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Large-Scale Pyrolysis Oil Production: A Technology Assessment and Economic Analysis
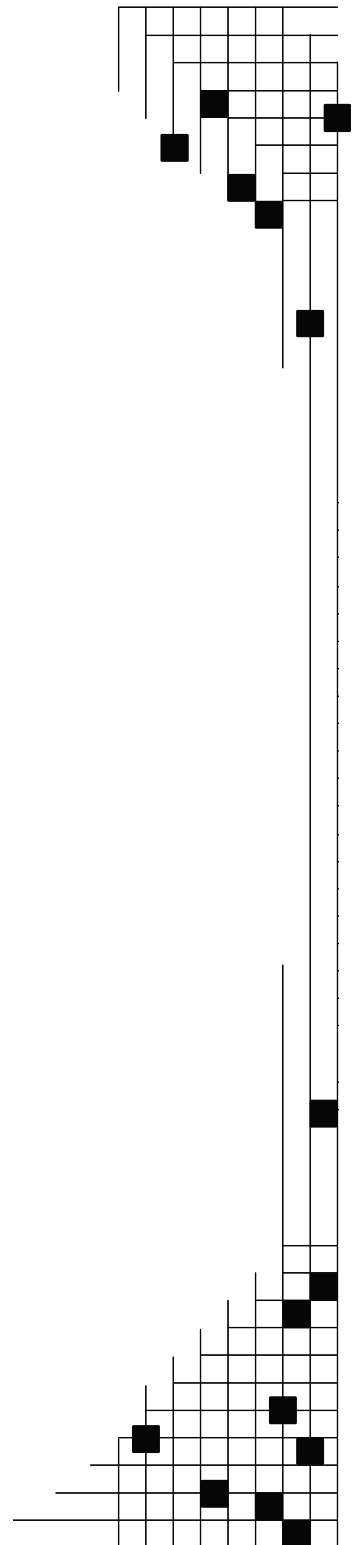
M. Ringer, V. Putsche, and J. Scahill

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Executive Summary

Pyrolysis is one of a number of possible paths for converting biomass to higher value products. As such, this technology can play a role in a biorefinery model to expand the suite of product options available from biomass. The intent of this report is to provide the reader with a broad perspective of pyrolysis technology as it relates to converting biomass substrates to a liquid "bio-oil" product, and a detailed technical and economic assessment of a fast pyrolysis plant producing 16 tonne/day of bio-oil.

The international research community has developed a considerable body of knowledge on the topic over the last twenty-five years. The first part of this report attempts to synthesize much of this information into the relevant issues that are important to advancing pyrolysis technology to commercialization. The most relevant topics fall under the following categories:

1) Technical requirements for converting biomass to high yields of liquid bio-oil

2) Reactor designs capable of meeting technical requirements

3) Bio-oil stability issues and recent findings that address the problem

4) Product specifications and standards that need to be established

5) Applications for using bio-oil in existing or modified end use devices

6) Environmental, safety, and health issues

For the bio-oil plant technical and economic analysis, the process is based on fast pyrolysis, which is composed of five major processing areas: feed handling and drying, pyrolysis, char combustion, product recovery, and steam generation. An ASPEN model was developed to simulate the operation of the bio-oil production plant. Based on a 550 tonne/day biomass (wood chips, 50% by mass water content) feed, the cost of the bio-oil for a fully equity financed plant and 10% internal rate of return is $7.62/GJ on a lower heating value (LHV) basis.

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1. Introduction

The vast stores of biomass available in the domestic United States have the potential to displace significant amounts of fuels that are currently derived from petroleum sources. Energy security, energy flexibility, and rural and urban job development are other drivers that support the use of biomass to produce fuels, chemicals, and other products. The loss of traditional biomass-based industries such as lumber and paper to overseas markets make it increasingly important to develop this domestic resource. The rationale is even more compelling if one considers the benefits of forest thinning to forest health and fire issues in the arid West. Proposed fuel reduction activities would involve removing enormous amounts of biomass that have no current market value. The only realistic market capable of consuming this volume of material is energy and/or commodity chemicals. The primary question of "what is the best way to convert biomass into higher value products" is then raised.

Pyrolysis is one of a number of possible paths by which we can convert biomass to higher value products. As such, this technology can play a role in a biorefinery model to expand the suite of product options available from biomass. The intent of this report is to provide the reader with a broad perspective of pyrolysis technology as it relates to converting biomass substrates to a liquid "bio-oil" product, and a detailed technical and economic assessment of a fast pyrolysis plant producing 16 tonne/day of bio-oil.

The international research community has developed a considerable body of knowledge on pyrolysis over the last twenty-five years. The first part of this report attempts to synthesize much of this information into the relevant issues that are important to advancing pyrolysis technology to commercialization. The most relevant topics fall under the following categories:

1) Technical requirements to effect conversion of biomass to high yields of liquid bio-oil
2) Reactor designs capable of meeting technical requirements
3) Bio-oil stability issues and recent findings that address the problem
4) Product specifications and standards need to be established
5) Applications for using bio-oil in existing or modified end use devices
6) Environmental, safety, and health issues.

The first two categories above represent topics that are well established and accepted in the research community. There is little argument on requirements for producing bio-oil in high yields. The principal technical requirement is to impart a very high heating rate with a corresponding high heat flux to the biomass. When exposed to this environment, thermal energy cleaves chemical bonds of the original macro-polymeric cellulose, hemicellulose, and lignin to produce mostly oxygenated molecular fragments of the starting biomass. These fragments have molecular weights ranging from a low of 2 (for hydrogen) up to 300-400. The lower molecular weight compounds remain as permanent gases at ambient temperature while the majority of compounds condense to collectively make up what is called bio-oil at yields up to 70 wt%. This 70 wt% also includes the water formed during pyrolysis in addition to moisture in the biomass feed that ends up as water in bio-oil. The yield of permanent gas is typically 10-15 wt% with the balance of the weight produced as char.

A number of reactor designs have been explored that are capable of achieving the heat transfer requirements noted above. They include:

- Fluidized beds, both bubbling and circulating

- Ablative (biomass particle moves across hot surface like butter on a hot skillet)

- Vacuum

- Transported beds without a carrier gas

Of these designs, the fluidized and transported beds appear to have gained acceptance as the designs of choice for being reliable thermal reaction devices capable of producing bio-oil in high yields.

Categories 3, 4, and 5 have important relationships to each other. The stability of the bio-oil product is critical to the design of end use devices such as burners, internal combustion (IC) engines, and turbines. As with devices that operate on petroleum-based fuels, these devices are designed to function properly with consistent fuel properties. To gain marketplace acceptance of bio-oils, the consumer must have confidence that this fuel will perform reliably in a given piece of equipment and not have deleterious effects on the equipment. The generally accepted way of providing this level of confidence is to establish a set of specifications for bio-oil that every producer would be required to meet. This, of course, needs to be done in concert with the designers and manufacturers of the end use application devices. One of the key specification issues is the level of char fines remaining in the bio-oil. While char is known to be a primary catalytic influence on the long-term stability of the oil, it is not known how it can be removed in a cost effective manner. The difficulty is tied to the sub-micron size of these char fines. In many respects the issue of "clean up" of char fines from the bio-oil can be considered analogous to the cleaning of tars and particulates from gasifier product streams. Both are critical technical hurdles that must be overcome before the technology gains widespread commercial acceptance.

The last category concerns environmental, safety, and health issues. These issues are important to both the producer and consumer of bio-oils. The producer must have a good understanding of the toxicity of bio-oil so as to design and build in the appropriate engineering controls for protecting plant operating personnel. Information about these issues is also required to meet the requirements of commerce with respect to transportation and consumer right-to-know safety issues.

Current pyrolysis systems are relatively small from a process industries throughput standpoint. The table below illustrates this point. Some of the mobile systems that are currently under development or were demonstrated in the late 1980s have capacities of about 5 tons /day, which is similar to some of stationary units noted below. The implication here is that this technology is still in its early development stages from a standpoint of its commercialization status. The Red Arrow plants can be considered commercial but they are focused on high value flavoring compounds that have limited markets. Large-scale systems to serve energy markets have not yet achieved commercial status.

Table 1. Worldwide Biomass Pyrolysis Units

Reactor Design	Capacity (Dry Biomass Feed)	Organization or Company	Products
Fluidized bed	400 kg/hr (11 tons/day)	DynaMotive, Canada	Fuel
	250 kg/hr (6.6 tons/day)	Wellman, UK	Fuel
	20 kg/ hr (0.5 tons/day)	RTI, Canada	Research / Fuels
Circulating Fluidized Bed	1500 kg/hr (40 tons/day)	Red Arrow, WI Ensyn design	Food flavorings / chemicals
	1700 kg/hr (45 tons/day)	Red Arrow, WI Ensyn design	Food flavorings / chemicals
	20 kg/hr (0.5 tons/day)	VTT, Finland Ensyn design	Research / Fuels
Rotating Cone	200 kg/hr (5.3 tons/day)	BTG, Netherlands	Research / Fuels
Vacuum	3500 kg/hr (93 tons/day)	Pyrovac, Canada	Pilot scale demonstration / Fuels
Other Types	350 kg/hr (9.3 tons/day)	Fortum, Finland	Research / Fuels

The application of heat in the absence of oxygen is well recognized as a method for breaking down the complex polymeric constituents of biomass (cellulose, hemicellulose, and lignin) to simpler molecular fragments. Some of the earliest recorded uses of this technique were in Egypt to produce pitch for water sealing boats and as an embalming agent. In more recent times, before the advent of the petrochemical industry, a number of chemicals such as methanol, phenol, carboxylic acids, and furfural were derived from the pyrolysis liquids generated during charcoal manufacturing. These were rather crude techniques and little effort was expended in trying to improve the yields or selectivity of the compounds of choice since charcoal was the primary product. In the late 1960s and early 1970s pioneering research in understanding the fundamental mechanisms of thermal processes as applied to biomass substrates began in earnest [1,2]. After the global petroleum supply restrictions in the early 1970s, and the subsequent price increases, the use of biomass as a source of energy saw renewed interest. This interest accelerated the research and development of thermal processes and investigators began to gain a better understanding of how the various components of biomass break down in high temperature environments [3]. By this time the community of researchers investigating thermochemical conversion pathways had grown substantially. In October 1980, a workshop sponsored by the Solar Energy Research Institute (SERI) —forerunner to the National Renewable Energy Laboratory (NREL)—was held at Copper Mountain CO. The workshop brought together most of the people who had been doing research in biomass pyrolysis. In retrospect this "Specialists'

Workshop on Fast Pyrolysis of Biomass" could be considered a watershed event that began extensive networking among researchers in this field. This then set the stage for rapid advancement of the chemical science and engineering that would be crucial in developing biomass fast pyrolysis into a commercial technology. The years from 1980 to 1990 can be considered the golden era of biomass pyrolysis development with many advances made by U.S. and Canadian research teams. By the end of the 90s Europe had taken the lead in advancing biomass fast pyrolysis technology. With the wide number of researchers involved in developing biomass pyrolysis, liquid products have taken on a variety of descriptors such as: biomass (or wood) pyrolysis oils, biocrude oils, wood oil, pyroligneous tar, liquid wood, biomass pyrolysis liquids, or simply bio-oil. For the remainder of this report the term bio-oil will be used for the liquid product.

2. Production of Bio-oil

2.1   Heat Transfer Requirements

Three primary products are obtained from pyrolysis of biomass. They are char, permanent gases, and vapors; that at ambient temperature condense to a dark brown viscous liquid. While pyrolysis of biomass has been practiced in some form for thousands of years, it wasn't until recently that the relationship between heat transfer rates into the biomass and product distribution yields were well understood. The practice of charcoal manufacture from biomass is generally referred to as a slow pyrolysis process based on the rate in which heat is imparted to the biomass. The distribution of products between liquid, char, and gas on a weight basis for this "slow" pyrolysis is approximately 30%, 35%, and 35% respectively, whereas under "fast pyrolysis" conditions the product distribution is dramatically altered and shifts the distribution primarily to a liquid bio-oil product. Under these conditions bio-oil yields of liquid, char, and gas are 75%, 12%, and 13% respectively [4]. It is generally recognized that two primary processing steps are required to meet the conditions for fast pyrolysis. They are:

- Very high heat flux to the biomass with a corresponding high heating rate of the biomass particle.

- The heat transfer to the biomass must occur in a very short time period with immediate quenching following product formation.

The rate of the heat transfer to the particle needs to be between 600-1000 W/cm^2 [5]. Some unpublished work done at SERI (now NREL) in the early 1980s indicated that the heat of pyrolysis (energy required to thermally break the macro polymer bonds) was relatively low, on the order of 230 KJ/kg. The reproducibility of the data was not very good so the accuracy of this number is questionable. Other published data report numbers as high as 1000 KJ/kg [6], which sheds some light on the relative magnitude of energy required for converting solid biomass to a liquid. For comparison, the amount of energy needed to reform methane to hydrogen is about 750 MJ/Kg. Even at the higher value these numbers imply that once the reaction vessels are brought up to temperature the amount of energy required to actually break apart the biomass is not significant. The energy needed to carry out this transformation is readily available in the co-products of pyrolysis gas and/or char.

Applying this heat to the macro-polymer components making up biomass will result in their cleaving into smaller fragments. Because of the oxygen present in these fragments, they tend to be unstable above 400°C and will continue to undergo chemical change unless they are thermally quenched. Hence, very short residence times are required in the thermal reaction zone, ideally only a few hundred milliseconds. These thermal breakdown reactions are very complex and have not been well characterized, but it is thought that many free radical-type compounds are present in the promptly formed products. We know however, that if not rapidly quenched these compounds can crack further into smaller molecular weight fragments and/or polymerize into larger fragments, both at the expense of fragments making up the desired liquid product [7,3]. The combination of these processing requirements, a short residence time, and immediate cooling of the vapors, can be thought of in terms of a "cracking severity" (combined effect of temperature and time), which generally defines the optimized operating parameters. Even though the "cracking severity" has the major impact on pyrolysis vapors, there are other factors that can

also influence the nature and yield of the pyrolysis products. For example, the amount of inert gas present in the reaction environment will determine the partial pressure of the resulting fragments and therefore affect the rate of their polymerization. It is also well known that mineral matter present in the biomass exhibits catalytic effects for both cracking and polymerization [8,9].

Because most forms of biomass are composed of lignin, cellulose, hemicellulose, and extractives; the thermal breakdown fragments from each of these will be chemically different and therefore affected differently by the cracking severity as well as any catalytic effects from mineral matter present in a given type of biomass. However, even with all the variables involved in producing bio-oil it is interesting to note that if oils are prepared from different biomass substrates and the amount of moisture in the resulting bio-oil is relatively constant then the heating value of the oil is relatively uniform at about 17 MJ/kg. If one compares this to the heating value of the starting biomass at 18 MJ/kg it is apparent that fast pyrolysis is primarily a process of changing the physical state of biomass from a solid to a liquid. However this needs to viewed from the context that approximately 25% of the starting biomass weight has been lost during the conversion process. But this only tells part of the story. Closer inspection of the resulting liquids reveals a complex yet rich mixture of compounds that may also serve chemical markets in addition to a useful form of energy.

2.2 Biomass Feedstock Preparation

To achieve the high bio-oil yields of fast pyrolysis it is also necessary to prepare the solid biomass feedstock in such a manner that it can facilitate the required heat transfer rates. There are three primary heat transfer mechanisms available to engineers in designing reaction vessels: convection, conduction, and radiation. To adequately exploit one or more of these heat transfer mechanisms as applied to biomass fast pyrolysis requirements, it is necessary to have a relatively small particle for introduction to the reaction vessel. This ensures a high surface area per unit volume of particle. Because of small linear dimensions the whole particle achieves the desired temperature in a very short residence time.

Another reason for small particles is the physical transition of biomass as it undergoes pyrolysis when char develops at the surface. Char has insulating properties that impede the transfer of heat into the center of the particle and therefore runs counter to the requirements needed for fast pyrolysis. The smaller the particle the less of an affect this has on heat transfer. Comminution (size reduction) of biomass however requires energy, and this in turn adds to the overall processing cost. As would be expected, the smaller the desired size the more expense added to the feedstock preparation costs. To put this in perspective, a study conducted by Himmel et al. [10] in 1985 showed that reducing biomass to particles in the size range of 2.5 mm to 250 micron would add $1.80/ton to $5.60/ton respectively. These operating costs were based on a 7 cents / kW-hr cost of power to drive the mill. Since feedstock cost is a primary driver in the cost of producing bio-oils, it is important to keep these feed preparation costs low. In the early days of fast pyrolysis development researchers thought that particle sizes of a few hundred microns were needed to facilitate the high heat transfer rates. However, more recent practical experience has demonstrated this is not the case, but sizes of approximately 2 mm are still necessary [4].

Moisture in the biomass is another feedstock preparation consideration. Any moisture present in the feed will simply vaporize and then re-condense with the bio-oil product. As we will discuss later in Section 4.4, the amount of moisture in the bio-oil product will impact the resulting

quality of these liquids. It should also be noted that water is formed as part of the thermochemical reactions occurring during pyrolysis. If bone-dry biomass is subjected to the thermal requirements for fast pyrolysis the resulting bio-oil will still contain 12-15 wt% water. This is thought to be a result of dehydration of carbohydrates and possibly free radical reactions occurring with the hydrogen and oxygen in the high temperature (500°C) pyrolysis environment. So water in the starting biomass will simply add to this base amount in the final bio-oil product. At 2.3 MJ/kg, the latent heat of evaporation of water is substantial and points out another important consideration with respect to drying the biomass feed prior to pyrolysis. Moisture in the feed becomes a heat sink and competes directly with the heat available for fast pyrolysis. Ideally it would be desirable to have little or no moisture in the starting biomass feed but practical considerations make this unrealistic. Commercial wood chip dryers, having reasonable throughput capacities, have lower limits of moisture that are difficult to exceed without risking volatile organic chemical (VOC) emissions and fires starting in the dryers. Additional costs are also incurred as the moisture is driven to levels approaching zero, so in practice a balance must be sought. Moisture levels of 5-10 wt% are generally considered acceptable for the pyrolysis process technologies currently in use. As with the particle size, the moisture levels in the feedstock biomass are a trade off between the cost of drying and the heating value penalty paid for leaving the moisture in.

2.3   Reactor Designs Capable of Achieving Fast Pyrolysis Conditions

During the last twenty-five years of fast pyrolysis development a number of different reactor designs have been explored that meet the heat transfer requirements noted above while also attempting to address the cost issues of size reduction and moisture content of the feed. These are described in more detail in a comprehensive survey published by Bridgewater and Paecocke [11] and fall under the following general categories:

- Fluidized bed
- Transported bed
- Circulating fluid bed
- Ablative (vortex and rotating blade)
- Rotating cone
- Vacuum

The rotating blade type of ablative reactor along with the rotating cone and vacuum pyrolysis reactors do not require an inert carrier gas for operation. When issues of product vapor collection and quality are considered, the lack of a carrier gas when conducting fast pyrolysis can be a real advantage. This is because the carrier gas tends to dilute the concentration of bio-oil fragments and enhances the formation of aerosols as the process stream is thermally quenched. This in turn makes recovery of the liquid oil more difficult. Another disadvantage is that high velocities from the carrier gas entrain fine char particles from the reactor, which then are collected with the oil as it condenses. As we will discuss in sections 2.5 and 3.2 these char fines have a deleterious effect

on the bio-oil quality. A general discussion of the advantages and disadvantages of each reactor design follows.

2.3.1 Bubbling Fluidized Bed

Bubbling fluidized bed reactors have been used in petroleum and chemical processing for over fifty years and therefore have a long operating history. As reactor designs, they are characterized as providing high heat transfer rates in conjunction with uniform bed temperatures, both being necessary attributes for fast pyrolysis. By selecting the appropriate size for the bed fluidizing media, the gas flow rate can be established such that gas/vapor residence time in the freeboard section above the bed can be set to a desired value, generally between 0.5-2.0 seconds. Experience has shown that an operating temperature of 500° -550°C in the bed will usually result in the highest liquid yields at about 0.5 sec residence time, however larger systems can operate at a somewhat lower temperature and a longer residence time. The temperatures may also vary depending on the type of biomass being processed. The largest units in operation are a 200 kg/hr unit by Union Fenosa in Spain and a 400 kg/hr unit by DynaMotive in Canada. Both were designed and constructed based on the Waterloo Fast Pyrolysis Process developed at the University of Waterloo and designed by its spin-off company Resource Transforms International in Canada.

Because of their long history of service and inherently simple operating design, this type of reactor is considered to be very reliable and virtually trouble free as a system capable of conducting fast pyrolysis of biomass. There are however, some practical constraints that must be taken into account when considering this design for larger-scale reactors. The reactor throughput depends on the amount and efficiency of heat supply. Some bubbling beds operate in an adiabatic regime with all the process heat supplied by the preheated fluidizing gas, which in many instances is recycled pyrolysis gas. This simplifies the reactor design but usually results in a smaller throughput. Better performance is obtained when the reactor sand is indirectly heated by the use of fired tubes. DynaMotive uses natural gas to heat their pilot reactor but larger-scale commercial units will need to integrate combustion of char and gas byproducts to supply the necessary heat. Direct heating using flue gases is not recommended because it can result in smaller oil yields due to oxidation from excess air in the flue gases.

