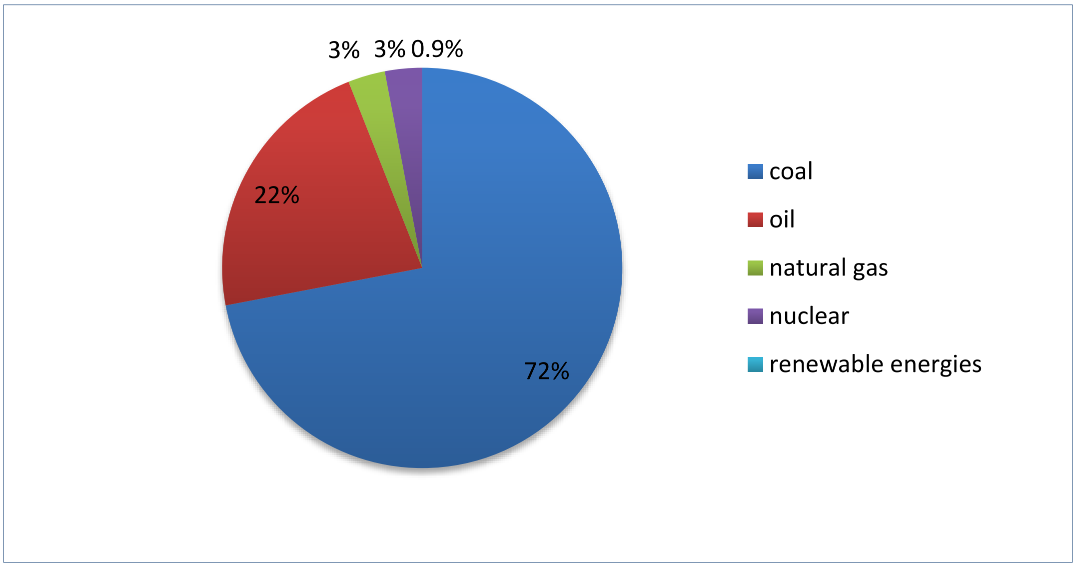


Figure 2-1: South Africa's energy consumption (2012) (Department of Energy, 2015)

Table 2-1: Liquid fuels facilities and production capacities (Department of Energy, 2015)

Facility	Raw material input	Production Capacity bbl/day	Location
Sapref	Crude oil	180 000	Durban
Enref	Crude oil	125 000	Durban
Natref	Crude oil	69 000	Sasolburg
Chevref	Crude oil	100 000	Cape Town
Synfuels	Coal and gas	150 000	Secunda
Petro SA	Gas	45 000	Mossel Bay

South Africa has rich coal deposits located in the north east in the Mpumalanga province. Approximately 80% of the total coal consumed domestically is used for electricity production. State owned power utility, Eskom, dominates the electricity sector in South Africa. It has 27 operational power plants which generate 95% of the country's electricity needs, as well as 40% of Africa's total electricity needs, making it one of the 10 largest power utilities in the world. Table 2-2 indicates Eksom's coal fired facilities and production capacities (Eskom, 2014).

Table 2-2: Eskom's coal fired power stations and production capacities (Eskom, 2014)

Power Station	Production Capacity (MW)	Location
Arnot	2 352	Middelburg
Camden	1 510	Ermelo
Duvha	3 600	Witbank
Grootvlei	1 200	Balfour
Hendrina	1 965	Hendrina
Kendal	4 116	Witbank
Komati	940	Middelburg
Kriel	3 000	Kriel
Lethabo	3 705	Sasolburg
Majuba	4 110	Volksrust
Matimba	3 990	Lephalale
Matla	3 600	Kriel
Tutuka	3 654	Standerton

2.1.2 Production and supply crisis

a Liquid fuels

Liquid fuels refer to transportation fuels such as petroleum and diesel, as well as oils and liquified petroleum gases (LPG) typically used for heating and electricity generation. In addition to the traditional refineries listed in Table 2-1, South Africa has PetroSA and Secunda coal to liquids plants, which specialize in synthetic fuels derived through the conversion of coal. These plants produce several liquid fuels of which more than 50% is unleaded petrol while the remainder consists of paraffin, diesel, propane, liquid oxygen and nitrogen, distillates, eco-fuels, process oils and alcohols which are fed to the domestic markets (U.S. Department of Energy, 2013).

Even with the Fischer-Trospch technology, South Africa’s current fuel refining capacity is unable to meet local demand for liquid fuels. As a result, the country has become increasingly dependent on liquid fuel imports to meet the national demand (Figure 2-2). From 2002 – 2013, there has been an 85% increase in petroleum imports, and a 60% reduction in exports of petroleum out of South Africa. Similarly for diesel, LPG and kerosene, from 2002 – 2013 there has been a significant increase in imports and a decrease in exports (Figure 2-3; Figure 2-4 and Figure 2-5).

According to Maqubela, head of petroleum and petroleum products branch of South Africa, several factors have contributed to increased imports which include: instability in crude oil exporters resulting in disruptions in crude oil supply, and existing refineries operating at approximately 80% of production capacity (The Citizen, 2015).

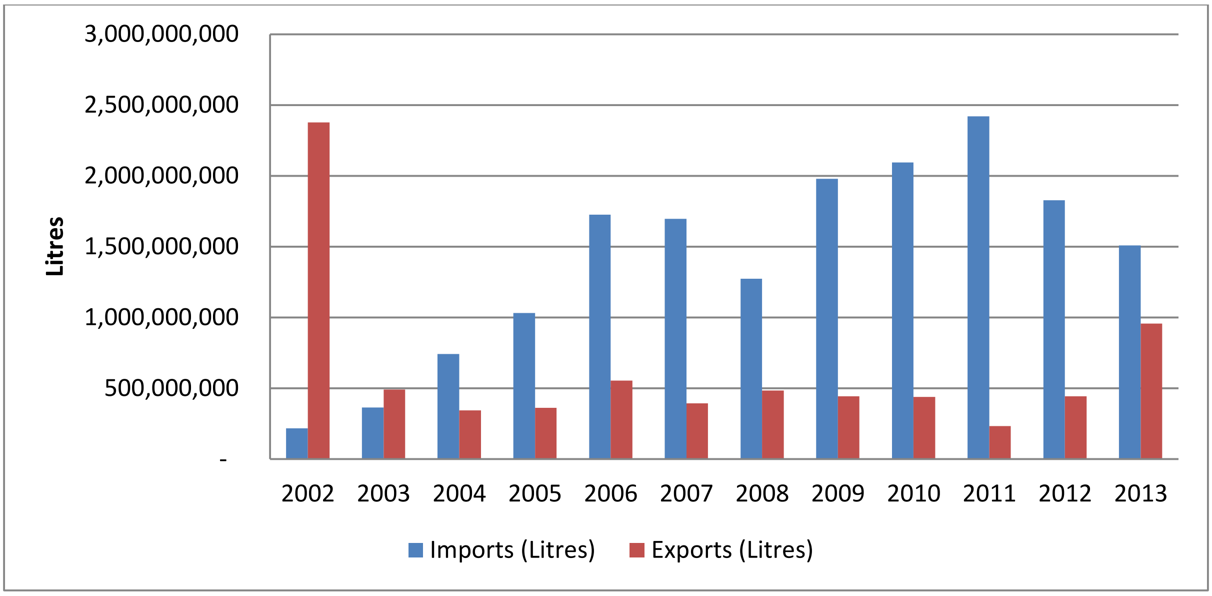


Figure 2-2: South Africa: South Africa's petroleum imports and exports (The Citizen, 2015)

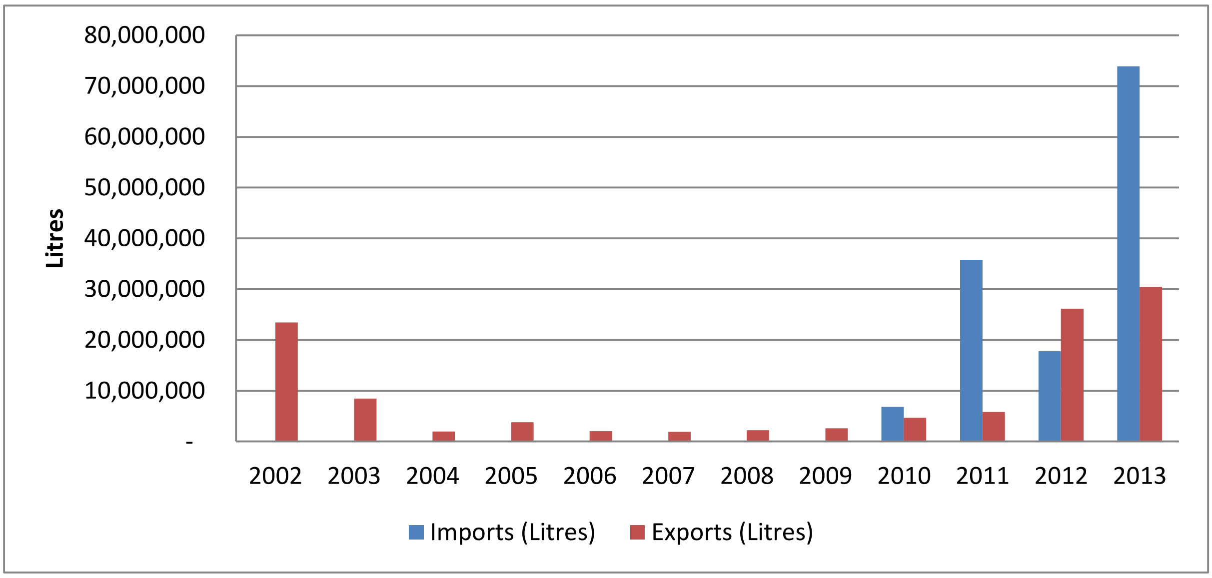


Figure 2-3: South Africa's LPG imports and exports (The Citizen, 2015)

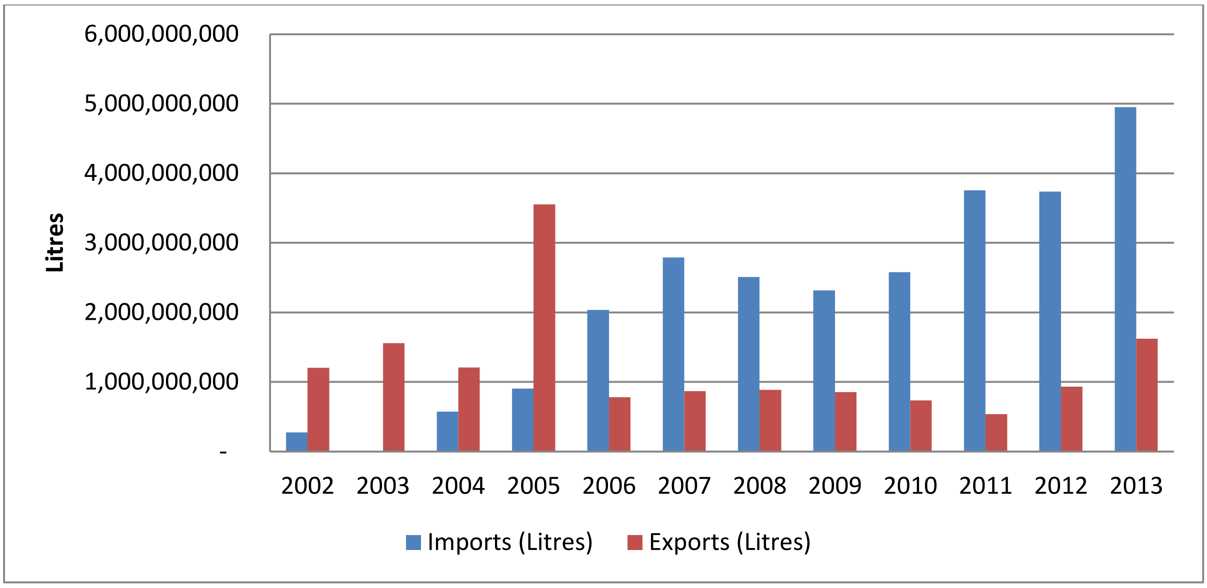


Figure 2-4: South Africa's diesel imports and exports (The Citizen, 2015)

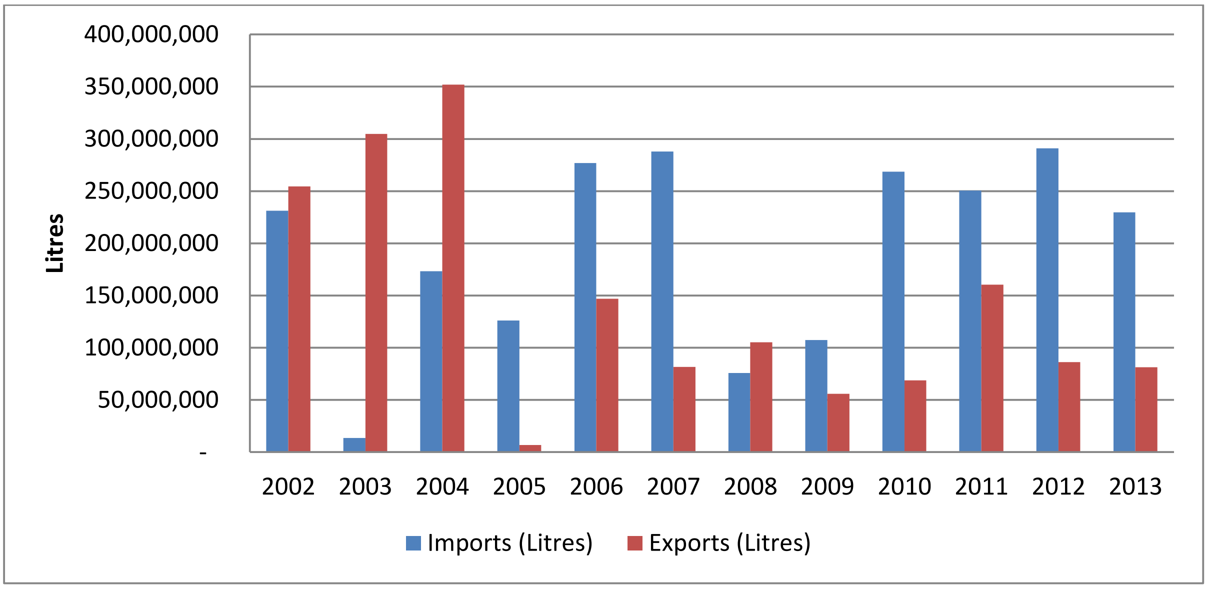


Figure 2-5: South Africa's kerosene and jet fuels import and exports (The Citizen, 2015)

b Electricity

Due to lack of investment, the government has been unable to maintain Eskom's production capacity in relation to economic and population growth. This has resulted in a large energy shortage and eventual energy crisis in late 2007. As a result Eskom, has been forced to implement load shedding to reduce pressure on the national grid. This has led to social speculation of a possible complete grid failure (Financial Media, 2015).

From 2004 – 2010 there has been an approximate increase of 10% in population growth, with only a 4% growth in energy production (Figure 2-6). From 2004 – 2010 there has only been a 6% growth in electricity production for domestic use and a 30% decrease in exportation of electricity to Africa (Figure 2-7). In response to this crisis, the state has developed a short, medium and long term plan which involves maintenance of existing power stations and enlarging capacity through the addition of 3 new power stations: Kusile, Madupi and Ingla; and in the long term pursue gas, petroleum, nuclear and hydropower as additional sources of energy (Zuma, 2013).

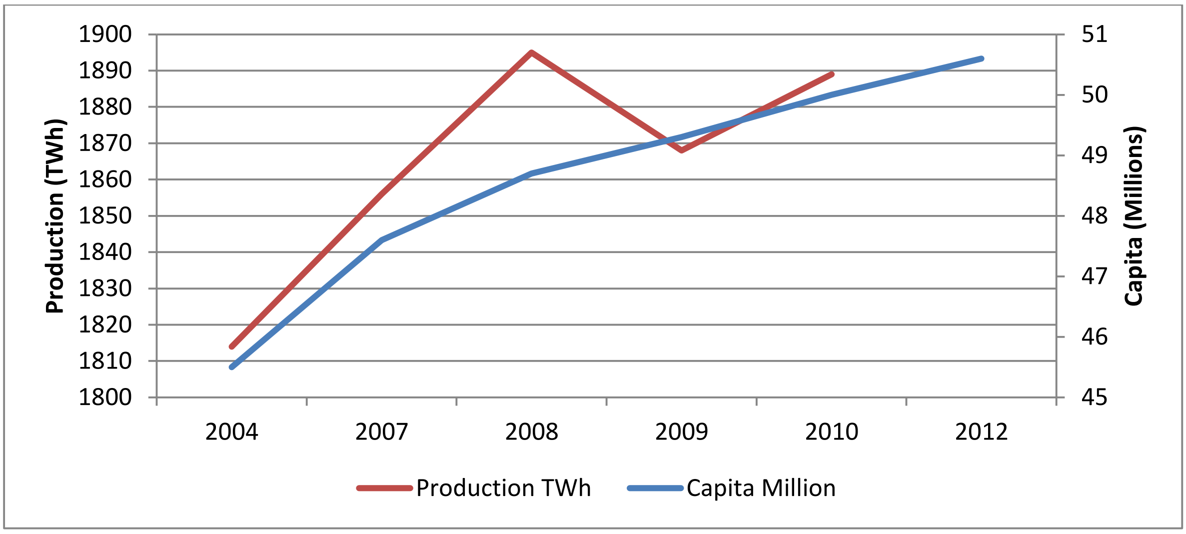


Figure 2-6: South Africa: population vs electricity production for 2004 – 2012 (Department of Energy, 2015)

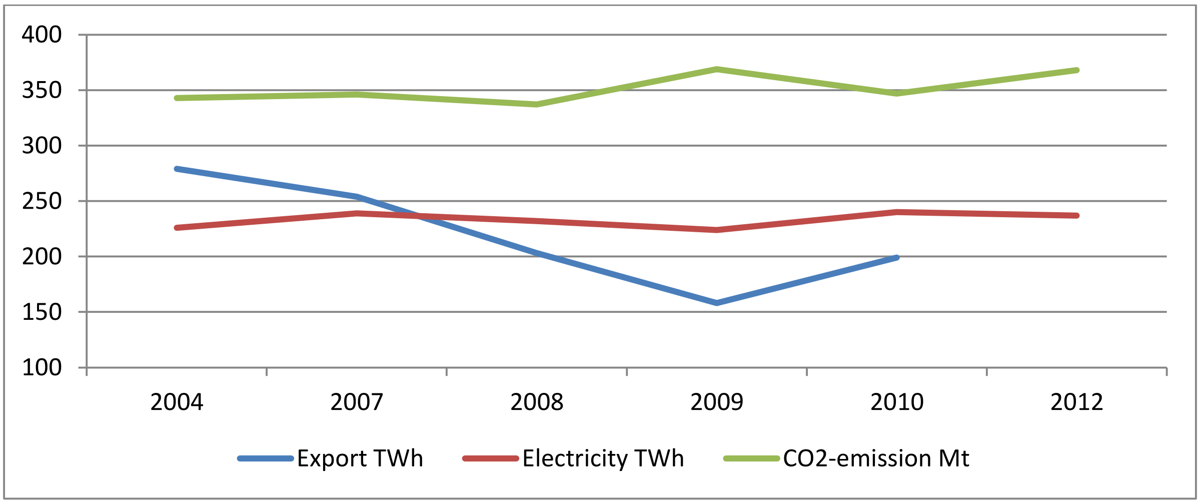


Figure 2-7: South Africa: electricity produced for domestic use vs electricity produced for exportation and CO_2 emissions (Department of Energy, 2015)

c Natural gas

Natural gas is one of the purest forms of available energy due to its ability to burn cleanly. It consists of mainly methane with small amounts of other hydrocarbons such as ethane, propane and butane. It is found within reservoirs beneath the surface of the earth with sulfur, carbon dioxide and nitrogen impurities, which are removed before use (Department of Minerals and Energy, 2005).

According to the South Africa energy analysis carried out by the U.S. Energy Information Administration, in 2012 South Africa consumed approximately 4.7 billion normal cubic metres of natural gas, of which 23% were produced locally and the balance imported from Mozambique via pipeline. This dependency on importation has been attributed to infrastructure constraints, which have limited the role of natural gas in South Africa’s electricity and energy sector. The government hopes that gas production from future projects known as the F-O field and Project Ikhwezi as well as regional imports from Mozambique, coupled with potential gas imports from Namibia in the future, will reduce the country’s reliance on coal in the electricity and industrial sector. Although these plants and processes exist, natural gas still only contributes 3% of South Africa’s total energy needs.

Sasol and Shell have proposed to build a second regional pipeline which will connect Namibia’s offshore Kudu natural gas field to both PetroSA’s Mossel Bay GTL plant, and PetroSA’s proposed oil refinery in Coega to feed a power station. However, plans to construct the pipeline have been halted due to lack of funds and investments (Department of Minerals and Energy, 2005).

d Renewable energy

The South African Department of Energy has started an initiative known as The White Paper target. The target of this initiative is to achieve 10 000 GWh obtained from renewable energy (Department of Minerals and Energy, 2007).

In addition, the Biofuels Industry Strategy (2007) was an initiative supported by government to generate bioethanol from agricultural residue. Ethanol is produced through the fermentation of sugars. Fuel ethanol is produced by removing excess water and concentrating the alcohol. It can be used alone as a fuel or is more typically blended up to a maximum of 10 -15% with other fuels such as petroleum (Department of Minerals and Energy, 2007).

Commercial production of fuel ethanol in the U.S.A, involves reducing the starch present in maize into simple sugars, and fermenting it through the use of yeast. There are two main industrial methods employed to produce fuel ethanol, which include wet milling and dry grind. Dry grind processing results in over 70% of the U.S fuel ethanol production at approximately 400 litres/ ton maize (Mosier & Ileleji, 2005). In 2005 approximately 35 million tons of maize were used to produce ethanol in America. This resulted in 15 million litres of fuel ethanol, which assisted in reducing dependence on foreign oil imports, positively impacted the environment, and improved the rural community and agricultural production (Mosier & Ileleji, 2005).

Despite successes in America, the Biofuels Industry Strategy has excluded maize as a crop used for biofuel production, as it is believed utilization of maize for this purpose will threaten food security. Sorghum has instead been selected as the crop for biofuel generation in South Africa (Department of Minerals and Energy, 2007). Despite these initiatives, renewable energy still only contributes less than 1% of South Africa's total energy needs.

2.1.3 South Africa liquid fuel production units: an environmental perspective

South Africa is a leading carbon dioxide emitter and must drastically reduce its greenhouse gas emissions by 34% by 2020, in order to comply with environmental legislation (Inglesi-Lotz & Blignaut, 2011). From 2002 to 2010, there has been an increase in total CO_2 emissions by 1% (refer to Figure 2-7). This is largely due to coal production and use, which results in coal combustion waste, coal mine wastes and toxic coal land fires. Coal combustion waste contains harmful substances such as arsenic, cadmium, chromium and lead. The coal mines are filled with sulfate salts, heavy metals, and carcinogenic substances like benzene and toluene. This adversely affects wildlife and the environment. An example of this is the Witbank region located near Mpumalanga. This area has an abundance of shallow seam coal deposits, and has been subjected to extensive surface and underground mining. Exploitation of this resource has resulted in a number of adverse impacts such as random land collapse, acid rain and acid seepage resulting in severe water pollution, and significant air pollution (Rapson, 2004).

Despite environmental groups continuing to target the coal industry for air, land and water pollution, the use of coal, especially by Eskom and Sasol, is expected to rise over the next few years (U.S. Department of Energy, 2013). Eskom plans to expand coal-fired electricity capacity to meet the growing energy demand. According to Eskom, plans have been approved to expand capacity at the coal-fired power stations Grootvlei and Komati by 30 and 90 Mega Watts (MW) respectively. In addition, the coal-fired power stations, Medupi and Kusile with capacities of 4764 MW and 4800 MW respectively, are expected to be brought online by 2018 (Eskom, 2014).

2.2 Syngas

Syngas is a synthetic gas produced through a reforming process involving the decomposition and stripping of hydrogen atoms from the hydrocarbon molecules existing in natural gas or carbonaceous solids such as coal or biomass. Oxygen is introduced in the form of a gasifying agent to substitute some of the hydrogen atoms producing a mixture of carbon monoxide and hydrogen. Syngas composition can vary significantly depending on feedstock and he gasification process involved. Typically syngas is 30 – 60% CO; 25 – 30% H_2; 0 – 5% CH_4; 5 – 15% CO_2 and some amount of water vapour. Impurities can also exist depending on the feedstock. These impurities may be sulfur compounds in the form of H_2S and COS, and some NH_3 (U.S. Department of Energy, 2017). Depending on the final uses of the syngas, the initial composition and impurities are significantly important – see Table 2-3.

Table 2-3: Desirable syngas characteristics for different applications (Ciferno & Marno, 2002)

Product	Synthetic fuels	Methanol	Hydrogen	Fuel Gas	
				Boiler	Turbine
H_2/CO ratio	Depending on catalyst type: Fe >0.6 Co around 2.0	Approximately 2.0	High	Not important	Not important
CO_2	Low	Low	Can use water-gas-shift reaction to adjust	High	High
Hydrocarbons	Low	Low	Low	High	High
N_2	Low	Low	Low	N_2 lowers heating value but level is unimportant as long as boiler and turbine efficiencies are satisfactory.	
Contaminants	<1 ppm S; low particulates	<1 ppm S; low particulates	<1 ppm S; low particulates	Small amounts of contaminants can be tolerated	
Heat value	Unimportant as long as H_2/CO ratio is achieved	Unimportant as long as H_2/CO ratio is achieved	Unimportant as long as H_2/CO ratio is achieved	High	

All current processes commercially available for syngas conversion are based on the Fischer-Tropsch catalytic conversion process. The product obtained from this process is dependent on the catalyst used, reactor type and operating conditions (Farias *et al.*, 2007). The reaction occurs through the growth of chains of hydrocarbons which is largely determined by reaction time (Farias *et al*., 2007).

The raw material for the Fischer-Tropsch (FT) synthesis conventionally involves coal, refinery residual or natural gas together with a hydrogen source in the form of the feed stock itself or the addition of water (Puskas & Hurlbert, 2003). The conversion of natural gas through the use of the FT process results in an extremely pure synthetic crude oil virtually free of contaminants such as sulfur, aromatics and heavy metals (Puskas & Hurlbert, 2003). This synthetic crude can then be further refined into products such as diesel fuel, naphtha, wax, and other liquid petroleum or specialty products.

Since transportation of natural gas poses such a problem, the areas interested in gas to liquids (GTL) projects are typically those in which natural gas reserves are high, and where gas constitutes a critical resource for economic development (U.S. Department of Energy, 2013). These areas include the Far East, The Persian Gulf, Africa, and South and North America. GTL projects are also implemented in existing industrial sites or in synergy with Liquid Natural Gas (LNG) plants such as Shell in Egypt. This helps to eliminate some of the costs associated with transport and capital (U.S. Department of Energy, 2013).

New technology is being developed and applied in order to obtain better efficiencies in the conversion process. The key factors which influence the competitiveness of GTL processing are the cost of feed stocks, capital, operating costs, and scale of the plant. In comparison to conventional oil production, GTL processing is not competitive due to the high cost and difficulty in transportation of natural gas (Inglesi-Lotz & Blignaut, 2011).

2.2.1 Fischer-Tropsch process

The Fischer-Tropsch process is the catalytic hydrogenation of carbon monoxide which results in a wide range of alkenes, alkanes, aldehydes, alcohols, ketones and acids (Tavakoli *et al.*, 2008). The reaction which takes place during catalytic Fischer-Tropsch synthesis is shown by equation 2-1. Carbon monoxide reacts with hydrogen to form mainly short straight chain carbons with small amounts of branched and unsaturated hydrocarbon chains. The Fischer-Tropsch process typically occurs at temperatures of 200-350°C and pressures of 25-60 bar (Yang *et al.*, 2017). This reaction is exothermic, and 20% of the chemical energy is released as heat (Mattei, 2004). Studies carried out by Farias *et al.* (2007) investigated the effects of different operating conditions on product distribution. The results indicated that low temperature and pressure of 240°C and 27 atm respectively favoured the production of middle distillates and heavy waxes which can be cracked via hydrocracking into liquid fuels, whereas direct conversion to liquid fuels was favoured by a comparatively high temperature of 270°C and pressure of 30 atm. Both cobalt and iron catalysts are suitable for this is application, but at the lower end of the temperature range cobalt is preferred (Selvatico *et al.,* 2016).

$$CO + 2H_2 \rightarrow -(CH_2)- + H_2O \qquad [2\text{-}1]$$

This process is widely applied for syngas conversion as the hydrocarbon products obtained from this process are very clean due to low sulfur and aromatics content. In Thailand and Greece, Shell uses the products from GTL processes as a blending component for fossil fuel diesel to reduce soot and SO_2 emissions (Department of Energy, 2015).

In some applications the H_2/CO ratio must be adjusted to meet the downstream process requirements for FT synthesis. This is achieved through passing the syngas through a multi-stage, fixed-bed reactor containing shift catalysts to convert CO and water into additional H_2 and carbon dioxide according to the following reaction (U.S. Department of Energy, 2017):

$$CO + H_2O \rightarrow H_2 + CO_2 \qquad [2\text{-}2]$$

The water-gas-shift reaction can operate with a variety of catalysts within the range of 200 - 480°C. The reaction does not change molar totals and therefore, the effect of pressure is minimal. The equilibrium for hydrogen is favoured by high moisture content and low temperature for the exothermic nature of the reaction (Ciferno & Marno, 2002). A significant difference between iron and cobalt based FT synthesis, is the ability of the iron catalyst to catalyse the WGS reaction. While cobalt catalysts show virtually no WGS activity. This implies that a cobalt catalyst is more sensitive to the H_2/CO ratio than iron, as the latter has the ability to can change the balance by shifting H_2 or CO (Dry, 1981).

2.2.2 Gas to Liquids (GTL) process

All GTL processes follow a series of similar process steps which are summarized by Figure 2-8. Natural gas undergoes three major stages to produce a primary liquid product. These stages include feed pre-treatment, syngas production and syngas conversion. The production and conversion steps require catalysts in order to start and maintain the relevant chemical reactions.

In addition, depending on the specifics of the process; there may be a need for the addition of steam, air or oxygen, and further treatment and upgrading of the primary raw product.

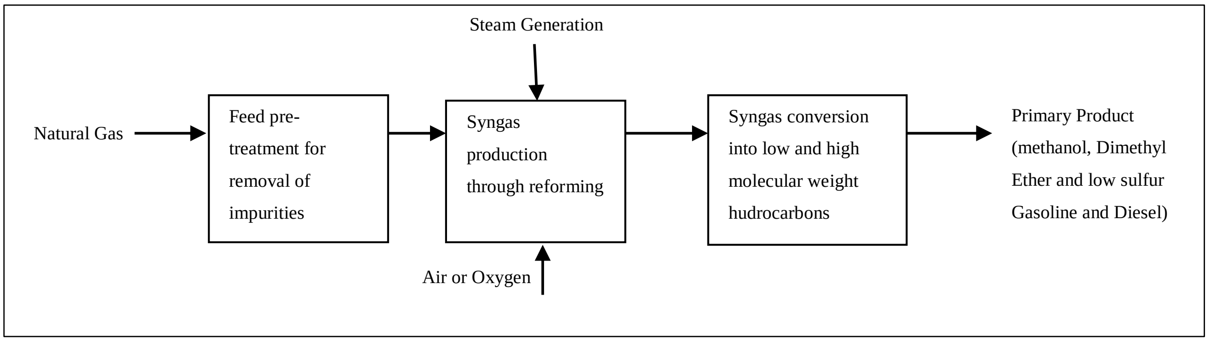


Figure 2-8: Illustration of major process steps which occur during GTL processes (Mattei, 2004)

a Feed pre-treatment

Natural gas is a complex mixture consisting of mainly gaseous hydrocarbons with the presence of nitrogen, carbon dioxide, hydrogen sulphide, helium and water vapour. The feed for syngas conversion requires further cleaning before it can be converted into syngas. Sulfur containing compounds need to be removed as these can poison the catalysts used during the conversion stage (Mattei, 2004).

There are two different types of pre-treatment available depending on the volume of gas to be treated. For smaller volumes of gas, either liquid or solid scavengers can be used. Liquid scavengers can be injected into the gas, or the gas can be passed through a vessel containing either a liquid or solid scavenger. The used scavengers are then collected and removed. Capital costs for this method of treatment are low, but the operating costs of this process are high as the scavengers are difficult to recycle and must be supplied continuously. For larger volumes of gas, amine washers are used. The gas is fed through a column fitted with trays and overflow weirs. The liquid amine flows downwards through the column, while gas bubbles through the liquid on the trays ensuring good contact and the dissolving of sulfur compounds. Once the amine solution reaches the bottom of the column, it can be removed and sent to a recovery system where the impurities can be removed (Mattei, 2004). This process requires a significant capital investment initially, due to the column and amine regeneration system, but has low operating costs as the amine solution can be recycled.

b Syngas production

There are three basic types of catalytic and non-catalytic reformers which consist of steam-methane reformer, an autothermal reformer and a partial oxidation reactor (Mattei, 2004).

- Steam-Methane reformer

In steam-methane reforming, natural gas and steam are passed over a nickel catalyst. Heat of the reaction is supplied by burning some of the feed stock (de Jong *et al.*, 2009). This method is the most widely applied technology for syngas production in the manufacture of methanol and other chemicals in the bulk chemicals industry. This process does not require a separate air or oxygen supply although steam must be supplied. However the composition of the produced syngas is not ideal for liquid fuels production (Mattei, 2004). Steam methane reforming occurs through endothermic reactions shown by equations 2-3 and 2-4.

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad [2\text{-}3]$$

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \qquad [2\text{-}4]$$

Due to the presence of CO_2 in the second reaction, it causes a secondary reforming reaction to occur as shown by equation 2-5.

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad [2\text{-}5]$$

- Autothermal reformer

In an autothermal reformer the gas is burned with oxygen and steam and then passed through a bed of nickel located in the same vessel. The combustion reaction is very fast and produces very high temperatures (Rice & Mann, 2007). It produces syngas suitable for most conversion processes; however the need for oxygen implies that an air separation plant is needed. Air blown reactors have also been developed for syngas production, however this reactor results in a significant nitrogen content in the syngas, which requires further processing before conversion can take place (Mattei, 2004).

- Partial oxidation reactor

The partial oxidation process involves a direct reaction between oxygen and hydrocarbon gas. There is no need for steam or a catalyst. This process operates at very high temperatures with the addition of oxygen making it very efficient (Laquaniello *et al.*, 2012).

The partial oxidation reaction occurs according to Reaction 2-6. Part of the carbon monoxide and hydrogen produced undergo combustion reactions illustrated by equations 2-7 to 2-8.

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2 \qquad [2\text{-}6]$$

$$CO + \frac{1}{2}O_2 \rightarrow CO_2 \qquad [2\text{-}7]$$

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \qquad [2\text{-}8]$$

Partial oxidation reactions are more compact than the steam reformers and have higher reactor efficiencies of 70-80%. The overall process efficiency of partial oxidation is, however worse due to the higher levels of temperature and heat loss.

c Syngas conversion

Typical catalysts used include iron, nickel and cobalt. Iron catalysts result in the production of low molecular weight hydrocarbons while cobalt produces higher molecular weight products, which require less upgrading (Mattei, 2004). Cobalt is however, very expensive and requires an inert material such as silica or alumina as a support. The most commonly used catalysts during the FT process are iron and cobalt. Cobalt catalysts have a higher conversion rate and life span of over 5 years, but are much more expensive than iron catalysts. In addition cobalt catalysts are comparatively more reactive than iron and result in greater hydrogenation producing less unsaturated hydrocarbon chains and alcohols. Iron catalysts however, have a greater tolerance for sulfur, are cheaper and produce more olefins and alcohols. The life span of an iron catalyst is very short and when used in commercial processes is limited to 8 weeks (Mattei, 2004).

2.2.3 Coal to Liquids (CTL) processing

Through the processing of direct or indirect liquefaction, coal can be converted to liquid products. In order to complete the transformation of the carbon rich solid, coal, there needs to be an external hydrogen feed introduced to the process. Coal, particularly anthracite, have extremely low hydrogen to carbon ratios. A minimum H/C ratio of 2:1 is required in order to convert coal to liquid fuels. Methane, a primary constituent in natural gas, has a ratio of 4:1 (National Petroleum Council, 2007). Figure 2-9 indicates the hydrogen to carbon ratios for coal feed relative to carbonaceous fuels. Coal to liquids processing is different to GTL processing as in order to make liquid fuels from coal it is necessary to add hydrogen or reject carbon, while the converse is true for natural gas processing.

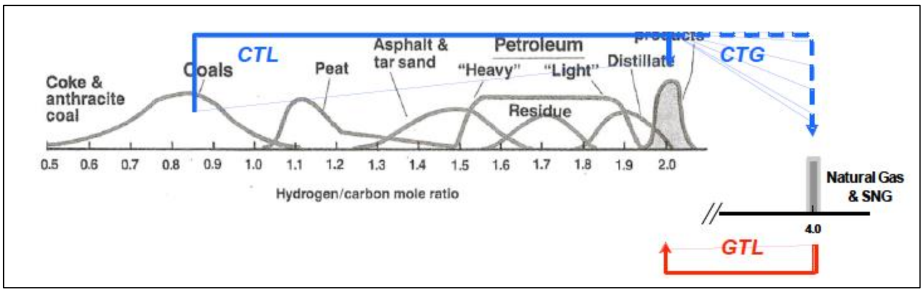
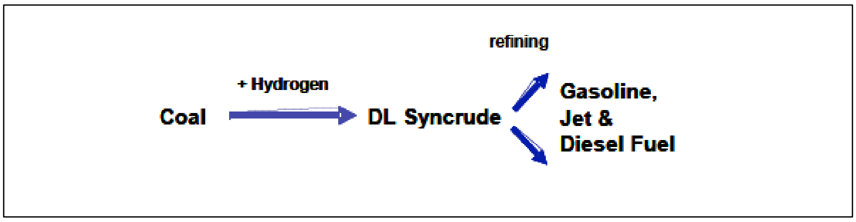


Figure 2-9: Hydrogen content of coal in comparison to other carbonaceous fuels (National Petroleum Council, 2007)

Direct liquefaction is shown by Figure 2-10. It is made of two stages which follow a similar route to hydrocracking processes used in oil refining. The first stage involves thermal decomposition of the coal in a high pressure hydrogen atmosphere; required to stabilize the coal fragments to prevent re-polymerization into a solid carbo mass. The crude liquids formed can then be further upgraded to produce commercial liquid fuels. The second reactor stage also requires a hydrogen feed which can be produced either through the water-gas shift reaction shown by equation 2-22 or through coal gasification (National Petroleum Council, 2007).



igure 2-10: Process of direct coal liquefaction (National Petroleum Council, 2007)

Indirect coal liquefaction is a multistep process involving the gasification of coal, which converts the carbonaceous material from solid to gas through partial oxidation. Gasifying agents in the form of high purity oxygen and steam are required in order to complete the conversion of coal to syngas. The produced syngas contains H_2, CO, H_2O, CO_2, and other compounds containing impurities found in the coal source. The H_2 and CO formed from gasification are the building blocks which can be used to synthesize a wide variety of hydrocarbons. Undesirable impurities such as sulfur, nitrogen and fly ash need to be removed from the syngas before further processing can take place.

2.2.4 Product distribution

There are a large variety of potential products which can be derived from syngas. These products can either be added to or replace existing commercial petroleum and chemical markets. Major products derived from syngas are indicated in

Figure 2-11.

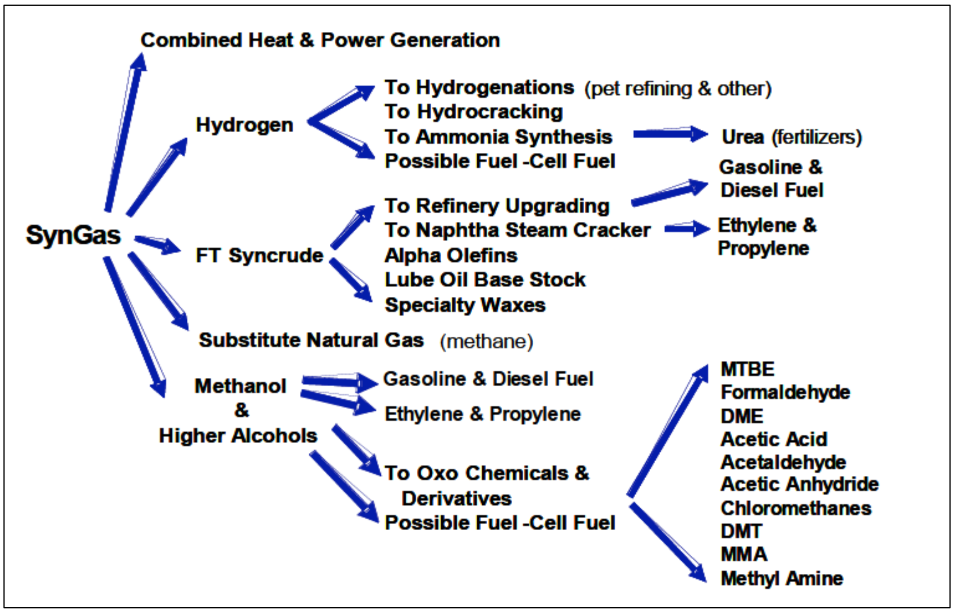


Figure 2-11: Potential products that can be produced based on further processing of Syngas (National Petroleum Council, 2007)

The polymerization which takes place during the Fischer-Tropsch process results in a range of products which consists of light hydrocarbons, liquefied petroleum gas, naphtha, diesel and wax. The product distribution can be theoretically described by the Anderson-Schulz-Flory equation which is illustrated by equation 2-9 (Puskas & Hurlbert, 2003).

$$\log\left(\frac{W_n}{n}\right) = nlog\alpha + log\frac{(1-\alpha)^2}{\alpha} \qquad [2\text{-}9]$$

Where W_n is the weight fraction of a product consisting of n carbons and α the chain growth probability factor. As α increases so does the molecular weight of the products. The chain growth probability factor is dependent on the catalyst; reactivity and process conditions used in the Fischer-Tropsch process. Thus based on the desired product, the production process, catalysts and process operation conditions can be altered toward the production of either low or high molecular weight hydrocarbon chains. Studies carried out by Puskas and Hurlbut (2003) involving a cobalt catalyst in a fixed bed reactor at 103-241 kPa generated growth factors of 0.66-0.82 which correlated to C6-C10 molecules.

Since the Anderson-Schulz-Flory equation is an ideal relationship, there are often deviations with regards to the lower hydrocarbon yields. The equation typically under predicts the yield of compounds containing a single carbon and over predicts the yields of compounds consisting of two carbons. In order to account for this deviation from the ideal distribution equation, the corrected yields for C1-C4 hydrocarbons can be determined through the use of equations 2-10 and 2-11 (Tavakoli *et al.*, 2008). Equation 2-10 is used for estimating the corrected yield of methane, while equation 2-11 is used to estimate the corrected product distribution of molecules containing 2, 3 and 4 carbons.

$$W_1 = \frac{1}{2} \times (1 - \textstyle\sum_5^\infty W_i) \qquad [2\text{-}10]$$

$$W_2 = \frac{1}{6} \times (1 - \textstyle\sum_5^\infty W_i) \qquad [2\text{-}11]$$

2.2.5 Syngas from biomass

Biomass is one of the most abundant renewable energy sources. It is formed through fixing carbon dioxide from the atmosphere during the process of photosynthesis. Currently biomass contributes 12% of the world's energy supply, while in some developing countries it is responsible for up to 50% of the energy supply. This indicates the potential possibility of biomass as a fuel source. A variety of biomass types exist, which can be converted into energy. These general categories include energy crops, agricultural residues and waste, forestry residues and waste, and industrial and municipal wastes (Lin *et al.,* 2001).

a Biomass conversion processes

The possible methods available for the conversion of biomass into energy can be separated into two categories known as biological and thermochemical processes. The five biological processes available are direct biophotolysis, indirect biophotolysis, biological water-gas shift reaction, photo-fermentation and dark-fermentation. The phenomenon of biological syngas and hydrogen fuels production was observed one century ago, and when the oil crisis happened in 1970s, the technology started receiving attention especially in hydrogen production by photosynthesis (Ni *et al.,* 2006). However, these works only exist on a laboratory scale and the large scale applications of these processes still need to be demonstrated. Thus for the purpose of this report syngas production obtained from biological processes will not be considered.

The thermochemical processes available for energy conversion include combustion, pyrolysis, liquefaction and gasification. Combustion is the direct burning of biomass in the presence of air to produce energy. Typically combustion of biomass is used to provide heat, electricity generation and fuels for stoves, furnaces, boilers or steam turbines. However the energy efficiency of combustion is low (10-30%) and it results in many toxic by-products which are released into the air as pollutants. Due to this, combustion is not a sustainable means for energy production. In the process of biomass liquefaction, biomass is heated in the absence of air to a temperature of 252-357ºC in water, under a pressure of 5-20 MPa, with the addition of a catalyst or solvent. The disadvantages associated with liquefaction are the difficulty in achieving the operating conditions, as well as low syngas and hydrogen yield (Ni *et al.*, 2006). Thus the remaining two thermochemical processes, gasification and pyrolysis, are feasible means of producing syngas and have been receiving much attention in recent years.

b Pyrolysis

Pyrolysis involves the heating of biomass to a temperature in the range of 400-800ºC to produce a carbon rich liquid phase and a volatile phase of gases and condensable organic vapours (DalmasNeto *et al.*, 2014). This process primarily results in liquid oils, and solid ash with some gaseous compounds. Pyrolysis can be further classified into slow and fast pyrolysis; however as slow pyrolysis results in large amounts of ash, it is not considered for syngas production. Fast pyrolysis is a high temperature process which involves the rapid heating of the feedstock to form vapour. This vapour can then be condensed to a dark brown bio-liquid which is suitable as a fuel source. The products of fast pyrolysis exist in gas, liquid and solid phases. The gaseous products depend on the organic nature of the biomass used, but it typically consists of H_2, CH_4, CO and CO_2. The liquid products include tar and oils while the solid products consist of mostly char and inert materials. Studies carried out by DalmasNeto *et al.* (2014) involved the fast pyrolysis of algae which resulted in the production of 17.4% (m/m) of bio oil with a LHV of 8.071 kcal/kg.

