A thesis submitted to the Department of Environmental Sciences and Policy of Central European University in part fulfilment of the Degree of Master of Science

An Overview of Biomass to Liquid (BTL) Fuels via Fisher Tropsch Synthesis: Pathways towards Developing a Smart BTL Facility

Waleed CHAUDHRY

July, 2017

Budapest

(3) For bibliographic and reference purposes this thesis should be referred to as:

Chaudhry, W. 2017. *An Overview of Biomass to Liquid (BTL) Fuels via Fisher Tropsch Synthesis: Pathways towards Developing a Smart BTL Facility*. Master of Science thesis, Central European University, Budapest.

Further information on the conditions under which disclosures and exploitation may take place is available from the Head of the Department of Environmental Sciences and Policy, Central European University.

Author's declaration

No portion of the work referred to in this thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning.

Waleed CHAUDHRY

CENTRAL EUROPEAN UNINVERSITY

ABSTRACT OF THESIS submitted by:

Waleed CHAUDHRY

for the degree of Master of Science and entitled: *An Overview of Biomass to Liquid (BTL) Fuels Via Fisher Tropsch Synthesis: Pathways Towards Developing a Smart BTL Facility*

Month and Year of submission: July, 2017

As a result of highly unpredictable oil prices in recent years, there has been an amplified demand for developing other liquid fuel alternatives. Biomass to liquid (BTL) conversion process produces fuels such as gasoline, jet fuel oil and diesel. This process not only harvest a variety of clean burning liquid fuels, but also produces a range of high quality chemicals. The process first converts biomass into syngas, a blend of hydrogen and carbon monoxide gases. The gas mix is then condensed over a catalyst to form liquid fuels with ultra-low sulphur content through the Fischer-Tropsch (FT) process.

One major concern of the process, however, is large amounts of carbon emissions and waste generated during the conversion process. The research overlooks at the BTL conversion process, highlights the potential environmental impacts and identifies ways to develop a smart BTL facility which effectively utilizes all major waste/by-product in order to minimize potential environmental hazard(s). The research also sheds light on the issues related to commercialization of the BTL technology for mass production.

Keywords: biomass, fisher tropsch, synthetic liquid fuels, syn gas, gasifier, environmental friendly, agriculture waste, biochar, emissions, waste water

---

Acknowledgements

I would like to extend my gratitude to my advisor Prof. Zoltan Illes for his continuous support, motivation and guidance throughout the academic year, and especially during the thesis writing period.

I would like to thank CEU and the department of Environmental Sciences and Policy for providing me with the knowledge, platform and resources to undertake this research study.

To Mr. Shahid Ansari, Dr. Dr Xinying Liu, MaPS team and all my interviewees who were always happy to share their knowledge and kept me motivated throughout the process, thank you.

To my parents for their unconditional love, support and encouragement. I love you. Lastly, my gratitude to Anam Ameen, Areeb Arshad and Jackie Moore, who inspired me in life.

Table of Contents

List of Tables

List of Figures

List of Abbreviations

BTL	Biomass to Liquids
FT	Fischer Tropsch
EIA	U.S. Energy Information Authority
UNISA	University of South Africa
MaPS	Material and Process Synthesis
GHG	Greenhouse Gas
OLGA	Oil - Gas
ECN	Energy research Center of the Netherlands
MEA	Monoethanolamine
WGS	Water Gas Shift
HTFT	High Temperature Fischer Tropsch
LTFT	Low Temperature Fischer Tropsch
CFB	Circulating fluidized bed
SFB	Stationary fluidized bed
CTL	Coal to Liquids
GTL	Gas to Liquids
CCS	Carbon Capture and Sequestration
C_4	Hydrocarbon compound containing 4 carbon atoms
COD	Chemical Oxygen Demand
NOx	Oxides of Nitrogen
BTE	Biomass to Energy
UV	Ultra Violet
CW	Constructed Wetland
TSS	Total Suspended Solids
FWS	Free Water Surface
HSSF	Horizontal Subsurface Flow

Chapter 1 Introduction

1.1 Background

Today we are highly dependent on fossil fuels to meet our energy demands. The use of fossil fuel based products, such as plastics and industrial chemicals, is also increasing every day and has led to the question about how many more years we can depend on the non-renewable reserves which will eventually deplete. Moreover, burning fossil fuels releases trapped carbon into the atmosphere which is responsible for causing global warming. (Kumar et al. 2009)

The EIA (Energy Information Administration) has estimated an increase of 43% in the annual CO2 emissions, from 29.7 billion tons in 2007 to 42.4 billion tons in 2035. This staggering increase of emissions has the potential of severely effecting our lives mainly due to the changes it will bring in climate (Maitlis and Klerk 2013). Thus, requiring a rapid transition from conventional non-renewable resources towards other alternatives which are low carbon, renewable and environment friendly (Demirbas 2007).

Biofuels are regarded as liquid or gaseous fuels which are derived from biomass such as forest residues, fruit and vegetable peels, bagasse, rice husk, rice straw, maize stalk and even cattle dung. As a consequence of the current energy crises, and increasing greenhouse gas emissions, biofuels have gained growing attention from researchers, scientists and policy makers (Gomiero 2015; Sharma 2013). Biofuels are classified as first, second and third generation (Lee and Ofori-Boateng 2013). First generation biofuels or conventional biofuels are produced directly from food crops such as sugarcane, grains and vegetable oils (Buckeridge and Souza 2017). These are produced using well developed technologies such as fermentation, distillation and transesterification (Naik et al. 2010). Second generation biofuels are produced by non-food feed stocks such as woody crops, forestry and agricultural wastes etc. and have several advantages over first generation fuels (Mabee et al. 2008; STI and URC 2012). Second generation biofuels do not have a conflict with food security, as in the case for first generation biofuel production (Thompson 2012). They are also associated with producing higher energy yield per area as compared to first generation fuels and can be produced from a much wider range of crops (FAO 2008). Additionally, low quality land could also be used to grow the crops (Sims et al. 2010). Second generation biofuels are produced by biochemical and thermochemical conversion processes. Biochemical processes include biocatalysts, such as enzymes, in presence of heat to convert biomass into an intermediate sugar stream which is then converted into biofuel through fermentation. Thermochemical processes use heat with or without a physical catalyst for conversion to gas or liquid phase, and finally to biofuel (Foust et al. 2009). Thermochemical processes include biomass conditioning, gasification, gas purification, and then Fischer Tropsch synthesis to produce fuels (Sen 2014).

Third generation biofuels are produced using highly specialised crops like algae which is harvested to extract oil that may be further processed into biodiesel (Alam et al. 2015). These fuels have higher energy density than the first and second generation biofuels and are considered more sustainable as they reduce stress on land and water usage. They can be grown using sewage or even salt water. Algae are nontoxic, biodegradable and can reproduce at a fast rate. However, additional research and development is required in order to make it economical and technologically viable. (Hughes et al. 2013; Ullah et al. 2014).

1.2 Aims & Objectives

The primary aim of this thesis is to investigate how an environment friendly and smart BTL (through FT Synthesis process) commercial scale facility can be developed. The aim is achieved by understanding the BTL process, identifying and thus managing the most important waste streams/by-products that could potentially raise environmental concerns if not dealt with properly.

The secondary aim of this research is to highlight the problems facing the BTL industry in its commercial implementation to produce fuels and chemicals as an alternative to conventional fossil fuel derived products.

The objectives of the thesis are the following:

- To have an in-depth understanding of the major components of BTL through Fischer Tropsch Synthesis process
- To become acquainted with the Fischer Tropsch reactions, as a part of BTL conversion process, for producing different variety of products.
- To analyze the effect of changing various operating parameters and conditions such as pressure, temperature, catalyst used, in the BTL conversion process.
- To identify major waste stream(s) and/or by-product(s) of the BTL process.
- To investigate methods that could effectively utilize all major waste/by-products identified and can be incorporated in a BTL facility to support a sustainable operation.
- To identify the most important hindrances within commercial implementation of BTL.

1.3 Research Questions

Apart from the aims and objectives mentioned above, two distinct research questions were formulated for the in-depth focus and narrowing down of scope of this research study. The research questions are:

- What are the advantages and the disadvantages of the BTL through FT Synthesis technology?
- What approaches can be adopted to develop an environment friendly BTL plant to produce second generation biofuels?
- What factors influence the development of BTL industry?

1.4 General Information about UNISA & MaPS

The research study for the thesis was undertaken in the University of South Africa (UNISA) with The Material and Process Synthesis (MaPS) research group. Details of tasks performed at UNISA are covered in the methodology chapter.

University of South Africa (UNISA), founded in 1873, is the largest university in the continent of Africa. The university has produced over 400,000 students from Africa and other parts of the world and is considered the most productive South African university; responsible for granting 12.8% of all degrees in the country. The university offers an extensive range of academic programs including short courses, certificates to 3 & 4 year degrees, and doctorates. UNISA is a multi-campus university with main campuses in Pretoria and Johannesburg, while several regional centres across South Africa (Wiki 2017; UNISA 2017).

MaPS or The Material and Process Synthesis research group based at the science campus of UNISA in Johannesburg focuses on innovative methods aimed at making various chemical processes more sustainable by reducing waste, energy consumption and GHG emissions (UNISA 2017). The MaPS team has over 15 years of experience in the field of process synthesis and Fischer Tropsch technologies (Coal/gas/biomass to liquid). The Fischer-Tropsch Synthesis group within MaPS is head by Dr Xinying Liu. MaPS have been effective in establishing connections with several major industries inside and outside South Africa and have been successful in providing their services for industrial research projects. The industries include Sasol, Anglo Coal, Golden Nest International, Anglo Platinum and Linc Energy (UNISA 2017).

Some of the industrial projects MaPS undertook are the following:

- MaPS was involved in building a Coal to Liquid via FT synthesis demonstration plant for LINC Energy in Australia. The plant constructed in 2008 is still under operation and serves as a pilot scale plant for a full scale facility that is being developed (UNISA 2017).
- In 2004 MaPS signed a contract with a Chinese company for designing and supervising the commissioning of a Coal to Liquid plant in China. The project was successful and the plant operated for a year and a half (UNISA 2017).

1.5 Methods

Research methods for this study included three parts: literature review and pilot plant study, in depth semi structured interviews and simulation plant design of the BTL facility.

- Document analysis and pilot plant study provided a base for the research to be conducted by developing a firm understanding of the major technical aspects of the Biomass to liquid conversion process.
- Semi structured interviews were conducted with experts (researchers and industry related) to gather relevant data.
- The plant design simulation study was aimed to supplement the data acquired by document analysis and semi structured interviews. It was also aimed at providing a better understanding of the BTL process with respect to the operating conditions of the components.

Details of how the research methods were conducted are presented in the Methodology Chapter of this thesis.

1.6 Thesis Outline

- Chapter 1 of the thesis presented the background, aim & objectives and research questions associated with the study. The background provides a brief overview of our current dependence on fossil fuels and the related GHG emissions. It discussed the trend in development of biomass derived fuels as an alternative to conventional fossil fuels.

The chapter also highlights the methods used to collect data along with brief introduction of the institute where the research works were conducted.

- Chapter 2 covers the literature review where it explains the entire Biomass to Liquid Fuels conversion process through Fischer Tropsch synthesis. The aim is to explain all major stages involved in the BTL conversion process as separate sections and with the help of a process flow diagram.

- Chapter 3 discusses in detail the methods used to conduct the research and gather relevant data.

- Chapter 4 presents simulation design of a basic small scale BTL plant modelled using Aspen Plus modelling and simulation software. The chapter provides quantitative data in form of simulation results.

- Chapter 5 provides an analysis of the interview discussions and their results.

- Chapter 6 provides suggestions on how BTL plants can better utilize waste and by-products in an eco-friendly manner.

- Chapter 7 concludes the thesis, provides recommendations and suggestions, based on the findings.

Chapter 2 Literature Review

2.1 Biomass to Liquid Fuels Conversion

An integral part of producing second generation biofuels through Biomass to Liquid (BTL) technology requires the thermal disintegration of the biomass feed into synthesis gas (Ehrig and Dallos 2009). Synthesis gas or syngas can be defined as a gas mixture containing Hydrogen and Carbon monoxide as the major combustible constituents. Raw syngas however, may also contain significant quantities of carbon dioxide and water (Van der Drift and Boerrigter 2006).

This biomass derived syngas is then converted into liquid hydrocarbons, in presence of a catalyst, through the Fischer Tropsch (FT) reaction. The flow diagram of Biomass to liquid fuels conversion through FT reaction is shown in figure 1:

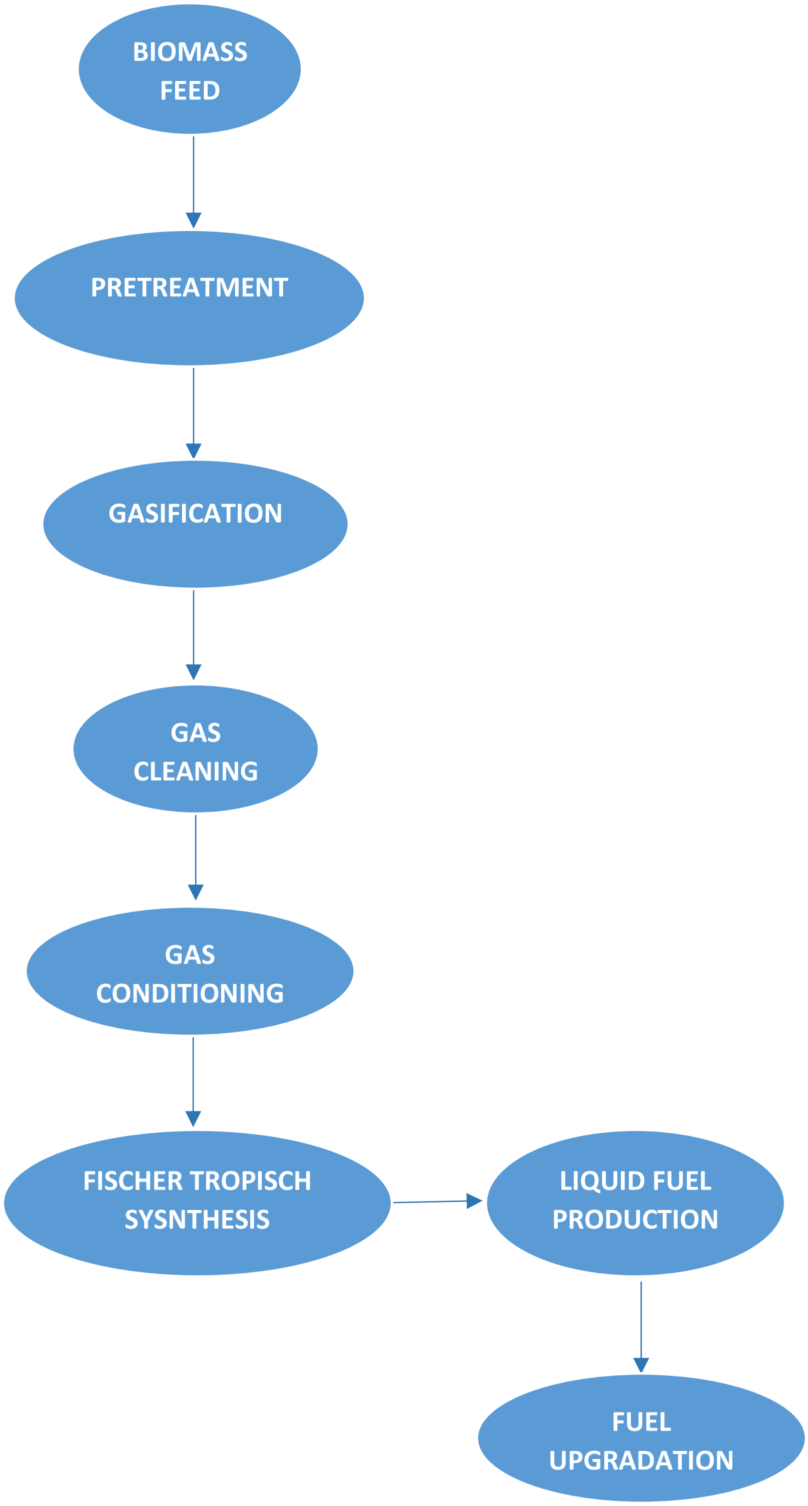


Figure 1. BTL through Fischer Tropsch synthesis process flow diagram
Information Source: (Ehrig and Dallos 2009)

2.2 Pre-treatment

The first step in the BTL process usually consists of washing then reducing the size of the biomass feed by shredding or crushing the biomass material. The size of the feed depends on the type of Gasifier used in the following step (Lee and Ofori-Boateng 2013). The washed biomass is then dried, which is an essential part of the pre-treatment as it reduces the moisture content of the biomass and helps optimize the gasification process (Varbanov et al. 2013).

2.3 Gasification

Gasification is a completely different process compared to combustion and pyrolysis. Combustion results in a complete oxidation of the fuel and occurs in an excess of air. This generates heat, exhaust gases and residue ash (Ehrig and Dallos 2009). While Pyrolysis is decomposition of carbon based matter in absence of oxygen at high temperatures (Paethanom and Yoshikawa 2012). However, in the gasification process, the carbon rich matter is partially oxidized, in presence of a limited oxygen supply (Goyal et al. 2008). This converts the carbonaceous matter into a combustible gas mixture of carbon monoxide (CO), carbon dioxide (CO_2), hydrogen (H_2), and methane (CH_4) at temperatures of 700 °C and above (Karlen 2014).

Gasification also results into hydrocarbons formation in minute quantities, along with tar and ash. The gasification process can be classified in several ways. Amongst the most important ones are the type of gasification agent and the method of heat supply (Couto et al. 2013). Common gasification agents include steam, oxygen-steam and air (Inayat et al. 2010).

Classification based on method of heat supply include two types of processes, Autothermal Process and Alothermal Process. Autothermal process is where the heat is provided by partial combustion of process material in the gasification stage, while in the alothermal process the heat provided comes from external source such as heat exchangers or a heat transferring medium. In Alothermal process, the heat may be generated by the combustion of the processed material (Ehrig and Dallos 2009).

2.4 Gasifier Types

Based on the method of contact of fuel with the gasification agent, gasifiers can be characterised in three major types. These include fixed bed gasifiers, Fluidized bed gasifiers and Entrained flow gasifiers (Ehrig and Dallos 2009). Common types of gasifiers used are described below:

Stationery Fluidized Bed Gasifier:

Stationary fluidized bed (SFB) also known as Bubbling fluidized bed (BFB) gasifiers are characterized by a relatively slow flowrate of the gasifying agent and thus promote a low concentration of particles entrained in the gas which leaves the reactor. Inside the Stationary Fluidized gasifiers, the bed material acts such as a turbulent fluid causing rapid mixing of the fuel with bed material. This leads to pyrolysis inside the reactor. The bed material forms an observable bed with a bubbling and turbulent surface. An example of the bed material in such a type of gasifier is quartz sand. The fluid bed gasifiers are typically used for processing materials with high ash-content such as biomass. Such gasifiers are mostly used for large scale operations of usually > 10 MWth (Bodhanwalla and Ramachandran 2017; Ehrig and Dallos 2009; Williams and Kaffka 2015). Design of a stationary fluidized bed gasifier is shown in Figure 2.

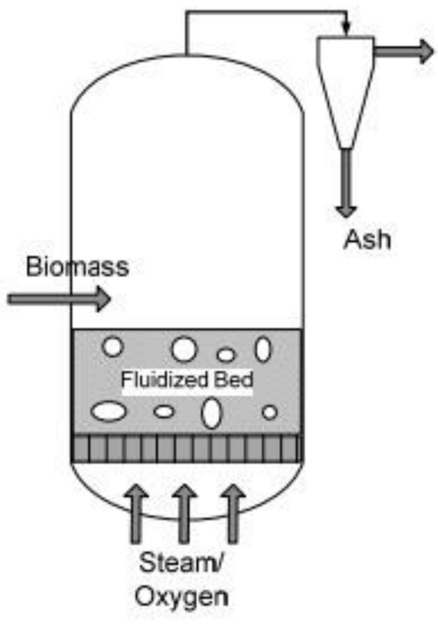


Figure 2. Schematic of a SFB gasifier
Source: (Swanson et al. 2010)

Circulating Fluidized Bed Gasifier:

As shown in Figure 3, the construction of the circulating fluid bed (CFB) gasifiers is quite similar to that of stationary fluid bed gasifiers, however, the gasification agent in CFB gasifier is sent to the reactor with a higher velocity and offers a higher rate of conversion. The bed material gets dispersed in the entire reactor with high concentration at the lower section. The bed material and the fluidized gas are carried into a cyclone where the particles are separated from the gas and sent back to the reactor. In such a gasifier, there is no observable bed surface (Ehrig and Dallos 2009; Williams and Kaffka 2015).

A CFB gasifier provides excellent mixing because of operating at higher velocities. They have several advantages over a BFB gasifier which includes processing a wider range of feed, reduced tar production and ease of scaling up. These benefits make CFB gasifier suitable for biomass gasification (Basu 2006).

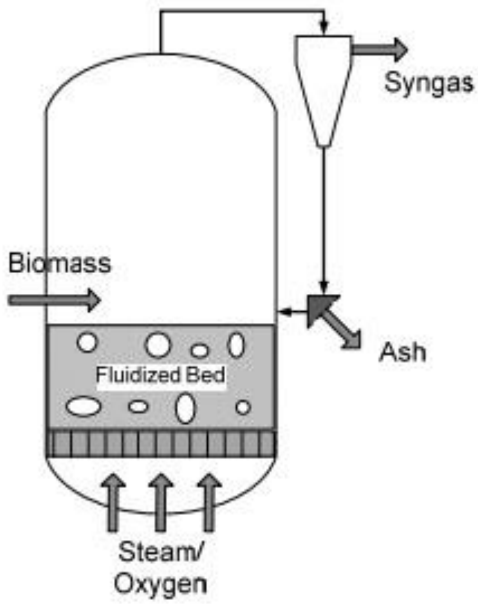


Figure 3. Schematic of a CFB gasifier
Source: (Swanson et al. 2010)

Entrained Flow Gasifier:

The constriction and working of the entrained flow gasifiers is quite different from the ones already described. In the entrained flow gasifiers, processed material is sent at the top of the gasifiers, along with the gasification agent. Unlike other gasifiers, there is an added pilot flame to meet the initial energy required (Ehrig and Dallos 2009).

The entrained flow gasifier is generally used for gasification of crude oil and coal, but integrating with an upstream pyrolysis stage, it can also be used for processing biomass material (Ehrig and Dallos 2009).

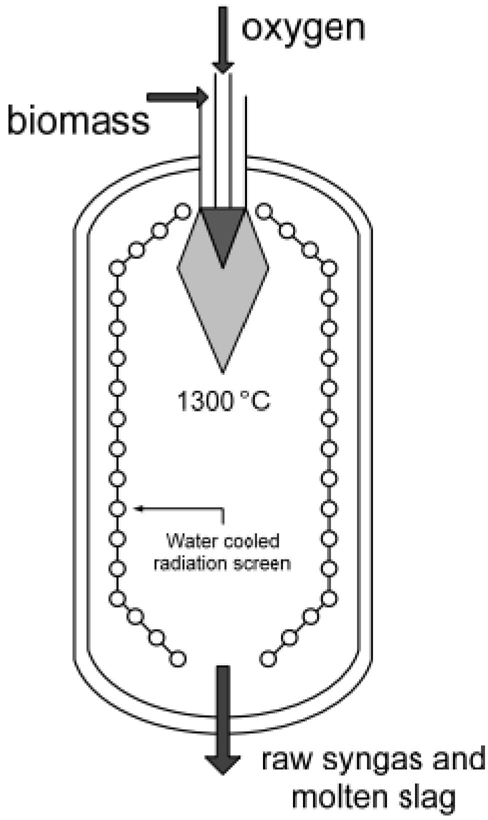


Figure 4. Schematic of an entrained flow gasifier
Source: (Swanson et al. 2010)

Fixed bed Updraft Gasifier:

Updraft gasifiers is the oldest and simplest type of gasifiers (FAO 1986). As illustrated in Figure 5, fuel enters the upper section of the gasifier and then flows down through the drying section followed by pyrolysis and finally the gasification sections. The ash that remains as a residue is then taken out from the reactor bottom. Steam along with air is given to the bottom section of the reactor from the grate. The resultant gas (product gas) is sent to a burner for combustion, through a pipe (Kurkela et al. 1989). Updraft gasifiers is easy to operate and is mainly used for efficient biomass gasification, but has a problem of generating high amounts of tar (FAO 1986).

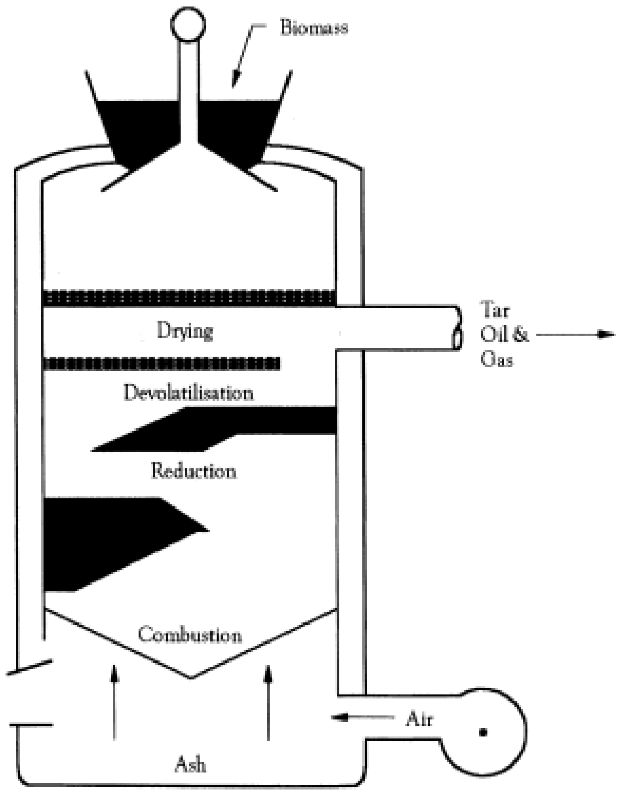


Figure 5. Schematic of a fixed bed updraft gasifier
Source: (McKendry 2002)

Fixed Bed Downdraft Gasifier:

The design of the downdraft gasifiers is very similar to that of the updraft gasifiers. It is designed to it help avoid the tar accumulation problem associated with the updraft gasifiers. The gasification agent in downdraft gasifier is either sent to the gasifier above or on the oxidation zone. The resultant gas then flows to the bottom of the gasifier, parallel to the direction of fuel, and is removed (FAO 1986). Figure 2 below shows the construction of a downdraft gasifier.

