ECONOMIC AND ENVIRONMENTAL ASSESSMENT OF BIOGAS TO LIQUID FUELS (BgTL) TECHNOLOGY VIA FISCHER-TROPSCH SYNTHESIS

by

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ABSTRACT

Production of drop-in renewable diesel from biogas derived from anaerobic digestion (AD) of *Miscanthus gigentus* cultivated from strip-mined soils was investigated to evaluate energy use, environmental impacts and economic feasibilities and compared with that of conventional fossil based diesel fuel. A process simulation model was developed for biogas to liquid fuels (BgTL) via Fischer-Tropsch (F-T) synthesis to assess overall mass and energy balances and to estimate the minimum selling price of renewable F-T fuels. A base case BgTL plant size of 2000 Nm^3/h required about $105 million capital investment and $12 million annual operating expenses with a minimum F-T fuels selling price of $5.6/GGE and the price could be reduced by up to $2/GGE, if the biogas plant capacity can be increased by tenfold (20,000 Nm^3/h). Life cycle assessment study concluded that the net greenhouse gas (GHG) emissions could be reduced by up to 26% compared with that of conventional diesel fuel with increased crop yield and soil carbon sequestration rate.

INDEX WORDS: Biogas, Renewable diesel, Aspen Plus, life cycle analysis, GHG.

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DEDICATION

This research work is dedicated to Almighty God for the graces and wisdom He bestowed on me during this project. And to Our Lady of Perpetual Help for Her ad-infinitum intercessions without which I would not have made this thus far.

Ad Maiorem Dei Gloriam

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INTRODUCTION

1.1 Motivation

In recent times, the global rate of energy consumption (1.4% increase) has outgrown the rate of energy production (0.6% increase) [1] causing an imminent shortage of energy supply. According to the 2008 report by Energy Watch Group, the maximum crude oil production limit termed the ‘peak-oil’ has been exceeded [2]. In this scenario, a world without energy can be envisioned to cause a shutdown of major energy dependent activities. Sequel to the aforementioned, a balance between energy production and consumption needs to be met. With an approximate world population of 7.2 billion people estimated by the United States Census Bureau [3], the energy need of the population is high with an estimated energy consumption of 12 billion gallons per day [4]. The high number of vehicles used for transportation in countries such as China [5] and the U.S [6], and the improvement in the standard of living especially in non-Organization for Economic Co-operation and Development (OECD) countries contribute to the growth in energy demand.

Over the years, the energy need has been supplied from petroleum derived fuels [7] with little concern on the sustainability of the energy source and its effect on climate change. It is very evident that the environment pays for the use of fossil fuel as the climate has accumulated a lot of carbon emissions due to the combustion of fossil fuels.

Environmental impacts such as global-warming, particulate matter, smog, sulphuric and nitrous oxide accumulation and ozone layer depletion being the adverse effects of fossil energy usage. The consequences of such impacts include health hazards when the particulates are inhaled, acid rain formation due to nitrous and sulfuric acid, and global warming due to accumulation of heat trapped by emitted carbon dioxide. With more awareness to these adverse effects, and uncertainty of energy security associated with fossil energy usage, a shift to alternative forms of energy is currently advocated.

1.2 Background

The use of biomass for energy production has been realized as an alternative route to reduce the carbon footprint caused by fossil fuels combustion. Hence, the Department of Energy (DOE) and United States Department of Agriculture (USDA) are on the collaborative Biomass Research and Development Initiative (BRDI) to enhance the use of biomass to produce biofuels. This initiative is aimed at advancing bioenergy technology with the ultimate goal of carbon emissions reduction and energy sustainability guaranteed by the renewable biomass feedstock.

Sequel to the aforementioned, interests in the use of lignocellulosic biomass sources has been explored by several researchers to produce various biofuel products. Given the 754 million acres of land potentially available for biomass production in the United States [8], it proves the sustainability of biomass feedstock needed for biofuels production. According to [9], there are 157,194 thousand dry tonnes per year of crop residues, 56,612 thousand dry tonnes per year of forest residues and a sum total of 144,895 thousand dry tonnes per year of energy crops in the United States that all can be used for bioenergy production. Hence, this biomass can be converted to bioenergy/biofuels sources either through the thermochemical and biochemical routes of which the thermochemical pathway has received a huge attention in recent times. The typical biomass thermochemical conversion route is the gasification approach which produces syngas.

Biomass gasification technology have been a proven source of syngas for multiple fuels production such as ethanol, mixed alcohols, hydrogen, methanol, Fischer-Tropsch liquids, etc. [10]. These products of syngas are very useful in achieving the increasing energy demands of the bio-based derived fuels. Of interest in the use of syngas produced from biomass is the production of drop-in liquid transportation fuels via Fischer-Tropsch synthesis. This process of converting biomass to liquid fuels has been studied by several authors using different biomass feedstock. In 2002, [11] studied the prospects of liquid fuels production using poplar wood. Willow wood was used by [12] to synthesis liquid fuels production pathway. [13] examined the coproduction of liquid fuels and electricity using switchgrass. Recently, corn stover low and high temperature gasification processes were studied by [14] to determine the process feasibility in liquid fuels production.

However, biomass gasification route to generate drop-in liquid fuels produces syngas with a high amount of impurities in the form of ash, char and particulate matter [12, 14]. Therefore, the syngas needs to be subjected to cleaning and upgrading to make it suitable for other process applications. Attempts to clean-up the syngas to remove the impurities has incurred high equipment and operating costs. According to [10], syngas cleaning contributes 60-65% of the operating cost of the process and ultimately makes the product cost expensive. This high cost of syngas production via gasification is due to the following:

1. More sophisticated gasifier equipment fabrication specification due to gasifier's high operating temperature and pressure.
2. Additional installation of equipment needed for tar and particulate matter removal from the syngas stream.
3. The syngas (H_2/CO) ratio produced in the BTL process needs to be conditioned via a reverse water gas shift process to meet the Fischer-Tropsch feedstock condition.
4. Some gasification process produces more methane gas which requires additional reforming unit to produce syngas.

Such overall process requires the use of expensive unit operations which impacts the total capital and operating cost of the BTL process. In addition, the extent of particulate matter removal is not certain after the syngas cleaning process. Hence, downstream equipment is subject to corrosion and rust effects.

With this established research challenges, we are proposing an alternative means of converting biomass to drop-in liquid fuels that eliminates the complex and high cost of unit operation requirement in the pathway to liquid fuels production. This pathway is an existing technology inherently safe and has been used over the years. We are specifically focusing on the biochemical conversion process, known as anaerobic digestion (AD) process to produce biogas which is cleaned and reformed into syngas that is processed further to produce drop-in fuels. Hence the research focuses on "Biogas conversion to drop-in fuels".

Biogas is a self-energy source produced from the anaerobic digestion and breakdown of organic matter. Sewage, agricultural residues, energy crops, and food wastes are among the feedstock used for the production of biogas via anaerobic digestion [15].

Liquid state anaerobic digestion has been the predominant AD process employed for the production of biogas. Currently in the United States, liquid state feedstock such as industrial and institutional organic wastes, landfills, wastewater, and animal manure are used in the for biogas production with a methane potential reported to be approximately 8 million tonnes per annum [16]. With 11,000 sites reported to be developed for biogas production, it is evident that the potential for biogas growth in the U.S is huge [17]. In Europe, unlike the U.S, Solid-State Anaerobic digestion has been used to produce biogas and digestate suitable for agricultural purposes. Lignocellulosic biomass feedstock such as energy crops, agricultural residues, and woody biomass with solid content of about 25-40% [18, 19] are generally used.

For the purpose of this research work, we are focusing on the solid state anaerobic digestion of lignocellulosic biomass either in a single SS-AD plant or in a plant capable of digesting both solid and liquid biomass feedstock typically referred to as an integrated anaerobic digester (iAD) plant to produce biogas. Then the biogas is cleaned to remove impurities and pipelined for renewable liquid fuel production via Fischer-Tropsch synthesis. Economic feasibility of this conversion technology is necessary in order to evaluate the technical and economic aspects of the project. This evaluation is conducted via Techno-economic assessment (TEA) which helps to determine the capital investment, operating cost and ultimately, the product minimum selling price which shows the economic standing of the project. The economic analysis of the gas to liquid (GTL), biomass to liquid (BTL) and coal to liquid (CTL) processes have been carried out by different authors [13, 20-23] with an estimated capital investment cost between 191 – 541 $MM while the product price was between 1.85 – 3.11 $/GGE. Comparing the price of these liquid fuels to the incessant change in oil price coupled with the future forecast of the depletion of fossil fuel [24], it enabled the thriving of biomass derived liquid fuels with future anticipation to be competitive with fossil fuels. On the contrary, the drop in oil price to $45/bbl since 2014 [25] has ultimately led to a dip in renewable energy projects due to the comparatively high capital and operating costs of renewable energy sources. According to EIA, the US biodiesel and renewable diesel imports declined 36% in 2014 [26]. From all indications, the future of bioenergy is in doubt due to the current low price of oil in short-term.

Nevertheless, several incidences of drop and rise in oil price over the decades indicate a need for continual research and development in alternative and renewable energy. The energy insecurity associated with fossil energy doubles the quest for more reliable energy sources. In addition, considering that emissions associated with fossil fuel combustion negatively impact the world’s climate, a renewable source of energy that emits biogenic carbons with little or no climate change, proves a healthy substitute to fossil sources [27]. Biomass and biomass-derived feedstock are promising sources to be used in various ways to generate alternative liquid fuels.

However, to ascertain the claim of an environmentally friendly liquid fuels from biomass derived sources, a systematic and quantitative evaluation of the entire liquid fuels production is conducted in a “cradle to gate” approach using life cycle assessment (LCA). LCA is an internationally recognized procedure of assessing the energy and environmental impacts of a product life cycle in order to determine their effects on the environment. In the past, [6, 28-33] have all conducted an environmental assessment on GTL, BTL, and petroleum diesel and gasoline products to evaluate the product performance on the environment. With different authors reporting different observations of their life cycle assessment, it can be understood that each process has a unique impact. Therefore, it becomes necessary to carry out the life cycle assessment of the biomass to liquid fuels process in order to estimate the energy and environmental impact.

1.3 Objectives

The overall goal of this research is to assess the economic and environmental impacts of biomass to liquid fuels technology via Fischer-Tropsch synthesis to produce drop-in diesel fuel. The overall process description is illustrated in figure 1 below showing a biomass to biogas via anaerobic digestion. The various applications of biogas are depicted with emphasis on the biogas to liquid fuels as highlighted by the boundary.

The specific objectives are to:

1. Develop a steady-state process simulation model of the biogas to liquid (BgTL) technology to produce drop-in fuels via Fischer Tropsch synthesis.
2. Conduct a techno-economic analysis of the biogas to liquid (BgTL) technology to estimate capital investment, and the operating cost of the drop-in fuel price to be compared with conventional fuels.
3. Perform a life-cycle assessment of the proposed technology to evaluate the energy and environmental impacts and compare with the conventional diesel fuel.

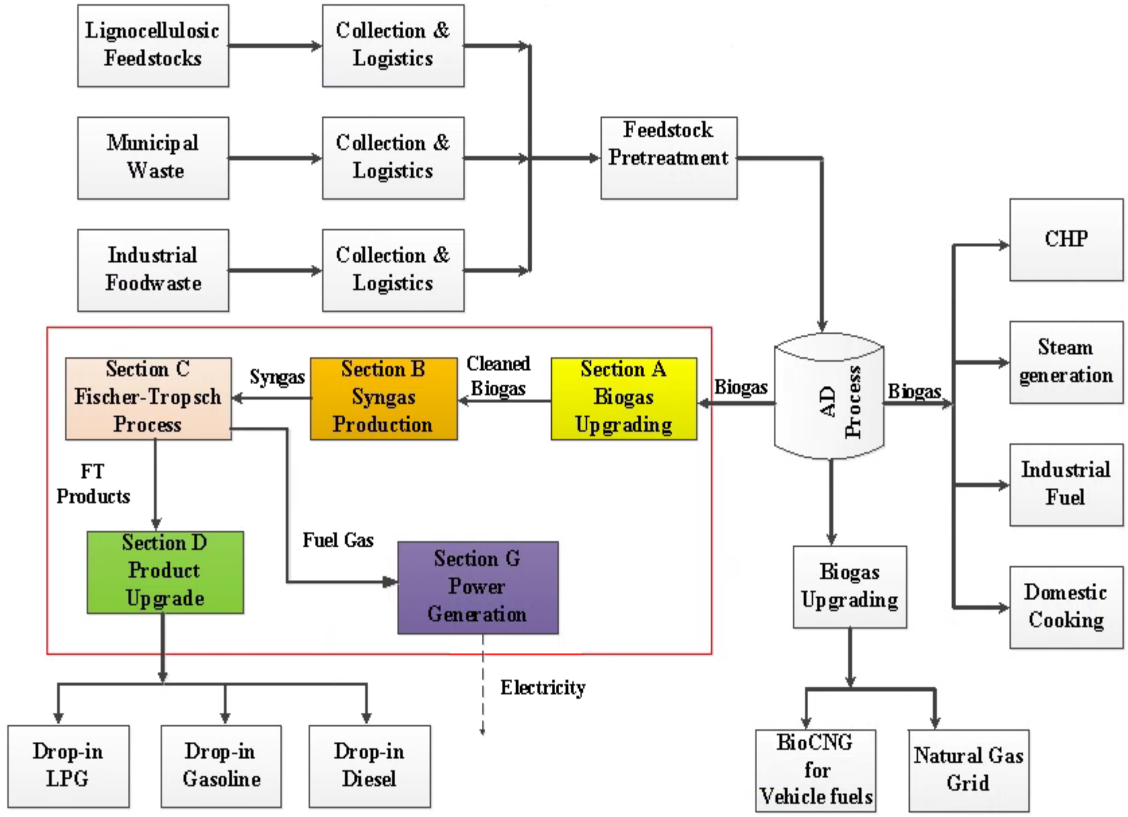


Figure 1-1: Overall process flow diagram of biogas co-generation with emphasis on biogas to liquid fuels production

CHAPTER 2

LITERATURE REVIEW

2.1 Background

The history of biogas can be traced back to the 10th century as reported in the National Renewable Energy Laboratory publication by [34]. Biogas is produced by the anaerobic breakdown of organic matter in the absence of air/oxygen. Traditional biogas production involves the decomposition of food wastes, sewage, animal manures in a digester such as AD or landfills as shown in figure 2-1.

Figure 2-1: Picture of an Agricultural Anaerobic Digester [35]

Generally, anaerobic digestion is carried out at a temperature of between 35 – 45^{o}C (mesophilic) and 55-65^{o}C (thermophilic) to produce a mixture of gas which consists of CH_4 (55-75%), and CO_2 (25-45%) with other impurities such as H_2S, NH_3, and siloxane [36, 37]. The composition, quality, and amount of biogas produced depends on carbon to nitrogen (C/N) ratio of feedstock, temperature of digestion, and the percentage of solids present in the feedstock (%Total Solid and %Volatile Solid) [38].

2.2 Biochemistry of Anaerobic Digestion

The fundamental reaction of the anaerobic digestion process starts with the microbial action on the feedstock subjected to the digestion process. Describing the biochemistry of anaerobic digestion by [39], the composition of the feedstock are basically proteins, fats and carbohydrate which undergoes hydrolysis and become reduced by multicellular enzymes to simple soluble molecules. Amino acids, long chain fatty acids, and sugars are the respective products of the hydrolysis of proteins, fats, and carbohydrates. The further action of fermentative bacteria converts the amino acids, sugars, and fatty acids to multiple products such as carbon dioxide, hydrogen, volatile fatty acids, and acetic acid. Acetic acid is converted to acetate by acetogenic bacteria. Finally, methanogens (methane loving bacteria) produces methane by converting the acetate, carbon dioxide, and hydrogen

2.3 Anaerobic Digestion Technology

Typically, biogas is produced in a digester with a total solid less than 15% [40]. This solid content has been used to differentiate between the traditional liquid state anaerobic digester (L-AD) operating at TS less than 15% and the solid state anaerobic digester (SS-AD) which operates at TS greater than 15%. The L-AD and SS-AD reactors are operated differently which gives rise to different product streams.

2.3.1 Liquid State Anaerobic Digestion

At the inception of anaerobic digestion, the Liquid state anaerobic digester (L-AD) has been the only method for the production of biogas. Operating with a high moisture content of about 85%, L-AD has been successfully used to digest animal and food waste.

According to [41], the L-AD produces biogas by the digestion of wastewater sludge and animal manure. The digestion action in an L-AD typically operates at a mesophilic temperature with a short retention time of about 15-20 days. The product of the L-AD is an effluent with high liquid content. According to [42], the effluent of L-AD plagues the process when considering the processing cost as only the handling cost of the effluent comprises 30% of the operating cost. In addition to the large volume of effluent, the odor of the effluents proves challenging when used as fertilizer in farmland. Similarly, [43] reported that the L-AD rector requires high volume and even higher energy demand. This disadvantages associated with L-AD tend to make the L-AD process economically unfeasible. Therefore, a shift to an anaerobic digestion process that requires less a smaller digester volume [18], lower energy and most importantly reduces the effluent handling with a concomitant reduction in cost is implemented in solid state anaerobic digestion.

Table 2-1: Summary of Liquid State Anaerobic Digestion

Feedstock	Operating conditions				Reactor type	Gas yield	Ref
	Temp	MC[a]	VS/TS[b]	HRT[c]			
Food waste	50°C	70%	83%	28	Batch	435 mL/g VS	[44]
Swine manure	37°C	N/a	5.8%	15	CSTR[d]	188 mL/g VS	[45]
Dairy manure	35°C	N/a	68%	31	SCSTR[e]	2.21 L/d	[46]

a= Moisture content
b= Volatile solid/Total solid
c= Hydraulic retention time in days
d= Continuous stirred tank reactor
e=Sequential continuous stirred tank reactor

2.3.2 Solid State Anaerobic Digestion

In solid state anaerobic digestion, feedstock with a total solid content greater than 15% are used [19]. Unlike the liquid state AD process which forms a slurry or solution with its substrate, the substrate of the SS-AD involves the formation of a bed of solid [47] due to the solid nature of the feedstock. These processes generally occur at a thermophilic temperature and a longer retention time of about 30-40 days. The high operating temperature and extent of retention in the digester helps to ensure a complete degradation of the feedstock. According to [15], the long retention time is due to slow mass transfer operation in the SS-AD. Since the SS-AD operates with a feedstock of a low moisture content, the residue (digestate) is suitable for use as fertilizer and is much easier to handle compared to L-AD [18]. Also compared to L-AD, there are minimal odor challenges when the digestate is used as fertilizer. Another advantage of the low water content of SS-AD is the formation of compost-like end product that can serve as a soil amendment [41]. Comparing the performance of L-AD with SS-AD, [47] reported that an efficiently designed SS-AD can digest more organic feedstock than the L-AD when carried out in a digester of the same size.

The SS-AD process utilizes lignocellulosic biomass feedstock such as energy crops, woody biomass, forest residues which has the solid content necessary for SS-AD process. Lignocellulosic biomass contains 55-75% carbohydrates by dry weight [48]. However, the structure of the feedstock is a heterogeneous complex mixture of cellulose, hemicellulose, and lignin which poses a challenge in the AD process. Also the particle size, pore volume, and total surface area available for enzymatic reaction affects the anaerobic biodegradability of lignocellulosic biomass [49]. Due to the complex nature of the SS-AD feedstock, a pretreatment is necessary to disrupt the barriers imposed by the lignin so that hydrolytic enzymes can penetrate and commence the hydrolysis of the feedstock. Also according to [49], pretreatment helps to increase the surface area and the size of the pores of the cellulose, decrease its crystallinity, and extent of polymerization. Pretreatment methods used to treat lignocellulosic biomass before the SS-AD process are evaluated in the following sections. The SS-AD process using different feedstocks were summarized in table 2.2 below.

Table 2-2: Summary of Solid State Anaerobic Digestion

Feedstock	Operating conditions				Reactor type	Gas yield	Ref
	Temp	MC[a]	VS[b]	HRT			
Corn Stover	37°C	<10%	92.6%	30	Batch	81.2 L/kg VS	[50]
Leaf Biomass	35°C	N/a	95%	35	PFR[d]	360 L/kg TS	[51]

a= Moisture content
b= Volatile solid
c= Hydraulic retention time in days
d= Plug flow reactor

2.3.3 Integrated Anaerobic Digestion (iAD)

The anaerobic digestion process whereby the effluent of the L-AD is combined with the SS-AD feedstock gives rise to the iAD process. Generally, the L-AD effluent serves as an inoculum that balances the microbial consortia which promotes a high methanogenic activity [41]. Different authors have reported the improved performance of the iAD process when lignocellulosic biomass is digested. According to [15], the use of iAD is more likely to reduce operating cost since L-AD effluent handling is eliminated. Therefore, biogas production via iAD seems to be the future of the AD process. Table 2-3 highlights a summary of iAD processes.

Table 2-3: Summary of Integrated Anaerobic Digestion

Feedstock	Operating condition				Reactor type	Gas yield	Ref
	Temp	MC[a]	VS/TS[b]	HRT[c]			
OFMSW & CM[d]	50°C	70%	83%	28	Batch	172m^{3}CH$_4$/t	[52]
CW and POME[e]	37°C	N/A	5.8%	15	CSTR	188 mL/g VS	[45]
SM & CO[f]	35°C	N/A	N/A	40	PFR	0.3 m^3/kg VS	[53]

a= Moisture content
b= Volatile solid/Total solid
c= Hydraulic retention time in days
d= Continuous stirred tank reactor
e=Cow manure and POME
f= SM and cooking oil

2.4 Pretreatment Methods

Several pretreatments of lignocellulosic biomass have been performed to enhance the biogas yield of lignocellulosic biomass. Pretreatment methods can be categorized as either chemical or physical [48, 49] pretreatment with some pretreatment method having both effects. Physical pretreatment methods include grinding, milling, extrusion categorized as mechanical pretreatment [49] and other irradiation processes that includes gamma rays, electron beams, microwaves, and ultrasound. Chemical pretreatment methods are alkaline pretreatment, acid hydrolysis, organolosv, and fungal pretreatment. [48] conducted an evaluation of several pretreatment methods such as lime pretreatment, dilute acid, uncatalyzed steam explosion, liquid hot water, pH controlled hot water, and flow-through liquid hot water. Pretreatment methods applied to different lignocellulosic biomass have been studied with a summary of the pretreatment methods shown in table 2-4 below.

Table 2-4: Summary of Pretreatment methods

Pretreatment Type	Agent	Advantage	Disadvantage	Ref
Acid hydrolysis	H_2SO_4,HCl,H_3PO_4	High solubilization of hemicellulose	Corrosive	[54]
Steam Explosion	High Pressure Steam	Improves enzymatic access	Explosive decompression	[48]
Alkaline hydrolysis	NH_3,CaOH,NaOH	Improves delignification of biomass	Converts agent into salts	[55]
Organosolv	C_2H_5OH, C_6H_5OH,	High solubilization of hemicellulose	High cost	[56]

2.5 Factors Affecting Biogas Yield

Biogas yield is typically affected by a combination of different factors that needs to be maintained to ensure optimal yield of the biogas. The following factors that affect the biogas yield are given in table 2-5 below.

Table 2-5: Summary of factors that affect biogas yield

Parameters	Typical conditions	Advantages	Disadvantages
Temperature	Mesophilic or Thermophilic	Microbial survival	Microbial death
Feed/Inoculum ratio	Depends on feedstock	Appropriate consortium of microbes	Drop in methane yield
Carbon/Nitrogen ratio	15 - 20	Optimal digestion at appropriate ratio	TAN and VFA accumulation

2.6 Biogas Applications and Challenges

Biogas can be used industrially as a thermal source to produce heat or steam, as fuels to drive process equipment, and in internal combustion engine to produce power mostly as combined heat and power (CHP). With a calorific value of 21.48MJ/m^3 [57] compared to natural gas with a calorific value of 38 MJ/m^3, biogas energy capacity is not effectively utilized when directly combusted. Hence, the need for upgrading of the biogas to a pure gas termed “biomethane”. Compression of biomethane to bioCNG is widely used in Europe as a fuel in the national grid for electricity production [36]. According to [58], after cleaning and conditioning, bioCNG satisfies the SAE J 1616 and engine manufacturers fuel standard and can be used the same way as compressed natural gas. Hence, this renewable fuel can power natural gas vehicles. Similarly, renewable diesel fuels that can power diesel vehicles can be produced using biogas as feedstock in the GTL process. Such use of biogas adheres to renewable fuels standard (RFS) which ensures that the fuels used in the U.S has a minimum amount of renewable fuel [59]. With focus on achieving the RFS target, routes on how to produce alternative diesel fuels via renewable sources are sorted of which biogas to liquid fuels seem viable.

2.6.1 Biogas Upgrading

Although biogas has been proven a reliable energy source, it has been plagued by the presence of contaminants that are corrosive, toxic and harmful to the system to which biogas is applied. According to [37], one of the challenges encountered with biogas application is the complex composition of biogas. As reported by several authors, the composition of biogas produced from AD process is dependent on the feedstock and digestion technology. Methane and carbon dioxide are the main composition of biogas with the presence of H_2S, N_2, O_2, NH_3, siloxane, water vapor, and H_2 [36-38] and even other uncharacterized components. The presence of H_2S in biogas mixture has been the most difficult component because of its poisonous effect on catalyst. If biogas is directly employed for the production of syngas in the presence of any metal catalyst, the catalyst that speeds up the reaction will be halted by the poisonous action of H_2S on catalyst. Moreover, the application of biogas as a vehicle fuel or its injection in the gas line for electricity generation requires the removal of CO_2 that reduces its heating value [37, 60]. Hence, biogas upgrading is performed to remove the unwanted components of the biogas that reduces its applicability.

Several upgrading technologies have been employed by different biogas facilities to upgrade their biogas product in other to meet specification. Pressure swing adsorption, Amine treatment, water scrubbing, membrane permeation, cryogenic method, and genosorb process are the common biogas upgrading technology. The inherent advantages and disadvantages of each upgrading processes are summarized in table 2-6.

Table 2-6: Summary of biogas upgrading methods

Method	Mechanism	Advantage	Disadvantages
Pressure Swing Adsorption	Gas adsorption rate	Low capital cost, energy requirement	Low CO_2 recovery, effect of water on adsorbates
Membrane Permeation	Gas permeability	Biogas dehydration	Low methane recovery
Amine Absorption	Absorption	High selectivity of CO_2	High energy demand
Water Scrubbing	Biogas component Solubility difference	High methane recovery, low operating cost	Off-gas handling

2.7 Syngas Production

Biomethane obtained from the biogas upgrading can be employed in the synthesis gas production process. Synthesis gas is a mixture of CO and H_2. This gas is generally called syngas and is used for the production of fuels and chemicals by petroleum and chemical industries [61]. Methanol, dimethyl ether, Fisher Tropsch gasoline, and diesel are the products to which syngas can be utilized. Syngas is produced from different feedstock such as natural gas, coal, or biomass via different production technologies.

Production of syngas from natural gas occurs by reforming the natural gas in the presence of a catalyst. Different reforming processes are utilized for the production of syngas. Steam methane reforming (SMR), partial oxidation reforming (POR), dry reforming (DR), auto thermal reforming (ATR), and combined reforming processes are the well-known reforming processes [62-64] that have been employed by the petroleum and pharmaceutical industries in a product development pathways [61].

Syngas is also produced from coal and biomass by gasification. Unlike the syngas produced from natural gas, the syngas produced from gasification of coal or biomass contains lots of impurities such as tar, ash and particulate matter [11, 14]. This increased amount of impurities creates the need for syngas cleaning and conditioning which adds to the capital and operating cost of the plant.

It is necessary to know that each of the reforming processes has its inherent challenges due to the reaction and operating conditions, cost involvement, and environmental issues. Therefore appropriate choice of syngas production process affects the overall efficiency of GTL process [65]. As it is evident that the syngas production contributes 60% to the overall liquid fuels production cost [65], good engineering practice decision is generally applied in the choice of syngas production to use. In addition to the cost of syngas formation, H_2/CO ratio which affects the downstream formation of liquid fuels helps in the decision making process of the choice of reforming.

The various reforming processes were reviewed to highlight each process reaction, operating conditions, typical catalyst choice, and H_2/CO ratio as tabulated in 2-7.

Table 2-7: Summary of Reforming Processes

Reforming type	Catalyst	Reaction	Operating Condition	H_2/CO
Steam Reforming	$Ni/MgAl_2O_3$	$CH_4 + H_2O \rightarrow CO + 3H_2$	700-1000°C & 15-30bar	≈ 3
Autothermal	Ni/Al_2O_3	$CH_4 + \frac{3}{2}O_2 \rightarrow CO + 2H_2O$ $CH_4 + H_2O \leftrightarrow CO + 3H_2$ $CO + H_2O \leftrightarrow CO_2 + H_2$	2000°C: Combustion Zone 1000-1200°C: Catalytic zone	
Partial Oxidation		$CH_4 + 0.5O_2 \rightarrow CO + 2H_2$	1200-1500° C & 50-70bar	≈ 1.7
Dry Reforming	Pt, Pd, Ni, Co, Ru, Rh, Ire	$CH_4 + CO_2 \rightarrow 2CO + 2H_2$	700-900°C & 1-14bar	≈ 1

2.8 Fischer Tropsch Process

The quest for alternative forms of liquid fuels led to the development of Fischer-Tropsch process. Initial attempt was made by Sabatier and Sanderens in 1902 to synthesize hydrocarbons by the hydrogenating of carbon monoxide [10]. In 1920, Fischer and Trospch devised a mechanism known as synthol process that produced rich oxygenated product when carbon monoxide was catalytically converted in the presence of iron (Fe) catalyst [10, 66]. This process was then termed the Fischer-Tropsch process. The development of the F-T process brought about a promising pathway for the production of fuels from biomass, natural gas and coal [61] which serves as carbon sources. According to [32], the wide range of feedstock for the F-T process, biomass, natural gas and coal, enhances transition from energy source which makes the process sustainable.