Most pyrolysis processes are designed primarily for bio fuel production, and further conversion processes need to be applied in order to maximize hydrogen production and increase the quality of the syngas produced. Alternatively fast pyrolysis can be employed using high temperatures and sufficient volatile phase residence time which increases the production of syngas components. Studies carried out by Moghadam *et al.* (2014) involving the pyrolysis of coconut shell at 500ºC resulted in a 485.9 g/kg syngas yield with a LHV of 12.54 MJ/Nm^3. The use of high temperatures for greater residence times or additional conversion processes implies greater complexity and cost (Ni *et al*, 2006).

c Gasification

Gasification involves the gasifying of biomass at temperatures above 700ºC in the presence of gasifying agents. This causes the biomass particles to undergo partial oxidation resulting in the production of gas and ash. The gaseous products consist of mostly H_2, CO, CO_2 and CH_4, while the ash can be further reduced into additional amounts of these components. The gasification of biomass occurs according to equation 2-12 and is applicable to biomass containing less than 35% moisture (Ni *et al,* 2006).

$$Biomass + Heat + O_2 \rightarrow H_2 + CO + CO_2 + CH_4 + light\ and\ heavy\ hydrocarbons + ash \qquad [2\text{-}12]$$

The process of gasification is aimed at the production of gaseous products while pyrolysis is aimed at bio oils and ash production. Based on this the thermochemical process of gasification was selected as the energy conversion means for biomass. However, one of the major disadvantages associated with gasification is the formation of tar which occurs during the process. Unwanted tar formation can result in the formation of tar aerosols and polymerisation to more complex molecules which is not conducive for syngas production. Currently there are three ways of minimizing tar formation which consists of proper design of the gasifier, optimum control and operation, and the addition of catalysts (Ni *et al.*, 2006).

The operation parameters such as temperature, gasifying agent and residence time, play an important role in both syngas formation, and in the formation and decomposition of tar. Studies have indicated that tar can be thermally cracked at temperatures exceeding 1000ºC. Also the use of certain additives such as dolomite, olivine and char, inside the gasifier can assist with the reduction in tar. These catalysts not only reduce the tar content, but can also improve the gas quality and conversion efficiency.

An additional problem of gasification is the formation of ash, which can cause deposition, sintering, slagging, fouling as well as agglomeration. In order to avoid these problems, fractionation and leaching have been employed to reduce ash formation inside the reactor. Fractionation has been proven to be quite successful in ash removal, however it can cause deterioration in quality of the remaining ash. While leaching can remove the inorganic fraction of biomass as well as improve the quality of the remaining ash. Studies carried out by Garcia-Ibanez *et al*. (2004) indicated that leaching as a pre-treatment technique for the gasification of olive oil was found to be successful and effective for gas production.

The products of gasification are mainly gases which makes it more favourable for syngas production than pyrolysis. Since the quality of syngas is directly related to the hydrogen content, the process of gasification can be optimised for the production of hydrogen. Several researchers have carried out studies on various biomass types, reactors and operating conditions in order to achieve high hydrogen production as indicated by Table 2-4. As shown by Table 2-4, using a fluidised bed gasifier in conjunction with suitable catalysts can result in 60% vol hydrogen. Such high conversion efficiencies make biomass gasification an attractive syngas production alternative. Studies carried out by Ni *et al.* (2006) also indicated that the costs of syngas production by biomass gasification are competitive with the syngas production obtained from natural gas reforming. In addition, taking account of account the environmental benefits, syngas production from biomass gasification should be a promising option based on both economic and environmental considerations.

Table 2-4: Investigations on biomass gasification for hydrogen production (Ni *et al*., 2006)

Reference	Yongie (1996)	Chaungzhi *et al*. (1997)	Xia & Dunsong (2000)	Turner *et al*. (1998)	Rapagna *et al*. (1998)	Jian-chun *et al*. (2001)	Zhiwei *et al.* (2002)	Courson *et al*. (2002)	Midilli *et al*. (2002)	Rapagna *et al*. (2002)	Brown (2003)	Brown *et al*. (2003)
Feedstock	Sawdust	Sawdust	Wood	Unknown	Sawdust	Pine Sawdust	Bagasse	Cotton stem	*Eucalyptus gobulus*	*Pinus Radiata*	Sewage sludge	Almond shell
Reactor	Unknown	Circulating fluidised bed	Fixed bed	Fluidised bed	Fluidised bed	Fluidised bed	700-800	700-800	700-800	700-800	Unknown	800
Catalyst	Na_2CO_3	None	None	Ni	K_2CO_3	Unknown	29-38	27-38	35-37	27-35	10-11	62.8
Temperature (ºC)	700 - 800	810	550	830	964	700-800	700-800	700-800	700-800	700-800	Unknown	800
H_2 Production (vol%)	48.31 55.40	10.50	7.70	62.10	11.27	26-42	29-38	27-38	35-37	27-35	10-11	62.8

As shown by Table 2-4, studies carried out by Yongie (1996), Zhiwei *et al.* (2002), Midilli *et al.* (2002) and Rapagna *et al.* (2002) make use of sawdust, bagasse and plants as feed stocks for gasification, which resulted in the highest hydrogen productions, ranging from 20-55 vol%. This indicates that woody or plant material biomasses tend to be better sources of carbon for hydrogen production, whereas wastes such as sewage sludge used in studies carried out by Brown (2003), only resulted in 10-11 vol% of hydrogen. In addition, the effects of reactor type and catalyst can be seen in studies carried out by Yongie (1996), Chuangzhi *et al*. (1997), Rapagna *et al.* (1998) and Jian-chun *et al.* (2001), which all made use of a sawdust feed and various catalysts. Yongie (1996) made use of a sodium carbonate catalyst, which resulted in the highest vol% of hydrogen in comparison to other studies at the respective temperatures. Jian-chun *et al.* (2001) made use of a fluidised bed reactor which resulted in the next highest production of hydrogen in comparison to the other sawdust studies. The effects of catalyst on reaction temperature and production, are also illustrated in studies carried out by Yongie (1997) and Chuangzhi *et al.* (1997). Chuangzhi *et al.* (1997) made use of a sawdust feed which resulted in a 7.7 vol% of hydrogen at a temperature of 810°C whereas Yongie's (1997) study resulted in the production of 55.4 vol% of hydrogen at a lower temperature and in the presence of a catalyst.

d Mechanism of biomass gasification

Gasification is the conversion of solid fuel feed stocks to combustible gases through the addition of a gasifying agent. Typical feed stocks are coal, wood, manure and agricultural wastes, as these sources of biomass consist of carbon, hydrogen and oxygen. Typically the gasifying agents are air, oxygen, steam and carbon dioxide. The product gas obtained from air gasification typically has a low heating value of 4-7 MJ/Nm^3, while pure oxygen gasification produces a higher quality gas of 10-18 MJ/Nm^3. However, the disadvantage associated with oxygen is that it has a high production cost (Che *et al.*, 2012). The process of biomass gasification can be divided into four stages: drying, pyrolysis, oxidation and reduction, as outlined below.

- Drying:

DDuring the drying stage the available free moisture is converted into gas phase; producing a dry biomass material. The drying process typically occurs within the temperature range of 50 - 150°C.

- Pyrolysis:

As the temperature begins to exceed 160ºC, the biomass starts to undergo the process of pyrolysis. Pyrolysis causes the separation of volatile matter from the dried biomass resulting in carbon, hydrogen, carbon monoxide, carbon dioxide, methane, tar and other hydrocarbons. Equation 2-13 represents the general chemical reaction for pyrolysis.

$$CH_xO_y \rightarrow \ n_1C + \ n_2H_2 + n_3H_2O + n_4CO + n_5CO_2 + \ n_6CH_4 \qquad [2\text{-}13]$$

In Requation 2-13 the chemical formula CH_xO_y is the characteristic general molecular formula for biomass. $n_1 - \ n_6$ are equilibrium constants determined by the specific circumstances of gasification.

- Oxidation:

Oxidation of the biomass begins to occur at temperatures of 1000 – 1200ºC. The chief chemical reactions which take place during oxidation occur according to equations 2-14 – 2-18 (Mavukwana *et al.,* 2013). The reaction heat produced as a result of oxidation can provide potential heat for biomass drying, pyrolysis and reduction. Typically gasification processes which involve the use of air or oxygen are self-supplying of heat. This heat is mainly consumed in the drying, pyrolysis and reduction stages. As shown by the reactions, if all the carbon material could be completely converted, the major products would be CO, CO_2, H_2, CH_4 and H_2O. In the case where air is the gasifying agent, then N_2 would also be a significant product.

$$C + \ O_2 \quad \rightarrow \quad CO_2 \qquad \Delta H = -393.51\ kJ \qquad [2\text{-}14]$$

$$2C + O_2 \quad \rightarrow \quad 2CO \qquad \Delta H = -221.34\ kJ \qquad [2\text{-}15]$$

$$2CO + \ O_2 \rightarrow \quad 2CO_2 \qquad \Delta H = -565.94 \ \ kJ \qquad [2\text{-}16]$$

$$2H_2 + \ O_2 \ \rightarrow \quad 2H_2O \qquad \Delta H = -483.68\ kJ \qquad [2\text{-}17]$$

$$CH_4 + \ 2O_2 \rightarrow \quad CO_2 + 2H_2O \qquad \Delta H = -890.36\ kJ \qquad [2\text{-}18]$$

- Reduction:

The reactions which take place during the reduction process occur according to equations 2-19 – 2-23 (Mavukwana *et al.,* 2013). The reactions which occur during reduction are endothermic which causes the temperature to decrease from approximately 900 to 600ºC.

$$C + \ CO_2 \quad \rightarrow \quad 2CO \qquad \Delta H = +172.43\ kJ \qquad [2\text{-}19]$$

$H_2O + C \rightarrow CO + 2H_2 \qquad \Delta H = +90.17\ kJ$ [2-20]

$H_2O + C \rightarrow CO + H_2 \qquad \Delta H = +131.72\ kJ$ [2-21]

$H_2O + CO \rightarrow CO_2 + H_2 \qquad \Delta H = +41.13\ kJ$ [2-22]

$3H_2 + CO \rightarrow CH_4 + H_2O \qquad \Delta H = +250.16\ kJ$ [2-23]

During the simulation of biomass gasification these stages are usually strictly divided without any attention to the effects of each stage on the next. This can contribute to the discrepancies observed between simulations and experimental data. This is especially true for gasifiers such as fluidised and spouted bed, where these stages cannot be separated due to good mixing, but must rather be regarded as occurring simultaneously throughout the reactor (Jarungthammachote & Dutta, 2008).

e Equivalence Ratio

Equivalence ratio is the actual oxidant/fuel mole ratio normalized by the stoichiometric oxidant/fuel mole ratio. It can be defined according to equation 2-24.

$$\Phi = \frac{\left(\frac{Oxidant}{Fuel}\right)actual}{\left(\frac{Oxidant}{fuel}\right)stoichiometric}$$ [2-24]

The fuel mixture is considered to be lean with an excess of oxidant when $\Phi > 1.0$, and fuel rich when the $\Phi < 1.0$. Incomplete combustion occurs when there is less than stoichiometric amounts of oxidant present (Turns, 1998).

2.3 Current research related to syngas production from biomass

2.3.1 Energy crops

Energy crops are defined as low cost and maintenance plants which have high energy content, and are harvested for use in direct combustion for electricity; heat generation or in the making of biofuels. These crops are characterised as woody or herbaceous plants such as grass, which grows specifically for use as fuel as they require low energy inputs and offer high energy outputs per hectare.

Commercially grown energy crops are usually densely planted, high yielding crop species, which will be burnt for power generation. For these types of applications, woody crops such as willow, poplar and temperate grasses such as elephant grass are utilized, whereas whole crops such as maize, Sudan grass and millet are converted into silage, and used for biogas production due to their high carbohydrate content.

Salix viminalis, Miscanthus X giganteus and *Andropogon gerardi* are Polish energy crops, which indicate potential suitability for combustion, pyrolysis and gasification processes for the production of bio-oils, biofuels, syngas and hydrogen. Smolinski *et al.* (2010) carried out studies involving steam gasification of these energy crops in a lab scale fixed bed reactor. In addition, the reactivity of each of these crops was investigated. Table 2-5 indicates the elemental and proximate analyses of *Salix viminalis, Miscanthus X giganteus* and *Andropogon gerardi*. Based on this analysis, Smolinski *et al*. (2010) were able to determine the chemica formuli, and steam reforming reactions for *Salix viminalis, Miscanthus X giganteus* and *Andropogon gerardi* which is indicated by equations 2-25 – 2-27.

Table 2-5: Elemental and proximate analyses for various energy crops

Reference	Smolinski *et al.* (2010)		
Biomass	*Salix viminalis*	*Miscanthus X giganteus*	*Andropogon gerardi*
Elemental Analysis (wt%)			
C	52.2	53.7	53.3
H	6.2	6.6	7.6
O	35.3	31.3	25.5
N	<0.1	<0.1	<0.1
S	0.05	0.05	0.06
Proximate Analysis (wt%)			
Moisture	4.7	6.8	9.7
Fixed Carbon	20.6	15.6	16.2
Volatiles	73.2	76	70.3
Heat of Combustion (kJ/kg)	18171	16546	16132
Calorific Value (kJ/kg)	16697	16546	16132

$$CH_{1.41}O_{0.51} + 0.49H_2O\ (g) \rightarrow CO\ (g) + 1.20H_2(g) \qquad [2\text{-}25]$$

$$CH_{1.46}O_{0.44} + 0.56H_2O\ (g) \rightarrow CO\ (g) + 1.29H_2(g) \qquad [2\text{-}26]$$

$$CH_{1.70}O_{0.36} + 0.64H_2O\ (g) \rightarrow CO\ (g) + 1.49H_2(g) \qquad [2\text{-}27]$$

The steam gasification of these energy crops was carried out at atmospheric pressure within a temperature range of 650-900°C.

According to Smolinski *et al.* (2010), reactivity is an important element in deciding the suitability of biomass for use in an industrial process such as combustion or gasification. Reactivity characterises the biomass in terms of its ability to undergo thermochemical transformations. It is dependent on factors such as chemical composition, content of volatiles, ash and carbon. In addition, reactivity is also influenced by the physical and chemical changes in the char as it develops, which is dependent on process conditions such as temperature, pressure and heating rate. The reactivity of biomass can be determined according to equation 2-28.

$$R_x = \frac{dm}{(m_o.dt_x)} \qquad [2\text{-}28]$$

$$x = \frac{m \times 100}{m_o} \qquad [2\text{-}29]$$

Where R_x is the reactivity for $x\%$ of carbon conversion, m_o is the initial carbon content in the sample, m is the carbon content in the gaseous products mixture and t_x is the time required to achieve carbon conversion of $x\%$. The carbon conversion $x\%$ can be determined according to equation 2-29.

Studies carried out by Smolinski *et al.* (2010) indicated that the products of steam gasification of these energy crops were hydrogen, carbon monoxide, methane and carbon dioxide. As indicated by Table 2-5, hydrogen was the largest constituent of the gas composition for all three energy crops. Table 2-10 indicates the produced syngas from gasification of these energy crops. It was also found for all tested crops that as the temperature increased, the total volume and calorific value of the produced gas increased. In addition, it was found that the effect of an increased process temperature resulted in an increased hydrogen production, decreased carbon dioxide production and relatively stable carbon monoxide and methane levels. The most significant differences found between the energy crops were observed in the reactivity. It was found that a higher R_{50} values of *Andropogon gerardi* and *MXG* corresponded with shorter times needed to reach 50% carbon conversion of these crops relative to *Salix viminalis*. In addition it was found that the highest reactivity values (R_{50} and R_{max}) was observed for *MXG* which had the lowest carbon content, while *Salix viminalis* had the lowest reactivity values and highest relative carbon content.

2.3.2 Municipal Solids Waste (MSW)

Municipal solids waste is defined as all types of solid waste generated by households or commercial establishments. This waste typically consists of product packaging, woods, plastics, papers, appliances, paint and batteries, and is typically collected by local municipalities for energy recovery, recycling, disposal in landfills or shipment to treatment and disposal facilities (U.S. Environmental Protection Agency, 2014).

The national waste baseline indicated that in 2011, South Africa generated approximately 108 million tons of general and hazardous waste. 90% of this waste was disposed of in landfills, while the remaining 10% was recycled (Department of Environmental Affairs, 2012).

As indicated, the majority of municipal waste is landfilled in South Africa. In recent years, South Africa has developed a detailed and rigorous waste policy which advocates proper municipal waste management practices. However, there is still a large scope for implementation and enforcing of this policy. According to the Council for Scientific and Industrial Research (CSIR), developing this compliance with the existing legislation will require enhanced technical skills which ensures sanitary and proper operation of landfills, as well as competent auditing and monitoring systems for enforcement. In addition, it is also vital to begin the implementation of effective and alternative technological solutions which can assist with waste management. This includes energy recovery, thermal treatment, beneficiation and recycling (United Nations Environment Programme, 2014).

A possible alternative to using landfills is to utilize municipal solids waste as a biomass for gasification. MSW gasification has been widely researched in America and Europe, from laboratory scale to pilot plant stage (Arena *et al*., 2010). There are also many gasification plants for MSW in Japan, which are under commercial operation for energy and material recovery (Tanigki *et al.*, 2012).

Tanigaki *et al.* (2012) carried out studies to evaluate the effect of co-gasification of bottom ash (ash obtained from a MSW incinerator), and municipal solid waste relative to gasification of only MSW. This study was carried out in two commercial plants. Tables 2.5 and 2.6 indicate the physical components and elemental and proximate analyses for the two respective feeds, while results of these experiments are indicated in Table 2-10. The results of this study indicated that from a production and operational view, there was no significant difference between co-gasification of bottom ash and MSW versus gasification of MSW. The effect of equivalence ratio (ER) was similar to results obtained for gasification of other biomass; as ER increased, there was a corresponding slight decrease in carbon monoxide production, and increase in carbon conversion, carbon dioxide production and process temperature (Tanigaki *et al.*, 2012).

Table 2-6: Physical components of various wastes

Reference	Tanigaki *et al.* (2012)					
	Plant A					Plant B
Waste	MSW	Bottom Ash	Combustible Residue	Incombustible Residue	Waste to be treated	MSW
Physical components						
Paper	55.7	0.0	14.6	1.0	42.4	55.8
Vinyl and Plastics	6.6	0.1	66.4	31.9	8.7	18.9
Wood	10.5	0.0	3.8	2.5	8.2	6.2
Biowaste	25.1	0.0	0.0	0.0	19.0	10.3
Incombustibles	0.7	42.9	10.1	19.4	10.4	5.2
Others	1.3	57.1	5.2	45.2	11.4	3.6

Table 2-7: Elemental and proximate analyses for various wastes

Reference	Tanigaki *et al.* (2012)					
	Plant A					Plant B
Waste	MSW	Bottom Ash	Combustible residue	Incombustible residue	Waste to be treated	MSW
Elemental Analysis (wt%)						

C	21.2	1.1	58.9	27.1	19.3	24.7
H	3.0	0.0	9.8	3.6	2.7	3.3
O	23.1	38.3	14.5	26.3	24.9	18.3
N	0.3	0.0	0.4	0.4	0.24	0.33
S	0.03	0.12	0.10	0.13	0.11	0.03
Cl	0.2	0.53	0.51	0.66	0.57	0.20
Proximate Analysis (wt%)						
Moisture	51.7	17.9	11.8	12.5	42.8	44.0
Reference	Tanigaki *et al.* (2012)					
	Plant A					Plant B
Waste	MSW	Bottom Ash	Combustible residue	Incombustible residue	Waste to be treated	MSW
Proximate Analysis (wt%)						
Moisture	51.7	17.9	11.8	12.5	42.8	44.0
Combustibles	44.2	5.8	68.9	40.3	38.7	46.9
Ash	4.1	76.4	19.3	47.2	18.5	9.1
LHV (MJ/kg)	6.8	0.0	27.3	11.3	6.5	9.1

2.3.3 Animal manure

Animal manure is an inevitable by-product of the agricultural and food industry, which is becoming a problem due to increasing accumulation and pollution. Due to this, it is increasingly being recognized as an industrial waste which needs to also be addressed in an environmentally friendly and sustainable manner (Zhang *et al*., 2011). Animal excrement is a potentially sustainable and renewable source of energy due to the organic matter it consists of. This makes it an attractive option as a low grade biomass for gasification due to its high availability, low cost and waste disposal management (Cantrell *et al*., 2008; Gao *et al*., 2009).

According to Zhang *et al.* (2011), syngas can be obtained from livestock manure via gasification using air or steam at high temperature. Fluidized bed reactors offer great advantages to solid waste treatments and has been used widely for many different sources of biomass. Gasification in a fluidized bed reactor is typically carried out at temperatures exceeding 800°C as this is appealing for practical applications due to increased gasification rate. However, based on previous studies carried out by Zhang *et al.* (2010, 2011), this system is not conducive for gasification of livestock manure, as this biomass has high ash yields, which results in fouling and slagging in fast and high temperature conversion systems. In addition, the gas produced from this gasification system typically contains heavy hydrocarbon chains, which are too refractory for cracking at low temperature resulting in the hindrance of gasification of further material. Higher efficiencies and easier operation can be obtained when this low calorific biomass is gasified at a lower temperature using an appropriate catalyst. In addition with the aid of a catalyst it assists with the avoidance of ash related problems such as sintering, agglomeration, deposition, erosion and corrosion which occur under high temperature conditions. The tar in the produced gas can also be eliminated through the use of nickel based catalysts which are very active in tar cracking (Zhang *et al.*, 2011).

Zhang *et al.* (2009) investigated the organic constituents of pig manure through thermogravimetric curves. This indicated that pig manure consists of hemicelluloses, celluloses and lignin. The significance of this is that there is a characteristic pyrolysis behaviour which corresponds to the organic makeup of the biomass. Cellulose decomposes within the temperature range of 300 – 430ºC, lignin decomposes with a temperature range of 250 – 550ºC and hemicellulose is most unstable thermally and can begins decomposition between the temperatures of 250 – 330ºC (Wang *et al.*, 2008). Based on these studies, there were two distinct peaks found at temperatures of 288 and 333ºC which corresponded to the decomposition of hemicellulose and cellulose respectively. In addition, it was found that under no condition was there a peak which corresponded with lignin decomposition. This was attributed to the slow decomposition behaviour of lignin which was further supported by a smooth gentle sloping temperature curve.

Zhang *et al.* (2011) conducted two separate studies on the low temperature catalytic gasification of pig and hen manure to produce syngas using a two stage fixed bed reactor. In addition, the effects of the mineral content on gasification under these conditions was also investigated, as the presence of inorganic material can significantly affect the pyrolysis behaviour of biomass (Raveendran *et al.*, 1996). , CO and total syngas yield.

Table **2-8** indicates the elemental and proximate analyses for both livestock manures.

Table **2-9** illustrates the inorganic impurities found in hen and pig manure (see p35). In both studies it was found that a high H_2, CO and total gas yields were obtained under these conditions. It was also found that a weak acid wash of HCl and HF were effective in the removal of K, Zn, Mn and Si. In both studies a Ni/Al_2O_3 catalyst and steam gasifying agent were used. This was especially effective in the pig manure biomass as it favoured the complete cracking of tar into H_2, CO and residual carbon.

The mineral content in the pig manure was found to have no significant effect on the pyrolysis behaviour of the biomass. While high calcium content in the form of mainly CaO and $Ca(OH)_2$ was found in the hen compost. Due to the reactivity sites for cracking on the inner and outer surface of the CaO molecule, it may have assisted in the catalysing of decomposition reaction to increase gas yield. The presence of CaO resulted in the absorption of CO_2, which promoted hydrogen production and provided the necessary energy through the carbonation reaction for the endothermic reactions required in gasification. As a result of the presence of these molecules in the hen manure ash, it was found that both the ash and the char, promoted the productivity of H_2, CO and total syngas yield.

Table 2-8: Elemental and proximate analyses for animal manure

Reference	Zhang *et al.* (2011)	Zhang *et al.* (2011)
Biomass	Fowl Manure	Pig Manure
Elemental Analysis (wt%)		
C	41.81	43.99
H	4.81	6.06
N	3.91	5.75
S	0.8	1.07
Proximate Analysis (wt%)		
Moisture	18.00	21.61
Ash	38.86	20.73
Volatile	90.35	85.58

Table 2-9: Inorganic impurities in animal manure

Reference	Zhang *et al.* (2011)	Zhang *et al.* (2011)
Biomass	Fowl manure	Pig Manure
Si	0.37	0.33
Fe	0.18	0.50
Ca	21.36	8.06
K	3.42	3.00
Reference	Zhang et al. (2011)	Zhang et al. (2011)
Biomass	Fowl manure	Pig Manure
Inorganic impurities (wt%)		
Zn	-	0.12
P	1.03	1.16

Table 2-10 compares gas yields for gasification of various types of biomass. As shown, maize residue has the high hydrogen and carbon monoxide contents in comparison to energy crops, municipal solids waste (MSW) and animal waste. This indicates that maize residue is a potentially good source for syngas production and a potentially good fuel source.

Table 2-10: Syngas production from various types of biomass

Reference	Smolinski *et al.* (2010)			Tanigaki *et al.* (2012)	Ioannidou *et al.* (2009)	Ioannidou *et al.* (2009)	Zhang *et al.* (2011)	Zhang *et al.* (2011)
Biomass	*Salix viminalis*	*Miscanthus giganteus*	*Andropogon gerardi*	MSW	Maize	Stalk	Fowl Manure	Pig Compost
Temp (°C)	650-900	650-900	650-900	400-1000	-	-	300-400	300-400
Gas Production (v/v%)								
H_2	49-61	58-68	61-68	-	360-730	380-680	62.5	58
CO	13-19	9-10	9-12	16.5	28-42.5	18-28	12.5	28
N_2	-	-	-	-	41-51	35-59	-	-
CO_2	23-28	21-30	9-30	18	-	-	18.6	9.5
CH_4	0-1	<1	0	-	3.5-24	2-39	0-5	4.2
C_2H_6/C_2H_4	-	-	-	-	7-9	8-12	0-1.4	<1
LHV (MJ/m^3)	9-14	10-14	9-14	5.9	0-1	0-1	-	-

2.3.4 Maize

Maize is an important agricultural crop all around the world. The reported global annual production is approximately 520 million tons. The major sources of production are North America (42%), Asia (26%), Europe (12%) and South America (9%). Almost 64% of this maize is used for animal food, 19% is utilized for human needs while 5% of global production is lost as waste. The residue of maize can be defined as the stalk, leaf, husk and cob which remain in the field following the harvest of cereal grain. This residue can make up to half of the yield of a crop and often also contains other weeds and grasses, and other non-grain parts of the harvested maize which are bulky and contain low water content (Ioannidou *et al.,* 2009).

Much of the wasted maize has been used in the past as a lucrative feedstock for bioethanol production. In America the cellulosic ethanol produced from maize residue has offered a way to derive an environmentally friendly fuel blending component without disrupting the food supply. However U.S. biofuel companies are beginning to suffer as the U.S. government's support and subsidies under the 2005 Renewable Fuel Standard have started to expire, making bioethanol production from maize economically unviable.

Recent studies have shown that maize residue may contain valuable materials which make the cost of transportation and processing economically feasible (Ioannidou *et al*., 2009). Due to this, maize residues have been studied as a raw material for energy and active carbon preparation.

Several researchers carried out studies on the effects of various parameters on pyrolysis products. Cao *et al.* (2004) and Sun *et al.* (2009) conducted studies on the behaviour of maize pyrolysis. Encinar *et al.* (1997), Zanzi *et al*. (2002) and Wei *et al.* (2006) investigated the rapid pyrolysis of various types of biomasses in a free fall reactor. In their studies, it was found that hydrogen content was favoured by a higher temperature, and higher cellulose and hemi-cellulose content. Table 2-11 indicates the cellulose and hemicellulose content of maize and maize stalk as reported by Garrote *et al.* (2007) and Banchorndhevakul (2002) respectively. As shown by Table 2-11, the cellulose and hemicellulose contents of both maize and maize stalk are high. This implies potentially high hydrogen content in the gasification product.

Table 2-12 indicates the elemental and proximate analysis found for various agricultural crops. Ioannidou *et al.* (2009) determined the elemental and proximate analysis for maize and maizestalk through the use of a thermogravimetric analysis (TGA). In addition, the heating value of the feedstock was determined by using a calorimeter, in which the combustion of each sample was done in the presence of pure oxygen. The moisture content of the maize residue was determined by heating it in an oven at 105°C for 3 hours. The results obtained by Ioannidou *et al*. (2009) for heating value and moisture content are reported in Table 2-12. The remaining data reported in Table 2-12 indicates the elemental and proximate analysis as well as heating value and moisture for similar types of agricultural crops obtained from other researchers. As shown by Table 2-12, maize residue has the highest lower heating value in comparison to maize, straw and legume. This indicates that it is a good source for fuel in comparison to these agricultural crops (Ioannidou *et al*., 2009).

Table 2-11: Chemical characteristics of maize and maize stalks

Reference	Garrote *et al.* (2007)	Banchorndhevakul (2002)
Biomass	Maize	Maize Stalk
Chemical Analysis (wt%)		
Cellulose	34.3	32.4
Hemicellulose	40.53	40.8
Lignin	18.8	2.5

Table 2-12: Elemental and proximate analysis of agricultural residues

Reference	Ioannidou *et al.* (2009)	Ioannidou *et al.* (2009)	Encinar *et al.* (1997)	Shuangning *et al.* (2005)	Zanzi *et al.* (2002)	(Wei *et al.* (2006)
Biomass	Maize	Maize stalk	Maize	Maize stalk	Straw	Legume
Elemental analysis (wt%)						
C	43.77	43.80	46.90	43.65	45.60	43.30
H	6.23	6.42	5.40	5.56	6.50	5.62
O	50	49.78	47.40	43.31	47.00	50.35
N	-	-	0.06	0.61	0.50	0.61
S	-	-	-	0.01	-	0.12

Table 2.11 continued.

Proximate analysis (wt%)						
Moisture	7.57	6.44	-	-	-	9.80
Light vol.	57.27	83.07	82.30	75.17	7.10	73.74
Heavy vol.	27.10	8.19	-	-	-	-
Fixed carbon	-	-	14.80	19.25	-	14.84
Ash	8.06	2.3	2.9	5.58	-	1.62
LHV (MJ/kg)	18.25	18.17	15.40	17.19	17.08	-

Ioannidou *et al.* (2009) also carried out studies which involved the investigation of the behaviour of maize residues during pyrolysis in two reactor configurations. Pyrolysis was carried out at 360, 520, 630 and 730°C for maize and 380, 520, 630 and 680°C for maize stalk. The main purpose of this research was to investigate the potential of maize residue for energy, fuel, materials and chemicals production according to the obtained quality and yields of product. The products of pyrolysis were found to exist in gaseous, liquid and solid phase. The yields of these products were influenced by temperature. Increasing the temperature resulted in greater volatiles release from the biomass, increasing the gaseous yield and decreasing the amount of char. The char yield for maize at 360°C was found to be 48 wt% and 49 wt% for stalk at 380°C. The highest gas yields for maize and maize stalk were found to be 63 wt% and 55 wt% at 760°C and 630°C respectively. This indicates that the higher yields of char are observed at lower temperatures, whereas the higher yields of gas are observed at temperatures exceeding 500°C.

The product gas comprised of mostly CO, CO_2, H_2, CH_4, C_2H_2 and C_2H_6. In this study it was found by Ioannidou *et al.* (2009) found that there was a high yield of syngas (H_2 and CO), which was attributed to the increased content of cellulose and hemicellulose within the maize residue. Biomass with higher cellulose and hemicellulose contents produce a relatively higher hydrogen yield than feeds containing lignin. The lower heating value (LHV) of the gas was determined according to equation 2-30 and was found to be 10-13 MJ/m^3 and 13-15 MJ/m^3 for maize and maize stalk respectively. According to Yang *et al*. (2006), these LHV's belong to the medium level gas fuels and can be used directly in engines, turbines and boilers for energy production.

$$LHV = (30.0 \times CO + 25.7 \times H_2 + 85.4 \times CH_4 + 151.3 \times C_nH_m) \times 4.2 \qquad [2\text{-}30]$$

2.3.5 Maize in South Africa

a Yield

South Africa is the highest maize producer on the African continent (Bureau for Food and Agricultural Policy, 2015). Figures 2.12 and 2.13 indicate the historical maize production and projection up to 2023, which is expected to remain stable at approximately 13 million tons per annum for combined white and yellow maize production. Major factors affecting maize yield include rainfall, season, temperature, soil conditions and maintenance. Maize is a seasonal crop which is typically planted from October to December due to the variation in rainfall pattern, temperature and duration of the growing season. Tillage practices vary from plough to no-till depending on the soil type and rainfall or irrigation. Areas which have in excess of 350 mm of annual rain promote maize production (National Department of Agriculture, 2015). In 2013/2014, approximately 20% of the 11.8 million tons of maize produced was exported, only 0.8% was imported making South Africa a net exporter in maize. The Bureau for Food and Agricultural Policy (BFAP) project South Africa to continue being a net exporter until 2023. The only exception to this trend is 2015/2016 due to the severe drought experienced, resulting in lower than expected maize production.

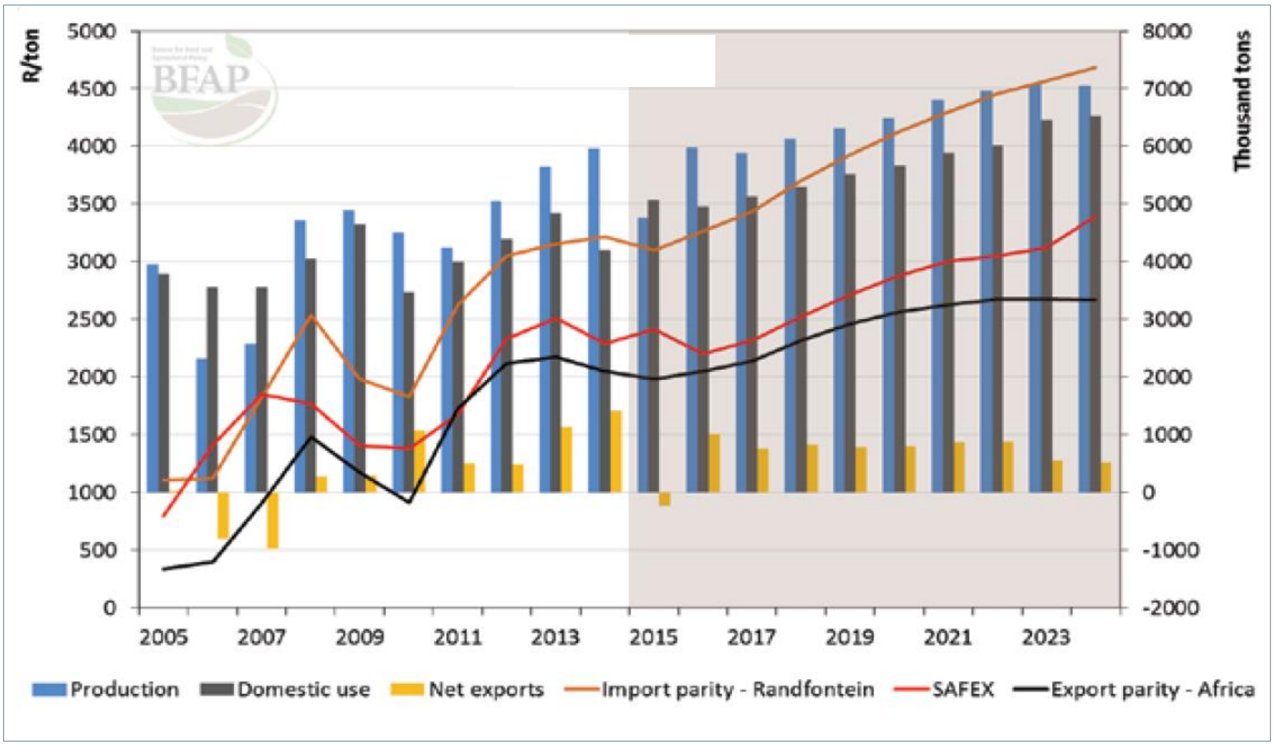


Figure 2-12: Yellow maize production, domestic use and net exports projection for South Africa (BFAP, 2015)

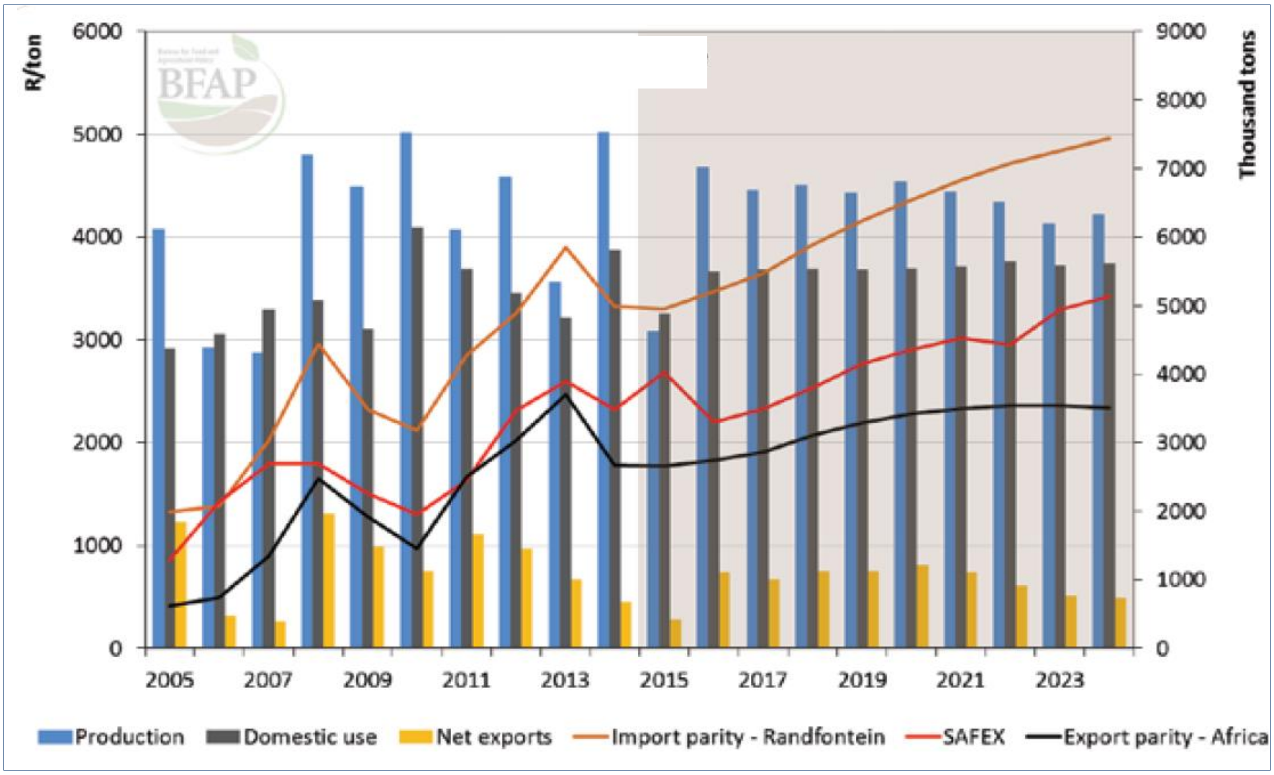


Figure 2-13: White maize production, domestic use and net exports projection for South Africa (BFAP, 2015)

b Land

As indicated by Figure 2-14, majority of maize production concentrated in the North West, Free State, Mpumalanga and KwaZulu Natal. These areas have medium to high potential soils which make up 25% of the country’s total arable land. Maize typically requires 450 – 600 mm of water per season. The balance not acquired from irrigation or rainfall is obtained from soil moisture reserves. A single maize plant will consume approximately 250 litres of water to reach full maturity with a resultant leaf area of over 1 square metre (du Plessis, 2003).

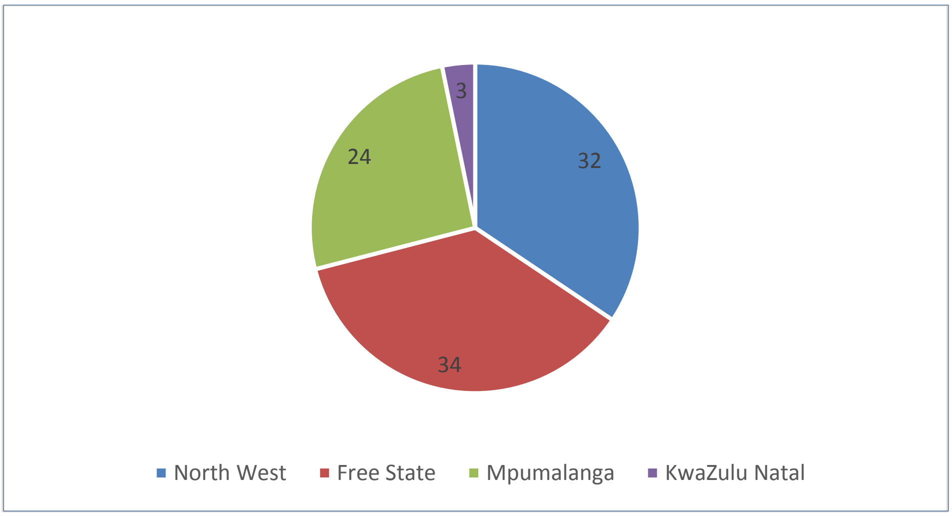


Figure 2-14: Maize production in South Africa

c Maize types and uses

There are predominantly two types of maize available in South Africa's maize production which are referred to as yellow and white maize. White maize is a sweeter maize which is harvested before reaching full maturity. As it grows on the stalk, white maize becomes wrapped in layers of green and white husk. White maize is considered as having a higher sugar to starch ratio and water content relative to yellow maize. It is typically treated as a vegetable which is either boiled or roasted for direct human consumption. Yellow maize is commonly used as grain product for livestock feed such as cows and chickens in the raw form found in the fields or processed as animal feed. Yellow maize is also used for indirect human consumption in the form of 'mealie meal', which is consumed as a thick porridge, maize-starch and used as a thickener for soups and maize syrup. Figure 2-15 indicates the South African maize production in 2013/14 and the corresponding domestic and international consumption. Of the 11.8 million tons of maize produced, 5.6 million tons consisted of white maize and 6.2 million consisted of yellow maize (Bureau for Food and Agricultural Policy, 2015). Table 2-13 indicates the maize consumption for South Africa in 2013/2014. There is potential to reduce the export tons of maize and use this additional capacity for liquid fuels generation should the returns on revenue be economically viable.

Table 2-13: Maize balance sheet and breakdown of consumption for South Africa 2013/2014 (Bureau for Food and Agricultural Policy, 2015)

Maize Balance Sheet		Breakdown of Domestic Consumption		
Description	Million tons	Description	Million tons	% of Total
Domestic production	11.8	Food (direct human consumption)	4.66	45.6
Domestic Consumption	10.2	Industrial (indirect human consumption)	0.6	5.9
Maize Imports	0.1	Animal Feed	4.96	48.5
Maize Exports	2.23			

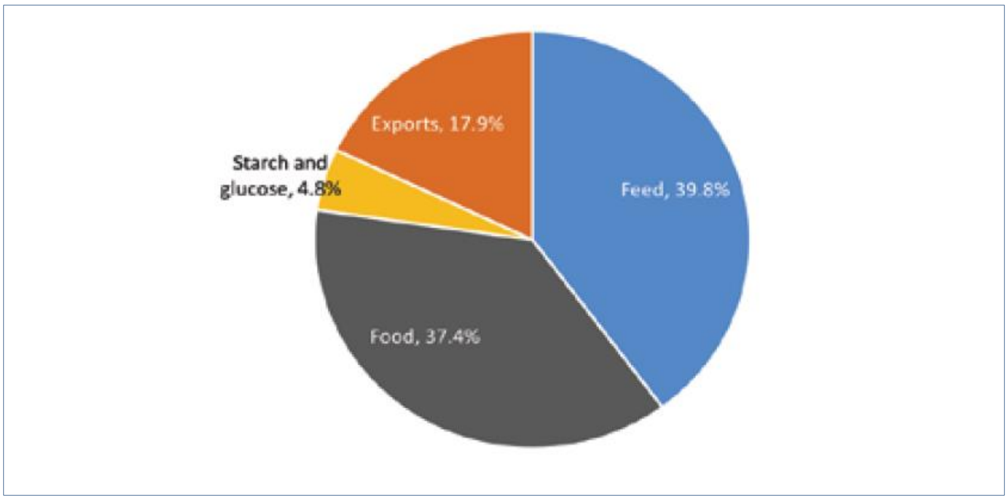


Figure 2-15: Maize consumption in South Africa 2013/2014 (Bureau for Food and Agricultural Policy, 2015)

d Food

Maize is the most important grain in South Africa as it is both a staple food and animal feed grain.

Figure **2-16** illustrate the trend of maize consumption for humans and animals from 2000 to 2014. Maize consumption as food has remained relatively stable at approximately 4 – 4.5 million tons per annum since 2008, while there has been a significant growth in animal feed consumption by approximately 45% over the same period (Bureau for Food and Agricultural Policy, 2015).

