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Bio-mass to Bio-oil: Direct Conversion vs Companion Coal Gasification

Gabriel Hayes

Western Michigan University, gjhayes13@yahoo.com

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Letter of Transmittal

April 20, 2020

Dr. James Springstead
Chemical Engineering Professor
Western Michigan University,
4061 Campus Dr,
Kalamazoo, MI 49008

Dr. James Springstead,

We are submitting our chemical engineering design report entitled “Biomass to Bio-oil: Direct Conversion vs Companion Coal Gasification” as partial fulfillment of the CHEG 4870 course requirement. The purpose of this report is to know the concepts and steps involved in the biomass pyrolysis process and attempt to optimize the process using companion coal gasification.

This design report includes a completed market survey, mass and energy balances both proposed process flow diagrams, plant optimization recommendations, and an economic analysis of the proposed plant designs. Detailed material flow rates, economic data, and energy use can be located in the appendix at the end of the report.

The group appreciates your help with the direction and advice during the completion of this report. If you have any questions concerning the report or the material included please contact the group members, found below, at their Western Michigan University email addresses.

Sincerely,

Alex Cook
Jared Cousino
Gabriel Hayes
Cammi Schneider
Noah Wood

Enclosed: Technical Report “Biomass to Bio-oil: Direct Conversion vs Companion Coal Gasification”

Executive Summary

Biomass is produced in agriculture and forestry, and can be converted to use as a fuel substitute for petroleum. Direct conversion of biomass to bio-oil is conventionally accomplished with a process called fast pyrolysis, in which the biomass is heated to promote the chemical breakdown of its components. This produces some condensable vapors which, when condensed, yield bio-oil. Such a process was compared to a process that gains heat from companion coal gasification instead of traditional heating media such as heated sand and superheated steam.

The economic analysis and optimization of the design consisted of a market survey and market projections based on the key products in both current and future markets. The key products of this analysis are bio-oil for the direct conversion process and bio-oil and diesel for the companion coal gasification, or “married” process. The value of the streams sold as product were calculated by hand using the flow rates provided by the material and energy balances and included as profit into the cash flow tables. After analyzing the total capital investment to build the facility and the profit of the facility after 10 years, it was determined that neither proposed process was a viable or profitable option for the production of bio-oil. Extremely high utility costs for both processes resulted in a negative annual cash flow and a return on investment (ROI) of -93.4% for the direct conversion process and -16.8% for the “married” process.

This report also analyzes the safety and environmental impacts of both processes discussed. The main safety concern in this project is that both of the processes discussed are dealing with highly flammable products. Manufacturing bio-oil safely and efficiently begins with good equipment design. The design process involves the functional specifications to be made, the development of a process flow diagram, the development of a process instrumentation diagram, a HAZOP study to be conducted, a detailed review of design and costing, and documentation. Environmental concerns arise in this analysis due to the waste streams present in the married process. The “married” process contains four waste streams that cannot be reused or recycled into a useful product.

The married process attempted to provide an economically feasible alternative to the direct conversion process of converting biomass to bio oil. The married process eliminated the high utility demands of the biomass pyrolysis reactor by heating the reactor with syngas from a coal gasification process. Although the utility costs for the reactor in the married process were eliminated through the use of syngas, the coal gasifier and Fischer-Tropsch process required for the married process offset these savings and the married process was not profitable. However, a sensitivity analysis revealed that the profitability of the married process relies heavily on the selling price of the product streams. Increases in the prices of bio-oil and diesel could result in the married process becoming economically feasible in the future.

Biomass to Bio-oil: Direct Conversion vs Companion Coal Gasification



**Western Michigan University
College of Engineering and Applied Sciences**

April 20, 2020

**Alex Cook
Jared Cousino
Gabriel Hayes
Cammi Schneider
Noah Wood**

**Faculty Advisors:
Dr. James Springstead and Dr. Abdus Salam**

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Introduction

Biomass is produced in agriculture and forestry, and can be converted to use as a fuel substitute for petroleum. Direct conversion of biomass to bio-oil is conventionally accomplished with a process called fast pyrolysis, in which the biomass is heated to promote the chemical breakdown of its components. This produces some condensable vapors which, when condensed, yield bio-oil. Such a process was compared to a process that gains heat from companion coal gasification instead of traditional heating media such as heated sand and superheated steam. The conversions were then compared to determine the more cost-effective method for producing bio-oil. Additional parameters investigated include the economic benefits of the fuel which are produced through coal gasification.

Almost half of the United States' petroleum products were imported in 2011, which is economically dangerous. While this percentage has decreased significantly in recent years, other incentives for increasing bio-oil production have risen. Chief among these is the rise in demand for carbon free or carbon neutral sources of energy. Biomass can provide a carbon neutral source of energy, since biomass removes CO₂ from the atmosphere while it is growing. With a rise in demand for such sources of energy, it is therefore a worthwhile endeavor to increase the efficiency and decrease the costs for processes that produce bio-oil.

The proposed process operating with companion coal gasification offers several potential advantages over the traditional fast pyrolysis process that may lead to cost reduction. The first advantage is that for this "married" process, it is not necessary to dry the biomass before heating it to promote pyrolysis. The second advantage is that the energy used to heat the biomass to the necessary reaction temperature is gained from the cooling of the syngas produced from coal gasification, eliminating the need for an intermediate heating medium such as sand. The ability to re-use the heat from coal gasification and elimination of the need for drying allows for a simpler design of the biomass pyrolysis reactor and potentially significant savings in terms of total energy costs.

Market Survey

The first price researched was for coal. In Figure 1 on page 7 it shows the price trend for coal over the last 5 years. The most recent listed price is at \$62.92/ton. This graph was taken from tradingeconomics.com

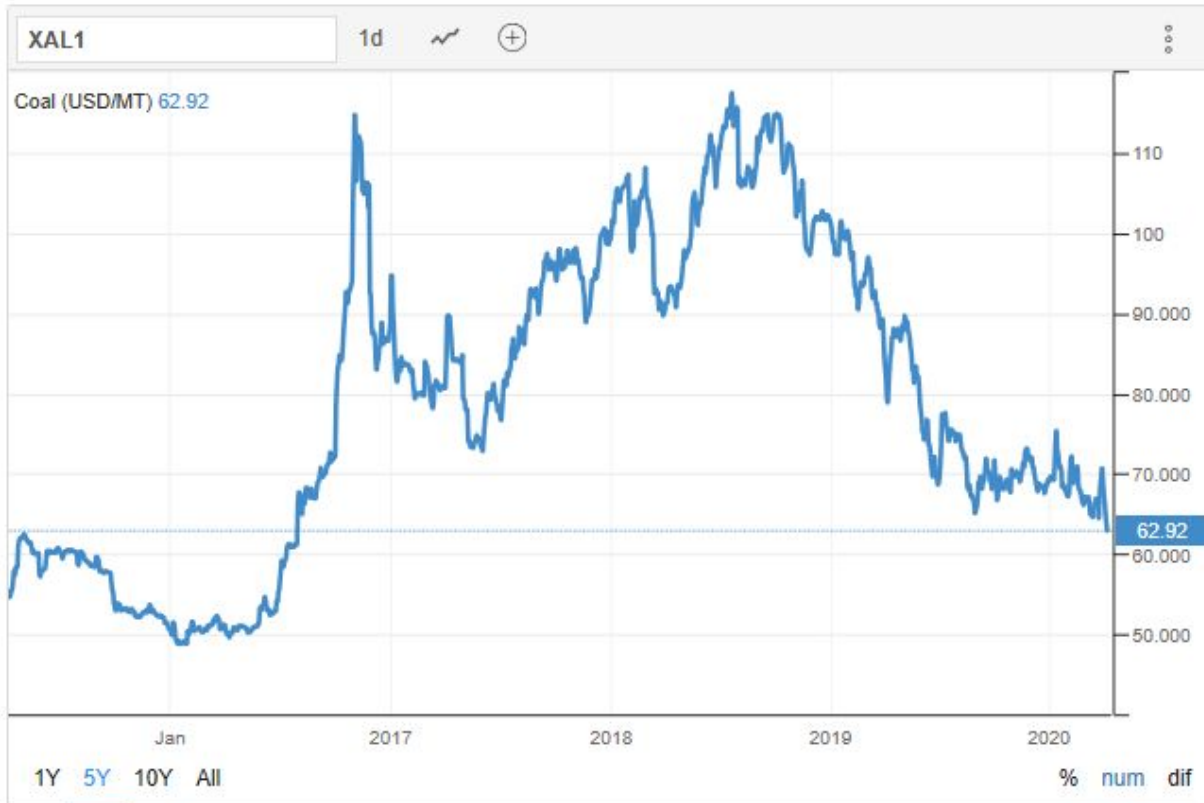


Figure 1: Price Trend for Coal

The price has been mostly declining since 2011 because of natural gas and biofuel becoming more widely used. It is forecast that prices will stay this low or continue to fall for the next 12 months.

The next most important price was for biomass. The website biomassbrokerage.com was used. There were a lot of sellers listed with many kinds of biomass available. To narrow down the results, only biomass listed as a source for ethanol was used since the term pyrolysis yielded no results. From the selection remaining, the sellers from the US and Canada with prices listed were recorded. For our biomass pyrolysis process, we stated wood chips would be used. A California company is selling hardwood wood chips at \$30/dry ton and they had 30,000 tons available.

We also need to know how much we can sell our products for. According to Biofuels Digest raw bio-oil is priced around \$2.00/gal and is on a small upward trend (Bauer, 2017). Converting

to units of U.S. dollars per ton, the average value of raw bio-oil is found to be approximately \$409.66/ton.