The U.S has large amount of natural gas, biomass and coal deposit that can be respectively utilized for GTL, BTL and CTL, thus increasing the nation's energy security and in turn reduce dependence on petroleum importation [6]. Sasol in South Africa has been the world largest CTL company which made them less dependent on crude oil derived fuels in addition to the economic benefits of the process [32]. Currently, Chevron, Shell, Syntroleum, even ConocoPhilips and Total are working towards the technology; GTL and CTL [10, 32]

Fischer-Tropsch process employs a hydrogenation mechanism to convert carbon monoxide (CO) and hydrogen (H_2) to desirable and undesirable hydrocarbons as illustrated in the following reaction below [67].

$$nCO + (2n+1)H_2 \rightarrow CnH_2n_{+2} + nH_2O \ldots\ldots\ldots\ldots\ldots\ldots 4$$

Conversion of the syngas to liquid fuels in the F-T process is a complex reaction. The target product of Fischer-Tropsch process is the formation of only the straight-chain aliphatic hydrocarbons although hydrocarbons of the branched chain type are inevitably formed as well [68] and the specific products are given below:

Paraffins Synthesis: $nCO + (2n+1)\ H_2 \leftrightarrow CnH_2n_{+2} + nH_2O \ldots\ldots\ldots 5$

Olefins Synthesis: $nCO + 2nH_2 \leftrightarrow Cn\ H_2n + nH_2O \ldots\ldots\ldots 6$

Alcohols Synthesis: $nCO + 2nH_2 \leftrightarrow Cn\ H_2n_{+1}OH + (n-1)\ H_2O \ldots\ldots\ldots 7$

In addition to the reaction products, other side products are formed during the reaction. These products are usually undesirable and efforts are made to reduce and/or minimize the occurrence of these reactions. The following undesired reactions below takes place during the FT process:

Water-gas shift reaction: $CO + H_2O \leftrightarrow CO_2 + H_2$……………………………8

Carbonaceous materials: $(x + (y/2))\ H_2 + xCO \leftrightarrow CxHy + xH2O$......................9

Boudouard reaction: $CO + CO \leftrightarrow C + CO_2$……………………………10

Bulk carbide formation: $yCO + xM \leftrightarrow MxOy + yC$…...11

Catalyst oxidation: $yCO2 + xM \leftrightarrow MxOy + yCO$…………………………12

Temperature, composition of feed gas, catalyst type and associated promoters, and pressure are the known variables that influence the product formation [69].The operating temperature and pressure for the Fischer Tropsch synthesis are typically 200-340^{o}C and 25-60bar [70]. The type and activity of catalyst used during the Fischer-Tropsch synthesis process affects the rate of reaction and likewise the conversion of syngas [71]. The following range of products are obtained during the Fisher Tropsch synthesis; light hydrocarbons methane (CH_4), ethane (C_2H_4) and ethane (C_2H_5), LPG (C_3–C_4, propane and butane), gasoline (C_5–C_{12}), diesel fuel (C_{13}–C_{22}), and light and waxes (C_{23}–C_{33}) range of products.

Primarily, a mole of CO in the presence of cobalt or iron catalyst reacts with two moles of H_2 to form a chain of hydrocarbon. According to [10], this is a polymerization reaction where the CO is adsorbed to the surface of the catalyst, followed by the initiation of the cleaving of the C-O bond and the formation of -CH_2- chain. The reaction completes when the growth in chain length terminates and the product desorbs from the catalyst. Basic F-T reaction is generally given by the equation:

$CO + 2H_2 \rightarrow - (CH_2) - + H_2O$ $\Delta H = -40$ kcal/gmol CO…................13

where:

- (CH_2) – = Hydrocarbon chain extension.

The extent of the formation of the hydrocarbon chain is determined by the Anderson-Schluz-Flory distribution [72]. Since the product selectivity during the F-T process is determined by the ability of a catalyst to maintain the chain growth against the chain termination, the polymerization rates are independent of the products formed. The Anderson-Schulz-Flory model is represented by the equation

$$W_n = n(1-\alpha)^2\alpha^{n-1} \ldots\ldots\ldots\ldots\ldots\ldots\ldots 14$$

Where

W_n= mass fraction of product with n carbon atoms

α = probability of chain growth

$(1-\alpha)$ = probability of chain termination

Assuming the probability of chain growth to be independent of chain length, a plot of $Log\left(\frac{W_n}{n}\right)$ against n gives a slope equals to the chain probability value,α, which is typically low for gasoline products and high (0.8-0.9) for diesel products.

$$Log\left(\frac{W_n}{n}\right) = nlog\ \alpha + \text{ constant} \ldots\ldots\ldots\ldots\ldots\ldots\ldots 15$$

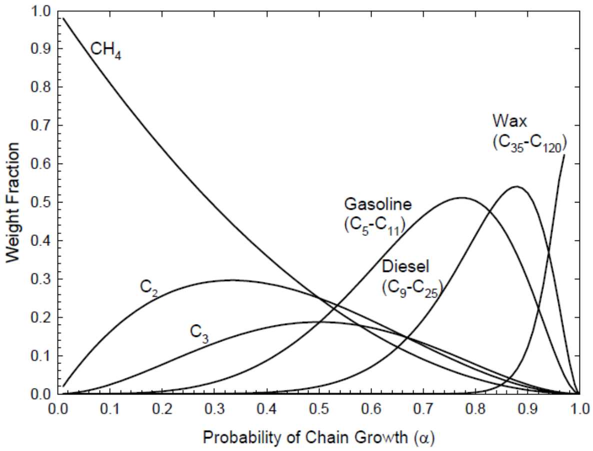


Figure 2-2: Anderson-Schulz-Flory chain growth distribution

The chain growth probability is also calculated using the equation developed by [73] as illustrated below by the partial pressure and temperature interaction.

$$\alpha_{ASF} = \left[0.2332\frac{y_{CO}}{y_{H_2}} + 0.663\right][1 - 0.0039\ (T - 533)]\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots16$$

y_{CO}= partial pressure of CO

y_{H_2}= partial pressure of H_2

T= temperature in K

The selectivity of the hydrocarbon product Sc_{5+} for cobalt catalyst has been empirically determined by with a correlation showing the relationship between temperature, pressure, and alpha value. The selectivity and alpha value relationship are shown by equations 17 and 18 below

$$Sc_{5+} = 1.7 - 0.0024T - 0.088[H_2/CO] + 0.18([H_2] + [CO]) + 0.0078P_{total}\ldots\ldots\ldots\ldots\ldots\ldots17$$

$$\alpha = 0.75-0.373*(-\log (Sc_{5+})) + 0.25\ Sc_{5+}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots18$$

2.9 Fischer Tropsch Catalysts

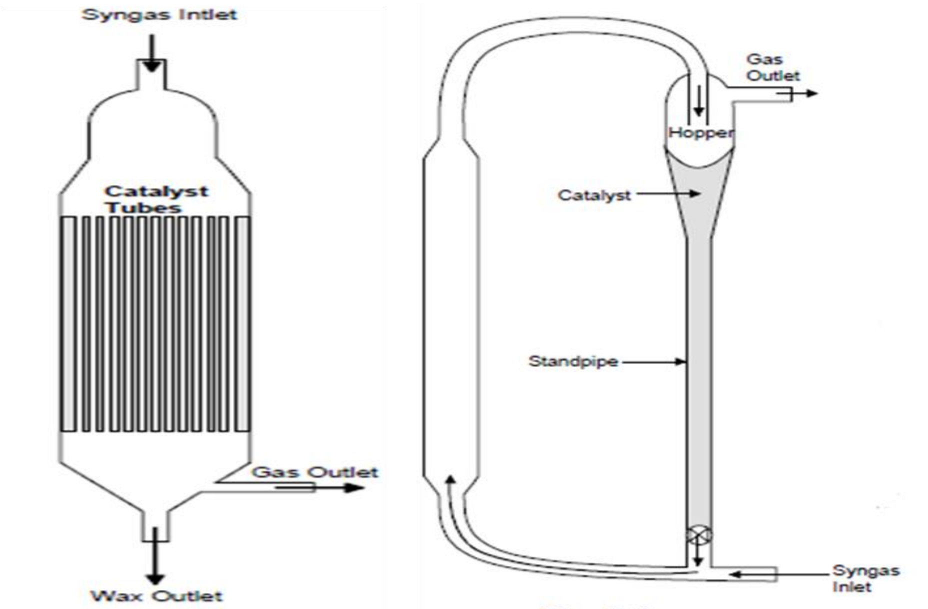
The choice of a catalyst over another during the Fischer Tropsch process is a challenging decision to be made as it depends on several factors. Cobalt (Co), potassium (K), iron (Fe) and ruthenium (Ru) are amongst the numerous catalysts used for Fischer-Tropsch synthesis [66]. Due to the better activity, considerate high life expectancy and low cost, cobalt and iron catalysts are preferentially considered for the gas to liquid process [61]. But according to [74], there is still no catalyst developed for the F-T process that can handle the challenge of the lifetime, activity and selectivity of the products.

The flexibility of the process variables, selectivity to the lower olefins, and higher conversion are the characteristics exhibited by Fe-based catalyst [75]. It is used in the high temperature FT (HTFT) process that operates at a temperature of about 300-340^{o}C. Fe catalyst proves a good resistance to sulphur, produces more olefin and alcohols and is affordable [69]. One of the limitations of a Fe catalyst is the short life spans of 8 weeks when used for commercial F-T application [76].

In as much as cobalt (Co) catalyst is 1000 times more expensive than Fe, it is more selective, efficient, less deactivated by water since water is an F-T synthesis product and hence has longer life span [67]. Dry et al., posited that for better activity, the cost of cobalt catalyst should not affect its use [77]. Co catalyst is more reactive for hydrogenation and when compared to Fe catalyst yields less unsaturated hydrocarbons and alcohols [78].

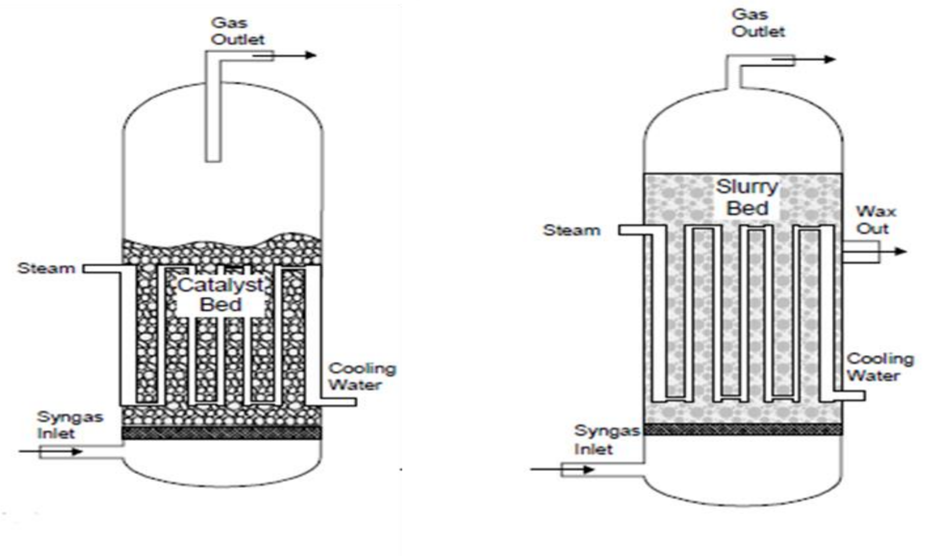
2.10 Fischer Tropsch Reactor

Over the years, the industrial and commercial reactor employed for the F-T process has been the fluidized bed and multi-tubular fixed-bed reactors [61]. In the late nineteenth century, the 3-phase slurry continuous stirred tank reactor has been investigated and proposed as a feasible reactor for F-T synthesis process [67]. Efficient heat removal produced during the exothermic F-T reactions and the solvent action of the “inert” are one of the advantage of the slurry reactor being its greater ability for [67]. The slower gas/liquid-solid interface diffusion rates obtained in comparison to both the fixed and fluidized bed reactors pose a disadvantage to the slurry reactor. Advances in the Fischer-Trospch process is in the development of new reactors for the technology. Fixed fluidized bed (FFB), circulating (synthol) fluidized bed (CFB), advanced synthol reactor, and multi-tubular fixed bed reactors were reported by [10] as the modification in the process technology as shown in figure 2-3. The design of the new reactor for the F-T process has resulted to a high capacity reactor and an increase in conversion efficiency to the order of 70% [10]. Replacing the circulating fluidized bed reactor, the fixed bed reactor has better heat removal, thermal efficiency and lower pressure drop with a scale-up trend to 20,000 bpd [79]. For the same reactor capacity, the FFB can be produced at half the cost and size of CFB. The challenge of catalyst separation have been reduced by the use of slurry bed reactor which is 75% less than the cost of multi-tubular fixed bed reactor [10].



Multi-tubular (ARGE) Fixed Bed

Circulating (Synthol) Fluidized Bed



Fixed (Sasol Advanced Synthol) Fluidized Bed

Fixed Slurry Bed

Figure 2-3: Fischer-Tropsch Reactors

2.11 Techno-Economic Assessment

Gas to liquid (GTL), biomass to liquid (BTL) and coal to liquid (CTL) processes need to be economically feasible in order to serve as a supplement or even replacement and/or substitute to the conventional fossil fuel pathway. Therefore, economic assessment is conducted to determine the cost analysis of the product.

An N^{th} plant assessment of the biorefinery for the production of liquid fuels via biomass is promising since these technologies in anticipation prove to be a future of the bioenergy. Different technological approaches have been evaluated by several researchers with focus on process and cost improvements. Of the techno-economic assessment of the GTL, BTL and CTL plants carried out by different authors, the estimated capital investment cost has been between \$191 – \$541 million [11-13]. The wide range difference in capital investment is due to difference in feedstock price, plant capacity, year value of money, process requirement, and cost estimation assumptions.

[11] performed an economic feasibility of biomass integrated gasification Fischer-Tropsch (BIG-FT) process using poplar wood of purchase cost of US \$2/GJ as feedstock. The plant operation time was 8000 h/year with a capital investment of \$380 million and an operating and maintenance cost of \$14 million per annum. The process involved in his evaluation is the advanced high temperature gas cleaning which is not commercially available. According to him, component level cost estimation was used which was obtained by consultation with manufacturers (vendor quote), literature, and communication with experts. For the calculation of the installed cost, the free on-board costs were multiplied by the installation factor obtained from [80] and industry communication. The capacity of each unit operation was obtained using mass and energy balance of the Aspen Plus model

and was scaled using a scaling exponent (n) between 0.6 and 0.8. The investment parameter used were straightforward discounting, interest rate of 10%, and depreciation period of 15 years. Production cost of the F-T liquid fuel with a hydrocracker was calculated to be between $13 and $30/GJ for 60% and 80% conversion scenarios respectively assuming an electric power price of $0.057/kWh. The addition of a hydrocracker with an estimated installed cost of $8.1 per 2000bbl/day increased the liquid fuel production cost by about 5%. Performing a sensitivity analysis, he observed the high effect of electricity on the overall process. The production cost of $14/GJ F-T liquid was for a short term project but comparing the long term effect of the plant, he observed that the advancement in technology will reduce the capital cost (contributed 50% of original production cost), the operating and manufacturing cost, feedstock cost, and the process energy efficiency. Hence, the production cost for the F-T liquid dropped from $14 to $9/GJ.

Economic assessment of Fischer Tropsch (FT) diesel produced from the gasification of wood was determined by [12]. The investment parameters used for estimating the plant cost were similar to that of [11] in areas of interest rate and operating time. However, he assumed a feedstock cost of $3/GJ, electricity cost of $0.03/kWh, and economic and technical lifetime of 15 and 25 years respectively. The annual operating costs were estimated as a percentage of the total capital investment. Estimating the total capital investment, [12] used the factored estimation method which has an accuracy of ± 30%. He applied the scale up method to estimate equipment costs for similar unit operations when the maximum capacity was not exceeded. Calculating the total capital investment, he obtained a value of €286 million which is 1.7 times higher than that reported by [23]. He attributed the difference in cost to the gasifier and air separation unit used in his process of which without pre-treatment and gasifier, the cost will be about €93 million.

Corn stover (2000 metric tons/day) feedstock was used by [14] to produce F-T liquid fuels alongside excess electricity in two temperature (HT & LT) scenarios of which he estimated a capital investment of $610 and $500 with a corresponding product value of $4.3/GGE and $4.8/GGE respectively. Comparing his product value with that obtained by [11] of approximately similar plant capacity and process technology, it can be inferred that the difference lies in the time value of money at which the estimation was performed, technology difference and most importantly, the investment parameter assumptions.

2.12 Life Cycle Assessment

Global liquid fuels consumption for the everyday transportation activities of humans are highly indispensable. Petroleum derived fuels have been the predominate source of transportation fuel contributing 92% of transportation fuels [81]. In 2013, the monthly energy review of the United States Energy Information Administration (EIA) reported an annual petroleum consumption of 203 million gallons by the transport sector [82]. This makes the transportation sector the highest consumer of petroleum derived fuel in the United States [82] as evident in the over 250 million registered vehicles in the U.S reported by the Research and Innovative Technology Administration of the Department of Transportation [83]. With rapid industrial, economic, and improved standard of living, more vehicles are acquired on daily basis which contributes to petroleum fuel consumption in the United States. The increase in the number of vehicles results to a higher demand of petroleum fuel to power the increasing number of vehicles of which the security of the fossil fuel is not guaranteed.

Traditionally, petroleum fuels are produced by exploration and production (E&P) companies through the process of hydrocarbon extraction from beneath the earth crust. The extracted product is a mixture of gas, oil, and water which are processed in their facility in a train of separators and compressors into the individual constituents. The crude oil is then sent to the refinery to obtain the different fractions of petroleum fuels. The combustion of this fuel leads to emissions of pollutants such as carbon dioxide (CO_2), volatile organic compounds (VOC), nitrogen oxides (NO_x), sulphur dioxide (SO_2) and other pollutants which primarily is as a result of the presence of sulphur in the fuel [84]. In the U.S, the greenhouse gas emissions from the transportation sector is the second highest source of GHG after the power sector [85, 86]. Increased climate change caused by the use of fossil derived fossils has led to the search for alternative ways whereby the emissions as a result of the production and use of fossil derived fuels will be reduced.

As a remedy to the environmental impacts fossil energy use, renewable energy sources are tipped to mitigate climate change impact due to the biogenic nature of its emissions. Therefore, reduction in energy use, increase in energy efficiency and carbon sequestration, and decarbonization of energy supply by renewable energy sources are advantages which the renewable energy tends to offer [87]. However, these assertions do not have any proven facts and have raised many concerns about its potential to reduce

In the past, [6, 28-33] have all conducted an environmental assessment on GTL, BTL, and petroleum diesel and gasoline products to evaluate the product performance on the environment. Evaluating the life cycle assessment of petroleum products, [28] opined in his assessment that the GHG of crude oil extraction, processing and storage contributed 4 - 12% GHG's more than the actual fuel combustion. For GTL and BTL process, [30] determined from his assessment that the emissions associated with transportation can be reduced by 28 – 69% using BTL from straw or forest wood. Also, [32] reported that vehicles operated with BTL can result to an emission of 32 – 63g CO_2/km but can be reduced to negative if carbon sequestration was employed. Reduction of GHG can be achieved according to [6] by substitution method of allocation and even more when GTL fuels are mixed with heavy crude oil. But on the contrary, [29] conducted the GHG emissions of GTL diesel fuel focusing on the GTL synthesis efficiency and compared it with conventional fuels using life cycle analysis (LCA). He observed that the GHG emissions of GTL fuel process was higher than the petroleum diesel at a GTL synthesis efficiency less than 75% with an improvement in emissions of GTL fuels at a synthesis efficiency of 75% or greater. Performing a cradle to grave LCA work on the hydrogenation-derived renewable diesel (HDRD) using three different biomass (whole tree, forest residues, and agricultural residues), a GHG reduction up to 61.1% compared to fossil derived fossil was estimated [88]. In the light of these conflicting results, the life cycle assessment for the production of drop-in fuels from the miscanthus generated biogas will be conducted to effectively evaluate and justify the environmental friendliness of the renewable fuels process.

2.13 Literature Summary

The overall study of the production of liquid fuels have been reviewed with specifics on the feasibility of biogas as a potential feedstock for liquid fuels production.

Biogas with a 60% methane content is proposed to be a possible replacement or co-feed for the production of renewable fuels via Fischer-Tropsch synthesis with potential reduction in the greenhouse gas (GHG) emission.

In addition to the conventional liquid state anaerobic digestion process, lignocellulosic biomass is used as feedstock in a solid state anaerobic digester (SS-AD) to produce biogas which is to be further converted to liquid fuels via Fischer-Tropsch synthesis. Biogas production from lignocellulosic biomass can be challenging due to inherent characteristics of the feedstock. Lignocellulosic biomass is composed of complex carbohydrate structure which typically does not promote the anaerobic digestion process. Hence, a breakdown of the structure to cellulose, hemicellulose and lignin is normally required in order to enhance the yield of biogas [38]. Pretreatment processes such as fungal pretreatment, wet oxidation, acid hydrolysis have been used in pretreating lignocellulosic biomass prior to AD process [89, 90]. Similarly, the carbon to nitrogen (C/N) ratio of lignocellulosic biomass is high than the optimum value of 25 [91].

Biogas methane potential from lignocellulosic biomass such as miscanthus have been reported to be within the range of 0.17-0.218 m^3/kg VS [92]. The produced biogas can be cleaned via several upgrading processes [36, 37, 60] which the high pressure water scrubbing (HPWS) process proves to be the most economical and efficient in terms of biogas methane recovery [93].

The cleaned biogas solely can be used as feed for the liquid fuels production via F-T synthesis or co-fed with natural gas in an existing GTL plant such as the Shell Bintulu's GTL plant in Malaysia [94]. The process of converting the cleaned biogas commences with the catalytic conversion of the methane in biogas to syngas (steam methane reforming) or the non-catalytic process (partial oxidation) and several other reforming processes depending on the desired syngas output composition [10, 23].

Liquid fuels production can be carried out in diverse reactors operating at 200 – 340°C temperatures in the presence of different types of catalysts (Fe or Co) depending on the selectivity of the final liquid fuels fraction (gasoline or diesel) [61, 64]. A temperature of 340°C in a slurry reactor packed with Fe catalyst is typically used for gasoline fraction fuels while Co catalyst in slurry phase reactor operating at 200°C offers a high selectivity for the diesel fuel fraction [10]. Another key parameter that determines the length of hydrocarbon formation is the probability of chain growth, α, which varies from 0.1-1 [70].

The techno-economic feasibility of the process reviewed showed that no available literature data on the process and economics of the biogas to liquid (BgTL) fuels is currently in existence which shows the novelty of this work. However, several reported works on the renewable liquid fuels production have focused on the biomass thermochemical conversion. Total capital investment (TCI) ranging from $191 – $541 million have been reported for different processes using different feedstocks [11-13] with a minimum selling price of F-T fuels of up to $4.3/GGE [14]. Such estimated minimum selling price is highly dependent on certain process and plant assumptions which are plant specific.

Environmental concerns in terms of greenhouse gas emission of the liquid fuels production using renewable feedstocks were ascertained. Life cycle analysis studies of the greenhouse gas emission (GHG) of various renewable derived fuels were conducted to determine the extent of climate change savings offered by renewables. GHG savings of up to 61.1% lower than diesel obtained from conventional refinery was estimated when renewable diesel was produced from agricultural residue in a cradle to grave life cycle analysis [88].

Overall, the review of the processes involved in the liquid fuels production via F-T synthesis, techno-economic assessment of F-T liquid fuels production, and the environmental impact assessment of the renewable fuels production served as the background, references for certain data, and rational in the F-T fuels biogas route employed in this thesis work.

CHAPTER 3

TECHNO-ECONOMIC ASSESSMENT OF BIOGAS TO LIQUID FUELS CONVERSION TECHNOLOGY VIA FISHER-TROPSCH SYNTHESIS[1]

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[1] Okeke, I.J., and Sudhagar Mani. To be submitted to the Biofuels, Bioproducts & Biorefining Journal

Abstract

Contrary to the recent biomass gasification to liquid fuels production, a unique biogas to drop-in fuels plant was simulated using Aspen Plus V8.8. With the aid of the process model, the mass and energy balance was estimated which was employed in the techno-economic analysis of BgTL model. A base case biogas feed capacity of 2000Nm^3/h was assumed which was upgraded to produce biomethane, reformed to yield syngas, catalytically converted to F-T syncrude, and finally upgraded to generate drop-in fuels. Electricity and steam were produced within this process utilizing the excess unconverted syngas and integration approach (pinch points) respectively while the excess electricity was sold. For the specified annual feed capacity, a total production capacity of 4.6 million gallons per annum of F-T drop-in fuels was achieved resulting to a 51% yield in mass basis. Calculating the discounted cash flow rate of return (DCFOROR) for this Nth plant (100% equity financed) with the estimated capital and operating costs, the least selling price of the F-T drop-in fuels was \$5.99/gal (\$5.59/GGE). Different biogas plant feed capacity was explored to determine its effect on the F-T drop-in fuels selling price. Finally, sensitivity analysis on the base case model was performed by varying critical process and cost parameters in order to ascertain their effects on the least selling price of the drop-in fuels.

Keywords: Biogas, F-T drop-in fuels, Aspen Plus, Process model, Plant Capacity, Syngas

3.1 Introduction

The global demand for transportation fuels is a “conditio sine qua non” for everyday living in the 21^{st} century. Sequel to aforementioned, there is a high global demand for these fuels that oil importation can be resorted to meet the domestic fuel needs of a country. The U.S Energy Information Administration [82] have reported a high consumption of petroleum products from the transportation sector consuming approximately 14 million barrels per day. The increase in global population and relative increase in standard of living of people from developing country can further fuel the demand for transportation fuels. High global dependencies on petroleum fuels could cause fuel price instability in addition to increasing the greenhouse gas (GHG) emissions.

Because of the increased interests in environmental sustainability, countries are making specific rules to accommodate the use of petroleum fuels but reduce the extent of emissions associated with its combustion. Hence, the U.S government in the Energy Independent and Security Act (EISA) enacted the renewable fuels standard (RFS) which regulates a number of renewable fuels blend in liquid transportation fuels [95]. Ethanol produced from corn grain, corn stover, switchgrass, etc. has been blended with gasoline to achieve the RFS target. In 2015, annual ethanol production in the United States has reached to about 14.8 million gallons with a world annual ethanol production of 25.68 million gallons [96]. On the other hand, lignocellulosic feedstock and other sources of unutilized organic sources (e.g. MSW, Food Waste and Animal Manures) can open a new pathway to produce transportation fuels via anaerobically generated biogas into drop-in liquid fuels.

Anaerobic digestion is a well-studied commercial technology to produce biogas from waste organic sources that can further be converted to produce compressed natural gas (Bio-CNG), and heat and power generation. A recent study [7] by National Renewable Energy Laboratory (NREL) reported that approximately 7.9 million tonnes of methane can be produced annually from organic waste sources in the U.S. Lignocellulosic biomass such as agricultural crop residues and energy crops can be either co-digested with organic wastes [8] or dry digested to produce biogas. Currently, a LemvigBiogas plant in Europe co-digests liquid and solid feedstocks that produce 10.2 million Nm^3 per annum of biogas[97]. This large amount of biogas from a single biogas plant illustrates the potential of an AD technology in producing huge volumes of biogas that can serve wide range of applications namely: a feedstock for both domestic and industrial possesses and production of multiple fuels and chemicals.

Biogas is a mixture of methane (40-60%) and carbon dioxide (30-40%) with other impurities such as H_2S, NH_3, O_2, N_2, etc. depending on the type of feedstock [37, 98]. Biogas in its raw form can be utilized in an internal combustion engine, to produce power and heat generation, cooking applications [99]. An upgraded form of biogas, biomethane, can be used as a substitute for natural gas or further converted in to drop-in diesel or gasoline fuels (biogas-to-liquid, BgTL) to meet both U.S and global transportation fuel demands [13]. However, the technical and economic feasibilities of this technology need to be further investigated. A study on biogas cleaning to remove CO_2 and H_2S has been experimentally carried out by [100] in a packed column reactor to achieve a 90% CO_2 reduction efficiency and H_2S reduction below detectable limit with a chemical solvents such as NaOH, $Ca(OH)_2$, monoethanolamine (MEA). Although the process was technically feasible, the economic aspect of this cleaning approach was high due to solvent cost, solvent regeneration challenges, and stability. However, high pressure water scrubbing (HPWS) is a commercially employed biogas cleaning method with an effective cost US$0.22 per Nm^3 of biogas upgraded (US $ 2015), 94% yield, and a biogas purity of 98% [93]. A Kristianstad biogas plant located in Sweden processes about 70,000 tonnes of organic wastes (50% organic manure, 45% food waste, and 5% household) [99] with an attached biogas water scrubbing facility that produces 50,000 MWh/yr upgraded biogas consisting of 97% methane that is primarily used as vehicle fuels [101]. The upgraded biogas can be reformed into syngas using steam and further converted into liquid fuels or power. A recent experimental study by Rakass et al., [102] conducted a steam reforming of methane in the presence of unsupported Ni catalyst that achieved a 98% conversion of methane at 700°C into syngas with high H_2 yield and CO selectivity. Other studies on the steam reforming of methane has reported a complete conversion of methane at a high steam to carbon (S/C) ratio of no less than 4 [103] in the presence of Ni/Al_2O_3 catalyst. The produced syngas can be subjected to F-T synthesis to produce liquid hydrocarbons operating at 473K and 20 bar in the presence of cobalt catalyst with high conversion of H_2 and CO at gas hourly space velocity (GHSV) of about 37 $Nml.g_{cat}^{-1}.h^{-1}$.

Gas-to-liquid (GTL) and coal-to-liquid (CTL) process technologies are established liquid fuels production processes operated by different companies such as Sasol, Shell, Syntroleum, and ExxonMobil in various parts of the world. Exploring the different GTL plants, Greene [104] reported the different plant capacity and capital investments by various companies that aimed at estimating the project profitability.