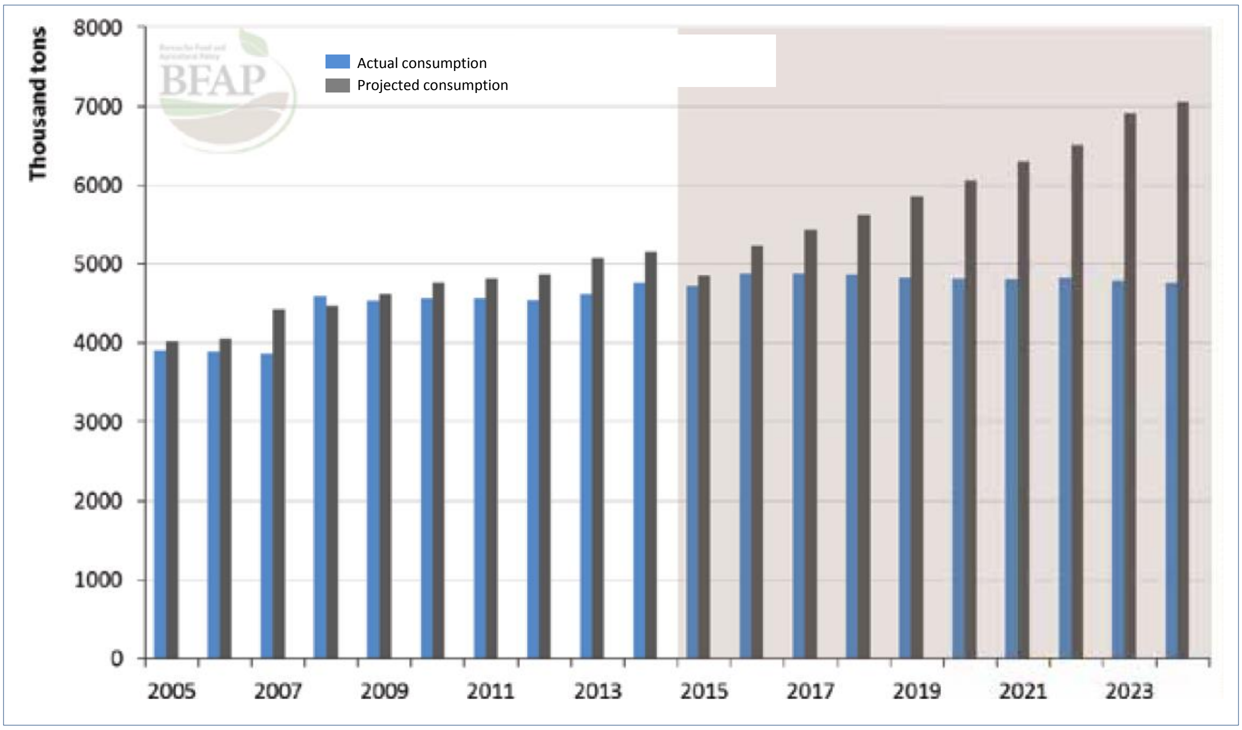


Figure 2-16: Projected human, animal feed and ethanol maize consumptions for South Africa (BFAP, 2015)

The BFAP expects the trend of white maize consumption to remain relatively stable due to the migration from lowest income groups to middle and upper income groups in South Africa. Since white maize has typically been an important staple food consumed by lower income groups in South Africa, this will have a negative impact on maize consumption. StatsSA indicated in 2012 that maize meal moved from being the biggest contribution to staple expenditure to contributing only 7% of a household budget. It was found that as income increased, a movement from maize meal to a variety of other starches such as bread, rice, potatoes and pasta was observed. A secondary effect of consumer income growth is an increase in consumption and production of animal based proteins. The growth in demands for meats, dairy products and eggs has resulted in yellow maize consumption increasing by 19% from 2005 to 2014 to produce additional animal feeds. A further increase in animal based proteins is expected in the next decade, while BFAP project that white maize consumption will remain stable at 4.77 million tons by 2023. This estimation is also supported by the milling industry. While government feeding programmes and new maize based food products may stimulate an increase in consumption, the industry’s long term projection is that this sector will remain stable due to lack of growth in demand for maize based food products (Bureau for Food and Agricultural Policy, 2015). The demand in yellow maize is expected to increase by a further 46% due to the expected consumption increase in animal proteins (Bureau for Food and Agricultural Policy, 2015).

2.3.6 Maize and bio fuel production

In response to the oil crisis in the 1970s, countries around the world have introduced policies to encourage diversification of energy sources to lower the use of fossil fuel dependency and reduce effects on the environment. These policies consist of extensive biofuel mandates supported by programmes which include government financing for biofuel project development, grants and favourable credit for biofuel production, tax credits for fuel blenders and tax rebates for fuel suppliers.

These policies have generated high levels of support for biofuel producers and expanded the markets for agricultural feed stocks used in biofuel production (Bureau for Food and Agricultural Policy, 2015). The Biofuels Industrial Strategy (BIS) for the South African biofuel industry is expected to provide sufficient incentives to support the kick off of a domestic biofuels industry. In this policy, maize was excluded as a feed stock to prevent a negative impact on food security. According to the Draft Position Paper (2014), sorghum was selected as the preferred crop for bioethanol production. During initial stages of implementation, the strategy plans to make use of underutilized land found in the former homelands. Two ethanol plants planned to use sorghum feed are located in Bothaville and Cradock. The expectation of the BIS is to achieve a 2% blending rate which is equivalent to 400 million litres of liquid fuels/annum which will require a consumption of over 600 thousand tons of sorghum. The BIS plans to incorporate maize as a feedstock only once the ability and yield of the underutilized land has been established and measures have been established to protect against extreme food inflation (Department of Minerals and Energy, 2007).

The Strategy proposed that bioethanol be sold at whole sale prices to cover operation, transportation and capital payback. The cost to the motorist will be equivalent to base fuel price of R 5.39/L crude oil and will present a benefit limited to 2% if the price of crude oil increases beyond this point. The biofuel supply required by the BIS will need to be low operational cost, high yield and consume agricultural residue typically not used for human consumption especially when crude oil prices are low. South Africa has a surplus of crop production which is estimated to potentially produce approximately 5% of South African petroleum demand through ethanol blending. In addition underutilized land could produce biofuels representing 5% of national diesel usage assuming ideal climate and soil characteristics. According to the BIS (2007) feasibility study accounting for practical weather and soil conditions, an achievable production level from surplus crops and underutilized land equates to 4.5% of national diesel and petroleum volumes.

It is estimated that 2% biofuels blending will create over 25 000 jobs reducing unemployment by 0.6% and boosting economic growth by 0.05%. In addition, it has the potential to achieve a greenhouse gas saving of R100 million per annum. According to the BIS, to achieve the required biofuel production, the biofuel plant would require 4 billion Rand investment over a 5 year period.

As stipulated by the Biofuels Industry Strategy (2007), maize has been excluded from ethanol production with sorghum rather selected as the preferred crop for biofuel production. However, recently South Africa has moved from being a net exporter to a net importer of sorghum. Since 1980s sorghum planting has decreased from 300 000 to 65 000 hectares in 2016. This reduction is due to low yields in comparison to maize, resulting in less competitive margins per hectare. This trend is projected to continue according to BFAP (2016), as sorghum yields have continued to stagnate for the past decade, especially since profit margins of maize have been significantly more than sorghum. This has resulted in maize yields increasing annually by over 2%. This has been attributed to the improvement in maize yield per hectare and genetic modification applications which are available in maize and not in sorghum. Due to both yields and profit margins being higher, it would be more feasible to promote maize production for biofuel generation. This will support and uplift local communities and farmers economically. Table 2-14 is an example of profit margins for maize, sorghum and sugar based on bioethanol production (Bureau for Food and Agricultural Policy, 2015). Maize used for ethanol production results in a higher profit than using a sorghum feed. This further supports the proposal that biofuel generation should be derived from maize and not sorghum.

Table 2-14: Comparison of profit margins for maize sorghum and sugar for ethanol production (BFAP, 2015)

	Maize (cents)	Sorghum (cents)	Sugar (cents)
Cost of Crop	533.9	623.22	518.17
Ethanol production variable costs	184.06	184.66	173.14
Ethanol production capital costs	104.21	104.55	105.18
Income from dried distillers grains	-176.85	-127.95	-
Total costs	654.31	784.48	796.69
Ethanol price at plant (c/Litre)	807.82	807.82	807.82
Profit Margin	162.51	23.34	11.14

In addition, sorghum production is exceptionally low in comparison to other agricultural crops in South Africa – see Figure 2-17. A year on year decline of over 25% in sorghum production is projected due to reduced area and low yields. This will result in the need of importing more than 50 000 tons in order to supply domestic demand of 200 thousand tons. BFAP (2016) projects for the next 10 years demand for sorghum will remain fairly stable with less than 1% annual increase, which will be as a result of population growth and not an increase in consumption per capita. Planting area is also projected to remain at 65 000 hectares. Production increase will only occur due to improvements in yield. Assuming stable weather conditions, the market will remain stable with limited trade. These existing conditions for sorghum are not favourable and implies farmers would prefer planting maize as indicated by Figure 2-17.

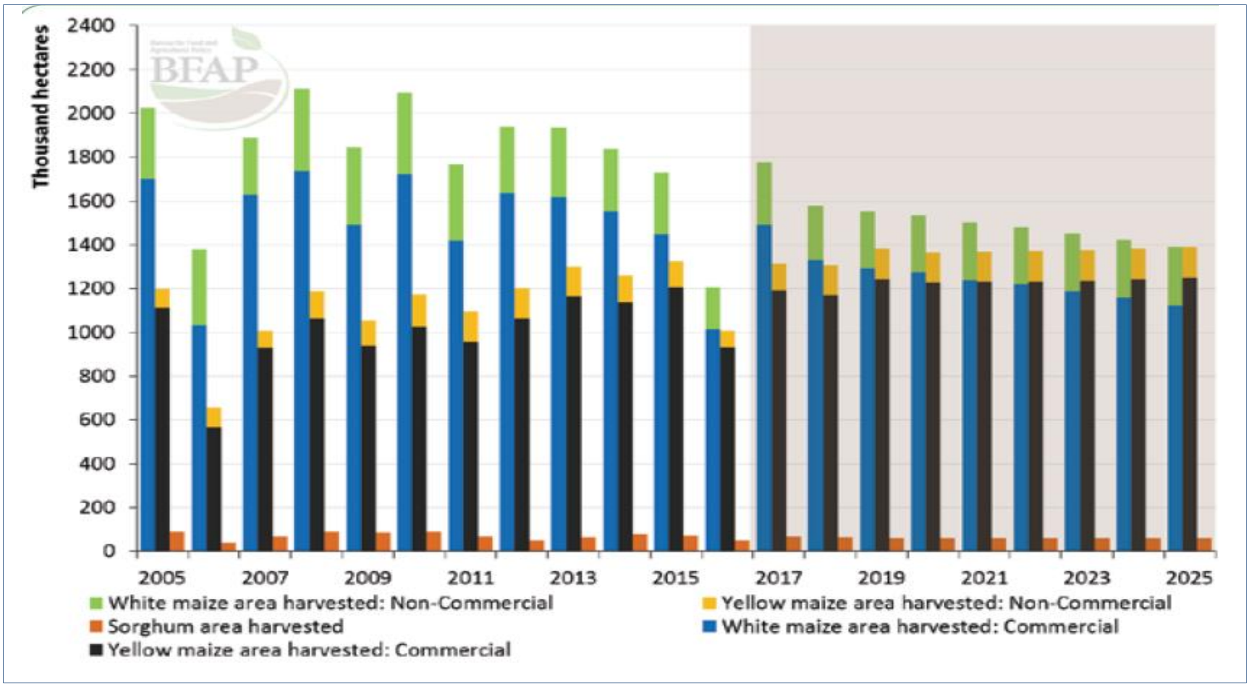


Figure 2-17: Agricultural crop production and future projections (BFAP, 2016)

2.3.7 Simulations of biomass gasification through equilibrium models

Equilibrium models have been developed according to two approaches. The first is an equilibrium model based on equilibrium constants. This approach requires that appropriate and specific chemical reactions and realistic equilibrium constants be defined in order to carry out the relevant calculations. The disadvantage of this approach is that it is not suitable for complex problems were extensive information on the reactions and equilibrium constants are unknown. The second approach is the Gibbs free energy minimization model, which is suitable for complex problems as no chemical reaction is needed to find the solution. Therefore the Gibbs free energy minimization approach will be used as the equilibrium model and will be carried out in Aspen Plus® due to the complex reaction nature of biomass gasification. The thermodynamics of the Gibbs free energy model, which will be used to generate the Aspen Plus® simulation are outlined below.

The total Gibbs free energy of a system can be defined according to equation 2-31. When equilibrium is reached, the total Gibbs free energy of the system is at a minimum.

$$G^t = \sum_{i=1}^{N} n_i \mu_i \tag{2-31}$$

Where G^t is the total Gibbs free energy of the system and n_i is the number of moles of species i. μ_i is the chemical potential of species i which can be represented by equation 2-32.

$$\mu_i = G_i{}^o + RTln(\frac{f_i}{f_i{}^o}) \tag{2-32}$$

Where R and T are the universal gas constant and temperature of the system respectively. f_i is the fugacity of species i and the subscript o indicates a standard thermodynamic quantity. $G_i{}^o$ is the standard Gibbs free energy of formation. Equation 13 can also be represented in terms of pressure as shown in equation 2-33.

$$\mu_i = G_{f,i}{}^o + RTln(\frac{\phi P_i}{P_i{}^o}) \tag{2-33}$$

Where ϕ is the fugacity coefficient. According to the laws of fugacity, fugacity tends to pressure as pressure approaches zero. At this condition, real gases also approach ideal gas state. Based on the assumption that all gases behave as ideal gases at a pressure of 1 atmosphere, Equation 14 can be rewritten as equation 2-34.

$$\mu_i = G_{f,i}{}^o + RTln(y_i) \tag{2-34}$$

Where y_i is the mole fraction of gas species i and is the ratio of n_i and the total number of moles in the reaction mixture. $\Delta G_{f,i}{}^o$ is the standard Gibbs free energy of formation and can be set to zero for all chemical elements or molecules in their natural state. Therefore by substituting equation 2-34 into equation 2-31, equation 2-35 can be obtained.

$$G^t = \sum_{i=1}^{N} n_i \Delta G_{f,i}{}^o + \sum_{i=1}^{N} n_i \, RTln(\frac{n_i}{n_{tot}}) \tag{2-35}$$

In order to find the values of n_i which minimize Gibbs free energy, Lagrange multipliers must be employed. The constraint of this model arises from the elemental balance which can be represented by equation 2-36.

$$\sum_{i=1}^{N} a_{ij}n_i = A_j, \quad j = 1, 2, 3, \dots k \qquad [2\text{-}36]$$

Where a_{ij} is the number of atoms of the jth element in a mole of i species. A_j is defined as the total number of atoms of the jth element in the reaction mixture. To form the LaGrange function (L), the Lagrange multipliers, $\lambda_j = \lambda_1, \dots, \lambda_k$ are used by multiplying them with the elemental balance constraints. These terms can then be subtracted from G^taccording to equation 2-37.

$$L = G^t - \sum_{j=1}^{k} \lambda_j \left(\sum_{i=1}^{N} a_{ij}n_i - A_j \right) \qquad [2\text{-}37]$$

The partial derivatives of Equation 18 are set to zero according to equation 2-38, in order to determine the extreme point.

$$\left(\frac{\partial L}{\partial n_i} \right) = 0 \qquad [2\text{-}38]$$

Equation 19 can be translated into the terms of a matrix with i rows and solved simultaneously using the constraints shown in Equation 17. The solutions to $n_i$must be real numbers which fall within the boundary $0 \le n_i \le n_{tot}$. Equation 19 creates a set of non-linear equations which are solved by an iterative technique in Aspen Plus® based on the extensive internal thermodynamic properties data base. Based on the Aspen Plus® simulation and the Gibbs free energy model, the composition of the product gases will be determined.

2.3.8 Current gasification simulation research

a Simulation of Maize Gasification in Aspen Plus®

Studies carried out by Mavukwana *et al.* (2014) involved the simulation of South African corncob gasification through the use of Aspen Plus®. This simulation was generated based on the Gibbs free energy minimization model, which is based on the assumption that at chemical equilibrium the total Gibbs free energy of the system is at its minimum. Based on this model, the operating parameters, i.e. equivalence ratio (ER) and steam to biomass ratio (SBR) were varied in order to investigate the effects of these parameters on syngas composition.

The simulation of corncob gasification involved two stages. The first stage involved the decomposition of dried corncob into its volatile components and ash. This was subsequently followed by the second stage of partial oxidation and gasification shown by equations 2-14 - 2-23. This Aspen Plus® simulation was generated based on a flow rate of 12 000 kg/hr of corncob. The Soave-Redlich-Kwong (SRK) method was chosen as the equation of state for the simulation of all conventional and non-conventional compounds, as the physical properties were readily available. HCOALGEN and DCOALGT models were chosen for the definition of the elemental and proximate analysis of maize as it is a non-conventional fuel. The flow sheet for this simulation model began with a dry feed of corncobs specified as a non-conventional solid, which was first converted into its elemental constituents as indicated by

Table 2-15. This analysis was generated by the RYield model. The elemental and proximate analysis assisted in specifying the yield distribution and was achieved through a Fortran statement which resulted in the mass flow rate of each component in the outlet. This outlet stream was then fed to a gasifier where the possible products were specified as H_2, CO, CO_2, CH_4, C_2H_4, H_2S, COS, HCl, NH_3, and H_2O. In order to simulate this gasification reaction as an isothermal system, the heat of reaction associated with corncob decomposition was added to the gasifier through an additional heat stream. The outlet stream of the gasification reactor then entered a cyclone to simulate the separation of ash from the produced gases. This gas stream was then passed through a condenser and flash separation unit to accommodate for the removal of water.

The model assumptions for this simulation are summarized below (Mavukwana *et al*., 2014):

- The gasification system is adiabatic and maintained under steady state conditions;
- The ash is unreactive and as a result, does not participate in any chemical reactions;
- All the sulfur in the feedstock reacts to form either H_2S or COS and all nitrogen is converted NH_3 with no formation of nitrogen oxide;
- All chlorine reacts to form HCl; and
- Heavy hydrocarbons such as tart are not considered in the product stream as these compounds are products of non-equilibrium reactions, which is not in agreement with the Gibbs free energy minimization model.

A sensitivity analysis carried out on the specified parameters revealed that temperature is the most significant output parameter in gasification. Temperature has a significant effect on the thermodynamics of the reaction. In addition, it was also found that the feed of the gasifying agents, oxygen and steam, also has a great effect on the temperature of the reactor. It was found that the amount of oxygen fed to the gasifier tends to favour exothermic reactions, causing an increase in temperature which in turn affects secondary reactions. Steam increases the formation of the endothermic products, which reduces the temperature of the gasifer. The results obtained from this study indicate that an increase in ER results in an increase in gasification temperature. In addition, as SBR increased, it was found that the hydrogen gas production increased while the methane and carbon monoxide formation decreased. Further analysis indicated that the temperature of the adiabatic gasifier was dependent on the steam and oxygen flow rates. Based on this study, the optimum ER and SBR were found to be 0.286 and 0.8-1 respectively. This corresponded to an optimum temperature of 854-890ºC for maize gasification.

Table 2-15: Maize elemental and proximate simulation analyses

Reference	Mavukwana *et al.* (2014)
Biomass	corncobs
Elemental analysis (wt%)	
C	49.28
H	5.79
N	0.412
O	42.69
S	0.029
Cl	0.216
Proximate Analysis (wt%)	
Moisture	4.6
Fixed carbon	14.39
Volatile matter	83.9
Ash	1.7

b Simulation of sugarcane bagasse gasification in Aspen Plus®

Limited research on the simulation of maize gasification is available, however much research has been carried out on gasification of biomass involving wood, coal and other carbon sources. Mavukwana *et al.*, (2013) developed a steady state Aspen Plus® simulation to study the gasification of sugarcane bagasse. The results obtained from the simulation where then validated through a comparison with experimental data obtained from literature. This gasification model was similarly based on the Gibbs free energy minimization model and was developed according to two stages. The first stage involved the modelling of the decomposition of dried bagasse into its volatile components and ash, which was used to specify the yield distribution according to the bagasse ultimate and proximate analyses shown by Table 2-16. Some assumptions had to be made in order to develop the Aspen Plus simulation: these are indicated below (Mavukwana *et al*., 2013):

- The system operates under steady state conditions and is adiabatic;
- The ash acts an as inert and is therefore unreactive;
- All the sulfur in the feed react to form H_2S, in addition all nitrogen is considered to form NH_3 and no nitrogen oxide is consider; and
- Heavy hydrocarbons such as tar are not considered as these compounds are products of non-equilibrium reactions which do not agree with the Gibbs free energy minimization model.

Similarly, the second stage involved the modelling of partial oxidation and gasification reactions according to the Gibbs free energy minimization model. The effects of the same operating parameters (equivalence ratio, steam to biomass ratio and temperature) were investigated and the results obtained from this study indicated that there was a slight disagreement in relation to the experimental data, which are also indicated by Table 2-16. The simulation resulted in an under prediction in methane formation and a slight over prediction in the hydrogen gas formation. These discrepancies were attributed to the equilibrium assumption of the Gibbs Free Energy Minimization model.

Table 2-16: Simulated sugarcane bagasse and actual cuban bagasse elemental and proximate analysis

Reference	Mavukwana *et al*. (2013)	De Philippis *et al*. (2004)
Biomass	Sugarcane bagasse	Cuban bagasse
Elemental Analysis (wt%)		
C	47.5	42.9
H	5.9	5.9
N	0.29	0.2

O	40.7	49
S	0.07	-
Ash	5.6	-

Reference	Mavukwana *et al.* (2013)	De Philippis *et al.* (2004)
Biomass	Sugarcane bagasse	Cuban bagasse
Moisture	6.8	11.1
Fixed carbon	11.9	9.3
Volatile matter	82.5	88.7
Ash	5.6	2

2.3.9 Modified Gibbs free energy model simulation

Equilibrium models such as the Gibbs Minimization model are often chosen for preliminary studies due to their simplicity and few input requirements. However, due to the potential existence of non-equilibrium conditions within the gasifier, there are often discrepancies between equilibrium models and experimental data, as shown by the investigations carried out by Mavukwana *et al*. (2013, 2014). According to the Gibbs free energy minimization model, the product gas obtained at equilibrium is tar free. However, under actual conditions, gasification processes usually produce tar as supported by several studies. Gil *et al.* (1999) and Herguido *et al*. (1992) observed tar yields of 9.5% and 2 - 8% of fuel mass within a temperature range of 650-800°C. The chemical composition of tar that is produced in biomass gasification varies according to feed stock and operating conditions. Haseli *et al.* (2011) carried out investigations involving the modelling of wood combustion particles in which tar was considered as $C_{3.878}H_{6.426}O_{3.561}$, while Barman *et al*. (2012) considered 5.5% of the product to be tar and considered its formula as $CH_{1.003}O_{0.33}$. The model developed by Barman *et al*. (2012) gives a better correlation with experimental data.

As indicated, many researchers modify their equilibrium models to obtain a better correlation between predicted and experimental results. Studies carried out by Ghassemi *et al*. (2010) involved the modification of a Gibbs free energy minimization model in order to account for carbon conversion. Based on the Gibbs free energy minimization model, a 100% conversion of the carbon material is assumed. Under actual conditions, usually some of the carbon remains unconverted. Lv *et al.* (2004) reported carbon conversions ranging between 0.6 - 0.95 when using an air-steam fluidised bed gasifier, while Kaewluan *et al.* (2011) indicated carbon conversions varying between 0.79 - 0.87 for woods with different moisture contents. Therefore, in order to avoid these inaccuracies, some studies have introduced correction systems based on experimental data. Li *et al.* (2004) investigated coal gasification in a fluidised bed and accounted for an amount of carbon and hydrogen which bypassed the equilibrium reactions.

Under actual conditions, not all the gasification products are gases; some solid outputs known as char may be found. The char mainly consists of carbon and is formed by the biomass which has not reached the reaction zone in the gasifier. In order to consider that not all the carbon in the feed participates in the equilibrium reactions, Azzone *et al.* (2012) introduced a factor α. This factor represents the carbon fraction which participates in the equilibrium reactions, while the remaining carbon bypasses the reaction zone. Thus, based on the model developed by Azzone *et al.* (2012), the reaction within the gasifier can be described according to equation 2-39. $\mathrm{H_aO_b + wH_2O(l) + qH_2O(l) + mO_2 +} \rho \mathrm{\,mN_2 = (1 -} \alpha \mathrm{)C(s) + xCO + xH_2 + xCO_2 + xH_2O + xCH_4 +} \rho \mathrm{\,mN_2}$ [20]

$\rho\alpha x_{H2}$2-

$$1 - \alpha = 1 - \delta_c \qquad [2\text{-}40]$$

where:

$$\delta_c = 0.32 + 0.82(1 - e^{\frac{-\varphi}{0.299}}) \qquad [2\text{-}41]$$

δ_c is a function of the equivalence ratio and is represented by equation 2-42 which was derived based on a biomass with empirical formula $CH_\varepsilon O_b$.

$$\varphi = \frac{m}{1+\frac{\varepsilon}{4}-\frac{b}{2}} \qquad [2\text{-}42]$$

where ε is the number of hydrogen atoms per carbon atom in the biomass molecule and b is the number of oxygen atoms per carbon atom in the biomass molecule.

The results from the studies carried out by Azzone *et al.* (2012) indicated that that the analysed and validated modified equilibrium model showed a behaviour which was coherent with the gasification process. Based on this modified model, the effects of gasification parameters such as ER, temperature and gasifying agents were evaluated for wood and agricultural residues such as maize stalks, rapeseed straw and sunflower seeds. The results from this model were found to correlate well with the experimental data obtained for these various types of biomass.

2.3.10 Simulation of liquid fuels production in Aspen Plus®

Studies carried out by Er-rbib *et al.* (2012) involve the simulation of dry reforming of methane for the production of synthetic petroleum and diesel fuel. The process of liquid fuels production was carried out by modelling a preheated natural gas feed to a reforming reactor in the presence of steam and carbon dioxide. The produced syngas undergoes a water removal step and cooling before entering the Fischer-Tropsch unit. Synthetic fuels produced in the Fischer-Tropsch reactor were sent to a distillation column which recovered petroleum, diesel and LPG.

The simulation was carried out in Aspen Plus®. The feed and product streams were specified as oxygen, nitrogen, carbon monoxide, carbon dioxide, hydrogen, water, alkanes, alkenes, and oxygenated hydrocarbons. The reactors and distillation columns were modelled thermodynamically based on the Peng-Robinson with the Boston-Mathias alpha function as all binary interaction parameters were available in Aspen Plus® (Er-rbib *et al.*, 2012).

The syngas unit was modelled by a two stage reactor. The first stage involved the conversion of the longer hydrocarbon chains to methane, carbon oxides and hydrogen based on a nickel catalyst. The reaction temperature was 550°C at an operating pressure of 5 bar. In the second stage the temperatures and pressures were varied from 700 – 1000°C and 1 – 5 bar. The steam to natural gas ratio was approximately 1.36 with a CO_2 feed ratio of 0.39. The Fischer-Tropsch unit was modelled based on a cobalt based catalyst. According to Sudiro *et al.* (2009), the Fischer-Tropsch synthesis requires a H_2/CO ratio in the range of 1.9 – 2.1. The process of low temperature Fischer-Tropsch was employed. This naturally has a higher selectivity for diesel and wax production. The Fischer-Tropsch synthesis was modelled on a temperature and pressure of 240°C and 20 bar respectively. Studies carried out by Sudiro *et al.* (2009) modelled conversion of syngas in the Fischer-Tropsch unit at 87%. Based on low temperature Fischer-Tropsch synthesis, the selectivity for liquid fuels production can be found according to Figure 2-18 (Sudiro *et al.*, 2009).

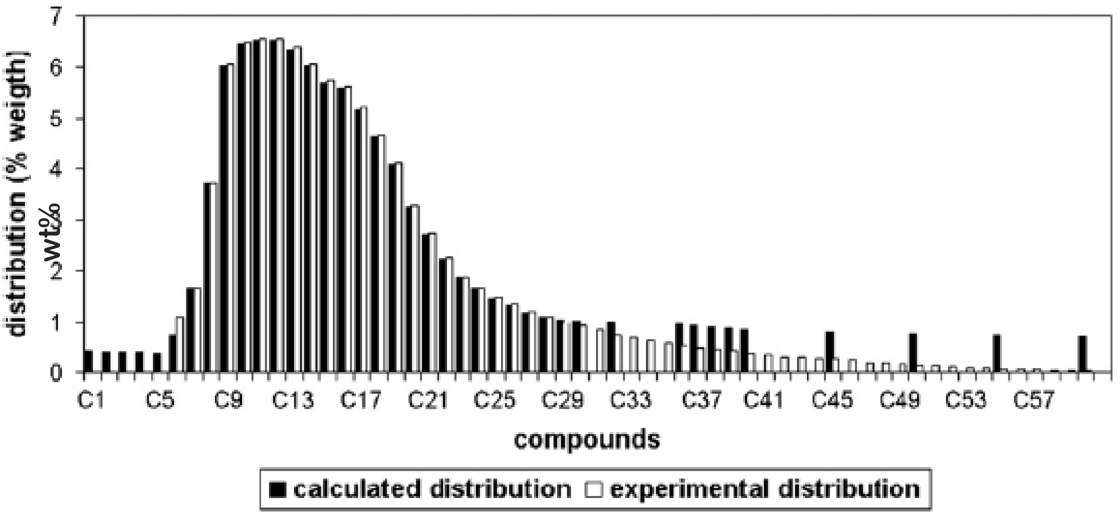


Figure 2-18: Selectivity of liquid fuels product distribution based on Low Temperature Fischer-Tropsch Synthesis (Sudiro & Bertucco, 2009)**.**

Results obtained from the study of Er-rbib *et al.* (2012) indicated that by increasing the H_2/CO ratio there is an increase in production rate of synthetic fuels (Figure 2-19). The effects of temperature and pressure on the H2/CO ratio was investigated (Figure 2-20). It was found that pressures varied between 1 – 5 bar had no effect As temperature increases the H_2/CO ratio increases.

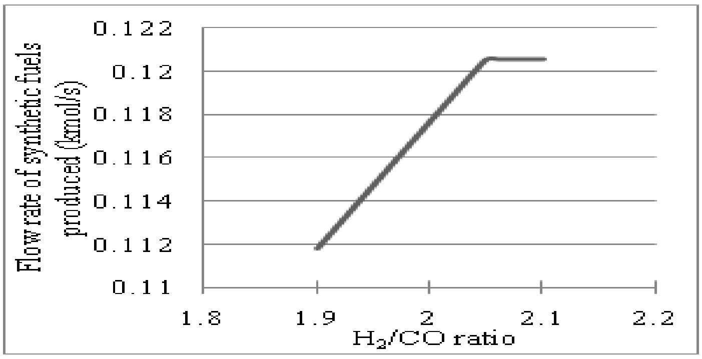


Figure 2-19: Effect of H_2/CO ratio on synthetic fuels production (Bezergianni & Kalogianni, 2009)

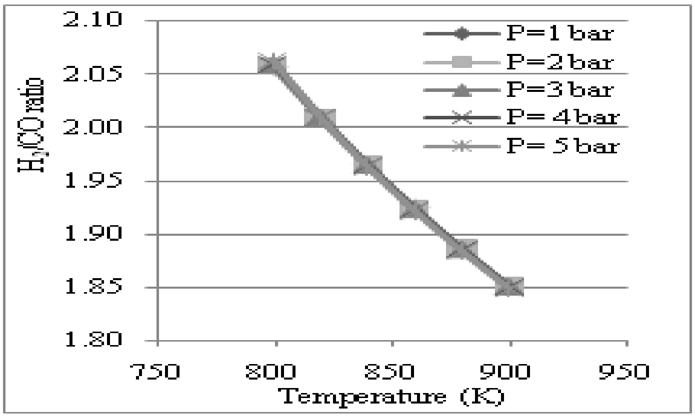


Figure 2-20: Effects of temperature and pressure on H_2/CO (Bezergianni & Kalogianni, 2009)

Waxes produced from the Fischer-Tropsch unit can be further processed through hydrocracking. Hydrocracking is the catalytic chemical process used to convert heavier hydrocarbon chains to ore valuable lower boiling point products such as petroleum, kerosene, jet fuel and diesel oil. The reaction takes place in the presence of hydrogen and a catalyst (U.S. Department of Energy, 2014). Hydrocracking is an alternative technology for biofuels production which employs existing process equipment of conventional petroleum refineries (Bezergianni & Kalogianni, 2009).

Bezergianni & Kalogianni (2009) conducted an investigation on used cooking oil as a hydrocracking feedstock and the impact of key process variables affecting yield and quality. In this study, the hydrocracking process occurred according to Figures 2-20 and 2-21. Bezergianni & Kalogianni (2009) found that temperature has a significant impact on catalyst effectiveness and life. Increasing temperature increases catalyst activity which also results in accelerated catalyst deterioration. The effects of temperature on selectivity of lighter hydrocarbon fuels was also examined.

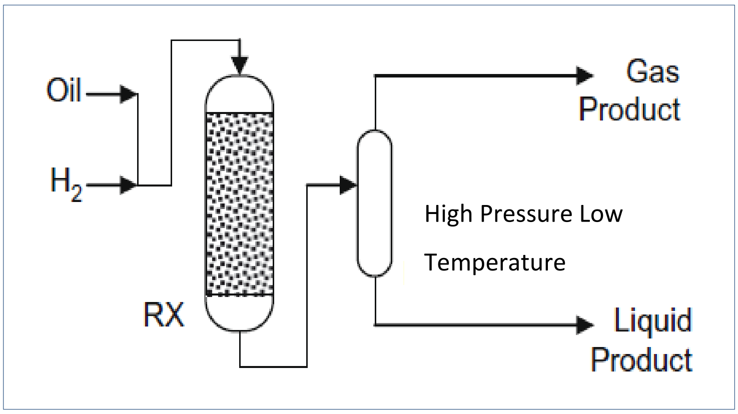


Figure 2-21: Hydrocracking process (Bezergianni & Kalogianni, 2009)

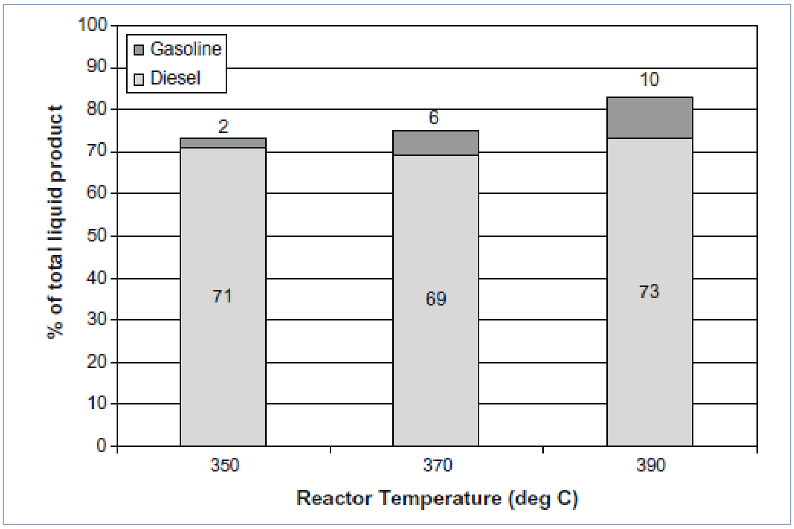
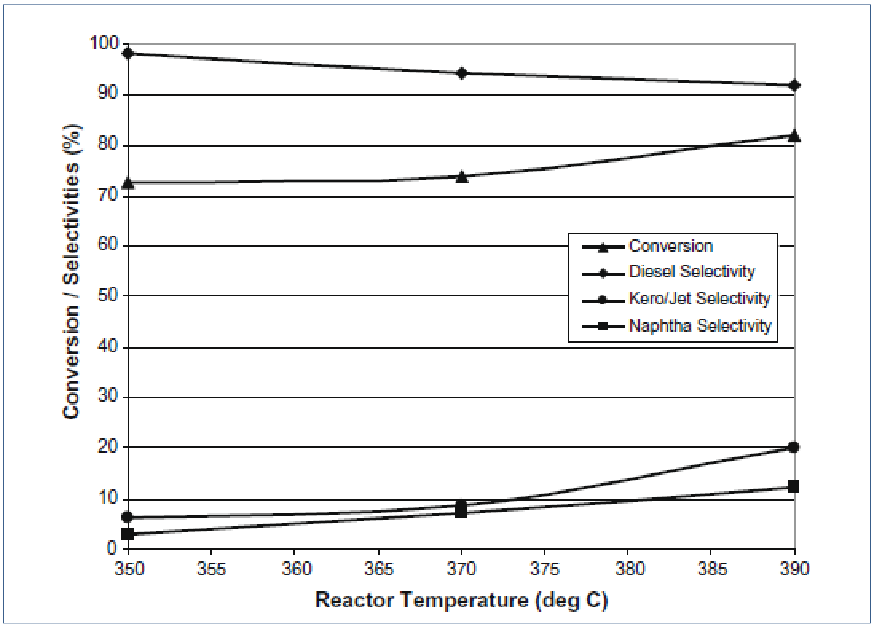


Figure 2-22: Effects of temperature on gasoline and diesel selectivity (Bezergianni & Kalogianni, 2009)

Product yields at three reactor temperatures: 350, 370 and 390°C are indicated by Figure 2-22. The diesel yield was estimated based on a boiling range of 180 – 360°C, while petroleum was estimated based on boiling range of 40 -200°C. All lighter products with a boiling point below 40°C were assumed to be in gaseous phase, while all products with a boiling point greater than 360°C were taken as unconverted feedstock, which cannot be used for liquid fuels production (Bezergianni & Kalogianni, 2009).

igure 2-23 indicates the conversion and selectivity of diesel, kerosene and naphta. The catalyst used for this study was not specified. As temperature increases, the conversion increases. At low temperatures however, diesel has a significant selectivity of greater than 90% while kerosene and naptha have a selectivity of less than 20%. Diesel selectivity is not favoured with increasing temperature as more intensive cracking occurs at increased temperature. This means at higher temperatures diesel molecules are cracked into lighter molecules (Bezergianni & Kalogianni, 2009; Suidiro & Bertucco, 2009).



igure 2-23: Effects of temperature on selectivity of liquid fuel products (Bezergianni & Kalogianni, 2009)

Coonradt & Garwood (1964) conducted studies on the dependency of hydrocracking on the activity of the hydrogenation component of dual function catalysts. The results obtained based on a platinum-silica-alumina catalyst are shown in Figure 2-24. It was found that the product composition was quite stable until conversion of 100% was reached. At this point secondary splitting started to occur at a more appreciable rate. Conversions of 53.1%, 81.6%, 98% and 100% occurred at temperatures of 370°C, 371°C, 394°C and 394°C respectively.

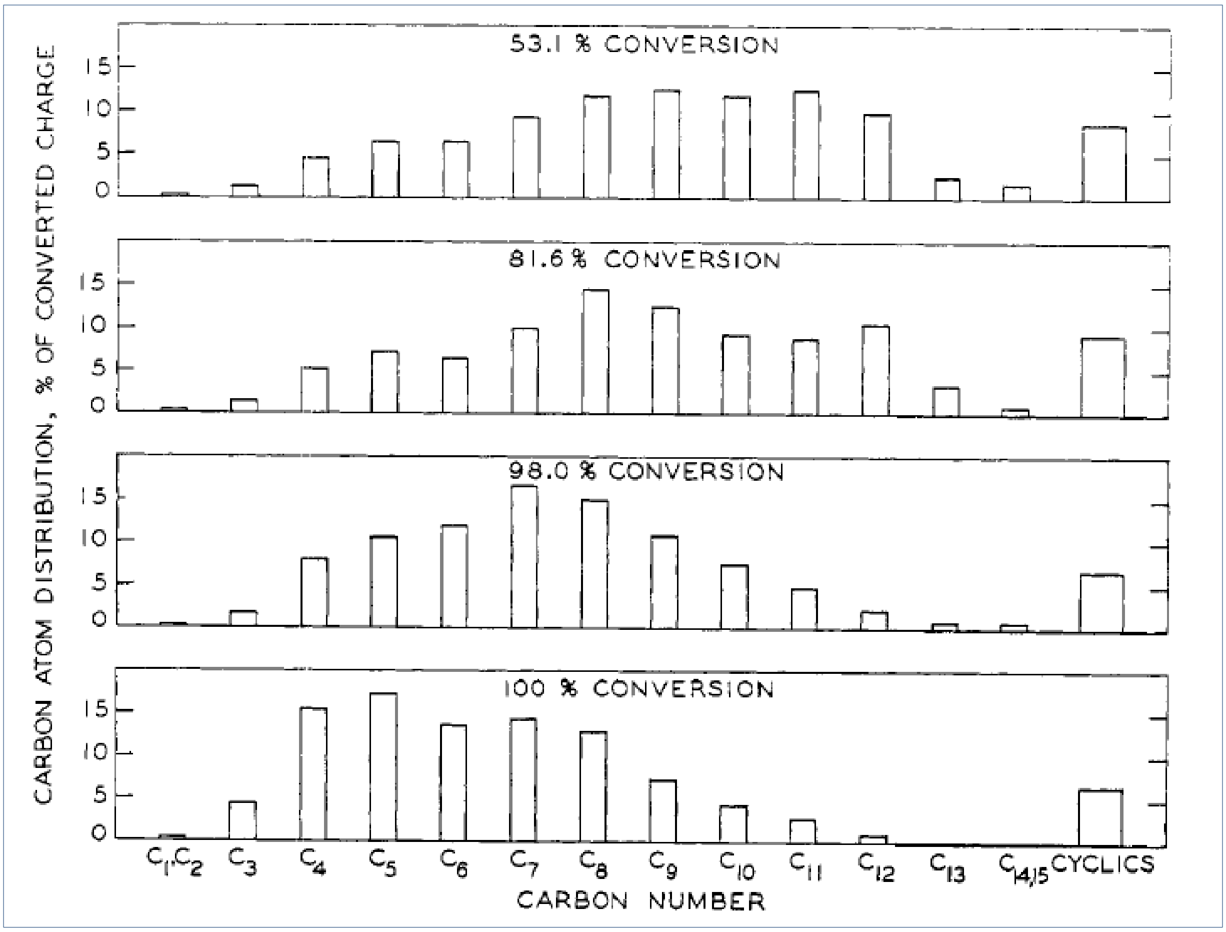


Figure 2-24: Hexadecane hydrocracked over a platinum-silica-alumina catalyst (Coonradt & Garwood, 1964)

2.4 Economic feasibility of FT processing

Studies carried out by Wood *et al.* (2012) indicate that there are a number of factors which affect the viability of a GTL operation. Major factors include:

- Cost of feedstock
- Price of end products
- Capital costs
- Plant efficiency, utilization and maintenance
- Logistical costs
- Operational costs
- Tax deductions and inflation/depreciation of assets

Due to the number of variables and unknowns, it is difficult to estimate the economic feasibility of maize on commercial scale operation. This is due to no existing commercial operation of biomass gasification and conversion to liquid fuels via Fischer-Tropsch synthesis to use as a basis. This makes it difficult to estimate capital investment and operating expenditure for maize conversion to liquid fuels.

Given the existing infrastructure in South Africa for syngas production and liquid fuels conversion for coal and natural gas, it is assumed that should maize be economically viable, it will be conducted on commercial scale through modification of existing operations to reduce capital investment. One major variable affecting economic feasibility is feed stock costs.

The change in raw material feed will result in huge process upset and affect production. Changes in logistics, processing and novelty of the process can lead to high operational costs, poor production and additional process modifications to address these issues. An example of this was the Sasol Oryx plant constructed in Qatar. Oryx was the first cobalt based low temperature Fischer-Tropsch commercial unit built by Sasol. The plant was commissioned in 2006 with a total investment cost of 1.4 billion U.S. dollars. This plant suffered from a number of initial challenges preventing it from reaching design capacity. It was described as ‘a source of disappointment felt throughout the entire GTL industry’. Sasol invested additional capital and capacity into addressing the faults. The plant is now able to produce at full design capacity (Meleloe & Walwayn, 2016).

Studies show that the GTL industry is exposed to significant risk regarding existing fossil fuel feed prices. There needs to be a sizeable deficit between raw material feed and petroleum product prices in order to support viability of a GTL plant. Volatile crude oil and natural gas prices makes it difficult for companies to commit the capital for new investment into a GTL plant which will only be commissioned 4 years into the future, where future market conditions can potentially change such that the plant is no longer economically viable. In addition, in order to compete with conventional oil refineries at oil prices less than 40 U.S. $/barrel, GTL plant raw material usage and operation either need to be significantly lower or more efficiently utilized to yield cost per ton of liquid fuels substantially lower than GTL plants in existence today.

Studies carried out by Wood *et al.* (2012) indicated that if the capital cost of a Fischer-Tropsch GTL plant was 100 U.S. $/barrel/day, with a feed gas cost of 5 U.S. $/mmBTU, the operating costs would be 20 U.S. $/barrel and the produced liquid products would cost in the vicinity of 100 U.S. $/ barrel. Based on these conditions, the economics of this plant would have already been unattractive in 2012. This production unit would have to achieve a lower operational cost or raw material cost to be economically viable.

Based on the above studies, raw material feed costs in relation to conventional feeds have a significant impact on securing the initial capital needed to construct a Fischer-Tropsch GTL plant. In addition, raw material feed costs in relation to conventional feeds have a continued impact on economic feasibility of a GTL plant once it is operational. Therefore the economic feasibility of liquid fuels production from maize will be expressed in terms of raw material cost differences between conventional fossil fuel feeds and maize.

Based on this literature study, a model of maize gasification and downstream processing for liquid fuels production will be developed to ascertain the feasibility of using maize as a feed for biofuels generation. Modelling gasification and FT synthesis based on a maize feed will give a reliable indication of the expected liquid fuels production and process parameters that can be expected without large capital investment. Results obtained from this study can provide a strong support to consider maize as a feed for biofuels production rather than sorghum. In addition, this agricultural crop can be considered as a supplement for synthetic fuels production via FT synthesis rather than bioethanol production as envisioned by the Biofuels Industry Strategy. Furthermore the results obtained from this model can be further contextualized based on existing environmental, economic and energy conditions in South Africa to indicate whether further investigation in the form of lab and pilot scale operations on maize as a feed for liquid fuels is worthwhile.