Since diesel will also be produced in the married process, the price that can be achieved by selling this product was also taken into consideration. The figure below shows the five year price trend of diesel, with the price shown on the y-axis in dollars per gallon.

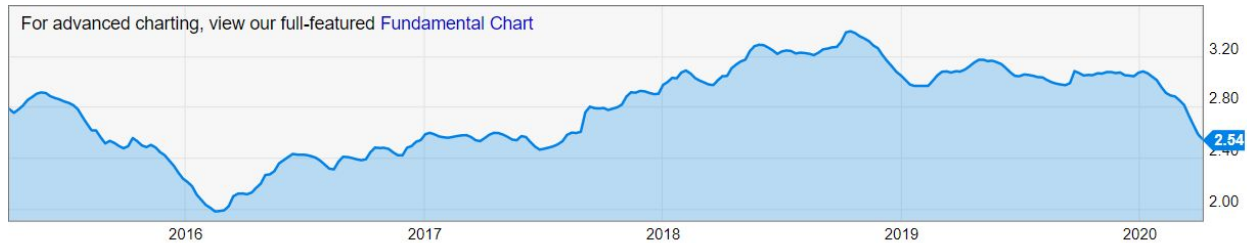


Figure 2: Price Trend for Diesel

It can be seen in Figure 2 above that though there have been significant fluctuations in the price of diesel, the average has remained fairly stable at around \$2.80/gallon. This price will be used for the economic analysis, and is equivalent to \$806.57/ton.

Lastly, a catalyst is needed for the FT synthesis in the married process, cobalt is the most widely used and recommended catalyst for this reaction. From sigmaaldrich.com one type of cobalt catalyst is available at \$90 per 100grams. Other cobalt catalysts can be much more expensive.

Process Flow Diagrams

Biomass Pyrolysis:

The main products formed in biomass pyrolysis are char and gases. The gases produced are split into two categories: gases that are condensed into a dark brown viscous liquid, referred to as bio-oil, and gases that are not condensed in the pyrolysis process. The bio-oil produced via pyrolysis can be used as a liquid fuel for static heating and electricity generation applications or can be used to produce a variety of chemicals. Two main methods of biomass pyrolysis exist, and are referred to as fast pyrolysis and slow pyrolysis. Fast pyrolysis is the preferred process, and the process that will be used in this project, because it yields a higher percentage of bio-oil in the product stream.

The biomass pyrolysis process flow diagram is shown below in Figure 3. The process begins with stream A, containing biomass in the form of wood chips, being fed to a dryer. The wood chips must be dried to remove any excess water because too much water will lead to poor quality bio-oil. After the pyrolysis process begins, it is very difficult to remove water from the bio-oil; simple distillation will not work to remove the excess water and can further degrade the quality of the bio-oil.

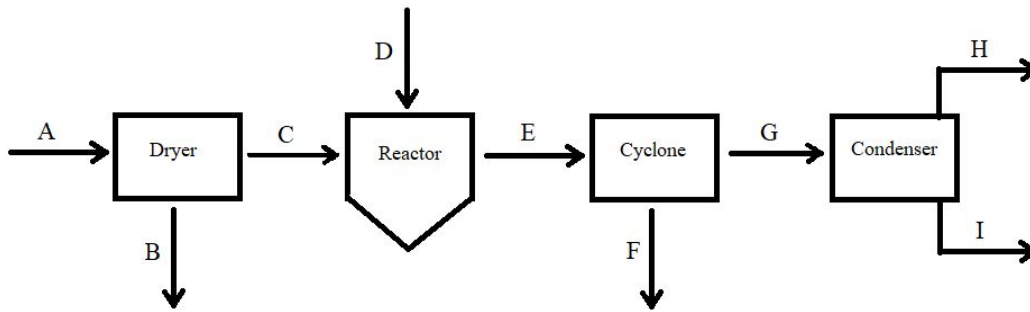


Figure 3: Biomass Pyrolysis Process Flow Diagram

After exiting the dryer, the oven dry wood is fed to the pyrolysis reactor. There are a variety of options for the reactor used in the biomass pyrolysis process. The type of reactor used depends on the desired product quantity and quality and also the desired cost and environmental impact of the process. The pyrolysis reaction chamber operates at a temperature of approximately 500°C and has a vapor residence time of less than 2 seconds to prevent undesirable secondary reactions from occurring. The stream leaving the reactor contains approximately 15% char, 10% incondensable vapors, and 75% vapors that will eventually be condensed into the bio-oil product. This stream enters a cyclone that removes any remaining solids from the gas and char mixture. The gases leaving the cyclone flow into a condenser to produce the desired bio-oil product.

“Married” Process:

The “married” process is a process that produces bio-oil by combining coal gasification, and biomass pyrolysis. Products that can be produced from coal gasification is diesel, and products that can be produced from biomass pyrolysis is char and bio-oil. In this specific process, the synthesis gas that is produced from the coal gasification will be used to heat the biomass pyrolysis reactor.

The “married” process uses the heat from the coal gasification process, as a utility to heat the biomass pyrolysis reactor in order to create bio-oil. Figure 4 on page 10 shows the process flow diagram of the “married” process. The process starts with stream A, that contains coal and water

in a slurry, and oxygen that will burn in a gasifier at extremely high temperatures to produce a mixture of carbon monoxide, carbon dioxide, and hydrogen, known as synthesis gas. The remainder of the coal will leave the gasifier as coal slag from the coal through stream B. The syngas stream, C, will then be used to heat the reactor for the biomass pyrolysis, some of the syngas will then go through the water shift to be cleaned, in stream K. Some of the syngas will bypass the water shift process, in L, and either leave through M as waste or be mixed back in with the clean syngas to form stream P. The mixture in stream P will then be sent to the Fischer-Tropsch Synthesis process where it is converted to a series of hydrocarbons that can be used to create diesel.

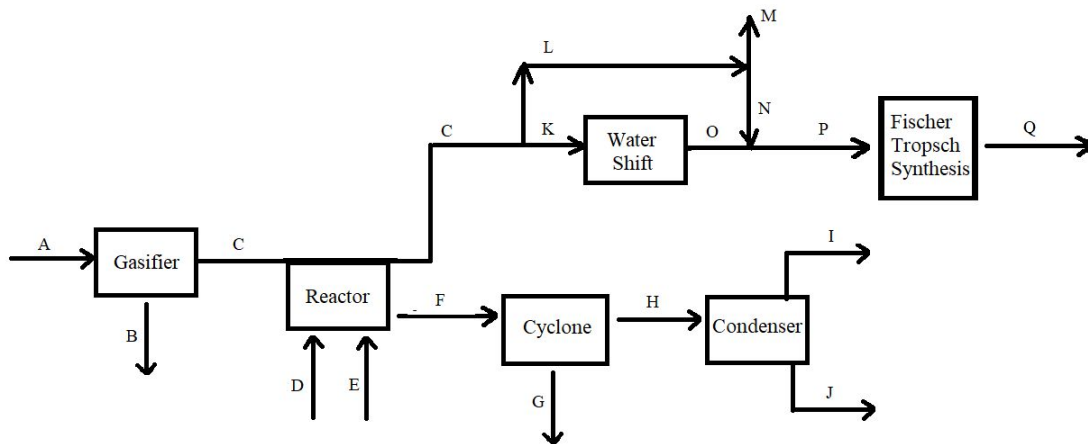


Figure 4: "Married" Process PFD

In stream D, a biomass of dried wood chips will enter the biomass pyrolysis reactor with stream E, that contains pure oxygen. The biomass reactor needs to at least be 500 °C for the reactions to occur. The pyrolysis of the biomass will produce a mixture of water, carbon dioxide, oxygen, and solid impurities from the wood chips (cellulose, hemicellulose, and lignin). This mixture (stream F) will then enter a cyclone where the solids and gas will be separated. The solids and char will leave through stream G, and the remaining gas will leave through stream H. The gas will then enter a condenser where gases will leave through stream I, and the desired product, bio-oil, in stream J, will be produced.

Material Balances

Biomass Pyrolysis:

The basis for the material balances in this analysis is 1000 tons/day of wood chips being fed to the dryer. Wood chips are composed of approximately 40% cellulose, 30% hemicellulose, 27% lignin, and 3% wood extractives, phenolic compounds, terpenes, fats, and water. The chemical

formulas and approximate molecular weights for cellulose, hemicellulose, and lignin are shown below in Table 1. Values for lignin were found from the journal article “Thermodynamic Properties of Plant Biomass Components. Heat Capacity, Combustion Energy, and Gasification Equilibria of Lignin” by Voitkevich et. al. The values for cuproammonium lignin were used for this analysis.

Table 1: Molecular Formula and Molecular Weights of Cellulose, Hemicellulose, and Lignin

Component	Molecular Formula	Molecular Weight
cellulose	$(C_6H_{10}O_5)_n$	162
hemicellulose	$(C_5H_8O_4)_n$	132
lignin	$C_{10}H_{11.9}O_{6.5}$	236

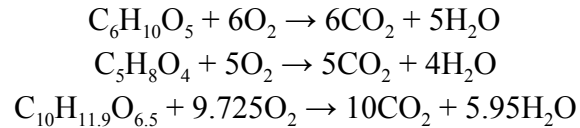
The dryer step of the biomass pyrolysis process removes the wood extractives, phenolic compounds, terpene, fats, and water from the woody biomass and yields an approximate oven dry wood composition of 41% cellulose, 31% hemicellulose, and 28% lignin. The molecular weights from Table 1 above and approximate stream compositions yield an average molecular weight of wood chips fed (stream A) equal to 168.66 and an average molecular weight of oven dry wood (stream C) equal to 173.42. The material balances for the dryer step are summarized below in Table 2. “Other” refers to the wood extractives, phenolic compounds, terpene, fats, and water that the dryer step removes from the woody biomass.

