Process Optimisation and techno-economic assessment of the slow pyrolysis of corn-stover

By

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Dedicated to the "Mpinga" family.

Thank you for the support. A special acknowledgement to my father (Mongesi Soka), mother (Mahali Soka) and sisters (Siphokazi and Nontombi)

DECLARATION

I, Ongama Soka, declare that the contents of this dissertation/thesis represent my own unaided work, and that the dissertation/thesis has not previously been submitted for academic examination towards any qualification. Furthermore, it represents my own opinions and not necessarily those of the Cape Peninsula University of Technology.

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Abstract

There is a growing need for the production and use of sustainable biofuels worldwide. One noteworthy approach is the production of biofuels via the pyrolysis of lignocellulose biomass. Benefits of such a process include carbon neutrality of the biofuels and alleviation of growing concerns on waste management. Moreover, the use of lignocellulose biomass does not upset the surrounding ecosystem through widespread deforestation.

In South Africa, corn-stover is an abundant lignocellulosic biomass with an estimated 9 million metric tonnes produced annually. The production of this is however seasonal. This study assumes a constant supply of corn-stover feedstock. The vast amounts of this biomass resource validates its potential as a suitable candidate for biofuel valorisation processes. This investigated the production of char and volatile by-products through the slow pyrolysis of corn-stover with particular emphasis on char as a prospective supplement or replacement of coal in industrial processes. The char quality was assessed according to ASTM D388, which ranks coals according to their higher heating value (HHV), volatile matter and fixed carbon. Furthermore, an evaluation of the techno-economic feasibility of an industrial scale 30 t/day slow pyrolysis plant was conducted. The techno-economic study was conducted at a char baseline price of $100/ton. A two-level three factor central composite design (CCD) making use of response surface methodology (RSM) was used to study slow-pyrolysis process conditions. Optimisation experiments were conducted at bench-scale gram-level to study the influences of process condition of char higher heating value (HHV) and yield. The results showed process temperature had the most significant influence on HHV and yield. By heating char from room temperature to 300°C, a 3.44 MJ/kg (29.13%) improvement in char HHV was attained. A 1.76 MJ/kg (11.37%) improvement was attained from 350°C to 450°C. Statistical analysis showed negative quadratic coefficient of temperature (-18.59) indicating that an increase in temperature had a detrimental effect on char yield. Optimal conditions for char productions were reactor temperature of 453°C and 5°C/min and 29 min for heating rate and holding time respectively. Under these conditions char with HHV of 26.25±1.5 MJ/kg and yield of 34.5% were produced. These chars are comparable to sub-bituminous A coals.

An economic study on a 30t/day slow pyrolysis process showed the process had a fixed capital investment requirement of $980 440, which was significantly less than other pyrolysis types. A profitability analysis that assessed the impact of feedstock availability and product prices on the feasibility of the process was conducted. Results showed the feasibility of the plant is highly sensitive to the price of char and cost of feedstock corn-stover. An economically viable

process was attained when the price of corn-stover and char were \$3/ton and \$200/ton respectively.

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Nomenclature

Abbreviation	Definition
ASTM	American Society for Testing and Materials
IEP	International Energy plan
CECPI	chemical engineering cost price index
EU	European Union
CS	Corn-stover
MJ	Mega Joule
kg	kilogram
HHV	Higher Heating Value
TBA	To be assessed
TGA	Thermogravimetric Analyser
RSM	Response Surface Methodology
CCD	Central Composite Design
BBD	Box Behnken Design

Chapter 1: Introduction

1.1. Background and context

Between 2015 and 2040 the world's energy consumption is expected to increase by 28% (EIA, 2017). This increase is attributed to strong economic growth, increasing populations leading to higher energy demands and access to marketed energy. The industrial sector will continue to account for the largest share of energy consumption, followed by transportation. Of the current global energy supply, 78% is comprised of fossil fuels, with consumption of coal being the second-largest closely behind petroleum (EIA, 2017). The use of fossil fuels poses serious environmental problems associated with the release of greenhouse gases and the eventual depletion of these energy sources.

Despite the majority of coal being used for electricity generation by the national utility Eskom, a minority of South Africans use coal domestically in low-income households (Balmer, 2007). This is most prevalent in communities located close to coal mines. The coal is used for cooking and heating of the homes. The intrinsic dangers with the use of coal in households are extreme air pollution, respiratory diseases associated with smoke inhalation as well as suffocation/poisoning due to carbon monoxide inhalation. Charcoal and firewood are also popular fuels in South Africa, particularly for rural domestic dwellers. The production of charcoal and firewood have devastating ecological and environmental issues associated with widespread deforestation (Chidumayo and Gumbo, 2013). The impacts of deforestation extend to rises in climate change and extensive damage to the land. The traditional production of charcoal via earth-kilns is highly inefficient with almost half of the energy input lost during production (Kammen and Lew, 2005; Adam, 2009; Chidumayo and Gumbo, 2013 and Chidumayo, 2013)

The production of biofuels from lignocellulose biomass is regarded as a cleaner and more sustainable replacement or supplement to coals and charcoals. It is common practice in many countries to utilise biomass for bio-energy production (Kretschmer *et al*., 2012). The European Union (EU) has identified bio-energy as one of the main renewable, low-carbon sources to achieve significant climate and energy targets (Directive 2009/28/EC, 2009). In 2013, 26% of the EU's electricity was generated from bio-energy. The target is to reach 45% power generation by 2030 (COM, 2015). In South Africa, the Department of Energy's Integrated Energy Plan (IEP) estimates 26% of the country's energy mix will be derived from renewable resources by 2030. (Department of Energy, 2015). Accounting a total systems capacity of 89

532 MW. From a socio-economic point of view, it is estimated bioenergy and biomass resources have the potential of creating 3700 jobs per MW (megawatt) energy produced.

Biomass is a sustainable energy source that not only reduces the unwanted impacts of waste on the environment but also serves as a regenerative energy source in comparison to the depleting fossil sources. The application of biofuels not only provides great economic opportunity but also promotes a sustainable future. In 2015 alone, 9-13% of the global energy supply was attributed to biomass resources, which amounts to approximately 60 exajoules of energy (Wang *et al.*, 2017). Biomass can be divided into five basic categories of materials namely; virgin wood, energy crops, agricultural residues, food wastes and industrial wastes and co-products (Dermirbas, 2000; Varol and Atimtay, 2007). Agricultural residues are considered to be less contentious, low cost, carry few risks (WBGU, 2009; Chum *et al*., 2011) and thus making them ideal for countries with a large agricultural base. South Africa, in particular, has great potential for bio-energy due to large agricultural production where significant amounts of biomass are available for energy purposes (Potgieter, 2011). South Africa remains the largest producer of maize in Africa followed by Nigeria and Egypt (Mohlala *et al.*, 2016). Approximately 9.7 million metric tonnes of maize residues are produced annually (FAO, 2015). These maize residues are commonly referred to as corn-stover (CS). A key advantage of CS is that their use leads to minimal to no land destruction as compared to energy crops (Batidzirai *et al.*, 2016). Mohlala *et al*. (2016) states that 30% of the agricultural residues in South Africa have a potential of 463 MW of power generation. Pyrolysis is a process that can valorise CS into char and volatile by-products.

The motivation of this study is to present an alternative and greener solution to the current use of coals in South Africa by proposing the production of chars and volatile by-products via the pyrolysis of CS. The study will explore the supplementation of chars into industrial and domestic uses. The study will also simulate and assess the economic feasibility of a pyrolysis plant.

1.2. Thesis outline

This dissertation consists of 6 main chapters. **Chapter 2** reviews the literature on biomass pyrolysis with emphasis on the constituents that have an effect on biofuel production, the operation, mechanisms, and feasibility of pyrolysis processes. The objectives and research motivation are also outlined. **Chapter 3** details the experimental and analytical methods that were used in the study, while also highlighting the experimental process that was studied. **Chapter 4** details the characterisation of feedstock and products and the results of bench-scale slow pyrolysis experiments, a study on the optimisation of process conditions for char yield and higher heating value (HHV) maximisation is presented. **Chapter 5** details the use of the Gibbs free model to simulate and study the evolution of pyrolytic volatiles during the process. **Chapter 6** details a techno-economic assessment of a 30t/day slow-pyrolysis plant.

1.3. Research motivation

Literature has identified 5.1 million tons of CS are produced annually in South Africa (Batidzirai *et al*., 2016). This abundant lignocellulosic biomass remains underutilised. As such an opportunity to produce high-value biofuels from CS presents itself. The production of combustion application chars from CS is a promising form of waste management. Secondly, the valorisation of this waste would adhere to South Africa's renewable energy framework which seeks to lower greenhouse gas emissions by relying more on greener fuels. Literature has shown that chars from lignocellulose biomass have good prospects in combustion applications, furthermore, they can be competitive with coal (Mundike *et al*., 2017). Such studies however usually relied on torrefaction to produce the chars. This study will use slow pyrolysis to produce biofuels. Slow pyrolysis has the added advantage of producing volatile biofuel by-products. In order to determine whether char could be competitive with coal, the slow pyrolysis process was investigated. In the current study, the most influential process conditions namely; temperature, heating rate and holding time were investigated and the process was optimised for the production of high energy chars. Additionally, the commercial economic viability of an industrial scale slow pyrolysis plant has seldom been studied. This current study will thus estimate the costs associated with the production of char and volatile by-products from the slow pyrolysis of CS. The study details the techno-economic feasibility of the process from start to end.

1.4. Problem statement

In recent years there has been enormous scrutiny over the use of fossil fuels in our daily lives. The issues with fossil fuels are their unsustainability, greenhouse gas emissions which contribute to the environment's depletion, as well as health and safety issues related to inefficient waste disposal systems. The current usage of CS in South Africa is inefficient in light of the valorisation possibilities that exist. Pyrolysis is a thermochemical process that can be used to convert this waste into commercial energy products. The energy products produced through the valorisation of CS have the potential to bridge the energy shortages in South Africa whilst providing environmentally cleaner fuels. However, there is a dearth of literature concerning a comprehensive assessment of its techno-economic feasibility. As such, there is a need to explore alternatives to the use of fossil fuels by exploring valorisation processes of CS into biofuels. Pyrolysis presents itself as a good candidate through which the valorisation of CS into biomass can be achieved.

1.5. Aims and objectives

The aim of the study is to assess the full potential of production char by means of the thermochemical process known as slow pyrolysis for application in combustion processes. The approach entails optimising the production of char and evaluating char as a substitute for coal. The char quality will be assessed in accordance with the American Standard Testing Method (ASTM) D388, which ranks the quality of coals according to fixed carbon content, HHV and volatile matter. The process factors affecting both char yield and HHV are defined as temperature, heating rate and holding time, and will thus be studied accordingly. Literature stipulates that with regards to char HHV and yield there is an inversely proportional relationship to temperature. At high temperatures chars with high HHV are produced, however, the yield is compromised. While lower temperatures produce higher char yields at the detriment of HHV. This study seeks the production of high char yields while maintaining char qualities comparable to those of coals. The benchmark requirement for optimisation of HHV and fixed carbon content was set at 25 MJ/kg and 56 wt% respectively. It is believed such an output would produce chars competitive with coal and be beneficial to the economics of the process. Hence the study also seeks to develop a pyrolysis plant that is techno-economically feasible. It is also believed the economic feasibility of the process will be enhanced by the commodification of the liquid and gaseous by-products. This study is in line with the current South African energy framework which seeks to produce energy from renewable sources.

1.5.1. Objectives

The aims of the study will be achieved by the following specific objectives:

- To optimise the slow pyrolysis of corn-stover as a function of temperature, heating rate and holding time (Chapter 4).

- To simulate a predictive model for the evolution of volatiles during the pyrolysis reaction. A Gibbs model was used for this function (Chapter 5).

- To perform a techno-economic feasibility study of the slow pyrolysis plant (Chapter 6).

1.6. Research hypothesis

By determining the optimum operating conditions for char production, it is envisaged that the chars produced will be suitable replacement for coals in industrial processes. The techno-economic feasibility of the slow pyrolysis process will be improved by the sale of gaseous and liquid by-products.

Chapter 2: Literature Review

2.1. Biomass

Biomass refers to biodegradable organic matter (Loppinet-Serani *et al*., 2008). The material originates from a variety of sources namely; plants, animals, residues, and waste from agriculture, forestry as well as organic fractions from industrial and municipal solid wastes (Demirbas, 2009). In addition to solids, biomass exists as liquid and gas residues from the decomposition of non-fossilised and biodegradable organic matter (Basu, 2010). There exist two major groups of biomasses, primary or virgin biomass and waste biomass (figure 2.1).

Virgin biomass describes all naturally occurring terrestrial plants; grasses, trees, cultivated crops (Basu, 2010). The use of such biomass in valorisation processes generally leads to widespread deforestation and land destruction (Batidzirai *et al.*, 2016). Waste biomass is referred to as low-value biomass by-products of virgin biomass. These include agricultural wastes such as corn-stover, corn-cobs, and bagasse, forestry waste such as sawmill and paper mill. The application of such biomass rarely upsets their ecosystem and have lower food uses (Basu, 2010).

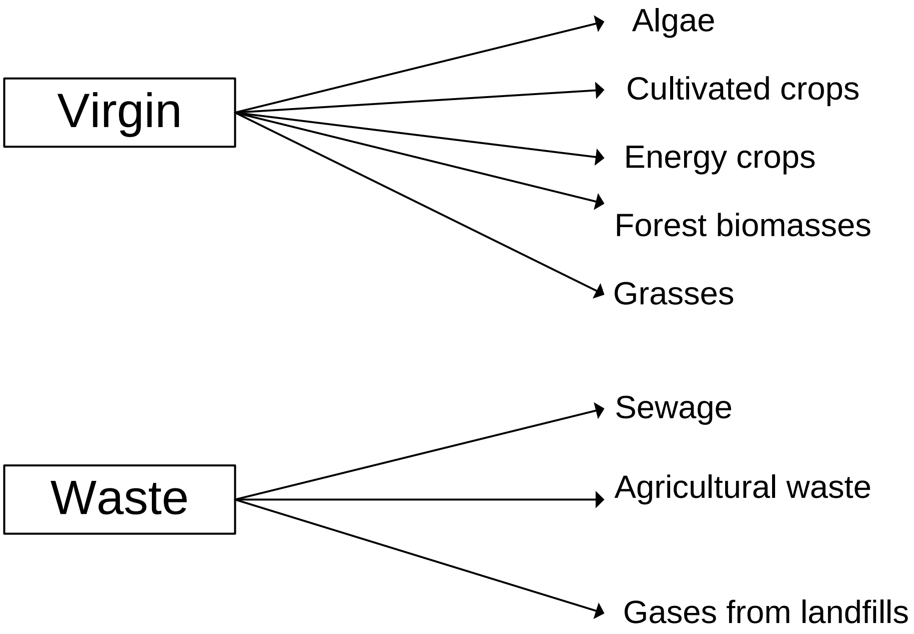


Figure 2. 1: The major groups of biomass (Basu, 2010)

2.2. Constituents of plant biomass

A major part of the biomass plant is the lignocellulose, a non-starchy, fibrous part of plant materials (Basu, 2010). Lignocellulose is a term used to describe the constituents of plant material, consisting of lignin, cellulose, and hemicellulose. It is made up of a complex matrix of different proteins, phenolic polymers, and polysaccharides (Zafar, 2018). The lignocellulose part of the plant is not digestible by humans, thus its use for biofuel does not pose a threat to the food supply. The major components that constitute lignocellulosic biomasses are lignin, cellulose and hemicellulose. As such the composition of the above-mentioned components in various lignocellulosic biomasses are presented (Table 2.1).

Table 2. 1: Typical composition of various lignocellulose biomass

Biomass	Lignin (%)	Cellulose (%)	Hemicellulose (%)	Source
Hardwood	20-25	45-50	20-25	Ortega *et al*. 2011 Agblevor *et al*. 2010
Softwood	27-30	35-40	20-25	Ortega *et al*. 2011
Corn stover	15-19	38	26-29	Shah *et al*. 2012
Switchgrass	18-19	37-43	24-29	Imam and Capareda, (2012)
Bagasse	18.9	44.3	26	Kelley *et al*. 2004
Rice straw	17	47	26	Moniruzzaman, 1996
Wheat straw	22.6	39.8	27.3	Kristensen *et al*. 2008
Corn cobs	15	45	35	Reshamwala *et al*. 1995
Ryegrass	19.8	33.1	22.2	Sun and Cheng, 2005
Miscanthus	17	24	44	Demirbas, 1997; Demirbas, 2004; Wang *et al*., 2006 and Fahmi *et al*., 2008
Tea waste	40	30.2	19.9	Demirbas, (1997)
Almond shell	20.4	50.7	28.9	(Yang *et al*., 2007; Abbasi and Abbasi, 2010)
Hazelnut shell	42.5	25.9	29.9	Demirbas, (1997)
Bamboo	26-43	21-31	15-26	Demirbas, 1997 and Wang *et al*., 2006

2.2.1. Lignin

Dhyani and Bhaskar, (2017) describe lignin as an aromatic, three-dimensional and cross-linked phenol polymer consisting of randomly bonded hydroxyl/methoxy-phenylpropane units. The empirical formula of lignin is $C_{20}H_{19}O_{14}N_{22}$. It is one of the most abundant organic compounds on earth after cellulose and chitin (Demirbas, 2009). It is responsible for structural stability and the holding of fibres of polysaccharides together. Physically, lignin fills the empty spaces between hemicellulose while cellulose micro-fibrils coats the hemicellulose (Lee *et al*., 2014). The percentage composition of lignin as high as 42.5% has been reported in some lignocellulosic biomass. Figure 2.2 illustrates the structure of lignin.

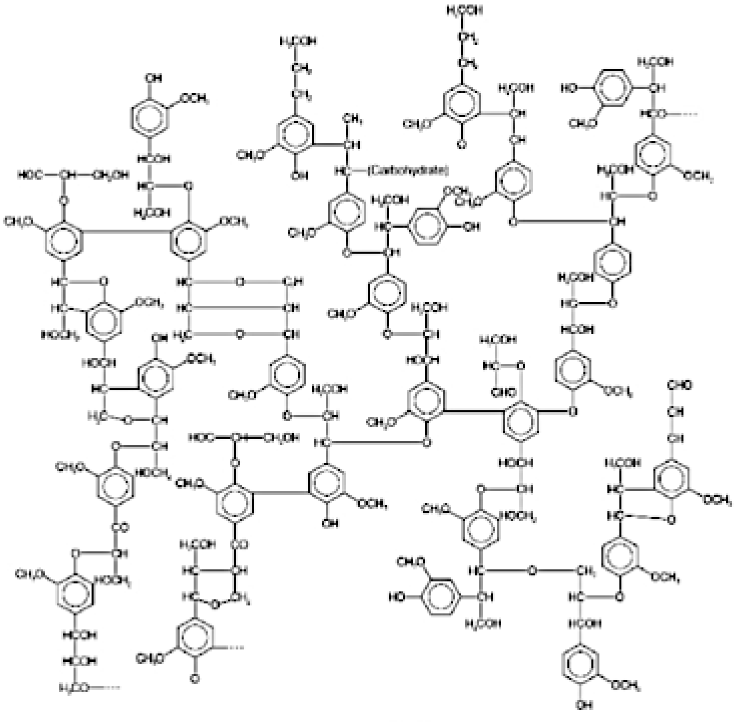


Figure 2. 2: Lignin structure (Dhyani and Bhaskar, 2017)

2.2.2. Cellulose

The most abundant organic polymer on earth and the predominant polymer in lignocellulosic biomass (Table 2.1), consisting solely of anhydroglucose units held together in a straight chain molecule (Demibras, 2000). The molecules of cellulose are thin strands called micro-fibrils. The arrangement of these micro-fibrils mesh-like patterns which link up the hemicellulose and lignin and assist in strengthening the cell wall (Klemm *et al*. 2005). Cellulose is characterised by its insolubility in most solvents and low accessibility to acid and enzymatic hydrolysis. Figure 2.3 illustrates the structure of the cellulose.

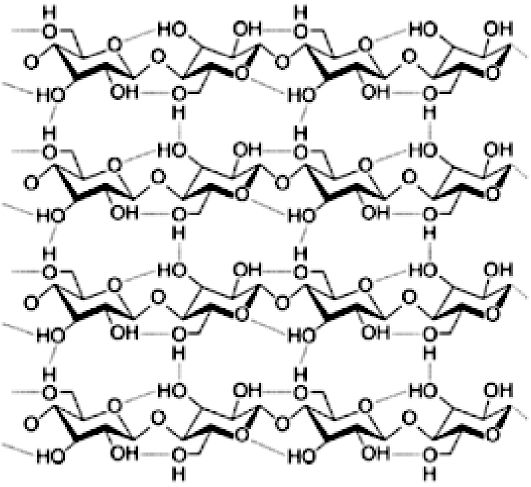


Figure 2. 3: Cellulose structure (Dhyani and Bhaskar, 2017)

2.2.3. Hemicellulose

The second most abundant polymer of lignocellulose biomass (Table 2.1) (Isikgor and Becer, 2015). Unlike cellulose which is derived from glucose, hemicellulose is derived from a variety of sugars (Mohan *et al*., 2006). It is a group of carbohydrates with a low degree of polymerization, the empirical formula is represented as $(C_5H_8O_4)_n$ (Klaas, 1998). Figure 2.4 illustrates the structure of the hemicellulose.

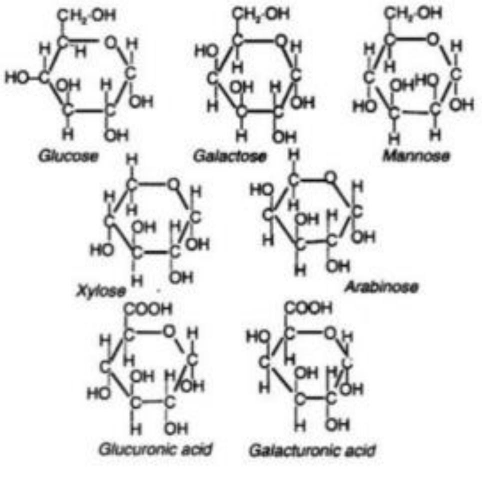


Figure 2. 4: Hemicellulose structure (Dhyani and Bhaskar, 2017)

2.3. Biomass used in this study

Corn-stover (CS) is an abundant agricultural residue in South Africa. It consists of the stem, the leaves and the stalk of the corn plant (Schechinger and Hettenhaus, 1999). CS is the surface residue that remains after corn kernels are harvested. Produced through natural atmospheric CO_2, water and sunlight through the photosynthesis process. The result is a carbon-neutral material, meaning the biofuels produced from CS have net-zero carbon emissions. It is estimated that 9.7 million tons of above-ground CS are produced annually in South Africa. A portion of approximately 47.4% of the biomass is used as animal feed and to provide nutrients to the soil. As a result, 5.1 million tons of corn-stover per annum (52.6%) are available for valorisation processes (Batidzirai *et al*., 2016). The advantage of CS over other biomass feedstock is that it does not interfere with food supplies. The lignocellulosic nature of CS makes it a strong candidate feedstock for renewable energy owing to its bio-compatibility and bio-degradability (Ahn *et al*., 2012). The dry matter percentages (Table 2.2) of typical corn plant (Myers and Underwood, 1992). CS constitutes about half the weight of the corn plant and is a readily available agricultural product in the area of large corn production (Danje, 2011). It is estimated about 1 kilogram of CS is produced per kilogram of grain (Glassner *et al*., 1999). Due to the lignocellulosic nature of CS, valorisation into biofuels and chemicals such as biodiesel and ethanol is viable.

Table 2. 2: Constituents of CS (Glassner et al., 1999)

Corn residue	% of residue (dry matter)
Stalk	50
Cob	20
leaf	20
Husk	10

2.4. Valorisation of biomass into biofuels

2.4.1. Biochemical processes

Biofuels can be produced via biochemical processes by chemical or enzymatic hydrolysis and subsequent microbial fermentation is applied (Kabir *et al.,* 2010). Two common forms of biochemical processes are bio-methanation and ethanol fermentation.

Bio-methanation can be applied to a variety of biomass including corn residues due to activities of complex microflora. This process occurs spontaneously when organic compounds are maintained at 5-70°C and neutral pH under anaerobic conditions. Biogas is often a product of the process. The process is composed of hydrolysis, acetogenesis, and methanogenesis (Achinas *et al*., 2017).

With regards to ethanol fermentation, the pathway to produce ethanol from lignocellulosic biomass generally involves chemical or enzymatic hydrolysis followed by microbial fermentation. The major issues associated with biochemical processing are the high costs of enzymes and anaerobic digesters. The operating equipment also require frequent maintenance due to the complexities of processing. These disadvantages favour the use of more sustainable processing routes such as thermochemical. Thermochemical processes are often cheaper, more reliable and often do not require expensive catalysts.

2.4.2. Thermochemical processes

Thermochemical processes are among the processes used to convert bio-renewable feedstock into useful biofuels and chemicals. The process utilises high temperatures to break down organic matter bonds. The advantages of this process include the destruction of pathogens, lower emissions, less processing times and recovery of nutrients (Thomas *et al.*, 2017). Thermochemical processes are most feasible for large-scale application of bioenergy due to the flexibility of biomass conversion to various fuels (Sanchez and Kammen, 2016). The main products obtained through thermochemical processes are potential alternatives to petroleum-based fuels. Biofuels such as ethanol, char, and biogas can be produced from thermochemical processes. The products can be utilised as solid, liquid or gaseous products used in electric power production, chemicals or gaseous and liquid biofuels (Demirbas, 2009). Thermochemical conversion can be divided into three subcategories, namely; combustion, gasification, and pyrolysis.

2.4.3. Direct Combustion: Co-firing

Biomass co-firing describes the process of producing electricity by simultaneously blending and combusting biomass with coal or natural gas in existing power plants (Agbor *et al.*, 2016). Coal/biomass co-firing is classified into two categories; direct and parallel co-firing. Indirect co-firing, the biomass is fed directly into the boiler with the coal, whereas parallel co-firing requires the installation of a separate external biomass-fired boiler (Canadian Clean Power Coalition, 2011 and Agbor *et al*., 2016). The resulting steam from the boilers is used to generate electricity. Biomass co-firing with natural gas requires the biomass to be initially gasified to syngas, which can then be co-fired with natural gas in a turbine (IEA-ETSAP IRENA, 2013). Co-firing has been identified as a prospect for the reduction of greenhouse gas emissions, particularly carbon dioxide (De and Assadi, 2009).

2.4.4. Torrefaction

The aim of this process is to transform biomass into higher energy char under low temperatures (200-300°C) and long residence times typically between 2 hours and 2 days (Bergman and Kiel, 2005). It is conducted under oxygen inert conditions (Zhang *et al.*, 2016). The process reduces liquid yield but, increases the yield of pyrolysis solids to typically around 80%. Torrefaction is often used as a pre-treatment method to other processes such as combustion and gasification processes, as a means of improving the properties of raw biomass (Uslu *et al*., 2008). The major concerns with the use of biomass not pre-treated using this approach, in industrial processes are high moisture and volatile contents, higher chlorine, and potassium contents, causing technical difficulties for existing plant equipment. Torrefied biomass has better properties such as an improved energy density, improved grindability and hydrophobicity (Ibrahim *et al*., 2013). Typically, torrefaction is combined with pelletisation which requires further energy input to complete (Rentizelas and Li, 2016). A disadvantage of the torrefaction process is the production of relatively low energy content biofuels, hence torrefied biofuels are typically used as feedstock for downstream upgrading processes.

2.4.5. Pyrolysis processes

Pyrolysis has been used since the dawn of civilisation. Wood distillation was used to collect tars and pyro-ligneous acid for use in the embalming industry in ancient Egypt (Demirbas, 2009). Fast forward to the 1800's, the pyrolysis of wood was a major industry used to supply fuel for the industrial revolution. In the early 20th-century wood pyrolysis remained profitable for the production of soluble tar, creosote oil, chemicals, and non-condensable gases often used to heat boilers. The industry however soon declined after the advent of the petrochemical industry (Osburn, 1989).

The method of pyrolysis is thermal decomposition by heating the biomass in oxygen inert conditions (Peters *et al*., 2017). The biomass is decomposed into char, bio-oil, and biogas (non-condensable gas, including CO_2, CO, H_2, CH_4, and heavier hydrocarbons) (Figure 2.5). During heating cellulose and hemicellulose mainly form the volatile products, due to the thermal cleavage of the sugar units. The lignin generally forms char since it is not easily cleaved under thermal energy to lower molecular weight fragments (Demirbas, 2009). Pyrolysis has been reviewed extensively in scientific research due to its carbon-neutral property. Emissions of CO_2 from the burning of biomass or pyrolytic products are considered carbon-neutral since the CO_2 released through the application of the pyrolytic products was previously absorbed from the atmosphere through the photosynthesis process (Brownsort, 2009; Thilakaratne, 2016). There are several factors affecting the pyrolysis process. Some of the important factors highlighted in the literature, are temperature, heating rate, sweeping gas flow rate and hold time which have a direct impact on the quality and distribution of pyrolytic products (Pütün, 2014).

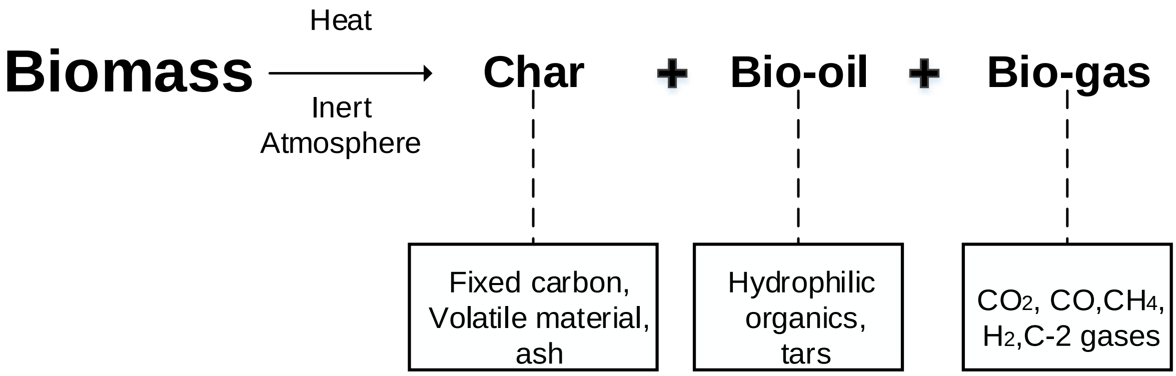


Figure 2. 5: Representation of the pyrolysis process (Brownsort, 2009)

The general changes that occur during pyrolysis are presented below (Mohan *et al*., 2006) :

1. A temperature increases inside the fuel due to heat transfer from an energy source.
2. Due to temperature rise, primary pyrolysis reactions are initiated which releases volatiles and forms char.
3. Heat transfer due to the interaction of volatiles and cooler unpyrolysed biomass.
4. The interaction between hot volatiles and cooler solids leads to the formation of tars and consequently secondary reactions.
5. While primary pyrolytic reactions occur, autocatalytic secondary reactions occur simultaneously. Secondary reactions are a result of volatiles reacting with the char which could produce more permanent gases or secondary chars.