Based on the above literature study, syngas derived from biomass and converted to liquid fuels via FT synthesis can be an advantageous solution to South Africa’s energy crisis.

3 CHAPTER 3: MODEL DEVELOPMENT

3.1 Selection of Aspen Plus® software

Aspen Plus® was selected for modelling the gasification of maize as it is a software package capable of giving a complete and integrated solution to chemical processes and reactors. This specific software was selected due to its ability to define non-conventional fuels in terms of their ultimate and proximate analysis. In addition, Aspen Plus® also has an extensive built in physical properties database which can be used to facilitate all necessary simulation calculations. The Fortran code found within Aspen Plus® can also allow the user to alter the given model in order to operate the system within the user's specified limits and constraints (Mavukwana *et al.*, 2013; 2014).

3.2 Process description

Gas to liquids processes have been recognized as alternative methods for synthetic fuel production, which is environmentally benign and potentially highly profitable relative to crude oil resources (Sudiro & Bertucco, 2009; Er-rbib *et al.*, 2012). However, the most commonly used feedstock is natural gas. In this study, maize will be considered as a renewable feedstock for synthetic fuels production. This will be done through combining the process of maize gasification to generate syngas, with traditional gas to liquids processing to produce synthetic fuels from maize.

This process consists of four stages obtained, and combined from various literature studies related to gasification of maize, and liquid fuels generation from conventional fossil fuels (Sudiro & Bertucco, 2009; Er-rbib *et al.*, 2012; Mavukwana *et al.*, 2014).

i) The production of syngas from maize;
ii) The Fischer-Tropsch synthesis to produce long chain hydrocarbons;
iii) Upgrading of liquids and hydrocracking of waxes; and
iv) Hydrogen recovery

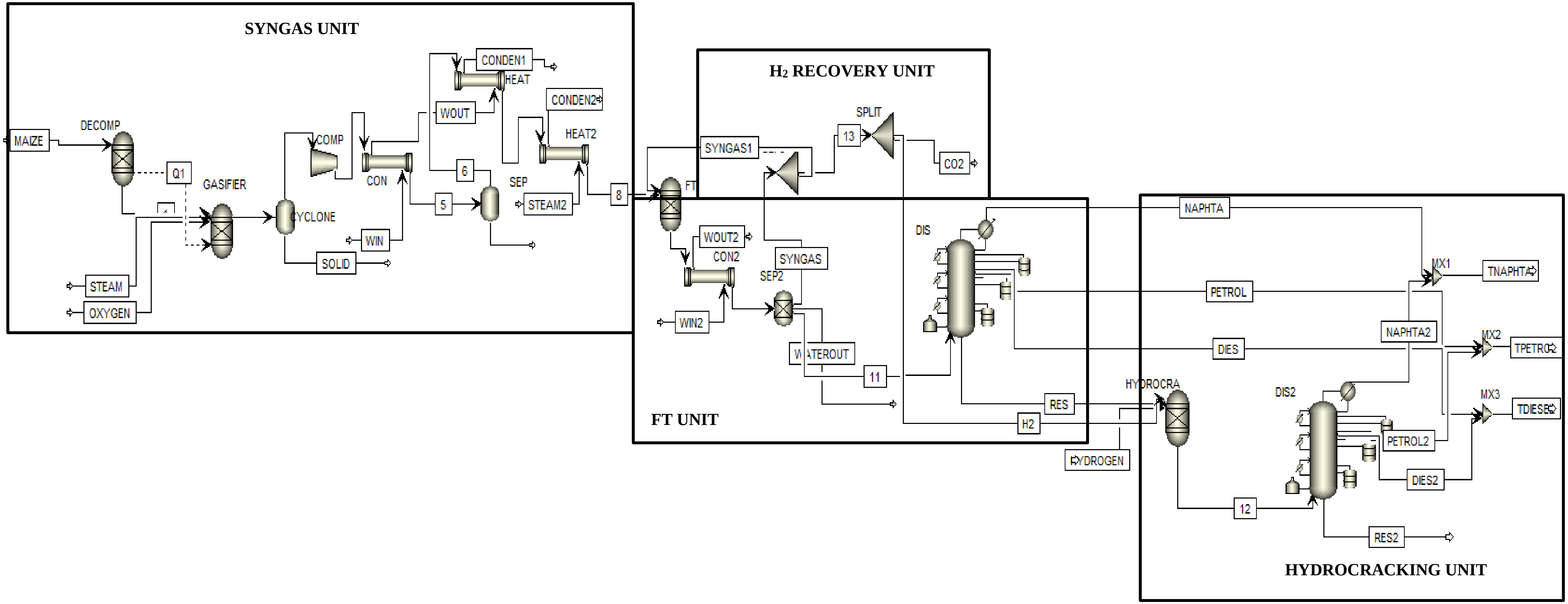


Figure 3-1: Process Flowsheet of Aspen Plus® simulation for maize gasification and FT processing for liquid fuels production

Figure 3-1 shows the overall process flowsheet generated from this study for maize gasification and FT processing. The maize is fed into a gasifier where it is reacted with steam and oxygen in order for gasification to take place. A similar setup was used by Mavukwana *et al.*, (2013; 2014). The gasification product is fed to a cyclone where solid material is removed. The resultant syngas undergoes cooling in order to condense and remove water. It is then re-heated before entering the Fischer-Tropsch reactor. The FT product is cooled to condense the reaction water and sent to a separator where water and unreacted syngas is removed from the produced synthetic fuels. The unreacted syngas is fed to a pressure swing adsorption unit modelled as two splitters, used to produce a high purity hydrogen stream and remove the undesired carbon dioxide. The remaining syngas is recycled to the FT reactor.

The produced synthetic fuel is sent to a distillation unit where it is separated based on boiling point, into naphta, petrol, diesel and residue. The heavy residue is sent to a hydrocracking unit together with a high purity hydrogen stream in order to crack the heavy hydrocarbon stream into more value lower boiling point products. The product stream from the hydrocracker is also sent to a distillation unit where it separated based on boiling point. The synthetic fuel product streams; naphtha, petrol and diesel from the FT and hydrocracker units, are combined to give the overall liquid fuels produced based on a maize feed.

3.3 Model construction

The simulation model was developed in Aspen Plus®. The thermodynamic model specified for gasification was Soave-Redlich-Kwong (SRK) (Mavukwana *et al.*, 2014), while the Fischer-Tropsch and hydrocracker reactors were modelled based on Peng-Robinson equation with Boston – Mathias alpha function (PR-BM) (Er-rbib *et al.*, 2012). All binary parameters needed for this simulation were available in Aspen Plus®.

3.3.1 Syngas unit

The process of maize gasification was broken into two stages, which were modelled through the use of a reactor yield block based on the Gibbs free energy model. The yield block first simulated the decomposition of the maize biomass into its elemental composition, based on its ultimate and proximate analysis, at ambient temperature and pressure. This product was then fed into the Gibbs reactor to simulate gasification. In order to account for non-equilibrium conditions, 5.5% of the overall product from the gasifier was considered to form tar based on the empirical formula $CH_{1.003}O_{0.33}$, obtained from studies carried out by Barman *et al.* (2012). The products of gasification were limited to H_2, CO_2, CO, CH_4, C_2H_4 and H_2O. A similar method for the modelling of biomass gasification was followed by Mavkwana *et al.* (2013; 2014) in the modelling of gasification of maize and sugarcane bagasse.

In order to model maize as a feedstock, it was specified as an unconventional solid. The property method Soave-Redlich-Kwong (SRK) was specifically chosen due to the availability of physical properties for nonconventional compounds. Maize was specified as a nonconventional fuel, as a result HCOALGEN and DCOALGT models were chosen in order to define the elemental and proximate analysis of maize (shown by Table 2-12). HCOALGEN is a coal enthalpy model and DCOALGT is the coal density model. This selection allows non-conventional solids to be modelled based on their ultimate and proximate analysis. The calculations used to determine the yield for the decomposition block are shown in Appendix A.1 Table 8-2. These calculations were determined based on a mass balance over the unit.

The outlet stream was then fed to a reactor block based on the Gibbs free energy model which was used to model the gasification process. Ash and tar were specified as inert, and oxygen and steam were used as gasifying agents for the process. Adiabatic conditions were assumed. The inputs for oxygen and maize were selected based on operation around the Free state/North West/Mpumalanga area, as maize cultivation occurs mostly in this region of South Africa (25°C and 101.325 kPa) (South Africa.com, 2017). Saturated steam at 8 bar was selected as the costs per kg were known for evaluations, which occur later on in this study (Omnia Fertilizer, 2017).

The outlet stream of the gasification reactor was then fed to a cyclone to model solid separation of the ash from the produced gases. The inputs of the cyclone were set as the outlet conditions of the gasification unit: 1 atm and 610°C. A cyclone is a device that separates particles from a gas stream using centrifugal force. The gas enters tangentially into the cyclone and is forced to follow the curved geometry of the cyclone, while the inertia of particles in the flow causes them to move towards the outer wall where they collide and collect. Cyclones can have an efficiency of up to 99% depending the particle size distribution (Paraschiv & Paraschiv, 2016). Centrifugal separators also have the ability to be used to separate liquid in the incoming stream. When cyclones are used within their design envelope, they effectively separate 99 percent of the liquid. Drops that are less than 10 microns in diameter are not usually separated (Peters, 2017). It is assumed that tar exits the gasifier as a liquid and is also removed from the syngas stream via cyclone separation.

The resultant hot gas stream was then passed through a heat exchanger to condense the excess water. Chilled water was used as a cooling medium. Water removal from the process was then modelled via a separator block which separated liquid and gas phase (Mavukwana *et al*., 2014; Er-rbib *et al*., 2012).

Figure 3-2 and Table 3-1 indicate the temperatures and pressures for each stream and the process flow sheet for the syngas unit.

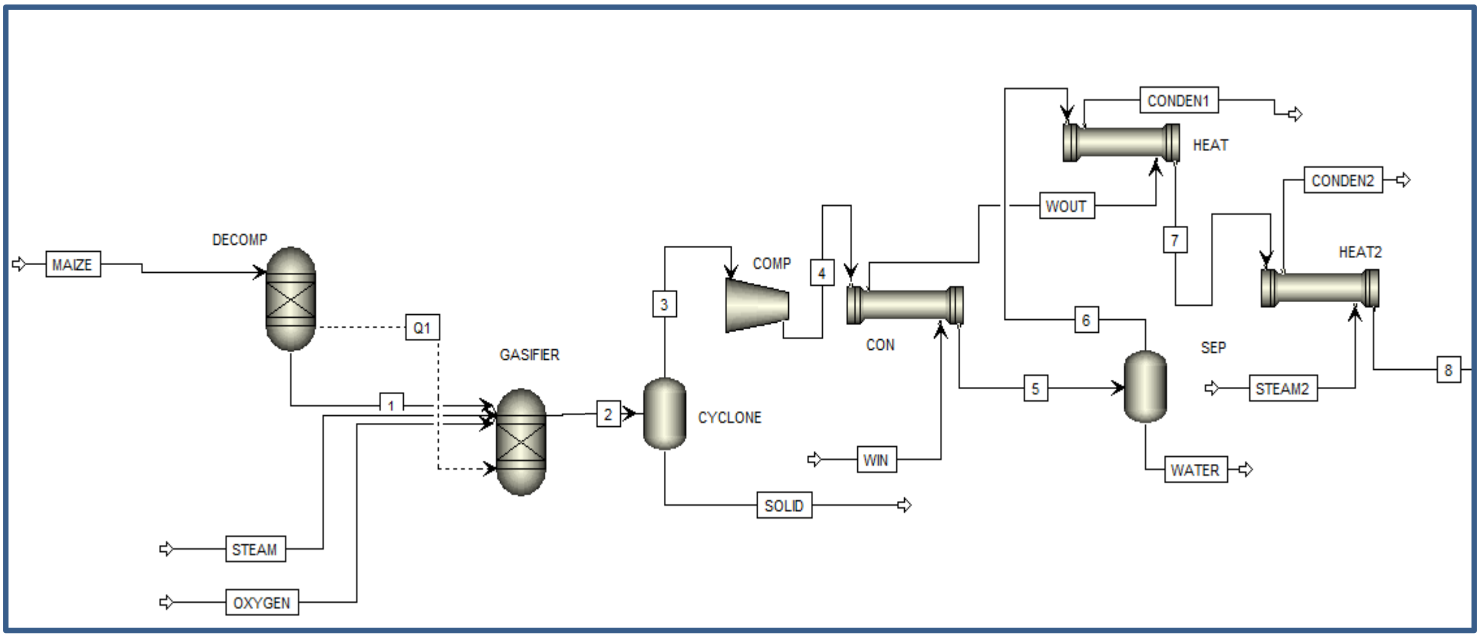


Figure 3-2: Aspen Plus® process flowsheet for syngas unit

Table 3-1: Key Process parameters for streams around syngas unit

Stream Name	Fluid	Temperature (°C)	Pressure (Bar)	Mass (kg/hr)
MAIZE	Maize	25	1	1000
STEAM	Steam	170.4	8	240
OXYGEN	Oxygen	25	8	220
1	Syngas	2906	1	1000
2	Syngas	611	1	1460
3	Syngas	611	1	1307
4	Syngas	519	3	1307
SOLID	Tar and Ash	611	1	1307
5	Syngas	55	3	153
6	Syngas	130	3	1307
7	Syngas	230	3	1071
8	Syngas	230	3	1071

3.3.1 Fischer-Tropsh (FT) unit

The catalytic reaction for the production of long chain hydrocarbons occurs in the Fischer-Tropsch reactor. The catalyst chosen was cobalt due its availability and selectivity for longer hydrocarbon chains in the form of petroleum, diesels and waxes. The Fischer-Tropsch reactor was modelled by a RYield reactor with the product distribution specified according to selectivity based on Table 3-3 (Sudiro *et al.*, 2009). The RYield block was chosen to represent the FT reactor, as it allows the yield of each product to be specified. This is a necessary approach when detailed information about the extents of the various reactions are unavailable. In the case of FT synthesis of syngas derived from maize, it is a bit difficult to define a set of reactions, which adequately describe the system. There is however, experimental data giving information about the products present and the quantities produced under certain conditions. In this case the yield for each product can be defined without knowing the exact stoichiometry of the reaction system. A mass balance was done based on reactions shown in Table 3-2, using the production distribution determined experimentally by Sudiro *et al.*, (2009). The property method Peng - Robinson equation with Boston - Mathias alpha function (PR-BM) was selected for the FT and hydrocracking units due to the available physical properties for liquid fuel products (Er-rbib *et al.*, 2012). The selectivity of the product compounds was determined by assuming low temperature Fischer-Tropsch synthesis and 87% conversion of syngas. (Sudiro *et al.*, 2009; Er-rbib *et al.*, 2012). This conversion was determined experimentally by Moulijn *et al.*, (2003). The FT process was specified to operate at a low temperature of 240°C to maximize diesel and wax production. (See appendix A.1 Table 8-3 Table for full calculation)

Table 3-2: Reactions used to model the reactions taking place in the FT reactor

1	CO	+	1	H_2O	------>	1	CO_2	+	1	H2
1	CO	+	3	H_2	------>	1	CH_4	+	1	H_2O
2	CO	+	5	H_2	------>	1	C_2H_6	+	2	H_2O
3	CO	+	7	H_2	------>	1	C_3H_8	+	3	H_2O
4	CO	+	9	H_2	------>	1	C_4H_{10}	+	4	H_2O
5	CO	+	11	H_2	------>	1	C_5H_{12}	+	5	H_2O
6	CO	+	13	H_2	------>	1	C_6H_{14}	+	6	H_2O
7	CO	+	15	H_2	------>	1	C_7H_{16}	+	7	H_2O
8	CO	+	17	H_2	------>	1	C_8H_{18}	+	8	H_2O
9	CO	+	19	H_2	------>	1	C_9H_{20}	+	9	H_2O
10	CO	+	21	H_2	------>	1	$C_{10}H_{22}$	+	10	H_2O
11	CO	+	23	H_2	------>	1	$C_{11}H_{24}$	+	11	H_2O
12	CO	+	25	H_2	------>	1	$C_{12}H_{26}$	+	12	H_2O
13	CO	+	27	H_2	------>	1	$C_{13}H_{28}$	+	13	H_2O
14	CO	+	29	H_2	------>	1	$C_{14}H_{30}$	+	14	H_2O

15 CO + 31 H_2 ------> 1 $C_{15}H_{32}$ + 15 H_2O
16 CO + 33 H_2 ------> 1 $C_{16}H_{34}$ + 16 H_2O
17 CO + 35 H_2 ------> 1 $C_{17}H_{36}$ + 17 H_2O
18 CO + 37 H_2 ------> 1 $C_{18}H_{38}$ + 18 H_2O
19 CO + 39 H_2 ------> 1 $C_{19}H_{40}$ + 19 H_2O
20 CO + 41 H_2 ------> 1 $C_{20}H_{42}$ + 20 H_2O
21 CO + 43 H_2 ------> 1 $C_{21}H_{44}$ + 21 H_2O
22 CO + 45 H_2 ------> 1 $C_{22}H_{46}$ + 22 H_2O
23 CO + 47 H_2 ------> 1 $C_{23}H_{48}$ + 23 H_2O
24 CO + 49 H_2 ------> 1 $C_{24}H_{50}$ + 24 H_2O
25 CO + 51 H_2 ------> 1 $C_{25}H_{52}$ + 25 H_2O
26 CO + 53 H_2 ------> 1 $C_{26}H_{54}$ + 26 H_2O
27 CO + 55 H_2 ------> 1 $C_{27}H_{56}$ + 27 H_2O
28 CO + 57 H_2 ------> 1 $C_{28}H_{58}$ + 28 H_2O
29 CO + 59 H_2 ------> 1 $C_{29}H_{60}$ + 29 H_2O
30 CO + 61 H_2 ------> 1 $C_{30}H_{62}$ + 30 H_2O
32 CO + 65 H_2 ------> 1 $C_{32}H_{66}$ + 32 H_2O
35 CO + 71 H_2 ------> 1 $C_{35}H_{72}$ + 35 H_2O
39 CO + 79 H_2 ------> 1 $C_{39}H_{80}$ + 39 H_2O
1 CO + 2 H_2 ------> 1 CH_3OH + 0 H_2O
2 CO + 4 H_2 ------> 1 C_2H_5OH + 1 H_2O
3 CO + 6 H_2 ------> 1 C_3H_7OH + 2 H_2O
4 CO + 8 H_2 ------> 1 C_4H_9OH + 3 H_2O
5 CO + 10 H_2 ------> 1 $C_5H_{11}OH$ + 4 H_2O
6 CO + 12 H_2 ------> 1 $C_6H_{13}OH$ + 5 H_2O

Table 3-3: Selectivity used to determine the product distribution for the FT product stream (Sudiro *et al.* 2009)

Carbon Number	Selectivity
C1	0.39%
C2	0.38%
C3	0.38%
C4	0.38%
C5	0.40%
C6	0.70%
C7	1.60%
C8	3.70%
C9	6.10%
C10	6.40%
C11	6.70%
C12	6.78%
C13	6.30%
C14	6.00%
C15	5.80%
C16	5.50%
C17	5.20%

C18	4.80%
C19	4.00%
C20	3.20%
C21	2.80%
C22	2.50%
C23	2.20%
C24	2.00%
C25	1.80%
C26	1.70%
C27	1.60%
C28	1.20%
C29	1.20%
C30	1.20%
C32	1.20%
C35	5.00%
COH1	0.15%
COH2	0.10%
COH3	0.10%
COH4	0.15%
COH5	0.15%
COH6	0.15%

The produced liquid fuels were then sent to a distillation unit modelled by the Aspen Plus® Petrofrac unit. The produced streams were defined as naphtha, petrol, diesel and residue, and were separated based on boiling points. Petroleum, diesel and wax were defined as C_5 – C_{11}, C_{12} – C_{18} and C_{20} – C_{60} respectively. The diesel yield was estimated based on a boiling range of 200 – 360°C, while petroleum was estimated based on a boiling range of 40 - 200°C. All lighter products with a boiling point below 40°C were assumed to be naphtha, while all products with a boiling point greater than 360°C were taken as unconverted feedstock and fed to the hydrocracking unit (Bezergianni & Kalogianni, 2009). Figure 3-3 and Table 3-4 indicate the temperatures and pressures for each stream and the process flow sheet for the FT unit.

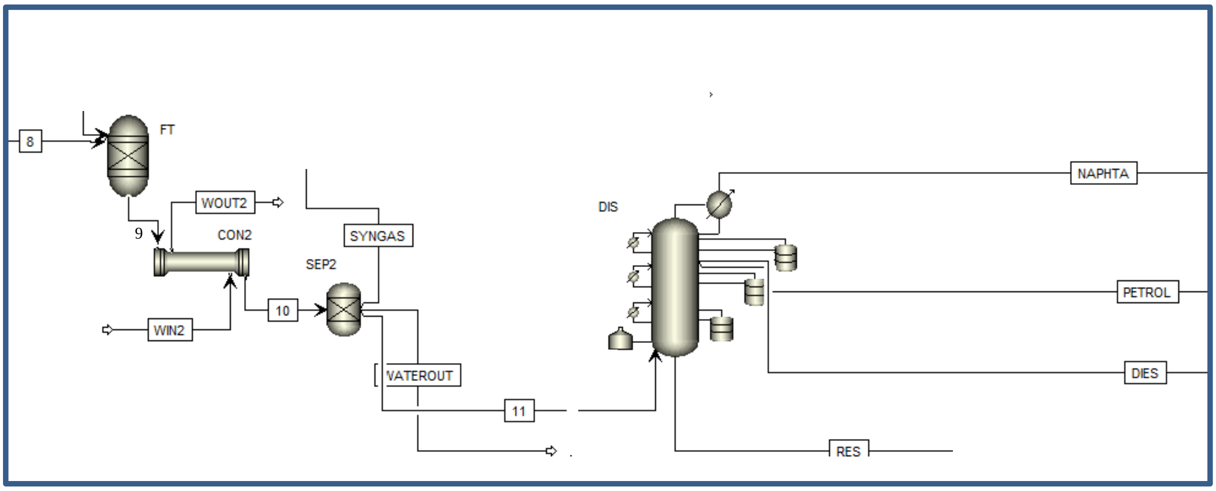


Figure 3-3: Aspen Plus® process flowsheet for FT unit

Table 3-4: Key process parameters for streams around FT unit

Stream Name	Fluid	Temperature (ºC)	Pressure (Bar)	Mass (kg/hr)
9	FT Product	240	15	1314
10	FT Product	90	15	1314
SYNGAS	Syngas	90	15	818
WATEROUT	Reaction Water	90	15	239
11	Synthetic Fuel	90	15	257
NAPHTHA	Naphtha	40	1	123
PETROL	Petrol	181	1	35
DIES	Diesel	221	1	60
RES	Heavy Residue	377	1	40

3.3.2 Hydrogen (H_2) recovery unit

Hydrocracking requires a hydrogen feed to support the reactions. As a result, a hydrogen recovery unit was required in order to provide a source of H_2. This process is known as pressure swing adsorption which is technology used for separating and purifying a gas mixture (Er-rbib *et al.*, 2012).

Major applications of the pressure swing adsorption (PSA) process include the recovery of high purity hydrogen, methane and carbon dioxide. PSA units provided by Linde Engineering, are designed for the recovery and purification of hydrogen obtained from syngas streams or off gases in petrochemical processes. The Linde hydrogen PSA units have a range of capacities from < 100 Nm3/hr to 400 000 Nm3/hr. The hydrogen product can be purified to 99.9999 mol% at high recovery rates of 70 - 90%. A minimum of 4 absorber vessels are required to ensure a continuous hydrogen supply (Linde Engineering, 2016).

The PSA process involves 2 main stages:

i) Adsorption
ii) Regeneration

Adsorption

PSA technology is based on the physical binding of gaseous molecules to an adsorbent material. The forces governing separation of the gas components are dependent on type of adsorbent material, partial pressure and operating temperature. The separation is based on differences in binding forces to the adsorbent material. Highly volatile components with low polarity such as H_2 are nearly non-absorbable in comparison to N_2, CO, CO_2, hydrocarbon vapours and water vapour. As a result, these impurities can be adsorbed producing a high purity hydrogen stream.

Adsorption of impurities occur at high pressures between 10 – 40 bar. The PSA process is isothermal and uses the effect of alternating pressure and partial pressure to perform adsorption and desorption. As a result of equilibrium being reached, the adsorption phase stops and regeneration of the absorbent takes place.

Regeneration

Regeneration involves the lowering of pressure slightly above atmospheric conditions resulting in a respective decrease in equilibrium loading. The impurities are desorbed at this point; regenerating the adsorbent material. Desorption is achieved through the use of highly pure hydrogen obtained from another adsorption unit, which moves impurities into the total gas stream. Re-pressurization is achieved by a split stream from the hydrogen product line. After termination of the regeneration step, pressure is increased back to adsorption pressure level and the process repeats.

The PSA process is assumed to be a turn-key unit and is modelled by two splitters which is fed by the unreacted syngas stream. 70% of the hydrogen in the syngas stream is assumed to exit as the pure hydrogen stream. A high purity CO_2 stream was also purged from the process at this stage (Linde Engineering, 2016). The remaining gaseous components from the unreacted syngas stream is recycled back to the FT reactor (Er-rbib *et al.*, 2012). Figure 3-4 and Table 3-5 indicate the temperatures and pressures for each stream and the process flow sheet for the H_2 Recovery Unit.

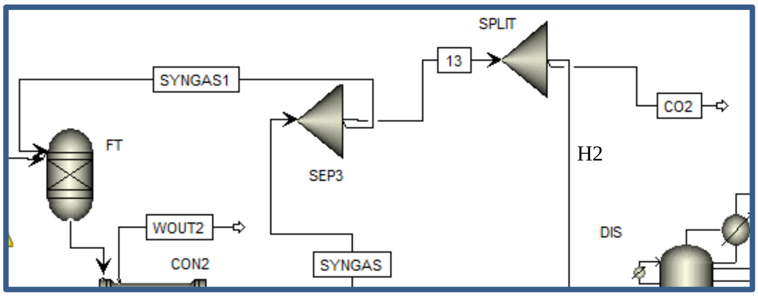


Figure 3-4: Aspen Plus® flowsheet for H_2 recovery unit

Table 3-5: Key process parameter for streams around the H_2 recovery unit

Stream Name	Fluid	Temperature (°C)	Pressure (Bar)	Mass (kg/hr)
SYNGAS1	Syngas	90	15	243
13	H_2/CO_2	90	15	575
H2	Hydrogen	90	15	29
CO2	Carbon dioxide	90	15	546

3.3.3 Hydrocracking unit

The heavy residue stream from the distillation unit was converted to lower weight hydrocarbons through hydrocracking. The hydrocracking operation was modelled through a RYield reactor. The product yield was determined based on 98% conversion of wax according to Figure 2-24 (Coonradt & Garwood, 1964). Full calculations can be found in Appendix A.1 Table 8-4. Based on these calculations it was found that additional hydrogen stream of 22 kg/hr was necessary to achieve the 98% conversion of residue.

The produced hydrocarbon stream was then fed to a second distillation unit, which was modelled similarly to the first. Petroleum, diesel and wax were defined as $C_5 – C_{11}$, $C_{12} – C_{18}$ and $C_{20} – C_{60}$ respectively. The diesel yield was estimated based on a boiling range of 200 – 360°C, while petroleum was estimated based on a boiling range of 40 - 200°C. All lighter products with a boiling point below 40°C were assumed to be in gaseous phase. While all products with a boiling point greater than 360°C were taken as unconverted feedstock unable to be converted to liquid fuels (Bezergianni & Kalogianni, 2009). Figure 3-5 and Table 3-6 indicate the temperatures and pressures for each stream and the process flow sheet for the hydrocracking unit.

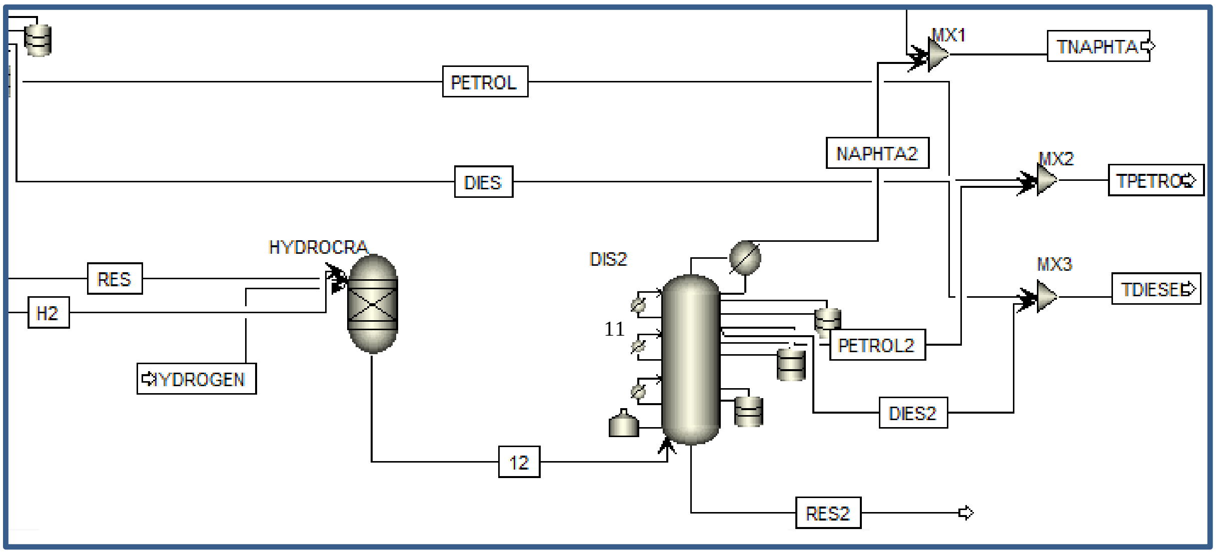


Figure 3-5: Aspen Plus® Flow sheet for hydrocracking unit

Table 3-6: Key process parameters for streams around hydrocracking unit

Stream Name	Fluid	Temperature (ºC)	Pressure (Bar)	Mass (kg/hr)
HYDROGEN	Hydrogen	25	14	22
12	Hydrocracked product	394	14	636
NAPHTHA2	Naphtha	40	14	29
PETROL2	Petrol	180	14	482
DIES2	Diesel	360	14	95
RES2	Residue	370	14	31

3.4 Assumptions used for model construction

The following assumptions were made throughout:

- Ash is an inert, as a result it does not participate in any chemical reactions and can be removed via solid separation (Mavukwana *et al.*, 2014). Tar is assumed to be in liquid phase and can also be removed via separation in the cyclone (Peters, 2017).

- Gasification occurs at atmospheric pressure 1.032 bar. The system is adiabatic, isobaric and occurs under steady state conditions (Azzone *et al.*, 2012; Mavukwana *et al.*, 2014).

- The gasification system tends to equilibrium and obeys the assumptions of the Gibbs free energy minimisation model (Mavukwana *et al.*, 2012; 2014):
    - At equilibrium the Gibbs free energy of the system is at a minimum; and
    - Real gases behave as ideal gases at a pressure of 1 atm.
    - Heavy hydrocarbon chains such as tar are not typically considered in the product stream as these compounds are not formed under equilibrium conditions. Since experimental data shows tar formation this indicates equilibrium conditions are not met. Therefore it was assumed 5.5% of the total product from gasification was assumed to form tar with the empirical formula of $CH_{1.003}O_{0.33}$ based on studies carried out by Barman *et al.*, (2012).

- Gasification products were specified as H_2, CO_2, CO, CH_4 and C_2H_4. No S, Cl or N was reported in the ultimate and proximate analysis (Ioannidou *et al.*, (2009), therefore no contaminants in the form of HCl, COS and H_2S were formed.

- 87% conversion of syngas to liquid fuels occurs in the Fischer-Tropsch unit (Sudiro e*t al.*, 2009)

- Selectivity of liquid fuels produced was based on Figure 2-18 (Sudiro *et al.*, 2009).

- Hydrocracking reactions are assumed to take place at 394°C and 14 bar on a platinum-silica-alumina catalyst. Selectivity of products obtained from the hydrocracking unit was based on Figure 2-24 (Coonradt & Garwood, 1964)

- Hydrogen recovery unit recovers H_2 at a purity of 99.95% (Er-rbib *et al.*, 2012; Linde Engineering, 2016).

- Petroleum, diesel and wax were defined as $C_5 – C_{11}$, $C_{12} – C_{18}$ and $C_{20} – C_{60}$ respectively. The diesel yield was estimated based on a boiling range of 180 – 360°C. Petroleum was estimated based on a boiling range of 40 - 200°C (Sudiro & Bertucco, 2009; Er-rbib *et al.*, 2012).

- All products with a boiling point greater than 360°C after the hydrocracking unit were taken as unconverted feedstock and composed the unconverted part of the feed that cannot be utilized as liquid fuels (Bezergianni & Kalogianni, 2009).

3.5 Process optimization

Sensitivity analyses were carried out over the gasification unit, in order to find the optimum operating conditions which maximize high quality syngas production from maize gasification. An optimal H_2/CO ratio of 1.9 – 2.15 is required for Fischer-Tropsch synthesis and liquid fuels production (Mavukwana *et al.,* 2014; Sudiro & Bertucco, 2009; Er-rbib *et al.,* 2012). The effects of the following process parameters: equivalence ratio, steam to biomass ratio, temperature and pressure on syngas composition and the H_2/CO ratio were investigated. The sensitivity analyses were carried out in Aspen Plus® by specifying each process parameter as the independent variable and examining its effects on syngas composition.

3.6 Analyses carried out on Aspen Plus® simulation

The following analyses were carried out on the generated Aspen Plus® simulation of maize gasification and FT processing for liquid fuels production. These analyses were done in order to address the objectives of this study listed below:

- Validate the Aspen Plus® simulation of maize gasification with experimental data obtained from literature in terms of product gas composition;
- Determine (based on the Aspen Plus® simulation) the optimum reactor conditions (equivalence ratio, steam to biomass ratio, temperature and pressure) and configuration which yields the highest quality syngas production in comparison to literature;
- Determine the feasibility of maize as a feed for syngas and liquid fuels production in South Africa; and
- Evaluate the viability of maize gasification to produce liquid fuels on a commercial scale from an economic and energy perspective.

3.6.1 Validation of Aspen Plus® simulation for maize gasification and liquid fuels production

The Aspen Plus® simulation for syngas production from maize was determined through optimizing the reactor operating conditions. The optimum reactor conditions for maximum quality and yield of syngas was determined via carrying out sensitivity analyses for each specified process parameter: ER, SBR, temperature and pressure. The resultant syngas composition based on these optimized parameters was then verified and evaluated against other simulation studies and experimental data obtained from literature.

The simulation of FT processing to produce liquid fuels from maize was evaluated against the ideal product distribution for FT synthesis represented by the Anderson-Shultz-Flory (ASF) equation, and real data obtained from industry for conventional fossil fuel conversions. The ASF equation, shown by equations 2-9 – 2-11, is a proposed kinetic model frequently used to describe the product distribution from Fischer-Tropsch synthesis. This model assumes an ideal polymerization reaction where a single growth probability factor α is able to determine the hydrocarbon chain length (Dry, 1981; Donnelly, 1989). Studies carried out indicate a cobalt based catalyst resulted in a product distribution, which can be represented by a α factor of 0.89 (Matsumoto, 1987; Donnelly, 1989). Therefore a α factor of 0.89 was chosen to represent the expected production from the ASF equation.

No optimization was carried out on these reaction units, as these process parameters were determined according to experimental data obtained from literature (Coonradt & Garwood, 1964; Sudiro *et al.*, 2009; Er-rbib *et al.*, 2012).

3.6.2 Feasibility of maize as a feedstock for syngas and liquid fuels production in South Africa

The feasibility of maize as a feedstock for syngas production was done based on an evaluation of quality and yield of syngas obtained from the simulation, compared to the quality requirements for syngas used for FT synthesis and liquid fuels production.

The feasibility of liquid fuels production from maize in South Africa was evaluated based on the constraints outlined in the Biofuels Industry Strategy (2007). This strategy stipulated that renewable energy sources must not affect food security, consume additional amounts of water and, ideally make use of underutilized land located in the Homelands of South Africa. Based on this available land and the average production of maize per hectare without irrigation, the feasibility of liquid fuels produced from maize in South Africa could be determined.

3.6.3 Economic feasibility of liquid fuels production from gasification of maize

The economic feasibility of liquid fuels production from maize was evaluated based on raw material costs for coal, natural gas and oil. In order to create the same basis for comparison, the H_2/CO ratio of 2.20 was fixed in order to keep the downstream operation and liquid fuels production the same. The coal and steam feed necessary to produce a H_2/CO ratio of 2.2 was determined according to the ultimate and proximate analysis shown in Appendix B.6 Table 9-13. (For full calculations refer to Tables 9-13 – 9-15). The natural gas and steam feed necessary to produce the H_2/CO ratio of 2.2 was determined according to the reactions outlined in Table 9-16.

The economic feasibility was determined by expressing raw material costs as a percentage of revenue generated through sales of liquid fuels. Sensitivity analyses were carried out on conventional fossil fuel feed costs, (natural gas, coal and crude oil) to determine the economic environment conducive for maize gasification and liquid fuels production. The sensitivity analyses were done by treating the coal, natural gas and oil price as independent variables. Through changing these variables the effect on economic feasibility of liquid fuels produce from maize could be examined. Further analysis was carried out on the Rand/U.S. Dollar exchange rate. By using the exchange rate as an independent variable, the effects on all fossil fuel feeds could be seen and the economic feasibility of maize could be determined.

3.6.4 Feasibility of liquid fuels production from maize gasification from an energy perspective

The Aspen Plus® simulation for maize gasification and liquid fuels production was examined from a thermal perspective to evaluate energy usage and feasibility of the process.

The process was further evaluated in terms of its steam requirements and CO_2 emissions per kg of maize feed in comparison to natural gas and coal. The steam requirements and CO_2 emissions for natural gas and coal, were determined by fixing the H_2/CO ratio from the gasifier to the FT reactor. The coal and steam feed necessary to produce a H_2/CO ratio of 2.2 was determined according to the ultimate and proximate analysis shown in Appendix B.6 Table 9-13. (For full calculations refer to Tables 9-13 – 9-15). The natural gas and steam feed necessary to produce the H_2/CO ratio of 2.2 was determined according to the reactions outlined in Table 9-16.

4 Chapter 4: ASPEN PLUS® MODEL VALIDATION

The Aspen Plus® simulation developed in this study was based on data obtained from literature. The gasification unit was modelled based on the ultimate and proximate analysis from studies carried out by Ioannidou *et al.* (2009) and followed a similar method to Mavukwana *et al.* (2014). In order to account for tar formation which occurs under experimental conditions, it was assumed that 5.5% of the total gasification product forms tar (Barman *et al.* 2012). The Fischer-Tropsch and hydrocracking unit was modelled based on product distributions experimentally determined by Sudiro & Bertucco (2009) and Coonradt & Garwood (1964). In the following sections, the outputs from each reactor will be compared to experimental data obtained from literature in order to validate and ensure the reliability of the developed Aspen Plus® simulation.

4.1 Gasification unit

Sensitivity analyses were carried out over the gasification unit in order to find the optimum operating conditions which maximized quality syngas production from maize gasification. Syngas quality for the purposes of this study, is defined as the maximum individual hydrogen and carbon monoxide molar volumes, as well as maximum H_2/CO ratio for the overall gas composition that can be achieved based on a maize feedstock. This is necessary in order to meet the requirements for liquid fuels production based on a Co catalyst for FT synthesis (Ciferno & Marno, 2002). Since the system was assumed to be adiabatic, the temperature of the gasifier was determined based on the air and steam feed. The effects of the following process parameters: equivalence ratio, steam to biomass ratio, temperature and pressure on syngas composition, and the H_2/CO ratio were investigated. Figures 4-1; 4-3 and 4-5 – 4 -7 indicate the results obtained for these process variables based on the Aspen Plus® simulation constructed in this study. It was found that the equivalence ratio and steam to biomass ratio had the biggest impact on syngas molar composition. Table 4-1 indicates the optimized process values which maximized syngas quality.

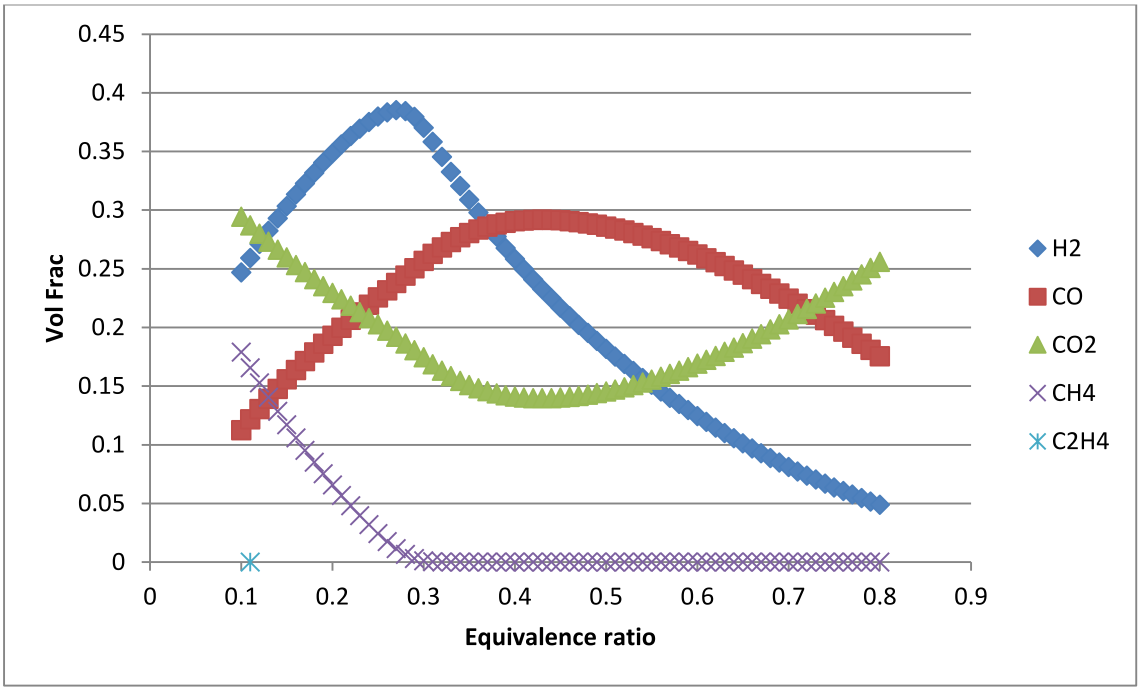


Figure 4-1: Effect of equivalence ratio on syngas composition at a pressure of 101.325 kPa and SBR of 0.2

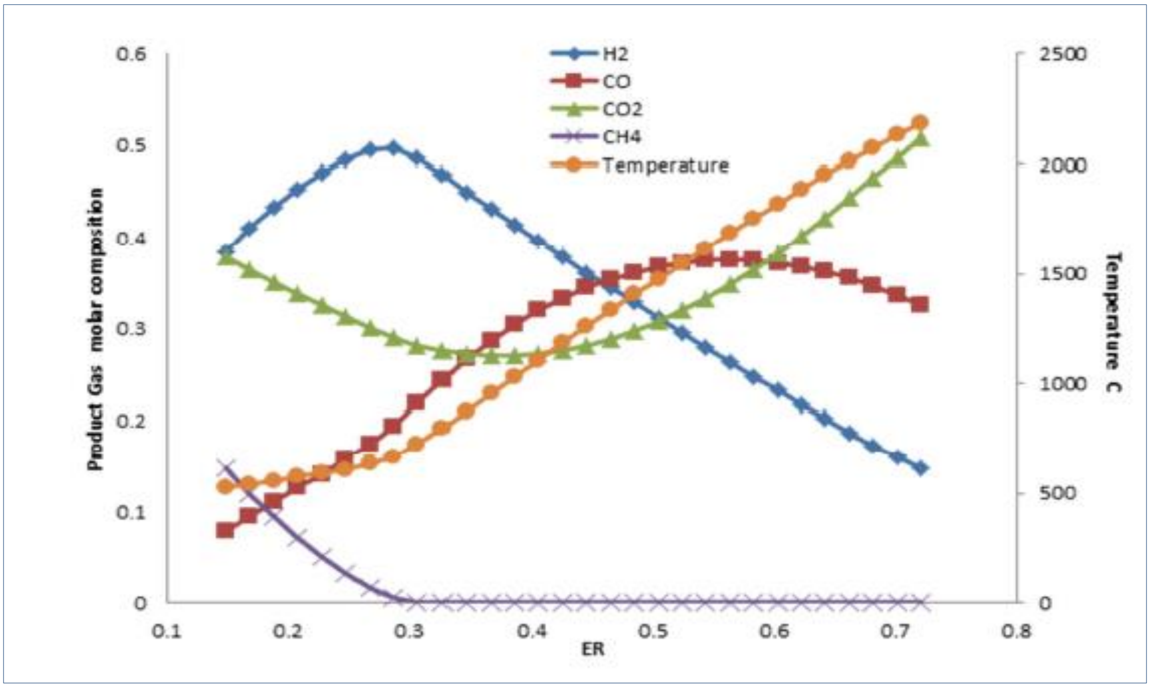


Figure 4-2: Effects of equivalence ratio on syngas molar composition (Mavukwana *et al.*, 2012)

a Effects of air on syngas molar composition:

Figure 4-1 indicates the effect of equivalence ratio on syngas composition based on the developed Aspen Plus® model. Based on the results obtained from this study, there was an increase in H_2 and CO molar composition when the equivalence ratio was within a range of 0.2 – 0.3. This is consistent with the reactions that take place during gasification which are shown by equations 2-19, 2-20, and 2-23. As the equivalence ratio increased the temperature of the system increased. This favoured the forward reaction represented by equation 2-19, which is endothermic resulting in the formation of CO and a corresponding decrease in CO_2. At equivalence ratios greater than 0.3 there is enough oxygen present for complete combustion of CO and H_2. This resulted in an increase in formation of CO_2 and H_2O and a corresponding decrease in CO and H_2.

