

# Pyrolysis of Switchgrass to Fuels



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## **Abstract**

The pyrolysis method is currently being considered as a potential process to convert biomass to a liquid fuel suitable for automobile engines. The process produces a bio-oil mixture of hydrocarbons, water, and oxygenates. Though this bio-oil can be used in boilers and furnaces, it must be upgraded by lowering the oxygen content before it is suitable for use in automobiles. The purpose of this project was to develop a pyrolysis system to produce bio-oil on an industrial scale and to determine the uses of bio-oil after it is produced. Three options were considered: 1) selling the bio-oil for use in electricity-generating plants, 2) upgrading the bio-oil using the hydrotreating method, and 3) upgrading the bio-oil using zeolite catalysis deoxygenation. The process design and economic analysis was performed for each of these three options. Though the first option was found to be the only one with a reasonable return on investment given current market conditions, the other two options could be brought to break-even profitability. Also, to further test economic feasibility of the catalytic deoxygenation process, four alternate scenarios were analyzed to determine which factors significantly affected profitability. It was found that increasing catalyst selectivity or decreasing the amount of catalyst used could make the process profitable.

## **Introduction**

The United States has been striving to develop alternate sources of energy to standard petroleum fuels. The motive for this is both the need for independence from foreign oil markets and an increasing interest in earth-friendly and renewable resources. To pursue this goal, the U.S. began a Biomass Research and Development Initiative to develop bioenergy and biobased products. Also, the federal government has issued an energy bill that sets requirements that increase annually for the percentage of fuel that must come from renewable resources.<sup>11</sup>

There are a variety of feedstocks under consideration for use as a renewable feed source including corn, soybeans, vegetable oil, and switchgrass. These feedstocks have then been used to produce several types of fuel including ethanol, syngas, and biodiesel. Ethanol is currently one of the most popularized fuel types. Already it is being mixed in with petroleum and gasoline-grade fuels. Syngas is a second form of fuel: a synthetic natural gas that can be used to produce electricity and fire boilers. However, the search still continues for an economical liquid fuel suitable for use in automobile engines.

Four major technological processes have been developed towards this goal: 1) acid hydrolysis followed by fermentation, 2) enzymatic hydrolysis followed by fermentation, 3) gasification followed by Fischer-Tropsch process, and 4) pyrolysis. The first two processes result in ethanol production as well as a number of side products. Gasification is currently used to produce syngas, but with the Fischer-Tropsch process, this can be turned into a liquid fuel. The pyrolysis method results in a mixture of liquid bio-oil, noncondensable gas, and solid charcoal. This bio-oil contains water and a mix of oxygenated hydrocarbons. It is suitable for use as fuel for boilers but must be upgraded before it can be used in an automotive engine. Two possible methods exist for upgrading this fuel: severe hydrotreating and catalytic deoxygenation. The Biofuels Group in the Chemical Engineering department at OU is currently performing research to upgrade the bio-oil produced during pyrolysis. Their primary research focus is catalytic deoxygenation of the liquid hydrocarbons.

The purpose of this Capstone project is to develop a pyrolysis process for producing bio-oil and to determine if there is an economically feasible method of upgrading the bio-oil to fuel suitable for automobiles. Three options will be considered: 1) selling the bio-oil to generate

electricity without upgrading, 2) upgrading the bio-oil through hydrotreating, 3) upgrading the bio-oil using a zeolite catalyst. A simulation of a pilot plant was created using excel spreadsheets, using a basis of 100 tons of switchgrass feed per hour. It was assumed that the biofuels process would run in connection with a petroleum refinery to save on transportation and separation costs. For the third option, four additional scenarios were considered, changing factors from the original scenario. The factors considered were 1) the amount of catalyst used, 2) the number of regeneration cycles for the catalyst, 3) the selectivity of the catalyst for the product oil, and 4) running the biofuels process as a separate plant, unconnected to a refinery. The purpose of considering these alternate scenarios was to determine which factors had significant impact on the economic feasibility of the catalytic deoxygenation option.

## Current Technological Processes

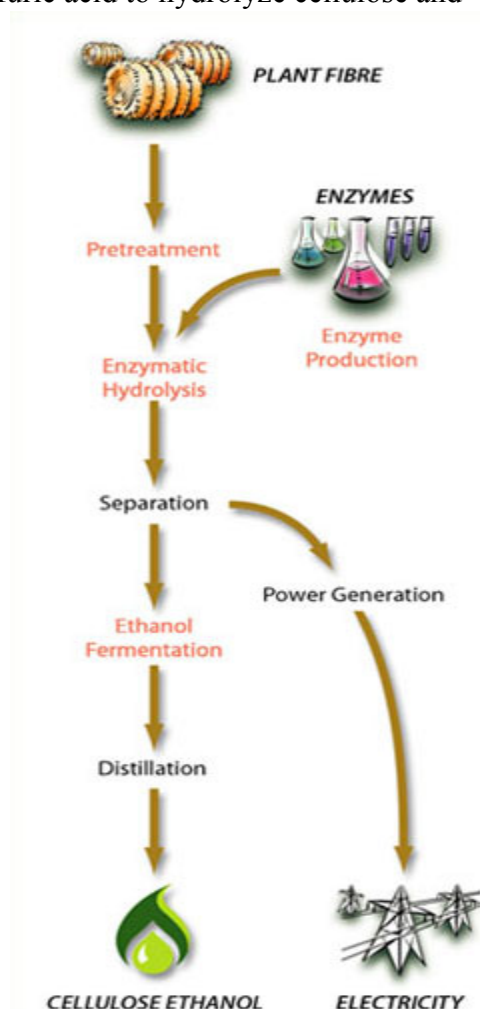
There are four technological processes currently being used to produce biofuels. This section presents a short summary of each of these processes.

### *Acid hydrolysis followed by fermentation*

The acid hydrolysis method is a process that utilizes sulfuric acid to hydrolyze cellulose and hemicelluloses. However, before cellulose can be depolymerized, they must first be pretreated to hydrolyze the hemicelluloses leaving the cellulose to be more accessible for depolymerization. After pretreatment, the cellulose can either follow the diluted acid hydrolysis or the concentrated method. In the diluted method, the cellulose is hydrolyzed into glucose utilizing a low sulfuric acid concentration in a reactor at a relatively higher temperature of about 473 K. As for the concentrated acid hydrolysis, it requires a higher sulfuric acid concentration but the process can operate at a lower temperature compared to the diluted method. Lignin is formed during the hydrolysis process and therefore needs to be separated from the mixture before the sugars are fermented. Lignin can be burned to produce energy to subsidize the energy required by the acid hydrolysis process. After the separation of lignin, simple sugars such as glucose and xylose follow the fermentation route using yeast to yield ethanol.

### *Enzymatic hydrolysis followed by fermentation*

Figure 1 described the process of enzymatic hydrolysis of biomass as a separate hydrolysis and fermentation (SHF) process. In enzyme hydrolysis method, biomass also needs to undergo a pretreatment phase similar to the acid hydrolysis before enzymes such as cellulase are added into the process to depolymerize cellulose to glucose. Similar to the acid



**Figure 1: Ethanol Production via Enzymatic Hydrolysis**

hydrolysis process, lignin that is produced is separated from the process for energy production uses. The sugars produced are then fermented into ethanol using yeast. The problem with the SHF process is with the product inhibition associated with enzymes which ultimately stops the process before all the cellulose can be degraded. Therefore, the simultaneous saccharification and fermentation (SSF) method is proposed. The SSF process combines the cellulase enzyme and the fermenting microbe in the same reactor so that ethanol is produced readily as glucose is being produced.

### *Gasification*

Gasification converts biomass into carbon monoxide and hydrogen by reacting the raw material at high temperatures with a controlled amount of oxygen. The product is a synthetic gas fuel called syngas. Syngas is more efficient than direct combustion of the original fuel, as more of the energy contained in the fuel is extracted. It can be burned directly in internal combustion engines or converted into liquid fuel using the Fischer-Tropsch process. The gas can also be used anywhere you would normally use natural gas, such as for electricity generation. Another benefit is that the high temperature reaction refines out the corrosive chemicals so that the produced gas is clean. The Fischer-Tropsch process is a catalyzed chemical reaction to convert CO and H<sub>2</sub> into liquid hydrocarbons using iron and/or cobalt as catalyst.

### *Pyrolysis*

Pyrolysis is the method that will be used in this project to generate bio-oil. It consists of heating the biomass to high temperatures in the absence of oxygen. Fast pyrolysis produces a high yield of liquid bio-oil as well as combustible gas similar to syngas and solid char. All three products have potential fuel use, as they can all be burned to produce energy for boilers. The bio-oil can also be upgraded to be used in combustion engines through hydrotreating or catalytic deoxygenation. The pyrolysis process is slightly endothermic, so heat must be supplied.

## **Switchgrass**

Switchgrass is a perennial grass native to North America. It grows fast and can stand up to ten feet high after one growing season. It is relatively easy to produce, and can be grown in marginal land that would otherwise not be used. Due to its root system, it can be useful to the farmer in preventing soil erosion<sup>5</sup>. Also, as it is a prairie grass, it provides a suitable habitat for birds and animals native to the Great Plains. The grass can be cut and baled with conventional mowers and balers and can be harvested either annually or semiannually for ten years before it needs to be replanted<sup>1</sup>. One field of switchgrass yields from 5.2 to 11.1 metric tons of grass bales per hectare, depending the amount of rainfall<sup>6</sup>. Because the grass only needs to be planted once, it will deliver an average of 13.1 megajoules of energy as ethanol for every megajoule of petroleum consumed in growing the plant.<sup>6</sup> This means that switchgrass ethanol returns 540% of the energy used to grow it while corn ethanol only returns about 25% more energy.<sup>6</sup> Aside from being turned into ethanol through a fermentation process, switchgrass can also be used for gasification and pyrolysis.

Switchgrass is sold in bales and costs approximately \$35 per ton. Thus it provides an inexpensive feed for the biofuels plant. This project uses a basis of 100 tons/hr of switchgrass feed. In order to generate enough switchgrass to supply the plant for a year, 108,000 acres or 170 mi<sup>2</sup> must be devoted to switchgrass production. This assumes two harvests a year, one in

spring and one in fall. If the switchgrass is only harvested once a year, then twice this area will be needed.

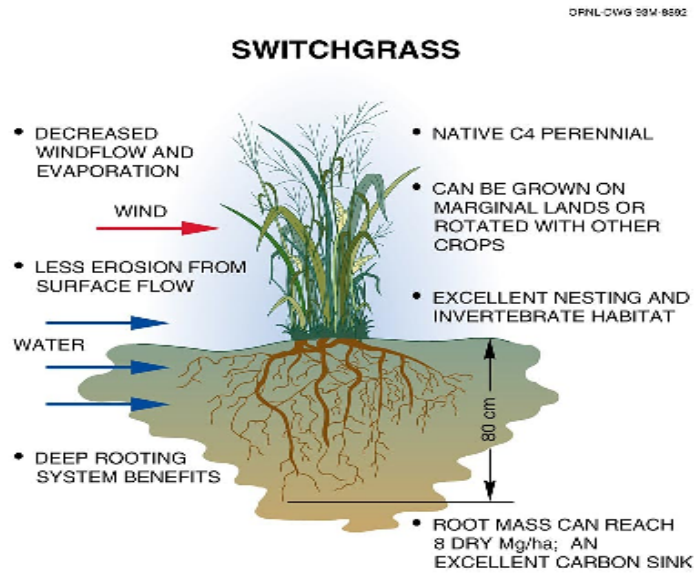


Figure 2: Switchgrass Benefits<sup>5</sup>

### Plant Location and Transportation Costs

The switchgrass to bio-fuel plant should be located in the Midwest so as to be located near farms producing switchgrass and thus minimize transportation costs. To transport switchgrass costs approximately \$0.10 per ton per mile<sup>4</sup>. It was assumed that this cost would be charged to the biofuels plant and not to the farmers. Therefore, additional costs due to transportation must be estimated. It was assumed that the feed supply for the plant would come from farms within a radius of 20 to 200 miles. A roughly standard normal distribution was assumed, with the majority of the switchgrass coming from the closer farms. The figure below shows the distance distribution of farms from the biofuels plant. Transportation costs were estimated to be \$862 per 100 tons of switchgrass.



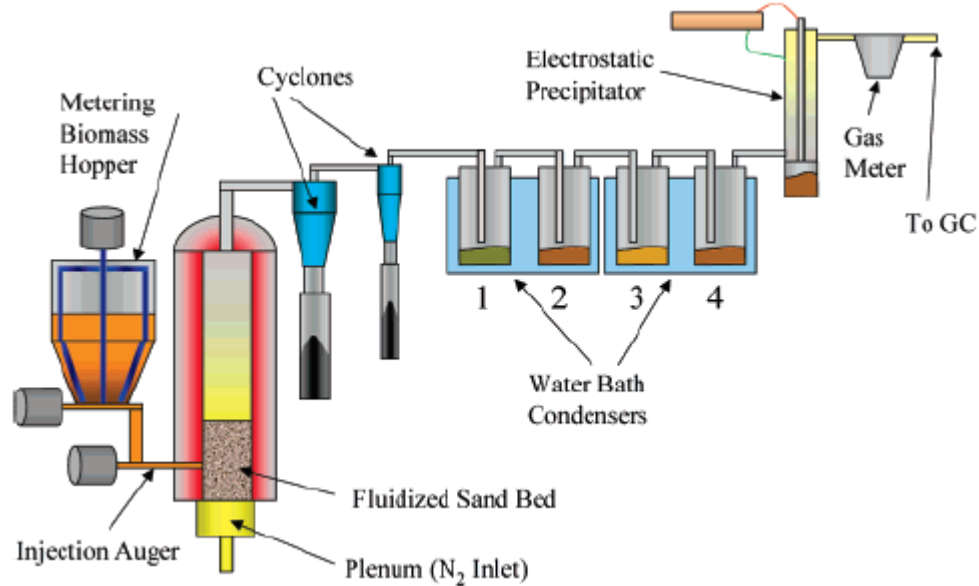
**Figure 3: Distance Distribution of Farms from Biofuels Plant**

It was decided to build the plant in Iowa as it is centered in the Midwest and so has good access to switchgrass farms. Also, there are four large refineries located in Iowa, two of them own by major oil companies that may be interested in purchasing the bio-oil from the plant. Also, research is currently being done in Iowa on the cultivation of switchgrass and the development of a biofuels plant.