During the pyrolysis process, different reactions occur at different temperatures, hence different products are produced (Table 2.3).

Table 2. 3: Pyrolysis reactions with respect to temperature. Adopted from Jahirul et al., (2012)

Condition	Reactions	Products
< 350°C	Dehydration and depolymerisation of biomass feedstock.	Production of carbonyl, carboxyl compounds and char
Between 350°C and 450°C	Breaking –OH bonds to form sugars	Production of tars and char.
> 450°C	Dehydration, reassignment of sugar compounds	Production of carbonyl group compounds and char.
> 500°C	Mixture of all the above reactions	Mixture of all the above products.
Condensation	Condensation of unsaturated products and attachment to char.	Char remains.

2.4.5.1. Vacuum pyrolysis

Vacuum pyrolysis is a newer technology relative to the other pyrolysis methods (Danje, 2011). The process is under vacuum instead of using oxygen inert atmospheric conditions. Due to the lower heat transfer rates associated with vacuum reactors lower bio-oil yields (relative to fast pyrolysis) of 35-50% are produced (Jahirul *et al.*, 2012). This type of pyrolysis is unique because it operates under slow heating rates but removes vapours rapidly which stimulates bio-oil production. The biggest downside of this mechanically complicated process is the high maintenance costs and capital investment required for large scale implementation.

2.4.5.2. Fast Pyrolysis

Fast pyrolysis favours the production of bio-oils. This is done by rapidly heating the feedstock at moderate temperatures in the absence of oxygen. The production of liquid fuels requires very low residence times to minimise secondary reactions which lead to char formation, typically 1 to 5 seconds (Uzun *et al*., 2010). Fast pyrolysis can achieve bio-oil yields up to 75-80% (Amutio *et al*., 2012). Bio-oil is a miscible mixture of polar organics and water (Bridgwater, Meier and Radlein, 1999).

2.4.5.3. Slow Pyrolysis

Slow pyrolysis also termed carbonisation has been historically applied for the production of charcoal. Unlike the other forms of pyrolysis, slow pyrolysis gives a near even yield distribution of products (35% char, 35% biogas and 30% bio-oil). Traditionally, the process has been applied to woody biomass for thousands of years by operating at low temperatures and long hold times to enhance char production (Jahirul *et al*., 2012). The modern slow pyrolysis process maintains oxygen inert conditions by flushing the reactor with nitrogen gas, which is also used to control the residence time. Longer residence times lead to secondary charring reactions which consequently increase the energy content of the char (Danje, 2011). Different pyrolysis process conditions lead to different products (Table 2.4)

Table 2. 4 Summary of pyrolysis types, process conditions and product distribution (Demirbas and Arin, 2002; Mohlala et al., 2016; Feng and Lin, 2017)

Pyrolysis Type	Process conditions			Product Distribution (%)		
	Temperature	Heating rate	Holding time	Char	Bio-oil	Biogas
Slow pyrolysis	400-600°C	5-30°C/min	5-50 min	35	30	35
Fast pyrolysis	600-800°C	10-200°C/s	0.5-10 s	12	75	13
Vacuum pyrolysis	500-600°C	5-30°C/min	2-30 s	10-30	35-50	20

2.5. Effects of process parameters and biomass feedstock

This section describes the effect process parameters have on the distribution of pyrolysis products. The influence of feedstock composition is discussed first followed by the effect of process operating conditions. The section will also highlight the product distribution. Authors have well established the main factors influencing the production of biofuels as feedstock composition, process temperature, heating rate and holding time (Demirbas and Arin, 2002; Feng and Lin, 2017). However, the researchers have rarely reported on the interaction among these variables, particularly as it pertains to the production chars for combustion applications and volatile by-products through the slow pyrolysis of agricultural residues. This is one of the objectives of the current study

2.5.1. Feedstock composition

As discussed in section 2.2, agricultural biomass is mainly composed of three main polymeric materials: cellulose, hemicellulose, and lignin. The other components present in small proportions are known as inorganic compounds and extractives (smaller organic polymers). These are present in varying proportions in biomass and these proportions can influence the yield distribution of the pyrolysis products (Antal and Grønli, 2003; Mohan *et al*., 2006).

Upon heating of biomass, the main constituents contribute to the product yields as follows; lignin mainly decomposes to gaseous and solid char products. Hemicellulose and cellulose are mainly decomposed into liquid and gaseous products. Inorganic compounds are found in the char where they are termed ash. Lastly, extractives contribute to liquid and gas products (Brownsort, 2009). It is understood that at lower temperatures the decomposition of cellulose and hemicellulose are favoured relative to that of lignin, while the lignin fraction of the biomass contributes most significantly to the final char yield (Orfão *et al*. 1999). In the case of CS, lignin composition is moderately high at 14-26% (Table 2.1). Subsequently having a positive influence on char production. Researchers rely on the composition of their feedstock as one of the criteria to predict the possible products. Martin-Lara *et al*. (2019) used knowledge of olive cake's composition to produce solid fuels and adsorbents through the slow pyrolysis process. Gura, (2017) relied on lignin produced from the paper and pulp industry to model the production of phenols. In the case of CS, all three constituents are presented in relatively high proportions (Table 2.1). The result is versatility regarding potential process products as can be seen by studies conducted by such as Danje, (2011) and Ravikumar *et al*. (2016) who investigated the production of liquid biofuels from CS.

A schematic representation of a typical product distribution from biomass components is shown in figure 2.6

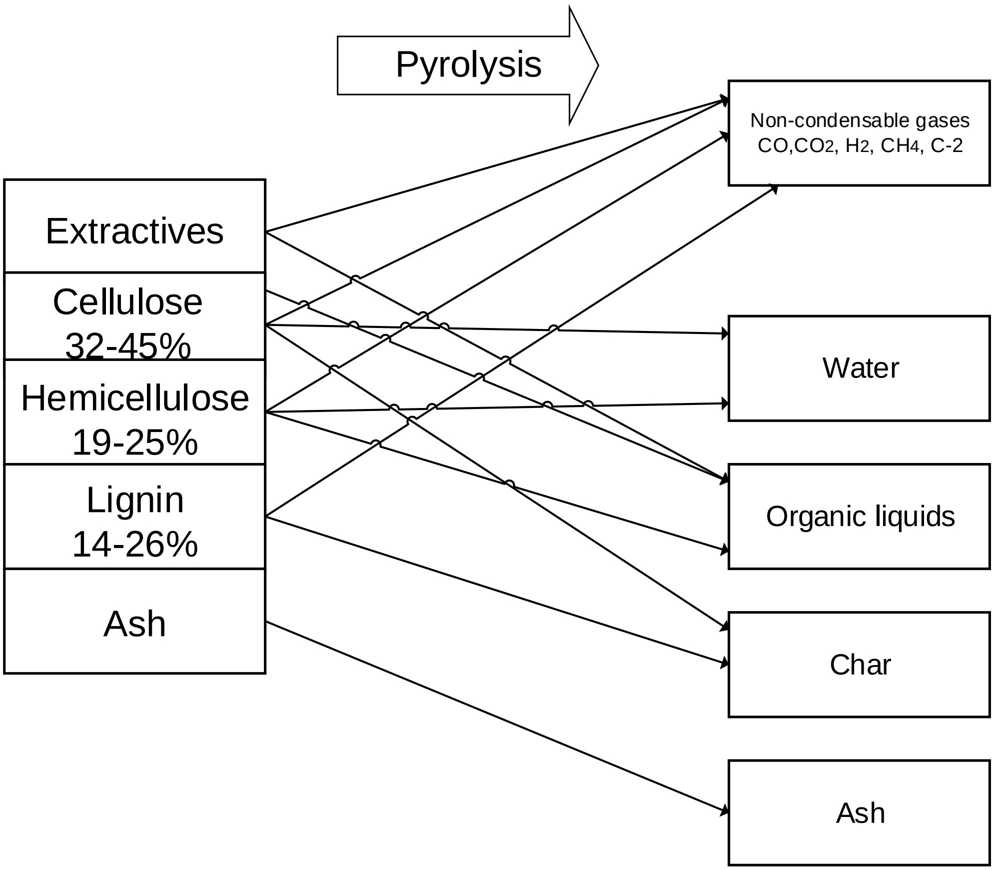


Figure 2. 6 : Product distribution of biomass components (Brownsort, 2009)

2.5.2. Process temperature

It is generally accepted that process temperature has the highest influence on the pyrolytic product yields and heating values (Horne and Williams, 1996; Garcia-Perez *et al*., 2008). With regards to char HHV, studies have reported increases in HHV for various lignocellulosic chars at temperatures in the range 300-600°C (Mafu *et al.*, 2017 and Volpe *et al.*, 2017). This development is seen as a result of lignocellulose deoxygenation, which typically occurs at temperatures in the range 250-500°C (Collard and Biln, 2014). It is important to note however there is a temperature threshold to this phenomenon. Some studies have noted a decrease in HHV at temperatures above 500°C. A study by Mundike *et al*. (2017) attributed the decrease in char HHV at higher temperatures to dehydrogenation. The dehydrogenation results in char having higher a higher percentage of inorganic materials such as potassium and silica. The presence of these elements is detrimental to char's HHV. The study by Mundike *et al*. (2017) however was performed under torrefaction conditions. Researchers have rarely studied the detriment of high-temperature conditions on the slow pyrolysis of lignocellulosic biomass.

With respect to product yields, at low-temperature conditions char formation increases. As the temperature is increased char yield decreases, this is true for all pyrolysis systems. The effect of temperature on char can be attributed to the fact that volatiles are forced out of the char at elevated temperatures resulting in a reduction in char yield but increasing the fraction of carbon in the char (Brownsort, 2009). It is important to note that Brownsort, (2009) investigated chars potential as soil nutrient supplement, as a result, measurements such as the porous structure of the char are considered. Such variables do not form part of this study.

With respect to liquids, the yields are proportional to temperature but only up to a maximum value, typically around 500°C. If the temperature is elevated further, the result will be a decrease in the liquid yield due to secondary reactions taking place (Hugo, 2010). At temperatures from 600 to 800 °C, the polar, aliphatic and aromatic fractions in the bio-oils are enhanced (Ates and Isikdag, 2008). At temperatures exceeding 700°C, the carbon content in the bio-oils is increased in the form of polycyclic aromatic hydrocarbons. This is a result of decarboxylation and dehydration reactions (Akhtar and Amin, 2012). This study evaluates the production of bio-oils as secondary to char at temperatures ranging from 300 to 500°C.

The effect of temperature on gas yield is more complex. At conditions that favour high liquid yield, temperature irregularly affects gas yield. However, at temperatures above this, gas yields are dependent strongly on temperature (Brownsort, 2009).

2.5.3. Heating rate

The heating rate is the central parameter that describes the type of pyrolysis process (i.e. fast or slow pyrolysis). High heating rates result in rapid fragmentation of the biomass which yields high volatiles and less char, as a result of the limitations on secondary reactions and improvements in mass and heat transfer (Kan *et al*., 2016). A study by Ozbay *et al*. (2006) showed that an increase in liquid yield was observed by elevating the heating rate from 5 °C/min (26 wt%) to 300 °C/min (35 wt%) via the pyrolysis of cottonseed cake. With regards to slow pyrolysis, heating rates are low, typically operated between 5-30°C/min (Mohlala *et al.*, 2016). A slower heating rate will result in high char yields, due to secondary char reactions. Typically, TGA equipment has been used to study heating rates on processes where heating rates are controllable such as in batch and fixed-bed systems.

2.5.4. Holding time

Holding time describes the duration at which the biomass sample is held isothermally at the peak temperature in the reactor. Typically, long holding times favour char formation, as they lead to further thermal degradation of the biomass resulting in further release of hot volatiles. Previous studies have reported that char HHV increased while the yield decreased with prolonged holding times (Gheorghe *et al*., 2010). The effects of holding time are most prevalent at lower reaction temperature, as the temperature is raised the effects of holding time on char HHV tend to decrease as reported by (Rossen *et al.*, 2013). In the case of systems that favour bio-oil production, hold time is kept as short as possible in an attempt to limit secondary and tertiary reactions taking place.

There is a dearth in the literature on the effects of the aforementioned conditions on the production of high energy content char, especially as it pertains to the slow pyrolysis process. Most studies typically focused on torrefaction or made use of slow pyrolysis to produce soil additive chars.

2.6. Pyrolytic products

The following section describes the products of pyrolysis processes based on their uses, composition and physicochemical properties. The potential uses of various pyrolysis products (figure 2.7) are provided.

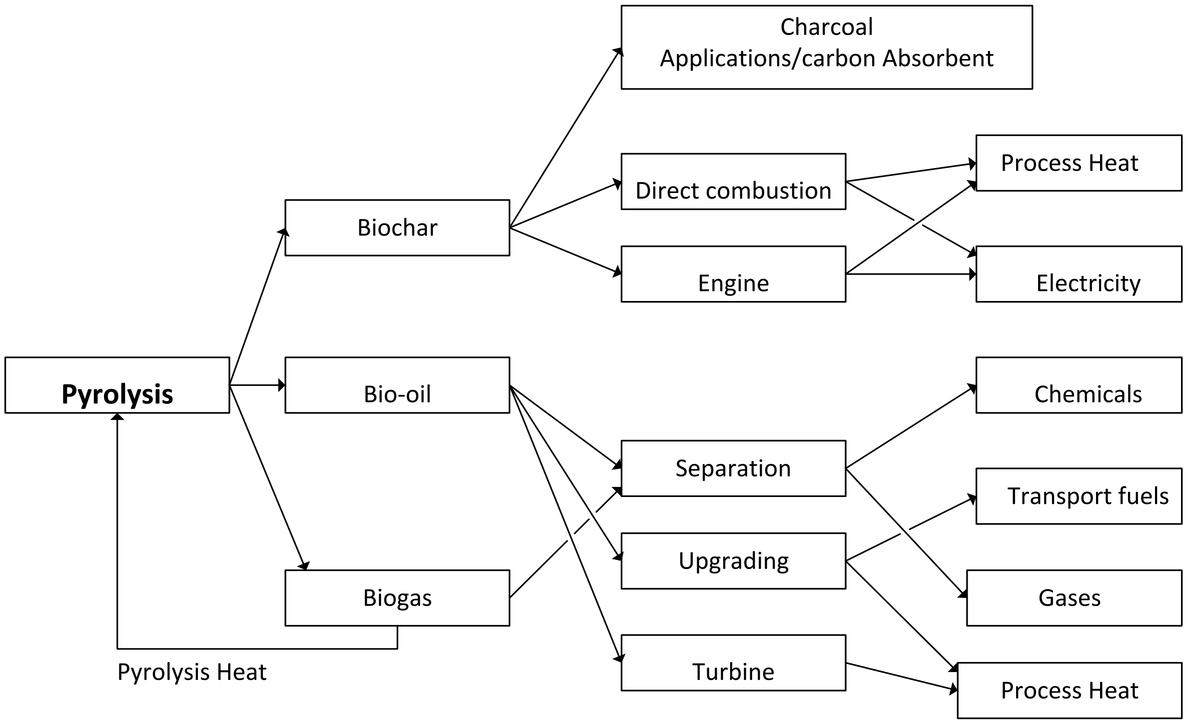


Figure 2. 7: Various end uses for pyrolysis products (Raveendran and Ganesh, 1996)

2.6.1. Char

The thermal degradation of lignin and hemicellulose in biomass results in a substantial mass loss in the form of volatiles. The solid material produced is an amorphous carbon structure referred to as char (Jahirul *et al.*, 2012). Char is a black/dark brown solid product consisting of carbonaceous residues and unconverted organic solids produced from the partial or complete decomposition of biomass material (Kan *et al*., 2016). The physical characteristics of char are significantly affected by the pyrolysis conditions such as reactor operating temperature, residence time, flow-rate of inert gas including the nature of biomass as shown was detailed in section 2.4.5.3. (González *et al*., 2009; Downie *et al*., 2009). For example, pyrolysis at high temperatures and heating rates (e.g. 500°C and 150°C/min), with a finely ground feedstock produce finer chars whereas slow pyrolysis with larger particle sizes will produce coarser chars.

A study by Lopez *et al*. (2013) showed chars produced from woody biomass have HHV similar to those of semi-anthracite and medium bituminous coal. The HHV of the chars obtained was 31-35 MJ/kg. Furthermore, their burnout temperatures, combustion intervals, and volatilisation were also similar to those of commercial coals (Lopez *et al*., 2013). Similar to coal, char can be used in industrial combustion applications either as the main feed or in co-firing scenarios for the production of electricity. There have been studies on the use of char as a soil supplement due to its nutrient composition (Ba *et al.,* 2018) however, in literature, char is most commonly seen as a coal contender. The combustion of char can be affected by several factors including carbon structure, total surface area and ash content. In the case of the study by Park *et al*. (2012) char was a by-product with the study focusing on the production bio-oil from garlic and red pepper stems. The authors assessed the quality of the char based on its ash content, HHV and molar ratios of carbon, hydrogen and oxygen. Similar to the study by Park *et al*. (2012) the current study will also assess the quality of char on its ash content, HHV and molar concentrations of carbon, hydrogen and oxygen.

The ash content is the powdery residue left after the combustion of char. Ash is made up of mainly calcium (Ca), iron (Fe), silica (Si), sodium (Na), aluminium (Al), potassium (K) and magnesium (Mg) (Sun *et al*., 2016). The presence of large quantities of ash changes the thermal properties of the char. Otero *et al.* (2010) indicated that an increase in ash content reduces the flammability of char by preventing contact with oxygen supply. The HHV, on the other hand, determines the primary energy utilisation of the char (Raveendran and Ganesh, 1996). A study by Pehlivan *et al*. (2017) showed that with the rise in the reactor temperature, the carbon content in the char also increased. However, oxygen and hydrogen contents decreased. A decrease in oxygen and hydrogen content indicates increased aromaticity and hence increased HHV of the char (Xie *et al.,* 2015). The quality of char (Table 2.5) can be assessed in accordance with its HHV, ash content and elemental percentages of hydrogen and oxygen.

Table 2. 5: Char quality assessment

Biomass	Pyrolysis type	Yield (%)	Ash content (wt%)	H/C molar ratio	O/H molar ratio	HHV (MJ/kg)	comment	Source
Garlic stem	Fast	n.d	0.27	n.d	n.d	17.2	The yields of pyrolytic products are highly dependent on temperature	Park *et al.*, 2012
Red pepper stem	Fast	n.d	0.13	n.d	n.d	22.1		
Waste wood samples	Fast and slow	23-29	2-8.5	0.32-0.34	0.02-0.06	31.0-35.0	Combustion properties of the char were similar to those of semi-anthracite and medium bituminous coal	Lopez *et al*., 2013
Cherry pulp	Slow	31.3	n.d	0.42-0.81	0.16-0.44	24.3-26.8	The properties of cherry pulp make it a suitable feedstock for valorisation processes.	Pehlivan *et al*., 2017
Algae waste	n.d	44	31.52	0.64	0.54	23.1	Char presents good properties as a solid fuel.	Aboulkas *et al*., 2017
Soft wood	Slow	n.d	0.7-0.8	0.7-1.0	0.20-0.30	23.2-28.8	Higher fixed carbon ratios are reported at higher pyrolytic temperatures.	Mafu *et al.*, 2017
Hard wood	Slow	n.d	0.6	0.6	0.20-0.40	23.2-28.1		
Switchgrass	n.d	25	n.d	n.d	n.d	28.9-29.0	The integrated process where all pyrolysis products are marketed may improve the project economics.	Iman and Capareda, 2012

n.d: not described.

2.6.2. Bio-oil

The second product produced through pyrolysis of biomass is a dark brown or dark red to green in colour organic liquid, depending on initial feedstock and pyrolysis mode, comprised of highly oxygenated organic compounds (Peacocke *et al*., 1994 and Czernik and Bridgwater, 2004). This product is also called pyrolysis oil, bio-crude, pyroligneous acid (Mohan *et al*., 2006). Bio-oils are produced by rapid depolymerizing and fragmentation of cellulose, hemicellulose, and lignin with the fast increase in process temperature. This thermochemical degradation of biomass results in a release in the volatile matter. By capturing and condensing the volatiles, bio-oils are formed. Chemically, bio-oil is a complex mixture of water, acetic acid, formic acid and major group compounds including sugars, carboxylic acids and phenols (Piskorz *et al*., 1988 and Mohan *et al*., 2006).

As for the physical state of bio-oil, the multiphase complex structure is attributed to the presence of char particles, aqueous droplets and formation of micelles as a result of a mixture of water and hollocellulose-derived compounds (Garcıa-Perez *et al*., 2006). Physical characteristics and properties of bio-oils (Table 2.6) can be further characterised in accordance with odour, density, viscosity, heating value and miscibility.

Table 2. 6: Properties of bio-oil (Bridgwater, 2003 and Jahirul et al., 2012)

Properties	Oil characteristics	Reasons
Odour	A metallic smoky smell	Lower molecular weight aldehydes and acids.
Density	Bio-oil density is 1.2 kg/L, which is higher than that of light fuel (0.85 kg/L).	High oxygen content and possible contamination of the molecule.
Viscosity	Varies from 25 cSt to 1000 cSt (measured at 40°C)	Highly dependent on feedstock, water content and amount of volatiles collected.
Heating value	About half that of fossil fuels	High oxygen content
Miscibility	Bio-oils are immiscible in water. Miscible with polar solvent such as acetone.	Polar in nature

The main advantages of bio-oils are (Chiaramonti *et al*., 2007 and Balat *et al*., 2009)

- Storability and transportation as a liquid fuel.
- High energy density.
- Potential use in existing power stations.

As a result of bio-oil being a complex mixture of organic substances such as ketones, phenols, aromatics hydrocarbons, etc., bio-oil can be processed and upgraded into a variety of biofuels and biochemicals. There is growing research on the upgrading of bio-oil into valuable products. Vispute *et al.* (2010) showed that bio-oil can be processed through catalytic hydroprocessing and fluid catalytic cracking into valuable industrial fuels. Elliot *et al*. (2009)

described the potential of using catalytic hydroprocessing followed with hydrocracking bio-oil into alkene and aromatics which could be used as petroleum refinery feedstock. Wright *et al*. (2010) studied the production of naphtha and diesel fuels through the pyrolysis of CS. Several authors including Wright *et al*. (2010) and Zhang *et al.* (2013) investigated the economic feasibility of such upgrading pathways and found the processes as expensive and their commercialisation potential subject to high uncertainty.

2.6.3. Biogas

The gases released during the pyrolysis of lignocellulose biomass can consist of hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), light hydrocarbons such as methane (CH_4), ethane (C_2H_6) and ethylene (C_2H_4), propane (C_3H_8) and a small number of other gases such as ammonia. With regards to origin, the CO and CO_2 originate from the decomposition and reforming of carboxyl (COO) and carbonyl (C=O) groups (Qu *et al*., 2011). Light hydrocarbons are attributed to the decomposition of weakly bonded methylene ($-CH_2-$) and methoxy ($-O-CH_3$). Hydrogen is produced from the secondary decomposition and reforming the aromatic C=C and C-H groups (Liu *et al*., 2008).

Pyrolysis gas has numerous potential applications, such as use as an energy source for the pyrolysis process itself by providing electricity through compression ignition engines, use in co-fired processes with coal for the production of individual gas components or in synthesis process for the production of liquid biofuels (Demirbas, 2000 and Goyal *et al*., 2008). Prior to use in industrial applications, the biogas requires processing to eliminate unwanted constituents such as aerosols and tars.

2.7. Pyrolysis reactors

At the heart of the pyrolysis processes are the reactors. The pyrolysis reactors are designed to meet the heat-transfer requirements of the reaction. As mentioned earlier, the fundamental difference between the various types of pyrolysis is the heat transfer mechanism.

2.7.1. Fluidised bed reactor

These types of reactors are well understood. The operation is simple and the design offers excellent heat transfer to the biomass particles (Mohan *et al*., 2006). Traditionally, these reactors are used when bio-oil is the product of interest. The construct is usually a cylindrical vessel through which biomass is fed. Inert sand is typically used as a heating medium by improving fluidisation and heat transfer (Bridgwater, 2002). Inert nitrogen is then used as a carrier medium for the vapours produced which are then condensed through a series of condensers.

2.7.2. Vacuum reactors

These reactors rely on the thermochemical breakdown of biomass under reduced pressure.

Similar to fixed bed reactors the biomass is fed into the reactor and pyrolysed from the solid phase over longer holding times. The vapour residence time, however, is similar to those of fast pyrolysis. The vapours are then quickly removed from the reactor via a vacuum. The extent of secondary reactions are limited due to the rapid volatilization under vacuum (Mohan *et al*., 2006). A downfall of this technology, however, is poor heat and mass transfer rates.

2.7.3. Fixed bed reactors

These types of reactors are simple in construct. Unlike fluidised bed reactors, they do not require a fluid medium to facilitate the heat transfer. The reaction is generally operated under atmospheric pressures and in an inert oxygen environment. The reactor is then operated under the set conditions. This arrangement is ideally suited for char favouring systems.

2.8. Thermogravimetric analysis

Thermogravimetric analysis (TGA) is a simple analytical tool used to provide general information on the overall kinetics of biomass. The analysis is used extensively to investigate the thermal behaviour of lignocellulosic feedstocks. It involves heating the biomass at different heating rates, then studying the change in mass due to thermal decomposition as a function of temperature and time (Müsellim *et al.*, 2018). The downside of TGA however is, it does not provide information about individual reactions.

The thermogravimetric (TG) data provides information regarding the rate of decomposition of biomass as a function of time and temperature under controlled atmospheric conditions (Müsellim *et al.*, 2018). The data obtained from TGA is useful in the determination of kinetic parameters of pyrolysis processes, which in turn can be used to study the chemical structure of materials and provide information on the operation of thermochemical systems (Jaroenkhasemmeesuk and Tippayawong, 2016; Olaokun *et al*., 2016). There have been few studies on the thermogravimetric analysis of corn residues (Kumar *et al.*, 2008; Li *et al.*, 2017; Cai *et al.*, 2018). Thermogravimetric studies are also useful in determining the proximate analysis of biomass which are used in the determination of fixed carbon, volatile matter, moisture and ash in the biomass. By applying mathematical models to TG data, pyrolytic decomposition of biomass and related kinetic parameters can be determined.

2.8.1. Kinetics of lignocellulosic pyrolysis

It is important to understand the kinetics of biomass pyrolysis before the conversion of biomass into fuel takes place. The information provided by knowledge of process kinetics can be used for process parameter optimisation as well as providing information that simplifies mathematical modeling. The rate equation is usually used to analyse the chemical kinetics of biomass decomposition (Biagini *et al*., 2008):

$$\frac{d\propto}{dt} = Aexp\left[-\frac{E}{RT}\right]f(\alpha) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..equation\ 2.1$$

In equation 1, A is the Arrhenius parameter pre-exponential factor, while E is the activation energy. f(α), T(K) and R (J/Kmol.k) describe the reaction model, temperature and gas constant respectively.

Kinetic evaluation involves determining the activation energy (E_a), reaction model and frequency factor (A). This data is essential in understanding the reaction mechanism of lignocellulose biomass and is useful in calculating the costs of thermal processes. There are two kinetic model techniques used to analysis biomass pyrolysis kinetics: isoconversional and model-fitting methods.

2.8.2. Isoconversional method

Isoconversional methods are the most effective techniques for assessing TGA data (Cai *et al.*, 2018). There are various isoconversional models such as the Ozawa-Flynn-Wall linear integral isoconversional method (Flynn and Wall, 1966) and the Kissinger- Akahira-Sunose linear integral isoconversional method (Kissinger, 1956). The most widely used isothermal model however is the Friedman isoconversional method owing to its accuracy and simplicity (Cai *et al.*, 2018). The isoconversional method is considered 'model-free' as it does not require selecting a reaction model. The primary principle for this method is that the reaction rate for a constant conversion varies only with temperature (Vyazovkin and Wight, 1999)

The isoconversional method is often used to describe the kinetics of solid-state processes. The theory of isoconversional methods is based on two fundamental assumptions:

i) The rate of processes in the condensed state is a function of temperature and conversion:

$$\frac{d\alpha}{dt} = \Phi(T,\alpha) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..equation\ 2.2$$

ii) A set of kinetic runs are used to obtain the activation parameters from the dependencies of time vs. temperature, reaction rate vs. temperature (for the differential Friedman method) or temperature vs. heating rate. (Šimon, 2004)

The benefits of using model-free method for kinetic analysis are (Vyazovkin and Wight, 1999):

- The method can be used to analyse both isothermal and non-isothermal data.
- Difficulties in reaction kinetics can be revealed by the unambiguous evaluation of the activation energy dependencies.

2.9. Model fitting methods

Model fitting methods involve fitting different models to conversion versus temperature curves and consequently determining the activation energy and frequency factor (Ebrahimi *et al*., 2007). The methods are an excellent approach of fitting isothermal data, however, it produces inexact values for Arrhenius data when applied to non-isothermal data. Vyazovkin and Wight (1999) states that by means of model-fitting, Arrhenius parameters are obtained by the form of an assumed reaction model. This is done by force-fitting a non-isothermal data to hypothetical reaction data. The danger of this method is almost any reaction model can be made to fit a set of data, this will come at the expense of variations in the Arrhenius parameters. Secondly, with regards to non-isothermal experiments both temperature and conversion vary at the same time, consequently, the model-fitting approach largely fails to assess the separation between temperature dependence and the reaction model. Usual model-fitting methods are utilised for extracting a single value of activation energy for an overall process.