In principle, the bubbling bed is "self cleaning," which means that byproduct char is carried out of the reactor with the product gases and vapors. However, in practice this requires using carefully sized feedstock with a relatively narrow particle size distribution. If biomass particles are too large the remaining char particles (after pyrolysis) may have too much mass to be effectively entrained out of the reactor with the carrier gas and product vapors. The density of this char will be less than that of the fluidizing media and, consequently, this char will "float" on top of the bed. In this location it will not experience enough turbulence with the bed media to undergo attrition into smaller particles that will eventually leave the reactor. Another issue with having the char on top of the bed is that it will have a catalytic influence on the vapors as they pass through it on their way out of the bed. This can affect the yields and the chemical nature of the resulting liquid product. On the other hand, if fines are present in the feed, then the feed must be introduced lower in the bed otherwise the fines will be quickly entrained out of the bed before complete pyrolysis can occur. In general, char accumulation in the bed should be prevented. The design should include a means for skimming and discharging char from the top of the bed. If this is not done the feed will need to be carefully screened to obtain a narrow particle size

distribution. This in turn will add considerably to the feedstock preparation costs. A schematic of a typical fluidized bed is shown below in Figure 1.
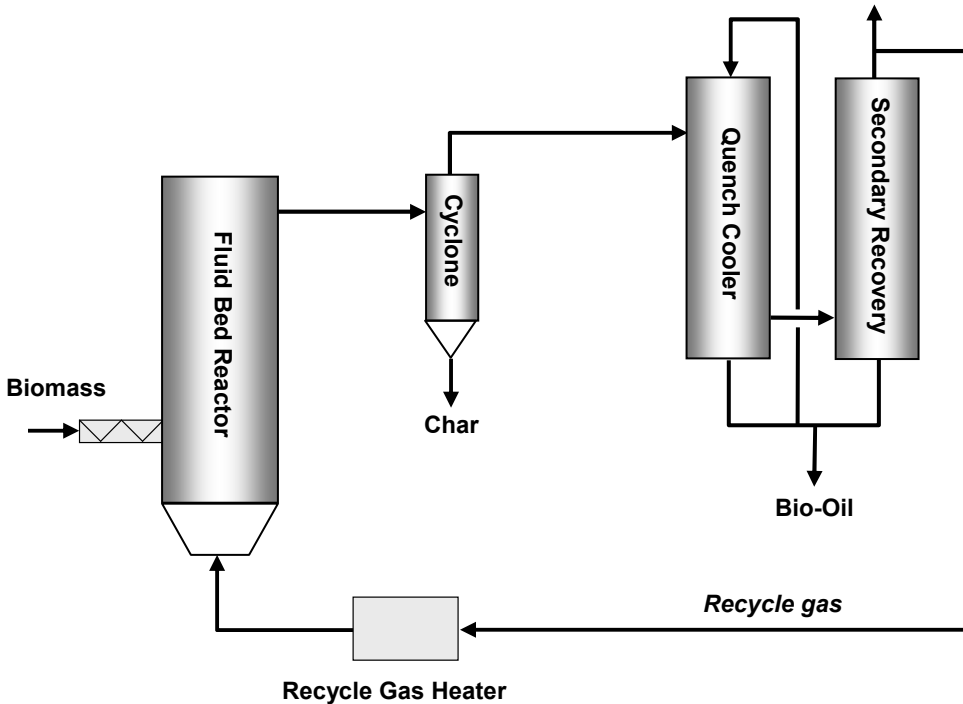
Figure 1. Process Schematic for a Bubbling Fluidized Bed Pyrolysis Design

Some design considerations in bubbling fluidized bed systems:

- Heat can be applied to the fluid bed in a number of different ways that offer flexibility for a given process.

- Vapor residence time is controlled by the carrier gas flow rate

- Biomass feed particles need to be less than 2-3 mm in size

- Char can catalyze vapor cracking reactions so it needs to be removed from the bed quickly

- Char can accumulate on top of the bed if the biomass feed is not sized properly, provisions for removing this char may be necessary

- Heat transfer to bed at large scales has not been demonstrated.

2.3.2 Circulating Fluidizing Bed

This reactor design also is characterized as having high heat transfer rates and short vapor residence times which makes it another good candidate for fast pyrolysis of biomass. It is somewhat more complicated by virtue of having to move large quantities of sand (or other fluidizing media) around and into different vessels. This type of solids transport has also been practiced for many years in refinery catalytic cracking units, so it has been demonstrated in

commercial applications. Circulating bed technology has been extensively applied to biomass pyrolysis by Ensyn Technologies under the name of Rapid Thermal Processing (RTP). Other organizations involved in developing this type of pyrolysis technology are CRES (Greece) and ENEL (Italy). Various system designs have been developed with the most important difference being in the method of supplying heat. Earlier units were based on a single indirectly heated reactor, cyclone, and standpipe configuration, where char was collected as a byproduct. Later designs incorporated a dual reactor system such as that operated by ENEL in Italy. In this design the first reactor operates in pyrolysis mode while the second one is used to burn char in the presence of the sand and then transfer the hot sand to the pyrolysis vessel. Such an option has advantages but also is more challenging because of solids transport and temperature control (overheating of sand in the combustor) in the system. Sand flow rate is also 10-20 times greater than the biomass feed rate and there is a high energy cost in moving this sand around the loop.

Feed particles sized for a circulating bed system must be even smaller than those used in bubbling beds. In this type reactor the particle will only have 0.5-1.0 seconds (s) residence time in the high heat transfer pyrolysis zone before it is entrained over to the char combustion section in contrast to the bubbling bed where the average particle residence time is 2-3 s. For relatively large particles this would not be enough time to transport heat to the interior of the particle. This is especially true as a char layer develops on the outside surface, which acts as an insulating layer preventing further penetration of heat. The movement of sand and particles through the system causes abrasion of this char layer but mostly at the elbows and bends where there is more forceful interaction between the particles and sand. The incompletely pyrolyzed larger particles will end up in the char combustor where they will simply be burned. Consequently, if larger feed particles are used, the oil yield will be reduced due to combustion of incompletely pyrolyzed particles. Particles in the 1-2 mm are the desired size range. A schematic of this type of pyrolysis system is shown below in Figure 2.
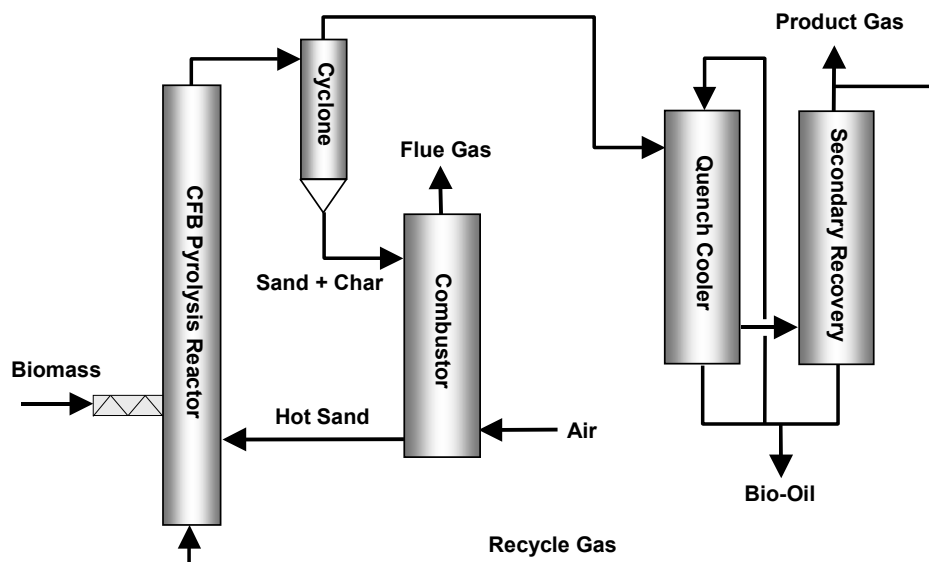
Figure 2. Process Schematic for a Circulating Fluidized Bed Pyrolysis Design

2.3.3 Ablative Pyrolysis

The vortex reactor was developed at SERI (now NREL) from 1980 until 1996 [12,13] to exploit the phenomena of ablation. In this approach the biomass particle is melted / vaporized from one plane or side of its aspect ratio. This design approach had the potential to use particle sizes up to 20 mm in contrast to the 2 mm particle size required for fluidized bed designs. Biomass particles were accelerated to very high velocities by an inert carrier gas (steam or nitrogen) and then introduced tangentially to the vortex (tubular) reactor. Under these conditions the particle was forced to slide across the inside surface of the reactor at high velocities. Centrifugal force at the high velocities applied a normal force to the particle against the reactor wall. The reactor wall temperature was maintained at 625°C, which effectively melted the particle in a fashion similar to butter melting on a hot skillet. Vapors generated at the surface were quickly swept out of the reactor by the carrier gases to result in vapor residence times of 50-100 milliseconds. So this design was also able to meet the requirements for fast pyrolysis and demonstrated yields of 65% liquids. A schematic of this design is shown in Figure 3.

In practice it was necessary to incorporate a solids recycle loop close to the exit of the reactor to re-direct larger incompletely pyrolyzed particles back to the entrance to insure complete pyrolysis of the biomass. Particles could escape the reactor only when they were small enough to become re-entrained with the vapor and gases leaving the reactor. While the solids recycle loop was able to effectively address the issue of insuring all particles would be completely pyrolyzed it also resulted in a small portion of the product vapors being recycled into the high temperature zone of the reactor. This portion of vapors effectively had a longer residence time at the pyrolysis reactor temperature and most likely resulted in cracking of the product to gases thus resulting in slightly lower yields compared to other fluidized bed designs.
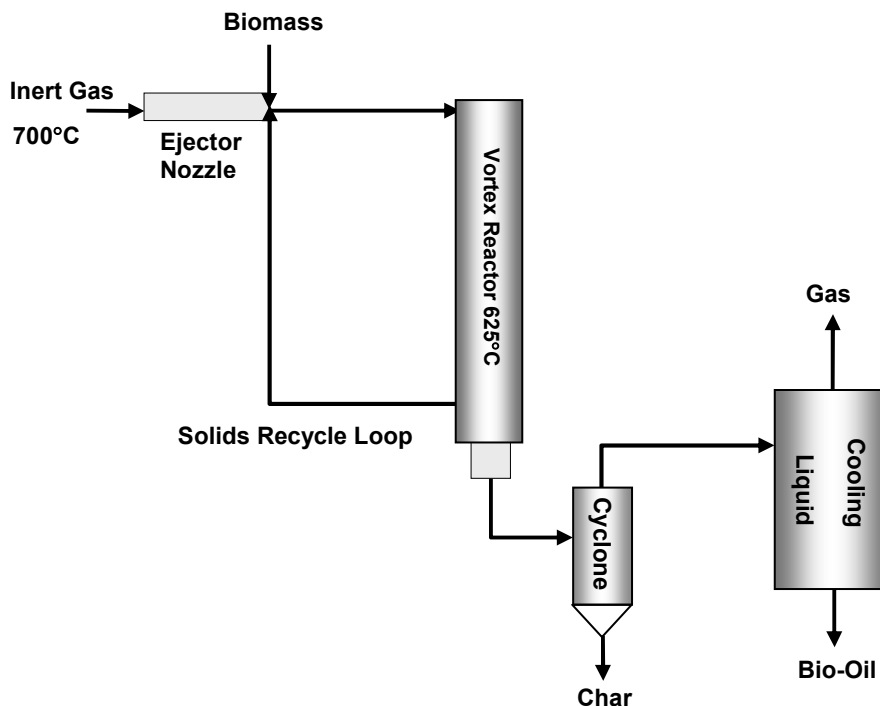
Figure 3. Schematic of the NREL Vortex Reactor Fast Pyrolysis Reactor Design

Other design issues with the vortex reactor were:

- High entering velocities of particles into the reactor caused erosion at the transition from linear to angular momentum.

- Excessive wear was also realized in the recycle loop. Both wear problems were exacerbated when inert tramp material (stones, etc.) were introduced with the feed.

- There were uncertainties about the scalability of the design related to maintaining high particle velocities throughout the length of the reactor. The high velocities are necessary for centrifugal force to maintain particle pressure against the reactor wall. The high sliding velocity and constant pressure of the particle against the 600°C reactor wall are necessary to achieve the high heat transfer requirements for fast pyrolysis.

Because of these issues the vortex reactor design concept was abandoned in 1997.

2.3.4 Vacuum Pyrolysis

Pyrovac in Québec, Canada has developed a vacuum pyrolysis process for converting biomass to liquids [14]. While this is a slow pyrolysis process (lower heat transfer rate) it generates a chemically similar liquid product because the shorter vapor residence time reduces secondary reactions. However, the slow heating rates also result in lower bio-oil yields of 30-45 wt% compared to the 70 wt% reported with the fluid bed technologies. The process itself is very complicated mechanically, involving a moving metal belt that carries the biomass into the high temperature vacuum chamber. There are also mechanical agitators that periodically stir the biomass on the belt; all of this mechanical transport is being done at 500°C. These design features are expected to have high investment and maintenance costs. Operating at a vacuum requires special solids feeding and discharging devices to maintain a good seal at all times. Heating efficiency is low and, in this particular design, unnecessarily complex in the use of a burner and an induction heater with molten salts as a heat carrier. Even with these drawbacks vacuum pyrolysis does have several advantages:

- It produces a clean oil (no or very little char) without using hot vapor filtration (this technique is discussed later in section 2.5).

- Liquid product condensation is easier than for fluidized bed or entrained flow technologies (higher vapor concentration, less, if any, aerosol formation).

- It can use larger feed particles than fluidized bed processes; up to 2-5 cm.

- The lignin-derived fraction of the oil can be of a lower molecular weight than that from fast pyrolysis processes, which may have advantages if extracting this component for phenolic type chemicals.

- Eliminates the requirement to sweep vapors out of the reaction vessel by a carrier gas through vacuum assistance. The lack of a carrier gas appears to be a key factor in minimizing aerosol formation.

However, vacuum pyrolysis technology also has serious drawbacks for producing liquids, especially for fuel applications because of the high yields required:

- It is a slow pyrolysis process that will not be able to provide oil yields as high as fast heating rate processes (vacuum pyrolysis has demonstrated yields of 47% organics and 17% water from spruce, 35% organics and 20% water from bark).

- It generates more water than other fast pyrolysis processes. In the Pyrovac plant the condensates are collected as two fractions, the second one being heterogeneous. Based on the published yields, after mixing these fractions the whole bark oil will contain 36% water and the wood oil 28% water, which can both result in phase separation.

- It generates liquid effluents as volatile material that is not collected in the scrubbers but absorbed in the liquid ring compressor pump. These would need to be recycled back to the scrubbers.

This process was successfully scaled up to 3000 kg/hr in 2000 but lack of markets for the bio-oil generated from this unit made continued operation untenable and operations were discontinued in 2002.

2.3.5 Rotating Cone Pyrolysis Reactor

The Rotating Cone Pyrolysis Reactor has been under development at the University of Twente in The Netherlands since the early 1990s. Recent activities have involved scale up of the system to 200 kg/hr [15]. This technology is analogous to the transported bed design (circulated fluidized bed) in that it co-mingles hot sand with the biomass feed to affect the thermal pyrolysis reactions. The primary distinction is that centrifugal force resulting from a rotary cone is used for this transport instead of a carrier gas. The biomass feed and sand are introduced at the base of the cone while spinning causes centrifugal force to move the solids upward to the lip of the cone. As the solids spill over the lip of the cone, pyrolysis vapors are directed to a condenser. The char and sand are sent to a combustor where the sand gets re-heated before introducing at the base of the cone with the fresh biomass feed. This design has demonstrated yields of 70% on a consistent basis. Advantages of this design are:

- It does not require a carrier gas for pyrolysis (but it does for sand transport) which makes bio-oil product recovery easier

- The transport dynamics of the sand and biomass are not as aggressive as in the Ensyn Rapid Thermal Processing (RTP) circulating fluid bed process therefore reducing wear problems

Some disadvantages for this process design are:

- The integrated process is complex, involving a rotating cone, a bubbling bed for char combustion, and pneumatic transport of sand back to the reactor

- Scale up issues are uncertain

2.4 Pyrolysis Vapor (Bio-oil) Recovery

Once the pyrolysis vapors are generated in the reaction vessel it is a critical processing requirement that they be thermally quenched from the high reaction temperatures. This is important to preserve the compounds that comprise the bio-oil; otherwise many of these compounds will further crack to permanent gases or polymerize to char.

Upon cooling, the pyrolysis vapors have a tendency to form aerosols, which are submicron droplets. This phenomenon is enhanced if large amounts of carrier gas are present with the oil vapors when condensation occurs. Because of their size these droplets are very difficult to separate from the permanent gas stream. A number of techniques have been used over the years with the most effective probably being liquid spray scrubbing. Simple column scrubbers and venturi scrubbers have both been used successfully. The key to these devices is generating spray droplets that are very small so they can effectively collide with the bio-oil aerosol droplets. Venturi scrubbers can also be effective but a high-pressure drop (>10 kPa) penalty must be paid, and this pressure loss may not be available from the process. Electrostatic precipitators have also been used successfully [16] for capturing pyrolysis aerosols but they can be tricky to operate and are more expensive than simple scrubbers.

Devices such as mist eliminators and coalescing filters are very effective in removing liquid mists and aerosols from gas streams but they are not practical for the pyrolysis processes described above because particulates are present along with the aerosol. The particulates will rapidly plug the small openings in these devices.

Staged condensation with a series of shell and tube heat exchangers has also been used but this was only about 90% efficient in capturing bio-oil aerosols. While not quite as efficient in capturing aerosols as the spray scrubber, the staged system [14] had the advantage of collecting the liquids as fractions or "thermal cuts". This may have some advantages if one is seeking to extract certain compounds from the whole oil such as in a bio-refinery application.

2.5   Char and Particulate Separation

Char is one of the co-products produced during the conversion of biomass to bio-oil. Because of the relatively low reaction temperatures (500º-600ºC) employed during pyrolysis, all of the mineral matter in the starting biomass ends up being sequestered in the char. This phenomenon has some benefits in offering techniques to effectively manage the minerals in biomass but can also impact the quality of the resulting bio-oil. Work done at NREL in the mid 1990s [17] showed that char played a major role in the long-term stability of bio-oils. This role will be discussed in more detail in the section on Properties of Bio-oil, but for now the discussion will focus on char and particulate removal techniques applied during the pyrolysis processing steps.

Ideally it would be desirable to separate the char while it is in the vapor stream before the vapor is cooled and condensed to a liquid. All of the processes described above attempt to do this by using cyclone separators at the exit of the high temperature reaction vessel. Proper design of cyclones specifies the required entering velocities, vortex finder length & diameter, cone angle, etc. for a given particle loading in the gas stream. When designed properly for optimum separation efficiency, the pressure drop across the cyclone needs to be at least 1.5 kPa. The limitation on cyclones, however, has to do with the particle size (or actually particle mass). They are not very effective on particles below 2-3 microns and all pyrolysis processes generate char particles under this size. The exception to this would be the vacuum pyrolysis system developed by PyroVac. Since this process does not involve carrier gas and sand attrition of the char, there is little to no entrainment of char with the vapor stream in this design. Instead the char is mechanically transported out of the reaction vessel. So in practice, almost all pyrolysis processes produce bio-oils that contain a certain level of char fines.

In the early 1990s NREL began a research effort to use hot gas filtration in lieu of cyclones in an attempt to remove essentially all of the char before condensing the pyrolysis vapors to liquids [18]. The approach was to use conventional baghouse type filters that were modified for biomass pyrolysis operation. These modifications involved reducing the volume and therefore the residence time that the vapors would spend in the high-temperature bag-house filter. The objective was to minimize cracking of the vapors to gases during filtration of char fines and therefore maximize bio-oil yields. The baghouse operating temperature was reduced to as low as 390°C to also minimize cracking of product vapors. This temperature is approximately where many of the compounds present in bio-oil will begin to condense so this was effectively the lower limit for hot vapor filtration. Although it was possible to remove almost all of the char with this technique it was fraught with difficulties. The char cake became very difficult to remove from the filter elements after a relatively short period of operation. There was also evidence of chemical reactions as indicated by a measured temperature rise across the filter elements. Both cracking and polymerization reactions among the various compounds in bio-oil are likely to have occurred as the pyrolysis vapors passed through the char cake on the filter elements [19]. It is suspected that polymerization reactions were responsible for bonding char particles together in the cake, making it difficult to remove from the filter elements. These reactions undoubtedly contributed to oil yield losses of 10%-15% observed when doing hot gas filtration. However, this loss should be weighed against a dramatic improvement in the quality of the resultant oil. This is especially true with respect to long term stability, which will be discussed in the next section on bio-oil properties.

3. Properties of Bio-oil

The properties of bio-oil can encompass a broad range of parameters because of the complex nature of this material. Even if one is able to perfectly reproduce all of the processing conditions necessary to produce bio-oil, the biomass feed, itself, can influence the nature of the final product. Not only are there differences between types of biomass species but also where a particular species is grown can affect things such as the composition of mineral matter present. Given this non-uniformity in the starting material and the high temperature reactive environment to which the prompt biomass vapor fragments are exposed during pyrolysis, it is not unusual to see variations in many of the physio-chemical properties of bio-oil. For some applications, the small variations will be of little consequence, but in situations where it is desirable to use bio-oil in devices that have been designed to operate on hydrocarbon fuels, some of these properties will make operation difficult or simply not feasible.

3.1 Chemical Nature of Bio-oil

Based on the Ultimate Analysis, the chemical formula for wood can be represented by $CH_{1.4}O_{0.6.}$ What this formula implies is that on a weight basis wood is composed of almost 42% oxygen. When biomass under goes pyrolysis, bonds are cleaved to produce fragments of the original macro polymers: cellulose, hemicellulose, and lignin. During this process most of the original oxygen is retained in the fragments that collectively comprise bio-oil. Research reports that bio-oil contains 45-50 wt% oxygen [20], but this is thought to be related to water content. Proximate analysis of bio-oil gives a chemical formula of $CH_{1.9}O_{0.7}$ which represents about 46% oxygen. The oxygen difference between the original biomass and the bio-oil is related to how the oxygen is coupled to compounds in the permanent gases and the amount tied up as water in the oil. The oxygen in bio-oil is embodied in most of the more than 300 compounds that have been identified [21] in bio-oil. Given the limitations of analytical techniques used to identify and quantify many of the higher molecular weight species, it is probably safe to assume there are many more compounds than those already identified.

We can classify these compounds into five broad categories [22]: hydroxyaldehydes, hydroxyketones, sugars, carboxylic acids, and phenolics. The phenolic compounds are present as oligimers having molecular weights ranging from 900 to 2500 [23]. These phenolics are primarily derived from the lignin component of biomass. A more detailed classification of compounds can be found [24, 25] that classifies compounds under the following categories: acids, alcohols, aldehydes, esters, ketones, phenols, guaiacols, syringols, sugars, furans, alkenes, aromatics, nitrogen compounds, and misc. oxygenates. While there is a rich mixture of known compounds in bio-oil, the vast majority are found in low concentrations. The highest concentration of any single chemical compound (after water) is hydroxyacetaldehyde at levels up to 10 wt%. This is followed by acetic and formic acids, at about 5 wt% and 3 wt%, respectively. This is the primary reason why bio-oils exhibit a pH in the range of 2.0-3.0.