Though the machinery for the biofuels plant may not take up more than a few acres, there also needs to be space allotted for administration offices. Also, as the feedstock of switchgrass will be taken in twice a year and then fed into the system at a steady rate the rest of the time, a large amount of space needs to be allotted for storage. Based on these considerations, it was estimated that 20 acres should be purchased for building the biofuels plant. Cost of land in Iowa is approximately \$5100 per acre. Therefore, the cost of land for the plant is \$102,000.

### **Pyrolysis Process**

For this project, a pyrolysis system will be use to convert switchgrass to bio-oil. This industrial-size system will be used in all three options considered by this project. It is based on the design of a bench-scale pyrolysis reactor developed by Boateng et al for switchgrass conversion<sup>2</sup>. The switchgrass is fed into a metering hopper that feeds it into the fluidized bed reactor. Following the reactor is a series of separators. First are cyclones to separate out and collect the solid char. Next the gaseous product is passed through a series of canisters set in a coldwater bath where the water and soluble bio-oil components are condensed out. Final capture of the bio-oil was achieved with an electrostatic precipitator (ESP). The noncondensable gas (NCG) passes to a gas meter as a product stream.



**Figure 4: Basic Flow Diagram for Pyrolysis Process<sup>2</sup>**

The product recovery from this bench-scale process was approximately 61% bio-oil, 13% char, and 11% NCG<sup>2</sup>. This high liquid recovery percent is average for fast pyrolysis reactors. The chemicals recovered in significant proportions in the liquid bio-oil were hydroxyacetaldehyde, levoglucosan, and their decomposition fragments, acetic acid and acetol<sup>2</sup>. These two larger molecules are both believed to be from the decomposition of cellulose. The NCG contained primarily CO and CO<sub>2</sub> in a 2:1 ratio respectively<sup>2</sup>. Also, the properties of the recovered charcoal are similar to some types of U.S. coal<sup>2</sup>. Thus, both the NCG and the char are of combustible quality and could be used to fuel the pyrolysis reactor.

In the industrial-sized system designed during this project, the water baths and ESP are combined into a quencher. The quencher will cool down the vapor and stop the pyrolysis reaction, as well as condensing out the bio-oil. Also, before the switchgrass enters the reactor, it will first pass through a heater and hammer mill. The heater will reduce the moisture content in switchgrass to less than 10% wt and the hammer mill will cut it into small uniform pieces. This serves two purposes: 1) the dry and evenly cut switchgrass is much less likely to clog up the reactor system than wet mass is, and 2) drying the switchgrass before it enters the reactor decreases the water content within the system and thus reduces energy costs as the reactor will then not have to expend energy vaporizing the water.



## Reactor Type and Temperature

There are several types of pyrolysis reactors, as described in the table below.

Property	Status	Bio-oil wt%	Complexity	Feed size	Inert gas need	Specific size	Scale up
Fluid bed	Demo	75	Medium	Small	High	Medium	Easy
CFB	Pilot	75	High	Medium	High	Large	Easy
Entrained	None	65	High	Small	High	Large	Easy
Rotating cone	Pilot	65	High	V small	Low	Small	Hard
Ablative	Lab	75	High	Large	Low	Small	Hard
Auger	Lab	65	Low	Small	Low	Medium	Easy
Vacuum	Demo	60	High	Large	Low	Large	Hard
The darker the cell color, the less desirable the process.				Lab: 1 – 20 kg h <sup>-1</sup> Pilot: 20 – 200 kg h <sup>-1</sup> Demo: 200 – 2000 kg h <sup>-1</sup>			

Adapted from PYNE IEA Bioenergy <http://www.pyne.co.uk>

**Table 1: Types of Pyrolysis Reactors<sup>3</sup>**

To optimize the maximum bio-oil throughput, the reactor that would yield the highest bio-oil weight percent will be of interest. Shown in table 1, the fluidized bed reactor, circulating fluidized bed (CFB) and the ablative pyrolyzer will all yield 75 wt % bio-oil from biomass feed. However, not all of these reactors can use switchgrass as the biomass feedstock. The ablative pyrolyzer requires wood exclusively. Therefore, both the fluidized bed reactors can be chosen to be the reactor of choice because they both accept switchgrass as a biomass feedstock. Nevertheless, the fluidized bed reactor is easy to scale up and the complexity, along with the specific size of the system, is lower compared to the CFB. Moreover, the fluidized bed reactor's system is closer to the industrial scale as there are currently demo plants producing bio-fuel built using that specific reactor type. Therefore, the fluidized bed reactor will be the reactor of choice for our pyrolysis system.

Figure 5 shows the relationship between the percent bio-oil yield and the pyrolysis reactor temperature. The optimum temperature for the reactor to yield the highest amount of bio-oil is between 470 °C to 490 °C. The data also shows that the percent bio-oil yield peaks at about 75 % when the pyrolysis reactor temperature is at about 480 °C. Therefore, our fluidized bed pyrolysis reactor will be operating at 480 °C to maximize the percent yield of bio-oil.

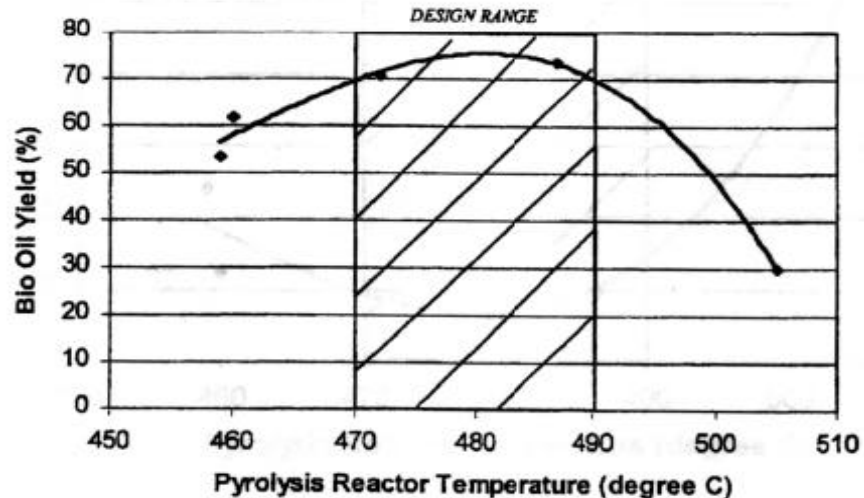


Figure 5: Yield vs. Reactor Temperature.<sup>8</sup>

### Three Options for Design of a Biofuels Plant

This project analyzed three possible processes to produce fuel from switchgrass using pyrolysis. They differ in complexity, capital costs, and end products. The three methods are 1) selling the bio-oil to generate electricity, 2) upgrading the bio-oil through hydrotreating, and 3) upgrading the bio-oil using a zeolite catalyst.

#### *Option 1: Selling the Bio-Oil to Produce Electricity*

This option is the simplest of the three that were considered, as it requires the least equipment. However, it should be noted that this option does not satisfy the goal of producing liquid fuel suitable for automobile engines. Therefore, this analysis was performed for this project as a comparison tool, but the process should be considered as a stepping stone towards an upgraded fuel and not as a final solution.

The end products are oxygenated bio-oil, NCG, and char. First the switchgrass is sent through a heater and hammer mill to prepare it for the pyrolysis reactor. In the heater, it is dried to less than 10% water content. In the hammer mill, the grass is ground up into smaller and more uniform pieces. Both of these steps aid in preventing the system from clogging up with wet and/or large pieces of the grass. From the hammer mill, the switchgrass passes into the pyrolysis system, consisting of the fluidized bed pyrolysis reactor, cyclones, and quencher. The thermal decomposition of switchgrass occurs in the pyrolysis reactor through an endothermic reaction. The pyrolysis product is then passed through the cyclone to remove the char from the gaseous products. In order to stop the aging of the bio-oil, it is quenched as soon as possible to room temperature. In addition, the quencher functions as a heat exchanger, cooling the high-energy gaseous pyrolysis products and producing steam. The steam can then be used to subsidize the energy needed to maintain the pyrolysis reactor at operating temperature.

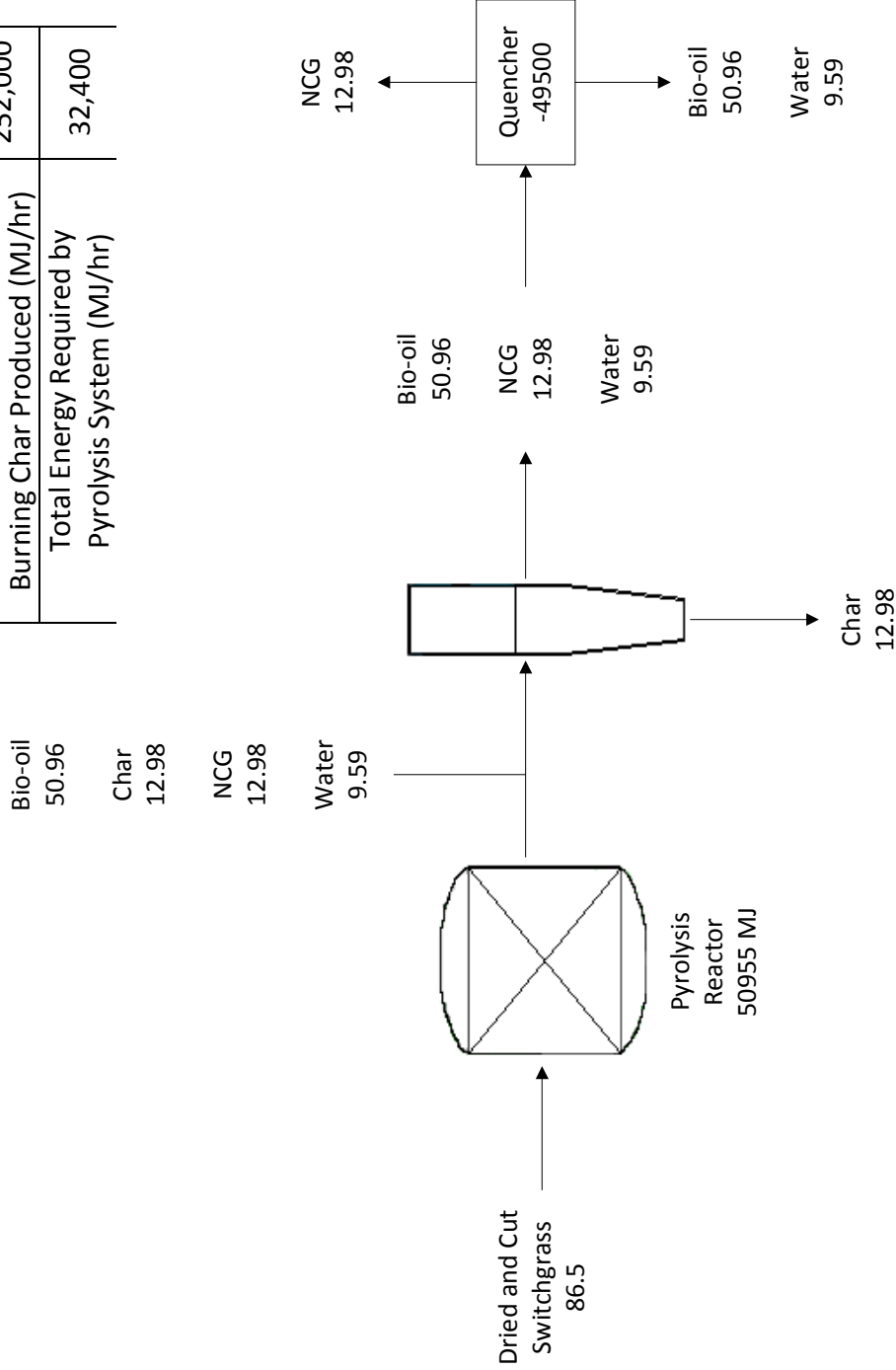
The total energy requirement for this system is 32,400 MJ. The char generated during the process is capable of providing 252,000 MJ of energy, so there is plenty of char to fuel the system. The left over char can be sold as solid fuel for \$0.35 per GJ produced. Also, the NCG can be sold as natural gas at \$8.9 per MMBTU. The process flow diagram (PFD) including mass

and energy balances is shown below. Pictures or diagrams of the major pieces of equipment are also shown below the PFD.

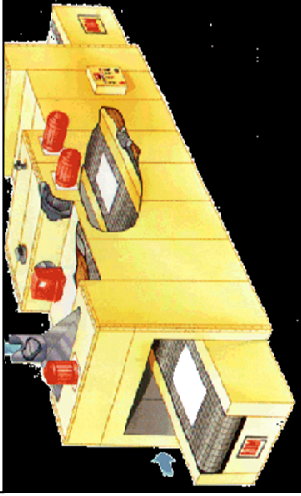


Units = Metric Tons/hr

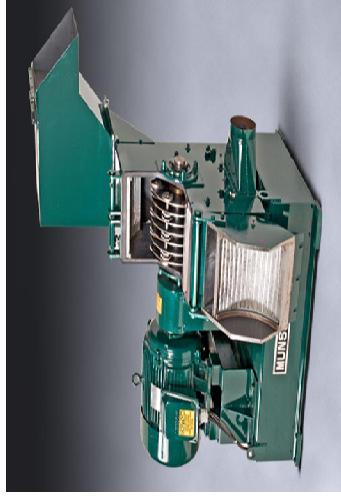
Total Energy Generated by Burning Char Produced (MJ/hr)	252,000
Total Energy Required by Pyrolysis System (MJ/hr)	32,400



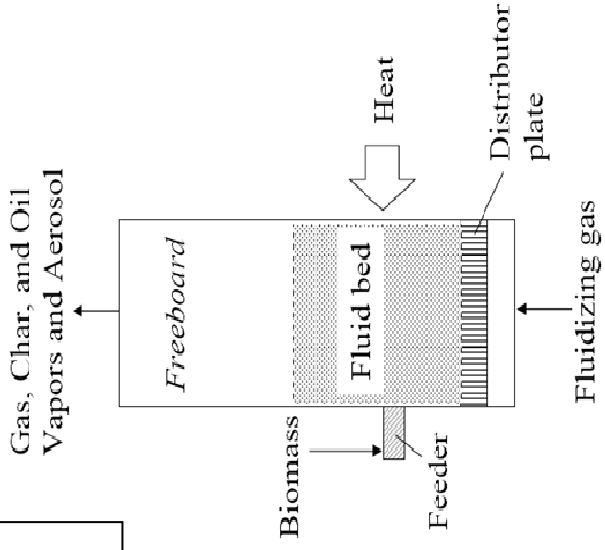
**Equipment used in Pyrolysis Process:**



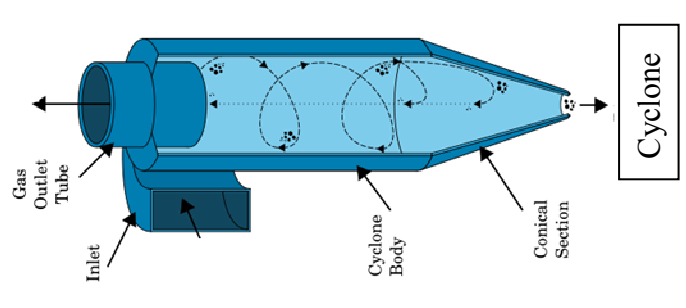
Heater Oven



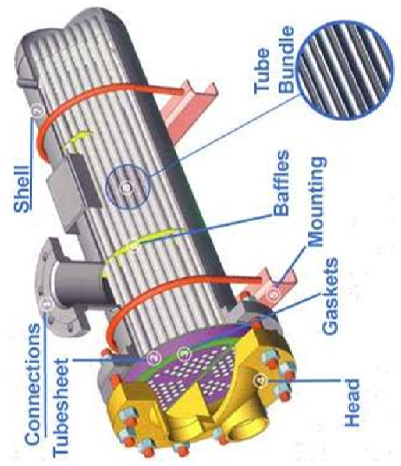
Hammer Mill



Fluidized Bed Pyrolysis Reactor



Cyclone



Quencher

### *Capital Costs:*

The pyrolysis system is sold as a unit that includes heater, hammer mill, reactor, cyclones, and quencher. The system costs approximately \$1.2 million<sup>8</sup>. An initial estimation of the capital costs for the biofuels plant is shown in the table below. Fixed capital investment (FCI) is approximately \$6.6 million and total capital investment (TCI) is approximately \$7.7 million. This option was the least expensive of the three options considered, both in capital investment and manufacturing costs.

