A Comparison of Biodiesel Processes for the Conversion of Jatropha Curcas

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ABSTRACT

With the reserves of fossil fuel declining worldwide, interest has been revived in search of alternative energy sources and in developing cost effective processes. Jatropha Curcas is a plant that has the capability of growing in harsh tropical climates, and is a good renewable source for biofuel production for countries such as Haiti. This report analyzes different biofuel production processes that have been developed and that can convert Jatropha Curcas into biodiesel usable in transportation. From the comparison of processes on a basis of energy consumption, yield and cost of the processes, the viability of one of these biodiesel production methods to be introduced in the Haitian community was established.

ACKNOWLEDGEMENTS

Contents

INTRODUCTION

As countries grow and become more industrialized their energy needs grow with them. One of the most readily available and economical sources of energy is fossil fuels. While abundant and inexpensive, fossil fuels are a finite source of energy that some estimates state will last only 40 more years [1]. In addition, combustion of fossil fuels produces harmful pollutants that are exhausted into the atmosphere. Many of these pollutants contribute to detrimental phenomenon such as acid rain and health problems which are caused respectively by an increased amount of sulfur emissions and smog production [2]. Although, global climate change from increased green house gas emissions remains one of the most prominent debatable issues today, the concentration of CO_2 in the atmosphere has almost doubled in the last 60 years, see Figure 1. This recent controversy has sparked more research in alternative and renewable energy sources [3].
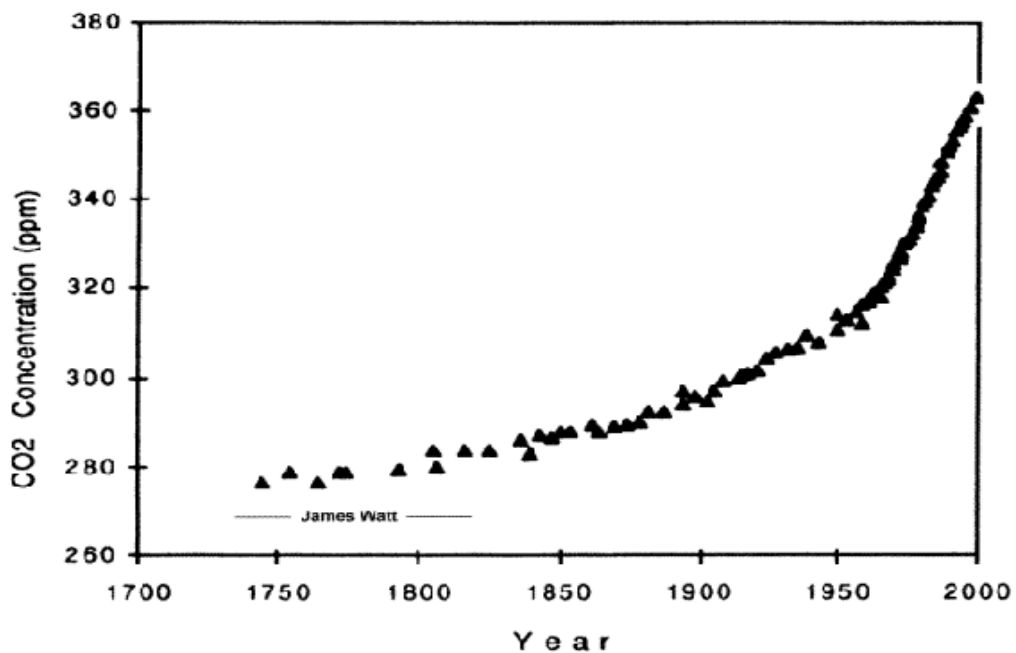
Figure 1: Concentration of Carbon Dioxide in ice cores taken in Antarctica[3]

Clean Energy can be generated from many sources; solar power collects radiation from the sun and converts it directly into electricity, wind power uses moving air masses to drive large propellers on electric generators, and hydroelectric power uses moving water to drive turbines. Another alternative has been the replacement of gasoline and diesel fuels with biofuels derived from plants. Some examples of biofuels are pyrolysis oil and methyl esters, commonly known as biodiesel. Biodiesel is combustible liquid fuel similar in properties to regular petroleum diesel. Biodiesel is produced from oils derived from plants such as coconut, soybeans, and more recently, Jatropha Curcas. Pyrolysis oil is similar to regular petroleum crude oil and is produced by thermally decomposing carbon feedstocks like corn stover, switchgrass, or Jatropha Curcas. Through past research and experience, biofuel has been proven a viable substitute for standard diesel fuel in motor vehicle engines and other machines due to a cleaner burn and its renewable sources [4].

Some agricultural societies have benefited politically, economically, and socially from the exploitation of biofuels. In Malaysia, an estimated 500,000 jobs associated with the production of palm oil for biodiesel were created. Meanwhile, it generated a taxable domestic product that lowered the dependency on foreign oil. This led to an overall strengthening of their economy and government [5]. Haiti, a predominantly agricultural society, could potentially reap the same benefits given that 66% of the employed population works in the agricultural sector; see Figure 2. With only one third of the nation's population engaged in formal employment [6], large biofuel production industries could create local jobs while lowering Haiti's reliance on imported foreign oil in the same way as in Malaysia.
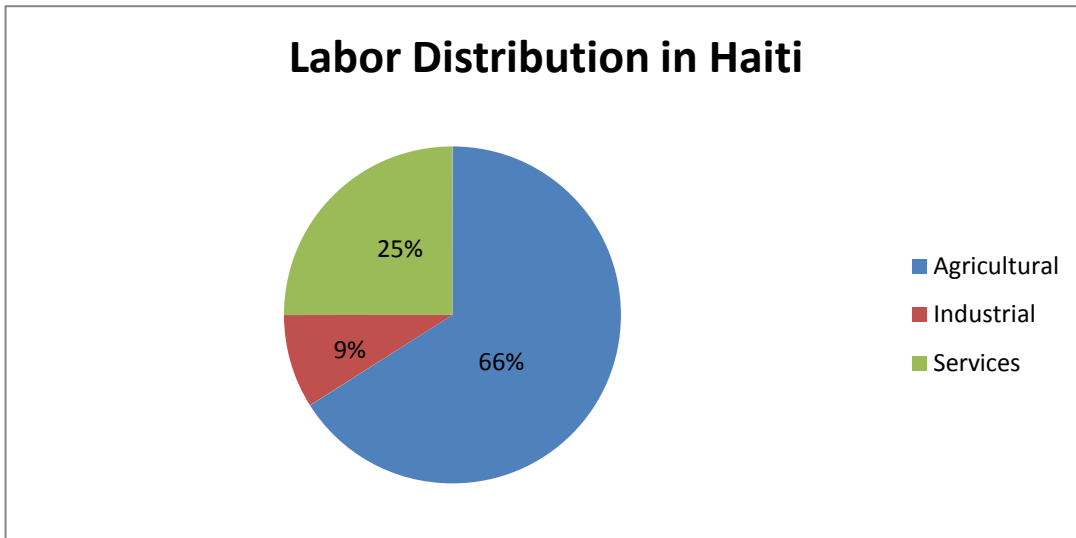
Figure 2: Distribution of the labor force by occupation in Haiti [6]

Jatropha Curcas offers many qualities that make it both a good biofuel source and a beneficial business venture for Haiti. One interesting quality is that Jatropha is toxic to most mammals; this means that it would not be eaten by local wildlife or used as a food source, allowing it to be used solely in oil production. Also, Jatropha grows best in warm, rainy climates and in Haiti the temperature is 60° F in the winter and 80° F in the summer, while the rainfall is about 55 inches annually [7]. The Jatropha Curcas plant has also been shown to slow or prevent land erosion which would benefit Haiti as much of its land has been affected by deforestation. In the 1920s, approximately 60% of Haiti was forested while today less than 2% of the country remains forested [8]. Since this has led to a loss of arable land, perhaps the best quality of Jatropha is its ability to grow in lands that are not suitable for other crops. Since about 60% of Haiti's land is not agriculturally profitable, Jatropha would allow a large portion of land to become economically viable through the production of biofuels.

One of the most widely used processes to produce biodiesel is batch transesterification. Its popularity is due to its low start up cost and ability to be used on a small scale. On the other hand, batch transesterification is slower than some newer and more innovative processes. A variation of batch

3

transesterification uses supercritical methanol to accelerate the reaction. Fast pyrolysis is a process that submits carbon-based feedstocks to a series of extreme conditions of temperature and pressure. This process mimics the natural way that oil was produced beneath the surface of the earth over thousands of years [9].

This report analyzes the standard batch transesterification using Jatropha oil at low temperature and transesterification using methanol at a supercritical temperature and pressure, and compares them to the thermal process of Pyrolysis followed by Hydrotreatment. The comparison is on a basis of the following parameters: yield, energy requirements, reaction time, raw materials, capital and operating costs of production. The results were obtained using a computer simulation called ASPEN PLUS to model of all the processes and through comparison of literature results. A cost analysis was done using current major studies to provide perspectives on the feasibility of large scale production in a country like Haiti.

In order to achieve these goals, computer simulations were carried out in a computer laboratory in Goddard Hall. The results were compared to past research while analyzing the best option for biofuel production from Jatropha Curcas in Haiti.

BACKGROUND

In the following section, we will present the energy situation of Haiti and examine one of the alternatives for the oil dependency which is biodiesel from the Jatropha plant. We will then establish some processes used to make the biodiesel from the seeds of the plant which in turn will set the ground for the evaluations of these processes.

HAITI ENERGY EVALUATION

In 2005, Haiti imported approximately 11,840 barrels of oil per day (B/day) while the consumption was estimated to be above 12,000 B/day[6], and it is paid for by a majority of the country's income[10]. The Illinois Sustainable Technology center has broken down the energy consumption of Haiti, see figure 3.
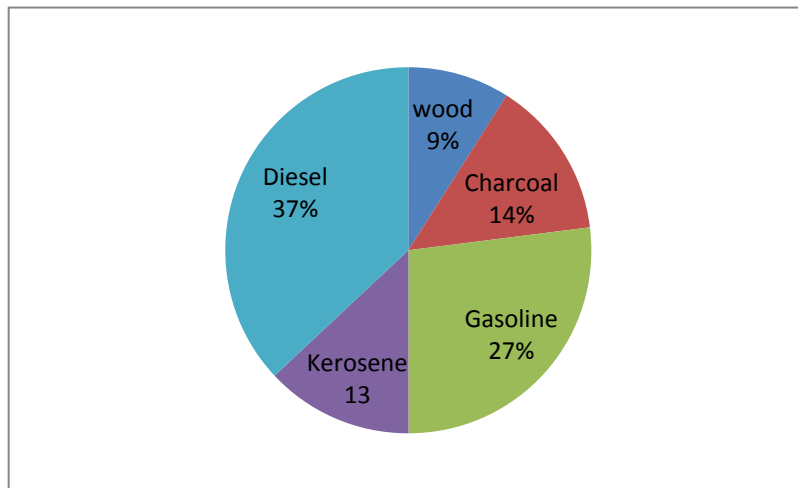

Figure 3: Energy sources in Haiti [11]

In recent years, gasoline prices in Haiti have been approximately 5 US dollars per gallon [11]. These facts show that the energy consumption of the country is neither economical nor profitable. Because of this, there has been increased interest in developing alternative sources of energy for the

Haitian people. There has been research to locally produce biodiesel, diesel fuel obtained from plants

that could potentially replace the imported diesel fuel used for transportation and electricity generation.

JATROPHA

Jatropha biodiesel

Unlike ethanol, biodiesel could be used pure in a diesel engine once it meets ASTM diesel

criteria. Although, due to biodiesel's solvent properties, some parts such as hoses, valves and gaskets

within a diesel engine may have to be replaced for those made of a different material [12]. The quality of

Jatropha biodiesel surpasses that of petroleum diesel on several levels. For instance, the Cetane

number, which is the measure of combustion quality, is 52 for Jatropha biodiesel and 47.5 for petroleum

diesel. Jatropha biodiesel also has a higher ignition point which is good for transportation safety. To

appreciate the quality of this alternative, a more thorough comparison between Jatropha diesel,

petroleum diesel and the established norms for diesel fuels can be seen in table 1.

Table 1: Comparison of biodiesel quality against diesel standards[13][14]

	Standard for ester fuel	Petroleum biodiesel	Jatropha Biodiesel
Density (g/ml)	>0.8	0.85	0.88
Flash point (^{o}C)	>55	55	192
Cetane number	>48	47.5	57
Carbon residue	<0.1	0.35	0.024
Sulfur Content	<0.55	0.5	0

The Jatropha plant is a relatively new crop to the biodiesel market and various sources have

reported different yields of fuel per hectare, depending on the extent of irrigation of the area. For the

purpose of this analysis, the lowest recorded yield, 375 gal/ha and the average value of 499 gal/ha were

used. Haiti's reported 2005 oil consumption estimate of 12,000 B/day is 57.8% diesel. When considering

a 375 gal/ha yield it would take 2094.2 km^2 of land to satisfy the diesel needs of the country. For 499

gal/ha, the land needed is 1573.8 km^2. In the 1980's the United States Department of Agriculture

evaluated that 11.3 percent or 3114 km^2 of land in Haiti was used for crops and close to 50 percent of

that land, or about 1567 km^2, is situated on steep slopes that are vulnerable to soil erosion [15]. If

Jatropha were planted on all of the steep, vulnerable lands, enough oil could be produced to satisfy

Haiti's diesel fuel needs. Growing Jatropha on these highlands would help in the reduction of soil

erosion and make these lands more profitable.

The Jatropha Plant

In Haiti, Jatropha is considered a viable biodiesel raw material because of its low cost of

production and its effects on society and the environment. However, Jatropha has not been recently

discovered. Its oil has been used since 1930s in parts of Africa, including Mali and Egypt where

shipments were made to France for use as fuel for cooking. More recently, the oil from the plant has

been used for electricity production by mixing Jatropha oil with Petroleum and pure vegetable oil. It has

also been used in soap production [16] and for many years as a source of medicine for diseases such as

cancer. It is also believed that the bark of the plant prevents the reoccurrence of cancer after it has gone

into remission [17].

The plant also produces several useful byproducts. For example, the pruned branches are used

for dye production. Once they are cut off from the plant, their bark is scraped off and used for

production of a blue colored dye. The Jatropha oil presscake contains high compositions of nitrogen,

phosphorous and potassium which make it a useful organic fertilizer for the rest of the Jatropha plants.

The seeds of Jatropha have recently been discovered to produce a chemical that can help the human

body repel parasites. This in turn has allowed this product to be used in areas like Brazil as an insecticide

for fumigating houses against household pests such as bedbugs. In other parts of the world, it has been used for fish nets and lines [17].