Table 2 lists the chemical properties of bio-oils produced from three different types of biomass: birch, pine, and poplar [26]. The birch and pine were produced at VTT in Finland using a circulating fluidized bed reactor while the poplar was produced in a vortex reactor at NREL. The column labeled "various" is a compilation of over 150 bio-oil samples produced from a variety of feedstocks by different organizations, so a range is given here. We should point out that the wide range of some of these properties is tied to certain processing methods employed by the

particular organization producing the oils. For example some producers may not have used bone dry feed as a starting material and the additional moisture ends up in the oil. This is clearly seen in the range of moisture contents for the various samples whereas the samples produced at VTT and NREL both used bone-dry feed. It is interesting to note that bio-oils from birch and poplar, both hardwoods, have identical moisture contents even though they were made in different laboratories with different reactor designs. Both reactor designs however employ similar heating rates and residence times. A similar issue applies for the mineral matter, which is a function of the amount of char permitted to carry over to the condensation system where the oils are recovered. The hot gas filtered oils produced at NREL clearly show the link between char content and minerals. In other production runs using the same poplar feedstock but employing cyclone separators instead of a baghouse filter, alkali metal levels of up to 300 ppm were measured.

Table 2. Properties of Bio-oil from Various Feedstocks

Property	Birch	Pine	Poplar	Various
Solids (wt%)	0.06	0.03	0.045	0.01-1
PH	2.5	2.4	2.8	2.0-3.7
Water (wt%)	18.9	17.0	16.8	15-30
Density (kg/m^3)	1.25	1.24	1.20	1.2-1.3
Viscosity, cSt @ 50°C	28	28	13.5	13-80
LHV (MJ/kg)	16.5	17.2	17.3	13-18
Ash (wt%)	0.004	0.03	0.007	0.004-0.3
CCR (wt%)	20	16	N/M	14-23
C (wt%)	44.0	45.7	48.1	32-49
H (wt%)	6.9	7.0	5.3	6.9-8.6
N (wt%)	<0.1	<0.1	0.14	0.0-0.2
S (wt%)	0.00	0.02	0.04	0.0-0.05
O (wt%)	49.0	47.0	46.1	44-60
Na + K (ppm)	29	22	2	5-500
Ca (ppm)	50	23	1	4-600
Mg (ppm)	12	5	0.7	N/M
Flash Point (°C)	62	95	64	50-100
Pour Point (°C)	-24	-19	N/M	-36 -9

It is also possible to manipulate the chemistry of bio-oils by changing the thermal conditions in which they are produced or carrying out the pyrolysis in the presence of catalysts (see section 4.5). Increasing the cracking severity (time/temperature relationship) is known to alter the chemical profile of the resulting oils. Elliot [26] described the relationship between compound classes and the temperature to which the vapors were exposed to before quenching. That relationship is described in the example shown below.

Mixed		Phenolic		Alkyl		Heterocyclic		Polycyclic Aromatic HC		Larger
Oxygenates	→	Ethers	→	Phenolics	→	Ethers	→	PAH	→	PAH
400° C		500° C		600° C		700° C		800° C		900° C
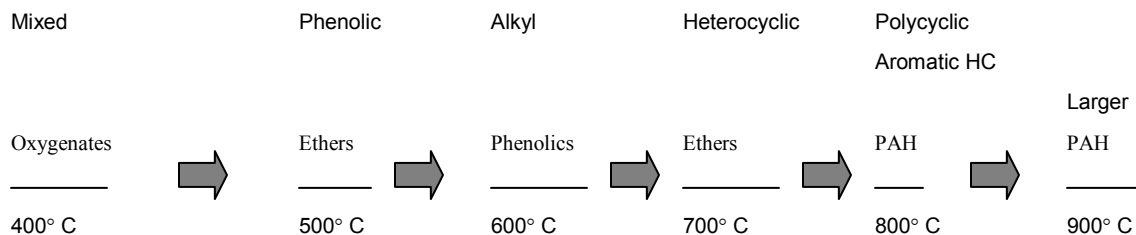
This relationship is also shown below in a series of molecular beam scans taken at different temperatures when using a common Pine biomass sample. As the temperature is increased, alkyl groups are split off aromatic compounds until eventually the aromatics condense into polycyclic aromatic hydrocarbons at the higher temperatures. Even though the desired high yields are realized at the lowest cracking severities, this thermal chemistry shows the potential for altering the chemical nature of bio-oils by shifting the temperature.
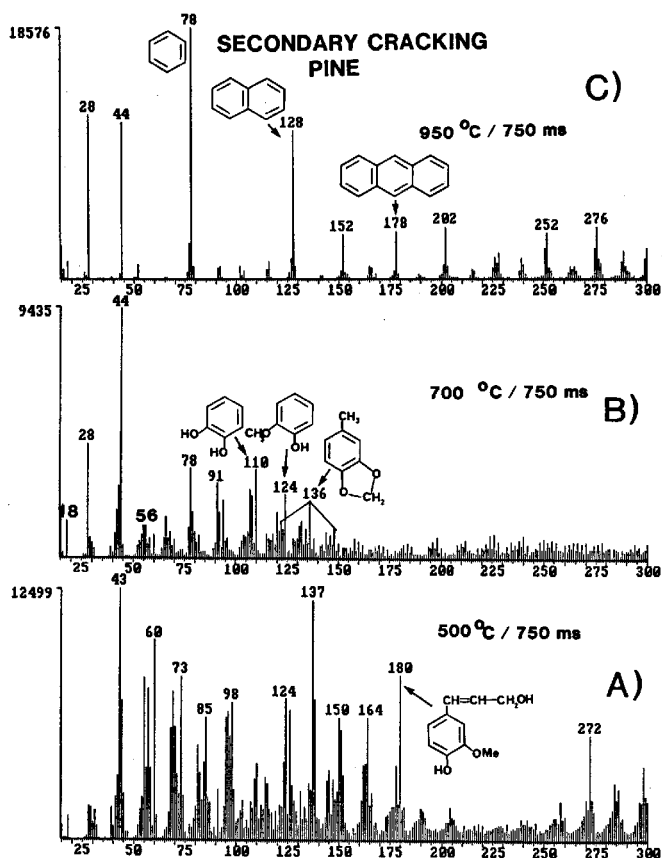
Figure 4. Molecular Beam Mass Spectrometer Scans of Pyrolysis Product Profile at Different Temperatures Using the Same Pine Wood Sample

Given the complex nature and number of different compounds making up bio-oil, it is not unreasonable to expect that one could effect some separation of compounds by exploiting the temperature profile on the quenching or condensation end of the process. Another approach to selectively producing specific compound classes was demonstrated by Pakdel et al. [27] by what

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they called "fractional pyrolysis." This involved ramping up the pyrolysis temperature in stages and collecting the products before ramping to the next temperature. In this manner they were able to almost double the amount of phenolic compounds produced compared to a conventional approach of simply ramping straight up to the final pyrolysis temperature. Again this demonstrates the potential of manipulating the product slate by creative application of the heating profile.

3.2 Physical Properties of Bio-oil (Stability)

One of the primary attributes of converting solid biomass to a liquid bio-oil is the ability to store bio-oil until needed for immediate energy use. In the early development stages of this technology the long-term storability of bio-oils was plagued by major problems; the principal one being a slow gradual increase in the viscosity of the freshly produced oils. This phenomenon also occurs with petroleum derived fuels but at a much slower rate. To put this in perspective, hydrocarbon fuels can be stored for periods of up to six months while bio-oils appear to have a shelf life of weeks or at most a few months depending on properties of the oil. However, recent studies (described below) have demonstrated that this shelf life can be greatly extended. Another significant issue observed in bio-oils was phase changes that appeared to coincide with the increase in viscosity. These can result in heavy molecular weight tars, sludges, waxes, and water as multiple phases in what originally started as a single-phase product. Since combustion burners, injector nozzles, and other end use devices are designed to operate with liquids that have consistent properties this became a major technical challenge to overcome to gain acceptance by end users of these oils.

Considerable effort was expended in the early 1990s and continues today to understand the mechanisms of this undesirable phenomenon. Much of the pioneering effort was done at NREL where both fundamental mechanisms were explored; and controlled studies were conducted to measure the rates of changing viscosity as a function of temperature. At the same time, work was being done to develop methods of removing char from pyrolysis vapors prior to condensing the vapors to liquid bio-oil. These efforts coincided to provide a considerable base of knowledge about bio-oil stability and revealed methods to address the problem.

The production of bio-oils from fast pyrolysis is a thermodynamically non-equilibrium process. The short residence times in the high temperature zone of the process followed by rapid thermal quenching results in a liquid product that is also not at equilibrium. The many oxygenated compounds present in bio-oil then attempt to achieve equilibrium during storage resulting in additional chemical reactions. These reactions cause increases in the average molecular weight and consequently increase the viscosity of the oil. As with most chemical reactions temperature increases the rate at which these reactions occur. The co-solubility of many of the compounds is also impacted by these reactions, which also adversely affect the viscosity. With the "soup" of various chemical compounds present in bio-oil and the low pH it is not surprising that chemical reactions occur within the bio-oil.

A major finding however was the influence of char on these reactions. Agblevor et al. [28,29] clearly showed that char fines present in the bio-oil had a major impact on the rate at which viscosity increased in these oils. In one experiment a freshly produced sample of pyrolysis oil was spiked with 5 wt% of char produced from the same biomass feed. Dramatic increases in the

viscosity of this oil sample were observed in a few days time and within a month the sample was solidified. Additional studies [30] identified the reason for this interaction of char on the rate of viscosity increase. X-Ray Photoelectron Spectroscopy (XPS) analysis of char particles revealed that the mineral matter sequestered in the char was randomly distributed within the char particle but a substantial amount was also exposed at the surface. The mineral matter is primarily composed of alkali (Na and K) and alkali earth (Ca and Mg) metals. The alkali metal potassium is a known catalyst for influencing char forming reactions during the pyrolysis step [31]. Not only is the alkali metal present on the surface of the char particles but the particles themselves are very small. Agblevor et al. [30] showed that over 90% of the char particles in bio-oils that used a cyclone for separation were less than 1 micron in size. This small size distribution implies a large surface area available for alkali exposure to the many compounds present in the oils.

Also during the 1990s, other researchers at NREL were developing hot vapor techniques to filter biomass pyrolysis vapors prior to cooling and condensation [19]. This work resulted in producing bio-oils that had very low levels of char and consequently alkali metal content, on the order of only a few ppm total alkalis. This char-free oil displayed remarkable stability characteristics compared to other bio-oils produced with the same feedstock but employing cyclone separators for the char removal. Indeed, samples of this hot vapor filtered oil were still fluid in 2003 after storage at ambient temperature in closed containers for seven years. This corroborates the work of Agblevor et al linking char (alkali) as the catalyzing agent for promoting the molecular building reactions tied to viscosity increases in these oils.

In 1997 Diebold and Czernik [32] investigated the addition of various solvents (including water) to bio-oils in an attempt to chemically interrupt molecular building reactions suspected of occurring between known compounds in bio-oil. Acetalization and esterification reactions induced by alcohol addition in the presence of mineral acids has been reported in the literature by Radlein et al. [33] to support this idea. The Diebold and Czernik work investigated various addition levels of methanol, ethanol, ethyl acetate, MiBK, acetone, and combinations of these. The findings were very promising, showing a strong effect in slowing the rate of aging of bio-oils both at ambient and elevated temperature. The study also indicated that adding the solvent when the oils were freshly produced had a more favorable impact than when added to older aged samples. Methanol showed the greatest benefit when added at 10 wt% levels; reducing the aging rate by a factor of 17! Fortuitously it was also the least expensive of all the solvents investigated. Adding a solvent also improves the quality of bio-oil by reducing its viscosity and increasing the heating value. For more detail on the issue of bio-oil stability the reader is referred to Diebold [34] who prepared a comprehensive report on this topic in January 2000.

Based on these two studies it appears there are demonstrated methods to stabilize biomass pyrolysis oils. Although filtration to remove the char before oil recovery was demonstrated, it also revealed difficulties with the technique that precluded the use of conventional filtration equipment. It also resulted in a yield loss penalty of about 10 wt%.

3.3   Physical Properties (Re-vaporization)

Another property of bio-oils that is closely tied to the complex chemical composition is the inability to revaporize the oils from a liquid state. Unlike hydrocarbon fuels that can be heated to develop a distillation curve, the complex and oxygenated nature of the compounds in bio-oil prevent this. As bio-oils are heated to increasingly higher temperatures the volatiles are first driven off, followed by water and soon the remaining compounds begin to polymerize. The result

is that 40%-60% of the original starting material will remain as a solid. This property of the oil will cause potential difficulties in fuel processing devices that require pre-heating of the fuel. In a closed system, such as a diesel injector loop, the volatiles and water will be preserved which can minimize this problem but as noted above, any residual char in the oil will exacerbate the problem. Little research effort has been devoted to solving this problem of re-volatilizing bio-oil liquids.

3.4   Environmental / Health

Given the large number of compounds in bio-oil, it obviously raises concerns about the human health and environmental effects of this material. As reported earlier in this document, more than 300 specific compounds have been identified in biomass pyrolysis oil and some of those compounds are known carcinogens such as benzene and phenanthrene. In addition there are many compounds in bio-oil that have not been identified and their toxicity or health effects are not known by the research community developing biomass fast pyrolysis technologies. Because this is an important issue to the eventual commercialization of this technology, researchers began to investigate the health effects of bio-oil in the mid 1980s. Elliot [26] used the Ames test to look at the mutagenic activity of bio-oil as a function of the thermal severity of the process used to generate the oils. With the low temperature "primary" oils, produced in the range of 500° - 600°C no mutagenic activity was observed. However, when the bacteria were exposed to oils produced at the highest severity a marked increase in mutagenicity occurred. When other investigators conducted similar studies with samples of bio-oil produced using different biomass feedstocks and different processes, they saw mixed results. Scott [35] exposed two different strains of bacteria to two separate bio-oil samples and also saw mixed results. One strain showed mutagenicity and the other did not. In a later series of Ames tests [36] with two separate bio-oil samples produced at NREL using a hardwood and a softwood; both samples displayed mutagenic activity but only slightly when compared to a benzo(a)pyrene standard. These results were considered to be inconclusive.

Elliot conducted additional studies with mammals using a subset of the same bio-oil samples used for the Ames test. Diluted samples of oil were applied to the skin of mice genetically bred to be susceptible to cancer. The low severity "primary" oil showed no statistically significant difference compared to controls that were only painted with the dilutent acetone. However, exposure to the higher severity oils definitely showed a positive carcinogenic response. The two oils from the Waterloo process used for the Ames test were also tested with ovary cell cultures from Chinese hamsters for chromosome damage. Over narrow ranges of dilution, both of these samples exhibited damage to the cells [35].

While some of these tests were inconclusive others showed a clear potential carcinogenic effect. The oils produced at a lower cracking or thermal severity appear to be relatively benign but as the severity goes up the cancer promoting activity also increases. If one refers to Figure 4, this is consistent with the experience seen in the coal tar industry where exposure to polycyclic aromatic hydrocarbons (PAH) was correlated with high incidence of cancer. These same PAHs can be made with biomass under severe cracking conditions. Fortunately the production of high yields of bio-oil requires process operating conditions based on the lowest cracking severity.

When investigating the health aspects of fast pyrolysis processes, the focus was entirely on the liquid product because some of the identified compounds are known carcinogens. The char from many of the processes used for fast pyrolysis can be attrited to very small sizes and some portion is likely to be in the PM 10 and PM 2.5 size range. This refers to particles in the 10 and 2.5 micron size range that pose unique respiratory hazards. Given that these particles are co-entrained with the organic vapors it is realistic to expect that some compounds become adsorbed on the surface. To protect workers in an emerging pyrolysis industry, and comply with OSHA reporting requirements, it would be prudent to include health and safety assessment of the char in any future toxicology studies.

The low pH of bio-oils is also a potential environmental and safety issue. In the studies reported in the literature there was no reference to investigations of damaging effects of physical contact with acidic bio-oil. In studies where mammals were dosed by application of oil to the skin the primary objective was to evaluate the cancer promoting potential of these liquids. With a pH of 2.0-2.5 the oil is likely to have damaging effects to the eyes but this has not been conclusively established by controlled studies.

Work done by Piskorz and Radlein [37] used respirometry techniques to show that bio-oil readily biodegrades in soils at rates significantly higher than hydrocarbon fuels. This was also true for biodegradation in water but neutralizing the oil first enhanced this process. Neutralizing the bio-oil was not necessary to see the biodegradability in soil. The low pH of these oils, however, would obviously have detrimental effects on aquaculture in the event of a large spill in a river, lake, or stream. Given how often one hears of hydrocarbon fuel tanker truck spills in rivers and streams next to roadways, it would be inevitable for this to happen with bio-oils as well.

Another environmental / health issues relates to the design and operation of the pyrolysis plant or biorefinery producing the bio-oils. Fugitive emissions from the collection, transfer, and further processing would need to be carefully controlled. Fugitive emissions from drying the biomass feed also need to be carefully controlled. Because of the large number of compounds present it is possible that some operating personnel may develop chemical sensitivities to vapors or liquids they are exposed to. Modern process design usually takes this into consideration but critical HAZOPs analysis should be applied to key processing steps where the potential exists.

4. Uses for Bio-oil

Bio-oil has the potential for multiple applications. These can range from a variety of combined heat and power options to the extraction of selected chemicals. Use as a substitute for hydrocarbon fuels in conventional prime movers to produce electricity or generate steam has been demonstrated but has not been commercially adopted. This is primarily due to lower cost for petroleum-based fuels compared to bio-oils. However, in some applications with more sophisticated prime movers such as internal combustion engines and aeroderivitive turbines, quality issues with the oil must still be addressed. Upgrading of bio-oils to higher value transportation fuels requires de-oxygenation and reforming of most of the compounds present in the bio-oil. Because of the large amount of oxygen present there will be a loss in mass (or volume) yield but this will be balanced against higher heating values. Overviews of these applications are provided below.

4.1 Combustion

Sandia National Laboratory [37,38] conducted fundamental single droplet combustion studies of bio-oils produced at NREL, including hot gas filtered oil. Despite the major differences between petroleum fuels compared to bio-oil, the burnout time for bio-oil was comparable to #2 fuel oil. The bio-oil however demonstrated a sequential burnout ending with formation and subsequent burnout of cenosphere particles. This property may present problems with soot formation during combustion. Also unique to the bio-oil was micro-explosion of the droplet as it transitioned through the combustion sequence. The phenomenon of the micro-explosion was also observed to be different depending on the cracking severity in which the oil was produced. It is not known if this droplet micro-explosion will cause combustion problems in large burner applications or impact the resulting combustion products. Full-scale combustion tests on bio-oil conducted in flame tunnels at MIT [39] and CANMET [40] did not show fundamental differences in combustion behavior compared to #2 fuel oil. However, the NOx, CO, and particulate emissions from bio-oil were higher. Other studies in Europe [41,42] have reported similar findings with a clear correlation of the emissions to the quality of the bio-oil, in particular the residual char fines content.

4.2 Diesel Engines

Medium and slow speed diesel engines are known for their ability to run on low quality fuels, even such fuels as coal slurries. In the early 1990s researchers began investigating the use of bio-oils in these engines. Solantausta [43] conducted pioneering work in this area using a high-speed single cylinder engine with a compression ratio of 15:1. It was very difficult to get the bio-oil to auto-ignite without substantial amounts of nitrated ignition additives. In addition, carbon deposits formed at the injectors causing plugging problems. Additional studies conducted on larger scale medium speed engines, equipped with pilot fuel capabilities, showed more promise [44]. While auto-ignition was not a problem it was difficult to maintain proper adjustment on the injectors, and excessive wear and corrosion were seen in the injector loop. Much of this was attributed to the acidity and particulate matter in the oil. Additional testing was done at the University of Kansas and MIT using the very clean hot gas filtered oil produced at NREL. When Suppes [45] at the University of Kansas blended methanol and a cetane enhancer with these clean oils they exhibited performance characteristics similar to conventional diesel fuel. If high

compression ratios are employed, the solvent blended oils would even perform well in high-speed engines. At MIT, Shihadeh [46] showed that the clean oils had much better combustion characteristics (shorter ignition delay, faster burn out, and less coking) than non-filtered oil. He also demonstrated that these clean oils would auto-ignite if the combustion air were preheated to 55°C. More recently [47], testing of emulsions of diesel fuel and bio-oil at 50:50 blends were successfully demonstrated as an alternative way to get around the auto ignition problem.

With only minor modifications to the engines, these early results indicate that bio-oils have the potential to replace conventional diesel fuel in low to moderate speed stationary diesel engines. The difficulties encountered with wear and corrosion appears to be solvable with proper selection of materials for key components and improved particulate removal from the oil.

4.3   Combustion Turbines

Combustion turbines are a well-established technology that offers the potential of producing power (and heat) at relatively high efficiencies. They are primarily fueled on petroleum distillates or natural gas but if properly designed, in conjunction with appropriate fuel specifications, they should be able to operate on any fuel including bio-oil. Of critical importance in these devices is particulates and alkali metal content in the fuel. This is especially important if sulfur is also present due to alkali sulfate formation during the combustion process. Alkali sulfates will stick to and aggressively corrode the turbine blades. Fortunately, biomass is very low in sulfur but it does contain alkali (K and Na) and alkali earth (Ca and Mg) metals that are sequestered in the char during pyrolysis. A small portion of this char is typically entrained with pyrolysis vapors and captured with the bio-oil product. Consequently one of the key issues to using bio-oils in combustion turbines is the effective removal of char from the oil. The acidic nature, low heating value, and higher viscosity properties of bio-oil can be addressed by appropriate design and material selection in the turbine.

Since 1995, Orenda Aerospace Corp. (Canada) has been investigating the use of bio-oils in a combustion turbine application. They have selected a turbine designed by Mashproekt in the Ukraine because of its robust design for low quality fuels. It also employs advanced coating in the entire hot section of the turbine to protect against alkali contaminants. Andrews et al [48] tested this 2.5 MW turbine on bio-oil fuel (after starting on diesel) and ran it through its full operating range from idle to full power without any difficulties. Measured emissions on bio-oil were lower for NOx, SOx, and HC but higher for particulates. The higher particulates may have been due to higher levels of char in the bio-oil but this property was not measured. Orenda has recently started to market this turbine for bio-oil applications, which implies they feel confident about the performance of the Mashproekt turbine operating on bio-oil fuel.