Similar to the GTL and CTL, thermochemical conversion of biomass to liquid fuels production has gained huge attention in the recent years. The pathways such as biomass-to-liquid (BTL), biomass-to-butanol (BTB), biomass-to-ethanol (BTE), and biomass-to-methanol (BTM) fuels processes have been studied recently as possible commercial routes to produce liquid biofuels [11, 13, 14, 20, 23, 105]. Considering the economic aspect of the liquid fuels processes, a techno-economic aseeesement (TEA) study on natural gas to liquid (GTL) fuels plant conducted by Betchel [23] reported that 44,940 BPD of liquid fuels could be produced from 412 MMSCF/day of natural gas with a total capital investment of $1842.5 milllion (US $ 1993). Williams et al., [20] conducted a TEA of a 3000 tonnes/day biomass to methanol plant estimated a methanol selling price of $12/GJ ($1.42/GGE) for a US $1995 cost year. Similarly, a techno-economic analysis performed by Phillips [106] for ethanol production from hybrid poplar wood with a feed plant capacity of 2000 tonnes/day estimated a minimum selling price of $1.01/gal ($1.49/GGE). Moreso, Tijmensen et al., [11] estimated a minimum selling price of $9/GJ of F-T fuels from an 80 tonnes/h (1741 tonne/day) poplar wood plant worth $380 million (US $1999) in capital investment. The cost analysis of 1327 tonnes/yr of switchgrass biomass to F-T fuels (gasoline and diesel) studied by Larson et al., [13] produced 3897 BPD of F-T fuels with a capital investment of $541 million (without spares) (US $ 2003) which was discounted to attain a fuel plant gate cost of $15.25/GJ. In 2010, the National Renewable Energy Laboratory (NREL) reported an economic-study of a 2000 tonnes/day corn stover to F-T fuels plant and estimated a product value of $4.80/GGE and $4.30/GGE respectively in a low and high temperature scenarios with a total capital investment (TCI) of $498 million and $606 million (US $2007) respectively [14]. Finally, Okoli et al., [107] carried out an economic study of butanol liquid fuel production from a 75 tonnes/h pine woody biomass plant with a TCI of $357 million (US $2012) and a minimum butanol selling price of $0.83/L. Although these biomass conversion routes are promising for liquid fuels production, limited study has been published on the techno-economic feasibility of biogas to liquid fuels production route and the interrelationship between the plant size and capital investment.

As already stated, biogas can be produced from anaerobic digestion of lignocellulosic biomass which can be further converted to drop-in fuels. Hence, drop-in-biofuels such as renewable diesel and gasoline can also be produced not only via the thermochemical conversion (gasification) of lignocellulosic biomass but also via biochemical conversion (anaerobic digestion) of biomass. By and large, these conversion routes are the future of green/renewable fuels production. However, each operating routes has its inherent advantages and disadvantages. Focusing on the liquid transportation fuels from biomass gasification, the economic feasibility of the process can be of doubt given the high capital cost of the process technology. For instance, biomass feedstock are typically preprocessed (screened, dried and size reduced) [80] upstream prior to downstream processing. And the work of Tijmensen et al., [11] estimated a preprocessing operation cost that contributed the highest installed cost (21%) compared with that of other process operations. In addition to the high gasifier cost, the presence of contaminants such as particulates, tars, alkali compounds [11] in the biomass-gasified syngas negatively affects the downstream process and poisons the catalysts [10] if not removed. Boerrigter et al., [108] reported that the technology in achieving biomass-gasified syngas cleaning and conditioning processes possess a challenge in the liquid fuels production pathway of which several authors [13, 14, 109] have estimated a high installed cost for those unit operations. Contrary to the challenges associated with the biomass gasification route, biogas reforming route has lower capital cost, less impurities and no further capital intensive investment after reforming due to the purity level of biomethane. Although biomass gasification route is relatively expensive, the rate of conversion of biomass to syngas is high when compared with biomass to biogas prior to biogas reforming. This high conversion achieved in biomass gasification route is an inherent advantage when compared with biogas reforming route where a retention time of at least 28 days is required to produce biogas prior to reforming. Nevertheless, given the proven technology in converting solid organic matter either as a standalone feed or in an integrated anaerobic digester (iAD), biogas production challenges have been considerably addressed.

Therefore, the main objectives of this paper is to develop a process simulation model to produce drop-in-biofuels from biogas via Fischer-Tropsch synthesis and to conduct a detailed techno-economic assessment of biogas to liquid fuels technology to estimate capital investment, operating cost and minimum selling price of biofuels.

3.2 Methodology

3.2.1 Process model description

A baseline Biogas to Liquid (BgTL) fuels production technology via F-T synthesis as shown in Figure 1 was developed with a biogas processing capacity of 2000Nm^3/h that could be delivered from a large scale anaerobic digestion plant. [97]

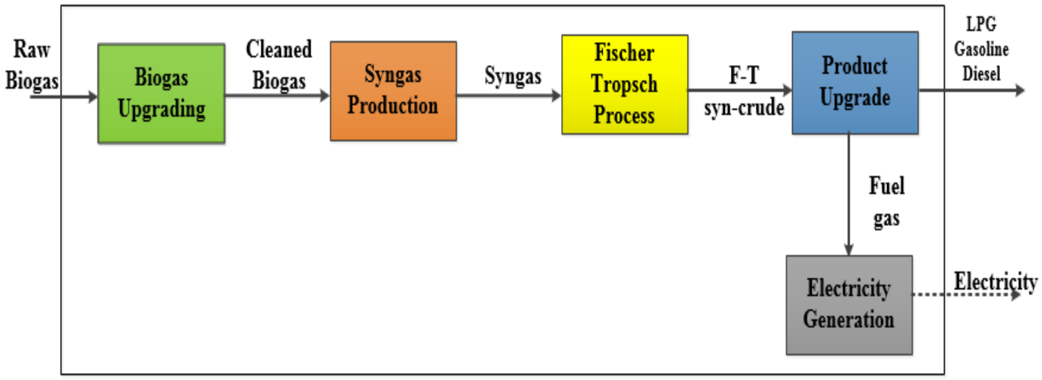

Figure 3-1: Block flow diagram of the biogas to liquid fuels (BgTL) process technology

Raw biogas from an anaerobic digestion plant consists of mainly CH_4, and CO_2, and trace amounts of H_2S, N_2, O_2 and saturated water vapors and serves as a feedstock for producing drop-in diesel fuel. The presence of trace gases and carbon dioxides should be removed or stripped to enhance downstream conversion process. In this study, it was sent to the biogas upgrading section of the plant with the overall goal of removing the impurities (CO_2 and H_2S) present in the biogas stream which affects the downstream process [10]. The upgrading approach employed for the biogas cleaning is the commercial high pressure water scrubbing process [36, 60] which produces biomethane with 97% methane composition. The biomethane (cleaned biogas) product was sent to the syngas production area where two reforming processes (steam and partial oxidation reforming) were employed in order to attain the desired syngas ratio [23] and maintain an energy efficient syngas production [110]. So, the biomethane stream was split and sent to the steam and partial oxidation reforming processes that produces syngas of different compositions. As the downstream liquid fuels production requires a hydrogen to carbon monoxide ratio ($H_2/CO=2$), the syngas products of the two processes were mixed and then cooled to remove excess water in the syngas before it was sent to the F-T synthesis process. Catalytic conversion of the syngas feed occurred in a low temperature slurry phase reactor in the presence of cobalt catalyst to yield F-T syncrude with high selectivity for the heavy chain fractions due to the probability of chain growth used for this model. The F-T syncrude undergoes product upgrading to obtain the different fuels fractions. Hydrocracking, hydrotreating, and distillation and separation were the upgrading operations that the syncrude mixture was subjected to obtain the desired final products of drop-in fuels fractions: LPG, gasoline, and diesel. Process steam was generated using the excess heat produced by exothermic reactions in certain processes. The unconverted methane and syngas were combusted to generate electricity through a combined cycle (gas and steam turbine) to meet internal electricity demand and the excess electricity was sold to the grid.

3.2.2 Process Design and Modeling

Our process design and modeling approach for the BgTL conversion technology used the optimal operating conditions from industry data and relevant literature sources using an ASPEN Plus simulation platform. The raw biogas composition was defined based on various literature sources as shown in Table 3-1.

Table 3-1: Raw biogas composition

Biogas Constituents	Unit	Monnet (2003) [20]	Appari (2014) [21]	Persson et al (2009) [9]	Dirkse (2007) [12]	Present work Aspen Model
Methane	Vol %	55-70	50-75	53-70	60-70	60
Carbon dioxide	Vol %	30-45	25-50	30-47	30-40	37.5
Nitrogen	Vol %	0-2	0-10	0.2	<1	0.5
Hydrogen sulphide	ppm	~500	0-300	<1000	10-4000	400
Oxygen	Vol %	0	0		<0.2	0.2
Water	RH %	0	0	0	100	0.0176

The raw biogas also consists of sediments and dust particles that should be separated using a settling tank prior to the upgrading process [30]. Two isentropic compressors were designed to operate at 2 and 8 bars respectively in order the satisfy the pressure demands on the system. And each of these two compressor outlet were connected to a 20^{o}C TEMA coolers so as to control the temperature of the process. The raw biogas existing the settling tank was then passed through series of compressors and coolers that brought its temperature and pressure to that of the absorber packed tower operating at 20^{o}C and 8 bar [60]. The absorber and stripping columns are counter current columns designed with a plastic intalox structured packed bed that enhanced mass transfer operation in the gas and liquid phases when they are in contact as a result of their interaction. This choice of packing material is due to the corrosive nature of the contaminants in the gas as the plastic intalox packing is resistant to corrosion, has minimum liquid holdup and causes lower pressure drop compared to other packing materials [31]. Non-random two-liquid (NRTL) with Henry's constant was used as the activity coefficient for the property method calculations. The solubility of biogas mixtures in water which occurred in the absorption column was estimated by Henry's law which is an intrinsic parameter of the property method used to simulate the biogas upgrading section of the plant. The loss of methane during the upgrading process was minimized by dropping the pressure of the solute-rich water stream to 2 bar in the flash drum before the recycling and stripping operation [60]. The top product of the flash drum containing some methane was sent back to the absorber column through the compressors and coolers, while the bottom product containing the solute-rich water was sent to a packed bed air stripping column. The air stripping column operating at 20^{o}C and 1 bar [60] was employed to regenerate the process water continuously for the absorption operation, while 10% of the recovered water was purged to reduce buildup of undesired gas before it was recycled into the absorber column.

Biomethane, the product of the absorption process, is the feedstock for syngas production via steam reforming and partial oxidation processes. The two reforming processes ensured that the F-T syngas ratio was achieved [110]. The two processes were coupled to attain proper energy efficiency by the use of exothermic heat from the partial oxidation reaction to drive the steam reforming process. The steam reformer modeled as a plug flow reactor (PFR) was operated at a temperature of 850^{o}C and a pressure of 15 bar [111], reforming the biomethane in the presence of $NiAl_2O_3$ catalyst. The feed to the PFR was maintained at a steam to carbon (S/C) ratio of 4.0 [103] which enhanced the complete conversion of methane to syngas. The reaction rate and conversion was predicted by the steam methane reforming (SMR) Langmuir Hinshelwood Hugton Watson (LHHW) kinetics developed by [112] as shown in equation (1-3). The temperature dependent Arrhenius expression for the reaction is also shown in equations (4& 5).

$$R_1 = \frac{k_1}{P_{H2}^{2.5}} \frac{P_{CH4}P_{H2O} - (P_{H2}^{3}P_{CO}/K_1)}{DEN_1^2} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

$$R_2 = \frac{k_2}{P_{H2}} \frac{P_{CO}P_{H2O} - (P_{H2}P_{CO2}/K_2)}{DEN_1^2} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2$$

$$R_3 = \frac{k_3}{P_{H2}^{3.5}} \frac{P_{CH4}P_{H2O}^{2} - (P_{H2}^{4}P_{CO2}/K_3)}{DEN_1^2} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3$$

where $DEN_1 = 1 + K_{CO}P_{CO} + K_{H2}P_{H2} + K_{CH4}P_{CH4} + \frac{K_{H2O}P_{H2O}}{P_{H2}}$

$$k_i = k_{oi} \times e^{-Ei/RT} \qquad i = 1, 2, 3\ldots\ldots 4$$

$$K_j = K_{oj} \text{ x } e^{-\Delta H_j/RT} \qquad j = CO, H_2, CH_4, H_2O\ldots.5$$

SMR catalyst consumption was estimated from the work of Swanson et al., [14] on hourly basis (kg/hr) assuming a catalyst life of 3 years. Syngas production via partial oxidation (POR) reaction is an exothermic non-catalytic reaction with an optimal operating condition of 1127^{o}C [113] and 50 bar [114] and the process was modelled as a Gibbs reactor (RGibbs) which follows the minimization of Gibbs free energy to perform a phase equilibrium and chemical equilibrium [115]. The two syngas streams from SMR and POR were mixed and cooled to 50^{o}C [12] and the excess water present in the syngas was removed prior to sending it to the slurry reactor. The overall syngas composition has a H_2/CO ratio of 2.19 and was necessary to produce drop-in fuels via Fischer-Tropsch synthesis process where the excess hydrogen was used for the syncrude upgrading. The various reaction that occurred during Steam and partial oxidation reforming and F-T synthesis are shown in Table 3-2

Since our target product is the diesel fraction, the F-T liquid fuels synthesis was modeled similar to the Bechtel's slurry phase reactor design [116]. The low temperature process took place at a temperature of 200°C and 26 bar in the presence of cobalt catalyst [10, 61, 77]. Sequel to the operating condition of the slurry reactor, the syngas feed was conditioned using a heater and compressor upstream the F-T slurry reactor. We assumed a 55% single pass conversion with separation and recycle to achieve an 80% overall conversion of the syngas in the slurry reactor which was similar to the conversions achieved by [11]. The reaction rate for the formation of the syncrude is proportional to the weight of catalyst which is a function of the gas hourly space velocity (GHSV) [116]. The catalyst consumption rate per m^3 of syngas processed was determined using the gas hourly space velocity of 2.38 $m^3/hr.kg_{catalyst}$ reported by [116]. Although the use of cobalt catalyst promotes the formation of diesel fractions, [10], it also eliminates the formation of water-gas shift reaction [77, 117]. Since the F-T process is an exothermic process, it served as a pinch point that was effectively recovered and used in other areas of the process. The length of hydrocarbon product formed during F-T synthesis is dependent on the alpha chain growth probability model predicted by Anderson-Flory mechanism [61] according to equation (6).

$$W_n = n(1-\alpha)^2\alpha^{n-1} \ldots\ldots\ldots\ldots\ldots 6$$

where

W_n= mass fraction of product with n carbon atoms

α = probability of chain growth

$(1-\alpha)$ = probability of chain termination

A basic Fortran expression was written in Aspen Plus that estimates the α_{ASF} value based on the syngas feed parameters and reactor operating condition using the alpha correlation parameter developed by [73] as shown in equation (7).

$$\alpha_{ASF} = \left[0.2332\frac{y_{CO}}{y_{H_2}} + 0.663\right][1 - 0.0039\,(T - 533)]\ldots\ldots\ldots 7$$

The estimated α_{ASF} variable solves the product distribution expressions that yields the Fischer-Tropsch syncrude products.

Table 3-2: Different process reactions

Processes	Reaction	Reference
Steam Reforming	$CH_4 + H_2O \rightarrow CO + 3H_2$	[112]
	$CO + H_2O \rightarrow CO_2 + H_2$	
	$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$	
Partial Oxidation	$CH_4 + 0.5O_2 \rightarrow CO + 2H_2$	[114]
Fischer-Tropsch synthesis	$nCO + (2n+1)H_2 \rightarrow CnH_2n_{+2} + nH_2O$	[67, 68]
	$nCO + 2nH_2 \leftrightarrow Cn\ H_2n + nH_2O$	
	$nCO + 2nH_2 \leftrightarrow Cn\ H_2n_{+1}OH + (n\text{-}1)\ H_2O$	

F-T syncrude predominantly consist of long chain paraffin's, olefins and oxygenates [77] as shown in table 2. In order to use F-T liquid fuels as conventional fuels, it has to be refined in somewhat similar fashion as crude oil product. Initially, the light gases in the syncrude were separated in high pressure hydrocarbon recovery unit which is collected as the LPG (C_3) fractions while the heavy hydrocarbons of wax, distillates and naphtha were further processed downstream. Hydrocracking of the wax fractions occurred at 380^oC and 50 bar [118] in the presence of platinum catalyst with a liquid hourly-space velocity (LHSV) of 1.1 hr^{-1} [119]. The distillate and naphtha fractions were selectively hydro treated in a distillate and naphtha hydrotreaters [23] on a $CoMo/Al_2O_3$ with a LHSV of 1.2 hr^{-1} [120]. Distillate hydrotreating specifically improved the diesel fraction cetane number while naphtha hydrotreating saturated the olefins [121] for higher paraffin formation, which is the inherent F-T products. The different drop-in fuel fractions of gasoline and diesel were obtained by distillation using the principle of relative volatility of the hydrocarbons with some wax (C_{30}) fractions recovered as heavy bottom products and sold as a co-product. The underwood equation of the DSTWU block was employed to achieve product slits by initially performing an iteration to determine the minimum reflux ratio (R_{min}). Hence, the actual reflux ratio was obtained using the correlation ($1.5*R_{min}$) [122] which calculated the corresponding number of stages.

The unconverted syngas in this process was used as a fuel gas for electricity generation. A combined cycle approach was employed in this analysis to effectively utilize the flue gas heat in a heat recovery steam generator (HRSG). For optimal fuel gas energy usage, the fuel gas was subjected to a laydown system operating at 8 bar which utilizes the internal energy of the fuel gas to produce electricity before the fuel gas was combusted in a burner in the presence of excess air and steam. Air with 20% excess oxygen served as an ignition medium in the burner which was calculated from the stoichiometric air fuel ratio using the Aspen Plus calculator block. Steam was used as a thermal NOx control medium and was varied according to [123] to reduce the amount of NOx in exhaust gas. The hot gas was fed to the gas turbine to generate electricity while the hot flue gas heat was recovered in a HRSG for steam and additional electricity generation in a steam turbine. The rate of water circulation for the Rankine cycle depended on the amount of heat recovered from the flue gas by the HRSG which was calculated using the calculator block. The operating conditions of the unit operations are given in table 3-3

Table 3-3: Operating condition for different unit operation

Unit Operation	Type	Temp (ºC)	Pressure (bar)
Inlet Tank	Fixed roof	20	1
Compressor 1	Isentropic	−	2
Compressor 2	Isentropic	−	8
Cooler (1&2)	TEMA	20	−
Valve	ASME	−	2
Absorber	Packed Tower	20	8
Flash	Fixed roof	20	2
Stripper	Packed Tower	20	1
Pump (1&2)	Centrigual	−	8
Air Compressor	Isentropic ASME	−	1.1
POX-Heater	TEMA	1127	50
SMR-Heater	TEMA	850	15
Partial Oxidation Reformer (POX)	POX	1127	50
Heat exchanger	TEMA	1127	−
Separator & Cooler	TEMA	50	−
Steam methane reformer (SMR)	SMR	850	15
Compressor	Isentropic ASME	−	90
Heater	TEMA	180	−
Pressure Swing Absorber (PSA)	Packed bed	−	Swing
Slurry Phase F-T reactor	Slurry Phase	200	40
Separator & Recycle	TEMA	50	−
Depropanizer	Tray Tower	−	20
Hydrocarbon Recovery	Tray Tower	250	Atm
Hydrocracker	UOP	380	50
Naphtha hydrotreater	UOP	300	41.37
Distillate hydrotreater	UOP	315	40
Distillation 1	Tray Tower/Vaccum	−	1.2
Distillation 2	Tray Tower/Vaccum	−	1.7
LPG Storage Tank	Fixed roof	Atm	Atm
Gasoline Storage Tank	Fixed roof	Atm	Atm
Diesel Storage Tank	Fixed roof	Atm	Atm
Boiler	TEMA	Sat	−
Pump	Centrigual	−	15
Laydown	Isentropic ASME	−	8
Burner	Generic	1370	−
Air Compressor	Isentropic ASME	−	1.1
Steam Turbine	Isentropic ASME	−	0.1
Gas Turbine	Isentropic ASME	−	6
Heat Recovery Steam Generator	TEMA	120	−
Pump	Centrigual	−	125

The mass and energy balance of the base case BgTL (2000 Nm^3/h) plant was obtained from the Aspen Plus model which was used in the estimation of the capital cost and operating cost. For subsequent evaluation of the effect of the assumed plant capacity on the overall project cost evaluation, we developed three additional models of different feed capacities: 500, 10,000, and 20,000 Nm^3/h employing the same design specification as the base case to ensure comparison. These four BgTL models were useful in evaluating the potential of biogas as a future possible drop-in fuels route when such capacity of biogas can be delivered for conversion to liquid fuels via F-T synthesis.

3.2.3 Techno-Economic Assessment

Techno-economic assessment of the biogas to liquid fuels (BgTL) was performed using Aspen Process Economic Analyzer (APEA) v8.8 on a (USD $ 2014) pricing basis. The sizing of the unit operation was carried out using the Icarus cost estimator and mapped to the appropriate equipment in APEA in order to obtain the base equipment cost (fob) and installed cost. The estimated installed cost was escalated to USD $2015 using the chemical engineering cost index. A discounted cash flow rate of return (DCFROR) at a net present value (NPV) of zero was performed using the estimated total capital investment (CAPEX) and operating cost (OPEX) obtained from the mass and energy balance of the BgTL model at an assumed plant life of 20 years to obtain the least selling price of fuel (LSPF). Internal rate of return (IRR) of 10% was used for this analysis [124]. The plant was assumed to be 100% equity financed which is one major assumption of an N^{th} plant [125]. Basic investment parameter assumptions are shown in table 3-4.

Table 3-4: Investment parameters

Parameter	Value	Units
Number of Periods for Analysis	20	
Construction duration	2.5	Period
Tax Rate	35	Percent/period
Rate of Return	10	Percent/period
Depreciation Method	MACRS	
Working capital	15	Percent/period
Length of start-up	20	Weeks
Operating Hours	8000	Hours

Period = year = 52 weeks

In addition to the use of Aspen Plus Economic Analyzer for the cost estimation, we used published literature costs data for certain equipment costs along with appropriate cost exponents (more details in the supplementary document). Also the equipment costs were inflated using the chemical engineering cost index to account for the time value of money. Other costs associated with equipment installation that constituted the total capital investment were estimated using Peter's et al., [126] capital costs estimation relationship as shown in table 3-5.

Table 3-5: Total Capital Investment Approach

Estimate	Approach
Base Equipment Cost (BEC)	Aspen Process Economic Analyzer
Direct Equipment Cost (DEC)	Aspen Process Economic Analyzer
Balance of Plant (BOP)	12% of BOE
Total Direct Equipment Cost (TDEC)	DEC + BOP
Indirect Equipment Cost (IEC)*	89% of TDEC
Total Plant Cost (TPC)	TDEC + IEC
Contingency fee	20.4% of TPC
Fixed Capital Investment	TPC + Contingency
Working capital	15% of FCI
Land	8% of BEC
Total capital Investment (TCI)	FCI + WC + Land
ISBL	Section (A-D)
OSBL	Section (E-F)

* (32% Engineering and supervision, 23% Contractors and legacy fees and 34%Construction expenses)

The mass and energy balance data obtained from the process simulation model was used to estimate the variable operating cost. The unit price of different resources used in this study are summarized in table 3-6. The fixed operating costs consisting of plant employees were estimated based on the work of Humbird et al., [127] [details in the supplementary document]

Table 3-6: Summary of Variable Operating Costs

Variable	Cost	Source
Biogas	\$4/GJ	[128]
Process Water	\$0.0002/kg	[126]
Cooling Water	\$0.0000792/kg	[126]
Electricity	\$0.1045/kWh	[129]
Waste Water disposal	\$0.000528/kg	[130]
Nickel Catalyst	\$35.36/kg	[14]
Cobalt Catalyst	\$35.36/kg	[14]
Platinum Catalyst	\$56.29/kg	[131]
Oxygen	\$0.09/kg	[132]
CoMo/Al_2O_3	\$35.36/kg	Assumed
Wax	\$1.13/kg	[133]

Performing a discounted cash flow rate of return (DCFROR) analysis on the estimated capital and operating cost for a plant life of 20 years, the selling price of the F-T drop-in fuel was obtained. This selling price was achieved by iterating the net present value of the accumulated financial inventory to zero using the revised version of the NREL DCFROR spreadsheet.

3.2.4 Sensitivity analysis

Sensitivity analysis on the base case BgTL plant was conducted to determine the effects of key input process and cost parameters on the least selling price of the F-T fuels. This analysis was classified into process and plant cost sensitive parameters in order to distinguish between parameters that are specific to the process (production dependent) and those that are plant cost dependent. The process specific input parameters analyzed were F-T conversion, plant availability, feedstock, oxygen, and catalyst costs, co-products price: electricity and wax while and plant cost parameters were internal rate of return (IRR), contingency fee, working capital, and income tax. The criteria for selecting these parameters that were evaluated was based on how sensitive they are in contributing to the fuels price. A 20% increase or decrease for each of these parameters while keeping other parameters constant was implemented. Catalyst life assumed to have a life time of 3 yrs was varied between 1 and 5 yrs assuming a worst case and advanced catalyst performance scenarios respectively. These variations pave an avenue for future research in drop-in fuels process improvement, optimization and cost analysis which ensures that drop-in fuels are competitive.

3.3 Results and Discussion

3.3.1 Process simulation

A base case process model for biogas to liquid fuels (BgTL) plant was successfully developed and the overall product distribution and energy data were presented in Table 3-7.

Table 3-7: BgTL product distribution and energy usage

Drop-in fuels		
LPG	0.309	million gallons/yr
Gasoline	1.331	million gallons/yr
Diesel	3.014	million gallons/yr
Co-Products		
Wax	233896	kg/yr
Electricity	1014.871	kWh
Energy use		
Thermal Energy	19.33	GJ/h
Electricity	623.41	kWh

The process analysis of converting 2000 Nm^3/h (2381 kg/h) of raw biogas produced 4.65 million gallons per year of liquid LPG, gasoline and diesel fractions (Table 3-7). The amount of liquid fuels produced from raw biogas showed a 53% (mass basis) overall product yield which is comparable to a typical GTL yield of 40-60% [104] and 63% natural gas to liquid fuels yield of Bechtel [23]. However, this yield value in the BgTL process differ from the liquid fuels production from biomass gasification works of Larson et al., [13] and Swanson et al.,[14]. Both authors reported a product yield less than 20% (mass basis). This is by and large understandable since a huge loss is usually encountered during the reforming and conditioning of syngas obtained from biomass gasification. The electricity co-product obtained in this work depended on the extent of conversion in the slurry reactor. Total energy consumption in the entire process in terms of heat and electricity can be found in table 3-7 with the breakdown of the energy balance shown in table 3-8.

Table 3-8: Electricity and Heat requirement in kWh

	Electricity Consumption	Process Heat
Biogas Upgrading	398.72	300.09
Syngas Production	166.39	-891.13
Fischer-Tropsch Synthesis	55.78	6656.77
Product Upgrade	-	179.25
Power Generation	-1014.89	-2971.17

Table 3-8 shows the heat and power demand for the BgTL plant. Biogas upgrading was the highest consumer (64%) of electricity in this process. The reason being that the series of compressors and pumps installed to achieve the process design operating condition amounts to a total power consumption of 0.2 kWh/Nm^3 of biogas upgraded. This corresponds to the HPWS specific energy consumption of 0.2-0.3 kWh/Nm^3 of biogas reported by Bauer et al., [134]. For this given amount of electrical energy consumed, a 75% of heat was recovered similar to the HPWS electrical power recovery achieved by Dirkse [60]. This heat recovered was used within the process accounting for a proper energy balance. Syngas production and F-T synthesis compressors used to condition the feed before being sent to the reformer and reactor were the consumers of electricity in each of these processes sections. Although the partial oxidation was an exothermic process which provided heat to drive the endothermic steam reforming process, additional amount of heat was needed in the overall syngas production section of the process. Net heat utilization in the syncrude upgrade from the reboiler and condenser served also as a pinch point. Fischer-Tropsch process known as a high exothermic process with heat removal challenge provided the most heat needed in the process heat integration approach. Overall, the amount of electricity required in this process was met from the internally generated power with a thermal efficiency of 36%. Of the total amount of electricity generated, 61% was used within the process while 39% was sold as co-product.

3.3.2 Techno-Economic Analysis

For the base case scenario of 2000 Nm^3/h feed capacity, a total production of approximately 4.65 million gallons/yr of F-T drop-in fuels with a capital expenditure (CAPEX) and operating expenditure (OPEX) of $104.8 million and $11.66 million dollars (US $ 2015) respectively was estimated. And for this investment, a discounted cash flow rate of return (DCFROR) analysis resulted to a least selling price of F-T drop-in fuels (LSPF) of $5.59 per gasoline gallon equivalent (GGE).

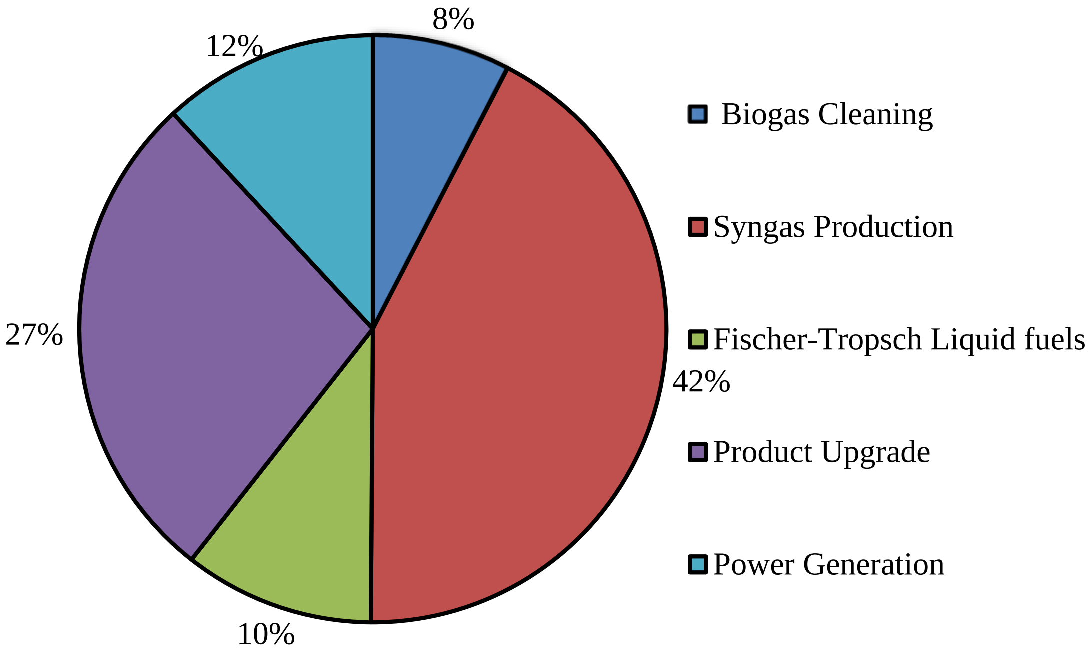

Figure 3-2: Percentage equipment installed cost distribution by section

Detail analysis of the equipment installed costs for each section of the process classified as the inside battery limit (ISBL) is shown in figure 3-2 above. The syngas production section contributed 42% of the total equipment cost which is typically the highest cost in all GTL process as reported by [10]. Syncrude upgrade and power generation contributed 27% and 12% respectively while the Fischer-Tropsch synthesis and biogas cleaning sections contributed the 10% and 8% of the ISBL cost.