Equation 2-23 is the methanation reaction which is exothermic. Based on the relationship of equivalence ratio and temperature, as equivalence ratio increased the reverse reaction was favoured. This resulted in the suppression of CH_4 formation which explains the observed trend of CH_4 molar composition with increasing air feed to the gasifier.

The sensitivity analysis obtained from the Aspen Plus® simulation for maize gasification in this study was found to be in good agreement with Aspen Plus® sensitivity analyses carried out by Mavukwana *et al.* (2013) shown by Figure 4-2.

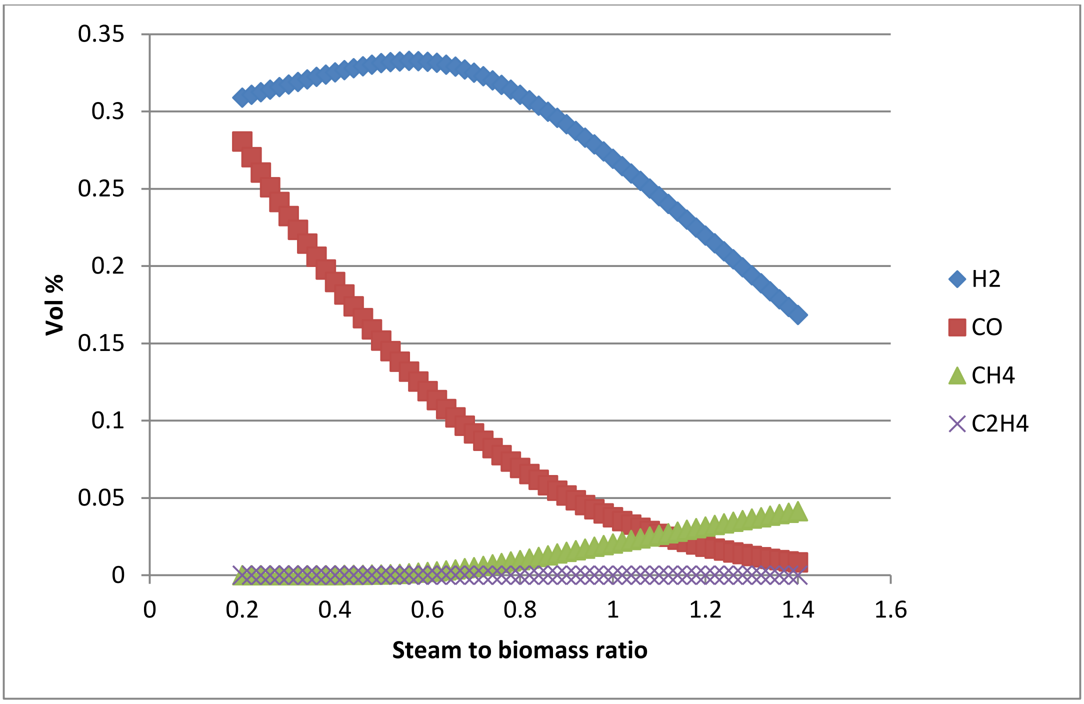


Figure 4-3: Effects of steam to biomass ratio on syngas composition at a pressure of 101.325 kPa and ER ratio of 0.22

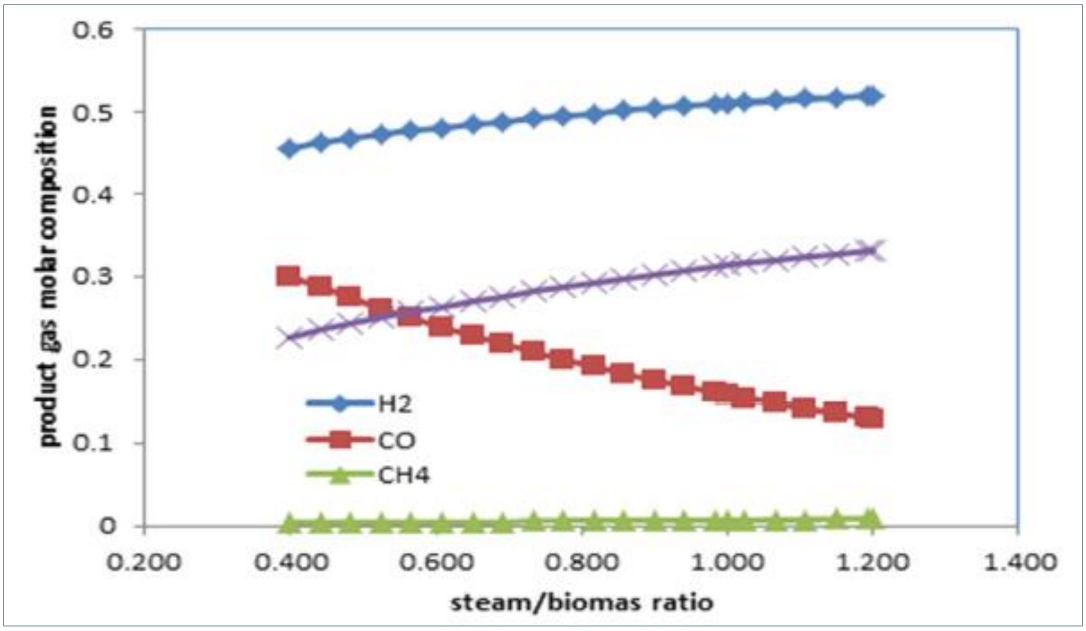


Figure 4-4: Effects of steam to biomass ratio on syngas molar composition (Mavukwana *et al.*, 2012)

b Effects of Steam on Syngas molar composition:

Figure 4-3 indicates the effect of steam to biomass ratio on syngas composition at a fixed equivalence ratio of 0.22 based on the developed Aspen Plus® simulation. As the steam to biomass ratio increased the H_2 molar composition increased while a decrease in CO and CO_2 is observed. This trend is as a result of equations 2-3, 2-20 and 2-22. The CH_4 production decreased due to the steam reforming reactions shown by equations 2-2 – 2-4. Mavukwana *et* *al.* (2013) found a similar behaviour for syngas composition with varied steam feed to the gasifier as shown by Figure 4-4.

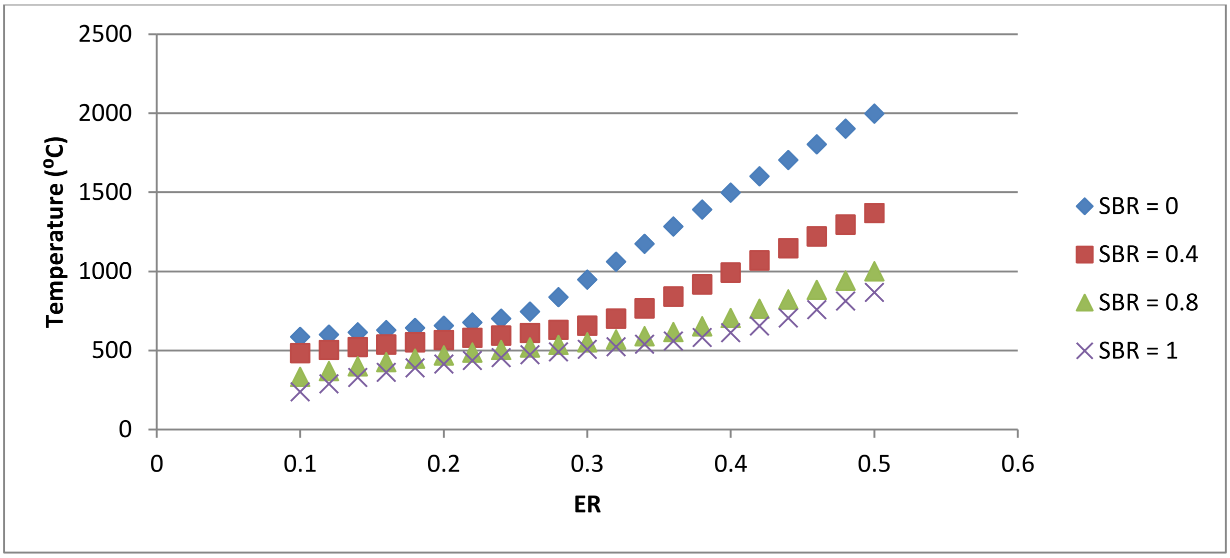


Figure 4-5: Effect of ER ratio and SBR ratio on temperature of the gasifier at a pressure of 101.325 kPa

c Effects of Temperature on Syngas molar composition:

Figure 4-5 shows the effects ER and SBR on temperature based on the Aspen Plus® simulation developed in this study. At a fixed pressure of 101.325 kPa, increasing temperature is mostly affected by increasing the equivalence ratio. This is due to the additional oxygen which favours exothermic reactions and allows the combustion process to proceed further. As a result of this, there is an observed increase in CO_2 and H_2O and corresponding decrease in H_2 and CO in the syngas molar composition. Azzone *et al.* (2012) reported similar results on the effect of temperature on syngas composition. They also found that increasing process temperature resulted in a decrease in the lower heating value of syngas due to the complete combustion reaction which took place (See Figures 4-6 and 4-7 for the effects ER and SBR on hydrogen and carbon monoxide content in the produced syngas).

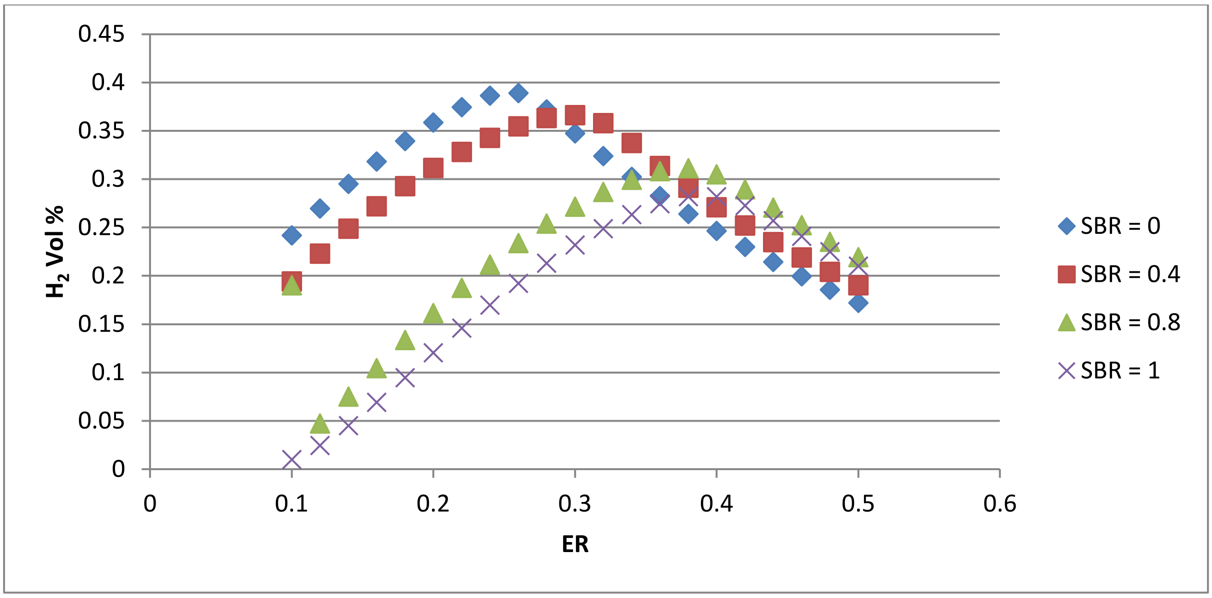


Figure 4-6: Effects of ER and SBR on hydrogen content in the produced syngas

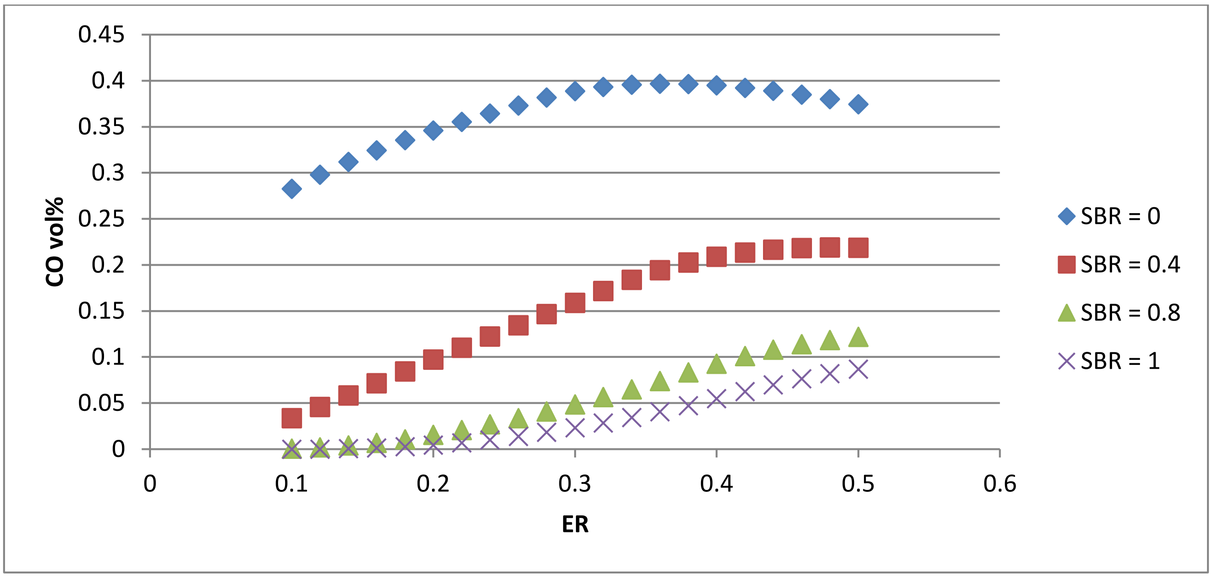


Figure 4-7: Effects of ER and SBR on carbon monoxide content in the produced syngas

d Effects of Pressure on Syngas composition:

Figure 4-8 shows the effect of pressure on syngas composition based on the developed Aspen Plus® simulation. As pressure increased there is slight decreasing trend observed for CO and H_2 molar volume, and an increasing trend in CH_4 formation. Increasing pressure results in the favouring of the forward reaction of 2-23, which is consistent with an increase in CH_4 molar volume. Azzone *et al.* (2012) found similar results and attributed this to the equilibrium constant which is inversely proportional to the process pressure which can be described by equation 4-1.

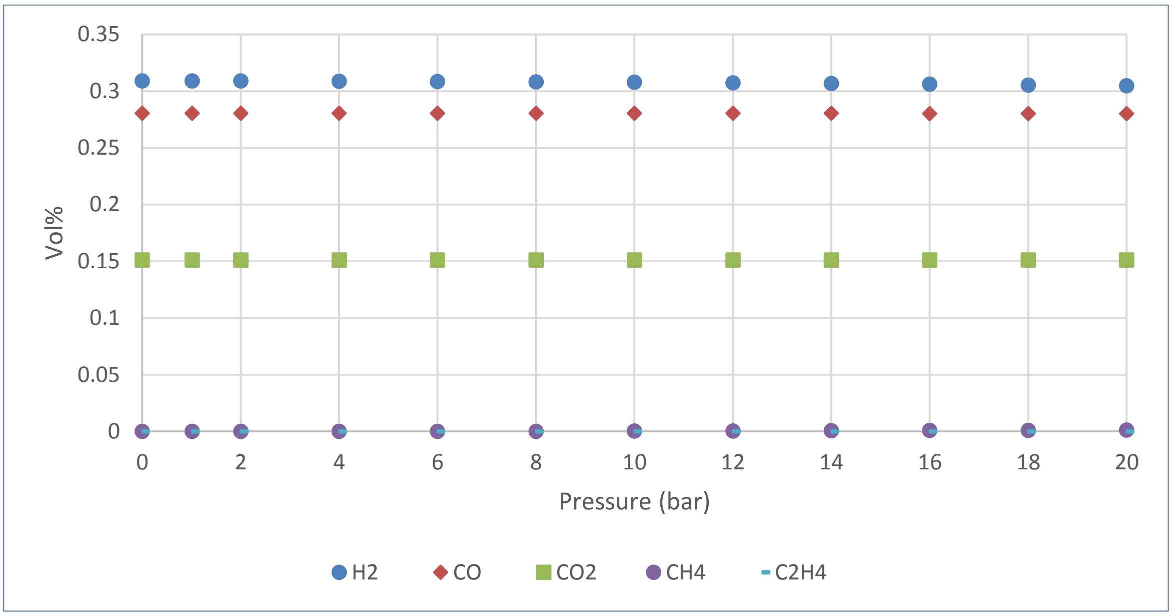


Figure 4-8: Effects of pressure on syngas composition at ER of 0.22, SBR of 0.20 and temperature of 611°C

$$K_1 = \frac{xCH_4}{(xH_2)^2}\left(\frac{P}{P_0}\right)^{-1} \quad [4\text{-}1]$$

Where K_1 is an equilibrium constant, x_{CH4} and x_{H2} are gas molar ratios with respect to biomass, P is pressure (Pa), and P_o is atmospheric pressure (Pa).

Table 4-1: Process parameters which maximized syngas molar composition based on the developed Aspen Plus® simulation

Process Parameter	Optimized values obtained from Aspen Plus® simulation
Equivalence Ratio	0.22
Steam to Biomass Ratio	0.20
Temperature (°C)	611
Pressure (kPa)	101.325

Table 4-1 is a summary of the process parameters found to maximize the syngas molar composition based on the developed Aspen Plus® simulation. These parameters were found through a sensitivity analysis on ER and SBR, which maximized molar volume of hydrogen and carbon monoxide, and resulted in the maximum H_2/CO ratio (See Appendix B Table 9-1). Since temperature was found to be dependent on the ER and SBR fed to the system, the temperature which corresponded to ER of 0.22 and SBR was 0.2, was 611°C. Pressure was kept at atmospheric conditions as increasing pressure was found to decrease CO and H_2 molar volume.

4.2 Comparison of simulated syngas composition to experimental data

Table 4-2 and Table 4-3 indicate the ultimate and proximate analyses, and corresponding syngas molar volume composition for the Aspen Plus® simulation developed in this study. It is compared to experimental and simulation data obtained from literature. Table 4-3 indicates the resultant syngas molar composition found based on the optimized process parameters shown in Table 4-1. The H_2/CO ratio found under these conditions was 2.20.

The developed Aspen Plus® simulation was based on the ultimate and proximate analysis shown in studies carried out by Ioannidou *et al*. (2009) on maize. The output from the gasifier was found to be 35% H_2, 16% CO, 24% CO_2 and 3% CH_4. In relation to experimental studies carried out by Ioannidou *et al*. (2009) on the pyrolysis of maize, this Aspen Plus® simulation showed good agreement for H_2 formation, but under predicted CO and CH_4 formation. This is a common discrepancy found between equilibrium models and experimentation. The difference in methane formation is due to generation of this hydrocarbon at low temperatures which bypasses the reaction zone ad avoids reduction into CO and H_2. In addition these differences in CO and CH_4 can be explained by insufficient residence time experimentally preventing chemical equilibrium from being reached. The Gibbs free energy model assumes fast reaction kinetics resulting in chemical equilibrium. Although, in this developed Aspen Plus® simulation, tar was accounted for as 5.5% of the total product from the gasifier (Barman *et al.*, 2012), it may have been an insufficient estimation. The difference in process may also have had an impact as pyrolysis is aimed at bio oils and char production, while gasification is used primarily for production of gaseous products. The difference in process can also contribute to the differences in molar gas composition of produced syngas.

The gasification results obtained from this simulation indicate a reduced hydrogen and carbon monoxide molar volume than results obtained from Mavukwana *et al.* (2013). This is as a result of the modified Gibbs free energy model used in this study. The results obtained from the developed simulation, based on a modified Gibbs free energy model, show a closer agreement with experimental data obtained from Ioannidou *et al.,* (2009), than the simulation based on the Gibbs free energy model, developed by Mavukwana *et al.*, (2013).

Table 4-2: Comparison of ultimate and proximate analysis for syngas production from various biomass

Reference	De Filippis *et al.* (2004)	Rapagna *et al.* (2000)	Mavukwana *et al.* (2013)	Loha *et al.* (2011)	Ioannidou *et al.* (2009)	Ioannidou *et al.* (2009)	Mavukwana *et al.* (2013)	Azzone *et al.* (2012)	Aspen Plus® Simulation
Biomass	Cuban bagasse	Almond shells	Sugarcane bagasse	Rice husk	Maize	Maize stalk	Corncobs	Maize stalk	Maize
Bed Type	Al_2O_3	olivine	Simulation	unknown	unknown	unknown	Simulation	Simulation	Simulation
Ultimate Analysis (wt %)									
C	42.9	46.7	42.9	38.4	43.8	43.8	49.3	43.8	43.8
H	5.9	5.6	5.9	2.9	6.2	6.4	5.8	6.4	6.2
N	0.2	-	0.2	0.49	-	-	0.4	-	-
O	49	38.7	49	36.4	50	49.8	42.7	49.8	50
S	-	-	-	0.07	-	-	0.03	-	-
Cl	-	-	-		-	-	0.22	-	-
Proximate Analysis (wt %)									
Fixed Carbon	9.3	18.5	9.3	15	-	-	14.4	-	-
Volatile matter	88.7	72.5	88.7	55.5	84.3	91.2	83.9	-	84.3
Ash	2	1.2	2	19.5	8.1	2.3	1.7	2.4	8.1
Moisture	11.1	7.9	11.1	10	7.6	6.4	4.6	6.4	7.6

Table 4-3: Comparison of syngas quality and production from various biomass

Reference	De Filippis *et al.* (2004)	De Filippis *et al.*, (2004)	Mavukwana *et al.* (2009)	Loha *et al.*, (2011)	Rapagna *et al.* (2000)	Rapagna *et al.* (2000)	Ioannidou *et al.* (2009)	Ioannidou *et al.* (2009)	Mavukwana *et al.* (2013)	Azzone *et al.* (2012)	Aspen Plus$^{®}$ Simulation
Biomass	Cuban Bagasse	Cuban Bagasse	Sugarcane Bagasse	Rice Husk	Almond Shells	Almond shells	Maize	Maize Stalk	Ccorncob	Maize stalk	Maize
Bed Type	Al_2O_3	Simulation	Simulation	unknown	olivine	dolomite	-	-	Simulation	Simulation	Simulation
Product Component (vol %)											
H_2	40.6	49.2		52.3	52.2	55.5	28-42.5	18-28	40-50	23.39	35
CO	17.2	14.12	59.5	17.8	23	24	41-51	35-59	28-30	20.80	16
CO_2	33.7	35.73	23.5	22.3	16.9	14.1	3.5-24	2-39	25-28	12.31	24
CH_4	8	4.00 x 10-4	16	7.4	7.9	6.4	7-9	8-12	0	0.75	3
Temperature (ºC)	850	850	0.1	750	770	770	360-730	380-680	854 - 890	570	611
H_2O/Biomass	1.9	1.9	770	1.32	1	1	-	-	0.8 - 1	-	0.20
Equivalence Ratio	0.38	0.38	1	-	-	-	-	-	0.286	-	0.22

4.3 Validation of Aspen Plus® simulation for liquid fuels production from maize gasification

4.4 Product distribution from Fischer-Tropsch synthesis

The product distribution from the Fischer-Tropsch synthesis was defined according to Table 4-4. Table 4-5 indicates the liquid fuels product distribution obtained from the FT unit in the developed Aspen Plus® simulation. These results were then compared to typical results obtained from the industrial Sasol process which makes use of low temperature Fischer-Tropsch (LTFT) synthesis, and the ideal Anderson Schulz Flory (ASF) equation for Fischer-Tropsch product distributions. α factor of 0.89 was used to determine product yields using the Anderson Schulz Flory equation which is graphically illustrated by Figure 4-9.

Table 4-4 Distinction of liquid fuel products (Bezergianni & Kalogianni, 2009; van der Laan, 1999)

Name	Component
LPG (liquefied petroleum gas)	$C_2 - C_4$
Petroleum	$C_5 - C_{11}$
Diesel	$C_{12} - C_{18}$
Soft Wax	$C_{19} - C_{23}$
Medium Wax	$C_{24} - C_{35}$
Hard Wax	C_{35+}

Table 4-5: Comparison of simulated Fischer-Tropsch product distribution with literature

Reference	Aspen Plus® Simulation	LTFT Sasol Process (Dlamini, 2012)	ASF distribution Based on Equation 1
Biomass	Maize	Coal	Ideal model
wt%			
Methane	2.54	4	3
LPG	2.21	4	11
Petrol	25.91	18	23
Diesel	40.64	19	39
Wax	31.62	48	24

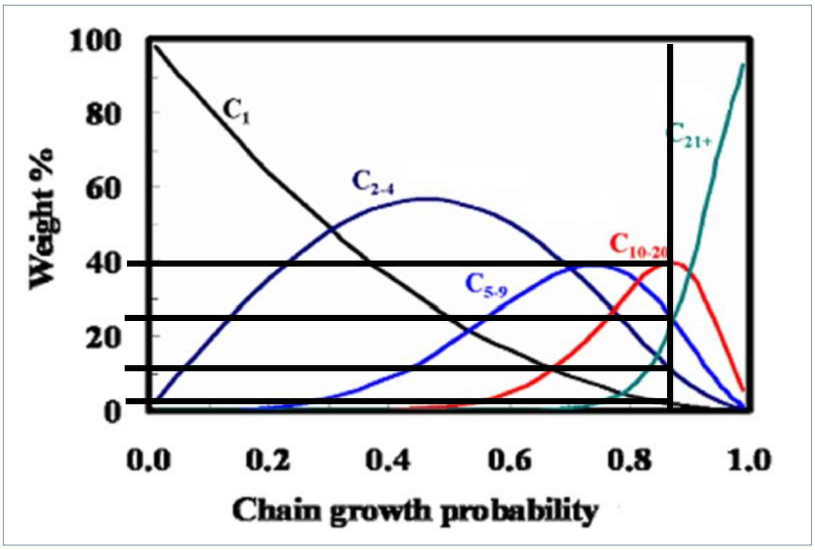


Figure 4-9: Graphical representation of Anderson-Shultz-Flory Equation with cobalt α factor superimposed

Fischer-Tropsch is a polymerization reaction where CO and H_2 are adsorbed and dissociated on the surface of a catalyst to form a chain initiator CH_3, methylene monomer CH_2 and H_2O. Selectivity for longer chain growth is influenced mainly by catalyst activity to enhance chain propagation rather than chain termination (van der Laan, 1999).

The simulation product distribution was modelled based on experimentally determined yields obtained by Sudiro *et al.* (2009). The FT synthesis of maize reported a significantly higher diesel weight percentage than the coal to liquids process reported by Sasol. This may be due to the difference in H_2/CO ratio. Low rank coal used for gasification has a low H_2/CO ratio of 0.8 in comparison to the maize H_2/CO ratio of 2.20. The LTFT process employed by Sasol, has a WGS reactor which would adjust the H_2/CO ratio. After the WGS step this resultant H_2/CO ratio may still be less than the H_2/CO ratio achieved for maize, which could account for the difference. Studies carried out by Pirola *et al.* (2014) indicated that with decreasing H_2/CO ratios, the CO conversion rapidly decreases affecting selectivity of liquid fuel products. Studies show that product selectivity moves toward heavier products and oxygenated compounds with increasing partial pressures of H_2/CO in the FT reactor. Higher H_2/CO ratios result in lighter hydrocarbons and lower olefin content (van der Laan, 1999). By decreasing H_2 content, the mechanism of hydrocarbon synthesis is affected. According to Table 4-6, reduced H_2 inhibits the adsorption reactions, chain initiation and chain growth accounting for the reduced diesel production indicated by the Sasol process.

Table 4-6: key reactions of the hydrocarbon synthesis mechanism influenced by H_2/CO ratio (van der Laan, 1999)

Adsorption	H2 + 2s ↔ 2Hs
Chain initiation	Cs + Hs ↔ CHs + s CHs + Hs ↔ CH_2s + s CH_2s + Hs ↔ CH_3s + s COs + H_2 ↔ CHOHs CHOHs + H_2 ↔ CH_2s + H_2O
Chain Growth	C_nH_2n + s + Hs → $C_{n+1}H_2$n+3s +s C_nH_{2n} + s + Hs → C_nH_{2n+2} + 2s

Cobalt catalysts form mostly straight chain hydrocarbons typically ranging from C_{10} – C_{20}, which correspond to products such as diesel and jet fuels. Based on this, cobalt is often used as the catalyst of choice for LTFT synthesis. Heavier hydrocarbons with a carbon number greater than 20 can be hydrocracked to lower molecular weight fuels with higher value. Cobalt catalysts are typically associated with higher α factors than iron catalysts. Studies carried out indicate a cobalt based catalyst resulted in a product distribution which can be represented by a α factor of 0.89 (Donnelly 1989; Matsumoto, 1987).

In comparison to the ASF product distribution, this simulation under predicts the formation of LPG and over predicts wax product formation. Studies indicate that measured product distributions from Fischer-Tropsch reactions rarely obey predictions from the ASF model. Common deviations include higher methane and lower ethane yields (van der Laan, 1999) (Mvukwana *et al.* 2012). This accounts for the lower LPG yields obtained from this simulation.

The ASF equation also does not distinguish between different types of products but rather produces a semi-logarithmic plot of the mole fractions versus carbon number. The gradient of this plot results in the chain growth probability factor α. This is not representative of experimental conditions where a multicomponent product mixture is formed. Practically main products are characterized by process conditions and catalysts, which result in the formation of oxygenated compounds, branched hydrocarbons and β – olefins (van der Laan, 1999). This could explain the differences observed in the simulated diesel and wax weight fractions relative to the ASF product distribution, as experimentall, the product distribution of hydrocarbons with C10 and greater show a significant deviation from the ideal ASF equation.

4.5 Product distribution from hydrocracking unit

Table 4-7 indicates the resultant product distribution obtained from the hydrocracking unit based on the developed Aspen Plus® simulation. A conversion of 98% of the wax feed was specified based on experimental data obtained on a platinum-silica-alumina catalyst from Coonradt & Garwood (1964). In order to validate this section, results obtained from this simulation were compared to experimental studies carried out by Bezergianni & Kalogianni (2009). In relation to this study, the Aspen simulation resulted in a greater selectivity for petrol than diesel.

Table 4-7: Aspen Plus® simulation of liquid fuels produced from hydrocracking unit

	Aspen Plus® Simulation	Bezergianni & Kalogianni (2009)
Liquid Fuel	Wt%	Wt%
LPG	10	Unknown
Diesel	10	73
Petroleum	78	10
Wax	2	7

A wax conversion of 98% shows good agreement with experimental studies carried out by Hodala *et al.* (2010) who achieved maximum conversions of 93 – 98%.

Synthetic fuels in liquid phase was found to be 88%.from this simulated hydrocracking unit. Liquid fuels production obtained from experimental data indicate a selectivity of 16% gaseous products and 83% liquid products (Calemma *et al.*, 2010). Good yield of liquid products is a function of operating parameters such as catalyst type and weight, time, temperature and pressure. The wax feed quality also has a significant impact on product yield (Hodala *et al.*, 2010). Parameters such as catalyst type or weight are not well defined in the studies carried out by Bezergianni & Kalogianni (2009), which has most likely contributes to the difference in liquid fuel distribution and wax conversion.

In comparison to Bezergianni & Kalogianni (2009), this simulation under predicts diesel yield and over predicts petroleum formation. In addition to catalyst operating parameters, this could also be attributed to differences in wax feed. Based on findings from John *et al.* (2006), it was found that higher molecular weight waxes were able to undergo hydrocracking easier than softer waxes. This is also consistent with the paraffin hydrocracking theory, where adsorption and reaction of heavier chains occur before lighter ones, which results in an overall greater reactivity for heavier feeds. In addition, it was also found that softer waxes showed higher selectivity for petroleum yields than heavier waxes. The average carbon number for the simulated wax feed to the hydrocracking unit was within the range of 23 – 24, which is consistent with soft waxes. The average carbon number is unspecified for the feed used in experiments carried out by Bezergianni & Kalogianni (2009). It is possible that the simulated wax feed was on average a lighter wax than the experimental feed, which would account for the deviations found between the liquid fuel yields.

Overall, the simulation of liquid fuels production via the Fischer-Tropsch synthesis and hydrocracking process shows fair agreement with literature. Where significant deviations were found, they can be reasonably explained and supported. This simulation is a suitable means to predict liquid fuels production from maize gasification and downstream processing.

5 Chapter 5: Results and Discussion

5.1 Feasibility of maize as a biomass for syngas and liquid fuels production

Results:

Figure 5-1, Tables 5-1 and 5-2, indicate the quality of syngas produced from maize based on the developed Aspen Plus® model. The results of this study were then compared to coal, natural gas and other conventional carbon feed stocks to determine the feasibility of maize as a feed for syngas generation.

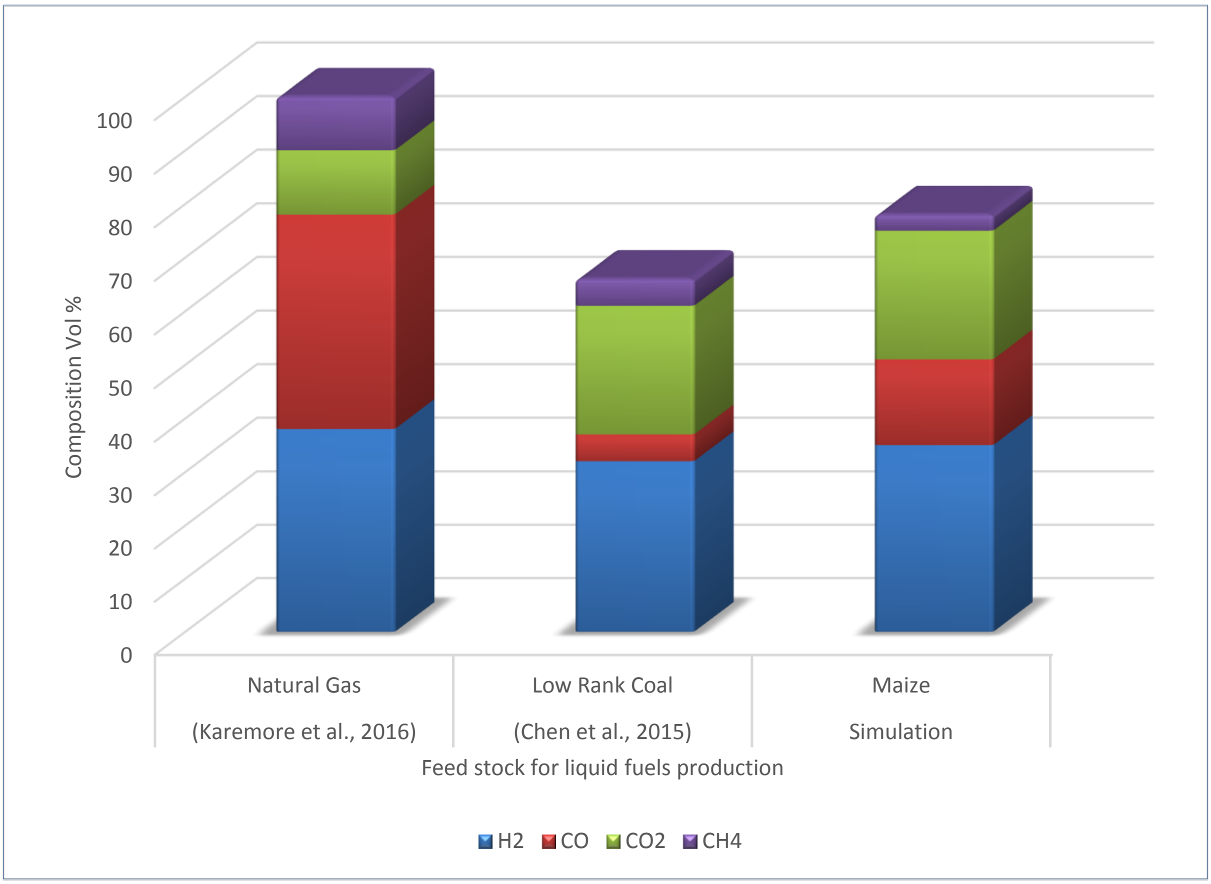


Figure 5-1: Comparison of syngas chemical composition produced from conventional feed stocks and maize

Table 5-1: H_2/CO ratios found in syngas produced from different coal feed stocks using a Slagging Gasifier (Karemore *et al.*, 2016; Chen *et al.*, 2015)

Feedstock	H_2/CO ratio
Natural gas	1.75
Naphtha	0.94
Heavy Oil	0.9
Vacuum residue	0.83
Coal	0.8
Petroleum Coke	0.61
Maize based on developed Aspen Plus® simulation	2.20

Table 5-2: H_2 and CO properties for different carbon feed stocks gasified using a shell gasifier

Feed stock	Units	Natural Gas	Liquefied Waste	Vacuum Residue	Liquefied Coke	Maize Aspen Plus® simulation
Reference		Karemore *et al.* (2016)	Karemore *et al.* (2016)	Karemore et al. (2016)	Karemore *et al.* (2016)	
C/H ratio	wt%	3.35	9.2	9.7	11.9	8.4
S	wt%	Trace	3.1	6.8	8.0	-
Ash	wt%	-	0.01	0.08	0.16	0.081
H_2, CO in product	vol%	95.3	94.0	92.9	92.8	92
H_2/CO ratio in syngas product	mol/mol	1.69	0.89	0.88	0.78	2.20

Table 5-3 indicates the impurity content found in the syngas produced in the Aspen Plus® model. In relation to syngas quality specifications for FT synthesis indicated by Hu *et al.* (2012).

Table 5-3: Quality specifications of syngas for Fischer-Tropsch synthesis (Hu *et al.*, 2012)

Impurity	Quality Specification	Maize Aspen Plus® simulation
H_2S; COS; CS_2	< 1 ppmv*	0 ppmv
NH_3; HCN	<1 ppmv	0 ppmv
HCl; HBr; HF	< 10 ppbv**	0 ppbv
Alkali Metals (Na; K)	< 10 ppbv	0 ppbv
Particles (soot; ash)	Trace	Trace

Hetero-organic compounds (S;N;O)	< 1 ppmv	0 ppmv

*ppmv – ppm by vol

*ppbv – ppb by vol

Discussion:

Gasification is a thermal decomposition achieved by partial oxidation at high temperature with a limited oxygen feed to prevent complete combustion, which results in a synthesis gas rich in CO and H_2. The typical H_2/CO ratio ranges between 0.5 -1.8 depending on technologies and the desired end product (Ricci, 2011). Natural gas and coal are used for liquid fuels production in South Africa and have typical H_2/CO ratios of 1.75 and 0.8 respectively (Jones & Thomas, 2008). When the H_2/CO ratio is as low as 0.8, further upgrading is required in the form of a water-gas-shift reactor, to achieve a higher ratio, or a Fe catalyst for FT synthesis must be used. The water-gas-shift reaction operates with a variety of catalysts within the range of 200 - 480°C. Cobalt catalysts show virtually no WGS activity. This implies that a cobalt catalyst is more sensitive to the H_2/CO ratio than iron, as the latter has the ability to can change the balance by shifting H_2 or CO (Dry, 1981).

The H_2/CO ratio of syngas derived from maize is higher than the conventional natural gas and coal feeds for liquid fuels production. This indicates that that maize can result in a syngas feed that is both renewable and richer in CO and H_2 than the current non-renewable sources without using a WGS reactor. The H_2/CO ratio of 2.20 obtained for maize gasification is slightly above the range of 1.9 – 2.0 and is suited for Fischer-Tropsh synthesis and conversion to liquid fuels (Mavukwana *et al.*, 2013; Er-rbib *et al.*, 2012). Studies carried out by Lillebo *et al.* (2017), involved FT experiments with different H2/CO ratios over a range of 1.04 – 2.56 over an alumina supported cobalt catalyst. It was found that H2/CO ratios above 2.1 have conversion of at least 85% CO, without significant de-activation of the catalyst or loss of selectivity towards heavier hydrocarbons – see Figure 5-2.

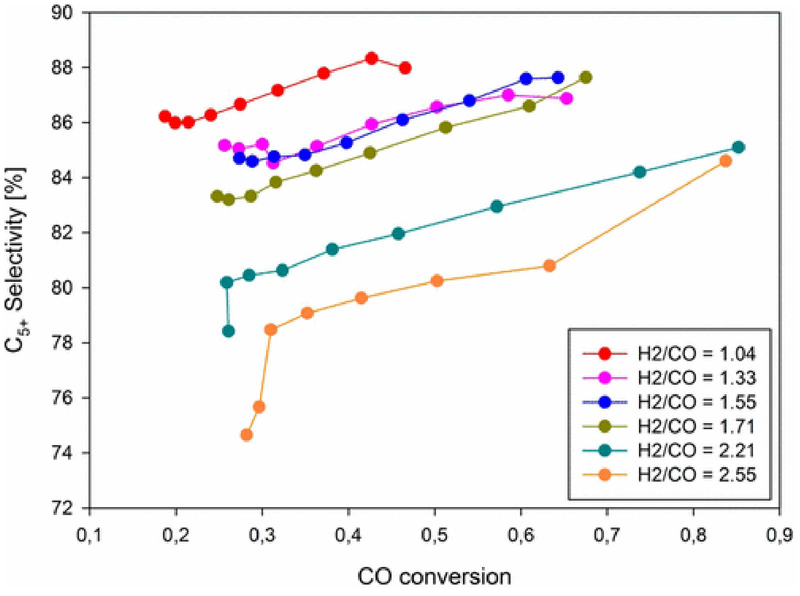


Figure 5-2: Results obtained for H2/CO ratios in the range of 1.04 – 2.55 (Lillebo *et al.* 2017)

In addition to the H_2/CO ratio, the impurities in syngas must be controlled according to specifications listed in Table 5-3. The presence of these impurities can reduce the Fischer-Tropsch activity during the catalytic conversion process of syngas. The Aspen Plus® simulation does not indicate presence of any impurities, as the ultimate and proximate analysis of the maize feed did not contain N, S, metals or halogens. However, the ultimate and proximate analysis used by Mavukwana *et al.*, (2013) shows presence of N and S, which can result in presence of ammonia and hydrogen sulfide in the produced syngas. Should these impurities exist, ammonia can be reduced through aqueous scrubbing or decomposed and selectively oxidized. While sulfur compounds can be addressed through the use of sulfur absorbents such as ZnO (Hu *et al.*, 2012). Similar methods are currently employed in the coal processing industry.

The Aspen Plus® simulation can only give an indication of deviations from quality specifications for the Fischer-Tropsch synthesis. This must be verified through experimentation as Aspen models typically assume all N is converted to NH_3 and all S is converted to H_2S with no tar formation (Mavukwana *et al.*, 2012; 2013). This assumption excludes the possible formation of all other N and S containing compounds.

5.2 Feasibility of liquid fuels production from maize in South Africa

Results:

Based on the developed Aspen Plus® simulation, Table 5-4 indicates the liquid fuels production possible based on the processing of 1 ton maize. Table 5-5 indicates the potential synthetic fuels production from maize cultivated solely on underutilised lands. The underutilized land of 450 000 hectares has the ability to support approximately 1.7 million tons of maize per annum which can be converted to approximately 1.2 billion litres per annum of liquid fuel. This is equivalent to 6% of the total liquid fuel consumption in South Africa.

Table 5-4: Liquid fuels production based on results from Aspen Plus® simulation from 1 ton of maize

	kg/hr	kg/m^3	m^3/hr	L/hr
LPG	151.77	510	0.30	297.59
Petrol	517.29	739	0.70	699.99
Diesel	155.01	820	0.19	189.04

Table 5-5: Potential synthetic liquid fuels production from Maize cultivated on underutilized land

Underutilized land	450 000	hectares
Underutilized land	450 000	hectares
maize production per hectare	3.8	t/hectare
maize production	1 710 000	tons/annum
safety factor	20%	
maize	136 8000	tons
Petrol	958	million L/annum
Diesel	259	million L/annum
Total	1.216	billion L/annum
Total liquid fuel requirements	20	billion L/annum
Possible renewable fuels supplement for South African liquid fuels demand	6%	

Discussion:

5.2.1 Domestic maize production

South African maize prices have reached record highs in 2016 due to severe drought conditions. Rainfall in 2015/2016 was the lowest reported annual rainfall since 1904. The severity of the drought resulted in a significant 30% decline of planted maize. The Crop Estimates Committee (CEC) project a 7.16 million ton maize production for 2016. This is 28% below 2015 production and 40% below the three year average. In addition the CEC also indicated a decline of 33% year on year of maize planting by informal settlements due to unfavourable planting conditions.

Although maize production for 2016 has been exceptionally low, this is due to the adverse drought and not to economic conditions. The BFAP (2016) projects a strong recovery in 2017 for yellow and white maize crops. Long term projections indicate that there will be an annual decline of 1.5% in commercial white maize and an increase in yellow maize by 1.4% over the same period. Figures 2-12 and 2-13 indicate that future maize production is not only expected to meet demand, but it is also projected that the country will return to a net exporting position in the medium term. This surplus of maize could also be redirected to synthetic fuels production should it be economically viable.

Based on 2015 crop estimates – see Figure 5-3, South Africa is able to produce an average of 3.8t of maize per hectare nationally (BFAP, 2016). Although the Northern Cape is able to produce significantly higher tons of maize per hectare relative to the national average, this is due to irrigation. Due to the challenges regarding domestic water, maize cultivation for liquid fuels is assumed to be achieved without irrigation.