Strenziok et al. [49], at the University of Rostock in Germany, tested a smaller commercial 75 kW turbine on bio-oils. In this demonstration the combustion chamber was modified to enable dual fuel operation with diesel and bio-oil. Under dual fuel operation they were able to achieve 73% of the full output power that would have been obtained from diesel alone. The ratio of fuel blend was 40% bio-oil and 60 % diesel. When compared to straight diesel operation the CO and HC emissions were higher while the NOx was lower.

As with diesel engine applications, these early results show that it is indeed possible to operate turbines on bio-oil fuels. These results were achieved with only minor modifications of existing

equipment and little effort was expended in tailoring the oil properties specifically for turbine operation.

4.4   Bio-Oil Standards and Specifications

The petroleum and automobile industries have a long history of working together in a symbiotic relationship to develop the fuels and engines that work in concert to provide reliable, efficient, and clean service. As with many engineering designs there are compromises that must be made because of conflicting performance objectives. For example internal combustion engines can be designed to be more efficient than they currently are by increasing the compression ratio of the engine. This in turn requires the petroleum industry to produce fuels with higher octane levels. Chemical engineers learned that a relatively easy and inexpensive way to do this is by adding tetra-ethyl lead. Environmental engineers however recognized the pervasive increases of lead in the environment, along with the long-term health costs tied to its continued use. After restricting this method of octane enhancement, the petroleum industry was forced to develop other ways to increase octane levels in motor fuels. The alternate approaches are not as effective as tetra-ethyl lead so the internal combustion engine designer also had to compromise on the upper limits of compression ratio. Cost of course also plays a major role in these design considerations. This is a good example of the importance of developing good technical relationships between the fuel producer and the end user of that fuel.

The situation with the auto / petroleum industry can also be applied to the emerging bio-oil industry. The examples noted above with pioneering efforts to utilize bio-oil in various prime movers, and even relatively simple combustion burners, demonstrates the need for standardization of bio-oil properties. If there was a uniform set of standard specifications for bio-oil, designers of the various end use devices could select the appropriate materials and make the necessary design changes to achieve much better performance than what has already been demonstrated. Commercial acceptance of biomass pyrolysis technology will demand that these specifications be established. Unfortunately there has been little progress in this area over the years.

To a large extent the petroleum industry has laid the foundation for what a set of standards and specifications should be based on. Because there are also quality variations in petroleum hydrocarbons, the industry has established separate specifications for a number of different grades of hydrocarbon fuels. The higher grades of course command a premium price and a similar situation would be expected with bio-oil grades. The specifications for petroleum fuels are established by an independent organization such as ASTM in the United States and similar organizations in other countries. These organizations also get involved in developing/establishing the methods and protocols used for quantifying the specification property. The specifications are usually based on the end use requirements of the consumer for the given fuel and typically are concerned with such things as the ability to properly atomize, flash points or ignition temperatures, energy content (LHV), and qualities that have environmental impacts such as sulfur content.

In 1996 the Pyrolysis Activity of the International Energy Agreement under Task XIII proposed a series of specifications for bio-oil [51] that were modeled after the ASTM specifications for hydrocarbon fuels. The proposed specifications attempted to mimic as much as possible the key

properties established for petroleum fuels that have major design considerations for end use devices. This was intentionally done to require the least effort on the part of the manufacturer of end use equipment to accommodate bio-oil fuels. The proposed specifications from this document are listed in Table 3.

Table 3. Proposed Specifications for Various Grades of Bio-oil [51]

Property	Light Bio-oil (~ASTM #2)	Light-Medium Bio-oil (~ASTM #4)	Medium Bio-oil (~PORL 100)	Heavy Bio-oil (~CAN #6)
Viscosity, cSt	1.9-3.4 FO 1.9-4.1 D 1.9-4.1 GT @40° C	5.5-24 @40° C	17-100 @50° C	100-638 @50° C
Ash, wt%	0.05 FO D 0.01 GT	0.05 FO 0.01 D	0.10 FO	0.10 FO
Pour point, °C min	Report	Report	Report	Report
Conradson carbon, wt%	Report	Report	Report	Report
Max. 0.1 µm filtered ethanol insol. solids, wt%	0.01 FO	0.05	0.10	0.25
Accelerated aging rate @90° C, cSt/hr	Report	Report	Report	Report
Water, wt% of wet oil, max	32	32	32	32
LHV, MJ/L min, wet oil	18	18	18	Report
C, wt% dry H, wt5 dry O, wt% dry S , wt% dry N, wt5 dry K+ Na, ppm	Report " " Max Max. Report 0.5 GT	Report " " Max. Max. Report	Report " " .2 Max. .3 Max Report	Report " " .4 max. .4 max Report
Phase stability @ 20° C after 8 hr @ 90° C	Single phase	Single phase	Single phase	Single phase
Flash point, ° C minimum	52	55	60	60
Density, kg/m^3	Report	Report	Report	Report

As with petroleum type fuels, these specifications are structured around viscosity and ash content, because these have significant impacts on end use devices. Requirements for pour point will generally be site specific depending on the climate but the information is necessary for the end user to determine storage requirements such as heating to maintain flow properties. While the water content may seem high, this is the amount that would be expected if the feedstock were dried to 8 wt% moisture. Because the water content of bio-oil can vary depending on feedstock and operating conditions it is expected that bio-oil will be sold based on the LHV. These are initial proposals for bio-oil specifications and adjustments to these values are likely to occur as more experience is gained in using these fuels in various end use devices.

4.5   Upgrading Bio-oil Properties to Higher Value Products

As noted in the previous section, bio-oil quality can be improved to move it into a different grade and therefore command a higher price for the producer. The simplest and least expensive methods involve adding solvents or limited amounts of water to bring the bio-oil into the desired viscosity range. If solvents such as alcohols are used, added benefits accrue by adjusting the heating value and gaining improved long term storage properties. Solids in the form of ash and attrited fluidizing media can be removed by filtration, either hot (vapor phase) or after the oil has been condensed. This processing step will add complexity and additional operating costs to the final product. We should point out that while filtration has been demonstrated, both approaches have inherent difficulties that will require additional development before they can be considered commercially viable. These physical upgrading techniques can improve the quality of the neat, as produced, bio-oil but will still require the designer of end use equipment to make significant modifications to address the chemical properties of bio-oil, including acidity and low heating values because of high oxygen content.

If bio-oils could be upgraded chemically to produce a product that looked more like petroleum hydrocarbons then the end use device would require little to no modification. This would be the fastest way to gain acceptance of biomass-based fuels into the existing infrastructure. This approach essentially involves de-oxygenation and subsequent reforming of the remaining hydrocarbons. Two approaches have been explored for chemical upgrading of these oils: catalytic cracking and catalytic hydrotreating.

Diebold and Scahill [52] and others investigated in situ cracking of promptly formed biomass pyrolysis vapors over zeolite cracking catalysts. A number of zeolite cage sizes along with different doping metals were explored but the standard Mobile ZSM-5 catalyst developed for the methanol to gasoline process gave the best results. Oxygen is rejected in the form of H_2O, CO_2, and CO and the remaining hydrocarbons are re-arranged to form mostly aromatic type hydrocarbons because of the shape selectivity of zeolite catalysts for these types of hydrocarbons. Although conversion efficiencies of 42 wt% are theoretically possible, in practice only about half of this value was obtained in C_2+ hydrocarbons. High coking rates on the catalyst (up to 15 wt%) were a major contributor to the low yield.

An alternate approach using catalytic hydrotreating showed more promise. Elliott et al [53] and others have been developing this approach to chemical upgrading. Early work using low-activity sulfided catalysts, showed that it was necessary to carry out the hydrotreating in two steps. The first step (at lower temperature) initially stabilized the more reactive lower molecular weight compounds, which was followed by higher temperature more aggressive hydrotreating of the more stable phenolic compounds. This effort resulted in higher yields than those seen for

catalytic cracking but also produced a similar highly aromatic product composition. Although aromatics have a relatively high-octane level, which makes these compounds good for gasoline blending stocks, other toxicity issues limit their concentration in present fuel specifications to about 3 wt%. Current work in this area is focused on a number of improvements in hydrotreating catalysts with the following objectives:

- Optimize the catalytic processing for the properties of a given bio-oil or bio-oil fraction feedstock

- Explore the efficiency and selectivity of these newly developed, non-sulfided catalysts, which can be operated at lower temperatures

- Direct the selectivity to produce de-oxygenated higher value (but less aromatic) transportation fuels in addition to chemical co-products

- Improve the hydrogen utilization for the process

- Establish the process economics with the improved catalysts

Other catalytic methods of upgrading bio-oil to hydrocarbon gases were demonstrated in the late 1980s. Researchers at the University of Waterloo in Canada [54] demonstrated that by using a catalyst in lieu of the sand in a fluidized bed pyrolysis reactor they were able to produce methane in relatively high yields. Using different catalysts in this fashion resulted in different hydrocarbon products.

More recent work at NREL is focused on developing processes to reform bio-oil to hydrogen using conventional steam reforming catalysts. Yields of greater than 80% of theoretical have been demonstrated [55]. However, the current economics are favorable only if higher value co-products are produced in conjunction with the hydrogen.

These examples show the potential for catalytic manipulation of bio-oil to produce gaseous hydrocarbons or hydrogen that could be used as feed streams for other biorefinery products.

5. Prior Investigations of Bio-Oil Production Costs

Islam and Ani [56] studied the cost of producing crude bio-oil and catalytically treated bio-oil based upon data from a 0.3 kg/h pilot plant. Both Fluidized Bed Fast Pyrolysis (FBFP) and FBFP with Catalytic Treatment were examined at 100 kg/hr and 1,000 kg/hr scales using rice husks. The base feed cost was $20/ton. The system was operated at 3,120 hours/year (10 hours/day). The interest rate on capital was 10%. The electricity cost was $0.04/kWh. Notable cost assumptions for this analysis were: (1) an extremely low labor rate of $1.00/hr for Malaysia and (2) feed preparation costs were not included. Sensitivities were performed around feedstock cost, labor cost, equipment cost, and char credit. The estimated crude bio-oil price was $0.38/kg for the 100 kg/hr plant and $0.18/kg for the 1,000 kg/hr plant. The total capital investments were $97,000 and $389,000 for the 100 kg/hr and 1,000 kg/hr plants, respectively. The authors identified feedstock cost, equipment cost, and operating labor as important variables.

A study done at the University of New Hampshire [57] looked at the conversion of low-grade wood chips to bio-oil, primarily for use as a substitute for No. 2 fuel oil. The study looked at using a DynaMotive fast pyrolysis reactor design at 100, 200, and 400 metric tonne/day wet wood feed rates. The base feed cost was $18/wet ton at 45% moisture. The electricity cost was $0.065/kWh. The plant operated 24 hours/day, 330 days/year (7,920 hours/year). The bio-oil cost was calculated to be $1.21/gal, $0.99/gal, and $0.89/gal for 100, 200, and 400 wet tonne/day plant sizes. The total capital costs were $6.6 million, $8.8 million, and $14 million, respectively. Cole Hill Associates and DynaMotive compared the University of New Hampshire results with similar studies. The bio-oil costs for the Cole Hill and DynaMotive studies ranged from $0.77/gal to $1.05/gal of bio-oil.

Cottom and Bridgwater [58] performed an analysis of a generic flash pyrolysis process using correlations from the University of Waterloo. Their base case was sized at 1,000 tonnes/day using 7% moisture wood at $43.2/dry tonne. The resulting crude bio-oil price was $78.4/ton of bio-oil. A sensitivity analysis was done that showed the effect of feedstock cost on bio-oil cost, but no details of other cost assumptions were provided. No capital costs were provided. The authors noted feedstock cost as an important cost driver.

NREL [59,60] performed an analysis of the cost of bio-oil production in the early 1990s. The base case design for this study was 900 dry tonne/day of 50% moisture wood. The total capital investment for this facility was $46 million and the bio-oil selling price was $0.11/kg for a 15% after-tax internal rate of return. The operating hours were 8,000 per year. The feed stock cost was $44/dry tonne. Some sensitivities were done regarding plant size, capital cost, return on investment, feedstock cost, online availability, and different approaches to debt financing. Important cost variables identified were financing method, feedstock cost, plant availability, plant size, and depreciation schedule.

Solantausta et al. [61] reviewed 11 different pyrolysis variations looking at wood, peat, and straw as possible feedstocks. The base case feedstock prices were $30/tonne, $20/tonne, and $42.50/dry for wood, peat, and straw, respectively. The base case process size was 1,000 tonne/day dry biomass feed. The electricity price was assumed to be $0.065/kWh and the capital was financed at 10% interest. With these assumptions, the crude bio-oil price ranged from $117/ton to $488/ton of bio-oil. The total capital costs for the different 1,000 tonne/day plants

ranged from $44-$143 million. Graphs showing the sensitivity to biomass cost and capital recovery were included.

Arthur J. Power and Associates, Inc. also completed a feasibility study for the conversion of 1,000 tpd of biomass to bio-oil in 1991 for SERI (now NREL) [62]. In that report, a 15% pre-tax return on investment was used with 100% equity financing, $0.037/kWh electricity price, and $40/dry ton wood price. The total capital investment for the 1,000 dry tpd plant was $37 million. The estimated cost of the bio-oil produced was $0.044/lb. A sensitivity case was also done for a 250 dry tpd plant, resulting in a bio-oil cost of $0.039/lb with a total capital investment of $14 million. Other sensitivity calculations included varying the feed cost, the rate of return on capital, and the product yield for the two different plant sizes.

Table 4 lists the plant size, feedstock price, estimated bio-oil cost, and capital investment as reported in the various reports. Where applicable, the crude bio-oil values were reported instead of the upgraded product price. No attempt was made to adjust these costs to current dollars or put all the costs on a consistent basis. For one of the studies [62], a higher biomass purchase price was assumed with the larger plant sizes.

Table 4. Bio-oil Production Cost/Selling Price

Plant Size (tonne/d)	Feed Cost ($/dry tonne)	Feed Cost ($/GJ)[1]	Bio-Oil Cost ($/kg)	Bio-Oil Cost ($/gal)[1]	Bio-Oil Cost ($/GJ)[1]	Total Capital Investment	Source
2.4	$22	$1.10	$0.38	$1.73	$21.20	$97,000	[56]
24	$22	$1.10	$0.18	$0.82	$10.10	$389,000	[56]
100	$36	$1.80	$0.26	$1.21	$14.50	$6.6 million	[57]
200	$36	$1.80	$0.21	$0.99	$11.70	$8.8 million	[57]
400	$36	$1.80	$0.19	$0.89	$10.60	$14 million	[57]
1,000	$46.50	$2.33	$0.09	$0.41	$5.00	(Not given)	[58]
1,000	$44	$2.20	$0.11	$0.50	$6.10	$46 million	[59]
250	$44	$2.20	$0.11	$0.50	$6.10	$14 million	[60]
1,000	$20-$42.50	$1.00-$2.13	$0.13-$0.54	$0.59-$2.46	$7.30-$30.00	$44-143 million	[61]
250	$11	$0.55	$0.10	$0.46	$5.60	$14 million	[62]
1,000	$44	$2.20	$0.09	$0.41	$5.00	$37 million	[62]

[1] Assumes 20 MJ/kg HHV for wood, 17.9 MJ/kg HHV of bio-oil and 4.55 kg/gal density of bio-oil. [57, 63]

6. Wood Chip Pyrolysis Facility Economic Analysis

A preliminary Stage 1 analysis was conducted for a wood chip pyrolysis facility producing bio-oils (i.e., bio-crude). Material and energy balances were developed using ASPEN Plus® 12.1 and an economic analysis was conducted based on ASPEN ICARUS Questimate® 11.1 and standard NREL economic protocols.

6.1 Design Basis and Process Description

The production of bio-oil from biomass is based on the fast pyrolysis process, which is composed of five major processing areas: feed handling and drying, pyrolysis, char combustion, product recovery, and steam generation. Figure 1 is a block flow diagram of a fast pyrolysis process.

In the feed handling section, the biomass is reduced in size to <1-5 mm and dried to 5%-10% moisture. It is then sent to pyrolysis where it is heated to 400-500ºC in an oxygen-deficient atmosphere to degrade the biomass into a mix of gases, bio-oils, and char. Char is removed using high-efficiency cyclones and is combusted to fuel the pyrolysis reaction. To maximize the yield of bio-oils, the reaction is rapidly quenched through heat exchange or direct liquid (e.g., water or recycled bio-oils) injection. The bio-oils are present in the gas stream as aerosols and require scrubbers and/or wet electrostatic precipitators for efficient capture. After cleaning, some of the clean pyrolysis gases are recycled to fluidize the bed and the remaining gases are combusted for process heat. Where feasible, heat is recovered from the pyrolysis gases to generate steam for electricity production.

Figure 5. Fast Pyrolysis Block Flow Diagram
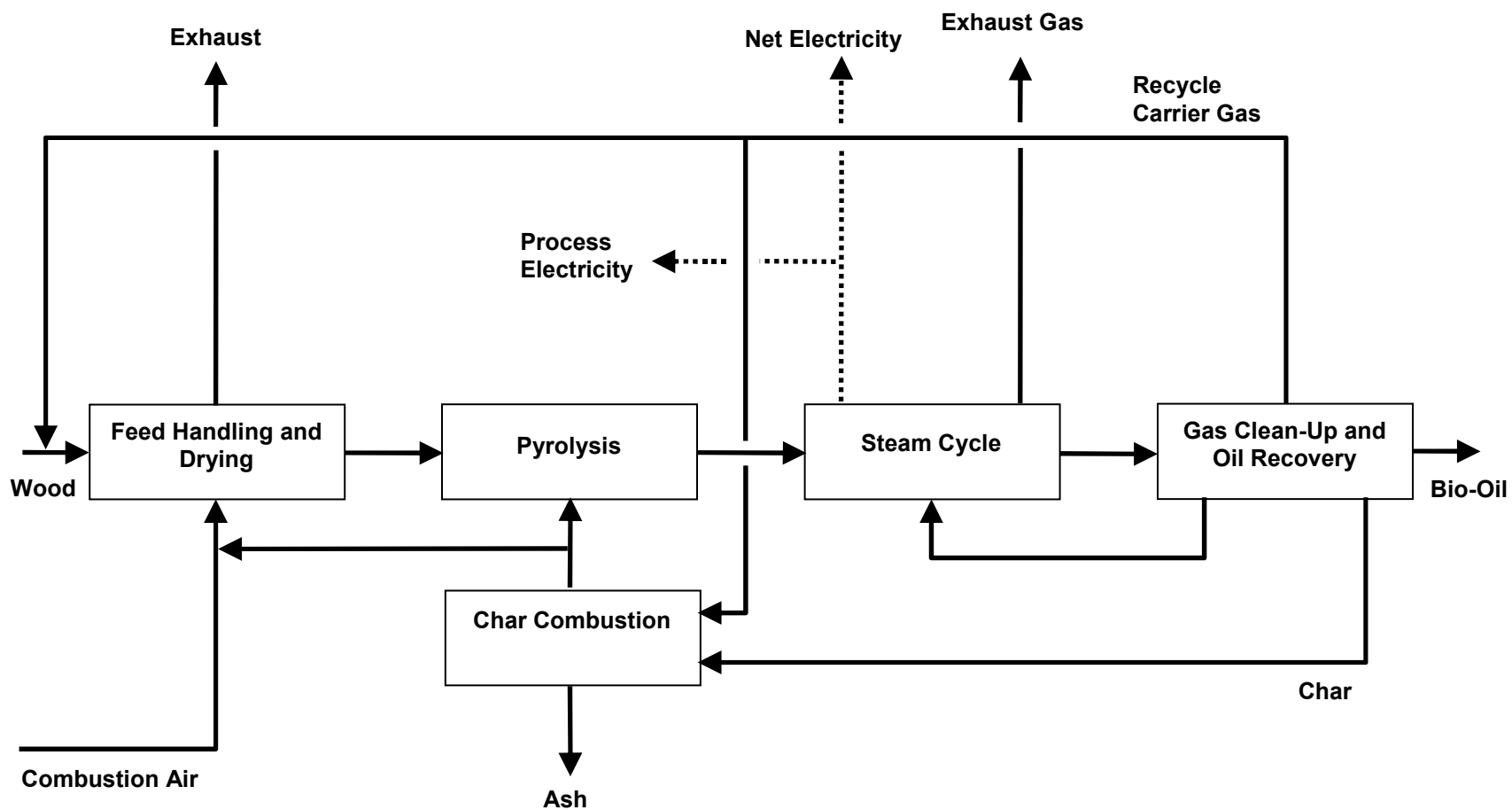
The pyrolysis facility was modeled using numerous assumptions and data sources. The following table summarizes the key design parameters and their sources.

Table 5. Design Basis

Parameter	Value	Source
Feedstock		
Type	Wood Chips	Engineering judgment
Moisture Content	50%	[64]
Cost	$30/dry ton	[64]
Throughput	550 dry tons/day	[64]
Particle size	3-45 mm	[65]
Feedstock Composition (wt%, dry)		
Carbon	50.93%	
Hydrogen	6.05%	Original feedstock composition in model; modified to eliminate S based on engineering judgment
Oxygen	41.93%	
Nitrogen	0.17%	
Sulfur	0.0%	
Chlorine	0.0%	
Ash	0.92%	
Pyrolysis Design		
Pyrolysis Type	Bubbling Fluidized Bed	Engineering judgment
Temperature	500 ºC	Original model
Air Carrier Ratio	2.75 lb air/lb pyrolysis feed	[66]
Feed Moisture Content	7%	[67/68]
Ground Particle Size	< 3 mm	[67/68]
Yields (Dry Basis)		
Oil	59.9%	[67/68]
Water	10.8%	Large-scale facility
Char and Ash	16.2%	
Gas	13.1%	

Table 5. Design Basis

Parameter	Value	Source
Oil Representative Components (lb/100 lb wood)		
$C_2H_4O_2$	5.93	
$C_3H_6O_2$	7.31	Estimated values
$C_7H_8O_2$	0.61	
$C_8H_{10}O_3$	3.80	
CH_2O_2	3.41	
$C_{10}H_{12}O_3$	16.36	
C_6H_6O	0.46	
C_7H_8	2.27	
$C_5H_4O_2$	18.98	
C_6H_6	0.77	
Projected Overall bio-oil composition (wt%)		
Carbon	59.27	Spreadsheet results
Hydrogen	6.03	
Oxygen	34.69	
Target Overall bio-oil composition (wt%)		[67/68]
Carbon	55-58%	
Hydrogen	5.5-7.0%	
Oxygen	35-40%	
Gas Composition (lb/100 lb dry wood)		
CO_2	5.42	
CO	6.56	Elemental balance
CH_4	0.035	From the ratios of the earlier model
C_2H_4	0.142	
H_2	0.588	
C_3H_6	0.152	
NH_3	0.0121	
		Material balance – all N in feed

Several of these assumptions, particularly the yields, require further explanation. The overall yields of the major streams: bio-oil, char, gas, and reaction water were taken from Bridgwater et al. [67/68] and are based on the dry feedstock. The composition of these major streams is highly variable. In fact, over 200 compounds have been identified in the bio-oil alone [69]. The original model, developed by Gregoire [60] used pseudo-components to represent the bio-oils, but it was since changed, but not documented, to have the representative components listed in the table above.