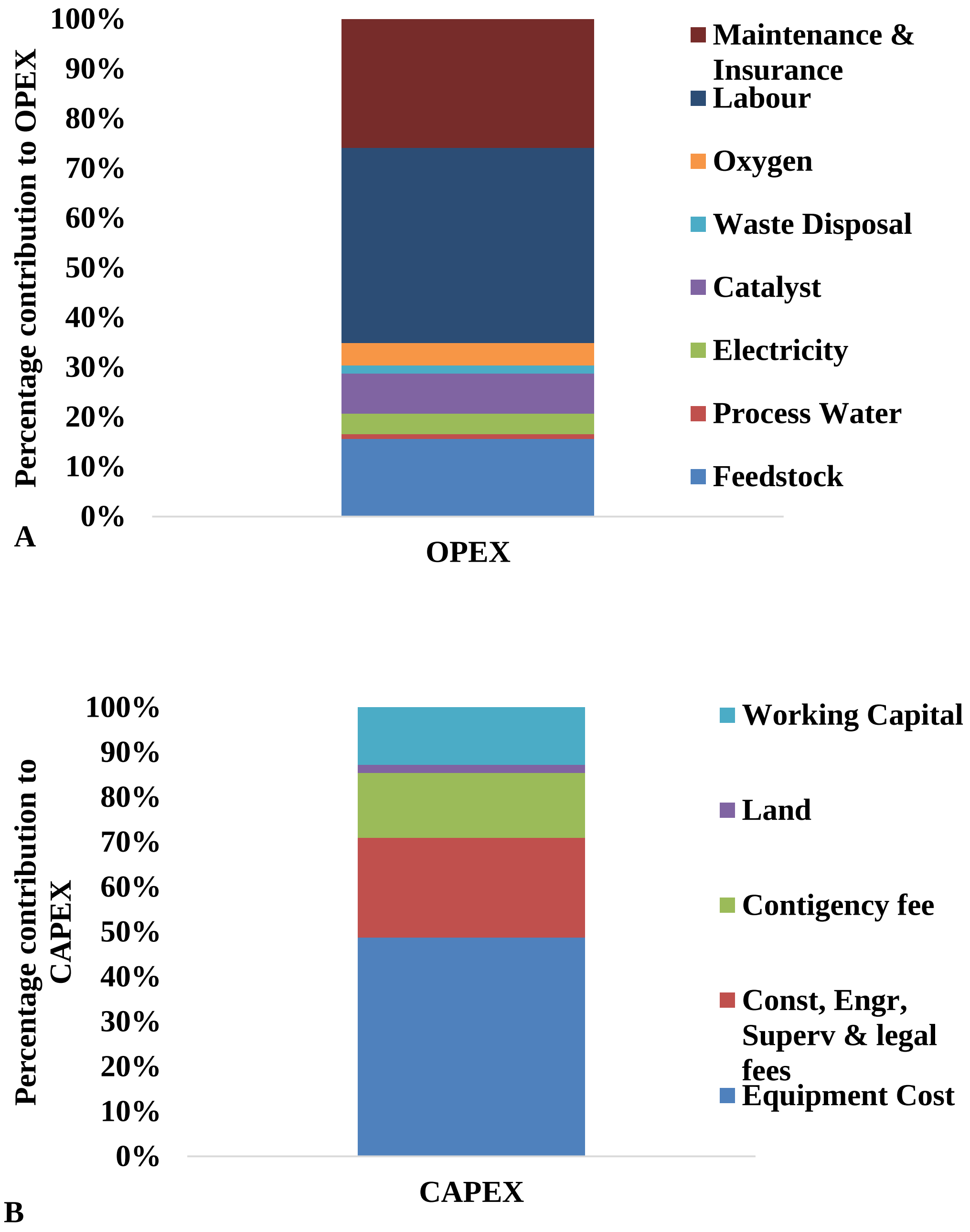

Figure 3-3: Individual costs contributing to OPEX (A) and CAPEX (B)

Factors contributing to the overall capital expenditure (CAPEX) and operating expenditure (OPEX) are depicted in figure 3-3. It can be observed that the equipment cost contributed 49% of the fixed capital investment which without doubt is usually the highest capital investment in a typical chemical process. Then the engineering and construction, and contingency fee contributed 22% and 14% respectively. Working capital and land contributed the rest of the capital investment with each contributing 13% and 2% respectively. Advancement in technology is vital as it will definitely enhance technical know-how needed in the design and fabrication of the unit operation thereby promoting competition amongst dealers. The result of these is a reduction in the investment cost tied to equipment procurement. Such achievement will invariably reduce the other costs (engineering, construction, and supervision, land, working capital, etc.) which are generally estimated from the equipment cost. For the operating cost, the fixed operating cost usually accounts for the highest expensive since it is independent of production. Labor and maintenance cost contributed 39% and 26% of the total operating cost followed by feedstock cost which contributed 16%. Other consumables such as catalyst, oxygen, electricity, waste disposal, and process water costs contributed 8%, 4%, 4%, 2%, and 1% respectively. The inherent cheap feedstock cost highlights the prospects of the use of biogas as feedstock in the GTL process.

We explored the effects of plant size on the CAPEX, OPEX, LSPF, and production capacity in order to ascertain the recommendable size of the BgTL process. Four biogas plant scenarios: 500Nm^3/h, 2000 Nm^3/h (base case), 10,000 Nm^3/h, and 20000 Nm^3/h were considered with their relations to investment shown in figure 3-4 below.

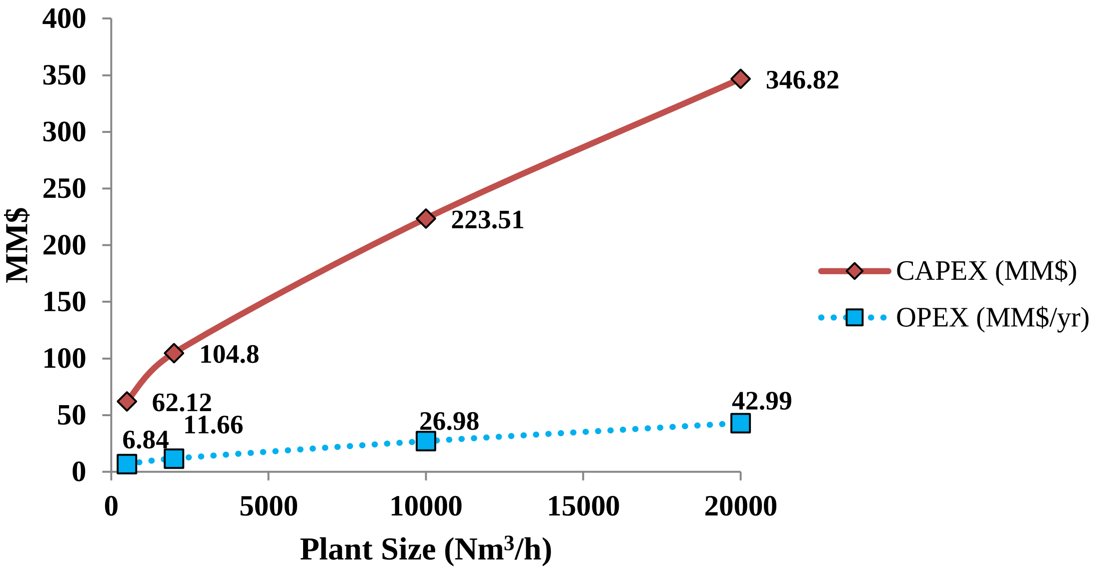

Figure 3-4: OPEX and CAPEX as a function of plant capacity

It can be observed that the CAPEX and OPEX increases as the plant size increases. However, this is not a linear relationship since the costs does not double or quadruple when the plant capacity is increased by similar magnitude. Interesting, a plot of CAPEX and OPEX per production capacity against plant size further explains the effect of large plant capacity which helps depict the recommendable size of a BgTL. Figure 3-5 shows the investment cost ($/gal) as a function of the plant size. It is clear that operating the plant at a feed capacity of 500Nm^3/h and 2000Nm^3/h is not economically feasible as the cost per production is extremely high compared to the 10,000 Nm^3/h and 20,000 Nm^3/h plant sizes.

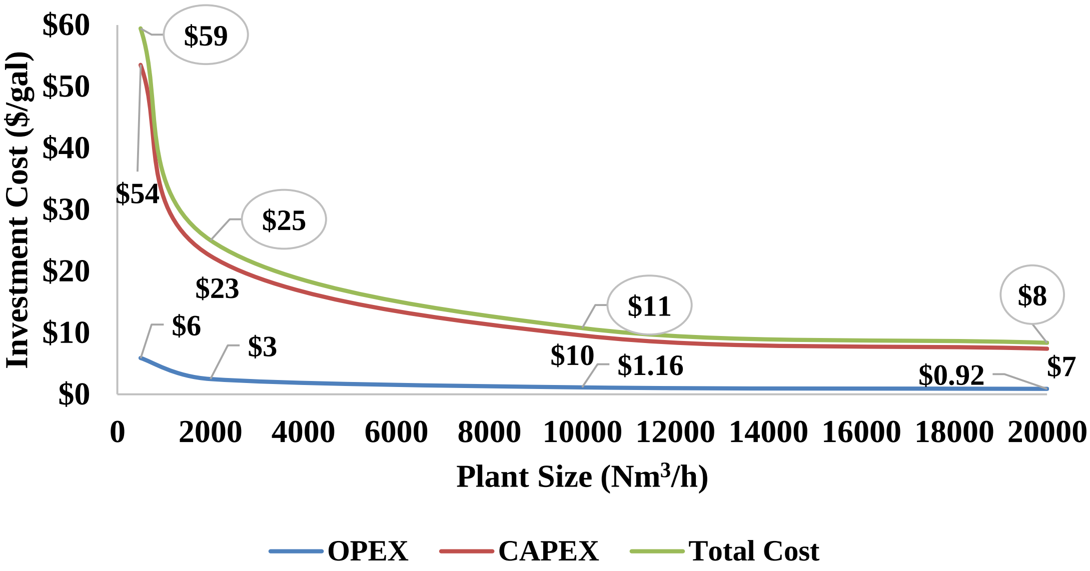

Figure 3-5: OPEX and CAPEX per production against plant size

Figure 3-6 illustrates the relationship between plant capacity and the product selling price which brings to limelight the effect of economy of scale on the proposed BgTL process.

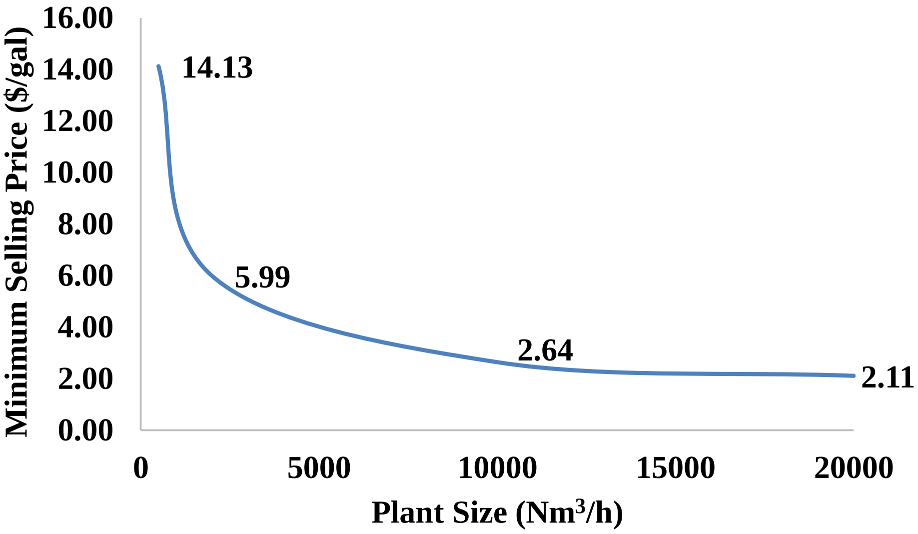

Figure 3-6: Product selling price as a function of plant size

The least selling price of our drop-in fuels for this analysis at a plant size of 500Nm^3/h was $14.13/gal which is unequivocally not feasible based on the market price of fossil fuels counterpart. But assuming a biogas plant with a size of 20,000 Nm^3/h, the LSPF was $2.11/gal which seems feasible and competitive in the energy market. However, the tendency that such biogas plant size would be achieved remains a doubt.

3.3.3 Sensitivity Analysis

Performing a sensitivity analysis on the process, factors that critically affect the selling price of the product were outlined for possible future advancement. Figs. 3-7 & 3-8 shows the parameters that were evaluated as arranged in the order of magnitude at which they affect the selling price. The highest impact on the selling price was the extent of conversion in the F-T slurry reactor. It is evident that the latest development in research on the conversion of syngas in a slurry phase reactor is 80% which is higher than the conversion achieved in the conventional fluidized reactor [109]. Focus on the advancement of the overall conversion during F-T synthesis is principally of utmost importance in this process as a higher conversion resulted to a high syncrude formation which significantly reduced the selling price of the liquid fuels due to the high production capacity achieved. Predicting a future technological development up to 96% conversion of syngas in a slurry reactor, the effect of selling price was evaluated. During the F-T process, sintering of catalyst by impurities in the feed can negatively affect the catalyst activity [10] which results to a reduction in catalytic conversion of syngas to F-T syncrude with a resultant effect on the selling price of the fuels. A 64% conversion was assumed to represent the overall conversion in the slurry reactor when the catalyst is poisoned and such effect on the selling price was evaluated as seen in figure 3-7.

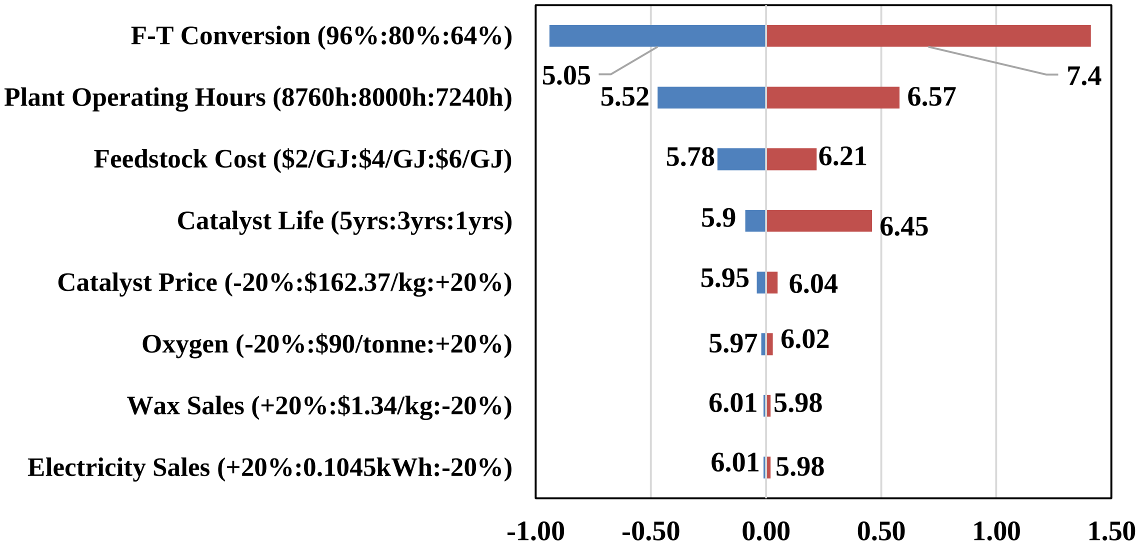

Figure 3-7: Sensitivity analysis for the effect of process parameter on the selling price of the base case model.

Process plant online time is also inadvertently critical to the profitability of the project. Since we assumed a 91% online time for the process without production interruption, the overall cost of production which includes the fixed operating cost (independent of production) can be recovered with a minimal selling price. This analysis showed the loss involved during a shutdown as the project handles payroll, employee benefits and equipment maintenance costs whereas no income from product sells are made. Feedstock cost is another sensitive parameter in the BgTL process. Biogas can be produced from a feedstock with no monetary value (manure) or highly expensive ligncellulosic biomass. For such scenarios, the selling price of biogas typically differs. Average feedstock cost of $4/GJ was used as the base case which when reduced to $2/GJ in the scenario were biogas feedstock was obtained as credit, the selling price dropped to $5.78/gal. In addition, technological development on the life span of catalyst is crucial to the chemical industry in terms of operating cost invested in catalyst purchase. Typical catalyst life of 3yrs achieved with catalyst in-situ regeneration alleviated the high purchase cost of catalyst that would have been recorded in the annual operating expenditure. This catalyst life cost contribution to the selling price is a function of the gas hourly space velocity (GHSV) and liquid hourly space velocity (LHSV) evaluated for a 3 yrs life cycle in this base case BgTL model. Variation of the catalyst life cycle to 1yr for this analysis shows an 8% increase in selling price which is undesirable. Similarly, the catalyst life determines the percentage of the operating cost invested in the purchase of a catalyst. Figure 3-7 shows that the effect of catalyst cost on the selling price which was really not significant as this is a function of the GHSV and LHSV used for this work. In similar process where different GHSV and LHSV are used in the analysis, it is certain that a significant effect on catalyst price will be observed. Purchase of oxygen for the partial oxidation process was more economically feasible in this BgTL process than investing money on an air separation unit (ASU). It can be observed that the oxygen cost of $90/tonne did not have a significant impact when the price was varied within ± 20%. Co-products such as electricity and wax obtained during the analysis played a vital role in minimizing the selling price of the fuel as co-product credits were obtained that offsets the project selling price of the fuel. It can be observed that a reduction in the co-product price selling price negatively affected the selling price as more money was needed from the sale of the liquid fuels to maintain cash flow. Therefore, the design of the process to produce high value co-products typically aids the project profitability. Overall, this is an arduous task of engineers to design and develop a more efficient and optimal system that can help attain the profit aims from a given investment.

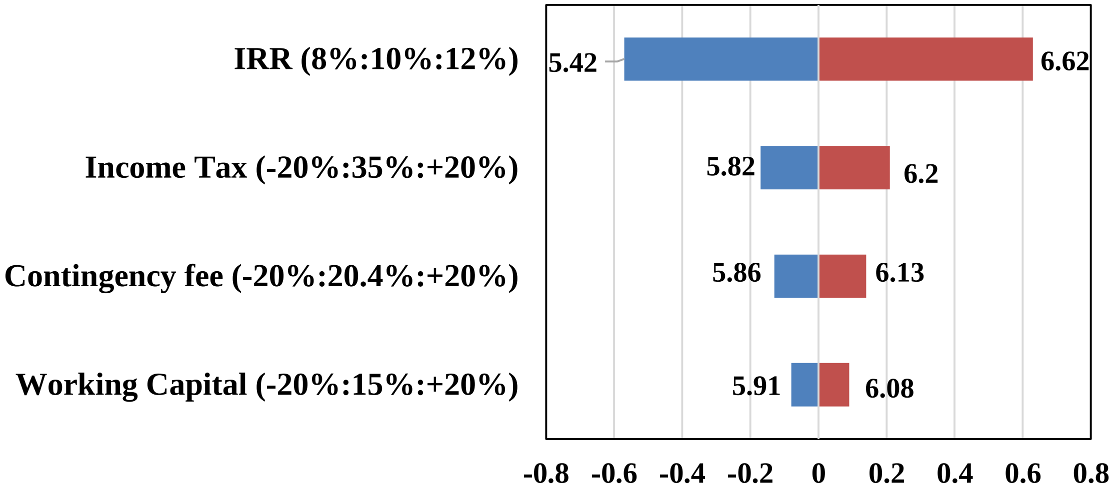

Figure 3-8: Sensitivity analysis for the effect of plant cost parameter on the selling price of the base case model.

Established concept of assessing the profitability of a project is the internal rate of return (IRR) which proves to have a significant effect on the selling price. For every project, IRR measures the extent of risk involved in the investment of which company managers tend to make the critical decision. Adopting an IRR of 10% [124], a 20% increase raises the selling price by 11% indicating a higher risk which no prospective investor would want to invest. Tax rate, which included the federal and state taxes, directly influenced the overall project as it is a direct function of the projects profit. Since states taxes differ in the U.S, the variation of the tax rate charged to a company annual profit varies based on plant location. Assuming the plant was situated in a state with no local tax, the selling price can reduce from \$5.99 to \$5.82. Hence it is vital to compare projects with similar tax rates. Factors related to capital investment such as contingency fee and working capital were similarly evaluated. Budget for contingency fee accounting for the uncertainties during a project can be open ended as different percentages of the fixed capital investment have been used. Likewise, the initial project running capital before the project starts making income from sell of product (working capital) which is generally recovered at the end of the plant life have been estimated as a percentage of FCI.

In conclusion, estimation of capital investment is usually within a magnitude of ± 30% that a proper estimation of the total capital investment reduces the amount of cash bequeathed to a project which invariably reduces the risk involvement of a project.

Table 3-9: Comparison of the techno-economic analysis of BgTL and related processes

	BgTL Model	Bechtel 1996	Tijmensen et al., 2002	Hamelinck et al., 2004	Larson et al., 2009	Swason et al., 2010	Bao et al., 2010
Feedstock	Biogas	Natural Gas	Poplar	Wood	Switch-grass	Corn Stover	Natural Gas
Feedstock Cost ($/dry tonne)	$72	N/A	$33	$38	$46	$75	$44.14[a]
Plant Size (dry metric ton/day)	57	8391	1741	400MW$_{th}$	4536	2000	21600
Product	F-T Liquids	F-T Liquids	FT Liquids	F-T diesel	Diesel, gasoline	LPG, Gasoline, Diesel	Synfuels
Cost Year	2015	1993	2000	2002	2003	2007	2010
TCI (MM$)	$105	$1842.5	$339	$303.46	$541[b]	$610[c]	$10800
Product Value ($/GGE)	$5.59	N/A	$2.00	$1.92	$1.85	$4.30	$1.41[d]
Product Value ($/GGE) 2015	$5.59	N/A	$2.86	$2.73	$2.59	$4.61	$1.44[d]

a = calculated based on $8/1000 SCF natural gas price with a density of 0.8 kg/m^3
b = without spare scenario
c = high temperature scenario
d = reported in $/bbl which was converted to $/gal

Table 3-9 summarizes the techno-economic analysis works of different authors for the production of F-T liquid fuels from natural gas and different biomass sources in comparison with our BgTL process model analysis. This comparison helps to explore the economic viablity of liquid fuel production from these routes. Gas to liquid (GTL) and coal to liquid (CTL) have been the commercial routes for liquid fuels production with no detailed economic analysis data available for such processes. The gas to liquid process analysis of Bechtel [23] provided no selling price of the F-T products while Bao et al., [135] reported a selling price of $58/bbl (US $ 2010). Recently, the thermochemical conversion (gasification) of biomass has received tremendous research attention as a promising route for F-T fuels production. Tech-economic analysis of converting different types of biomass feedstock have been conducted by several authors for which a product value range of $2.86/GGE - $4.61/GGE were estimated [11-14].

Table 3-9 shows that the gas to liquid fuels product price proves to be competitive ($1.44/GGE) whereas the thermochemical route seemed to be higher when compared to the product price ($5.59/GGE) of our base case model. We could make this assertion due to the average plant feed capacity of 1,728 tonnes/day for the thermochemical pathways which is approximately 30 times the size of our base model plant capacity. At a plant capacity of 20,000Nm^3/h, the product value was estimated to be $1.97/GGE which offers a better prospect for the liquid fuels production from biogas. Critical parameters that contributed to the high product value of the thermochemical process were the feedstock preprocessing and gasification (including syngas cleaning and conditioning) investments, and feedstock cost. It is also noteworthy to understand that each process analysis employed different assumptions for the plant life time, process conversion, plant availability, catalyst life time and costs, and other process consumable costs during the analysis which would make the comparison of different processes not very realistic.

3.4 Conclusion

Drop-in fuels production via biogas was successfully modeled using Aspen Plus to obtain the mass and energy balance which was employed in the techno-economic analysis. For the base case plant capacity of 2000 Nm^3/h, the drop-in fuels selling price of \$5.99/gal (\$5.59/GGE) was estimated. This selling price for a biofuel is not very competitive judging from the \$3/gal target set by the EPA's renewable fuels standard (RFS). And given the current drop in crude oil price, the feasible of the process stands no chance. Although the price of the fuel is not possible in the market, certain factors contributed to these selling price as evident in the sensitivity analysis. The yield of syngas and extent of conversion of the syngas to liquid fuel if advanced through R&D, an acceptable selling price can be attained. Nevertheless, these technology is absolutely achievable at a higher plant size as a selling price of \$2.46/GGE was obtained at a size of 10,000 Nm^3/h which further drops to \$2/GGE for a size of 20,000Nm^3/h. Therefore, a feasible N^{th} plant model for a biogas to drop-in F-T liquid fuels can be explored in the future for possible implementation.

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CHAPTER 4

LIFE CYCLE ANALYSIS OF RENEWABLE DIESEL PRODUCTION VIA AD AND F-T SYNTHESIS FROM MISCANTHUS GROWN IN STRIP-MINED SOILS.[2]

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[2] Okeke I.J., and Sudhagar Mani. To be submitted to Environmental Science & Technology, ACS Publications.

Abstract:

Climate change resulting from the production and use of transportation fuels have raised a global concern which environmental friendly fuels are sorted. Renewable fuels obtained from biomass and other organic carbon sources are proposed to mitigate these climate chance challenges. In this study, a cradle to gate attributional life cycle assessment (LCA) approach which considered the whole life cycle of the cultivation of the energy crop till the production of the fuel (drop-in diesel). TRACI 2 v4.0 was used to calculate the overall emissions from cradle (miscanthus cultivation) to the gate (drop-in diesel production). The functional unit of this analysis was 1 gasoline gallon equivalent (GGE) of drop-in diesel fuel which was compared to the conventional diesel fuel in a typical U.S refinery. For the entire life cycle of the drop-in diesel production, a net greenhouse gas (GHG) emission reduction of 41% and 26% were estimated when carbon sequestered during the feedstock cultivation was accounted in scenarios where lime addition and no lime addition were used for the cultivation of miscanthus. Other impact assessments such as eutrophication potential, smog formation, acidification potential, respiratory effects, carcinogenic and non-carcinogenic formations, ozone depletion, and ecotoxicity were assessed and reported in comparison to the fossil derived diesel. Cumulative energy demand (CED) v1.08 was used to assess the total energy usage for the entire life cycle of the drop-in diesel from miscanthus which was estimated to be 29.178 MJ/GGE with a net energy balance of 100.421 MJ/GGE. With such reduction in GHG and a positive net energy balance, the drop-in renewable diesel from miscanthus is proven to be a sustainable pathway.

Keywords: Energy crops, biogas, renewable diesel, GHG emissions.

4.1 Introduction

Anaerobic digestion of lignocelluosic biomass to produce biogas used for the production of drop-in renewable diesel fuels is a viable route to attain the EPA's renewable fuels standard (RFS) biomass-based diesel target of 1 billion gallons [136]. These RFS target is in the bid to reduce the amount of greenhouse gas emissions that causes climate change in the U.S. For example, the use of the biomass-based diesel is expected to reduce the emission of the fossil fuel it substituted by 20% [95]. In order to ascertain this claim, these renewable sources of energy need to be critically analyzed in terms of their energy consumptions and greenhouse gas emissions impacts on the environment.

With a 2014 greenhouse gas emission of 6,870 million metric tons CO_{2eq} [137], the United States is considered a high emitter of greenhouse gases which significantly contributes to climate change. The Unite States Environmental Protection Agency (EPA) quantified the GHG emissions and estimated that CO_2 emission contributed 81% of total emissions which the electricity generation and transportation sectors are the highest contributors [137]. Depending on the source of electricity generation, it is evident that power generation contributes significantly to climate change however, this work focuses on the emission from the transport sector which the use of biomass-derived diesel tends to reduce.

Lignocellulosic biomass is digested under anaerobic condition in a solid state anaerobic digester to produce biogas and digestate [40, 90, 138]. These process is commercially applicable as the biogas is employed for multiple applications such as home cooking, industrial methane source, combined heat and power (CHP), while the digestate is used for fertilizer. As opposed to other biomass conversion, the energy efficiency of this process for the production of methane compared to other biological and thermos-chemical processes [139] and its reduced methane emissions [140] makes anaerobic digestion desirable. Anaerobic digestion and the production of biogas is of interest in Europe because it is a renewable source of energy with less greenhouse (GHG) emissions and guaranteed energy security [36] . Substituting fossil derived fuels with biogas contributes to the reduction in climate change due to less greenhouse gas emissions [27]. EPA's AgSTAR program reported in 2010 an energy production of 1600 megawatts from biogas equivalent to the removal of 6.5 million cars off the road as it reduces global warming potential by 1.8 million metric ton of methane [141].

To employ lignocellulosic biomass in an AD process, pretreatment of the lignocellulosic biomass is carried out. According to Zheng, Y., et al., [44], pretreatment causes structural reduction of lignocellulosic biomass and exposes the cellulose and hemicellulose to enhanced microbial breakdown which raises the rate of biomass degradation and biogas yield. Amongst the other pretreatment methods, fungal pretreatment of the ground miscanthus was performed to enhance the digestibility of the feedstock. After pretreatment, the lignin content of miscanthus was reduced to about 25.7% with a corresponding 25% increase in specific methane yield [89].