Table 2: Biomass Pyrolysis Dryer In/Out Table

Unit	Dryer		
	A	B	C
stream (tons/day)			
cellulose	400	0	400
hemicellulose	300	0	300
lignin	270	0	270
other	30	30	0
total	1000	30	970

After leaving the dryer, the oven dry wood in stream C enters a reactor where the pyrolysis process occurs. Due to the limitations of hand calculations, it was assumed that primarily combustion reactions occur in the pyrolysis reactor and side reactions were neglected. It was

assumed that the following three reactions occurred in the biomass pyrolysis step:



Stream D contains oxygen that is fed to the reactor to fuel the combustion reaction. Complete combustion of the oven dry wood yields a theoretical oxygen demand of 1193.74 tons/day in stream D. From the AIChE packet provided for this project, it is stated that 15% of the material leaving the reactor is unreacted ash and char. Thus, a conversion rate of 85% of the oven dry wood was assumed. This results in oxygen being present in the reaction product, stream E. The material balances for the reactor step are summarized below in Table 3.

Table 3: Biomass Pyrolysis Reactor In/Out Table

Unit stream (tons/day)	Reactor		
	C	D	E
cellulose	400	0	60
hemicellulose	300	0	45
lignin	270	0	40.5
other	0	0	0
O ₂	-	1193.74	179.74
CO ₂	-	0	1405.8
H ₂ O	-	0	431.84
total	970	1193.74	2162.88

After leaving the reactor the pyrolysis products in stream E are fed to a cyclone to separate out the unreacted material, ash, and char. This results in only the gases from the pyrolysis reaction being fed to the condenser in stream G. Stream G is composed of 1405.8 tons/day CO₂, 431.84 tons/day H₂O, and 179.74 tons/day O₂. Based on these values, stream G is composed of 19% carbon, 78.6% oxygen, and 2.4% hydrogen. From the AIChE packet provided for this project, bio-oil contains an approximate elemental composition of 56.4% carbon, 37.1% oxygen, 6.2% hydrogen, and the remainder ash and char. In order to be able to solve the material balance, it was assumed that all of the carbon in stream G was condensed into the bio-oil product. This means that the off-gasses for the biomass pyrolysis system in stream H are composed of only hydrogen and oxygen. The material balances for the condenser step are summarized in Table 4 on page 13.

Table 4: Biomass Pyrolysis Condenser In/Out Table

Unit stream (tons/day)	Condenser		
	G	H	I
C	383.28	-	383.28
H	1585.6	5.35	42.13
O	48.42	1332.36	252.12
total	2017.3	1337.71	677.53

The biomass pyrolysis processes resulted in a 67.7% yield of bio-oil compared to the amount of woody biomass fed to the system. This is just under the estimated 75% liquid bio-oil yield from the AIChE packet provided for this project.

“Married” Process:

The coal gasification process starts out with 3433.00 tons/day of coal ($C_{240}H_{90}O_4NS$), 5123.07 tons/day of water in the form of steam, and 3507.89 tons/day of oxygen going into the coal gasifier. The gasifier is operating at very high temperatures, around 1730 °C and moderate pressure, 44 bar, where it will burn and break down coal, water, and oxygen into carbon monoxide, carbon dioxide, water, hydrogen, hydrogen sulfide, nitrogen, and coal slag. The coal slag from the coal will leave separately from the gasifier. It was assumed that 3% wt of the coal didn't participate in the reaction and came off as coal slag. While the rest of the components, shown in Table 5 on page 14, will be used for the syngas. Syngas is a gas that is composed mainly of carbon monoxide and hydrogen. Since the gasifier is operating at the same conditions as the Texaco Gasifier (Zheng and Furinsky, 2005), it was assumed that the $CO:CO_2$ ratio was the same. The gas leaving the coal gasification process will need to be cleaned and stripped of the impurities, namely carbon dioxide and sulfur. In the water-gas shift process, some steam is reacted with carbon monoxide to form carbon dioxide and hydrogen gas. These separations are needed in order for it to go through the Fischer-Tropsch Synthesis where it will then be formed into diesel. Table 5 shows the flow rates, in tons/day, of the syngas and the coal slag leaving the gasifier, using the coal feed basis of 3433.00 tons/day. The following combustion reaction is an approximation of what happens in the gasifier:

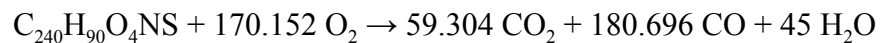


Table 5: Coal Gasification Output

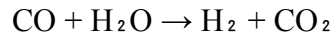
Synthesis Gas Leaving Gasifier (tons/day)		Coal Leaving Gasifier (tons/day)
CO	5470.16	-
CO ₂	2821.18	-
H ₂ O	3322.54	-
H ₂	293.04	-
H ₂ S	36.75	-
N ₂	15.12	-
Coal Slag	-	102.997
total	11958.79	103

After the syngas leaves the gasifier it is used to heat the pyrolysis reactor of the “married” process. The syngas is then cleaned and turned into diesel using the Fischer-Tropsch Synthesis process. Table 6 below shows the flow rate of the streams in this process.

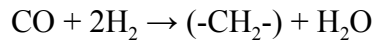
Table 6: Fischer-Tropsch Synthesis

Components	Streams (tons/day)						
	C	K	L	O	P	Q	M
CO	5470.16	2430.94	3039.22	-	3039.22	-	-
CO ₂	2821.18	-	2821.18	3820.05	3820.05	3820.05	2821.18
H ₂ O	3322.54	1562.75	1759.79	-	-	1953.78	1759.79
H ₂	293.04	-	293.04	173.64	434.17	32.50	-
H ₂ S	36.75	-	36.75	-	-	-	36.75
N ₂	15.12	-	15.12	-	-	-	15.12
CH ₂	-	-	-	-	-	1519.61	-
total	11958.8	3993.69	7965.1	3993.69	7293.44	7325.94	4632.84

The water-gas shift reaction is performed so that the ratio of carbon monoxide and hydrogen gas is two moles of hydrogen gas for every mole of carbon monoxide, which is the ideal ratio for the reaction in the FT synthesis reactor. The water-gas shift reaction is simple:

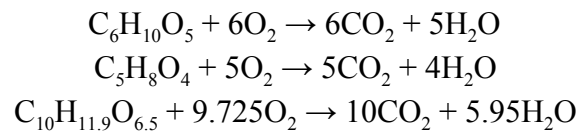


This reaction creates carbon dioxide as a byproduct that must be sent to an exhaust. The hydrogen gas that is created is sent to the Fischer Tropsch reactor with the other hydrogen from the syngas and the left-over carbon monoxide. The water-gas shift reaction and the FT synthesis reaction are exothermic reactions. The catalytic reaction that takes place in the FT reactor is:



The $-\text{CH}_2-$ monomers join to become diesel ($\text{C}_{10}\text{H}_{20}$). The cobalt catalyst must be present in the reactor for the reaction to be feasible. From the production rate of CH_2 monomers, we can estimate a production rate of about 152 tons of biodiesel per day.

The biomass pyrolysis process starts out with a basis of 1000 tons/day of dry wood chips going into the reactor. The wood chips are composed of 40% cellulose ($\text{C}_6\text{H}_{10}\text{O}_5$), 30% hemicellulose ($\text{C}_5\text{H}_8\text{O}_4$), and 30% lignin ($\text{C}_{10}\text{H}_{11.9}\text{O}_{6.5}$). Assuming that a combustion reaction will occur, a stream of 1950.25 tons/day of oxygen will also enter the biomass pyrolysis reactor. The components that are formed from the reaction are carbon dioxide, and water. The three reactions that occur are:



In the AIChE packet, it is stated that 15% of the material leaving the reactor is unreacted solids and char from the biomass. Therefore, there is an 85% conversion of biomass to the remaining product that will be sent to the condenser. Table 7 on page 16 shows the flow rate of each component in the stream coming out of the reactor in tons/day.

Table 7: Stream out of Pyrolysis Reactor in Married Process

Components	Stream (tons/day)
Cellulose	340
Hemicellulose	256.08
Lingin	254.88
O ₂	198.91
CO ₂	1456.13
H ₂ O	444.25
total	2950.25

After the stream leaves the reactor it will go through a cyclone where the solids and char will be separated from the gas. 850.96 tons/day of the solid and char will be wasted through stream G, and 2099.29 tons/day of gas will be sent to the condenser where it will then be condensed into bio-oil in stream J, or it will leave through stream I as waste. The gas will then be condensed by an elemental basis. Using the information provided in the AIChE packet, biomass pyrolysis into bio-oil yields 56.4% carbon, 6.2% hydrogen, and 37.1% oxygen; the remainder is undesirable. Assuming a complete conversion of carbon to the stream that makes bio-oil, the only components leaving stream T are hydrogen and oxygen. From the biomass entering the reactor, it will yield 70.1% bio-oil. Table 8 below shows a table that has the flow rates of the stream going into the condenser, the stream of undesirable gases leaving the condenser, and the stream of desired bio-oil coming out of the condenser, in tons/day.