Jatropha as a biodiesel crop

The Jatropha plant is native in most tropical parts of the world including Central America, India and Africa. The plant is resistant to drought and pests, and it produces seeds that contain about 27-40% oil [18]. Additionally when compared to other oil producing crops, Jatropha offers certain advantages:

- It can be cultivated in different types of soil and in areas that have low rainfall.

- When grown, Jatropha will not be disrupted by animal activity, as it is harmful to most animals, although, small insects help in pollinating the female flowers to produce seeds that will be used for oil production.

- It is among the best non-edible seeds that produce high yields of oil, and thus does not compete with the food industry. None of its products are used for human food consumption unlike soybeans and other oil producing crops.

- Growing the Jatropha plant reduces the amount of carbon dioxide that is in the atmosphere. Since it grows much faster than other bushes, carbon dioxide is removed from the atmosphere in larger quantities. "1 acre of Jatropha plantation absorbs and reduces 500 kg of CO_2 every year. A 1 hectare plantation (2500 plants) will reduce the CO_2 in the atmosphere by 20 tons yearly for 40 years" [19].

- After pressing the seeds to extract the oil, the presscake, which is 65% of the seed, can be burned and used to produce methane which could replace the wood or kerosene that are commonly used in cooking in Haiti [19].

Growing Conditions

The Jatropha plant requires 4 to 5 yrs to fully develop into an adult bush, but can start producing seeds for oil in the first 2 yrs of cultivation if the plantations are well irrigated. It grows well in poor soil, thus establishing its existence in sub-Saharan parts of Africa that don't receive adequate amounts of rain. The plant can withstand drought for three consecutive years and will still produce seeds. Without special care and attendance, a Jatropha plant can last for an average of 25 years, but with care it can last for over 40 years producing seeds and, in turn, oil for biodiesel [17].

The best Jatropha selection is the Jatropha Curcas. This species is drought resistant and holds well in desert-like ground. However, if planted in irrigated areas or on land with a sufficient amount of rain, the oil yield from the seeds is much higher than when planted in arid conditions.

Yield and water footprint

Jatropha produces about 0.35 to 0.375 gallons of oil per tree every harvest, which is equivalent to an oil content of about 37 wt %. Different parts of the plant have various oil contents. For the seed itself, the oil produced is about 25-30 wt% but if the kernel of the seed is used this oil content would increase to 50-60 wt %. Thus, it would be wise to allow the seeds to ripen in order to let the oil content grow.
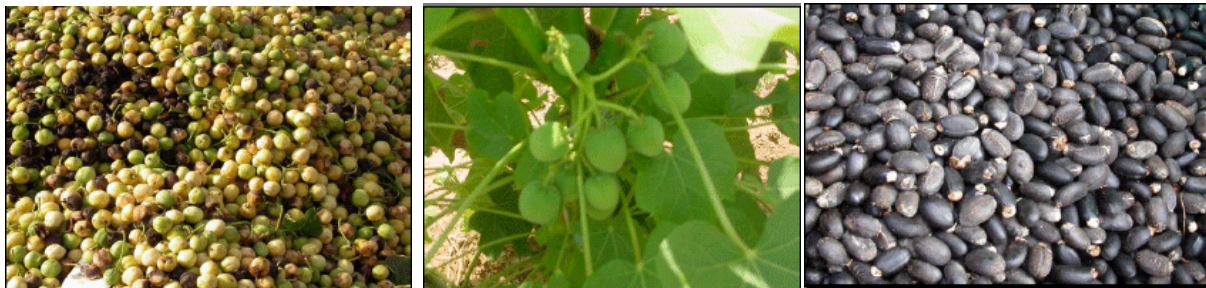

Figure 4: Jatropha ripe fruits, Fruits in the tree and the seeds [17]

When the plant is well irrigated, the amount of oil obtained from each plant increases to about 0.79 to 1.3 gallons. This will be over 375 gallons per hectare of land [17]. Since Jatropha oil is not used for any other human consumption, comparison is made between Jatropha and other edible plants oils that have been tested as biodiesel feedstock Coconut and palm tree. Jatropha 's oil production potential is close to the production value of the others.

Table 2: Oil yield comparison of Jatropha to other edible plants [17][20]

CROP	KG OIL/HA	LITRES OIL/HA
Jatropha	1590	1892
Coconut	2260	2689
Palm Oil	5000	5950

A major controversy in the use of Jatropha as a biodiesel source is its water footprint. Well known professors and scientists such as Gerbens-Leenesa, Arjen Y. Hoekstraa and Theo H. van der Meerb argue that though Jatropha is a viable plant for biodiesel, its water consumption is higher than other competing plants. Jatropha's water footprint is calculated to be 1,400 gallons of water for every gallon of Jatropha oil produced [21]. When compared to sugar beets, a plant that is known for its high consumption of water, Jatropha's water footprint is found to be higher by $92500\frac{gal}{Gj}$. When compared to rapeseed, a plant also favorable for biodiesel production, Jatropha water footprint is higher by $53000\frac{gal}{Gj}$. Still some scientists refute these allegations, because none of the institutions have been able to provide evidentiary calculations to come to these conclusions. Prof. E.N.van Loo and his colleague H.H.G. Savenije strongly contest the methods used for calculation of water footprint for Jatropha. They believe that this method has brought about wrong conclusions and bias to the integrity of this plant. They believe that the water footprint should be calculated by relating "the energy yield of the crop to its actual water use under actual climatic conditions" rather than just depending on precipitation and

irrigation crop water requirements [22]. Compared to the other crops that have been employed to produce oil, Jatropha's research is still at an early stage and since Jatropha has not been properly domesticated and studied the controversy over its water footprint is ongoing.

From fruit to biodiesel

Each Jatropha tree can produce 15 to 20kg of fruits per harvest and can be harvested between 3 to 5 times per year[23]. According to Achten etal it is safe to estimate a yield of 4 to 5 tonnes per hectare[24]. After the harvest, the fruits are sun dried then de-hulled, which removes the seeds protective layer [18]. The seeds are then either solar heated for several hours or roasted for 10 minutes to fluidize the contained oil before the extraction. The oil could be extracted by mechanically pressing the seeds or using a chemical solvent process.

Mechanical extraction

The mechanical extraction that uses a press to squeeze the oil out of a pack of seeds is recommended for plantation sizes smaller than 5,000 hectare, approximately 50 km^2. The seeds are crushed then humidified before being sent into a press that will squeeze the seeds until the oil sieves through. The remaining solid matter is called the presscake and will be processed in another stream where it will be pressed further before being collected and used as a fertilizer. According to the *African Centre for Plant Oil Technology*, three to four kilograms of Jatropha seeds yields one liter of oil and two to three kilograms of valuable presscake rich in Nitrogen and phosphates[25]. A screw press is the machine of choice with a capacity of processing up to 100 tons of seed per day. Some accounts say the mechanical method's limit is in the machine overheating and breaking, and a lower oil yield than with other methods. The oil content of the presscake is around 12-15 wt %.[14]

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┌─────────────┐     ┌─────────────┐     ┌─────────────┐     ┌─────────────┐
│ Separation  │     │ Seeds are   │     │ Press of    │     │ Presscake   │
│ of seed and │ ──▶ │ heated      │ ──▶ │ crushed     │ ──▶ │ repressed   │ ──▶
│ dried skin  │     │ crushed and │     │ seeds       │     │             │
│             │     │ humidified  │     │             │     │             │
└─────────────┘     └─────────────┘     └─────────────┘     └─────────────┘
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                                                           │ Oil to biodiesel│
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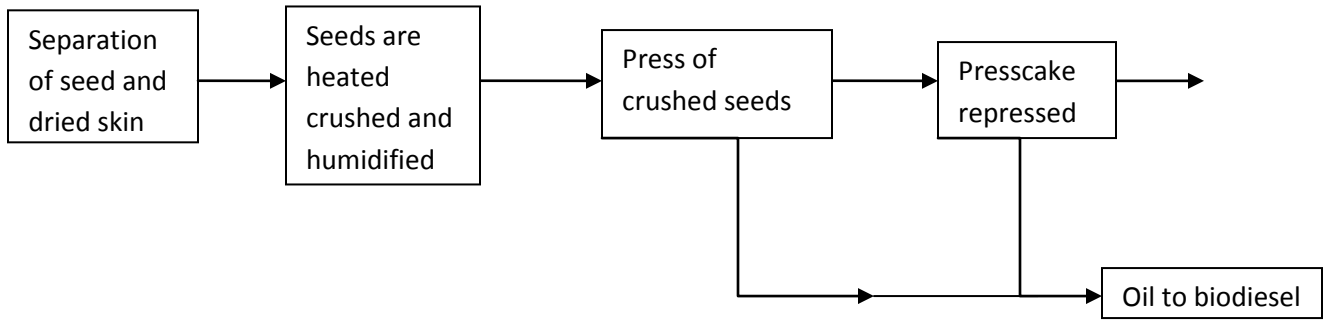
Solvent extraction

For solvent extraction, the seeds would be pressed as well but the presscake that still contains around 15% of oil would be treated with a solvent [26]. The final treated presscake would have a residual oil content of less than one percent when the mechanical extraction allows higher than 4% to remain in the presscake. The solvent of choice for Jatropha oil has been determined to be hexane because of the high solubility of oils and fats in it [27].Even though the solvent extraction is the most efficient and preferred form of oil extraction, it adds one more step of product preparation before the biodiesel conversion; the separation of Hexane and oil through distillation is easily done downstream, because hexane evaporates at a very low boiling point. For these reasons, it is used on plantations that are larger than 50 km^2.

BIODIESEL PRODUCTION PROCESSES

Batch Transesterification

The most widely used process to produce biodiesel is batch transesterification. Transesterification is the reaction of alcohol and triglycerides to form the methyl esters that are used as the biodiesel, and a byproduct of glycerol.
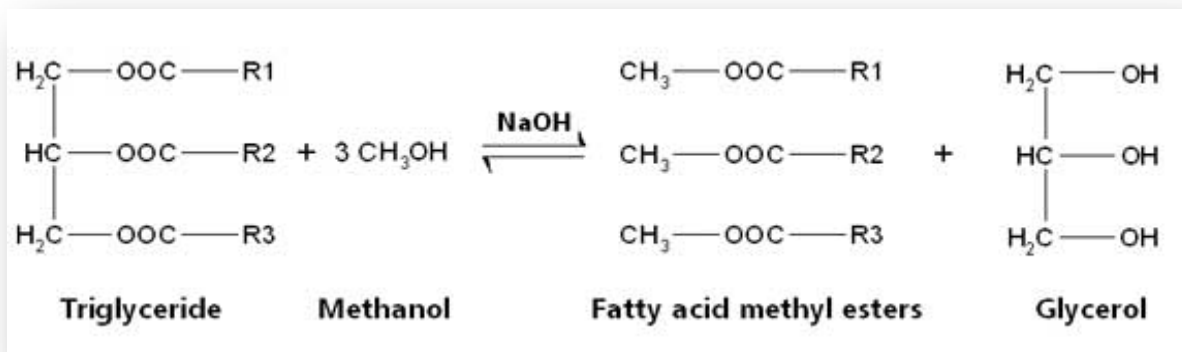
The incoming oil is filtered to remove any solids while the levels of free fatty acids and water are monitored. Free fatty acids are unbound hydrocarbon chains with a –COOH group on one end. First, the oil is pumped into a reaction vessel. Next, the catalyst, usually lye (NaOH), is mixed with the alcohol, usually methanol, to form sodium methoxide that is charged into the closed reaction vessel with the oil. The system from here on is totally closed to the atmosphere to prevent the loss of alcohol through evaporation. The vessel is stirred with an impeller while being heated to temperatures of $55^{\circ} - 70^{\circ}$ C in order to speed the reaction. After 1 -4 hours of reaction, the liquid phases are separated [29]. The two preferred methods to separate the methyl esters from the other byproducts are decanting or centrifuging. When decanting, the heavier glycerol is allowed to settle and will sink to the bottom where it can be drawn off along with the residual catalyst. To accelerate the rate of separation of the liquid phases, a centrifuge can be used for high volume processes. The glycerol byproduct is treated to remove the unused catalyst and excess free fatty acids. The glycerol is stored to be sold to other industries.

After the separation, the methyl esters are distilled to remove the unreacted alcohol which is collected to be recycled back into the methoxide feed. The biodiesel is then washed, generally with warm water, to remove any residual impurities and unused catalyst. Another method to purify the biodiesel is to use a dry wash system that consists of a packed column of magnesium silicate powders or

13

some sort of resin[30]. The dry wash can be done continuously to reduce production time. A schematic

diagram of the process can be seen in Figure 5.
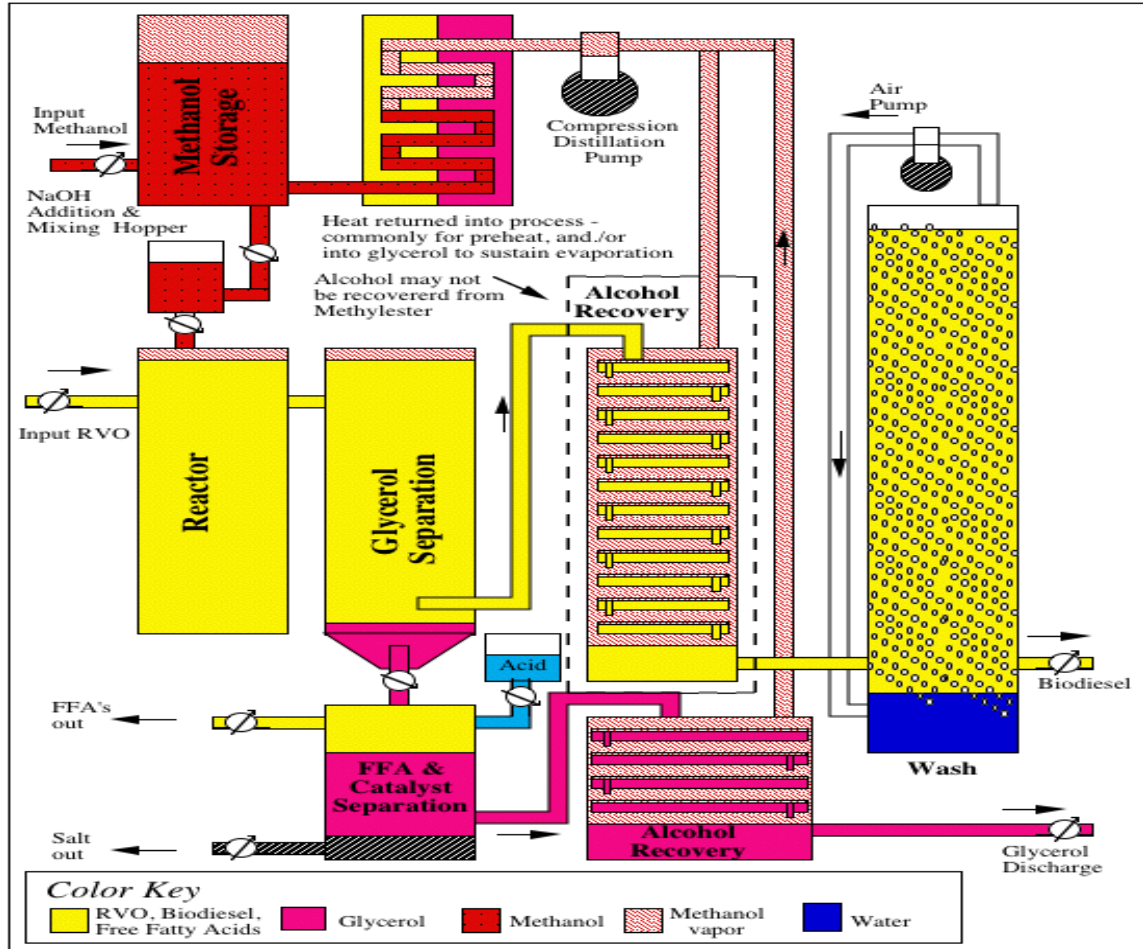
Figure 4: Schematic of a batch process

Supercritical Methanol Transesterification

The supercritical methanol method has the same basic principles as batch transesterification.

