Water Footprint Of Aviation Fuel Synthesis By The Fischer Tropsch Process Using Sugar Cane Waste & Landfill Gas As Feedstocks

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WATER FOOTPRINT OF AVIATION FUEL SYNTHESIS BY THE FISCHER TROPSCH PROCESS USING SUGAR CANE WASTE & LANDFILL GAS AS FEEDSTOCKS

by

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B.E. Ecole Polytechnique de Tunisie, 2004

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in the Department of Mechanical, Materials & Aerospace Engineering in the College of Engineering and Computer Science at the University of Central Florida Orlando, Florida

Fall Term 2008

Major Professor: Jayanta Kapat
The recent spikes in oil prices have spurred an already bullish demand on biofuels as a source of alternative energy. However, the unprecedented price records set simultaneously by staple food have raised high concerns about potential impacts of biofuels on the global agricultural landscape as fuel and food markets are being inextricably coupled. The revival of interest in the Fischer-Tropsch (FT) process comes into full force since it offers a promising way to produce carbon-neutral liquid fuels which are readily usable with today’s existing infrastructure. The FT synthesis offers the possibility of using crop waste as feedstock instead of the crop itself thus avoiding the risk of further straining water and land resources while helping to alleviate the national energy bill and to achieve independence from foreign oil.

As the airline industry is the hardest-hit sector with fuel jumping ahead of labor as the primary cost item, this thesis investigates the prospects of the FT process to transform sugar cane waste (namely bagasse, tops and green leaves) and landfill gas in order to produce kerosene (C_{12}H_{26}) as jet fuel for civil aviation. Established chemical correlations and thermodynamics of chemical reactions are used to assess the water footprint inherent to kerosene production using the above feedstocks at optimal conditions of temperature, pressure, catalyst and reactor type. It has been estimated that 9 to 19 gallons of water are needed for every gallon of kerosene produced. In addition, for the case of sugar cane, less land area per unit energy is required compared to ethanol production since all non-food waste of the plant can be used to produce FT fuel as opposed to ethanol which would utilize only the sugar (food) portion of the plant. This translates into a much lower water footprint for irrigation and consequently a lower water footprint overall.
Dedicated to my parents
ACKNOWLEDGMENTS

I would like to thank my graduate advisor, Dr. Jay Kapat, for his supervision and guidance throughout this project. I would also like to thank Dr. Louis Chow and Dr. Saptarshi Basu for serving as members of my graduate committee.

A special thought goes to Dr. John Brandenburg for his insightful remarks and for sharing his vision on energy and environment. I also appreciate the occasional emails I exchanged with some faculty from the chemistry department namely Dr. Richard Blair and Dr. Li Yiao.

I am privileged to have received the Fulbright scholarship and I thank the Amideast staff for their logistical help as well as my fellow Fulbrighters who stood by me during the last weeks of summer.

I am fortunate enough to have made friends in graduate school and I am indebted to them for their help, friendship and sporadic sympathy. My utmost gratitude goes to my parents and brothers for their patience and prodding to make a positive change in the world by helping address a few energy issues.
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<th>Description</th>
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</thead>
<tbody>
<tr>
<td>FT</td>
<td>Fischer-Tropsch</td>
</tr>
<tr>
<td>C-T-L</td>
<td>Coal to liquids</td>
</tr>
<tr>
<td>B-T-L</td>
<td>Biomass to liquids</td>
</tr>
<tr>
<td>G-T-L</td>
<td>Gas to liquids</td>
</tr>
<tr>
<td>EIA</td>
<td>Energy Information Administration</td>
</tr>
<tr>
<td>(\alpha)</td>
<td>Carbon chain growth probability</td>
</tr>
<tr>
<td>Sasol©</td>
<td>South African Synthetic Oil©</td>
</tr>
<tr>
<td>JP-5/8</td>
<td>Jet Propellant 5/8</td>
</tr>
<tr>
<td>ASF</td>
<td>Anderson-Schultz-Flory Distribution</td>
</tr>
<tr>
<td>(W_n)</td>
<td>Weight Fraction of a given FT final product of a carbon number (n)</td>
</tr>
<tr>
<td>(C_p)</td>
<td>Specific Heat</td>
</tr>
<tr>
<td>(\nu_k)</td>
<td>Modified stoichiometric coefficient relative to the (k^{th}) reactant/product</td>
</tr>
<tr>
<td>(Syn)gas/fuel</td>
<td>Synthetic gas/fuel</td>
</tr>
<tr>
<td>(\Delta h_f)</td>
<td>Enthalpy of formation</td>
</tr>
<tr>
<td>(X_k)</td>
<td>Molar fraction of the chemical species (k)</td>
</tr>
<tr>
<td>(K(T))</td>
<td>T-dependent equilibrium constant</td>
</tr>
<tr>
<td>(T)</td>
<td>Temperature (K)</td>
</tr>
<tr>
<td>(P)</td>
<td>Pressure (psi)</td>
</tr>
<tr>
<td>(d\tilde{N})</td>
<td>Consumed number of moles during a reaction at a given state</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>R</td>
<td>Ideal gas constant (8.3144 J/mol.K)</td>
</tr>
<tr>
<td>CO</td>
<td>Carbon Monoxide</td>
</tr>
<tr>
<td>Co</td>
<td>Cobalt</td>
</tr>
<tr>
<td>$X_n$</td>
<td>Mole fraction of the hydrocarbon product with carbon atoms of number n</td>
</tr>
<tr>
<td>WGSR</td>
<td>Water gas-shift reaction</td>
</tr>
<tr>
<td>Bpd</td>
<td>Barrels per day</td>
</tr>
<tr>
<td>Lfg</td>
<td>Landfill gas</td>
</tr>
</tbody>
</table>
CHAPTER I
INTRODUCTION

As of July 2008, crude oil prices reached an unprecedented record of $145 a barrel (West Texas). Even in terms of real prices (as compared to nominal prices before the adjustment to inflation indices), oil prices have exceeded those witnessed during the oil shocks of 1973 or 1980. The increasingly bullish demand on crude oil has been mainly supported by the robust growth rates of the BRIC (Brazil, Russia, India and China) economies in addition to a number of reemerging Asian economies in the Asia Pacific region. The Middle East, unbeatably the powerhouse of crude oil, is now awash with oil windfalls and is seeing its own oil demand on the rise with several mega-projects underway. This upward trend does not appear to be stopping anytime soon with new record prices being broken on a daily basis. Energy experts agree that the era of cheap oil is gone without return predicting prices will possibly break past new records [3].

Figure 1 Nominal price of crude oil (West Texas Intermediate), 2002-2008
1.1 Liquid Fuels & Transportation Sector

The transportation sector, being the single biggest consumer of liquid fuels with more than 55 percent of the global liquid fuel demand in 2004, is projected to increase up to 67 percent through 2030 according the Energy Information Administration as shown by figure 2.

![Figure 2 Global Liquid Fuel Consumption by Sector (2004-2030)](image)

The conventional wisdom has always linked oil spikes and the economy crunch inherent to them with the need to implement alternative solutions namely solar and wind. While alternative energy forms like these can help curb demand on fossil fuels by displacing the need for oil to produce electricity, or heat in some cases, they do not directly address the problems inherent to transportation. The issue with the transportation sector is that there are only a few off-the-shelf alternative technologies which are readily both available and usable with today’s infrastructure to power the millions of vehicles hitting the roads every day. Indeed, the same applies to air and
maritime transportation as well. These gloomy scenarios are pushing governments and businesses to rethink their energy policies and to come up with action plans such as cutting consumption, boosting energy efficiency and most of all increasing supply. It is increasingly clear that, in order not to undermine economic growth and development, a policy of generation along that of conservation is of primary importance. As shown by figure 3, gas-to-liquids (GTL), coal-to-liquids (CTL) and biofuels will be the fastest growing liquid fuels sources apart from Canadian oil tar sands. Combined, they will account for roughly half of the world’s production of liquid fuels by 2030. The problem with feedstocks like coal or natural gas though is that there is no real shift being made away from fossil fuels in order to make a fully-fledged transition into a post fossil fuel era. While these CTL and GTL fuels can partly alleviate the burden on the national energy, foreign dependency on oil (in the case of gas-to-liquids technology) will still be an issue. Using non-fossil feedstock would help resolve the behemoth transportation problem. Biomass-to-liquids (BTL) are part of the solution provided they are not crop-based in order to avoid displacing food markets as witnessed during the recent staple food price spikes and as explained later in the chapter. Using Landfill Gas (LFG) is yet another viable option given the similar properties of LFG and natural gas (methane) and the advent of FT technology using natural gas as feedstock to make jet fuel.
This is where the prospects of the Fischer-Tropsch synthesis technology basically lie. The Fischer-Tropsch synthesis is a proven, feasible and an increasingly economically viable process with the oil prices way above the $30 cut-off price [4]. The eight-decade old process is a promising way to curb demand on foreign oil by supplying an “in-house”, reliable and environmentally-friendly source of energy for the nation’s fleet of trucks or ships (for diesel-like fuels) and aircrafts (kerosene-like fuels). These synthesized fuels are readily usable with the existing infrastructure without any needs for modifications on conventional internal combustion engines for diesel-like synfuels. The same is valid for aircraft jet engines as demonstrated recently by Syntroleum© gas-to-liquids jet fuels for the US Air Force. The development for the civil aviation seems imminent following advancements in the military with more feedstocks to investigate and explore since the airline industry is far more fuel-guzzling as a business than the army. There is a cornucopia of feedstocks to investigate and experiment with. For instance, Virgin Atlantic Airlines has recently used a fuel blend of Babasu oil mixed with traditional jet
fuel to power one engine on a 747 flight from London to Amsterdam, a milestone for the ailing airline industry towards less dependency on conventional fuels.