The exact distribution of these components was not found, but a range of typical values for bio-oil was obtained by Bridgwater et al. [67/68]. The yields of the representative compounds were manipulated until the analysis approximated that found in Bridgwater et al. [67/68]. No effort was made to ensure that other important properties of the bio-oil (e.g., density and LHV) matched that of the mixture of components. However, all of the economic calculations are based on a typical bio-oil densities and LHVs and so this should not be a concern. If a better representation of the composition of the bio-oil is obtained, the slate and distribution of the components should be modified.

Similarly, the exact composition of the gaseous product varies depending upon the operating conditions and the feedstock. In this case, the number of components is much lower and the relative concentrations are better known. To estimate the dry gas composition, we assumed that all of the nitrogen in the fuel converted to ammonia. The remaining gaseous product was apportioned in the same ratios as the original model.

Finally, the composition of char is variable. For this analysis, we determined char composition based on an elemental balance using the assumed feedstock composition and the slate of products. All ash was assumed to be present in the char. The heat of combustion of char was then determined using an IGT estimation correlation presented in Domalski et al. [70]:

$HHV = 146.58C + 568.78H - 51.53(O+N) - 6.58A + 29.45S$ in Btu/lb

Where C - % carbon

  H - % hydrogen

  O - % oxygen

  N - % nitrogen

  A - % ash

  S - % sulfur

From this, the standard heat of formation is calculated. The density and heat capacity of the char were assumed the same as elemental carbon.

6.2   Model Description

An ASPEN Plus® model was developed for the pyrolysis process, based largely on the work by Gregoire [60]. Significant design changes include:

- Elimination of steam generation for sale

- Combining all steam generated into a single steam drum, similar to the Combi System by Clayton Industries [71].

- Substitution of condensing turbine for original turbine

- Modification of process parameters to correspond to literature values rather than in-house data

- Changed pyrolysis type to fluidized bed vs. ablative

- Increased carrier gas rate to 2.75 lb/lb feed for fluidized bed vs. 1.3 lb/lb feed for ablative

- Addition of power requirements for size reduction

- Modification of quench section to include a scrubber and wet electrostatic precipitator (WESP) after heat recovery

- Recycle of cooled product as the scrubbing medium in the quench section.

Other modeling changes included:

- Removal of several unit operation models by simplifying the modeling methodology

- Modification for heat flow design convention and heat integration design-specs

- Use of characteristic components instead of pseudo-components

- Elimination of unused components

- Conversion of non-conventional components (e.g., ash) to conventional solids (e.g., SiO_2)

- Addition of utility flowsheet

- Modification of flash specifications to account for free water.

The modeling changes had only small effects on the overall material and energy balances. In general, they only simplified the model and increased its utility.

6.3 Material and Energy Balance Results

Using the assumptions outlined above, the overall material and energy balances were completed for the process. The mass balances for the model are included with the ASPEN model write-up in Appendix A.

The facility produces 16,091 kg/hr of bio-crude with a moisture content of 23.6%. It also produces almost 4,900 kW of electricity, but uses roughly 80% of that value for recycle gas compression (2,600 kW) and feedstock size reduction (1,400 kW). The net electricity output for the facility is 588 kW.

6.4 Economic Basis

The economic analysis for the pyrolysis process is based on standard NREL analysis protocol and the most recent NREL ethanol economic analysis [72]. The basis for the capital and operating costs as well as the financial calculations are addressed in this section.

All costs were projected in 2003$.

6.5 Capital Costs

Using the material and energy balance as well as standard sizing procedures in Perry's Chemical Engineers' Handbook [73] and similar references, each major piece of equipment was sized. The equipment and setting charges for each component were then estimated primarily using ASPEN ICARUS Questimate® Version 11.1. For non-standard equipment (e.g., the pyrolysis unit), other methods such as comparison with other similar equipment were employed. Each of these non-standard methods is discussed in the capital cost results section.

Installation factors were applied for each component type based on the most recent NREL ethanol economic analysis [72]. After estimating the equipment costs, a contingency factor of 35% was applied to project the total equipment costs. This conservative contingency factor was designed to account for any miscellaneous equipment left out of the analysis, uncertainty in the analysis due to its early stage of development, and the conceptual nature of the analysis.

Using the total equipment cost, the total project investment (TPI) was projected using a factored method based on the methodology used in the most recent NREL ethanol economic analysis [72]. Table 6 outlines the factors used.

Table 6. Total Project Investment Factors

Component	Basis
Total Equipment Cost	Questimate® and Literature
Warehouse	1.5% of Equipment Costs
Site Development	9% of ISBL
Total Installed Cost (TIC)	Sum of Above
Indirect Costs	
Field Expenses	20% of TIC
Fee Home Office & Construction	25% of TIC
Project Contingency	3% of TIC
Total Capital Investment (TCI)	Sum of Above
Other Costs (Startup)	10% of TCI
Total Project Investment	Sum of Above

6.6 Operating Costs

Annual costs were projected for both variable and fixed operating costs. Variable operating costs are incurred for feedstock and incidental chemicals such as cooling tower chemicals. Unit operating costs were obtained from the literature or similar NREL studies. Unit costs for the cooling tower chemicals and boiler feed water chemicals were obtained from the most recent NREL ethanol economic analysis [72].

Table 7 summarizes the unit costs associated with these items.

Table 7. Unit Costs

Input	Unit Cost	Source
Wood chip feedstock	$30/dry ton	Bain 2003
Cooling tower chemicals	$1.00/lb	Ruth 2003
Boiler feed water chemicals	$1.03/lb	Ruth 2003

Fixed operating costs, composed of labor, maintenance, overhead, taxes and insurance were also determined. The number, expertise, and salaries of personnel required to operate the facility was estimated based on NREL experience. Salaries were scaled using the Bureau of Labor Statistics' labor index for Chemical and Allied Trade Workers [74].

Table 8 summarizes the salaries and number of employees required.

Table 8. Employee Requirements

Employee	Number Required	Annual Salary
Plant/General Manager	1	$121,600
Plant Engineer	1	$79,000
Maintenance Supervisor	1	$72,940
Lab Manager/Chemist	1	$60,780
Shift Supervisor	4	$45,000
Maintenance Tech	5	$34,000
Shift Operators	20	$30,400
Administrative Assistants	2	$24,300

The remaining fixed operating costs were calculated as percentages of the total labor cost or capital costs.

- Overhead/maintenance – 60% of labor [72]
- Maintenance – 2% of equipment [72]
- Insurance and taxes – 1.5% of total installed capital [72]

6.7 Economic Analysis

The economic viability of the process is evaluated using a discounted-cash flow-rate of return (DCFROR) calculation. An internal rate of return (IRR) of 10% was specified for a plant life of 20 years and straight-line depreciation over 7 years. The plant will be constructed over a 3-year period with capital outlays of 8%, 60%, and 32% each year. Working capital is estimated at 5% of the fixed capital investment and the start-up period is projected to be six months. These assumptions are from the Bain [64] analysis.

6.8 Capital Cost Results

A majority of the equipment costs were determined using ASPEN Icarus Questimate® 11.1. Two large component costs, the pyrolysis system and the feed handling system were estimated using other cost quotes.

As noted earlier, the pyrolysis unit is a non-standard unit operation. Although there are numerous commercial pyrolysis units, most of these units are slow pyrolysis units and as such, may not be directly applicable to the proposed fast pyrolysis unit. The cost for the pyrolysis system was estimated from a fluidized bed boiler system designed by Energy Products of Idaho [75]. The heat recovery equipment would likely be the most similar between the systems (e.g., both are composed of air preheater, economizer, and superheater) and was thus used as the basis for scaling. The cost of the pyrolysis system was projected to be $3.8 million based on the steam flow rates of the two systems with a 0.6 equipment cost exponent.

This estimate should be conservative based on several factors. The pyrolysis chamber should be significantly smaller than the combustion chamber of a fluidized bed boiler based on the lower gas flow rates in the pyrolysis system. The steam pressure and temperature for the EPI system is higher (950 psi) than that for the pyrolysis system (620 psi). Finally, the EPI cost quote included NO_x and SO_2 control and other systems that may not be required for the pyrolysis system.

The cost of the wood feed handling system was estimated from the Gregoire [59] report and scaled up to 2003$. The system has provisions for rail car or truck delivery and accommodates 4 weeks of storage. Rocks and tramp metal are removed using a flume and two front-end loaders are used to feed the wood chips to the process conveyor. Additional small metal pieces are removed with a magnet. The Gregoire [59] report estimated the cost of this system at $400,000. For this analysis, the cost is projected at a little more than $450,000.

Solids handling within the facility was estimated using Questimate® based on the design presented in Bridgwater et al. [65]. This design includes screening, re-chipping of oversized components, drying, grinding, screening, and re-grinding of overs.

The costs for the WESP and scrubber were estimated from literature values [76]. The power requirement for the WESP was estimated at 5.17E-4 kW/acfm [76].

The equipment costs were developed assuming a minimum of sparing. In general, each pump has a spare, but other unit operations were designed without redundancy. Table 9 summarizes the installed equipment costs by unit area.

Table 9. Installed Equipment Costs

Plant Area	Installed Equipment Cost ($ Million)
A1000- Feedstock Handling and Drying	$5.57
A2000 – Pyrolysis	$3.92
A3000 – Quench	$1.94
A4000 – Heat Recovery	$1.14
A5000 – Product Recovery and Storage	$0.80
A6000 – Recycle	$1.38
A7000 – Steam and Power Production	$3.16
A9000 – Utilities	$3.13
Equipment Contingency – 35%	$7.37
Total Installed Equipment Cost	$28.41

Using the installed equipment costs and the factors outlined in Table 6, the TPI was estimated at $46.1 million. Table 10 provides a breakdown of the TPI.

Table 10. Total Project Investment

Component	Cost
Total Equipment Cost	$28,410,567
Warehouse	$426,159
Site Development	$826,448
Total Installed Cost (TIC)	$29,663,173
Indirect Costs	
Field Expenses	$5,932,635
Home Office & Construction Fee	$7,415,793
Project Contingency	$889,895
Total Capital Investment (TCI)	$43,901,497
Other Costs (Startup)	$4,390,150
Total Project Investment	$48,291,646

6.9 Operating Cost Results

Variable operating costs were determined from the material and energy balance. The largest variable operating cost, by far is the feedstock at $5.5 million annually. Make-up water and miscellaneous chemicals have negligible costs. Waste treatment, both water and solid, contribute almost $1 million to the annual costs. After accounting for plant electricity demands, the facility has a net export of 4.70 MM kWh of electricity annually, resulting in a revenue stream of $0.21 million. Overall variable operating costs are thus estimated at $6.13 million annually.

Labor costs were estimated as outlined earlier in Table 10 and resulted in a direct labor cost of $1.34 million. An additional $800,000 was estimated for overhead labor charges.

At 2% of the equipment and TPI costs, respectively, the costs for maintenance and insurance/taxes are estimated at $568,000 and $724,000. The total fixed operating costs are thus estimated at $3.4 million and the total operating costs are roughly $9.6 million.

The operating cost spreadsheet is provided in Appendix B.

6.10 Financial Analysis Results

A DCFROR analysis was conducted using the parameters outlined earlier. The selling price of the bio-oil was projected to be $7.62/GJ, LHV.

6.11 Discussion

As discussed in Section 4.4 of this report, pyrolysis oils have several concerns including their shelf life, high ash content, volatility, heat content, and their overall quality. Table 3 showed some proposed specifications for the various grades of bio-oil.

The IEA Bioenergy Pyrolysis committee, which developed the specifications in Table 3, focused on four grades of fuel oil: #2, #4, #5, and #6 corresponding to similar petroleum-based distillate and residual fuels. The committee does not believe that pyrolysis oils will be able to meet the viscosity, volatility and residue specifications for #1 fuel oil and so they did not develop specifications for these oils [77]. ASTM #2 fuel oil is also considered a volatile fuel as the specifications are not as strict as for #1 fuel oil. In addition, applications using ASTM #2 fuel oil generally have some preheating, which would likely also be required for an IEA #2 fuel oil [77].

Three example bio-oils were highlighted in the Diebold [77] report; one that had been upgraded with hot gas filtration and two that had only cyclones. The two oils using cyclones only generally met the proposed IEA specifications for #6 heavy bio-oil; they failed to meet only the flash point, LHV, and filtered solid specs [77]. The upgraded bio-oil (i.e., via hot gas filtration) met the flash point and filtered solid specifications for the IEA #6 heavy bio-oil oil and almost achieved the LHV. This oil closely parallels the #4 specification. With further upgrading to remove alkali and other solids, it could meet the IEA #2 light bio-oil specification. The #2 specification is important as this type of fuel could likely be used in applications such as gas turbines without significant equipment modifications.

The IEA committee did not include shelf life as a specification, but the literature shows that this is a concern. To account for these differences, it is assumed that pyrolysis oils, as currently produced have a value similar to #6 residual fuel oil and that the ultimate goal is to develop a fuel oil that meets the specifications of #2 fuel oil and will have a shelf life of at least 6 months. Thus, when evaluating process improvements, the product oil will be referred to as either IEA #6 heavy bio-oil or IEA #2 light bio-oil and their values will be assigned based on this specification.

The market values of the petroleum fuel oils that correspond to the two end points of the proposed fuel oil specifications (i.e., #2 and #6) differ considerably. In fact, in 2000, distillate fuel (#2) sold for $9.30/MM Btu ($10.12/GJ) while residual fuel oil (#6) sold for less than half of that at $4.50/MM Btu ($4.75/GJ), on an LHV basis [78]. Residual oil is generally used as an industrial heating oil and distillate oil is used for residential heating, power generation, or for vehicles. For this study, only non-highway uses of distillate are considered. The markets for both oils are significant. In 2001, over 12,400 million gallons of residual fuel oil and 22,900 million gallons of non-highway distillate fuel oil was purchased in the United States [79].

Although this analysis is portraying these oils as IEA #2 light bio-oil and IEA #6 heavy bio-oil, it is critical to note that the pyrolysis oils are not fungible with petroleum fuels (e.g., #2 distillate and #6 residual fuel oils). A separate fuel handling and transport system must thus be developed. In addition, the fuel specifications proposed by the IEA committee have not been accepted by conventional standards organizations (e.g., ASTM) and many properties of bio-oils will never be equivalent to their petroleum-based counterparts (e.g., heating value). However, the proposed comparison should provide a useful method to assess the potential for fuel upgrading and to provide appropriate cost goals and markets.

6.12 Sensitivity Studies

Several sensitivity studies were conducted and the cost barriers were identified. From this, researchers devised a roadmap of the improvements necessary to be cost competitive with petroleum fuels. It is envisioned that there will be parallel development efforts, focusing on the low-end IEA #6 heavy bio-oil and the higher-end IEA #2 light bio-oil markets.

Based on the above analysis as well as the earlier analysis by Bain [64], the following sensitivity studies were conducted in series to determine their cumulative effect and whether the #6 fuel oil goal of $4.75/GJ, LHV based on the current price of #6 residual fuel oil was feasible. Table 11 summarizes the results of these analyses.

Table 11. Crude Bio-oil Sensitivity Studies

Sensitivity Study	Resulting Bio-Oil Cost
Increase facility size to 2000 dtpd	$5.65/GJ (LHV)
Increase bio-oil yield; 59.9% to 70%	$4.84/GJ (LHV)
Reduce contingency factor; 35% to 10%	$4.44/GJ (LHV)

As shown in the table, the cost goal of $4.75/GJ, LHV appears to be feasible for a larger facility, decreased capital costs and an increase in bio-oil yield. None of these achievements is unreasonable. The 70% bio-oil yield has been achieved and the capital contingency factor should decrease as the equipment becomes better specified [66]. In addition, the facility size of 2000 dtpd is well within the projected range of biomass facility sizes. Finally, while the stated goal for the crude IEA #6 fuel oil is that for #6 residual fuel oil, the actual value of the IEA #6 bio-oil may be higher due to its extremely low sulfur content. In general, residual oils have sulfur contents of > 1% [80].

6.13 Upgrading of Crude Bio-Oil

Bio-oil can be upgraded through both chemical (e.g., hydrotreating) and physical (e.g., filtering) methods into chemicals and fuels. If the bio-oil can be upgraded to an ASTM #2-type fuel oil, suitable for use in residential heating or power production (e.g., gas turbines), it would likely demand a price that is double that of the crude pyrolysis oil.

NREL researchers have proposed a process to upgrade the crude bio-oil, which involves a direct solvent (e.g., ethanol or methanol) quench, scrubbing, a wet ESP, and bio-oil filtration [66]. Figure 6 provides a block flow diagram of the proposed upgrading process.
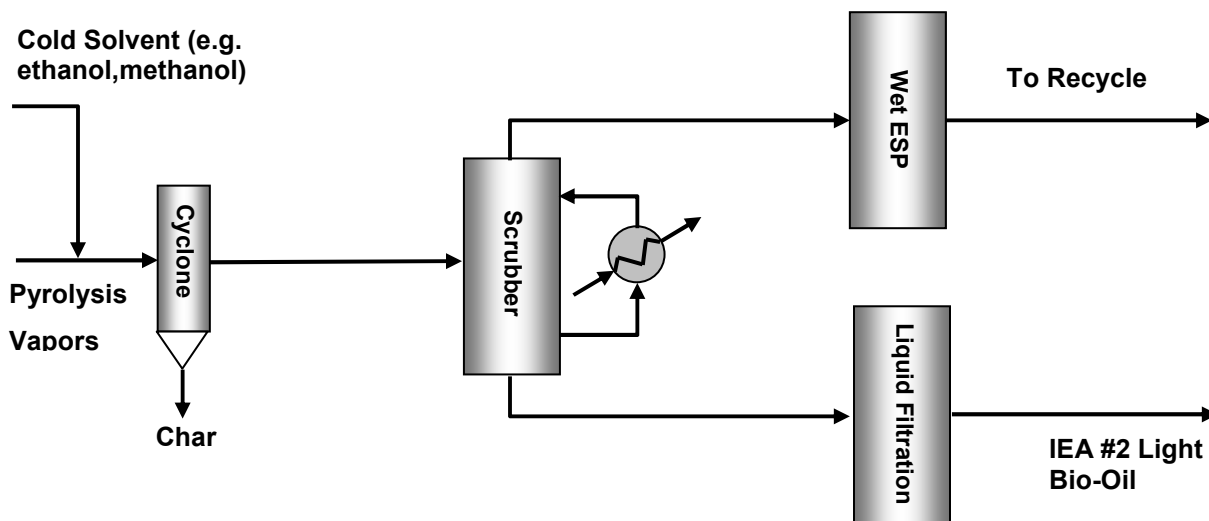
Figure 6. Proposed Heavy Bio-Oil Upgrading Process

The proposed process is relatively simple, adding only a solvent quench and liquid filtration to the current design. The solvent should help stabilize the product and the filtration can remove fine solids. It is not clear if the design would also impact the current heat integration/steam generation design. If the solvent quench can be employed after the heat recovery, then it will not be impacted. Further research and analysis is required to test the feasibility of this design. In addition, it is not clear that it would meet the proposed #2 IEA specifications. In fact, reviewers of this report are skeptical that the proposed process would improve the volatility of the oil sufficiently for use in #2 fuel oil applications and would employ a chemical modification [81].

Costs for this process were not estimated, as it is not clear whether this process is feasible and will achieve the proposed IEA specifications for a refined bio-oil. However, all of the unit operations are based on standard equipment and no exotic chemicals are employed.

The actual potential for this technology is tremendous. Assuming that, based on the analysis above, the crude bio-oil can be produced for the current residual fuel oil price of $4.75/GJ, LHV, then the proposed upgrading process would have an allowable cost of over $5/GJ, LHV to meet the $10.12/GJ, LHV cost goal for IEA #2 light bio-oil. Although the margin of error is relatively high given the scope of this analysis, the tremendous potential increase in product value (i.e., > 100%) for the upgrade is attractive. In fact, even if none of the projected process improvements for the current crude bio-oil design are implemented, the upgrading process, if successful, has an allowable cost of $2.50/GJ, LHV (i.e., $10.12/GJ-$7.62/GJ).

6.14 Limitations of the Analysis

The current analysis has several limitations, many due to the lack of current laboratory data as well as the conceptual nature of the analysis itself. The following is a summary of the most significant limitations of this analysis.

- Lack of current data

- Untested, proposed design for bio-oil upgrading

- Quench section design with heat recovery may be infeasible due to the rapid quenching required (i.e., Ensyn uses direct quench without heat recovery)

- Fungibility issues and the resulting storage and distribution system requirements of bio-oil have not been addressed

- Large contingency factor due to the large uncertainty

- Proposed development approach is based on proposed fuel standards that have not been accepted by traditional standardization bodies (e.g., ASTM)

7. Conclusions and Recommendations

Researchers have learned much about the science and engineering of pyrolysis of biomass especially in the last twenty-five years. This knowledge base has contributed to rapid advances in process hardware design improvements in addition to a broad understanding of the physical and chemical properties of the resulting bio-oil product during the same time period. Even with these advances, significant technical and economic challenges remain to be addressed before fast pyrolysis technology gains commercial acceptance. The following section will summarize the current state-of-the-technology, where it needs to go, and suggested paths to get it there.