2.10. Optimisation studies

Optimisation is referred to as the method of improving the performance of a process to achieve maximum potential throughput from it. In chemical engineering, the term optimisation is generally applied to a process that produces the best response. Traditionally, the optimal conditions of a process are investigated by monitoring the influence of one factor at a time on an experimental response. One parameter at a time would be changed while the other parameters are kept constant. This optimisation technique is known as one variable at a time (Bezerra *et al.*, 2008). The main disadvantage of using this method is it does not assess the interaction among the selected parameters. Secondly, using this method will lead to an unnecessary increase in the number of experimental runs required to perform optimisation on the experimental data. A way of overcoming these issues is by multivariate statistic techniques to perform optimisation studies. One of the most widely used multivariate techniques in optimisation studies is response surface methodology (RSM)

2.10.1. Response surface method

Over the past decade, RSM has been useful in studying the interactive effects of independent parameters for numerous chemical processes (Rajeshkannan *et al*., 2009; Vimalashanmugam and Viruthagiri, 2012). RSM was developed in the 50's to model experimental responses but was then later used to model numerical responses (Bezerra *et al.*, 2008). RSM makes use of statistical techniques to fit empirical models to experimental data. The model is then described by linear or square polynomial functions. The functions are then studied before modeling and optimisation of the conditions. According to (Bezerra *et al.*, 2008) the methodology of optimisation via application of RSM is as follows:

- Screening studies are used to select the independent parameters with a major effect on the system, subsequently, the definite limits of the parameters are defined by the researcher.
- Selection of experimental design and careful implementation experiments in accordance with an appropriate experimental matrix.
- Assessment of the experimental data using mathematic-statistic treatment for the fitted polynomial function.
- Evaluation of the fitness of the model.
- Locating optimum values for each parameter from the RSM plot.

2.10.2. Central composite designs

Central composite designs are common designs used for RSM for fitting second-order models. Quadratic surfaces are appropriately fitted while independent parameters are optimised using minimal experimental runs. The experimental centre points are used to assess the errors and reproducibility of the results. A comprehensive CCD with three design parameters is represented in Figure 2.8.

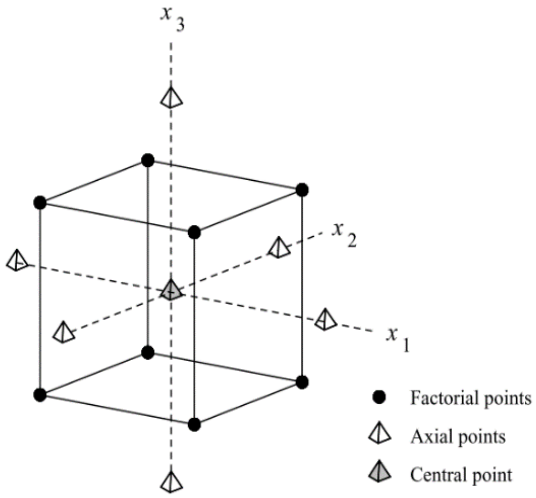


Figure 2. 8: Central composite design for three parameters at two levels

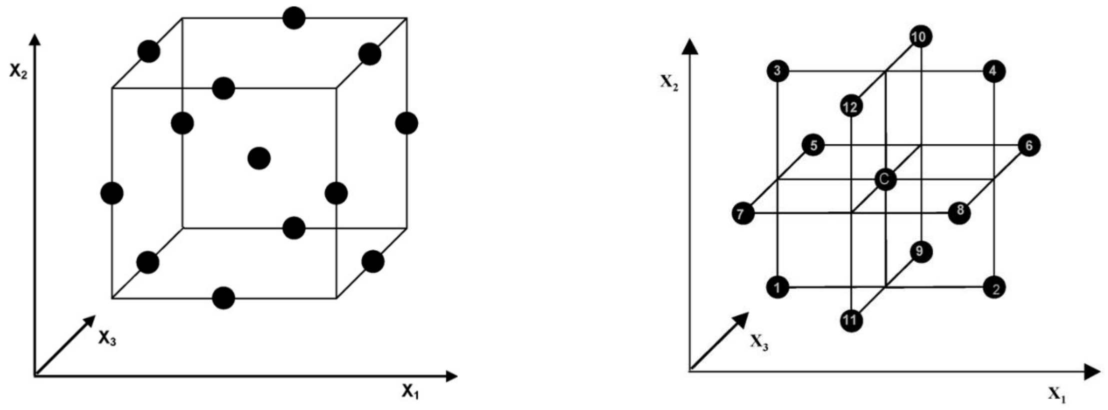
The CCD consists of a 2^n factorial runs with $2n$ axial runs and n_c centre runs. The number of experiments necessary for a CCD is defined by $N= 2^n + 2n + n_c$. There exist two types of central composite design: uniform precision and orthogonal. The distinction relates to the number of centre points in the design and the axial values (SAS Institute Inc, 2009):

- With regards to the uniform precision, the centre points are chosen to allow the prediction variance near the centre of the design space to be flat.

- Orthogonal designs, on the other hand, the number of centre points are selected to reduce the correlation between the second-order parameter estimates with other parameter estimates.

2.10.3. Box-Behnken designs

This method was developed by Box and Behnken (1960) as a design that allows for the accurate estimation of first and second-order coefficients of the model from the three-level factorial arrangement. The number of experimental runs for BBD is defined by $N = 2n\ (n-1)+ n_c$ These designs are often used for 3^k designs with a large number of independent parameters (Bezerra *et al.*, 2008). Like to CCD, Box-Behnken Designs express the experimental design via an experimental run matrix. An advantage of BBD's is the combinations expressed by the design matrix never result in an experimental run in which all factors are simultaneously at the highest of the lowest (Ferreira *et al.*, 2007). The result is operation at extreme conditions is avoided. Equally, such designs are not ideal when responses at extreme conditions are required. For three factors the graphical representation is as follows:



(a) *(b)*

Figure 2. 9 : (a) Box-Behnken Design cube (b) three interlocking 2^2 factorial design

Box-Behnken Designs are suitable for RSM because they allow for (Ferreira *et al.*, 2007):

- An accurate estimation of the quadratic model
- Building of designs
- Good detection of lack of fit model

In the past, researchers have typically focussed on the optimisation of pyrolysis processes for volatile biofuel production. Issa *et al*. (2011) employed CCD to optimise the pyrolysis of rice husk for bio-oil production. The results from the study showed that bio-oil production was only affected by the main process factors such as temperature, heating rate, particle size, holding time and gas flow rate. The interaction of these factors had no significant influence on the production of bio-oil. The authors also noted high char production at 400°C, as such bio-oil yield was reduced. No further work was done on studying the production of char in the study. Similarly, Kolokolova, (2014) optimised the production of bio-bitumen through the pyrolysis of sawdust. The author detailed maximum bio-oil yields were obtained at temperatures above 450°C. The author went further to state that by-product chars produced at 450°C had a higher calorific value to those produced at 350°C, this the author stated demonstrated char's potential to be used as a solid fuel. The author produced char with a calorific value of 25 MJ/kg, which was higher than the 22 MJ/kg average of New Zealand coal. A noteworthy case study was by Mundike *et al*. (2017), who successfully employed CCD to optimise the production of chars for combustion applications through the slow pyrolysis of alien invasive plants. The study, however, did not extend to the commercial viability of the process. The current study will not only investigate the optimisation coal competitive chars but will also assess the commercial techno-economic feasibility of the process.

2.11. Techno-economic analysis

The following section evaluates previous techno-economic studies performed on pyrolysis process. Before any process is implemented on an industrial scale it must prove that it can provide good returns on investment through an extensive techno-economic assessment. Kung *et al.* (2013) who studied the techno-economics of pyrolysis-based energy production concluded that neither slow nor fast pyrolysis was profitable. The authors further highlighted the results of the techno-economics are highly sensitive to construction costs, feedstock costs, char value, and utility costs. It is important to mention the study was centered on the sale of bio-oil and char. The third pyrolysis product, biogas, which can be used as a valuable by-product in the process was not considered in their study.

Shabangu *et al.* (2014) studied the techno-economic of methanol-char producing pyrolysis systems. At the time of the study, value of char had not been generally established by commercial markets, thus the selling prices were estimated. The authors claimed that if both methanol and chars are considered as commercial products, the profitability of the plant will depend on the selling price of char. When the sale of char was not considered in their study, syngas produced through the refining of the pyrolysis volatiles was not enough to make methanol prices competitive in the United States market. The authors recommended further research on the establishment of char markets, this they believed could help reduce the cost of biofuels.

McCarl *et al*. (2009) conducted a techno-economic analysis of the slow and fast pyrolysis of CS, concluding both processes to be economically not feasible. In their conclusion, the authors demonstrated they made assumptions that did not rely heavily on evidence, such as the value of the products. The study determined that char and bio-oil were most lucrative when used as fuel for electricity generation. Wright *et al*. (2010), study disputes this claim by stating that utilisation of the products in that respect produces lower economic returns as compared to the returns obtained by using bio-oil as feedstock for the production of 'green' gasoline. The latter compared the profitability of two pyrolysis scenarios; fast pyrolysis producing char and transportation fuel versus slow pyrolysis producing fuel gas and char. The fast pyrolysis scenario produced products with substantially higher economic value compared to those of slow pyrolysis. A downside of the fast pyrolysis scenario was that it required a capital investment of $200 million which was significantly higher than $132 million capital investment required for the slow pyrolysis scenario. The slow pyrolysis internal rate of return (IRR) was estimated for two scenarios, firstly assuming a feedstock price of $0 per metric ton, the resultant IRR ranged from 8% to 17%. A realistic price of biomass feedstock is $83 per metric ton according to the authors, at this price the process is not profitable. Ultimately, the authors concluded a process that centers on the production of char is likely to be unprofitable due to the low value of char assumed in their study.

According to Mullaney *et al*. (2002), it is possible to produce enough energy to heat both the pyrolysis process and provide process heat for other applications using pyrolysis products. By refining bio-oil, 'green' gasoline and diesel can be produced. Biogas, on the other hand, can be used as a substitute for natural gas for heating or power generation purposes (Wright *et al*., 2010). Finally, char has various uses such as solid fuel in boilers, production of activated carbon, soil amendment properties and production of hydrogen-rich gas (Jahirul *et al.*, 2012). The design and efficiency of the pyrolysis plant will dictate the properties of the products and hence their use and economic value. Table 2.7 displays a summary of techno-economic assessments on lignocellulosic biomass pyrolysis processes by detailing the cost of feedstock and products, capital investment requirements and overall profitability of the process. The table highlights that the profitability of the process is highly dependent on the pricing of pyrolysis biofuel products, feedstock and type of process.

Table 2. 7 : Summary of techno-economic assessments on pyrolysis processes

Plant size (t/d)	Pyrolysis Type	Feed type	Feed cost ($/dry/t)	Bio-oil cost ($/t)	Char cost ($/kg)	Biogas cost ($/kg)	Capital investment ($ million)	Profitability assessment	Comments	Reference
2000	Fast	Corn-stover	0-83	$3.7/gallon (gasoline)	not given	not given	200	Profitability dependent on product price	High-value products are produced via fast pyrolysis at a substantially higher investment cost than slow pyrolysis	Wright *et al.* (2010)
100	Fast	Woody L.B	36	260	not given	not given	6.6	Not profitable	Fast pyrolysis has proven to be technically viable for 0 to 45 ton/day plant ranges. Economically however markets for bio-oil consumption need to be established before it can be an economically viable alternative.	Mullaney *et al*. (2002)
2000	Fast	Corn-stover	75	not given	20	not given	247	Profitability dependent on product pricing and fuel upgrading	The transportation fuels produced in this study can potentially be produced from biomass at a competitive product value of $3.09–2.11 per gallon ($0.82–0.56 per litre), this however depends on hydrogen production or purchased for bio-oil upgrading scenarios, respectively	Wright *et* al. (2010)
2000	Slow	Corn-stover	0-83	not given	10-55	not given	132	Not profitable	A process that centres on the production of char is likely to be infeasible. Note: biogas was not recycled into the system.	Wright *et al.* (2010)
2400	Slow	Corn-stover	50	not given	0.25	422 (methanol)	685	Not profitable if biochar is not considered	Pyrolysis is not viable if biochar is not valued as a product. Biochar-methanol production systems improved the viability of slow pyrolysis concepts. The internal rates of return for all concepts studied lie between 10.1% and 14.2%	Shabangu *et al.* (2014)

*****L.B lignocellulose biomass

Chapter 3: Materials and Methods

This chapter describes the research methodology and laboratory equipment used for this study which involved sampling, characterisation, and optimisation. The chapter details the sampling of CS feedstock in order to obtain a proper representative sample, the characterisation of the CS both using elemental and proximate analyses. The analyses on CS coupled with preliminary experimental runs assisted in establishing processing conditions and further provided information on optimisation conditions. The characterisation of the experimental products provided knowledge of the fuel capabilities as well as information on the comparability of char and coal.

3.1. Materials and equipment

3.1.1. Biomass

Corn stover (CS) biomass was harvested from a farm in the North West province, South Africa. The biomass was then packed into 20L polyethylene bags and transported to the University of Stellenbosch. Upon arrival, the biomass was stored in a cool dry storage room before processing. Pre-processing of the biomass entailed milling approximately 40 kg CS using a lab-scale Type SM 100 mill (Retsch GmbH, Haan, Germany). A particle size distribution (PSD) of 0.8 to 3.5 mm was selected using appropriate sieves. The selected PSD was sufficient to allow higher heating rates during the pyrolysis reaction. The milled CS was then packed back into the polyethylene bags prior to the experimental runs. In order to ensure a good representation of the CS, sampling was done by taking a sample of CS from the top, mid-way and bottom of the polyethylene bag. The samples were then mixed into a different bag. From this bag, CS was scooped and weighed for each experimental run.

3.1.2. Thermogravimetric analysis

The thermogravimetric analysis of samples was carried out on a TGA/DSC Star Systems analyser (Mettler Toledo, Ohio, USA). The standard ASTM E1131 test method was used. For the experiment, a 20 mg CS sample was heated from 30 to 900°C at a specified heating rates of 1- 20°C/min. A nitrogen inflowing at 100 mL/min was used as the inert gas medium. Whilst the sample was being heated, the weight loss (wt.%) of the sample was continuously measured by the TGA software. A graph that presents the rate of change of the fuel was then provided by the software. The mass loss was due to the pyrolysis heating step. The proximate analysis was then calculated using equation 3.1 based on the graphical representation of figure 3.1.

$$100\ wt.\% = a(wt.\%) + b(wt.\%) + c(wt.\%) + d(wt.\%) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..equation\ 3.1$$

Where:

$a(wt.\%)$= Moisture content

$b(wt.\%)$ = volatile matter

$c(wt.\%)$ = Fixed carbon

$d(wt.\%)$ = Ash content

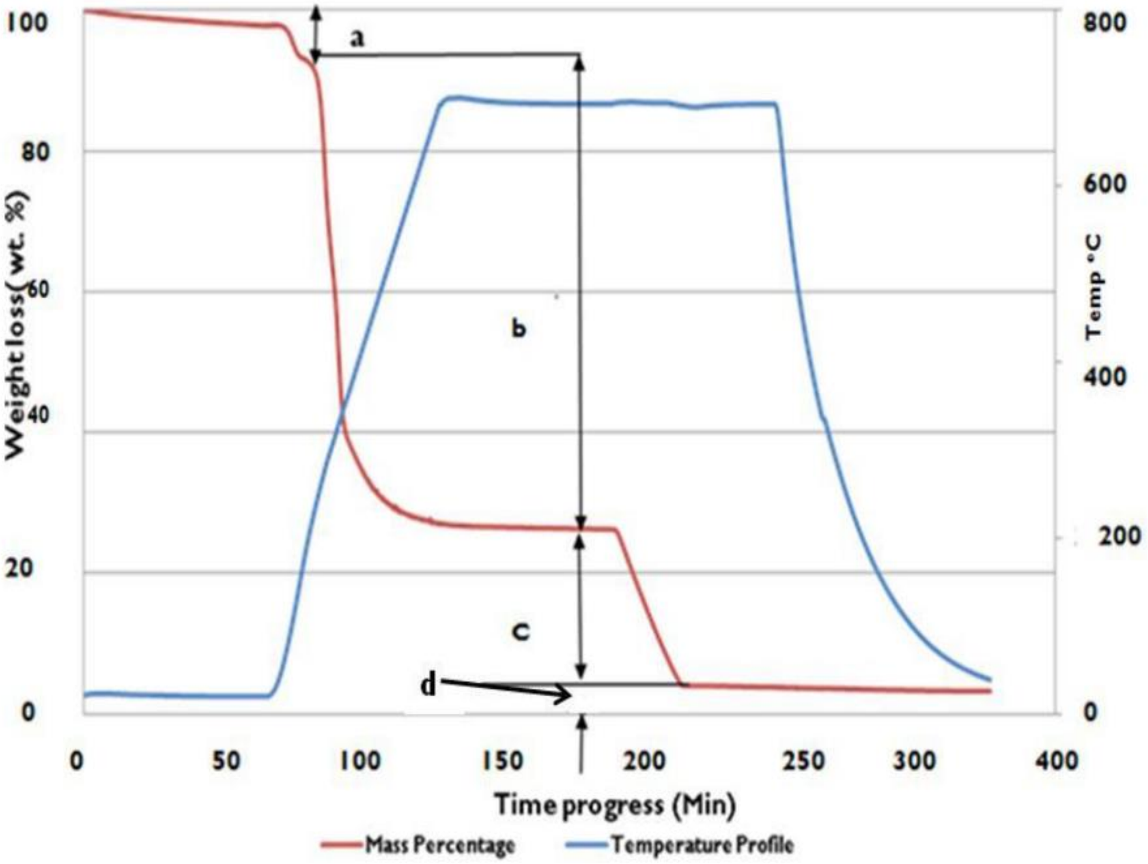


Figure 3. 1 : TGA mass loss and temperature adapted from Danje, (2011)

3.1.3. Elemental analysis

The analysis was conducted using a Vario EL Cube elemental analyser (Elementar, Langenselbold, Germany). The test determined the elemental percentage of carbon (C), nitrogen (N), hydrogen (H) and oxygen (O) of the sample in accordance with DIN 51721 standard method. The C and H contents were analysed by infrared detector and N content by thermal conductivity detector. A sample mass of 100 mg was combusted in the elemental analyser at a temperature of 950°C.

3.1.4. Bomb Calorimetry

For this study, a bomb calorimeter model Cal^{2}K ECO 2013 (DDS Instruments, Rheinland, Germany) was used to determine the higher heating value (HHV [MJ/kg]) of samples. The operation of the bomb calorimeter was as follows:

Approximately 0.2g of the sample was weighed and placed on a metallic crucible. A fuse wire used to deliver the ignition current was then connected to the roof of the bomb vessel and an ignition thread was run from the fuse wire to the material. The bomb vessel was then sealed with the sample inside, 1500 kPa of oxygen was then purged into the vessel. The vessel was subsequently placed into the vessel compartment and the weighed mass of sample entered on the keyboard instrument. The ignition of the fuse wire led to the combustion of the fuel sample. The HHV of the fuel was captured on the instrument.

3.1.5. Gas chromatography

Gas chromatography is ideal for measuring gases and light hydrocarbons in laboratory operations. A CompactGC$^{4.0}$ (Global Analyser Solutions^{TM}, Breda, Netherlands) was employed for this purpose due to its reliability and highly sensitive detectors. The analysis produced the volume composition of each compound in the sampled gas. The CompactGC$^{4.0}$ operation was as follows:

The gas exiting the pyrolysis system was collected into 10L Tedlar bags within two-minute intervals. The collection was done throughout the duration of the experiment. The CompactGC$^{4.0}$ instrument was calibrated to analyse C_1 – C_6 hydrocarbons, including H_2, N_2, O_2, CO and CO_2 gases in terms of their volume per mole composition.

The mass of the gas was then determined using equation 3.2.

$$X_x = \frac{Vol(x\%)}{Vol(N_2\%)} . \frac{N_2\ feedrate\ to\ pyrolyisi\ reactor\ (L/min)}{Standard\ gas\ volume\ (L/mol)} . MM_x \left(\frac{g}{mol}\right) . sampling\ time(min) \ \ldots\ldots\ equation\ 3.2$$

X= mass yield (%)

x = gas compound

MM = molar mass gas compound

3.2. Biomass characterisation

The CS biomass was characterised according to its elemental and proximate analyses in accordance to the method detailed in sections 3.1.2 and 3.1.3 respectively. The determination of HHV (section 3.1.4) was also conducted.

3.3. Pyrolysis experimental setup

The slow pyrolysis setup consists of a furnace that houses a removable 1m long stainless-steel reactor and a condensation train consisting of 5 condensers, firstly a condenser at room temperature connected to four glass condensers in series immersed in a dry ice (CO_2)**.** The set-up encompasses utilities consisting of a flow meter**,** which was used to regulate the flow of nitrogen into the reactor as well as two thermocouples for reactor temperature regulation. A vacuum pump was fed to the stainless steel batch-wise reactor. The volatiles produced during the reaction flow via the carrier gas from the reactor to the condensation train. Bio-oil was condensed while the non-condensable gases were captured into 10L Tedlar bags proceeding the last condenser and are analysed on the gas chromatography instrument (Compact GC 4.0). The instrument was calibrated to determine the concentrations of N_2, CO, CO_2, CH_4, H_2, C_1 to C_6. Once the experiment was completed and the reactor temperature was cooled to below 90°C, the system was then dismantled and char collected from the crucible. The description of the experimental runs were as follows:

The initial step of the process involved weighing and assembly of each of the individual parts of the setup. Consisting of the reactor, each of the condensers, crucibles and the rubber pipes connecting the condensers. Knowledge of the initial weight of the components is crucial as the difference in weighed weight after the experiment will be recorded as the mass of the product in the respective fraction. Once weighing is complete the unit was assembled. 20g of CS was then weighed and placed into the crucible. The crucible was then placed in the centre of the vertical reactor using a wooden rod. Thereafter, leak and purge tests were conducted to ensure the system was isolated. The system was checked for leaks by connecting the vacuum pump to the exit point of the last condenser. A pressure gauge reading of between 100 and 150 kPa is an indication that the system was well sealed. The vacuum was then removed and purging commenced. The system was purged with nitrogen (1L/min, 15 minutes). In the meantime, dry ice was placed around the glass condensers immersed in flasks. Polystyrene chips were placed over the dry ice in the flask to limit sublimation. Once the set-up was completed the reaction start-up was initiated. The desired process condition for the specific each run was keyed entered into on the control board. The variable parameters employed in this study were holding time (5-30 minutes), heating rate (5-20°C/min) and reactor temperature (300-500°C). Once the parameters were keyed the reaction commences by pressing the "Start" key. The reaction begins at room temperature until the set-point temperature. As the reaction commenced, gases are were captured at 2-minute time intervals into Tedlar bags from the outlet of the last condenser and were sent to the compact GC for analysis. Once the reaction was complete, the final set-point temperature begins to drop automatically, the "stop" button is then pressed on the control panel to signify the reaction is complete. The furnace was then allowed to cool below 90°C before it was opened. Once the system reached the appropriate temperature, it was dismantled and the individual components weighed. After weighing the bio-oil and char, they were stored in plastic cylinders and containers respectively, for future analysis. The components of the system were then cleaned using acetone. The components were then weighed and reassembled for the next experimental run.

Figure 3.2 below illustrates the process flow diagram of the experimental pyrolysis set-up

3.4. Product characterisation:

3.4.1. Char

The quality of the char produced during the experiments was assessed according to ASTM D388 which classifies coal by ranking them according to their HHV, volatile matter and fixed carbon based on method detailed in section 3.1.2 and 3.1.4. The elemental analysis of the char was likewise determined (section 3.1.3). These three properties are important in determining the use of char in energy applications. Industrially accepted South African coals typically have minimum energy and fixed carbon content of 25 MJ/kg and 56 wt% respectively (Mundike, 2018). This was used as the benchmark for the chars produced in this study.

3.4.2. Bio-oil

The HHV of bio-oil was determined using the method outlined in section 3.1.4. The elemental analysis of the bio-oil products was then determined in accordance with section 3.1.3 using a ThermoScientific Flash 2000 Elemental Analyser (Thermo Fisher Scientific, Inc., Massachusetts, USA) at the University of KwaZulu Natal.

3.4.3. Biogas

The non-condensable gases from the pyrolysis experiments were determined by gas chromatography as described in section 3.1.5.

3.5. Design of experiments and optimisation

The optimisation and statistical analysis was performed following the response surface methodology (RSM) and design of experiments (DoE) (Table 3.1) generated using Design-Expert® Software Version 11 (Stat-Ease, Inc., Minneapolis, USA). A full-factorial central composite design (CCD) with three process variables was used to generate a 20 run experimental design matrix. Temperature (°C), heating rate (°C/min) and holding time (min) were selected as the input variables, while char HHV (MJ/kg) and yield (%) were two process responses. The choice of process variables was based on screening tests and literature. Screening tests on char yield defined the conditions of the process variables in question.

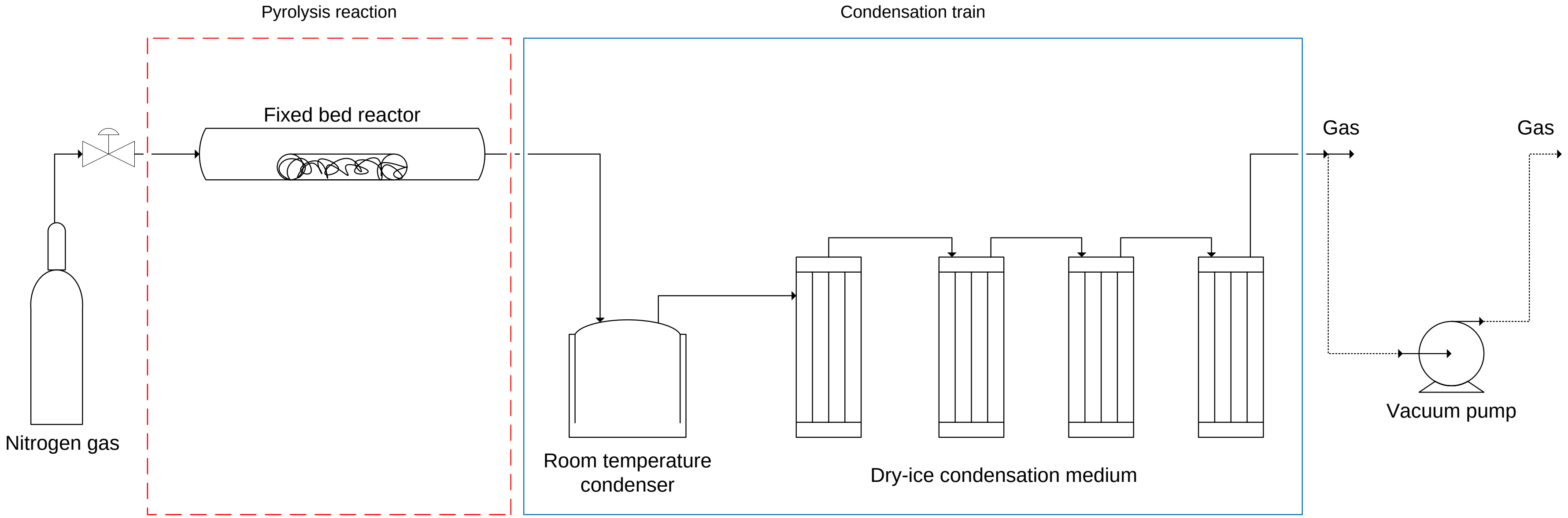


Figure 3. 2 : PFD of pyrolysis process bench-scale set-up

The char yield screening tests were conducted through experimental pyrolysis runs as described in section 3.3, at temperatures between 200°C and 600°C. Once the char yield range was clearly established, the experiment variable ranges were defined. Based on char product yields from screening tests, minimum and maximum temperature were defined as 300 and 500°C respectively. With a centre temperature point at 400°C. The heating rate minimum and maximum were defined as 5 and 20°C/min respectively. With a centre heating rate point at 12.5°C/min. Finally, the holding time was defined as 5 and 30 minutes with a centre point at 17.5 minutes. The aim of the optimisation study was to produce chars with a minimum HHV of 25 MJ/kg while maintaining a minimum yield of 30%. All experiments were duplicated for repeatability.

Table 3. 1 : Design of experiments

Factor	Variable Type	-1(Lower Level)	0 (Centre Point)	+1 (Upper Level)
Temperature (°C)	Variable	300	400	500
Heating rate (°C/min)	Variable	5	12.5	20
Holding Time (Min)	Variable	5	17.5	30
Sample Amount (g)	Constant			
Particle Size (mm)	Constant			
Char HHV (MJ/Kg)	**Response**			
Char Yield (%)	**Response**			

For optimisation of the char yield and energy content, a RSM was utilised by applying CCD. The method modelled various responses and expressed them as quadratic functions. For model validation, regression method was used to gauge the significance of the model. The significance was expressed by the R^2 statistic. The significance of the independent variable were assessed according to their p-values. A $p < 0.5$ denoted a significant variable.

3.6. Process modeling

The first step of building the model entailed selection of the appropriate physical property package that would be able to describe the behaviour of each of the components or pseudo components. The physical property package includes a thermodynamic property method used to calculate properties such as enthalpy and k-values. Advanced System for Process Engineering (Aspen Plus®) software (Aspentech, Massachusetts, USA) provides a large database of thermodynamic properties based on chemical and physical components of the feed. Despite the ideal gas method being suitable for this simulation due to the process operating at high temperatures and pressures, the Peng-Robinson property method was used as the global property method for this model. The Peng-Robinson property method is well suited because it is based on a cubic equation of state. The importance of the cubic equation of state is that it can consider possible non-ideal behaviours due to the non-polar mixtures (Aspentech, 2001 and Visconti *et al*., 2015).

The second step is to define the input components, CS and ash were defined as non-conventional solids. CS and ash do not participate in the chemical or phase equilibrium. As a result, CS and ash were defined in accordance with HCOALGEN and DCOALIGT properties models. HCOALGEN determines the enthalpy of the CS based on its proximate, ultimate and sulphur analysis in addition to using empirical correlations for heat of combustion, heat of formation and heat of capacity (Sun, 2017). DCOALIGT model was used to determine the density of CS and ash. The DCOALIGT model uses equations from IGT (Institute of Gas Technology) to estimate the density of non-conventional solids. The global stream class was specified as “MIXCINC” which is suitable for a mixed stream containing both conventional and non-conventional solids with no particle size distribution. The model input also requires a sulphur analysis with specification of the relative sulphate, pyritic and organic sulphur quantities. This data was not determined in this study, it was therefore assumed the sulphur within the CS is equally distributed among the three species. The following assumptions were made when developing the model for pyrolysis of CS:

- Steady state operation.
- Char is 100% carbon.
- No particle size distribution.
- No volatile condensation
- Equilibrium reached in pyrolysis reactor.
- Ash is inert.