Table 8: In/out Table of Condenser, Married Process

Component	Going in Condenser (tons/day)	Bio-Oil Coming Out (tons/day)	Gases Coming Out (tons/day)
C	397.08	397.08	-
H	49.36	43.58	13.96
O	1651.84	260.86	1381.17
Total	2098.28	701.52	1395.13

Energy Balances

Biomass Pyrolysis:

The thermodynamic properties of the biomass elements in this analysis were required to complete the energy balances for the biomass pyrolysis process. The following equation for the relationship between the heat capacity of sulfuric lignin and cuproammonium lignin was found from the journal article “Thermodynamic Properties of Plant Biomass Components. Heat Capacity, Combustion Energy, and Gasification Equilibria of Lignin” by Voitkevich et. al:

$$\frac{C_{p, \text{sulfuric lignin}}}{C_{p, \text{cuproammonium lignin}}} = 0.9006 - (3.232 \times 10^{-4})T(\text{K})$$

Voitkevich et. al. provided tabulated values for the heat capacity of sulfuric lignin at various temperatures. Using the equation above and the tabulated values, the heat capacity of cuproammonium at various temperatures was calculated. The data from Voitkevich et. al. was only available in the temperature range between 0K - 440K. For temperatures greater than 440K the heat capacity of lignin was assumed to be constant at 564.35 J/mol K. This is equivalent to the calculated heat capacity of lignin at 440K. A reference temperature of 0K was used for all calculations in this analysis. The table containing the calculated values of cuproammonium lignin for the temperature range of 0K - 440K can be found in Table B.1 in Appendix B.

Several assumptions had to be made for the heat capacities of the remaining two biomass components in this analysis, cellulose and hemicellulose. “The specific heat capacities for lignin and amorphous cellulose differ by $\leq 0.015c_p$ below $T = 180\text{K}$ ” (Voitkevich et. al, 2012). In addition to this, Figure 5 on page 18 was retrieved from the journal article “Explaining the heat capacity of wood constituents by molecular vibrations” by Thybring. This figure reveals that there is very little deviation in the heat capacity values of cellulose, hemicellulose, and lignin. Therefore, for the purposes of this analysis, it was assumed that the heat capacities of cellulose, hemicellulose, and lignin were equivalent.

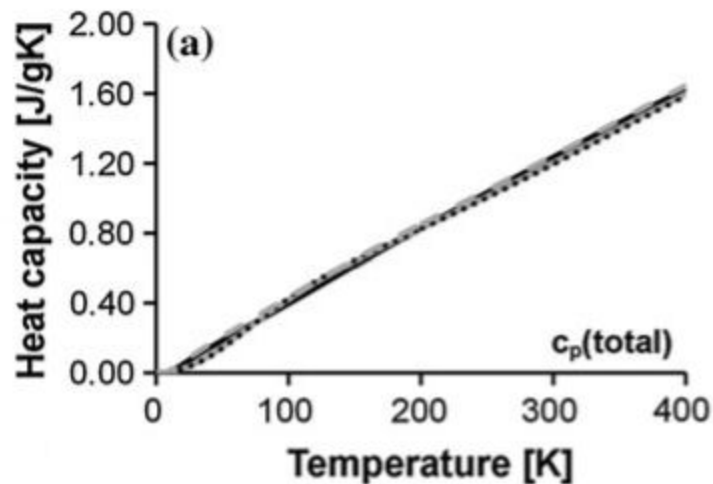


Figure 5: Comparison of the Total Heat Capacities of Cellulose, Hemicellulose and Lignin
(Retrieved from Thybring, 2018 - Figure 8a)

As discussed in the biomass pyrolysis material balances, the dryer step of the biomass pyrolysis process removes wood extractives, phenolic compounds, terpenes, fats, and water from the woody biomass feed, these compounds are referred to as “other” in the energy balance calculations. Since the main objective of the dryer step is to remove excess water from the woody biomass feed, it was assumed that the thermodynamic properties of “other” were equivalent to the thermodynamic properties of water. Energy balance calculations yielded a dryer heating duty, Q_D , equal to 290,728,290.7 kJ/day or 3364.91 kJ/sec.

The reactor step of the biomass pyrolysis process requires the largest heating duty. Superheated steam is required to heat the reactor feed up to the reaction temperature of 500 degrees Celsius. This will be discussed more in depth in the utility summary section of this report. The required reactor heating duty, Q_R , is equal to 17,413,459,465 kJ/day or 201,544.67 kJ/sec.

To complete the energy balance analysis, assumptions about the heat capacity of bio-oil (stream I) and the non-condensable pyrolysis gases (stream H) in the condenser step had to be made. The journal article “Estimation of Enthalpy of Bio-Oil Vapor and Heat Required for Pyrolysis of Biomass” by Yang et. al. provided the following estimates for the heat capacities of bio-oil and non-condensable pyrolysis gases:

$$\begin{aligned} C_{p, \text{bio-oil}} &= 0.022 \text{ kJ/mol K} \\ C_{p, \text{gas}} &= 0.019 \text{ kJ/mol K} \end{aligned} \quad (\text{Yang et.al, 2013})$$

Energy balance calculations using the listed heat capacities yielded a condenser heating duty, Q_C , equal to -17,320,058,211 kJ/day or -200,463.64 kJ/sec. The heating duties for the dryer, reactor, and condenser step of the biomass pyrolysis process are summarized below in Table 9. The reactor and the condenser step provide the largest heating/cooling duty requirements and are a significant source of utility costs.

Table 9: Summary of Biomass Pyrolysis Heating Duties

	Heating Duty (kJ/day)	Heating Duty (kJ/sec)
Dryer	290728290.70	3364.91
Reactor	17413459465.06	201544.67
Condenser	-17320058211.08	-200463.64

“Married” Process:

The heating duty for the gasifier was found using the equation $Q_g = m_B \hat{H}_B - m_C \hat{H}_C - m_A \hat{H}_A$ where stream A is the gasifier feed, B is the coal slag, and C is the raw gas. Finding the H values for all components, except for the coal, by using $C_p = R(A + BT + CT^2 + DT^2)$ and the mass flow rates, it was found that the heating duty on the gasifier is 31,734,414,776.60 kJ/day or 367,296.30 kW. For the coal, an average value of 13 BTU/lb was found and used.

The reaction enthalpy for the water-gas shift reaction and Fischer-Tropsch process were taken from chapter 24 in Perry’s engineering handbook, 9th edition. Equation 24-29 is for the water-gas shift and equation 24-38 is for hydrogen rich syngas in a FT reactor. These equations give the reaction enthalpies: $\Delta H = -40.6$ kJ/mol for the water-gas shift and $\Delta H = -165$ kJ/mol of $-\text{CH}_2-$. The heating duties could then be calculated by multiplying the enthalpies by the number of moles/time. In the water-gas shift material balance it was calculated that 86819253.70 mol of each component was consumed or produced per day, so the heating duty is calculated as $(-40.6 \text{ kJ/mol}) \cdot (86819253.70 \text{ mol/day}) = -3,524,861,700$ kJ/day. The heating duty for the FT reactor was calculated as $(-165 \text{ kJ/mol of } \text{CH}_2) \cdot (108543603.40 \text{ mol } \text{CH}_2 \text{ produced/day}) = -17,909,694,600.00$ kJ/day.

To find the heating duty on the reactor, there is a simple exchange between the syngas and the biomass with no reaction occurring. The syngas is at a temperature of 1644 K, and using the equation $\hat{H} = C_p \Delta T$, using the heat capacity correlation for each component, $C_p = R(A + BT + CT^2 + DT^2)$, (A, B, C, D values used from “Intro to Chemical Engineering Thermodynamics by Smith, Van Ness, et al”), and using solver on excel, the heat capacity can be found. The heating duty on the reactor is 17,413,459,363 kJ/day or 201,544.67 kJ/sec.

In order to find the heating duty on the condenser, the equation $Q_c = m_H \widehat{H}_H - m_I \widehat{H}_I - m_J \widehat{H}_J$ was used. In order to calculate it the flow rate, heat capacity, and operating temperature of the condenser has to be known for streams H, I, and J. The condenser is operating at 298.15 K. The heat capacity for bio-oil is 0.022 kJ/molK and the heat capacity for the gas is 0.019 kJ/mol K. $\widehat{H} = C_p \Delta T$ can be used to find the enthalpy. The heating duty on the condenser is -17,998,925,394.20 kJ/day or -201,320.89 kJ/sec.

Table 10 below shows a summary of all of the heating duties, in kJ/day and kJ/second, for each unit used in the “married” process.

Table 10: Summary of Married Process Heating Duties

	Heating Duty (kJ/day)	Heating Duty (kJ/sec)
Gasifier	31,734,414,776.60	367,296.30
Reactor	17,413,459,363.00	201,544.67
Condenser	-17,998,925,394.20	-208,320.89
Water Gas Shift	-3,524,861,700.00	-40,797.01
FTS	-17,909,694,600.00	-207,288.13

Utility Summary

Biomass Pyrolysis:

As described in the biomass pyrolysis energy balances, the dryer and reactor steps require heating duties to operate and the condenser step requires a cooling duty. The pyrolysis reactor has the largest energy demand and significantly contributes to the utility costs of the system. The following utility cost analysis yields an annual utility expense of \$106,793,470.25 for the direct conversion process.

The dryer in the direct conversion process is heated using saturated steam at a pressure of 600 psig. Just like in the energy balances, it was assumed that the thermodynamic properties of stream B were equal to those of water. Saturated steam at 600 psig has a temperature of 252.3°C. To avoid temperature cross in the system and to maintain technical feasibility, it was assumed that the logarithmic mean temperature of the system (ΔT_{LM}) was greater than zero. This

assumption, modeled in the equation below, was used to solve for the temperature of the steam leaving the dryer. T1 and T2 represent the entering and exiting temperatures of the saturated steam and t1 and t2 represent the entering and exiting temperatures of the biomass feed.

$$0 = \Delta TLM = \frac{(T1 - t2) - (T2 - t1)}{\ln\left(\frac{T1 - t2}{T2 - t1}\right)}$$

The temperature of the steam leaving the dryer was calculated to be 177.3°C. To solve for the required mass flow rate of saturated steam the following equation was used. Q_D is the calculated heating duty of the dryer, m_{steam} is the required mass flow rate of saturated steam, C_p is the heat capacity of steam (assumed to be constant at 4.18 kJ/kg°C), and ΔT is the change in temperature of the saturated steam.

$$Q_D = m_{steam} C_p \Delta T$$

This calculation yielded a required flow rate of saturated steam of 927,362.97 kg/day. It was assumed that saturated steam at 600 psig could be purchased for \$9/1000lbs. This resulted in a dryer utility cost of \$18,361/day.