1.2 The Case for the Aviation Industry

The ascent of already high fuel prices since October 2004 has been eating away most of the profits many US companies have been making after their relative recovery from the post 9-11 recession era back in 2001. The hardest-hit businesses are obviously airliners and shipping and transportation companies given that fuel is already a significant operating cost for them. Since the start of 2008, a number of US airlines have filed for bankruptcy and major airlines started to cut domestic flights by up to 12 percent of their daily activities. Delta and Northwest Airlines are on their way to an imminent merger. United and American Airlines are on early stages of negotiation for a similar deal. This wave of consolidation is just yet another attempt from the part of airline companies to partially cut fuel costs. By sharing infrastructure namely newer and more fuel-efficient aircrafts as well as global fuel contracts and jet fuel depots (in order to avoid refueling in costly places), airliners can create room for much needed savings and higher operations efficiency. United Airlines decided to ground its least efficient aircrafts, old 737’s and 747’s. American Airlines also recently announced that it is withdrawing old gas-guzzling airplanes altogether (their MD 80’s). The company is even charging for the first checked-in piece of luggage to partially make up for the money lost to rising fuel expenses.

Even though the airline industry has been a leader in energy efficiency thanks to continuous and substantial improvements in aerodynamics and jet engine technology, demand on jet fuel has
been steadily increasing. The Energy Information Administration (EIA) statistics show that civilian air transport of passengers and freight will account for 86 percent of aviation fuel in 2025. Fuel cost has also overtaken labor cost as the single most expensive item incurred by airlines following the sharp increases in fuel prices in recent years. So far the new price average for 2008 is $124.5/b adding some $63 billion for the global airline industry fuel bill. As a rule of thumb, every extra cent/gallon costs the airline industry some $180 million per year.

<table>
<thead>
<tr>
<th>Index (*)</th>
<th>$/b</th>
<th>Cents/gallon</th>
<th>$/metric ton</th>
<th>March 08</th>
<th>April 07</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jet Fuel Price</td>
<td>401.3</td>
<td>146.8</td>
<td>349.6</td>
<td>1157.1</td>
<td>12.2 %</td>
</tr>
</tbody>
</table>

(*) 100 in 2000 (87 cents/gallon)

This upward trend leaves only one option: increase the supply of jet fuel by an alternative, reliable and renewable way. Mass-scale supply of such fuels will curb (and then maybe reverse) the rising trend of fuel prices. Fischer-Topsch (FT) fuels have received growing attention in recent years since they are readily usable with today’s existing infrastructure in addition to their environmentally friendly nature (carbon neutral with zero sulfur content). The composition of both Jet A-1 and Jet A (main civil jet fuels) is basically the same as kerosene, with the exceptions that they are made under more stringent conditions and contain various additives not found in kerosene. The same applies to military fuels like JP-5 and JP-8 with even more stringent requirements to follow for these latter fuels. Throughout this study we will not make the difference between any of these slightly different fuels. We will assume that the variations
brought up by the different additives relative to each blend of fuel is not of an importance. We will also assume that there are only simple carbon bonds in the molecule of kerosene, an alkane, whose chemical formula is $\text{C}_{12}\text{H}_{26}$. This assumption is important to take into account in order to be in line with the mechanisms of the carbon chain growth as described in Chapter II. Table 2 sums up the main physical properties of kerosene.

Table 2 Physical Properties of kerosene

<table>
<thead>
<tr>
<th>Physical Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flash Point</td>
<td>37 °C</td>
</tr>
<tr>
<td>Auto-Ignition Point</td>
<td>220°C</td>
</tr>
<tr>
<td>Relative density (water =1)</td>
<td>0.8</td>
</tr>
<tr>
<td>Boiling point</td>
<td>170°C</td>
</tr>
<tr>
<td>Melting point</td>
<td>-20°C</td>
</tr>
<tr>
<td>Solubility in water</td>
<td>none</td>
</tr>
<tr>
<td>Explosive limits, vol. % in air</td>
<td>0.7-5</td>
</tr>
<tr>
<td>Relative vapor density (air = 1)</td>
<td>4.5</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>170 g/mol</td>
</tr>
</tbody>
</table>

The full approval of FT fuels by the US Air Force following extensive tests on a B-52 powered solely by a 50-50 blend of JP-8 and of Syntroleum©'s FT fuel will undoubtedly boost the “renaissance” of FT fuels first for military use and then inevitably for civil aviation [2].

The Fischer-Tropsch synthesis also offers another edge over other biofuel technologies. In fact, the need to meet increasing energy demands in the US (25 percent of the world’s crude oil consumption and over 40 percent of its gasoline) has spawned feverish efforts to boost fuel production out of crop-based feedstock, namely ethanol. This is obviously driving up competition on land and water resources and is putting more strain on food production unless
non-edible parts of the crop are used. For instance, filling the 25-gallon tank of an SUV with pure ethanol requires over 450 pounds of corn which contains enough calories to feed one person for a year [3]. Unlike corn-based ethanol, which is not a sustainable solution since it displaces staple food resources, FT biodiesel or kerosene produced from sugar cane trash are more sustainable and viable options. Sugar cane waste is an abundant and cost-effective feedstock providing substantially important energy potential to tap into. While the Fischer-Tropsch process does not directly address the insatiable thirst for gasoline, it does help partially displace the need for diesel and kerosene from foreign oil imports to domestic fuel production. The benefit is two-fold 1) independence from fossil fuel/crop based fuels and 2) recycling of waste that would otherwise be disposed of. As shown in table 8 in Chapter V, Florida is the biggest sugar-cane producer nationwide (almost 50 percent of the national production) which provides for more abundant and cheaper feedstock for Florida-based Fischer-Tropsch bioplants. This also results in lower transportation costs and translates into better competitiveness of the final product when benchmarked against fossil fuels. Subsequently, this reduces the need for government subsidies at least in the medium to long term.

The environmental concerns are of no less urgency amid rising voices to address global warming. As shown in Figure 4, the aviation industry is estimated to contribute 12 percent of the world’s transport CO$_2$ emissions tantamount to 2 percent of the world’s total CO$_2$ emissions.
The FT synthesis is therefore good news for the aviation industry since it has been proven that synthetic fuels are sulfur-free with substantially less carbon emissions than their fossil peers [2].

The current analysis is mainly explorative in nature when considering sugar cane and biomass in general as viable feedstock as the revival of interest in Fischer-Tropsch synthetic fuels still heavily focuses on fossil fuel feedstocks such as coal or natural gas. This study does not try to prove the feasibility of the process as much as it tries to derive the optimal conditions of the chemical reaction at the heart of a large-scale production plant of kerosene from sugar cane waste and assess the demand on water needed when using this synthesis technology.

Chapter I provided an introduction to the present energy crisis faced by the aviation industry. Chapter II serves as a literature review on the Fischer-Tropsch synthesis with an emphasis on the mechanism of the reaction and ways to optimize the distribution of the desired final product. In
Chapter III, a procedure is presented to assess the water footprint in a typical bio-refinery for a given volume of kerosene produced using sugar cane waste as feedstock. In Chapter IV, the same is done as in the previous chapter but considering landfill gas as feedstock instead. Chapter V deals with basic economics of a pilot plant to convert biomass into jet fuel. Chapter VI enumerates the limitations of this study and suggests a set of recommendations for possible future work. Chapter VII serves as a general conclusion for the present thesis.
CHAPTER II
LITERATURE REVIEW: FISCHER-TROPSCH PROCESS

2.1 Historical Background

The Fischer-Tropsch synthesis is a chemical process invented, proven and patented by two German chemists Franz Fischer and Hans Tropsch at the then Kaiser Wilhelm Institute (today’s Max Planck Institute) in the 1920’s. The technology had been heavily exploited during the extremely high energy-intensive Second World War to meet oil-poor but coal-rich Germany’s fuel demands on diesel and kerosene. According to the US Department of Energy data “more than 92 percent of Germany's aviation gasoline and half its total petroleum during World War II had come from synthetic fuel plants. At its peak in early 1944, the German synfuels output was around 124,000 barrels per day produced by a total of 25 plants” [33]. The interest in the FT process faded away as post-war economies heavily shifted to conventional oil and low prices were affordable in the 1950’s. By 1985 the Synthetic Liquid Fuels Program run by the US Bureau of Mines and enacted by the congress in 1944 was abolished amidst the mid 80’s oil gluts. Only did South African Synthetic Oil (Sasol©) keep developing the technology due to the embargo imposed on the apartheid regime. Sasol© also used coal as feedstock at the start. With the increasing volatility of crude oil prices notably on the aftermath of 9-11 events, there has been a growing attention to the FT synthesis again. Oklahoma-based Syntroleum© conducted a series of successful tests with the US Air Force and obtained full approval for their fuels in late 2007. According to the US Air Force official web site “the USAF intends to certify every one of its aircraft models for the fuel by 2011. This is a major step in the U.S. military's goal of
obtaining about half of its aviation fuel from alternative sources by 2016 to reduce its dependence on foreign-sourced crude oil”. Both Syntroleum© and Sasol© use fossil fuel feedstocks though namely natural gas or coal. However, the same process is common to all feedstocks including biomass like sugar cane waste, switch grass, woodchips, algae or any other organic (carbon-based) materials. A growing number of companies have been fine tuning the process and experimenting with different feedstocks and improved processes. Shell Malaysia in Bintulu, Choren© of Germany and Rentech© in California are some other prominent market players for the time being with the most advanced area of the research involving understanding the catalysis mechanism and orienting the reaction towards a maximum conversion ratio of the desired product using the optimal catalyst for a given feedstock.