7.1 Current State-of-the-Art for Fast Pyrolysis of Biomass

The method to produce bio-oils in high yield is well established. Numerous researchers throughout the world, using a variety of biomass feedstocks and a number of uniquely different reactor designs, have demonstrated this. As long as the thermal requirement of imparting high heat fluxes to the biomass immediately followed by rapid thermal quenching of the resulting vapors is followed, product yields and the chemical nature of the bio-oil product will be reasonably consistent. This will be true regardless of the specific reactor design or its relative size. Scale up to commercial size plants has yet to be demonstrated and there are questions related to being able to get enough heat into the reaction vessel. There may be other reasons to select one particular reactor design over another based on certain operating conditions that impact another processing step; but the thermal "cracking severity" or time / temperature relationship is the overriding principle to employ in any reactor design.

The requirements needed to produce a bio-oil that has a reasonably long shelf life (equivalent to petroleum fuels) is also fairly well established. The principle technical issue here is producing oil containing little or no char. A substantial body of evidence has implicated the alkali metal sequestered in the char as a catalytic agent for promoting polymerization reactions between certain compounds known to be present in the bio-oil. While it is understood that this is an important issue for bio-oil stability, it is not known how to remove the char effectively and inexpensively. The challenge is primarily related to the very small (sub-micron) size of the char fines. Complementary to the absence of char fines for improving the storage stability is the addition of alcohol or other solvents. Based on the known types of compounds present in bio-oil and the chemical reactions between alcohols and some of these compounds, a convincing argument can be made that these reactions tie up the compounds suspected of undergoing polymerization reactions. The combination of these two approaches is expected to result in a bio-oil product capable of having a shelf life of up to six months.

Although the need to remove char fines from the bio-oil is recognized by the biomass pyrolysis community, there is not a consensus in how this can be done easily at a reasonable cost. Filtration at elevated temperatures before condensing the bio-oil vapors to liquids created major operational problems. Vapors passing through the char cake captured on the filter surface are exposed to the same alkali metal in the char that has been linked to the polymerization reactions thought responsible for impacting long term stability in the liquid oils. In fact evidence of vapor phase polymerization reactions occurring within the char cake on the filters was observed. The consequence of this polymerization was a bonding of the char particles making up the cake on the filter surface. This bonding then made removal of the char cake from the filter very difficult. The polymerization is also thought to contribute to a yield loss of approximately 10% of the

product bio-oil. Filtering liquid bio-oil after condensation has its own set of problems. As particulate is collected on the filter surface, the viscous bio-oil passing through the particulate cake tends to agglomerate the char fines into a thick sludge. As the sludge is removed from the filter to recover pressure drop, a considerable amount of bio-oil is also rejected with the sludge. So this strategy also results in a yield loss. As with gasification and the need to clean up the synthesis gas product from tars and particulates, a similar analogy applies to bio-oil. These are both difficult technical challenges that do not lend themselves to easy solutions. This is a critical technical challenge because of the link to both stability of the bio-oil and the need to meet stringent specification standards for particulate and alkali metal content.

It is imperative to establish a set of standard specifications for bio-oils that have broad acceptance in the international community. Without this set of specifications designers and manufacturers of burners, IC engines, and turbines will not know how to design their equipment to accommodate the properties of this new fuel. At this point in time a set of standards has been proposed but no formal acceptance has been established between producers, users, and organizations involved with developing methods and protocols for measuring each specification.

Preliminary studies of the health effects of bio-oil indicate that when produced at the relatively moderate temperature (500°C) used for fast pyrolysis conditions, the oils are not overly toxic. However these studies were preliminary in nature and some of the data showed inconclusive results. More definitive answers to the health and safety aspects of bio-oil will be required before this product can gain widespread public acceptance. In addition to the oils, the char produced as a byproduct also needs to be assessed from a chronic exposure standpoint. This information will be critical in both gaining public acceptance of the use of bio-oil and in designing plants to minimize chronic exposure to these materials. Along with the health aspects of working with bio-oil the effects on the environment also need to be better understood. Little to no effort has been expended in this area to date. The impact of a major spill of bio-oil on land and /or aquatic systems needs to be assessed.

It is possible to upgrade bio-oil to hydrocarbon-like fuels through catalytic hydrotreating or cracking. These processes remove the oxygen in bio-oil and then reform the remaining carbon and hydrogen into hydrocarbon compounds. The yield of liquid product is reduced substantially because of efficiency losses and the fact that much of the mass of the original bio-oil is oxygen that gets rejected in the form of carbon oxides or water. Yields are lower when doing catalytic cracking instead of hydrotreating. In both cases the resulting hydrocarbon product is dominated by aromatic compounds, which have limits for blending into motor fuels. Methods for redirecting the type of hydrocarbons produced will need to be developed. Upgrading the bio-oil to a hydrocarbon fuel would be the fastest way to gain acceptance of biomass pyrolysis-based fuels into the existing market. We expect that the resulting product would be used directly in prime movers that have been designed for hydrocarbon fuels with little or no modification.

Moderate scale fast pyrolysis plants have gained enough operating experience that reasonably good economic data is available to assess the economic viability of this emerging technology. No large scale plants have been built to date. This is primarily due to the lack of demand for the pyrolysis product. There have been modest size pilot plants built and operated at a number of locations worldwide. These have mostly been for demonstration purposes and are listed in the table below. The two plants at Red Arrow WI can be considered commercial operations but they are producing food flavoring compounds and there is a limited market for those products. Larger scale plants needed for producing fuels have yet to be developed from a commercial status.

Table 12. Worldwide Current Biomass Pyrolysis Operating Plants

Reactor Design	Capacity (Dry Biomass Feed)	Organization or Company
Fluidized bed	400 kg/hr (11 tons/day)	DynaMotive, Canada
	250 kg/hr (6.6 tons/day)	Wellman, UK
	20 kg/ hr (0.5 tons/day)	RTI, Canada
Circulating Fluidized Bed	1500 kg/hr (40 tons/day)	Red Arrow, WI; Ensyn design
	1700 kg/hr (45 tons/day)	Red Arrow, WI; Ensyn design
	20 kg/hr (0.5 tons/day)	VTT, Finland; Ensyn design
Rotating Cone	200 kg/hr (5.3 tons/day)	BTG, Netherlands
Vacuum	3500 kg/hr (93 tons/day)	Pyrovac, Canada
Other Types	350 kg/hr (9.3 tons/day)	Fortum, Finland

A technoeconomic analysis using discounted cash flow methodology (10% IRR, 100% equity financing) on a bio-oil production facility showed that heavy bio-oil (i.e., IEA #6 heavy bio-oil) is projected to have a selling price of roughly $7.62/GJ, LHV. The facility analyzed produced 16,091 kg/hr of bio-crude with a moisture content of 23.6%. The feed rate to the pyrolyzer was 550 dry tones/day. The pyrolysis reactor was modeled using yields from Bridgewater, et al. [67/68].

The pyrolysis unit also produced almost 4,900 kW of electricity, but used roughly 80% of that value for recycle gas compression (2,600 kW) and feedstock size reduction (1,400 kW). The net electricity output for the facility was 588 kW.

7.2 Recommendations for Advancing Fast Pyrolysis Technology

There are a number of barriers that must be overcome to advance the technology of biomass fast pyrolysis. They can be listed as follows:

- No universally accepted specifications or standards for bio-oil

- Bio-oil quality and reproducibility must be established, especially with respect to storage stability of the oil

- Effects on the environment and safety and health of production personnel potentially exposed to bio-oil needs to be established. This need is also present for consumers using the product.

- Public acceptance or perception may be an issue, particularly if the health and safety issues are unknown. Odor is another issue related to public acceptance. Bio-oil has a strong smoky smell that is unlikely to be masked by other compounds.

- A near term technical barrier is lack of adequate supplies of bio-oil for long term testing in burners and prime movers for power generation. There are currently a limited number of sources for bio-oil production and little support for funding bio-oil production runs.

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- A policy barrier is the need to secure long term supplies of the biomass resource. This is a ubiquitous problem for all biomass utilization technologies and will prevent the flow of investment capital unless it can be resolved. A minimum of a guaranteed ten year supply will be necessary to create a favorable investment climate.

The first two barriers are somewhat related in that if the appropriate specifications are established for key properties of the oil then the oil stability and quality will be enhanced. Given what is already known about char fines and their relationship to storage stability, their effective removal should be a priority. One approach worth investigating would be to add alcohol solvents to the bio-oil prior to doing liquid filtration. Adding the alcohol will reduce the viscosity to the point where sludge buildup on the filter surface may no longer present a problem. Previous studies have shown that addition of the alcohol solvent is more effective in stabilizing oils when it is added shortly after the oils are produced. An approach that should be explored is adding the alcohol solvent directly into the hot bio-oil vapor stream. Two benefits could possibly result from this method of addition. Vaporization of the alcohol will have a cooling effect on the hot vapor stream, which is desirable from a standpoint of quenching the thermal reactions from pyrolysis and preserving the biomass fragments that comprise the liquid product. Addition of the alcohol at this location in the process would provide a small amount of residence time in an elevated temperature zone to enhance the reactivity of alcohol with some of the reactive compounds in bio-oil. This may further improve the stability over what has already been observed with the addition of alcohol to liquid bio-oil. There may also be benefits of co-condensing the alcohol solvent with bio-oil vapors to minimize the formation of aerosols during cooling.

Establishing a moisture specification for bio-oil will require the producer to dry the biomass feed to a certain level prior to pyrolysis. This requirement can be set to levels that insure bio-oil will always remain a single phase. What currently happens in practice is that various organizations make their own determination as to the moisture content of the starting feed. This results in a wide range of moisture contents for bio-oil produced by different organizations.

It will be necessary to stay involved the international pyrolysis research community in developing specifications for bio-oil. The best vehicle in which to do this would be the International Energy Agency. Indeed, the first set of standards promulgated for bio-oil was done through the Pyrolysis Activity under Task XIII within the IEA. There continues to be a lot of activity in developing protocols and standard methods for measuring the properties of bio-oil in the European biomass pyrolysis community. This is even being done in collaboration with equipment manufacturers. The United States should re-engage with this activity. An organization such as ASTM also needs to be brought into the loop to provide credibility to the final specifications and methods for measuring them. The manufacturers of the end use equipment also must be involved in establishing these specifications. NREL and PNNL both have extensive experience in analyzing bio-oils and can provide technical assistance in developing the measuring protocols.

A better understanding of the environmental impacts along with safety and health issues of exposure to bio-oil needs to occur. This analysis should also include particle size distribution and toxic compounds that may be adsorbed on the surface of particles for the char, particularly the fines.. Having this information will be critical in gaining public acceptance of bio-oil as a new fuel source. These studies should be more rigorous and therefore more definitive than the preliminary studies previously conducted. They also need to include biodegradability of the oil in

soils and an assessment of the impacts on aquaculture resulting from a major spill in a river or lake.

Collaborative activities with the U.S. Department of Agriculture (USDA) Forest Service should continue because of their close connection with the biomass resource and the need to establish long-term access to this resource by investors willing to provide capital for the emerging conversion technologies. The Forest Service also conducts R&D on biomass harvesting and size reduction equipment. There may be opportunities to guide this development toward equipment that can be multi-purpose with respect to feed preparation for biomass conversion technology. An example would be equipment that could simultaneously grind and dry the biomass, thus reducing process feed costs.

Upgrading of bio-oil to hydrocarbon fuels or high value chemical products should continue. Since the performance characteristics, toxicity, and public acceptance of these types of fuel are well known this will present the fastest path to market for biomass based transportation fuels. Additional opportunities should be explored in catalytic manipulation of the promptly formed pyrolysis vapors. All technologies employing heat transfer media (fluid or transported beds) lend themselves to this approach by replacing the transfer media with a catalyst. Some effort has been expended in this area in the past so it may offer novel pathways to chemicals or other fuels from biomass pyrolysis. The University of Waterloo in Canada demonstrated (69) an example of this approach during the late 1980s where they conducted pyrolysis of biomass in the presence of hydrogen with a catalyst as the fluidizing media. They were able to convert the carbon in biomass primarily to methane at very high yields. At the time methane was an inexpensive commodity fuel so there was little commercial interest. However, recent trends in the supply / demand dynamics of natural gas are changing this situation and may offer new opportunities to exploit this technology.

The technoeconomic analysis also showed that research on upgrading the bio-oil should continue. For example, in order for pyrolysis oil to be cost competitive with #6 fuel oil and to compete in the industrial heating market, further cost reductions are necessary. Potential areas for improvement include increased yields, larger facility sizes, and reduced pyrolysis unit capital costs. With further research and development, it is likely that the cost goal of $4.75/GJ, LHV for this grade of bio-oil is achievable.

Developing a higher-value bio-oil (e.g., IEA #2 light bio-oil) will require some type of gas cleanup or liquid fuel upgrade. This higher value oil could be used in applications such as gas turbines without extensive equipment modifications. This trade-off should be explored using studies such as Thamburaj [82].

NREL researchers have proposed a simple bio-oil upgrading process that may cost effectively convert the crude bio-oil into a gas turbine fuel with properties similar to a #2 distillate. Due to the large cost differential between residual ($4.75/GJ, LHV) and distillate ($10.12/GJ, LHV) fuel oils, there is an attractive economic incentive   for evaluating this process. For the current bio-oil design, the upgrading process has an allowable cost of $2.5/GJ, LHV to meet the proposed cost goal of $10.12/GJ, LHV and if the projected crude oil process improvements are achieved, the allowable cost doubles to $5/GJ, LHV.

Figure 7 summarizes these results graphically.
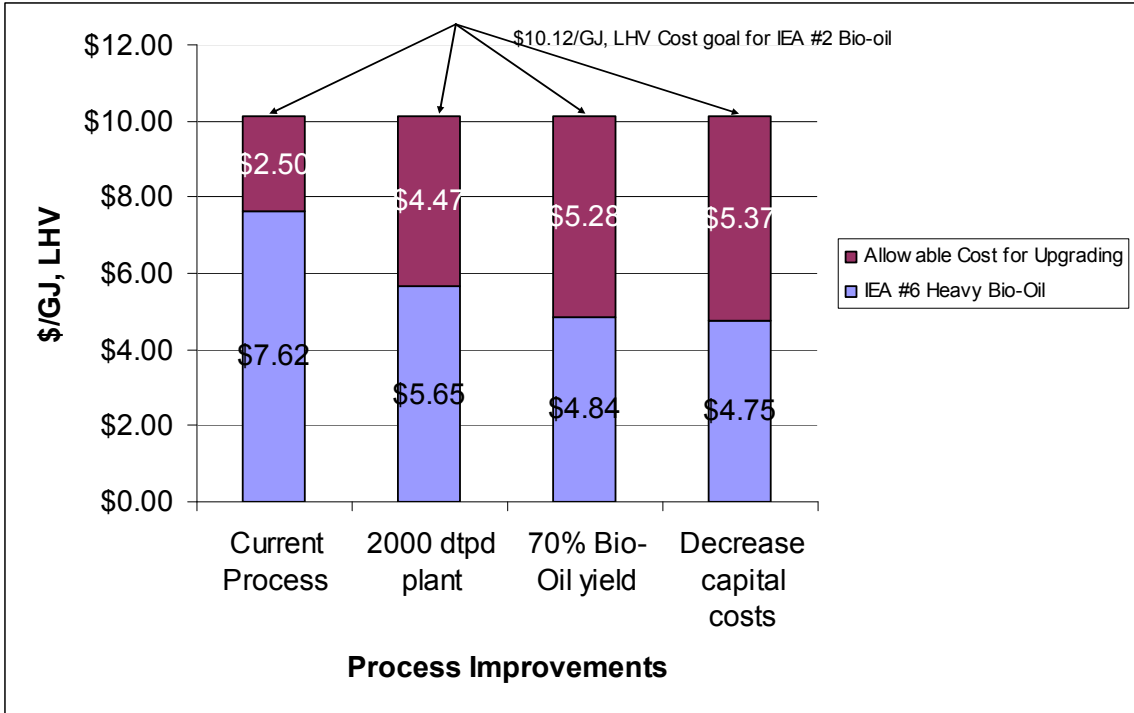
Figure 7. Bio-Oil Production and Upgrading Cost Goals

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Appendix A: ASPEN Plus® Model Implementation / Mass Balances

The ASPEN Plus® pyrolysis model is divided into eight flowsheets:

- A1000 – Feed Handling and Drying
- A2000 – Pyrolysis
- A3000 – Quench
- A4000 – Heat Recovery
- A5000 – Product Recovery and Storage
- A6000 – Recycle
- A7000 – Steam and Power Production
- A9000 – Utilities

Each of these areas will be briefly discussed and flow diagrams from ASPEN Plus® will be presented. The flow diagrams show only those unit operations modeled in ASPEN Plus®. Equipment used for operations such as conveyance, size reduction, and storage are generally not included in the model. The power requirements of this equipment, however, are included and are modeled as work streams in the utility section, A9000. Also, costs for all of the equipment are included in the economic analysis.

The mass for each section is included with each of the flow diagrams.

A1.1 A1000 – Feed Handling and Drying

Figure A1 shows the flowsheet for the feed drying area. Two unit operation models, a heater and a flash, model the wood chip dryer. The wood chip feed (1001) is milled and dried (DR-1001) using the preheated flue gases (1002) from the secondary condenser (HX-3002). The outlet moisture content is controlled to 7% [68] using a design-spec AIRDRY. The evaporated water (1004) is flashed in DR1001FL and sent off the flowsheet. The dried wood chips (1005) are sent to Pyrolysis (A2000).

All of the necessary heat for drying is supplied from gases heated from the condensing pyrolysis vapors (A3000). Due to convergence issues, the recycle stream (1007) was broken. However, the model ensures that the heat added to the recycle is more than sufficient to heat the incoming dryer air (1002).

The feed handling section has several pieces of equipment, (e.g., conveyors) which are not modeled in ASPEN Plus®. In fact, one of the most significant energy demands is the feedstock grinder. The power requirements to grind the wood to < 2 mm are estimated at 50 kWh/ton [83] and are calculated in the utility section (A9000).
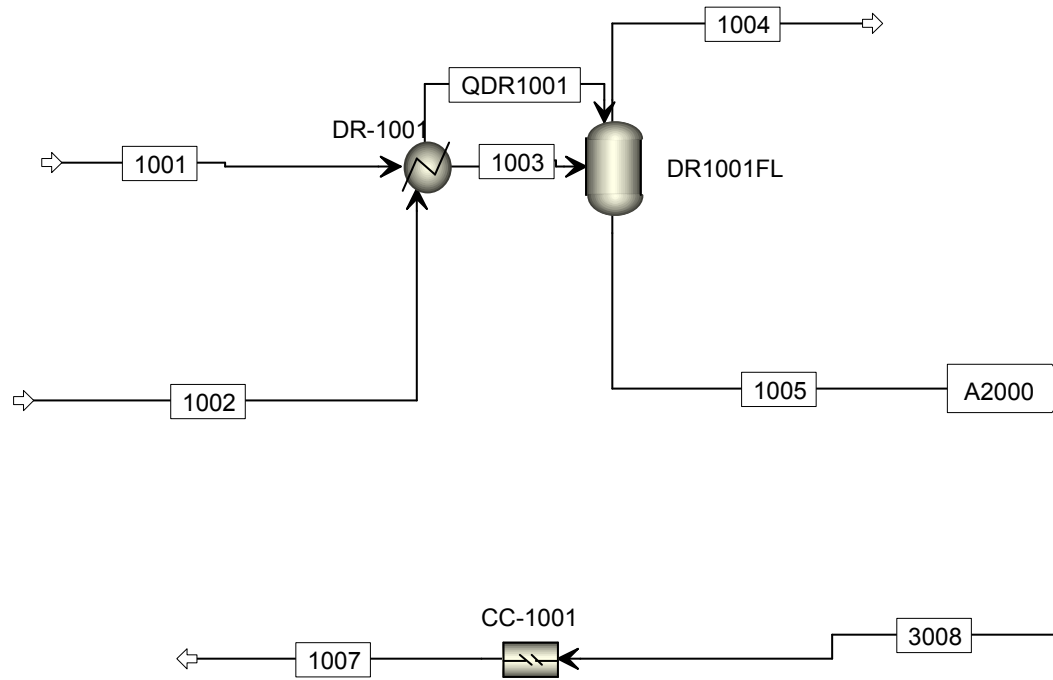
Figure A1 A1000 – Feedstock Handling and Drying

	1001	1002	1003	1004	1005	1007	3008
Mass Flow kg/hr							
N2	0.0	267209.0	267209.0	267209.0	0.0	264954.0	264954.0
O2	0.0	81135.4	81135.4	81135.4	0.0	81194.4	81194.4
H2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CO	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CO2	0.0	0.0	0.0	0.0	0.0	161.6	161.6
H2O	20789.6	0.0	20789.6	19222.5	1567.2	2315.4	2315.4
H3N	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CH4	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C2H4	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C3H6-2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
AR	0.0	0.0	0.0	0.0	0.0	4498.6	4498.6
C2H4O2-1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C3H6O2-D	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C7H8O2-E	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C8H10O3	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CH2O2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C10H12O3	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C6H6O	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C7H8	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C5H4O2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C6H6	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CHAR	0.0	0.0	0.0	0.0	0.0	0.0	0.0
ASH	0.0	0.0	0.0	0.0	0.0	0.0	0.0
WOOD	20789.6	0.0	20789.6	0.0	20789.6	0.0	0.0
Total Flow kg/hr	41579.3	348344.4	369134.0	367566.8	1567.2	353123.9	353123.9

Temperature	C		25.0	200.0	110.0	52.0	52.0	200.3	200.3
Pressure	psi		20.0	20.0	20.0	20.0	20.0	14.8	14.8
Enthalpy	MJ/hr		-427852.3	62125.2	-336599.0	-247680.0	-118056.0	30515.2	30515.2

Table A1. Mass Balance for Section A1000

A1.2 A2000 – Pyrolysis

As shown in Figure A2, the dried wood chips are fluidized (MX-2001) using recycled pyrolysis vapors (6008) at 200ºC in a 2.75:1 gas-to-feed ratio. The fluidizing gas rate is maintained with the design spec GASSPLT that controls the split in SP-6001. The solid/gas mixture is heated (HX-2001) to the pyrolysis temperature of 500ºC using heat from the char combustor (CB-4001).