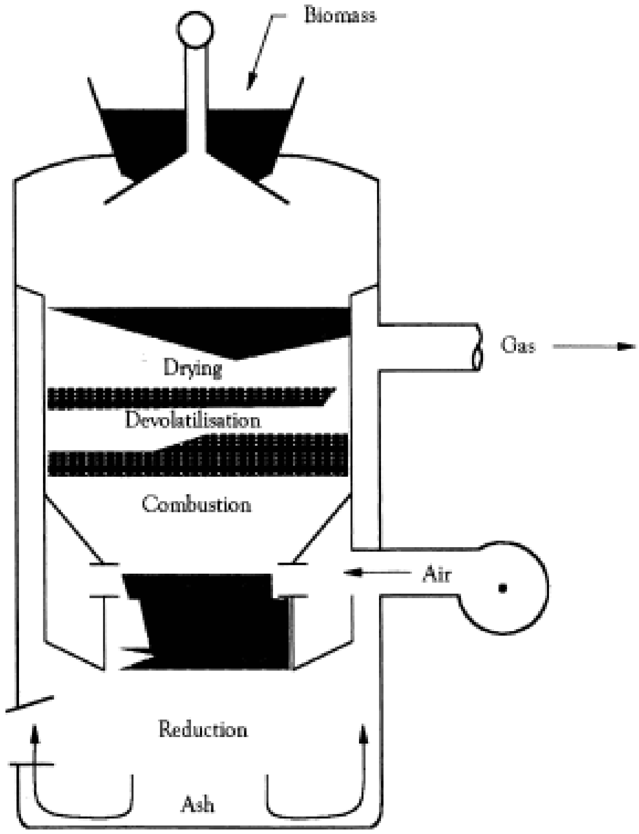


Figure 6. Schematic of a fixed bed downdraft gasifier
Source: (McKendry 2002)

2.5 Gas Cleaning and Conditioning

The product gas from the gasification stage has to be cleaned before it can be sent to the FT reactor for catalytic conversion into fuel (Boerrigter and Rauch 2006).

Gas Cleaning:

Gas cleaning is an important step after any gasification process as the product gas typically contains particulate matter, organic compounds and trace elements such as hydrogen sulphide (H_2S), ammonia (NH_3) and hydrogen cyanide (HCN). These contaminants cause erosion in process lines and deactivate the catalyst due to catalyst impairment (Zeisler et al. 2010).

Particulate matter may find its way in the gas from the biomass ash, as dust or unconverted carbon. There are various methods to eliminate particulate matter from the syn gas. Such methods include use of cyclones, electrostatic filters or scrubbers (Hofbauer et al. 2007).

Gasification processes operated under 1000°C results into organic compounds being present in the product gas. This includes, methane, aliphatic compounds such as ethylene, aromatics such as benzene and tars. In case of gasification at higher temperatures, the organic material is almost completely converted into H_2, CO and CO_2 (Hofbauer et al. 2007).

Tar removal is an essential part of the gas cleaning process. The OLGA process, developed by ECN is effective in removal of tar and other aromatic organic compounds. The gas is passed through a scrubber where the tars are washed, and the washing liquid is then regenerated in a stripper. The OLGA process is effective in bringing the aromatics to very low levels (Boerrigter et al. 2004; Hofbauer et al. 2007).

Levels of H_2S in the product gas originating from the gasification of biomass is significantly lower when compared to that of coal gasification, but still needs removal as it can deactivate the catalyst even when present in minute quantities. This can be achieved by either wet or dry processes. The wet processes are based on absorption principle in which the H_2S is absorbed by a solvent such as Monoethanolamine (MEA) and potassium carbonate. While dry processes are based on the adsorption principle which use solid adsorbers such as Zinc Oxide or Activated Carbon (Hofbauer et al. 2007).

Gas Conditioning:

Gas conditioning involves the gas treatment processes taken in order to ensure the desirable syngas composition so it adheres to the requirements to undergo FT synthesis. This includes regulating the H_2/CO ratio and the removal of undesired CO_2. Carbon monoxide produced from the biomass feedstock is usually higher than required for the FT synthesis, hence maintaining an appropriate and higher H_2/CO ratio becomes essential (Hofbauer et al. 2007).

The water gas shift (WGS) reaction favours Hydrogen gas production and decreases the amount of CO in the syngas (Hofbauer et al. 2007). Water gas shift reaction occurs during the gasification stage and may be additionally introduced after the gas cleaning process by incorporating a WGS reactor in the process for a higher H2/CO ratio (Kumar et al. 2009; Lee et al. 2014)

The water gas shift reaction is:

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

The equilibrium of the reversible reaction depends highly on temperature, while change in pressure shows almost negligible effect on shift in reaction equilibrium. For temperatures around 1000°C and higher, the reaction reaches equilibrium without a catalyst, while lower temperatures require catalytic activity to promote hydrogen generation (Hofbauer et al. 2007).

Removal of CO_2 is beneficial as is it an inert gas and increases the energy requirements of the overall process. Carbon dioxide can be removed by chemically absorbing with a solvent or by physical adsorption or both. Both H_2S and CO_2 are typically removed together (Hofbauer et al. 2007).

2.6 Fischer-Tropsch Synthesis

Fischer Tropsch synthesis was developed in the 1920's by German scientists Franz Fisher and Hans Tropsch. At present, Fischer Tropsch synthesis is effectively employed for production of synthetic fuels by using coal, natural gas and biomass as feed compounds (Andrews and Logan 2008; Ehrig and Dallos 2009). The BTL derived fuels have received much popularity as they are considered renewable, are much cleaner than conventional fuels, and contain very small or no sulfur content and other contaminants (Hu et al. 2012).

In the FT synthesis process, 1 mole of carbon monoxide reacts with 2 moles of hydrogen to produce paraffins, olefins, alcohols, aldehydes, acids, esters and aromatic compounds in varying quantities. Major FT products include the linear olefins and paraffins, while the nonlinear products, such as monomethyl-substituted alkenes and alkanes are also produced in smaller quantities (Hofbauer et al. 2007; Henrici-Olivé and Olive 1976).

The Fischer Tropsch Synthesis can be categorized into two types based on the operating pressure and temperature of the process - High Temperature Fischer Tropsch (HTFT) Synthesis and Low Temperature Fischer Tropsch (LTFT) Synthesis. HTFT usually operates under the temperature range of 300 to 350°C and pressures of 20 to 40 bar. Whereas LTFT operates at 200 to 220°C and pressures usually below 20 bar. HTFT typically results into light hydrocarbon chain compounds such as ethylene, propylene etc. While LFTF is used to produce long chain molecules such as waxes (Ehrig and Dallos 2009; Maitlis and Klerk 2013). Most common FT reactors include the multi-tubular fixed-bed reactor, the slurry reactor, fluidized bed reactor, and circulating fluidized-bed reactor (Ail and Dasappa 2016).

Major reactions occur during the FT synthesis are shown as following equations:

Alkanes:	$n\mathrm{CO} + (2n + 1)\mathrm{H_2} \rightarrow \mathrm{H(CH_2)}_n\mathrm{H} + n\mathrm{H_2O}$	Eq 2.1
Alkenes:	$n\mathrm{CO} + 2n\mathrm{H_2} \rightarrow (\mathrm{CH_2})_n + n\mathrm{H_2O}$	Eq 2.2
Alcohols:	$n\mathrm{CO} + 2n\mathrm{H_2} \rightarrow \mathrm{H(CH_2)}_n\mathrm{OH} + (n - 1)\mathrm{H_2O}$	Eq 2.3
Carbonyls:	$n\mathrm{CO} + (2n - 1)\mathrm{H_2} \rightarrow (\mathrm{CH_2})_n\mathrm{O} + (n - 1)\mathrm{H_2O}$	Eq 2.4
Carboxylic acids:	$n\mathrm{CO} + (2n - 2)\mathrm{H_2} \rightarrow (\mathrm{CH_2})_n\mathrm{O_2} + (n - 2)\mathrm{H_2O}, n>1$	Eq 2.5
Water gas shift:	$\mathrm{CO} + \mathrm{H_2O} \rightarrow \mathrm{CO_2} + \mathrm{H_2}$	Eq 2.6

(Klerk 2011)

Fischer Tropsch synthesis of the syngas into hydrocarbons takes place in presence of a catalyst which is a transition metal (Damartzis and Zabaniotou 2011). Iron, cobalt, ruthenium, nickel are FT active metals and can be used as catalysts. Ru has the advantage of highest catalytic activity, but is uneconomical to use owing to a very high cost of the metal (Maitlis and Klerk 2013). Hence the most commonly used catalysts are Iron and cobalt (Damartzis and Zabaniotou 2011). Iron catalysts are used in high temperature high temperature FT synthesis, while, low temperature FT synthesis employs either iron or cobalt catalyst (Ail and Dasappa 2016). When compared to Iron, Cobalt based catalysts provide a higher conversion rate and produce more saturated hydrocarbons and less amount of unsaturated hydrocarbons and alcohols. The life time of Co catalysts are also much higher than Iron (Boerrigter et al. 2004). For example, shell uses Co based catalyst to produce waxes (alkanes) which are then broken down to make smaller chain hydrocarbons (Maitlis and Klerk 2013).

Cobalt based catalysts are effective for syngas that has a higher H_2/CO ratio of around 2. While Iron based catalysts have the advantage of handling syngas even with lower H_2/CO ratios because of their ability to support water gas shift reaction which promotes hydrogen production (Damartzis and Zabaniotou 2011). Iron based catalysts have the benefit of being cheaper too. Cobalt catalysts can be up to 250 times the price of Iron catalysts (Lualdi 2012).

The composition of syncrude produced from the FT synthesis depends on the catalyst used and the operating conditions, because of which the FT synthesis process directly effects the overall quality of the syncrude (Klerk 2011). Therefore, it is essential for operating an FT plant to run based on accurately designed FT reactors (Maitlis and Klerk 2013). The reaction equations Eq. 2.1 to 2.5, demonstrate that Fischer Tropsch synthesis is a water producing process, as most of the reactions involved during the FT synthesis has water as one of the products.

2.7 Type of FT Reactors

Multi-Tubular Fixed-Bed Reactor:

As shown in figure 7, the multi-tubular fixed bed reactor consists of a shell and a bundle of tubes. The tubes are filled with the catalyst and are submerged in boiling water, allowing the removal of heat through the shell of reactor. Syngas enters through top of the reactor and flows over the catalyst present inside the tubes, allowing for fisher Tropsch synthesis. The unreacted syngas, along with the syncrude produced exit the tubes and enters the bottom section of the reactor where the wax and gas phases are separated. The gases are removed from the gas outlet present at the upper section of the base of reactor, while the wax is removed from the bottom. Multi-tubular Fixed bed reactors have been employed in industries since many decades because of their rigid design and operation. The design provides resistance to pollutants such as H_2S and allows easy separation and removal of wax (Maitlis and Klerk 2013).

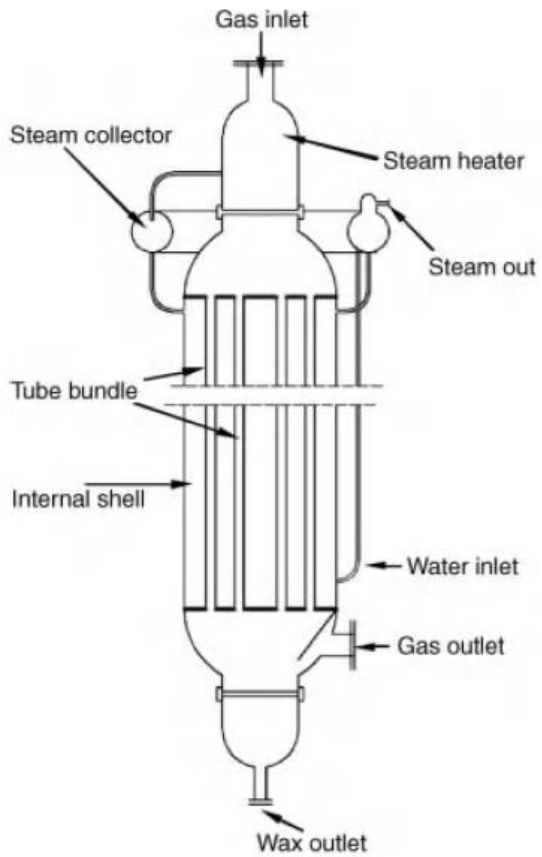


Figure 7. Schematic of a multi-tubular fixed bed reactor
Source: (Maitlis and Klerk 2013)

Slurry Bed Reactors:

Figure 8 shows the design of a slurry bubble column reactor. In the reactor, the syngas enters through the gas distributor present at the lower section of the reactor. From the gas distributor, it passes in the slurry phase in the reactor, where Fischer Tropsch synthesis occurs. The gas passes through the slurry bed and exits at the top of the reactor from the gas outlet. At the upper section of the reactor, a mist separator insures removal of any mist which may accompany the gas stream. Light fractions of the syncrude are extracted in the downstream processes, while heavy fractions, such as wax, is recovered using in-situ filtration technique. Heat produced by the reaction is removed with heat exchangers submerged in the slurry. Major advantages of this type of reactor includes a relatively lower cost of construction, higher production of heavier hydrocarbons, a lower catalyst consumption and more stable operating temperature (Maitlis and Klerk 2013).

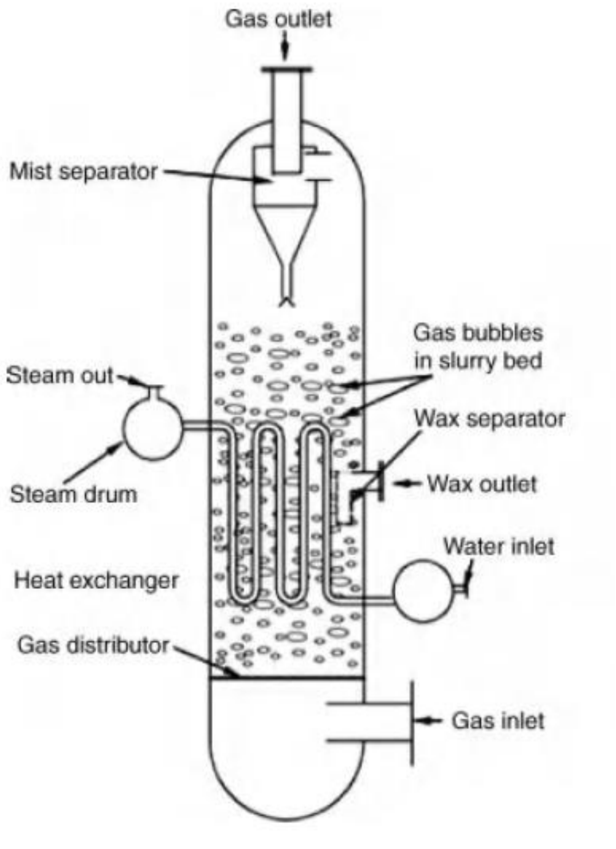


Figure 8. Schematic of a slurry bed reactor
Source: (Maitlis and Klerk 2013)

Circulating and Fixed Fluidized Bed Reactors:

Circulating fluidized bed (CFB) and fixed fluidized bed (FFB) reactors are utilized in High Temperature Fischer Tropsch synthesis applications only. In a CFB reactor design, the syngas makes contact with the catalyst inside the stand alone pipe, illustrated in figure 9, where the FT synthesis takes place. The catalyst-gas mixture flows through the pipe and moves into the transportation reactor body, where heat exchangers are employed to effectively remove the reaction heat. The catalyst-gas mixture then flows through the transportation reactor and exits from the top to reach the catalyst separation vessel where the catalyst gets separated in the vessel, and gas exits the FT reactor. CFB reactor is characterized by a high gas flow rate which results into a short life of the catalyst. The reactor also entails a high quantity of unreacted catalyst in the separation vessel and stand pipe, contributing to a low catalytic efficiency (Maitlis and Klerk 2013).

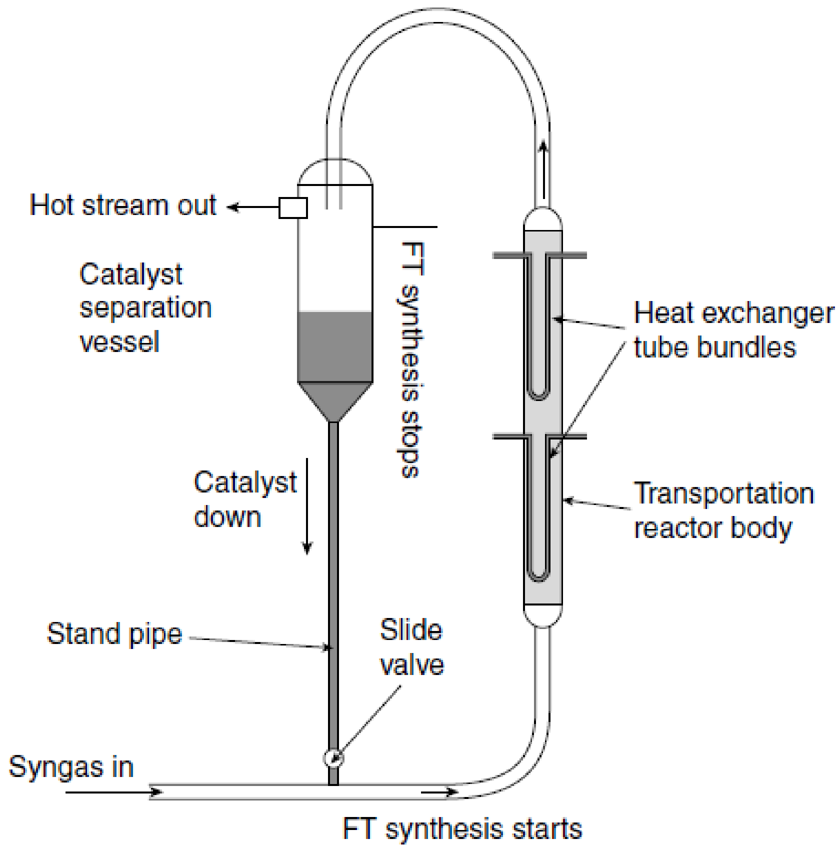


Figure 9. Schematic of a circulating fluidized bed reactor
Source: (Maitlis and Klerk 2013)

The FFB, however is deigned in a way that the catalyst remains inside the FFB reactor, avoiding the need to recycle it as in the case with CFB reactors. The syngas enters at the lower section of the reactor to flow through the gas distributor and then enter in the fluidized bed where Fisher Tropsch synthesis occur. The gas exits the fluidized bed from the upper section of the rector after being passed through cyclones which separate out any catalyst present in the gas exiting the reactor. Tubes of heat exchanger are submerged in the fluidized bed for reaction heat removal. Major advantages of FFB reactors over CFB reactors include low catalyst consumption, cheaper maintenance & operation and a significantly lower construction cost due to the simple design (Maitlis and Klerk 2013).

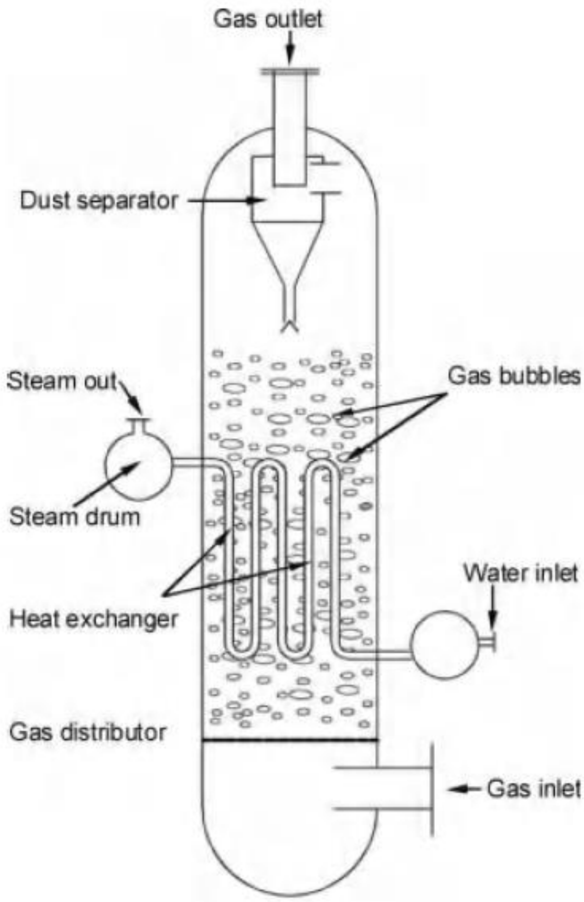


Figure 10. Schematic of a fixed fluidized bed reactor
Source: (Maitlis and Klerk 2013)

2.8 Upgrading of the Raw FT Product

The raw Fischer Trophic product from the syngas catalytic conversion is synthetic crude oil or syncrude (Klerk 2011). The raw product needs to be upgraded to yield high quality products such as naphtha diesel or jet fuel. The liquid fractions are hydrotreated in order to saturate the unsaturated olefins present in the FT product. While the solid product (wax at room temperature) is hydrocracked to produce shorter chain hydrocarbons including gases, diesel, jet fuel etc (Gray et al. 2007). The upgrading of the raw FT product process results into production of value added products (Klerk 2011).

Other additional upgrading processes commonly used include Distillation, Isomerization and Reforming. Distillation is used to separate out the various fractions of the FT raw product which can then be further processed as per the requirement (Ehrig and Dallos 2009). Isomerization is used primarily for C_5 to C_6 fractions to produce a higher octane number fuel. The fractions are converted into highly branched isomers with better octane rating and results in better performance (Abbas et al. 2017; Jones and Pujadó 2006). Reforming of higher fractions, C_7 to C_{10}, is done for the same purpose and is used to convert low octane linear hydrocarbons to high octane aromatic hydrocarbons (Ehrig and Dallos 2009; Klerk 2011).

Chapter 3: Methodology

The research was approached by combining qualitative and quantitative methods of gathering data. The qualitative methods included:

- Document Analysis
- Pilot plant study
- Semi Structured Interviews

While the quantitative data was collected by Plant Design Simulation of a small scale BTL facility on Aspen Plus simulation and modelling software.

3.1 Document Analysis

Detailed document analysis was performed after defining the Aims and Objectives and finalizing the research questions. This was performed with the purpose of drafting a strong Literature Review to convey the audience precise and accurate information pertaining to the area of research.

The sources utilized included journal articles, relevant books and reports published by universities or relevant research institutes. Recently published articles and reports were found by searching on Google scholar using keywords. The documents were downloaded and the abstracts were read in order to choose relevant studies, focused on the research area. While some books were provided by MaPS research group at UNISA. Two of the books from where extensive information was used were Greener Fischer-Tropsch Processes for Fuels and Feed stocks and Fischer–Tropsch Refining. Additional material such as reports and publications were also searched based on key authors who were acknowledged in the preliminary searches. These authors would often show up in different search results related to the topic.

The literature review was written in a way that interesting information and data was noted simultaneously while reading. This helped prepare a rough draft with several sentences and bits and pieces of information under each section of the literature review. This scattered information was then rewritten and organized to construct a consistent text and form a clear argument. Referencing of the text was done concurrently from the beginning to avoid any confusing arising later.

The subject of BTL via FT synthesis is highly scientific, for which it is important to develop the basic understanding of the technology. Therefore, the biomass conversion process was divided into sections or parts and written in a simple style to make it easily comprehendible. A systematic structure was then developed based on step by step working principle of the BTL process. A process flow diagram and various diagrams were presented to supplement the text and help readers relate more to the information being delivered. Moreover, all scientific or technical terms used in the writing were defined.

3.2 Pilot Plant Study

The pilot scale study was undertaken at UNISA during the first two days of the visit. It was conducted in supervision of the MaPS research group and the nature of the study was an observatory one. PhD students from the MaPS research group conducted gas analysis experiment by gasifying wood pallets in a downdraft gasifier with air as the gasifying agent and then collected gas samples to analyse the syn gas composition at different gasification temperatures. Passive participation was taken during these experiments which not only helped develop a sound understanding of the gasification process but at the same time aided to verify some claims made by MaPS researchers during preliminary discussions and later during the interviews. Following are some of the pictures taken during the pilot scale study:

Figure 11. Downdraft gasifier with wood pellets as feed

Figure 12. Biochar (Gasification residue)

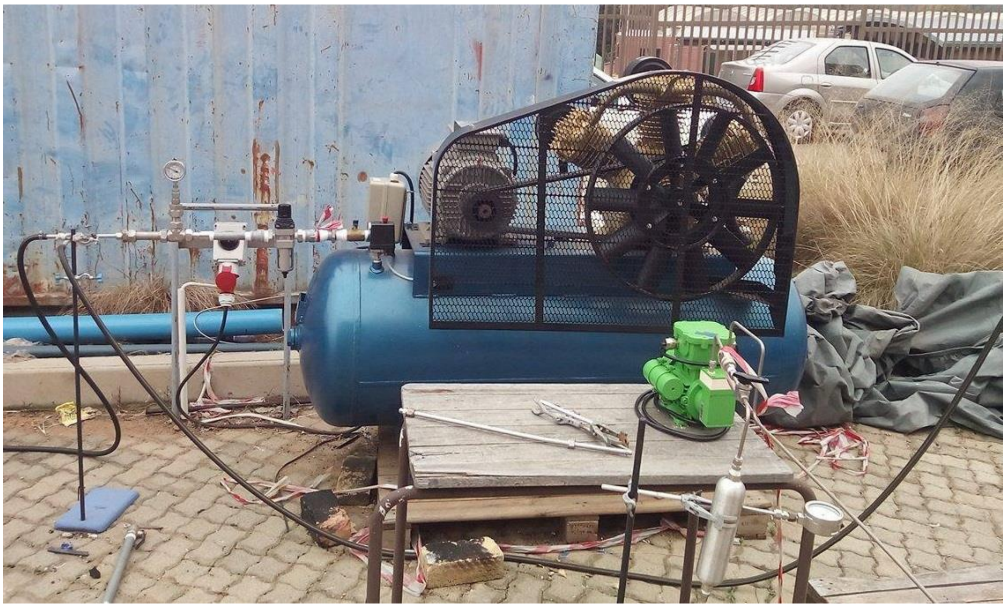


Figure 13. Air Compressor

Figure 14. Tar produced during gasification of biomass

Figure 15. Gas Sampler

Figure 16. Gas Chromatograph

- Figure 11 shows top of a down draft gasifier which is being loaded by wood pellets biomass.
- Figure 12 shows residue bio char produced from the gasification of wood pallets. Bio char is produced from combustion of biomass during pyrolysis or gasification at temperatures in the range of 300 to 1000°C (Novotny et al. 2015; Roos 2010). Properties and use of biochar has been discussed in detail in the analysis chapter.
- Figure 13 shows air compressor which provides constant air flow to the gasifier.
- Figure 14 shows tar production during gasification process.
- Figure 15 shows gas sample being collected. This is syn gas formed after gasification stage.
- Figure 16 shows gas chromatography being performed to analyse syn gas composition.