Similar approaches were used to calculate the utility costs of the reactor and the condenser in the biomass pyrolysis process. Saturated steam at 600 psig was not sufficient for heating the reactor in this process. Therefore, it was assumed that superheated steam at 1 bar and 500°C could be purchased for \$11/1000lbs. The required flow rate of superheated steam was calculated to be 10,414,748.48 kg/day and resulted in a reactor utility cost of \$252,036.91/day. The condenser was cooled using cooling water with an entrance temperature of 26.6°C and an exit temperature of 48.8°C (an assumption suggested by Dr. James Springstead in CHEG 4600). The required flow rate of cooling was calculated to be 186,638,558.3 kg/day and resulted in a condenser utility cost of \$22,186.94/day. Table 11 below summarizes the utility costs for the biomass pyrolysis process.

Table 11: Biomass Pyrolysis Utility Cost Summary

	Daily Utility Cost (USD/day)
Dryer	18,361.00
Reactor	252,036.91
Condenser	22,186.94
total	292,584.85

“Married” Process:

With such a high temperature to achieve, it is no surprise that the gasifier has the highest heating duty in this process. It was assumed that we could purchase this steam for \$20/1000 lbs at 44 bar and 1644 K. To heat the gasifier feed to 1644 K, it was determined that 12,423,029.05 lbs/day of steam were needed. This resulted in over $\frac{3}{4}$ of the utility costs for this process.

The utilities in this process that cost the next most are the condenser and the Fischer-Tropsch synthesis. Shown in table 12 below, the condenser and the Fischer-Tropsch Synthesis have the next highest heating duty in this process. The overall utility cost of all of the systems is \$325,154.06/day. In order to find the cost of the equipment, the equation $Q = mC_p\Delta T$, is used. With Q being the heat duty, m being the flow rate of the steam that will heat or cool a system, C_p being the heat capacity of the stream, and ΔT being the change in temperature. Once the flow rate of steam is found, in kg/day, the price of saturated steam is found to be \$11/1000 lbs, then the price per day of each utility can be calculated.

The water gas shift operates at 200 °C, while the stream from the gasifier is 529.55 °C after it heats the pyrolysis reactor. The cooling stream will cost around \$8820.05/day.

The stream that bypasses the water gas shift and mixes back in with stream O will heat the stream to 364.77°C. The stream will need to be cooled back to 200 °C in order for the Fischer-Tropsch synthesis to operate correctly. Using the website “engineering tool box” the heat capacity value of coal gas is $C_p = 2.14$.

Since the reactor is being heated from the coal gasification stream of syngas, the utility cost will be \$0/day.

The condenser will cost \$23,059.05 a day. The reason that it is so expensive is because the stream coming off the reactor is very hot and needs to be cooled down a lot.

Table 12 on page 23 shows a summary of the utility costs for each unit in the married process.

Table 12: Married Process Utility Cost Summary

	Daily Utility Cost (USD/day)
Gasifier	248,460.58
Water Gas Shift	8,820.05
FTS	44,814.38
Reactor	-
Condenser	23,059.05
total	325,154.06

Equipment Information Summary

Biomass Pyrolysis:

Table X shows a summary of the size, temperature, and pressure used for the equipment in the “married” process. A lot of this information was provided in the AICHE packet.

Table 13: Biomass Pyrolysis Equipment Information Summary

	Temperature (°C)	Pressure (bar)
Dryer	100	1
Reactor	500	1
Cyclone	500	1
Condenser	25	1

“Married” Process:

Table 14 on page 24 shows a summary of the size, temperature, and pressure used for the equipment in the “married” process. The majority of this information was provided in the AICHE packet.

Table 14: Married Process Equipment Information Summary

	Temperature (°C)	Pressure (bar)
Reactor	500	1
Condenser	25	1
Gasifier	1250-1550	44
Water Gas Shift	200	1
Fischer-Tropsch Synthesis	200	1

Capital Estimate

The Fixed Capital Investment (FCI), Working Capital (WC) and Total Capital Investment (TCI) were estimated using Table 6-9 from the textbook “Plant Design and Economics for Chemical Engineers” by M. Peters, K. Timmerhaus, and R. West. Chapter six of this textbook is for estimating operating costs and other economic factors. Table 6-9 is used for estimating the capital investment based on delivered equipment cost and ratio factors. There are different ratio factors for a solid processing plant, solid-liquid processing plant, and a fluid processing plant. The ratio factors for this process were taken from the solid processing plant column.

Table 15: Estimating Capital Investment for the Biomass Pyrolysis Process

Direct Costs	
Purchased Equipment (delivered) E	\$4,321,000
Equipment Installation 45% E	\$1,944,450
Instrumentation/controls 18% E	\$777,780
Piping (installed) 16% E	\$691,360
Electrical Systems 10% E	\$432,100
Buildings (including services) 25% E	\$1,080,250
Yard Improvements 15% E	\$648,150

Service Facilities (Installed) 40% E	\$1,728,400
Total Direct Plant Cost, D	\$11,623,490
Indirect Costs	
Engineering and Supervision 33% E	\$1,425,930
Construction Expenses 39% E	\$1,685,190
Legal Expenses 4% E	\$172,840
Contractor's Fee 17% E	\$734,570
Contingency 35% E	\$1,512,350
Total Indirect Plant Cost, I	\$5,530,880
<i>Fixed Capital Investment = D+I</i>	\$17,154,370
<i>Working Capital</i>	\$3,027,242
Total Capital Investment (TCI)	\$20,181,612

The delivered equipment cost was calculated as \$4,321,000. This value was set as “E” and all of the other direct and indirect costs were estimated using the ratio factors multiplied by E. The total of the direct costs (D) and the total of the indirect costs (I) were summed to find the fixed capital investment. FCI is about 85% of the total capital investment, so FCI was calculated by dividing the value for FCI by 0.85. The working capital makes up the other 15%. A similar table was created for the married process. The purchased equipment cost (E) was increased by \$89,000 to purchase the coal gasifier and FT synthesis reactor. The FCI for the married process only came out to be \$17,507,700.00 which is \$353,330 more than the biomass pyrolysis process. The FCI was then used to estimate more costs in the operating expense checklist.

Operating Cost Summary

The operating cost was calculated on a yearly basis. The FCI calculated above was used to estimate the cost for about half of the items on the following checklist. For example, the materials cost for maintenance was estimated as 1.9% of the FCI. Table 16 on page 26 outlines the operation expenses for the biomass pyrolysis process.

Table 16: Biomass Pyrolysis Operation Expenses Checklist

		\$/year
1. Raw Materials		
	Biomass- Wood Chips	\$10,950,000.00
2. Operating Labor		\$346,078.40
3. Supervisory and Other Labor		\$51,911.76
4. Maintenance		
	Labor	\$291,624.29
	Materials	\$325,933.03
	Contract Labor	\$85,771.85
5. Catalyst and Solvent		\$0.00
6. Supplies		
	Operating	\$17,154.37
	General	\$600,402.95
7. Utilities		
	Steam	\$98,695,233.5
	Water	\$8,098,233.10
8. Auxiliaries		
	Control Lab and Experimental	\$171,543.70
	Garage	\$34,607.84
	Pumping	\$69,215.68
9. Burden		
	Employee Benefits	\$310,154.52
	Administration	\$289,389.82

	Mechanical Overhead	\$203,793.92
	Technical	\$171,543.70
10. Patent and Royalty Charge		\$514,631.10
11. Corporate Overhead		\$263,007.21
12. <i>Ad Valorem</i> Tax		\$343,087.40
13. Research Expenses		\$343,087.40
Total		\$114,270,437.50

The utility costs are derived from the energy balances for the biomass pyrolysis. Calculating the cost for labor was done using table 6-13 from the textbook by Peters, Timmerhaus and West and the website bls.gov. That table was used to determine how many workers were needed to run the process based on the type and number of unit operations and equipment. Then the website was used to find the mean salary for chemical process workers. From this data the yearly cost of operating labor was calculated. Other costs could be estimated from the operating labor cost, for example, supervisory and other labor is estimated as 15% of the operating labor.

Table 17: Married Process Operation Expenses Checklist

		\$/year
1. Raw Materials		
	Biomass- Wood Chips	\$10,950,000.00
	Coal	\$12,812,655.77
2. Operating Labor		\$519,117.60
3. Supervisory and Other Labor		\$77,867.64
4. Maintenance		
	Labor	\$297,630.90
	Materials	\$332,646.30
	Contract Labor	\$87,538.50
5. Catalyst and Solvent		\$270.00

6. Supplies		
	Operating	\$17,507.70
	General	\$612,769.50
7. Utilities		
	Steam	\$90,688,111.70
	Water	\$27,993,120.20
8. Auxiliaries		
	Control Lab and Experimental	\$175,077.00
	Garage	\$51,911.76
	Pumping	\$103,823.52
9. Burden		
	Employee Benefits	\$392,861.86
	Administration	\$135,643.05
	Mechanical Overhead	\$207,991.48
	Technical	\$175,077.00
10. Patent and Royalty Charge		\$525,231.00
11. Corporate Overhead		\$364,645.72
12. <i>Ad Valorem</i> Tax		\$350,154.00
13. Research Expenses		\$350,154.00
Total		\$145,201,833.00

The values for the operation expenses of the married process in Table 17 above were calculated the same way as for the biomass pyrolysis process. This process included a row for coal in the raw materials section, and increased labor and utility costs to run the extra machinery. The cost of running the married process is much higher than that of the biomass pyrolysis. There is a difference of \$52,459,138.66 every year.