The reaction is methanol and triglycerides combine to form methyl esters. There are two main

differences with this process and the standard batch process. First, the methanol being used is at a high

enough temperature and pressure that it is considered supercritical, a state where it is neither liquid nor

gas but retains properties of both. For methanol, the critical temperature and pressure are 240 $^{\circ}$C and

1140 PSI (7-8 MPa) respectively. One of the main advantages is that this process is faster than the normal batch transesterification. It is able to react similar amounts of oil as the standard batch process in as little as 6 minutes. Another advantage to using supercritical methanol is that the reaction is completely spontaneous, meaning no catalyst is needed. A third advantage is that this process is much more tolerable of excess water and free fatty acids in the feedstock. That means that the supercritical process can accept and successfully react a much wider range of feedstock since the quality does not need to be as high [31].

Pyrolysis

The direct use of vegetable oil as transportation fuel is impeded by several undesirable properties of those oils. This includes the absence of aromatics when diesel fuel has between 20-40% and a lower energy/volume burning capacity of 20MJ/L when diesel releases 40MJ/L.

Pyrolysis is the thermal decomposition and transformation of a compound in an oxygen free environment and at high temperatures from as low as 170^oC for things like sugars to as high as 2000^oC for making coke used in metallurgy. In the case of vegetable oil, the triglycerides are cracked because the average length of the molecular chains is of 57 carbon groups and for diesel that acceptable number usually goes from 4 to 25. A study from the Chemistry Institute of the University of Brazil reports that the pyrolysis of palm, castor and soybean oils was conducted and produced a diesel-like fuel [32]. In 2003 Ozlem Onay et al. found a gas-swept fixed-bed tubular reactor, when fed with ground rapeseed gave a diesel like oil as well.

However, due to the variety of results possible, and the ASTM standard for diesel components, the pyrolysis oil cannot directly substitute diesel fuel. One of the primary issues with the pyrolysis oil, often referred to as bio-oil, is the amount of oxygenates which makes the mixture acidic and unstable. There have been processes to upgrade the bio-oil by converting the undesired components. The two

main ones we have analyzed are catalytic cracking using an aluminosilicate zeolite HZSM5 and

Hytrotreatment HDO.
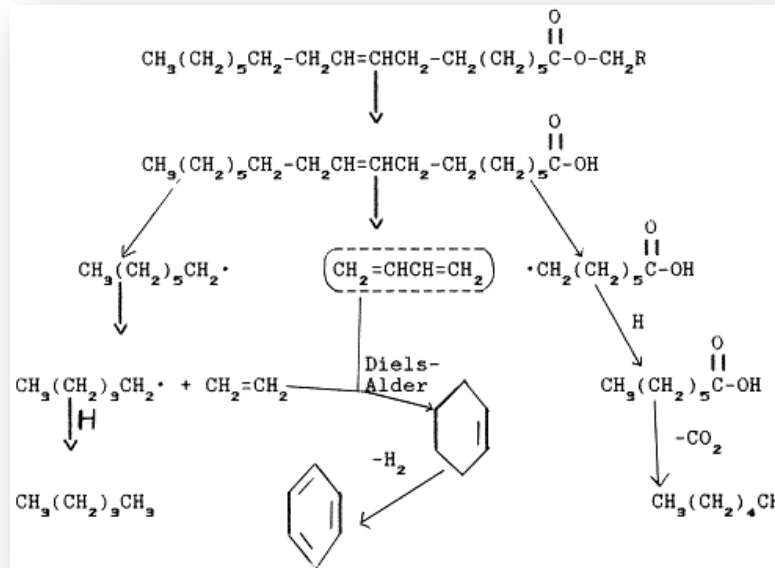
Figure 6 Thermal decomposition Mechanism [33]

Several studies on the thermal decomposition of triglycerides have shown that the

decomposition of the protein is done via many mechanisms to yield a variety of components. Due to

the fact that vegetable oils have both saturated and unsaturated chains of molecules, the

decomposition of triglycerides can yield to the formation of aromatics, hydrocarbons and carboxylic

acids, as shown in figure 4. In the case of Jatropha oil, there are several double bonds, approximately

two per branch. The acidity of the product is to be corrected, because it could react with the interior of

the car fueling system, rapidly damaging the engine. In Wisniewski et al. a standard of gasoline

composition can be compared with the biodiesel product.

There have been several types of reactors for the pyrolysis however the "circulating fluidized

bed CFB" reactor is the one that has been scaled up to tens of tons per day of feedstock throughput[34].

Hot sand is conveyed by compressed air from a heater to a chamber where it is mixed with fluidized dry grinded pieces of biomass. A gaseous mixture of evaporated oil, flue gas and water as well as ash and sand are then conveyed to a cyclone that recuperates the sand and ash particles. The gases are then condensed and separated into incondensable gases and the oil. The incondensable gases that include a significant amount of carbon monoxide, carbon dioxide, propylene, and hydrogen are partially used as fluidizing gas and recycled as fuel gas for the sand heater. The condensed oil represents between 70 to 76% wt of dried inlet biomass and is moved to the next treatment step of the process.

Catalytic cracking

HZSM-5 zeolites are crystalline aluminosilicates, rich in silica used for their catalytic character. Their high thermal stability and their acidity allow them to react with oxygenated compounds to form hydrocarbons, aromatics and gasoline like products effectively [35]. Structurally, they are networks of tetrahedra of silica and aluminum linked together by shared oxygen atoms. It has been proven that the selectivity of the catalyst is dependent both on the product and on the shape. In a study by Adjahe and Bakshi, HZSM-5 was found to have a good catalyst effectiveness ($\frac{1}{Yield * Selectivity}$) in conversion of bio-oil to hydrocarbons, aromatics and in minimal coke formation [36].

One pyrolysis was conducted using tires as feedstock and showed that HZSM-5 increased the overall yield of gases and favored the formation of tar with the hydrocarbon formation lower to the non-catalytic simulation. Martin Olazar et al. reported 18% wt of organic liquid which is about half of the yield without a catalyst [37]. However the oxygen content was significantly lower- from 36% without the catalyst to 18% with HZSM-5.

Hydrotreating

Presently, the most effective way to remove the excess oxygen from the pyrolysis oil is a process called hydrotreating which is a high pressure hydrogenation treatment for the oxygen rich bio-oil. The

oil is put through a packed-bed catalytic reactor operating at high pressures and temperatures where the hydrogen reacts with the oxygen to form water. There are several different catalysts that can assist this process; the most common ones are made of a Ni/Mo silica [38]. Some of these newer catalysts are able to lower the amount of organic acids, aldehydes, ketones, and ethers, and raise the amounts of the desired products: phenolics, aromatics, and alkanes.
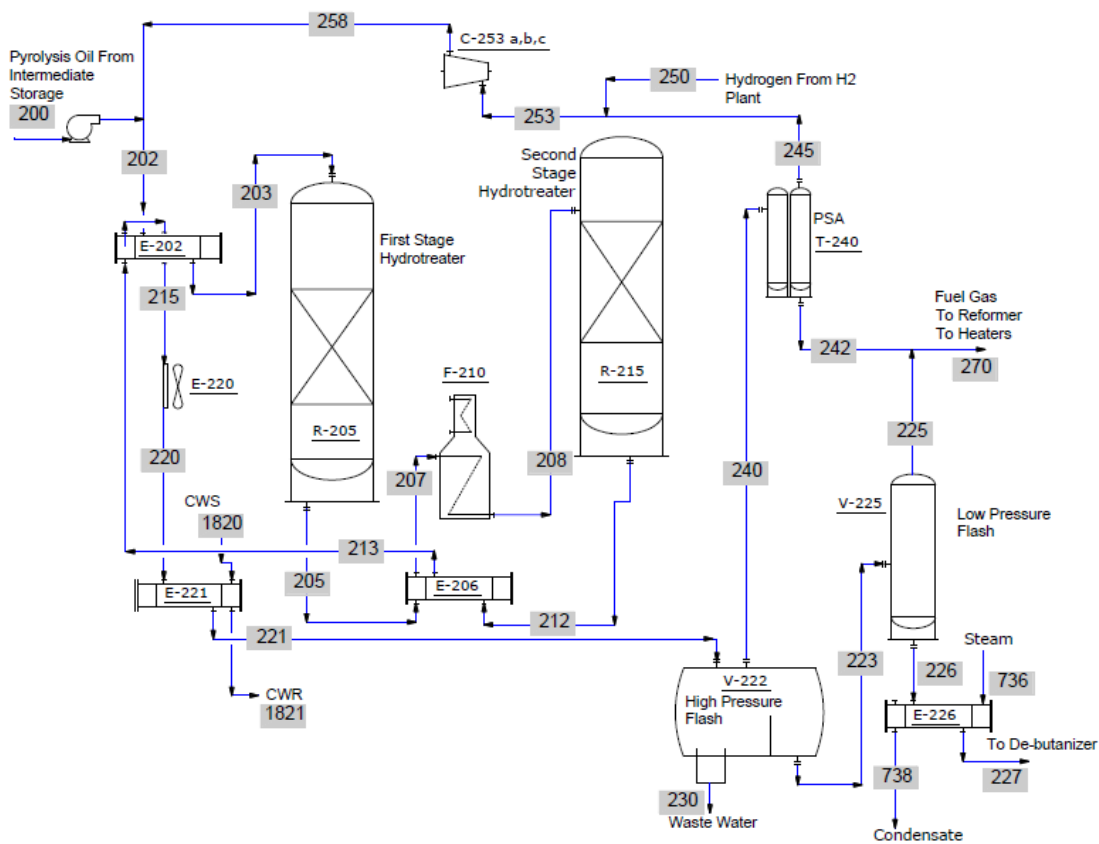
Figure 7: A detailed PFD of a hydrotreatment process[39]

Mild-hydrotreating allows the removal of O2 in the pyrolysis oil which then can be used as crude oil to be refined into gas and diesel, while using less hydrogen to help keep costs down. Heavy duty pumps are needed to boost the oil and hydrogen to high pressures, while heat exchangers and furnaces

are needed to raise it to high temperatures. Then, the deoxygenated oil passes through two flash stages to remove the fuel gases and excess carbon dioxide. The fuel gas is sent to the steam reformer unit to produce more Hydrogen [39].

METHODOLOGY

The goal of this study was to compare standard transesterification, supercritical transesterification and pyrolysis on a basis of energy consumption/efficiency, yield, capital and operating costs and quality of the out coming fuel. For the transesterification processes, Aspen was used to simulate the reaction in a batch setting. For the pyrolysis process, information was gathered from major works including a wood pyrolysis design case submitted to the US Department of Energy [39]. From the results of the simulations and research, the processes were compared to each other in a decision matrix in order to get an appreciation of their different parameters.

Transesterification using Aspen

The Aspen simulation for the transesterification was done using R-batch reactor. Table 3 shows

Table 3: Input in ASPEN for transesterification

Components	Triolein, Methyl ester named Methyl Oleate, glycerol, water
Property model	RK-Soave
Input stream	25^oC, methanol and triolein ratio varied
Reactor	Constant temperature
	Stop criteria :0.95 conversion of triolein
Reaction	1 triolein+3 methanol→3 FAME + 1 glycerol
	Pre-exponential factor k_o=2.2*10^6
	Activation Energy E= 85kj/mol

From the MSDS of Jatropha Oil, triolein was determined to be the main triglyceride which is why its transesterification was closely analyzed. The pre-exponential factor and the Activation Energy values were found in a study of the kinetics of triolein transesterification from the Chemical Engineering Department of Tsinghua University in China [40].

For the purpose of the simulation the catalyst was left out of the chemical equation. As for supercritical and subcritical transesterification, the main difference was temperature.

Heat Balance

In order to calculate the heat balance for the respective processes it was assumed that the separation stages would have similar heat duties in all processes and therefore the energy balance was focused around the reactor. The general balance equation used allowed for the calculation of total heat input required for the reaction or for the heat loss.

$$Hin + Hgen = Hout + Hused + Hloss$$

Transesterification

H_{loss} was attributed to conduction through the stainless steel reactor shell with an overall heat transfer coefficient:
$$U = \frac{\Delta H}{\Delta T * A} = 14.4 \frac{W}{m^2.k}$$

H_{used} was the energy used to heat up the oil from an initial temperature of 25 degrees to the reaction temperature of 70^0C for normal transesterification and 250^0C for super critical transesterification. H_{used} also considered the amount of heat needed to drive the reaction. This required the calculation for C_p, the specific heat of triglycerides by using the following Rowlinson-Bondi equation for vegetable oils [41].

$$C^{\circ}_{p\ triolein} = \int a + bT + cT^2 + dT^3$$

$$C^{\circ}_{pTriolein} = aT + \frac{bT^2}{2} + \frac{cT^3}{3} + \frac{dT^4}{4}$$

$$mC_p(T) = \Delta H$$

Pyrolysis and Hydrotreatment

For the Pyrolysis and Hydrotreatment processes, the heat balance was done around each individual reactor. The heat duties of each stream H_{in}, H_{out} as well as H_{gen}, which was the heat duty of the furnace, were all found in the appendix PFD stream sheets resulting from the Aspen simulation of the process found in the Design case of "Gasoline and Diesel Production Through Pyrolysis" [39]. Several assumptions were made for the heat calculations:

- The similarity between Canola oil (from rapeseed) and Jatropha oil was noticed. The literature on the pyrolysis of rapeseed confirmed the feasibility of the process for crushed seeds [42]. With a similarity in seed oil composition between rapeseed and jatropha- approximately 40%wt of oil in both seeds [32] the composition of the rest of the fruit was assumed to be 16% cellulose 22% protein and 22% hemicelluloses and lignin.