2.2 Mechanisms of the Fischer Tropsch Process

The Fischer-Tropsch synthesis is basically summarized in the following two-step procedure:

**Step 1:** Cane trash is a carbohydrate that is almost 50 percent oxygen by mass. Kerosene (C_{12}H_{26}) by contrast is oxygen free. In order to produce a fully reduced hydrocarbon from the carbohydrate, the trash must be combusted to drive the oxygen out of the rest of the carbohydrate. The natural gas, coal or in our case trash is gasified by partial combustion and turned into a mixture of carbon dioxide, carbon monoxide, hydrogen and water vapor. This mixture is called “syngas”. The generic chemical equation is the following:

\[
\text{Biomass}(C) + O_2 \rightarrow CO + H_2
\]  

(1)
The shredded mixture goes through a partial pyrolysis. Ideally, moisture content should not exceed 40 percent so as to avoid spending a substantial amount of heating energy to dry and gasify the feedstock.

**Step 2**: The syngas is passed through a catalyst bed and undergoes a Fischer-Tropsch process to be converted into long chain hydrocarbons to form a kerosene-like fuel. A hydro cracking and refining phase is finally carried out to obtain high quality, market-like fuels.

![Figure 5 Fischer-Tropsch Synthesis (hydro cracking not shown)](image)

**2.2.1 Chemical Equations**

As explained by the section above, the synthesis process is a combination of three sub-processes: First, gasification of the biomass then a water gas shift reaction and finally the core Fischer Tropsch process, the hydro cracking phase not included. In the following section we will present
the chemical reactions describing each stage of the process and which we will use throughout this study.

2.2.1.2 Fischer Tropsch Reaction

The FT synthesis is in principle a carbon chain building process, where CH₂ clusters are attached to the carbon chain. The reaction can be presented as two simultaneous sub-reactions

\[ nCO + \left( n + \frac{m}{2} \right)H₂ \rightarrow C_nH_{2n} + nH₂O \]  \hspace{1cm} (2)

\[ CO + 2H₂ \rightarrow -CH₂- + H₂O \]  \hspace{1cm} (3)

Where -CH₂– is the organic cluster below

```
H
|   C   |
H
```

Both n and m vary with the process conditions namely the nature of the catalyst, temperature, pressure and reactor type. The above sequence of chemical equations can be represented by the figure below
For alcanes, $n$ and $m$ are related by the formula

$$m = 2n + 2 \quad (4)$$

In the case of kerosene where $n = 12$ and $m = 26$, the FT reaction becomes the following

$$12CO + 25H_2 \rightarrow C_{12}H_{26} + 12H_2O \quad (5)$$

2.2.1.3 Water Gas-Shift Reaction

Ideally, the FT process requires a syngas ratio of $H_2:CO$ of 2. This is not the case for most if not all feedstocks. In order to shift the ratio around 2 a water gas-shift reaction (WGSR) is essential.
\[ CO + H_2O \rightarrow CO_2 + H_2 \quad (6) \]

This is carried out by injecting hot steam on the gasified biomass to produce hydrogen and carbon dioxide. Although Carbon dioxide is not a reactant in the FT reaction but its presence inhibits the production of carbon chains of a carbon number higher than 5 [13]. Therefore it is of primary importance to remove carbon dioxide. Generally, a physical absorption technology (PSA) or ceramic membranes are applied for this purpose with PSA able to remove both water and CO$_2$ at the same time.

2.2.2 Optimizing the Reaction for Kerosene Production

The outcome of Fischer-Tropsch synthesis can not be closely controlled. It is impossible to obtain a particular product distribution in a narrow range of carbon numbers let alone to individually obtain a single product corresponding to an exact carbon number. This is because the mechanisms of the Fischer-Tropsch reaction are probabilistic and still remain a subject of controversy and extensive research.

However with the advent of new catalysis technologies, better built FT reactors and improved control techniques of temperature and pressure, it is being increasingly possible to manipulate the reaction in a direction generating the highest yield of a particular desired product from the start. For instance it is known that FT product distribution is highly catalyst-dependent and is largely influenced by temperature, pressure and reactor type.
In the following section, we will present the effect of each parameter on product distribution (selectivity) with recommendations relevant to kerosene production. The objective of this section

2.2.2.1 Catalyst Effect

Four main catalyst types are used in FT synthesis: Iron (Fe), Cobalt (Co), Nickel (Ni) and Ruthenium (Ru). However, we will only consider Fe and Co catalysts. In fact, even though Ru is the most active FT catalyst of all working at temperatures as low as 150 °C and yielding very high molecular weight products, it is both very expensive and scarce, which discards it for large-scale commercial applications. On the other hand, Ni can react with Co at high pressures to produce Nickel Carbonyl or generate excessive methane at high temperatures.

Iron however is abundant, cheap and offers good selectivity to olefins. Its methane selectivity remains relatively low at temperatures as high as 350 °C. Iron catalysts are flexible and sweep a large enough spectrum of products but are limited when it comes to the degree of conversion. Cobalt is also widely used in industry especially for diesel production with natural gas as feedstock. Reductions up to 30 percent in the capital costs required for the FT section of the plant can be achieved because of higher conversions with Cobalt. Cobalt catalysts are more expensive than Iron and less flexible towards lower carbon numbers. By and large, different synthesis gas compositions can be used. Cobalt-based catalysts tend to work better for H₂:CO ratios of a range around 1.8-2.1 while Iron-based catalysts promote the water-gas-shift reaction and thus can tolerate significantly lower ratios. This can be important for synthesis gas derived from biomass, which tend to have relatively low H₂:CO ratios (<1) [18].
2.2.2.2 Temperature Effect

Generally, the Fischer-Tropsch process is operated in a temperature range of 150-300°C. It has been experimentally shown that higher temperatures lead to faster reactions and higher conversion rates, but also tend to simultaneously favor methane production. Consequently, the temperature is usually kept at the low to middle part of the range. Higher temperatures favor the formation of lower molecular weight hydrocarbons, for distillates C12-C19 the optimal temperature is around 200°C to 250 °C. As for Naphtha C5-C11, it is slightly higher around 275°C [18].

2.2.2.3 Pressure Effect

Typical pressures are in the range of a few to tens of atmospheres. Chemically, even higher pressures would be favorable, but the benefits maybe offset by the additional costs of high-pressure equipment. Increasing the pressure leads to higher conversion rates and also favors formation of long-chained alkanes both of which are desirable. While higher pressure favors heavier FT hydrocarbons distribution, total pressure does not have a direct impact on the product selectivity; it is rather the partial pressure of the syngas components H₂ and CO who does [18].

2.2.2.4 Reactor Type Effect

A brief comparative study benchmarking the performance of the three main types of Fischer Tropsch reactors in different operation aspects (heat removal, catalyst loading/unloading) is presented in appendix B. The effect of reactor type on product conversion & selectivity with the syngas ratio as a parameter (H₂:CO) is provided in Appendix C [18].
For the case of kerosene, slurry bubble column are preferred for two main reasons: the possibility to produce important daily quantities (as it is the case for the aviation industry), excellent heat removal performance is expected [18].

2.3 Product Distribution

Product distribution when using the Fischer Tropsch technology has always been a subject of controversy. The chain growth probability, \( \alpha \), represents “the probability that an oligomer with \( n-1 \) carbon atoms will grow to an oligomer with \( n \) carbon atoms and is the single parameter of this model” [26]. Therefore the probability to grow to a carbon chain of \( C_{n-1} \) is \( \alpha^{n-1} \) and subsequently the probability of chain termination at a carbon atom of \( C_n \) is given by the following formula

\[
X_n = \alpha^{n-1}(1 - \alpha)
\]  

(7)

\( X_n \) is also the mole fraction of the hydrocarbon product with carbon atoms of number \( n \) and can be written as

\[
\log X_n = n \log \alpha + \log[(1 - \alpha) / \alpha]
\]  

(8)

Given that the molecular weight of the chain sequence that add ups every step of the process i.e \( \text{CH}_2 \) (see figure 6) is 14 g/mol, the corresponding mass is then given by

\[
w_n = 14n\alpha^{n-1}(1 - \alpha)
\]  

(9)
Which leads to the expression of the

\[ W_n = n\alpha^{n-1}(1-\alpha)^2 \]  \hspace{1cm} (10)

For the step-by-step calculations leading to the above equation, please refer to Appendix A.