The model can be divided into three parts, namely DECOMP, PYRO and CYCLONE. DECOMP represents the initial stage where the CS is decomposed into its elemental constituents namely C, H_2, O_2, Cl_2, N_2, ash H_2O and S. The PYRO stage represents the pyrolysis reaction whereby the CS is reacted into char and gas. Lastly CYCLONE represents the stage at which char and gas are separated.

3.7. Techno-economic analysis

In order to understand the costs associated with an industrial scale slow pyrolysis plant, the techno-economics of the process were conducted as follows:

- A block flow diagram (BFD) for the plant was developed highlighting all major processing units of the plant.

- The costs associated with the purchase, delivery and installation of these units were then estimated using CapCost® database. CapCost® made use of its database of equipment with reference to CECPI to estimate equipment costs.
- The cost of raw material, utilities and products were then estimated based on historical data (Wright *et al*., 2010; Indexmundi, 2018 and City of Cape Town, 2018).
- The profitability of the process was then estimated using net present value (NPV), discounted cash flow (DCF) and payback period (PBP).

Chapter 4: Slow Pyrolysis Process Optimisation

4.1. Introduction

The composition of biomass and process conditions play an influential role on the composition and end uses of the biofuels (char and volatiles) produced through pyrolysis processes (Mohan *et al*., 2006 and Ravikumar *et al*., 2016). Biofuels are primarily influenced by feedstock physical and chemical properties such as volatile matter, ash content and elemental constituents as they affect biofuel's HHV and process stability (Feng and Ling, 2017). Thus, in order to fully understand and optimise the slow pyrolysis process, it is important to determine the characteristics of CS and pyrolysis products. The distinct nature of CS was characterised in accordance with proximate and elemental analysis. Comparisons and differences were drawn between the pyrolysis products of this study and those in published literature.

Furthermore, this study explored the dearth in the literature regarding the optimisation of the slow pyrolysis process centring on the production of coal competitive char. The study focused on the effect of process parameters; temperature, hold time and heating rate on char production. To achieve the optimisation goal, a benchmark requirement for HHV and fixed carbon content of 25 MJ/kg and 56 wt% respectively was designated whilst maintaining a minimum production yield of at least 30%.

4.2. Elemental analysis

4.2.1. Corn-stover

The characteristics of the CS used in this study were comparable to those previously used in literature with regards to the H and N content (Table 4.1). This implies the CS used in this study is suitable for pyrolysis processing into various biofuels such as char and gasoline. Variance was with regard to the C and O contents. The variance could be a result of geological differences which could affect the properties of the corn-stover.

Table 4. 1: Elemental analysis for corn-stover

Elements (%)	**Tortosa *et al.* 2007**	**Wright *et al.* 2010**	**Danje 2011**	**This study**
C	48.8	47.28	48.9	40.97 ± 1.91
H	6.41	5.06	6.01	5.10 ± 0.19
O	44.1	40.63	44.4	53.23 ± 2.11*
N	0.65	0.8	0.61	0.71 ± 0.14
S	0.64	0.22	0.05	-

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*calculated by difference

The analytical instrument used in this study to determine the elemental analysis was not designated to measure oxygen and sulphur. As a result the oxygen content of CS was calculated by difference. It is thus likely that the oxygen content is overestimated in this regard.

4.2.2. Char

The elemental analysis for chars was determined over temperatures ranging from 300°C to 500°C (Table 4.2).

Table 4. 2: char elemental analysis at various temperatures

Char samples	H (%)	C (%)	N (%)	O* (%)
300°C	4.71 ± 0.18	50.07 ± 2.01	0.98 ± 0.13	44.25 ± 2.21
400°C	4.13 ± 0.06	59.36 ± 1.02	1.29 ± 0.14	35.22 ± 1.19
500°C	3.04 ± 0.07	57.90 ± 3.38	1.12 ± 0.23	37.94 ± 3.63

*calculated by difference

The char elemental properties were different from those of raw CS biomass. Increasing temperature had a positive effect on the carbon content of char from 300 to 400°C (Table 4.2) from 50.07 to 59.36% respectively. The degree of carbonisation and the development of aromatic carbon structures were accelerated by increasing temperature. The increase in char carbon concentration with increasing temperature is collaborated with those previously reported in biomass pyrolysis literature by Naik *et al*. (2017) and Dhanavath *et al*. (2019). The study on slow pyrolysis of neem seed cake by Dhanavath *et al*. (2019) reported an improvement from 57.39 to 64.12% when char was heated from 450 to 575°C. Likewise, Naik *et al*. (2017) reported an 18.29% improvement as a result of the pyrolysis of sorghum from 350 to 500°C. The authors attributed this to the cleavage and cracking of weak char bonds as a result of increasing temperature.

This study however also reported a 1.46% from 59.36 to 57.90% (Table 4.2) reduction in char carbon content when the temperature was raised from 400 to 500°C. It is believed this reduction is linked to the breaking of C-H chains under high temperature conditions. Similarly, the study by Chandra and Bhattacharya, (2019) of the slow pyrolysis neem press seed cake also noted a drop in carbon concentration at elevated temperatures above 500°C. The study linked the reduction to an increased rate of loss of long-chain aliphatic groups due to homolytic dissociation and thermal breaking of C-C and C-H bonds as a result of the char’s thermal exposure that crosses the threshold dissociation energy of bonds.

Loss in hydrogen from 4.71 to 4.13% and oxygen concentration from 44.25 to 35.22% was noted when temperature was raised from 300 to 400°C. The loss in hydrogen and oxygen concentrations could be linked to losses in water vapour, hydrocarbons, carbon dioxide, hydrogen and carbon monoxide through the production of volatiles as the pyrolysis reaction progresses. From 400°C to 500°C a slight increase in oxygen concentration (35.22 to 37.94%) was observed. It is believed the formation of volatiles was limited under these conditions. The study by Chandra and Bhattacharya, (2019) noted an increase in oxygen concentration as temperature was raised from 500°C to 600°C during the production of biochar through the pyrolysis of rice straw. It is however important to note the study by Chandra and Bhattacharya, (2019) intended the production of biochar for soil applications. The trend was also noted by Gai *et al*. (2014) who studied the pyrolysis of corn-straw, wheat straw and peanut shell.

Nitrogen concentration increased from 0.98% to 1.29% when the char was heated from 300°C to 400°C (Table 4.2). This positive trend is likely due to the formation of amine functional groups such as NH_4-N, NO_3-N. However, at 500°C a decline in nitrogen concentration was observed. It is believed the decline in nitrogen suggests elevated temperatures above 500°C prohibit the formation of amine functional groups. The decline of this group at 500°C was also noted by Gai *et al*. (2014) and Chandra and Bhattacharya, (2019). The authors noted a decline in nitrogen concentration at temperatures above 500°C was a result of loss of volatiles and nitrogen groups such as NH_4-N, NO_3-N.

The composition of char, particularly its high carbon concentrations >50% suggests the char produced in this study is suitable for biofuel use (Dhanavath *et al*. 2019) as high carbon concentrations are linked to improved biofuel properties. Similarly, the reduction of hydrogen and oxygen concentrations with respect to rising temperature implies improvement in fuel properties. The above-mentioned deductions are to be tested in section 4.4 by measuring the energy content of the chars with respect to temperature.

4.2.3. Bio-oil

Carbon concentration of the bio-oils produced at 300 - 500°C was in the range of 32.64 - 50.32% (Figure 4.1). Whereas hydrogen increased slightly from 6.35 to 6.74%. This indicates slow pyrolysis can be used to produce liquid products concentrated with organic compounds and energy. The concern with the bio-oil results of this study are the oxygen concentration results (> 40%). High oxygen concentrations > 10% affect the homogeneity, polarity, HHV and viscosity of the bio-oil. The consequence of such high concentrations of oxygen is a reduction in the fuel properties of the bio-oil (Zhang *et al*., 2007 and Mullen *et al*., 2010). A possible solution to this result is upgrading. Bio-oil upgrading through processes such as hydroprocessing removes oxygenated compounds from the bio-oil resulting in improved fuel capabilities (Mortensen *et al*., 2011).

In comparison, the bio-oils produced through fast pyrolysis generally have carbon and hydrogen products of 55-65% and 5-7% respectively, with oxygen concentrations <30% (Holmgren *et al*., 2008; Venderbosch *et al*., 2010 and Mullen *et al*., 2010).

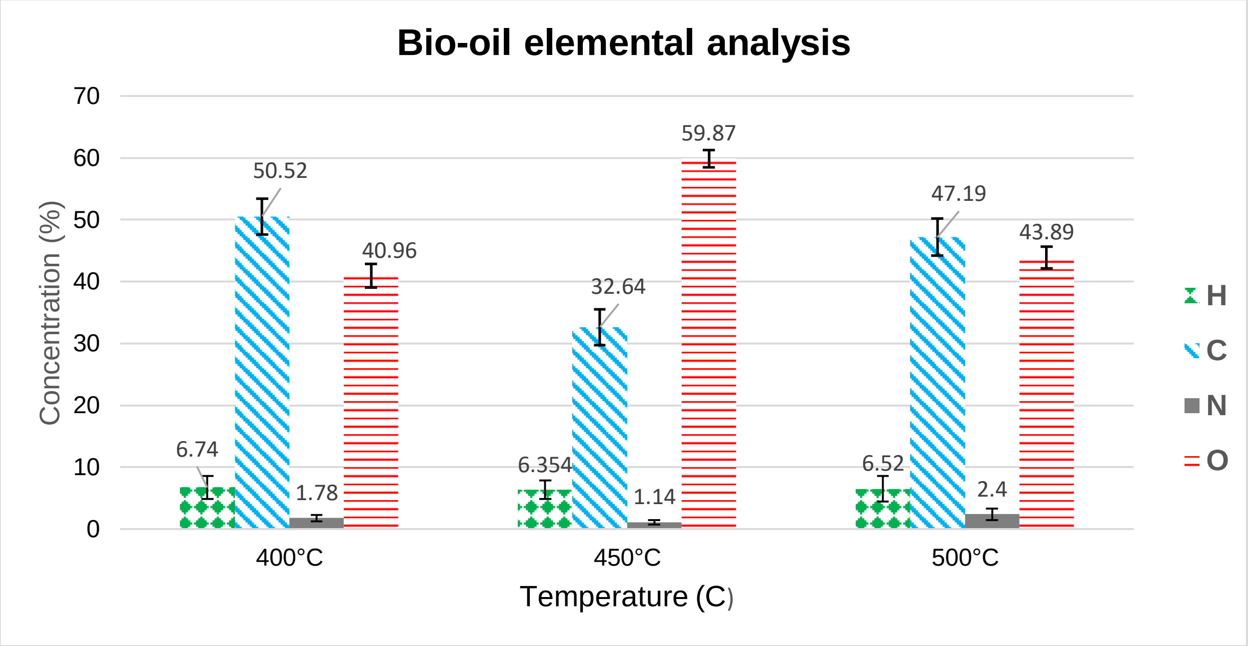

Figure 4. 1: Bio-oil elemental analysis

4.3. Proximate analysis

The section below presents the proximate analysis results for corn-stover and char.

4.3.1. Corn-stover

Table 4. 3: Corn-stover proximate analysis relative to previous studies

Proximate analysis	Evans et al., 1988	Wright et al. 2010	This study
Ash content (%)	7.3	4.5	4.96
Volatile matter (%)	78.1	52.8	68.86
Moisture (%)	-	25	8.64
Fixed carbon (%)	-	17.7	17.54

The volatile matter of the char reduced steadily with rising temperature of 300 to 500°C from 62.24 to 29.36% respectively (Figure 4.2). The volatile matter represents the fraction of biomass that will likely degrade to light molecular organics in the form of syngas in the presence of high temperature (Kim *et al*., 2012). Thus the loss in volatile matter correctly represents the devolatilisation of the biomass as it was pyrolysed into char. Similarly, the study by Chandra and Bhattacharya showed a 12.61% reduction in volatile matter when rice-straw char was heated from 400 to 500°C.

The fixed carbon in the char in this study increased from 29.81% to 51.01% with a rise in temperature from 300 to 400°C (Figure 4.2). A rise in fixed carbon is linked to improved fuel properties through the increase in aromatic carbon (Wu *et al.,* 2012). Hence, the rise in fixed carbon correlates to a rise in HHV (Rafiq *et al*., 2016). After the initial rise in fixed carbon content, a reduction from 51.02 to 44.87% in fixed carbon was then observed at 500°C. The reduction implies a drop in the energy content of the char. HHV tests were conducted in the proceeding section to verify this claim. The ash content of the char increased from 7.95 to 25.77% when the temperature was raised from 300 to 500°C respectively. Rise in ash content was related to amplification of the mineral concentration during the release of volatiles from the char during heating. Amplification of the mineral concentration is known to cause a reduction in fuel properties as evidenced by Rafiq *et al*. (2016), the authors showed an ash content increase from 5.7% to 18.7% when corn-stover biomass was heated from 300 to 500°C.

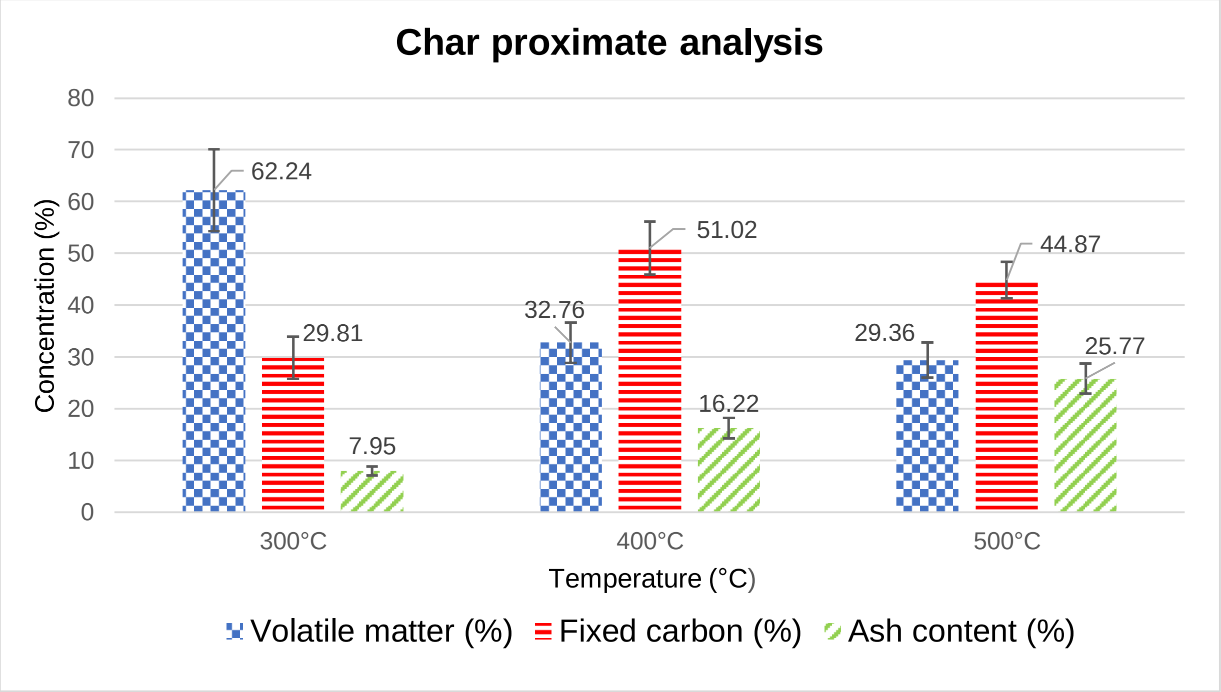

Figure 4. 2: Char proximate analysis

4.4. Energy content

The energy content of the materials was determined by measuring their HHV’s. The heating rate and hold time were maintained at 12.5°C /min and 17.5 minutes respectively when producing the respective chars. An increase in temperature from 300 to 400°C improved the HHV from 21.42 to 23.79 MJ/kg. This is evident in the fixed carbon concentration in section

4.2.1. Further heating to 500°C led to a 1.95 MJ/kg drop in HHV. This drop could validate the claim made in section 4.2.1. The assertion was that the reduction in fixed carbon and an increase in ash content had a detrimental effect on the HHV at 500°C. A previous study by Mundike *et al.* (2017) attributed dehydrogenation as the cause in the reduction of HHV at higher (above 450°C) temperatures. Dehydrogenation resulted in char having a higher percentage of inorganic material such as potassium and silica. The presence of these elements are detrimental to the char's HHV decrease in char's HHV at higher

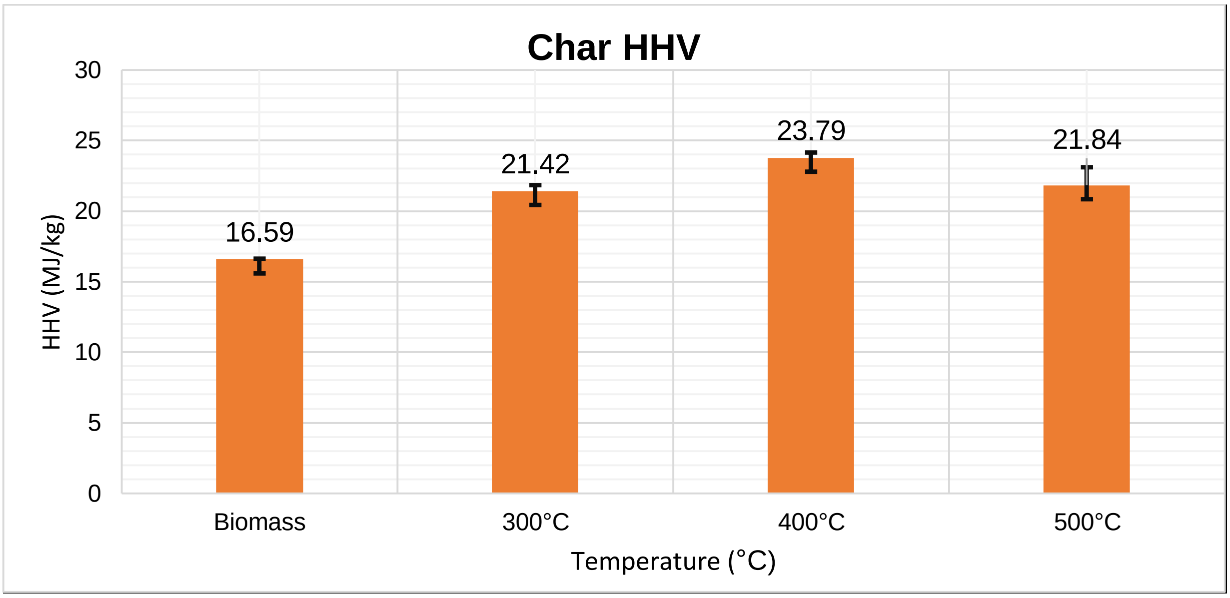

Figure 4. 3 : Char HHV's relative to temperature

4.5. Experimental product yields

The product yields of bio-oil and biogas showed a positive response to a process temperature increase from 300 to 500°C. Bio-oil increased from 20.05 to 35.88% while biogas increased from 12.51 to 33.64% relative to the 200°C temperature increase (Figure 4.4). Alongside this, the mass yield of char dropped from 66.5% to 27.95%. This is consistent with the theory of pyrolysis (Jahirul *et al.,* 2012; Dhanavath *et al*., 2019 and Chandra and Bhattacharya, 2019). The reduction in char yield with respect to temperature can be linked to the loss of volatiles and organic liquids resulting from the thermal degrading of cellulose and lignin structure of the biomass (Zhan *et al*., 2015; Chandra and Bhattacharya, 2019).

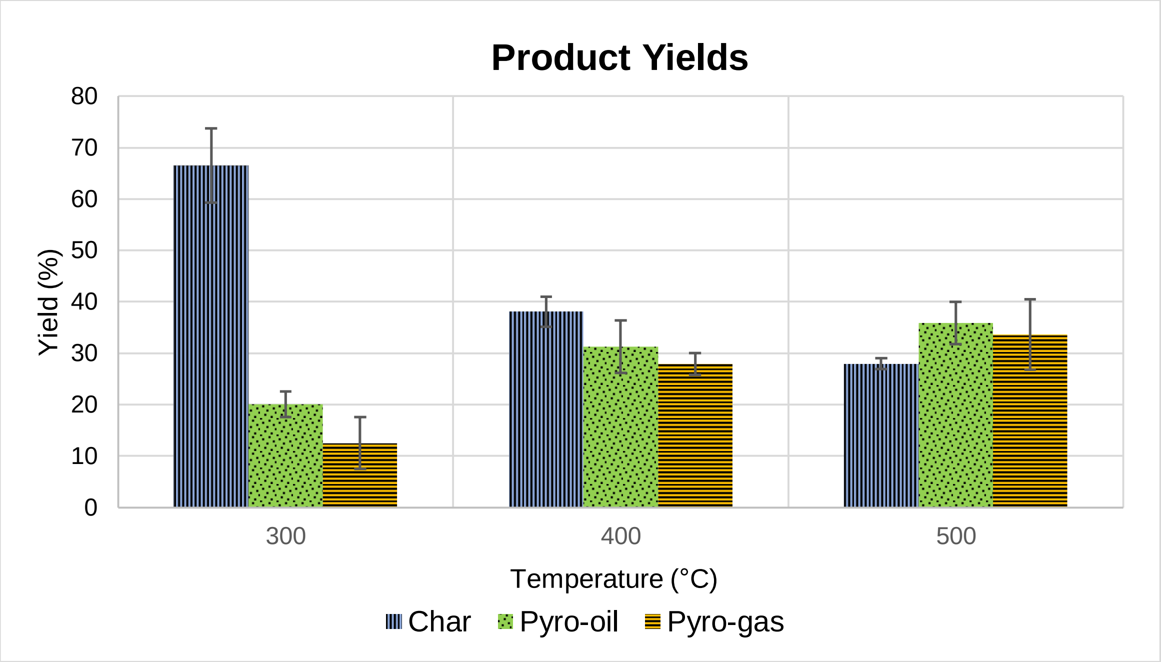

Figure 4. 4 : Bench-scale product yields

4.6. Optimisation results

The section below describes the results for the optimisation experiments for char yield (Xchar, wt.%) and char energy content (HHV, MJ/kg). The purpose of the study was to optimise the slow pyrolysis of CS to produce chars with HHV > 25 MJ/kg with a yield of at least 30%. The statistical analysis using Design Expert® version 11 was conducted using a CCD with three process variables; temperature, heating rate and holding. The temperature was varied from 300 to 500°C, while the heating rate and holding time were varied at 5–20°C/min and 5–30 minutes respectively. The goal of the experiments was to maximise the HHV of char while producing a char yield above 30 wt.%.

4.6.1. Char yield

The char yield (Xchar) regression model was relatively high $R^2 = 99.57$. The adjusted R^2 was 97.20. This indicated the model agreed with experimental results. ANOVA was utilised to determine the significance of the RSM model. The effect of all variables on Xchar were significant ($p < 0.05$) (Table 4.4). The F-value of temperature was highest (F=158.51), indicating it had the highest influence on Xchar. Design Expert® was used to fit the experimental results to quadratic models. The effects of each of the variables were studied using three-dimensional surface plots of the model. The process model (equation 4.1) illustrates the magnitude and interactions of the process variables.

$$char\ yield = 17.98 - 18.59x_1 - 1.26x_2 - 1.57x_3 + 0.924x_2x_3 - 2.94x_1^2 + 0.67x_1x_2 \ldots\ldots\ldots equation\ 4.1$$

Table 4. 4: ANOVA for char yield

	Variable	F-value	p-value	comment
Adjusted R^2 = 99.57	(X_1) Temperature (L)	158.51	0.0001	Significant
	Temperature (Q)	132.2	0.008	Significant
R^2= 97.20	(X_2) Heating rate (L)	14.26	0.013	Significant
	Heating rate (Q)	0.08	0.52	Insignificant
	(X_3) Holding time (L)	3.35	0.046	Significant
	Holding time (Q)	0.042	1.22	Insignificant
	(X_1)L by (X_2)L	64.1	0.032	Significant

*L: linear *Q: quadratic

Optimisation of char HHV sought to produce char with a yield of at least 30%. Analysis of the results indicated that if the temperature is maintained below 470°C (Figure 4.5 and 4.6), Xchar above 30% can be produced. Provided that holding time is maintained below 15 minutes. Heating rate on the other hand should ideally be maintained below 10°C/min. Based on the ANOVA table 4.4 "L" represents the linear coefficient while "Q" represents the quadratic coefficient. A linear coefficient describes a linear relationship between the dependent variable and quadratic coefficients imply the response varies parabolically with the dependent variables. The section below details the independent variable effects on Xchar as well as the relationships amongst them.

4.6.1.1. Relationship of process variables on char yield

The three-dimensional surface plot for Xchar as a function of temperature from 300 to 500°C and holding time from 5 to 30 minutes at a constant heating rate of 12.5°C/min is shown in figure 4.5. The figure shows there was a general decrease in Xchar with respect to temperature and holding time until around 400°C and 30 minutes. As the temperature increased beyond 400°C, the rate of char mass loss decreased slowly and plateaued, ANOVA describes this relationship as linear. It is believed at this point (beyond 400°C) the quadratic effect of temperature cancelled the linear effect (Table 4.4). Despite temperature having a dominant effect on Xchar, the interaction between temperature and holding time had an insignificant ($p > 0.05$) effect on Xchar. This suggests an optimum holding time for Xchar maximisation under the prescribed conditions does not exist. Figure 4.6 shows a three dimensional surface plot of Xchar as a function of temperature from 300 to 500°C and heating rate from 5 to 20°C/min, with holding time maintained at 12.5 minutes. The interaction between the two variables was significant ($p < 0.05$) and linear (Table 4.4). Equation 4.1 suggests this interaction as having a positive effect on Xchar. However the progression of figure 4.6 suggests a reduction in Xchar relative to increasing temperature and heating rate. This is likely because the magnitude (F-values and p-values) the individual effects of temperature and holding time which have a detrimental effect on Xchar supersede that of the interaction between them (Table 4.4).

4.6.1.2. Influence of Temperature on char yield

Temperature had the highest overall influence on the yield of char with $p < 0.0001$ (Table 4.4). This is consistent with reports from other authors (Solar *et al*., 2016; Gómez *et al*., 2016). The effect of temperature was the most pronounced as it is the principal variable that stimulates the pyrolysis reaction. A maximum char yield of 71.45% was obtained at 300°C (Figure 4.5). The figure illustrates that increasing temperatures have a negative effect on Xchar. This is further validated by the negative linear coefficients of temperature -18.59 (Equation 4.1) which indicates that an increase in temperature had a detrimental effect on Xchar. Accordingly, when CS was heated from 300 to 400°C the Xchar dropped from 66.5 to 38.08% respectively. This observation is consistent with results from previous reports (Wu *et al*. 2012 and Khanmohammadi *et al*. 2015). The study by Dhanavath *et al*. (2019) on the slow pyrolysis of neem press seed cake, the reaction temperature was the most predominant process variable and it had negative effects on Xchar. Their study found that by raising the temperature from 450 to 575°C, the net result was an 18.52% reduction in Xchar. The study by Brown and Brown, (2012) also showed that an increase in temperature resulted in a decrease in Xchar. The reduction in Xchar in this study could be attributed to the degradation in the hemicellulose, cellulose and lignin constituents in CS.

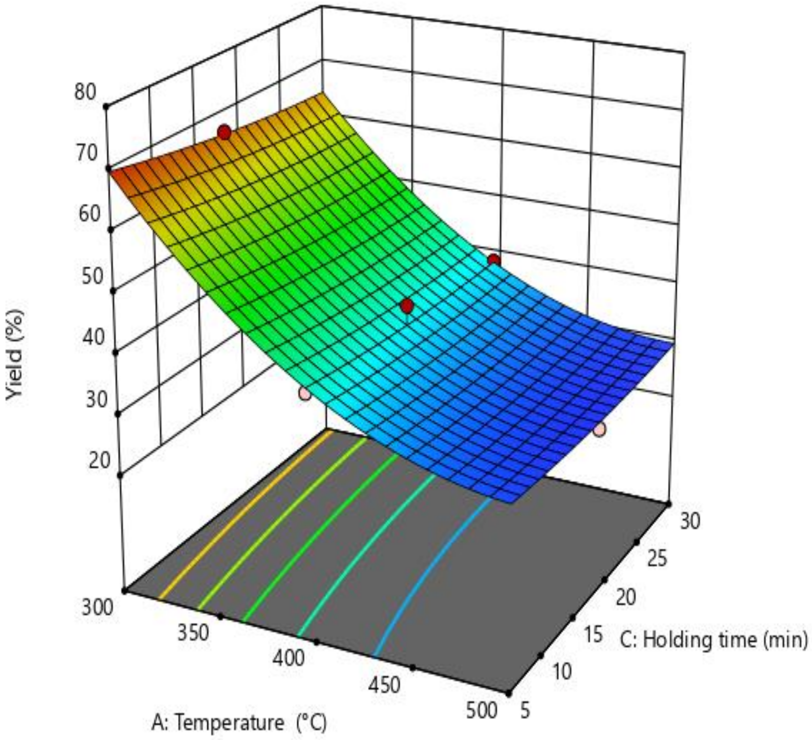

Figure 4. 5 : Relationship of temperature and holding time with respect to char yield.

4.6.1.3. Influence of hold time on char yield

The effect of hold time on Xchar was significant (p = 0.046). The linear coefficient of holding time was -1.57 (Equation 4.1). The linear coefficient suggests that Xchar had an inversely proportional relationship with hold time. Prolonged reaction times resulted in the degradation of biomass constituents, thus leading to the production of secondary products such as gases and liquids (Xu and Lancaster, 2008 and Dhanavath *et al*. 2019). Under reaction conditions of 300°C and 5 minutes, the degree of pyrolysis of biomass into char was favourable, as could be observed by the relative high Xchar of 71.45% (Figure 4.5). In comparison to when holding time was raised to 30 minutes, Xchar dropped to 63.85%.

4.6.1.4. Influence of heating rate on char yield

The linear coefficient of heating rate was -1.26, (Equation 4.1) which suggests an increase in heating rate will result in a reduction in Xchar. Heating rate had a significant effect on char yield (p = 0.013) (Table 4.4). However, it was observed that when the heating rate was increased from 5 to 20°C/min there was a 1.91% increase in char yield when the temperature was maintained at 300°C. This is contrary to the theory on pyrolysis. The theory on pyrolysis systems suggests volatile production is favoured with increases in heating rate (Amutio *et al*., 2012). Pyrolysis literature generally ascribes such theory when operation is at elevated temperature > 450°C, this study suggests the theory does not hold true at 300°C likely because temperature is not high enough to initiate rapid devolatilisation of the char.