#### **Capital Costs**

<b>Equipment Cost</b>	
Pyrolysis unit	\$1,200,000
Land (acres)	\$100,000
<i>Total Equipment Costs</i>	\$1,300,000
<b>Direct Costs</b>	
Purchased equipment	\$1,303,000
Purchased-equipment installation	\$612,000
Instrumentation and controls	\$469,000
Piping	\$886,000
Electrical systems	\$143,000
Buildings	\$235,000
Yard improvements	\$130,000
Service facilities	\$912,000
<i>Total Direct Costs</i>	\$4,690,000
<b>Indirect Costs</b>	
Engineering and supervision	\$430,000
Construction expenses	\$534,000
Legal expenses	\$52,000
Contractor's fee	\$287,000
Contingency	\$573,000
<i>Total Indirect Costs</i>	\$1,876,000
<b>Fixed Capital Investment</b>	\$6,566,000
Working Capital	\$1,159,000
<b>Total Capital Investment</b>	\$7,726,000

### *Manufacturing Costs:*

The direct production costs come from the switchgrass feed and transportation costs. The table below summarizes the manufacturing costs for the plant in millions of dollars. These estimates were based on an economic model for predicting the cost of biofuels plants<sup>7</sup> as well as the Peters and Timmerhaus textbook<sup>10</sup>. Also, the cost of operating labor was based on three operators with pay of \$12.50 an hour plus labor benefits.

**Manufacturing Cost (in millions \$/yr)**

<b>A. Direct production costs</b>	<b>\$8.86</b>
Operating labor	\$0.46
Direct supervisory and clerical labor	\$0.07
Maintenance and repairs	\$0.39
Utilities	\$3.9
Patents and royalties	\$3.92
Wastewater treatment	\$0.1
<b>B. Fixed charges</b>	<b>\$7.80</b>
Local taxes	\$0.66
Insurance	\$3.28
Financing	\$3.86
<b>C. Plant Overhead</b>	<b>\$3.92</b>
<b>D. General Expenses</b>	<b>\$9.16</b>
Administrative costs	\$3.28
Distribution and marketing	\$3.92
Research and development	\$1.96
<i>Total</i>	<b>\$29.75</b>

*Profitability:*

The economic feasibility of this project was analyzed for a ten year time period. An inflation rate of 3% was assumed. The table below shows the economic breakdown of the process in millions of dollars. For this analysis, it was assumed that the bio-oil would be sold for \$50/bbl. From this breakdown, we conclude that the process would be profitable with a reasonably good return on investment.

**Economic Analysis (in million \$/yr)**

<b>Year</b>	<b>Sales</b>	<b>Cost</b>	<b>Revenue</b>	<b>Depreciation</b>	<b>Net Profit</b>	<b>ROI</b>
1	\$143.46	\$29.75	\$113.72	\$0.66	\$74.62	9.66
2	\$147.77	\$30.64	\$117.13	\$0.66	\$76.87	9.95
3	\$152.20	\$31.56	\$120.64	\$0.66	\$79.19	10.25
4	\$156.76	\$32.50	\$124.26	\$0.66	\$81.58	10.56
5	\$161.47	\$33.48	\$127.99	\$0.66	\$84.04	10.88
6	\$166.31	\$34.48	\$131.83	\$0.66	\$86.57	11.21
7	\$171.30	\$35.52	\$135.78	\$0.66	\$89.18	11.54
8	\$176.44	\$36.58	\$139.86	\$0.66	\$91.87	11.89
9	\$181.73	\$37.68	\$144.05	\$0.66	\$94.64	12.25
10	\$187.18	\$38.81	\$148.37	\$0.66	\$97.49	12.62

To further evaluate profitability, a plot of the ROI at various sale prices of bio-oil was created. The cheapest price the bio-oil could be sold at and still break even is \$1.68/bbl. Operating in the breakeven range is not recommended however, as return on investment is essentially zero. An ROI of 8% is generally necessary to consider a process a good investment. A bio-oil price of \$55/bbl will give a 10% ROI, so this would be a good price to sell the product for. This can be seen in the graph below, which evaluates ROI at various product bio-oil prices.

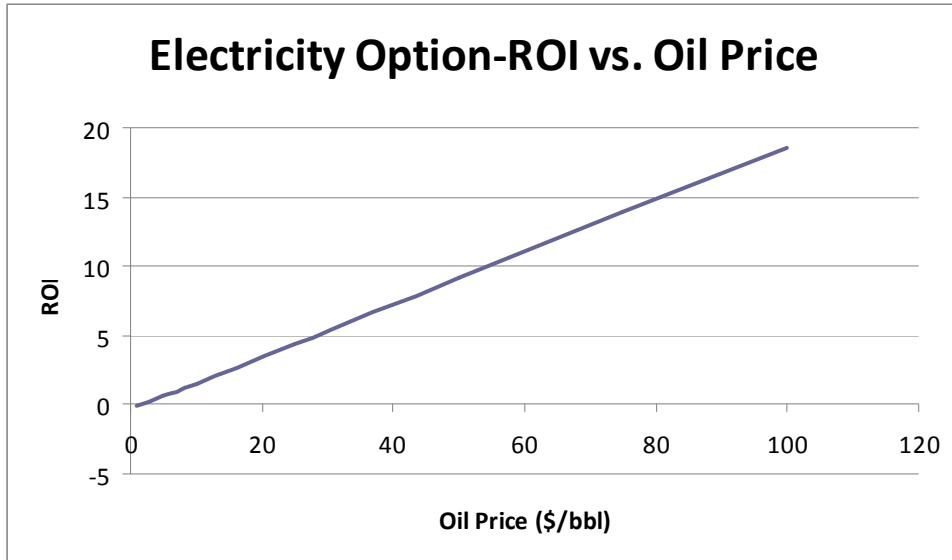


Figure 6: ROI at various Product Bio-Oil Prices

In addition to the price of bio-oil, the effect of changing the production rate of the process was also examined. For a bio-oil price of \$50/bbl, the process reached a breakeven point at 13 ton/hr of switchgrass feed. As this production rate is increased, the ROI will increase. In order to make an ROI of 10% and sell the bio-oil at \$50/bbl, the switchgrass feed needs to be 105 ton/hr, or 2.36 million barrels of bio-oil produced per year.

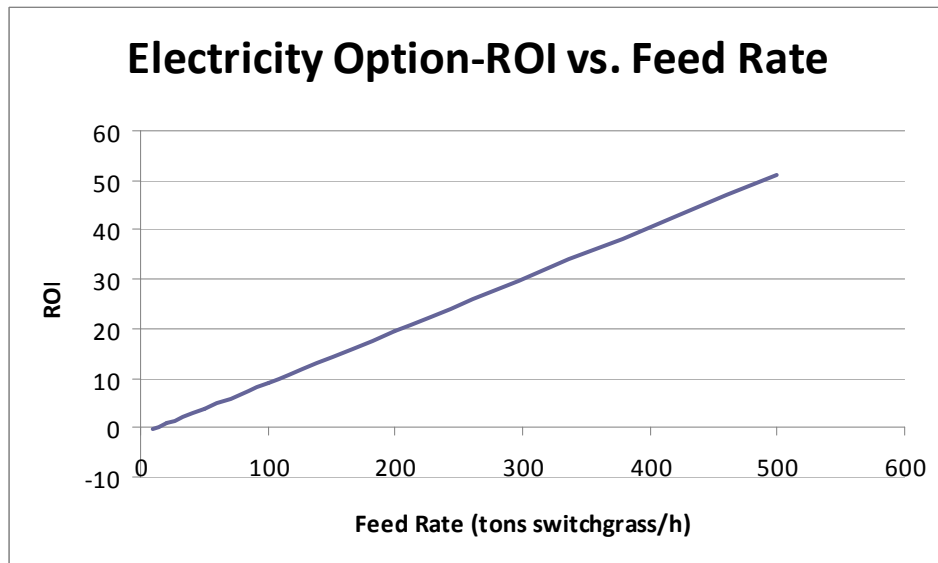


Figure 7: ROI for Various Sizes of Plants

From this economic analysis, it can be seen that using the pyrolysis process to produce bio-oil and selling this bio-oil without upgrading to produce electricity is a profitable process. A plant producing 2.36 million bbl/yr and selling the bio-oil for just over \$50/bbl will obtain a 10% ROI. Thus it is concluded that this option is economically profitable. However, as mentioned at

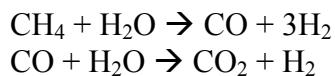


the beginning of this section, this process will not result in a fuel suitable for automobile engines. While the bio-oil can be used as fuel for boilers to generate electricity, additional processing must be performed on the bio-oil to upgrade it. Hydrotreating and catalytic deoxygenation were the two processes considered for this.

### *Option 2: Upgrading the bio-oil to liquid fuel with Hydrotreating*

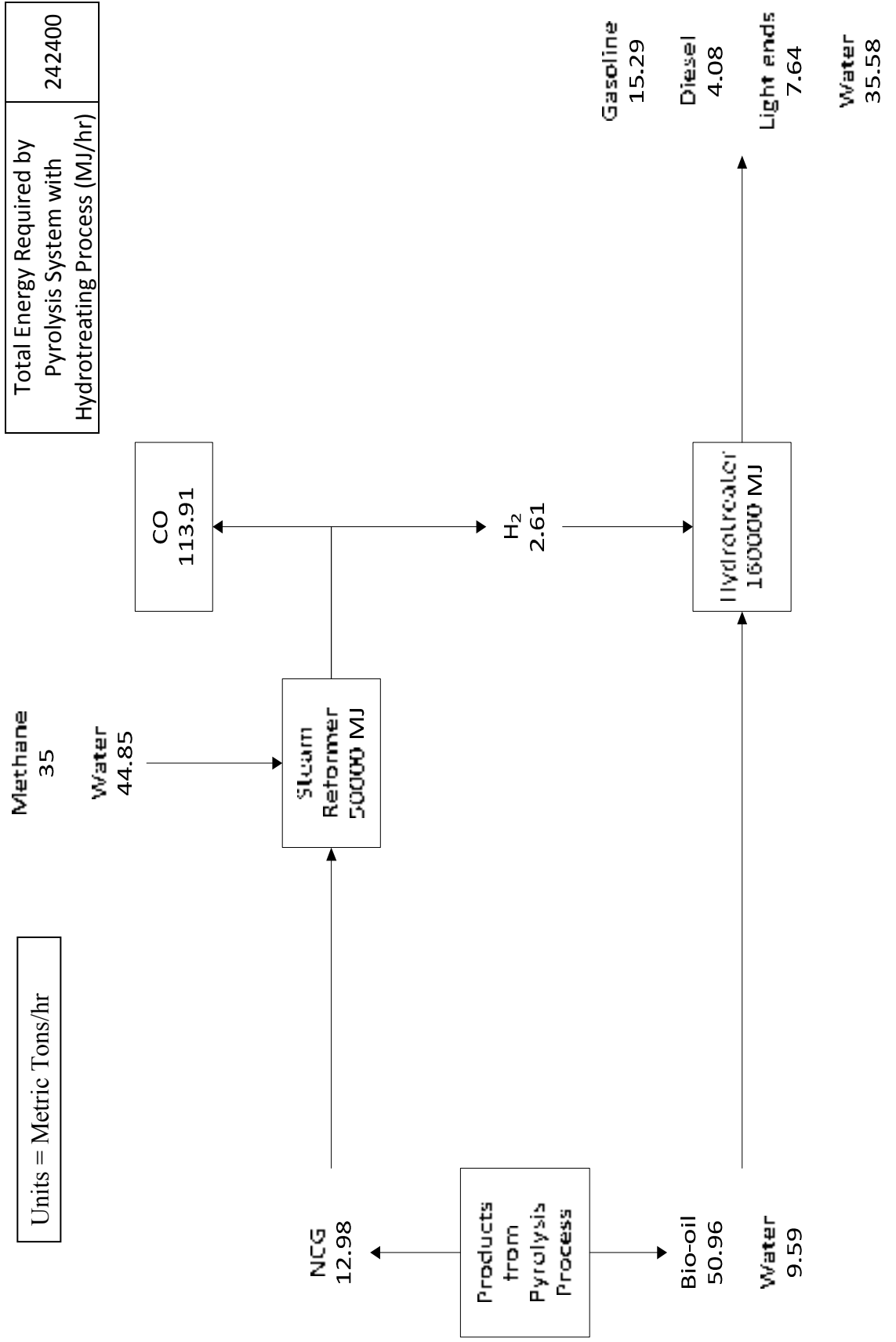
The bio-oil produced through pyrolysis contains too much oxygen to be suitable in a combustion engine and so it needs to be upgraded. One method is to feed the bio-oil from the pyrolysis system into a hydrotreater where it is reacted with hydrogen to produce liquid fuel and water. The products from this process are gasoline grade oil, diesel grade oil, and some light end hydrocarbons. Once again, the char from the pyrolysis system is used to fuel the plant.