Finally dividing by \( n \),

\[ \frac{W_n}{n} = \alpha^{n-1}(1-\alpha)^2 \]  \hspace{1cm} (11)

It is clear from the above equation that the largest single product will always be methane (CH\(_4\)) since it corresponds to a carbon number of 1. However, by increasing \( \alpha \) close to one, the total amount of methane formed can be minimized compared to the sum of all of the various long-chained products. Increasing the parameter \( \alpha \) favors the formation of long-chained hydrocarbons by the very definition of \( \alpha \). The very long-chained hydrocarbons are waxes, which are solid at room temperature. Therefore, in order produce liquid transportation fuels it may be necessary to crack some of the Fischer-Tropsch products. This is done as the final phase after products come out of the FT reactor to obtain the final synfuels.

The corresponding Anderson-Schultz-Flory (ASF) polymerization equation is given by Figure 7.
Kerosene (a distillate) lies on the red curve (carbon number between 12 and 18). Dividing both sides of the equation above by \( n \) and applying the log operator

\[
\log\left(\frac{W_n}{n}\right) = n \log \alpha + \log\left(\left[1 - \alpha\right]^2 / \alpha\right)
\] (12)

Consequently one would expect a linear relation between \( \log(W_n/n) \) and \( n \) with \( \log \alpha \) as a slope.

The product distribution is schematized in the following graphic by class of product. Kerosene is bounded by the red ellipse area which is a narrow range to aim at and requires a good control of the reaction parameter to optimize the yield of the desired product i.e kerosene.
The control of the FT reaction to obtain an exact carbon number at equilibrium remains the subject of controversy and not a fully understood. However we know the parameters involved in deciding which final product will be obtained with a certain probability. The curve for kerosene can be obtained by plotting equation (10) for $n = 12$. 

Figure 8 FT product distribution for different probabilities of carbon chain growth
<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical Reaction</th>
<th>H2:CO Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>$CO + 3H_2 \rightarrow CH_4 + H_2O$</td>
<td>3</td>
</tr>
<tr>
<td>Ethane</td>
<td>$2CO + 5H_2 \rightarrow C_2H_6 + 2H_2O$</td>
<td>2.5</td>
</tr>
<tr>
<td>Propane</td>
<td>$3CO + 7H_2 \rightarrow C_3H_8 + 3H_2O$</td>
<td>2.33</td>
</tr>
<tr>
<td>Butane</td>
<td>$4CO + 9H_2 \rightarrow C_4H_{10} + 4H_2O$</td>
<td>2.25</td>
</tr>
<tr>
<td>Pentane</td>
<td>$5CO + 11H_2 \rightarrow C_5H_{12} + 5H_2O$</td>
<td>2.2</td>
</tr>
<tr>
<td>Kerosene</td>
<td>$12CO + 25H_2 \rightarrow C_{12}H_{26} + 12H_2O$</td>
<td>2.08</td>
</tr>
<tr>
<td>-</td>
<td>$nCO + (2n+1)H_2 \rightarrow C_nH_{2n+2} + nH_2O$</td>
<td>$\frac{2n+1}{n} \rightarrow 2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>As $n \rightarrow \infty$ (theoretically)</td>
</tr>
</tbody>
</table>

Let us consider the set of the chemical equations gathered in the table below according to the corresponding carbon number. The above table can be represented by the chart below linking the syngas ratio to the carbon number.
Figure 9 H2:CO ratio as a function of carbon number
CHAPTER III
WATER FOOTPRINT USING SUGAR CANE WASTE AS FEEDSTOCK

3.1 Overview

According to waterfootprint.org, “water footprint is an indicator of water use that includes both direct and indirect water use of a consumer or producer. The water footprint of an individual, community or business is defined as the total volume of freshwater that is used to produce the goods and services consumed by the individual or community or produced by the business. Water use is measured in water volume consumed (evaporated) and/or polluted per unit of time. A water footprint can be calculated for any well-defined group of consumers (e.g. an individual, family, village, city, province, state or nation) or producers (e.g. a public organization, private enterprise or economic sector). The water footprint is a geographically explicit indicator, not only showing volumes of water use and pollution, but also the locations.”

Increased use of biofuels puts higher pressure on water resources in at least two ways: water use for the irrigation of crops used as feedstocks for biodiesel production and water use for the production of biofuels in refineries, mostly for boiling and cooling. In this section, we assess the amount of water necessary to produce 1 unit of kerosene. The findings will be benchmarked against ethanol and coal-to-liquids fuels.
3.2 Sugar Cane as Feedstock

Sugar cane is a sub-tropical to tropical crop mainly grown in countries like Brazil, India, the US, the Caribbean, Egypt and Sudan among others. It is mainly used for producing sugar in mills but the use of choice is increasingly being ethanol with Brazil and the US being the two biggest producers with over 95 percent of the global ethanol production combined. One of the other possible energy usages for sugar cane is the burning of bagasse that remains after sugarcane crushing to provide both heat - used in the mill, and electricity - typically sold to the consumer electricity grid.

The average heating value for the sugar cane trash taken from the field is approximately 17.5 MJ/kg. According to Hassuani et al, “this higher heating value does not vary much among the three components of trash and bagasse, when expressed as dry matter” as shown in table 5 [7]. This value is approximately 40 percent of the heating value of an equal mass of a kerosene-like fuel which is 45MJ/kg.
Figure 10 Drawing of Sugar Cane Plant

Figure 11 Dry and cut stalks
3.3 Water Footprint

The amount of water necessary for kerosene production by the Fischer-Tropsch is mainly divided into two main categories:

3.3.1 Irrigation Water Needs

This is the water required to grow sugar cane crops on land. The figures are readily available on agricultural statistics and vary across regions. This part is obviously beyond the scope of this research work but studies show a big disparity between regions and countries depending on the sugar cane variety, climate, soil quality/humidity among other factors. By and large and for the case of ethanol which is the primary user of sugar cane crops for liquid fuel purposes, the range is between 900 and 1600 gallons of water for every gallon of ethanol produced [23].

3.3.2 Biorefineries Water Needs

Although marginal compared to that needed for irrigation, it remains a key parameter to evaluate in order to decide on the right location for such plants, to properly size equipment along the production chain and to accurately assess the impact on aquifers and the ecosystem in general. Water used in biorefineries as a source of hydrogen for the production of syngas as well as other processes particularly for cooling accounts for up to 70% of the overall water use in biorefineries [19].

28
Water used in biorefineries is further divided into two sub-categories:

3.3.2.1 Water Gas Shift Reaction Needs

This is the water needed to carry out the water shift reaction in order to adjust the H₂:CO ratio prior to feeding the syngas into the Fischer-Tropsch reactor. This reaction is given by the following chemical equation:

$$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \quad \Delta H = -41 \text{kJ/mol} \quad (13)$$

This is achieved by injecting steam into the syngas right after the gasification process. In fact, during the gasification process (a limited combustion in the presence of Oxygen), a transformation occurs converting the moisture content in the biomass into water vapor. This gaseous water can be recovered from the gasifier as hot steam and injected downstream in the water shift phase. The benefit is two-fold. First, it partially saves thermal energy that would otherwise have gone to heat an external source of water to feed the water shift reaction. Secondly, it saves some water that would otherwise have been brought from the same external source. The moisture percentage for each section of the plant on a dry basis is presented in the following table:

<table>
<thead>
<tr>
<th>% Weight Moisture Content</th>
<th>Tops</th>
<th>Green Leaves</th>
<th>Bagasse</th>
</tr>
</thead>
<tbody>
<tr>
<td>82.3</td>
<td>67.7</td>
<td>50.2</td>
<td></td>
</tr>
</tbody>
</table>

So it is expected that tops will consume the least amount of water since their moisture content is higher in the case it’s recovered for the later steam injection phase even though this will
tantamount to providing more heating energy during the biogasification process. The gasification is described by the chemical reaction below

$$Biomass + O_2 \rightarrow CO + H_2$$  \hspace{1cm} (14)

Note that the above chemical equation is well balanced since the biomass here – sugar cane waste – contains hydrogen and oxygen indeed so as to balance the equation. The table below gives the chemical composition in percent of weight for each types of sugar cane waste.