Economic Analysis

This project was assumed to be battery limits, meaning that all investments will be made in equipment and operation of the process. Additionally, a ten year plant life was assumed for the economic analysis, and a minimum acceptable return rate of 20% was also assumed. The capital investment for this project was estimated using the Lang factor method. The equipment costs were estimated, and the Lang factors were then used to estimate the fixed capital investment (FCI) and total capital investment (TCI). The Lang factors for a solid processing plant were found using Table 6-9 from the textbook “Plant Design and Economics for Chemical Engineers” by M. Peters, K. Timmerhaus, and R. West, with the factor for FCI being 3.97 and the TCI factor being 4.67. This means that

$$FCI = 3.97 \times (\text{Delivered Equipment Cost})$$

$$TCI = 4.67 \times (\text{Delivered Equipment Cost})$$

Which results in FCI values of \$17,154,370 (biomass pyrolysis) and \$17,507,700 (married process), and TCI values of \$20,181,612 (biomass pyrolysis) and \$20,597,294.12 (married process).

The operating costs can be found in Table 16 for the biomass pyrolysis process, and Table 17 for the married process. A large portion of the operating expenses are incurred as utilities, since the processes require incredibly high amounts of heating and subsequent cooling.

The revenue source for the biomass pyrolysis process is the bio oil product. For the married process, the revenue sources are the bio oil and diesel products. As outlined in the market survey, a price of \$409.66 per ton can reasonably be achieved by selling the raw bio oil, and a price of \$806.57 per ton can be achieved by selling the diesel.

Tables 18 and 19, shown on page 30, are cash flow tables for each of the two processes. The FCI and WC were both taken from calculations shown earlier. The income (INC) comes from the revenues discussed earlier. The expenses (EXP) come from the operational checklist shown earlier in the report (Tables 16 and 17). The depreciation fraction (and consequently the yearly depreciation, DEP) were calculated using 7 year MACRS values. The book value (BV) of the FCI per year is determined by subtracting the current year’s depreciation from the previous year’s book value. The profit is calculated by subtracting EXP and DEP from INC. The tax rate was assumed to be 21% of profits, but with negative profits for all years, there will not be any taxes charged. The cash flow (CF) is calculated by subtracting FCI, WC, EXP, and TAX from the INC column. The discount factor (DF) comes from the assumed minimum acceptable return

rate of 20%. Discounted cash flow (DCF) results from multiplying CF by DF, and PV is simply the summation of the DCF up to that year.

Table 18. Biomass Pyrolysis Cash Flow Table (MM \$)

Year	FCI	WC	INC	EXP	DEP Fraction	DEP	BV	PROFIT	TAX	CF	DF	DCF	PV
0	17.154	3.027	0	0	0	0	17.154	0	0	-20.182	1	-20.182	-20.182
1	0	0	97.14	114.27	0.1429	2.451	14.703	-19.577	0	-17.126	0.833	-14.271	-34.453
2	0	0	97.14	114.27	0.2449	4.201	10.502	-21.327	0	-17.126	0.694	-11.893	-46.346
3	0	0	97.14	114.27	0.1749	3.000	7.502	-20.126	0	-17.126	0.579	-9.910	-56.256
4	0	0	97.14	114.27	0.1249	2.142	5.359	-19.268	0	-17.126	0.482	-8.259	-64.515
5	0	0	97.14	114.27	0.0893	1.532	3.827	-18.657	0	-17.126	0.402	-6.882	-71.397
6	0	0	97.14	114.27	0.0892	1.530	2.297	-18.656	0	-17.126	0.335	-5.735	-77.133
7	0	0	97.14	114.27	0.0893	1.532	0.765	-18.657	0	-17.126	0.279	-4.779	-81.912
8	0	0	97.14	114.27	0.0446	0.765	0	-17.890	0	-17.126	0.232	-3.983	-85.895
9	0	0	97.14	114.27	0	0	0	-17.126	0	-17.126	0.194	-3.319	-89.214
10	0	-3.027	97.14	114.27	0	0	0	-17.126	0	-14.098	0.162	-2.277	-91.491

Table 19. Married Process Cash Flow Table (MM \$)

Year	FCI	WC	INC	EXP	DEP Fraction	DEP	BV	PROFIT	TAX	CF	DF	DCF	PV
0	17.508	3.090	0	0	0	0	17.508	0	0	-20.597	1	-20.597	-20.597
1	0	0	143.5	145.2	0.1429	2.502	15.006	-4.220	0	-1.719	0.833	-1.432	-22.030
2	0	0	143.5	145.2	0.2449	4.288	10.718	-6.006	0	-1.719	0.694	-1.194	-23.223
3	0	0	143.5	145.2	0.1749	3.062	7.656	-4.781	0	-1.719	0.579	-0.995	-24.218
4	0	0	143.5	145.2	0.1249	2.187	5.469	-3.905	0	-1.719	0.482	-0.823	-25.046
5	0	0	143.5	145.2	0.0893	1.563	3.906	-3.282	0	-1.719	0.402	-0.691	-25.737
6	0	0	143.5	145.2	0.0892	1.562	2.344	-3.280	0	-1.719	0.335	-0.576	-26.313
7	0	0	143.5	145.2	0.0893	1.563	0.781	-3.282	0	-1.719	0.279	-0.480	-26.792
8	0	0	143.5	145.2	0.0446	0.781	0	-2.500	0	-1.719	0.232	-0.400	-27.192
9	0	0	143.5	145.2	0	0	0	-1.719	0	-1.719	0.194	-0.333	-27.525
10	0	-3.090	143.5	145.2	0	0	0	-1.719	0	1.371	0.162	0.221	-27.304

As can be seen from these cash flow tables, neither process manages to make a profit. As will be discussed in the conclusions, this means that it is not recommended to pursue either investment opportunity in their current design. The fact that the present value at the end of 10 years (or the net present value, NPV) is negative means that the MARR of 20% was not achieved.

Other economic parameters of interest include the return on investment (ROI), which can be calculated by

$$ROI = \frac{\text{Annual Cash Flow}}{TCI} \times 100\%$$

This results in an ROI of -93.4% for the biomass pyrolysis process, and -16.8% for the married process. Another parameter of interest is the payback period (PBP), calculated by

$$PBP = \frac{FCI}{\text{Annual Cash Flow}}$$

Which results in a PBP of 0.176 years for the biomass pyrolysis process, and 0.122 years for the married process.

The final economic factor taken into consideration was the internal rate of return (IRR). The IRR is defined as the MARR for which the process has an NPV of 0. The IRR for these processes was not found to exist, because both processes fail to achieve any profit even with no rate of return expected. The results of this economic investigation show that while neither process would achieve profitability, the married process comes much closer to doing so than the biomass pyrolysis process does.

A sensitivity analysis was also conducted to determine how changes in raw material and/or product prices would affect the two processes. If the price of biomass changes by 15%, then the NPV of each process would either increase or decrease by \$6.886 million (depending on if the price rises or falls). If the price of coal changes by 15%, then the NPV of the married process changes by \$8.057 million (the biomass pyrolysis process does not use coal). If the price of bio oil changes by 15%, then the NPV of both processes changes by \$61.093 million. If the price of diesel changes by 15%, then the NPV of the married process would change by \$26.978 million (the biomass pyrolysis process does not generate diesel).

These findings indicate that the price of the products has a much bigger impact on the NPV of the processes than the price of the raw materials. In fact, if price increases were seen for the bio oil close to 15% with no other changes, then the married process could actually become profitable and achieve the MARR of 20% assumed for this analysis. Therefore, the price of both bio oil and diesel should be closely monitored, and if these prices trend upward then the married process may be a viable investment.

Innovation & Optimization

The married process attempts to drive the direct conversion of biomass pyrolysis toward economic optimum. Using the syngas to heat the biomass pyrolysis reactor saves money by not having to pay as much for the superheated steam necessary to heat the reaction. Also, the diesel being made from the syngas could be sold which can account for another source of income. Unfortunately, the savings from heating the pyrolysis reactor with steam are offset by the utility costs of the coal gasifier and the Fischer-Tropsch process needed to make diesel. These utility costs could be reduced by using the heat from the solid waste streams of the cyclone and the gasifier that contain char and unreacted material at very high temperatures.

An alternative design that could have been done for this project is the actual mixture of coal gasification and biomass pyrolysis. The mixed process would have coal gasification and biomass pyrolysis reactions occurring in the same processing unit. This process could yield a higher outcome of bio-oil, and save money by cutting back on utilities. However, the combination of the coal gasification and biomass pyrolysis processes could cause complications due to an excess of char and unreacted material in the system.

Safety

The main safety concern in this project is that both of the processes discussed are dealing with highly flammable products. Manufacturing bio-oil safely and efficiently begins with good equipment design. The design process involves the functional specifications to be made, the development of a process flow diagram, the development of a process instrumentation diagram, a HAZOP study to be conducted, a detailed review of design and costing, and documentation. Before approving the final design, it is a good idea to go over a series of checklists to make sure that all the important factors have been considered. Checklists may include health and safety requirements, environmental requirements, technical and economic considerations, and training and staffing needs.