- To calculate the heat used to raise the temperature of the mixture from 66° C to 500° C, the average specific heat c_p for triglycerides was found to be $1800 \frac{J}{kg\ C}$ and for molasses the value was found to be $2512 \frac{J}{kg\ C}$.

$$H_{used} = (M_{oil}\, cp_{\ oil} + M_{Molasse}\, cp_{Molasse})\, \Delta T$$

Therefore, the Heat loss was calculated as the Heat remaining after the balance.

For the Hydrotreating process, the balance differed by the importance of the heat of reaction.

$$\Delta H_{f\ products} - \Delta H_{f\ reactants} = \Delta H_{reaction}$$

	Amount used(lbs/hr)	ΔH_f(kJ/mol)
Lignin	64000	-1092
Cellaboise	23000	-2226
Furfural	12000	-151
Acetic Acid	8000	-483
Hydrogen		

Product	Amount created(lbs/hr)	ΔH_f(kJ/mol)
Water	40000	-241
Carbon Dioxide	9000	-393.5
Methane	3000	-74.9
Ethane	2000	-83.8
Propane	1500	-104.7
Butane	1500	-125.6
2-5Xylenol	8000	-237
Heptane	3000	-187
Cyclohexane	10000	-156
Cis-Decalin	3000	-207
Biphenyl	4000	-182
Diamantane	9000	-193
Phenanthrene	6000	-201
Chrysene	6000	-152

ΔH_f for cellabiose came from sucrose, a similar molecule in size, shape and chemical make up.

In addition to the heat of reaction, the heat of vaporization was calculated because of the amount of water formed during hydrogenation. The Heat of vaporization of water at temperatures of 240 and 371 degrees Celsius were 13650BTU/lb.mol and 7868 BTU/lb.mol, respectively. The total heat used for the vaporization of water was given by $M_{water} * H_{vap}$.

Comparison of Processes

After analyzing each of the parameters for the comparison, the importance of the parameter was rated on a scale from 1 to 10 and it was later determined how well each process performed on that scale. The weights for each parameter were determined by team members brainstorming for educated, reasoned judgments. For each parameter a maximum score of 10 was possible, meaning the parameter would be very important . For example, capital cost was assigned a score of 8.5 which means that it is important, but not as critical as the yearly operating cost a recurring cost which was assigned a 10. The same reasoning was applied to determining the weight of the other parameters. Table 4, shown below, will help to visualize the comparisons made later for the various parameters.

Table 6 Matrix table for comparison of processes

	Wt	Transesterification subcritical	Transesterification supercritical	Pyrolysis + Hydrotreating
Wt % yield of biofuel	5			
Energy used(MMBTU/hr)	5			
Utilities MM$/yr	5			
Speed of reactions	4			
Complexity of process	4			
Byproducts	4			
Capital cost	8.5			
Operating cost $MM	10			
Total RM cost	7			
Total	52.5			

The performance of the process for the corresponding parameter was rated from 0 to 1, 1 being the ideal condition. This value was also determined from reasoning of the team.

Although the results might be considered subjective, a decision matrix is used in industry to evaluate and compare multiple processes, or factors, taking into account a variety of pros and cons. We also note that this process was applied consistently to each of the three processes. This is why this method was used in this case.

The economical values that were entered in the comparison sub-section of the results are a combination of three major papers: the Design Case by PNNL, a Technoeconomic Study of Supercritical Biodiesel production Plant and The Centre for Jatropha Promotion in India.

RESULTS AND ANALYSIS

Transesterification Results

Transesterification results were acquired by running simulations with the program Aspen PLUS. Standard and supercritical transesterification processes were both simulated in order to compare both processes. Data were acquired about how the processes varied by fluctuating the molar ratio, the temperature and the pressure of both systems. By varying these three parameters, an analysis was made to find out how each of the parameters changed the reaction time of the processes, and heat of the process.

In most published papers, such as "Comparing Cost of Biodiesel Production from Transesterification" [43], the authors investigated the effect of varying the operating parameters on the total yield. Significantly, the data recovered from our Aspen Simulations differed greatly from published information due to the fact that for the purpose of the simulation a constant 95% conversion of Triglycerides had to be maintained. This was the only way that significant errors and fatal warnings would not be generated.

Additional assumptions made in the Aspen simulation were that the reactor was completely adiabatic and conversion was constant at 95% of the triglycerides. Perfect mixing within the tank was assumed while pure components were theorized to have been used in the process.

Molar Ratio

Reaction Time

Figure 8 represent a comparison of molar ratio to the reaction time. In both processes, the reaction time decreased as the ratio of methanol to triglyceride increased. At a molar ratio of 5 to 1, the trends that had been similarly linear underwent a significant decrease in reaction time for both the standard and the supercritical transesterifications. In the standard process, the reaction time dropped

by about 10 min while in the supercritical process, the reaction time decreased by about 2 min. By increasing the amount of methanol, the transesterification reaction is accelerated and thus time required to acquire a 95% conversion is lessened.
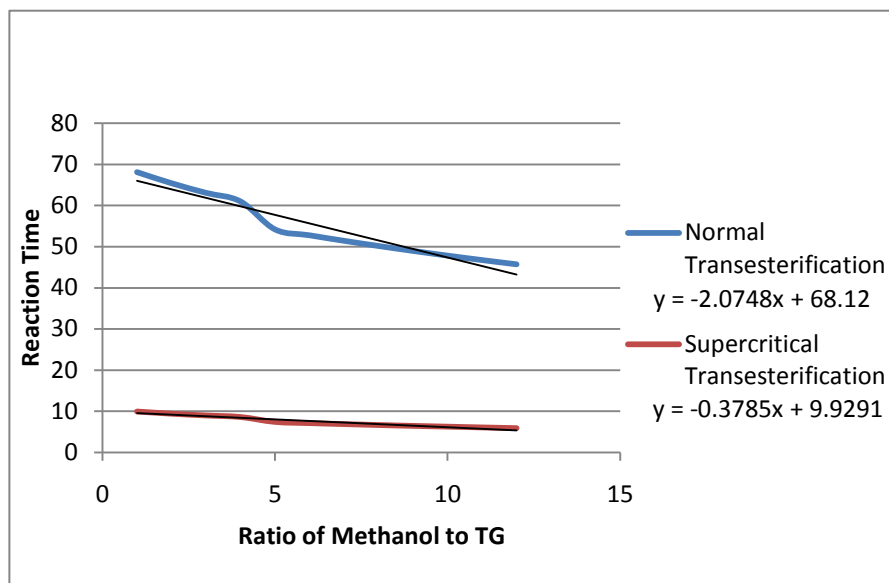

Figure 8: variation of reaction time with changes in molar ratio for standard and supercritical transesterification

Several published journals available today agree that as molar ratio of methanol to oil is increased the reaction time decreases. In "Development of mathematical correlation for the transesterification reaction" [44], the researchers used a real world assumptions and actual reactions and also found that an increase in the molar ratio of methanol to triglycerides from 5:1 to 10:1 resulted in an increase in the yield from 88% to 97 %. "Alternatively as molar ratio increases, reaction time decreases, but higher molar ratio requires higher amount of methanol which reasonably increases the cost of transesterification" [44]. Also, as the methanol is increased, it becomes harder for the methanol to be totally separated from the methyl esters downstream [44].

Heat Load

The molar ratio affects the heat duty in a way similar to the reaction time. The heat duty decreased following the same trend in both processes with a sudden drop at a molar ratio of 5 to 1. It can be noticed in Figure 8, 9, and 10 that the heat load varies in the same trend as the reaction time; this shows the close relationship that reaction time and heat load have in that less time reacting means less heat will be needed

Since increasing the amount of methanol utilized reduces the reaction time, one can infer the system uses less heat to drive the reactions and carry out the transesterification. These results are consistent with reaction kinetics because adding methanol in greater excess allows the triolein to be reacted faster.
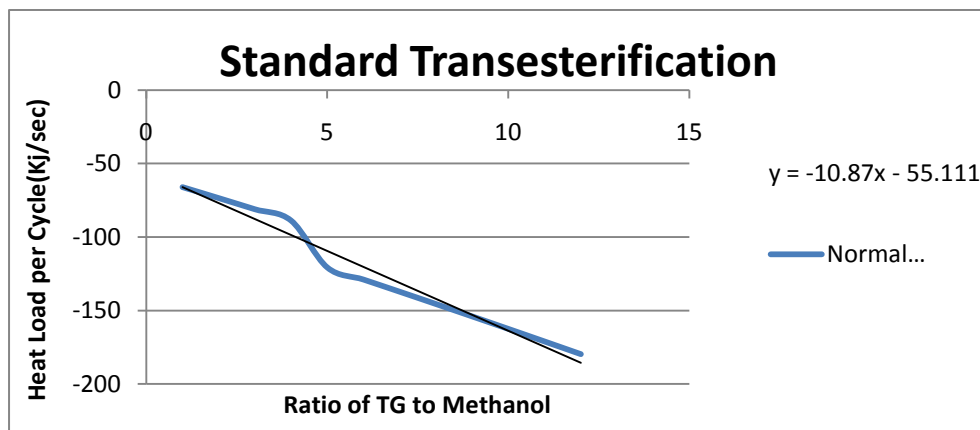

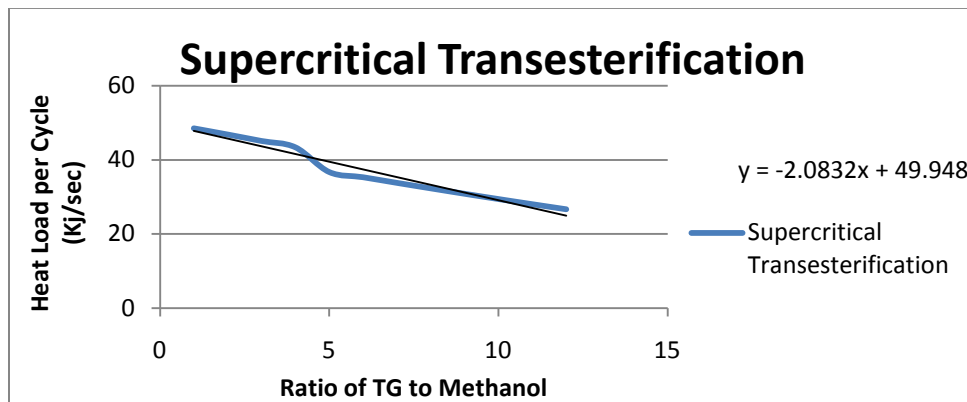Figure 9: Variation of heat load with changes in molar ratio for standard transesterification

Figure 10: Variation of heat load with changes in molar ratio for supercritical transesterification

28

Temperature

Reaction Time

From the Aspen simulation, it resulted that as the reactor temperature increased, the reaction time decreased significantly. Eventually in both cases, it will reach a point that the temperature will increase but the reaction time would approach zero, and thus the reaction will be almost instantaneous. As temperature increases, the time for the reaction to reach a certain conversion decreases, though not as drastically as shown in figure 11. According to data obtained, a 10 degree Celsius increase in temperature more than decreases the reaction time to a 95% conversion by over 50%; in the first 10 degree temperature elevation the time varied from 23 minutes to 8 minutes in supercritical transesterification and from 169min to 84 min for standard transesterification. Another increase of 10 degrees Celsius would bring the standard transesterification reaction time to less than 1 minute, which is neither a realistic nor an achievable result in real world conditions.
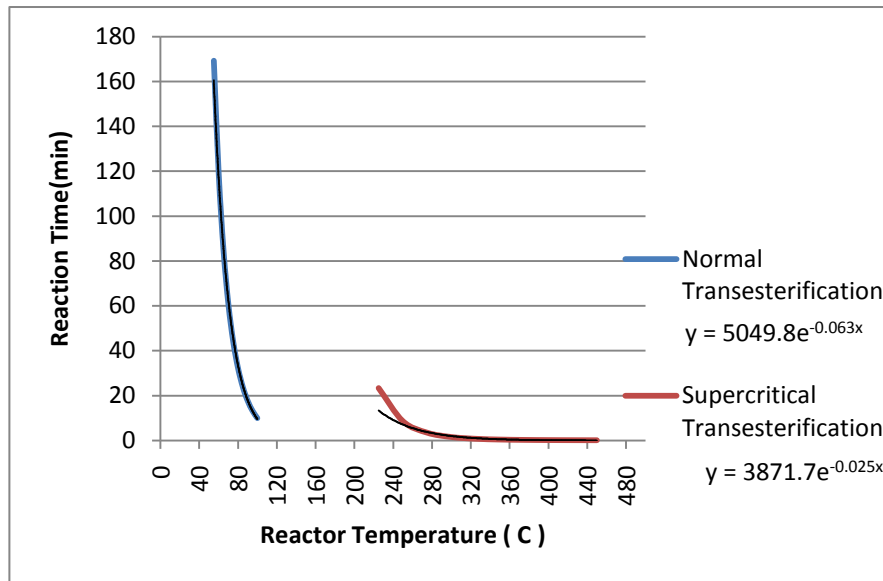
Figure 11: Variation of reaction time with change in the reaction temperature for both standard and supercritical transesterification