<table>
<thead>
<tr>
<th>%</th>
<th>Tops</th>
<th>Green Leaves</th>
<th>Bagasse</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>43.9</td>
<td>45.7</td>
<td>44.6</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>6.1</td>
<td>6.2</td>
<td>5.8</td>
</tr>
<tr>
<td>Oxygen</td>
<td>44</td>
<td>42.8</td>
<td>44.5</td>
</tr>
<tr>
<td>Energy Content (MJ/Kg)</td>
<td>16.4</td>
<td>17.4</td>
<td>18.1</td>
</tr>
</tbody>
</table>

The percentages in the above table do not add up to 100 percent since we did not include other chemical constituents like Sulfur, Chlorine, and Nitrogen among other present species and traces. Table 5 shows that we can equally treat all sections of a sugar cane plant when it comes to chemical composition and energy content [7]. We will take the following values for the rest of paper: Carbon (45%), Hydrogen (6%) and Oxygen (44%). The general formula for sugarcane can be taken as $C_{12}H_{22}O_{11}$ which gives a good count of the above table (42% carbon, 6% Hydrogen and 51% Oxygen). Thus equation (14) can be rewritten as

$$C_{12}H_{22}O_{11} + \frac{1}{2}O_2 \rightarrow 12CO + 11H_2$$  \hspace{1cm} (15)
3.3.2.2 Cooling Needs

Water needed to cool down the highly exothermic Fischer-Tropsch. According to Caldwell (1980), it is estimated that 20 percent of the chemical energy is converted into heat thus requiring a substantial amount of water to cool down the reactor. This is essential to conserve the catalyst life, maintain a constant reaction rate and avoid the excessive production of methane as well as carbon deposition at higher temperatures. This is one main reason why slurry bubble column reactors are preferred to solid or fluidized bed reactors since slurry phase reactors offer substantially better heat removal capability. For the particular case of Kerosene, a great attention has to be paid to cooling efficiency so that the reactor temperature does not exceed the auto-ignition point of kerosene (220°C) and in order to avoid catalyst attrition (Cobalt is preferred to Iron in the case of kerosene because of its better yield for higher carbon number products).

3.4 Calculation of Water Gas Shift Needs

The following cookbook procedure shall be followed step by step:

3.4.1 Equilibrium Constant (Moe’s Correlation)

In order to assess the amount of water needed during the water-shift process, the constant of equilibrium in Equation (15) needs to be determined first. Moe established in 1962 the following correlation to determine the equilibrium constant of the water-gas shift reaction as a function of temperature [28]
\[
K(T) = 0.0132 \exp\left(\frac{38.1}{RT}\right)
\]  

(16)

Therefore \( K(200 \, ^\circ C) = 0.0133 \).

3.4.2 Mass Action Law

Since the sum of the stoichiometric coefficients in the water shift reaction is zero (the convention is that the stoichiometric coefficients of products are positive while those of reactants are negative), the equilibrium is only temperature-dependent. In fact, the mass action law states:

\[
\frac{X_{CO_2}X_{H_2}}{X_{CO}X_{H_2O}} = P^{-\sum_{i=1}^{4}v_{ki}} K(T)
\]

(17)

Where

\( X \) is the molar fraction of a certain product or reaction

\( v_{ki} \) are the modified stoichiometric coefficients

\( T \) and \( P \) are respectively the temperature and the pressure at which the reaction in question is carried out. It is immediate to notice that

\[-\sum_{i=1}^{4}v_{ki} = -(1+1-1-1) = 0\]

(18)

Hence the independence of the equilibrium state vis-à-vis pressure.
The mass action law can be applied here since all species are in gaseous state and since we assume here that they behave like ideal gases. Since $H_2$:$CO$ is greater than 1 ($25/12=2.08$), we need more hydrogen than CO thus the reaction is carried out in the forward direction so as to produce $H_2$. We assume that we depart from 12 moles of carbon monoxide and $X$ mole of water (to be determined by the upcoming calculations) with 11 moles of $H_2$ and zero moles of $CO_2$

$$CO + H_2O \rightarrow CO_2 + H_2$$

*Initially*  
\[
\begin{array}{cccc}
12 & X & 0 & 11
\end{array}
\]

*At equilibrium*  
\[
\begin{array}{cccc}
12-d\tilde{N} & X-d\tilde{N} & d\tilde{N} & 11+d\tilde{N}
\end{array}
\]

With the total number of moles equaling $23+X$

Where $d\tilde{N}$ is the advancement of the chemical reaction once it reached the equilibrium, this is again the number of moles consumed from the reactants or generated in the form of products.

\[
\frac{X_{H_2}}{X_{CO}} = \frac{2n+1}{n} = \frac{25}{12} = 2.08 \quad \text{(19)}
\]

\[
\frac{(11 + d\tilde{N})}{(12 - d\tilde{N})}(23 + X) = \frac{11 + d\tilde{N}}{12 - d\tilde{N}} = 2.08 \quad \text{(20)}
\]

We therefore obtain

\[
d\tilde{N} = 4.53 \quad \text{(21)}
\]
The reaction is being carried out at a temperature of 200 °C or 473 °K [2] therefore the equilibrium constant is 0.013 by Moe’s correlation.

\[
\frac{d\tilde{N}(11 + d\tilde{N})}{(12 - d\tilde{N})(X - d\tilde{N})} = K(473) \tag{22}
\]

Hence \( X = 73 \) moles or 0.034 gallon (one mole of water weighing 18 grams so this amounts to 131.4 grams i.e. 0.131 liters or 0.034 gallon). Consequently, so for every mole of feedstock \( C_{12}H_{22}O_{11} \), this amount of water is needed in order to achieve a transition from a \( H_2:CO \) ratio of 11/12 to 25/12 (=2.08).

Assuming each mole of biomass yields one mole of carbon monoxide and using real plant data (Mobile) confirmed by a series of simulations using ASPEN Plus software, Lu (2003) estimated that one ton of feedstock (coal) yields around 18 percent of its weight as the final product in the range of distillates (carbon number from 12 to 18). Vessia (2005) gives a range of 10 percent of the feedstock’s initial weight in the case of lignocellulosic materials (namely wood). Taking an average yield ratio in this range for the case of sugar cane (around one sixth of the feedstock’s initial weight turned into the final desired product) then it is calculated that 1 mole of sugar cane waste (\( C_{12}H_{22}O_{11} \) thus weighing 342 grams) yields 57 grams of kerosene whose molecular weight is 170 g or roughly 1/3 of a mole.
3.5 Calculation of Cooling Water Needs

3.5.1 Twenty percent rule (of thumb)

Literature review reveals that some 20 percent conversion ratio from chemical energy to thermal energy in the combustion reaction of syngas [15], we proceed as follows to assess the amount of this heat.

The equation is

\[12CO + 25H_2 \rightarrow C_{12}H_{26} + 12H_2O + \text{Heat}\]  \hspace{1cm} (23)

Clearly to calculate the heat released by this reaction, we can not directly use heats of formation since we have compounds as reactants (instead of elementary or simple chemical elements).

\[CO + H_2 + O_2 \rightarrow H_2O + CO_2\]  \hspace{1cm} (24)
3.5.2 Hess’ Law

The above equation can be written as the combination of the following two equations

\[ 2H_2 + O_2 \rightarrow 2H_2O \]  \hspace{1cm} (25)

For which \( \Delta h_f = -241.83 \text{kJ/mol} \) and since we get one mole of water as described by Equation (24) then we consider the value of \( \Delta h_f = -120.91 \text{kJ/mol} \)

and

\[ C + O_2 \rightarrow CO_2 \]  \hspace{1cm} (26)

For which \( \Delta h_f = -393 \text{kJ/mol} \)  \hspace{1cm} (27)

Now assuming both specific heat capacities for carbon dioxide and water are kept constant during the process

\[ \text{CO}_2 : \quad C_p = 0.839 \text{J.g}^{-1}\text{.K}^{-1} = 36.94 \text{J.mol}^{-1}\text{.K}^{-1} \]  \hspace{1cm} (28)

\[ \text{H}_2\text{O (steam) : } \quad C_p = 2.080 \text{J.g}^{-1}\text{.K}^{-1} = 37.47 \text{J.mol}^{-1}\text{.K}^{-1} \]  \hspace{1cm} (29)

\( \Delta T = T_{\text{combustion}} \text{ since } T_{\text{combustion}} >> T_{\text{room}} \); the combustion temperature being 600K

And using

\[ \Delta h = C_p \Delta T \]  \hspace{1cm} (30)

We get the heats of formation at the reaction temperature for each reaction above
\[ \Delta h = 74.94 \text{ kj/mol therefore } \Delta h(600) = -45.97 \text{ kj/mol} \quad (31) \]

\[ \Delta h = 73.88 \text{ kj/mol therefore } \Delta h(600) = -319.12 \text{ kj/mol} \quad (32) \]

Then, according to Hess’ Law, using the heat of formation at standard conditions (room temperature & pressure), we can compute the heat produced by the combustion of syngas:

\[ \Delta h = -365.09 \text{ kj/mol} \quad (33) \]

and therefore determine how much heat is released by the kerosene-producing equation.

\[ \text{Heat} = 73 \text{ kj/mol} \quad (34) \]

Therefore we need 195 moles of water to absorb that amount of heat (since the water specific heat is a known tabulated value) and to bring the reaction temperature back to a temperature of 200 °C (a minimum gradient of temperature of 20 °C/K in order to avoid reaching the critical and hazardous auto-ignition temperature of 220 °C). One mole of water weighing 18 g corresponding to a volume of 3.5 liters or 0.925 gallons (assuming water is constantly supplied at 25 °C say from a nearby lake) for every mole of kerosene.