The NCG from the pyrolysis product is reacted in a steam reforming process to produce hydrogen to fuel the hydrotreater. Steam reforming is a commonly used industrial process to generate hydrogen. In the process, steam is reacted with methane at high temperatures of 700-1100 °C in the presence of a metal-based catalyst. This forms carbon monoxide and hydrogen. The carbon monoxide can then be reacted in a lower temperature reaction to produce more H<sub>2</sub>. The two reactions are:



However, there is not enough NCG generated by pyrolysis to supply all of the necessary hydrogen for the hydrotreater, so natural gas must be purchased to make up the deficit, as well as extra water for steam. Due to these extra costs, the process was determined to be unprofitable.

The same pyrolysis system is shown in the PFD below to produce the needed bio-oil along with the mass balances of the system. The NCG produced by the pyrolysis system, along with additional methane and water, is then used in the steam reformer to produce the hydrogen required in the hydrotreater to upgrade the bio-oil into fuel suitable for automotive engines. Figure 8 shows the steam reforming process to produce the necessary hydrogen. The energy required by the system is estimated to be 50,000 MJ/hr. Figure 9 below shows the hydrotreating process that upgrades the bio-oil into fuels. The energy required by the hydrotreating process is 160,000 MJ/hr. The total amount of energy required by the pyrolysis system along with the processes required to upgrade bio-oil to fuel is found to be 242,400 MJ/hr. Although that is a huge amount, the energy acquired from burning the char produced in the pyrolysis system can fully account for energy needed by this process.



Energy Required (MJ/hr)	
Steam Reformer	50000

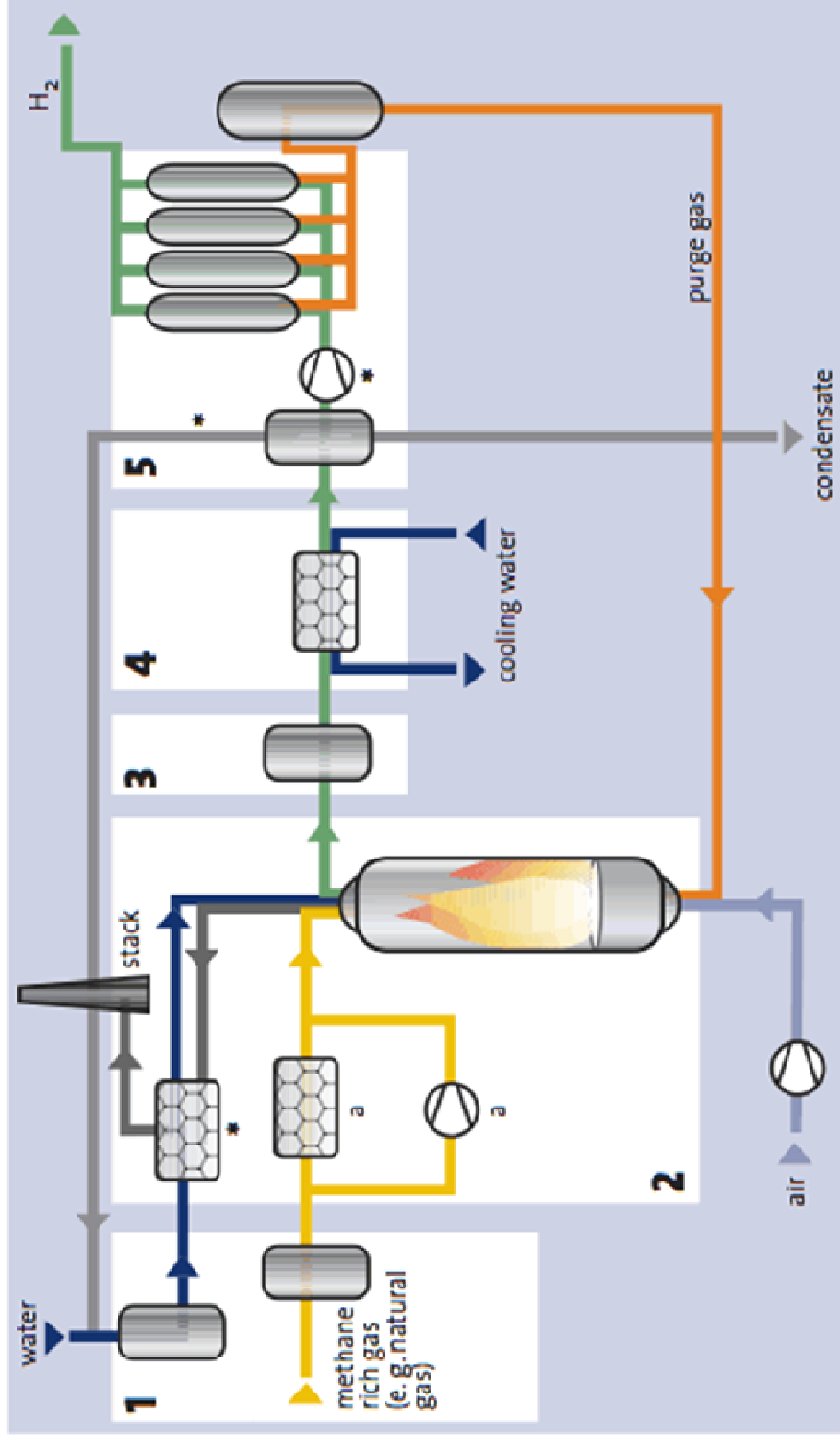


Figure 8: PFD of a Steam Reformer: 1 Feed Pre-Treatment 2 Reforming & Steam Generation 3 High Temperature Conversion 4 Heat Exchanger Unit 5 Purification Unit \* optional, depending on reformer design a either heat exchanger for low pressure reformer or compression to 1 bar for high pressure reformer Flow Chart of a Steam Reformer.<sup>13</sup>

Energy Required (MJ/hr)	
Hydrotreater	160000

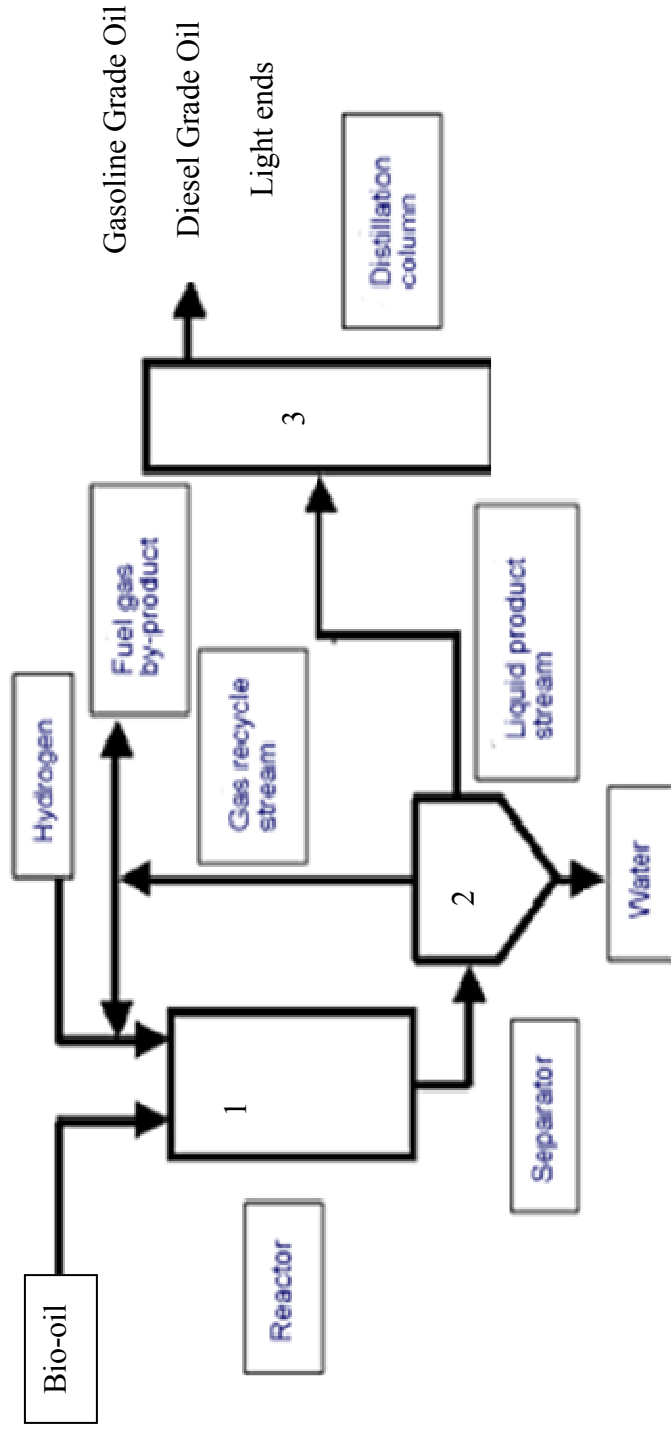


Figure 9: PFD of a Hydrotreating Process: 1 Hydrotreater 2 Separator 3 Distillation Column.<sup>14</sup>

### Possible Chemical Reactions

The bio-oil produced during the pyrolysis process is composed of a mixture of over twenty different compounds, each making up a small percentage of the overall mixture. (For a list of these compounds, see the description of the third option considered by this project.) Four compounds that make up larger percentages of the bio-oil than the rest are hydroxyacetaldehyde ( $C_2H_4O_2$ ), levoglucosan ( $C_6H_{10}O_5$ ), acetol ( $C_3H_6O_2$ ), and acetic acid ( $CH_3COOH$ )<sup>2</sup>. A number of different reactions can occur with just these four compounds in combination with hydrogen during the hydrotreating process. A sample of the possible reactions is shown in the table below. Also shown are approximate values for the Gibbs energy of reaction and the equilibrium constant for each reaction. These values were calculated for a temperature of 700 K, as this is the temperature of the hydrotreater. A negative  $\Delta G$  value and large K value indicates a favorable irreversible reaction.

**Possible Chemical Reactions During Hydrotreating**

#	Reaction	$\Delta G$ (kJ/mol)	K
1	$C_2H_4O_2 + 3H_2 \rightarrow C_2H_6 + 2H_2O$	-190	1.6E14
2	$C_6H_{10}O_5 + 6H_2 \rightarrow C_6H_{12} + 5H_2O$	-695	7.4E51
3	$CH_3COOH + 3H_2 \rightarrow C_2H_6 + 2H_2O$	-79	7.9E5
4	$C_3H_6O_2 + 3H_2 \rightarrow C_3H_8 + 2H_2O$	-153	2.9E11
5	$C_6H_{10}O_5 + 8H_2 \rightarrow 2C_3H_8 + 5H_2O$	-735	6.5E54
6	$C_6H_{10}O_5 + 5H_2 \rightarrow C_6H_{14}O_2 + 3H_2O$	-640	6.1E47
7	$C_6H_{10}O_5 + 4H_2 \rightarrow C_6H_{12}O_2 + 3H_2O$	-645	1.5E48
8	$C_6H_{10}O_5 + 9H_2 \rightarrow 3C_2H_6 + 5H_2O$	184	1.8E-14
9	$C_3H_6O_2 + H_2 \rightarrow C_2H_6O + H_2O$	-93	8.2E6
10	$C_3H_6O_2 + 2H_2 \rightarrow C_3H_8O + H_2O$	-97	1.9E7
11	$CH_3COOH + H_2 \rightarrow C_2H_4O + H_2O$	-5.6	2.6
12	$CH_3COOH + H_2 \rightarrow C_2H_6O + H_2O$	6.5	0.33
13	$C_2H_4O_2 + H_2 \rightarrow C_2H_4O + H_2O$	-102	3.9E7
14	$C_2H_4O_2 + 2H_2 \rightarrow C_2H_6O + H_2O$	-92	7.5E6

### Capital Cost:

This option had the highest capital cost of the three options that were considered. In addition to the pyrolysis system and land for the biofuels plant, there are also capital costs associated with the hydrotreater and steam reformer. These initial estimates for capital costs are shown in the table below.

**Capital Costs (in million \$)**

<b>Equipment Cost</b>	
Pyrolysis unit	\$1.20
Hydrotreater	\$5.00
Steam Reformer	\$0.69
Land (acres)	\$0.10
<b>Total Equipment Costs</b>	<b>\$6.99</b>
<b>Direct Costs</b>	
Purchased equipment	\$6.99
Purchased-equipment installation	\$3.29

Instrumentation and controls	\$2.52
Piping	\$4.76
Electrical systems	\$0.77
Buildings	\$1.26
Yard improvements	\$0.70
Service facilities	\$4.89
<i>Total Direct Costs</i>	\$25.17
<b>Indirect Costs</b>	
Engineering and supervision	\$2.31
Construction expenses	\$2.87
Legal expenses	\$0.28
Contractor's fee	\$1.54
Contingency	\$3.08
<i>Total Indirect Costs</i>	\$10.07
<b>Fixed Capital Investment</b>	
Working Capital	\$6.22
<b>Total Capital Investment</b>	\$41.47

*Manufacturing Costs:*

This option also had the highest manufacturing costs of all three options. There are production costs from the natural gas and water for the steam reformer in addition to the switchgrass feed and transportation costs. The table below summarizes the manufacturing costs for the plant. These estimates were based on an economic model for predicting the cost of biofuels plants<sup>7</sup> as well as the Peters and Timmerhaus textbook<sup>10</sup>. Also, the cost of operating labor was based on five operators with pay of \$12.50 an hour plus labor benefits. There are more operators hired for this option than for the first option due to the increased complexity of the plant.