Heat Duty

Aspen simulations showed that as the temperature is increased in the transesterification systems, the reaction time decreases while the heat duty increases. Data acquired signifies that the heat duty increases linearly. As reaction time decreases, the time to heat up the reactor decreases, although there is more energy put into the system per time.
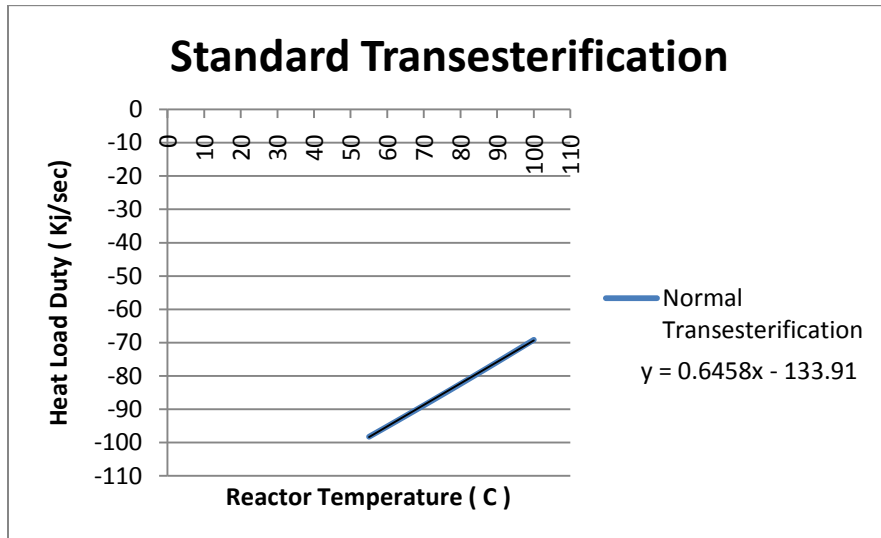
Figure 12: Variation of Heat load with respect to Reactor Temperature
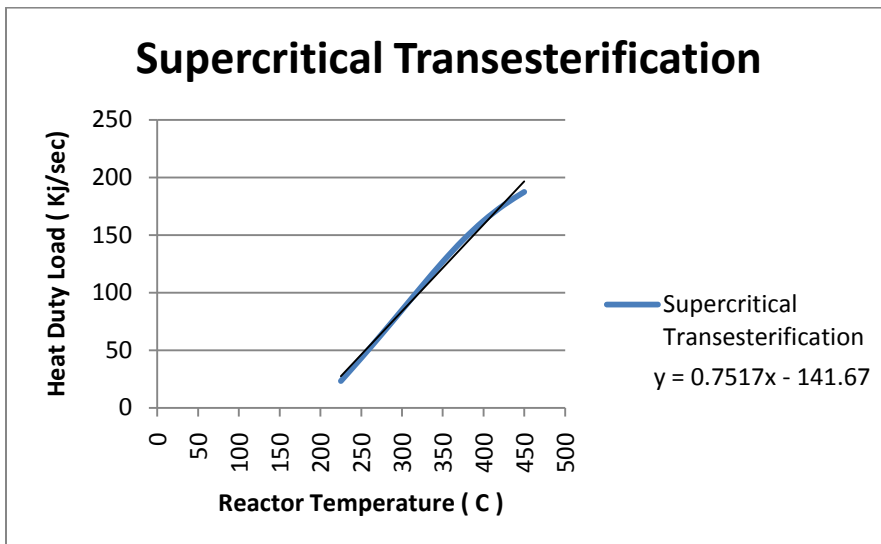
Figure 13: Variation of Heat load with respect to Reactor temperature

Pressure

Reaction Time

As the pressure was varied in the standard transesterification process, the reaction time did not noticeably change. The reaction time dropped from 61.05 min to 60.94 min, a difference of about 0.11 min which is less than a 0.2% decrease.

For supercritical transesterification, varying the pressure had little effect on the reaction time, with a difference of about 0.004 min from the highest reaction time to the lowest. The difference is so small that it can be assumed to have no effect in reaction time. Tang et al in their "Transesterification of the crude *Jatropha curcas* L. oil catalyzed by micro-NaOH in supercritical and subcritical methanol" [40] established that pressure had no significant effect on yield of methyl ester.

Normal Transesterification

$y = 7E\text{-}05x^2 - 0.0052x + 61.039$
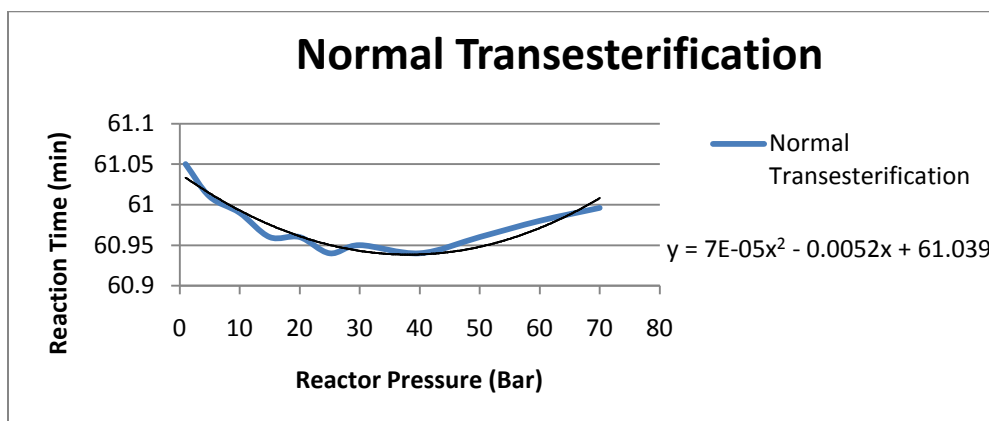
Figure 14: Variation of reaction time with change of pressure in standard transesterification

Supercritical

$y = -0.0001x^2 + 0.0016x + 8.6053$
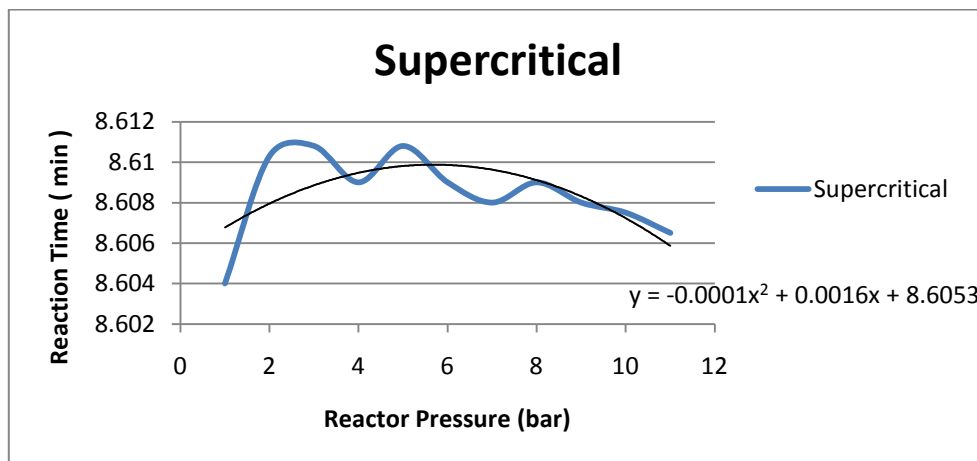
Figure 15: Variation of reaction time with change of pressure in supercritical transesterification process

Pyrolysis results

Results on Composition of bio-oil and Effect of catalyst

As predicted, the pyrolysis oil had a significant variance from the ideal diesel fuel liquid standard. From the pyrolysis of wood, this trend can be observed, where the amount of oxygen detected is around 40% when the acceptable range is below 3 % [16].

The total bio-oil yield of the pyrolysis of a Jatropha Curcas cake was 64wt% in a fluidized bed reactor at $500^{o}C$ using Nitrogen as fluidizing gas with particle diameter of 1mm [45]. For the pyrolysis of wood in the PNNL design, the bio-oil represented 83% of the incoming dried biomass, 20% of which was water. The bio-oil composed of 35-40 wt% of oxygenates with significant amounts of furfural, acetic acid, hydroxyacetone and levoglucosan. The levoglucosan is from the depolymerization of cellulose/hemicellulose which represents more than 50% of wood material. These products would therefore be present in the bio-oil of Jatropha seeds since close to 40% of its weight is composed of hemicelluloses and cellulose.

 In the PNNL experiment, hybrid poplars were used because of their high carbohydrate composition, of more than 70% [46]. In an experiment conducted where the pyrolysis bio-oil from beech wood [47] was followed by a hydrotreatment, showed significant improvement of the bio-oil quality when treated with Ru on carbon catalyst table 7.

Table 7 Chemical composition of different stages of pyrolysis[47]

	Pyrolysis Beech oil	Expected Conversion	HDO Pd-C catalyst	HDO Ru-C catalyst
Acid	8.3	less	7.8	7
Aldehydes	18.7	less	10	4.2
Furans	5.3	less	0.3	0.2
Guaiacol & Syringols	19.7	less	4	1.9
Sugar	21.4	less	0	0
Phenolics	7.4	higher	9.2	15
Alkylbenzenes	1.8	higher	29.5	24.7
Hydrocarbon	0.4	higher	3.3	10.9
Not classified	5.3	less	9.9	9.5

Table 7 demonstrates the improvement in bio-oil oxygenate content when hydrotreated. Generally mild-hydrotreating occurs in several in-line reactors operating at pressures around 100-200 bar and temperatures ranging from 175°C to 400°C [48]. The hydrotreating used in the PNNL industrial model is a two step process in which the bio-oil goes through a hydrogenation at 220^{0}C followed by a decarboxylation at 371^{0}C.

There are several different catalysts that can assist this process, the most common ones are made of a Ni/Mo alumina (Ni-Mo/ Y-Al$_2$O$_3$, 3% NiO, and 15% MoO$_2$) [38]. According to a study by Wildschut, et al, other catalysts such as Ru/C performed better than traditional catalysts, raising yields and allowing for better deoxygenation[48][49]. Table 7 demonstrates catalysts effect on the concentration of both undesired and desired products, all of which affect the fuel's quality and properties.

Effect of operating pressure and temperature

Putun's 1996 studies proved that the hydrogen's pressure impacted the hydrodeoxygenated oil yield and content. A hydrogen input of 15MPA and reaction of 550 degrees gave the best results for that study. PNNL's model had the hydrogen enter at about 15 MPA and in the reactors the highest temperature used is 371^0C. The temperature was chose to be less than 550, because subsequent studies found that the severity of the process, which is the operating temperature, has an effect on the products and byproducts made.

In general a more severe hydrotreatment will give better deoxygenation, but also results in a higher average molecular weight and more residual coke. Ardiyanti, Venderbosch and Heeres found that as the temperature increase or as the space velocity decreased, the oxygen content of the product decreased[48]. While the oxygen content became more favorable, the average molecular weight and the coke residue increased. The optimal operating conditions were found to be at either 350 or 400 degrees Celsius, which allowed for a final oxygen content of 14.2 wt% from an original of 40.1 wt% while keeping the bio oil from polymerizing or excess coke residue to be formed [48].
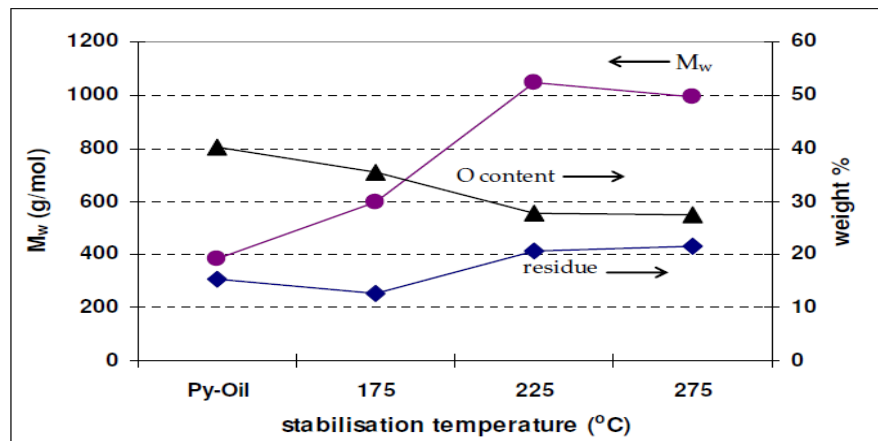
Figure 16 Effect of temperature on oxygen content of bio-oil during hydrotreating [48]

Results of properties at each stages

From a study conducted in the Netherlands in association with BTG, 2 stage hydrotreated oil catalyzed by Ru/C was tested on an engine and showed no sign of corrosion or erosion like the non-treated bio-oil did over a period of 30minute period[50]. This can be explained by the similarity in composition and properties shown by the treated oil to ASTM diesel standards tabulated in Table 8. The second stage oil is the closest to the Diesel fuel properties but still needs improvement. Put table 8 on a single page.

Table 8 Properties of bio-oil and different stages of upgrades [50]

Properties	Diesel	Beech Bio-Oil	HDO1	HDO2
HHV (MJ/kg)	49	15.7	31.8	37.5
LHV (MJ/kg)	46	13.9	30.1	35.6
Density at 20 °C (kg/l)	0.8	1.2	1	0.9
Flash point (°C)	66	40-65	31.1	30.4
Viscosity at 40 °C (mm^2/s)	5.0	33.3-83.3	1000	144.4
Water content (%)	0.007	27.8	4.3	1.6
pH	n.a.	2-3	5	6
Elemental comp. (dry)				
C (%-wt.)	86.4	39.95	71.6	79
H (%-wt.)	13.7	8	7.8	9
N (%-wt.)	0	0.04	0.29	n.a
O (%-wt.)	0	52.05	20.31	12

It is believed that by removing the naphthalene, and butane and refining the crude treated bio-oil in the same manner in which petroleum crude oil is refined, the properties could be further

enhanced[39][50].The viscosity of HDO2 is approximately 33 times higher than that of diesel fuel. It was found that the viscosity of the bio-oil was dependent on the biomass type [51]. From Heeres, the viscosity was found to decrease linearly with decrease of oxygen content lower than 20%.

However, it is important to specify that the scope of the project that resulted in the property table above was to test the different stages of pyrolysis beech oils. The hydrotreatment was done in a batch setting with a reaction time of 3-4hr.

Comparison of Three Processes

Heat Balance

Table 9 Energy balances around the reactors (in MMBTUs)

Processes	Subcritical Trans.	Super critical Trans.	Pyrolysis	HDO
Heat in (MMBTU)	398	1003	6141	494
Heat out			6192	533
Heat generated				+40
Heat of vap	21.26	627	1165	21
Heat of reaction	377	377	46	+77
Heat loss/acc	0.01	0.05	1160	57

The energy balance around the different reactors gave the results tabulated in table 9. From the heat balances, the energy need of each process was identified for processing an equal amount of 183,000 lb/hr dry seeds. Although the numbers for the pyrolysis might seem unfavorable, approximately 5000 MMBTU that are carried by the sand particles will be recycled back from the reactor to heater. The net heat loss comes down to a significant 35 MMBTU, perhaps dissipated during the residence of the sand in the cyclone recovery units. The fuel for the heating unit of the pyrolizer is a byproduct of the reaction. Glushkov V. A. estimated that the gas fuel obtained from the combustion of 1kg of cellulosic matter has a calorific value of 6-9MJ of energy [52]. Considering that the amount of 183,000lb/hr of

plant matter processed, the gas fuel could provide as much as 550 MMBTU of energy per hour significantly decreasing the fuel expenses for the plant.

The energy demand of the transesterification reactions vary from low for standard transesterification to significant for the supercritical transesterification. From standard to supercritical, the heat duties of the heating apparatus will triple as well as the need for a more sophisticated reactor able to withstand the pressure build-up and minimize energy loss. Marchetti et al. related that annual utilities cost in operating the transesterification goes from $305,000 to $1.5 million[53]. On the energy basis, the press cake can be burned to produce energy with a calorific value of 11.1MJ/kg burned[54]. Since the cake represents 60 wt% of the seed, on a basis of 183,000lbs/hr of dry seeds there is a potential of 524 MMBTU/hour.