3.3 Semi Structured Interviews

Face to face in depth interviews were conducted during the three-week research trip to UNISA and some Skype based virtual interviews were conducted after the trip. The nature of the interviews was semi structured which means that follow up questions were asked where it felt necessary. The interviews were based on a questionnaire (attached in appendix) with 8 pre-determined questions. The draft questionnaire was prepared on grounds of literature review, aims of the research and discussions with PhD students at UNISA. The draft was then discussed in detail with the supervisor, and finalized after incorporating few changes. Although sufficient literature exists on gasification and Fisher Tropsch synthesis but majority is related to either CTL (Coal to Liquid) or GTL (Gas to Liquid) processes especially for commercial scale production facilities. One likely reason can be that since BTL commercial scale plants do not exist yet and the subject still exists on research and experimental level, hence most information is CTL or GTL related (Ail and Dasappa 2016). This was kept in mind while preparing the questionnaire and some questions were focused on the practicality and commercialization of the technology.

A total of 9 interviews were conducted with experts in the field mainly from academia and industry. Most of the interviews were conducted within the MaPS research group, owing to their expertise and easy access. While the rest of the interviews were arranged by MaPS using their external connections with the industry and other institutes. Notes were taken during all 9 interviews, while the face to face interviews were audio recorded as well. The details of the interviews are presented in table 1 below:

	UNISA	**Stellenbosch University**	**FMT GLOBAL**
Professors	4		
Senior Researcher	2		
Post Doc Researchers		2	
Professionals			1

Table 1. Number of interviews

The length of the interviews varied from 25 minutes to almost an hour with an average time of 40 minutes. As per the nature of the selected research topic, the drafted questions were quite straight forward and aimed at gathering facts rather than assumptions, hence many of the participants had similar views on most of the questions discussed. This made analysis of the interviews quite straight forward and less time consuming.

3.4 Plant Design Simulation Model

Computer simulation approach was used to model the functioning of a small scale BTL plant. Simulation and modelling helps determine how real systems would work and provide results which are precise and accurate. The main aim was to gather quantitative data by identifying the quantity and composition of the liquid fuels that can be produced by a small scale BTL plant using a biomass feed that is available in surplus. This was performed by identifying optimum operating conditions of the BTL plant by performing simulation runs on a range of different parameters. The simulation also helped identify the amount of emissions and by-products/waste generated by the plant.

A model of BTL process based on High Temperature Fischer Tropsch was designed by the MaPS research group at University of South Africa, using ASPEN PLUS. The model was adopted to run a simulation based on a widely available biomass feed. The gasifier was set at suitable operational parameters to obtain an appropriate syngas composition from the gasification stage, which would further be converted to a range of liquid fuels after undergoing High temperature FT synthesis in a FT reactor. Although FT synthesis can occur using syngas with a H2/CO ratio in the range 1:2 to 5:1, but a preferred H_2/CO ratio lies in the range of 1.5:1 to 2.6:1 (Hugues and Marion 2012).

3.5 Limitations

One of the major limitations faced while conducting this research was the number of interviews conducted from the industrial professionals. Although several attempts were made to approach relevant industrial specialists; most did not have time to be interviewed, while others did not respond to the emails. The total number of BTL industrial experts contacted was not too high as well, since most people are related to the more developed CTL industry in South Africa.

Another limitation was the complexity of the topic. The BTL via FT Synthesis is a highly technical subject. Often while going through the documents there would be parts which were difficult to comprehend, mostly with respect to various chemical reactions within different sections of the process. This problem was however resolved by the help of PhD students and researchers at MaPS group who were always available to lend their support in anyway related to the subject.

One limitation within pilot scale study was that the pilot plant was not fully functional. The plant comprised of gasifier and gas cleaning units but the FT reactor, although available, was not connected to plant because plant's structure at that time was undergoing some modifications. Hence the syn gas was produced but was not further converted into liquid fuel by the pilot plant. It would have been very interesting to observe the fully functional pilot plant and syngas conversion into syncrude as the final product.

Another limitation was related to the simulation design software. MaPS used Aspen Plus simulation and modelling software, a more advanced version of Aspen Hysys. I have experience of working only on Aspen Hysys during my undergraduate studies, hence I was unable to work independently on Aspen Plus while designing the BTL plant and required continuous support from the MaPS team. The software installation file was also found to be incompatible with my laptop computer which limited me to work on simulation design only during office hours at UNISA on the university computers.

Time was another limitation; not only for the field research in South Africa, but for preparing the overall thesis. The scope of research had to be redefined and narrowed down several times considering the limited time frame for the study.

Even though all the above limitations existed, the quality of data gathered and analysed was not compromised. This makes the research consistent and focused towards achieving the aims and objectives by providing a clear understating of the BTL process, its advantages and disadvantages, along with suggestions on developing a smart BTL commercial scale plant.

Chapter 4: Simulation of Small Scale BTL Plant

4.1 Black Locust as Feed in Hungary

The biomass feed used for the simulation was Black locust (Robinia pseudoacacia L.), a fast growing deciduous tree species which constitutes to 19% of the total timber output per year of Hungary and contributes to 23% of the entire forested area (Hazpra 2010; Rédei et al. 2008). Black locust is characterized by a low ash content and high heating value making it a favourable option to be used as a source of energy production (Barta-Rajnai et al. 2016).

The ultimate and proximate analysis of Hungarian Black locust sample to run the simulation were taken from the article "Comprehensive compositional study of torrefied wood and herbaceous materials by chemical analysis and thermoanalytical methods" published in the scientific journal Energy and Fuels in 2011 by Barta-Rajnai et al. (2016). The proximate and ultimate analysis used in the simulation were:

Proximate Analysis	
Moisture % m/m	6.08
Fixed Carbon % m/m	14.32
Volatile Matter % m/m	77.85
Ash % m/m	1.75

Table 2. Proximate Analysis of Black Locust

Ultimate Analysis	
Carbon % m/m	48.10
Hydrogen % m/m	4.74
Oxygen % m/m	45.41 – 1 = 44.41
Sulphur % m/m	1

Table 3. Ultimate Analysis of Black Locust

Concentration of Sulphur present in the sample was assumed as 1%, and was adjusted from original oxygen concentration. This is because concentration of oxygen is usually calculated by difference while performing ultimate analysis (Speight 2015).

4.2 Simulation of the BTL Process

Process Flow Sheet:

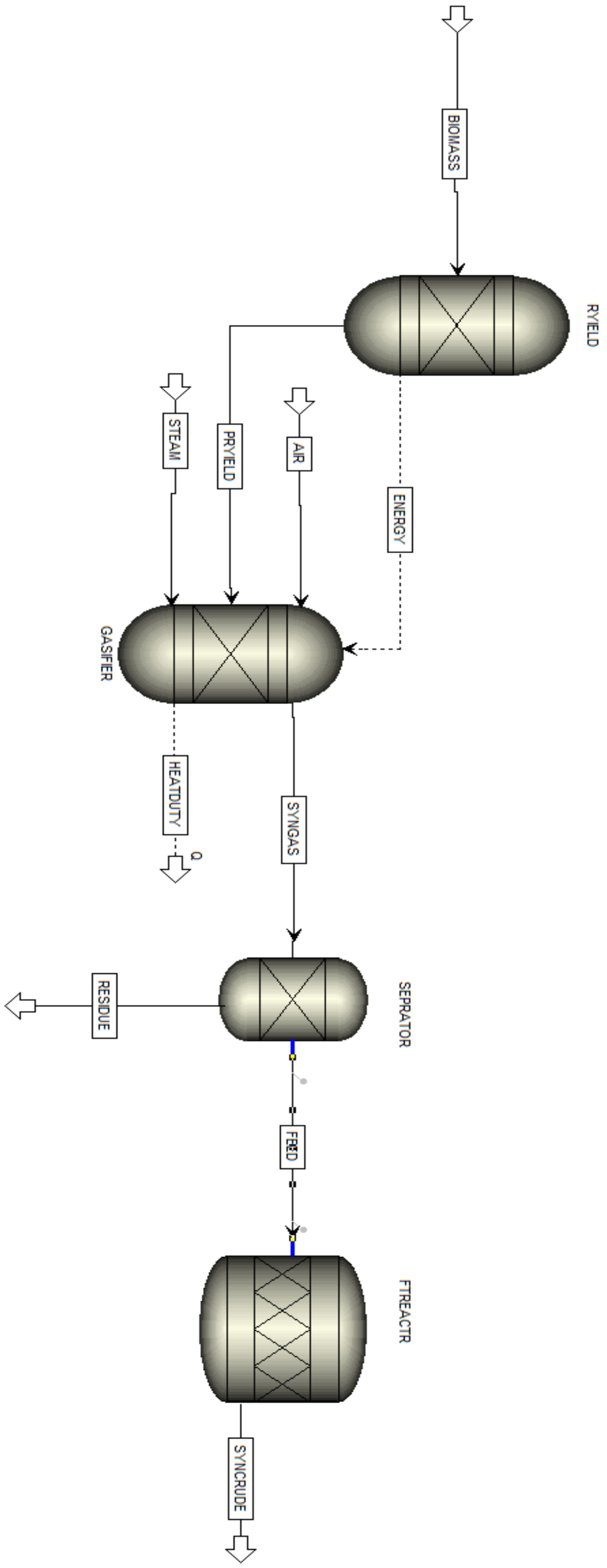


Figure 17. Process Flow Sheet of Biomass to Liquid via FT Synthesis Simulation
Source: Self-generated using Aspen Plus

Unit operations required to produce syncrude from Biomass in the BTL simulation setup consists of yield reactor (RYEILD), fixed bed Down Draft Gasifier, Separator and a Fixed Fluidized Bed Fischer–Tropsch reactor. To maintain simplicity of the simulation, clean up units for gaseous compounds such as H_2S and CO_2 were not added.

The unit operation RYIELD simulates the decomposition of the biomass by converting it into its constituents, by identifying the yield distribution based on the ultimate analysis (Nayak and Mewada 2011).

Air, along with steam were used as the gasifying agents, because the resultant H_2/CO ratio using air gasification is around 1, which is considered low. Adding steam as a gasifying agent ensures a higher and desirable ratio (Rodríguez-Olalde et al. 2015).

The following assumptions were made in the modelling and simulation approach:

1. Gasifier will operate in a steady state condition.
2. Reactions in the gasifier progress in isothermal conditions and constant volume.

Effect of Temperature:

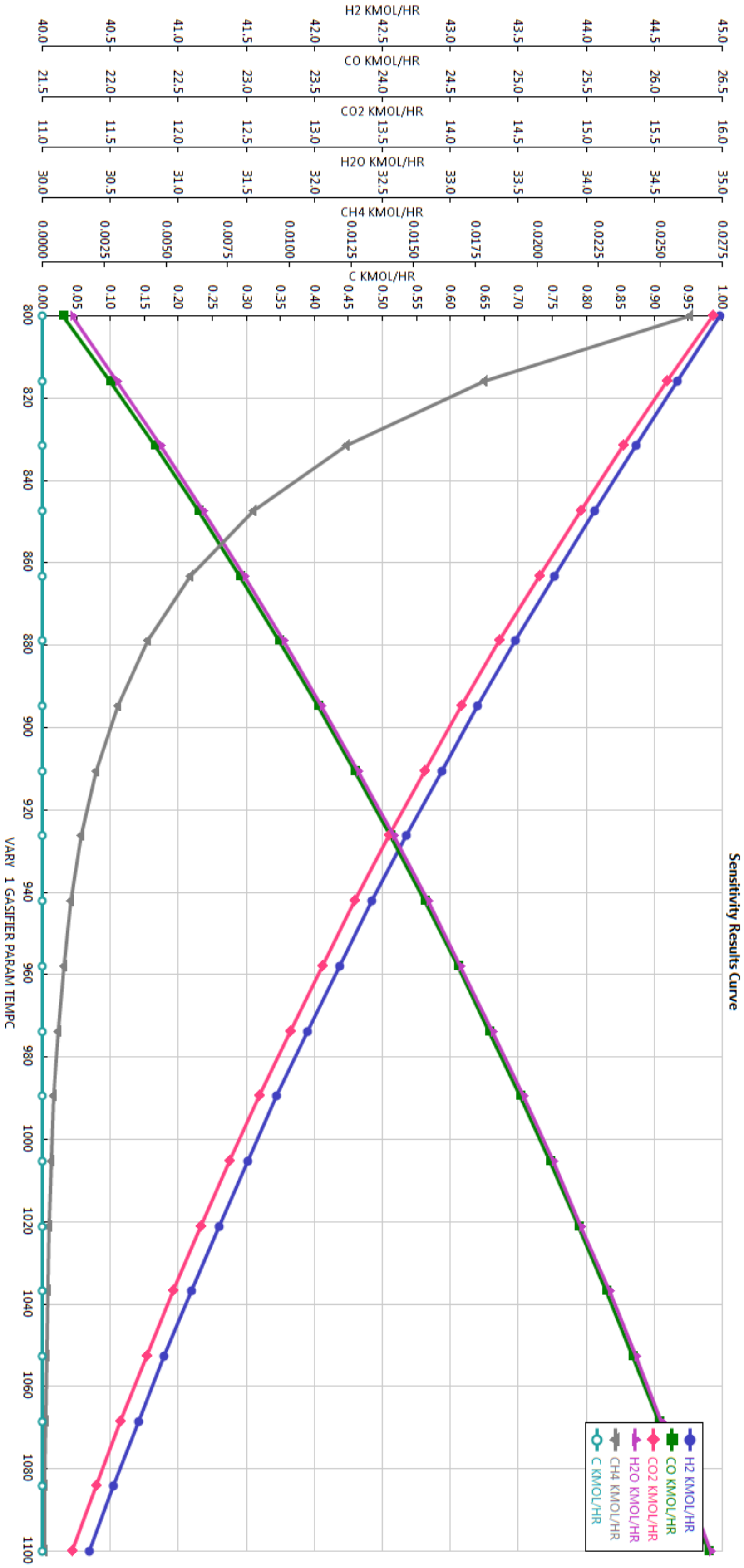


Figure 18. Effect of gasifier temperature on syngas composition
Source: Self-generated using Aspen Plus

The curve above illustrates the composition of the syngas mix produced in the gasifying stage at a range of temperatures (800 to 1100 °C). The results confirm that at 1100 °C, the H_2/CO ratio is desirable and production of other undesired compounds such as CO_2, CH_4 and water remain at minimum. At lower temperatures, the amount of H_2 and CO is reducing while other gases are produced in much higher quantities. Therefore, the gasifier temperature of 1100 °C was selected.

Effect of Pressure:

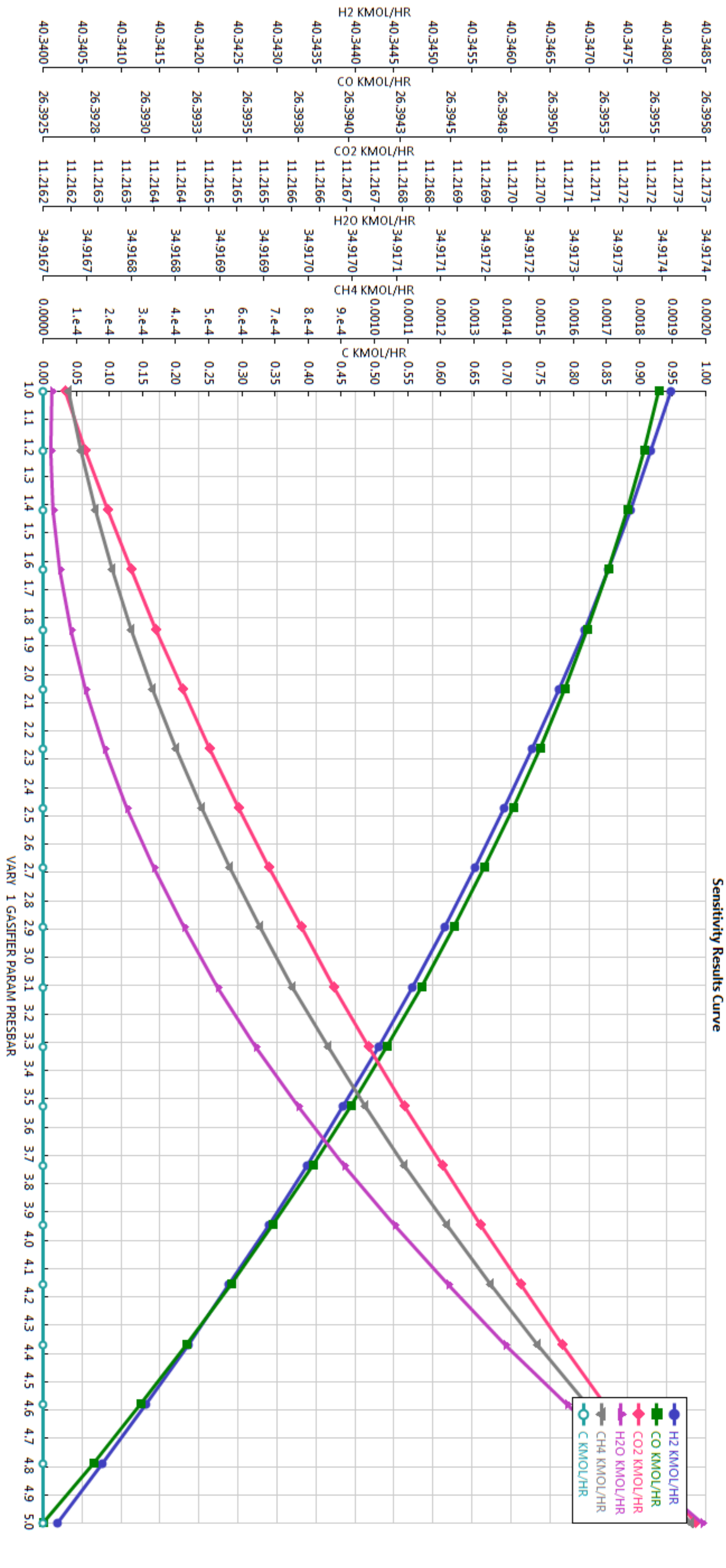


Figure 19. Effect of gasifier pressure on syngas composition
Source: Self-generated using Aspen Plus

As illustrated by the curve, a low pressure of 1 Bar results in a desirable H_2/CO ratio along with keeping CH_4, H_2O and CO_2 production at a minimum. As the pressure is increased it decreases the amount of Hydrogen produced, and favours CO_2, H_2O and CH_4 production. Therefore, a pressure of 1 Bar was selected to be used for the gasifier.

Effect of Steam Flowrate:

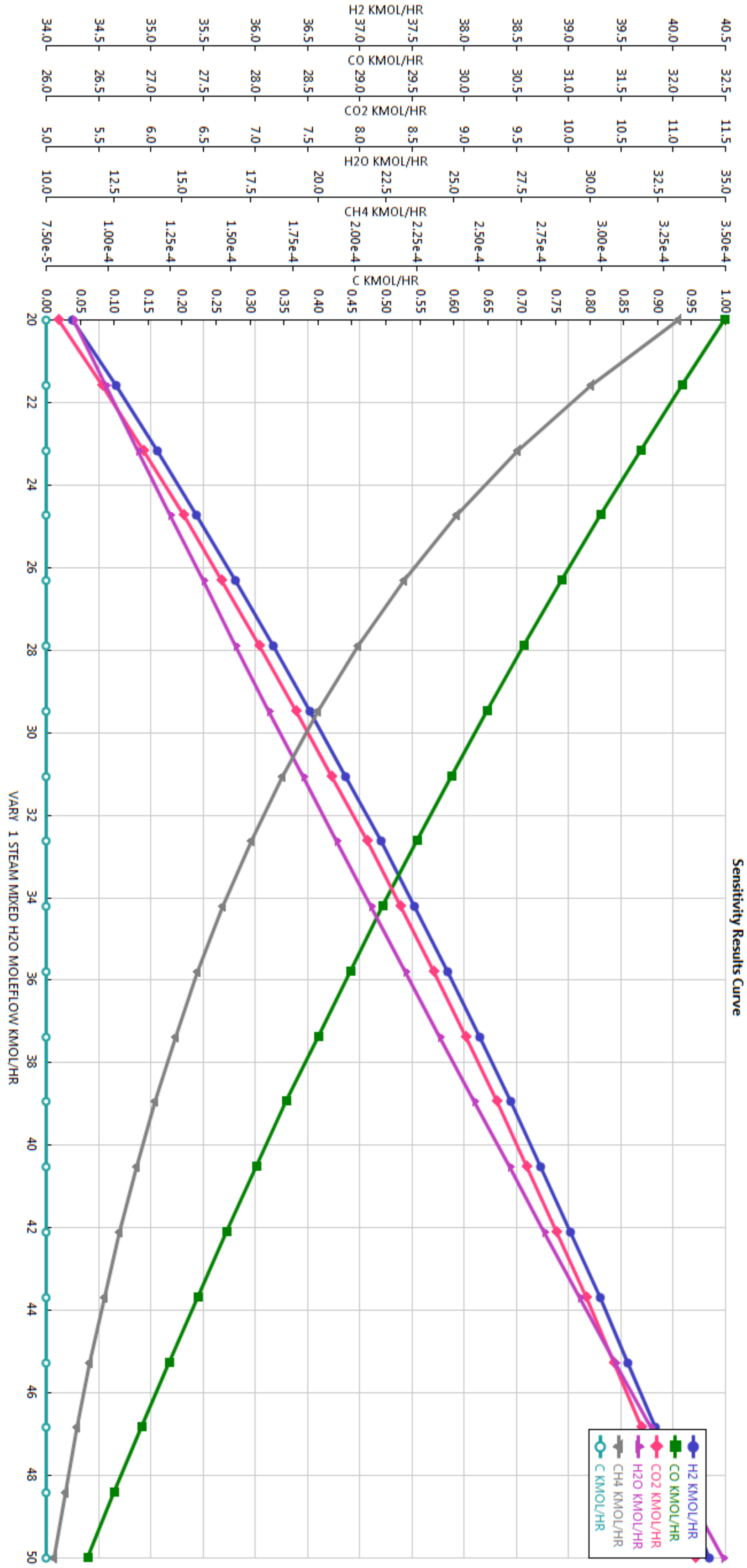


Figure 20. Effect of flowrate of steam (gasifying agent) on syngas composition
Source: Self-generated using Aspen Plus

The figure demonstrates change in composition of the product gas in the 20 – 50 KMOL/HR steam flow rate range. The effect of increasing steam to biomass ratio results in an increased mole fraction of hydrogen and decreases carbon monoxide and methane production.

Steam as a gasifying agent increases the yield of Hydrogen production and improves the H_2/CO ration as it allows for water gas shift reaction:

$$CO + H_2O \quad \leftrightarrow \quad CO_2 + H_2$$

Hence a steam flow rate of 50 KMOL/HR was selected which promises a high yield of H_2 production.

Effect of Air Flowrate:

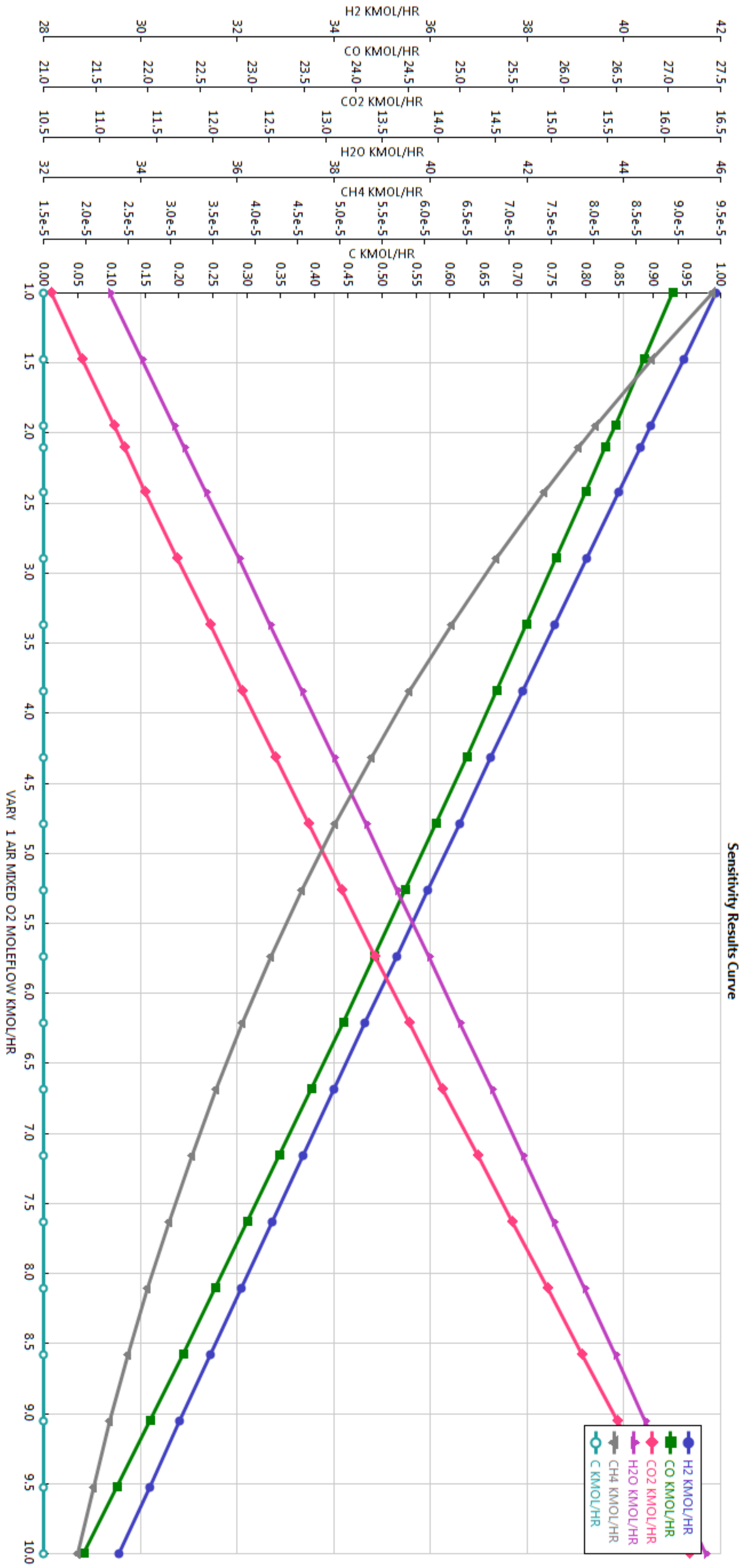


Figure 21. Effect of flowrate of air (gasifying agent) on syngas composition
Source: Self-generated using Aspen Plus

As illustrated by the curve, most favourable conditions for H2 production exist at lower flow rates of air. However, a practical flow rate of 10 KMOL/HR was selected, which produces lower CH_4 quantities, and at the same time ensures a higher degree of gasification.