Since lignocellulosic biomass exists in abundance in the United States which are also available for bioenergy production, possible anaerobic digestion feedstock challenges have been addressed. Another noteworthy development is presence of 191 anaerobic digesters in the U.S which indicates a growth in the production of biogas [17]. The methane potential of biogas in the United States was reported to be about 7.9 million tonnes per annum (420 billion cubic feet of methane gas) [16]. Such growth in production of biogas ensures adequate sustainability of the feedstock to supply the drop-in diesel production plant. In order to assess the environmental impacts and evaluate the RFS requirement, a detailed life cycle analysis of biomass to drop-in biofuel via AD technology is required. In addition, we will further evaluate the potential of this conversion pathway in comparison with gasification routes to produce drop-in-biofuels.

Production of drop-in fuels from biogas obtained from either any other source or lignocellulosic biomass requires the upgrading of the biogas to a clean state since it has an average composition of 50–75% CH_4, 25–50% CO_2, 0–10% N_2, 0–5%O_2, 1000-2000ppm H_2S [142]. Once biogas is upgraded, it predominately becomes methane or what is conventionally regarded as biomethane [60] and can be converted through several unit operations to produce the drop-in diesel fuels.

The focus of this study is to examine the energy use and environmental emissions in the production of drop-in diesel using biogas obtained from miscanthus SS-AD and compare with the fossil based diesel. In order to achieve such comparison, the entire life cycle of the production of drop-in diesel was conducted in a cradle to gate attributional life cycle analysis approach. Life cycle assessment is an internationally recognized procedure for the systematic and quantitative evaluation of environmental impacts on the entire stages of a product life cycle which is compared to a similar product based on the same functional unit.

4.2 Methodology

This is an attributional life cycle analysis (LCA) study based on the ISO 14000 environmental management standards (ISO 14040:2006 and 14044:2006) approach. As defined by the standard, a life cycle assessment was conducted in four separate but collective segments namely: Goal and scope definition, Inventory analysis, Impact assessment, and Interpretation. During the life cycle inventory (LCI) phase, all inputs (raw materials and energies) required to produce the product of interest alongside the co-products and emissions (air, water, and land) were accounted for. SimaPro.7, a life cycle analysis tool, and TRACI 2 v4, an impact calculation method, were used to estimate the emissions attributed to the entire life cycle of drop-in renewable diesel production from miscanthus. In-built U.S LCI database in SimaPro was predominantly used for this assessment of which the GREET model was used in the absence of any input data. Similarly, our logistics model was used in estimating the inputs for the miscanthus cultivation through the feestock delivery at plant gate. Data for the pretreatment (tub grinding and fungal treatment) of the feedstock and biogas production were obtained from related literature. Inputs for the conversion of the biogas conversion drop-in renewable diesel were obtained from our biogas to liquid fuels (BgTL) Aspen Plus model. Impact assessments categories such as global warming, eutrophication, acidification, carcinogenic and non-carcinogenic, respiratory effects, ozone depletion, ecotoxicity, and smog potentials were analyzed. The CED 1.02 (Cumulative Energy Demand LCA) method was also used to evaluate the non-renewable fossil energy used in the system entirely.

4.2.1 Goal and Scope definition

The overall goal of this study was to systematically assess and evaluate the energy and environmental impacts of producing renewable diesel from biogas produced via solid-state AD of

Miscanthus cultivated from strip-mined land. Strip-mined lands are lands originally used for the production of minerals by excavating the soil. Miscanthus feedstock cultivation was performed in a strip-mined land at Ohio with the downstream processing facility located also in Ohio were input data were considered to be within this geographical location. The overall assessment in this study is to compare the emissions and impacts of the production of renewable drop-in diesel with the production of petroleum-based diesel. The scope of the life cycle inventory (LCI) included emissions from the energy input in the entire process which encompasses the cultivation of miscanthus, feedstock logistics, pretreatment, anaerobic digestion of the pretreated miscanthus to biogas, transportation and use of digestate in farmland, biogas cleaning operation, biomethane conversion to syngas, catalytic c0onversion of syngas to Fischer-Tropsch syn-crude, electricity generation using unconverted syngas in the F-T process, and the F-T syn-crude upgrade to drop-in diesel.

4.2.2 System Boundary, Functional Unit and Reference System

The system examined in this work is depicted in figure 4-1. As can be seen in the outlined boundary, the system included the cultivation of miscanthus to its anaerobic digestion to produce biogas which was subsequently converted to drop-in renewable diesel. Inputs includes the strip-minded land, fertilizers, pesticides, diesel for cultivation and harvesting, fungal used for pretreatment, process water, catalyst, oxygen, and atmospheric air. All thermal and electrical energy used in this system were internally generated and hence excludes any external supply of energy.

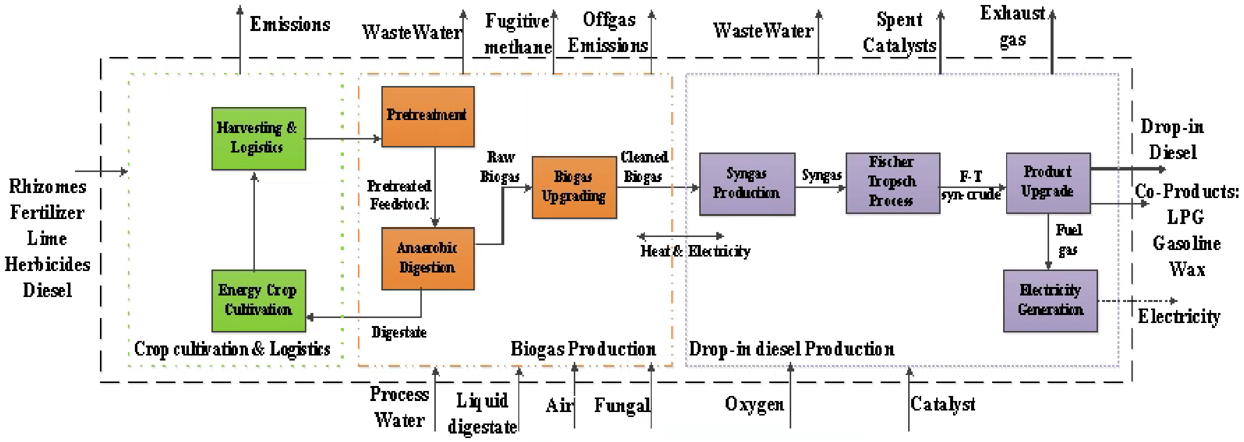


Figure 4-1: System boundary of GTL production from anaerobic digestion of miscanthus

4.2.2.1 Feedstock Cultivation

Miscanthus, a perennial energy crop, was used as feedstock for the production of biogas employed for the drop-in renewable diesel pathway. Miscanthus has a high biomass yield which makes it a potential feedstock for the production of biogas via solid state anaerobic digestion. Currently, Illinois is regarded as the highest producer of miscanthus in the United States with an estimated yield of about 30-60 t DM ha^{-1} yr^{-1}[143]. For this study, a cultivation life cycle of 20 years on a stripped-mined land located in Ohio with an average spring yield of 10 Mg DM ha^{-1} yr^{-1} was assumed. These assumptions were judged as reasonable since the land for cultivation of miscanthus is not arable and has lower yield compared to when grown in an arable land. All input data (rhizome, fertilizers, herbicides, lime, and diesel) for the cultivation of miscanthus were calculated based on an average yield of 10 Mg DM ha^{-1} yr^{-1}. Miscanthus harvested in spring was reported to have total solid (TS) and volatile solid (VS) of 90.1% and 87.2% respectively [89]. The composition of miscanthus used in this process is reported in table 4-1. During the cultivation and harvesting of the miscanthus, some carbon is sequestered on the farmland which helps to improve the soil quality of the land used for cultivation. For miscanthus cultivation, the soil organic carbon (SOC) sequestration have been reported to be within the values of 0.16-0.82 Mg C ha^{-1} yr^{-1} [144]. A key assumption made for this cultivation operation is the land use change which was assumed to be negligible since the land used in this analysis does not compete with food cultivation.

Table 4-1: Elemental composition and heating value of Miscanthus

Component	weight % (dry)
Carbon (C)	47.92
Nitrogen (N)	0.54
Hydrogen (H)	5.5
Oxygen (O)	41.0
Sulphur (S)	0.11
Ash	2.78
Fixed Carbon	25.40
Net Heating Value (GJ/ Mg)	17.86

4.2.2.2 AD Feedstock Logistics

The optimum harvest time for miscanthus is between late November and early December [145] with a higher biomass yield. According to [145], the harvest of miscanthus in late winter and spring reduces the yield by 30-50% but with a higher specific methane yield of about 25% after fungal pretreatment with Ceriporiopsis subvermispora [89]. For the functional unit of produce 1 GGE (gasoline gallon equivalent) of drop-in renewable diesel production, an estimated amount of 0.024 Mg DM/hr of miscanthus was harvested. Harvesting operations of swathing, stalking, and bailing into a large square bale were carried out and piled on farmland prior to transportation to the biorefinery intermediate storage location. During the logistics operation (storage and transportation), approximately 10% of the harvested feedstock were lost. A single direction distance of 30 km (farmland – intermediate storage – biorefinery) for the transportation of the feedstock using a diesel-powered truck was estimated based on the AD plant annual capacity. The entire logistics operation was carried out with a diesel-powered machine (tractor with attachment) for which all emissions data from the use of diesel fuel and organic matter losses during the logisitcs were considered in the overall life cycle of the process.

4.2.2.3 Feedstock Pretreatment

The cell wall composition of miscanthus giganteus consists of 52.13% cellulose, 25.76% hemicellulose and 12.58% lignin [146]. The direct use of lignocellulosic biomass for anaerobic digestion results to poor yield of biogas [15, 90] because of the complex carbohydrate components which are insoluble and are covalently bounded to each other. Therefore, to achieve a high biogas yield, pretreatment of the material is vital before the AD process. Feedstock pretreatment process included the tub grinding of miscanthus (15% moisture content) for size reduction and then fungal pretreatment of the chopped miscanthus to enhance breakdown of the carbohydrate structure of miscanthus, which eventually rises methane yield. The tub grinding operation comprised the debailing and grinding of the feedstock. Due to the bulk nature of the feedstock, grinding to reduce the bulk feedstock to smaller particle size was carried out using a 630 hp diesel-powered tub-grinder with an energy consumption of 3.72 liters/tonne [147]. After the grinding of miscanthus, a front-end loader was used to convey the chopped feed to the pretreatment location. The moisture content of the ground miscanthus was raised to 60% followed by the addition of fungal (Ceriporiopsis subvermispora) at room temperature for 28 days [89] in an assumed bunker silo. Dry matter loss of 12.5% was considered during the fungal pretreatment process [148]. Finally, a front-end loader (100 hp) was used to feed the AD reactor with the pretreated feedstock.

4.2.2.4 Anaerobic Digestion

Digestion of pretreated miscanthus was carried out in a solid-state anaerobic digester (SS-AD) due to the solid content (>10%) of the feedstock. In this analysis, the feedstock was conditioned to a moisture content of 75% before it was subjected to an SS-AD that operated at a mesophilic temperature of 35°C and atmospheric pressure. The heat and electricity required to maintain the digester operating temperature and for stirring of the feed were estimated from the work of [149] as 110 MJ/tonne and 66 MJ/tonne respectively. These heat and electricity demand were supplied from the excess heat and electricity generated within this process analysis. Hence, there was no external thermal or electrical energy requirement. Optimum carbon to nitrogen (C/N) ratio for AD process is typically between 25-30 [91] which the C/N ratio of miscanthus is about 88. Liquid digestate from an anaerobic digester plant was used as an inoculum to maintain the required ratio. Feed to inoculum (F/I) ratio of 2 was maintained for every batch of feed processed in the digester [89]. An estimated distance of 30 km for the transportation of the liquid digestate to the plant was assumed for which we account for the direct emissions in the transportation process. According to the [92], methane yield of miscanthus is approximately between 0.179-0.218 m^3 per kg volatile solid. Similarly, a miscanthus methane potential of 0.2 m^3/kg VS was reported by [150]. Therefore, an average methane yield of 0.18 m^3/kg VS was used in this work to estimate the methane production rate based on the feedstock volatile solid of 87.2% while the unconverted solid were withdrawn from the AD reactor as digestate. For the amount of methane produced in the process, the fugitive emission was estimated to be 5% of the total biogas produced [151]. Product allocation for the AD process was on product value (cost) basis [152]. Finally, biogas was upgraded to natural gas quality for the production of drop-in diesel while the digestate was transported back to the miscanthus farmland to be used as fertilizer replacement.

4.2.2.5 Transportation of Digestate

The unconverted biomass (non-volatile solids) in the SS-AD process were collected as digestate and used as organic fertilizers in the farmland for the cultivation of the feedstock, which serves as replacement for the chemical fertilizers. Using digestate in place of chemical fertilizer serves as a recycle of nutrients in the raw material. Biogas yield of each feedstock determines the amount of digestate produced which invariably influences the nutrient concentration of the digestate and the amount to be spread on farmland [153]. It was assumed that the means of transportation of the digestate from the biogas plant back to the farmland was the same as that from the farmland to biogas plant. Hence, the diesel-powered truck traveled a round trip of 60 km. Spraying of the digestate was with a tractor and manure spreader [27] of which the energy consumption for the operation was estimated. In these analysis, the use of digestate as a fertilizer substitute was not considered as a scenario to ascertain the impact assessment reduction.

4.2.2.6 Biogas Cleaning Operation

The produced biogas is a mixture of methane and carbon dioxide with other impurities like nitrogen, oxygen, ammonia, hydrogen sulphide, water particles, dust [60]. Since biogas is to be converted downstream into drop-in renewable diesel via F-T synthesis, impurities present in biogas was stripped off [37] to ensure the F-T process impurity tolerance level (0.1 H_2S) was maintained [10]. High Pressure Water Scrubbing (HPWS) of biogas was employed in this operation which generated biomethane (>96% methane) [36] product which is analogues to the natural gas (methane) used for the GTL process [93]. During the biogas cleaning process, some amount of thermal energy was recovered which was utilized in the overall process while the electrical energy demand was met with the internally generated electricity. HPWS off-gas emission consisting of 2% methane loss [57] and the scrubbed impurities in biogas were considered as biogenic emissions in this work. Our developed biogas to liquid fuels (BgTL) Aspen Plus model was used in estimating the mass and energy balance for the HPWS process, which was used to access the energy and environmental contribution of this process to the entire drop-in diesel production.

4.2.2.7 Biomethane Conversion to Syngas

In this analysis, biomethane was converted to syngas via a combination of partial oxidation and steam reforming processes in order to achieve the overall syngas H_2/CO ratio required for the drop-in fuels production. The steam reforming process is a catalytic process that employed Ni/Al_2O_3 for the conversion of biomethane to syngas. All process inputs such as catalyst, oxygen, steam, heat, and electricity were accounted based on our process mass and energy balance obtained from Aspen Plus model as shown in table 4-2 of life cycle inventory. Similarly, the emissions of the process to water, land and air were considered when assessing the impact of the syngas production to the overall drop-in fuels process.

4.2.2.8 Fischer Tropsch Synthesis

Syngas produced from biomethane was converted to synthetic crude in a similar fashion as the commercial Fischer-Tropsch gas to liquid (GTL) process [10, 61, 77]. This technology has grown so widely since its invention and it is renowned for its quality fuels and chemicals supply [77]. In our model, a slurry cobalt catalyst-bubbled phase F-T reactor with an overall conversion of 80% was employed for the liquid hydrocarbons production. The unconverted syngas stream was used as fuel for electricity generation while the hydrocarbon product of the F-T process was sent to the upgrading unit. An assumed 0.1% of catalyst consumed in the liquid fuels production was estimated as solid emission to soil.

4.2.2.9 Product Upgrading

The products of F-T process are long chain hydrocarbons which includes paraffins, waxes, and oxygenates depending on temperature of the F-T reaction process and catalyst used [10]. For our process, the upgrading process considered consists of the hydrocarbon recovery, wax hydrocracking, distillate hydrotreating, naptha hydrotreating, and product distillation in accordance with the work of [23]. The desired product of this process, drop-in renewable diesel, was obtained alongside other co-products such as LPG, drop-in gasoline, and wax. Product allocation was based on energy value which corresponded to how the emissions were attributed.

4.2.2.10 Electricity Generation

The unconverted syngas was used as fuel to produce electricity in a combined cycle process. Steam dilution was used in fuel combustion process to reduce the amount of NOx formation [123]. Heat was recovered in a HRSG and used for the production of steam in a boiler, which was used in the steam turbine and other plant processes while the exhaust gas was emitted to the atmosphere. This electricity generated was used internally in whole process while the excess was sold. The exhaust gas emission was also considered as biogenic.

The functional unit of this system was based on the main product of the process analysis. Since the final product is a fuel, the unit was reported in energy basis: 1 gasoline gallon equivalent (GGE) of drop-in renewable diesel. All material and energy balance were normalized based on the functional unit. The reference system is fossil based diesel which is assumed to have the same energy characteristics as drop-in diesel and can be used interchangeably.

4.2.3 Life Cycle Inventory (LCI) Analysis

The LCI for the Fischer Tropsch GTL process applied to the production of renewable diesel from miscanthus includes inputs and outputs data obtained from literatures, reports and validated miscanthus supply-chain logistics. All values were normalized based on the functional unit (1 GGE of diesel). TRACI 2 v4.0, a life cycle assessment tool was used for the computation of the input data and the resultant emissions associated with the inputs were generated. These emissions were classified into water, air and soil in order to evaluate/categorize each impacts appropriately. Table 4-2 shows the detailed input parameters, values and source of the data used in this process analysis according to the specified system boundary. Detailed input data can be found in the supplementary information document (includes ASPEN Plus data, basic assumptions to estimate below numbers and any other emission data included for specific input from other sources e.g. GREET model)

Table 4-2: Input parameters and values for the production of 1 GGE drop-in renewable diesel from miscanthus

Miscanthus Cultivation				
Inputs from nature (resources)	Value	Unit	Comment	Ref
Occupation, arable, non-irrigated, fallow	0.002480351	ha	Hectare based on yield	Estimated
Inputs from technosphere (materials/fuels)				
Rhizome	1.75	kg	Average value of rhizome required	[154, 155]
Nitrogen fertilizer, production mix, at plant/US	0.084	kg	Nitrogen input average value	[156, 157]
Phosphorous fertilizer, production mix, at plant/US	0.011	Kg	Estimated average input value	[156, 158]
Potassium	0.175	kg	Estimated average input value	[156, 158]
Herbicide	0.001	kg	Estimated average input value	[159, 160]
Diesel, combusted in industrial equipment/US	0.013	l	Calculated based on operations	Estimated
Feedstock Logistics				
Inputs from technosphere (materials/fuels)	Value	Unit		
Diesel, combusted in industrial equipment/US	0.073	l	Diesel required for harvesting	Estimated
Transport, single unit truck, diesel powered/US	1.286	t km	Based on plant capacity (60 km)	Estimated
Feedstock Pretreatment				
Inputs from nature (resources)	Value	Unit		
Water, process and cooling, unspecified natural origin	0.032	m^3	Water needed to pretreat feedstock (60% MC)	[89]
Inputs from technosphere (materials/fuels)				
Diesel, combusted in industrial equipment/US	0.154	l	Diesel for tub grinding operation and pretreated feed loading to reactor	[147]
Anaerobic Digestion				
Inputs from nature (resources)	Value	Unit		
Water, process and cooling, unspecified natural origin	0.027957895	t/hr	Water to attain 75% MC of feed	[89]
Inputs from technosphere (materials/fuels)				
Transport, single unit truck, diesel powered/US	0.284188	tkm	Based on assumed digestate transport distance	Estimated
Inputs from technosphere (electricity/heat)				
Electricity	0.10	kWh	AD reactor electricity requirement	[149]
Heat	0.17	kWh	AD reactor thermal requirement	[149]
Biogas Cleaning				
Inputs from nature (resources)	Value	Unit		
Air	10.44286227	kg	Air for water scrubbing	Aspen Plus
Water, process and cooling, unspecified natural origin	0.105110744	m^3	Biogas absorption medium	Aspen Plus
Inputs from technosphere (electricity/heat)				
Electricity	0.93	kWh	Biogas upgrading electricity required	Aspen Plus
Syngas Production				
Inputs from technosphere (materials/fuels)	Value	Unit		
Steam	6.46	kg	Steam biomethane reforming	Aspen Plus
Oxygen	1.86	kg	Partial oxidation oxygen	Aspen Plus
Nickel Catalyst	0.01	kg	Catalyst for steam reforming	Aspen Plus
Inputs from technosphere (electricity/heat)				
Electricity	0.39	kWh	Unit operation electrical requirement	Aspen Plus
Heat	2.08	kWh	Endothermic steam reforming heat requirement	Aspen Plus
Fischer-Tropsch Synthesis				
Inputs from technosphere (materials/fuels)	Value	Unit		
Cobalt, at plant/GLO S	0.00022303	kg	F-T process catalyst requirement	Aspen Plus
Inputs from technosphere (electricity/heat)				
Electricity	0.13	kWh	Compressor electricity requirement	Aspen Plus
Product Upgrade				
Inputs from technosphere (materials/fuels)	Value	Unit		
Platinum Catalyst	0.000101915	kg	Hydrocracking catalyst	Aspen Plus
Cobalt Catalyst	0.000507718	kg	Hydrotreating catalyst	Aspen Plus
Electricity Generation				
Inputs from nature (resources)	Value	Unit		
Water, cooling, unspecified natural origin/kg	22.28	kg	Circulating water for steam cycle	Aspen Plus
Air	6.22	kg	Excess air for fuel ignition	Aspen Plus

4.2.4 Life Cycle Impact Assessment (LCIA)

The LCIA includes the natural resources used, energy, water and environmental impacts. The environmental impacts to produce renewable diesel from miscanthus were estimated by TRACI 2 developed by U.S EPA [161]. The impacts considered were ranked according to global, regional and local impact categories showing the magnitude of its effect. Typically, global impacts such as Global warming potential (GWP [kg CO2-eq]), Ozone depletion (kg CFC-11 eq), and Ecotoxicity (kg 2, 4-D eq) are impacts that affects the international community. This impacts have raised global concerns as the climate is adversely plagued. Acidification potential (H moles-eq]) is generally classified as either regional or local while Eutrophication (kg N eq) and Smog (g NOx eq) are predominately a local impact. Other impacts such as Carcinogenic (kg benzene eq), Non-carcinogenic (kg toluene eq), Respiratory effects (kg PM2.5 eq) are multi-ranked and can be either of the three ranks.

4.2.5 Sensitivity Analysis

For the whole life cycle of the drop-in fuels production, a sensitivity analysis was conducted for the critical parameters to determine the extent of impact when the parameters were varied. This analysis is vital due to the extent of uncertainty in estimating the input parameters used in the drop-in diesel process. In this study, factors for variation were based on the system boundary input parameters that were judged to be sensitive to the entire process. Fertilizer inputs for the miscanthus cultivation and the corresponding yield were key input to the process. The amount of carbon sequestered on the soil which depends on the multiple factors was estimated from literature data based on a range of value. Also feedstock transport distance to the bioenergy refinery is another parameter that depends on the size of the biorefinery, yield, and other logistics. Fugitive biogas emissions, extent of methane yield from miscanthus during AD process, methane conversion to syngas, and the syngas conversion to drop-in fuels were all critical parameters that determines the energy and environmental impacts of this process. In order to forestall the possibility of capturing the impacts all these data, sensitivity analysis was carried out on the abovementioned parameters. Environmental impact categories such as greenhouse gas (GHG), smog formation, acidification, eutrophication, ecotoxicity, and fossil fuel energy consumption were examined as the parameters were varied by 25%.

4.3 Results and Discussion

4.3.1 Impact Assessment

The analysis of the environmental impacts of the production of renewable diesel from miscanthus was critically evaluated. Table 4-3 shows the inventory emissions data for the entire life cycle of the miscanthus to drop-in fuel production.

Table 4-3: Inventory emissions for the production of 1 GGE of Renewable Diesel

Substance	Unit	Miscanthus Cultivation	Logistics	Feedstock Pretreatment	Anaerobic Digestion	Biogas Upgrading	Syngas Production	Fischer-Tropsch Synthesis	Product Upgrade
Emissions to Air									
Carbon dioxide, biogenic	g	0.142	2146.059	4763.876	725.122	3740.136	497.329	51.845	0.105
Carbon dioxide, fossil	g	265.285	468.289	469.661	54.362	0.000	189.972	0.031	14.075
Carbon monoxide, biogenic	µg	0.000	0.000	0.000	378.047	247.005	106.714	29.352	0.000
Carbon monoxide, fossil	µg	417.316	3187.932	4087.434	276.944	0.000	99.671	0.187621	32.838
Dinitrogen monoxide	mg	264.216	8.308	0.369	1.851	0.035	0.635	0.004244	0.072
Methane, biogenic	g	0.000	0.000	0.000	235.780	2.136	0.000	0.000	0.000
Methane, fossil	mg	147.161	36.977	43.430	3.639	0.000	35.256	0.224	6.657
Nitrogen dioxide	mg	0.000	0.000	0.000	2.422	1.582	24.588	0.188	0.000
Nitrogen monoxide	mg	0.000	0.000	0.000	396.690	259.186	111.976	30.799	0.000
Nitrogen oxides	g	352.524	5.829	8.570	0.392	0.000	0.572	0.002	0.049
Particulates, unspecified	mg	73.099	43.174	44.972	4.841	0.000	117.388	0.094	21.467
Sulfur dioxide	g	2.092	0.230	0.239	0.026	0.000	1.357	0.003	0.164
Sulfur oxides	g	0.324	0.459	0.474	0.053	0.000	1.569	0.031	0.092
VOC, volatile organic compounds	mg	85.811	222.618	224.740	25.706	0.000	23.968	0.370	4.028
Emissions to Soil									
Cobalt	mg	0.000	0.000	0.000	0.008	0.000	0.008	0.408	1.015
Nickel	mg	0.000	0.000	0.000	0.000	0.000	7.185	0.000	0.000
Emissions to Water									
BOD5, Biological Oxygen Demand	mg	69.151	95.081	99.040	10.657	0.000	13.164	0.100	73.474
Chloride	g	14.249	18.771	19.552	2.104	0.000	2.707	0.021	15.228
Cobalt	µg	8.752	11.515	11.994	1.291	0.000	1.661	0.013	9.338
COD, Chemical Oxygen Demand	mg	116.983	180.521	188.037	20.232	0.000	22.401	0.168	123.649
Nickel	µg	238.780	140.454	146.301	15.741	0.000	14.420	0.106	75.657
Suspended solids, unspecified	g	0.396	1.381	1.439	0.155	0.000	0.084	0.001	0.314

These emissions were categorized into air, soil and water with the top emissions represented. It can be observed that some of the greenhouse gases contributing to global warming such as CH_4 and CO_2 accrued from biogic origin for which CO_2 participates in photosynthesis and hence reduces the amount of GHG emissions from this process.

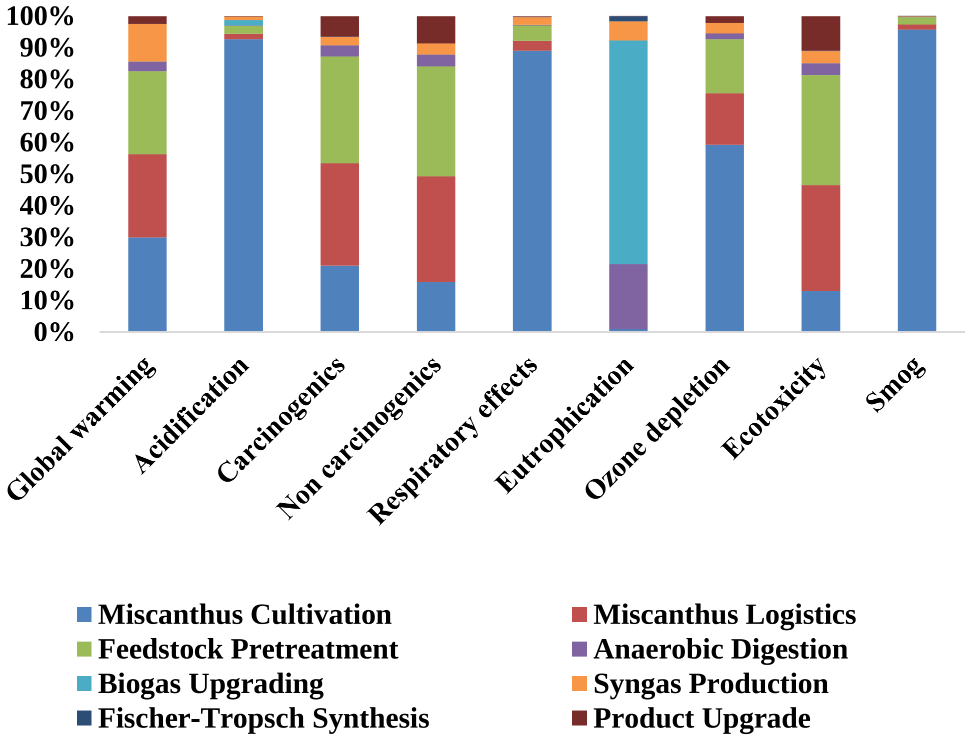


Figure 4-2: Cradle to gate impact analysis of the production of 1 GGE of diesel from Miscanthus

Fig. 4-2 shows the categories of impacts considered in this study according to the different processes in the renewable diesel pathway that made up the entire emission. Miscanthus cultivation, feedstock logistics, and pretreatment contributed 80% of the total greenhouse gas (GHG) emission. This is not far-fetched as they were the highest consumer of fossil energy. The miscanthus cultivation was responsible for the 90% of acidification potential due to the use of fertilizer (NPK) which is primarily the cause of acidification. Biogas cleaning was chiefly accountable for the high eutrophication potential of the entire process as 10% of the scrubbing water was purged in this process to minimize build up of impurities. This purge water joins the local water bodies contributing to the eutrophication formation. We discussed the different impact categories in the subsection below to highlight key factors contributing to the various categories.