Byproducts

A recent research paper by Elliott et al. [39] projected that the byproducts created by the production of crude oil through fast pyrolysis are a fuel gas mixture and ash. The fuel gas stream contains mostly methane, ethane, propane and butane; it also contains a large amount of carbon dioxide. Elliott et al. showed that these fuel gas streams that come from several different parts of the process including pyrolysis and hydrotreatment can have a total flow rate of 12wt% of the feedstock input. The gas is rerouted to fuel the steam reformer and the heaters elsewhere in the process. By using the off gas, a large pyrolysis plant can significantly decrease its need for an outside source of fuel for heat and power in the steam reformer and heaters. The same study found that 13wt% of the feedstock would be converted into an ash and char mix, this char mixture can be used as soil amendment, allowing for better growth and yield from the land [55] Karayilderim et al. found that 20 wt% of the feedstock was converted into a gaseous product and 40% was converted to char [56]. The two experimental char yields differed because the latter resulted from the semi-batch fixed-bed pyrolysis of mixed waste water

treatment sludge while the first one resulted from the continuous fluidized bed pyrolysis of fresh ground poplar wood.

The process of transesterification produces two distinct byproducts, glycerol and a feedstock presscake. The presscake, left over from the extraction of the oils, accounts for about 60% of the weight of the original feedstock. This presscake is fairly energy rich and could be burned to produce much of the power and heat needed for the biodiesel production process or used as a nutrient rich fertilizer. Assuming a good conversion in the transesterification reaction, 10 wt% of the oil feedstock will be converted into glycerol [57]. Glycerol can be used in the production of soap or in the food industry to produce mono and di-glycerides, it also has many uses in today's pharmaceutical industry. Today prices of glycerol can be as much as 600 dollars per ton [58]. However, with increase biodiesel production will come an increased glycerol production and the market would soon become depressed as the need for glycerin in the cosmetic industry, soap industry and food industry lessens.

Raw Materials

The first material needed for the pyrolysis process is the carbon feedstock, in many cases wood or another biocrop. A common cellulosic feedstock such as poplar can cost $50 per ton, although others like corn stover and sugar cane begasse may cost as little as $30 per ton [59].Jatropha on the other hand costs about $140[60]. The other resources needed for pyrolysis are hydrogen, natural gas and certain catalysts. Hydrogen today cost about $1 per kg [61], but in a large scale pyrolysis plant the hydrogen will most likely be produced on site, powered by the off gas from earlier in the process, which will lower costs significantly. The natural gas used in the steam reformation process in the PNNL design case estimated the cost at almost $3000 per hour for a large scale production facility. The catalysts used in the pyrolysis process as well as the hydro treating process are expensive, some estimates have been at $15 a pound, and that the life span of the hydrotreating catalyst about one year [39]. In a large scale

facility a buildup of impurities would occur much faster than in a laboratory scale experiment, this would cause the cost of the catalyst to increase over time.

The raw materials used in standard transesterification are the bio-oil, methanol and NaOH. The oil is extracted from the seeds in one of several different methods: with solvents, or through mechanical extraction. The cost of hexane, a common solvent used for oil extraction, is about $14 per gallon, and along with the added equipment cost and operating cost of an extra distillation step, solvent extraction would be better suited for a large scale operation. Mechanical extraction is less costly, but also less efficient and possibly more dangerous. It requires a piece of machinery that would generally be run by a gasoline motor and cannot handle as great a load as a solvent extractor could, meaning that several would be needed for an operation of decent size. The second important reactant is methanol, which when purchased on large scale can cost as low as 1.15 dollars per gallon [62]. Since only 1/8 gallons of methanol is consumed for every gallon of oil, costs would be low, especially if an efficient distillation step is employed to recycle the unused methanol. The catalyst, usually NaOH, goes for a more than 2 dollars per pound [62].Unfortunately this catalyst is very difficult to recapture and reuse, so it needs to be replaced at the beginning of every run.

Emissions

According to Searchinger and Hiemlich, the production and use of biodiesel through transesterification, cuts the total green house gas emissions by 54% in comparison to the production and use of diesel fuel. The energy input needed to prepare the land, pretreat the Jatropha feedstock and transesterify the oil into biodiesel is larger than the energy input needed to extract and refine petroleum diesel. This is due to the energy intensive pretreatment of the land for planting, the oil extraction, the lengthy transesterification, and washing and distillation process. However, the carbon dioxide drawn out of the atmosphere by developing Jatropha plants greatly reduces the net gain of greenhouse gases

in the air[57]. Table 10 gives a numeric value of the emissions for biodiesel and petrodiesel production

and use. A study from the Center for Industrial Ecology at Yale University reported that the net savings

of green house gas emissions was approximately 540 kg per year per hectare [63]. Another paper by

Prueksakorn and Gheewala, report that the net gain of GHG emissions are 27% of that of petroleum

diesel [64]. The Prueksakorn article used a life cycle assessment to calculate the net CO_2 reduction. The

life cycle assessment included a more detailed view of the processes, activities, materials, use and

disposal of waste products associated with the transesterification process. They found the most energy

consumed came from transesterification, irrigation and fertilization respectively accounting for 40%,

23% and 22 % of the total energy used. This is why Prueksakorn's analysis gives a lower reduction value

of the greenhouse gases. When biodiesel is burned in a diesel motor the carbon dioxide emissions are

almost identical. The burned biodiesel exhausted 595.7 grams of CO_2 per horsepower for every hour the

engine was running. By comparison, the diesel motor exhausted 595.12 g/hp*hr [63]. Since the

greenhouse gas emissions from the burning of the fuel are so similar, the net CO_2 reduction comes from

the fact that the biodiesel is derived from a renewable source that replenishes itself from the carbon

dioxide in the atmosphere.

Table 10 Petrodiesel and biodiesel life cycle CO2 consumption in grams of Greenhouse Gasses CO2 /mile

Source of Fuel*	Making Feedstock	Refining Fuel	Vehicle Operation (Burning Fuel)	Feedstock Uptake from Atmosphere (GREET)	Land Use Change	Total GHGs*	% Change in Net GHGs for Biodiesel vs. Diesel
				Net Land Use Effects			
Diesel	+18	+40	+246	0	—	+304	—
Biodiesel /(GREET)	+82	+81	+248	-272	—	+139	-54%

A study by Roberts et al. shows the pyrolysis of several feedstocks, such as, corn stover, can

reduce the overall green house gases through slow pyrolysis by over 800 kg of CO_2 per metric ton of

feedstock, this shows an 80% recycling of CO_2 [65]. Consequently, the plant designed by The Pacific

Northwest National Laboratories that processes about 2000 metric tons of dry poplar wood feedstock per day, could theoretically lower carbon dioxide emissions by almost 620,000 metric tons per year, 0.1% of the total CO_2 emissions of the US. [62]The theoretical reduction in CO2 emissions predicted by the PNNL paper may have been less than that of Roberts et al. study, because it took into account more parts of the process, such as the production of hydrogen through steam reformation and the cracking and refining of the hydrotreated bio-oil. From "Experimental Studies on the Performance of Catalytically Hydrotreated Fast Pyrolysis oil in a Stationary Diesel Engine" it was concluded that the CO2 emissions of a treated pyrolysis diesel were similar to that of a fossil fuel diesel emission [50].

Potential as substitutes for diesel fuel in engine

The value of the biofuel as diesel replacement will be evaluated based on how it measures to the ASTM standards from 2010 and on various results comprised in this analysis.

Table 11 Typical properties of wood pyrolysis bio oil and heavy fuel oil

Physical property	2010 ASTM Standards Diesel	Sample Bio-oil From jatropha [45]	HDO2 [49]	Jatropha Methyl ester [66]	2010 ASTM standards B100 methyl ester
Moisture content (wt%)	1 max	15–30	1.6	-	0.05
Acid value (mgKOH/g)	0.2	87.84	Ph=6	0.24	0.50
Specific gravity (20°C)	0.85	1.2	0.9	0.87	-
Ash	0.01	0–0.2			0.02%max
Flash point	52	140	30.4	191	93
HHV (MJ/kg)	42	16–19	37.5		
Viscosity (at 50° C) (mm²/s)	2.6-4	7.4	6	4.84	1.9-6.0
Pour point	-20	4			

None of the renewable fuels can directly replace petroleum diesel because they come short in satisfying the established requirements for transportation fuel. The viscosity as well as the pour point is

higher than that of petroleum diesel which would cause damage and clogs to the fueling system. The high acidity tends to erode the interior of the car. From an engine test conducted by J. Florijn [49] using the double hydrotreated bio-oil from beech tabulated as HDO2, there seem to be coke residue in the engine as well as visible erosion on the nozzle hole when the oil was fed at a low inlet air temperature. Since the B100 product cannot be used in the diesel engines alone, it is often mixed with diesel to produce B10 and B20 fuel.

Matrix for the evaluation of the processes

All processes were scaled to a production of approximately 2000 ton per day with a 350 day/24h per day plant operations. This would include the cultivation of 8.27 field s of 10 000ha per year which produces about 5811 Barrels per day. This is around half of the diesel consumption of Haiti for the year 2006 and 827 square kilometers is approximately 3% of the nation's land area. The economical values are a combination of three major papers: the Design Case by PNNL [39], Technoeconomic Study of Supercritical Biodiesel production Plant [53] and The Centre for Jatropha Promotion in India [60].

	Weight	Transesterification subcritical	Transesterification supercritical	Pyrolysis + Hydrotreating
Wt % yield of biofuel	5	37.6 (0.6)	36.2 (0.5)	36 (0.5)
Energy used(MBTU)	5	398 (0.9)	1003 (0.2)	1300 (0.2)
Utilities MM$/yr	5	2.42 (0.9)	7.97 (0.4)	12.4 (0.2)
Speed of reactions	4	60mn (0.2)	15-28mn (.5)	<10 s (1)
Complexity of process	4	(0.7)	(1)	(0.1)
Byproducts	4	Glycerol Presscake Soap (0.6)	Glycerol Presscake (0.7)	Ash Tar Fuel Gas (0.8)
Capital cost	8.5	$45,500,000 (1)	$151,000,000 (0.6)	303,190,000 (0.4)
Yearly operating cost	10	$143,000,000 (0.1)	$293,000,000 (0.05)	$102,000,000 (0.8)
Methanol		$32,000,000	$32,000,000	0
NaOH		$4,7000,000		0
Natural Gas		-		$26,300,000
catalyst RM costs		-		$10,850,000
Hexane		$11-45,000,000	$11-45,000,000	
Total RM cost	7	$47-81,600,000 (0.3)	$43-77,000,000 (0.4)	$37,150,000 (0.6)
Total points achieved	**52.5**	**27.4**	**23.3**	**28.7**

For the transesterification process, even at the lowest scales, the operating costs compete with any revenue from the sale of the biodiesel produced. To confirm the numbers calculated in this report, several studies have estimated that the cost of production of transesterification biodiesel has been the main obstacle to the development [13] [53].The US department of Energy Information Administration, evaluated that Methyl Ester biodiesel's cost of production is higher than that of petroleum diesel; when made from soybean, the cost of production is $2.54 when for diesel it is $0.76 [67]. Unlike the transesterification, the pyrolysis process is profitable, with a minimal selling price of the diesel of $1.80-2.04 depending on the source when biodiesel's cost of production alone is $2.54[57] [31].Although the pyrolysis process appears to have a heavy initial cost it can be compared to the investment for a new oil rig which can cost anywhere between $200million and over 1 billion dollars [68][69].

Additionally, when talking about the complexity of the process, it was only considered the amount of different stages the process included. Having a batch system could be most inconvenient and inefficient for a production of this scale. For a reaction of 1 hour and a well-mixed solution, the size of the reactor would be limited and the number of reactors would depend on that volume. It can already be predicted that this number would be large and the process would become complex in the management of that many more pieces of equipment.

CONCLUSION AND FUTURE WORK

This report analyzed the processes of standard transesterification, supercritical transesterification and pyrolysis in order to compare them to one another on a basis of the following parameters: yield, energy requirements, reaction time, raw materials, capital and operating costs of production. From the matrix created, pyrolysis scored only slightly higher than standard transesterification, and the supercritical transesterification was least favorable. For pyrolysis, the energy demand and equipment sophistication weighed most for that process. For transesterification, the yearly cost of production due to raw material needs like methanol and NaOH, made this process economically unattractive on a large scale. Additionally, the pyrolysis diesel fuel can be used independently of the petroleum diesel, which makes this option ideal for Haiti considering the desire to reduce the burden of imported transportation fuel on their economy.

Although the method of determination is relatively subjective, as noted in our description of the matrix analysis, our team recommends that further investigation be done on the feasibility of establishing a large scale fast pyrolysis operation in Haiti, since it was established to be the most economical process. It is recognized that there is still a great deal of research to be attended to. We recommend that the following be the focus of studies and experiments to come.

- Design lab scale unit for Pyrolysis and Hydrotreating of Jatropha Curcas oil and of crushed seeds with in-line Chromatography to study conversions

- Investigate Changing World Technologies treatments after their pyrolysis as an alternative to Hydrotreatment.

- Address the pherbol ester content (toxicity factor) of Jatropha and how that affects the quality of the outcoming fuels and design extraction treatment for this element.

- Test long term reactivity of the biodiesel and pyrolysis fuels as well as engine performance evaluations to decide on which fuel is superior.

- Contact companies, like BTG, Dynamotive, PYNE.co.uk, leaders in the pyrolysis industry for collaboration in future projects.

While we recommend pyrolysis as the best option for this application, we recognize that transesterification has attractive characteristics including low capital investments and low energy demand. However, for the production of Haiti's oil needs, the cost of raw materials would significantly decrease profitability. Therefore in the domain of standard transesterification, more research should be conducted towards

- Diminishing the raw material needs of the process

- Lowering reaction time in a non energy intensive manner

- Minimizing negative byproducts such as soap

Appendix: Calculations and Data

I).TRANSESTERIFICATION HEAT DUTY CALCULATIONS:

All values assume a 1 hour reaction time

Since all calculations will be estimated to the amount used in Pyrolysis Process, our Triolein will come in at about $78,800 \frac{lbs}{hr}$, which is 40% of the feed going into the pyrolysis process where $197,000 \frac{lbs}{hr}$ of seeds are used. This is because the Jatropha oil takes up only about 40% of the seed itself.

The ratio used for the transesterification processes was a 1:6 molar ratio which is in comparison to a ratio of 0.238:1 in weight magnitude.