An essential part of the design phase of the project is a risk assessment/HAZOP analysis. During all phases of the process (loading, startup, operation, shut down, unloading, and storage) the following risks should be considered: fire and explosion (including dust explosions and combustion during storage), particulate and gaseous emissions, gas leakage (particularly carbon monoxide), and noise pollution (Lynch, 2010).

Environmental

Although bio-oil is a promising source of clean energy, the married process presents several environmental concerns. In the married process, there are 4 waste streams that cannot be reused or recycled into a useful product. One of these streams is a concentrated CO₂ stream that cannot be directly released into the atmosphere due to it being a greenhouse gas. The married process also creates a reliance on coal gasification for the production of bio-oil. Bio-oil is a promising source of green energy, but fueling the production of bio-oil with fossil fuels takes away from its environmental benefits. The married process provides another application for the syngas produced in coal gasification, but it is not a sustainable, long-term solution for the elimination of fossil fuels.

Computer Programs

The use of the computer software ASPEN Plus V11 would have been ideal for the analysis conducted in this project. Modeling this project in ASPEN Plus was attempted, but was ultimately not successful. One of the most significant issues was inputting the wood chips biomass feed as a component. Wood chips are composed of cellulose, hemicellulose, and lignin. Unfortunately, ASPEN Plus does not have these components in its existing database. Several sources were found regarding the modeling of biomass pyrolysis in ASPEN Plus. However, due to the time limitations of this project and the complications encountered with the simulation software, the group was forced to proceed with the analysis via hand calculations. The software would have provided more accurate estimates of the pyrolysis reaction products by taking into account all of the reactions that occur in the pyrolysis process, not just the combustion reactions. The software would have also provided a better estimate of the composition of the bio-oil produced in each of the two processes.

Conclusion

The direct conversion of biomass pyrolysis uses fast pyrolysis to produce bio-oil, while the “married” process uses coal gasification as a utility for the biomass reactor to achieve the production of bio-oil, and diesel. It was thought that the “married” process was more economically optimal, compared to the direct conversion process due to the elimination of the need for superheated steam to fuel the pyrolysis reaction. Although the “married” process was slightly more economically friendly than the direct pyrolysis of biomass, between the two processes, neither seemed to make a profit. Therefore, it is not recommended to proceed with

either process. However, a sensitivity analysis revealed that the profitability of the married process relies heavily on the selling price of the product streams. Increases in the prices of bio-oil and diesel could result in the married process becoming economically feasible in the future.

Recommendations

The next steps to make both of the processes, direct biomass pyrolysis and the “married” process, more profitable would be using the waste streams from the cyclone and coal gasification to heat the reaction. The waste streams from both of these profits contain char and unreacted material at very high temperatures. Another recommendation would be to mix the synthesis gas from the coal gasification in the reactor with the biomass instead of using the synthesis gas to heat the reactor. This would eliminate the profits from selling the diesel produced from the Fischer-Tropsch process, but would also eliminate the large utility costs of the Fischer-Tropsch process.

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Appendix A: Material Balance Data

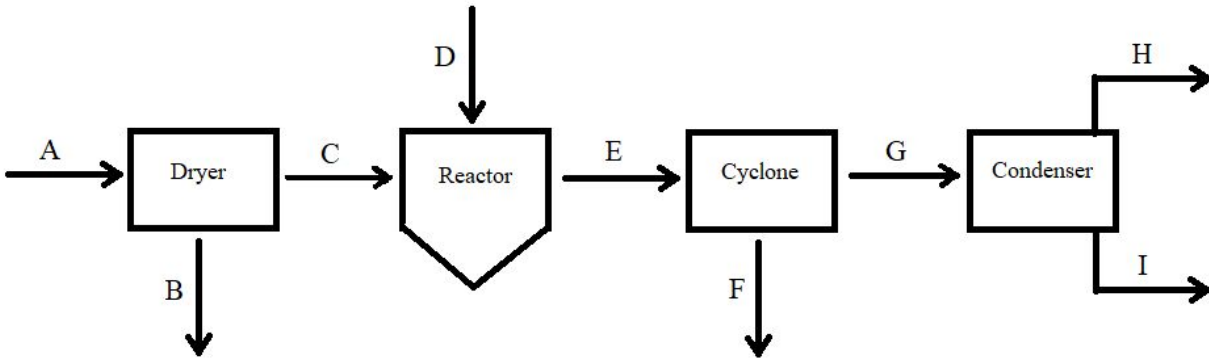


Figure A.1: Biomass Pyrolysis Process Flow Diagram

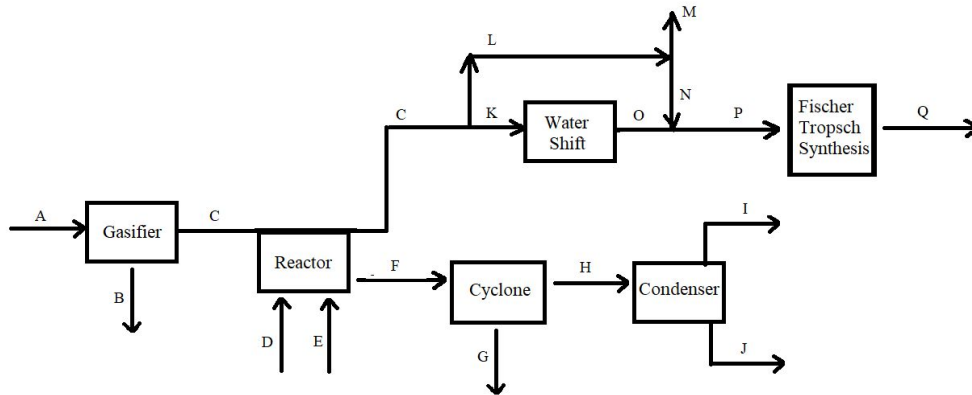


Figure A.2: "Married" Process PFD

Table A.1: Biomass Pyrolysis Material Balance In/Out Table

Unit	Dryer			Reactor			Cyclone			Condenser		
stream (tons/day)	A	B	C	C	D	E	E	F	G	G	H	I
cellulose	400	0	400	400	0	60	60	60	0	0	-	-
hemicellulose	300	0	300	300	0	45	45	45	0	0	-	-
lignin	270	0	270	270	0	40.5	40.5	40.5	0	0	-	-
other	30	30	0	0	0	0	0	0	0	0	-	-
O ₂	-	-	-	-	1193.74	179.74	179.74	0	179.74	-	-	-
CO ₂	-	-	-	-	0	1405.8	1405.8	0	1405.8	-	-	-
H ₂ O	-	-	-	-	0	431.84	431.84	0	431.84	-	-	-
C	-	-	-	-	-	-	-	-	-	383.28	-	383.28
H	-	-	-	-	-	-	-	-	-	1585.6	5.35	42.13
O	-	-	-	-	-	-	-	-	-	48.42	1332.36	252.12
total	1000	30	970	970	1193.74	2162.88	2162.88	145.5	2017.38	2017.3	1337.71	677.53

Table A.2: Coal Gasification Output

Synthesis Gas Leaving Gasifier (tons/day)		Coal Leaving Gasifier (tons/day)
CO	5470.16	-
CO ₂	2821.18	-
H ₂ O	3322.54	-
H ₂	293.04	-
H ₂ S	36.75	-
N ₂	15.12	-
Coal Slag	-	102.997
total	11958.79	103

Table A.3: Fischer-Tropsch Synthesis

Components	Streams (tons/day)						
	C	K	L	O	P	Q	M
CO	5470.16	2430.94	3039.22	-	3039.22	-	-
CO ₂	2821.18	-	2821.18	3820.05	3820.05	3820.05	2821.18
H ₂ O	3322.54	1562.75	1759.79	-	-	1953.78	1759.79
H ₂	293.04	-	293.04	173.64	434.17	32.50	-
H ₂ S	36.75	-	36.75	-	-	-	36.75
N ₂	15.12	-	15.12	-	-	-	15.12
CH ₂	-	-	-	-	-	1519.61	-
total	11958.8	3993.69	7965.1	3993.69	7293.44	7325.94	4632.84

Table A.4: Stream out of Pyrolysis Reactor in Married Process

Components	Stream (tons/day)
Cellulose	340
Hemicellulose	256.08
Lingin	254.88
O ₂	198.91
CO ₂	1456.13
H ₂ O	444.25
total	2950.25

Table A.5: Married Process In/out Table of Condenser

Component	In (tons/day)	Bio-Oil Out (tons/day)	Gases Out (tons/day)
C	397.08	397.08	-
H	49.36	43.58	13.96
O	1651.84	260.86	1381.17
Total	2098.28	701.52	1395.13

Appendix B: Energy Balance Data

Table B.1: Calculated Values of Cuproammonium Lignin

T (K)	Cp of sulfuric lignin (J/mol*K)	Cp cuproammonium lignin (J/mol*K)
0	0	0
20	11.87	13.2753854
40	32.9	37.06323957
60	53.68	60.91637843
80	72.74	83.15575757
100	89.55	103.1349334
120	105.4	122.2998877
140	120.5	140.8776738
160	135.5	159.620586
180	150.5	178.6511305
200	165.6	198.0956027
220	180.8	217.9636791
240	196.5	238.7513487
260	212.3	259.9905948
273.15	222.5	273.9075361
280	227.7	281.0750225
298.15	242	300.9059807
300	243.5	302.9963665
320	260	326.1513141
340	274.1	346.6496019
360	288.8	368.2508594
380	307.3	395.0968392
420	413.3	540.3631533
440	428	564.3519446