After summing up the two contributing parts, we obtain the amount of water needed to produce one mole of kerosene (170 g with a density of 800 g/liter or 0.21 liter or 0.06 gallons). Put in other terms in order to produce 1 gallon of kerosene we roughly need 19 gallons of water.

Taking also into account that we assumed a constant supply of cool water instead of circulation via a cooling tower, we should get lower water consumption than the 19 gallons of water per one gallon of kerosene produced.
This figure is very conservative in that 19 gal/gal is a high estimate. Still it does not rule out the feedstock as a potential candidate to make aviation fuel if further adjustments to the model are taken into account.

The assumption of constant supply of cool water to evacuate the heat generated by the highly exothermic reaction is obviously not applied in industry as coolant water is recycled through the cooling towers back to the heat exchanger at the level of the Fischer-Tropsch reaction. The calculations above show that the bulk of water consumption is indeed relative to the cooling part of the process or nearly 75 percent. Assuming a ratio of 50 percent recycling of cooling water (if the heat exchangers and the cooling circuit can use half the amount of water compared to a constant supply of cool water scenario) the figure drops to 12 gal/gal.
This figure still remains marginal compared to the amount of water needed for irrigation (900 to 1600 gallons of water for the case of ethanol for instance) but is important to evaluate in order to appropriately seize equipment and location of such bioplant [7]. Most importantly, Fischer-Tropsch based biomass-to-liquids plant production can use the whole plant instead of only some parts of it. In our case, it is possible to use tops, green leaves and bagasse to feed into the biogasifier. This will automatically translate to less land area required per unit energy compared to other processes which translates again into a lower water footprint in the irrigation part. This clearly more than offsets the 50 percent or so extra amount of water (12 gal/gal vs. 8 gal/gal) needed in the biorefineries.
CHAPTER IV
WATER FOOTPRINT USING LANDFILL GAS AS FEEDSTOCK

4.1 Overview

Landfill gas (LFG) is generated as a natural byproduct of decomposing organic matter disposed of in landfills. LFG consists of about 50 percent methane (CH₄), the primary component of natural gas, about 50 percent carbon dioxide (CO₂), and a trace amount of non-methane organic compounds. However, we will equate both throughout this analysis since we are considering the fuel synthesis to start after the landfill gas (LFG) has been processed and purified from carbon dioxide (CO₂) and these non-methane organic traces. Globally, landfills are the third largest anthropogenic (human influenced) emission source, accounting for about 13 percent of global methane emissions or over 223 million metric tons of carbon equivalent (MMTCE). The figure below shows the global potential of the United States to harness this type of feedstock for other energy resources while cutting its carbon footprint [36].

Figure 15 Global landfill methane emissions in 2000
In the US alone in 2003, both residents and businesses produced more than 236 million tons of municipal solid waste (MSW), which is approximately 4.5 pounds of waste per person per day [36].

4.2 Chemical Equations

For the case of Landfill gas as feedstock and like the sugar cane waste, syngas is produced by partial combustion of the feedstock. Recalling the general chemical equation of the pyrolysis

\[ C_nH_{(2n+2)} + \frac{1}{2} nO_2 \rightarrow (n+1)H_2 + nCO \]  (35)

And since methane corresponds to a carbon number of one (n=1), the above equation can be rewritten for the particular case of methane as follows:

\[ 2CH_4 + O_2 \rightarrow 4H_2 + 2CO \]  (36)

The same methodology used in the previous chapter for the case of sugar cane waste will be applied for landfill gas to assess the water footprint when considering such a feedstock.

\[ H_2:CO = 4/2 = 2 \]  but since the ratio to be obtained for kerosene is 2.08 , the amount of water needed to shift the syngas ratio to 2.08 will be considerably lower than that in the case of sugar cane waste (since again the ratios are close to each other).
4.3 Calculation of Water Footprint in biorefineries

Just like in the previous chapter, the same cookbook procedure will be followed to assess the amount of water needed in a typical Fischer Tropsch refinery to produce one gallon of kerosene.

4.3.1 Water Gas Shift Reaction

4.3.1.1 Equilibrium Constant (Moe’s Correlation)

Referring to Moe’s correlation in equation (16), the equilibrium constant \( K \) is the same in the case of Landfill gas since it is only temperature-dependent i.e 0.013.

4.3.1.2 Mass Action Law

Recalling again the equation of mass action law

\[
\frac{X_{CO_2}X_{H_2}}{X_{CO}X_{H_2O}} = P \sum_{k=1}^{4} \nu_k K(T)
\]

where

\( X \) is the molar fraction of a certain product or reaction

\( \nu_k \) are the modified stoichiometric coefficients
T and P are respectively the temperature and the pressure at which the reaction in question is carried out.

\[ CO + H_2O \rightarrow CO_2 + H_2 \]  \hspace{1cm} (38)

Initially

\[
\begin{array}{cccc}
2 & X & 0 & 4 \\
\end{array}
\]

At equilibrium

\[
\begin{array}{cccc}
2-d\tilde{N} & X-d\tilde{N} & d\tilde{N} & 4+d\tilde{N} \\
\end{array}
\]

With the total number of moles equaling 6+X

Once again, the mass action law can be applied here since all species are in gaseous state and since we assume here that they behave like ideal gases. Since H\(_2\):CO is greater than 1 (=2.08), more hydrogen needs to be generated than CO. The reaction is therefore carried out in the forward direction so as to produce H\(_2\). We assume that we depart from 2 moles of carbon monoxide and X mole of water (to be determined by the upcoming calculations) with initially 4 moles of H\(_2\) and no CO\(_2\) as shown in equation (38).

\[
\frac{X_{H_2}}{X_{CO}} = \frac{2n+1}{n} = \frac{25}{12} = 2.08 \hspace{1cm} (39)
\]

\[
\frac{(4+d\tilde{N})}{(6+X)} = \frac{4+d\tilde{N}}{2-d\tilde{N}} = 2.08 \hspace{1cm} (40)
\]

we therefore obtain

\[
d\tilde{N} = 0.376 \hspace{1cm} (41)
\]
The reaction is being carried out at a temperature of 200 °C or 473 °K therefore the equilibrium constant is 0.0133 following Moe’s correlation

\[
\frac{(4 + d\tilde{N})d\tilde{N}}{(2 - d\tilde{N})(X - d\tilde{N})} = K(473)
\]  (42)

Hence X= 11.6 moles or nearly 0.005 gallon (one mole of water weighing 18 grams with water density being equal to 1). Consequently, for every mole of carbon monoxide we need this amount of water to achieve a transition from a H₂:CO ratio of 2 to 2.08. Again, recalling figure 12 and using real plant data (Mobile) confirmed by a series of simulations using ASPEN Plus software, Lu (2003) estimated that one ton of feedstock (coal) yields around 18 percent of its weight as the final product in the range of distillates (carbon number from 12 to 18). It is then calculated that 16 grams of methane (the mass of one mole of CH₄) yields 2.88 grams of kerosene whose molecular weight is 170 g or exactly 0.017 moles.

4.3.2 Cooling Needs

Applying Caldwell’s twenty percent rule (of thumb) and Hess’ law, we derive that some 73 kJ need to be removed for every mole of kerosene produced. Therefore we need 195 moles of water to absorb that amount of heat and to bring back the reaction to a temperature of 200 °C (a minimum gradient of temperature of 20 °C/°K in order to avoid reaching the critical and hazardous auto-ignition temperature of 220 °C). One mole of water weighing 18 g corresponding
to a volume of 3.5 liters or 0.925 gallons (assuming water is constantly supplied at 25 °C say from a nearby lake) for every mole of kerosene.

After summing up the two contributing parts, we obtain the amount of water needed to produce one mole of kerosene (170 g with a density of 800 g/liter or 0.21 liter or 0.06 gallons). Put in other terms in order to produce 1 gallon of kerosene, we roughly need 14 gallons of water. Taking also into account that we assumed a constant supply of cool water instead of circulation via a cooling tower, we should get lower water consumption than the 14 gallons of water per one gallon of kerosene produced.

Assuming a ratio of 50 percent recycling of cooling water (if the heat exchangers and the cooling circuit can use half the amount of water compared to a constant supply of cool water scenario) the figure drops to 9.1 gal/gal.
Figure 17  Water consumption per gallon of kerosene produced (with 50% reutilization of water) with LFG as feedstock
CHAPTER V
ECONOMICS

In this chapter we provide an economic analysis of the total capital investment needed to get a synthetic kerosene plant up and running using sugar cane waste (bagasse) as raw material. Cost estimates are based on three different reports by the Norwegian University of Science and Technology, the Utrecht University/Energy Research Centre of the Netherlands [12, 13] and a report by the Bechtel Corporation “Baseline Design Economics for Advanced Fischer Tropsch Technology” [35]. Both coal and natural gas were considered in the Bechtel studies. The estimated overall cost of such biorefinery was found to be around $1.5 billion.