**Manufacturing Cost (in millions \$/yr)**

<b>A. Direct production costs</b>	\$50.8
Operating labor	\$0.8
Direct supervisory and clerical labor	\$0.1
Maintenance and repairs	\$2.1
Utilities	\$28.4
Patents and royalties	\$18.9
Wastewater treatment	\$0.5
<b>B. Fixed charges</b>	\$41.9
Local taxes	\$3.5
Insurance	\$17.6
Financing	\$20.7
<b>C. Plant Overhead</b>	\$18.9
<b>D. General Expenses</b>	\$46.0
Administrative costs	\$17.6
Distribution and marketing	\$18.9
Research and development	\$9.5
<i>Total</i>	\$157.7

*Profitability:*

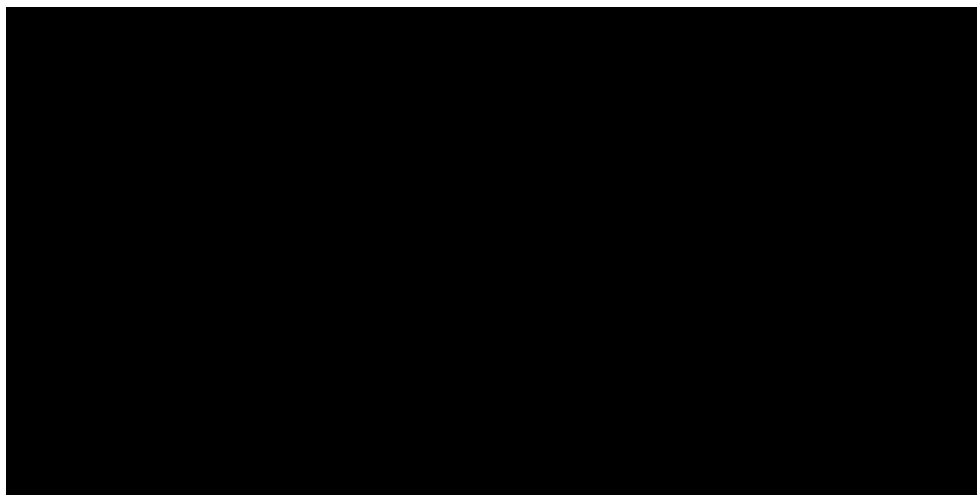
The economic feasibility of this project was analyzed for a ten year time period. An inflation rate of 3% was assumed. As mentioned, this project was the most expensive in terms of capital and manufacturing costs. Therefore, it was not surprising to find that the process is not profitable. The table below shows the profitability assuming that the product oil is sold for \$100/bbl and the feed rate of switchgrass is 100 tons/hr.

**Economic Analysis (in million \$)**

Year	Sales	Cost	Revenue	Depreciation	Net Profit	ROI
1	\$140.42	\$157.70	-\$17.27	\$3.52	-\$13.73	-0.33
2	\$144.64	\$162.43	-\$17.79	\$3.52	-\$14.07	-0.34
3	\$148.97	\$167.30	-\$18.33	\$3.52	-\$14.42	-0.35
4	\$153.44	\$172.32	-\$18.88	\$3.52	-\$14.78	-0.36
5	\$158.05	\$177.49	-\$19.44	\$3.52	-\$15.16	-0.37
6	\$162.79	\$182.81	-\$20.03	\$3.52	-\$15.54	-0.37
7	\$167.67	\$188.30	-\$20.63	\$3.52	-\$15.94	-0.38
8	\$172.70	\$193.95	-\$21.25	\$3.52	-\$16.35	-0.39
9	\$177.88	\$199.77	-\$21.88	\$3.52	-\$16.77	-0.4
10	\$183.22	\$205.76	-\$22.54	\$3.52	-\$17.20	-0.41

Below, three factors were examined to try and make the process profitable. These were the selling price of the product oil, the scale of the plant, and the cost of methane that is supplied to the steam reformer. The breakeven prices were determined for each of these factors. However, a process that breaks even only means that net profit is zero. In other words, the process is neither losing nor gaining money. Return on investment will be essentially zero. It is not recommended that a process be operated in this breakeven range long term. In fact, it is recommended that the process not be built unless 8% or larger ROI can be assured. Nevertheless, it is useful to know the requirements for a process to meet in order to break even.

In order for the process to break even, the price of product oil would have to be raised to \$119/bbl. This is seen in the table below where ROI has been determined over a range of product oil prices.



**Figure 10: ROI at Various Prices of Product Oil**

Though making the plant smaller will not increase the profitability of the process, increasing its size will. If the rate of switchgrass feed is increased to 165 ton/hr, then this process will break even. This is the equivalent of producing 1.1 million bbl/yr of product oil.

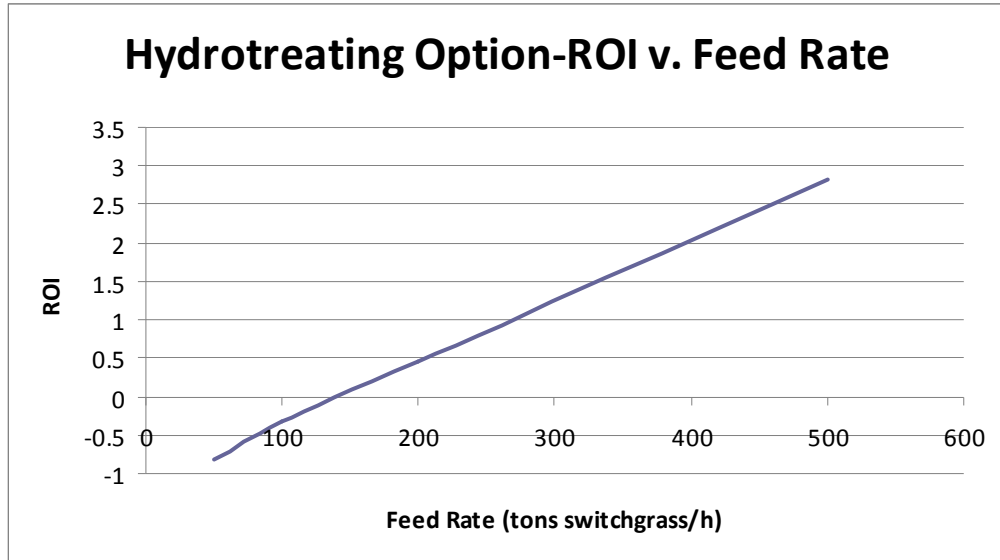


Figure 11: ROI for Various Plant Sizes

One final factor to consider is the price of natural gas, as this is the most significant manufacturing cost. If the price of natural gas were reduced to \$6.30/MMBTU, then this process would break even. The current price of natural gas is \$8.9/MMBTU. This suggests that perhaps though this process is not economical as a stand-alone process, if it were combined with an existing plant that had extra natural gas, or where natural gas was lower priced, then the process may become feasible.

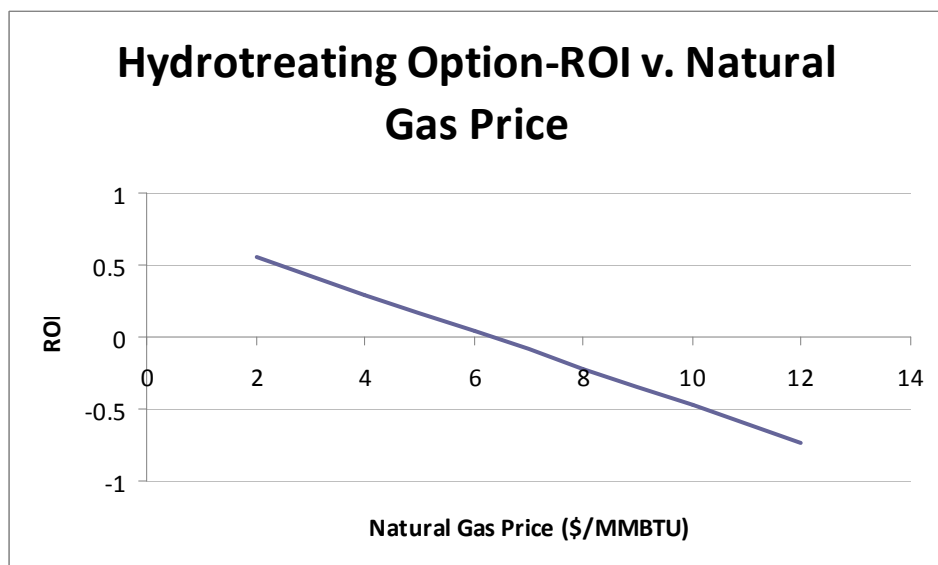


Figure 12: ROI for Various Prices of Natural Gas



As a final consideration, an optimized process scenario was considered. For this scenario, the price of the product oil was raised to the breakeven price of \$119/bbl. Also, the scale of the plant was increased to 500 tons/hr of switchgrass feed. The price of natural gas was not changed, however, as this price is unlikely to decrease. When this optimal scenario was generated, the following profitability table was obtained. From this table we see that it is possible to obtain a positive net profit and ROI. However, the ROI does not reach the desired 8% ROI.

**Economic Analysis for Optimized Scenario (in million \$)**

Year	Sales	Cost	Revenue	Depreciation	Net Profit	ROI
1	\$808.07	\$501.92	\$306.15	\$3.52	\$199.73	4.82
2	\$832.31	\$516.97	\$315.33	\$3.52	\$205.79	4.96
3	\$857.28	\$532.48	\$324.79	\$3.52	\$212.04	5.11
4	\$883.00	\$548.46	\$334.54	\$3.52	\$218.47	5.27
5	\$909.48	\$564.91	\$344.57	\$3.52	\$225.09	5.43
6	\$936.77	\$581.86	\$354.91	\$3.52	\$231.91	5.59
7	\$964.87	\$599.32	\$365.56	\$3.52	\$238.94	5.76
8	\$993.82	\$617.29	\$376.52	\$3.52	\$246.18	5.94
9	\$1,023.63	\$635.81	\$387.82	\$3.52	\$253.63	6.12
10	\$1,054.34	\$654.89	\$399.45	\$3.52	\$261.31	6.3

Hydrotreating and steam reforming are both well-established technologies. However, they cannot be used in a stand-alone biofuels plant to economically upgrade bio-oil produced from switchgrass under current market conditions. Though a plant could be built which would break even, a significant ROI of 8% or greater could not be assured and so it is concluded that this method should not be pursued.

### *Option 3: Upgrading the bio-oil to liquid fuel with a Zeolite Catalyst*

The final option examined by this project was to upgrade the bio-oil using a zeolite catalyst. The zeolites HZSM-5 and H-Y were considered as potential catalysts for the biofuels plant. When the bio-oil was upgraded using HZSM-5, the resulting liquid fraction consisted of two phases, one organic and one aqueous<sup>14</sup>. When the H-Y catalyst was used, only a single phase was obtained, which would make separating the fuel from the water difficult<sup>14</sup>. Also, the HZSM-5 had a larger yield of upgraded oil than the H-Y, which tended to produce higher yields of char, coke, and tar.<sup>14</sup>

Due to this, it was decided to use HZSM-5 catalyst in the biofuels plant. Next, the temperature of the reactor and the residence time were considered. The upgrading experiment was carried out at temperatures of 410°C, 450°C, and 490°C. The highest yield of upgraded bio-oil was obtained at 450°C, while more gas was generated at 490°C<sup>14</sup>. Therefore the catalytic reactor should be operated at 450°C. All of these runs were performed with a residence time of 17 g cat/g oil/min. To study the affect of residence time, the reactor was run again at 450° C, this time with half the residence time, or 8.5 g cat/g oil/min. It was found that this lower residence time resulted in a greater yield of upgraded oil<sup>14</sup>. However, when the heating value of the oil was tested, it was found that a residence time of 17 g cat/g oil/min resulted in higher quality oil. The oil obtained with the longer residence time had a heating value of 8901 kcal/kg, while at the shorter residence time its heating value was only 8281 kcal/kg<sup>14</sup>.

In summary, the catalyst reactor will use HZSM-5 catalyst at 450°C and a residence time of 17 g cat/g oil/min. This will result in a high yield of liquid fuel with a heating value of 8900 kcal/kg. For comparison, the heating value of gasoline is 11,300 kcal/kg and diesel is 10,700 kcal/kg. However, the heating value of ethanol is only 7,100 kcal/kg. So while the upgraded oil contains less energy than petroleum fuels, it does have more than ethanol.

Table 2 below shows many of the different compounds found in the bio-oil produced through pyrolysis. It is easily apparent that almost none of the different compounds found in the sample from the raw bio-oil constitute more than 10 % of the total each. Also, there is a large number of ketones and alcohols in the bio-oil. These oxygenated compounds make the bio-oil unsuitable for use in car engines.

Compound	Identified compounds (%) <sup>a</sup>		
	Sample A	Sample B	Sample C
Vinyl formate	1.7	2.2	0.2
Vynil acetate	3.7	3.7	2.4
Acetic acid	0.5	0.6	0.5
2-Furaldehyde	1.4	2.4	1.5
2-Methylbutanol	2.8	3.1	2.8
2(5H)-Furanone	3.5	2.5	3.7
Cyclohexanone	1.4	1.3	1.4
Cyclopentenone	0.6	1.4	0.6
Phenol	1.3	2.2	1.3
Methylcyclopentadione	3.0	3.2	3.0
2-Methoxyphenol	4.2	3.2	4.3
2-Methoxy-4-methylphenol	3.7	2.8	3.8
4-Ethyl-2-methoxyphenol or			
2-Methyl-1,4-dimethoxybenzene	2.1	1.3	1.8
2-Methoxy-5-(1-prop-2- enyl)phenol	2.4	2.8	3.5
2-Methoxy-4-propylphenol	1.2	1.3	1.1
Ethyl butyrate	0.7	0.2	0.2
1-(4-Hydroxy-3- methoxyphenyl)etanone	1.3	0.5	1.1
1-(4-Hydroxy-3- methoxyphenyl)propan-2-one	1.6	1.3	1.7
1-(4- Hydroxymethoxyphenyl)propanol	1.7	1.7	1.6
Hexanoic acid	12.4	7.9	4.7
4-Ethyl-2-methoxyphenol	2.2	4.1	11.8
Decanol	2.1	1.1	1.9

<sup>a</sup> The amount (%) of the products were evaluated through the gc-area; no response factors were introduced.