Operating Conditions for Simulation:

Hence the basis to run the simulation of BTL process was determined and set as the following;

- Feed Input = 1000 kg/hr at 25°C and 1 Bar
- Gasifier Temperature: 1100°C
- Gasifier Pressure: 1 Bar
- Steam Flow Rate: 50 kmol/hr at 100°C and 1 Bar
- Air Flow Rate: 10 kmol/hr at 25°C and 1 Bar
- FT Catalyst: Iron Based
- FT Reactor Conditions: 350°C and 20 Bar (HTFT)

4.3 Results

Product Gas Composition:

The set basis and operating conditions in the simulation yielded the composition of the raw syn gas produced after gasification, as shown in table 4:

Components	Mole Flow kmol/hr
O_2	8.07 E-12
CO	26.39552
H_2	40.34805
CO_2	11.21619
H_2O	34.91666
CH_4	7.83 E-05
H_2S	0.2928949
N_2	7.799719
H_3N	0.000562864
C	0
S	9.79 E-07

Table 4. Syngas Composition
Source: Self-generated using Aspen Plus

The simulation run results into a syngas H2/CO of 1.54:1, which is considered suitable for Fischer Tropsch synthesis.

Separator Phase:

The function of the separator is to remove any tar, char or ash that is accompanied with the gases, in order to obtain only a gas phase that can be fed to the FT reactor (Rupesh et al. 2016).

Syn crude:

After passing through the separator, the syngas enters the FT reactor which converts it into syncrude at high temperature and pressure. The FT reactor was set to function with a 90% constant syngas conversion rate. Operating temperature for the FT reactor was set at 350 °C. As a result of the complete simulation run, 1000 kg per hour of Black locust as biomass produced 298.7 kg/hr of syncrude in a BTL Fe-HTFT process. The composition of syncrude produced is of a typical HTFT synthesis process and mainly consists of gasoline and light olefin (Nafees and Al Hashimi 2017; Hu et al. 2012). Gasoline fraction, C_4 to C_{12} (Demirel 2012), is produced at 72 kg/hr and light olefins, C_2 to C_5, are produced at 96.3 kg/hr, representing 24.1% and 32.2% of the syncrude respectively. Rest of the mix majorly consist of heavier alkanes (C_{13} to C_{30}). Detailed composition of syncrude is attached in the appendix.

As per the by-products of the process, CO_2 is produced at a rate of 654.9 kg/hr from both gasification and FT synthesis without any CO_2 removal system. While 945.3 kg/hr of water is produced from the entire BTL process. 16.4 kg/hr of char and ash is produced as residue of the biomass gasification.

Depending on process operating conditions, gasifying agent and feed type, it can be deduced that every kg of syn crude produced in a BTL process may be accompanied with approximately 2 kg of CO_2 and 3 kg of water.

*Further details about simulation process conditions and results are attached in the appendix.

Chapter 5: Interview Analysis

5.1 Interview Discussions

Responses from semi structured interviews were gathered and based on the outcome, the responses were divided into 8 themes to form an unbiased analysis. The responses are discussed below based on the following themes:

- Advantages of BTL over other technologies
- Carbon Foot Print of BTL technology
- Issues in the BTL process and its commercialization
- Suitable size and geographical location of plant
- Most valuable products
- Major Environmental Impacts and solutions
- Effect of Policy of a country on BTL development
- Common Opinion of Policy makers on Future of BTL

Advantages of BTL over other technologies:

When questioned about the advantages that BTL have over other technologies, the respondents argued that one of the biggest benefits is biomass availability in abundance. Biomass as a feedstock for the process brings independence over the use of fossil fuels which is a limited resource. Thus, it can help countries limit their reliance on imported oil and be less effected by the constantly varying oil prices in the international market.

A response by one of the senior researchers indicated that the produced liquid fuels have the flexibility of being easily stored and transported by ship, tanks or by pipe and have high energy density. He explained that in the previous 200 years, the majority of the development has been done based on liquid fuels, because of which the infrastructure to produce and use liquid fuels already exists. The liquids produced by BTL are very similar to those produced through conventional fossil fuels, because of which the same infrastructure can be used for further processing and utilization.

Another respondent pointed out the versatility of BTL and suggested that the process has the freedom to use a wide variety of feedstock. Most other technologies require a specific type of feed as input but BTL can process a wide range of biomass feed.

BTL processes can yield multi-products, unlike fermentation based processes which generates a single product. Having similar properties to conventional fuels, BTL derived liquid fuels do not require blending and can be directly used in engines unlike first generation biofuels, such as bioethanol, which requires blending with conventional oil derived products.

A BTL plant can serve in providing off grid solutions. A professor shared an example of a BTL facility based in a remote area to generate electricity. Such a facility can offer the advantage of producing power while at the same time generating fuels. Demand of electricity varies by time of the day and season of the year, so during low demand the syngas can be directed towards producing fuel and chemicals which can be sold in the market or simply be stored to burn and produce electricity later when demand is at peak and cannot be reached by generating capacity of the plant. Hence a BTL plant can generate more electricity and limiting fuel production in high demand period and likewise, produce more fuels and less electricity in low demand period.

Another professor explained that BTL process, even on a small scale, has the potential of providing a very positive social change especially in developing countries and said "Development of BTL can provide jobs to the people who are currently out of the economic system". These people include farmers and other unskilled workers who are unemployed.

Carbon Footprint of the BTL Technology:

All respondents had a general opinion on the process emissions and acknowledged that BTL processes can be considered as carbon neutral. This is because the CO_2 emitted from the process itself and from burning the BTL derived fuels is the same which was present in the atmosphere and was utilized by plants during photosynthesis. Therefore, the CO_2 released back into the atmosphere by burning biofuels and/or through the BTL process, will be captured by plants again to complete the closed loop carbon cycle. This means no additional carbon was released in the atmosphere.

In case of other technologies which are based on fossil fuels, such as CTL or GTL, the source of emissions is from the fossils. The fossil fuels can be considered an underground source of carbon which once released in the form of CO_2 emissions, cannot be trapped underground again as the total life cycle for CO_2 is in the order of millions of years to return in the form of non-renewable fossil deposits. Hence this is considered surplus CO_2 being released in the atmosphere which will not be utilized and only add to global warming.

A properly designed BTL process theoretically can achieve almost negligible carbon foot print. Although if the biomass feed in the BTL process has been grown using fertilizers coming from non-renewable resources, usually natural gas, it will definitely have a carbon footprint. Therefore, it is a better option to use fertilizers derived from renewable sources such as biomass. The respondent added that the current focus of development is not on energy crops but simply on utilizing agricultural and forestry waste as a feed for BTL. Based on life cycle assessment of the BTL process including all the energy spent in order to grow the crops, BTL can achieve around a 90% savings on carbon emissions compared to conventional oil use. GTL has a similar carbon footprint as oil, while CTL has a carbon footprint twice that of oil without going on the lines of carbon capture and sequestration (CCS). The respondent discussed about recent developments in proper utilization of CO_2 emissions from the BTL processes. This includes the utilization of CO_2 generated during the BTL process by supplying it to greenhouses for the purpose of increasing the yield of plants.

It was suggested by one of the respondents that BTL processes results lower environmental stress since the environmental damages related to coal mining, oil extraction and release of methane are not associated with this technology. BTL processes avoid major sulphur emissions which are related to other non-renewable source based technologies. These claims by the respondent are also supported by the literature review.

Problems Faced in Commercial Implementation of BTL:

While speaking about the commercial implementation of the BTL technology, the respondents had a common opinion that it relies on technological advancement and economy of BTL process. One respondent said "Success of commercialization of BTL relies on two aspects, first; maturity of the technology, and second; maturity of financing or making it economical. These are the two biggest problems".

The respondents suggested that a major issue in BTL's commercial implementation is its limited scale. A senior professor discussing the same subject said "This industry needs scale to survive". He shared an example of Sasol in South Africa, that it uses more than 30 million tonnes of coal per year to produce around 6.5 million tonnes of fuel and chemicals annually, while another CTL plant in China produces 3 million tonnes of fuel per year. BTL cannot reach that kind of scale. He also suggested that coal and natural gas have a centralized supply of feed and transportation is easy, while biomass cannot be centralized. In case of fossil fuel based industries such as CTL or GTL, a plant can be set up just next to the mine and the process of extracting the resource can continue at the same location for even 20 to 30 years. While in the case of biomass, it is a resource scattered over large pieces of land. Hence, a BTL facility set up is limited to a certain radius for biomass collection, otherwise transportation costs will severely affect the economy of plant. He explained that a hector of land can produce a few tonnes of biomass depending on the location, while only some energy crops can produce around 30 to 40 tonnes per hector. The truck carrying biomass has to move its own weight as well. 5 to 10 tonnes of truck transporting 2 tonnes of biomass one way is not efficient. Other methods for transport include rail, which can give a better radius but then it needs infrastructure to be built. The respondent said for now in the BTL industry people consider a plant size of about

5000 barrels per day, whereas Sasol (CTL) is producing 160,000 barrels per day. So the scale difference is huge if a BTL plant is compared to conventional CTL plants. Even one of the smallest GTL plants, based in Qatar, runs at 34,000 barrels/day, which is still much bigger than what a BTL facility can handle. The chemical industry needs a certain scale to be profitable: if the plant is small, the capital investment per unit capacity becomes huge and vice versa. However, the cost of operation is not too high. He said, “So we are trying to make the BTL process as simple and robust as possible” and added, “For that we sacrifice some efficiency, but not a lot, in order to deliver a process suitable for a BTL plant”.

When speaking about the technical issues faced in the BTL process, most respondents believed that biomass processing in the gasification stage is one of the biggest challenges faced in BTL conversion process. A senior researcher said “I’ve been involved in the study (BTL via FT synthesis) for about 7 years and the biggest headache is in the gasification part”. He said that development of gasifiers for biomass should be different from gasifiers for coal. Due to energy density difference per volume feed between biomass and coal and the dissimilar characteristics, the approach for manufacturing coal and biomass gasifiers should also be different. Coal gasifiers are much more developed than those for biomass handling. The respondent supported his claim and said that biomass gasifiers started development in 1940s to 50s without much progress in the 1970s to 90s. Then in 2000s they became important in the scientific world again and progression restarted. Thus, biomass gasifiers are underdeveloped, whereas coal gasifiers have been established for more than 100 consecutive years. When people develop gasifiers for biomass, they still follow the same criteria used for coal gasification resulting into technical issues. Another respondent explained that due to inefficient gasification of biomass a lot of undesired tar is produced, which was also observed during the pilot scale study and can be seen in figure 14. He suggested that ash handling is another concern. If the gasification temperature is not maintained, the ash melts which may solidify and block the reactor. Most respondents suggested that in comparison to the FT synthesis part of BTL process, gasification of biomass is more complex and needs to be improved. Another respondent suggested that the problem of tar production can be avoided by developing efficient catalytic gasification processes that cracks the tar compounds into lighter hydrocarbons. Speaking on the same topic a senior professor said that there are several technical issues in BTL but mainly associated with gasification. He shared an example of Choren, a German company, which had a small commercial demonstration BTL plant consisting of an entrained flow gasifier using high pressure multi stage gasification and Shell's FT technology. He mentioned that Choren's process worked well and the company decided to scale up in 2010, but failed in scaling up the gasifier successfully and eventually became bankrupt. He said, "That's how bad the industry can be". Talking about difficulties in handling biomass, he said that steam reforming by gasification using steam, to produce highly quality syn gas might be one solution. He concluded with "I have given up on conventional biomass gasification".

Another issue lies in the FT synthesis, which hinders implementation of BTL. One of the respondents developed the argument by saying that FT is a very unique reaction but it cannot be pushed to either produce extremely large proportions of heavy or light hydrocarbon products. He said that a balance is always maintained, therefore optimizing the production towards producing highly marketable products only is challenging. He said that for bigger facilities such as CTL or GTL it is easier to have a downstream product upgrading section to finally produce those marketable products, but it is very difficult to adopt the same approach in a much smaller BTL facility. This is because the scale of BTL is too small and it would not be economically feasible. Respondent explained that for a BTL process, the pre-treatment of biomass is already an expensive process and adding more expenses is not practical. It is better to try and keep the plant as simple as possible. He said that it is desirable to extract the marketable products in one step only and said “It’s a dream but it’s also a direction for BTL. I know it’s difficult but we are doing this. We are trying to do this”.

One of the researchers also suggested that the economic profitability is a huge concern and BTL process can only thrive if the BTL derived synthetic fuels can compete with the prices of crude oil derived fuels. The drastic drop in oil price from $115 in June 2014 to $35 in February 2016 has negatively affected the BTL industry.

Suitable Size and Geographical Location of Plant:

Seven out of nine respondents answered in favour of a small size BTL plant while only two answered in favour of a larger plant. For the geographical location, all respondents contributed with a same opinion of BTL plant(s) being developed near biomass rich source(s). A researcher described plants of 100 tons per hour capacity feedstock as large, while small ones of the capacity 30 tons per hour.

A senior professor responded that developing multiple small size plants in various locations has its benefits. The idea not only increases the cumulative scale of production which is desirable for higher profits, but also provides easy access to biomass. Which means that biomass will be available in a relatively short radius and transportation will become much cheaper and efficient unlike in case of a large biomass facility. Another benefit is that small projects can rely on some sort of subsidies from the government while huge projects cannot be satisfied by government support. He added that a small project brings lower risk as well, and by starting with a small scale it is easy to grow and construct more plants one after the other. This approach provides an opportunity to learn about the mistakes in previous projects and avoid them in the next ones during the process. While in case of a big plant once that the main process has been set, it becomes almost impossible to make major changes since its costly and risky. He said "We have designed some small scale FT plants in the past 10 years and we have made some considerable changes in the next ones to follow, for improvement". The smallest scale MaPS is currently working on is 50 L per day only. He said another benefit is that in following this approach it is easy to develop something simple and not too complicated. Another senior professor supporting the same idea said "We can look into smaller plants, as small as a tonne of biomass a day. The chemical industry has been built on the basis of chemical engineering which is to build one big thing to bring the costs down, but I believe in this case we need to scale down and follow what the computer industry has done. We have to learn from them how to build lots of smaller units, which are multipurpose and user can adapt to what they want. So I believe there are more system challenges than technical challenges…" Such an idea can provide a solution to developing countries where there is an abundant biomass resource but a limited capital investment. They can have a small start as phase 1 and then slowly move to a second phase which is of a larger scale and grow the industry.

The two respondents supported larger facilities on the basis of economies of scale, as larger plants would bring down the overall cost per unit production. Their argument seemed to overlook the important aspects of biomass availability in a short radius, transportation costs and high capital investment for large scale pants. During discussions, a respondent with ten years of experience in the industry pointed out that large plants can cost as much as 15 to 20 billion USD while small scale plant could be around 1 billion USD. Therefore, even developing a small scale plant is a large investment in itself. Another respondent pointed that transportation for biomass is expensive since the energy density of biomass per unit area harvested is low. It is around half that of coal, which means it requires a much larger quantity of biomass as compared to coal to produce fuel of the same amount.

All respondents stated that a BTL plant should be developed where biomass residues are readily available from agriculture or in an area where forestry waste can be easily collected and transported. The agricultural waste only becomes available twice or may be three times a year. After collection, it should be stored in a place which is easily accessible, doesn't burn or get wet. It may require another transportation system from the storage to BTL facility, adding difficulty and extra expenses. Transportation by sea, compared to trucks, is an alternative which is cheaper and more energy efficient given location.

Most valuable products:

The general opinion was that a BTL plant can be made profitable when it produces a range of various products. Liquid fuels, chemicals and power are considered as major BTL products while there are some secondary products as well. Although most chemicals products do have the advantage of a higher profit margin, but the importance of producing relatively lower value fuels cannot be ignored. One of the respondents said "What people have been trying to do is co-produce low value products along with high value products as well. They are trying make a multitude of products to make the process more economical".

A senior researcher explained that although the fuel market is huge, it has a lot of competition because of which the profit margins become low. Whereas the profit margins are relatively higher in chemicals, but the market is not as big. Hence a balance between fuel and chemical production should be maintained. He further discussed that co-production of power and liquids will be a reasonable selection. Producing kerosene and diesel is better than producing petrol as petrol requires further isomerisation for obtaining the desired octane number. While C_1 to C_4 products (gas fraction) from the FT process can be used to generate power.

A senior professor preferred chemical production over fuel production and fuel over power production for most valuable products. He said it's viable to generate power only when the government provides some incentives in form of subsidies or tax rebates. He said that the problem with fuel production is a small scale plant entering into the market may be challenging but then the product can be sold as a blend to refineries. It is beneficial for a small facility entering in the BTL industry to focus on chemicals in the initial stages. Starting off with one plant makes it easy to focus on producing and selling chemicals, and when the business grows into several plants, fuel should also be produced. He stated that fuel prices are constantly changing in the international market. Chemical prices vary too, as they are based on crude oil, but not to a large extent. Hence another advantage of producing chemicals is that the profits are much more predictable. He suggested that BTL can produce some higher quality chemicals compared to what can be derived from conventional crude oil. The long chain hydrocarbons produced from BTL are more desirable and difficult to obtain from the crude oil industry. BTL products are regarded as clean products, BTL derived Naphtha for example, is sulphur free, comes from nature and is widely used in the cosmetics industry. It can be marketed as "bio-naphtha" or as a "natural product". Same is the case with BTL derived Wax, he said.

A senior professor said that producing electricity, liquids and utilizing process heat (otherwise wasted) can lead to very high efficiency of the plant. Co-producing them on site can make the overall process cheaper yet simple. The professor suggested that it is more about designing a system where a user can balance the products, in a certain range, as per the requirements. She presented an example that the liquid produced can be used at site for engines or can be blend it into other fuels for similar purposes. She said, “I think that’s what we should aim for. Empower the person that has the equipment, to maximize its usefulness within his environment. I think it’s a different thinking to the classical approach of targeting high efficiency of a single aspect.”

“BTL is not meant to make just one product because it will just never be economical. You have to try to make a whole range of products”, said one of the professors at UNISA. He discussed how a balance should be maintained between fuels and chemicals production and pointed out that middle and higher fractions such as paraffin, diesel and wax are marketable. He suggested to properly utilize the biochar, a residue of biomass gasification, as it is a valuable by product of the BTL process. A senior researcher discussed about several applications of bio char including its use as a fuel and in water purification systems.

Major Environmental Impacts and solutions:

Waste water, one of the most discussed environmental concerns related to BTL, was regarded as the major by-product of the process by the interviewees. A senior professor explained that waste water is generated from two parts of the BTL process; Gasification and FT synthesis. Gasification waste water mainly consists of phenols, tar and ash. A dedicated water treatment process should be in place to remove the contaminants from the gasification waste water before it could be released in the environment. While, the water produced during FT synthesis consists of some alcohols, hydrocarbons and acids. He pointed that water from FT synthesis is much cleaner than the one produced from gasification stage and said "COD is high for FT water but it is not a big issue". He discussed that FT water can be recovered in the process by constructed wetlands method which is efficient in cleaning up the hydrocarbons and shared that research is being conducted on wetlands and its effectiveness in treating FT water by the MaPS research group. Upon reaching out to MaPS, I was told that the project is in the initial stages and they are currently starting testing on waste FT water samples provided by SASOL. A senior researcher in the MaPS group discussed that the FT water can be treated by biological processes to break down the hydrocarbons and release the treated water in the environment safely. For this purpose, bio digesters or even wetlands can be used and said "Their (wetlands) efficiency is good; the study is underway but we are getting there". Another researcher said that wetland is a unique structure and if you dig into the core of the technology, wetlands provides an environment for bacteria to grow. It is a cheap and environmental friendly method for water treatment and can drastically reduce COD value. A professor discussing about waste water said that for a small scale plant the issues related to water can be dealt with in a different way. If the water is returned to the field and spread on a large area, the hydrocarbons present will be degraded by bacterial action. The treated water can then be used for irrigation following some dilution. She recommended that the effluent shouldn't be released directly into the rivers, and to the soil at a rate existing ecosystems can efficiently degrade the contaminants present in waste water.

The use of land and soil are important concerns that were pointed out. A senior researcher suggested that if the process efficiency can be improved, higher energy can be extracted using lesser feed material. This will lead to less use of land water to grow biomass. Ideally, land that is underutilized and not suitable for growing food crops can be used to grow the biomass. He said if forests have to be removed to grow your biomass it would definitely have a negative environmental impact. A senior professor at MaPS suggested that it is essential to return all lost nutrients, trace minerals and elements to the soil and ensure that a system is developed which supports such a cycle and works well. She proposed the idea to avoid gasification to completion, but to a point where a substantial amount of bio char is left over, and can then be used to return the lost nutrients back to the soil. Another researcher at UNISA explained that char is composed of carbon, calcium and potassium and the components exist purely in elementary phase or as oxides. If the char is added in the soil, it enhances the soil quality. Although all heavy metals in char comes from the soil but still a proper management is required, because if the char comes in contact with running water it may pose a health and environmental hazard. Some companies in China collect bio char and mix it with fertilizer to add in the soil. Hence it should be treated as a valuable product instead of a by-product, so it can be beneficial and utilized it in an effective way.

While discussing emissions, one of the researchers claimed that gasification is one of the cleanest methods to utilize biomass and coal. This is because when the feed is converted into gas phase, it is passed through the process of gas clean-up which collects and removes most of the toxic materials and pollutants to provide a pollutant free gas. He suggested that the down side for any combustion or gasification process is that oxides of nitrogen (NOx) and dioxins (persistent organic pollutants) are produced, which are toxic in nature and harmful to human health. At higher temperatures, he explained, higher NOx and lower dioxin concentrations will be produced while at lower temperatures higher dioxin and lower NOx concentrations will be produced. So either way there's a toxic pollutant being released. Fortunately, there are technologies to reduce NOx and dioxin to very low levels (up to 99% removal), but the cost to incorporate these technologies is fairly high. He said that a high efficiency removal system can cause economy of the plant to suffer and suggested that if scientists could develop cost effective technologies for this purpose, it will be beneficial for BTL process in the gas clean up sector. He concluded "Emissions are not avoidable; you need to control them".

Discussing CO_2 emissions, a respondent explained that BTL generated CO_2 comes from biomass and not from coal or natural gas, the impact is much lower than CTL and GTL. She suggested that it is still important to minimize these emissions even though they are produced from a renewable resource. A post-doc researcher had similar views and said the CO_2 emitted may be carbon neutral, but it is still an emission that could impact the environment negatively. Another respondent suggested that CO_2, in theory can be converted back to fuel but it is a very difficult process. He explained that CO_2 already exists at a very low energy level and it would require a lot of work to convert it into fuel. He concluded by saying "You would have to add more energy in it than you can extract". Two professors from UNISA suggested that the CO_2 generated can be effectively utilized if sent to green houses. One of them said that growth rate of plants increases in a CO_2 rich environment so the CO_2 generated can used to improve plant yields. He said it's a cyclic process, coming from nature and going back to nature. This is one of the ways that CO_2 released from BTL can be effectively utilized.

Effect of Policy of a country on BTL development:

While questioning how the policy of a country can be a driver or a restriction for BTL development a researcher suggested that generally the energy policy only drives the development of a technology if it incentivises the production of renewable fuels. Otherwise, environmental policies that penalises excessive fossil fuel emissions can be used to incentivise renewables to develop BTL based fuel industry. Furthermore, environmental policies that promote a cheap supply of biomass feedstock for BTL, such as an invasive alien plant clearing program, may as well help developing BTL. If the energy policy dictates that the fuel prices of a country will be based on the international oil prices, then it is either advantageous or disadvantageous to a BTL industry depending on the oil prices in the international market. High oil prices will lead to feasibility for BTL development, while low oil prices will be otherwise.

If the energy policy promotes feed in tariff, then there is a huge potential for BTL or BTE (biomass to energy) to grow. If other policies related to fuel use and its specification are relaxed, then that could also be a huge driver. Most of the cost in producing BTL derived fuels is spent on product upgrading to meet mainstream fuel specifications, so with relaxed policies a significant cost of the process can be saved to make the overall process economically viable. The respondent said "If one can blend these fuels with conventional fuels, it will open up another market".

Another researcher argued that BTL technology comes under the category of renewable energy. Several countries recognize the urgency for renewable energy development but not as many are implementing those claims into actions. Policy can play a huge role in terms of development of BTL. The government may support developing projects by providing subsidies, but it is important to realize that it is only a temporary solution. For the incubation stage subsidies are supportive but the industry has to be self-sustained because the government cannot keep pumping money into it. He explained that manufacturing several mini plants for mass production is one way to go which could bring down the cost per plant and the other way is to make the process as simple as possible. He said that this is what they are working on in MaPS at UNISA, aiming to make BTL profitable and self-sustaining.