However, when the final reactor temperature was maintained at 500°C, a heating rate increase from 5 to 20°C/min resulted in reduced Xchar from 32.65 to 29.49%. It can be deduced that at higher heating rates of approximately 20°C/min, particularly at elevated temperatures above 450°C, the reaction decomposes the feedstock more rapidly. The rapid decomposition of the feedstock into volatiles limits the effect of secondary catalytic reactions between the char and volatiles. The limitation of these reactions favours the production of liquid, hence a reduction in Xchar was observed. This was consistent with the study by Gonzalez *et al*. (2005). The study showed that char yield increased by 4.2% when the heating rate was reduced from 20 to 5°C/min while maintaining the reaction at 500°C (Figure 4.6).

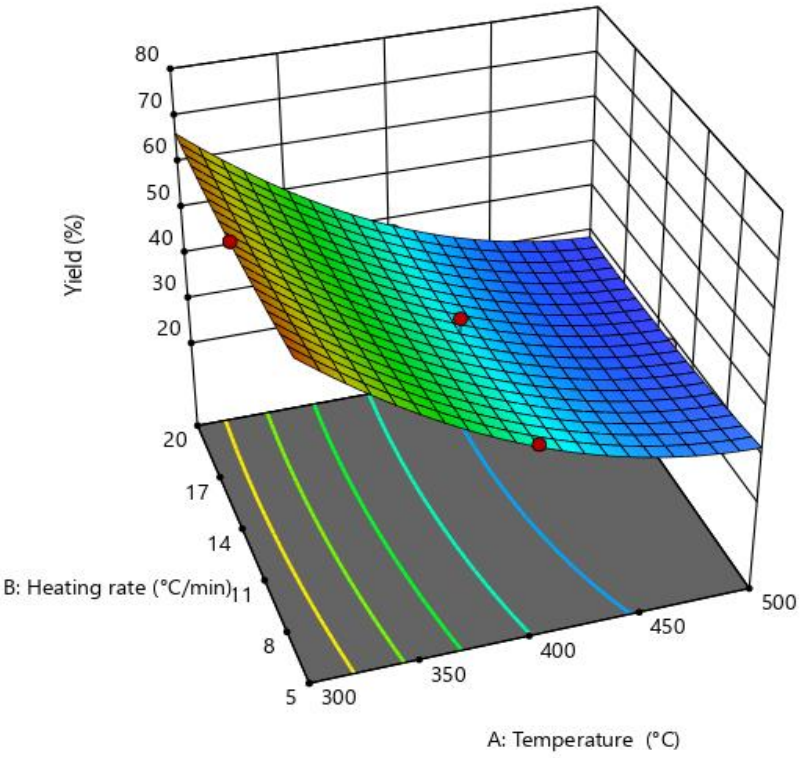

Figure 4. 6: Relationship of temperature and heating rate on char yield

4.6.2. Char HHV

Based on ANOVA the model had a confidence level of 96.20%. The p-value and F-value of the model were 0.0001 and 28.16 respectively, indicating model significance. Based on the p-value significance criteria, the coefficients of X_1 , X_2, X_1X_2, X_2X_3, X_1^2 quadratic terms were significant. The ANOVA for the optimisation of char HHV is presented (Table 4.5). Figure 4.7 illustrates the prediction curve for HHV experimental runs. The experimental model for the estimation of HHV is as follows:

$$Char\ HHV = 24.26 + 1.69x_1 - 0.501x_2 - 0.539x_1x_2 - 0.414x_2x_3 - 1.69x_1^2 \ldots\ldots\ldots\ldots\ldots\ldots.\ equation\ 4.2$$

Table 4. 5 : ANOVA for HHV optimisation

	Variable	**F-value**	**p-value**	**comment**
	(X_1) Temperature (L)	142.51	<0.0001	Significant
Adjusted R^2 = 92.79	Temperature (Q)	39.27	<0.0001	Significant
	(X_2) Heating rate (L)	12.6	0.0053	Significant
R^2= 96.20	Heating rate (Q)	0.78	0.0815	Insignificant
	(X_3) Holding time (L)	1.35	0.2723	Insignificant
	Holding time (Q)	0.04	0.8512	Insignificant
	(X_1)L by (X_2)L	11.65	0.0066	Significant
	(X_2)L by (X_3)L	6.87	0.0255	Significant

In order to produce char competitive with commercial coals, char with an energy content of above 25 MJ/kg was desired. Optimisation of slow pyrolysis experimental process variables yielded char with an energy content of 26.25 MJ/kg. This was achieved via slow pyrolysis at 453°C, 5°C/min and 29 min. Under these process conditions a desired Xchar of 34.5% was attained, which eliminated the need to further maximise the yield production of char. The section below details the independent variable effects on char HHV as well as the relationships amongst them

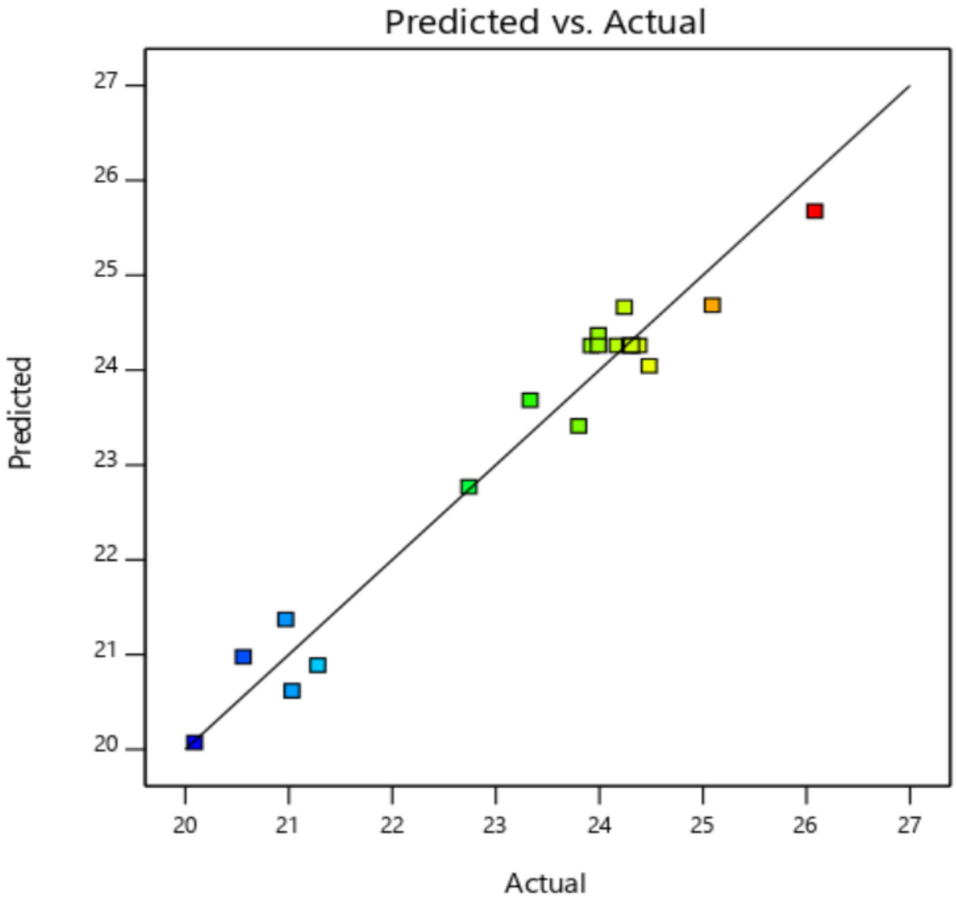

Figure 4. 7: HHV model prediction

4.6.2.1. Relationship of process variables on char HHV

The three dimensional surface plot for char HHV as a function of temperature from 300 to 500°C and heating rate from 5 to 20°C/min at a constant holding time of 12.5 minutes is shown in figure 4.8. The figure shows there was a generally parabolic relationship between temperature and heating rate validates there exists optimum process conditions for temperature and heating rate which would result in maximal char HHV production. This point is further validated by the significance ($p = 0.0066$) of the variables interaction (Table 4.5). Figure 4.9 also highlights a parabolic relationship between temperature and holding time, however the interaction of the variables did not meet the significance test ($p > 0.05$). With regards to relationship between holding time and heating rate their effects were significant and linear (Table 4.5). This is consistent with their individual variable effects on char HHV, which suggest an increase in holding time or heating rate results in a reduction in HHV.

4.6.2.2. Influence of temperature on char HHV.

Temperature had the highest effect on char HHV with $p < 0.0001$. The relationship between temperature and HHV is presented (Figure 4.8). The char HHV increased steadily with rising temperatures as indicated by the positive temperature linear coefficient (+ 1.69) (Equation 4.2). The linear and quadratic coefficients of temperature as having a significant effect of char HHV, with the quadratic coefficient being negative (-1.69). This further indicates the possibility of an optimum temperature for char HHV maximisation. By heating corn-stover biomass from room temperature to 300°C, a 3.44 MJ/kg (29.13%) fuel improvement was attained. Peak temperature effects were observed at temperatures exceeding 350°C. By raising the temperature from 350 to 450°C a 1.76 MJ/kg (11.37%) improvement in HHV was attained while maintaining heating rate and holding time at 12.5°C/min and 17.5 minutes respectively. As mentioned earlier, proximate analysis tests on chars within this temperature range indicate an increase in fixed carbon concentration, which is a primary indicator of improved fuel properties. A similar trend was reported by Xiong *et al*. (2014) as bamboo sawdust was heated from 400 to 600°C, an HHV increase from 28 to 32 MJ/kg was noted. Within 300 to 500°C temperature range is where the degradation of lignin and cellulose constituents takes place. These constituents are primarily responsible for char formation. The results of this study also showed that when an increase in temperature from 450 to 500°C was associated with HHV decrease from 24.27 to 21.84 MJ/kg. As previously mentioned dehydrogenation and amplification of the mineral concentration were linked to the decline in HHV. The results of Kumar and Chandrahekar, (2013) and Mundike *et al*. (2017) are in agreement with this finding. Mundike *et al*. (2017) describes a release of hydrocarbons composed of C-C and C-H bonds when temperature was raised from 525 to 570°C as the cause of their 0.74 MJ/kg loss in HHV.

4.6.2.3. Influence of heating rate on char HHV

The heating rate as a parameter had a significance of p-value = 0.0053 on the HHV of char. While its linear coefficient was -0.501 (equation 4.2), suggesting that an increase in heating rate resulted in a reduction in the char's HHV. Indeed when by raising the heating rate from 5 to 20°C/min a 1.76 MJ/kg (7.01%) reduction in char HHV was attained while the temperature and holding time were maintained at 400°C and 17.5 minutes respectively.

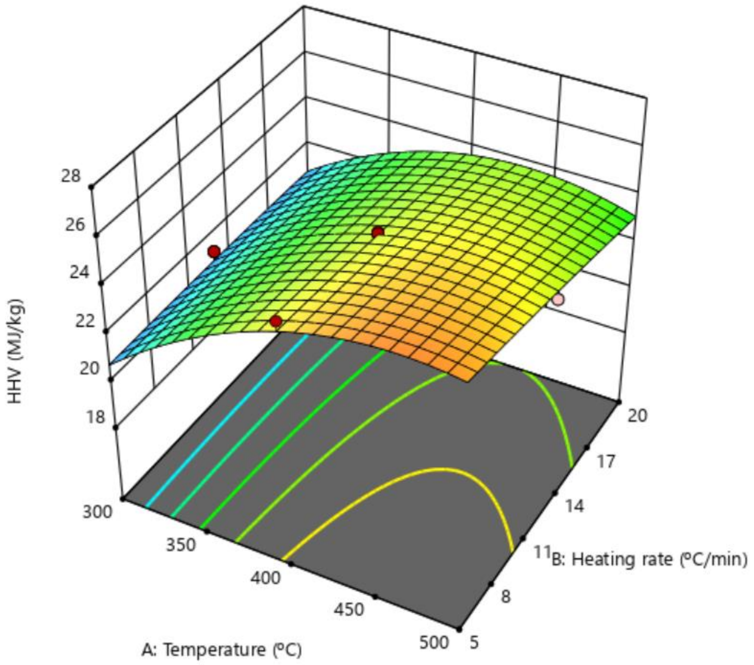

Figure 4. 8: Relationship of temperature and heating rate on HHV

This study also showed that at 500°C, a 1.56 MJ/kg (7.9%) reduction in HHV was attained when the heating rate is raised from 5 to 20°C/min. It was clear the negative effects of heating rate on HHV were more prominent at higher temperatures > 400°C. Higher heating rates lead to rapid devolitisation, which may limit secondary and tertiary char reactions. By limiting secondary and tertiary char reactions the pyrolysis mechanism does not favour the production of carbon-rich volatiles. Interestingly the study by Angin, (2013) produced results contrary to this fact. Rising heating rates showed positive effects on HHV, especially at 400°C. However, these results could be considered negligible as the rise accounted in energy differences of <0.2 MJ/kg per 100°C increases.

4.6.2.4. Influence of holding time on char HHV

In the case of the influence of holding time on char HHV, hold time had a statistically insignificant effect on char HHV. As evidenced by the $p > 0.05$ (Table 4.5). However, it is important to note that hold time had a positive linear coefficient of + 0.1640 (equation 4.2). This suggests that increasing holding time would have a positive effect on char HHV. Literature on slow pyrolysis systems describes how prolonging holding times affect the fuel properties of char positively (Gheorghe *et al*., 2010). Rossen *et al.* (2013), showed that by increasing the holding time from 15 to 30 minutes a + 0.6 MJ/kg was attained when heating cherry sawdust at 450°C. Although this study detailed hold time as having no significant effects on HHV, deductions could be drawn from the statistical analysis. Positive trends were observed. By raising the holding time from 5 to 30 minutes at 300°C, a 0.47 MJ/kg improvement was attained. Similarly a 0.29 MJ/kg fuel improvement at 400°C (Figure 4.9). The constituents of CS are readily decomposed under temperatures above 300°C, as such prolonging the reaction time theoretically accelerates degradation, hence an increase in HHV.

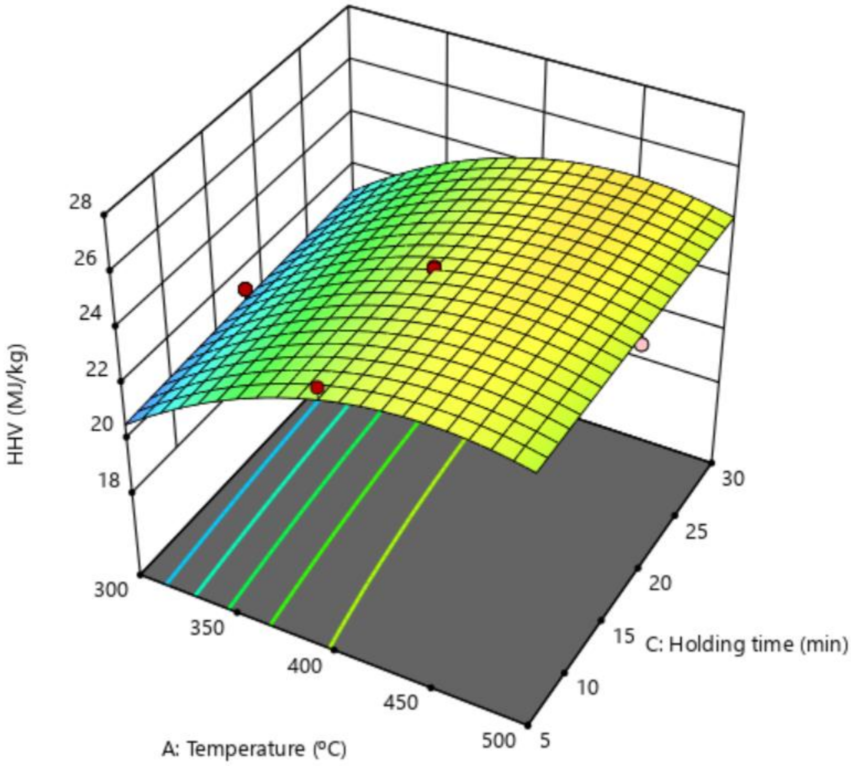

Figure 4. 9: Relationship of temperature and holding time on char HHV

4.7. Material balance of process

The material balance of the process provides an estimate of the anticipated product yields under the defined process conditions. The material balance of the process was determined under the optimum conditions for the slow pyrolysis of CS. The conditions were 453°C, 5°C/min and 29 min. A benefit of the slow pyrolysis process is it does not require any additional feedstock additives such as catalysts. The process requires a single input of CS under ideal process conditions for the reaction to take place. The material balance of the process was determined by assuming a CS feed-rate of 100kg/hr. The mass-loss during the process was estimated at 0.5%.

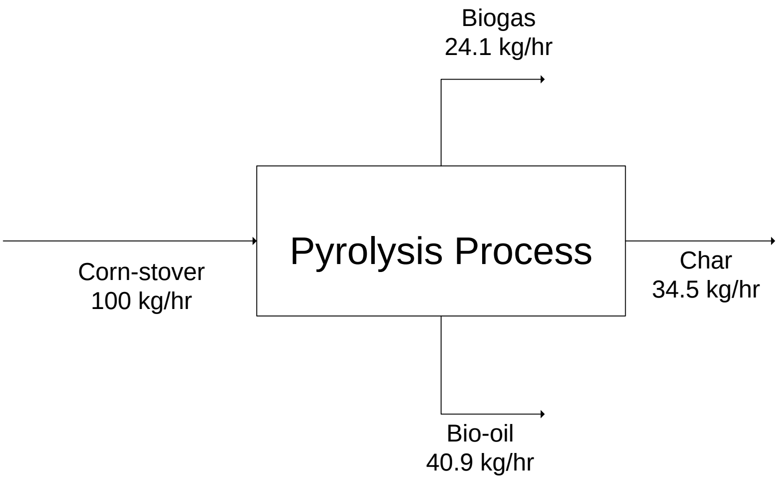

Figure 4. 10: Material balance of the pyrolysis process under optimum process conditions

The material balance was based on experimental feed and product yields. Under optimum process conditions, the slow pyrolysis process was effective in producing product outputs of 34.5% char, 40.9% bio-oil and 24.1% biogas. The results are consistent with the study by Dhanavath *et al*. (2019). Under conditions of 450°C and 60 minutes holding time, the authors produced product yields of 38.3% char, 28.8% bio-oil and 32.9% biogas through the slow pyrolysis of neem press seed cake.

4.8. Chapter summary

The energy applications of the chars produced were assessed in accordance with ASTM D388, which ranks the quality of coals according to fixed carbon content, HHV and volatile matter. The chars in this study were ranked according to their HHV relative to those of coals. From the experiments, it was determined that pyrolysis at 300 °C produced chars with an energy content of 20.09 to 21.28 MJ/kg. These chars have HHV consistent with sub-bituminous C coals (19.30- 22.09 MJ/kg). At 400 °C, the chars produced had the same energy content as sub-bituminous B coals (22.09-24.41 MJ/kg). Finally, when the experiments were conducted at 500 °C, the chars produced were comparable to sub-bituminous A coals (24.41-26.74 MJ/kg) (John Thompson, 2019).

This work investigated the effect of process conditions on char yield and HHV from the pyrolysis of CS. The purpose of the study was to optimise the slow pyrolysis of CS to produce chars with HHV > 25 MJ/kg with a yield of at least 30%. The work showed that temperature had statistically significant influences on both char yield and HHV. The study also showed that the chars produced via the slow pyrolysis of corn-stover are comparable and can be used as replacements or supplements for coal in energy applications

With temperature and heating rate having the most significant effects on char production, statistical analysis was performed to determine the optimal conditions for char HHV improvement. The analysis indicated that optimal conditions for char production attainment were at were 453°C, 5°C/min and 29 min. Under these conditions a char HHV of 26.25 ± 1.5 MJ/kg with a yield of 34.5% was determined. The char also had a fixed carbon content of 53.28% which was slightly below the 56% targeted. Taking into account the high HHV and yield, the optimisation of char production was considered successful.

Chapter 5: Process Modeling

5.1. Introduction

In spite of the rigorous investigations aimed at improving the pyrolysis of lignocellulose biomass (Sun, 2014), there exists a lack in the literature regarding the process modeling of the slow pyrolysis reaction in particular. The evolution of gases during the slow pyrolysis process was not highlighted in chapter 4 when the optimum conditions for char production were determined. As such, this chapter aims to use experimental optimum conditions for char production (Section 4.7) to develop a predictive model of the evolution of pyrolysis gases during the slow pyrolysis of corn-stover (CS). Limited data on the role of process temperature on biogas evolution during slow pyrolysis is available. Biogas typically contains mostly H_2, CO, CO_2, H_2O and CH_4 (Visconti *et al*., 2015). This work presents a process model of a steady-state, continuous slow pyrolysis of CS simulated using Advanced System for Process Engineering (Aspen Plus®) software. The simulation of the process was described through an equilibrium based, non-stoichiometric model. The model relies on experimental process conditions and feedstock composition detailed in chapter 4.

5.2. Overview of process models

It is imperative that model simulations be able to predict product over a range of process conditions. Aspen Plus® software allows the user to build a model of the proposed plant by inputting the necessary process information, using “Blocks” to represent calculation procedures in the software which rely on the user's input process information. In addition, the Aspen Plus® model is especially useful when working with solids in chemical processes. Solids present heat and mass balance difficulties that require physical property models fit for solid components (Aspentech, 2004). The software provides an extensive database of both conventional and non-conventional components which makes it possible to simulate solid chemical processes. Previous studies on pyrolysis models suggest that steady-state models are ideally suited for predicting gas compositions and performing a sensitivity analysis of the process variables (Alembath, 2016 and Mavukwana, 2016).

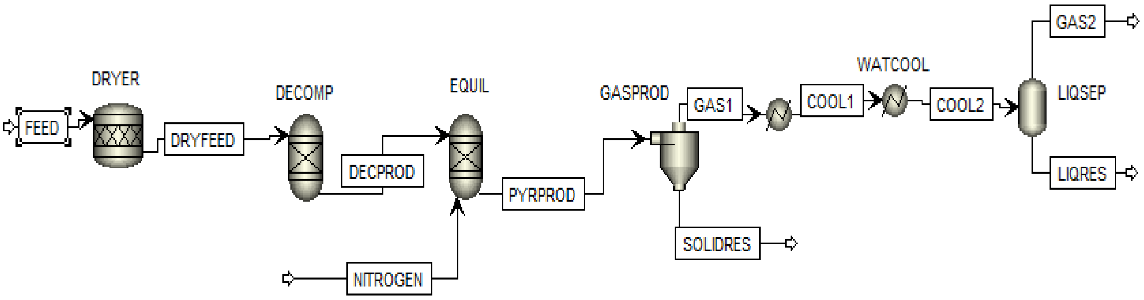

Figure 5. 1: Flow sheet for pyrolysis model developed by Visconti et al. (2015)

Visconti *et al*. (2015) studied the fast pyrolysis of biomass using a steady-state, continuous Aspen Plus® model (Figure 5.1). The objective of the study was to assess the effect of process variables on volatile production for slow pyrolysis using Gibbs free energy minimisation. The first block called DRYER made use of an "RYield Block" to simulate the drying of the feed biomass. The drying removed water from the biomass. The DECOMP unit modeled the dried biomass as a non-conventional solid fuel, as a result, the biomass was defined in accordance to its proximate and elemental properties. The third unit EQUIL modeled the pyrolysis reaction making use of an "RGibbs Block" (Figure 5.1). The main process assumptions made in the model are described in the following section.

5.3. Model approach

The model can be divided into three parts, namely DECOMP, PYRO and CYCLONE. DECOMP which made use of a "RYield" block represents the initial stage where the CS is decomposed into its elemental constituents namely C, H_2, O_2, Cl_2, N_2, ash H_2O and S. FORTRAN calculations were used to determine the balance of the constituents based on proximate and elemental analysis. The PYRO stage represents the pyrolysis reaction whereby the CS is reacted into char and biogas. The unit was modeled using an "RGibbs" block. The unit used Gibbs free energy minimisation to calculate the thermodynamic equilibrium. Lastly CYCLONE represents the stage at which char and gas are separated. The methodology of the model was described in section 3.6. The simulation utilised the elemental and proximate characteristics described in chapter 4 (Table 5.1). Sulphur analysis (pyritic, organic and sulphate) of CS was not determined experimentally, as a result, for simulation purposes the sulphur composition of the CS was assumed to be 0.01% of the CS.

Table 5. 1: Characterisation of CS

	Evans *et al*., 1988	Wright *et al*., 2010	This study
Ultimate Analysis (%wt dry basis)			
C	46.5	47.28	40.97 ± 1.91
H	5.81	5.06	5.20 ± 0.20
N	0.56	0.8	0.71 ± 0.14
O	39.7	40.63	53.23 ± 2.11
S	0.11	0.22	0.002 ± 0.004
Cl	7.32	0	-
Proximate analysis (%wt dry basis)			
Ash content	7.3	4.5	4.96
Volatiles	78.1	52.8	68.86
Moisture	-	25	8.64
Fixed carbon	-	17.7	17.54
Sulphur analysis (%wt dry basis)			
Pyritic sulphur	-	-	0.003
Organic sulphur	-	-	0.003
Sulphate sulphur	-	-	0.004

5.3.1. Process parameters

The model relied on the optimised experimental results of section 4.7. The decomposition section of the model operated at 25°C while the pyrolysis reaction was maintained at 453°C (Table 5.2). A 3:5 ratio of nitrogen gas and CS was fed to the process.

Table 5. 2: Aspen Plus® model operating conditions

Blocks	Temperature (°C)	Pressure (bar)
DECOMP	25	1
PYRO	453	1
CYCLONE	453	1
Material	**Feed rate (kg/hr)**	**Mole Composition (%)**
CS	1250	Refer to table 5.1
Nitrogen gas	750	99.9% nitrogen

The following assumptions were made when developing the model for pyrolysis of CS:

- Ash is inert.
- Char is 100% carbon.
- Equilibrium reached in pyrolysis reactor.
- The formation of intermediates was not considered.
- No particle size distribution.
- No volatile condensation

- Residence time was long enough to reach the thermodynamic equilibrium.
- Steady-state operation.
- The blocks were considered to be zero-dimensional and regarded as perfectly insulated.

5.4. Results and discussion

Figure 5.2 shows the modeled slow pyrolysis process used in this study

5.4.1. Model validation

To validate the model, simulation results were compared to biogas experimental results under the same process conditions (Table 5.3). Analysis of gas products using gas chromatography detailed the composition of the gas produced during the experimental runs. The CO and CO_2 simulation results are in reasonable agreement with those obtained experimentally (Table 5.3). The simulation, however, overestimates the composition of H_2 and CH_4. The deviation could be explained by the fact the simulation was based on Gibbs model which assumed the chemical reaction was fast enough and had reached equilibrium. In actual fact, it is likely the experimental reaction did not reach equilibrium during the slow pyrolysis experimental runs. The low molecular hydrocarbons is a consequence of non-equilibrium experimental reactions (Nikoo and Mahinpey, 2008).

Table 5. 3: Comparison of experimental and simulated results

Product	Experimental (vol.%)	Aspen simulation (vol.%)
H_2	18.7	48.1
CO	2.2	3.1
CO_2	6.4	8.9
CH_4	0.1	22.7
Temperature (°C)	453	453

Previous studies by Mavukwana, (2016) on the pyrolysis and gasification of sugarcane bagasse reported an agreement of experimental and simulated results with regards to CO and CO_2. Their model however under-predicted CH_4 and over-predicted H_2. The authors attributed the cause to non-equilibrium experimental results. The under prediction of methane was also experienced by Dorhety *et al*. (2009) in their gasification of biomass model.

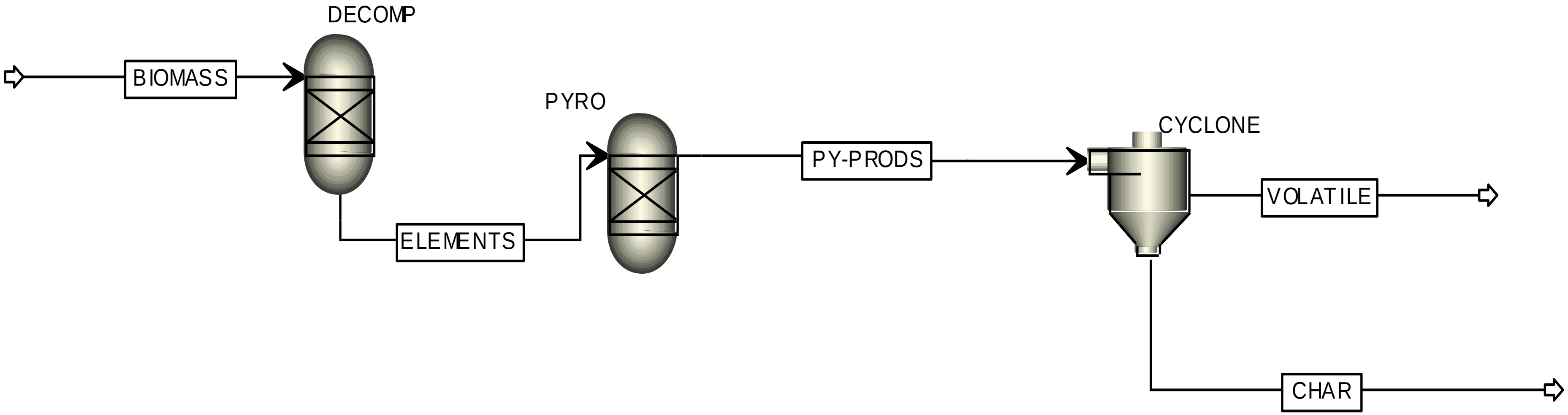

Figure 5. 2: Aspen Plus® slow pyrolysis flow sheet

Despite the deviation, this model still provides useful insight into how the reaction would progress under ideal equilibrium conditions. The insights could in future reduce the need for bench-scale laboratory experiments, process model simulations could be more relied on to assess production of pyrolysis products.

5.5. Sensitivity analysis

A sensitivity analysis of the effect on varying process temperatures (100 to 1000°C) on volatile production was performed. The analysis is a useful tool for predicting products over a range of process conditions.