Since the weight ratio is about 0.238:1 and we have Triolein coming in at $78,800 \frac{lbs}{hr}$, then Methanol the other component in the process will come in at

$$78,800 \frac{lbs}{hr} * \left(\frac{1}{0.238}\right) = \frac{331,100 lbs}{hr}$$

Energy Needed to Drive Reaction

$$Energy\ needed\ to\ drive\ reaction = Activation\ Energy \left(\frac{kJ}{kmol}\right) * moles\ used\ in\ reaction$$

$E_A = 84100\ kJ/kmol$ [40]

Total moles in the feed stream:

Triolein = $\frac{78,800 lbs}{hr} * \frac{0.4536 kg}{lb} * \frac{1000g}{1kg} * \frac{mol}{885.45g} = \mathbf{40,368\ moles/hr}$

$$Methanol = \frac{331{,}100\,lbs}{hr} * \frac{0.4536\,kg}{lb} * \frac{1000\,g}{1\,kg} * \frac{mol}{32.04\,g} = 4{,}687{,}483\ moles/hr$$

$$Total\ Moles = 40{,}368 + 4{,}687{,}483 = 4{,}727{,}851\ moles$$

Energy needed to drive reaction is:

$$= \frac{84100\,J}{mol} * 4{,}727{,}851\ moles = 3.976 * 10^{11}\,J = 377\,Mbtu$$

Calculation of Specific Heat

❖ **Specific Heat of Methanol:**

$$C_{pmet\ hanol} = \int a + bT + cT^2 + dT^3$$

$$a = 21.152 : b = 0.07092 : c = 2.59 * 10^{-5} : d = -2.85 * 10^{-8}$$

$$C_{pmet\ hanol} = \int 21.152 + 0.07092T + 2.59 * 10^{-5}T^2 + (-2.85 * 10^{-8})T^3$$

$$C_{pmet\ hanol} = aT + \frac{bT^2}{2} + \frac{cT^3}{3} + \frac{dT^4}{4}$$

$$C_{pmet\ hanol} = 21.152T + \frac{0.07092T^2}{2} + \frac{(2.59 * 10^{-5}T^3)}{3} + \frac{-2.85 * 10^{-8}T^4}{4}$$

Integrate from 25 degrees Celsius which is 298 K to Reaction Temperature.

Specific Heat from 25 Degrees Celsius to 70 Degrees Celsius:

$$C_{pmet\ hanol\ from\ 25C\ to\ 70C} = 11676.737 - 9624.567 = \frac{2052.17\,J}{kg * k} = \frac{2052\,J}{kg * k}$$

$$C_{pmet\ hanol\ from\ 25C\ to\ 70C} = \frac{2052.17\,J}{kg * k} * \frac{1\,Kg}{1000\,g} * \frac{32.04\,g}{mol} = \frac{65.75\,J}{mol * k}$$

Specific Heat from 25 Degrees Celsius to 250 Degrees Celsius:

$$C_{p\,met\,hanol\,from\,25C\,to\,250C} = 21463.091 - 9624.567 = \frac{11838J}{kg*k} = \frac{11840J}{kg*k}$$

$$C_{p\,met\,hanol\,from\,25C\,to\,250C} = \frac{11838J}{kg*k} * \frac{1Kg}{1000g} * \frac{32.04g}{mol} = \frac{379.306J}{mol*k} = \frac{379.3J}{mol*k}$$

❖ *Specific Heat of Triolein:*

At 70 Degrees Celsius from paper:

$$C_{p\,TRIOLEIN\,at\,70C} = \frac{2.10J}{g.k} * \frac{885.45g}{mol} = \frac{1859J}{mol.k}$$

Specific Heat Calculated:

$$T_c = 954.1K$$

$$\omega = 1.6862$$

$$C_p = \sum x_i * C_{pi}^{\circ}$$

$$T_{R\,at\,70C} = \frac{T}{T_C} = \frac{343}{954.1} = 0.3595$$

$$T_{R\,at\,250C} = \frac{T}{T_C} = \frac{523}{954.1} = 0.54816$$

$$C^{\circ}_{p\,triolein} = \int a + bT + cT^2 + dT^3$$

$$a = 5.9592 : b = 0.269695 : c = 1.5379 * 10^{-4} : d = 0.033981 * 10^{-6}$$

$$C^{\circ}_{pTriolein} = \int 5.9592 + 0.269695T + 1.5379 * 10^{-4}T^2 + 0.033981 * 10^{-6}T^3$$

$$C^\circ_{pTriolein} = aT + \frac{bT^2}{2} + \frac{cT^3}{3} + \frac{dT^4}{4}$$

$$C^\circ_{pTriolein} = 5.9592T + \frac{0.269695T^2}{2} + \frac{(1.5379 * 10^{-4}T^3)}{3} + \frac{0.0033981 * 10^{-6}T^4}{4}$$

$$C^\circ_{pTriolein \; from \; 25C \; to \; 70C} = \frac{4984.948J}{(kg * k)}$$

$$C^\circ_{pTriolein \; from \; 25C \; to \; 70C} = \frac{4984.948J}{kg * k} * \frac{1Kg}{1000g} * \frac{885.45g}{mol} = \frac{4413.92J}{mol * k} = \frac{4414J}{mol * k}$$

$$C^\circ_{pTriolein \; from \; 25C \; to \; 250C} = \frac{32284.2836J}{(kg * k)}$$

$$C^\circ_{pTriolein \; from \; 25C \; to \; 250C} = \frac{32284.2836J}{kg * k} * \frac{1Kg}{1000g} * \frac{885.45g}{mol} = \frac{28586.12J}{mol * k} = \frac{28590J}{mol * k}$$

Calculating Enthalpy for the System:

Using a 1 to 6 oil to methanol molar ratio, and **4,727,851moles**

mols of oil:

$$mC_p \Delta T = \Delta H$$

❖ *At 70 Degrees Celsius:*

$$\mathbf{40,368}mol * \frac{4414J}{molK} * (343K - 298K) = (8.02 * 10^9)J$$

$$\mathbf{4,687,483}mol * \frac{65.75J}{molK} * (343K - 298K) = (1.39 * 10^{10})J$$

$$(8.02 * 10^9)J + (1.39 * 10^{10})J = 2.192 * 10^{10}J = \mathbf{20.78Mbtu}$$

❖ *At 250 degrees Celsius:*

$$40,368 \, mol * \frac{28590J}{molK} * (523K - 298K) = (2.60 * 10^{11})J$$

$$4,687,483 mol * \frac{379.306J}{molK} * (523K - 298K) = (4.00 * 10^{11})J$$

$$(2.60 * 10^{11})J + (4.00 * 10^{11})J = 6.60 * 10^{11}J = \textbf{626Mbtu}$$

Energy loss out of the reactor

Assumptions:

- That the reactor is a cylinder 8ft by 41 ft which translates to 2.4384m by 12.4968m which is the same dimension specifications as used in the pyrolysis process.

- The Area of the Reactor thus becomes:

$$A = \pi * r^2 = \frac{\pi * D^2}{4}$$

$$A = \frac{\pi * 2.4384^2}{4} = 4.6698m^2 = 4.670m^2$$

Temperature Changes:

$$\Delta T \, at \, 70 \, Degrees \, Celsius = 343 - 298 = 45K$$

$$\Delta T \, at \, 250 \, Degrees \, Celsius = 523 - 298 = 225K$$

Therefore Heat Loss :

$$\Delta H = U * \Delta T * A$$

$$U(Internal \, Energy \, for \, Steel \, Reactor) = 14.4 \frac{W}{m^2.k}$$

- ❖ *70 Degrees Celsius is:*

$$\Delta H = U * \Delta T * A$$

$$\Delta H = \frac{14.4W}{m^2.k} * 45k * 4.6698m^2 = 3026.03W = 10\,324.814btu = \textbf{0.01Mbtu}$$

- ❖ *250 Degrees Celsius is:*

$$\Delta H = U * \Delta T * A$$

$$\Delta H = \frac{14.4W}{m^2.k} * 225k * 4.6698m^2 = 15130.15W = 51\,624.072btu = \textbf{0.052Mbtu}$$

Total Heat needed for the reactor to operate:

- ❖ *70 Degrees Celsius is:*
$$377 + 20.78 + 0.01 = \textbf{397.79Mbtu} = \textbf{398 Mbtu}$$

- ❖ *250 Degrees Celsius is:*
$$377 + 626 + 0.052 = \textbf{1003Mbtu}$$

II).PYROLYSIS HEAT DUTY CALCULATIONS:

Assumptions

- The values from heat input are taken from an Aspen Simulation run on a continuous fluidized bed with sand.

- Assumptions were made using the similarity between Canola oil(from rapeseed) and Jatropha. For the energy generated, the biomass composition of rapeseed was used as a basis that we believe is close to Jatropha seed as well.

- Approximately 40%wt of oil in both seeds "lima et al and msds" which is similar for both (Onay). We assume 16% cellulose 22% protein and 22% hemicelluloses and lignin based on rapeseed info and they are considered molasses in these calculations.
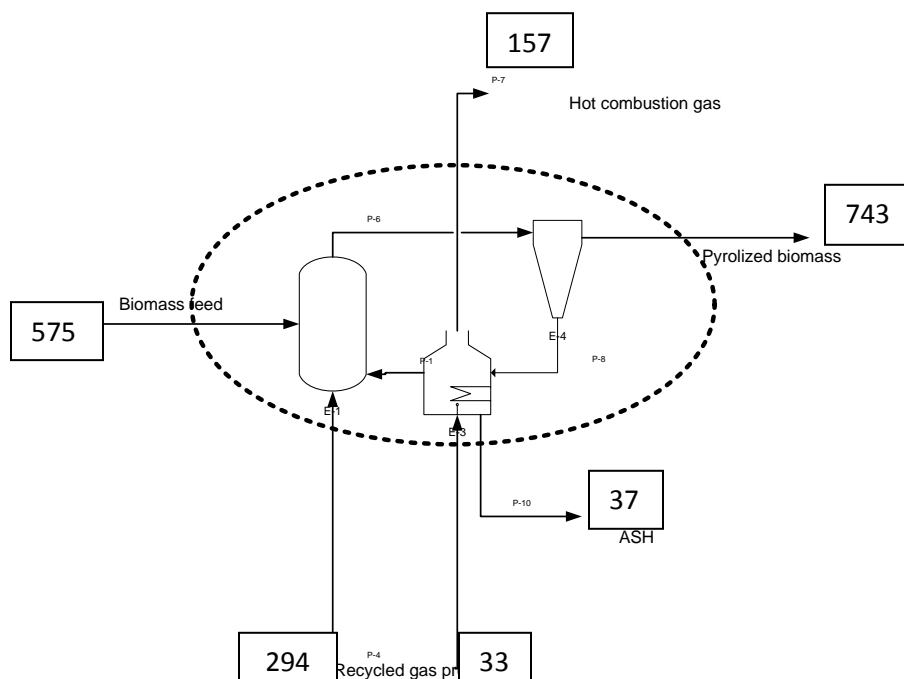

Figure 17: Pyrolysis Reactor

Energy Balance around Reactor:

$$Hin + Hgen = Hout + Hused + Hloss$$

H_{in} = Heat in biomass(575)+Heat of incoming fuel gas (294+33)= 902MMBTU

H_{gen}= 5322 MMBTU (PNNL simulation)

H_{used}=(triglyceride breaking (activation energy 84.1MJ) and evaporation/heating of mass)

$$Heat\ used\ to\ break\ triglycerides = E * mol\ reacted$$

$$84.1 \frac{MJ}{Kmol} * \left(40\% * 2.1 * 10^6 kg * \frac{1}{885} \frac{kmol}{kg}\right) = 46552\ MJ\ or\ \boldsymbol{46.123\ MMBTU}$$

Heat used to heat mixture from 66 to 500 Degree Celsius

$$H = (Mcp_{oil} + Mcp_{Molasses})\ \Delta T$$

$$H = \left(40\% * 2.1 * 10^6\ kg * 1800 \frac{J}{kg\,^0C} + 60\% * 2.1 * 10^6\ kg * 2512 \frac{J}{kg\,^0C}\right) * 434^0 C$$

$$H = 362MMBTU + 759\ MMBTU = \boldsymbol{1121MMBTU}$$

Total Heat Used:

$$1121MMBTU + 46.123MMBTU = \boldsymbol{1167MMBTU}$$

Heat Loss

$$Hin + Hgen = Hout + Hused + Hloss$$

$$Hloss = 902MMBTU + 5322MMBTU - 937MMBTU - 1167$$

$$Hloss = \boldsymbol{4120MBTU}$$
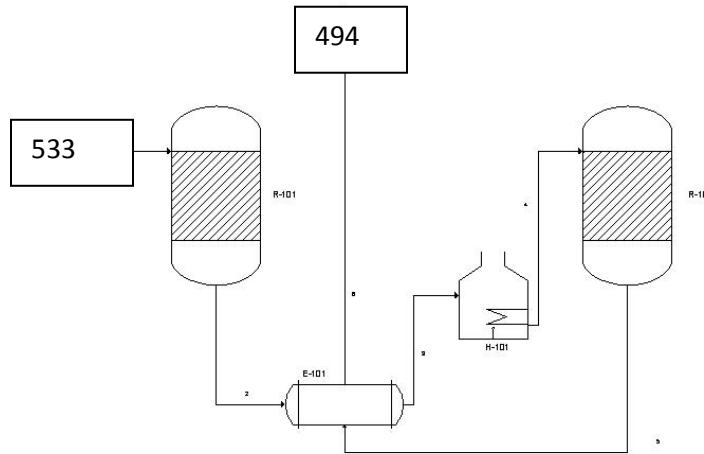
II).ENERGY BALANCE AROUND HYDROTREATING OF BIO-OIL :

Figure 18: Hydrotreating of Bio-Oil

$$Heat_{in} = Energy\ from\ stream\ 203 = \frac{533 Mbtu}{hr}$$

$$Heat_{gen} = Heat\ released\ from\ the\ reaction\ (Calculated\ Below)$$

$$Heat_{out} = Energy\ in\ stream\ 213 = \frac{494 Mbtu}{hr}$$

$$Heat_{used} = Energy\ to\ raise\ the\ temperature\ of\ the\ stream\ and\ to\ vaporize\ the\ water\ formed$$

Seeing that the partial vapor fraction corresponds to the amount of water created in the system. From 15% vapor entering the reactors to 70% of stream exiting in the vapor phase. With temperatures going from 240 to 341 degrees C

With cp of water above 533K is 89 kJ/kmol K

For water in reactor1

$$M * H_{vap} = 6.698 * 10^6 kJ = 6.3\ Mbtu$$

For water in reactor 2

$$M * H_{vap} = 1.616 * 10^7 kJ = 15 Mbtu$$

Heat of Reaction

The heat of reaction was determined by finding the difference of the heat of formation of the products and the reactants. Using the stream information tables and the pfd in the Pacific Northwest National Labs paper by Jones et al tables 1 and 2 were made. Only components with a major change were accounted for.