4.3.1.1 Greenhouse Gas (GHG)

Emission of carbon dioxide, methane and nitrogen oxides are greenhouse gases emitted during this process that contributed to global warming potential. This impact is categorized by global warming potential (GWP) reported in CO_2 eq. A global warming potential of 1.8485 kg CO_2 eq/GGE of renewable diesel was calculated for the base case scenario without lime addition in the miscanthus cultivation. This high amount of emission was due to the conversion of the carbon content in miscanthus lost during transportation, storage, and pretreatment to carbon dioxide which adds up to the overall GHG emission.

4.3.1.2 Smog Formation

Formation of smog are as a result of the emission of volatile organic compounds (VOC) and nitrogen oxides which leaves airborne particles and ground-level ozone in the atmosphere. It is estimated by the amount of ozone level and reported in mass ozone equivalent (kg O_3eq) which for this analysis a 9.1265 kg O_3eq/GGE of renewable diesel was obtained. 96% of the photochemical smog formation is from the combustion of the diesel fuel during miscanthus cultivation which releases nitrogen oxides and other smog formation causing compounds.

4.3.1.3 Acidification

Sulfur and nitrogen related emissions causes acidification which the alteration in the pH level of the environment. Emission of nitrogen oxides, ammonia, nitrogen dioxides, sulfur oxides, sulfur dioxides leads to atmospheric acidification. Miscanthus cultivation is higest contributor to acidification potential due to the amount of nitrogen related emissions accruing from the process. The production of 1 GGE of renewable diesel resulted to a acidification emissions of 15.37 H+ moles eq.

4.3.1.4 Eutrophication

The use of chemical fertilizers (NPK) are primarily the causes of eutrophication emissions. This emission was as a result of miscanthus cultivation which required fertilizer application. Environmental consequence of the use of chemical fertilizers is the leaching of the chemicals to ground water which generally causes algae bloom. This action occurred at the biogas cleaning process as the water used for the absorption process is purged and would have made its way to the ground water. A eutrophication potential of 2.0164 kg N eq was estimated for the renewable diesel production which raises the eutrophication level by approximately 99% compared to the fossil derived diesel.

4.3.1.5 Ecotoxicity

Toxic emissions from natural or synthesized pollutants results to adverse effects on the ecosystem. Such emissions are comparatively measured alongside other toxic emissions to the atmosphere and reported in CTUe. 1 GGE of renewable diesel causes 3.82 CTUe of ecotoxic emissions. Logistics and pretreatment processes are chiefly the operations that jointly consistuted 68% of the total ecotoxic emissions. Toxic emissions such as diesel emissions and feedstock loss raises the ecotoxicity level.

4.3.1.6 Ozone Depletion

Main constituent of ozone depletion is the emission of chlorofluorocarbon (CFC) and other halogenated compounds with chlorine and bromine effects being more severe. Compared to fossil diesel, ozone depletion potential of renewable diesel from miscanthus was calculated as 1.1734E-10 kg CFC-11eq which 147% lower than that of fossil diesel.

4.3.2 Comparison with Fossil Derived Diesel

The cradle to gate (CTG) life cycle of miscanthus to drop-in renewable diesel was compared with the fossil derived diesel in a typical U.S refinery. This comparison was performed for the miscanthus cultivation without lime addition (base scenario) and that with lime addition. The lime addition scenario was considered due to the pH level of some strip-mined soil which might have a high acid level and would need the soil condition to be balanced. For the scenario without lime addition shown in fig 4-3, it shows that the GHG emission of the renewable diesel from miscanthus contributed 65% of the emissions which is approximately 86% higher than the fossil derived diesel. And for the scenario that used lime for miscanthus cultivation, there is a 157% increase in the greenhouse gas emission (GHG) when compared to the fossil derived derived diesel as depicted in fig 4-4. From all indications, this defeats the assertion of a greenhouse gas reduction from renewable sources which several authors have reported.

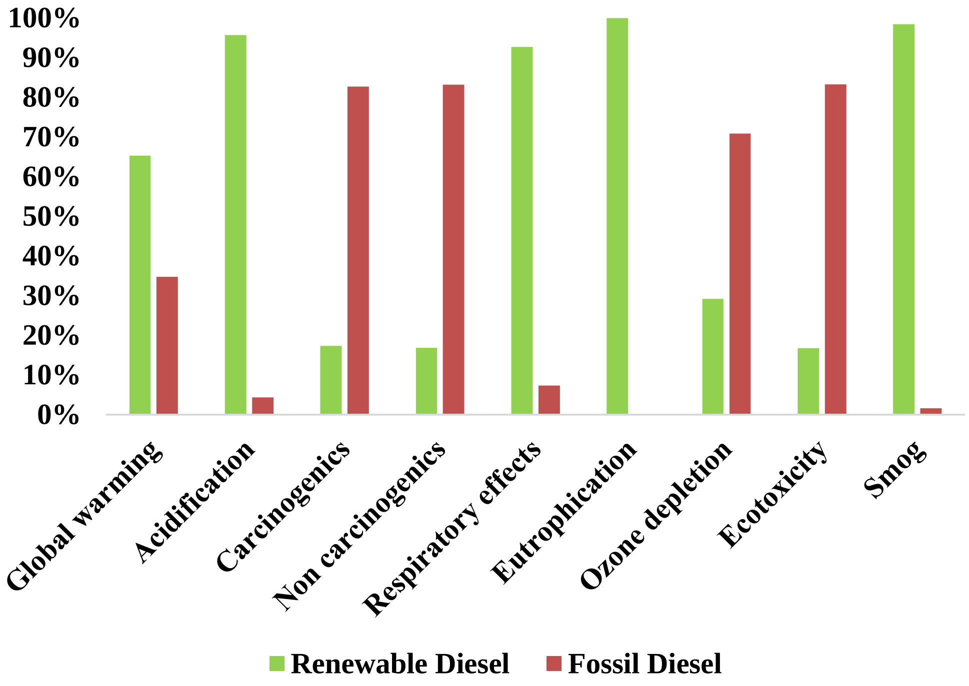


Figure 4-3: Cradle to gate life cycle of miscanthus to drop-in renewable diesel (without lime)

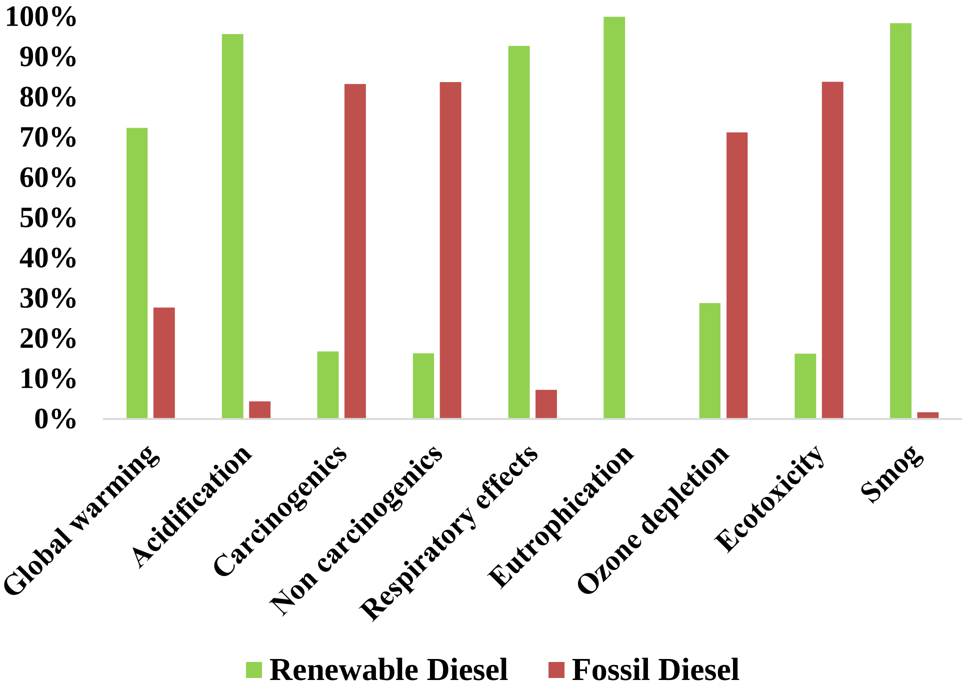


Figure 4-4: Cradle to gate life cycle of miscanthus to drop-in renewable diesel (with lime)

However, it should be noted that the analysis did not consider the effect of soil organic carbon sequesteration when accounting for the greenhouse gas emission. Typically, some amount of carbon sequestered during the cultivation of feedstock (biomass) is ususally taken as credit when reporting the greenhouse gas (GHG) emission. Therefore when the amount of carbon sequestrated during the feedstock culitvation is considered, there is a net GHG emission reduction of 41% and 26% compared to the fossil diesel for the base scenario without lime and that with lime addition respectively as shown in figs 4-5 and 4-6.

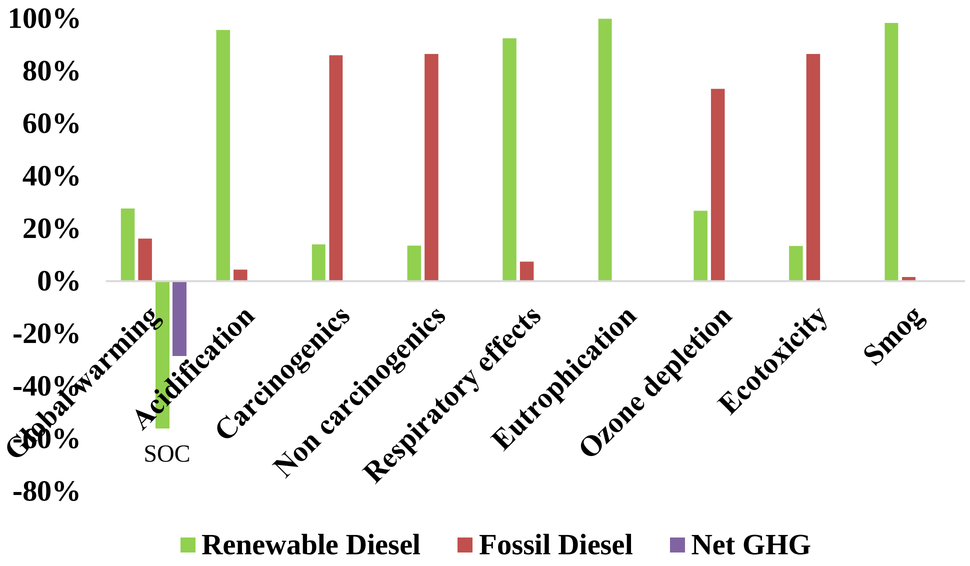


Figure 4-5: Comparison of the impact of production of 1 GGE of renewable diesel from miscanthus without lime addition and 1 GGE of fossil diesel

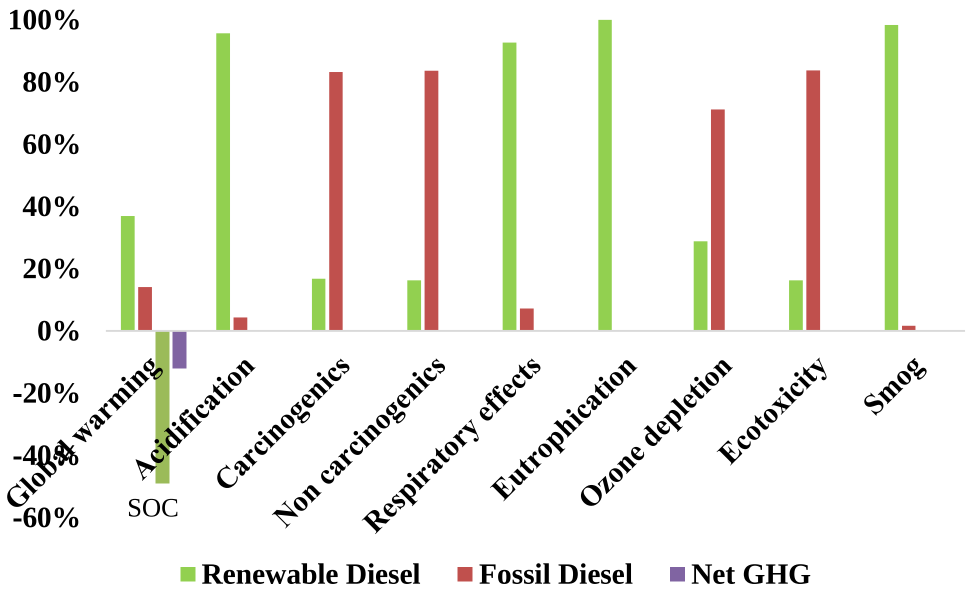


Figure 4-6: Comparison of the impact of production of 1 GGE of renewable diesel from miscanthus with lime addition and 1 GGE of fossil diesel

4.3.3 Sensitivity Analysis

Variation of the critical input parameters in the sensitivity analysis showed the impact of certain data in the life cycle of the drop in fuels production. Fig 4-7 – 4-12 shows the impact of F-T conversion, methane conversion, miscanthus methane yield, feedstock cultivation yield, nitrogen input, fugitive biogas emission, transport distance, and pretreatment loss on the impact categories studied.

Production of the drop-in renewable diesel is highly dependent on the F-T process and the extent of conversion to liquid fuel is vital in all respect (economic and life cycle perspective). A drop in conversion (40% syngas conversion) during the F-T process raises the GHG emission, acidification potential, ecotoxicity, fossil energy consumption and smog formation to approximately 80-100%. In the evident of an advancement in technology in terms of better catalyst performance resulting to a 100% conversion

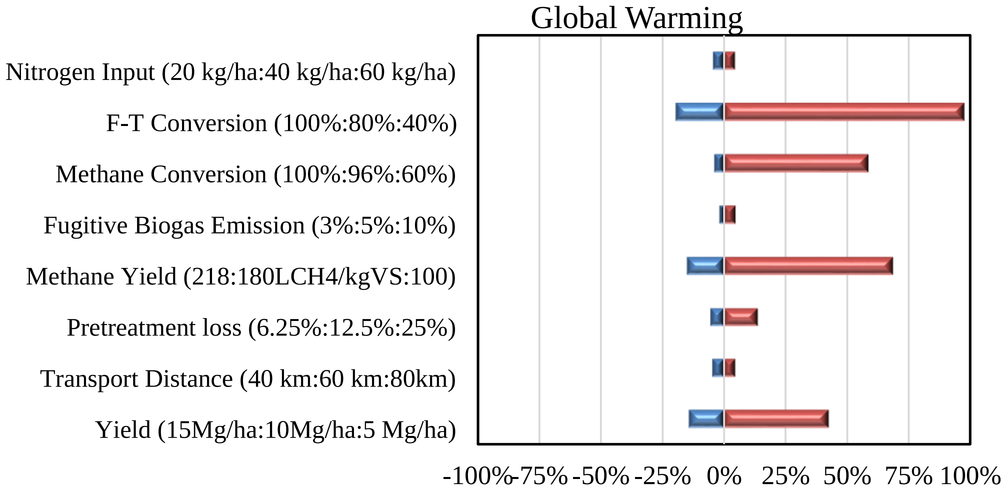


Figure 4-7: Sensitivity analysis for global warming potential

from the 80% maximum attainable conversion used for this analysis, approximately 20% reduction in GHG emission, acidification potential, ecotoxicity, fossil energy consumption and smog formation was achieved. Another aspect of the renewable diesel production is methane conversion during syngas production. If the presence of impurities causes catalyst sintering, the 96% conversion achieved in the syngas productuion can drop up to 60% with the formation of coke. As seen in figs 4-11, a 52% increase in fossil energy use occurred while recording approximately 95% increase in photochemical smog formation. Methane potential of miscanthus after pretreatment during anaerobic digestion process has been reported to be within 0.179-0.218 m^3CH4/kg VS.

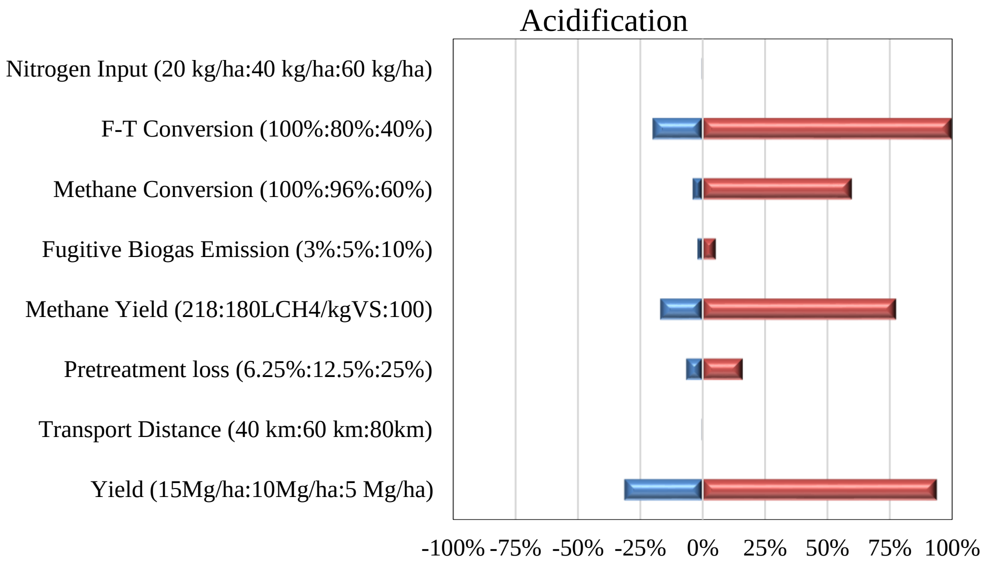


Figure 4-8: Sensitivity analysis for acidification potential

We employed an average value of 0.180 m^3CH_4/kg VS as the possible methane yield in the base case process. However in unforeseen circumstances surronding the performance of microbial activity during AD process, a 0.1 m^3CH_4/kg VS can be achieved. In such condition, fossil energy use increased by 54% contributing to the GHG emission that increased by 70%. Miscanthus cultivation on a strip-mined soil has an average yield of 10 Mg/ha which can drop as low as of 5 Mg/ha or increase upto as 15 Mg/ha depending on complex soil behavior. Conditions were the amount of harvestable biomass is 5 Mg/ha, there is a significant increase in emissions with acidification potential being the most signigificant (96% increase). This is reasonable since more fertilizers are required to achieve the amount of biomass needed for downstream conversion.

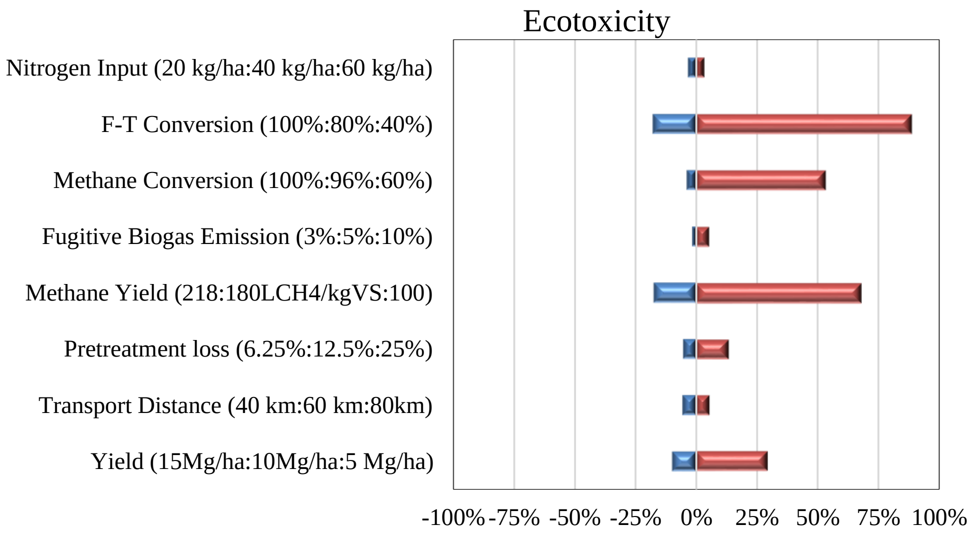


Figure 4-9: Sensitivity analysis for Ecotoxicity potential

As a result, N_2O emissions from the use of Nitrogen fertilzers raises the acid level of the atmosphere. It is not surprising that the drop in F-T conversion, methane conversion during syngas production, and miscanthus methane yield led to an increased demand for feedstock needed to achieve the functional unit. Such situations raises the acidification level to 100%, 55% and 78% respectively.

Wide range of amount of nitrogen required for miscanthus cultivation has been reported by several authors with some authors reporting that no nitrogen is required for miscanthus cultivation.

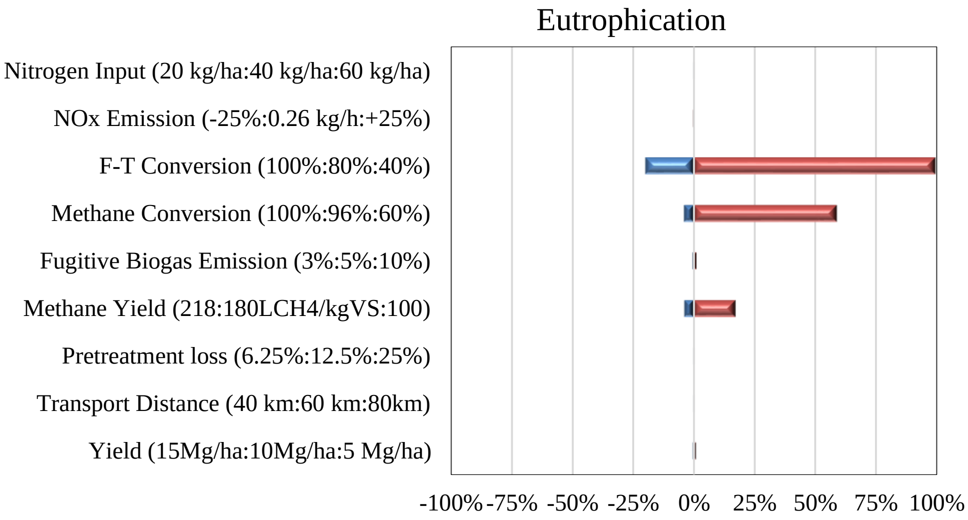


Figure 4-10: Sensitivity analysis for Eutrophication potential

Our analysis showed that the use of 20 kg/ha or 60 kg/ha of nitrogen for cultivation did not result to a very significant change in emissions showing that an optimum nitrogen input is established.

To enhance the breakdown of the carbohydrate structure of miscanthus, the fungal pretreatment was employed. During the pretreatment process, a 12.5% dry matter loss of the feedstock was reported [148].

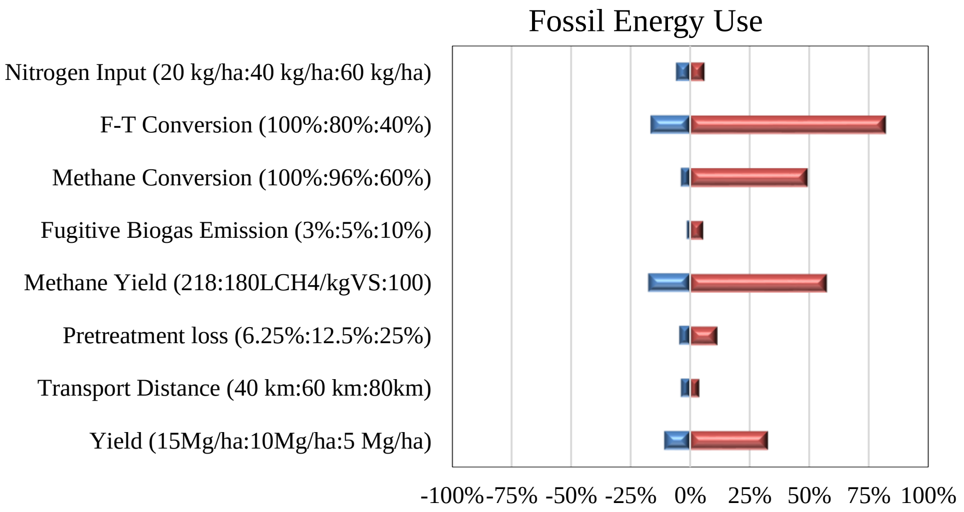


Figure 4-11: Sensitivity analysis for Fossil Energy use

Increased loss of biomass during pretreatment led to high demand of feedstock to cover for the losses encountered during the pretreatment process. The impact category with the most significant effect when the amount of dry matter lost during pretreatment doubled was photochemical smog formation (73%). Increase in fossil energy used for harvesting additional feedstock, logistics, and pretreatment was the parameter that contributed to this extent of emission. Biogas leaks from the digester referred to as fugitive biogas emission was also significant when the 5% biogas fugitive emission was doubled.

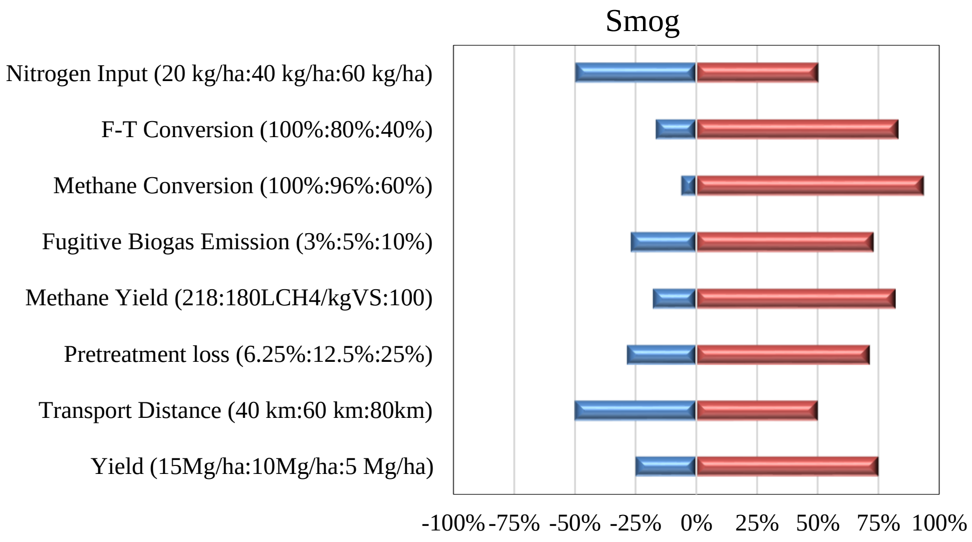


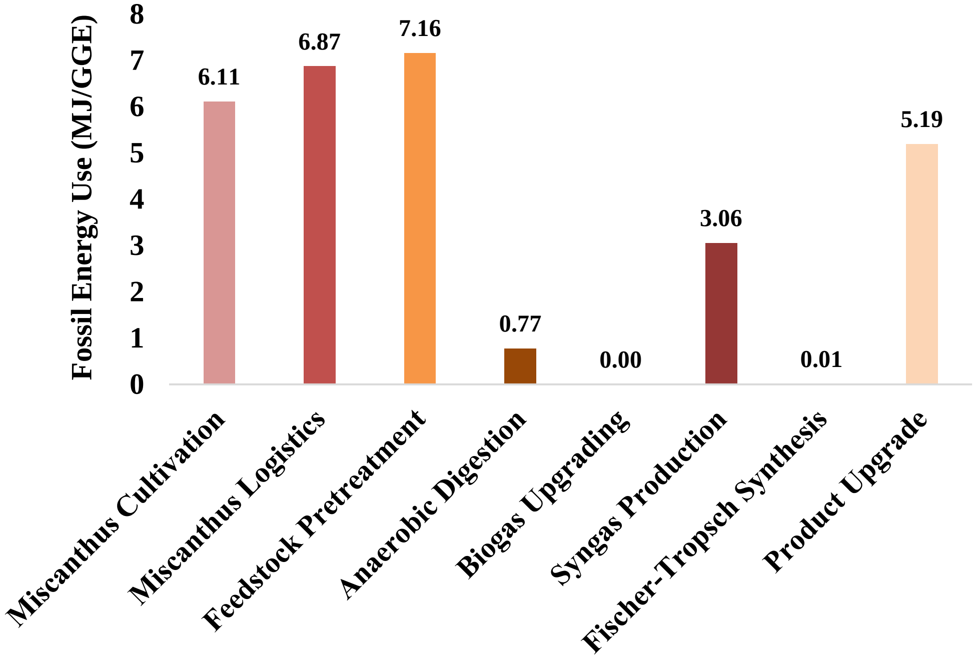
Figure 4-12: Sensitivity analysis for Photochemical Smog formation potential

The biogas plant capacity was used to estimate an average transport distance from the farmland to the biorefinery using GIS model. An increase or decrease in yield was modeled as the 40 km and 80 km transport distance to the biorefinery respectively which showed the same magnitude of change in both respects.

4.3.4 Other Impacts Analysis

4.3.4.1 Fossil Fuel Energy Consumption

Energy put in form of diesel for the cultivation, logistics (harvesting and transportation), and pretreatement were accounted for in this analysis. The production of 1 GGE of renewable diesel from miscanthus consumed a total of 29.178 MJ of fossil energy in its crade to gate life cycle. Fig 4-10 shows that the pretreatment of miscathus is the highest consumer of fossil energy given the amount of diesel used in the tub grinder and front-end loader.



The total energy consumed in the enitre life cycle of the drop-in diesel production results to a positive net energy balance of 100.421 MJ/GGE. This shows a sustainable energy production since the energy value in the product is approximately 3 times the energy utilized for its production.

4.4 Conclusion

Drop-in renewable diesel production from miscanthus grown in the strip-mined land have been explored. This process analysis was developed based on the mass and energy balance obtained from our Aspen Plus model, certain specific literature data and estimated GIS logistics. SimaPro v8 was used to model the process via input and output basis and its energy and environmental impacts calculated using TRACI 2 v4. For the entire cradle to gate (CTG) life cycle of the renewable diesel from miscanthus, a greenhouse gas (GHG) emission of 1.8485 kg CO_2/GGE was emitted to the environment when miscanthus was cultivated without the addition of lime. This emission is approximately 86% higher than the fossil derived diesel which offers no advantage to the use of renewable feedstock for the production of drop-in fuels. Greenhouse gas (GHG) emission increased from 86% to 161% when lime was used for the cultivation of miscanthus.