It should be noted outright that while “the Fischer-Tropsch process is a well proven technology, it requires a large capital investment in equipment followed by high operation and maintenance costs. Also, the gasification to create carbon monoxide and hydrogen is very energy intensive.” However and again, as petroleum prices spike upward, making synthetic fuels from coal, natural gas and biomass become more economically competitive. Along with advanced energy companies focusing exclusively on alternative fuels, many oil companies (namely Shell Malaysia in Bintulu) also have dedicated synthetic fuel development programs in place which is already driving operating costs down and paving the way to a better economical exploitation of the Fischer Tropsch synthesis.
The syngas clean up plant (Plant 2) is needed for cracking and scrubbing since syngas inevitably contains impurities (BTX, NH₃, HCl, H₂S, dust and soot, etc). Syngas also needs to be cooled and the water in it removed. After going through the Fischer Tropsch reaction (Plant 4), the obtained liquid fuel still needs to be upgraded and refined (Plant 6) for the sake of better cold flow properties before obtained the final desired product (kerosene). This is mainly done by condensation step. The product is then sent to recovery and upgrading sections. Syngas out of the gasifier contains carbon dioxide which needs to be eliminated since it negatively influences the selectivity and generates excessive undesirable methane (Plant 5). The CO₂ removal unit can either use the Physical Absorption Technology (PSA) or Ceramic membranes with the advantage of PSA of removing both water and CO₂ at the same time.

The following figure gives a rough breakdown of investment costs of a typical Fischer-Tropsch plant when adding other components like a pretreatment unit, an oxygen plant, a gas turbine (for cogeneration purposes) among other units and accessories.
One thing to be noted is the marginal cost of the Fischer Tropsch reactor compared to the overall cost, which gives excellent incentive for future plant enlargement and production growth. This modular approach of phasing out a smaller FT reactor and plugging in a bigger (or better) one is appealing to keep up with rising aviation fuel demand without adding a significant cost.

It should be also noted here that the gas turbine (7 percent of the overall cost) is for cogeneration purposes. In fact, as mentioned earlier, the heat generated by the highly exothermic Fischer Tropsch reaction can be captured, driven off line in order to boil water into steam which will be injected into a Rankine cycle for electricity production. This combined Fuel and Power cycle will clearly boost the economic yield of such investment.

According to Energy Research Centre of the Netherlands [13], economies of scale for Fischer Tropsch plants are of primary importance. The bigger the plant, the lower the operating costs and
the faster economics will converge to breakeven point then into profit if adequate government subsidies are offered such as those to the ethanol and biodiesel industries (51 cents per gallon). In fact, building a small FT plant is out of the question as production has to be in excess of around 25 000 bpd in order to fully exploit the expensive equipment invested in upfront [12]. By and large, Fischer Tropsch liquid fuels still cost 4 times their fossil peers hence the need for tax incentives such as exemption from excise duty but also environmental tax breaks since the produced fuel are sulfur free.

The competitiveness of future large FT plants also strongly depends on the evolvement of an international biomass market with large quantities of biomass against low prices. The Caribbean is an ideal market to tap into for feedstock in case the technology matures and extra feedstock is needed (beyond the local production) for Florida’s based bioplants. Florida is an obvious choice when considering sugar cane waste given the abundance of feedstock which translates into cheaper prices (less than $5 per ton of bagasse for the case of Brazil) [7]. This is promising for many parts of the US like Texas, Louisiana, Hawaii and Florida (it has been estimated that in 2004-05, Florida contributed an estimated 51.3% of the US sugar cane production, some 20 percent of the US biomass potential is also thought to be in Florida).

<table>
<thead>
<tr>
<th>State</th>
<th>Yield per acre (tons)</th>
<th>Production (1000 tons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FL</td>
<td>34.9</td>
<td>31.4</td>
</tr>
<tr>
<td>HI</td>
<td>90.8</td>
<td>80.8</td>
</tr>
<tr>
<td>LA</td>
<td>23.8</td>
<td>22.9</td>
</tr>
<tr>
<td>TX</td>
<td>37.3</td>
<td>38.3</td>
</tr>
<tr>
<td>US</td>
<td>31</td>
<td>28.8</td>
</tr>
</tbody>
</table>

Table 7 US Sugar cane production (2002-2006), [11]
In Hawaii, harvest continues throughout the year and production statistics are on a calendar year basis. In other states, harvest is seasonal and the production statistics year relates to the year in which the season begins.

The Fischer Tropsch synthesis is promising in that it is extensible to a large number of feedstocks. This versatility is important in that it is capable of replacing fossil based feedstocks namely natural gas and coal by renewable carbon neutral feedstocks like the ones mentioned above. We believe other feedstocks should be considered across the world depending on their local or regional availability, whether their exploitation for energy purposes will displace food markets and of course their water footprint. Among these potential feedstocks one can name Jatropha, olive pomace or pits, switch grass, wood chips, etc.
CHAPTER VI
LIMITATIONS OF THIS STUDY AND FUTURE IMPROVEMENTS

Since this study was mainly of explorative nature, the model needs to be further fine-tuned most notably on two different fronts: the chemical aspect of the process (Fischer-Tropsch reaction) and optimization of the final yield by selecting an accurate enough distribution model.

The use of an off-the-shelf commercial software to simulate the process by means of flow charts such as the Aspen Plus software will yield more detailed and more accurate results. The output of different chemical species can be known based on the catalyst, pressure, temperature and type of the reactor. Different scenarios can be investigated by changing and adjusting input data for a maximal output of a desired final product for the sake of optimization.

Access to recent data from the industry will offer a precise benchmark against which the proposed process will be assessed. Data like coolant quantities needed in daily operations in typical bioplants, heat transfer coefficients in the heat exchangers, amount of steam needed during the gasification phase as well as operating temperatures and pressures will clearly be useful when feeding the model into the simulating tool like Aspen Plus.

Another aspect that needs to be investigated further is a better way to assess the heat released by the Fischer-Tropsch reaction. Obviously, an access to a vast enough empirical data from the industry can address this issue. Although sugar cane waste has not been used before as feedstock
to produce aviation fuel, one can substitute for this by looking up figures from the coal-to-liquid or gas-to-liquid industry and consider a conservative value.

Among the three types of sugar cane waste, bagasse is the most adequate to produce liquid fuel since its moisture content is the lowest but still in an acceptable range (15 to 25 percent being the optimal). If it is too dry, the hydrogen content of the produced syngas decreases and the water footprint increases as more water (in the form of super steam) is needed during the gas shift phase. On the other hand if it too humid, too much heating energy is required to gasify the biomass.
A simple calculation method was undertaken to quickly estimate the water usage inherent to producing kerosene using the Fischer-Tropsch process. This method is also applicable to other olefin, paraffins, distillates or waxes. Reaction conditions have been assumed to be optimal based on literature findings (cobalt-based catalyst, slurry bubble column reactor at a temperature of 200 °C and a pressure of 20-30 bar).

It is recommended that bagasse be used as a primary feedstock due to the moderate moisture content. While tops and to a lesser extent green leaves offer a higher moisture content that could be captured, recovered and injected back in the waster-gas shift phase to reduce the net amount of water needed, these two types of waste will need higher heating energy to carry out the gasification process. This could offset the overall economics especially with the necessity to introduce costly water recovery equipment. Another recommended way is to inject the hot water out of the reactor back into the waster-gas shift phase. The benefit is two-fold: save water and energy (in the form of heat).

Overall, the figures seem of the same order of magnitude as those for ethanol or coal-to-liquid figures which does not rule out the biomass-to-liquid technology in general as a potential contender to replace conventional fossil fuels. In addition to offering a reliable source of liquid jet fuel readily usable with today’s infrastructure, the FT synthesis seems to be a promising way towards less dependency on foreign fossil fuel sources not only oil but also natural gas. This is
probably the single most important advantage of biomass-to-liquids over gas-to-liquids namely getting rid of fossil fuel feedstock altogether.