A senior professor at UNISA explained that with respect to the Policy in South Africa, while counting CO_2 emissions, the life cycle assessment is not taken into consideration. Hence, only the amount of CO_2 being released is taken into account, ignoring the nature of the source of emissions (carbon neutral biomass in this case). This hinders the development of the BTL industry and it is very difficult to make changes in the legislature once these policies are already in place. He explained how government support can help develop this industry but unfortunately that too is not in place. In theory, the carbon tax that government collects from other industries should be put into developing such industries which doesn't seem to happen. He said they almost received some funding from South African government for a project but unfortunately it died in the bureaucracy involved. Another problem is that BTL produces multiple products; electricity, fuels and chemicals and at the government level there are different departments that look into these. So one has to deal with several departments and ministries, where they are not sure about the correct authority that should be dealing and are confused. He said this is what they experienced not only in South Africa but even in China. Another professor discussed that they find policies in South Africa very restricted. She said "The government wants to tax anything that produces CO_2 but how can you compare a biomass process to a fossil fuel process?" and added that the energy policies are restraining BTL development. It is understood that government needs to make sure there are no damages but while developing a new technology, policies should be a little more open in the initial stages to allow the process to function and then put a system in work based on the identified problems. At the moment even garbage cannot be used as feed since it is legislated. It is a major issue in South Africa and probably many other developing countries as well.

Common Opinion of Policy makers on Future of BTL:

A senior researcher explained that a lot of policy makers have realized that they would have to focus more on renewable sources in order to promote sustainability. In the future, adapting this type of technology might be easier given that it also shows potential and economic advantages apart from the environmental benefits. Especially for countries that depend on input of crude oil, BTL development can be advantageous. The next step is to showcase that the technology can be economically viable and more environmental friendly than traditional ones. There is a lot of work that needs to be done before it happens, he added. There is a gap between policy makers and researchers due to differing incentives. He concluded, "I think if researchers were making these policies, things would have been much better".

A senior professor believes that BTL is the technology of future because once the fossil fuels are exhausted, biomass is the only carbon resource left in abundance. He said that policy makers acknowledge that but they also realize there is seemingly no urgency for the upcoming decades. When liquid fuel is available at a cheap price in the market, which it is as of this writing, the need to develop BTL perishes. Furthermore, policy making does not rely only on scientific findings but societal and economical as well. He explained that "I personally think there is not an urgency for the BTL industry I don't feel that way even when I am pushing it, currently I am pushing for chemicals rather than fuels. Even for climate change related issues in South Africa, carbon emissions are dropping because the economy is not growing". Most people believe that BTL is not ready yet and we still need a first demo to ensure that it works as per the predictions. For now, the simulations are available but are only estimates until the first model is built and operated, providing us its capital costs and real operational costs. More reliable numbers will then be available and policy makers will have something substantial for cost-benefit analysis. He said that currently BTL is at a very young age, where the government should intervene and allow it to develop against more mature substitutes. Choren's company failure also gave the industry some troubles and did not leave a good reputation to policy makers. Now we need something different, a new setup to convince them (policy makers) again. He said "It is reasonable, they have seen one project fail, and it's completely fair."

Two professors explained that policy makers in South Africa mostly follow the footsteps of Europe and USA. One said that issues in developing countries, such as South Africa, are different and require other approaches and different legislation. She mentioned that it is important to have the right people working in the right positions at the government level and shared that during one of her visits to China, she met with government officials who were PhDs, scientists and engineers that could understand their work. She shared another instance where she was in contact with the national utilities of South Africa for a proposal that was refused because they didn't want to work on a small scale. She added that they don't have the mindset for it and when people look into small systems they assume it cannot work or create jobs. They should realize that it is not only about the employment of engineers and skilled workers but also how to employ unskilled workers. She said "I don't think the government can see that the drivers are very different. We are not trying to create those jobs in America or Europe."

Another professor discussed that policy makers might be optimistic for BTL but most of them are likely to confuse it with the first generation technologies that produce bioethanol or biodiesel, which are more developed and known. In South Africa however, BTL should receive considerable support because a well-developed CTL industry already exists and BTL is just an extension of the same technology, but by far he said he has not heard about building a BTL plant in South Africa.

An industrial expert shared that BTL technology is considered to be in the innovation phase by funders which in turn frames the attitude of policy makers as risky and for venture capitalists. In South Africa, where a modular and efficient FT plant was developed off the back of the existing Sasol technology, there is less of a push-back. In other regions the successful commissioning and operation of a BTL plant in a third party location would encourage policy-makers to be more inclined to include this category in future planning.

5.2 RESULTS

The semi structured interviews proved to be an effective tool for the thesis research and assisted in providing a deeper understanding of several aspects associated with the BTL technology because of the first-hand experience of the experts and researchers in the BTL industry. The most important points relevant to the research have been:

- BTL derived fuels are of similar characteristics as the fuels derived from conventional oil. BTL can serve as an excellent alternative to produce clean burning fuels and high quality chemical products.
- BTL is established as a carbon neutral process and hence its development and reduced reliance on fossil fuels will help condense environmental stress and reduce GHG emissions.
- Commercial implementation can be made successful by technological advancements in order to optimize the process efficiency and by bringing down the plant construction as and operational costs.
- Technologically, gasification stage should be improved by developing high efficiency gasifiers to effectively process biomass.
- Several small scale plants should be set up at multiple distant locations instead of a large single facility. This approach will supply adequate feed for each plant in a short radius, bring down the cost per plant and provide a large cumulative output.
- Utilization of major wastes and by products generated from the BTL process is a key element to develop an environmental friendly smart BTL facility. Details are presented in the next chapter.

Chapter 6: Developing a Smart BTL Facility

The concept of a smart BTL facility is based on the idea that the BTL plant operates sustainably by effectively utilizing all the waste and by-product streams in a cost effective way and produce extra value. The plant should be self-sufficient and operate at high efficiency to maximize yield of the desired output while reducing the waste generated. The major waste or by-products of the process are identified as CO_2 emissions, waste water and biochar. The methods described below can be integrated with a small scale BTL facility to promote sustainability:

6.1 CO_2 Emission Reduction

Although it has been drawn from the literature and interviews that CO_2 produced is carbon neutral, it is of added environmental benefit to limit these emissions through Carbon Capture and Sequestration (CCS). CCS is capable to collect up to 90% of the CO_2 emitted, which can be transported and stored deep under the earth's surface between rock formations (Backus 2017). The technology however is very expensive to integrate with industrial processes (Rissman and Orvis 2017). Hence, CCS is not a viable option for the BTL, especially at this point when the industry is in early phase of development. Therefore, other cost effective and efficient methods should be employed.

One promising method to utilize the CO_2 emitted is by supplying it to greenhouses through CO_2 supplementation. According to the experts and researchers interviewed, it is considered a practical and cost effective approach for BTL towards minimizing CO_2 emissions. There are numerous studies that have shown the benefit of supplying CO_2 in greenhouses and one study conducted by Oklahoma State University demonstrates that some plants displayed 40% to

100% of an increase in yield when exposed to higher concentrations of CO_2 levels. This can be seen in Figure 5.1 (Poudel and Dunn 2017).

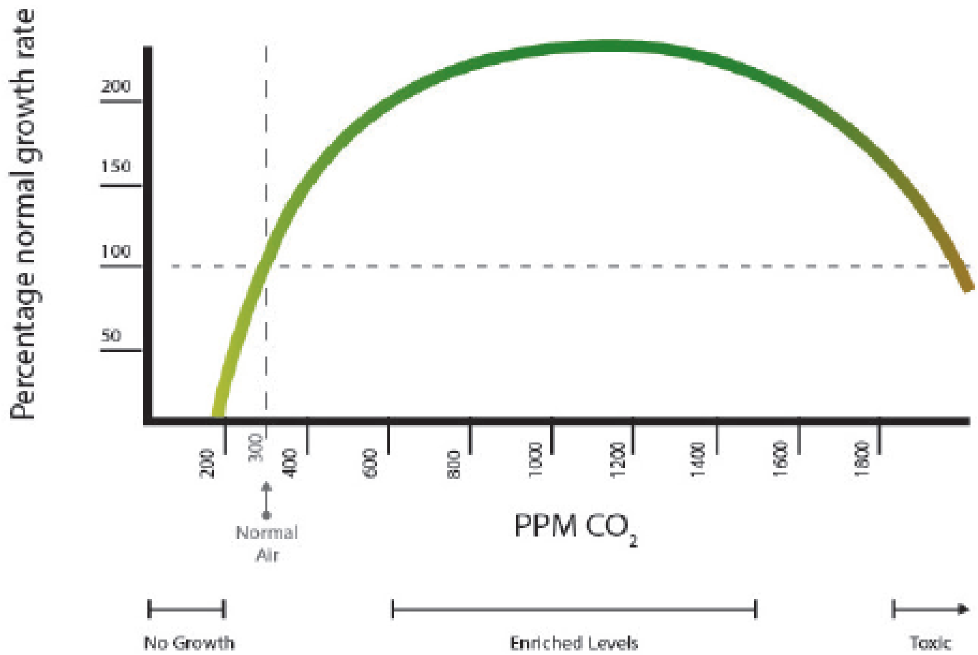


Figure 22. Effect of CO_2 concentration on plant growth
Source: (Poudel and Dunn 2017)

The CO_2 is utilized during photosynthesis; a chemical process that occurs in plants which uses light energy to convert carbon dioxide and water into glucose and oxygen (Blom et al. 1984). Photosynthesis reaction is the following:

$$6\ CO_2 + 12\ H_2O + \text{light} \longrightarrow C_6H_{12}O_6 + 6\ H_2O + 6\ O_2 \text{ (Paerl 2007)}$$

Carbon dioxide concentration in ambient air is around 400 ppm, which can drop significantly to only 150 to 200 ppm, inside a closed environment such as greenhouse. This is because during the day the carbon dioxide available gets used up by the plants. The study reveals that maximum growth rate of plants occur in the range 800 to 1000 ppm, while very high CO_2 concentrations can cause damage to the plants (Poudel and Dunn 2017).

Other benefits of CO_2 supplementation in greenhouses include higher plant growth rates and biomass production, reduced fertilizer costs and reduction in water use. Although, it should be acknowledged that CO_2 supplementation by itself cannot provide a higher yield. Other elements such as temperature, water, sunlight and nutrients need to be provided in the correct amounts to facilitate plant growth and obtain a higher output (Poudel and Dunn 2017).

6.2 Waste Water Treatment

As discussed during the interviews, waste water in the BTL process is produced from Gasification and Fischer Tropsch synthesis stages.

Gasification waste water is a result of wet scrubbing cleaning method, which uses water as a cleaning agent to remove a range of organic and inorganic contaminants from the raw producer gas (Mehta and Chavan 2009). The composition and concentration of the contaminants in the waste water may vary greatly depending on the gasifier type, feed used and the operating conditions, but mainly consists of tars, soot and ash which heavily pollute the cleaning water (Jeswani and Mukherji 2015; Tripathi et al. 2013). Therefore, the waste water must be treated before it is released in the environment (Mehta and Chavan 2009).

Major organic component in gasification waste water is tar, which consists of several acidic, alkaline and neutral compounds. Polyaromatics are mainly the alkaline compounds while phenols and acids are the acidic compounds. Major inorganic component of this waste water includes ammonia and some concentrations of hydrogen sulphide and chlorides (Tripathi et al. 2013). Physico-chemical Treatment of such tar rich waste water can be done by first treating the waste water with lime and alum to remove inorganic compounds and then adsorption over activated carbon to remove the organic compounds (Mehta and Chavan 2009). Activated carbon, also known as activated charcoal, is a carbon rich material that has high porosity and a large surface area, making it an excellent absorbent for several industrial and environmental applications (Çeçen 2014).

Charcoal for this treatment becomes readily available on site as a residue from biomass gasification. The charcoal can be thermally treated for activation and then can be used for water treatment purposes (Tripathi et al. 2013). Since the charcoal comes from biomass, it can also be called "Biochar". This water treatment method has been studied and experimented by Mehta & Chavan (2009) and Tripathi et al. (2013).Their work proved that the treatment method using biochar is effective at cleaning the polluted water and making it more suitable to be recycled in the process for gas cleaning which reduces the water requirement the plant (Tripathi et al. 2013). The treated water is also fit for being disposed-off in the environment safely or to be used for irrigation purposes (Mehta and Chavan 2009).

This method is relatively simple, cost effective and efficient for treating gasification waste water compared to other physical and chemical water treatment techniques. Physical methods make use of UV light to promote wet-oxidation while chemical treatment involves precipitating using iron and aluminium salts. These methods are efficient at treating waste water but are not recommended because of high energy consumption for UV light and the high cost of chemicals (Mehta and Chavan 2009).

Fischer Tropsch waste water in the BTL process is a result of water producing reactions occurring during FT synthesis of syngas into syncrude. These reactions are presented in the literature review (Eq. 2.1 to 2.5). The FT water is produced in large amounts; depending on the process conditions, 1 ton of hydrocarbon produced can be accompanied with around 1.1 to 1.3 tons of FT waste water (Wang et al. 2017).

The FT water is considered the most undesirable by-product of the Fischer Tropsch process (Dalai and Davis 2008). It is characterised by a high COD value (30g/L) and a low pH due to its acidic nature and needs to be properly treated before it is released in the environment (Wang et al. 2017). The chemical oxygen demand (COD) value is commonly used to indicate the amount of organic compounds present in wastewater, and it can be defined as the amount of oxygen required for the oxidation of organic compounds present in water (Yao et al. 2014). Such type of industrial waste water, high in COD value and low pH, is considered best treated using techniques based on anaerobic digestion (Majone et al. 2010).

Constructed Wetlands (CWs) are highly efficient in treating wastewater and are considered a cost effective and simple solution for water purification (Herath and Vithanage 2015). They are designed to function using the same processes that occur in natural wetlands, involving plantation and microbes, to improve the quality of wastewater (Lesikar 1999; Shelef et al. 2013). Constructed Wetlands not only effectively reduce the COD of waste water, but are reliable for removing metals, total suspended solids (TSS) and organic compounds (USEPA 2000). Additionally, they are efficient at neutralizing acidic water (Prasad and Shih 2016). A SRM University study showed a drastic decrease of 76.16 % for COD of sewage water sample treated by a pilot scale constructed wetland (Sudarsan et al. 2015). While several other studies have confirmed the ability of CWs to raise the pH of waste water from pH levels lower than 4 to above 7. (Eger and Wagner 2003).

Major types of CWs are Surface flow and Sub surface flow. Surface flow constructed wetlands, also called free water surface (FWS) CWs are characterised by a shallow depth of waters with floating, submerging and emergent aquatic plantation (Halverson 2004; Hiraishi et al. 2014).

Surface flow CWs are capable of effectively removing organic compounds present in wastewater by the help of microbial degradation and by settling suspended particles. Successful utilization of Surface flow CW has treated a range of wastewater from agriculture, mining, paper, refinery and metal industries (Vymazal 2010). Figure 23 shows a diagram of a surface flow constructed wetland.

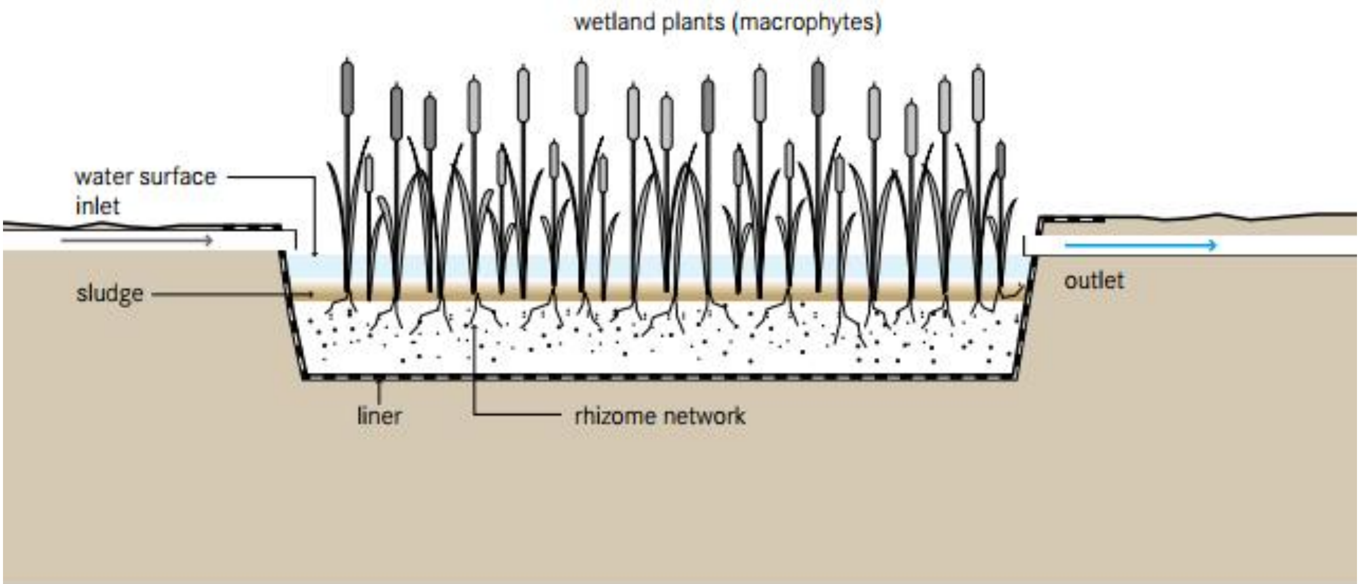


Figure 23. Schematic of a free water-surface constructed wetland
Source: (Tilley et al. 2014)

Horizontal subsurface flow constructed wetlands (HSSF CWs) are comprised of a bed of gravel, covered by an impermeable layer. The wastewater flows from the inlet and passes the porous medium under the surface of the bed, planted with emergent vegetation, horizontally to be discharged at the outlet. This way the wastewater gets in contact with aerobic, anaerobic and anoxic zones where the contaminants are removed by microbial activity and various physical and chemical processes. Most of the bed consists of anaerobic zone. HSSF CWs can be used for wastewater treatment in petrochemical, chemical, textile, paper and food industry (Vymazal 2010; Hiraishi et al. 2014). Figure 24 shows a diagram of a HSSF CW.

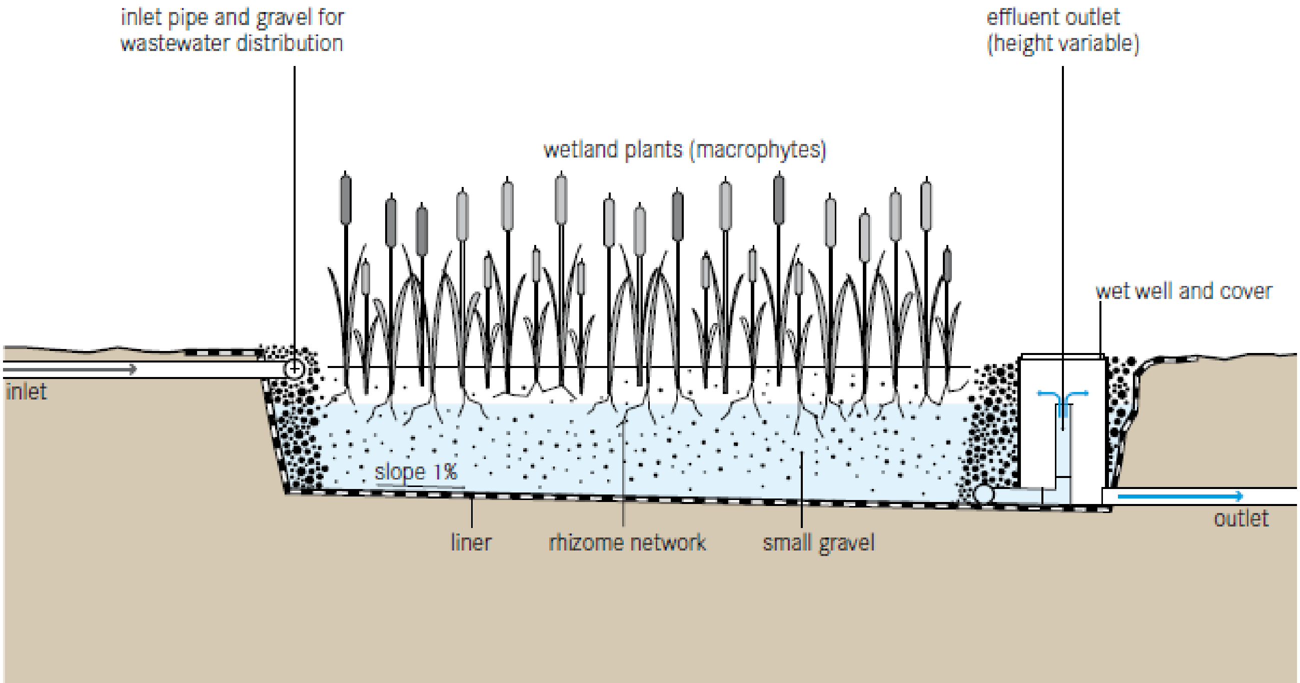


Figure 24. Schematic of a horizontal subsurface flow constructed wetland
Source: (Tilley et al. 2014)

Constructed wetlands are an ideal option for small to medium water treatment applications, up to 60 gallons/day. Apart from their high efficiency in water treatment applications, other advantages include minimum energy, labor and maintenance requirements. CWs are not only cost effective to build but also to operate (USEPA 2000). All these advantages make constructed wetlands an excellent choice for treating FT waste water in BTL facilities, which are much smaller in scale compared to GTL and CTL plants. Use of CWs will develop a BTL facility towards higher sustainability and reduce environmental stress which other energy intensive methods demonstrate.

6.3 Biochar Utilization

Biochar, a residue of biomass gasification in the BTL process has several applications in the field of environmental management. This includes soil improvement, waste management, climate change mitigation and energy production (Benedetti et al. 2017; Amin et al. 2016). Apart from its use in waste water treatment applications, this research will highlight the utilization and effectiveness of biochar in soil improvement.

The physical properties of biochar, such as its low density and high adsorptive characteristics, makes it suitable for use in agricultural and industrial applications (Quinn 2017). Properties of biochar produced are highly influenced by the type of feedstock and process conditions such as temperature, processing time and particle size etc. (Amin et al. 2016).

Biochar is characterized by macropores (<50 nm pore dia) and micropores (< 2 nm pore dia). The micropores are useful in filtration applications, while the macropores are excellent for soil amendment. Due to a highly porous structure, biochar facilitates good water absorptivity, soil aeration and provides a habitat for healthy microbial organisms. Biochar also helps increase cation exchange capacity, macronutrient and organic matter content in the soil (Quinn 2017). Biochar can directly be fed in the soil or can be mixed with other solid or liquid soil amendments (Camps and Tomlinson 2015). Application of Biochar may also promote a rise in total pH of soil, which makes it a substitute of the customary method of using lime to increase soil pH (Quinn 2017).

Several studies have successfully demonstrated improvements in crop yield by addition of biochar to the soil. For example, a field experiment by Yang et al. (2015) shows a 20% increase in yield of corn, peanut and wheat crops when rice straw derived biochar was added at to the soil 4 ton/ha. Another study by Carter et al. (2013) demonstrated higher yield output, by application of rice husk derived biochar, on lettuce and cabbage, in sandy and acidic soil, both with and without use of local fertilizer.

During gasification, the biochar is accompanied with production of some ash. Ash primarily contains metals and minerals such as iron, copper, manganese, potassium, calcium and phosphorus, and has a low carbon content (Klinghoffer et al. 2011). Biomass derived ash can also be used as a natural soil amendment to return the lost metals and minerals to the soil and improve its quality. The study by Saletnik et al. (2016) confirms that application of ash, both with and without biochar, results in significant plant growth.

Other advantages of biochar include reduction in odor, nitrogen loss and greenhouse gas emissions when mixed with other soil amendments such as manure and compost (Camps and Tomlinson 2015). A BTL facility should consider biochar and ash as valuable by products and utilize them to return the nutrients to the soil. This can be practiced at the source of biomass production, to encourage a higher yield of biomass output which can then be used in the BTL process again.