However, considering the merits of the carbon sequestered on the soil during the cultivation of miscanthus, the greenhouse gas (GHG) emission reported for the entire life cycle of the drop-in renewable diesel from miscanthus is the net value. Therefore, there is a net greenhouse gas emission reduction of 41% when the analysis is considered without the use of lime for the cultivation of miscanthus. Even for the scenario were miscanthus was grown with lime, there is still a 26% GHG reduction compared to the fossil derived diesel which meets the renewable fuel standard target.

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CHAPTER 5

CONCLUSIONS

Economic assessment of converting biogas to renewable transportation fuels via Fischer-Tropsch synthesis was investigated as a feasible route to attain the renewable fuels standard (RFS). Biogas is traditionally produced by the anaerobic digestion (AD) of food wastes, animal manure, and waste water either at a farm scale level or in a commercial scale. The farm scale AD plant have been generally used for heating and electricity generation that serves the farm needs while the industrial scale AD plants generates purified biogas for direct heating or electricity production or for the production of Compressed Natural Gas (CNG).

A process simulation model was developed using an ASPEN Plus software platform to simulate biogas to liquid fuels (BgTL) technology via F-T synthesis. Biogas primarily composed of methane, carbon dioxide, and other impurities was cleaned using the high pressure water scrubbing (HPWS) process technology which has an efficiency of 98%. By scrubbing the impurities (CO_2 and H_2S) in biogas, the product of the cleaning process called, biomethane composed of 97% methane. The energy requirement of the biogas cleaning process was 0.2 kWh/Nm^3 raw biogas upgraded. Such energy consumption is feasible when compared to the energy value of upgraded biogas which has same energy value as natural gas (39 MJ/Nm^3). Hence, there is a positive net energy balance in the biogas cleaning process which makes the process technology viable. In addition to the minimal electrical energy requirement of the process, proper heat integration approach recovered 75% of the input electrical energy in the form of heat.

The biomethane product obtained after biogas cleaning was reformed using a combination of steam and partial oxidation reforming processes to achieve an overall methane conversion of 96% and a product yield of 68%. Such extent of methane conversion was achieved by maintaining the steam to carbon ratio (vol/vol) at approximately 4 in the steam reforming process while keeping the reformer temperature at 850^{o}C. For this combination of reforming processes, a hydrogen to carbon monoxide ratio syngas ratio of 2.19 was achieved which is necessary for the downstream conversion to hydrocarbon fuels. Based on the syngas composition and slurry phase reactor (200^{o}C and 26 bar) employed for the F-T process, Aspen Plus Fortran calculator was used to estimate an alpha value of 0.9. An overall liquid fuels fractions yield of 53% (mass basis) was obtained when the F-T syncrude was upgraded and distilled.

Techno-economic analysis of the biogas to drop-in renewable fuels conducted using Aspen Process Economic Analyzer (APEA) resulted to a total capital investment (TCI) and annual operating costs of \$104.8 million and \$11.66 million for a plant size of 2000 Nm^3/h. A discounted cash flow rate of return was performed at a net present value of zero to estimate a selling price of \$5.99/gal (\$5.59/GGE). A selling price of \$2.64/gal (\$2.46/GGE) was obtained when the plant operates at a size of 10,000Nm^3/h which further reduces to \$2.11/gal (\$2/GGE) at a plant size of 20,000Nm^3/h.

The cradle to gate life cycle analysis of the production of drop-in diesel from miscanthus was also evaluated using TRACI 2 V4.0 based on the mass and energy balance of the entire process. This analysis was conducted for a functional unit of 1 gasoline gallon equivalent (GGE) of renewable drop-in diesel which was compared to the 1 GGE of fossil derived diesel in U.S refinery. All input and output were normalized based on the functional unit. Processes such as miscanthus cultivation, feedstock logistics, miscanthus pretreatment, anaerobic digestion (AD), biogas cleaning, syngas production, Fischer-Tropsch synthesis, product upgrade, and power generation were considered in this analysis accounting in details all the direct and indirect emissions.

For the entire life cycle of the process, the greenhouse gas emission of drop-in renewable diesel from miscanthus when miscanthus was cultivated without the use of lime was 1.8485 kg CO_2eq/GGE compared to the fossil derived diesel of 0.987 kg CO_2eq/GGE. This showed an 86% increase in the greenhouse gas emission of the renewable diesel compared to the fossil derived diesel. Analyzing the processes that contributed to the overall GHG of the renewable diesel pathway, it was observed that miscanthus cultivation, feedstock logistics, and feedstock pretreatment contributed 30%, 26% and 28% of the total 1.8485 kg CO_2eq GHG emission respectively.

In an alternative case, where lime was needed to maintain the soil pH level, the GHG emission increased from 1.8485 kg CO_2eq to 2.57 kg CO_2eq which is approximately a 40% increase in overall greenhouse gas (GHG) emission for the renewable diesel. Compared with that of the fossil derived diesel, a greenhouse gas (GHG) emission increased to a magnitude of 161%. Nevertheless, the proposition for a greenhouse gas emission reduction from the use of lignocellulosic biomass for the production of drop-in fuels is still feasible when carbon sequestration is put into consideration. The greenhouse gas emission of the renewable diesel produced from miscanthus cultivated without the addition of lime has a net greenhouse gas emission reduction of 41% compared to the fossil derived diesel when carbon sequestration was considered. Even when lime was used for the cultivation of miscanthus, the net greenhouse gas emission was reduced by 26% compared with that of the fossil derived diesel.

In conclusion, the production of renewable diesel from miscanthus has shown to offer a reduction in greenhouse gas emission when carbon sequestration is considered. And the extent of reduction in emission is within the stipulated target of 25% set by EPA’s renewable fuels standard (RFS).

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APPENDIX

Supporting Information (SI) for

Techno-Economic assessments of biogas to liquid fuels conversion technology via Fisher-Tropsch synthesis

1. Introduction

1.1. Biogas methane potential in the United States

Globally, food waste, animal manure and other organic solid wastes are co-digested in an anaerobic digester to produce biogas. In the United States, the reported methane potential from animal manure, landfill, wastewater, and industrial, institutional and commercial organic waste is estimated to be about 8 million tonnes per year.

8 million tonnes x 1000 kg / 1 tonne x $1m^3$ /0.656 kg = 12 billion m^3 per annum of methane

This high annual amount of methane makes biogas a potential feedstock for the production of drop-in fuels via Fischer-Tropsch synthesis, which formed the basis of our work.

1.2. Biogas Plant and F-T process integration

Although biorefineries such as an ethanol production plant are normally constructed as a stand-alone facility with feedstock sourced within some radius away, biogas plant can be expanded to include an F-T liquid fuels processing facility. Conventionally, biogas is pipelined for further downstream processing such as in a liquid fuels production facility that converts the biogas to drop-in fuels, which is the rationale for this study.

2. Aspen Plus model kinetics and equations

2.1. Simulation methods:

We employed the aid of a process simulation tool, Aspen Plus v8.8, to model the biogas to liquid (BgTL) drop-in fuels plant. The components specification that represents the overall feed and products compositions include: N_2, CO_2, H_2S, H_2, O_2, H_2O, Air. CH_4 and C_2-C_{20} alkanes and akenes compounds that are conventional compounds in Aspen Plus were specified. C_{21}-C_{29} and C_{30} (Wax) compounds were specified to represent the hydrocarbon chains in order to accurately account for the paraffins, olefins and oxygenates composition of each respective carbon number in the liquid fuels product distribution. The activity coefficient method, non-random two liquid (NRTL) with Henry's constant, was used for the thermodynamic calculations of the biogas cleaning. Henry's constant and the default binary parameter in Aspen Plus V8.8 predicted the performance of the absorption process in the biogas mixture and the liquid absorbent. The equation of state (EOS) Peng-Robinson (PR) was used to model the syngas production and Fischer-Tropsch reaction sections while Peng-Robinson with Boston-Mathias (PR-BM) was used to model the product upgrading section of the BgTL. The combined-cycle electricity generation process employed a STEAM-TA and PR methods respectively for the steam Rankine and gas Brayton cycles.

During the simulation of each sections of the BgTL process, several assumptions were made:

1. The process was carried out in a steady-state
2. All reactors were modeled using a continuous reactor
3. The PFR catalyst density and bed voidage were specified for Ni/Al_2O_3.
4. Heat and work streams represented thermal and electrical energy

2.2. Biogas Cleaning

The solubility action of the components of the biogas in water is based on Henry's law. The absorption operation is based on the partial pressure of the individual component of the biogas and concentration of the components of the biogas as illustrated in eqn 1.

$$\sum p_i = H_i x_i \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(1)}$$

where

p_i = partial pressure of biogas component i

H_i = Henry's constant

x_i = mole fraction of component i

The mass balance over the absorber that determines the amount of liquid required to absorb a certain amount of gas is given by the eqn 2:

$$Y_{n+1} - Y_1 = \frac{L'}{G'}(X_o - X_n) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(2)}$$

where:

Y_{n+1}= entering gas mole fraction into the absorber

Y_1= exiting gas mole fraction from the absorber

L'= Liquid flow rate into the absorber

G'= Gas flow rate into the absorber

X_o= entering liquid mole fraction into the absorber

X_n= exiting liquid mole fraction into the absorber

With known values of Y_{n+1},X_o, and G' , the desired absorber liquid flowrate (L') required to achieve the optimum methane composition in the biomethane stream (Y_1,) is obtained after several iterations.

The calculations for the amount of methane recovered from biogas, the ratio of liquid (water) to biogas ratio needed for absorption, and the air to biogas ratio needed to scrub the saturated water prior to recycling are shown in the excel sheet of this supporting information.

2.3.Syngas Production

Peng-Robinson (PENG-ROB) EOS was used to model the vapor-liquid equilibrium interaction of the components. This equation of state is utilized for natural gas systems and have been modified to enhance its thermodynamic predictions.

The Peng-Robinson equation of state is given by

$$P + \frac{\alpha a}{\tilde{v}^2+2b\tilde{v}-b^2}(\tilde{v}-b) = RT \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (3)$$

Steam reforming of the biomethane employed for the production of syngas followed a kinetic rate expression. Kinetic model developed by [112] for the steam methane reforming on Ni/Al_2O_3 catalyst was based on the Langmuir Hinshelwood Watson (LHHW) kinetics. To simulate the steam reforming process in Aspen Plus, the LHHW was used to predict the reaction rate expression. The reaction rates developed by [112] are shown below

$$R_1 = \frac{k_1}{P_{\mathrm{H2}}^{2.5}} \frac{P_{\mathrm{CH4}}P_{\mathrm{H2O}} - (P_{\mathrm{H2}}^{3}P_{\mathrm{CO}}/K_1)}{\left(1 + \mathrm{KCOPCO} + \mathrm{KH2PH2} + \mathrm{KCH4PCH4} + \frac{K_{\mathrm{H2O}}P_{\mathrm{H2O}}}{\mathrm{P_{H2}}}\right)^2} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (4)$$

$$R_2 = \frac{k_2}{\mathrm{P_{H2}}} \frac{P_{\mathrm{CO}}P_{\mathrm{H2O}} - (\mathrm{P_{H2}}\mathrm{P_{CO2}}/K_2)}{\left(1 + \mathrm{KCOPCO} + \mathrm{KH2PH2} + \mathrm{KCH4PCH4} + \frac{K_{\mathrm{H2O}}P_{\mathrm{H2O}}}{\mathrm{P_{H2}}}\right)^2} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (5)$$

$$R_3 = \frac{k_3}{P_{\mathrm{H2}}^{3.5}} \frac{P_{\mathrm{CH4}}\mathrm{P_{H2O}^{2}} - (\mathrm{P_{H2}^{4}}\mathrm{P_{CO2}}/K_3)}{\left(1 + \mathrm{KCOPCO} + \mathrm{KH2PH2} + \mathrm{KCH4PCH4} + \frac{K_{\mathrm{H2O}}P_{\mathrm{H2O}}}{\mathrm{P_{H2}}}\right)^2} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (6)$$

where R_1, R_2, and R_3 represents the SMR, Water gas shift process and Global SMR

The Arrhenius equation describes the rate coefficients and adsorption coefficients of the gases as illustrated by the equations [103]:

$k_i = k_{oi} \times e^{-Ei/RT}$ i = 1, 2, 3 ………………………………….…… (7)

$K_j = K_{oj}$ x $e^{-\Delta H_j/RT}$ j = CO, H_2, CH_4, H_2O ……………………………… (8)

The rate-based model of the LHHW is given by the expression

$$rate = \frac{(kinetic\ factor)(driving\ force\ term)}{(adsorption\ term)} \qquad (9)$$

where:

kinetic factor = $k[(T/T_o)^n]exp\left[(E/R)\left(\frac{1}{T} - 1/T_o\right)\right]$

driving force = $k_1 \prod_{i=1}^{N} C_i^{\alpha i} - k_2 \prod_{j=1}^{N} C_j^{\beta i}$

adsorption term = $\left(\sum_{i=1}^{M} K_i\left[\prod_{j=1}^{N} C_j^{mj}\right]\right)^m$

where

r = rate of reaction

k = pre-exponential factor

T = absolute temperature

To = reference temperature

n = temperature exponent

E = activation energy

R = gas law constant

C = Component concentration

m = Adsorption expression exponent

K_1, K_2, Ki = Equilibrium constants v = Concentration exponent

i, j = Component Index

A, B, C, D = Constants

Kinetic data obtained from the work of [112] as given shown in the table S1 below were employed for calculating the input parameters in Aspen Plus to determine the reaction rate.

Table S1. Kinetic and adsorption parameters for the kinetic rate of SMR in Ni/Al_2O_3 catalyst.

Reaction parameters			
K_{SMR} (mol Pa0.5/(kg s))	1.16×10^{16}		
K_{WGS} (mol/(kg s Pa))	5.41×10^{4}		
K_{GSMR} (mol Pa0.5/(kg s))	2.79×10^{15}		
E_{SMR} (kJ/mol)	240.1		
E_{WGS} (kJ/mol)	67.13		
E_{GSMR} (kJ/mol)	243.9		
K_{CO} (Pa−1)	8.25	ΔH_{CO}(kJ/mol)	-70.65
K_{H2} (Pa−1)	6.15×10^{-4}	ΔH_{H2}(kJ/mol)	-82.9
K_{CH4} (Pa−1)	66.6	ΔH_{CH4}(kJ/mol)	-38.28
K_{H2O} (Pa−1)	1.77×10^{10}	ΔH_{H2O}(kJ/mol)	88.68

1) Kinetic factor = 2.79e15 exp (243.9[kJ/kmol]/RT)

In Aspen Plus, the form of the equation is

kinetic factor = k exp (E/RT)

Hence, the inputs are as follows:

pre-exponential factor k = 2.79e15

Activation Energy E = 243.9 kJ/kmol

2) Driving Force

The Aspen Plus form of the driving force equation is

driving force expression = K_1 productsum (Ci^ai) - K_2 productsum (Ci^bi)

Aspen Plus calls the first product sum term1 and the second term2.

driving force expression = term1 - term2

For this problem,

driving force expression = (Ca)

In the Aspen Plus form of the driving force expression:

driving force expression = K_1 (Ca) - K_2 (Ca)

and

Term 1 = Ca where $K_1 = 1$

Term 2 = 0 where $K_2 = 0$

driving force expression = 1 (Ca) - 0 (Ca)

Since K is in a log form

$$\ln(K) = A + B/T + C \ln(T) + D T$$

For term 1:

ln 1 = 0 where A = 0

For term2:

ln 0 = -infinity

Since infinity cannot be entered, it is approximated as -1000:

ln 0 ~ -1000 where A = -1000

3) Adsorption term

The Aspen Plus form of the adsorption term is

$$\text{adsorption term} = (\text{sum Ki [productsum (Cj\^{}nuj)]})^m$$

For this problem,

$$\text{adsorption term} = (1 + K_{CO}P_{CO} + K_{H2}P_{H2} + K_{CH4}P_{CH4} + K_{H2O}P_{H2O})$$

Any number of terms are possible. For this problem there are five terms and the adsorption expression exponent m = 2.

$$\text{adsorption term} = (\text{term1} + \text{term2} + \text{term3} + \text{term4} + \text{term5})^m$$

For term 1:

$K = 1$

$\text{Ln } 1 = 0$

$\text{Ln } K = A$

For term 2:

$K_{CO} = 8.25\exp(70.65/RT)$

$\text{Ln }(K_{CO}) = \ln(8.25) + (70.65/0.00831/T)$

$= 15.602 + 8497.71/T$

$\text{Ln } K = A + B / T$

For term 3:

$K_{H2} = 6.15 \times 10^{-4}\exp(82.90/RT)$

$\text{Ln }(K_{H2}) = \ln(6.15 \times 10\text{-}4) + (82.90/0.00831/T)$

$= -7.39 + 9975.93/T$

$\text{Ln } K = A + B / T$

For term 4:

$K_{CH4} = 66.6\exp(38.28/RT)$

$\text{Ln}(K_{CH4}) = \ln(66.6) + (38.28/0.00831/T)$

$= 4.199 + 4606.50/T$

$\text{Ln } K = A + B / T$

For term 5:

$K_{H2O} = 1.07 \times 10^7 \exp(-5.78/RT)$

$\text{Ln}(K_{H2O}) = \ln(1.07 \times 10^7) + (-5.78/0.00831/T)$

$= 16.203 – 695.213/T$

$\text{Ln } K = A + B / T$

Table S2. Summary of Aspen Plus LHHW input

Kinetic factor	
k	2.79×10^{15}
E	243.9 kJ/kmol
Driving force expression:	
Term 1	CH_4 exponent = 1; H_2 exponent = 1; A = 0
Term 2	A = -100000
Adsorption term:	
Term 1	no exponents; A = 0
Term 2	CO exponent = 1; A = 2.11; B = 8497.71
Term 3	H_2 exponent = 1; A = -7.39; B = 9971.13
Term 4	CH_4 exponent = 1; A = 4.198; B = 4604.28
Term 5	H_2O exponent = 1; A = 16.203; B = -695.213

Detailed calculations on the overall conversion of methane, syngas yield, and syngas ratio (H_2/CO) can be found in the excel sheet of this supporting information.

2.4. Fischer Tropsch synthesis

The slurry reactor design equation modeled as a RYield reactor is given by

Design Equation: $V = F_{CH4o} \int_0^x \frac{dX}{-r_{CH4}}$…………………(10)

The length of hydrocarbon product formed is dependent on the alpha chain growth probability model predicted by Anderson-Flory mechanism [61]. Fischer- Tropsch Product distribution was calculated in Aspen Plus model using the temperature and feed composition dependent correlation developed by [73] for cobalt catalyst as shown by equation 11 below. The calculations for the alpha value can be found on the excel sheet of this supporting document.

$$\alpha_{ASF} = \left[A \frac{y_{CO}}{y_{H_2}+y_{CO}} + B\right] [1 - 0.0039\ (T - 533)] \text{……………… (11)}$$

where;

y_{CO} = mole fraction of carbon monoxide in syngas

y_{H_2} = mole fraction of hydrogen in syngas

A = constant = 0.2332

B = constant = 0.663

T = temperature in K

The calculated alpha distribution was fitted into the Anderson-Flory product distribution model of equation 12 to predict the F-T product weight calculated using the Aspen Plus calculator block and the results exported as output stream. The product weight distribution calculation model was developed in the excel sheet of this supporting information.

$$W_n = n(1 - \alpha)^2 \alpha^{n-1} \text{…………………………… (12)}$$

where

W_n= mass fraction of product with n carbon atoms

α = probability of chain growth

$(1-\alpha)$ = probability of chain termination

2.5. Product Upgrade

The F-T product distillation in a plate distillation column employed the principle of relative volatility of the hydrocarbons shown in equation 13.

$$\alpha_i = \frac{K_i}{K_{HK}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(13)}$$

where:

α_i = Relative volatility of i components

K_i= Equilibrium K-value of i component

K_{HK} = Equilibrium K-value of heavy component resp.

The product distillation was simulated using the DSTWU block that performs the Winn-Underwood shortcut distillation calculation. Being a complex mixture of hydrocarbons, a trial and error approach was used to determine the minimum reflux ratio (R_m) necessary to achieve the required product separation. Then the actual reflux ratio was obtained using the minimum and actual reflux ratio correction of 1.2 – 1.5 times R_m [122]. Obtaining the reflux ratio, the minimum number of stages for the process was calculated using equation 14.

$$N_{min} = \frac{\ln\left[\left(\frac{x_{LK}}{x_{HK}}\right)_{Dist}\left(\frac{x_{HK}}{x_{LK}}\right)_{Bot}\right]}{\ln \alpha_{LK-HK}} \ldots\ldots\ldots\ldots\ldots \text{(14)}$$

where:

x_{HK}, x_{LK}= mole fraction of heavy & light component resp.

N_{min}= minimum number of stages

The underwood equation as given by equation 15 below according to [122] was used to determine the distillation feed point location for optimal separation of the vapor liquid mixture.

$$q(1-F) = \sum \frac{\alpha_i n_{i,F}}{\alpha_i - \varphi} \ldots\ldots\ldots\ldots \text{(15)}$$

The sizing of the column to determine the diameter and height was carried out to help in the accurate estimation of cost. The column diameter is given by equation 16 below:

$$D_c = \sqrt{\frac{4 * \hat{V}_w}{\pi \rho_v \hat{u}_v}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(16)}$$

Estimation of column height is dependent on the plate spacing of which recommended a plate spacing between 0.15m to 1m [162].

The final liquid fuels product distribution (mass fraction) for LPG, gasoline and diesel is shown in table S3 with the detailed calculation in the excel sheet of the supporting document.

Table S3. Drop-in fuels product mass distribution

	Our model	Swanson et al., 2010	Bechtel, 1996
Temperature	220	220	
Alpha value	0.87	0.9	N/A
Products		Mass Fraction	
LPG	0.07	0.0877	0.03
Gasoline	0.32	0.261	0.37
Diesel	0.61	0.6167	0.61

3. Economic Evaluation

Capital and operating cost estimation for the BgTL model was performed using Aspen Process Economic Analyzer, referenced cost data, and mass and energy balance of the process to determine the overall project investment.

Unit operation costs estimated from a similar equipment were scaled-up applying the appropriate exponent value as shown in equation ….to determine the cost for the new equipment.

$$Equipment_{new\ cost} = Equipment_{\ old\ cost} \left[\frac{Flow\ rate_{new}}{Flow\ rate_{old}}\right]^{n} \ldots\ldots\ldots\ldots\ldots\ldots (17)$$

Where n = scaling factor.

The fixed operating cost data for the various positions occupied in our BgTL plant is shown in table S4 below

Table S4. Fixed Operating Cost

Employee Position	(Salary 2007)	Number of positions
Plant Manager	$ 147,000	1
Plant Engineer	$ 70,000	2
Maintenance Supervisor	$ 57,000	1
Maintenance Technician	$ 40,000	12
Lab Manager	$ 56,000	1
Lab Technician	$ 40,000	2
Shift supervisor	$ 48,000	4
Shift Operators	$ 48,000	20
Clerks & Secretaries	$ 36,000	3
Total salaries		46
	Other Fixed Operating Cost (OFOC)	
Labor burden	90% of Salaries	
Maintenance	3% of FCI	
Property Insurance	0.7% of FCI	
Total Fixed Operating Costs	∑ Total Salary + OFOC	

The modified accelerated cost recovery system (MACRS) used for calculating the depreciation of the process plant unit operation recovered the investment for the electricity/steam section and general plant section for 20 and 7 years respectively. Detailed depreciation calculation using the MACRS equation shown in 18 below which switched to straight line depreciation method (eqn.

19) when the recovery of the later is higher than the former can be found in the supporting excel sheet

MACRS depreciation: 2 * (1/N) …………………………. (18)

Straight-line depreciation: $\frac{Cost - Scrap\ value}{Life\ span}$ ……………… (19)

Calculations for critical cost parameters such as discount factor, annual present value, net present value of income tax and F-T income, and discounted cash flow are shown in the excel sheet of this supporting information.

Table S5A. Mass Balance of Biogas Cleaning

Stream Name	RAWBIOGA	TO-COMP1	TO-COOL1	TO-MIX	TO-COMP2	TO-COOL2	GAS-IN	LIQ-IN	LIQ-OUT	RE-GAS
Destination	SEP	COMP1	COOL1	MIXER	COMP2	COOL2	ABSORBER	ABSORBER	FLASH	MIXER
Source		SEP	COMP1	COOL1	MIXER	COMP2	COOL2	PUMP	ABSORBER	FLASH
Stream Fraction	VAPOR	VAPOR	VAPOR	VAPOR	MIXED	VAPOR	MIXED	LIQUID	LIQUID	VAPOR
Temperature										
Pressure										
Mole Flow kmol/hr										
Volume (Nm3/h)										
Mass Flow kg/hr										
METHANE	53.5779	53.5779	53.5779	53.5779	55.70335	55.70335	55.70335	0	2.173639	34.09807
CO2	33.48619	33.48619	33.48619	33.48619	91.14886	91.14886	91.14886	0	90.78895	2537.723
N2	0.4464825	0.4464825	0.4464825	0.4464825	0.4543394	0.4543394	0.4543394	0	7.94E-03	2.20E-01
O2	0.178593	0.178593	0.178593	0.178593	0.1848763	0.1848763	0.1848763	0	6.41E-03	2.01E-01
H2O	1.571618	1.571618	1.571618	1.571618	2.278767	2.278767	2.278767	2493.075	24935.41	12.73948
H2S	0.0357186	0.0357186	0.0357186	0.0357186	0.0652213	0.0652213	0.0652213	0	0.0798902	1.00551
CO	0	0	0	0	0	0	0	0	0	0
H2	0	0	0	0	0	0	0	0	0	0
C2H4	0	0	0	0	0	0	0	0	0	0
C2H6	0	0	0	0	0	0	0	0	0	0
C3H6	0	0	0	0	0	0	0	0	0	0
C3H8	0	0	0	0	0	0	0	0	0	0
BUTANE	0	0	0	0	0	0	0	0	0	0
1-BUT-01	0	0	0	0	0	0	0	0	0	0
1-BUT-02	0	0	0	0	0	0	0	0	0	0
ISOBU-01	0	0	0	0	0	0	0	0	0	0
N-PEN-01	0	0	0	0	0	0	0	0	0	0
1-PEN-01	0	0	0	0	0	0	0	0	0	0
2-MET-01	0	0	0	0	0	0	0	0	0	0
1-HEX-01	0	0	0	0	0	0	0	0	0	0
N-HEX-01	0	0	0	0	0	0	0	0	0	0
2-MET-02	0	0	0	0	0	0	0	0	0	0
1-HEP-01	0	0	0	0	0	0	0	0	0	0
N-HEP-01	0	0	0	0	0	0	0	0	0	0
1-OCT-01	0	0	0	0	0	0	0	0	0	0
N-OCT-01	0	0	0	0	0	0	0	0	0	0
N-NON-01	0	0	0	0	0	0	0	0	0	0
1-NON-01	0	0	0	0	0	0	0	0	0	0
1-DEC-01	0	0	0	0	0	0	0	0	0	0
N-DEC-01	0	0	0	0	0	0	0	0	0	0
1-UND-01	0	0	0	0	0	0	0	0	0	0
N-UND-01	0	0	0	0	0	0	0	0	0	0
1-DOD-01	0	0	0	0	0	0	0	0	0	0
N-DOD-01	0	0	0	0	0	0	0	0	0	0
1-TRI-01	0	0	0	0	0	0	0	0	0	0
N-TRI-01	0	0	0	0	0	0	0	0	0	0
C30WAX	0	0	0	0	0	0	0	0	0	0
OXHC	0	0	0	0	0	0	0	0	0	0
C29OP	0	0	0	0	0	0	0	0	0	0
C28OP	0	0	0	0	0	0	0	0	0	0
C27OP	0	0	0	0	0	0	0	0	0	0
C26OP	0	0	0	0	0	0	0	0	0	0
C25OP	0	0	0	0	0	0	0	0	0	0
C24OP	0	0	0	0	0	0	0	0	0	0
C23OP	0	0	0	0	0	0	0	0	0	0
C22OP	0	0	0	0	0	0	0	0	0	0
C21OP	0	0	0	0	0	0	0	0	0	0
1-EIC-01	0	0	0	0	0	0	0	0	0	0
N-EIC-01	0	0	0	0	0	0	0	0	0	0
1-NON-02	0	0	0	0	0	0	0	0	0	0
N-NON-02	0	0	0	0	0	0	0	0	0	0
N-OCT-02	0	0	0	0	0	0	0	0	0	0
1-OCT-02	0	0	0	0	0	0	0	0	0	0
1-HEP-02	0	0	0	0	0	0	0	0	0	0
N-HEP-02	0	0	0	0	0	0	0	0	0	0
N-HEX-02	0	0	0	0	0	0	0	0	0	0
1-HEX-02	0	0	0	0	0	0	0	0	0	0
1-PEN-02	0	0	0	0	0	0	0	0	0	0
N-PEN-02	0	0	0	0	0	0	0	0	0	0
N-TET-01	0	0	0	0	0	0	0	0	0	0
1-TET-01	0	0	0	0	0	0	0	0	0	0
AR	0	0	0	0	0	0	0	0	3.73E-18	0
TEG	0	0	0	0	0	0	0	0	0	0