**Table 2: Compounds identified by GC/MS in the raw bio-oil.<sup>15</sup>**

The upgraded oil also has many different compounds that which are mostly less than 10% each as well. These are shown in table 3 below. The compounds in the upgraded oil are mostly aromatic compounds and form an organic layer that can be separated easily from the aqueous

layer. Table 3 also shows the octane number and boiling points of each of the individual compounds. The chemical compounds ranging from benzene through 1,2,3,5-tetramethylbenzene can be found in today's liquid fuel. Also, the octane numbers of these compounds exceed the required octane number of 87 – 91 that is typically found at fuel pumps today. Chemical compounds ranging from naphthalene through dimethylantracene are not typically found in today's fuel and they are not desirable in today's engines. However, utilizing the difference in boiling points between the desired and undesired compounds, the chemical compounds found at the top section of table 3 can be separated easily from the bottom section using a distillation column. The benzene and toluene fractions can also be removed if preferred, as they are classified as carcinogens and thus may not be desirable in the fuel.

<b>Chemical</b>	<b>% wt. fraction</b>	<b>Octane #</b>	<b>Boiling Point (°F)</b>
<i>Benzene</i>	<i>1.2</i>	<i>101</i>	<i>176.18</i>
<i>Toluene</i>	<i>3.1</i>	<i>114</i>	<i>231.1</i>
<i>Ethylbenzene</i>	<i>2.6</i>	<i>115.5</i>	<i>277.1</i>
<i>1,3-dimethylbenzene</i>	<i>9.4</i>	<i>145</i>	<i>358</i>
<i>Propylbenzene</i>	<i>0.2</i>	<i>127</i>	<i>318.6</i>
<i>1,2,4-trimethylbenzene</i>	<i>11.8</i>	<i>136</i>	<i>336.9</i>
<i>Butylbenzene</i>	<i>0.3</i>	<i>97.5</i>	<i>361.9</i>
<i>2-methylphenol</i>	<i>3.3</i>	<i>---</i>	<i>359.3</i>
<i>1-Methyl-4-benzene</i>	<i>2.4</i>	<i>---</i>	<i>394</i>
<i>1,2,3,5-tetramethylbenzene</i>	<i>0.5</i>	<i>100</i>	<i>388.4</i>
<i>Naphthalene</i>	<i>6.2</i>	<i>Not a component in today's liquid fuel.</i>	<i>424.3</i>
<i>Methylnaphthalene</i>	<i>9.2</i>		<i>472.3</i>
<i>1-ethylnaphthalene</i>	<i>3.4</i>		<i>496.9</i>
<i>2,3-dimethylnaphthalene</i>	<i>6.3</i>		<i>511.3</i>
<i>Methylantracene</i>	<i>2.6</i>		<i>646.1</i>
<i>Dimethylantracene</i>	<i>0.5</i>		<i>Expected to be above the methylantracene.</i>

**Table 3: Compounds identified by GC/MS in the oils obtained by upgrading of the raw bio-oil sample using HZSM-5/50 (residence time 17 g cat/g oil/min), octane numbers and boiling points associated to the compounds.<sup>15</sup>**

The selectivity of the upgraded compounds using the zeolite catalyst can play a significant role in the production of liquid fuel. From table 3 above, 1,3-dimethylbenzene and

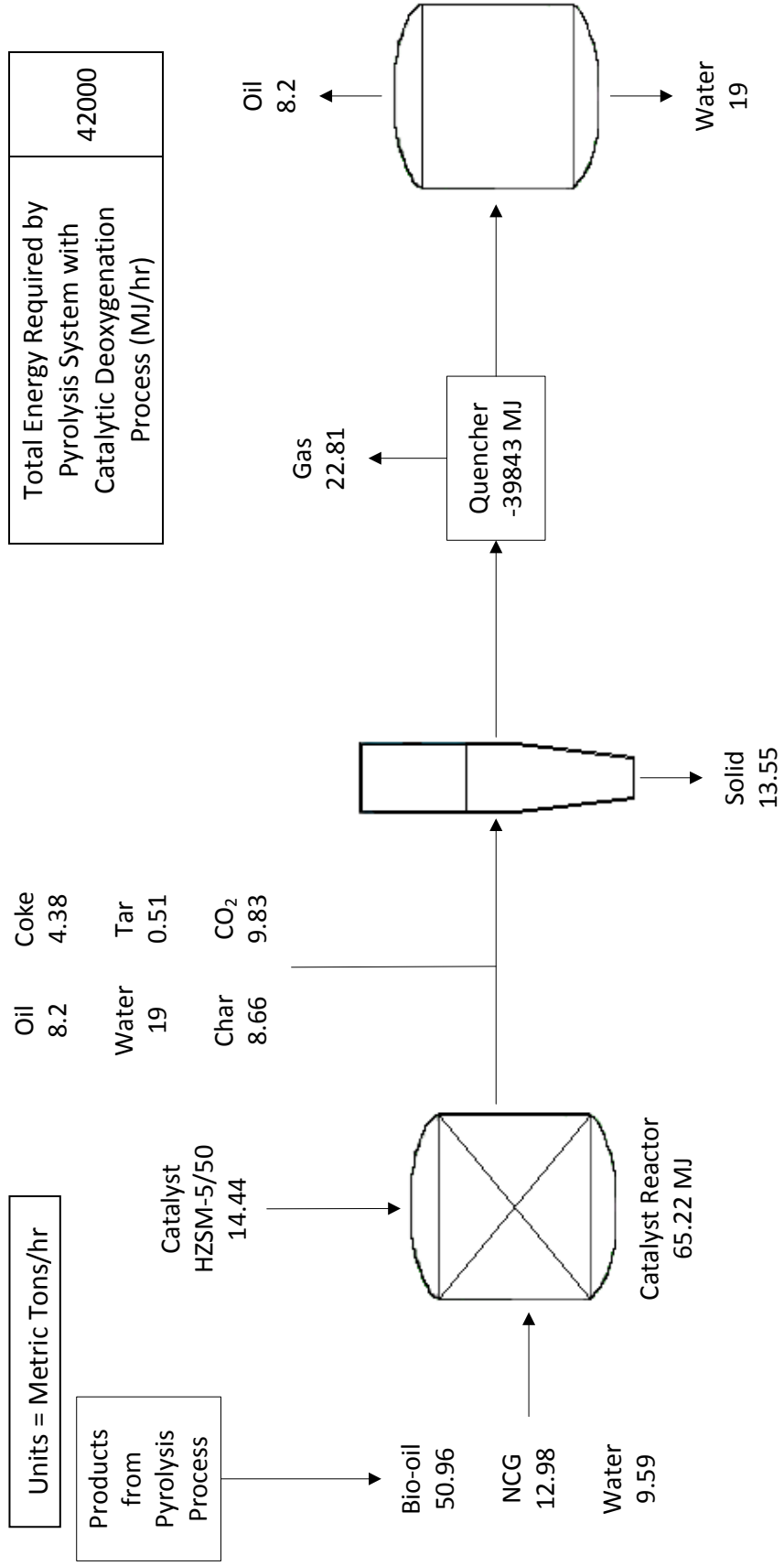
1,2,4-trimethylbenzene have the highest weight percent of around 10. Furthermore, these two compounds are gasoline-grade compounds that can be used in automotive engines. Therefore, it would be preferred for the catalyst to selectively upgrade the pyrolysis oil into oil that contains more of these two compounds instead of the undesired compounds found at the bottom section of table 3. This increase in selectivity will increase the quality of the fuel produced and decrease the amount of post-processing required. Other than having the catalyst selectively upgrade bio-oil to yield a higher weight fraction for the two compounds of interest, it would also be beneficial for the process if the catalyst upgrading yielded more upgraded oil compared to the side products of char, coke and tar. As the value of the upgraded oil is much more than these side products, increasing the yield of upgraded oil would have a significant effect on the economics of this process.

The regeneration of the catalyst was also considered when designing this process. Regeneration was accomplished by heating the catalyst in a furnace in the presence of air at 500°C for an hour<sup>15</sup>. In the experiment, catalyst was used in the reactor until deactivated and then regenerated until it was unable to be regenerated anymore. The table below summarizes the findings<sup>15</sup>.

<b>Number of Regenerations</b>	<b>Reaction Time until Deactivation</b>
Fresh catalyst	90 minutes
2	60 minutes
4	30 minutes
5	Unable to be regenerated

It was decided that the catalyst would be used in the reactor three times (regenerated twice) before disposal. This would allow the plant to operate on an hour basis. Once the reactor is filled with catalyst, it can upgrade the bio-oil for one hour<sup>15</sup>. After upgrading, the catalyst will be removed from the reactor and sent to the regenerator to be regenerated for an hour. Therefore, for a system that is operating on an hourly basis, it is best to only regenerate the catalyst two times. If it were regenerated more often than this, there would be a loss of product quality due to catalyst deactivation. After the regeneration cycle, the catalyst can be used again and is distributed to the catalyst reactor.

The PFD shown on the next page has additional processes added downstream of the original pyrolysis process which will upgrade the produced bio-oil into product oil similar to gasoline. The mass balance and the energy required are shown in the PFD as well. After upgrading the bio-oil using the zeolite catalyst HZSM-5/50, the products of the catalytic deoxygenation process will consist of solids and high-energy gaseous product. A cyclone is used to separate the solids away from the gaseous product. The high-energy gaseous product is then sent to a quencher to recover some of that energy used and also to separate the oil away from CO<sub>2</sub>. Since the zeolite catalyst HZSM-5/50 upgrades the bio-oil into mostly aromatics, the water and oil mixture will form two phases. The organic oil layer can then be separated easily using a tank separator. The total amount of energy required by the pyrolysis system coupled with the catalytic deoxygenation process is found to be approximately 49,000 MJ/hr. This takes into account the energy recovered from the quenchers and the energy spent to regenerate the catalyst.



**Catalyst Regeneration Process**

**Amount of catalyst used for upgrading**

Units = Metric Tons/hr

Energy Required (MJ/hr)	
Regenerator	7100



**Catalyst  
HZSM-5/50  
14.44**

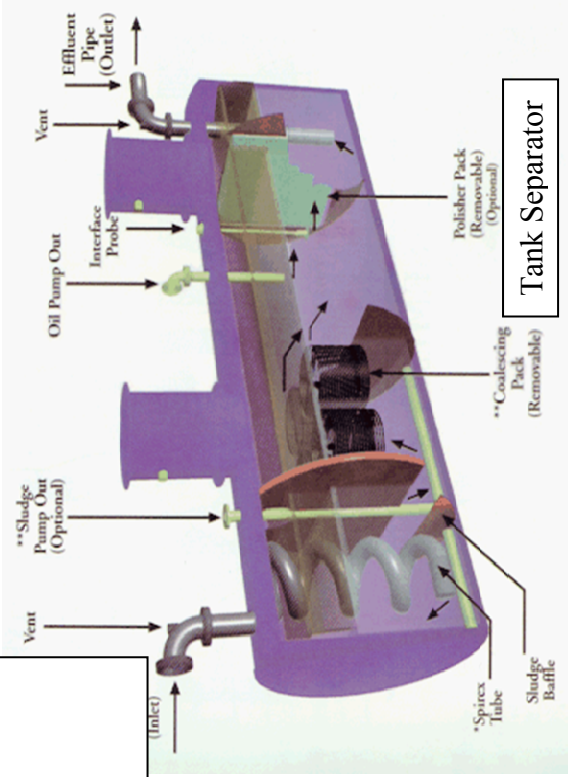
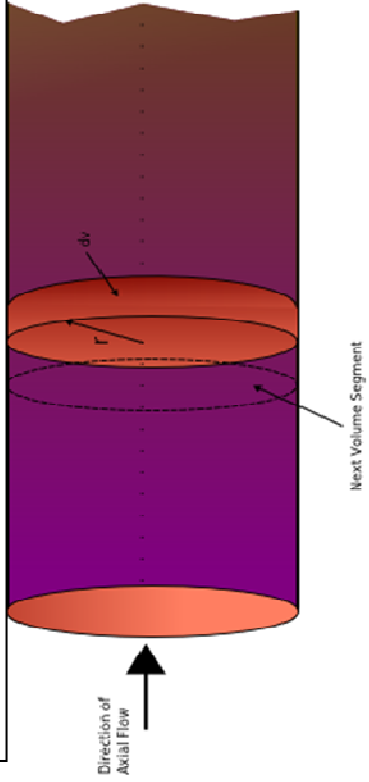


**Regenerator**

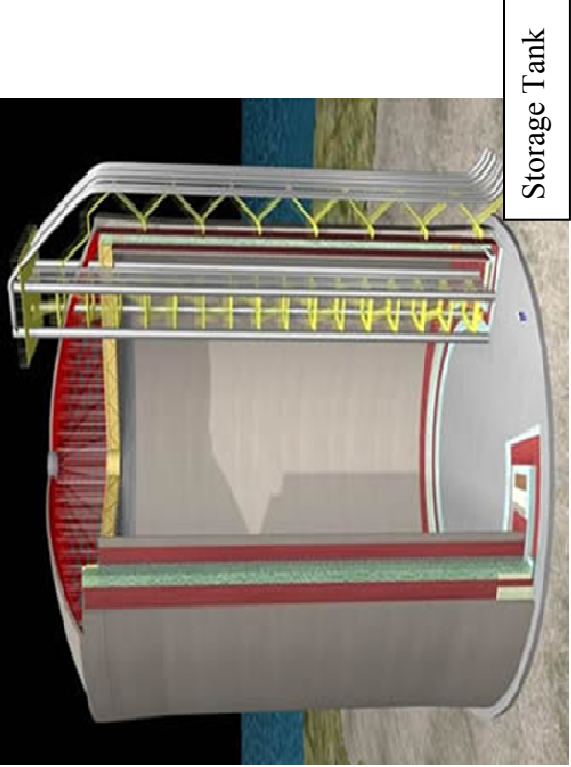


**Regenerated Catalyst  
HZSM-5/50  
14.44**

**Equipment used in Catalytic Deoxygenation Upgrading Process:**



**Tank Separator**



**Storage Tank**



**Regenerator Oven**

*Capital Costs:*

The capital costs associated with this process are summarized in the table below. They consist of the pyrolysis unit, land for the plant, the catalytic reactor, and regenerator. Also, after the catalytic reactor, there is a second quenching step and a separator to remove the aqueous phase from the product fuel.