6.4 BTL Smart Facility Schematic

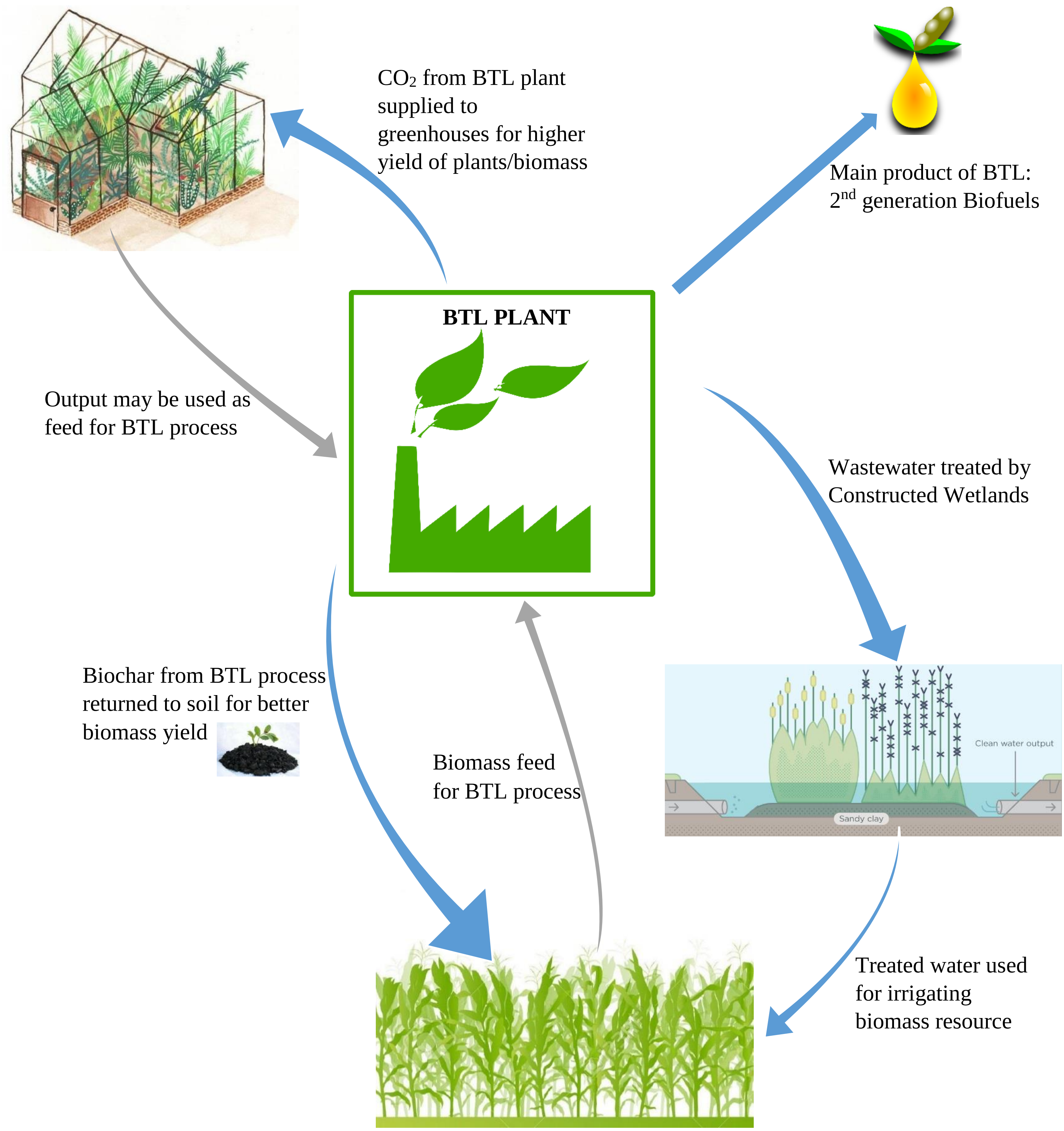


Figure 25. Schematic of a BTL facility integrating waste management system for all major waste streams and utilizing by-products

Chapter 7: Conclusion & Recommendations

The study demonstrated that BTL processes can have significant environmental benefits, especially with respect to reduced emissions, when compared to conventional fossil fuel production and use. Though it should be realized that the BTL industry is relatively new, because of which the costs related to construction and operation of BTL processes are high. The industry will only thrive if the cost of BTL derived fuel competes with conventional oil prices. BTL processes can be made economical by making advancements in technology and strategically developing the industry. The idea of starting with small scale BTL facilities and building several facilities one after the other, brings an opportunity to grow. It should also be taken into account that favorable environmental and energy policies, alongside appropriate government support are also important variables that can steer the industry towards progression in the future.

Moreover, the thesis has discussed methods by which a BTL facility can be enhanced to promote sustainability and device opportunities to self-sustain. The concept of a smart BTL facility promotes a waste management system, which is easy to adopt and reduces our existing reliance on expensive and energy intensive mechanical/engineering methods. The system however should be properly maintained ensuring all the by-products, originating from biomass feed and BTL process, are safely returned to nature and thus, forms a closed loop cyclic system as demonstrated in figure 25. This would not only add to the economic value of the process, but also create social value by safeguarding the environment. The simulation design of a small BTL facility demonstrated effectiveness of producing substantial quantities of liquid fuel mix using forest waste. Such a small sized facility has the potential to be developed in protected areas/national parks where biomass is abundant and the produced fuel can be effectively utilized within the park or sold in the market. Such a system has the capacity to provide jobs for farmers and other unskilled workers and can prove to be advantageous especially for developing countries where biomass resources are abundant. National parks also offer the advantage of easily integrating the BTL facility with wetlands for wastewater treatment due to the availability of space, and CO_2 supplementation because of abundance of plants. Biochar can find its application in nurturing soil to facilitate growth of indigenous plant and tree species being protected in the national park/protected area, forming a similar waste management system as witnessed in figure 25.

Although BTL requires time to reach a point when the process becomes economically feasible, it is only then that is able to provide considerable environmental benefits by replacing fossil fuels. BTL has the potential to become the technology of the future as fossil fuels near depletion, until this point extensive work needs to be done to research and develop this technology.

References

Alam, F., Mobin, S., and Chowdhury, H. 2015. Third Generation Biofuel from Algae. *Procedia Engineering* 105: 763–68.

Abbas, S.K., Ibrahim, W., and Hameed, Zahra. 2017. Improvement of Gasoline Production. Accessed July 29. URL: https://www.researchgate.net/profile/Sajjad_Abbas2/publication/301754872_Improvemet_of_Gasoline_Production/links/5725ec6308aee491cb3eb4ef.pdf.

Amin, F.R., Huang, Y., He, Y., Zhang, R., Liu, G., and Chen, C. 2016. Biochar Applications and modern techniques for characterization. *Clean Technologies and Environmental Policy* 18 (5): 1457–73.

Andrews, A.P., and Logan, J. 2008. *Fischer-tropsch fuels from coal, natural gas, and biomass: background and policy*. Congressional Research Service, Library of Congress. http://large.stanford.edu/courses/2012/ph240/jorna1/docs/RL34133.pdf.

Ail, S.S., and Dasappa, S. 2016. Biomass to liquid transportation fuel via fischer tropsch synthesis – technology review and current scenario. *Renewable and Sustainable Energy Reviews* 58 (May): 267–86.

Backus, W. 2017. Carbon Capture Technology. *Technoeconomic Evaluation of Absorption, Gasification, and Oxy-Coal Combustion for Coal Power Plants.-2010.-20 P*. Accessed July

Benedetti, V., Patuzzi, F., and Baratieri, M. 2017. Gasification char as a potential substitute of activated carbon in adsorption applications. *Energy Procedia* 105 (May): 712–17.

Blom, T.J., Straver, W.A., Ingratta, F.J., Khosla, S., and Brown, W. 1984. *Carbon Dioxide in Greenhouses*. Ontario: Ministry of Agriculture and Food. URL: http://webinfotech.tzo.com/Gardening101../How%20to%20PDF's/Greenhouses.CarbonDioxideInGreenhouses.pdf.

Bodhanwalla, H., and Ramachandran, M. 2017. Parameters Affecting the Fluidized Bed Performance: A Review. *REST Journal on Emerging trends in Modelling and Manufacturing* 3(1): 17–21

Boerrigter, H., and Rauch, R. 2006. Review of applications of gases from biomass gasification. *ECN Biomass, Coal & Environmental research*. Vienna, University of Technology, Institute of Chemical Engineering

Boerrigter, H., Calis, H.P., Slort, D.J., and Bodenstaff, H. 2004. *gas cleaning for integrated biomass gasification (BG) and fischer-tropsch (FT) systems; Experimental Demonstration of Two BG-FT Systems*. Report no. RX--04-041. Sint Maartensvlotbrug: Energy research Centre of the Netherlands (ECN)

Buckeridge, M.S., and Souza, A.P.D. 2017. *Advances of Basic Science for Second Generation Bioethanol from Sugarcane*. Cham: Springer International Publishing.

Barta-Rajnai, E., Jakab, E., Sebestyén, Z., May, Z., Barta, Z., Wang, L., Skreiberg, Ø., Grønli, M., Bozi, J., and Czégény, Z. 2016. Comprehensive compositional study of torrefied wood and herbaceous materials by chemical analysis and thermoanalytical methods. *Energy & Fuels* 30 (10): 8019–30.

Basu, P. 2006. *Combustion and Gasification in Fluidized Beds*. CRC press.

Couto, N., Rouboa, A., Silva, V., Monteiro, E., and Bouziane, K. 2013. Influence of the biomass gasification processes on the final composition of syngas. *Energy Procedia* 36: 596–606.

Çeçen, F. 2014. Activated Carbon. In *Kirk-Othmer Encyclopedia of Chemical Technology*, edited by John Wiley & Sons Inc, 1–34. Hoboken: John Wiley & Sons, Inc.

Damartzis, T., and Zabaniotou, A. 2011. Thermochemical Conversion of Biomass to Second Generation Biofuels through Integrated Process Design—A Review. *Renewable and Sustainable Energy Reviews* 15 (1): 366–78.

Demirbas, A. 2007. Progress and recent trends in biofuels. *Progress in Energy and Combustion Science* 33 (1): 1–18.

Demirel, Y. 2012. Energy and Energy Types. In Energy, 27–70. Green Energy and Technology. London: Springer.

Ehrig, R. and Dallos, M. 2009. *Survey on European 2nd generation biofuels technology suppliers.* Report prepared for the Department of Foreign Affairs and International Trade – Embassy of Canada and Agriculture and Agri-food Canada. Wieselburg: BIOENERGY 2020+.

Food and Agriculture Organization of the United Nations (FAO). 2008. Biofuels: prospects, risks and opportunities. The state of food and agriculture 2008. Rome: Food and Agriculture Organization of the United Nations

Foust, T.D., Aden, A., Dutta, A., and Phillips, S. 2009. An Economic and Environmental Comparison of a Biochemical and a Thermochemical Lignocellulosic Ethanol Conversion Processes. *Cellulose* 16 (4): 547–65.

Food and Agriculture Organization (FAO). 1986. *Wood gas as engine fuel*. FAO Forestry Paper 72. Rome.

Gray, D., White, C., Tomlinson, G., Ackiweicz, M., Schmetz, E., and Winslow, J. 2007. *Increasing Security and Reducing Carbon Emissions of the U. S. Transportation Sector: Transformational Role for Coal with Biomass*. Noblis, Incorporated

Gomiero, T. 2015. Are Biofuels an Effective and Viable Energy Strategy for Industrialized Societies? A Reasoned Overview of Potentials and Limits. *Sustainability* 7 (7): 8491–8521.

Goyal, H.B., Seal, D., and Saxena, R.C. 2008. Bio-Fuels from thermochemical conversion of renewable resources: a review. *Renewable and Sustainable Energy Reviews* 12 (2): 504–17.

Hughes, S., Gibbons, W., Moser, B., and Rich, J. 2013. Sustainable multipurpose biorefineries for third-generation biofuels and value-added co-products. In *Biofuels - Economy, Environment and Sustainability*, ed. by Z. Fang. Rijeka: InTech.

Hofbauer, H., Rauch, R., and Ripfel-Nitsche, K. 2007. Work package 2e: gas treatment. Vienna, University of Technology Institute of Chemical Engineering. URL:

https://ec.europa.eu/energy/intelligent/projects/sites/iee-projects/files/projects/documents/thermalnet_report_on_syngas_cleaning.pdf

Hugues, F., and Marion, M.-C. 2012. *Method for optimizing the operation of a unit for the synthesis of hydrocarbons from a synthesis gas*. Google Patents. URL: https://www.google.com/patents/US8278364.

Henrici-Olivé, G., and Olive, S. 1976. The fischer-tropsch synthesis: molecular weight distribution of primary products and reaction mechanism. *Angewandte Chemie International Edition* 15 (3): 136–141

Hu, J., Yu, F., and Lu, Y. 2012. Application of Fischer–Tropsch Synthesis in Biomass to Liquid Conversion. *Catalysts* 2 (4): 303–26.

Haszpra, L. 2010. *Atmospheric greenhouse gases: the Hungarian perspective*. Singapore: Springer Science & Business Media.

Inayat, A., Ahmad, M.M., Yusup, S., and Mutalib, M.I.A. 2010. Biomass Steam Gasification with In-Situ CO2 Capture for Enriched Hydrogen Gas Production: A Reaction Kinetics Modelling Approach. *Energies* 3 (8): 1472–84.

Lualdi, M. 2012. Fischer-tropsch synthesis over cobalt-based catalysts for btl applications. Stockholm: Chemical Science and Engineering, KTH Royal Institute of Technology.

Klerk, A. de. 2011. *Fischer-Tropsch Refining*. Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA.

Karlen, D.L. 2014. *Cellulosic Energy Cropping Systems*. Chichester, West Sussex: John Wiley & Sons.

Kumar, A., Jones, D.D., and Hanna, M.A. 2009. Thermochemical biomass gasification: a review of the current status of the technology. *Energies* 2 (3): 556–81.

Lee, S.-W., Park, J.-S., Lee, C.-B., Lee, D.-W., Kim, H., Ra, H.W., Kim, S.-H., and Ryi, S.-K. 2014. H2 recovery and co2 capture after water–gas shift reactor using synthesis gas from coal gasification. *Energy* 66 (March): 635–42.

Lee, K.T., and Ofori-Boateng, C. 2013. Sustainability of Biofuel Production from Oil Palm Biomass. Singapore: Springer Science & Business Media.

Mabee, W., and Saddler, J. 2008. *From 1st-to 2nd-Generation BioFuel technologies*. An Overview of Current Industry and RD&D Activities. Paris: IEA Bioenergy. URL: http://environmentportal.in/files/2nd_Biofuel_Gen.pdf.

Maitlis, P.M., and Klerk, A. de. 2013. *Greener Fischer-Tropsch Processes for Fuels and Feedstocks*. Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA, owned by John Wiley & Sons.

McKendry, P. 2002. Energy production from biomass (part 3): gasification technologies. *Bioresource Technology* 83 (1): 55–63.

Naik, S.N., Goud, V.V., Rout, P.K., and Dalai, A.K. 2010. Production of first and second generation biofuels: a comprehensive review. *Renewable and Sustainable Energy Reviews* 14 (2): 578–97.

National Science Technology and Innovation Policy Office (STI) and UNEP Risø Centre on Energy, Climate and Sustainable Development (URC). 2012. *Technology needs assessments report for climate change – mitigation.* Thailand: National Science Technology and Innovation Policy Office

Paethanom, A., and Yoshikawa, K. 2012. Influence of pyrolysis temperature on rice husk char characteristics and its tar adsorption capability. *Energies* 5 (12): 4941–51.

Ullah, K., Ahmad, M., Sofia, Sharma, V.K., Lu, P., Harvey, A., Zafar, M., Sultana, S., and Anyanwu, C.N. 2014. Algal biomass as a global source of transport fuels: overview and development perspectives. *Progress in Natural Science: Materials International* 24 (4): 329–39.

University of South Africa (UNISA). Facts & Figures. 2017. Accessed July 31. URL: http://www.unisa.ac.za/sites/corporate/default/About/Facts-&-figures.

________. 2017. Material and Process Synthesis Research Unit. Accessed July 26. URL: http://www.unisa.ac.za/sites/corporate/default/Colleges/Science,-Engineering-&-Technology/Research/Material-and-Process-Synthesis.

_______. 2017. Commercialisation at MaPS. Accessed July 31. http://www.unisa.ac.za/sites/corporate/default/Colleges/Science,-Engineering-&-Technology/Research/Material-and-Process-Synthesis/Commercialisation-at-MaPS.

________. 2017. Research at MaPS. Accessed July 26. URL: http://www.unisa.ac.za/sites/corporate/default/Colleges/Science,-Engineering-&-Technology/Research/Material-and-Process-Synthesis/Research-at-MaPS.

________.2017. Commercialisation at MaPS. Accessed July 26. URL: http://www.unisa.ac.za/sites/corporate/default/Colleges/Science,-Engineering-&-Technology/Research/Material-and-Process-Synthesis/Commercialisation-at-MaPS.

Van der Drift, A., and Boerrigter, H. 2006. Synthesis gas from biomass for fuels and chemicals. ECN Biomass, Coal and Environmental research. Report is the result of the workshop, Hydrogen and synthesis gas for fuels and chemicals. URL: http://www.ecn.nl/docs/library/report/2006/c06001.pdf

Varbanov, P., Thessalonikēs, A.P., and Associazione Italiana di Ingegneria Chimica (AIDIC). 2013. 16th Conference on Process Integration, Modelling and Optimisation for Energy Saving and Pollution Reduction, PRES'13: 29 September - 2 October 2013, Rhodes, Greece. Chemical Engineering Transactions 35. Milano: Associazione Italiana di Ingegneria Chimica.

Wikipedia (Wiki). 2017. University of South Africa. Accessed July 26. URL: https://en.wikipedia.org/w/index.php?title=University_of_South_Africa&oldid=791567850.

Williams, Robert B. and Kaffka, Stephen. 2015. Biomass gasification. Report prepared for California Energy Commission. Davis: California Biomass Collaborative, University of California.

Swanson, R.M., Satrio, J.A., Brown, R.C., Platon, A., and Hsu, D.D. 2010. *Techno-Economic Analysis of Biofuels Production Based on Gasification.* Report prepared for the National Renewable Energy Laboratory. Colorado: National Renewable Energy Laboratory.

Sims, R.E.H., Mabee, W., Saddler, J.N., and Taylor, M. 2010. An Overview of Second Generation Biofuel Technologies. *Bioresource Technology* 101 (6): 1570–80.

Sen, B. 2014. Technical Barriers to Advanced Liquid Biofuels Production via Biochemical Route. In *Liquid Biofuels: Emergence, Development and Prospects*, eds. A.D., Padula, M. S., dos Santos, O.M., Santos, and D., Borenstein, 27:189–204. London: Springer London.

Sharma, A., Verma, R., and TARA. 2013. *Biomass estimation and methodology - village electrification through sustainable use of renewable energy (VE-SuRE)*. Report prepared for the Swiss Agency for Development and Cooperation (SDC).

Thompson, P. 2012. The Agricultural Ethics of Biofuels: The Food vs. Fuel Debate. *Agriculture* 2 (4): 339–58.

Zeisler, J., Kleinhappl, M., and Hofbauer, H. 2010. *Reliable sampling of impurities in product gas and syngas*. Vienna University of Technology, Institute of Chemical Engineering. URL: http://bioenergy2020.eu/app/webroot/files/file/Download/ICPS10_paper_Zeisler_final.pdf.

Jones, D.S.J., and Pujadó, P.R. 2006. *Handbook of Petroleum Processing*. Cham: Springer Science & Business Media.

Novotny, E.H., Maia, C.M.B. de F., Carvalho, M.T. de M., Madari, B.E., Novotny, E.H., Maia, C.M.B. de F., Carvalho, M.T. de M., and Madari, B.E. 2015. BIOCHAR: pyrogenic carbon for agricultural use - a critical review. *Revista Brasileira de Ciência Do Solo* 39 (2): 321–44.

Roos, C.J. 2010. *Clean Heat and Power Using Biomass Gasification for Industrial and Agricultural Projects*. Olympia: Washington State University Extension Energy Program URL: https://pdfs.semanticscholar.org/8cc5/08891bdef421e671726842513bbf65f45738.pdf.

Rédei, K., Osvath-Bujtas, Z., Veperdi, I., and others. 2008. Black locust (robinia pseudoacacia l.) improvement in Hungary: a review. *Acta Silvatica et Lignaria Hungarica* 4: 127–132.

Speight, J.G. 2015. *Ultimate Analysis. Handbook of Coal Analysis*. John Wiley & Sons, Inc.

Nayak, R., and Mewada, R.K. 2011. Simulation of coal gasification process using ASPEN PLUS. In Proceedings of the International Conference On Current Trends In Technology: Nuicone. http://nuicone.org/site/common/proceedings/Chemical/oral/CH_18.pdf.

Rodríguez-Olalde, N.E., Mendoza-Chávez, E.A., Castro-Montoya, A.J., Saucedo-Luna, J., Maya-Yescas, R., Rutiaga-Quiñones, J.G., and Ortega, J.M.P. 2015. Simulation of syngas production from lignin using guaiacol as a model compound. *Energies* 8 (7): 6705–14.

Rupesh, S., Muraleedharan, C., and Arun, P. 2016. ASPEN plus Modelling of Air–steam Gasification of Biomass with Sorbent Enabled CO2 Capture. *Resource-Efficient Technologies* 2 (2): 94–103.

Nafees, A., and Al Hashimi, S.H. 2017. Fischer Tropsch Gas To Liquid Technology (GTL). Accessed July 26. http://www.energy-2030.com/08/pdfs/r-t2-1.pdf.pdf

Rissman, J. and Orvis, R. 2017. Carbon Capture and Storage: An Expensive Option for Reducing U.S. CO2 Emissions. *Forbes*. July 10.

Poudel, M. and Dunn, B. 2017. Greenhouse carbon dioxide supplementation. Oklahoma State University.

Paerl, H. W**.** 2007. Primary Productivity and Producers. *Manual of Environmental Microbiology, Third Edition*, eds. C. J. Hurst, R. L. Crawford, J. L. Garland, D. A. Lipson, A. L. Mills, L. D. Stetzenbach, 407-420. Washington DC: ASM Press.

Mehta, V., and Chavan, A. 2009. Physico-Chemical Treatment of Tar-Containing Wastewater Generated from Biomass Gasification Plants. *World Academy of Science, Engineering and Technology*. 57: 161–168.

Jeswani, H., and Mukherji, S. 2015. Treatment of Simulated Biomass Gasification Wastewater of Varying Strength in a Three Stage Rotating Biological Contactor. *Chemical Engineering Journal* 259 (January): 303–12.

Tripathi, L., Dubey, A.K., Sandip, G., and Singh, P.L. 2013. Waste Water Treatment of Biomass Based Power Plant. *International Journal of ChemTech Reseacrch* 5 (2): 761–764.

Wang, D., Ma, W., Han, H., Li, K., and Hao, X. 2017. Enhanced Treatment of Fischer–Tropsch (F-T) Wastewater by Novel Anaerobic Biofilm System with Scrap Zero Valent Iron (SZVI) Assisted. *Biochemical Engineering Journal* 117 (January): 66–76.

Dalai, A.K., and Davis, B.H. 2008. Fischer–Tropsch Synthesis: A Review of Water Effects on the Performances of Unsupported and Supported Co Catalysts. *Applied Catalysis A: General* 348 (1): 1–15.

Yao, N., Wang, J., and Zhou, Y. 2014. Rapid Determination of the Chemical Oxygen Demand of Water Using a Thermal Biosensor. *Sensors* 14 (6): 9949–60.

Majone, M., Aulenta, F., Dionisi, D., D'Addario, E.N., Sbardellati, R., Bolzonella, D., and Beccari, M. 2010. High-Rate Anaerobic Treatment of Fischer–Tropsch Wastewater in a Packed-Bed Biofilm Reactor. *Water Research* 44 (9): 2745–52.

Herath, I., and Vithanage, M. 2015. Phytoremediation in Constructed Wetlands. In *Phytoremediation*, edited by Abid Ali Ansari, Sarvajeet Singh Gill, Ritu Gill, Guy R. Lanza, and Lee Newman, 243–63. Cham: Springer International Publishing.

Shelef, O., Gross, A., and Rachmilevitch, S. 2013. Role of Plants in a Constructed Wetland: Current and New Perspectives. *Water* 5 (2): 405–19

Lesikar, B.J. 1999. *Constructed Wetlands*. Texas Agricultural Extension Service, Texas A & M University System. URL: http://lubbock.tamu.edu/files/2011/10/2074410-L52301.pdf

Prasad, M.N.V., and Shih, K. 2016. *Environmental Materials and Waste: Resource Recovery and Pollution Prevention*. London: Academic Press.

Sudarsan, J.S., Roy, R.L., Baskar, G., Deeptha, V.T., and Nithiyanantham, S. 2015. Domestic Wastewater Treatment Performance Using Constructed Wetland. *Sustainable Water Resources Management* 1 (2): 89–96.

Eger, P., and Wagner, J. 2003. Wetland Treatment Systems–How Long Will They Really Work. In *Sudbury 2003 Mining and the Environment Conference*. URL: http://pdf.library.laurentian.ca/medb/conf/Sudbury03/Wetlands/38.pdf.

Halverson, N. 2004. *Review of Constructed Subsurface Flow vs. Surface Flow Wetlands*. Savannah River Site (US). URL: https://www.osti.gov/scitech/biblio/835229

Hiraishi, T., Krug, T., Tanabe, K., Srivastava, N., Baasansuren, J., Fukuda, M., and Troxler, T.G. 2014. *2013 supplement to the 2006 ipcc guidelines for national greenhouse gas inventories: wetlands*. URL: http://www.ipcc-nggip.iges.or.jp/public/wetlands/

Vymazal, J. 2010. Constructed wetlands for wastewater treatment. *Water* 2 (3): 530–49.

Tilley, E., Ulrich, L., Lüthi, C., Reymond, Ph., Schertenleib, R. and Zurbrügg, C. 2014. *Compendium of Sanitation Systems and Technologies. 2nd Revised Edition*. Dübendorf: Swiss Federal Institute of Aquatic Science and Technology (Eawag).

United States Environmental Protection Agency (USEPA). 2000. *Wastewater Technology Fact Sheet – Wetlands: Subsurface Flow*. Washington, D.C.: United States Environmental Protection Agency Office of Water.

Quinn, D. 2017. Biochar: industrial applications a white paper. Accessed July 29. URL: http://whole-energy.com/wp-content/uploads/2015/04/Biochar-White-Paper-Mar-6.pdf.

Camps, M., and Tomlinson, T. 2015. The use of biochar in composting. *International Biochar Initiative. Www. Biochar International. Org*. URL: http://www.terutalk.com/Articles/201502-Compost_and_biochar_IBI.pdf.

Klinghoffer, N., Castaldi, M.J., and Nzihou, A. 2011. *Beneficial use of ash and char from biomass gasification*. In Proceedings of the 19th Annual North American Waste-to-Energy Conference NAWTEC19 May, 16–18. URL: http://proceedings.asmedigitalcollection.asme.org/pdfaccess.ashx?url=/data/conferences/nawtec19/70269/13_1.pdf.

Carter, S., Shackley, S., Sohi, S., Suy, T., and Haefele, S. 2013. The impact of biochar application on soil properties and plant growth of pot grown lettuce (lactuca sativa) and cabbage (brassica chinensis). *Agronomy* 3 (2): 404–18.

Yang, Y., Ma, S., Zhao, Y., Jing, M., Xu, Y., and Chen, J. 2015. A field experiment on enhancement of crop yield by rice straw and corn stalk-derived biochar in northern China. *Sustainability* 7 (10): 13713–25.

Saletnik, B., Bajcar, M., Zaguła, G., Czernicka, M., and Puchalski, C. 2016. influence of biochar and biomass ash applied as soil amendment on germination rate of virginia mallow seeds (sida hermaphrodita R.). *ECONTECHMOD: An International Quarterly Journal on Economics of Technology and Modelling Processes* 5 (3): 71-76

Appendix

QUESTIONARE
Biomass to Liquid via Fischer Tropsch

This Questionnaire is designed to interview experts in the field of Biomass to Liquid (BTL) conversion technology. The purpose is to gain first-hand knowledge about the benefits, drawbacks and opportunities of the concerned technology.