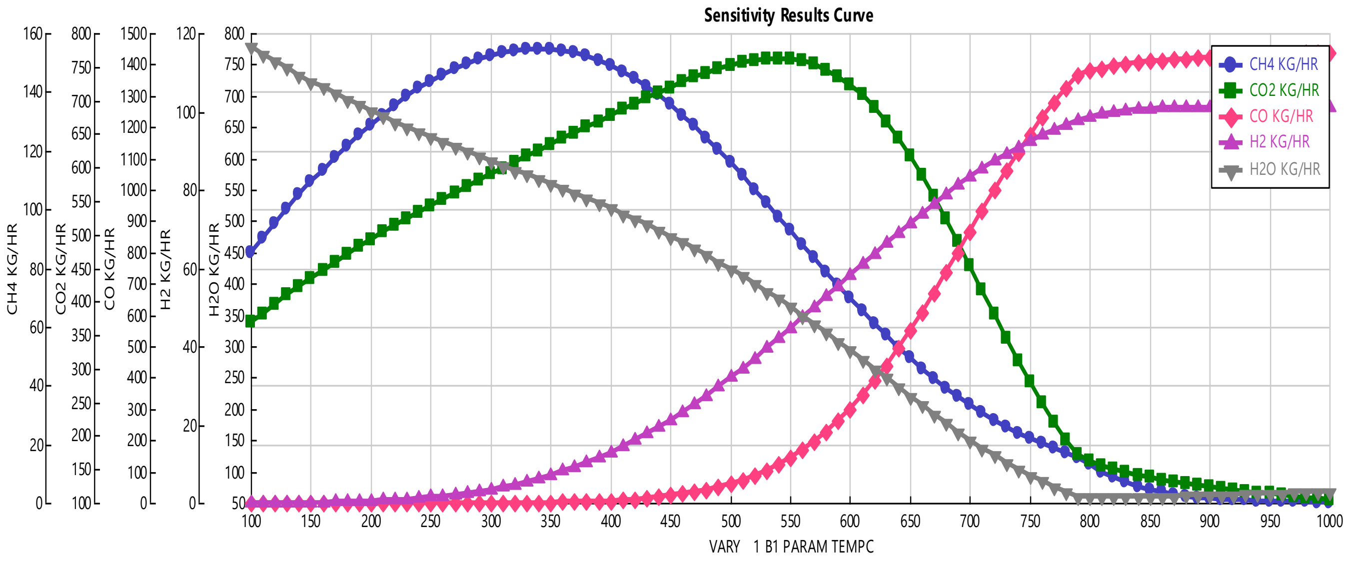

Figure 5. 3: Evolution of primary volatile throughout pyrolysis

The evolution of volatiles during the pyrolysis reaction over a range of temperatures is shown in Figure 5.3. The formation of CO and H_2 are highly favoured by temperature. A similar trend was described by Visconti *et al*. (2015). Their production is described by the following reactions:

$$CH_{4(g)} + H_2O_{(g)} \rightleftarrows CO_{(g)} + 3H_{2(g)} \qquad \Delta H_r = 205.8\ kJ/mol \qquad (5.1)$$

$$C_{(s)} + CO_{2(g)} \rightleftarrows 2CO_{(g)} \qquad \Delta H_r = 172.5\ kJ/mol \qquad (5.2)$$

$$C_{(s)} + H_2O_{(g)} \rightleftarrows CO_{(g)} + H_{2(g)} \qquad \Delta H_r = 131.3\ kJ/mol \qquad (5.3)$$

The formation of CO and H_2 result in endothermic reactions. CH_4 and CO_2 are consumed during the endothermic reactions. This is evidenced by their mass drop (Figure 5.3), whereas CO and H_2 increased steadily with temperature. This is consistent with the work done by Visconti *et al*. (2015). The authors similarly detailed the Boudouard's equilibrium as had taken place. The equilibrium presented by reaction (5.3) describes the equilibrium CO and CO_2 in the presence of char. In contrast, the presence of oxygen in the biomass results in various oxidation reactions which are exothermic.

$$H_{2(g)} + 0.5O_{2(g)} \rightleftarrows CO_{(g)} + H_2O_{(g)} \qquad \Delta H_r = -241.8\ kJ/mol \tag{5.4}$$

$$CO_{(g)} + 0.5O_{2(g)} \rightleftarrows CO_{2(g)} \qquad \Delta H_r = -283\ kJ/mol \tag{5.5}$$

The figure also shows that H_2O reduces steadily with increasing temperature. This could be attributed to the drying of the biomass. Visconti *et al*. (2015) describes this as the steam reforming reaction. The reaction yielded carbon monoxide and molecular hydrogen by reacting methane and water.

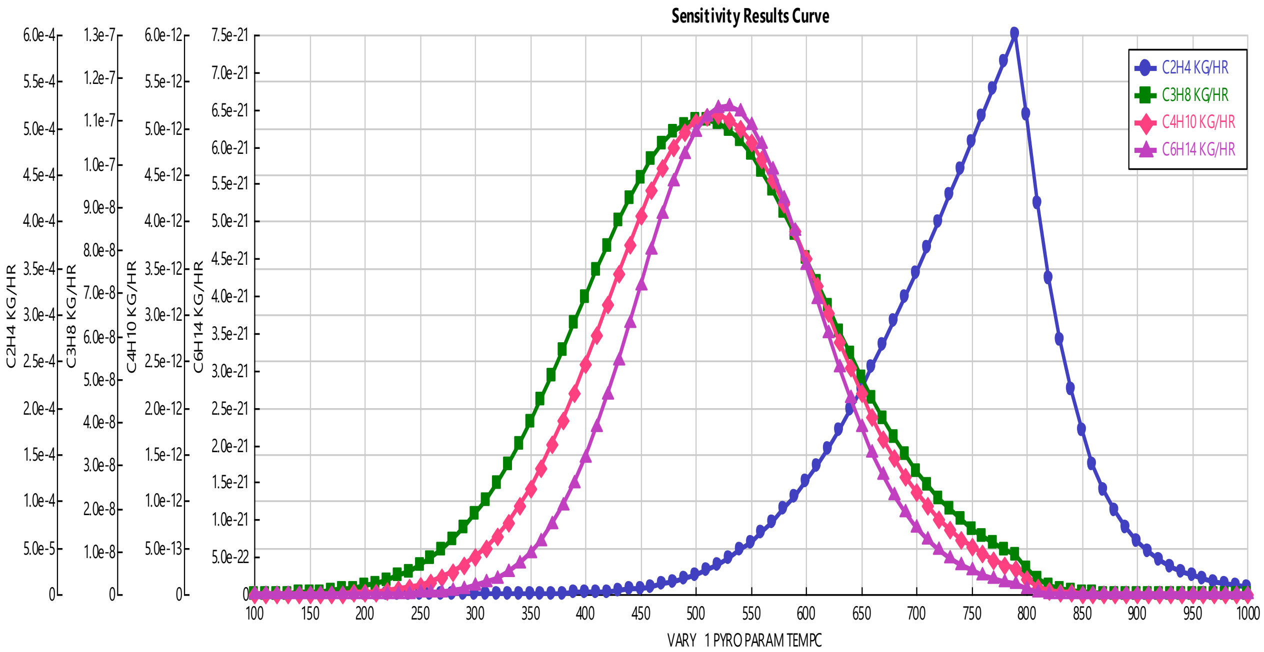

Figure 5. 4: Evolution of secondary volatiles throughout pyrolysis

The gases displayed in Figure 5.4 are seldom reported in the literature. The reason being that their presence is less significant than those presented in Figure 5.3, at times such gases are not detected by laboratory analysis instrumentation. The GC analysis conducted in the lab showed small traces of longer chained hydrocarbons such as ethylene, propane, butane and hexane. In order to fully understand the progression of the pyrolysis reaction, it was deemed necessary to model the evolution of these gases as the pyrolysis reaction progressed with temperature. C_3H_8, C_4H_{10} and C_6H_{14} follow near-identical trends. Their production follows the same trend of increases sharply to about 500°C. Thereafter they dropped steadily. The steep drop indicates that the devolatilisation has reached completion and possible equilibrium.

These results suggest the equilibrium of the slow pyrolysis process is achieved at about 500°C. The production of C_2H_4 is similar, with its production peaking at 780°C.

5.6. Chapter summary

The model was useful in predicting the evolution of volatiles during the slow pyrolysis reaction. Despite the Gibbs free energy method's overstatement of H_2 and CH_4 production, likely due to an inadequate equilibrium during laboratory experimental run. If it is unknown whether equilibrium was reached during laboratory experiments, the model provides good prediction of CO and CO_2 compounds. The successful modeling of volatiles indicates there could be a potential use of such a model in predicting products when laboratory experiments are not desired. The sale of gaseous products produced through the slow pyrolysis process could greatly improve the economic feasibility of the process, as such the modeling of gaseous products was imperative.

Chapter 6: Techno-economic Assessment

6.1. Introduction

Chapter 4 reported the necessary conditions to achieve optimal quality char while chapter 5 detailed a process model of the slow pyrolysis process. This chapter uses information from both chapters 4 and 5 to develop a continuous 1250kg/hr slow pyrolysis plant. The scale of the plant is based on the feedstock potential of South Africa and published studies on large-scale pyrolysis processes (Wright *et al*., 2010 and Batidzirai *et al*., 2016). The techno-economic feasibility study of a plant producing char as a primary product and volatile by-products is detailed in the current chapter. The volatiles were then separated through condensation into bio-oils and non-condensable biogas. A comprehensive literature review has shown that seldom are the economic values of volatiles from slow pyrolysis processes estimated (Wright *et al*., 2010 and Shabangu *et al*., 2014). The aim is to use the techno-economic assessment of the plant to determine the feasibility of the implementation of a 1250 kg/hr slow pyrolysis plant in South Africa. The plant processes corn-stover (CS) biomass into coal-competitive char and volatile (biogas and bio-oil) by-products. If successful, the implementation of such a processing plant could produce valuable biofuels for South Africa's energy requirements. The techno-economic feasibility of the plant was assessed using net present value (NPV), discounted cash flow (DCF) and payback period (PBP) as economic indicators. Finally, a sensitivity analysis was conducted to study the effect of product pricing on the economic feasibility of the plant.

The mass balance provided in figure 6.1 was based on the bench-scale experimental results (Chapter 4). The results are based on the optimum conditions for char production, as described in chapter 4. The capacity of the plant was selected to mirror the corn-stover production in South Africa.

6.2. Input and output of process

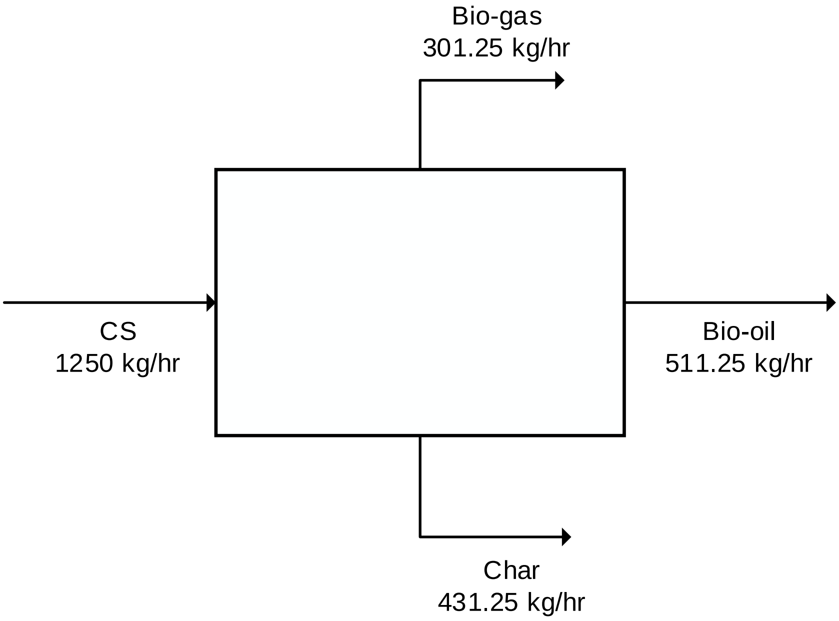

Figure 6. 1: Mass balance of the process

6.3. Development of process flow diagrams.

The development of the process was based on the literature of past pyrolysis plants and some of the technical knowledge that was gained when conducting bench-scale experiments. This section also provides several processing scenarios and information specific to the processing route.

6.3.1. Raw materials

CS is an abundant agricultural residue, which renders it the perfect lignocellulose candidate for pyrolysis valorisation. From an ecological point of view, it is essential the collection of CS mirrors the harvest of grain crop, so as not to upset the agricultural eco-system. From an economic point of view, major costs associated with the harvest are labour, equipment, fuel and transportation (Shechinger and Hettenhaus, 1999). A benefit of the proposed process is that it requires no catalyst or additives to the process thus reducing the costs associated with the operation of the plant.

6.3.2. Pre-treatment System

Prior to the biomass being fed for reaction, pre-treatment is performed to achieve specific processing requirements. The pre-treatment section of the plant consists of a feedstock storage tank with temperature regulation to initiate the drying of CS. It is important that the CS is dried, if left untreated the moisture in the CS might cause decomposition. A feedstock moisture content of below 10% is generally accepted (Danje, 2011). The drying is preceded by a milling section, lignocellulose pyrolysis is most efficient when feedstock is milled. The mill reduces the CS to the size range of 0.85-3.5mm. The milled feedstock is then passed through a sieve which serves two purposes. Firstly, it removes the unwanted CS which is not within the desired size ranges. Secondly, it discards unwanted impurities such as sand and rock which were entrained during the harvest of the maize plant. Figure 6.2 is a flow diagram of the proposed pre-treatment system.

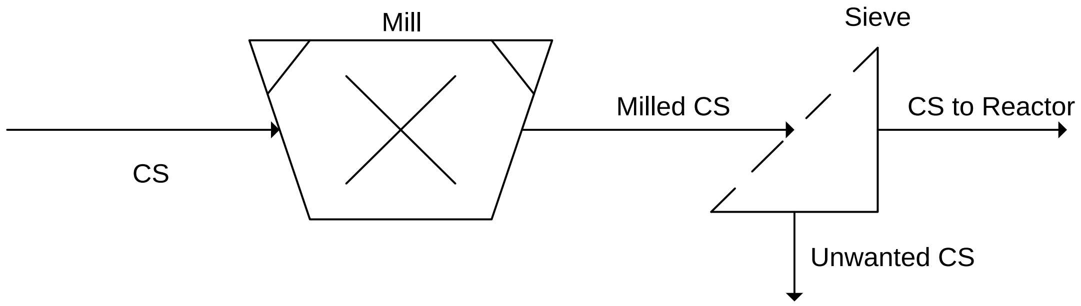

Figure 6. 2: Pre-treatment section

6.3.3. The refinement section

This section of the plant is responsible for the thermochemical reaction that results in various products and the separation of these products for their specific end uses.

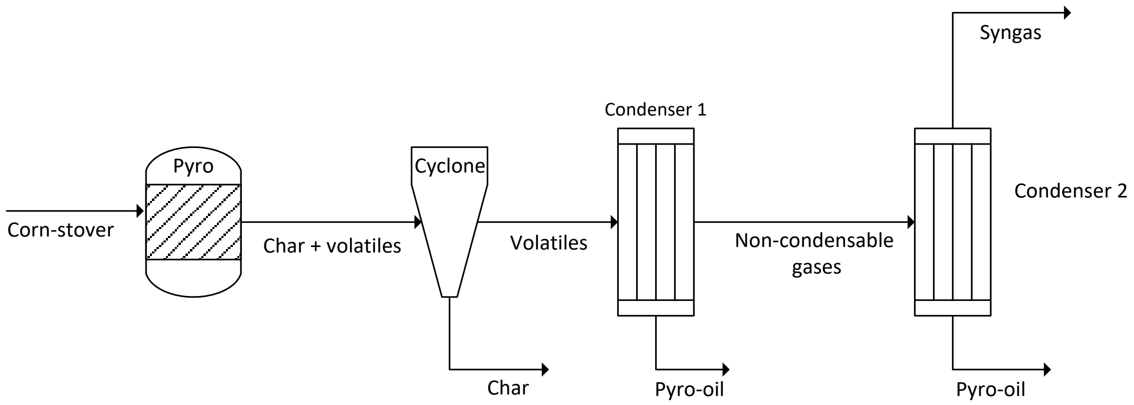

Figure 6. 3: Pyrolysis refinement section

CS is fed directly into a cyclone reactor under oxygen inert conditions, the CS is then thermochemically decomposed into char and volatiles (Figure 6.3). The products of the reactor then enter a cyclone where char is separated from the volatiles. The char exits the underflow of the cyclone and is kept in storage pots prior to pelletisation. At the overflow of the cyclone are the volatiles. Which are fed into a condenser that utilises cooling water at 25°C. This leads to the condensation of bio-oils. The bio-oil leaves the underflow of the condenser and is stored. At the overflow, is where the non-condensable gas which contain unwanted aerosols escape. In order to achieve the desired product, two condensers are required. This results in the condensation of bio-oil rich in water and overflow of aerosol-free gas. The bio-oil obtained in this process is likely to have a high oxygen content, which may reduce its economic value.

An important step in the development of a techno-economic feasibility evaluation is the articulation of fundamental process baselines and assumptions. These assumptions (Table 6.1) describe the foundation of the evaluation. The assumptions are based on defined chemical engineering standards (Peters and Timmerhaus, 1991; Amigun, 2008 and Turton *et al*., 2013) and published literature on pyrolysis studies (Jahirul *et al*., 2012; Thilakaratne, 2016; Peters *et al*., 2017 and Martin-Lara *et al*., 2019).

Table 6. 1: Production assumptions

Parameter	**Value**
Depreciation method	Straight line
Depreciation duration	10
Yearly operating days	300
Construction period (years)	2
Project life after start-up (years)	20
Income tax	28%
CECPI (2018)	603.1

*CECPI (chemical engineering cost price index)

6.4. Proposed slow-pyrolysis plant

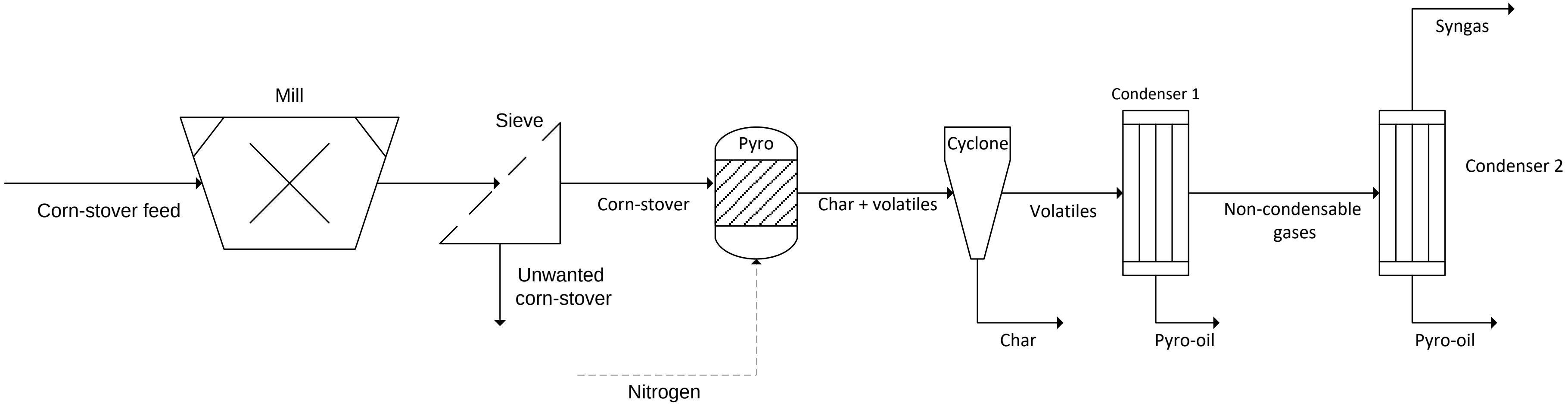

Figure 6. 4: Slow pyrolysis BFD

6.5. Process cost assumptions

The price of raw material (CS) and process utility costs regarding the slow pyrolysis process were not well defined in literature. Consequently price assumptions were made based on product purity and reports from fast pyrolysis systems (Table 6.2).
The conversion to Rand (SA) was average at $1 = R13.92 for the year 2018.

Table 6. 2: Economic assumptions

	$/unit	Source
Raw materials		
Corn-stover	20/ton	Wright *et al*. (2010)
Products		
Char	100/ton	www.indexmundi.com
By-products		
Bio-oil	50/ton	*a**
Biogas	1.5/m^3	*a**
Disposal services		
Disposal (solid and liquid)	53.48/ton	Turton *et al*. (2013)
Utilities		
Electricity	148.27 c/kWh	City of Cape Town (2018)
Cooling water	9.95/m^3	Gura (2017)
Medium pressure steam	10.86/ton	Gura (2017)
Labour		
Process engineer	27 168/year	Payscale (2018)
Operator	9 190/year	Payscale (2018)

a* estimate based on purity

The cost of equipment also plays a pivotal part on the economics of the process. The estimated purchased and bare module cost of equipment were calculated (Table 6.3). The cost of equipment is highly dependent on the 1250kg/hr plant capacity.

6.6. Results and discussion

Table 6. 3: Costs of equipment

Process stage	Equipment	Unit	Purchased Equipment Cost ($)	Bare Module Cost ($)
Reaction	Reactor	Autoclave	73 500	29 4000
Pre-treatment	Screen	Sieve	25 500	34 100
Storage	Storage Tanks	Feed Tank	81 000	89 100
		Char Tank	71 900	79 100
		Oil Tank	61 600	67 700
Separation	Centrifuge	Cyclone	32 800	51 600
	Heat exchanger	Condenser 1	33 700	110 800
	Heat exchanger	Condenser 2	32 500	106 900
Cost indicators				
Purchased cost of equipment (C_p)				350 900
Bare module cost (C_{BM})				765 600

Contingency cost (C_{cc}=0.18C_{BM})	137 808
Fixed capital investment incl. land (FCI_L)	980 440
Salvage value (0.1FCI_L)	88 044

The purchased and bare module cost (Table 6.3) of equipment was determined to be $350 900 and $765 600 respectively. The plant cost calculations following the procedures detailed in Turton *et al*. (2013) produced a fixed capital investment requirement of $980 440. This value is far less than those previously reported for pyrolysis in the literature. Unlike fast pyrolysis, slow pyrolysis focusses on the production of char which eliminates the need to upgrade the volatile products into more valuable biofuels, as a result, production costs were lowered. In recent years, researchers such as Gura, (2017) have reported extensively on the high capital requirements of liquid biofuel producing pyrolysis plants. The pyrolysis plant developed by Gura, (2017) which processed 5525 kg/hr of lignin extracted from solid organic matter waste from the paper and pulp industry into phenols had a fixed capital investment requirement of $53.57 million (Table 6.4). Shabangu *et al*. (2014) detailed a 100 t/hr slow pyrolysis bio-refinery which processed woody biomass into methanol and biochar by-product (soil amendment), the authors estimated a total investment cost of $671 million and that the minimum selling price of methanol fuel can be reduced substantially if the by-product biochar is sold as a soil amendment at a price of at least $220/ton. Thilakaratne *et al*. (2014) investigated a 2000 t/day catalytic pyrolysis plant, processing woody biomass into transportation fuels such as diesel and gasoline. The authors estimated the fixed capital requirement of the plant at $457 million. Similarly, the 2000t/day fast pyrolysis and hydroprocessing of red oak into diesel plant by Zhang *et al*. (2013) detailed a $379 million fixed capital investment requirement. Many pyrolysis case studies involve pyrolysis processing followed by further processing units such as hydroprocessing in order to obtain the desired liquid biofuel product quality. The inclusion of additional processing units, however, drives up production costs. In the study by Bridgwater, (1996) biofuels market selling prices were 158% higher than contemporary diesel fuel. It is believed that the emphasis on solid biofuel (char) eliminates the need for liquid biofuel upgrading.

The cost breakdown (Figure 6.5) of each processing section based on the costs of the equipment described in table 6.3. The breakdown shows that the separation stage accounts for 50% of the production costs.

Table 6. 4: Summary of previous process costs

Source	Pyrolysis type	Process purpose	Scale	Feedstock cost	operating costs	Profitability	Total investment cost
This study	Slow	corn-stover into char, bio-oil and biogas	1250 kg/hr	$208 050/yr	$115 200/yr	TBA	$980 440
Thilakaratne *et al.* (2014)	Fast	biomass into diesel and gasoline	2000 t/day	-	$142 million/yr	Yes, if appropriate market for products is found	$457 million
Zhang *et al.* (2013)	Fast	pyrolysis and hydroprocessing of red oak into diesel	2000 t/day	-	-	Highly dependent on price of products	$379 million
Gura, (2017)	Fast	lignin into phenols	5525 kg/hr	$790 000/yr	-	Yes, biogas sold as a by-product	$53.57 million

*TBA to be assessed

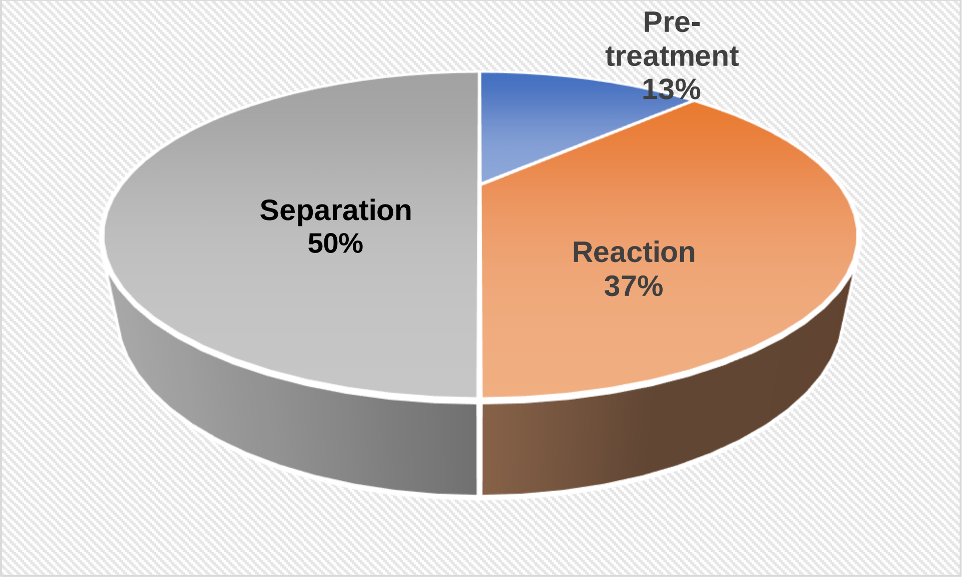

Figure 6. 5: Breakdown of cost of equipment excluding storage facilities

6.6.1. Profitability analysis

A profitability analysis for the proposed slow pyrolysis plant was developed using cost estimates and assumptions (Tables 6.1, 6.2 and 6.3) by assessing the techno-economic viability of the plant using NPV and producing DCF's. The PBP was then estimated based on the appropriate DCF. NPV is defined as the project worth at the end of the project life. The parameter considers the cash flows of the project and uses the interest rate to discount the cash flows (Turton *et al.*, 2013). It is desired the NPV be positive and high as possible. A negative NPV implies the project is not economically feasible.

The revenues estimated from the sale of the product and by-products of this study were $575 167. DCF of the process estimated the valued of the investment based on future cash flow projections.

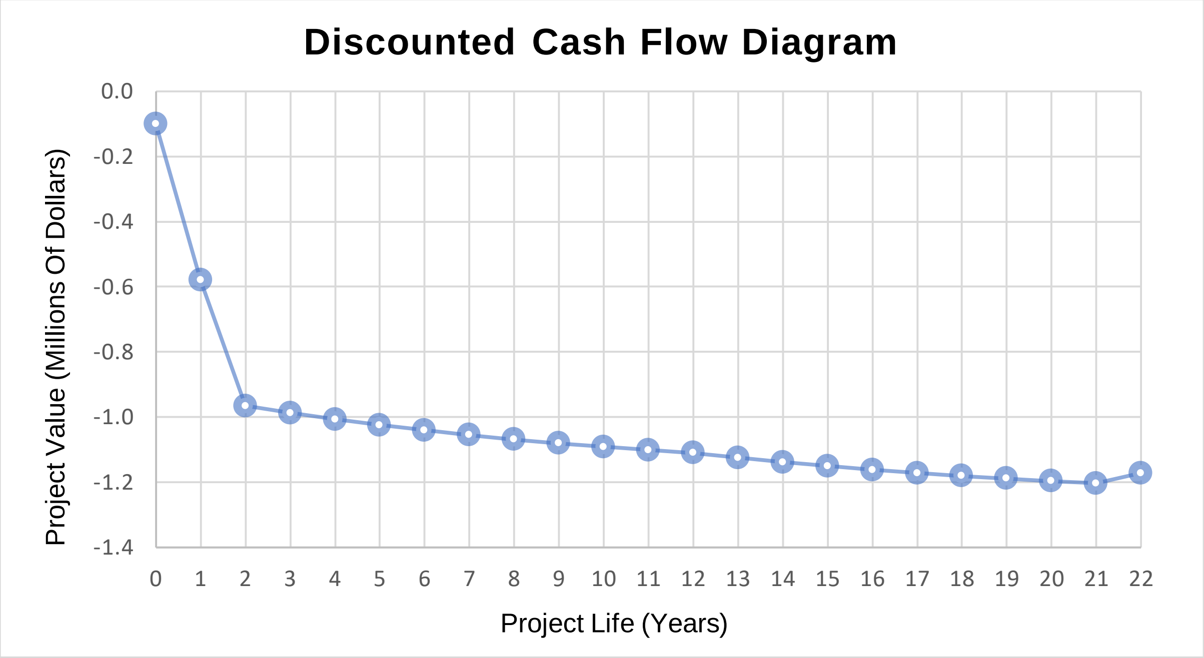

Figure 6. 6: Discounted cash-flow diagram

The discounted cash-flow (Figure 6.6) estimates that after a 20-year operation period the plant never generates enough income to become cash-flow positive. The rate of process expenses exceeds that of positive cash-flow generated by the sale of products. The NPV of the plant was -$1.17 million. Under these conditions, the process is economically infeasible. A sensitivity analysis focusing on the price/cost of the feedstock and products is required in order to quantify their impact on the economic feasibility of the plant.

6.6.2. Sensitivity cost analysis

This section assesses the impact feedstock costs and product pricing have on the economic viability of the pyrolysis plant. The techno-economics of the slow-pyrolysis process are challenging because of the relatively low price of the main product as compared to other types of pyrolysis that focus on the manufacturing of bio-oils. The uncertainties also arise from a lack of clear price definitions of slow pyrolysis products. The upper and lower cost price limits

(Table 6.5) were defined based on market reports and pyrolysis literature (Brown *et al*., 2010 Shabangu *et al*. 2014; Gura, 2017 and Indexmundi, 2018), these limits are defined as the probable maximum or minimum the market would pay for a product.