Even though the United States boasts abundant resources of coal, the FT process still enjoys an edge compared to coal-to-liquids which is the possibility to produce environmentally-friendly fuels, carbon-neutral and sulfur free which is yet another advantage for the aviation industry, which is responsible for 2 percent of the global greenhouse gas emissions.
APPENDIX A
CALCULATION STEPS OF THE ASF PRODUCT DISTRIBUTION
We first start from the equation below linking the molecular weight to the carbon chain growth probability

\[ w_n = 14n\alpha^{n-1}(1-\alpha) \]

Hence the mass fraction is given by

\[ W_n = \frac{w_n}{\sum_{k=1}^{\infty} w_k} \]

Computing the denominator in the above equation yields

\[ \sum_{k=1}^{\infty} w_k = \sum_{k=1}^{\infty} 14k\alpha^{k-1}(1-\alpha) = 14(1-\alpha)\sum_{k=1}^{\infty} k\alpha^{k-1} \]

The infinite sum in the right hand side of the above equation can be calculated as following

\[ \sum_{k=1}^{\infty} k\alpha^{k-1} = \sum_{k=0}^{\infty} (k+1)\alpha^k = \sum_{k=0}^{\infty} k\alpha^k + \sum_{k=0}^{\infty} \alpha^k \]

With

\[ \sum_{k=0}^{\infty} \alpha^k = \frac{1}{1-\alpha}; \ \alpha < 1 \]

And

\[ \sum_{k=0}^{\infty} k\alpha^k = 0 + \alpha + 2\alpha^2 + 3\alpha^3 + 4\alpha^4 + ... = \alpha(1 + 2\alpha + 3\alpha^2 + 4\alpha^3 + ...) \]
It is clear to notice that

\[
(1 + 2\alpha + 3\alpha^2 + 4\alpha^3 + ...) = (1 + \alpha + \alpha^2 + \alpha^3 + ...) \left( 1 + \alpha + \alpha^2 + \alpha^3 + ... \right) = \left( \sum_{k=0}^{\infty} \alpha^k \right)^2 = \frac{1}{(1 - \alpha)^2}
\]

We then obtain

\[
\sum_{k=0}^{\infty} k\alpha^k = \frac{\alpha}{(1 - \alpha)^2}
\]

\[
\sum_{k=1}^{\infty} k\alpha^{k-1} = \frac{\alpha}{(1 - \alpha)^2} + \frac{1}{1 - \alpha} = \frac{\alpha + 1 - \alpha}{(1 - \alpha)^2} = \frac{1}{(1 - \alpha)^2}
\]

Finally

\[
\sum_{k=1}^{\infty} w_k = 14(1 - \alpha)/(1 - \alpha)^2 = 14/(1 - \alpha)
\]

This leads to expression found previously of the weight Fraction of a given FT final product of a carbon number \( n \) in function of the carbon chain growth probability

\[
W_n = n\alpha^{n-1}(1 - \alpha)^2
\]
APPENDIX B
TYPES OF FISCHER-TROPSCH REACTORS
There are three kinds of FT reactor. We will briefly discuss each type and benchmark them against each other.

1. Fixed Bed

Source: K.Sudsakorn

Tubular Fixed Bed FT Reactor
2. Fluidized bed reactor
3. Slurry Reactors

“Slurry reactors are the most efficient and easy to operate. They contain no moving parts and provide for the easy removal of product and the replacement of catalyst as it becomes spent.”

Source: K.Sudsakorn

Slurry Bubble Column Reactor
APPENDIX C
COMPARATIVE STUDY OF DIFFERENT FISCHER TROPSCH REACTORS
<table>
<thead>
<tr>
<th></th>
<th>Fixed Bed</th>
<th>Fluidized Bed</th>
<th>Slurry Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Construction</strong></td>
<td>complex</td>
<td>-</td>
<td>simple</td>
</tr>
<tr>
<td><strong>Heat exchange</strong></td>
<td>Limited conversion per pass and large particle size necessary to obtain even temperature profile</td>
<td>Excellent heat transfer results in isothermal conditions</td>
<td>Excellent heat removal efficiency</td>
</tr>
<tr>
<td><strong>Solids separation</strong></td>
<td>Not needed</td>
<td>Filtering may be necessary</td>
<td>Filtering is necessary</td>
</tr>
<tr>
<td><strong>Gas-liquid separation</strong></td>
<td>-</td>
<td>Foam formation occurs</td>
<td>-</td>
</tr>
<tr>
<td><strong>Reactant distribution</strong></td>
<td>difficult</td>
<td>Automatically lateral mixed</td>
<td>Automatically lateral mixed</td>
</tr>
<tr>
<td><strong>Catalyst settling or Agglomeration</strong></td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>Catalyst deactivation</strong></td>
<td>The top region where the syngas enters acts as a sulphur trap whereas in the bottom region almost no sulphur is found</td>
<td>-</td>
<td>Sulphur poisoning and water inhibition have even effect over the reactor – continuous circulation- leading to 1.5 to 2 times higher conversion loss than in fixed bed. High costs of cobalt catalysts necessitates a more effective sulphur removal</td>
</tr>
<tr>
<td><strong>Loading/unloading catalyst</strong></td>
<td>Difficult, shut down necessary</td>
<td>On-line</td>
<td>On-line</td>
</tr>
<tr>
<td><strong>Maximum capacity</strong></td>
<td>-</td>
<td>-</td>
<td>2.5 to 6 times larger than fixed bed 2500 ton/day or roughly 20 000 bpd</td>
</tr>
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</table>
APPENDIX D
EFFECT OF REACTOR TYPE ON PRODUCT CONVERSION & SELECTIVITY WITH H2:CO AS A PARAMETER
CSTR: Continually Stirred Tank Reactor; FB: Fixed Bed

<table>
<thead>
<tr>
<th>(H₂/CO) feed</th>
<th>0.50</th>
<th>0.67</th>
<th>1.0</th>
<th>2.0</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>CSTR</td>
<td>FB</td>
<td>Slurry</td>
<td>CSTR</td>
</tr>
<tr>
<td>100/[CO] (%)</td>
<td>86.4</td>
<td>96.2</td>
<td>75.0</td>
<td>95.1</td>
</tr>
<tr>
<td>100/[H₂] (%)</td>
<td>93.6</td>
<td>99.9</td>
<td>84.5</td>
<td>87.5</td>
</tr>
<tr>
<td>100/[H₂+CO] (%)</td>
<td>88.2</td>
<td>97.5</td>
<td>78.2</td>
<td>92.0</td>
</tr>
<tr>
<td>(H₂/CO) usage</td>
<td>0.548</td>
<td>0.519</td>
<td>0.564</td>
<td>0.616</td>
</tr>
<tr>
<td>n</td>
<td>4.31</td>
<td>5.91</td>
<td>3.97</td>
<td>3.33</td>
</tr>
<tr>
<td>m/n</td>
<td>2.13</td>
<td>2.08</td>
<td>2.22</td>
<td>2.24</td>
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</tbody>
</table>

Weight % of hydrocarbons

<table>
<thead>
<tr>
<th>CH₄</th>
<th>6.24</th>
<th>3.75</th>
<th>7.64</th>
<th>10.3</th>
<th>4.99</th>
<th>10.4</th>
<th>15.3</th>
<th>7.10</th>
<th>14.7</th>
<th>23.9</th>
<th>11.2</th>
<th>24.1</th>
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<tbody>
<tr>
<td>C₂-C₄</td>
<td>27.0</td>
<td>16.8</td>
<td>30.2</td>
<td>36.5</td>
<td>16.5</td>
<td>36.2</td>
<td>44.8</td>
<td>18.0</td>
<td>43.5</td>
<td>52.0</td>
<td>21.3</td>
<td>51.3</td>
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<tr>
<td>C₅-C₁₁</td>
<td>47.1</td>
<td>39.1</td>
<td>43.1</td>
<td>44.6</td>
<td>37.3</td>
<td>41.6</td>
<td>36.2</td>
<td>35.7</td>
<td>35.4</td>
<td>23.4</td>
<td>34.3</td>
<td>23.1</td>
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<tr>
<td>C₁₂+</td>
<td>15.7</td>
<td>40.4</td>
<td>19.1</td>
<td>9.26</td>
<td>41.2</td>
<td>11.8</td>
<td>3.70</td>
<td>39.2</td>
<td>5.40</td>
<td>0.70</td>
<td>33.2</td>
<td>1.60</td>
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Weight % olefin content

<table>
<thead>
<tr>
<th>C₂-C₄</th>
<th>93.7</th>
<th>96.5</th>
<th>88.9</th>
<th>85.7</th>
<th>87.8</th>
<th>82.8</th>
<th>73.2</th>
<th>74.2</th>
<th>73.1</th>
<th>62.3</th>
<th>61.6</th>
<th>71.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₅-C₁₁</td>
<td>93.9</td>
<td>96.1</td>
<td>62.9</td>
<td>86.1</td>
<td>87.2</td>
<td>53.3</td>
<td>73.8</td>
<td>72.8</td>
<td>48.8</td>
<td>63.0</td>
<td>59.0</td>
<td>53.1</td>
</tr>
<tr>
<td>C₁₂-C₁₉</td>
<td>94.0</td>
<td>95.6</td>
<td>13.1</td>
<td>86.2</td>
<td>86.9</td>
<td>9.17</td>
<td>74.0</td>
<td>72.6</td>
<td>7.84</td>
<td>63.3</td>
<td>58.9</td>
<td>6.07</td>
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<tr>
<td>C₂₀+</td>
<td>94.0</td>
<td>95.5</td>
<td>683</td>
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<td>86.7</td>
<td>473</td>
<td>74.1</td>
<td>72.5</td>
<td>433</td>
<td>63.4</td>
<td>58.8</td>
<td>339</td>
</tr>
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LIST OF REFERENCES