Interviewee name:

Interviewee Profession:

Company:

Date of Interview:

Interview Duration:

Q1. Why are we investing in the BTL technology when we have other technologies to produce various value added chemicals and generate power? What advantages does BTL bring that those other technologies don't?

Q2. What is the carbon foot print of the BTL technology? What effect does it bring to global warming? How can you compare it with that of CTL or GTL technology?

Q3. Relative to the BTL technology, what are the top technical problems faced and what can be done to solve or avoid these problems?

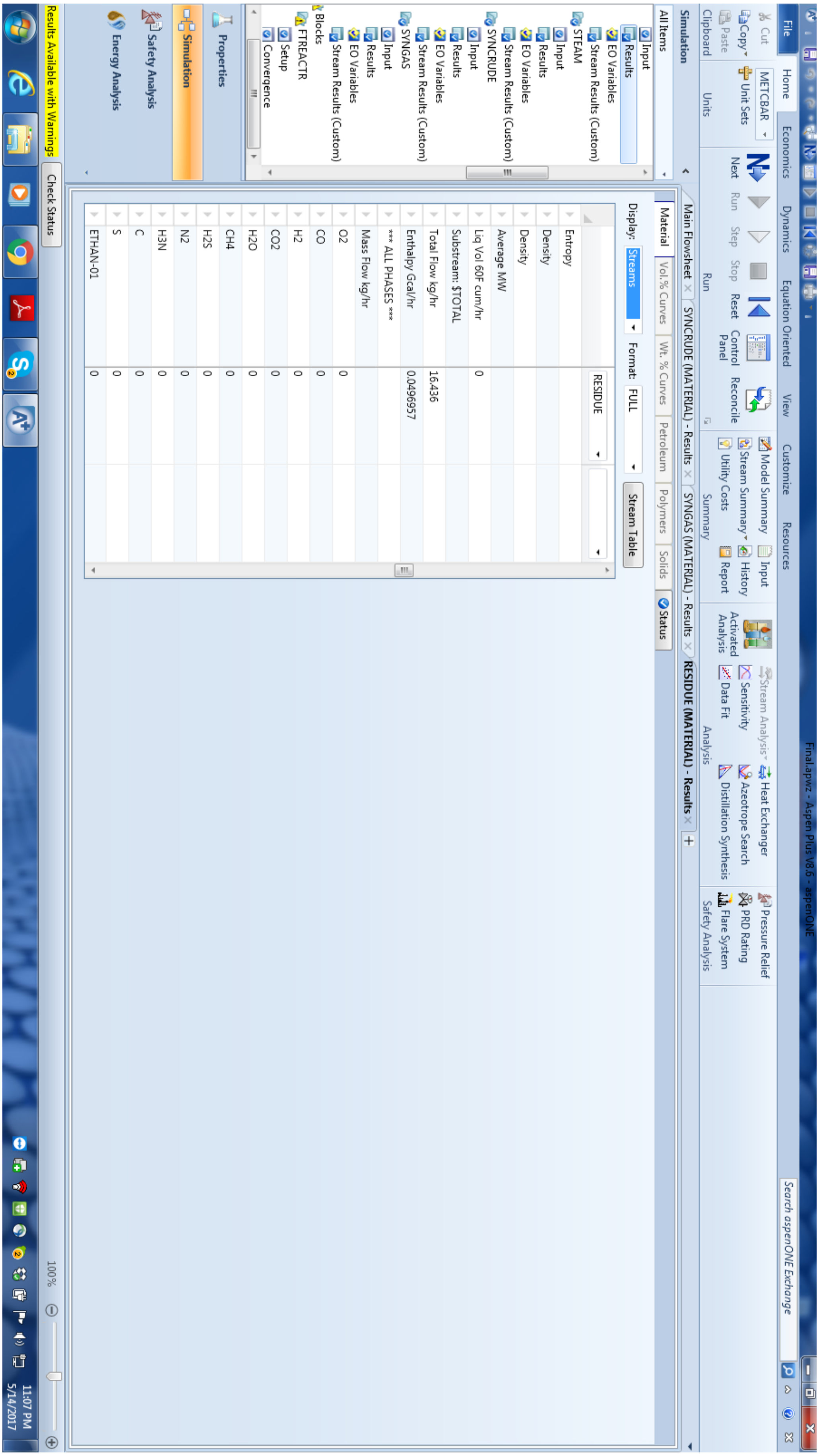
Q4. What are the problems faced in commercialization of BTL technology for mass production? What capacity of plants are suitable small, medium or large? What type of geographical location is best suited to set up a plant?

Q5. What are the most valuable products? Which markets can be targeted?

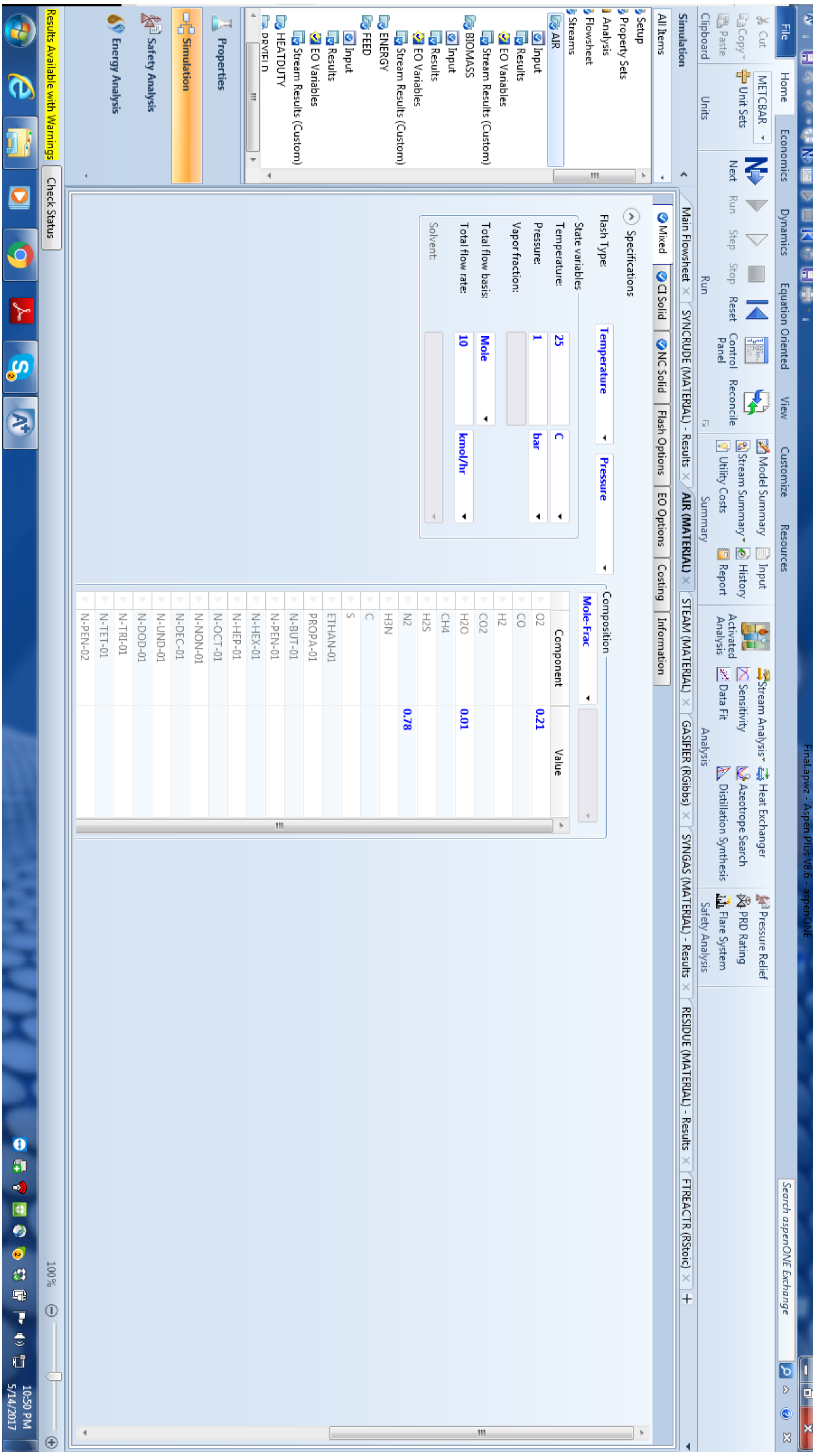
Q6. What are the major environmental impacts related to the technology and how can they be avoided?

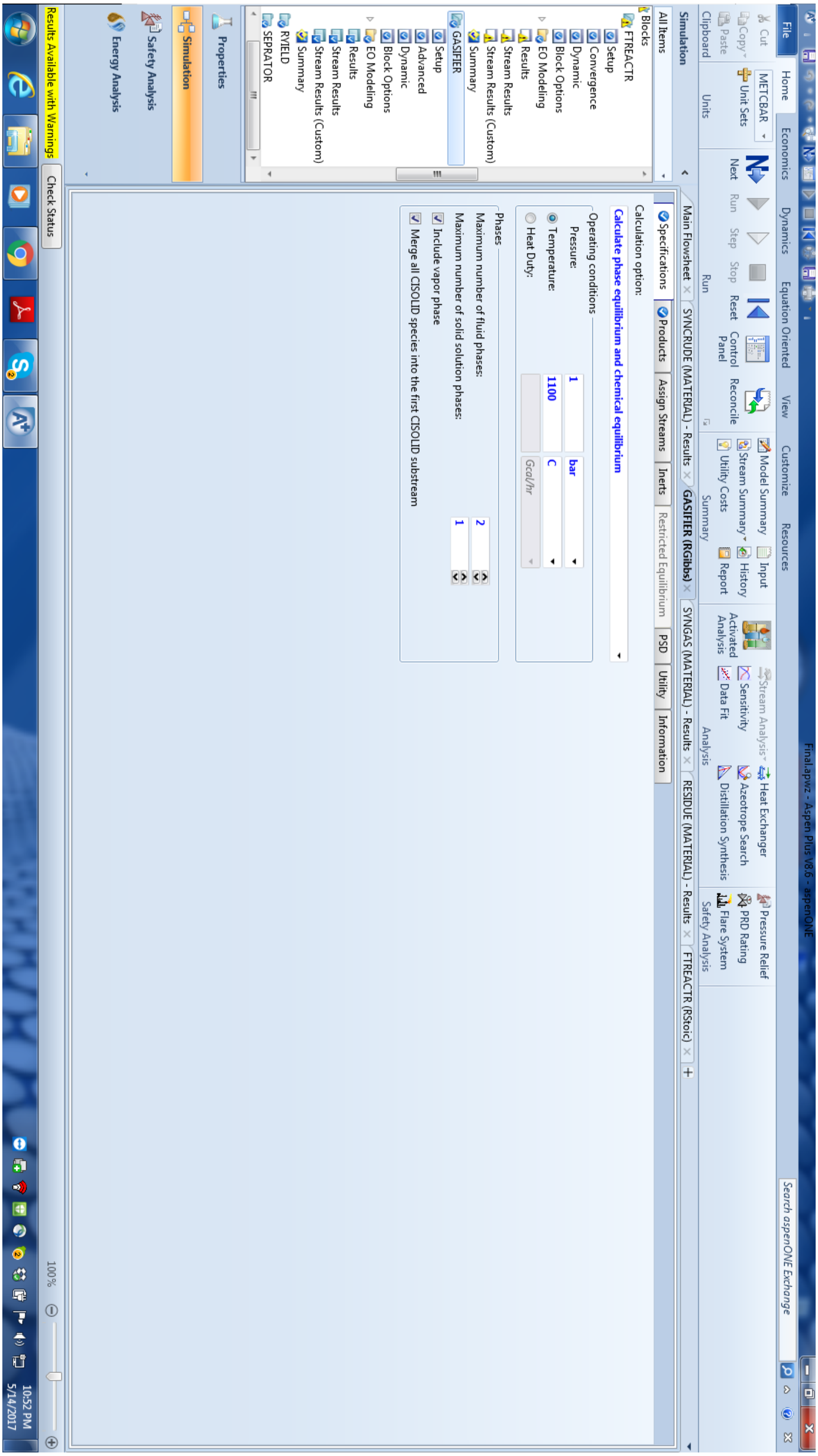
Q7. How the energy policy of a country more a driver or a restraint for the development of BTL?

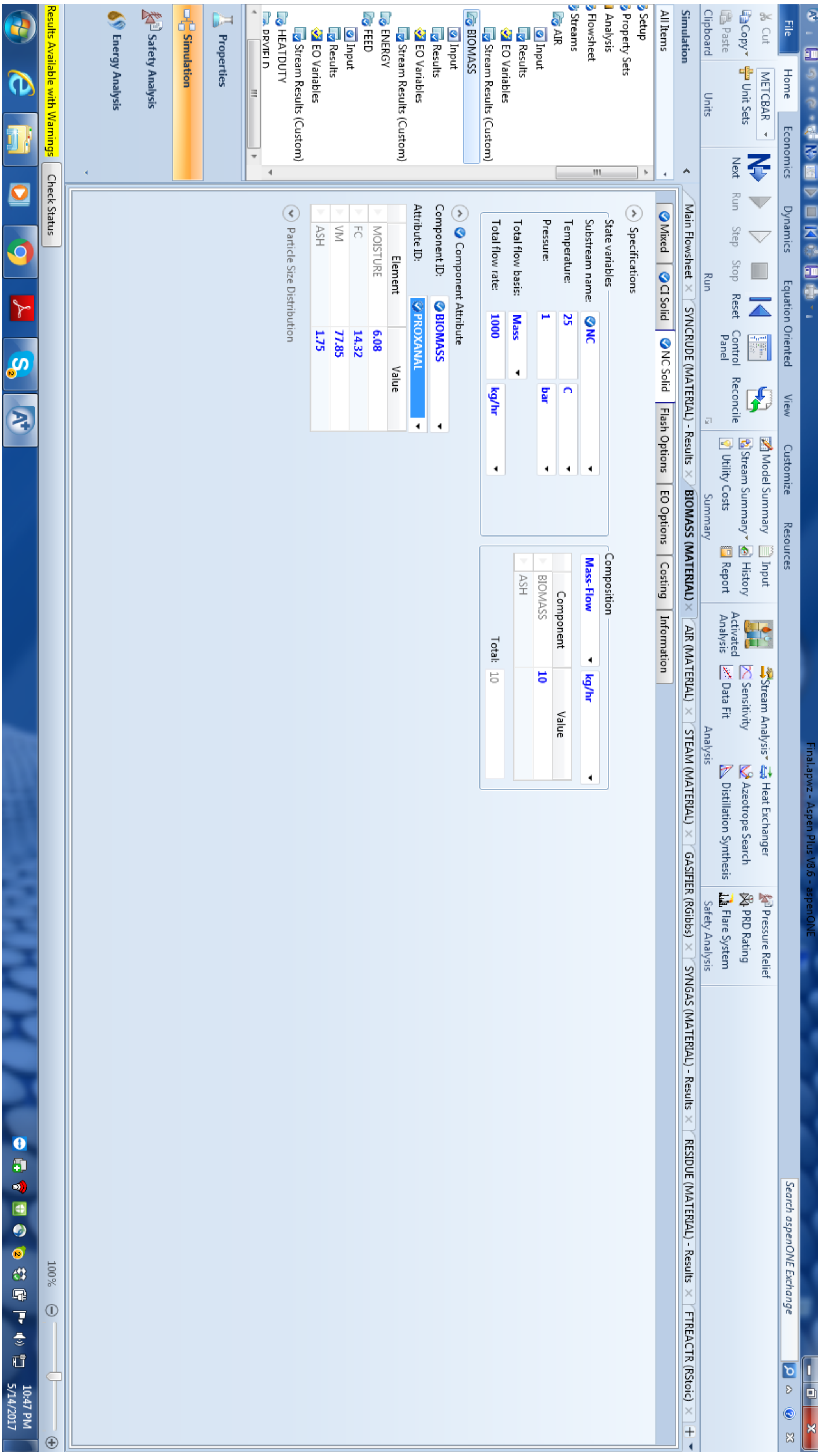
Q8. What is the common opinion among policy-makers about the future of the technology?

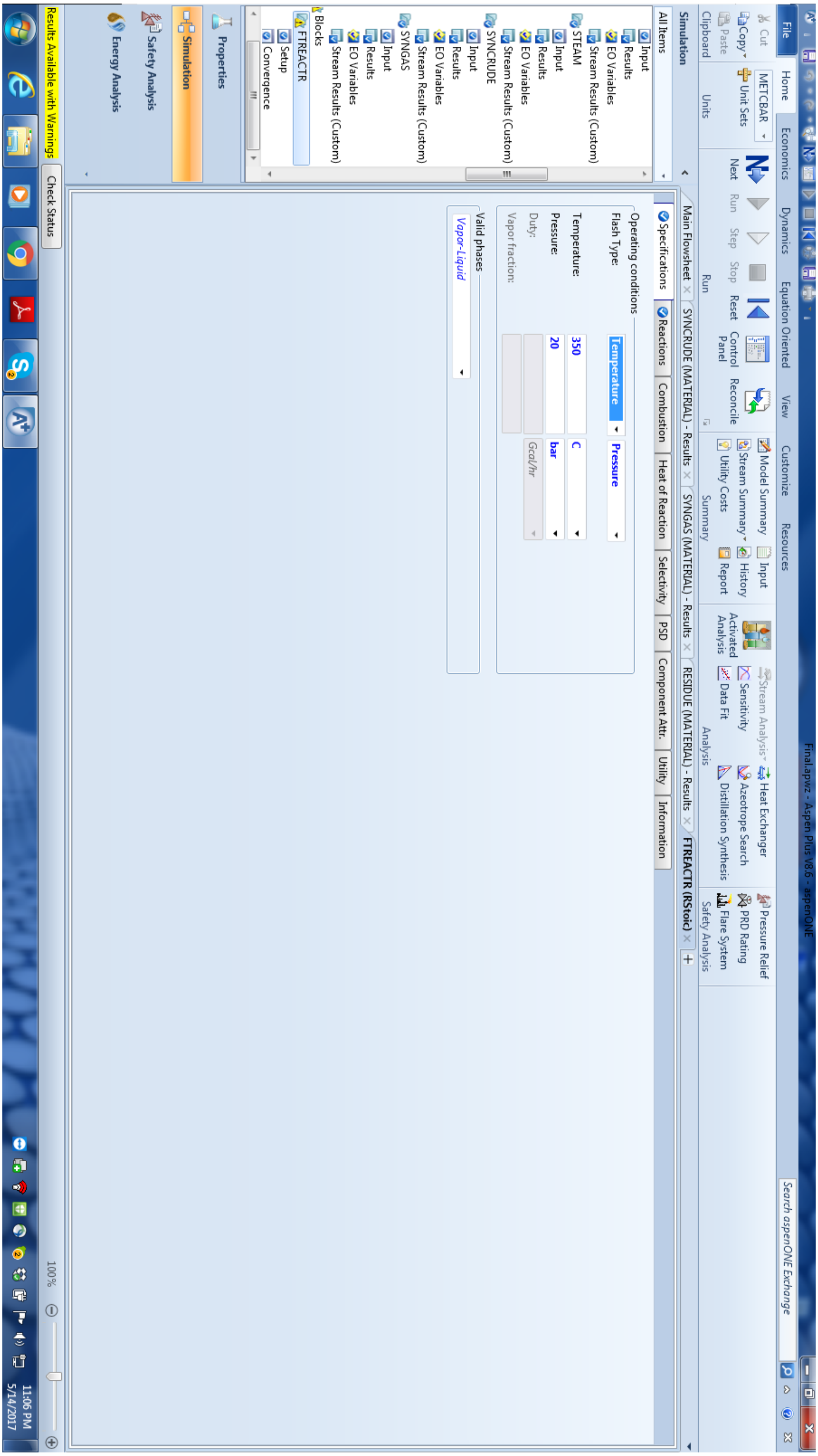


Final.apwz - Aspen Plus V8.6 - aspenONE
File
Home
Economics
Dynamics
Equation Oriented
View
Customize
Resources
Search aspenONE Exchange
Cut
Copy
Paste
Clipboard
METCBAR
Unit Sets
Units
Next
Run
Step
Stop
Reset
Control Panel
Reconcile
Run
Model Summary
Stream Summary
Utility Costs
Input
History
Report
Summary
Activated Analysis
Stream Analysis
Sensitivity
Data Fit
Heat Exchanger
Azeotrope Search
Distillation Synthesis
Analysis
Pressure Relief
PRD Rating
Flare System
Safety Analysis
Simulation
All Items
Input
Results
EO Variables
Stream Results (Custom)
STEAM
Input
Results
EO Variables
Stream Results (Custom)
SYNCRUDE
Input
Results
EO Variables
Stream Results (Custom)
SYNGAS
Input
Results
EO Variables
Stream Results (Custom)
Blocks
FTREACTR
Setup
Convergence
Properties
Simulation
Safety Analysis
Energy Analysis
Main Flowsheet
SYNCRUDE (MATERIAL) - Results
SYNGAS (MATERIAL) - Results
RESIDUE (MATERIAL) - Results
Material
Vol.% Curves
Wt. % Curves
Petroleum
Polymers
Solids
Status
Display: Streams
Format: FULL
Stream Table
RESIDUE
Entropy
Density
Average MW
Liq Vol 60F cum/hr 0
Substream: $TOTAL
Total Flow kg/hr 16.436
Enthalpy Gcal/hr 0.0496957
*** ALL PHASES ***
Mass Flow kg/hr
O2 0
CO 0
CO2 0
H2 0
H2O 0
CH4 0
H2S 0
N2 0
H3N 0
C 0
S 0
ETHAN-01 0
Results Available with Warnings
Check Status
100%
11:07 PM
5/14/2017

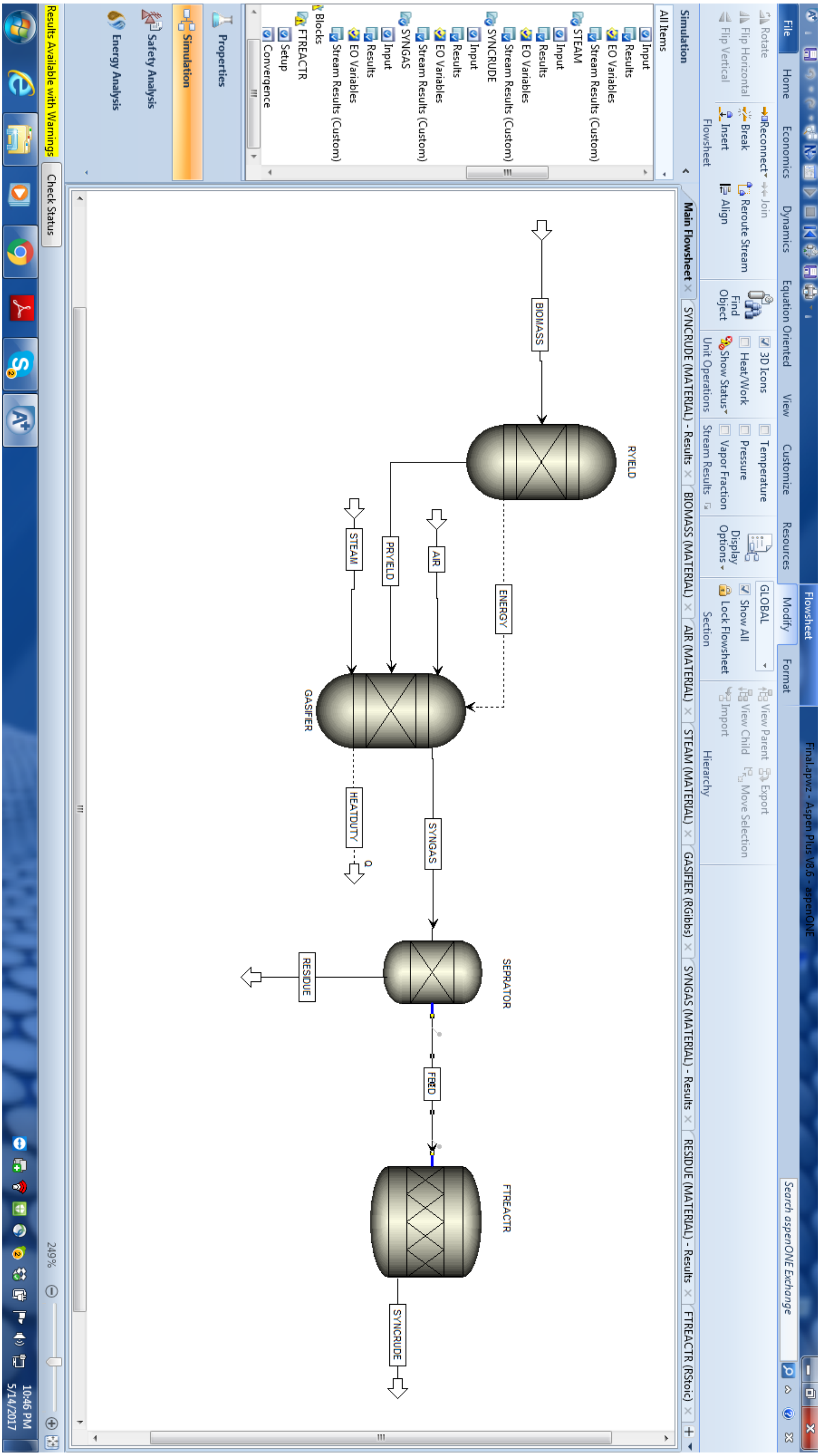

Final.apwz - Aspen Plus V8.6 - aspenONE
File
Home
Economics
Dynamics
Equation Oriented
View
Customize
Resources
Main Flowsheet
SYNCRUDE (MATERIAL) - Results
AIR (MATERIAL)
STEAM (MATERIAL)
GASIFIER (RGibbs)
SYNGAS (MATERIAL) - Results
RESIDUE (MATERIAL) - Results
FTREACTR (RStoic)
Mixed
CI Solid
NC Solid
Flash Options
EO Options
Costing
Information
Specifications
Flash Type:
Temperature
Pressure
State variables
Temperature:
25
C
Pressure:
1
bar
Vapor fraction:
Total flow basis:
Mole
Total flow rate:
10
kmol/hr
Solvent:
Composition
Mole-Frac
Component
Value
O2
0.21
N2
0.78
H2O
0.01
Results Available with Warnings
Check Status