<b>Equipment Costs</b>	
Pyrolysis unit	\$1.20
Cat Reactor	\$0.67
regenerator	\$1.63
storage tank	\$0.04
separator	\$0.07
land (acres)	\$0.10
<i>Total Equipment Cost</i>	\$3.72
<b>Direct Costs</b>	
Purchased equipment	\$3.72
Purchased-equipment installation	\$1.75
Instrumentation and controls	\$1.34
Piping	\$2.53
Electrical systems	\$0.41
Buildings	\$0.67
Yard improvements	\$0.37
Service facilities	\$2.60
<i>Total Direct Costs</i>	\$13.39
<b>Indirect Costs</b>	
Engineering and supervision	\$1.23
Construction expenses	\$1.52
Legal expenses	\$0.15
Contractor's fee	\$0.82
Contingency	\$1.64
<i>Total Indirect Costs</i>	\$5.36
<b>Fixed Capital Investment</b>	
Working Capital	\$3.31
<b>Total Capital Investment</b>	\$22.06

*Manufacturing Costs:*

The direct production costs come from the switchgrass feed, transportation costs, and cost of zeolite catalyst. The zeolite catalyst is sold for \$1320/ton. The table below summarizes the manufacturing costs for the plant. These estimates were based on an economic model for predicting the cost of biofuels plants<sup>7</sup> as well as the Peters and Timmerhaus textbook<sup>10</sup>. Also, the cost of operating labor was based on four operators with pay of \$12.50 an hour plus benefits.



**Manufacturing Cost (in millions \$/yr)**

<b>A. Direct production costs</b>	\$20.6
Operating labor	\$0.6
Direct supervisory and clerical labor	\$0.1
Maintenance and repairs	\$1.1
Utilities	\$9.3
Patents and royalties	\$9.3
Wastewater treatment	\$0.2
<b>B. Fixed charges</b>	\$22.3
Local taxes	\$1.9
Insurance	\$9.4
Financing	\$11.0
<b>C. Plant Overhead</b>	\$9.3
<b>D. General Expenses</b>	\$23.3
Administrative costs	\$9.4
Distribution and marketing	\$9.3
Research and development	\$4.6
<i>Total</i>	\$75.4

*Profitability:*

The economic feasibility of this project was analyzed for a ten year time period. An inflation rate of 3% was assumed. The table below is based on a 100 ton/hr feed rate of switchgrass and a \$100/bbl price of the product oil.

**Economic Analysis (in million \$)**

Year	Sales	Cost	Revenue	Depreciation	Net Profit	ROI
1	\$72.34	\$75.37	-\$3.03	\$1.87	-\$3.24	-0.15
2	\$74.51	\$77.63	-\$3.12	\$1.87	-\$3.30	-0.15
3	\$76.75	\$79.96	-\$3.21	\$1.87	-\$3.36	-0.15
4	\$79.05	\$82.36	-\$3.31	\$1.87	-\$3.42	-0.16
5	\$81.42	\$84.83	-\$3.41	\$1.87	-\$3.49	-0.16
6	\$83.86	\$87.37	-\$3.51	\$1.87	-\$3.55	-0.16
7	\$86.38	\$89.99	-\$3.62	\$1.87	-\$3.62	-0.16
8	\$88.97	\$92.69	-\$3.72	\$1.87	-\$3.70	-0.17
9	\$91.64	\$95.47	-\$3.84	\$1.87	-\$3.77	-0.17
10	\$94.39	\$98.34	-\$3.95	\$1.87	-\$3.85	-0.17

Again, three factors were examined to try and make the process profitable. These were the selling price of the product oil, the scale of the plant, and the cost of zeolite catalyst. The price of each of these that would result in the process breaking even was determined. Though once again, these prices were determined for purpose of analysis and it is not recommended that a process be operated in the breakeven range.

The table below compares ROI to the price of the product oil. The breakeven price is \$110/bbl.

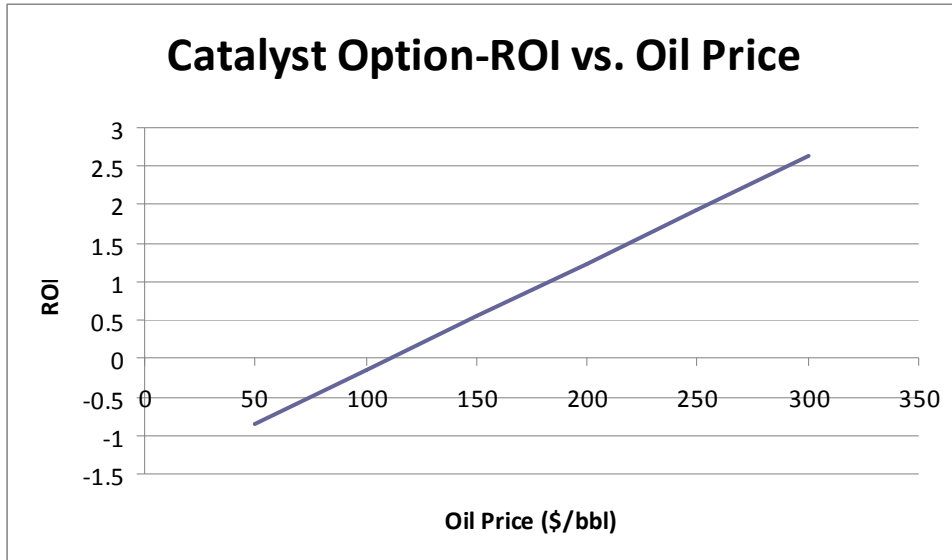


Figure 13: ROI at Various Prices of Product Oil

The ROI was also plotted at various switchgrass feed rates to determine if changing the scale of the plant would make the process profitable. However, as catalyst costs are the largest manufacturing costs and the amount of catalyst used parallels the amount of feed, changing the feed rate does not cause a significant change in the profitability of the process. Though the process will break even at 66 ton/hr of switchgrass feed, or 310 thousand bbl/yr of oil produced, an 8% ROI is not achieved.

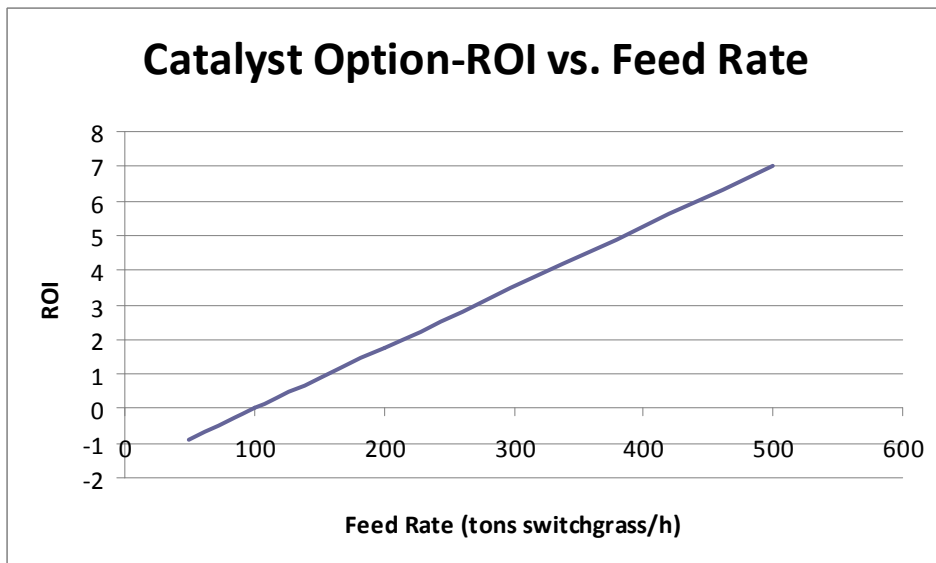
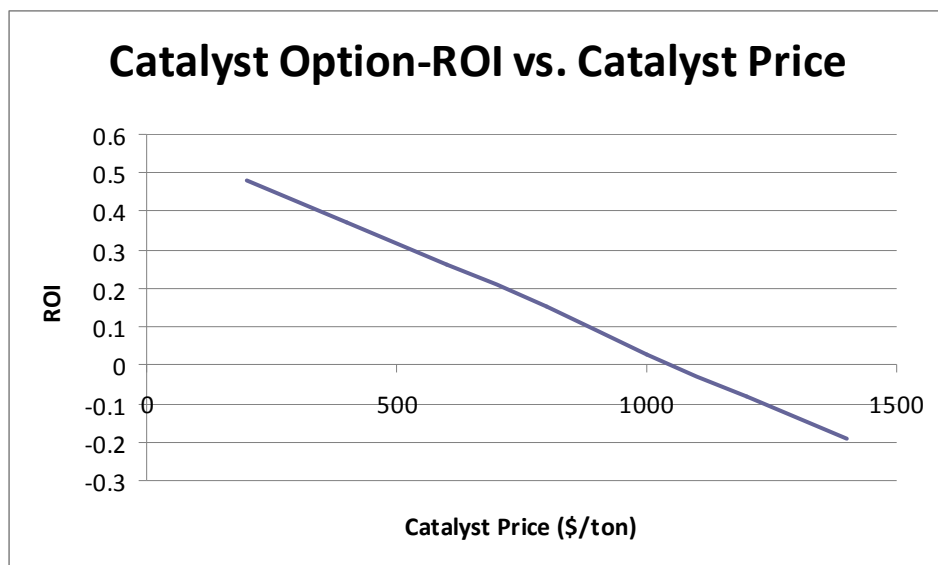


Figure 14: ROI for Various Plant Sizes

Zeolite catalyst is currently sold for \$1320/ton. While this is only \$0.60/lb, so much catalyst is used in the process that it creates a significant cost. In order for this process to break even, the cost of catalyst must decrease to \$996/ton. As this catalyst is currently used primarily

in lab scale experiments, it is not a common bulk chemical. However, if bio-fuel upgrading with this zeolite was pursued enough to create a market shift so that the demand for this chemical increased, then the bulk generation of this zeolite may become more popular. In which case, the price of the zeolite could substantially decrease.



**Figure 15: ROI for Various Catalyst Prices**

For this basic scenario, and given current market conditions, a plant using this option could be built, but it would only result in a break even or insubstantial net profit. However, there is potential for this process, given more research. Thus, additional economic analysis was performed for this method. Four alternate scenarios were considered, each changing one factor from the original scenario in order to determine which factors significantly affected the profitability of this process. Thus, the resulting five scenarios are:

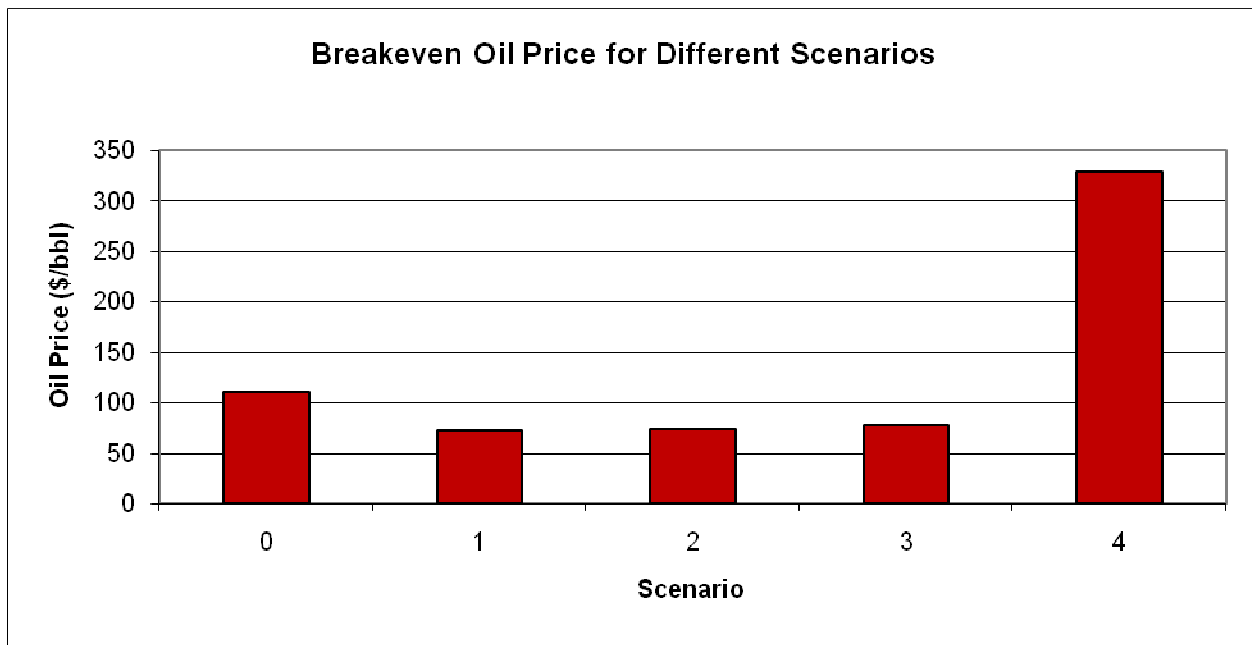
- Scenario 0: Original scenario.
- Scenario 1: Effect of the amount of catalyst used in process. Decrease amount of catalyst used from 17 g cat/g oil/min to 8.5 g cat/g oil/min.
- Scenario 2: Effect of the number of catalyst regeneration cycles. Regenerate catalyst 10 times instead of 2; run on 30 minute cycles instead of hour cycles.
- Scenario 3: Effect of the selectivity of the catalyst. Increase the yield of the upgraded product oil to 23 wt %, reduce the amount of char produced.
- Scenario 4: Consider the process as a stand-alone plant separate from a refinery. Adds separation process and transportation costs.

The net profit and return on investment were calculated for each of these scenarios. This is shown in the table below. All of the alternate scenarios show an improvement in profitability over the original scenario except for scenario 4. From this we can conclude that this biofuels process should be operated in combination with a refinery. Also, scenarios 1 and 3 showed the largest improvement in net profit over the original scenario. Scenario 1 uses less catalyst while

scenario 3 uses a more selective catalyst. Thus scenario 1 increases profitability by decreasing manufacturing cost while scenario 3 increases product sales.