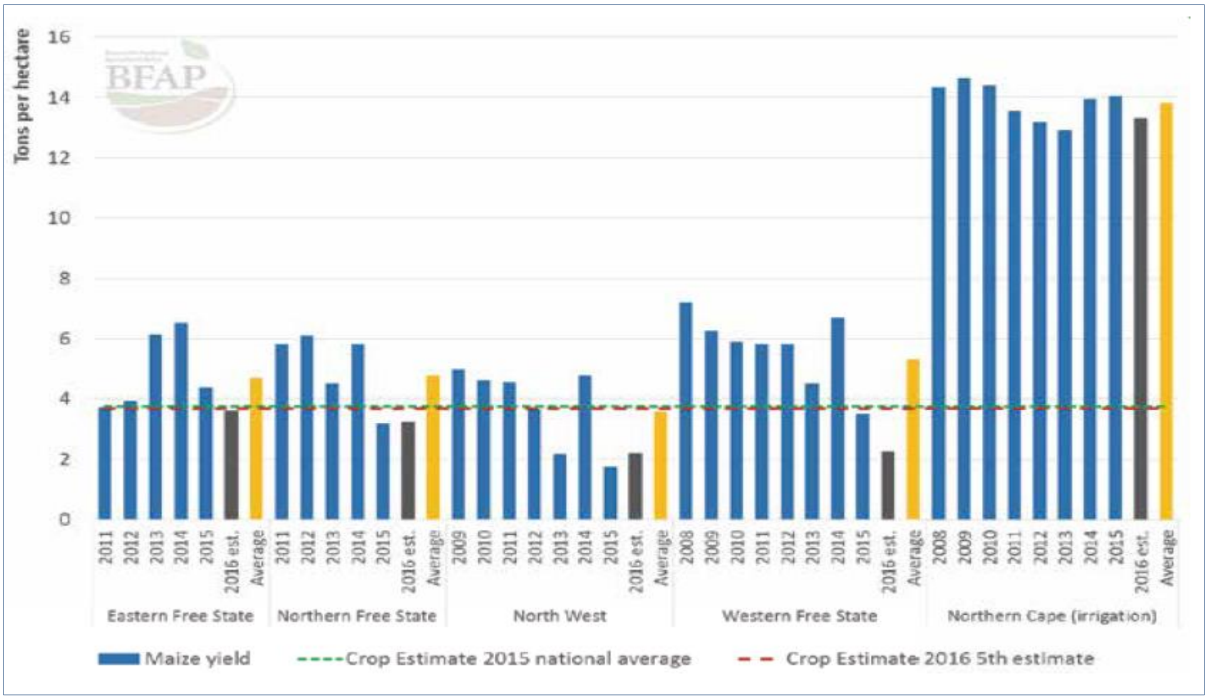


Figure 5-3 Maize yield trends and CEC's averages (BFAP, 2016)

According to BFAP (2016) the average cost incurred to produce one ton of maize is approximately R 1366.20. This is significantly higher than the international cost of R1 108.80. This is an indication that South African farming practices are not as competitive internationally, and there is room for optimization to improve production costs. Despite higher costs of production and unfavourable weather conditions, profit margins still exist - refer to Figure 5-4. The average revenue generated for 1 ton of maize is R 3208 in South Africa based on 2016 maize prices (Grain SA, 2016).

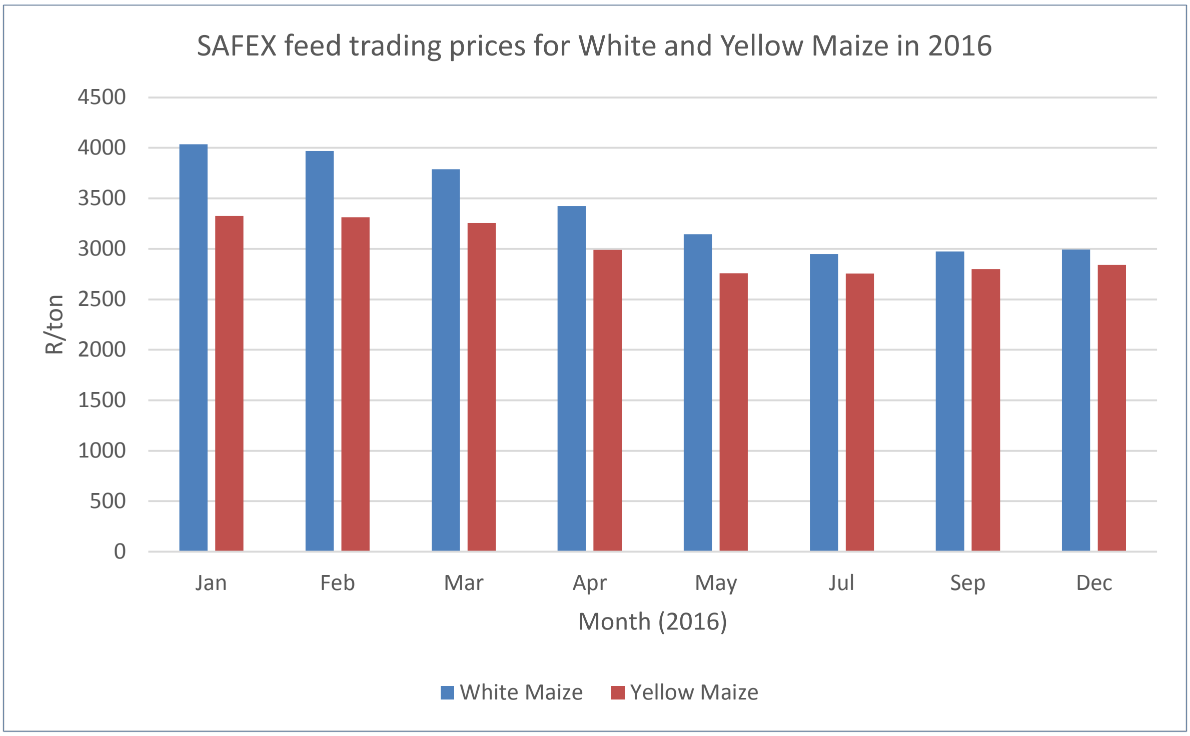


Figure 5-4: SAFEX feed trading prices for white and yellow maize in 2016 (Grain SA, 2016)

5.2.2 Arable land

South Africa is approximately 122 million hectares in size. While 12% of South Africa's total land can be used for crop production only 22% of this amount is considered high potential arable land, which is equivalent to approximately 3.1 million hectares (National Department of Agriculture, 2015), (SAinfo Reporter, 2012). According to the Biofuels Industrial Strategy (2007) there is approximately 14% of arable land that is underutilized in South Africa which is equivalent to approximately 450 thousand hectares. This land is found mostly in the homeland regions which consists of Transkei, Bophuthaswana, Ciskei, Venda Gazankulu, KaNgwane, KwaNdebela, Kwazulu, Lebowa and QwaQwa. Based on this data, by utilizing the arable land in the homelands, South Africa can potentially increase maize production to an additional 1.7 million tons per annum. Due to the stable and small incremental increase in demand for maize it means the underutilized land should be able to support maize cultivation for liquid fuels production without impacting food security.

5.2.3 Water consumption

South Africa is unable to make use of the total arable land available due to the uneven and inconsistent rainfall. Most of the high potential arable land is irrigated which results in approximately 60% of South Africa's total water consumption. This is equivalent to 7.83 million cubic metres per annum (National Department of Agriculture, 2015). The Biofuels

Industrial Strategy (2007) is firmly against irrigating crops for biofuel generation, stating that crops must find water from existing allocations. Maize is considered to be a dryland crop and is not listed as a water user. Dryland crops are defined as crops which are able to survive in arid regions through a number of mechanisms such as short life cycle where germination, growth and production can take place during a very short period when moisture is available. These plants also typically have a deep or extensive root systems which have the ability to gather water over a large area. These are also plants which have the ability to store water in their tissue and release it very slowly, or are protected by a wax layer to prevent moisture loss (Creswell & Martin, 1993).

To support the growth of dryland crops, there are also dryland farming practices which can assist with effective production. Dryland farming is the profitable production of crops on land with a low average, or highly variable rainfall without the use of additional irrigation. These techniques include reducing the runoff of water, preventing crust formation on soil surface and, reducing soil evaporation (Creswell & Martin, 1993). Based on this, additional maize production for synthetic fuels generation should not increase the water consumption as irrigation is not required.

5.2.4 Liquid fuels generation from maize in South Africa

Table 5-5 indicates the potential synthetic fuels production from maize cultivated solely on underutilised lands. The underutilized land of 450 000 hectares has the ability to support approximately 1.2 billion litres per annum of liquid fuels obtained from maize. This is equivalent to 6% of the total liquid fuel consumption in South Africa. Using maize to produce synthetic fuels via gasification and Fischer-Tropsch synthesis in South Africa would be able to exceed the original objective of the BIS which envisioned a biofuel blending rate of 2% equivalent to 400 million litres per annum. In addition, this also supports the original vision outlined by the BIS which targets underutilised lands for the development of a biofuels sector ensuring minimal impact on food security and water usage in South Africa.

5.3 Feasibility of liquid fuels generation from maize: an economic perspective

5.3.1 Economic feasibility of liquid fuels production via gasification and FT processing of maize in current conditions

Results:

The feasibility of synthetic fuels produced from maize was determined by expressing raw material costs as a percentage of revenue generated through sales of liquid fuels. The raw material was determined based on fixing the H_2/CO ratio exiting the gasifier, and determining the raw material feeds necessary to achieve this ratio for coal and natural gas. Figure 5-5 was determined based on existing costs of 49 U.S. $/bbl Brent Crude, 40 U.S. $/MT of coal and 6.5 U.S. $/mmBTU of natural gas at R/U.S. $ exchange rate of R 14.06/U.S. dollar (Statistics South Africa, 2016).

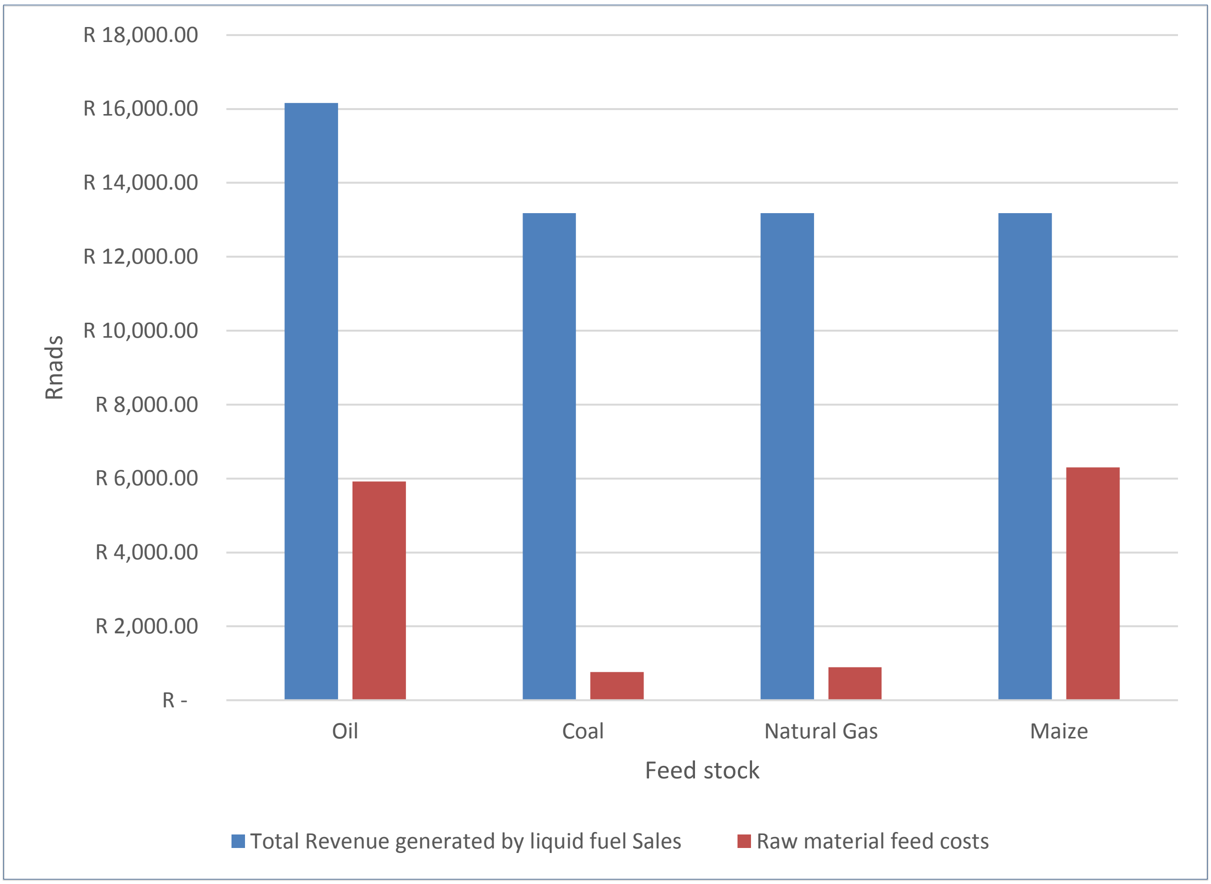


Figure 5-5: Economic feasibility of liquid fuels production from FT processing of maize in comparison to conventional feeds based on 2016 commodity pricing

Discussion:

Figure 5-5 indicates a comparison of raw material costing and total revenue generated per feed stock. Based on these economics, Brent crude raw material costs are 37% of total revenue generated, natural gas is 7%, coal is 6% and maize is 48%. Based on existing conditions, it is more economically feasible to produce liquid fuels from crude oil, coal and natural gas than considering maize as a feed.

Critical variables found to impact feasibility of liquid fuels production from maize was liquid fuel pricing, rand/U.S. dollar exchange rate and raw material feed costing. Sensitivity analyses were carried out on these variables to identify what market conditions are conducive for FT processing of maize for liquid fuels production.

5.3.2 Effects of crude oil price and Rand/Dollar exchange rate on liquid fuel prices in South Africa

Results:

Fuel prices for petroleum products in South Africa has a dependency on crude oil global trading price and the Rand/US dollar exchange rate. South Africa is heavily dependent on crude oil imports, as a result the global trading price and import inflation have a significant impact on domestic fuel prices. In addition, since world oil sales are carried out in US dollars, the Rand Dollar exchange rate also contributes to the fuel price movements.

Figure 5-6, Figure 5-7 and Figure 5-8 were developed based on historical relationship between crude oil trading price (US $/bbl), Rand/US $ exchange rate and fuel prices in South Africa. As indicated by these three dimensional plots, Brent crude trading prices have experienced larger fluctuations than the R/US $ exchange rate. As a result, over the last year the price of Brent crude has had a greater effect on domestic fuel pricing.

Equations 5-1 – 5-3 were developed based on historical data obtained from Statistics South Africa (2016) with a standard deviation of 47, 59 and 65 cents for petroleum, diesel and LPG fuel prices in South Africa respectively. These equations were used to determine the fluctuation of fuel prices as a result of changes to the crude oil price when examining the sensitivity of fossil fuels price on the feasibility of liquid fuels production from maize.

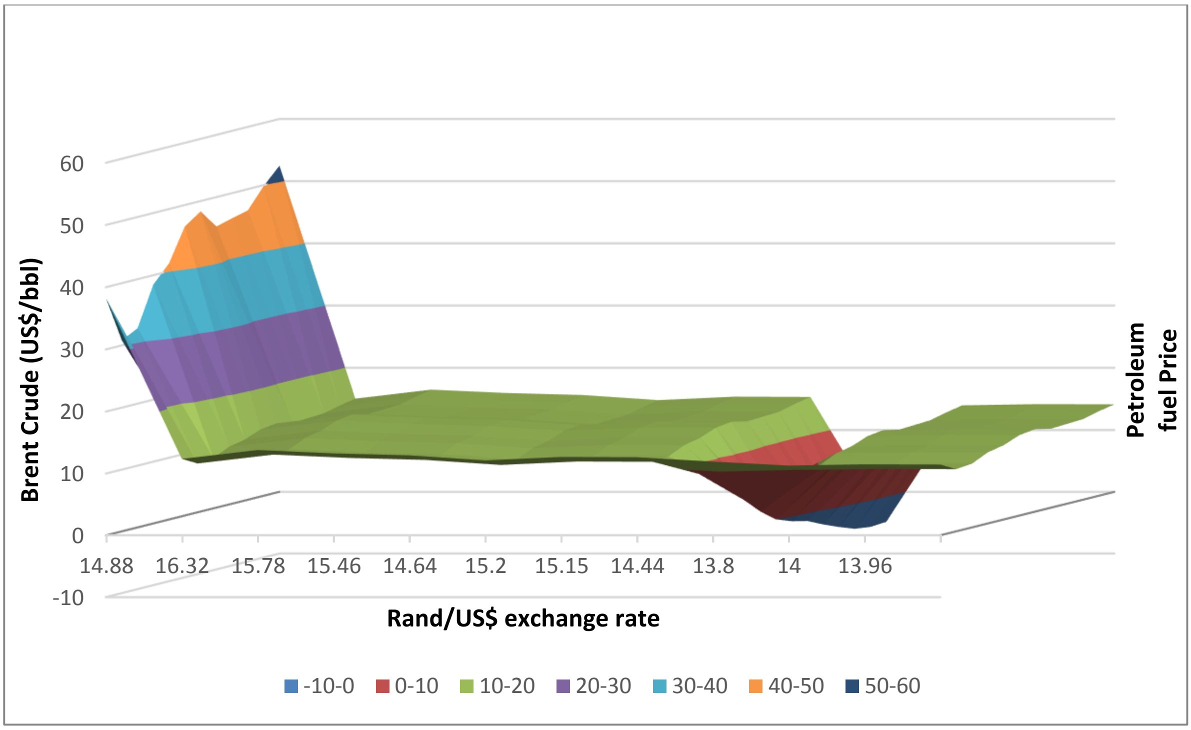


Figure 5-6: Effects of Rand/US Dollar exchange rate and Brent crude oil prices on petroleum fuel price in South Africa

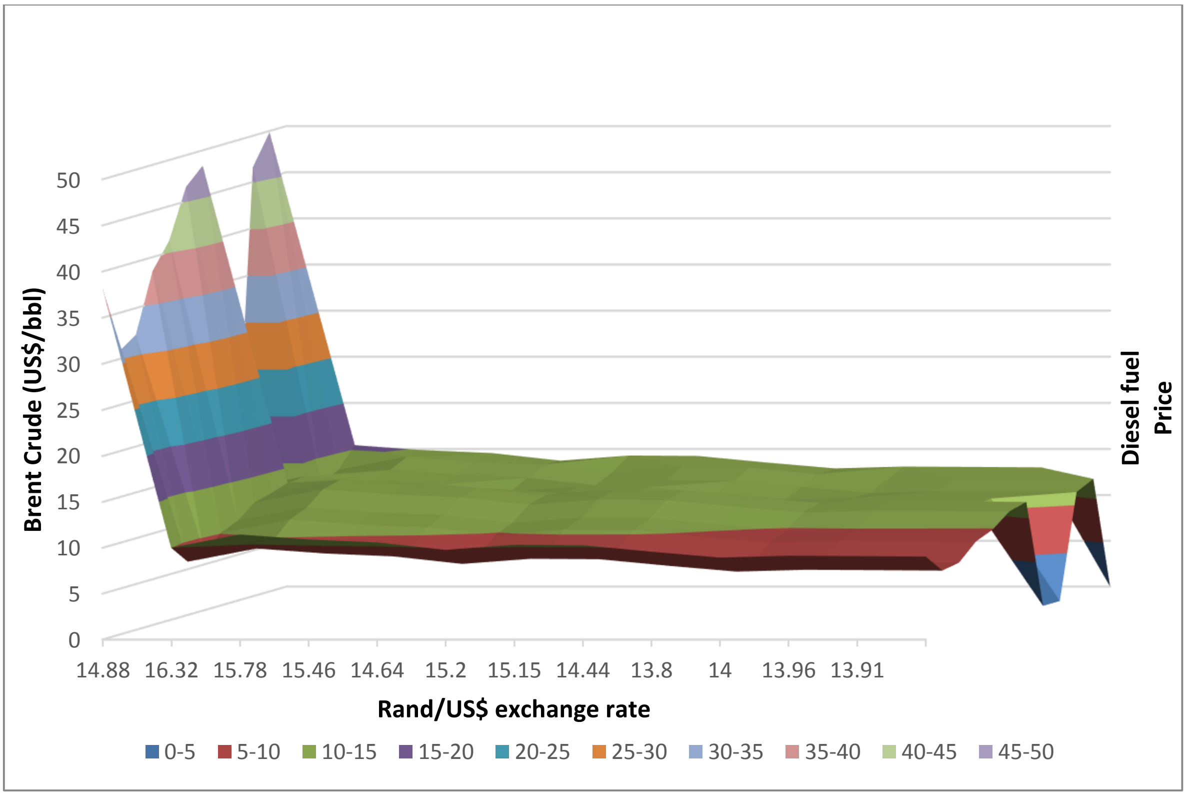


Figure 5-7: Effects of Rand/US Dollar exchange rate and Brent crude oil prices on diesel fuel price in South Africa

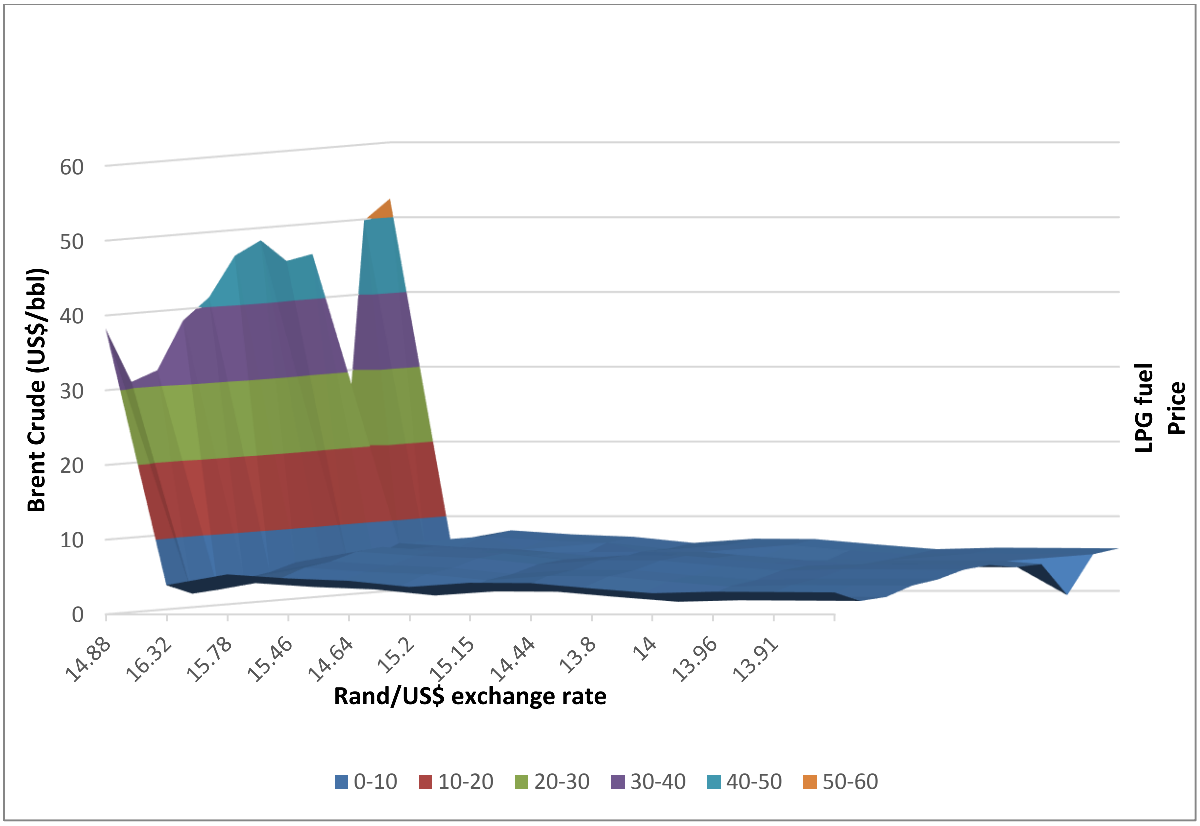


Figure 5-8: Effects of Rand/US Dollar exchange rate and Brent crude oil prices on LPG fuel price in South Africa

$$z_{petrol} = y + 0.187x - 9.65 \quad [5\text{-}1]$$

$$z_{diesel} = y + 0.278x - 15.484 \quad [5\text{-}2]$$

$$z_{LPG} = y + 0.1935x - 18.365 \quad [5\text{-}3]$$

Where x is the Brent crude oil price, y is the Rand/US \$ exchange rate and z is the fuel price in South Africa.

5.3.3 Effects of crude oil price on maize feasibility

Results:

Figure 5-10 indicates the effect of crude oil price on the feasibility of liquid fuels from maize based on a fixed R/US $ exchange rate of R14.06. According to this plot, provided the exchange rate is fixed, when the crude oil price escalates to 65 US $/bbl and greater, then FT processing of maize becomes economically feasible.

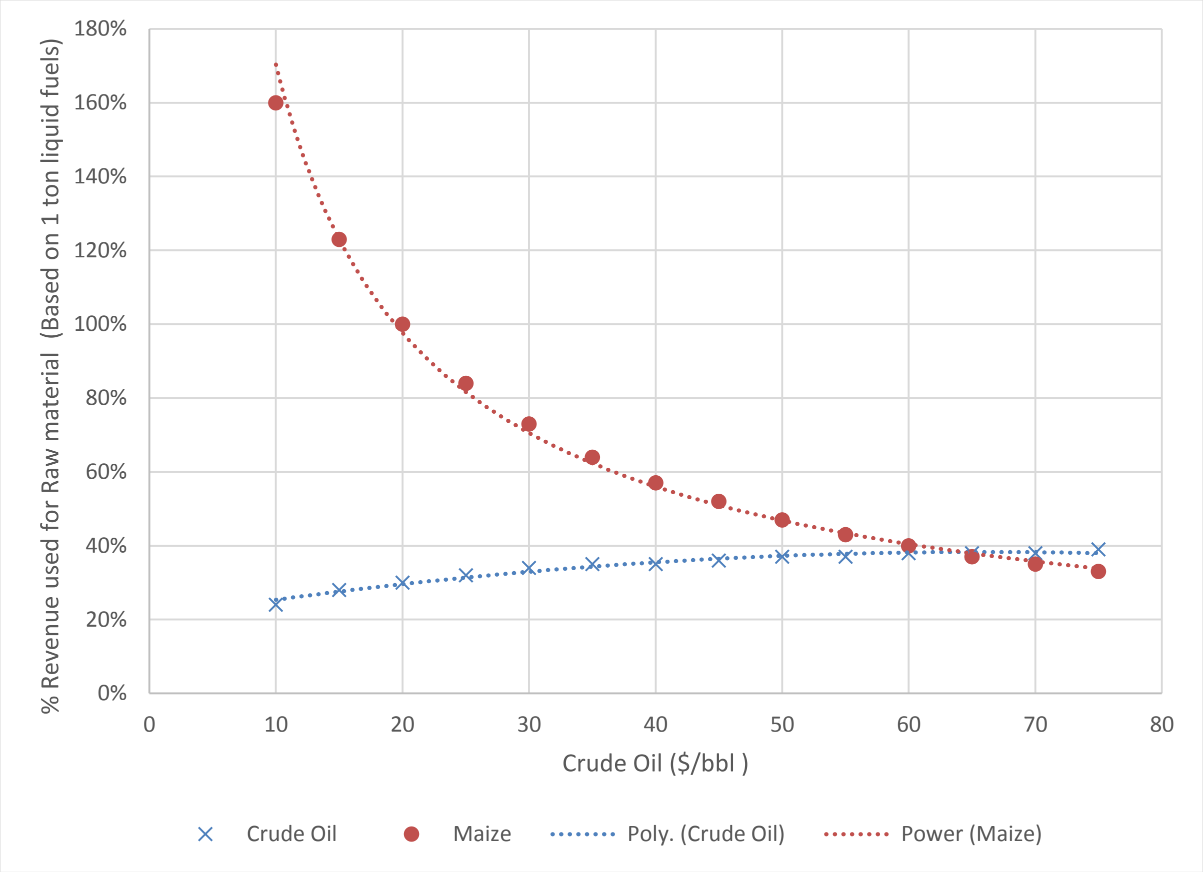


Figure 5-9: Effect of crude oil prices on feasibility of liquid fuels production from maize

Discussion:

The organization of the Petroleum Exporting Countries (OPEC), are countries which have the majority of crude oil reserves and rely heavily on oil exports as a source of revenue and foreign exchange. As a result, the OPEC has a stake in oil prices and movements. The countries involved attempt to steer production and price agreements through policy announcements. The OPEC's fuel pricing is based on a formula which uses West Texas Intermediate and Brent Crude oil prices as a benchmark (Nkomo, 2006). Since crude oil exports contribute significantly to growth and economy for the members of the OPEC, this makes them vulnerable to world oil prices and acts as motivation to unite and undertake unanimous decisions.

However, since crude oil prices determine growth around the world, factors responsible for high oil prices and fluctuations are mostly political rather than market related. Political instability in members of the OPEC or superpowers, such as the Iranian revolution in 1979, invasion of Kuwait by Iraq in 1990 and, the U.S. fear of Iraqi invasion in 2003 have resulted in significant and negative impact on world economic growth (Nkomo, 2006). Political incidents such as these has severe consequences on oil importers such as South Africa; affecting the country's domestic trading and exports into global markets.

All factors impacting crude oil pricing are outside of South Africa's control. This means escalations in crude oil prices can occur which can cripple the South African economy unless an alternative domestic fuel source can be found that can allow elimination of crude oil dependency. At crude oil costs of 65 US $/bbl and greater, maize becomes economically feasible and can assist as an alternative and renewable feed for domestic liquid fuels production.

5.3.4 Effects of coal price on maize feasibility

Results:

Figure 5-10 indicates the effect of coal pricing on the feasibility of liquid fuels from maize based on a fixed R/US $ exchange rate of R14.06 and Crude oil price of 49 US $/bbl. Maize only becomes an economically feasible feedstock when the coal price is 340$/MT and greater.

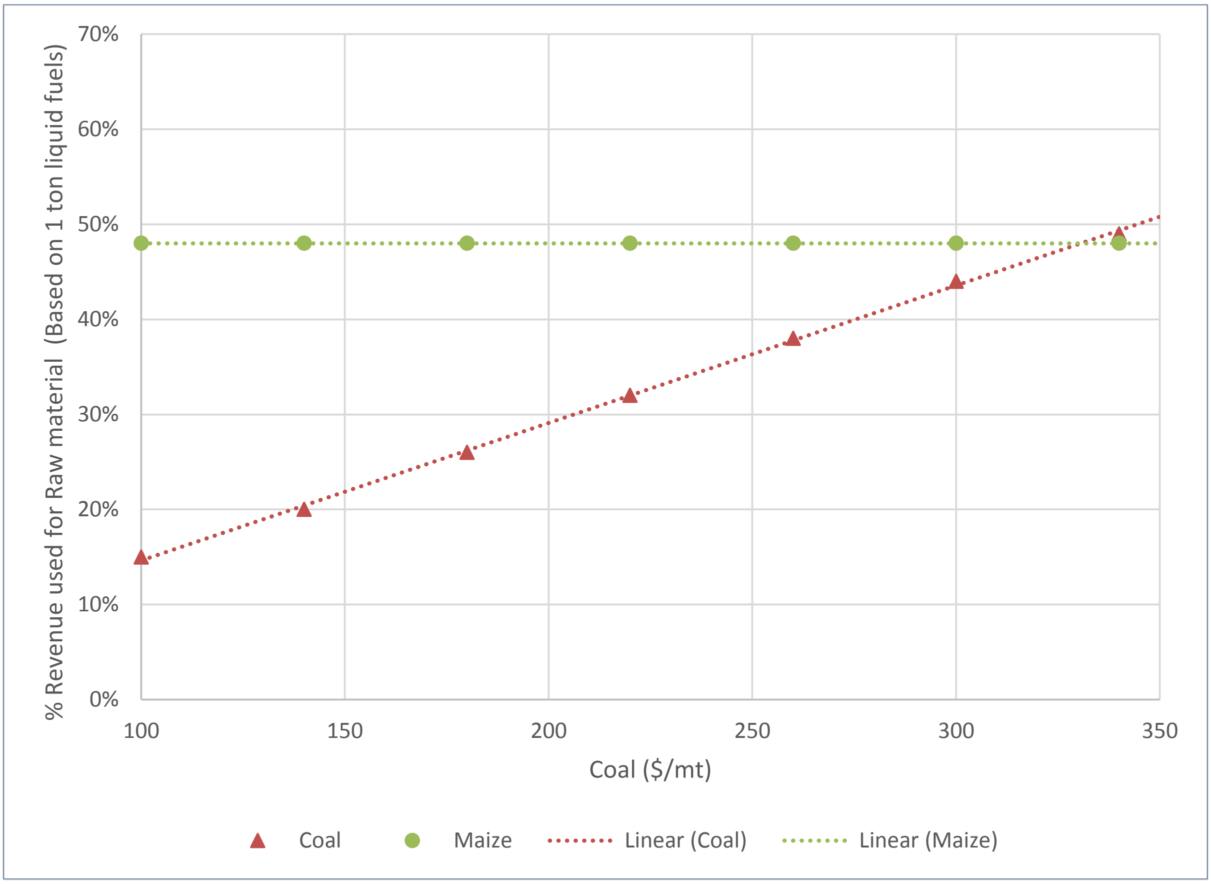


Figure 5-10: Sensitivity analysis: effect of coal prices on Feasibility of liquid fuels production from maize

Discussion:

Due to large coal reserves in South Africa, coal has provided an inexpensive and attractive energy source in comparison to crude oil. As a result, this fossil fuel supports electricity generation, synthetic fuels production and is also used as a direct fuel in steel, cement and brick manufacturing.

Environmentally coal is not a sustainable fuel source for South Africa. Coal fired power stations contribute 70% of CO_2, sulfur and particulate matter emissions. Despite poor environmental sustainability and being a signatory of the Kyoto Protocol, South Africa plans to increase coal consumption. Eskom plans to recommission 3 previously mothballed coal fired power stations and bring on line 2 new ones. Sasol has also expanded its synthetic fuels production capacity. This equates to a 75 million ton increase in coal demand. In addition, South Africa's coal is also in huge demand in China, India and the European Union due to low ash and sulfur content (Nyanjowa, 2014).

The existing coal production capacity in South Africa cannot sustain the forecasted growth with coal production capacity stagnating at 250 million tons/annum. This is as a result of depleted coal mines (in Witbank, Ermelo and the Highveld coal fields), difficult geological conditions, decreasing coal recovery grades, high operating costs and poor infrastructure at Transnet. Sources from industry have indicated that an additional two collieries in KwaZulu Natal have closed, and predict that most existing coal mines in Mpumalanga province will be exhausted by 2020 (Nyanjowa, 2014).

Based on rapidly increasing demand and constrained supply, coal prices are on the rise. This has resulted in large mining companies exporting more to take advantage of the higher pricing, and escalations in Eskom's electricity costs over the last 3 years.

Although maize is currently not economically attractive in comparison to coal, it may become a viable option should coal prices escalate to a price of 340 U.S. $/MT due to constraints in supply. Should coal reserves diminish critically, maize can provide a renewable alternative for support of synthetic liquid fuels production. This will allow further exporting of coal to support national GDP. In 2013, the economic value of coal to the South African economy was 51 billion rand providing employment to 500 000 people. Coal contributed more to the economy and employment than gold and platinum in 2013 (Statistics South Africa, 2016). Farming and processing of maize can assist with job creation to reduce the unemployment when further mines are depleted.

5.3.5 Effects of natural gas price on maize feasibility

Results:

Figure 5-11 indicates the effect of natural gas pricing on the feasibility of liquid fuels from maize based on a fixed R/US $ exchange rate of R14.06 and Crude oil price of 49 US $/bbl. Since domestic natural gas reserves are limited in South Africa, in order for maize to be more economically feasible than natural gas, the import cost will need to be greater than 48 U.S. $/mmBTU.

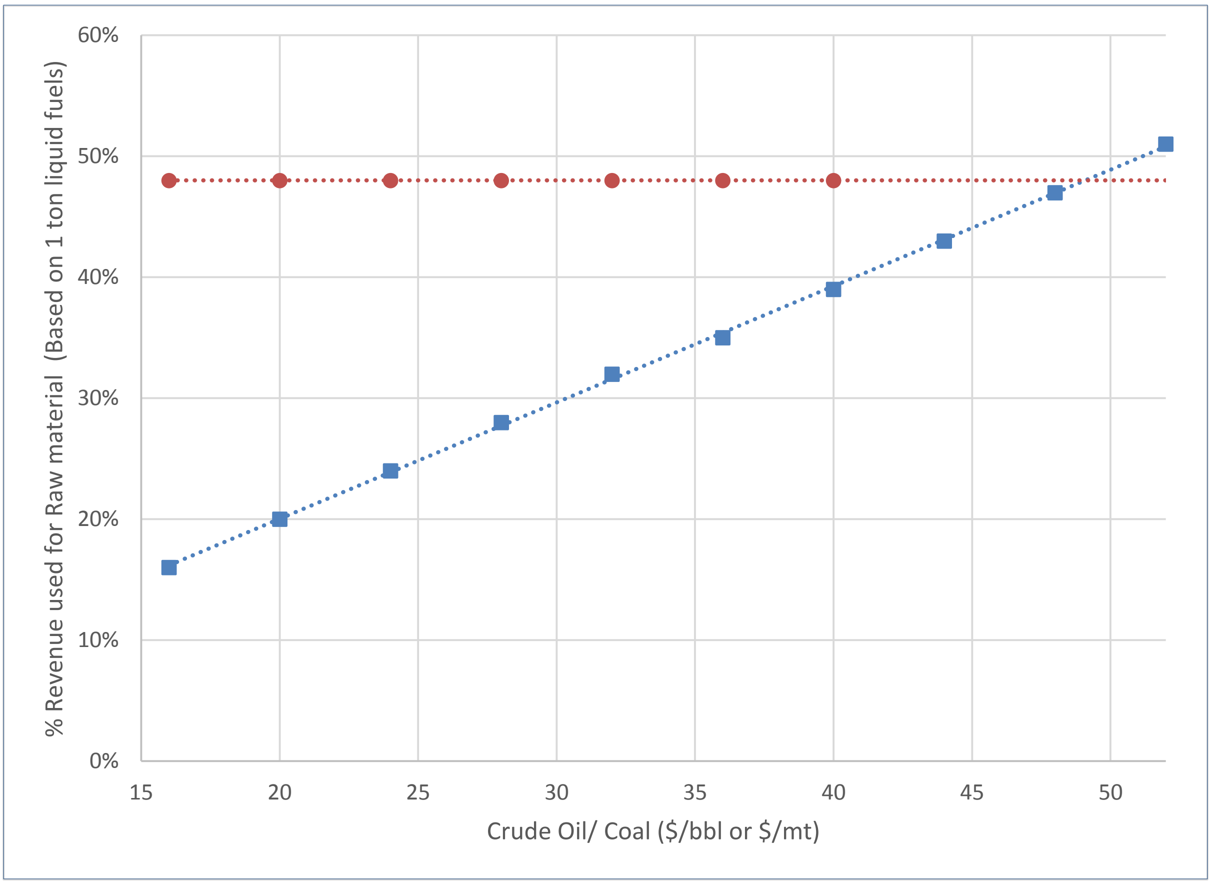


Figure 5-11: Sensitivity analysis: effect of natural gas prices on feasibility of liquid fuels production from maize

Discussion:

The entire gas and condensate production in South Africa is as a result of State owned PetroSA liquid fuels plant. PetroSA accounts for 1.5% of national energy needs (South African Department of Energy, 2016). However, this GTL plant has struggled to produce at its design capacity of 45 000 barrels/day due to shortage of indigenous natural gas supply. In addition, there have been challenges with feedstock from offshore wells resulting in imports of liquid gas condensate at much higher cost. Exploration projects to find additional supply require large capital investment, and take up to 5 year before seeing a return. According to Moagi, acting group CEO for CEF (owner of PetroSA), with low oil prices, the international trend for GTL processing assets is to be mothballed and all capital investments to be stopped (eNCA, 2016).

PetroSA has continued with exploration projects and capital investments in an effort to support the sustainability of the GTL plant. The Ikhwezi project initiated in 2010 by PetroSA, was expected to yield 242 billion ft^3 through 5 wells based on a cost estimate of R 1.344 billion. This project only resulted in 25 billon ft^3 after 3 wells were drilled. According to PetroSA executives 'the failure of the project to realize the initially estimated reserves resulted in a net loss of R 14.5 billion during 2014/2015 financial year' (eNCA, 2016). The unsuccessfulness of this Ikhwesi project has had serious ramifications for the sustainability of the GTL plant with a high risk of the refinery having to close by March 2017.

The lack of domestic supply and high natural gas import costs is a serious obstacle for synthetic fuel production from GTL processing in South Africa. Considering maize as a feed for liquid fuels production will allow South Africa the chance to control its own supply through years of experienced farming and remove the dependency on natural gas imports or investing capital into costly and risky explorations for domestic natural gas supply.

5.3.6 Effects of R/U.S. $ exchange rate on maize feasibility

Results:

Similarly to crude oil, fluctuations in the R/U.S. $ exchange rate also impact the liquid fuels price in South Africa. Equations 5-1 – 5-3 were used to determine the fluctuations in domestic fuel price based on a fix crude oil price of 49 U.S $/bbl.

The effect of changes in the R/U.S. $ exchange rate on the feasibility of maize as a feed for GTL processing is indicated in Figure 5-12. Changes in the R/US $ affects the costs of all fossil fuels. Maize used for FT processing becomes a viable option when the R/U.S. $ exchange rate is greater than R18.00 per US Dollar in comparison to crude oil refining. Natural gas and coal processing are still more economically feasible feeds than maize, when fluctuations in the R/US dollar exchange rate are within the range of R6.00 – R30.00 per U.S. dollar.

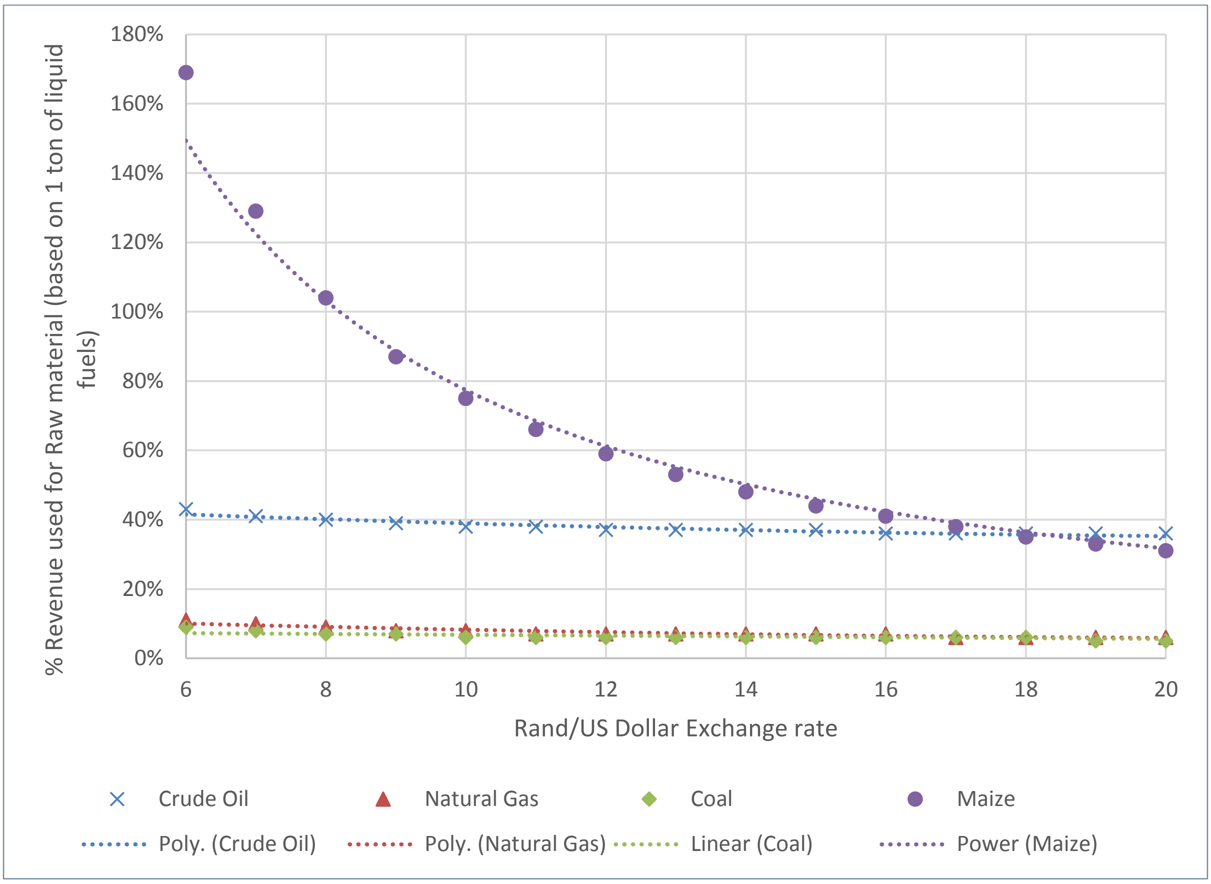


Figure 5-12: Effects of Rand/US Dollar Exchange rate on the feasibility of liquid fuels production from maize

Discussion:

The Rand Dollar exchange is dependent on a number of factors. According to Bhoola (2016) the main aspects affecting currency value are:

- Demand for a country's goods and services
- Domestic interest rate
- Current account deficit

In addition, political instability and poor economic performance also reduces attractiveness for foreign investment. This results in foreigners withdrawing capital and reinvesting in more stable countries. Currencies can also be treated as financial assets which can be traded. This also has an impact on value of a currency.

Recently political instability and perceived poor economic performance has affected the strength of the South African Rand. The Rand weakened substantially due to sudden changes in the finance ministry which was perceived to undermine the economic stability of South Africa in the market.