Table 13: Enthalpies of the Reactants

Reactant	Amount used(lbs/hr)	Molecular weight(g/mol)	Amount used(mols/hr)	ΔH_f (kJ/mol)	Total ΔH kJ
Lignin	64000	196	148200	-1092	-1.62E8
Cellaboise	23000	342	30500	-2226	-6.79E7
Furfural	12000	96	56800	-151	-8.58E6
Acetic Acid	8000	60	60500	-483	-2.92E6

Product	Amount created(lbs/hr)	Molecular weight(g/mol)	Amount created(mols/hr)	ΔH_f (kJ/mol)	Total ΔH kJ
Water	40000	18	1010000	-241	-2.43E8
Carbon Dioxide	9000	44	92900	-393.5	-3.66E7
Methane	3000	16	85100	-74.9	-6.37E6
Ethane	2000	30	30300	-83.8	-2.54E6
Propane	1500	44	15500	-104.7	-1.62E6
Butane	1500	58	11700	-125.6	-1.47E6
2-5Xylenol	8000	122	29800	-237	-7.06E6
Heptane	3000	100	13000	-187	-2.43E6
Cyclohexane	10000	110	42300	-156	-6.60E6
Cis-Decalin	3000	138	9900	-207	-2.11E6
Biphenyl	4000	154	11800	-182	-2.15E6
Diamantane	9000	136	30000	-193	-5.79E6
Phenanthrene	6000	178	15300	-201	-3.08E6
Chrysene	6000	228	11900	-152	-1.81E6

Numbers for cellabiose came from sucrose, a similar molecule in size, shape and chemical make up.

Using the equation:

$$\Delta H_{f\ products} - \Delta H_{f\ reactants} = \Delta H_{reaction}$$

$$\Delta H_{f\ products} = -3.22E8\ kJ$$

$$\Delta H_{f\ reactants} = -2.414E8\ kJ$$

The enthalpy of the reaction is

$$H_{reaction} = -8.123E7 \frac{kJ}{hr} = \boldsymbol{-77 Mbtu/hr}$$

Heat Loss

$$Heat\ Loss = Heat\ Lost\ through\ the\ Reactor\ and\ Pipe\ Walls(Calculated\ from\ the\ difference)$$

$$Heat_{loss} = Heat_{gen} + Heat_{in} - Heat_{out} - Heat_{used}$$

$$Heat_{loss} = 77.04 + 533 - 494 - 21.3 = \boldsymbol{107 MMbtu/hr}$$

References

[1] Shafiee, S., and Topal, E., 2009, "When Will Fossil Fuel Reserves be Diminished?" Energy Policy, 37(1) pp. 181-189.

[2] Robin Greenhalgh, 2002, "Fossil Fuel and it's Impact on the Environment," Pagewise, .

[3] University of California, San Diego, 2009, "GLOBAL WARMING: The Rise of CO2 & Warming," .

[4] Anonymous 2009, "Advantages of Biodiesel Fuel for Transportation," Alternative Energies, .

[5] Christiansen, R. C., 2008, "Description of the Harmfull Impact on the Environment from the Retrieval and Conversion of Fossil Fuels to Energy." Biodiesel Magazine, (Handling Hotwork Hazard) .

[6] CIA, 2009, "Haiti," World Factbook, .

[7] Southern Travels, 2009, "Weather and Climate in Haiti," .

[8] intute, 2009, "World Guide – Haiti," .

[9] Grennaholic, 2009, "Biodiesel Production Methods," .

[10] Marquez, H., 2008, "PrintSend to a Friend OIL-CARIBBEAN: Petrocaribe Building 'Anti-Crisis, Anti-Hunger Shield," IPS, .

[11] Sprague, Jed, and Wadner Pierre, 2007, "PrintSend to a Friend HAITI: Pain at the Pump Spurs Strike Actions," IPS, .

[12] NREL, 2009, "Clean Cities," US DOE.

[13] "Nazir, N. "., Ramli, N. "., "Mangunwidjaja, D. "., 2009, "Extraction, Transesterification and Process Control in Biodiesel Production from Jatropha Curcas," European Journal of Lipid Science and Technology, 111(12) pp. 1185-1200.

[14] Lele, S., 2007, "Jatropha, Managing Costs, Yields and Productivity," .

[15] Malik, B., 1989, " A Country study: Haiti, Land Use and Farming Technology," .

[16] Mittelbach, M., and Remschmidt, C., 2006, "Biodiesel : the comprehensive handbook," M. Mittelbach, Austria, pp. 332.

[17] Satish, L., "Jatropha Curcas, Castor Plantation," 2010(january/23) .

[18] Anonymous 2005, "Building a Successful Biodiesel Industry," CJP, .

[19] Brijesh, R., 2001, "Plant Jatropha - Go Green - Reduce Poverty," Altenergy Mag, .

[20] "Gui, M., "Lee, K., and "Bhatia, S. "., 2008, "Feasibility of Edible Oil Vs. Non-Edible Oil Vs. Waste Edible Oil as Biodiesel Feedstock," Energy, 33(11) pp. 1646-1653.

[21] Anonymous 2009, "Concerns Raised Over Water Thirsty Jatropha," Bio Industry News, .

[22] Jongschaap, R., R. Besgraaf, T. Bogaard, E. Van Loo, and H. Savenije, 2009, "The Water Footprint of Bioenergy from Jatropha Curcas," Proceedings of the National Academy of Science, 92.

[23] Brighton, A., "Jatropha Trees," 2010(02/12) .

[24] "Achten, W., "Verchot, L. "., "Franken, Y., 2008, "Jatropha Bio-Diesel Production and use," Biomass and Bioenergy, 32(12) pp. 1063-1084.

[25] African Centre for Plant Oil Technology, "MFC Jatropha Activities," 2009(10/28) .

[26] Buikema, Brooke, Stephan Gabadon, Michael Workman, and Hwok-Chuen Lee, 2008, "*Biodiesel Produced from Jatropha Seed Oil. Biodiesel Produced from Jatropha Seed Oil*," .

[27] oilgae.com, 2009, "Algae Oil Extraction," .

[28] Ryan C. Christiansen, 2008, "U.N. Report: Biodiesel Creates Jobs Worldwide," Biodiesel Magazine, .

[29] Gwi-Taek Jeong, D. P., 2006, "Batch (One- and Two-Stage) Production of Biodiesel Fuel from Rapeseed Oil," Applied Biochemistry and Biotechnology, 131pp. 1-3.

[30] "Clifford, T., "Millar, D., "Parish, D., 2008, "Design of a containerised biodiesel production plant," University of Exeter, .

[31] Pickowitz, Joe, and Tim Lindsey, 2009, "Growing Jatropha Curcas for Renewable Energy: Biodiesel Production in Haiti," The Illinois Sustainable Technology Cente, .

[32] "Lima, D. G. "., "Soares, V. C. D. "., "Ribeiro, E. B. "., 2004, "Diesel-Like Fuel obtained by Pyrolysis of Vegetable Oils," Journal of Analytical and Applied Pyrolysis, 71(2) pp. 987-996.

[33] Srivastava, A., and Prasad, R., 2000, "Triglycerides-Based Diesel Fuels," Renewable and Sustainable Energy Reviews, 4(2) pp. 111-133.

[34] PYNE, "Science and Technology: REACTOR," 2010(4/23) .

[35] Maher, K., and Bressler, D., 2007, "Pyrolysis of Triglyceride Materials for the Production of Renewable Fuels and Chemicals," Bioresource Technology, 98(12) pp. 2351-2368.

[36] Adjaye, J., and Bakhshi, N., 1995, "Production of Hydrocarbons by Catalytic Upgrading of a Fast Pyrolysis Bio-Oil. Part II: Comparative Catalyst Performance and Reaction Pathways," Fuel Processing Technology, 45(3) pp. 185-202.

[37] Olazar, M., Aguado, R., Bilbao, J., 2004, "Pyrolysis of Sawdust in a Conical Spouted-Bed Reactor with a HZSM-5 Catalyst," AICHE Journal, 46(5) pp. 1025-1033.

[38] "French, R. J. "., "Hrdlicka, J., and "Baldwin, R., 2010, "Mild Hydrotreating of Biomass Pyrolysis Oils to Produce a Suitable Refinery Feedstock," Environmental Progress & Sustainable Energy, 29(1) .

[39] "SB Jones", "JE Holladay", "C Valkenburg", 2009, "Production of Gasoline and Diesel from Biomass via Fast Pyrolysis, Hydrotreating and Hydrocracking: A Design Case," PNNL 18284, .

[40] "Zhiyong Tang", "Lianyuan Wang", and "Jichu Yang", 2007, " Transesterification of the Crude *Jatropha Curcas* L. Oil Catalyzed by Micro-NaOH in Supercritical and Subcritical Methanol." European Journal of Lipid Science and Technology, 109pp. 585-590.

[41] "Morad, N. A., "Kamal, A. A. M., "Panau, F. "., 2000, "Liquid Specific Heat Capacity Estimation for Fatty Acids, Triacylglycerols, and Vegetable Oils Based on their Fatty Acid Composition," Journal of American Chemists Society, 77pp. 1001-1005.

[42] Onay, O., and Koēkar, M., 2004, "Fixed-Bed Pyrolysis of Rapeseed (Brassica Napus L.)," Biomass and Bioenergy, 26(3) pp. 289-299.

[43] Kulchanat, P., 2007, "Comparing Cost of Biodiesel Production from Transesterifiction," Dept of ChemicalEngineering, Prince of Songkla Univ., .

[44] Bhuyar, T. a. D., 2009, "Development ofMAthematical Correlations for the Transesterificatino Reaction," Internation Journal of Applied Engineering Research, .

[45] "Raja, A. S., "Kennedy, D. Z. R., and "Pillai, D. B. C., 2009, " Flash Pyrolysis of Jatropha Oil Cake in Fluidized Bed Reactor," Electronic Newsletter on Renewable Energy and Environment, 6(4) pp. 2-8.

[46] "Coleman, H. D. "., "Canam, T., " Kang, K., 2007, "Over-Expression of UDP-Glucose Pyrophosphorylase in Hybrid Poplar Affects Carbon Allocation," Journal of Experimental Botany, 58pp. 15-16.

[47] "Marsman, J. H. "., "Wildschut, J. "., "Eversb, P. "., 2008, "Identification and Classification of Components in Flash Pyrolysis Oil and Hydrodeoxygenated Oils by Two-Dimensional Gas Chromatography and Time-of-Flight Mass Spectrometry," Journal of Chromatography A, 1188pp. 17-25.

[48] "Ardiyanti, A., "Heeres, H., and "Venderbosch, R. H. "., 2009, "Process-product studies on pyrolysis oil upgrading by hydrotreatment with Ru/C catalysts," The 2009 Spring National Meeting, Anonymous University of Groningen, Netherlands, .

[49] "Wildschut, J., "Mahfud, F. H. "., "Venderbosch, R. H. "., 2009, "Hydrotreatment of Fast Pyrolysis Oil using Heterogeneous Noble-Metal Catalysts," Ind. Eng. Chem. Res, 48pp. 10324-10334.

[50] "Wildschut, J., 2008, "Pyrolysis Oil Upgrading to Transportation Fuels by Catalytic Hydrotreatment. Chapter 6 Experimental Studies on the Performance of Hydrotreated Fast Pyrolysis Oil in a Stationary Diesel Engine," University of Groningen, .

[51] Steele, Hasann, Yu, Mitchell, Ingram, " from Whole-Tree Feedstocks to Biofuel Via Pyrolysis," Mississippi University, .

[52] Glushkov, 2007, "Production of Fuel Gas in Pyrolysis of Plant Mass," Chemistry and Technology of Fuels and Oils, 43.

[53] "Marchetti, J., and "Errazu, A., 2008, "Technoeconomic Study of Supercritical Biodiesel Production Plant," Energy Conversion and Management, 49(8) pp. 2160-2164.

[54] "Sotolongol, J. A., "Beatón, P., "Díaz, A., "Jatropha Curcas L. as a Source for the Production of Biodiesel: A Cuban Experience," .

[55] Liard, Brown, Amonette, Lehmann, 2009, "Review of the Pyrolysis Platform for Coproducing Bio-Oil and Biochar," Biofuels, Bioprod. Bioref, 3pp. 547-562.

[56] Karayildirim, T., Yanik, J., Yuksel, M., 2006, "Characterisation of Products from Pyrolysis of Waste Sludges," Fuel, 85(10-11) pp. 1498-1508.

[57] Searchinger, H., 2007, "ESTIMATING GREENHOUSE GAS EMISSIONS FROM SOY-BASED U.S. BIODIESEL WHEN FACTORING IN EMISSIONS FROM LAND USE CHANGE," Agricultural Conservation Economics, .

[58] Ben Lefebvre and Judith Taylor/Houston, 2010, " US Glycerin Prices Ready to Rocket, Fatty Alcohols and Acids See Upward Pricing Pressure," ICIS Chemical Business, .

[59] Paturau, 1986, "ALTERNATIVE USES OF SUGARCANE AND ITS BYPRODUCTS IN AGROINDUSTRIES," FAO Expert Consultation, .

[60] "Kumar, D. N., "Shekhawat, D. "., 'Benniwal, D. "., 2004-2009, "Jatropha World," Jatrophaworld.Org.

[61] Doty, D., 2004, "A Realistic Look at Hydrogen Price Projections," Doty Scientific, .

[62] AAAChemicals, 2010, "BULK CHEMICALS - TESTING - STANDARDS - BIODIESEL, SOAP AND CANDLE

MAKING SUPPLIES," .

[63] Knothe, S., Ryan, 2006, "

Exhaust Emissions of Biodiesel, Petrodiesel, Neat Methyl Esters, and

Alkanes in a New Technology Engine," National Center for Agricultural Utilization Research, 20pp. 403-

408.

[64] Prueksakorn, G., 2006, "Energy and Greenhouse Gas Implications of Biodiesel Production from

Jatropha Curcas L," Sustainable Energy and Environment, .

[65] Roberts, Gloy, Joseph, Scott, Lehmann, 2010, " Life Cycle Assessment of Biochar Systems: Estimating

the Energetic, Economic, and Climate Change Potential," Environ. Sci. Technol, 44pp. 827-833.

[66] Manurung, R., 2007, "Valorisation of Jatropha curcas using the Biorefinery Concept," FACT Jatropha

Expert Seminar Wageningen, Anonymous Biotechnologi Research Center ITB, .

[67] Radich, A., "Biodiesel Performance, Costs, and use," 2010(april/12) .

[68] "Gallardo, C., 2010, "ConocoPhillips to Build 1.7 Billion Dollar Ekofisk Rig ," Ordons News, Europe-

Nordic countries.

[69] African oil Journal, 2007, "Qatar to Build New Oil Refinery in Tunisia," Africanoiljournal.Com,

Tunisia.