Table B.2: Biomass Pyrolysis Energy Balance In/Out Table

	Unit	Stream								
		A	B	C	D	E	F	G	H	I
Temperature	C	25	100	100	25	500	500	500	25	25
Mass Enthalpy	kJ/ton	471662.6	369815.1	774532.41	259056.16	8541390	2281961.68	8955662.81	322398.91	465869.53
Mass Flowrate	tons/day	1000	30	970	1193.74	2162.88	145.5	2017.38	1337.71	677.53
Stream Energy	kJ/day	471662600	11094453	751296437.7	309245700.4	18474001603	332025424.4	18066975040	431276245.9	315640582.7

Table B.3: Summary of Biomass Pyrolysis Heating Duties

	Heating Duty (kJ/day)	Heating Duty (kJ/sec)
Dryer	290728290.70	3364.91
Reactor	17413459465.06	201544.67
Condenser	-17320058211.08	-200463.64

Table B.3: Summary of Married Process Heating Duties

	Heating Duty (kJ/day)	Heating Duty (kJ/sec)
Reactor	17413459363	2015.44
Condenser	-17998925394.20	-208320.89
Water Gas Shift	-105816582	-1224.72
FTS	-537844395	-6225.05

Table B.4: Biomass Pyrolysis Utility Cost Summary

	Daily Utility Cost (USD/day)
Dryer	18,361.00
Reactor	22,912.45
Condenser	22,186.94
total	63,460.39

Table B.5: Married Process Utility Cost Summary

	Daily Utility Cost (USD/day)
Gasifier	248,460.58
Water Gas Shift	8,820.05
FTS	44,814.38
Reactor	-
Condenser	23,059.05
total	325,154.06

Table B.6: Biomass Pyrolysis Equipment Information Summary

	Temperature (°C)	Pressure (bar)
Dryer	100	1
Reactor	500	1
Cyclone	500	1
Condenser	25	1

Table B.7: Married Process Equipment Information Summary

	Temperature (°C)	Pressure (bar)
Reactor	500	1
Condenser	25	1
Gasifier	1250-1550	44
Water Gas Shift	200	1
Fischer-Tropsch Synthesis	200	1

Appendix C: Capital Estimate, Operating Cost, and Economic Analysis Data*Table C.1: Estimating Capital Investment, Biomass Pyrolysis*

Direct Costs	
Purchased Equipment (delivered) E	\$4,321,000
Equipment Installation 45% E	\$1,944,450
Instrumentation/controls 18% E	\$777,780
Piping (installed) 16% E	\$691,360
Electrical Systems 10% E	\$432,100
Buildings (including services) 25% E	\$1,080,250
Yard Improvements 15% E	\$648,150
Service Facilities (Installed) 40% E	\$1,728,400
Total Direct Plant Cost, D	\$11,623,490
Indirect Costs	
Engineering and Supervision 33% E	\$1,425,930
Construction Expenses 39% E	\$1,685,190
Legal Expenses 4% E	\$172,840
Contractor's Fee 17% E	\$734,570
Contingency 35% E	\$1,512,350
Total Indirect Plant Cost, I	\$5,530,880
<i>Fixed Capital Investment = D+I</i>	\$17,154,370
<i>Working Capital</i>	\$3,027,242
Total Capital Investment (TCI)	\$20,181,612

Table C.2: Estimating Capital Investment, Married Process

Direct Costs	
Purchased Equipment (delivered) E	\$4,410,000.00
Equipment Installation 45%E	\$1,984,500.00
Instrumentation/controls 18%E	\$793,800.00
Piping (installed) 16%E	\$705,600.00
Electrical Systems 10%E	\$441,000.00
Buildings (including services) 25% E	\$1,102,500.00
Yard Improvements 15%E	\$661,500.00
Service Facilities (Installed) 40%E	\$1,764,000.00
Total Direct Plant Cost, D	\$11,862,900.00
Indirect Costs	
Engineering and Supervision 33%E	\$1,455,300.00
Construction Expenses 39%E	\$1,719,900.00
Legal Expenses 4%E	\$176,400.00
Contractor's Fee 17%E	\$749,700.00
Contingency 35%E	\$1,543,500.00
Total Indirect Plant Cost, I	\$5,644,800.00
<i>Fixed Capital Investment</i> = D+I	\$17,507,700.00
<i>Working Capital</i>	\$3,089,594.12
Total Capital Investment (TCI)	\$20,597,294.12

Table C.3: Operation Expenses Checklist, Biomass Pyrolysis

		\$/year
1. Raw Materials		
	Biomass- Wood Chips	\$10,950,000.00
2. Operating Labor		\$346,078.40
3. Supervisory and Other Labor		\$51,911.76
4. Maintenance		
	Labor	\$291,624.29
	Materials	\$325,933.03
	Contract Labor	\$85,771.85
5. Catalyst and Solvent		\$0.00
6. Supplies		
	Operating	\$17,154.37
	General	\$600,402.95
7. Utilities		
	Steam	\$15,064,809.25
	Water	\$8,098,233.10
8. Auxiliaries		
	Control Lab and Experimental	\$171,543.70
	Garage	\$34,607.84
	Pumping	\$69,215.68
9. Burden		
	Employee Benefits	\$310,154.52
	Administration	\$289,389.82
	Mechanical Overhead	\$203,793.92

	Technical	\$171,543.70
10. Patent and Royalty Charge		\$514,631.10
11. Corporate Overhead		\$263,007.21
12. <i>Ad Valorem</i> Tax		\$343,087.40
13. Research Expenses		\$343,087.40
Total		\$38,282,974.07

Table C.4: Operation Expenses Checklist, Married Process

		\$/year
1. Raw Materials		
	Biomass- Wood Chips	\$10,950,000.00
	Coal	\$12,812,655.77
2. Operating Labor		\$519,117.60
3. Supervisory and Other Labor		\$77,867.64
4. Maintenance		
	Labor	\$297,630.90
	Materials	\$332,646.30
	Contract Labor	\$87,538.50
5. Catalyst and Solvent		\$270.00
6. Supplies		
	Operating	\$17,507.70
	General	\$612,769.50
7. Utilities		
	Steam	\$25,172,491.45
	Water	\$8,098,233.10

8. Auxiliaries		
	Control Lab and Experimental	\$175,077.00
	Garage	\$51,911.76
	Pumping	\$103,823.52
9. Burden		
	Employee Benefits	\$392,861.86
	Administration	\$135,643.05
	Mechanical Overhead	\$207,991.48
	Technical	\$175,077.00
10. Patent and Royalty Charge		\$525,231.00
11. Corporate Overhead		\$364,645.72
12. <i>Ad Valorem</i> Tax		\$350,154.00
13. Research Expenses		\$350,154.00
Total		\$61,811,298.84

Table C.5. Biomass Pyrolysis Cash Flow Table (MM \$)

Year	FCI	WC	INC	EXP	DEP Fraction	DEP	BV	PROFIT	TAX	CF	DF	DCF	PV
0	17.154	3.027	0	0	0	0	17.154	0	0	-20.182	1	-20.182	-20.182
1	0	0	97.14	114.27	0.1429	2.451	14.703	-19.577	0	-17.126	0.833	-14.271	-34.453
2	0	0	97.14	114.27	0.2449	4.201	10.502	-21.327	0	-17.126	0.694	-11.893	-46.346
3	0	0	97.14	114.27	0.1749	3.000	7.502	-20.126	0	-17.126	0.579	-9.910	-56.256
4	0	0	97.14	114.27	0.1249	2.142	5.359	-19.268	0	-17.126	0.482	-8.259	-64.515
5	0	0	97.14	114.27	0.0893	1.532	3.827	-18.657	0	-17.126	0.402	-6.882	-71.397
6	0	0	97.14	114.27	0.0892	1.530	2.297	-18.656	0	-17.126	0.335	-5.735	-77.133
7	0	0	97.14	114.27	0.0893	1.532	0.765	-18.657	0	-17.126	0.279	-4.779	-81.912
8	0	0	97.14	114.27	0.0446	0.765	0	-17.890	0	-17.126	0.232	-3.983	-85.895
9	0	0	97.14	114.27	0	0	0	-17.126	0	-17.126	0.194	-3.319	-89.214

10	0	-3.027	97.14	114.27	0	0	0	-17.126	0	-14.098	0.162	-2.277	-91.491
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Table C.6. Married Process Cash Flow Table (MM \$)

Year	FCI	WC	INC	EXP	DEP Fraction	DEP	BV	PROFIT	TAX	CF	DF	DCF	PV
0	17.508	3.090	0	0	0	0	17.508	0	0	-20.597	1	-20.597	-20.597
1	0	0	143.5	145.2	0.1429	2.502	15.006	-4.220	0	-1.719	0.833	-1.432	-22.030
2	0	0	143.5	145.2	0.2449	4.288	10.718	-6.006	0	-1.719	0.694	-1.194	-23.223
3	0	0	143.5	145.2	0.1749	3.062	7.656	-4.781	0	-1.719	0.579	-0.995	-24.218
4	0	0	143.5	145.2	0.1249	2.187	5.469	-3.905	0	-1.719	0.482	-0.823	-25.046
5	0	0	143.5	145.2	0.0893	1.563	3.906	-3.282	0	-1.719	0.402	-0.691	-25.737
6	0	0	143.5	145.2	0.0892	1.562	2.344	-3.280	0	-1.719	0.335	-0.576	-26.313
7	0	0	143.5	145.2	0.0893	1.563	0.781	-3.282	0	-1.719	0.279	-0.480	-26.792
8	0	0	143.5	145.2	0.0446	0.781	0	-2.500	0	-1.719	0.232	-0.400	-27.192
9	0	0	143.5	145.2	0	0	0	-1.719	0	-1.719	0.194	-0.333	-27.525
10	0	-3.090	143.5	145.2	0	0	0	-1.719	0	1.371	0.162	0.221	-27.304