The Rand is expected to remain under pressure. Many analysts predict that it will fall further during the course of 2016 and 2017 (Bhoola, 2016). Based on this, economic feasibility of liquid fuels production from maize may be realized in the near future as a result of a weakening currency, making maize more economically feasible than crude oil refining for liquid fuels production. Coal and natural gas however, will remain more economically viable than maize despite further weakening of the Rand.

5.4 Feasibility of liquid fuels production from maize from an energy perspective

Results:

Total steam requirements of liquid fuels production from maize was found to be 910 kg/hr based on 1 000 kg/hr feed of maize. Table 5-6 indicates the thermal energy conditions determined for feeding, heating, distillation, as well as the thermal energy released from the reactor units.

Table 5-7 indicates the thermal energy requirements of this process in comparison to conventional fossil fuel feeds. The data for the fossil fuels was obtained through fixing the H_2/CO ratio of the developed simulation, and determining the necessary feeds for each fuel source based on each fuel source's unique composition. Since the H_2/CO ratio is fixed, the downstream operation from the gasifer onwards would be the same. Therefore the steam requirement indicated in Table 5-7 is only the feed required to attain an H_2/CO ratio of 2.20 based on each feed. Table 5-7 indicates the CO_2 production per kg feed for maize in comparison to the fossil fuel feeds.

Table 5-6: Thermal energy requirements for liquid fuels production from maize base on Aspen Plus® simulation

Steam consumed			
	kg/hr	Pressure (Bar)	kW
For distillation	250	10	142
For feeding	200	8	42
For heating	360	30	49
Steam generated	kg/hr		kW
by cooling operation	1802	8	459
by Fisher Tropsch synthesis	1804	10	377
by Hydrocracking	763	10	160

Table 5-7: Comparison of CO_2 production from a maize feed in relation to conventional fossil fuels processing

	Natural Gas	Coal	Maize
Raw material Feed (kg/hr)	169.10	1360.99	1000.00
Steam Feed (kg/hr)	287.47	531.49	199.83
Oxygen Feed (kg/hr)	0.00	345.89	220.01
CO2 emissions (kg/hr)	-352.00	662.62	662.62
CO2 emissions/Feed (kg/kg)	-2.08	0.49	0.66
Ash (kg/kg)	0	0.2	0.081
Steam requirement (kW/kg)	340.43	78.21	40.02

Discussion:

Assuming the steam generation from the FT and hydrocracking reactors is in the form of medium pressure steam at 10 bar, it can be sent to steam turbines for the generation of electricity to assist with the overall energy efficiency of the process (Er-rbib *et al.*, 2012).

The CO_2 production from liquid fuels processing based on a maize feed was found to be the highest at 0.66 kg/kg feed. The coal feed was found to have a lower CO_2 emission than maize, however 20% of the raw material forms ash, and 48.7% exists as fixed carbon. This indicates that there would be more solid toxic waste removal required from the gasifier than there would be for maize gasification. Natural gas treated by dry reforming performed the best in terms of CO_2 emissions. This process is a net consumer of CO_2, but has significantly higher steam requirements in order to achieve the same H_2/CO ratio as maize. This indicates that although maize results in more CO_2/kg feed, it is 88% more energy efficient than dry methane reforming.

6 CHAPTER 6: CONCLUSIONS AND RECOMMENDATIONS

6.1 Evaluation of the Aspen Plus® simulation for liquid fuels production from maize gasification in relation to experimental and simulation data from literature

The developed Aspen Plus® simulation was based on a modified Gibbs free energy model, using the ultimate and proximate analysis shown in studies carried out by Ioannidou *et al.* (2009) on maize. Equivalence ratio, steam to biomass ratio, temperature and pressure were investigated to ascertain the effects of these variables. Since the purpose of this report was to supplement liquid fuels production in South Africa via FT processing of maize, the syngas produced from maize gasification needed to have a high a H_2/CO ratio of 1.9 – 2.15 to be suitable for FT synthesis (Mavukwana *et al.*, 2014; Er-rbib *et al.*, 2012). As a result sensitivity analyses were conducted on these variables to maximum the H_2/CO ratio of syngas produced from maize, and the molar volume of hydrogen and carbon monoxide.

The optimum reactor conditions for maize gasification were found to be an equivalence ratio of 0.22 and steam to biomass ratio of 0.2 at a temperature of 611°C. As pressure increased there was a slight decreasing trend observed for CO and H_2 molar volume, and an increasing trend in CH_4 formation. Therefore optimum conditions were found to be at atmospheric conditions of 101.325 kPa, in order to maximize CO and H_2 molar volumes. Based on these conditions, the resultant H_2/CO ratio was found to be 2.20 suitable for FT synthesis, with a syngas composition of 35% H_2, 16% CO, 24% CO_2 and 3% CH_4.

In relation to experimental studies carried out by Ioannidou *et al.* (2009) on the pyrolysis of maize, this Aspen Plus® simulation showed good agreement for H_2 formation, but under predicted CO and CH_4 formation. This is a common discrepancy found between equilibrium models and experimentation. The difference in methane formation is due to generation of this hydrocarbon at low temperatures which bypasses the reaction zone ad avoids reduction into CO and H_2. In addition these differences in CO and CH_4 can be explained by insufficient residence time experimentally preventing chemical equilibrium from being reached. The Gibbs free energy model assumes fast reaction kinetics resulting in chemical equilibrium. Although, in this developed Aspen Plus® simulation, tar was accounted for as 5.5% of the total product from the gasifier (Barman *et al.*, 2012), it may have been an insufficient estimation. The difference in process may also have had an impact, as pyrolysis is aimed at bio oils and char production, while gasification is used primarily for production of gaseous products. The difference in process can also contribute to the differences in molar gas composition of produced syngas.

The gasification results obtained from this simulation indicate a reduced hydrogen and carbon monoxide molar volume, than results obtained from Mavukwana *et al.* (2013). This is as a result of the modified Gibbs free energy model used in this study. The results obtained from the developed simulation, based on a modified Gibbs free energy model, show a closer agreement with experimental data obtained from Ioannidou *et al.,* (2009), than the simulation based on the Gibbs free energy model, developed by Mavukwana *et al.*, (2013). Further experimentation should be carried out on maize gasification to establish and verify these results for South African maize.

The liquid fuels section of the developed Aspen Plus® simulation was modelled on experimental data obtained from literature. The product distribution from the Fischer-Tropsch synthesis was defined according to experimental data obtained from Sudiro *et al*., (2009). While the hydrocracking conversion and product distribution was based on results obtained from Coonradt & Garwood (1964). The results from the developed simulation was then validated against results from the industrial Sasol process, which makes use of low temperature Fischer-Tropsch (LTFT) synthesis, and the ideal Anderson Schulz Flory (ASF) equation for Fischer-Tropsch product distributions. This was done to validate the developed model and ensure its reliability. Based on the comparison, it was found that FT synthesis of maize reported a significantly higher diesel weight percentage than the coal to liquids process reported by Sasol. This may be due to the difference in H_2/CO ratio. Low rank coal used for gasification has a low H_2/CO ratio of 0.8 in comparison to the maize H_2/CO ratio of 2.20. The LTFT process employed by Sasol, has a WGS reactor which would adjust the H_2/CO ratio. After the WGS step this resultant H_2/CO ratio may still be less than the H_2/CO ratio achieved for maize, which could account for the difference. Studies carried out by Pirola *et al.* (2014) indicated that with decreasing H_2/CO ratios, the CO conversion rapidly decreases affecting selectivity of liquid fuel products. Low H_2/CO ratios reduce reactivity and affect selectivity of liquid fuels by inhibiting the adsorption reactions, chain initiation and chain growth associated with high H_2 content (van der Laan, 1999).

The discrepancy between the ASF equation and the liquid fuels distribution achieved by the simulation is as a result of the idealistic nature of the ASF product distribution. Studies indicate that common deviations between the ASF equation and experimental FT synthesis product distributions are lower LPG and higher wax formation achieved in practice. This is as a result of the characteristic ASF semi-logarithmic plot of mole fraction versus carbon number which is not representative of experimental conditions where a multi-component product mixture exists. These deviations from the ASF ideal product distribution can be expected as the liquid fuels section of the simulation was modelled based on experimental data obtained from literature.

The Aspen Plus® simulation of FT processing based on syngas from maize showed good agreement with literature. Where significant deviations were found, they could be explained and supported. The Aspen Plus® simulation was found to be a suitable means to predict liquid fuels production from maize gasification and FT processing.

6.2 Feasibility of maize as a biomass for syngas and liquid fuels production

The feasibility of maize as a feed for gasification was examined based on quality of syngas for FT synthesis. The syngas derived from maize was found to have a H_2/CO ratio of 2.20, which is higher than fossil fuel feeds: crude oil, coal and natural gas. This implies that maize can result in a syngas feed which is both renewable and richer in CO and H_2, making it a suitable feed for FT processing. The Aspen Plus® simulation does not indicate presence of any impurities, as the ultimate and proximate analysis of the maize feed did not contain N, S, metals or halogens. However, the ultimate and proximate analysis used by Mavukwana *et al.*, (2013) shows presence of N and S, which can result in presence of ammonia and hydrogen sulfide in the produced syngas. These impurities are not suitable for FT synthesis, as these compounds reduce reactivity during the catalytic conversion to liquid fuels. This means that the resultant syngas produced from maize, may require further processing in the form of aqueous ammonia scrubbing, with the use of sulfur absorbents prior to FT processing.

The Aspen Plus® simulation can only give an indication of the deviations in quality specifications for syngas prepared for FT synthesis. Typically Aspen® model limits formation of sulfur and nitrogen compounds to only NH_3 and H_2S; excluding all other possible N and S compounds. This assumption must therefore, be verified through experimentation to verify all possible deviations in syngas quality.

Simulated conversion of maize to liquid fuels indicated high conversions of syngas feed with greater selectivity for LPG and petrol in comparison to conventional fossil fuel feeds. Higher conversion indicates smaller amounts of gasification sludge and solid waste removal in relation to oil and coal processing. In addition, high feed stock conversion implies more efficient use of catalyst resulting in reduced catalyst spent in relation to a natural gas feed.

6.3 Feasibility of liquid fuels production from maize in South Africa

Based on findings from this study, it was found that maize is a feasible feed for gasification and FT processing for liquid fuels production. The feasibility of liquid fuels production from maize in South Africa was examined based on the country's resource capacity to support additional generation of maize. The examination was based on factors including domestic maize production, arable land, water and political stance in South Africa.

It was found that based on 450 000 hectares of underutilized land found in the Homelands of South Africa, an additional 1, 216 billion litres/annum of synthetic liquid fuels in the form of diesel and petrol could be produced. This has the potential to supplement South African liquid fuels demand by 6% using a renewable fuel source. This fuel generation from maize will not impact food security or water supply as it does not require irrigation since maize is classified as a dry land crop. In addition fuel generation in this manner supports the Biofuels Industry Strategy (2007) by targeting the use of underutilized land ensuring minimal impact on food security and exceeds its primary objective of achieving a 2% blending rate equivalent to 400 million litres/annum of liquid fuels derived from renewable sources.

6.4 Feasibility of liquid fuels generation from maize: economic perspective

Due to the number of unknown factors influencing economics of a FT commercial operation based on a maize feed, it was difficult to estimate the economic feasibility of a commercial maize GTL plant in terms of capital investment and operating expenditure. Based on literature, raw material costs in relation to commercial feeds have a significant impact on securing initial capital to construct a GTL plant. In addition raw material feed costs have a continued impact on economic feasibility of a GTL plant once it is operational. The economic feasibility of liquid fuels production from maize in South Africa was therefore, based on raw material cost difference between maize and conventional fossil fuel feeds.

Based on current economic conditions in 2016 of 49 U.S. $/bbl Brent Crude, 40 U.S. $/MT coal, and 6.5 U.S. $/mmBTU of natural gas at a Rand-Dollar exchange rate of R 14.06/U.S. $, it was found that coal to liquid fuels processing is still the most economically viable feed for fuel generation. Under these conditions, natural gas is the next most economically feasible feed followed by crude oil refining then maize processing. The raw material costs, domestic fuel prices and exchange rate have a significant impact on the economic feasibility of maize. Therefore sensitivity analyses were carried out on these variables.

Based on projected market conditions for South Africa, the R/U.S.$ exchange rate is expected to weaken further, the coal supply is expected to diminish resulting in limitations to existing consumers such as Sasol and Eskom, and natural gas supply will continue to be an issue for South Africa, especially with recent failure of the Ikhwezi project. Crude oil prices are subjected to world oil benchmarks and political issues outside of South Africa’s control which have the potential to adversely affect domestic fuel prices. Therefore, from an economic perspective maize should be considered as a fuel source to assist with the diminishing, costly non-renewable fossil fuel reserves in South Africa. Maize can potentially form an indigenous renewable feed, removing the dependency on crude oil and its associated impacts on the South African economy due to fluctuations in world oil prices and Rand Dollar exchange rates.

6.5 Feasibility of liquid fuels production from maize: an energy perspective

The energy feasibility of liquid fuels production from GTL processing of maize was only considered from a thermal energy perspective. Further work needs to be carried out on the electrical energy requirements of this process. It was found that maize gasification and FT processing requires 0.91 kg steam/kg feed. This 0.91kg of steam accounts for the raw material feed, distillation and heating required for every 1kg of maize processed. It was found that 2.56 kg steam/ kg feed was generated from the reactor units. This was assumed to be in the form of 10 bar steam, as in this form it can be sent to steam turbines for electricity generation to assist with overall efficiency of energy usage for this process.

In addition, the amount of CO_2 (kg/kg feed) produced, was examined for maize processing in comparison to fossil fuel feeds: natural gas and coal. The CO_2 production from liquid fuels processing based on a maize feed, was found to be the highest at 0.66 kg/kg feed. The coal feed was found to have a lower CO_2 emission than maize, however 20% of the raw material forms ash, and 48.7% exists as fixed carbon. This indicates that there would be more solid toxic waste removal required from the gasifier than there would be for maize gasification. Natural gas treated by dry reforming performed the best in terms of CO_2 emissions. This process is a net consumer of CO_2, but has significantly higher steam requirements in order to achieve the same H_2/CO ratio as maize. This indicates that although maize results in more CO_2/kg feed, it is 88% more energy efficient than dry methane reforming.

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7 CHAPTER 7: REFERENCES

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8 Appendix A:

Appendix A contains all data generated from the model developed in Aspen Plus ® for the production of liquid fuels from maize through gasification and Fischer-Tropsch synthesis.

8.1 Appendix A1:

Table A.1 indicates the mass and energy balance as well as all stream conditions.

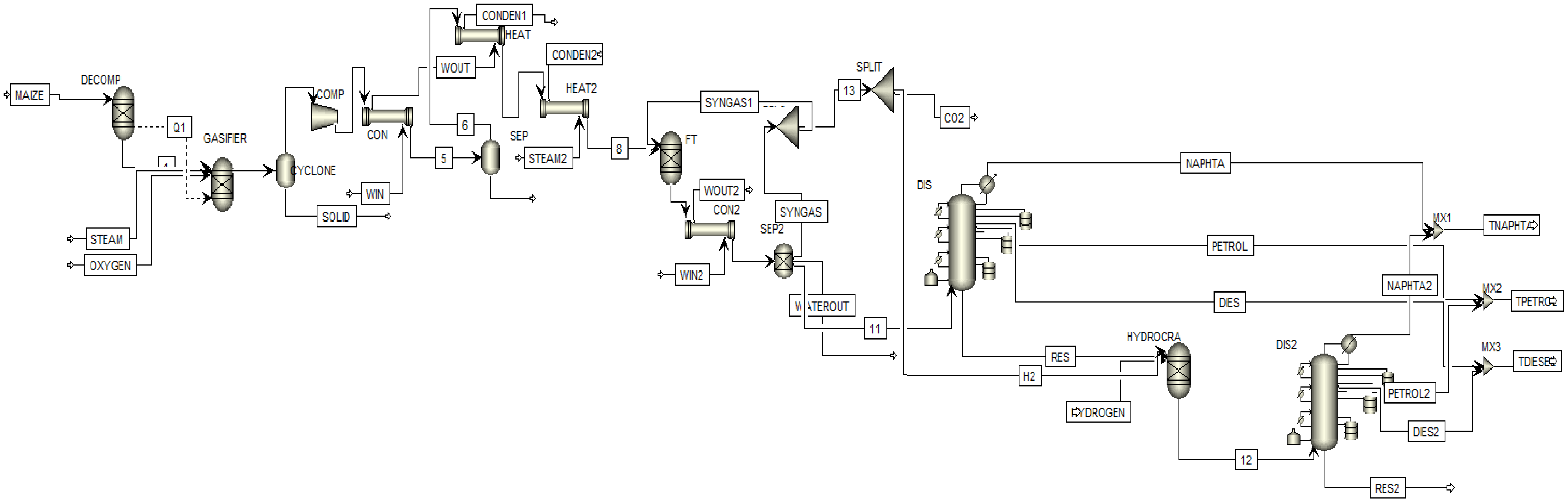


Figure 8-1 *Flow sheet of Aspen Plus ® model for liquid fuels production from maize gasification and downstream processing*

Table 8-1: Mass and Energy Balance for maize gasification and downstream processing for liquid fuels production

	1	2	3	4	5	6	7	8	9	10	11	12	13	CO2	CONDEN1	CONDEN2	DIES	DIES2
Substream: MIXED																		
Mole Flow kmol/hr																		
C	27	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
H	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
N	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
O	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
S	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
H2	24	22	22	22	22	22	22	22	3	3	0	-	2	-	-	-	0	-
O2	13	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
N2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CL2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
WATER	4	16	16	16	16	2	2	2	13	13	-	-	-	-	100	20	-	-
CO	-	9	9	9	9	9	9	9	1	1	0	-	1	-	-	-	0	-
CO2	-	16	16	16	16	16	16	16	20	20	2	-	12	12	-	-	0	-
CH4	-	2	2	2	2	2	2	2	2	2	2	-	0	-	-	-	0	-
C2H4	-	0	0	0	0	0	0	0	0	0	0	0	-	-	-	-	0	-
C3	-	-	-	-	-	-	-	-	0	0	0	0	-	-	-	-	0	-
C4	-	-	-	-	-	-	-	-	0	0	0	0	-	-	-	-	0	-
C5	-	-	-	-	-	-	-	-	0	0	0	1	-	-	-	-	0	-
C6	-	-	-	-	-	-	-	-	0	0	0	1	-	-	-	-	0	-
C7	-	-	-	-	-	-	-	-	0	0	0	1	-	-	-	-	0	-
C8	-	-	-	-	-	-	-	-	0	0	0	1	-	-	-	-	0	-
C9	-	-	-	-	-	-	-	-	0	0	0	1	-	-	-	-	0	-
C10	-	-	-	-	-	-	-	-	0	0	0	1	-	-	-	-	0	-
C11	-	-	-	-	-	-	-	-	0	0	0	0	-	-	-	-	0	0
C12	-	-	-	-	-	-	-	-	0	0	0	0	-	-	-	-	0	0
C13	-	-	-	-	-	-	-	-	0	0	0	0	-	-	-	-	0	0
C14	-	-	-	-	-	-	-	-	0	0	0	-	-	-	-	-	0	-
C15	-	-	-	-	-	-	-	-	0	0	0	-	-	-	-	-	0	-
C16	-	-	-	-	-	-	-	-	0	0	0	-	-	-	-	-	0	-
C17	-	-	-	-	-	-	-	-	0	0	0	-	-	-	-	-	0	-

C18	-	-	-	-	-	-	-	-	0	0	0	-	-	-	-	-	0	-
C19	-	-	-	-	-	-	-	-	0	0	0	0	-	-	-	-	0	-
C20	-	-	-	-	-	-	-	-	0	0	0	-	-	-	-	-	0	-
C21	-	-	-	-	-	-	-	-	0	0	0	-	-	-	-	-	0	-
C22	-	-	-	-	-	-	-	-	0	0	0	-	-	-	-	-	0	-
C23	-	-	-	-	-	-	-	-	0	0	0	-	-	-	-	-	0	-
C24	-	-	-	-	-	-	-	-	0	0	0	-	-	-	-	-	0	-
C25	-	-	-	-	-	-	-	-	0	0	0	-	-	-	-	-	0	-
C26	-	-	-	-	-	-	-	-	0	0	0	-	-	-	-	-	0	-
C27	-	-	-	-	-	-	-	-	0	0	0	-	-	-	-	-	0	-
C28	-	-	-	-	-	-	-	-	0	0	0	-	-	-	-	-	0	-
C29	-	-	-	-	-	-	-	-	0	0	0	-	-	-	-	-	0	-
C30	-	-	-	-	-	-	-	-	0	0	0	-	-	-	-	-	0	-
COH1	-	-	-	-	-	-	-	-	0	0	0	-	-	-	-	-	0	-
COH2	-	-	-	-	-	-	-	-	0	0	0	-	-	-	-	-	0	-
COH3	-	-	-	-	-	-	-	-	0	0	0	-	-	-	-	-	0	-
COH4	-	-	-	-	-	-	-	-	0	0	0	-	-	-	-	-	0	-
COH5	-	-	-	-	-	-	-	-	0	0	0	-	-	-	-	-	0	-
COH6	-	-	-	-	-	-	-	-	0	0	0	-	-	-	-	-	0	-
C32	-	-	-	-	-	-	-	-	0	0	0	-	-	-	-	-	0	-
C35	-	-	-	-	-	-	-	-	0	0	0	-	-	-	-	-	0	-
Total Flow kmol/hr	68	65	65	65	65	51	51	51	40	40	5	6	15	12	100	20	0	1
Total Flow kg/hr	847	1,307	1,307	1,307	1,307	1,071	1,071	1,071	1,314	1,314	257	636	575	546	1,802	360	60	95
Total Flow l/min	298,119	77,996	50,565	23,619	7,774	7,769	9,563	11,948	1,866	912	147	331	500	474	251	306	221	20
Temperature C	2,906	611	611	519	55	55	130	230	240	90	90	394	90	90	171	233	289	360
Pressure bar	1	1	1	3	3	3	3	3	15	15	15	14	15	15	8	30	1	14
Vapor Frac	1	1	1	1	1	1	1	1	1	1	1	1	1		0	1	1	1
Liquid Frac	-	-	-	-	0	-	-	-	0	0	0	-	-		1	0	-	-
Solid Frac	-	-	-	-	-	-	-	-	-	-	-	-	-		-	-	-	-
Enthalpy cal/mol	84,542	(36,277)	(39,075)	(37,129)	(43,249)	(36,909)	(36,312)	(35,486)	(65,892)	(70,489)	(55,146)	(25,740)	(76,968)		(65,525)	(58,506)	(52,695)	(39,184)
Enthalpy cal/gm	6,755	(1,791)	(1,929)	(1,833)	(2,135)	(1,772)	(1,743)	(1,704)	(2,016)	(2,157)	(1,093)	(231)	(2,057)		(3,637)	(3,248)	(261)	(236)
Enthalpy cal/sec	1,589,310	(650,180)	(700,320)	(665,440)	(775,120)	(527,060)	(518,530)	(506,730)	(735,620)	(786,940)	(78,121)	(40,790)	(328,340)		(1,820,100)	(325,030)	(4,374)	(6,210)
Entropy cal/mol-K	32	12	8	9	(5)	4	5	7	(6)	(17)	(51)	(127)	(1)		(32)	(18)	(254)	(204)
Entropy cal/gm-K	3	1	0	0	(0)	0	0	0	(0)	(1)	(1)	(1)	(0)		(2)	(1)	(1)	(1)

Density mol/cc	0	0	0	0	0	0	0	0	0	0	0	0	0		0	0	0	0
Density gm/cc	0	0	0	0	0	0	0	0	0	0	0	0	0		0	0	0	0
Average MW	13	20	20	20	20	21	21	21	33	33	50	112	37		18	18	202	166
Liq Vol 60F l/min	36	48	48	48	48	44	44	44	30	30	7	15	14	-	30	6	1	2
Substream: $TOTAL																		
Total Flow kg/hr	1,000	1,460	1,307	1,307	1,307	1,071	1,071	1,071	1,314	1,314	257	636	575	-	1,802	360	60	95
Enthalpy cal/sec	1,571,740	(667,750)	(700,320)	(665,440)	(775,120)	(527,060)	(518,530)	(506,730)	(735,620)	(786,940)	(78,121)	(40,790)	(328,340)	-	(1,820,100)	(325,030)	(4,374)	(6,210)
Substream: NC																		
Mass Flow kg/hr																		
MAIZE	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
ASH	81	81	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
TAR	72	72	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Total Flow kg/hr	153	153	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Temperature C	2,906	611																
Pressure bar	1	1	1	3	3	3	3	3	15	15	15	14	15		8	30	1	14

	H2	HYDROGEN	MAIZE	NAPHTA	NAPHTA2	OXYGEN	PETROL	PETROL2	RES	RES2	SOLID	STEAM	STEAM2	SYNGAS	SYNGAS1	TDIESEL	TNAPHTA	TPETROL	WATER
Substream: MIXED																			
Mole Flow kmol/hr																			
C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
H	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
N	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
O	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
S	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
H2	2	12	-	0	-	-	0	-	0	-	-	-	-	3	1	0	0	0	0
O2	-	-	-	-	-	7	-	-	-	-	-	-	-	-	-	-	-	-	-
N2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CL2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
WATER	-	-	-	-	-	-	-	-	-	-	-	13	20	-	-	-	-	-	13
CO	1	-	-	0	-	-	0	-	0	-	-	-	-	1	0	0	0	0	0
CO2	-	-	-	2	-	-	0	-	0	-	-	-	-	18	5	0	2	0	0
CH4	0	-	-	2	-	-	0	-	0	-	-	-	-	0	0	0	2	0	0
C2H4	-	-	-	0	0	-	0	-	0	-	-	-	-	-	-	0	0	0	0
C3	-	-	-	0	0	-	0	-	0	-	-	-	-	-	-	0	0	0	-
C4	-	-	-	0	0	-	0	-	0	-	-	-	-	-	-	0	0	0	-

C5	-	-	-	0	-	-	0	1	0	-	-	-	-	-	-	0	0	1	-
C6	-	-	-	0	-	-	0	1	0	-	-	-	-	-	-	0	0	1	-
C7	-	-	-	0	-	-	0	1	0	-	-	-	-	-	-	0	0	1	-
C8	-	-	-	0	-	-	0	1	0	-	-	-	-	-	-	0	0	1	-
C9	-	-	-	0	-	-	0	1	0	-	-	-	-	-	-	0	0	1	-
C10	-	-	-	0	-	-	0	1	0	-	-	-	-	-	-	0	0	1	-
C11	-	-	-	0	-	-	0	-	0	-	-	-	-	-	-	0	0	0	-
C12	-	-	-	0	-	-	0	-	0	-	-	-	-	-	-	0	0	0	-
C13	-	-	-	0	-	-	0	-	0	-	-	-	-	-	-	0	0	0	-
C14	-	-	-	0	-	-	0	-	0	-	-	-	-	-	-	0	0	0	-
C15	-	-	-	0	-	-	0	-	0	-	-	-	-	-	-	0	0	0	-
C16	-	-	-	0	-	-	0	-	0	-	-	-	-	-	-	0	0	0	-
C17	-	-	-	0	-	-	0	-	0	-	-	-	-	-	-	0	0	0	-
C18	-	-	-	0	-	-	0	-	0	-	-	-	-	-	-	0	0	0	-
C19	-	-	-	0	-	-	0	-	0	0	-	-	-	-	-	0	0	0	-
C20	-	-	-	0	-	-	0	-	0	-	-	-	-	-	-	0	0	0	-
C21	-	-	-	0	-	-	0	-	0	-	-	-	-	-	-	0	0	0	-
C22	-	-	-	0	-	-	0	-	0	-	-	-	-	-	-	0	0	0	-
C23	-	-	-	0	-	-	0	-	0	-	-	-	-	-	-	0	0	0	-
C24	-	-	-	0	-	-	0	-	0	-	-	-	-	-	-	0	0	0	-
C25	-	-	-	0	-	-	0	-	0	-	-	-	-	-	-	0	0	0	-
C26	-	-	-	0	-	-	0	-	0	-	-	-	-	-	-	0	0	0	-
C27	-	-	-	0	-	-	0	-	0	-	-	-	-	-	-	0	0	0	-
C28	-	-	-	0	-	-	0	-	0	-	-	-	-	-	-	0	0	0	-
C29	-	-	-	0	-	-	0	-	0	-	-	-	-	-	-	0	0	0	-
C30	-	-	-	0	-	-	0	-	0	-	-	-	-	-	-	0	0	0	-
COH1	-	-	-	0	-	-	0	-	0	-	-	-	-	-	-	0	0	0	-
COH2	-	-	-	0	-	-	0	-	0	-	-	-	-	-	-	0	0	0	-
COH3	-	-	-	0	-	-	0	-	0	-	-	-	-	-	-	0	0	0	-
COH4	-	-	-	0	-	-	0	-	0	-	-	-	-	-	-	0	0	0	-
COH5	-	-	-	0	-	-	0	-	0	-	-	-	-	-	-	0	0	0	-
COH6	-	-	-	0	-	-	0	-	0	-	-	-	-	-	-	0	0	0	-
C32	-	-	-	0	-	-	0	-	0	-	-	-	-	-	-	0	0	0	-
C35	-	-	-	0	-	-	0	-	0	-	-	-	-	-	-	0	0	0	-

Total Flow kmol/hr	3	12	-	4	1	7	0	4	0	0	-	13	20	22	6	1	5	5	13
Total Flow kg/hr	29	24	-	123	29	220	35	482	39	31	-	240	360	818	243	155	152	517	236
Total Flow l/min	25	659	-	925	1	353	178	15	1	1	-	5	415	711	211	693	1,188	1,611	5
Temperature C	90	25		40	40	25	182	180	377	370		170	236	90	90	322	(82)	122	55
Pressure bar	15	14	1	1	14	8	1	14	1	14	1	8	30	15	15	1	1	1	3
Vapor Frac	1	1		1	-	1	1	-	-	-		-	1	1	1	1	1	1	-
Liquid Frac	-	-		-	1	-	-	1	1	1		1	-	-	-	-	0	0	1
Solid Frac	-	-		-	-	-	-	-	-	-		-	-	-	-	-	-	-	-
Enthalpy cal/mol	(76,968)	(0)		(51,799)	(28,229)	(18)	(46,104)	(46,779)	(83,515)	(64,792)		(65,792)	(56,382)	(76,968)	(76,968)	(43,828)	(49,090)	(46,738)	(68,101)
Enthalpy cal/gm	(2,057)	(0)		(1,854)	(555)	(1)	(383)	(432)	(245)	(241)		(3,652)	(3,130)	(2,057)	(2,057)	(246)	(1,606)	(429)	(3,780)
Enthalpy cal/sec	(328,340)	(1)		(63,212)	(4,473)	(35)	(3,753)	(57,823)	(2,662)	(2,054)		(243,470)	(313,240)	(467,090)	(138,750)	(10,584)	(67,685)	(61,577)	(248,060)
Entropy cal/mol-K	(1)	(4)		(11)	(88)	(4)	(160)	(164)	(437)	(345)		(32)	(13)	(1)	(1)	(218)	(19)	(162)	(38)
Entropy cal/gm-K	(0)	(2)		(0)	(2)	(0)	(1)	(2)	(1)	(1)		(2)	(1)	(0)	(0)	(1)	(1)	(1)	(2)
Density mol/cc	0	0		0	0	0	0	0	0	0		0	0	0	0	0	0	0	0
Density gm/cc	0	0		0	1	0	0	1	0	0		1	0	0	0	0	0	0	1
Average MW	37	2		28	51	32	120	108	341	269		18	18	37	37	178	31	109	18
Liq Vol 60F l/min	14	10	-	4	1	6	1	12	1	1	-	4	6	20	6	3	5	12	4
Substream: $TOTAL																			
Total Flow kg/hr	575	22	1,000	123	29	220	35	482	39	31	153	240	360	818	243	155	152	517	236
Enthalpy cal/sec	(328,340)	(1)	(424,240)	(63,212)	(4,473)	(35)	(3,753)	(57,823)	(2,662)	(2,054)	(17,573)	(243,470)	(313,240)	(467,090)	(138,750)	(10,584)	(67,685)	(61,577)	(248,060)
Substream: NC																			
Mass Flow kg/hr																			
MAIZE	-	-	847	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
ASH	-	-	81	-	-	-	-	-	-	-	81	-	-	-	-	-	-	-	-
TAR	-	-	72	-	-	-	-	-	-	-	72	-	-	-	-	-	-	-	-
Total Flow kg/hr	-	-	1,000	-	-	-	-	-	-	-	153	-	-	-	-	-	-	-	-
Temperature C			25								611								
Pressure bar	15	7	1	1	14	8	1	14	1	14	1	8	30	15		1	1	1	3

	WATEROUT	WIN	WIN2	WOUT	WOUT2
Substream: MIXED					
Mole Flow kmol/hr					
C	-	-	-	-	-
H	-	-	-	-	-

N	-	-	-	-	-
O	-	-	-	-	-
S	-	-	-	-	-
H2	-	-	-	-	-
O2	-	-	-	-	-
N2	-	-	-	-	-
CL2	-	-	-	-	-
WATER	13	100	150	100	150
CO	-	-	-	-	-
CO2	-	-	-	-	-
CH4	-	-	-	-	-
C2H4	-	-	-	-	-
C3	-	-	-	-	-
C4	-	-	-	-	-
C5	-	-	-	-	-
C6	-	-	-	-	-
C7	-	-	-	-	-
C8	-	-	-	-	-
C9	-	-	-	-	-
C10	-	-	-	-	-
C11	-	-	-	-	-
C12	-	-	-	-	-
C13	-	-	-	-	-
C14	-	-	-	-	-
C15	-	-	-	-	-
C16	-	-	-	-	-
C17	-	-	-	-	-
C18	-	-	-	-	-
C19	-	-	-	-	-
C20	-	-	-	-	-
C21	-	-	-	-	-
C22	-	-	-	-	-
C23	-	-	-	-	-
C24	-	-	-	-	-

C25	-	-	-	-	-
C26	-	-	-	-	-
C27	-	-	-	-	-
C28	-	-	-	-	-
C29	-	-	-	-	-
C30	-	-	-	-	-
COH1	-	-	-	-	-
COH2	-	-	-	-	-
COH3	-	-	-	-	-
COH4	-	-	-	-	-
COH5	-	-	-	-	-
COH6	-	-	-	-	-
C32	-	-	-	-	-
C35	-	-	-	-	-
Total Flow kmol/hr	13	100	150	100	150
Total Flow kg/hr	239	1,802	2,702	1,802	2,702
Total Flow l/min	5	35	52	497	55
Temperature C	90	-	-	171	63
Pressure bar	15	8	8	8	8
Vapor Frac	-	-	-	0	-
Liquid Frac	1	1	1	1	1
Solid Frac	-	-	-	-	-
Enthalpy cal/mol	(67,413)	(69,166)	(69,166)	(65,218)	(67,934)
Enthalpy cal/gm	(3,742)	(3,839)	(3,839)	(3,620)	(3,771)
Enthalpy cal/sec	(248,000)	(1,921,300)	(2,881,900)	(1,811,600)	(2,830,600)
Entropy cal/mol-K	(36)	(42)	(42)	(31)	(38)
Entropy cal/gm-K	(2)	(2)	(2)	(2)	(2)
Density mol/cc	0	0	0	0	0
Density gm/cc	1	1	1	0	1
Average MW	18	18	18	18	18
Liq Vol 60F l/min	4	30	45	30	45
Substream: $TOTAL					
Total Flow kg/hr	239	1,802	2,702	1,802	2,702
Enthalpy cal/sec	(248,000)	(1,921,300)	(2,881,900)	(1,811,600)	(2,830,600)
Substream: NC					

Mass Flow kg/hr					
MAIZE	-	-	-	-	-
ASH	-	-	-	-	-
TAR	-	-	-	-	-
Total Flow kg/hr	-	-	-	-	-
Temperature C					
Pressure bar	15	8	8	8	8

MAIZE ULTANAL	1	2	MAIZE	SOLID
ASH			-	
CARBON			44	
HYDROGEN			6	
NITROGEN			-	
CHLORINE			-	
SULFUR			-	
OXYGEN			50	
MAIZE SULFANAL				
PYRITIC			-	
SULFATE			-	
ORGANIC			-	
ASH ULTANAL				
ASH	-	-	-	-
CARBON	53	53	53	53
HYDROGEN	4	4	4	4
NITROGEN	-	-	-	-
CHLORINE	-	-	-	-
SULFUR	-	-	-	-
OXYGEN	71	71	71	71
ASH SULFANAL				
PYRITIC	-	-	-	-
SULFATE	-	-	-	-
ORGANIC	-	-	-	-
ASH PROXANAL				
MOISTURE	-	-	-	-
FC	-	-	-	-
VM	-	-	-	-

ASH	-	-	-	-
TAR PROXANAL				
MOISTURE	-	-	-	-
FC	-	-	-	-
VM	-	-	-	-
ASH	-	-	-	-
TAR ULTANAL				
ASH	-	-	-	-
CARBON	47	47	47	47
HYDROGEN	4	4	4	4
NITROGEN	63	63	63	63
CHLORINE	-	-	-	-
SULFUR	-	-	-	-
OXYGEN	-	-	-	-
TAR SULFANAL				
PYRITIC	-	-	-	-
SULFATE	-	-	-	-
ORGANIC	-	-	-	-
PYRITIC		-		

Calculations carried out to determine the yield from the Decomposition Block in the Aspen Plus® model.

Table 8-2: Mass Balance calculations carried out to determine yield of decomp block in Aspen Plus® model

Total product stream from gasification	1307	kg/hr
Tar	72	kg/hr
Tar	5.5%	(Barman et al., 2012)

Tar	7.2%	% of the maize feed
Tar	72	

Tar	C	H	O	
	1	1.003	0.33	Tot Mw
Mw	12	1	16	18.283
Act mol	3.9	3.94	1.30	

Ioannidou et al., 2009	
Ultimate analysis	
C	43.8
H	6.2
N	-
O	50
S	-
Cl	-
Proximate Analysis	
Fixed Carbon	-

	kg/hr	kmol/hr
Maize	1000	
H2O	76	
Ash	81	
Volatile material	843	
C	369.2	30.8
H	52.266	52.3
O	421.5	26.3

Outlet		
	kmol/hr	kg/hr
H2	24	48
O2	13	401
H2O	4	76
C	27	322
Ash		81

Volatile matter	84.3
Ash	8.1
Moisture	7.6

Elemental Balance	In	Out	
C	30.8	30.8	kmol/hr
H	52.3	52.3	kmol/hr
O	26.3	26.3	kmol/hr

Tar	3.9	72

Elemental Balance over the Gasifer

Table 8-3: Mass Balance over Gasification unit to confirm results from Aspen Plus®

Ash/Tar	C	H	O
	1	1.003	0.33
	12	1	16

inlet	kmol/hr	kg/h
h2	24.14096	48.28192
o2	12.51162	400.3718
Water	4.221246	75.98243
C	26.80301	321.6361
ASH		81
Tar		72

outlet	kmol/hr	kg/h
h2	22.09024	44.18048
Water	13.94731	251.05158
CO	10.03029	280.84812
CO2	15.05955	662.6202
CH4	1.713173	27.410768
C2H4	1.23E-06	3.43753E-05

	Kmol/hr	Mol %	H2/CO
H2	22.09024	35%	2.20
Water	13.94731	22%	
CO	10.03029	16%	
CO2	15.05955	24%	
CH4	1.713173	3%	
C2H4	1.23E-06	0%	
	62.84056		

	kmol/h	kg/h
o2	6.875258	220.0083
h2o	11.10169	199.8304

Elemental Balance			
	In	Out	
H	78.92779	78.93	100%
C	26.80301	26.80	100%
O	54.09669	54.0967	100%

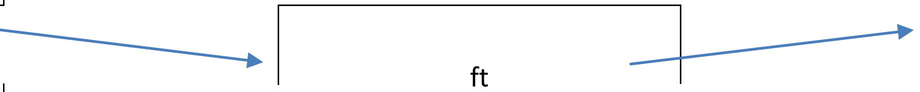
Calculations used to determine yield of FT reactor

Table 8-4: Calculations carried out to determine product distribution yield for FT reactor

		Inlet from gasifier	mol frac		diff
H2	KMOL/HR	22.9884545	0.397057	19.99996	2.988499
O2	KMOL/HR	0	0	0	0
N2	KMOL/HR	0	0	0	0
CL2	KMOL/HR	0	0	0	0
WATER	KMOL/HR	2.461421	0.042514	2.141436	0.319985
CO	KMOL/HR	9.2350686	0.159508	8.03451	1.200559
CO2	KMOL/HR	21.163938	0.365544	18.41263	2.751312
CH4	KMOL/HR	2.0482619	0.035378	1.781988	0.266274
C2H4	KMOL/HR	1.11922E-06	1.93E-08	9.74E-07	1.45E-07
		57.89714512		50.37052	7.526629

87% Conversion as per (Sudiro et al., 2009)

Inlet based on 87% conversion		
H2	KMOL/HR	19.99996
O2	KMOL/HR	0
N2	KMOL/HR	0
CL2	KMOL/HR	0
WATER	KMOL/HR	2.141436
CO	KMOL/HR	9.09451
CO2	KMOL/HR	18.41263
CH4	KMOL/HR	1.781988
C2H4	KMOL/HR	9.74E-07



(Sudiro et al., 2009) product distribution				
			mol%	wt%
Wax	31.60%	C19-30	32.25%	31.6162%
Petrol	25.60%	C5-11	25.60%	25.9170%
Diesel	40.30%	C12-18	40.38%	40.6439%
Light gas	1.60%	<C5	1.53%	1.1949%
oygenates	1%	OH		1.0338%
	100.00%			100.%

Table 8-5: Yield of each product determined for FT product based on selectivity and reactions in Table 3.2 and 3.3

	As per Sudiro et al., 2009				
	Selectivity	mol/h			mass%
CO2		20.10394	884.5733	0.50608	67.3942%
CO		1.21	33.84	0.03043	2.5786%
H2		3.05597	6.111939	0.07693	0.4657%
H2O		12.57811	226.406	0.31663	17.2495%
C1	0.39%	2.08373	33.33969	0.05245	2.5401%
C2	0.38%	1.73E-02	5.18E-01	0.00044	0.0395%
C3	0.38%	0.01152	0.506867	0.00029	0.0386%
C4	0.38%	0.00864	0.501107	0.00022	0.0382%
C5	0.40%	0.007276	0.523844	0.00018	0.0399%
C6	0.70%	0.01061	0.912482	0.00027	0.0695%
C7	1.60%	0.020787	2.078745	0.00052	0.1584%
C8	3.70%	0.042062	4.79508	0.00106	0.3653%
C9	6.10%	0.061641	7.889992	0.00155	0.6011%
C10	6.40%	0.058205	8.26509	0.00147	0.6297%
C11	6.70%	0.055394	8.641438	0.00139	0.6584%
C12	6.78%	0.051384	8.735277	0.00129	0.6655%
C13	6.30%	0.044073	8.109504	0.00111	0.6179%
C14	6.00%	0.038976	7.717341	0.00098	0.5880%
C15	5.80%	0.035165	7.455073	0.00089	0.5680%
C16	5.50%	0.031262	7.065297	0.00079	0.5383%
C17	5.20%	0.027819	6.67644	0.00070	0.5087%
C18	4.80%	0.024252	6.160015	0.00061	0.4693%
C19	4.00%	0.019146	5.131218	0.00048	0.3909%
C20	3.20%	0.014551	4.103443	0.00037	0.3126%
C21	2.80%	0.012126	3.5893	0.00031	0.2735%
C22	2.50%	0.010335	3.203748	0.00026	0.2441%
C23	2.20%	0.008699	2.818507	0.00022	0.2147%
C24	2.00%	0.007579	2.56162	0.00019	0.1952%
C25	1.80%	0.006548	2.304913	0.00016	0.1756%
C26	1.70%	0.005946	2.093136	0.00015	0.1595%
C27	1.60%	0.005389	2.047949	0.00014	0.1560%
C28	1.20%	0.003898	1.535673	0.00010	0.1170%
C29	1.20%	0.003763	1.535404	0.00009	0.1170%
C30	1.20%	0.003638	1.535153	0.00009	0.1170%
C32	1.20%	0.00341	1.534699	0.00009	0.1169%
C35	5.00%	0.012992	6.392141	0.00033	0.4870%
C39		0	0	0.00000	0.0000%
COH1	0.15%	0.013642	0.436536	0.00034	0.0333%
COH2	0.10%	0.004547	0.209174	0.00011	0.0159%
COH3	0.10%	0.003032	0.18189	0.00008	0.0139%

COH4	0.15%	0.00341	0.252373	0.00009	0.0192%
COH5	0.15%	0.002728	0.240095	0.00007	0.0183%
COH6	0.15%	0.002274	0.000527	0.00006	0.0000%
	99.9%	39.7245	1312.535		100.0000%

Table 8-6: Balanced chemical reactions used to model FT product distribution

	1	CO	+	1	H2O	------>	1	CO2	+	1	H2
Mols		1.06			1.06			1.06			1.06
Mw		28			18			44			2
Mass		29.68			19.08			46.64			2.12
					mass in	48.76				mass out	48.76

	1	CO	+	3	H2	------>	1	CH4	+	1	H2O
Mols		0.035469			0.106406			0.035469			0.035469
Mw		28			2			16			18
Mass		0.99312			0.212812			0.567497			0.638435
					mass in	1.205931984				mass out	1.205932

	2	CO	+	5	H2	------>	1	C2H6	+	2	H2O
Mols		0.034559			0.086398			0.01728			0.034559
Mw		28			2			30			18
Mass		0.967656			0.172796			0.518387			0.622064
					mass in	1.140451514				mass out	1.140452

	3	CO	+	7	H2	------>	1	C3H8	+	3	H2O
Mols		0.034559			0.080638			0.01152			0.034559
Mw		28			2			44			18
Mass		0.967656			0.161276			0.506867			0.622064
					mass in	1.128931802				mass out	1.128932