Table 6. 5: Limits of cost estimates

Limits	**CS ($/ton)**	**Char ($/ton)**	**Bio-oil ($/ton)**	**Biogas ($/m^3)**
Lower limit	3	90	20	1.2
Base	20	100	50	1.5
Upper limit	83	200	80	1.8

The base cost of corn-stover in this study was assumed to be $ 20/ton. The assumption is in line with a comprehensive study by Wright *et al*. (2010) and takes into account the cost of ploughing, packaging, delivery to the production site and other farm-related costs. The study by Wright *et al*. (2010) describes how the cost of corn-stover can vary from $0 to $83/ton. Shabangu *et al*. (2014) estimated the cost of corn-stover at $50/ton. In order to assess the effect the cost of CS has on the profitability of the plant, the lower limit cost of CS was assumed at $3/ton taking into consideration transportation and fuel costs, while the upper limit was $83/ton. With regards to char, the base price of $100/ton for this study is similar to the price of comparable coals exported in South Africa (Indexmundi, 2018). Since the price of coal is already well established the possible lower price limit of the char price was assumed to be -10% ($90/ton) of the established base price while the upper limit was assumed to be +100% ($200/ton) of the base price.

The price of bio-oil from slow pyrolysis has rarely been reported on. This is due to the relatively poor quality of bio-oils produced via slow pyrolysis as compared to other pyrolysis types as a result of high oxygen concentrations. Previous prices of high-value fast pyrolysis bio-oils were estimated to range from $260 to $6000/ton (Wright *et al*., 2010 and Gura, 2017). However, since the quality of bio-oil produced via slow pyrolysis is lower than that of fast pyrolysis a conservative price estimate of $50/ton was assumed as the base case. While the upper and lower limits were +60% ($80/ton) and -60% ($20/ton) respectively.

The production and sale of the biogas by-product has the potential of good economic return (Gura, 2017). Biogas is rich in CO_2, CO, H_2, CH_4 as well as alkanes and alkenes. This study does not extend to the separation of CO_2 from the biogas. As a result, this was factored into the price estimate of the gas. The base price of biogas was $1.5/m^3 while the upper and lower limits were +20% ($1.8/m^3) and -20% ($1.2/m^3) respectively.

Firstly, a single parameter sensitivity was performed. This study determined the magnitude each of the product pricing and feedstock cost has on the overall economics of the process.

6.6.3. Single parameter sensitivity analysis

In order to fully understand the influence of each cost and price point on NPV, each parameter was plotted with respect to NPV. The slope of the plot highlights the effect of incremental changes to the parameter has on the profitability of the process. The profitability of the process is highly sensitive to the cost of CS (Figure 6.7). For every ±20% change in the cost of CS, the resultant change in NPV is approximately ±$0.27 million. This implies the profitability of the process is highly sensitive to the cost of CS. For this reason, it is crucial that the cost of CS is kept at the lowest possible cost, so as to keep process input costs at a minimum. If the cost of CS was $2/ton, the resultant NPV would be $0.15 million. Whereas if the cost of CS was raised to $3/ton, the process becomes economically infeasible (NPV < 0). The steepness of the slope (m=-1.3) indicates the cost of corn-stover is the second most impactful on the NPV of the process. Second only to the price of char.

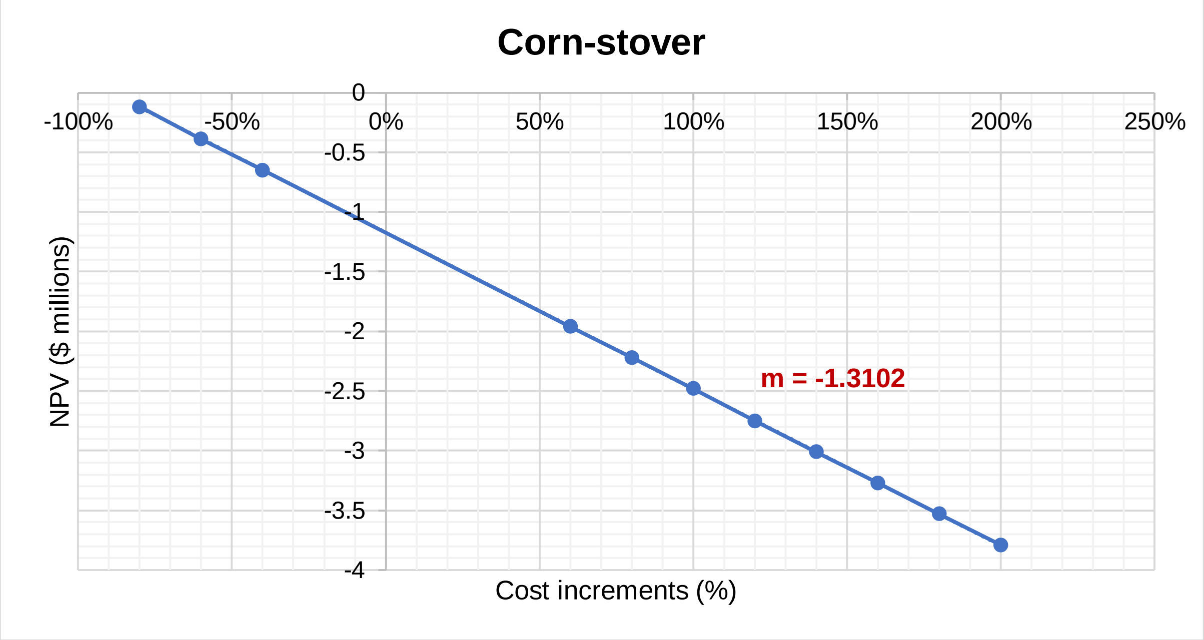

Figure 6. 7: % change in corn-stover cost

The steepness of the slope (m=1.8) indicates NPV is most sensitive to the pricing of char (Figure 6.8). For every ±20% change in char pricing, a resultant ±$0.36 million change in NPV was obtained. At approximately +65% ($165/ton) of the char base cost, the NPV of the plant is zero. A zero NPV is known as break-even, under these conditions the process has generated enough income to cover the fixed capital investment that was made commission the plant. The process, however, provides no profits to the possible investors or service providers of the plant. Such returns are seldom ideal for investors (Turton *et al*., 2013).

The influence bio-oil pricing had on NPV was less pronounced than that of char (Figure 6.9). For every ±20% price increment in bio-oil pricing, the resultant change in NPV was approximately ±$0.11 million. A +108% ($104/ton) change in the bio-oil base price would result in a zero NPV. It is possible to produce bio-oils priced at over $100/ton (Laclaire *et al*., 2002 and Gura, 2017). However, such conditions a more comprehensive quality usually through process upgrading is required.

With regards to biogas, Figure 6.10 shows that increments of ±20% in biogas pricing had little to no impact on the NPV. A ±40% price increment resulted in a $0.01 million change in NPV. A +200% increase in pricing resulted in an NPV of -$1.15 million. The results show that for slow pyrolysis processes the price of biogas has no major influence on the profitability of the process under the current base assumption price of $1.5/m^3. As such it is favourable to prioritise the pricing of the char and bio-oil products.

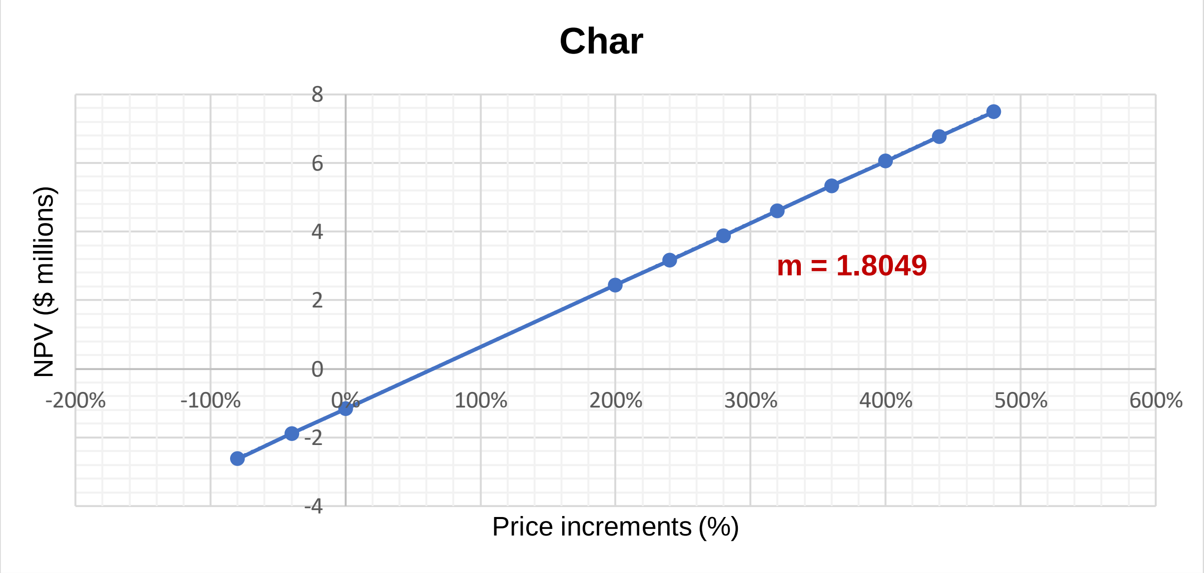

Figure 6. 8: % change in char price

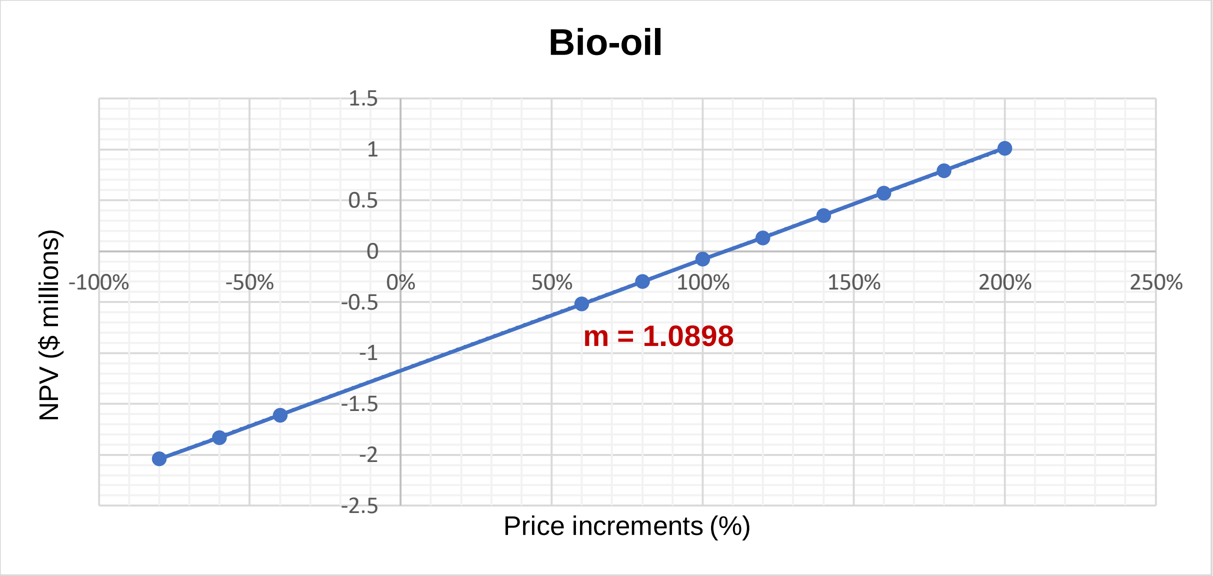

Figure 6. 9: % change in bio-oil price

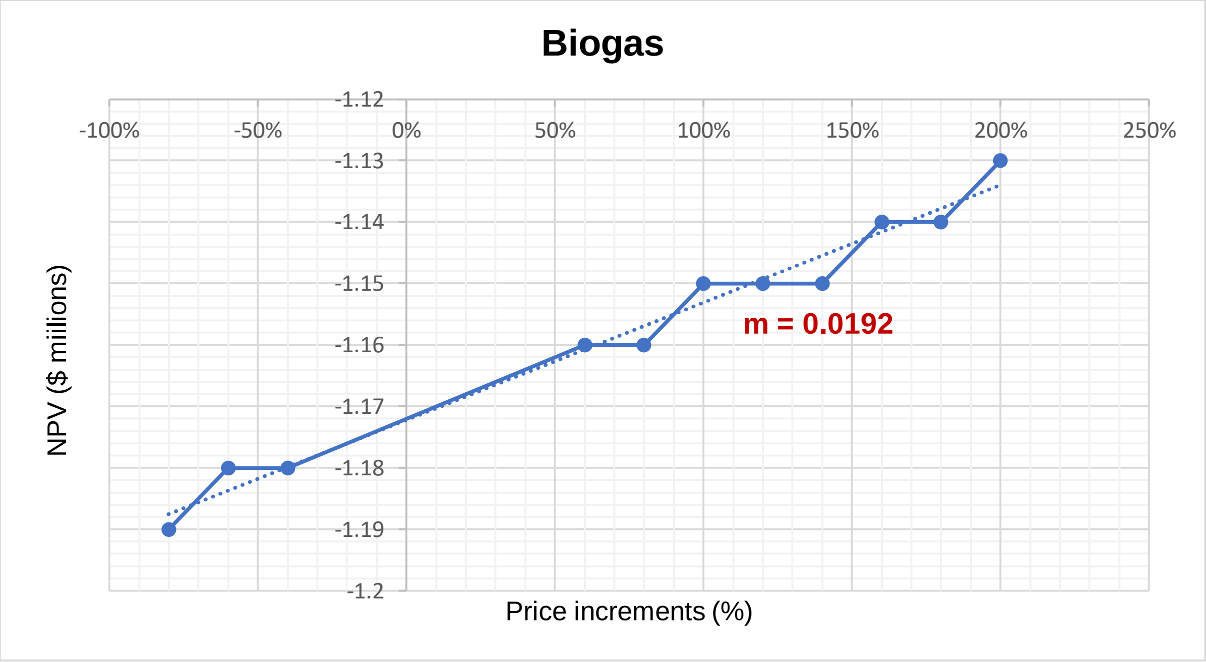

Figure 6. 10: % change in biogas price

6.6.4. Multi-parameter sensitivity

The section below provides a multiple parameter sensitivity analysis for the cost of feedstock, products and by-products. The multi-parameter sensitivity analysis (Figure 6.11) graphically illustrates the effect of each parameter on the plant's NPV.

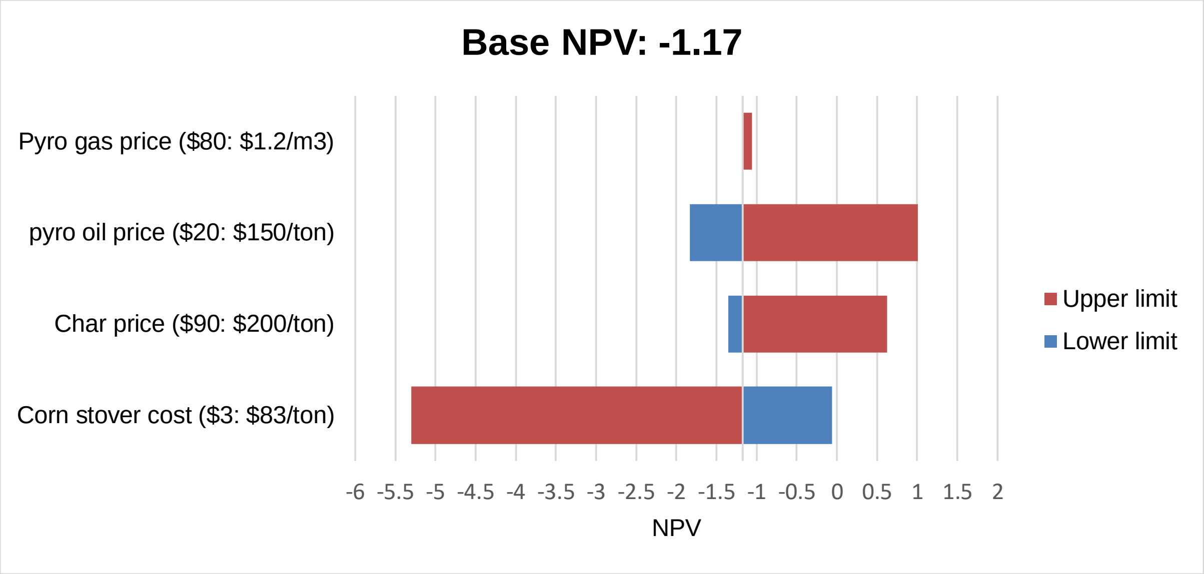

Figure 6. 11: Multi-parameter sensitivity analysis

The results from the profitability assessment of the pyrolysis plant indicate that under the base feedstock and product price assumptions, the plant is not economically viable, hence NPV of -$1.17 million (Figure 6.11). The cumulative effects of the costs were studied at the upper limit prices (Figure 6.12). Under these conditions, the cost of CS is kept at a minimum ($3/ton) while the prices of the products are raised to the maximum prices the markets would potentially allow.

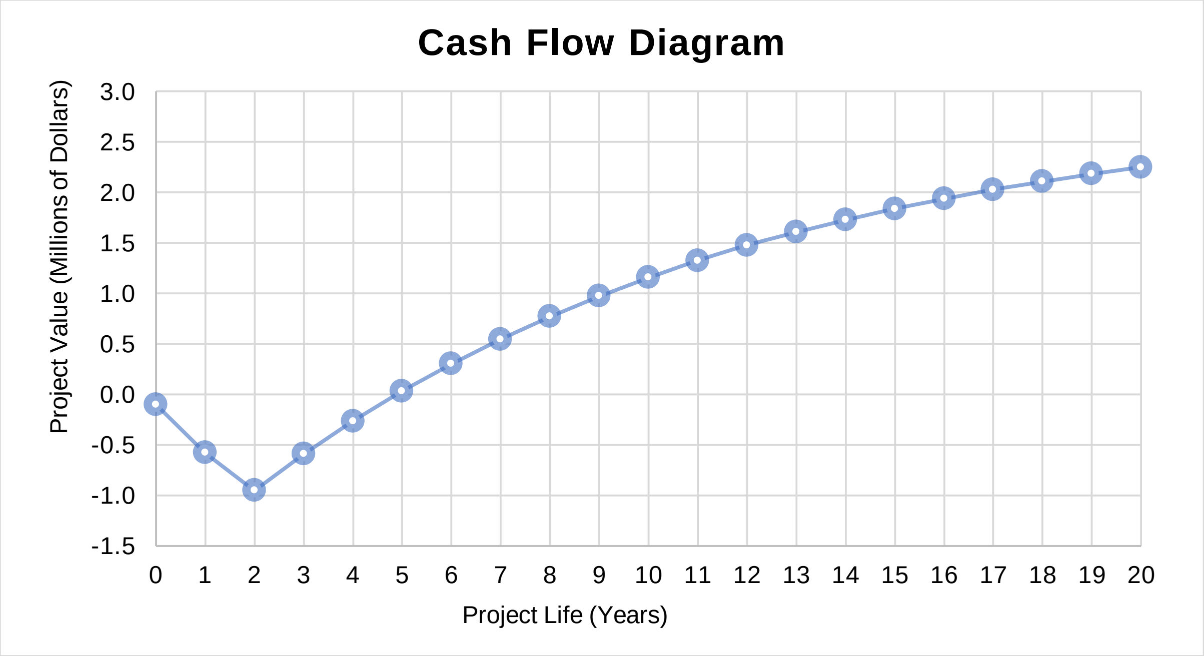

Figure 6. 12: Upper price limit conditions

The use of the upper limit prices (Figure 6.12) results in a positive cash-flow with NPV improved to $2.41 million. Under these conditions, the process would break-even after 5 years.

Provided these price estimates are accepted by the market, such returns could possibly draw investment. The study suggests the payback period of slow pyrolysis is longer than that of faster forms of pyrolysis. Comparatively, the study by Kolokolova, (2014) on the techno-economics of biomass pyrolysis into bio-bitumen had a break-even period of 3 years. While the NPV after 20 years of operation is $8.55 million.

6.7. Chapter summary

Corn-stover derived char is a commodity that can compete with traditional fossil fuels used in the South African energy sector. A pyrolysis plant that emphasises only on the production of char is not economically viable under base condition assumptions. Moreover, when the bio-oil and biogas by-products are accounted for, the price of char should be twice as much as that of traditional coals in order to make the process economically viable. It is unlikely the commercial markets would be receptive to such pricing. The NPV of the plant was highly dependent on the cost of CS and the price of char. At base price conditions, the valuation of by-products do not improve the profitability of the process significantly. An observation that is worthy of noting in this study is that a capital investment of $980 440, which is a far less capital investment than other forms of pyrolysis which could cost up to $200 million (Table 6.4) (Wright *et al*., 2010; Zhang *et al*., 2013 and Gura, 2017). The low cost is a consequence of the primary product not requiring further extensive processing before sale and use as energy fuel. As such this study balances the capital investment of the project with the estimated profitability of the process. For example, if char were sold at a coal competitive price of $100/ton, the process would as a result be not economically profitable, however if this fact is contrasted with the low capital investment requirement of $980 440, an interesting result which could possibly offset how such processes are viewed and discussed emerges. The positive consequences of such a process such as providing eco-friendly biofuel at a low process capital investment as well as the social aspects of employment creation make for a compelling argument for such a process despite of the apparent low financial losses.

7. Conclusion and Recommendations

7.1. Impact of study

The study showed technically the production of char and volatile by-products was feasible through the slow pyrolysis of corn-stover (CS). Economically, it was proved that when the price and cost of CS and products were maintained at market competitive prices, the process does not generate sufficient cash-flows to be attractive to yield positive returns. However, when the prices are raised to their assumed upper-limits, the process becomes economically attractive over its 20-year life cycle. Though at this level the price of char will be twice as much as its fossil fuel counterpart. At this price, taking into account market competitiveness, it is unlikely there would be an economic market for such a product.

From a social point of view, the process would create approximately 8 permanent jobs (excluding delivery drivers) and possibly many others in the construction phase of the plant. Environmentally, the process is in alignment with South Africa’s energy and waste framework (Department of Energy, 2015). The process can be viewed as a viable waste and energy management initiative, which not only assists with the disposal of CS but creates economic value synchronously.

7.2. Conclusion

This study focussed on the production of char that could be used as a supplement or replacement for coal in industrial processes. The char was produced through bench-scale laboratory slow-pyrolysis experiments. The process also produced liquid and gaseous by-products. Optimisation of the bench-scale experiments in Chapter 4 showed that chars produced under optimal conditions are comparable to sub-bituminous A coals. Chapter 5 built on the successes of optimising the process by developing a Gibbs model capable of predicting the volatile production during pyrolysis. From an economic feasibility point of view, the study showed that at market competitive pricing the process was economically infeasible. However, considering the estimated low costs of the process coupled with the positive environmental and social aspects of the process, a good case can be made for such a process. To ensure profitability, the cost-price of char would have to be twice that of traditional coals. Under such conditions, it is unlikely the markets would be welcoming to such a product.

7.3. Future work

The author recommends future studies on slow pyrolysis to consider the following:

- More research should be focused on the commodification of bio-oil and biogas produced through slow pyrolysis.
- Pilot-scale slow pyrolysis experiments using corn-stover as feed. Similarities and disparities should be drawn between pilot and bench-scale pyrolysis experiments.
- Research should go into the sustainability of recycling by-products for energy revitalisation in the process.
- Study the possibility of slow pyrolysis followed by by-product upgrading in order to add more economic value to the by-products.

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9. Appendices

Appendix A

Pictorial representation of experimental products as detailed in section 3.4

Figure A 1: Representation of char at 400°C

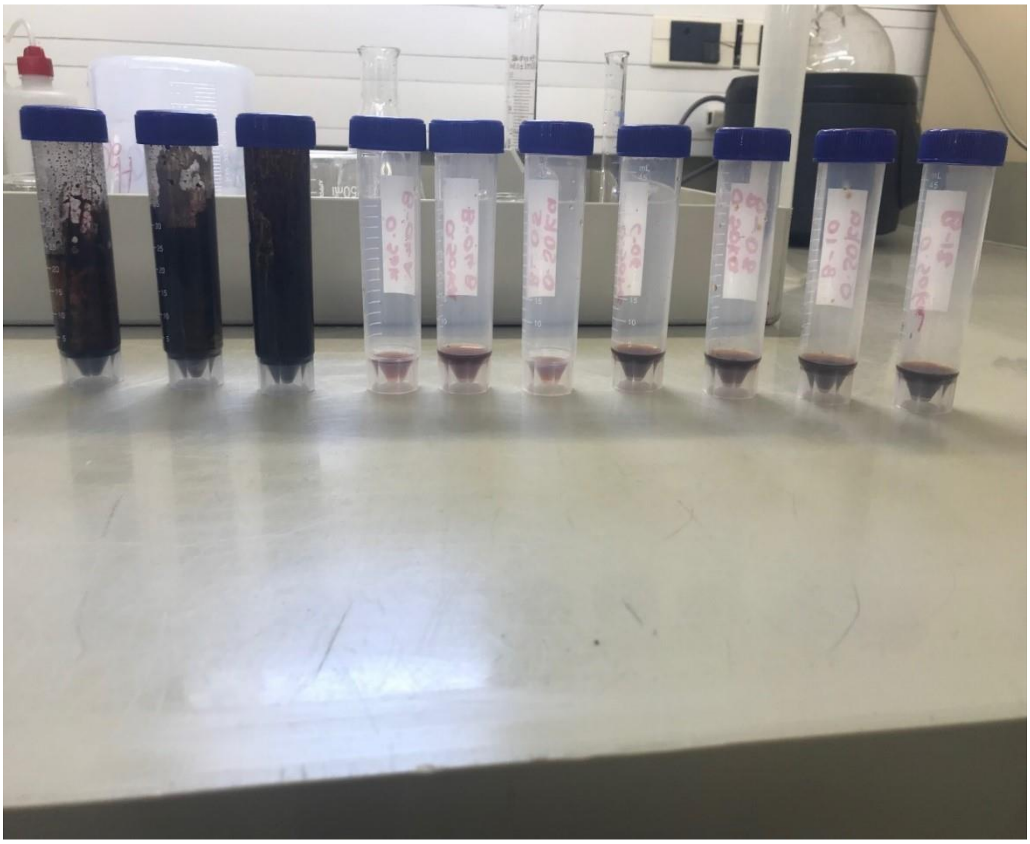
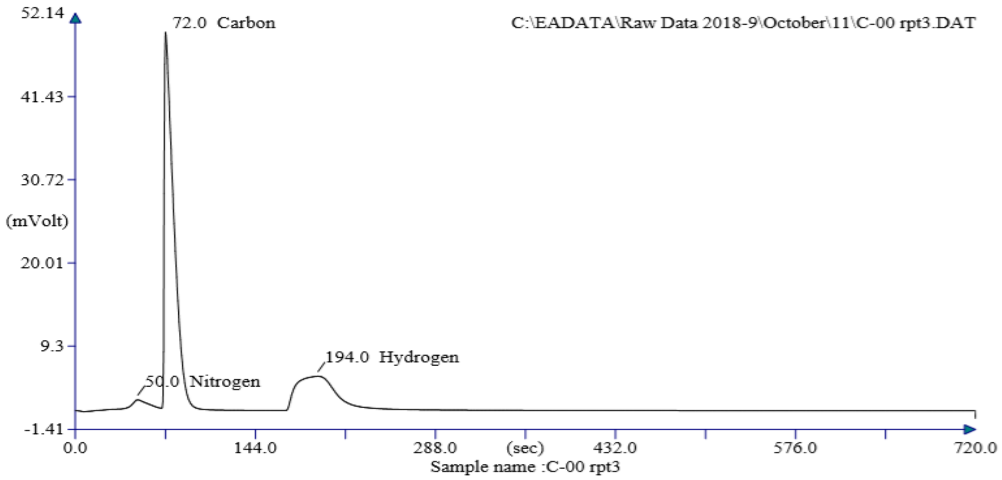


Figure A 2: Representation of bio-oils produced at various temperatures

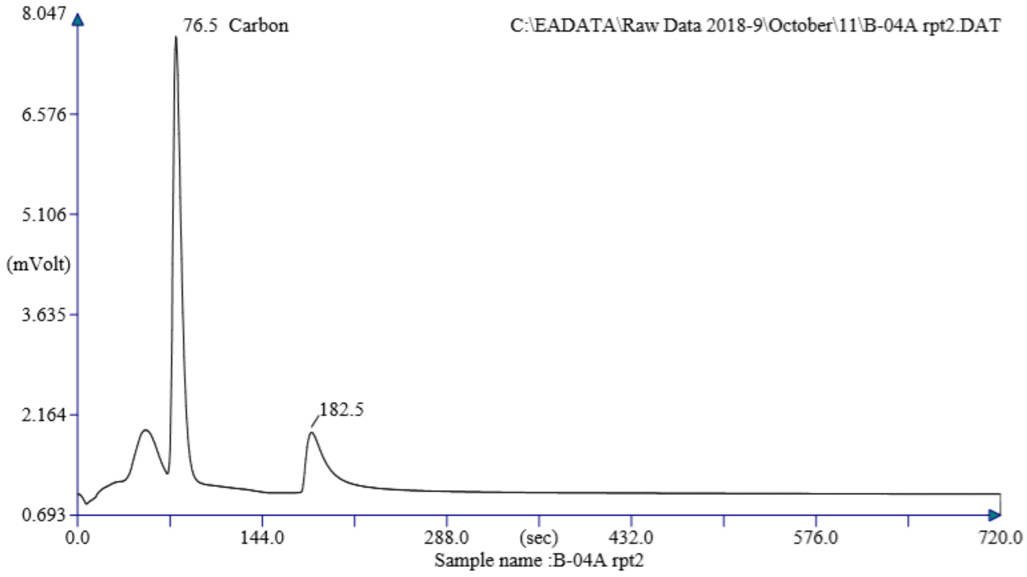
Appendix B

Analytical instrumentation proximate and elemental results detailed in section 3.1.2 and 3.1.3.



```
Retention Time   Element Name     Element %
(min)
---------------  ---------------  ---------------
0.833            Nitrogen         0.910
1.200            Carbon           41.209
3.233            Hydrogen         5.196
                                  ______
                                  47.315
```