The pyrolysis unit is modeled as an RSTOIC reactor. All of the incoming wood is converted to gas (e.g., CO, H_2), water, ash, char, or biocrude constituents (e.g., $C_2H_4O_2$). As noted in the design basis, the yield of biocrude is estimated at 59.9% of the dry wood feed. Heat for pyrolysis (QPY-2001) is supplied from the char combustor (CB-4001). The hot mix of solids, liquids and gases are sent to a bank of high efficiency cyclones (CY-2001) where the solids (e.g., ash and char) are separated (2005) from the gases and biocrude liquids (2004).

A1.3 A3000 – Quench

The pyrolysis reaction is rapidly quenched and the biocrude vapors are condensed in a series of two condensers: HX-3001 and HX-3002 shown in Figure A3. The first condenser is used to generate 515-psig steam (3010), which is then sent to the steam drum (V-7001). A design-spec BOILSTM is used to control the amount of steam generated. No biocrude is condensed from this stage.

In the second condenser (HX-3002), air (3007) is used as the cooling medium. The heated (200ºC) air is recycled back to the feedstock dryer (DR-1001). A design-spec, AIRFLOW1, controls the airflow to achieve the specified outlet temperature.

Any remaining aerosols in the vapor stream are removed in a scrubber (SC-3001) and wet ESP (ES-3001). The recovered liquids are sent to Product Recovery (A5000). The cleaned vapors (3006) are sent to Recycle (A6000) for recycle as the fluidizing medium.

A1.4 A4000 – Heat Recovery

The first unit operation in the heat recovery section (Figure A4) is the char and gas combustor (CB-4001). In reality, this combustor will be integral to the pyrolysis unit, but for modeling purposes, it is broken out. The combustor supplies the heat (QHX-2001) to preheat the feed/gas mixture (2001) before pyrolysis as well as the pyrolysis reactor (QPY-2001). A design-spec COMBADIA manipulates the temperature of the combustor to ensure adiabatic (i.e., QCB-4001 = 0) combustion. The combustor is modeled as an RSTOIC reaction, with ASPEN Plus® calculating the appropriate reactions; complete combustion is assumed.

Combustion air (4010) is combined with recycled product gases (2006) prior to the combustor. The amount of combustion air is maintained at 15% excess and is controlled with design-spec COMBAIR.

A6000 — 6008 → MX-2001 (MIXER)
A1000 — 1005 → MX-2001 (MIXER)
MX-2001 → 2001 → HX-2001+ → 2002 → PY-2001 → 2003 → CY-2001
CY-2001 → 2005 → MX-2002 (MIXER)
6006 — A6000 → MX-2002
MX-2002 → 2006 → A4000
2004
A3000
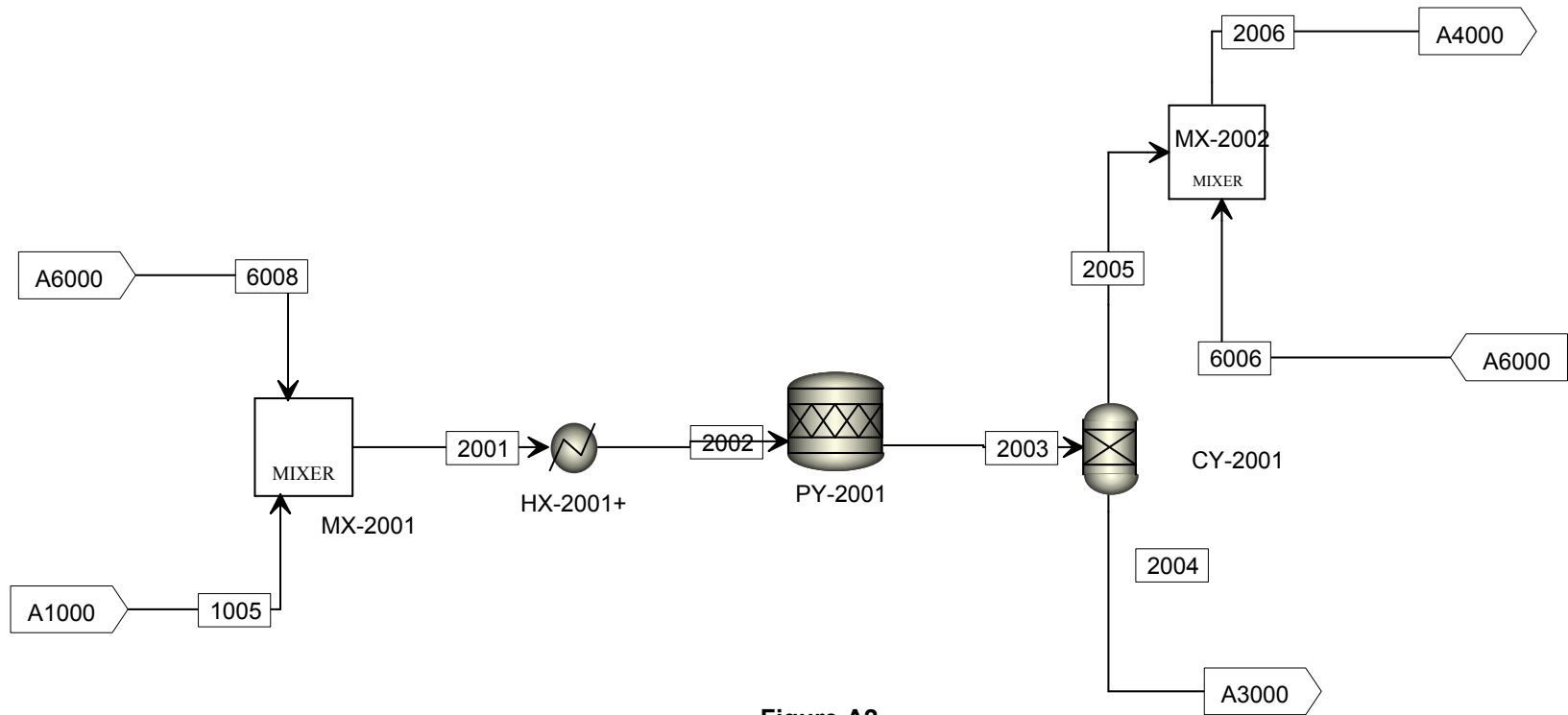
Figure A2

A2000 - Pyrolysis

	1005	2001	2002	2003	2004	2005	2006	6006	6008
Mass Flow kg/hr									
N2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
O2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
H2	0.0	2614.0	2614.0	2737.2	2737.1	0.0	123.1	123.1	2614.0
CO	0.0	28919.3	28919.3	30283.0	30281.5	0.0	1362.2	1362.2	28919.3
CO2	0.0	23953.2	23953.2	25080.1	25081.5	0.0	1128.3	1128.3	23953.2
H2O	1567.2	1571.5	1571.5	3818.6	3818.5	0.0	0.2	0.2	4.3
H3N	0.0	911.6	911.6	954.6	954.5	0.0	42.9	42.9	911.6
CH4	0.0	154.1	154.1	161.3	161.3	0.0	7.3	7.3	154.1
C2H4	0.0	628.6	628.6	658.2	658.2	0.0	29.6	29.6	628.6
C3H6-2	0.0	0.0	0.0	31.7	31.7	0.0	0.0	0.0	0.0
AR	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C2H4O2-1	0.0	0.3	0.3	1232.6	1232.6	0.0	0.0	0.0	0.3
C3H6O2-D	0.0	0.3	0.3	1520.6	1520.5	0.0	0.0	0.0	0.3
C7H8O2-E	0.0	0.0	0.0	127.5	127.5	0.0	0.0	0.0	0.0
C8H10O3	0.0	0.0	0.0	791.0	791.0	0.0	0.0	0.0	0.0
CH2O2	0.0	0.2	0.2	708.5	708.5	0.0	0.0	0.0	0.2
C10H12O3	0.0	0.0	0.0	3400.2	3400.2	0.0	0.0	0.0	0.0
C6H6O	0.0	0.0	0.0	96.7	96.7	0.0	0.0	0.0	0.0
C7H8	0.0	0.1	0.1	472.9	472.9	0.0	0.0	0.0	0.1
C5H4O2	0.0	0.9	0.9	3944.5	3944.5	0.0	0.0	0.0	0.9
C6H6	0.0	0.0	0.0	160.3	160.3	0.0	0.0	0.0	0.0
CHAR	0.0	0.0	0.0	3176.6	0.0	3176.6	3176.6	0.0	0.0
ASH	0.0	0.0	0.0	191.2	0.0	191.2	191.2	0.0	0.0
WOOD	20789.6	20789.6	20789.6	0.0	0.0	0.0	0.0	0.0	0.0
Total Flow kg/hr	1567.2	58754.0	58754.0	79547.4	76179.2	3367.8	9429.4	2693.7	57186.9

Temperature C		52.0	454.4	500.0	500.0	500.0	500.0	499.5	105.6	700.0
Pressure psi		20.0	20.0	20.0	20.0	20.0	20.0	20.0	45.0	45.0
Enthalpy MJ/hr		-118056.0	-380690.3	-372838.6	1179320.0	-372270.0	1551570.0	1536357.0	-15211.3	-262630.0

Table A2. Mass Balance for Section A2000.

Figure A3

A3000 - Quench

Mass Flow kg/hr														6001
N2	0.0	0.0	0.0	0.0	0.0	264954.0	264954.0	264954.0	0.0	0.0	0.0	0.0	0.0	0.0
O2	0.0	0.0	0.0	0.0	0.0	81194.4	81194.4	81194.4	0.0	0.0	0.0	0.0	0.0	0.0
H2	2737.1	2737.1	2737.1	0.0	2737.1	0.0	0.0	0.0	0.0	0.0	2737.1	0.0	0.0	2737.1
CO	30281.5	30281.5	30281.5	0.0	30281.5	0.0	0.0	0.0	0.0	0.0	30281.5	0.0	0.0	30281.5
CO2	25081.5	25081.5	25081.5	0.0	25081.5	161.6	161.6	161.6	0.0	0.0	25081.5	0.0	0.0	25081.5
H2O	3818.5	3818.5	3818.5	0.0	4491.6	2315.4	2315.4	2315.4	1470.9	1470.9	4.5	4487.1	673.1	4.5
H3N	954.5	954.5	954.5	0.0	954.5	0.0	0.0	0.0	0.0	0.0	954.5	0.0	0.0	954.5
CH4	161.3	161.3	161.3	0.0	161.3	0.0	0.0	0.0	0.0	0.0	161.3	0.0	0.0	161.3
C2H4	658.2	658.2	658.2	0.0	658.2	0.0	0.0	0.0	0.0	0.0	658.2	0.0	0.0	658.2
C3H6-2	31.7	31.7	31.7	29.8	7.5	0.0	0.0	0.0	0.0	0.0	0.0	7.5	5.6	0.0
AR	0.0	0.0	0.0	0.0	0.0	4498.6	4498.6	4498.6	0.0	0.0	0.0	0.0	0.0	0.0
C2H4O2-1	1232.6	1232.6	1232.6	1160.1	290.0	0.0	0.0	0.0	0.0	0.0	0.3	289.7	217.5	0.3
C3H6O2-D	1520.5	1520.5	1520.5	1431.1	357.8	0.0	0.0	0.0	0.0	0.0	0.4	357.4	268.3	0.4
C7H8O2-E	127.5	127.5	127.5	120.0	30.0	0.0	0.0	0.0	0.0	0.0	0.0	30.0	22.5	0.0
C8H10O3	791.0	791.0	791.0	744.5	186.1	0.0	0.0	0.0	0.0	0.0	0.2	185.9	139.6	0.2
CH2O2	708.5	708.5	708.5	666.8	166.7	0.0	0.0	0.0	0.0	0.0	0.2	166.5	125.0	0.2
C10H12O3	3400.2	3400.2	3400.2	3200.2	800.0	0.0	0.0	0.0	0.0	0.0	0.8	799.2	600.0	0.8
C6H6O	96.7	96.7	96.7	91.0	22.7	0.0	0.0	0.0	0.0	0.0	0.0	22.7	17.1	0.0
C7H8	472.9	472.9	472.9	445.0	111.3	0.0	0.0	0.0	0.0	0.0	0.1	111.1	83.4	0.1
C5H4O2	3944.5	3944.5	3944.5	3712.3	928.1	0.0	0.0	0.0	0.0	0.0	0.9	927.2	695.9	0.9
C6H6	160.3	160.3	160.3	150.9	37.7	0.0	0.0	0.0	0.0	0.0	0.0	37.7	28.3	0.0
CHAR	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
ASH	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
WOOD	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total Flow kg/hr	76179.2	76179.2	76179.2	11751.7	67303.7	353123.9	353123.9	353123.9	1470.9	1470.9	59881.6	7422.1	2876.2	59881.6

Temperature C													-	33.1
Pressure psi	20.0	20.0	20.0	20.0	20.0	14.7	14.8	14.8	515.0	515.0	20.0	20.0	40.0	20.0
Enthalpy MJ/hr	-372270.0	-376540.0	-442880.0	-42921.3	-421880.0	-36184.4	-35824.5	30515.2	-23544.2	-19275.6	-345170.0	-81619.8	-124530.0	-345170.0

Table A3. Mass Balance for Section A3000.
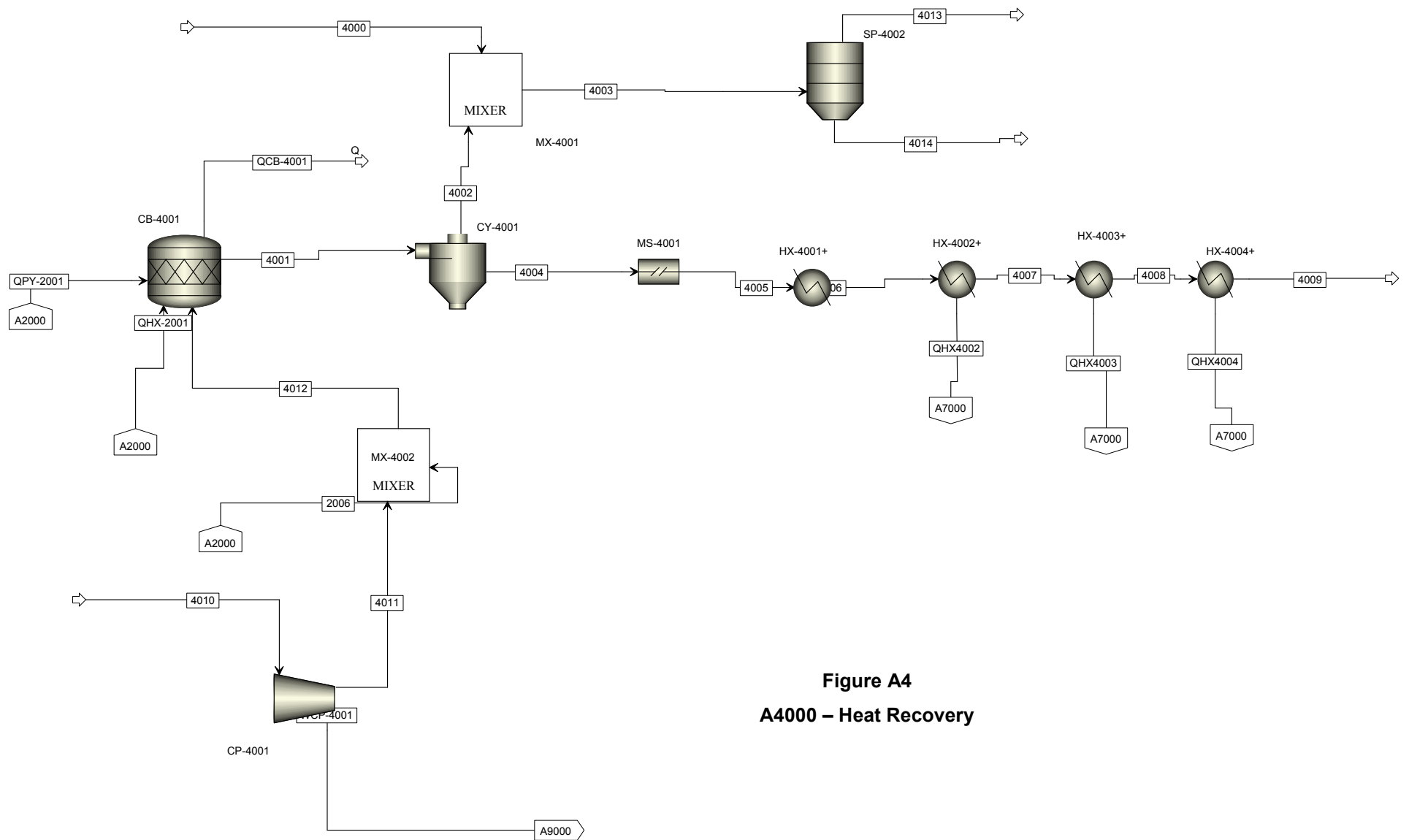
Figure A4

A4000 – Heat Recovery

															4014
Mass Flow kg/hr															
N2	0.0	0.0	37351.3	0.0	0.0	37351.3	37351.3	37351.3	37351.3	37351.3	37351.3	37351.3	37351.3	37351.3	0.0	0.0
O2	0.0	0.0	2349.6	0.0	0.0	2349.6	2349.6	2349.6	2349.6	2349.6	2349.6	11446.2	11446.2	11446.2	0.0	0.0
H2	123.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	123.1	0.0	0.0
CO	1362.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1362.2	0.0	0.0
CO2	1128.3	0.0	12780.9	0.0	0.0	12780.9	12780.9	12780.9	12780.9	12780.9	12780.9	22.8	22.8	1151.1	0.0	0.0
H2O	0.2	3316.1	2492.0	0.0	3316.1	2492.0	2492.0	2492.0	2492.0	2492.0	2492.0	326.4	326.4	326.6	2984.5	331.6
H3N	42.9	0.0	42.9	0.0	0.0	42.9	42.9	42.9	42.9	42.9	42.9	0.0	0.0	42.9	0.0	0.0
CH4	7.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	7.3	0.0	0.0
C2H4	29.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	29.6	0.0	0.0
C3H6-2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
AR	0.0	0.0	634.2	0.0	0.0	634.2	634.2	634.2	634.2	634.2	634.2	634.2	634.2	634.2	0.0	0.0
C2H4O2-1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C3H6O2-D	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C7H8O2-E	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C8H10O3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CH2O2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C10H12O3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C6H6O	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C7H8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C5H4O2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C6H6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CHAR	3176.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3176.6	0.0	0.0
ASH	191.2	0.0	191.2	191.2	191.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	191.2	1.9	189.3
WOOD	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Total Flow kg/hr																520.9
Temperature C	499.5	25.0	1796.6	1796.6	60.0	1796.6	1796.6	982.1	792.4	402.9	155.0	25.0	26.0	492.4	60.0	60.0
Pressure psi	20.0	20.0	14.8	14.8	14.8	14.8	14.8	14.8	14.8	14.8	14.8	14.7	14.8	14.8	14.8	14.8
Enthalpy MJ/hr	1536357.0	-53170.9	-28218.3	-2334.4	-55505.3	-25883.9	-25883.9	-86183.3	-99468.0	-125220.0	-140330.0	-4597.1	-4544.6	1531810.4	-47379.6	-8125.7

Table A4. Mass Balance for Section A4000.

The hot (> 1850ºC) combustion products are sent to a cyclone (CY-4001) where ash and non-combusted solids are removed (4002). The temperature of the solids is reduced to 60ºC through the addition of process water (4000). The addition of the water is controlled by H2OQUENH. A rotary filter (SP-4002) is used to separate the solids from the quench water. Both waste streams are sent off the flowsheet. The quench water (4013) is sent to wastewater treatment while the solids (4014) are landfilled.

The clean, hot flue gases (4004) are sent through a series of heat exchangers to recover heat for the process. The first exchanger, HX-4001+, is used to preheat the recycled product gases in HX-6002. The next three exchangers, HX-4002+ - HX-4004+, simulate the process side of a typical steam production system comprised of a superheater, economizer, and boiler feed water heater. These exchangers are coupled with the steam side of several exchangers in the steam production area (A7000).

The superheater is modeled as HX-4002+ (process side) coupled to HX-7003 (steam side). The 515 psig-saturated steam (7004 and 3010) is superheated to 620ºC prior to introduction into the steam turbine. The outlet temperature of the process side is manipulated by design-spec AIRPRHT to provide enough heat for superheating the steam. Additionally, if outside air is needed for the dryer (7006), it is heated here.

The economizer is modeled as HX-4003+ (process side) coupled to HX-7002). The design-spec ECOMZER manipulates the flue gas temperature to vaporize all of the inlet water to HX-7002.

The boiler water preheater is modeled by coupling HX-4004+ and HX-7001. The flue gas outlet (4009) temperature is specified at 155ºC. The boiler feed water (7001) rate is manipulated by the design-spec H2ORECY.

A1.5 A5000 – Product Recovery and Storage

The Product Recovery and Storage flowsheet, shown in Figure A5, is very simple and consists of a mixer (MX-5001), a pump (P-5001), and a cooler (HX-5001). The mixer combines products recovered from areas A3000 and A6000. It is pumped to the cooler (HX-5001), where it is cooled to 20 ºC using cooling water.

The area will also include a storage tank (T-7001), sized for 7 days storage, and a product transfer pump (P-7002). These are not modeled, but are included in the equipment costs.

A1.6 A6000 – Recycle

As shown in Figure A6, vapors (6001) from the initial product condensation steps in A3000 are sent to a tertiary condenser (HX-6001) where chilled water is used to cool the stream to 7ºC, resulting in further product recovery. The chilled stream is flashed (FL-6001) and the condensed product is sent to A5000, Product Recovery and Storage where it is combined with additional product.

The flashed vapor stream (6004) is compressed for recycle as a fluidizing medium. The amount of gas required for fluidization is estimated at 2.75 lb gas/lb pyrolysis feed [66] and is controlled by the design-spec GASSPLT, which specifies the split of recycle gas (6007) in SP-6001. The recycle gas is heated to 700ºC in HX-6002 using heat from the char combustor flue gas (CB-4001) in the air preheater, HX-4001. This heat transfer is controlled with design-spec AIRPRHT.

The vapors that are not needed for fluidization (6006) are recycled back to Heat Recovery, A4000, to provide heat for the process.