	4	CO	+	9	H2	------>	1	C4H10	+	4	H2O
Mols		0.034559			0.077758			0.00864			0.034559
Mw		28			2			58			18
Mass		0.967656			0.155516			0.501107			0.622064
					mass in	1.123171946				mass out	1.123172

	5	CO	+	11	H2	------>	1	C5H12	+	5	H2O
Mols		0.036378			0.080032			0.007276			0.036378
Mw		28			2			72			18
Mass		1.018585			0.160063			0.523844			0.654805

					mass in		1.178648455				mass out	1.178648
	6	CO	+	13	H2	------>		1	C6H14	+	6	H2O
Mols		0.063662			0.137933				0.01061			0.063662
Mw		28			2				86			18
Mass		1.782524			0.275867				0.912482			1.145908
					mass in		2.058390691				mass out	2.058391
	7	CO	+	15	H2	------>		1	C7H16	+	7	H2O
Mols		0.145512			0.311812				0.020787			0.145512
Mw		28			2				100			18
Mass		4.07434			0.623624				2.078745			2.619219
					mass in		4.697963859				mass out	4.697964
	8	CO	+	17	H2	------>		1	C8H18	+	8	H2O
Mols		0.336497			0.715056				0.042062			0.336497
Mw		28			2				114			18
Mass		9.421912			1.430112				4.79508			6.056943
					mass in		10.85202368				mass out	10.85202
	9	CO	+	19	H2	------>		1	C9H20	+	9	H2O
Mols		0.554765			1.171171				0.061641			0.554765
Mw		28			2				128			18
Mass		15.53342			2.342341				7.889992			9.985772
					mass in		17.87576403				mass out	17.87576
	10	CO	+	21	H2	------>		1	C10H22	+	10	H2O
Mols		0.582049			1.222302				0.058205			0.582049
Mw		28			2				142			18
Mass		16.29736			2.444604				8.26509			10.47688
					mass in		18.74196555				mass out	18.74197
	11	CO	+	23	H2	------>		1	C11H24	+	11	H2O
Mols		0.609332			1.274058				0.055394			0.609332
Mw		28			2				156			18
Mass		17.0613			2.548116				8.641438			10.96798
					mass in		19.60941642				mass out	19.60942
	12	CO	+	25	H2	------>		1	C12H26	+	12	H2O
Mols		0.616608			1.284599				0.051384			0.616608

Mw		28			2			170				18
Mass		17.26502			2.569199			8.735277				11.09894
					mass in	19.83421617				mass out		19.83422

	13	CO	+	27	H2	------>	1	C13H28	+		13	H2O
Mols		0.572954			1.189982			0.044073				0.572954
Mw		28			2			184				18
Mass		16.04272			2.379963			8.109504				10.31317
					mass in	18.42267831				mass out		18.42268

	14	CO	+	29	H2	------>	1	C14H30	+		14	H2O
Mols		0.545671			1.130318			0.038976				0.545671
Mw		28			2			198				18
Mass		15.27878			2.260635			7.717341				9.82207
					mass in	17.53941153				mass out		17.53941

	15	CO	+	31	H2	------>	1	C15H32	+		15	H2O
Mols		0.527482			1.090129			0.035165				0.527482
Mw		28			2			212				18
Mass		14.76948			2.180257			7.455073				9.494668
					mass in	16.94974084				mass out		16.94974

`	16	CO	+	33	H2	------>	1	C16H34	+		16	H2O
Mols		0.500198			1.031658			0.031262				0.500198
Mw		28			2			226				18
Mass		14.00554			2.063317			7.065297				9.003565
					mass in	16.06886179				mass out		16.06886

`	17	CO	+	35	H2	------>	1	C17H36	+		17	H2O
Mols		0.472915			0.973648			0.027819				0.472915
Mw		28			2			240				18
Mass		13.24161			1.947295			6.67644				8.512461
					mass in	15.18890111				mass out		15.1889

`	18	CO	+	37	H2	------>	1	C18H38	+		18	H2O
Mols		0.436536			0.897325			0.024252				0.436536
Mw		28			2			254				18

Mass		12.22302			1.79465			6.160015			7.857656
					mass in	14.01767092				mass out	14.01767
`	19	CO	+	39	H2	------>	1	C19H40	+	19	H2O
Mols		0.36378			0.746707			0.019146			0.36378
Mw		28			2			268			18
Mass		10.18585			1.493414			5.131218			6.548047
					mass in	11.67926507				mass out	11.67927
`	20	CO	+	41	H2	------>	1	C20H42	+	20	H2O
Mols		0.291024			0.5966			0.014551			0.291024
Mw		28			2			282			18
Mass		8.148681			1.1932			4.103443			5.238438
					mass in	9.341880345				mass out	9.34188
`	21	CO	+	43	H2	------>	1	C21H44	+	21	H2O
Mols		0.254646			0.521419			0.012126			0.254646
Mw		28			2			296			18
Mass		7.130096			1.042837			3.5893			4.583633
					mass in	8.172932701				mass out	8.172933
`	22	CO	+	45	H2	------>	1	C22H46	+	22	H2O
Mols		0.227363			0.46506			0.010335			0.227363
Mw		28			2			310			18
Mass		6.366157			0.93012			3.203748			4.092529
					mass in	7.296277086				mass out	7.296277
`	23	CO	+	47	H2	------>	1	C23H48	+	23	H2O
Mols		0.200079			0.408858			0.008699			0.200079
Mw		28			2			324			18
Mass		5.602218			0.817715			2.818507			3.601426
					mass in	6.419933009				mass out	6.419933
`	24	CO	+	49	H2	------>	1	C24H50	+	24	H2O
Mols		0.18189			0.371359			0.007579			0.18189

Mw		28			2			338			18
Mass		5.092925			0.742718			2.56162			3.274023
					mass in	5.835643713				mass out	5.835644
`	25	CO	+	51	H_2	------>	1	$C_{25}H_{52}$	+	25	H_2O
Mols		0.163701			0.33395			0.006548			0.163701
Mw		28			2			352			18
Mass		4.583633			0.667901			2.304913			2.946621
					mass in	5.251533671				mass out	5.251534
`	26	CO	+	53	H_2	------>	1	$C_{26}H_{54}$	+	26	H_2O
Mols		0.154607			0.31516			0.005946			0.154607
Mw		28			2			366			18
Mass		4.328987			0.630319			2.176386			2.78292
					mass in	4.959306087				mass out	4.959306
`	27	CO	+	55	H_2	------>	1	$C_{27}H_{56}$	+	27	H_2O
Mols		0.145512			0.296414			0.005389			0.145512
Mw		28			2			380			18
Mass		4.07434			0.592827			2.047949			2.619219
					mass in	4.667167635				mass out	4.667168
`	28	CO	+	57	H_2	------>	1	$C_{28}H_{58}$	+	28	H_2O
Mols		0.109134			0.222166			0.003898			0.109134
Mw		28			2			394			18
Mass		3.055755			0.444332			1.535673			1.964414
					mass in	3.500087012				mass out	3.500087
`	29	CO	+	59	H_2	------>	1	$C_{29}H_{60}$	+	29	H_2O
Mols		0.109134			0.222031			0.003763			0.109134
Mw		28			2			408			18
Mass		3.055755			0.444063			1.535404			1.964414
					mass in	3.499818209				mass out	3.499818
`	30	CO	+	61	H_2	------>	1	$C_{30}H_{62}$	+	30	H_2O
Mols		0.109134			0.221906			0.003638			0.109134

Mw		28			2			422			18
Mass		3.055755			0.443812			1.535153			1.964414
					mass in	3.499567326				mass out	3.499567

`	32	CO	+	65	H2	------>	1	C32H66	+	32	H2O
Mols		0.109134			0.221679			0.00341			0.109134
Mw		28			2			450			18
Mass		3.055755			0.443357			1.534699			1.964414
					mass in	3.4991126				mass out	3.499113

`	35	CO	+	71	H2	------>	1	C35H72	+	35	H2O
Mols		0.454725			0.922443			0.012992			0.454725
Mw		28			2			492			18
Mass		12.73231			1.844886			6.392141			8.185059
					mass in	14.5771998				mass out	14.5772

`	39	CO	+	79	H2	------>	1	C39H80	+	39	H2O
Mols		0			0			0			0
Mw		28			2			548			18
Mass		0			0			0			0
					mass in	0				mass out	0

	1	CO	+	2	H2	------>	1	CH3OH	+	0	H2O
Mols		0.013642			0.027284			0.013642			0
Mw		28			2			32			18
Mass		0.381969			0.054567			0.436536			0
					mass in	0.436536			mass out		0.436536

	2	CO	+	4	H2	------>	1	C2H5OH	+	1	H2O
Mols		0.009095			0.018189			0.004547			0.004547
Mw		28			2			46			18
Mass		0.254646			0.036378			0.209174			0.081851
					mass in	0.291024			mass out		0.291024

	3	CO	+	6	H2	------>	1	C3H7OH	+	2	H2O
Mols		0.009095			0.018189			0.003032			0.006063
Mw		28			2			60			18
Mass		0.254646			0.036378			0.18189			0.109134

					mass in	0.291024				mass out	0.291024

	4	CO	+	8	H2	------>	1	C4H9OH	+	3	H2O
Mols		0.013642			0.027284			0.00341			0.010231
Mw		28			2			74			18
Mass		0.381969			0.054567			0.252373			0.184164
					mass in	0.436536				mass out	0.436536

	5	CO	+	10	H2	------>	1	C5H11OH	+	4	H2O
Mols		0.013642			0.027284			0.002728			0.010913
Mw		28			2			88			18
Mass		0.381969			0.054567			0.240095			0.196441
					mass in	0.436536				mass out	0.436536

	6	CO	+	12	H2	------>	1	C6H13OH	+	5	H2O
Mols		0.013642			0.027284			0.002274			0.011368
Mw		28			2			102			18
Mass		0.381969			0.054567			0.23191			0.204626
					mass in	0.436536				mass out	0.436536

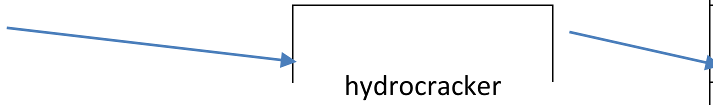
Calculations carried out to determine yield from hydrocracking unit.

Table 8-7: Elemental balance used to determine yield from hydrocracking unit

	in	out	
C	2.76	2.76	100%
H	5.75	30.21	100%
H required	24.46		

LPG	10%
Petrol	78%
Diesel	10%

	kmol/hr in
C	2.76
H	5.75



	C	H		C	H
C2	2	6	1%	0.027591721	2.055183
C3	3	8	3%	0.082775162	2.16555
C4	4	10	6%	0.165550324	2.331101
C5	5	12	10%	0.275917207	2.551834
C6	6	14	12%	0.331100648	2.662201
C7	7	16	14%	0.386284089	2.772568
C8	8	18	17%	0.469059251	2.938119
C9	9	20	15%	0.41387581	2.827752
C10	10	22	10%	0.275917207	2.551834
C11	11	24	5%	0.137958603	2.275917
C12	12	26	3%	0.082775162	2.16555

C13	13	28	2%	0.055183441	2.110367
Conversion			98.0%	2.70	29.41

0.114766

C19	19	40	2%	0.06	0.80
			Total	2.76	30.21
Additional Kmol/hr H required	24.46				
Additional H2/hr required kmol/hr	12.23005				

8.2 Appendix A.2: sensitivity analyses data

Appendix A.2 contains all data obtained from sensitivity analyses carried out over the gasification unit in the Aspen Plus® model.

Table 8-8: Aspen Plus® Sensitivity analysis: Effects of steam to biomass ratio on Syngas composition

VARY 1	H2	CO	CO2	CH4	C2H4
STEAM					
MIXED					
TOTAL MASSFLOW					
SBR					
0.2	0.30898	0.280523	0.151041	5.05E-06	3.50E-12
0.22	0.310705	0.270421	0.155014	6.96E-06	4.66E-12
0.24	0.312423	0.260558	0.15892	9.60E-06	6.21E-12
0.26	0.314131	0.250926	0.162758	1.32E-05	8.27E-12
0.28	0.315825	0.241521	0.166527	1.82E-05	1.10E-11
0.3	0.317498	0.232337	0.170226	2.51E-05	1.47E-11
0.32	0.319147	0.223369	0.173854	3.46E-05	1.95E-11
0.34	0.320763	0.214613	0.177409	4.75E-05	2.59E-11
0.36	0.322341	0.206066	0.180888	6.53E-05	3.43E-11
0.38	0.32387	0.197723	0.184289	8.95E-05	4.55E-11
0.4	0.325339	0.189583	0.18761	0.000123	6.00E-11
0.42	0.326737	0.181643	0.190846	0.000167	7.90E-11
0.44	0.328046	0.173901	0.193995	0.000228	1.04E-10
0.46	0.329245	0.166357	0.197051	0.000309	1.35E-10
0.48	0.330311	0.159011	0.200006	0.000416	1.75E-10
0.5	0.331214	0.151863	0.202855	0.000557	2.25E-10
0.52	0.331923	0.144915	0.205589	0.000741	2.86E-10
0.54	0.332403	0.13817	0.208198	0.000974	3.60E-10
0.56	0.332618	0.131631	0.210672	0.001267	4.46E-10
0.58	0.332538	0.1253	0.213002	0.001626	5.45E-10
0.6	0.332138	0.119179	0.215179	0.002056	6.54E-10
0.62	0.331401	0.113271	0.217195	0.002561	7.71E-10
0.64	0.33032	0.107577	0.219047	0.00314	8.93E-10
0.66	0.3289	0.102096	0.220731	0.003791	1.01E-09
0.68	0.32715	0.096825	0.222248	0.004509	1.13E-09
0.7	0.325089	0.091762	0.223599	0.005289	1.25E-09
0.72	0.322734	0.086902	0.224787	0.006124	1.35E-09
0.74	0.320109	0.082242	0.225817	0.007007	1.44E-09
0.76	0.317234	0.077776	0.226693	0.007932	1.51E-09
0.78	0.314131	0.073499	0.22742	0.008893	1.58E-09
0.8	0.310818	0.069406	0.228002	0.009884	1.63E-09
0.82	0.307314	0.065492	0.228446	0.010901	1.66E-09
0.84	0.303635	0.061752	0.228756	0.011939	1.68E-09
0.86	0.299795	0.058179	0.228937	0.012994	1.69E-09

0.88	0.295808	0.05477	0.228995	0.014064	1.68E-09
0.9	0.291687	0.051519	0.228932	0.015145	1.66E-09
0.92	0.287442	0.048422	0.228755	0.016234	1.64E-09
0.94	0.283085	0.045474	0.228468	0.017329	1.60E-09
0.96	0.278624	0.042669	0.228075	0.018429	1.56E-09
0.98	0.274068	0.040002	0.227581	0.019532	1.51E-09
1	0.269426	0.03747	0.226989	0.020636	1.46E-09
1.02	0.264705	0.035068	0.226305	0.02174	1.40E-09
1.04	0.259912	0.032791	0.225532	0.022842	1.34E-09
1.06	0.255055	0.030634	0.224674	0.023941	1.28E-09
1.08	0.250142	0.028593	0.223736	0.025036	1.22E-09
1.1	0.245176	0.026664	0.222721	0.026127	1.15E-09
1.12	0.240165	0.024842	0.221634	0.027213	1.09E-09
1.14	0.235115	0.023123	0.220479	0.028292	1.02E-09
1.16	0.230033	0.021502	0.219259	0.029364	9.58E-10
1.18	0.224922	0.019976	0.217978	0.030428	8.96E-10
1.2	0.21979	0.018541	0.21664	0.031483	8.35E-10
1.22	0.21464	0.017192	0.215249	0.032529	7.76E-10
1.24	0.209479	0.015925	0.213809	0.033566	7.20E-10
1.26	0.204311	0.014737	0.212322	0.034592	6.66E-10
1.28	0.199141	0.013623	0.210793	0.035607	6.14E-10
1.3	0.193975	0.012581	0.209225	0.03661	5.65E-10
1.32	0.188816	0.011607	0.207621	0.037602	5.18E-10
1.34	0.183668	0.010696	0.205985	0.038581	4.75E-10
1.36	0.178538	0.009846	0.20432	0.039547	4.33E-10
1.38	0.173429	0.009054	0.202628	0.040499	3.95E-10
1.4	0.168345	0.008316	0.200913	0.041438	3.59E-10

Table 8-9: Aspen Plus® Sensitivity Analysis: Effects of Equivalence ratio on Syngas Composition

VARY 1	H2	CO	CO2	CH4	C2H4
OXYGEN					
MIXED					
ER					
0.1	0.247066	0.112582	0.294468	0.17911	9.44E-08
0.11	0.259334	0.121728	0.287148	0.165774	9.85E-08
0.12	0.271095	0.130625	0.280009	0.152922	1.01E-07
0.13	0.28237	0.13927	0.273059	0.14054	1.03E-07
0.14	0.293174	0.147662	0.2663	0.128612	1.03E-07
0.15	0.303519	0.155804	0.25973	0.117123	1.02E-07
0.16	0.313413	0.163702	0.253347	0.106058	9.91E-08
0.17	0.322861	0.171363	0.247143	0.095406	9.55E-08
0.18	0.33186	0.178797	0.241112	0.085155	9.07E-08
0.19	0.340402	0.186014	0.235245	0.075297	8.49E-08

0.2	0.348471	0.193026	0.229529	0.065826	7.81E-08
0.21	0.356038	0.199847	0.223952	0.056741	7.04E-08
0.22	0.363056	0.20649	0.218499	0.048047	6.21E-08
0.23	0.369455	0.212975	0.213149	0.039756	5.32E-08
0.24	0.375121	0.219325	0.207875	0.031896	4.38E-08
0.25	0.379871	0.225567	0.202642	0.024517	3.43E-08
0.26	0.383397	0.231744	0.197397	0.017709	2.50E-08
0.27	0.38517	0.237912	0.19206	0.011638	1.64E-08
0.28	0.384284	0.244145	0.186517	0.006597	9.03E-09
0.29	0.379486	0.250499	0.180654	0.003009	3.89E-09
0.3	0.370248	0.25685	0.174567	0.001085	1.28E-09
0.31	0.358156	0.262853	0.168665	0.000345	3.66E-10
0.32	0.345296	0.268249	0.163301	0.000109	1.04E-10
0.33	0.332662	0.272974	0.158586	3.67E-05	3.12E-11
0.34	0.320541	0.27705	0.154513	1.32E-05	1.01E-11
0.35	0.30898	0.280523	0.151041	5.05E-06	3.50E-12
0.36	0.29796	0.283442	0.148123	2.05E-06	1.30E-12
0.37	0.287442	0.285852	0.145712	8.83E-07	5.09E-13
0.38	0.277386	0.287799	0.143766	4.00E-07	2.11E-13
0.39	0.267753	0.289322	0.142243	1.89E-07	9.20E-14
0.4	0.258508	0.290457	0.141107	9.36E-08	4.19E-14
0.41	0.249617	0.291238	0.140327	4.81E-08	1.99E-14
0.42	0.241053	0.291691	0.139874	2.56E-08	9.78E-15
0.43	0.23279	0.291844	0.139721	1.40E-08	4.97E-15
0.44	0.224806	0.291718	0.139847	7.92E-09	2.61E-15
0.45	0.217081	0.291332	0.140233	4.59E-09	1.41E-15
0.46	0.209598	0.290705	0.14086	2.73E-09	7.77E-16
0.47	0.202343	0.28985	0.141715	1.66E-09	4.39E-16
0.48	0.195301	0.288781	0.142784	1.03E-09	2.54E-16
0.49	0.188463	0.287509	0.144056	6.48E-10	1.49E-16
0.5	0.181817	0.286044	0.145521	4.16E-10	8.94E-17
0.51	0.175356	0.284395	0.14717	2.71E-10	5.44E-17
0.52	0.169071	0.282569	0.148995	1.79E-10	3.36E-17
0.53	0.162956	0.280574	0.150991	1.20E-10	2.10E-17
0.54	0.157005	0.278414	0.153151	8.13E-11	1.33E-17
0.55	0.151213	0.276096	0.155469	5.57E-11	8.49E-18
0.56	0.145576	0.273623	0.157942	3.85E-11	5.49E-18
0.57	0.140088	0.271	0.160565	2.69E-11	3.59E-18
0.58	0.134748	0.26823	0.163335	1.90E-11	2.36E-18
0.59	0.12955	0.265318	0.166247	1.35E-11	1.56E-18
0.6	0.124492	0.262265	0.1693	9.63E-12	1.04E-18
0.61	0.119572	0.259074	0.17249	6.93E-12	7.00E-19
0.62	0.114786	0.25575	0.175815	5.01E-12	4.72E-19
0.63	0.110133	0.252293	0.179272	3.65E-12	3.20E-19

0.64	0.105609	0.248706	0.182859	2.67E-12	2.18E-19
0.65	0.101213	0.244992	0.186573	1.96E-12	1.49E-19
0.66	0.096942	0.241152	0.190413	1.44E-12	1.02E-19
0.67	0.092794	0.23719	0.194375	1.07E-12	7.00E-20
0.68	0.088766	0.233107	0.198458	7.93E-13	4.82E-20
0.69	0.084857	0.228906	0.202659	5.90E-13	3.33E-20
0.7	0.081065	0.224588	0.206977	4.40E-13	2.30E-20
0.71	0.077386	0.220156	0.211409	3.29E-13	1.59E-20
0.72	0.073819	0.215613	0.215952	2.46E-13	1.10E-20
0.73	0.070362	0.21096	0.220605	1.84E-13	7.58E-21
0.74	0.067011	0.2062	0.225365	1.38E-13	5.24E-21
0.75	0.063765	0.201335	0.23023	1.04E-13	3.61E-21
0.76	0.060621	0.196369	0.235196	7.79E-14	2.49E-21
0.77	0.057578	0.191302	0.240263	5.84E-14	1.71E-21
0.78	0.054631	0.186138	0.245427	4.38E-14	1.17E-21
0.79	0.051779	0.180879	0.250686	3.28E-14	8.01E-22
0.8	0.04902	0.175528	0.256037	2.45E-14	5.03E-22

Table 8-10: Aspen Plus® Sensitivity Analysis: Effects of Temperature on Syngas Composition

VARY 1	VARY 2	TEMP	H2	CO	H2/CO
STEAM	OXYGEN				
MIXED	MIXED				
TOTAL MASSFLOW	TOTAL MASSFLOW				
KG/HR	KG/HR	C			
0	100	587.0776	0.241936	0.282577	0.856175
0	120	601.0432	0.269496	0.297977	0.904419
0	140	614.6333	0.294934	0.311806	0.945891
0	160	628.2748	0.318281	0.324281	0.981495
0	180	642.5006	0.339504	0.335597	1.01164
0	200	658.1284	0.358436	0.345933	1.036143
0	220	676.7191	0.374581	0.355468	1.053767
0	240	702.1163	0.386463	0.364431	1.060458
0	260	746.9077	0.388935	0.373214	1.042122
0	280	836.479	0.372124	0.381895	0.974416
0	300	948.8168	0.347277	0.388759	0.893297
0	320	1062.126	0.323837	0.393316	0.82335
0	340	1174.041	0.302312	0.395897	0.763612
0	360	1284.17	0.28241	0.396849	0.71163
0	380	1392.341	0.263854	0.396455	0.665534
0	400	1498.478	0.246432	0.394926	0.623995
0	420	1602.568	0.229988	0.392419	0.586079
0	440	1704.629	0.214412	0.389044	0.551126
0	460	1804.703	0.199625	0.38488	0.518669

0	480	1902.842	0.185573	0.379982	0.488373
0	500	1999.104	0.172217	0.374387	0.459996
400	100	483.9653	0.19425	0.033741	5.757144
400	120	503.753	0.22297	0.045836	4.86449
400	140	521.2409	0.248793	0.058543	4.249737
400	160	537.1451	0.272024	0.071515	3.803715
400	180	552.0209	0.292916	0.084517	3.465782
400	200	566.3499	0.311643	0.097396	3.199748
400	220	580.6214	0.328273	0.110069	2.982424
400	240	595.4368	0.342726	0.122504	2.797667
400	260	611.7158	0.354667	0.134725	2.632517
400	280	631.1977	0.363209	0.146833	2.473627
400	300	657.9018	0.366053	0.159059	2.301365
400	320	701.1046	0.35797	0.171724	2.084559
400	340	766.4311	0.337294	0.184083	1.832289
400	360	841.052	0.313546	0.194514	1.611943
400	380	917.3912	0.291265	0.202732	1.436703
400	400	993.9637	0.270865	0.208971	1.296185
400	420	1070.325	0.252161	0.213501	1.181076
400	440	1146.221	0.234922	0.216562	1.084783
400	460	1221.476	0.218947	0.218358	1.002697
400	480	1295.966	0.204067	0.219061	0.931553
400	500	1369.616	0.190143	0.218806	0.868999
800	100	334.1021	0.047396	0.00077	61.51889
800	120	370.7592	0.07519	0.001995	37.68616
800	140	400.9787	0.104513	0.004039	25.87293
800	160	426.6621	0.133626	0.006983	19.13642
800	180	449.0572	0.161534	0.01083	14.91579
800	200	469.0295	0.187708	0.01553	12.08671
800	220	487.2227	0.211893	0.021	10.09025
800	240	504.16	0.233981	0.02714	8.621373
800	260	520.3097	0.253913	0.033849	7.501425
800	280	536.1626	0.271626	0.04104	6.618563
800	300	552.3155	0.286953	0.048647	5.898694
800	320	569.6558	0.299499	0.056636	5.288108
800	340	589.7767	0.308355	0.06503	4.741718
800	360	615.968	0.31143	0.073926	4.212731
800	380	654.1405	0.305081	0.083381	3.65887
800	400	706.0602	0.289326	0.092775	3.118585
800	420	764.0754	0.270622	0.101141	2.675698
800	440	823.4662	0.252419	0.108194	2.33303
800	460	883.1058	0.235349	0.113972	2.064966
800	480	942.6899	0.219429	0.118573	1.850583

800	500	1002.07	0.204576	0.122103	1.675439
1000	100	237.78	0.009939	2.81E-05	353.7521
1000	120	288.2226	0.024549	0.000166	148.3131
1000	140	328.8551	0.045059	0.000559	80.57666
1000	160	362.207	0.069113	0.001355	51.01714
1000	180	390.3513	0.094732	0.002664	35.55721
1000	200	414.7363	0.120569	0.004561	26.4373
1000	220	436.3575	0.145766	0.00708	20.58825
1000	240	455.9307	0.16979	0.010228	16.60008
1000	260	474.0064	0.192313	0.013987	13.74933
1000	280	491.0505	0.213117	0.018322	11.63164
1000	300	507.5078	0.232029	0.023191	10.00511
1000	320	523.8851	0.248859	0.028555	8.715178
1000	340	540.8557	0.263287	0.034384	7.657274
1000	360	559.5073	0.274691	0.040675	6.753279
1000	380	581.8995	0.281748	0.047469	5.935412
1000	400	612.0453	0.281812	0.054837	5.139059
1000	420	654.2521	0.272437	0.062601	4.351955
1000	440	705.2527	0.257078	0.070027	3.671123
1000	460	758.9327	0.240696	0.076587	3.142781
1000	480	813.1032	0.224911	0.082174	2.736996
1000	500	867.2771	0.210004	0.086812	2.419063
200	350	980.0386	0.30898	0.280523	1.101441

Table 8-11: Aspen Plus® Sensitivity Analysis: Effects of Pressure on Syngas Composition

VARY 1	H2	CO	CO2	CH4	C2H4
GASIFIER					
PARAM					
PRES					
BAR					
0	0.293647	0.161545	0.184881	1.87E-05	6.82E-12
1.01325	0.293645	0.161545	0.184881	1.92E-05	7.10E-12
2	0.293433	0.161549	0.184856	7.41E-05	5.40E-11
4	0.292638	0.161541	0.184784	0.000285	4.14E-10
6	0.291448	0.161513	0.184691	0.000605	1.31E-09
8	0.289985	0.161469	0.184585	0.001	2.86E-09
10	0.288356	0.161412	0.184474	0.001441	5.10E-09
12	0.286644	0.161345	0.184364	0.001905	8.01E-09
14	0.284902	0.161271	0.184258	0.002378	1.15E-08
16	0.283168	0.161191	0.184158	0.002849	1.56E-08
18	0.281462	0.161106	0.184064	0.003313	2.03E-08
20	0.279797	0.161019	0.183977	0.003766	2.53E-08

9 Appendix B: Calculations

Appendix B contains all calculations carried out outside of Aspen Plus®.

9.1 Appendix B.1.: Syngas production from gasification of maize

Table 9-1: Sensitivity analysis carried out in Aspen Plus® to find optimum operating conditions in Gasifier

VARY 1	VARY 2	H2	CO	CO2	CH4	H_2/CO
OXYGEN	STEAM					
MIXED	MIXED					
TOTAL MASSFLOW	TOTAL MASSFLOW					
KG/HR	KG/HR					
140	0	0.301479	0.244092	0.23882	0.104562	1.235103
140	200	0.271213	0.090605	0.292295	0.112899	2.993366
140	400	0.193893	0.024266	0.284601	0.122309	7.990249
140	600	0.103427	0.004117	0.24778	0.129577	25.12397
140	800	0.034664	0.000332	0.208623	0.130465	104.4547
140	1000	0.004702	5.42E-06	0.179016	0.122488	867.429
160	0	0.326161	0.262243	0.22148	0.075908	1.243738
160	200	0.296483	0.108812	0.278783	0.088329	2.724742
160	400	0.226141	0.03499	0.280569	0.100523	6.463063
160	600	0.13851	0.0079	0.251355	0.110904	17.5321
160	800	0.061735	0.001079	0.214289	0.116573	57.21265
160	1000	0.015503	5.59E-05	0.182945	0.11477	277.5736
180	0	0.347551	0.278691	0.205755	0.050296	1.247084
180	200	0.318484	0.126382	0.265507	0.065854	2.520014
180	400	0.254431	0.046757	0.275039	0.080215	5.441618
180	600	0.171537	0.013033	0.253354	0.092806	13.16133
180	800	0.091671	0.002507	0.219689	0.101781	36.56653
180	1000	0.033584	0.00026	0.187844	0.104872	129.2219
200	0	0.364537	0.293833	0.191248	0.027844	1.240627
200	200	0.337094	0.14328	0.252507	0.045446	2.352684
200	400	0.278949	0.059191	0.268384	0.061398	4.71271
200	600	0.201697	0.0194	0.253781	0.075567	10.39663
200	800	0.122012	0.004751	0.224343	0.08684	25.68379
200	1000	0.056669	0.000761	0.193212	0.093492	74.49523
220	0	0.373035	0.308281	0.177312	0.009727	1.210047
220	200	0.351528	0.159615	0.239647	0.027262	2.202354
220	400	0.299717	0.072035	0.260852	0.044104	4.160707
220	600	0.228625	0.026832	0.252746	0.059336	8.520716
220	800	0.151276	0.007874	0.227982	0.072193	19.21268
220	1000	0.082261	0.001687	0.198532	0.081378	48.7504
240	0	0.358523	0.322963	0.16288	0.000887	1.110106

240	200	0.359113	0.17572	0.226452	0.012032	2.043662
240	400	0.316323	0.085162	0.252529	0.028462	3.714371
240	600	0.252098	0.035154	0.250384	0.044211	7.17115
240	800	0.178583	0.011884	0.230476	0.058103	15.02744
240	1000	0.108532	0.003138	0.203429	0.069066	34.58411
260	0	0.325775	0.335288	0.150579	3.68E-05	0.971628
260	200	0.351164	0.192295	0.211718	0.002393	1.82617
260	400	0.327233	0.098613	0.243241	0.014907	3.318352
260	600	0.271753	0.04423	0.246782	0.03032	6.144158
260	800	0.203361	0.016749	0.231779	0.044742	12.14156
260	1000	0.134263	0.00518	0.207658	0.056905	25.91955
280	0	0.295202	0.343293	0.142574	2.46E-06	0.85991
280	200	0.322861	0.208155	0.196282	0.000176	1.551063
280	400	0.327656	0.112696	0.232254	0.004826	2.90742
280	600	0.286649	0.053994	0.241895	0.017945	5.308895
280	800	0.225104	0.022422	0.231868	0.032261	10.03949
280	1000	0.158616	0.007852	0.211058	0.04513	20.20052

Table 9-2: Molar Volume Composition for Syngas produced from Gasification unit based on Maize feed

Mole Flow kmol/hr	VOL%
CO2	19%
CO	25%
H2	48%
H2O	0%
C	0%
CH4	7%
N2	0%
O2	0%
H2/CO	1.935072

9.2 Appendix B.2. Liquid fuels conversion based on feed: economic feasibility analysis

Compressed Air cost Europe	1.25	Euro/Nm3		
R/Euro Exchange	14.64	R/Euro		
Compressed Air cost South Africa	18.3	R/Nm3		
Density of air	1.225	kg/m3	at 15oC and 101.325kPa	

Steam cost per ton	153	R/ton	Omnia Fertilizer	
Natural gas cost $	6.5	$/mmBTU		
Natural gas Energy	0.036	mmBTU/Nm3		
Density of Natural gas	0.668	kg/m3		
Feed of Natural gas	1000	kg		
Feed of Natural gas	1497.006	Nm3		
Cost of Natural gas feed	350.2994	$/ton		
$/Rand Exchange rate	20	Rand/$		
Cost of Natural gas feed	7005.988	Rand/ton		
Cost of Crude	49	$/bbl		
Cost of Coal	40	$/mT		
		original		
Petrol Price	19.513	12.85		
Diesel price	18.138	11.02		
LPG price	11.1165	3.83		

Table 9-3: Raw material costs for 1 ton of liquid fuels generation based on existing economic conditions in 2016

	Total Revenue generated by liquid fuel Sales	Raw material feed costs
Oil	R 16,161.96	R 5,919.13
Coal	R 13,176.06	R 765.43
Natural Gas	R 13,176.06	R 897.53
Maize	R 13,176.06	R 6,302.89

Table 9-4: Sensitivity of domestic fuel prices based on changing Rand Dollar exchange rate

Sensitivity Analysis	Crude Oil	Natural Gas	Coal	Maize	petrol price	diesel price	LPG price
R/US $ exchange rate	%Raw material cost	%Raw material cost	%Raw material cost	%Raw material cost			
6	43%	11%	9%	169%	5.50	4.13	
7	41%	10%	8%	129%	6.50	5.13	
8	40%	9%	7%	104%	7.50	6.13	
9	39%	8%	7%	87%	8.50	7.13	

10	38%	8%	6%	75%	9.50	8.13	1.11
11	38%	7%	6%	66%	10.50	9.13	2.11
12	37%	7%	6%	59%	11.50	10.13	3.11
13	37%	7%	6%	53%	12.50	11.13	4.11
14	37%	7%	6%	48%	13.50	12.13	5.11
15	37%	7%	6%	44%	14.50	13.13	6.11
16	36%	7%	6%	41%	15.50	14.13	7.11
17	36%	6%	6%	38%	16.50	15.13	8.11
18	36%	6%	6%	35%	17.50	16.13	9.11
19	36%	6%	5%	33%	18.50	17.13	10.11
20	36%	6%	5%	31%	19.50	18.13	11.11
21	35%	6%	5%	30%			
22	35%	6%	5%	28%			
23	35%	6%	5%	27%			
24	35%	6%	5%	25%			
25	35%	6%	5%	24%			
26	35%	6%	5%	23%			
27	35%	6%	5%	22%			
28	35%	6%	5%	21%			
29	35%	6%	5%	21%			
30	35%	6%	5%	20%			

Table 9-5: Sensitivity analysis of domestic fuel prices based on Crude oil price Fluctuations

Sensitivity Analysis	Crude Oil	Maize	petrol price	diesel price	LPG price
$/barrel crude	%Raw material cost	%Raw material cost			
10	24%	160%	6.28	1.356	
15	28%	123%	7.215	2.746	
20	30%	100%	8.15	4.136	
25	32%	84%	9.085	5.526	0.5325
30	34%	73%	10.02	6.916	1.5
35	35%	64%	10.95	8.306	2.467
40	35%	57%	11.89	9.696	3.435
45	36%	52%	12.825	11.086	4.4025
50	37%	47%	13.76	12.476	5.37
55	37%	43%	14.69	13.86	6.337
60	38%	40%	15.256	15.256	7.305
65	38%	37%			
70	38%	35%			
75	39%	33%			

Table 9-6: Liquid fuels conversion based on Maize Feed

Feed	kg/hr	Cost	Final	kg/hr		% of Feed	Density kg/m3	Litres	Rand/Litre	Revenue	
Maize	1000	R 3,208.00	LPG	151.77	151.77	3%	510	297.5882	5.1765	R 1,540.47	
Air	220	R 3,064.29	Petroleum	517.19	517.19	25%	739	699.8512	13.573	R 9,499.08	
Steam	200	R 30.60	Diesel	155.01	155.01	50%	885	175.1525	12.198	R 2,136.51	
Total	1420	R 6,302.89		2052.646	823.97					R 13,176.06	48%

Table 9-7: Liquid fuels conversion based on Natural Gas Feed

Natural Gas											
Feed	kg/hr	Cost		Final	%Feed	kg/hr	Density kg/m3	Litres	Rand/Litre	Revenue	
Natural Gas	169	R 832.85		LPG	0.1%	151.77	510	298	5.1765	R 1,540.47	
Steam	287	R 43.91		Petroleum	7.2%	517.19	739	700	13.573	R 9,499.08	

				Diesel	19.0%	155.01	885	175	12.198	R 2,136.51	
	456	R 876.76				823.97				R 13,176.06	7%

Table 9-8: Liquid fuels conversion based on Crude oil feed

Crude Oil											
Feed		Cost	Final	%Feed	Gallons	Litres	Density kg/m3	kg	Rand/Litre	Revenue	
bbl	9	R 5,919.13	LPG	4%	14.434	65.6	510	33.5	5.1765	R 339.67	
Gallons	361		Petrol	45%	162.382	738.2	739	545.5	13.573	R 10,019.44	
			Diesel	29%	104.646	475.7	885	421.0	12.198	R 5,802.85	
								1000.0		R 16,161.96	37%

Table 9-9: Liquid fuels conversion based on Coal feed

Coal											
Feed	kg/hr	Cost	Final	%Feed	kg/hr		Density kg/m3	Litres	Rand/Litre	Revenue	
Coal	1361	R 765.43	LPG	0.3%	151.77		510	298	5.1765	R 1,540.47	
Air	1060.219		Petroleum	5.1%	517.19		739	700	13.573	R 9,499.08	
Steam	531		Diesel	11.2%	155.01		885	175	12.198	R 2,136.51	
Total	2952.219				824					R 13,176.06	6%

9.3 Appendix B.3: Data for white maize and yellow maize trading price

Table 9-10: Selling price of white and yellow maize in 2016 (Grain SA, 2016)

Year 2016	White Maize	Yellow Maize

	Rand	Rand
Jan	4037	3326
Feb	3969	3315
Mar	3790	3257
Apr	3423	2989
May	3145	2760
Jul	2949	2755
Sep	2975	2800
Dec	2993	2841

9.4 Appendix B.4: Maize production for liquid fuels generation in South Africa

Table 9-11: Volumetric flowrate of liquid fuels produced from Maize feed

	kg/hr	kg/m^3	m^3/hr	L/hr
LPG	151.77	510	0.30	297.59
Petrol	517.29	739	0.70	699.99
Diesel	155.01	820	0.19	189.04

Table 9-12: Potential maize production and liquid fuels generation based on underutilized land in South Africa

Underutilized land	450 000	hectares
Underutilized land	450 000	hectares
maize production per hectare	3.8	t/hectare
maize production	1 710 000	tons/annum
safety factor	20%	
maize	136 8000	tons
Petrol	958	million L/annum
Diesel	259	million L/annum
Total	1.216	billion L/annum
Total liquid fuel requirements	20	billion L/annum
Possible renewable fuels supplement for South African liquid fuels demand	6%	

9.5 Appendix B.5. Determination of net thermal energy release from maize gasification and FT processing

Distillation Unit

Energy Requirement	4119.01	cal/s	
	17.23393784	kJ/s	
Steam requirement	752.42	Kj/kg	10 bar pressure
	82.5	kg/hr	
	0.08	t/hr	

Distillation Unit 2

Energy Requirement	29769.885	cal/s	
	124.5571988	kJ/s	
	448405.9158	kJ/hr	
Steam requirement	2675.43	Kj/kg	10 bar pressure
	167.60	kg/hr	

FT Unit

Energy Released			
	-90140	cal/s	
	-377.14576	kJ/s	
		kJ/hr	
		kJ/kg	
		MJ/kg	
Steam produced	752.42	Kj/kg	10 bar saturated steam
	1804.48	kg/hr	
	1.80	t/hr	

Hydrocracking

Energy Released	-38126.3385	cal/s	
	-159.5206003	kJ/s	
Steam produced	752.42	Kj/kg	10 bar saturated steam

-763.24	kg/hr
-0.76	t/hr

	Cooling		
Energy requirement	-49900	cal/s	
	-208.782	kJ/s	
Steam requirement	752.42	Kj/kg	10 bar pressure
	998.9285	kg/hr	

9.6 Appendix B.6: Determining Coal and Natural gas feeds which result in the same H_2/CO ratio in order to compare liquid fuels production, steam requirements and CO_2 emissions

9.6.1 Coal Decomposition from Ultimate and Proximate analysis

a Coal ultimate and proximate analysis

Table 9-13: Ultimate and proximate analysis for South African coal (de Kock & Frazidis, 1973)

South African Coal	(de Kock & Frazidis, 1973)
Ultimate analysis	
%C	83.2
%H	4.82
%N	2.03
%S	0.34
%O	9.6
Promixate Analysis	
Volatile matter	28.4
Ash	20
Moisture	2.9

Table 9-14: Decomposition of South African coal based on ultimate and proximate analysis

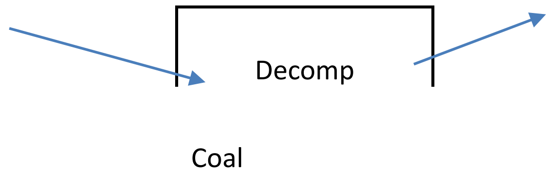
Total product stream from gasification	1266.111182	kg/hr
Tar	69.63611503	kg/hr
Tar	5.50%	(Barman et al., 2012)

Tar	5.12%	% of the maize feed
Tar	69.6	

Tar	C	H	O	
	1	1.003	0.33	
Mw	12	1	16	18.283
Act mol	3.81	3.82	1.26	3.80879

Ioannidou et al., 2009	
Ultimate analysis	
C	83.20
H	4.82
N	2.03
O	9.60
S	0.34
Mineral matter	0
Proximate Analysis	
Fixed Carbon	48.7
Volatile matter	28.4
Ash	20
Moisture	2.9

	kg/hr	kmol/hr
Coal	1360.989	
H2O	39.4687	
Ash	272.1979	
Volatile material	386.521	
Fixed C	662.8019	
Mineral matter	0	
C	321.5855	26.79879
H	18.63031	18.63031
O	37.10602	2.319126
S	1.314171	
N	7.846377	
Moisture	11.20911	



Outlet			
	kmol/hr	kg/hr	
H2	7	48	14.81
O2	0.531113	401	17.00
H2O	0.62	76	11.21
C	22.99	322	275.88
Ash		272.1979	0
Tar	3.80879	0	69.63612
N2	0.280228		7.846377
S	0.041068		1.314171

Elemental Balance	In	Out	

b Gasification of coal based on decomposition of ultimate and proximate analysis

Table 9-15: Gasification and goal seeked values for coal feed to obtain a H_2/CO ratio of 2.20

Ash/Tar	C	H	O
	1	1.003	0.33
	12	1	16

inlet	mol/hr	kg/h
h2	7	14.8101
o2	0.531113	16.9956
Water	0.62	11.20911
C	22.99	275.88
ASH		0
N2	0.280228	7.846377
S	0.041068	1.314171
Tar	3.80879	69.6

outlet	mol/hr	kg/h
h2	22.09024	44.18048
Water	13.94731	251.0516
CO	10.03029	280.8481
CO2	15.05955	662.6202
CH4	1.713173	27.41077
C2H4	1.23E-06	3.44E-05
Tar	3.80879	

			H2/CO
H2	22.09024	35%	2.20
Water	13.94731	22%	
CO	10.03029	16%	
CO2	15.05955	24%	
CH4	1.713173	3%	
C2H4	1.23E-06	0%	
	62.84056		

	mol/h	kg/h
o2	10.80891	345.8852
h2o	29.52722	531.49

18%

Elemental Balance			
	In	Out	
H	75.11	75.11	100%
C	22.99	22.99	100%
O	52.83	52.8398	100%

9.6.2 Natural gas

Natural gas was modelled based on the below reactions obtained from Er-bib *et al.*, (2012). The natural gas stream was assumed to be 94.9% pure methane Er-bib *et al.* (2012)

The amount of steam and methane was Goal seeked in order to obtain the same H_2/CO ratio and molar compositions of hydrogen and carbon monoxide.

Table 9-16: Reaction scheme for dry methane reforming and goal seeked values to obtain the same H_2/CO ratio of 2.20

			In	Out		mol/hr
		C	10.02998	10.02998	CO_2 feed	8
Natural Gas	169.1039	H	60.18048		Steam feed	5.94

	1	CH_4	1	H_2O	→	1	CO	3	H_2		
MW		16		18			28		2	H_2	22.09
Mol		10.02998		10.02998			10.02998		30.08993	CO	10.03
Mass		160.4796		180.5396			280.8393		60.17985	CO_2	8.00
										H_2O	13.94
	1	CO	1	H_2O	→	1	CO_2	1	H_2		
Mw		28		18			44		2		
Mol		0.000315		0.000315			0.000315		0.000315		
Mass		0.00882		0.00567			0.01386		0.00063		
	1	CO_2	1	H_2	→	1	CO	1	H_2O		
Mw		44		2			28		18		
Mol		8		8			8		8		
Mass		352		16			224		144		