Figure B 1: Sample of elemental analysis results for char



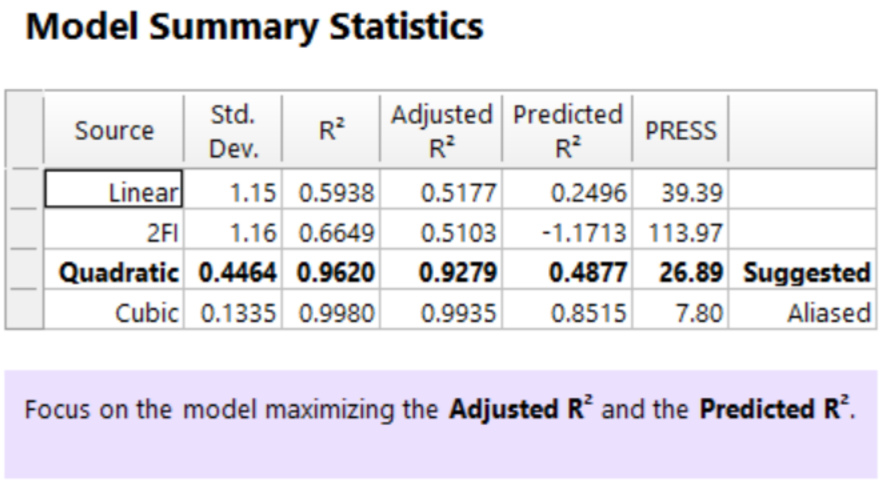
```
Retention Time   Element Name     Element %
(min)
---------------  ---------------  ---------------
1.275            Carbon           8.826
3.042            Hydrogen         2.694
                                  ______
                                  11.520


Warning Chromatogram has been subjected to manual inte
```

Figure B 2: Sample of elemental analysis results for bio-oil

Appendix C

Results from statistical and optimisation studies of section 4.6

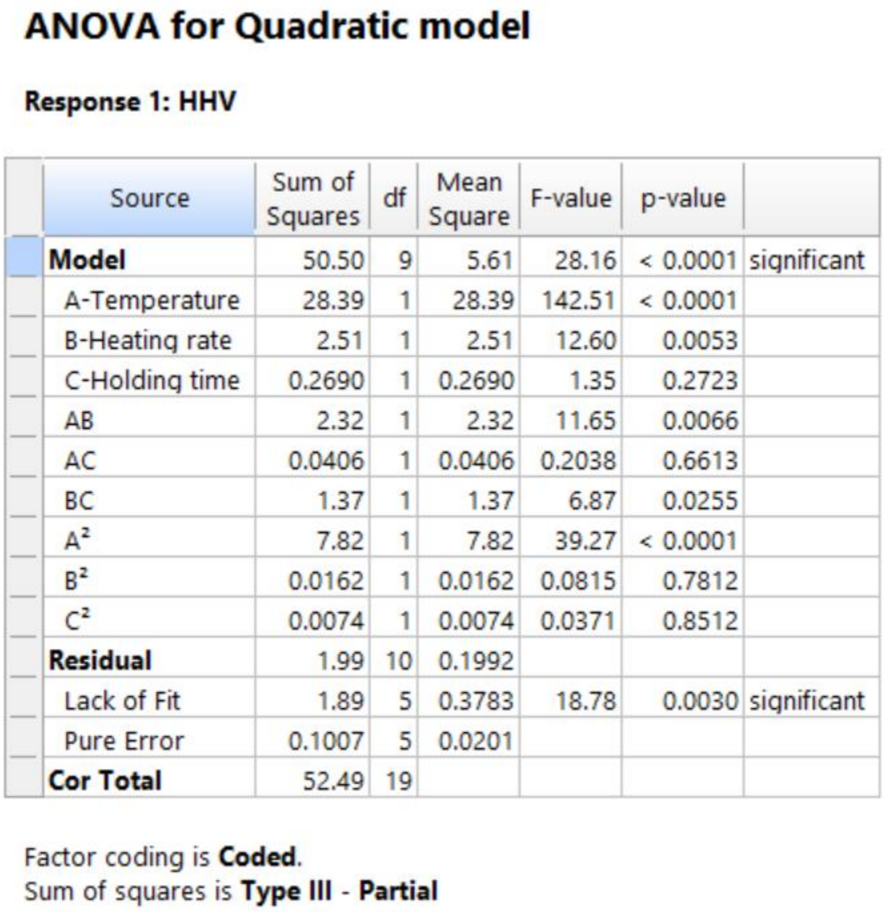


Model Summary Statistics

Source	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	PRESS	
Linear	1.15	0.5938	0.5177	0.2496	39.39	
2FI	1.16	0.6649	0.5103	-1.1713	113.97	
Quadratic	**0.4464**	**0.9620**	**0.9279**	**0.4877**	**26.89**	**Suggested**
Cubic	0.1335	0.9980	0.9935	0.8515	7.80	Aliased

Focus on the model maximizing the **Adjusted R^2** and the **Predicted R^2**.

Figure C 1: Summary of model results



ANOVA for Quadratic model

Response 1: HHV

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	50.50	9	5.61	28.16	< 0.0001	significant
A-Temperature	28.39	1	28.39	142.51	< 0.0001	
B-Heating rate	2.51	1	2.51	12.60	0.0053	
C-Holding time	0.2690	1	0.2690	1.35	0.2723	
AB	2.32	1	2.32	11.65	0.0066	
AC	0.0406	1	0.0406	0.2038	0.6613	
BC	1.37	1	1.37	6.87	0.0255	
A^2	7.82	1	7.82	39.27	< 0.0001	
B^2	0.0162	1	0.0162	0.0815	0.7812	
C^2	0.0074	1	0.0074	0.0371	0.8512	
Residual	1.99	10	0.1992			
Lack of Fit	1.89	5	0.3783	18.78	0.0030	significant
Pure Error	0.1007	5	0.0201			
Cor Total	52.49	19				

Factor coding is **Coded**.
Sum of squares is **Type III - Partial**

Figure C 2: Illustration of ANOVA results

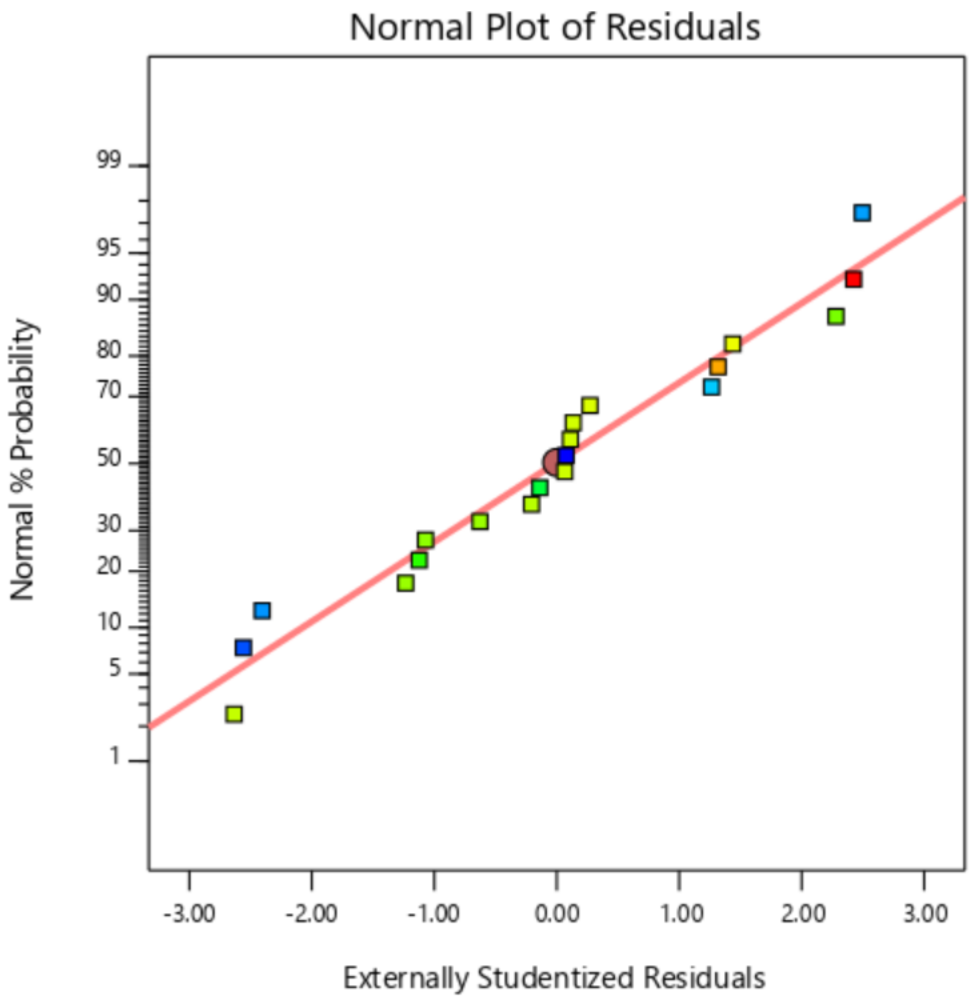


Figure C 3: Normal plot of residues for char yield

Table C 1: Sequential model sum of squares Type I

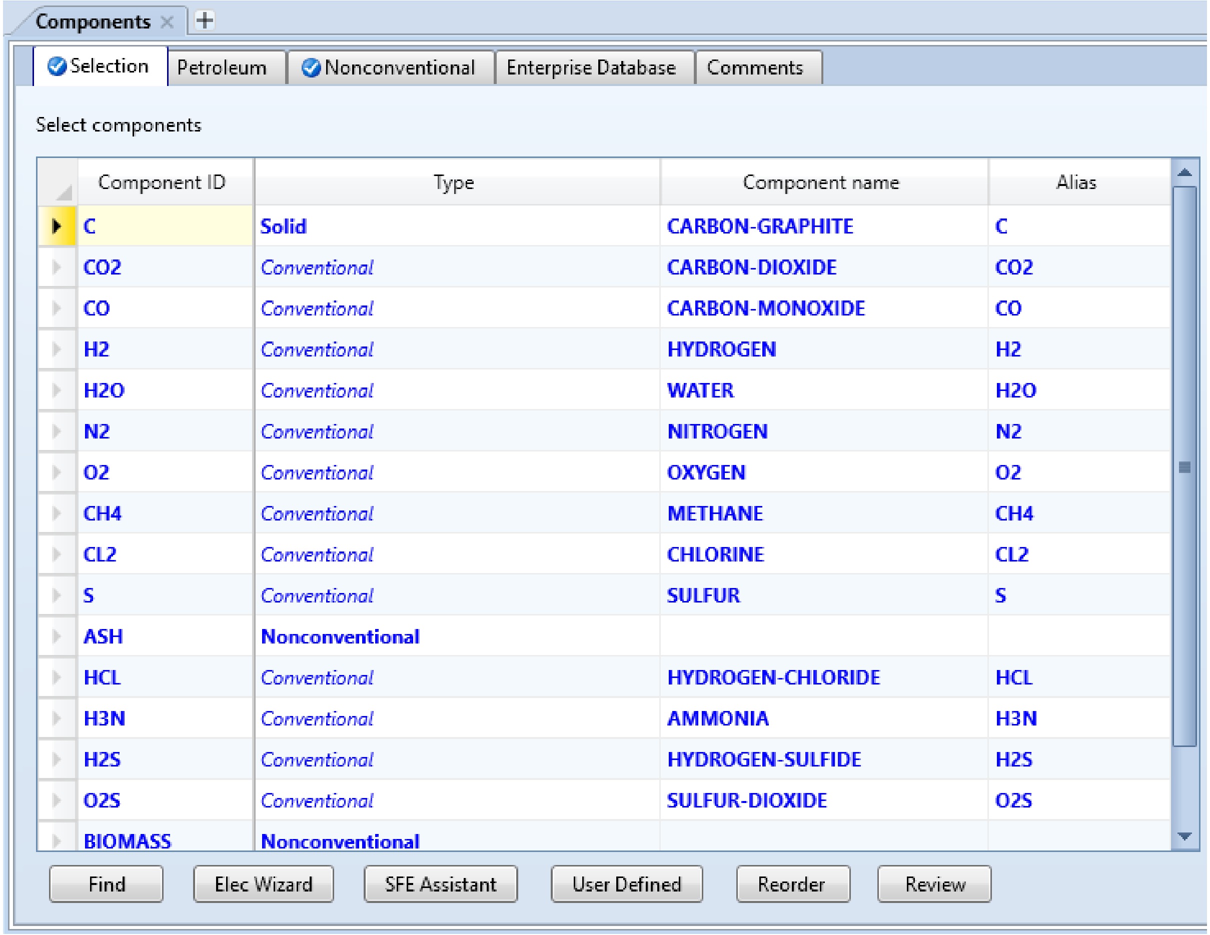
Source	Sum of Squares	df	Mean Square	F-value	p-value	
Mean vs Total	10907.3	1	10907.3			
Linear vs Mean	31.17	3	10.39	7.8	0.002	
2FI vs Linear	3.73	3	1.24	0.9195	0.4586	
Quadratic vs 2FI	**15.6**	**3**	**5.2**	**26.09**	**<0.0001**	**Suggested**
Cubic vs Quadratic	1.89	4	0.4713	26.44	0.0006	Aliased
Residual	0.107	6	0.0178			
Total	10959.7	20	547.99			

Table C 2: Lack of fit

Source	Sequential p-value	Lack of Fit p-value	Adjusted R^2	Predicted R^2	
Linear	0.002	< 0.0001	0.5177	0.2496	
2FI	0.4586	< 0.0001	0.5103	-1.1713	
Quadratic	**< 0.0001**	**0.003**	**0.9279**	**0.4877**	**Suggested**
Cubic	0.0006	0.6018	0.9935	0.8515	Aliased

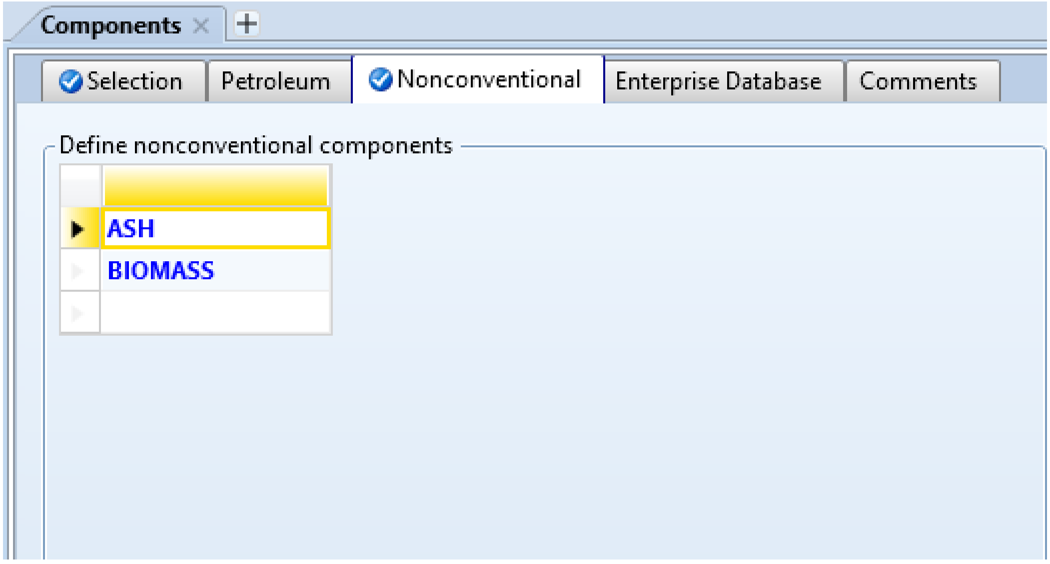
Appendix D

Development of Aspen Plus® model as detail in section 3.6



Component ID	Type	Component name	Alias
C	Solid	CARBON-GRAPHITE	C
CO2	Conventional	CARBON-DIOXIDE	CO2
CO	Conventional	CARBON-MONOXIDE	CO
H2	Conventional	HYDROGEN	H2
H2O	Conventional	WATER	H2O
N2	Conventional	NITROGEN	N2
O2	Conventional	OXYGEN	O2
CH4	Conventional	METHANE	CH4
CL2	Conventional	CHLORINE	CL2
S	Conventional	SULFUR	S
ASH	Nonconventional		
HCL	Conventional	HYDROGEN-CHLORIDE	HCL
H3N	Conventional	AMMONIA	H3N
H2S	Conventional	HYDROGEN-SULFIDE	H2S
O2S	Conventional	SULFUR-DIOXIDE	O2S
BIOMASS	Nonconventional		

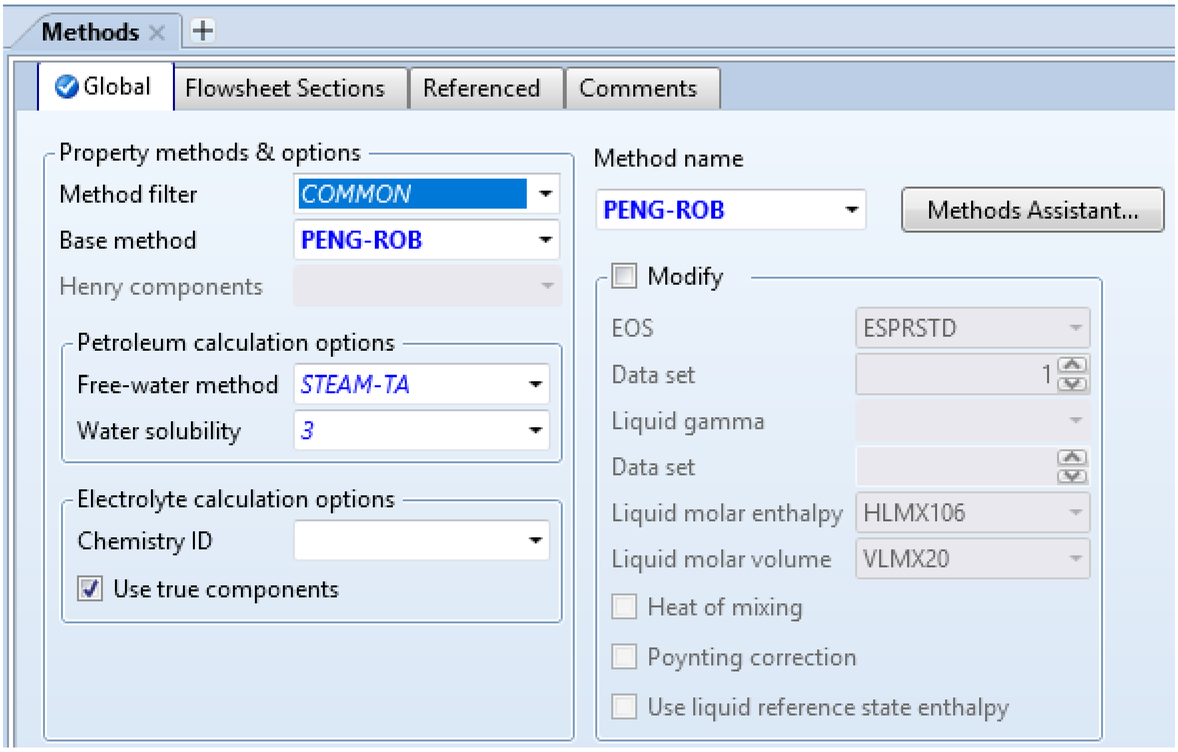
Figure D 1: Selection of conventional and non-conventional components



Define nonconventional components

ASH
BIOMASS

Figure D 2: Classification of biomass and ash as non-conventional components



Property methods & options

Method filter: COMMON
Base method: PENG-ROB
Henry components:

Petroleum calculation options

Free-water method: STEAM-TA
Water solubility: 3

Electrolyte calculation options

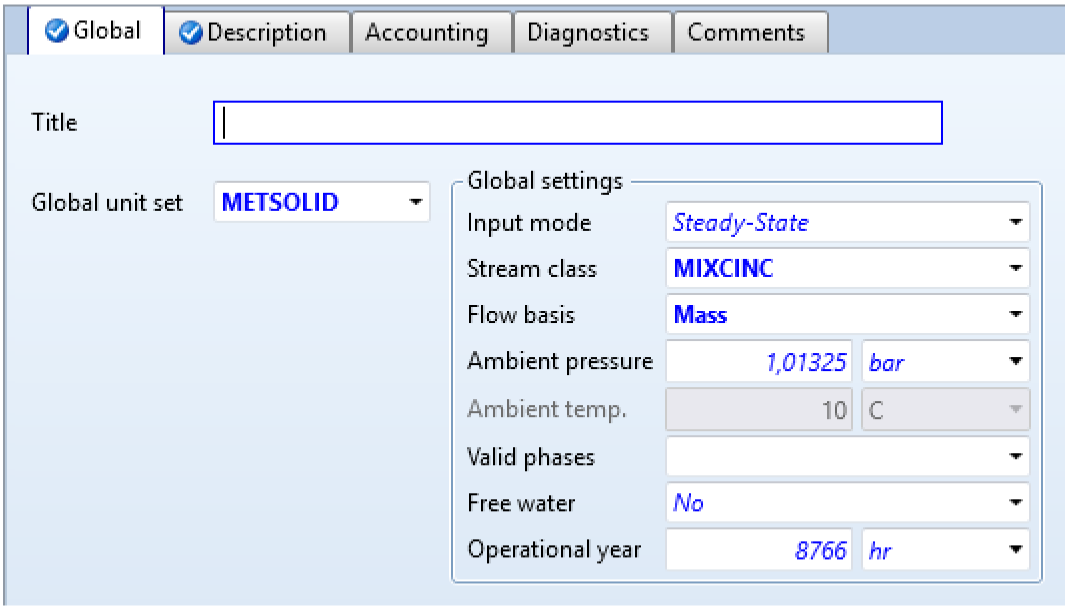
Chemistry ID:
☑ Use true components

Method name: PENG-ROB

☐ Modify

EOS: ESPRSTD
Data set: 1
Liquid gamma:
Data set:
Liquid molar enthalpy: HLMX106
Liquid molar volume: VLMX20
☐ Heat of mixing
☐ Poynting correction
☐ Use liquid reference state enthalpy

Figure D 3: Selection of model thermodynamic property



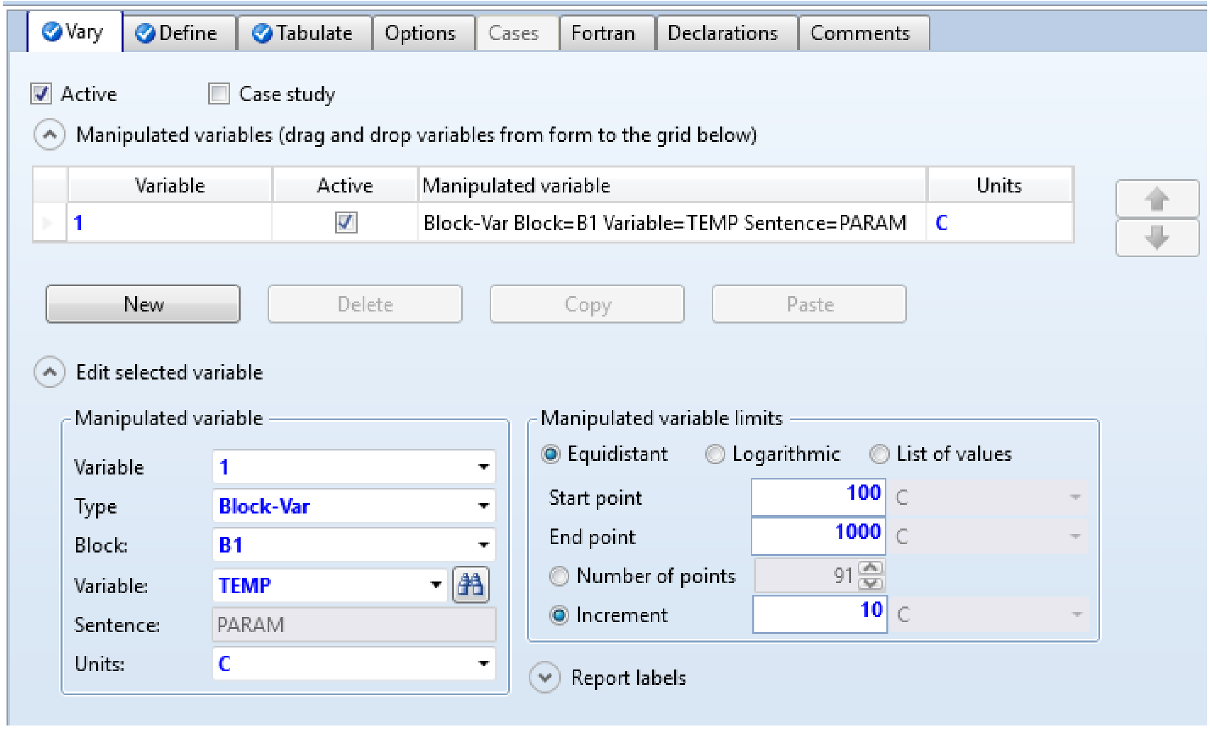
Title

Global unit set: METSOLID

Global settings

Input mode: Steady-State
Stream class: MIXCINC
Flow basis: Mass
Ambient pressure: 1,01325 bar
Ambient temp.: 10 C
Valid phases:
Free water: No
Operational year: 8766 hr

Figure D 4: Classification of stream class



☑ Active ☐ Case study

Manipulated variables (drag and drop variables from form to the grid below)

Variable	Active	Manipulated variable	Units
1	☑	Block-Var Block=B1 Variable=TEMP Sentence=PARAM	C

Edit selected variable

Manipulated variable

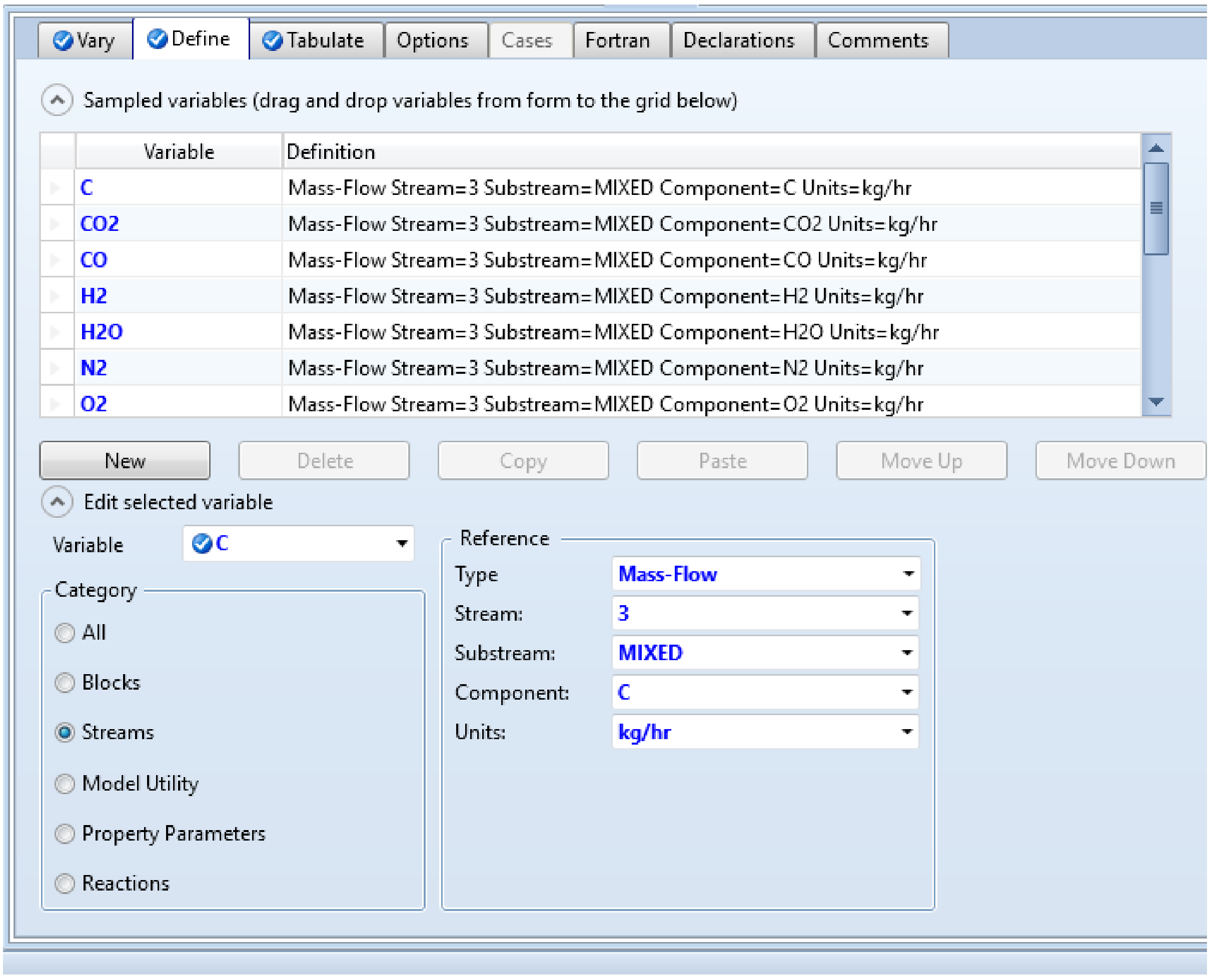
Variable: 1
Type: Block-Var
Block: B1
Variable: TEMP
Sentence: PARAM
Units: C

Manipulated variable limits

● Equidistant ○ Logarithmic ○ List of values

Start point: 100 C
End point: 1000 C
○ Number of points: 91
● Increment: 10 C

Figure D 5: Sensitivity input and variable selection



Sampled variables (drag and drop variables from form to the grid below)

Variable	Definition
C	Mass-Flow Stream=3 Substream=MIXED Component=C Units=kg/hr
CO2	Mass-Flow Stream=3 Substream=MIXED Component=CO2 Units=kg/hr
CO	Mass-Flow Stream=3 Substream=MIXED Component=CO Units=kg/hr
H2	Mass-Flow Stream=3 Substream=MIXED Component=H2 Units=kg/hr
H2O	Mass-Flow Stream=3 Substream=MIXED Component=H2O Units=kg/hr
N2	Mass-Flow Stream=3 Substream=MIXED Component=N2 Units=kg/hr
O2	Mass-Flow Stream=3 Substream=MIXED Component=O2 Units=kg/hr

Edit selected variable

Variable: C

Category
○ All
○ Blocks
● Streams
○ Model Utility
○ Property Parameters
○ Reactions

Reference
Type: Mass-Flow
Stream: 3
Substream: MIXED
Component: C
Units: kg/hr

Figure D 6: Variables for sensitivity analysis