Table S5B. Mass Balance of Biogas Cleaning continues

Stream Name	TO-COOL3	TO-STRIP	AIR-IN	AIR	OFF-GAS	TO-RECYC	PURGE	RECYCLE	LIQ-RCYC
Destination	VALVE	STRIPPER	AIR-COMP	STRIPPER		SPLITTER		PUMP2	ABSORBER
Source	FLASH	VALVE		AIR-COMP	STRIPPER	STRIPPER	SPLITTER	SPLITTER	PUMP2
Stream Fraction	LIQUID	MIXED	VAPOR	VAPOR	VAPOR	LIQUID	MIXED	MIXED	LIQUID
Temperature									
Pressure									
Mole Flow kmol/hr	24955.43	24955.43	154.1918						
Volume (Nm3/h)	450.6887	848.1853	3910.204						
Mass Flow kg/hr									
METHANE	0.9348956	0.9348956	0	0	0.0481896	9.07E-17	9.07E-18	8.16E-17	8.16E-17
CO2	1445.96	1445.96	0	0	32.49279	0.6334891	0.0633489	0.5701402	0.5701402
N2	2.79E-03	2.79E-03	3374.051	3374.051	10.99498	0.2294232	0.0229423	0.2064809	0.2064809
O2	5.01E-03	5.01E-03	1033.959	1033.959	2.88951	0.121857	0.0121857	0.1096713	0.1096713
H2O	448986	448986	0	0	1.111162	24933.59	2493.359	22440.23	22440.23
H2S	1.217313	1.217313	0	0	0.0316844	0.018703	1.87E-03	0.0168327	0.0168327
CO	0	0	0	0	0	0	0	0	0
H2	0	0	0	0	0	0	0	0	0
C2H4	0	0	0	0	0	0	0	0	0
C2H6	0	0	0	0	0	0	0	0	0
C3H6	0	0	0	0	0	0	0	0	0
C3H8	0	0	0	0	0	0	0	0	0
BUTANE	0	0	0	0	0	0	0	0	0
1-BUT-01	0	0	0	0	0	0	0	0	0
1-BUT-02	0	0	0	0	0	0	0	0	0
ISOBU-01	0	0	0	0	0	0	0	0	0
N-PEN-01	0	0	0	0	0	0	0	0	0
1-PEN-01	0	0	0	0	0	0	0	0	0
2-MET-01	0	0	0	0	0	0	0	0	0
1-HEX-01	0	0	0	0	0	0	0	0	0
N-HEX-01	0	0	0	0	0	0	0	0	0
2-MET-02	0	0	0	0	0	0	0	0	0
1-HEP-01	0	0	0	0	0	0	0	0	0
N-HEP-01	0	0	0	0	0	0	0	0	0
1-OCT-01	0	0	0	0	0	0	0	0	0
N-OCT-01	0	0	0	0	0	0	0	0	0
N-NON-01	0	0	0	0	0	0	0	0	0
1-NON-01	0	0	0	0	0	0	0	0	0
1-DEC-01	0	0	0	0	0	0	0	0	0
N-DEC-01	0	0	0	0	0	0	0	0	0
1-UND-01	0	0	0	0	0	0	0	0	0
N-UND-01	0	0	0	0	0	0	0	0	0
1-DOD-01	0	0	0	0	0	0	0	0	0
N-DOD-01	0	0	0	0	0	0	0	0	0
1-TRI-01	0	0	0	0	0	0	0	0	0
N-TRI-01	0	0	0	0	0	0	0	0	0
C30WAX	0	0	0	0	0	0	0	0	0
OXHC	0	0	0	0	0	0	0	0	0
C29OP	0	0	0	0	0	0	0	0	0
C28OP	0	0	0	0	0	0	0	0	0
C27OP	0	0	0	0	0	0	0	0	0
C26OP	0	0	0	0	0	0	0	0	0
C25OP	0	0	0	0	0	0	0	0	0
C24OP	0	0	0	0	0	0	0	0	0
C23OP	0	0	0	0	0	0	0	0	0
C22OP	0	0	0	0	0	0	0	0	0
C21OP	0	0	0	0	0	0	0	0	0
1-EIC-01	0	0	0	0	0	0	0	0	0
N-EIC-01	0	0	0	0	0	0	0	0	0
1-NON-02	0	0	0	0	0	0	0	0	0
N-NON-02	0	0	0	0	0	0	0	0	0
N-OCT-02	0	0	0	0	0	0	0	0	0
1-OCT-02	0	0	0	0	0	0	0	0	0
1-HEP-02	0	0	0	0	0	0	0	0	0
N-HEP-02	0	0	0	0	0	0	0	0	0
N-HEX-02	0	0	0	0	0	0	0	0	0
1-HEX-02	0	0	0	0	0	0	0	0	0
1-PEN-02	0	0	0	0	0	0	0	0	0
N-PEN-02	0	0	0	0	0	0	0	0	0
N-TET-01	0	0	0	0	0	0	0	0	0
1-TET-01	0	0	0	0	0	0	0	0	0
AR	0	0	57.34637	57.34637	0.127847	5.93E-03	5.93E-04	5.34E-03	5.34E-03
TEG	0	0	0	0	0	0	0	0	0

Table S6. Mass balance of Syngas Production

Stream Name	BMETHANE	TO-POX-H	TO-SMR	TO-POX	OXYGEN	TO-MIX	STEAM	TO-PFR	P-STEAM	P-WATER	POX-HOT	S4	POX-SYNG	SMR-SYN	SYNGAS	W-WATER	TO-FT
Destination	SPLITTER	POX-HX	SMR-HX	POX	POX	MIXER	MIXER	SMR		B4	PROP	B4	B5	B5	B2		$C-7
Source	$C-1	SPLITTER	SPLITTER	POX-HX	$C-6	SMR-HX	$C-3	MIXER	B4		POX	PROP	B4	SMR	B5	B2	B2
Stream Fraction	VAPOR	MIXED	MIXED	VAPOR	VAPOR	VAPOR	VAPOR	VAPOR	VAPOR	LIQUID	VAPOR	VAPOR	VAPOR	VAPOR	VAPOR	VAPOR	VAPOR
Temperature	32.77557	33.57395	33.57395	1127	1127	850	198.5386	366.6021	850	20	1127	1127	1116.62	850	949.889	949.889	50
Pressure	35	35	35	50	50	15	15	15	1	1	50	50	50	15	15	15	15
Mole Flow kmol/hr	55.09079	33.05447	22.03631	33.05447	42.13022	22.03631	110.7753	132.8117	0.5550844	0.5550844	98.67819	98.67819	98.67819	175.3306	274.0087	140.6477	133.3611
Volume (Nm3/h)	1234.784	740.8701	493.9134	740.8701	944.2905	493.9134	2482.876	2976.789	12.44145		2211.735	2211.735	2211.735	3929.791	6141.526	3152.422	2989.104
Mass Flow kg/hr																	
METHANE	852.6422	511.5853	341.0569	511.5853	0	341.0569	0	341.0569	0	0	0.713679	0.713679	0.713679	0	0.713679	0	0.713679
CO2	43.97149	26.38289	17.5886	26.38289	0	17.5886	0	17.5886	0	0	551.0997	551.0997	551.0997	17.5886	568.6883	511.8194	56.86883
N2	18.21841	10.93105	7.287364	10.93105	18.89961	7.287364	0	7.287364	0	0	29.83065	29.83065	29.83065	7.287364	37.11802	37.11802	0
O2	9.154762	5.492857	3.661905	5.492857	1280.711	3.661905	0	3.661905	0	0	2.36E-11	2.36E-11	2.36E-11	3.661905	3.661905	3.661905	0
H2O	6.73E-04	4.04E-04	2.69E-04	4.04E-04	0	2.69E-04	1995.649	1995.649	10	10	659.7852	659.7852	659.7852	1612.655	2272.441	2272.441	0
H2S	0.0608842	0.0365305	0.0243537	0.0365305	0	0.0243537	0	0.0243537	0	0	0.0365305	0.0365305	0.0365305	0.0243537	0.0608842	0.0608842	0
CO	0	0	0	0	0	0	0	0	0	0	558.015	558.015	558.015	595.4837	1153.499	0	1153.499
H2	0	0	0	0	0	0	0	0	0	0	54.56019	54.56019	54.56019	128.5691	183.1293	0	183.1293
C2H4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C2H6	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C3H6	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C3H8	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
BUTANE	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1-BUT-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1-BUT-02	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
ISOBU-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
N-PEN-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1-PEN-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2-MET-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1-HEX-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
N-HEX-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2-MET-02	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1-HEP-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
N-HEP-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1-OCT-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
N-OCT-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
N-NON-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1-NON-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1-DEC-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
N-DEC-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1-UND-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
N-UND-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1-DOD-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
N-DOD-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1-TRI-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
N-TRI-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C30WAX	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
OXHC	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C29OP	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C28OP	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C27OP	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C26OP	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C25OP	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C24OP	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C23OP	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C22OP	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C21OP	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1-EIC-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
N-EIC-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1-NON-02	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
N-NON-02	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
N-OCT-02	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1-OCT-02	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1-HEP-02	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
N-HEP-02	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
N-HEX-02	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1-HEX-02	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1-PEN-02	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
N-PEN-02	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
N-TET-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1-TET-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
AR	0.210829	0.1264974	0.0843316	0.1264974	57.19955	0.0843316	0	0.0843316	0	0	57.32605	57.32605	57.32605	0.0843316	57.41038	57.41038	0
TEG	2.55E-03	1.53E-03	1.02E-03	1.53E-03	0	1.02E-03	0	1.02E-03	0	0	0	0	0	1.02E-03	1.02E-03	1.02E-03	0

Table S7. Mass balance of Fischer-Tropsh Synthesis

Stream Name	TO-FT	TO-COMP	TO-RXC	FT-PRODT	CO2-STRM	TO-FTSEP	TO-DRUM	TO-UPGD	FUEL	H2-STRM
Destination	F-T-HX	FT-COMP	FT-RXC	CO2-SEP		FT-SEP	KOUT-DRM	$C-13	$C-9	$C-15
Source	$C-8	F-T-HX	FT-COMP	FT-RXC	CO2-SEP	CO2-SEP	FT-SEP	FT-SEP	KOUT-DRM	KOUT-DRM
Stream Fraction	VAPOR	VAPOR	VAPOR	MIXED	VAPOR	MIXED	VAPOR	MIXED	VAPOR	VAPOR
Temperature	50	150	199.6981	220	220	220	220	220	220	220
Pressure	15	15	20	20	20	20	20	20	20	20
Mole Flow kmol/hr	133.3611	133.3611	133.3611	80.88689	1.324495	79.5624	72.22246	7.339942	70.61988	1.602578
Volume (Nm3/h)	2989.104	2989.104	2989.104	1804.3	29.68671	1774.428	1618.766	102.4962	1582.847	35.91955
Mass Flow kg/hr										
METHANE	0.713679	0.713679	0.713679	0.6519273	0	0.6519273	0.6519273	0	0.6519273	0
CO2	56.86883	56.86883	56.86883	58.29075	58.29075	0	0	0	0	0
N2	0	0	0	0	0	0	0	0	0	0
O2	0.00E+00	0.00E+00	0	0	0	0	0.00E+00	0	0	0
H2O	0	0	0	4.571841	0.00E+00	4.571841	4.571841	0	4.571841	0
H2S	0	0	0	0	0	0	0	0	0	0
CO	1153.499	1153.499	1153.499	518.4387	0	518.4387	518.4387	0	518.4387	0
H2	183.1293	183.1293	183.1293	107.6868	0	107.6868	107.6868	0	104.4562	3.230604
C2H4	0	0	0	17.87039	0	17.87039	0	17.87039	0	0
C2H6	0	0	0	19.07593	0	19.07593	0	19.07593	0	0
C3H6	0	0	0	22.26707	0	22.26707	0	22.26707	0	0
C3H8	0	0	0	23.25987	0	23.25987	0	23.25987	0	0
BUTANE	0	0	0	12.69365	0	12.69365	0	12.69365	0	0
1-BUT-01	0	0	0	12.26816	0	12.26816	0	12.26816	0	0
1-BUT-02	0	0	0	12.26816	0	12.26816	0	12.26816	0	0
ISOBU-01	0	0	0	12.69365	0	12.69365	0	12.69365	0	0
N-PEN-01	0	0	0	12.9773	0	12.9773	0	12.9773	0	0
1-PEN-01	0	0	0	25.24547	0	25.24547	0	25.24547	0	0
2-MET-01	0	0	0	12.9773	0	12.9773	0	12.9773	0	0
1-HEX-01	0	0	0	25.03272	0	25.03272	0	25.03272	0	0
N-HEX-01	0	0	0	12.76456	0	12.76456	0	12.76456	0	0
2-MET-02	0	0	0	12.76456	0	12.76456	0	12.76456	0	0
1-HEP-01	0	0	0	27.30198	0	27.30198	0	27.30198	0	0
N-HEP-01	0	0	0	24.46541	0	24.46541	0	24.46541	0	0
1-OCT-01	0	0	0	22.62164	0	22.62164	0	22.62164	0	0
N-OCT-01	0	0	0	22.97621	0	22.97621	0	22.97621	0	0
N-NON-01	0	0	0	21.20336	0	21.20336	0	21.20336	0	0
1-NON-01	0	0	0	20.9197	0	20.9197	0	20.9197	0	0
1-DEC-01	0	0	0	19.14684	0	19.14684	0	19.14684	0	0
N-DEC-01	0	0	0	19.35958	0	19.35958	0	19.35958	0	0
1-UND-01	0	0	0	17.30307	0	17.30307	0	17.30307	0	0
N-UND-01	0	0	0	17.51582	0	17.51582	0	17.51582	0	0
1-DOD-01	0	0	0	15.53022	0	15.53022	0	15.53022	0	0
N-DOD-01	0	0	0	15.67205	0	15.67205	0	15.67205	0	0
1-TRI-01	0	0	0	13.9701	0	13.9701	0	13.9701	0	0
N-TRI-01	0	0	0	13.82827	0	13.82827	0	13.82827	0	0
C30WAX	0	0	0	27.12682	0	27.12682	0	27.12682	0	0
OXHC	0	0	0	2.269256	0	2.269256	0	2.269256	0	0
C29OP	0	0	0	2.694741	0	2.694741	0	2.694741	0	0
C28OP	0	0	0	3.19114	0	3.19114	0	3.19114	0	0
C27OP	0	0	0	3.68754	0	3.68754	0	3.68754	0	0
C26OP	0	0	0	4.325768	0	4.325768	0	4.325768	0	0
C25OP	0	0	0	5.105825	0	5.105825	0	5.105825	0	0
C24OP	0	0	0	5.956795	0	5.956795	0	5.956795	0	0
C23OP	0	0	0	6.949594	0	6.949594	0	6.949594	0	0
C22OP	0	0	0	8.084222	0	8.084222	0	8.084222	0	0
C21OP	0	0	0	9.360679	0	9.360679	0	9.360679	0	0
1-EIC-01	0	0	0	5.460396	0	5.460396	0	5.460396	0	0
N-EIC-01	0	0	0	5.460396	0	5.460396	0	5.460396	0	0
1-NON-02	0	0	0	6.311367	0	6.311367	0	6.311367	0	0
N-NON-02	0	0	0	6.240453	0	6.240453	0	6.240453	0	0
N-OCT-02	0	0	0	7.233252	0	7.233252	0	7.233252	0	0
1-OCT-02	0	0	0	7.233252	0	7.233252	0	7.233252	0	0
1-HEP-02	0	0	0	8.296965	0	8.296965	0	8.296965	0	0
N-HEP-02	0	0	0	8.296965	0	8.296965	0	8.296965	0	0
N-HEX-02	0	0	0	9.573422	0	9.573422	0	9.573422	0	0
1-HEX-02	0	0	0	9.431593	0	9.431593	0	9.431593	0	0
1-PEN-02	0	0	0	10.77896	0	10.77896	0	10.77896	0	0
N-PEN-02	0	0	0	10.92079	0	10.92079	0	10.92079	0	0
N-TET-01	0	0	0	12.33908	0	12.33908	0	12.33908	0	0
1-TET-01	0	0	0	12.26816	0	12.26816	0	12.26816	0	0
AR	0	0	0	0	0	0	0	0	0	0
TEG	0	0	0	0	0.00E+00	0.00E+00	0	0.00E+00	0	0

Table S8. Mass balance of Syn-crude Upgrade

Stream Name	FEED	LPG	TO-CRCK	H2-STRM	TO-DIST	GASOLINE	TO-DIST2	DIESEL	WAX
Destination	DEPROZE	LPG-STO	HYDROCRK	HYDROCRK	DIST1	GAS-STO	DIST2	DIES-STO	DIES-STO
Source	F-T Section	DEPROZE	DEPROZE	$C-16	HYDROCRK	DIST1	DIST1	DIST2	DIST2
Stream Fraction	LIQUID	LIQUID	LIQUID	VAPOR	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID
Temperature	200	5.03969	249.3066	200	354	3.050677	280.9733	261.3634	446.6425
Pressure	40	20	20	40	50	1.7	1.7	1.2	1.2
Mole Flow kmol/hr	6.890431	1.627622	5.262809	0.1661752	5.707071	3.474824	2.232248	2.205936	0.026312
Volume (m3/h)	1.647851	0.1214779	1.656083	0.1656965	2.437541	0.4114772	1.005752	0.9577213	0.0255899
Mass Flow kg/hr	860.7821	58.04112	802.741	0.3349893	803.076	276.9149	526.1611	515.0362	11.1249
METHANE	0	0	0	0	0	0	0	0	0
CO2	0	0	0	0	0	0	0	0	0
N2	0	0	0	0	0	0	0	0	0
O2	0	0	0	0	0	0	0	0	0
H2O	0	0	0	0	0	0	0	0	0
H2S	0	0	0	0	0	0	0	0	0
CO	0	0	0	0	0	0	0	0	0
H2	0	0.3349893	0	0	0	0	0	0	0
C2H4	2.69E-13	0	0	0.2114896	2.24E-11	12.12453	0.2114896	2.69E-13	2.69E-13
C2H6	1.39E-11	0	0	3.518668	2.82E-09	12.99334	3.518668	1.39E-11	1.39E-11
C3H6	6.60E-10	0	0	7.761569	2.11E-03	16.0205	7.761569	6.60E-10	6.60E-10
C3H8	8.17E-10	0	0	6.327304	0.0167897	16.78972	6.327304	8.17E-10	8.17E-10
BUTANE	3.99E-08	0	0	9.742579	9.682822	9.692515	9.742579	3.99E-08	3.99E-08
1-BUT-01	2.96E-08	0	0	11.84193	18.6669	18.71129	11.84193	2.96E-08	2.96E-08
1-BUT-02	2.96E-08	0	0	11.84193	0	0	11.84193	2.96E-08	2.96E-08
ISOBU-01	1.51E-08	0	0	8.758978	9.614727	9.692515	8.758978	1.51E-08	1.51E-08
N-PEN-01	1.32E-06	0	0	12.49688	10.51381	10.51383	12.49688	1.32E-06	1.32E-06
1-PEN-01	9.14E-07	0	0	14.59238	20.44175	20.44178	14.59238	9.14E-07	9.14E-07
2-MET-01	1.32E-06	0	0	23.16569	10.51381	10.51383	23.16569	1.32E-06	1.32E-06
1-HEX-01	2.36E-05	0	0	16.4924	21.41081	21.41081	16.49243	2.36E-05	2.36E-05
N-HEX-01	3.25E-05	0	0	12.91798	10.96238	10.96238	12.91802	3.25E-05	3.25E-05
2-MET-02	2.48E-05	0	0	21.62021	10.96238	10.96238	21.62024	2.48E-05	2.48E-05
1-HEP-01	5.65E-04	0	0	18.84968	21.78972	21.78972	18.85024	0.000564992	5.65E-04
N-HEP-01	7.26E-04	0	0	14.20452	22.23803	22.23803	14.20524	0.000725676	7.26E-04
1-OCT-01	5.88E-03	0	0	9.874661	21.71551	21.71551	9.880543	0.00588235	5.88E-03
N-OCT-01	0.01643	0	0	16.4136	22.10259	22.10259	16.43003	0.01643	0.01643
N-NON-01	0.2699057	0	0	14.64621	21.63277	21.63277	14.91612	0.2699057	0.2699057
1-NON-01	0.1899211	0	0	16.66573	21.29528	21.29528	16.85565	0.1899211	0.1899211
1-DEC-01	1.141962	0	0	5.453486	20.62135	20.62135	6.595448	1.141962	1.141962
N-DEC-01	3.929016	0	0	11.70368	20.91552	20.91552	15.63269	3.929016	3.929016
1-UND-01	17.03035	0	0	4.682292	19.75988	19.75988	21.71264	17.03035	17.03035
N-UND-01	14.08855	0	0	2.482506	20.02899	20.02899	16.57105	14.08855	14.08855
1-DOD-01	27.21082	0	0	0.4618295	18.78808	18.78808	27.67265	27.21082	27.21082
N-DOD-01	15.25436	0	0	0.1638508	19.01135	19.01135	15.41821	15.25436	15.25436
1-TRI-01	9.291712	0	0	9.30E-03	17.73278	17.73278	9.301013	9.291712	9.291712
N-TRI-01	17.01303	0	0	0.0119095	17.92732	17.92732	17.02494	17.01303	17.01303
C30WAX	0	0	0	0	0	0	0	0	0
1-EIC-01	20.53128	0	0	0	10.38101	10.38101	20.53128	20.53128	20.53128
N-EIC-01	13.13265	0	0	0	10.45503	10.45503	13.13265	13.13265	13.13265
1-NON-02	20.40209	0	0	0	11.32262	11.32262	20.40209	20.40209	20.40209
N-NON-02	14.06085	0	0	0	11.40759	11.40759	14.06085	14.06085	14.06085
N-OCT-02	14.84563	0	0	0	12.41274	12.41274	14.84563	14.84563	14.84563
1-OCT-02	20.80045	0	0	0	12.31516	12.31516	20.80045	20.80045	20.80045
1-HEP-02	21.12414	0	0	0	13.35306	13.35306	21.12414	21.12414	21.12414
N-HEP-02	15.88985	0	0	0	13.46508	13.46508	15.88985	15.88985	15.88985
N-HEX-02	0	0	0	0	14.55973	14.55973	0	0	0
1-HEX-02	38.03182	0	0	0	14.42468	14.42468	38.03182	38.03182	38.03182
1-PEN-02	52.90186	0	0	1.61E-04	15.52415	15.52415	52.90202	52.90186	52.90186
N-PEN-02	16.92285	0	0	2.81E-05	15.67917	15.67917	16.92288	16.92285	16.92285
N-TET-01	17.21316	0	0	8.01E-04	16.80614	16.80614	17.21397	17.21316	17.21316
1-TET-01	10.87483	0	0	6.74E-04	16.63664	16.63664	10.87551	10.87483	10.87483
AR	0	0	0	0	0	0	0	0	0
N-HEN-01	15.67066	0	0	0	19.05195	19.05195	15.67066	15.67066	15.67066
N-DOC-01	17.71725	0	0	0	17.38113	17.38113	17.71725	17.71725	17.71725
N-TRI-02	16.45279	0	0	0	15.82407	15.82407	16.45279	16.45279	16.45279
N-TET-02	15.3778	0	0	0	14.37927	14.37927	15.3778	15.3778	15.3778
N-PEN-03	15.03308	0	0	0	13.0437	13.0437	15.03308	15.03308	15.03308
N-HEX-03	13.75705	0	0	0	11.81324	11.81324	13.75705	13.75705	13.75705
N-HEP-03	14.02532	0	0	0	10.68304	10.68304	14.02532	14.02532	14.02532
N-OCT-03	12.3813	0	0	0	9.647707	9.647707	12.3813	12.3813	12.3813
N-NON-03	12.435	0	0	0	8.701601	8.701601	12.44745	12.435	12.44745
N-TRI-03	0.0111235	0	0	0	85.12502	85.12502	11.12357	0.0111235	11.12357
NO	0	0	0	0	0	0	0	0	0
NO2	0	0	0	0	0	0	0	0	0
N2O	0	0	0	0	0	0	0	0	0

Table S9. Mass balance of Electricity Generation

Stream Name	FUEL	FUEL-GAS	AIR	TO-MIX	NOXSTEAM	TO-TURB	TO-HRSG	FLUEGAS	CONDNSAT	HP-WATER	TO-STMTB	TO-COND	C-WATER
Destination	LAYDOWN	BURNER	AIRCOMP	BURNER	BURNER	GASTURB	HRSG		PUMP	BOILER	STMTRBN	CONDENSR	
Source	F-T Section	LAYDOWN		AIRCOMP		BURNER	GASTURB	HRSG		PUMP	BOILER	STMTRBN	CONDENSR
Stream Fraction	VAPOR	VAPOR	VAPOR	VAPOR	VAPOR	VAPOR	VAPOR	VAPOR	LIQUID	LIQUID	VAPOR	MIXED	LIQUID
Temperature	200	27.47081	32	367.7176	171.0811	1134.489	1079.536	120	20	20.19915	327.7763	20	20
Pressure	40	8	1	8	8	8	6	1	0.0233586	125	125	0.0233586	0.0233586
Mole Flow kmol/hr	79.14289	79.14289	218.5791	218.5791	338.7126	598.2639	598.2639	598.2639	467.6914	467.6914	467.6914	467.6914	467.6914
Volume (m3/h)	79.04257	247.9901	5543.026	1459.532	1495.1	8760.085	11221.18	19475.74	8.440059	8.393263	113.8814	3.01E+05	8.440059
Mass Flow kg/hr	780.7264	780.7264	6329.998	6329.998	6102.003	13212.73	13212.73	13212.73	8425.592	8425.592	8425.592	8425.592	8425.592
METHANE	37.22756	37.22756	0	0	0	1.48E-23	1.48E-23	1.48E-23	0	0	0	0	0
CO2	12.26991	12.26991	0	0	0	1085.701	1085.701	1085.701	0	0	0	0	0
N2	0	0	4782.985	4782.985	0	4782.348	4782.348	4782.348	0	0	0	0	0
O2	0	0	1465.719	1465.719	0	95.06698	95.06698	95.06698	0	0	0	0	0
H2O	3.624054	3.624054	0	0	6102.003	7166.945	7166.945	7166.945	8425.592	8425.592	8425.592	8425.592	8425.592
H2S	0	0	0	0	0	0	0	0	0	0	0	0	0
CO	618.1989	618.1989	0	0	0	3.85E-03	3.85E-03	3.85E-03	0	0	0	0	0
H2	109.406	109.406	0	0	0	2.05E-03	2.05E-03	2.05E-03	0	0	0	0	0
C2H4	0	0	0	0	0	0	0	0	0	0	0	0	0
C2H6	0	0	0	0	0	0	0	0	0	0	0	0	0
C3H6	0	0	0	0	0	0	0	0	0	0	0	0	0
C3H8	0	0	0	0	0	0	0	0	0	0	0	0	0
BUTANE	0	0	0	0	0	0	0	0	0	0	0	0	0
1-BUT-01	0	0	0	0	0	0	0	0	0	0	0	0	0
1-BUT-02	0	0	0	0	0	0	0	0	0	0	0	0	0
ISOBU-01	0	0	0	0	0	0	0	0	0	0	0	0	0
N-PEN-01	0	0	0	0	0	0	0	0	0	0	0	0	0
1-PEN-01	0	0	0	0	0	0	0	0	0	0	0	0	0
2-MET-01	0	0	0	0	0	0	0	0	0	0	0	0	0
1-HEX-01	0	0	0	0	0	0	0	0	0	0	0	0	0
N-HEX-01	0	0	0	0	0	0	0	0	0	0	0	0	0
2-MET-02	0	0	0	0	0	0	0	0	0	0	0	0	0
1-HEP-01	0	0	0	0	0	0	0	0	0	0	0	0	0
N-HEP-01	0	0	0	0	0	0	0	0	0	0	0	0	0
1-OCT-01	0	0	0	0	0	0	0	0	0	0	0	0	0
N-OCT-01	0	0	0	0	0	0	0	0	0	0	0	0	0
N-NON-01	0	0	0	0	0	0	0	0	0	0	0	0	0
1-NON-01	0	0	0	0	0	0	0	0	0	0	0	0	0
1-DEC-01	0	0	0	0	0	0	0	0	0	0	0	0	0
N-DEC-01	0	0	0	0	0	0	0	0	0	0	0	0	0
1-UND-01	0	0	0	0	0	0	0	0	0	0	0	0	0
N-UND-01	0	0	0	0	0	0	0	0	0	0	0	0	0
1-DOD-01	0	0	0	0	0	0	0	0	0	0	0	0	0
N-DOD-01	0	0	0	0	0	0	0	0	0	0	0	0	0
1-TRI-01	0	0	0	0	0	0	0	0	0	0	0	0	0
N-TRI-01	0	0	0	0	0	0	0	0	0	0	0	0	0
C30WAX	0	0	0	0	0	0	0	0	0	0	0	0	0
1-EIC-01	0	0	0	0	0	0	0	0	0	0	0	0	0
N-EIC-01	0	0	0	0	0	0	0	0	0	0	0	0	0
1-NON-02	0	0	0	0	0	0	0	0	0	0	0	0	0
N-NON-02	0	0	0	0	0	0	0	0	0	0	0	0	0
N-OCT-02	0	0	0	0	0	0	0	0	0	0	0	0	0
1-OCT-02	0	0	0	0	0	0	0	0	0	0	0	0	0
1-HEP-02	0	0	0	0	0	0	0	0	0	0	0	0	0
N-HEP-02	0	0	0	0	0	0	0	0	0	0	0	0	0
N-HEX-02	0	0	0	0	0	0	0	0	0	0	0	0	0
1-HEX-02	0	0	0	0	0	0	0	0	0	0	0	0	0
1-PEN-02	0	0	0	0	0	0	0	0	0	0	0	0	0
N-PEN-02	0	0	0	0	0	0	0	0	0	0	0	0	0
N-TET-01	0	0	0	0	0	0	0	0	0	0	0	0	0
1-TET-01	0	0	0	0	0	0	0	0	0	0	0	0	0
AR	0	0	81.29305	81.29305	0	81.29305	81.29305	81.29305	0	0	0	0	0
N-HEN-01	0	0	0	0	0	0	0	0	0	0	0	0	0
N-DOC-01	0	0	0	0	0	0	0	0	0	0	0	0	0
N-TRI-02	0	0	0	0	0	0	0	0	0	0	0	0	0
N-TET-02	0	0	0	0	0	0	0	0	0	0	0	0	0
N-PEN-03	0	0	0	0	0	0	0	0	0	0	0	0	0
N-HEX-03	0	0	0	0	0	0	0	0	0	0	0	0	0
N-HEP-03	0	0	0	0	0	0	0	0	0	0	0	0	0
N-OCT-03	0	0	0	0	0	0	0	0	0	0	0	0	0
N-NON-03	0	0	0	0	0	0	0	0	0	0	0	0	0
N-TRI-03	0	0	0	0	0	0	0	0	0	0	0	0	0
NO	0	0	0	0	0	1.361198	1.361198	1.361198	0	0	0	0	0
NO2	0	0	0	0	0	6.26E-03	6.26E-03	6.26E-03	0	0	0	0	0
N2O	0	0	0	0	0	1.89E-04	1.89E-04	1.89E-04	0	0	0	0	0