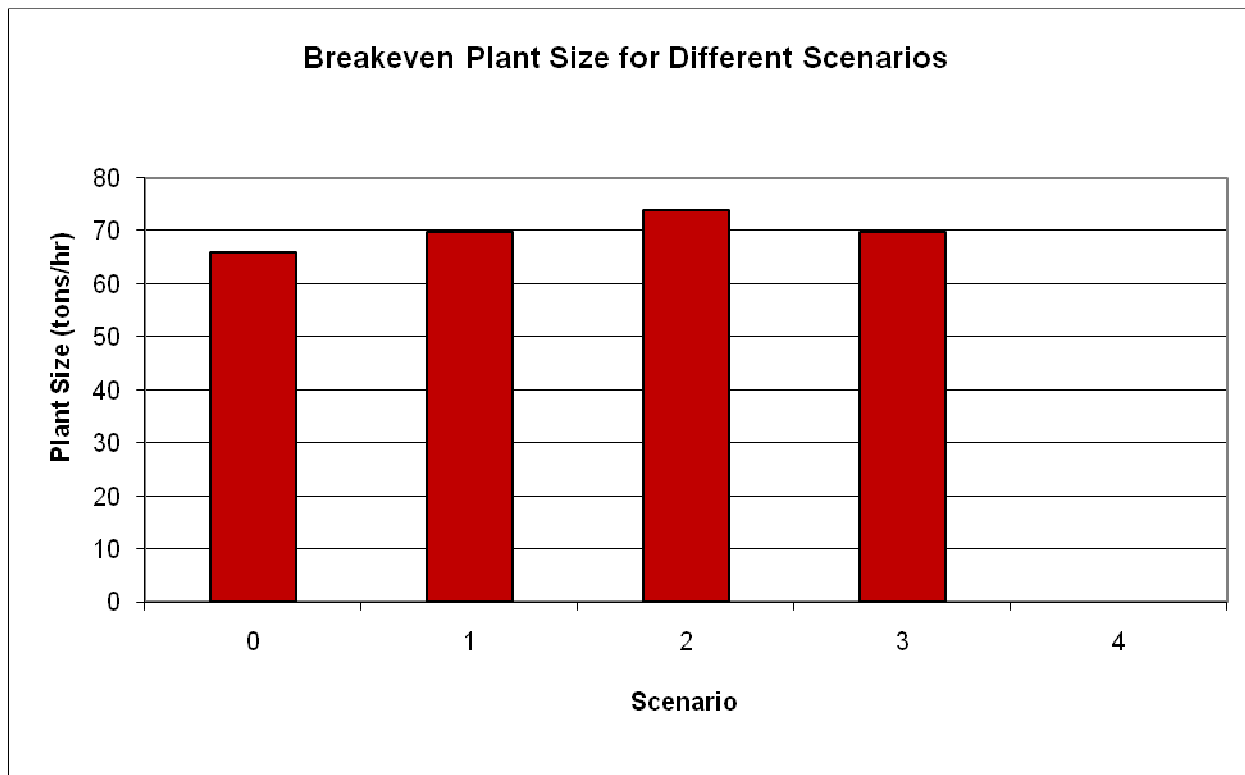
<b>Scenario</b>	<b>Net Profit (million \$)</b>	<b>ROI</b>
<i>Cat. Deox. Original</i>	<i>-\$3.24</i>	<i>-0.15</i>
<i>Cat. Deox. 1</i>	<i>\$10.09</i>	<i>0.46</i>
<i>Cat. Deox. 2</i>	<i>\$8.24</i>	<i>0.37</i>
<i>Cat. Deox. 3</i>	<i>\$10.07</i>	<i>0.46</i>
<i>Cat. Deox. 4</i>	<i>-\$24.32</i>	<i>-1.06</i>

In addition to net profit and ROI, the three criteria considered earlier were again analyzed; namely, breakeven oil price, catalyst price, and plant size. First, a comparison of breakeven oil prices for each of the five scenarios, including the original one, is shown in the chart below. Scenarios 1 through 3 give reasonable and nearly equivalent breakeven prices of \$75 per barrel of product oil. The current price of crude oil is approximately \$100 per barrel.

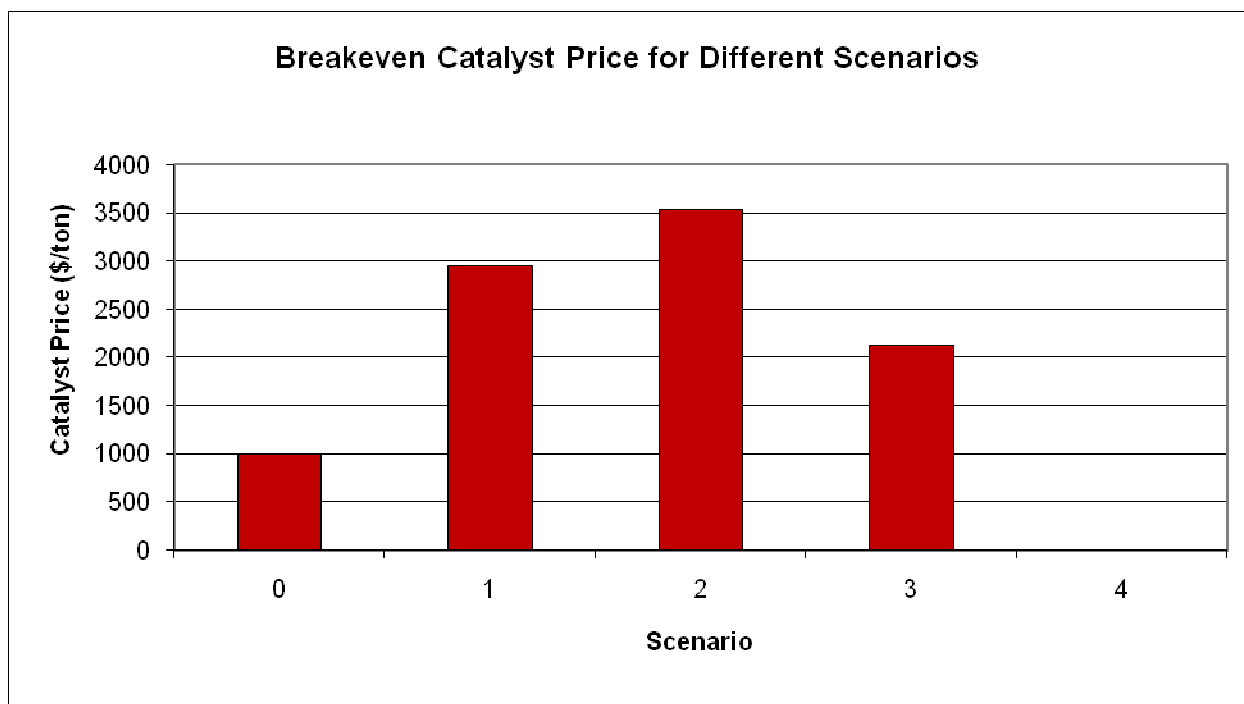


Next, the effects of scale were considered to determine what size of plant would be necessary to break even for each of the scenarios. This is shown in the table below. All

scenarios except scenario 4 give approximately the same size, at around 70 tons of switchgrass feed per hour. Thus, we can conclude that plant size is a relatively stable factor, as it does not change greatly between the different scenarios. So while a certain minimum plant size needs to be built, when trying to increase the efficiency and profitability of bio-oil upgrading, other factors are more important to study.



The last variable considered was catalyst price, as the catalyst is the most expensive of the operating costs. For this graph, a higher bar is actually better as it indicates that a scenario can still break even at higher catalyst cost. The lower the bar, the cheaper the catalyst must be for the process to break even, but higher bars imply that even though catalyst providers may charge more, the process will still break even. This is especially useful given current market conditions, as HZSM-5 catalyst is not currently produced in bulk for industry and is primarily used for lab scale experiments. The current price is \$1320 per ton, but this price is expected to decrease if this catalyst becomes widely used in the biofuels industry. The graph below shows the catalyst price for which each of the scenarios will break even. It can be concluded that for this factor, scenario 2 is best because it is the process that will breakeven at the highest catalyst price. Also, the breakeven catalyst price varies widely across the scenarios, so we can conclude that this is a significant factor in making the process profitable. For scenario 2, the catalyst was regenerated up to ten times, reducing the amount of fresh catalyst that needed to be purchased. Once again we see that catalyst amount is an important factor in profitability.



It should again be reiterated here that these are breakeven values and thus not suitable for long-term economic stability. However, from evaluating each of the scenarios not just through overall profitability but also in terms of the break even points of three factors, we can draw several conclusions about how to make a bio-oil upgrading process profitable. First, we see that the amount of catalyst used must be reduced, either through using less catalyst in the process or regenerating and re-using the catalyst more. Second, increasing the selectivity of the catalyst and thus producing a larger fraction of upgraded oil will also increase profitability. These two factors are more important than the scale of the plant, though a minimum size of process must be built. Finally, as seen from scenario 4, this process should be connected with a refinery and not built independently. A refinery will offset the cost of separating out the final upgraded oil, as well as shipping costs of the product.

As a final consideration, an optimized scenario was created. Scenario 1 was used as the basis for the optimized scenario, as it gave the highest net profit. Also, the price of product oil was increased to the breakeven price of \$110/bbl, the price of the catalyst was decreased to the breakeven price of \$996/ton, and the scale of the plant was increased to 500 tons/hr of switchgrass feed. The resulting profitability table is shown below.

**Optimized Economic Analysis (in million \$)**

Year	Sales	Cost	Revenue	Depreciation	Net Profit	ROI
1	\$427.28	\$165.60	\$261.69	\$1.87	\$171.48	7.77
2	\$440.10	\$170.56	\$269.54	\$1.87	\$176.66	8.01
3	\$453.30	\$175.68	\$277.62	\$1.87	\$181.99	8.25
4	\$466.90	\$180.95	\$285.95	\$1.87	\$187.49	8.5
5	\$480.91	\$186.38	\$294.53	\$1.87	\$193.15	8.76
6	\$495.34	\$191.97	\$303.37	\$1.87	\$198.99	9.02
7	\$510.20	\$197.73	\$312.47	\$1.87	\$204.99	9.29
8	\$525.50	\$203.66	\$321.84	\$1.87	\$211.18	9.57

9	\$541.27	\$209.77	\$331.50	\$1.87	\$217.55	9.86
10	\$557.51	\$216.07	\$341.44	\$1.87	\$224.11	10.16

From this table, it is seen that given improved conditions, an ROI of 8% can be obtained with the catalytic deoxygenation process. This optimal scenario is reasonable. The current price of crude oil is over \$100/bbl, and so setting the price at \$110/bbl for product oil is suitable. Also, if this process becomes used in industry, it is probable that the price of catalyst will decrease. The uncertain factor in this analysis is still the yield and amount of catalyst that is used for the process. Further research needs to be performed in order to generate conditions similar to Scenario 1.

## Conclusions and Future Work

The biofuels plant created in this study was based on 100 tons/hr of switchgrass feed. The plant's location was chosen to be Iowa and the transportation costs associated with shipping switchgrass to the plant were estimated. A fluidized bed pyrolysis reactor operated at 480°C was determined to give the highest yield of bio-oil. There were three options considered for what to do with the produced bio-oil.

Option 1: Sell the bio-oil to produce electricity. This was found to be economically profitable as a stand-alone process with bio-oil being sold as the final product. A 10% ROI was achieved with current market conditions. However, as the bio-oil is an unstable and corrosive liquid, it would be best to use it as a fuel as soon as it is produced. Therefore, it may be preferable for this process to be integrated into an electricity-producing plant rather than as a stand-alone process. Also, this option does not meet the goal of producing a liquid fuel suitable for use in automobile engines and can thus only be considered as a stepping-stone to achieving that goal.

Option 2: Upgrade the bio-oil using hydrotreating. This process was not found to be economically feasible with high capital and manufacturing costs. One potential way to make this process profitable would be to integrate it with a plant that has an excess supply of natural gas and water. If these costs were removed or lowered sufficiently, then the process may become economical. Also, as the capital costs are so large, this process would be most advantageous integrated into a plant that already has the equipment for hydrotreating and/or steam reforming.

Option 3: Upgrade the bio-oil using zeolite catalyst. For this project, zeolite HZSM-5 catalyst was used, with a residence time of 17 g cat/g oil/min in a 450°C reactor. The catalyst was regenerated two times before switching to fresh catalyst. Though this was used as a basis for economic evaluation of this method, catalytic deoxygenation is currently an ongoing research area. Though this project found this process to be unprofitable given current research knowledge and market conditions, we recommend this option be pursued.

The table below gives all of the possibilities considered that resulted in an upgraded bio-oil, including hydrotreating and each of the scenarios for catalytic deoxygenation. Based on this analysis, we do *not* recommend pursuing hydrotreating as a viable upgrading process given its high capital cost and negative net profit. On the other hand, most of the scenarios using catalytic deoxygenation resulted in a positive return on investment, and thus this further research on option should be pursued.

<b>Scenario</b>	<b>TCI (million \$)</b>	<b>Net Profit (million \$)</b>	<b>ROI</b>
<i>Hydrotreating</i>	<i>\$41.5</i>	<i>-\$13.73</i>	<i>-0.33</i>
<i>Cat. Deox. Original</i>	<i>\$22.06</i>	<i>-\$3.24</i>	<i>-0.15</i>
<i>Cat. Deox. 1</i>	<i>\$22.06</i>	<i>\$10.09</i>	<i>0.46</i>
<i>Cat. Deox. 2</i>	<i>\$22.06</i>	<i>\$8.24</i>	<i>0.37</i>
<i>Cat. Deox. 3</i>	<i>\$22.06</i>	<i>\$10.07</i>	<i>0.46</i>
<i>Cat. Deox. 4</i>	<i>\$22.06</i>	<i>-\$24.32</i>	<i>-1.06</i>

By looking at the five catalytic deoxygenation scenarios, it was apparent that the most important factor to study is the zeolite catalyst. By reducing the amount of catalyst used, either directly through the feed to the reactor or indirectly by increasing the number regeneration cycles it is put through, the process could give a positive net profit. In addition to the amount of catalyst used, the selectivity of the catalyst was also shown to be significant in making the process economical.

We recommend that future lab work focus on increasing the selectivity of the catalyst as well as determining the least amount of catalyst that must be used in order to obtain a suitably upgraded fuel. In current literature, reducing the amount of catalyst used reduced the heating value of produced oil<sup>14</sup>. It is necessary to determine the minimum amount of catalyst that can be used and still produce a worthwhile product. Also, the regeneration cycle of the catalyst needs to be studied more. Current research has focused on how long the catalyst would continue to work after a certain number of regeneration cycles<sup>15</sup>. For industrial use however, it will be necessary to know how many cycles a batch of catalyst could undergo given a specific cycle time, such as thirty minutes or one hour rather than just letting the catalyst be used until deactivation.

Renewable energy sources are assuming an important role in the energy industry due to government mandates, public interest, and environmental policy. It is important that these alternative energy sources are environmentally friendly, but they must also be profitable or they will not be pursued by business interests. Though there is more work that needs to be done before bio-oil can be economically upgraded into automobile fuel, progress is being made. We feel that this project presents a good overview of the design of a biofuels plant based on the pyrolysis method and the potential economic means of upgrading the bio-oil.



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