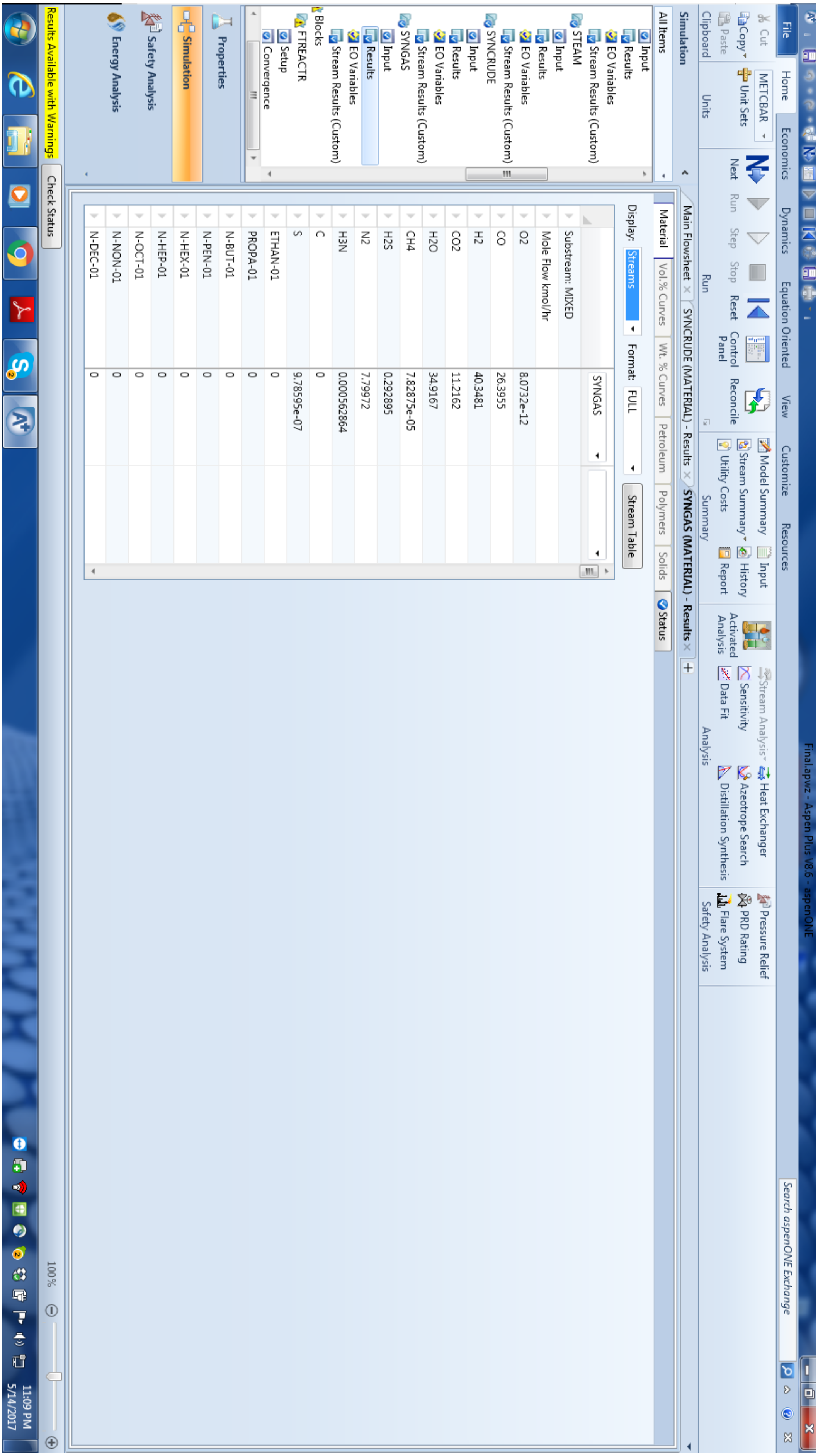

Final.apwz - Aspen Plus V8.6 - aspenONE
File
Home
Economics
Dynamics
Equation Oriented
View
Customize
Resources
Cut
Copy
Paste
Clipboard
METCBAR
Unit Sets
Units
Next
Run
Step
Stop
Reset
Control Panel
Reconcile
Run
Model Summary
Stream Summary
Utility Costs
Input
History
Report
Summary
Activated Analysis
Stream Analysis
Sensitivity
Data Fit
Heat Exchanger
Azeotrope Search
Distillation Synthesis
Analysis
Pressure Relief
PRD Rating
Flare System
Safety Analysis
Search aspenONE Exchange
Simulation
All Items
Blocks
FTREACTR
Setup
Convergence
Dynamic
Block Options
EO Modeling
Results
Stream Results
Stream Results (Custom)
Summary
GASIFIER
Setup
Advanced
Dynamic
Block Options
EO Modeling
Results
Stream Results
Stream Results (Custom)
Summary
RYIELD
SEPRATOR
Properties
Simulation
Safety Analysis
Energy Analysis
Main Flowsheet
SYNCRUDE (MATERIAL) - Results
GASIFIER (RGibbs)
SYNGAS (MATERIAL) - Results
RESIDUE (MATERIAL) - Results
FTREACTR (RStoic)
Specifications
Products
Assign Streams
Inerts
Restricted Equilibrium
PSD
Utility
Information
Calculation option:
Calculate phase equilibrium and chemical equilibrium
Operating conditions
Pressure:
1
bar
Temperature:
1100
C
Heat Duty:
Gcal/hr
Phases
Maximum number of fluid phases:
2
Maximum number of solid solution phases:
1
Include vapor phase
Merge all CISOLID species into the first CISOLID substream
Results Available with Warnings
Check Status
100%
10:52 PM
5/14/2017

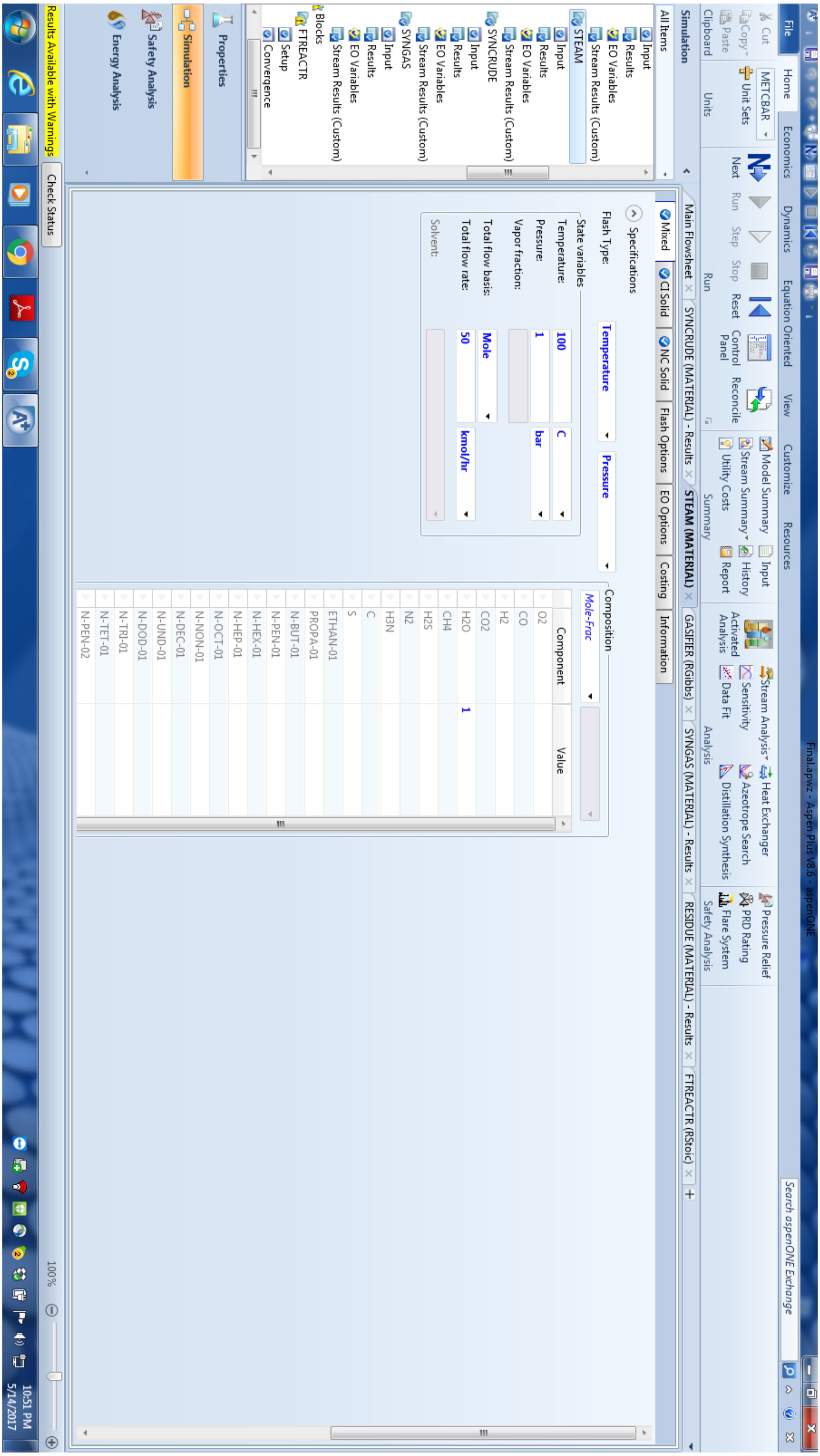

FinalAp.wz - Aspen Plus V8.6 - aspenONE
File
Home
Economics
Dynamics
Equation Oriented
View
Customize
Resources
Main Flowsheet
SYNCRUDE (MATERIAL) - Results
BIOMASS (MATERIAL)
AIR (MATERIAL)
STEAM (MATERIAL)
GASIFIER (RGibbs)
SYNGAS (MATERIAL) - Results
RESIDUE (MATERIAL) - Results
FTREACTR (RStoic)
Mixed
CI Solid
NC Solid
Flash Options
EO Options
Costing
Information
Specifications
State variables
Substream name:
NC
Temperature:
25
C
Pressure:
1
bar
Total flow basis:
Mass
Total flow rate:
1000
kg/hr
Composition
Mass-Flow
kg/hr
Component
Value
BIOMASS
10
ASH
Total:
10
Component Attribute
Component ID:
BIOMASS
Attribute ID:
PROXANAL
Element
Value
MOISTURE
6.08
FC
14.32
VM
77.85
ASH
1.75
Particle Size Distribution
Simulation
All Items
Setup
Property Sets
Analysis
Flowsheet
Streams
AIR
Input
Results
EO Variables
Stream Results (Custom)
BIOMASS
ENERGY
FEED
HEATDUTY
Properties
Simulation
Safety Analysis
Energy Analysis
Results Available with Warnings
Check Status
100%
10:47 PM
5/14/2017

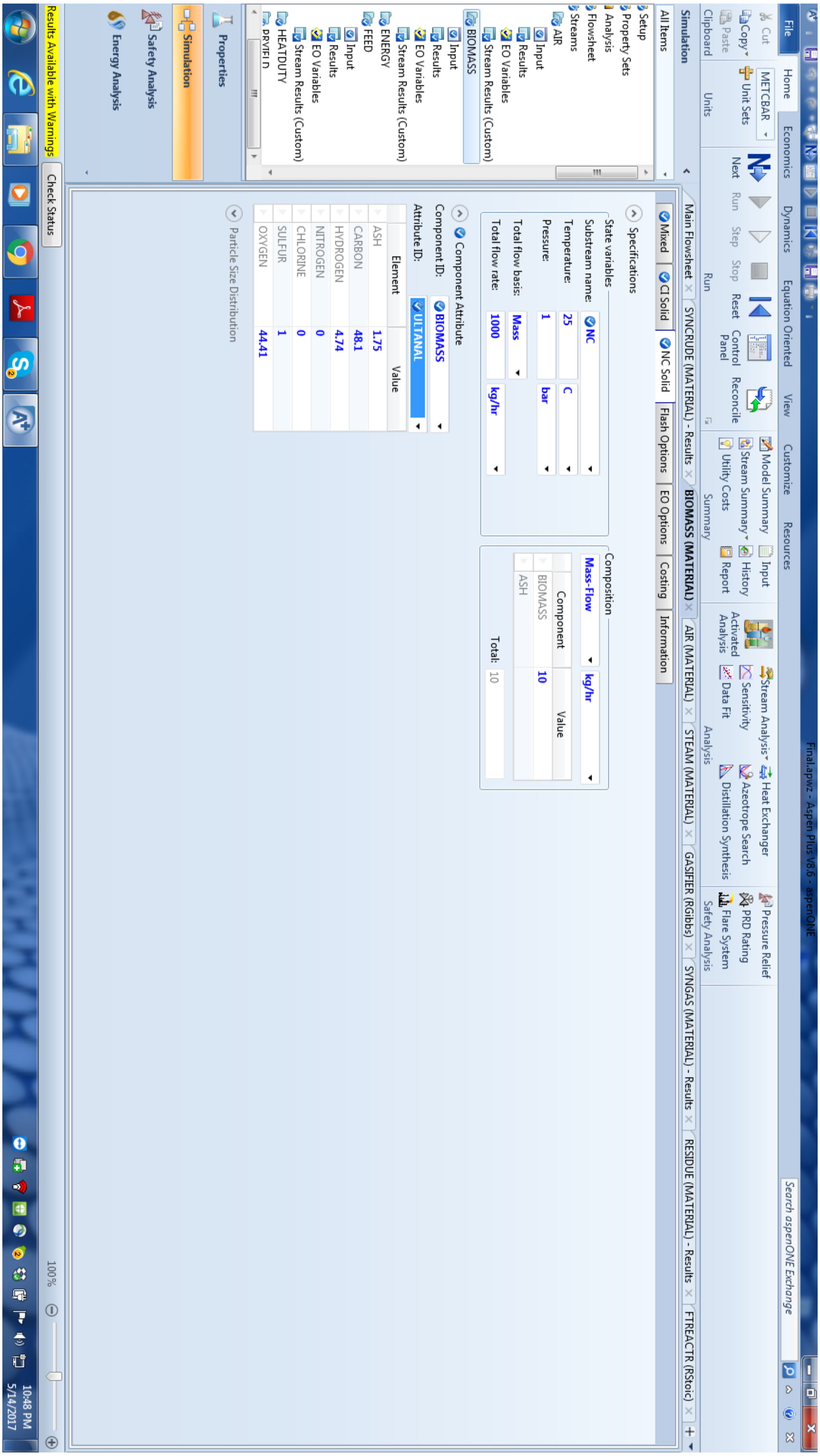


CEU eTD Collection

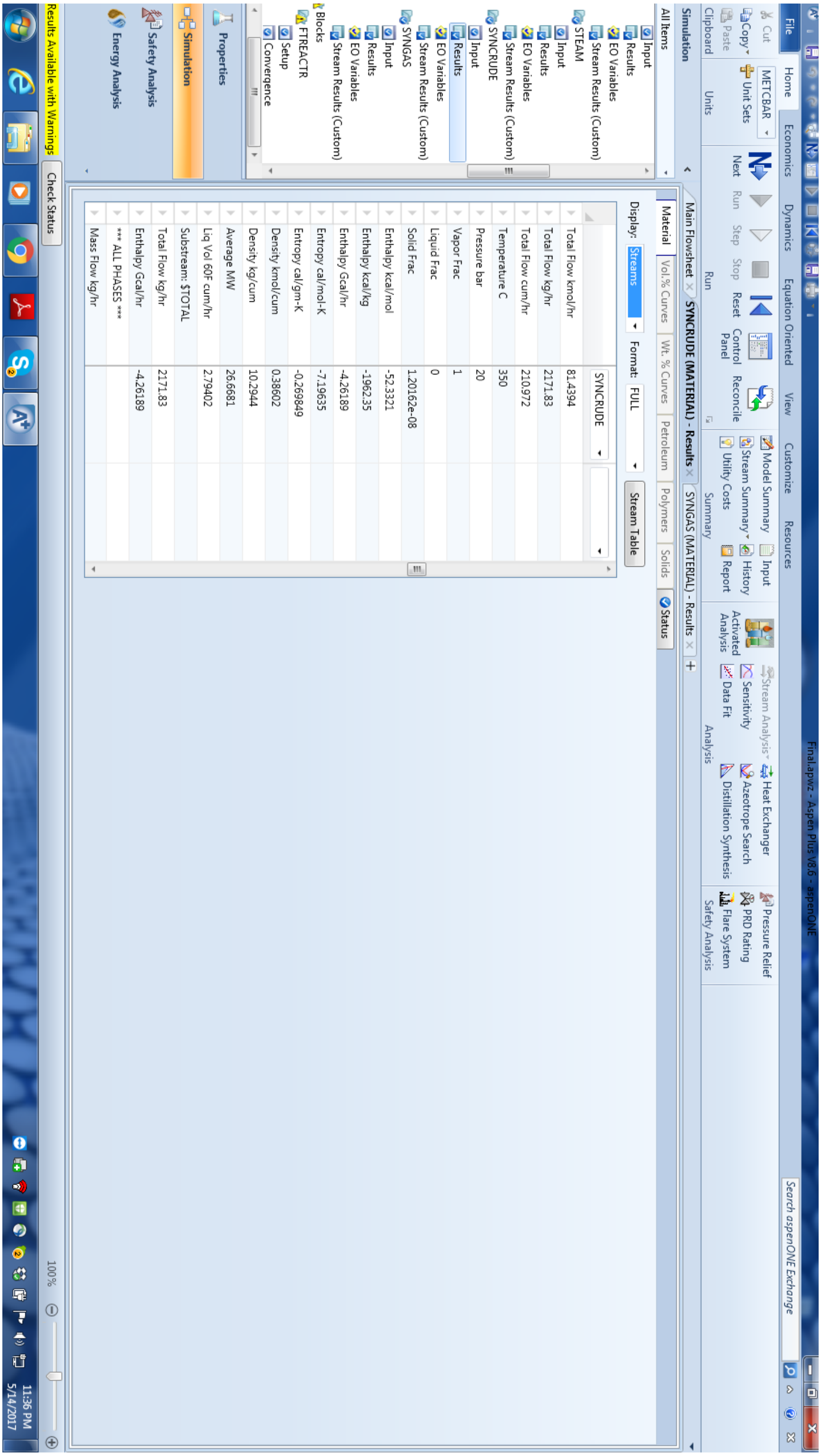

Final.apwz - Aspen Plus V8.6 - aspenONE
Main Flowsheet
BIOMASS
RYIELD
ENERGY
AIR
PRYIELD
STEAM
GASIFIER
HEATDUTY
SYNGAS
SEPRATOR
RESIDUE
FEED
FTREACTR
SYNCRUDE
Results Available with Warnings


Final.apwz - Aspen Plus V8.6 - aspenONE
File
Home
Economics
Dynamics
Equation Oriented
View
Customize
Resources
Search aspenONE Exchange
Cut
Copy
Paste
Clipboard
METCBAR
Unit Sets
Units
Next
Run
Step
Stop
Reset
Control Panel
Reconcile
Run
Model Summary
Stream Summary
Utility Costs
Input
History
Report
Summary
Activated Analysis
Stream Analysis
Sensitivity
Data Fit
Analysis
Heat Exchanger
Azeotrope Search
Distillation Synthesis
Pressure Relief
PRD Rating
Flare System
Safety Analysis
Simulation
All Items
Input
Results
EO Variables
Stream Results (Custom)
STEAM
Input
Results
EO Variables
Stream Results (Custom)
SYNCRUDE
Input
Results
EO Variables
Stream Results (Custom)
SYNGAS
Input
Results
EO Variables
Stream Results (Custom)
Blocks
FTREACTR
Setup
Convergence
Properties
Simulation
Safety Analysis
Energy Analysis
Main Flowsheet
SYNCRUDE (MATERIAL) - Results
SYNGAS (MATERIAL) - Results
Material
Vol.% Curves
Wt. % Curves
Petroleum
Polymers
Solids
Status
Display: Streams
Format: FULL
Stream Table
SYNGAS
Substream: MIXED
Mole Flow kmol/hr
O2 8.0732e-12
CO 26.3955
H2 40.3481
CO2 11.2162
H2O 34.9167
CH4 7.82875e-05
H2S 0.292895
N2 7.79972
H3N 0.000562864
C 0
S 9.78595e-07
ETHAN-01 0
PROPA-01 0
N-BUT-01 0
N-PEN-01 0
N-HEX-01 0
N-HEP-01 0
N-OCT-01 0
N-NON-01 0
N-DEC-01 0
Results Available with Warnings
Check Status
100%
11:09 PM
5/14/2017


Final.apwz - Aspen Plus V8.6 - aspenONE
File
Home
Economics
Dynamics
Equation Oriented
View
Customize
Resources
Search aspenONE Exchange
Cut
Copy
Paste
Clipboard
METCBAR
Unit Sets
Units
Next
Run
Step
Stop
Reset
Control Panel
Reconcile
Run
Model Summary
Stream Summary
Utility Costs
Input
History
Report
Summary
Activated Analysis
Stream Analysis
Sensitivity
Data Fit
Heat Exchanger
Azeotrope Search
Distillation Synthesis
Analysis
Pressure Relief
PRD Rating
Flare System
Safety Analysis
Simulation
All Items
Input
Results
EO Variables
Stream Results (Custom)
STEAM
SYNCRUDE
SYNGAS
Blocks
FTREACTR
Setup
Convergence
Properties
Simulation
Safety Analysis
Energy Analysis
Main Flowsheet
SYNCRUDE (MATERIAL) - Results
STEAM (MATERIAL)
GASIFIER (RGibbs)
SYNGAS (MATERIAL) - Results
RESIDUE (MATERIAL) - Results
FTREACTR (RStoic)
Mixed
CI Solid
NC Solid
Flash Options
EO Options
Costing
Information
Specifications
Flash Type:
Temperature
Pressure
State variables
Temperature:
100
C
Pressure:
1
bar
Vapor fraction:
Total flow basis:
Mole
Total flow rate:
50
kmol/hr
Solvent:
Composition
Mole-Frac
Component
Value
O2
CO
H2
CO2
H2O
1
CH4
H2S
N2
H3N
C
S
ETHAN-01
PROPA-01
N-BUT-01
N-PEN-01
N-HEX-01
N-HEP-01
N-OCT-01
N-NON-01
N-DEC-01
N-UND-01
N-DOD-01
N-TRI-01
N-TET-01
N-PEN-02
Results Available with Warnings
Check Status
100%
10:51 PM
5/14/2017



CEU eTD Collection


Final.apwz - Aspen Plus V8.6 - aspenONE
Main Flowsheet
SYNCRUDE (MATERIAL) - Results
SYNGAS (MATERIAL) - Results
Material
Vol.% Curves
Wt. % Curves
Petroleum
Polymers
Solids
Status
Display: Streams
Format: FULL
Stream Table
SYNCRUDE
Total Flow kmol/hr 81.4394
Total Flow kg/hr 2171.83
Total Flow cum/hr 210.972
Temperature C 350
Pressure bar 20
Vapor Frac 1
Liquid Frac 0
Solid Frac 1.20162e-08
Enthalpy kcal/mol -52.3321
Enthalpy kcal/kg -1962.35
Enthalpy Gcal/hr -4.26189
Entropy cal/mol-K -7.19635
Entropy cal/gm-K -0.269849
Density kmol/cum 0.38602
Density kg/cum 10.2944
Average MW 26.6681
Liq Vol 60F cum/hr 2.79402
Substream: $TOTAL
Total Flow kg/hr 2171.83
Enthalpy Gcal/hr -4.26189
*** ALL PHASES ***
Mass Flow kg/hr
Results Available with Warnings
Check Status
11:36 PM
5/14/2017

Syncrude Composition

I519

	A	B	C
121	1-NON-03	7.07E-10	
122	1-EIC-01	4.57E-10	
123	Mass Flow kg/hr		
124	O2	2.58E-10	
125	CO	42.25178	
126	H2	0	
127	CO2	654.8567	
128	H2O	945.3797	
129	CH4	2.174322	
130	H2S	9.98241	
131	N2	218.4973	
132	H3N	0.00958589	
133	C	0	
134	S	3.14E-05	
135	ETHAN-01	5.498646	
136	PROPA-01	6.450922	
137	N-BUT-01	7.174346	
138	N-PEN-01	7.694547	
139	N-HEX-01	8.041652	
140	N-HEP-01	8.243772	
141	N-OCT-01	8.325829	
142	N-NON-01	8.309504	
143	N-DEC-01	8.213479	
144	N-UND-01	8.053757	
145	N-DOD-01	7.843973	
146	N-TRI-01	7.595699	
147	N-TET-01	7.318704	
148	N-PEN-02	7.021196	
149	N-HEX-02	6.710037	
150	N-HEP-02	6.390922	
151	N-OCT-02	6.068548	
152	N-NON-02	5.746754	
153	N-EIC-01	[illegible]	

181	1-NON-03	1.53E-05
182	1-EIC-01	1.04E-05
183	Total Flow kmol/hr	81.43939
184	Total Flow kg/hr	2171.832
185	Total Flow cum/hr	210.9718
186	Temperature C	350
187	Pressure bar	20
188	Vapor Frac	1
189	Liquid Frac	0
190	Solid Frac	1.20E-08
191	Enthalpy kcal/mol	-52.33208
192	Enthalpy kcal/kg	-1962.349
193	Enthalpy Gcal/hr	-4.261893
194	Entropy cal/mol-K	-7.19635
195	Entropy cal/gm-K	-0.2698488
196	Density kmol/cum	0.3860203
197	Density kg/cum	10.29442
198	Average MW	26.66808
199	Liq Vol 60F cum/hr	2.79402
200	Substream: $TOTAL	
201	Total Flow kg/hr	2171.832
202	Enthalpy Gcal/hr	-4.261893
203	*** ALL PHASES ***	
204	Mass Flow kg/hr	
205	O2	2.58E-10
206	CO	42.25178
207	H2	0
208	CO2	654.8567
209	H2O	945.3797
210	CH4	2.174322
211	H2S	9.98241
212	N2	218.4973
213	H3N	0.00958589
214	C	0
215	S	3.14E-05
216	ETHAN-01	5.498646
217	PROPA-01	6.450922
218	N-BUT-01	7.174346
219	N-PEN-01	7.694547