A1.7 A7000 – Steam and Power Production

Many of the unit operations and much of the logic in this area (Figure A7) have already been discussed in A4000 and will not be repeated here. Steam from the economizer (HX-7002) and the waste heat recovery boiler (HX-3001) are combined in the steam drum, V-7001, and sent to the steam turbine, TB-7001. Here, power is generated in a condensing turbine with an outlet pressure of 1.47 psig. Over 5,000 kW of electrical power is generated. The turbine outlet (7011) is condensed in the turbine condenser (CD-7001) with cooling water. Blowdown (7013) is estimated at 3% of the steam system requirement. This blowdown value is used to determine the steam system make-up.

A1.8 A9000 – Miscellaneous Utilities

The miscellaneous utilities flowsheet shown in Figure A8 is basically a summary flowsheet that calculates the total utilities (e.g., cooling water, power) for the other flowsheets.

The overall power requirements for the facility are calculated in MX-9000. This block sums all of the power demands from the modeled pumps and compressors as well as the solids handling equipment that were not specifically modeled. The power requirements for the solids handling equipment are specified in the FORTRAN block MISCPOW and are based on the Questimate® equipment specifications. Each power demand, except grinding, is scaled from the dry wood feed rate (1001). The grinding power demand (50 kWh/ton) is scaled from the total dried wood rate (1005).

The cooling tower is sized based on a supply temperature of 16 ºC and a maximum temperature rise of 8ºC. The heat demands from the turbine condenser (9002) and the product cooler (9004) are summed in MX-9001 and an overall cooling water demand is projected (9005).

The pyrolysis system also requires chilled water to recover product in the tertiary condenser. The chilled water system is designed for a –18˚C supply temperature and a –12 ˚C return temperature.

Process water is also required for quenching and other uses. The overall process water demand is calculated as the sum of the quench water (4000) and boiler blowdown (7013). The facility will also require process and instrument air. These utilities were not included in the ASPEN Plus® model, but their capital costs will be included in the economic analysis.
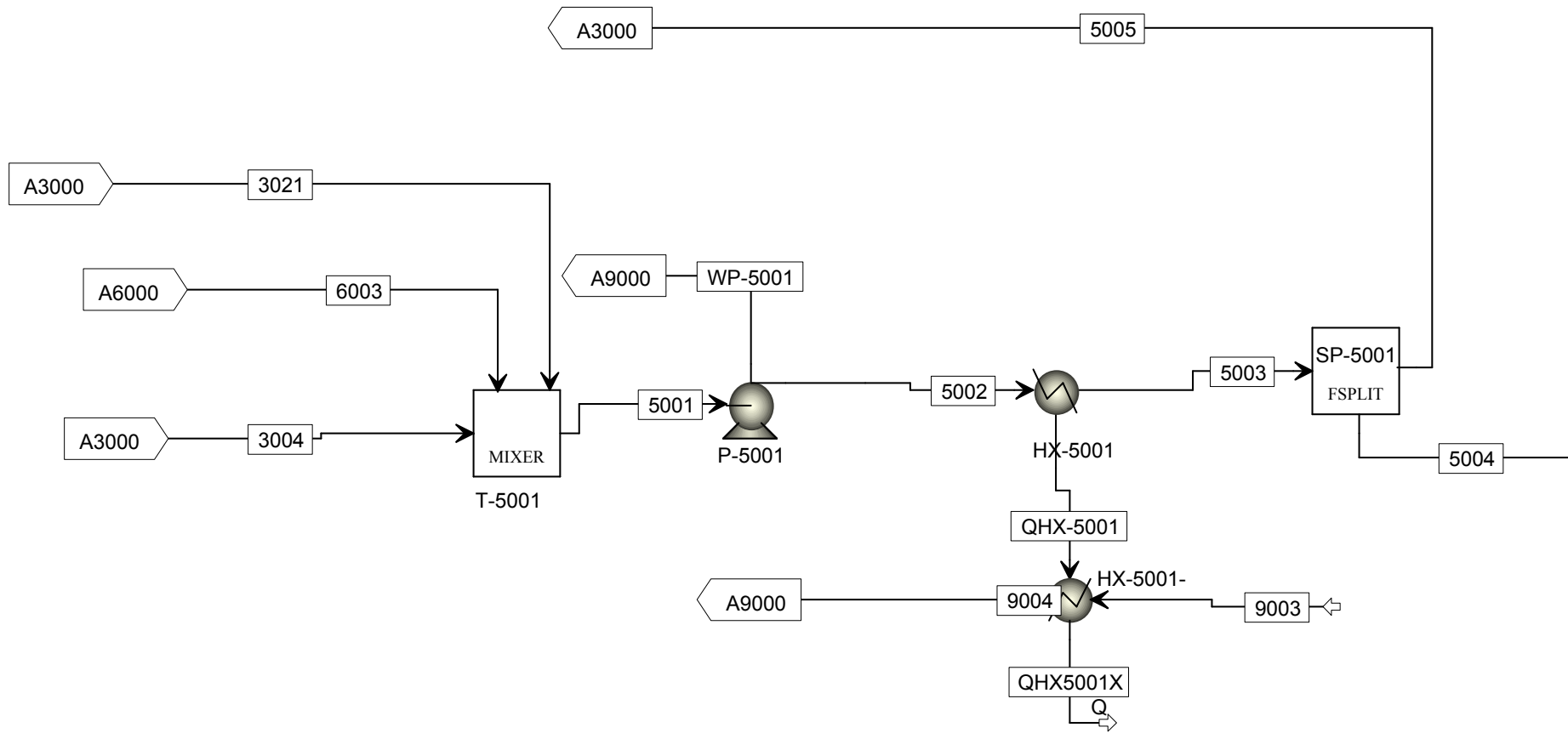
Figure A5

	3004	3021	5001	5002	5003	5004	5005	6003	9003	9004
Mass Flow kg/hr										
N2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
O2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
H2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CO	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CO2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
H2O	0.0	4487.1	4487.2	4487.2	4487.2	3814.2	673.1	0.0	14804.8	14804.8
H3N	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CH4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C2H4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C3H6-2	29.8	7.5	37.3	37.3	37.3	31.7	5.6	0.0	0.0	0.0
AR	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C2H4O2-1	1160.1	289.7	1449.8	1449.8	1449.8	1232.4	217.5	0.0	0.0	0.0
C3H6O2-D	1431.1	357.4	1788.5	1788.5	1788.5	1520.2	268.3	0.0	0.0	0.0
C7H8O2-E	120.0	30.0	150.0	150.0	150.0	127.5	22.5	0.0	0.0	0.0
C8H10O3	744.5	185.9	930.6	930.6	930.6	791.0	139.6	0.2	0.0	0.0
CH2O2	666.8	166.5	833.4	833.4	833.4	708.4	125.0	0.0	0.0	0.0
C10H12O3	3200.2	799.2	4000.2	4000.2	4000.2	3400.2	600.0	0.8	0.0	0.0
C6H6O	91.0	22.7	113.7	113.7	113.7	96.7	17.1	0.0	0.0	0.0
C7H8	445.0	111.1	556.2	556.2	556.2	472.8	83.4	0.0	0.0	0.0

C5H4O2	3712.3	927.2	4639.5	4639.5	4639.5	3943.6	695.9	0.0	0.0	0.0
C6H6	150.9	37.7	188.6	188.6	188.6	160.3	28.3	0.0	0.0	0.0
CHAR	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
ASH	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
WOOD	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total Flow kg/hr	11751.7	7422.1	19175.0	19175.0	19175.0	16298.7	2876.2	1.0	14804.8	14804.8
Temperature C	33.1	33.1	35.7	35.9	25.0	-6.4	-6.4	7.0	21.1	35.1
Pressure psi	20.0	20.0	26.0	40.0	40.0	40.0	40.0	20.0	15.0	15.0
Enthalpy MJ/hr	-42921.3	-81619.8	-124530.0	-124530.0	-125530.0	-106700.0	-18829.4	-2.9	-237660.0	-236660.0

Table A5. Mass Balance for Section A5000.
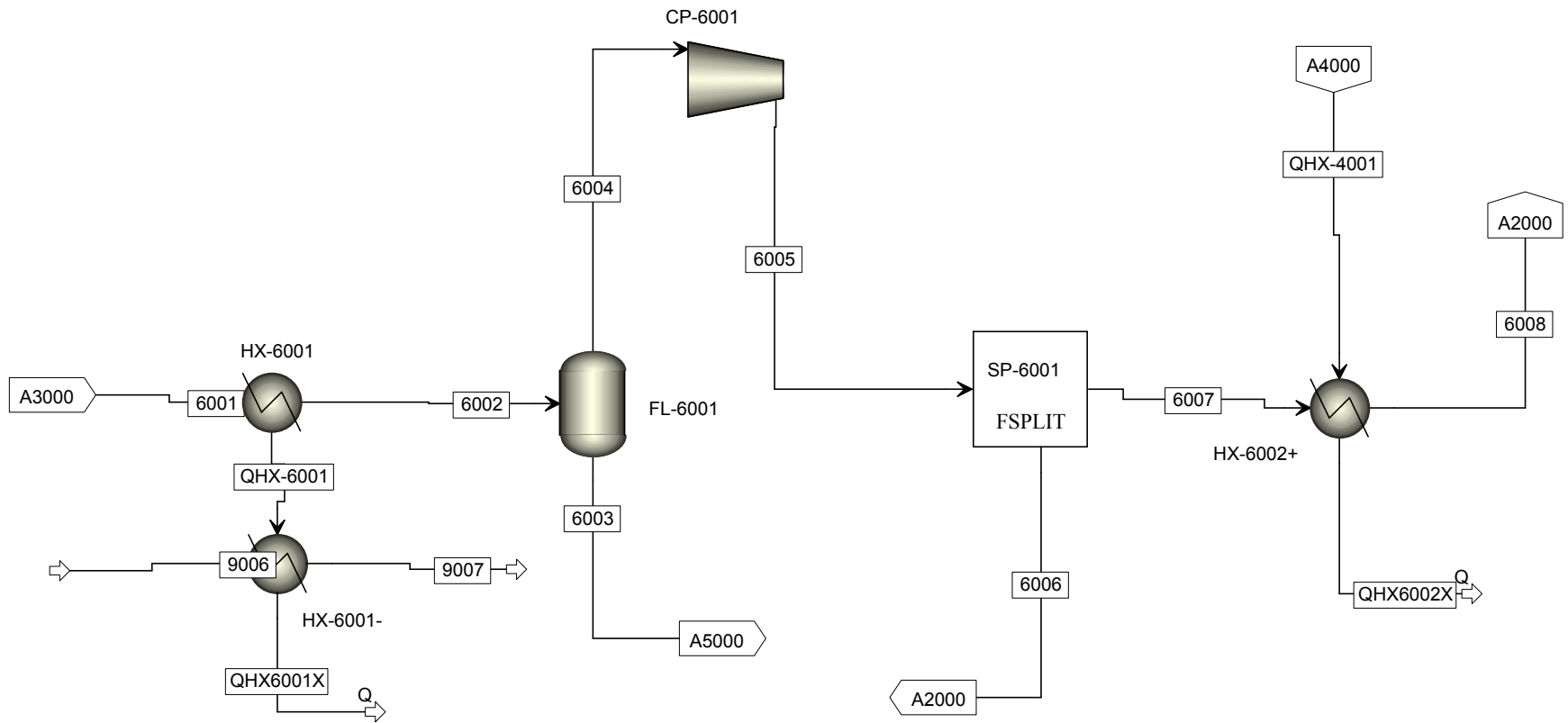
Figure A6

A6000 – Product Storage

	6001	6002	6003	6004	6005	6006	6007	6008	9006	9007
Mass Flow kg/hr										
N2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
O2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
H2	2737.1	2737.1	0.0	2737.1	2737.1	123.1	2614.0	2614.0	0.0	0.0
CO	30281.5	30281.5	0.0	30281.5	30281.5	1362.2	28919.3	28919.3	0.0	0.0
CO2	25081.5	25081.5	0.0	25081.5	25081.5	1128.3	23953.2	23953.2	0.0	0.0
H2O	4.5	4.5	0.0	4.5	4.5	0.2	4.3	4.3	64197.7	64197.7
H3N	954.5	954.5	0.0	954.5	954.5	42.9	911.6	911.6	0.0	0.0
CH4	161.3	161.3	0.0	161.3	161.3	7.3	154.1	154.1	0.0	0.0
C2H4	658.2	658.2	0.0	658.2	658.2	29.6	628.6	628.6	0.0	0.0
C3H6-2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
AR	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C2H4O2-1	0.3	0.3	0.0	0.3	0.3	0.0	0.3	0.3	0.0	0.0
C3H6O2-D	0.4	0.4	0.0	0.4	0.4	0.0	0.3	0.3	0.0	0.0
C7H8O2-E	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C8H10O3	0.2	0.2	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CH2O2	0.2	0.2	0.0	0.2	0.2	0.0	0.2	0.2	0.0	0.0
C10H12O3	0.8	0.8	0.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C6H6O	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C7H8	0.1	0.1	0.0	0.1	0.1	0.0	0.1	0.1	0.0	0.0

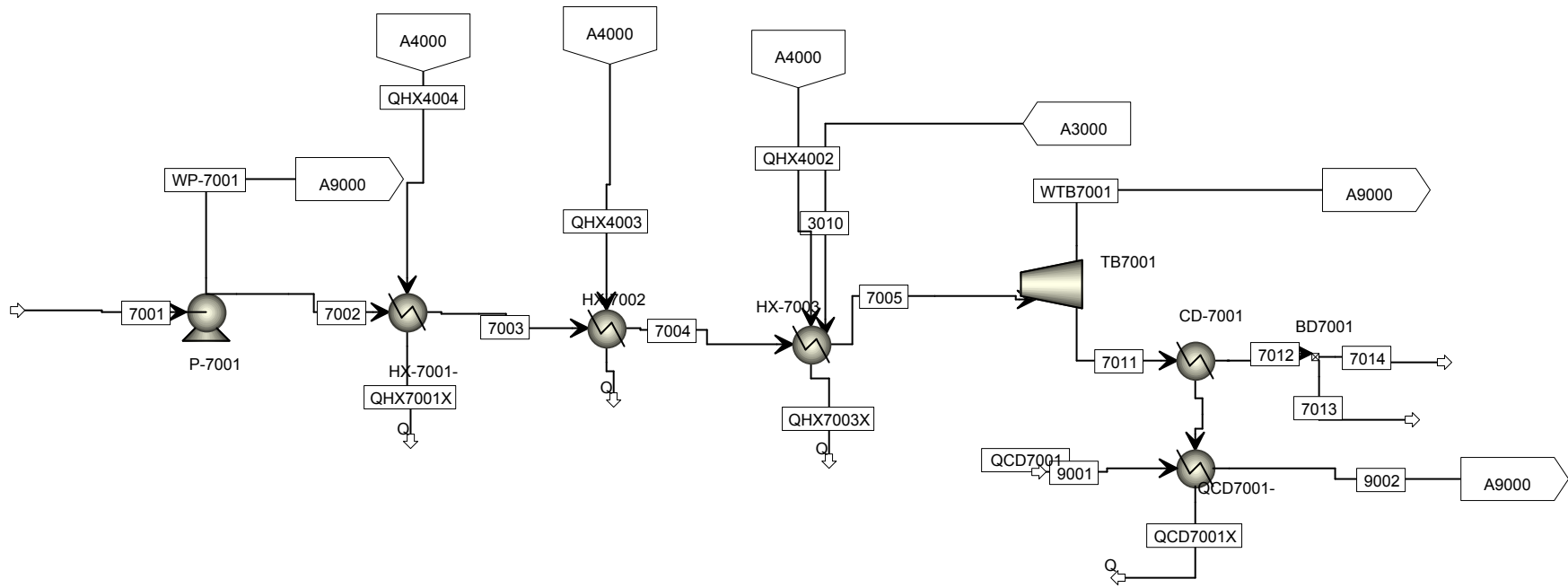|									
C5H4O2	0.9	0.9	0.0	0.9	0.9	0.0	0.9	0.9	0.0	0.0
C6H6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CHAR	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
ASH	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
WOOD	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total Flow kg/hr	59881.6	59881.6	1.0	59880.6	59880.6	2693.7	57186.9	57186.9	64197.7	64197.7
Temperature C	33.1	7.0	7.0	7.0	105.6	105.6	105.6	700.0	4.0	12.0
Pressure psi	20.0	20.0	20.0	20.0	45.0	45.0	45.0	45.0	15.0	15.0
Enthalpy MJ/hr	-345170.0	-347650.0	-2.9	-347650.0	-338140.0	-15211.3	-322930.0	-262630.0	-1035900.0	-1033400.0

Table A6. Mass Balance for Section A6000.

Figure A7

A7000 – Product Storage

	3010	7001	7002	7003	7004	7005	7011	7012	7013	7014	9001	9002
Mass Flow kg/hr												
N2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0	0
O2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0	0
H2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0	0
CO	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0	0
CO2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0	0
H2O	1470.9	14106.5	14106.5	14106.5	14106.5	15577.4	15577.4	15577.4	467.3	15110.0	585107	585107
H3N	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0	0
CH4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0	0
C2H4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0	0
C3H6-2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0	0
AR	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0	0
C2H4O2-1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0	0
C3H6O2-D	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0	0
C7H8O2-E	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0	0
C8H10O3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0	0
CH2O2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0	0
C10H12O3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0	0
C6H6O	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0	0
C7H8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0	0

|												
C5H4O2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0	0
C6H6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0	0
CHAR	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0	0
ASH	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0	0
WOOD	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0	0
Total Flow kg/hr	1470.9	14106.5	14106.5	14106.5	14106.5	15577.4	15577.4	15577.4	467.3	15110.0	585107	585107
Temperature C	242.1	30.0	31.1	242.0	242.1	620.0	50.3	50.3	50.3	50.3	21.1	35.0
Pressure psi	515.0	20.0	515.0	515.0	515.0	515.0	1.5	1.5	1.5	1.5	16.0	16.0
Enthalpy MJ/hr	-19275.6	-225850.0	-225720.0	-210610.0	-184860.0	-190850.0	-208740.0	-247880.0	-7436.3	-240440.0	-9392700.0	-9353600.0

Table A7. Mass Balance for Section A7000.
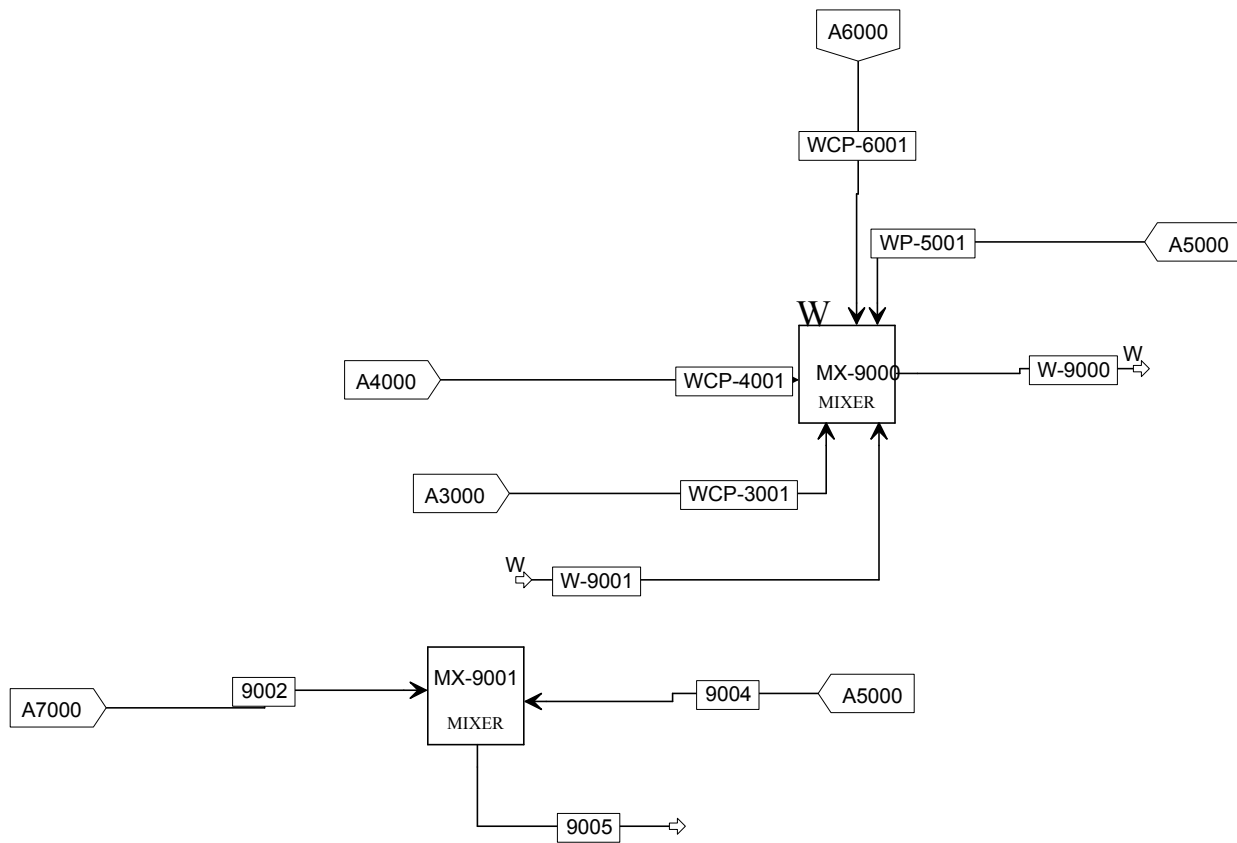
Figure A8

A9000 – Product Storage

		9003	9004	9005
Mass Flow kg/hr				
N2				0
O2		0	0	0
H2		0	0	0
CO				0
CO2		0	0	0
H2O		14804.79	14804.79	599912
H3N				0
CH4		0	0	0
C2H4		0	0	0
C3H6-2				0
AR		0	0	0
C2H4O2-1		0	0	0
C3H6O2-D				0
C7H8O2-E		0	0	0
C8H10O3		0	0	0
CH2O2				0
C10H12O3		0	0	0
C6H6O		0	0	0
C7H8		0	0	0

C5H4O2	0	0	0
C6H6			0
CHAR	0	0	0
ASH	0	0	0
WOOD			0
Total Flow kg/hr	14804.79	14804.79	599912
Temperature C	21.11111	35.11111	35.00334
Pressure psi			15
Enthalpy MJ/hr	-237660	-236660	-9590200

Table A8. Mass Balance for Section A9000.

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