

DEPARTMENT OF  
**ECOLOGY**  
State of Washington

WASHINGTON STATE  
 UNIVERSITY

# **Methods for Producing Biochar and Advanced Bio-fuels in Washington State**

## **Part 3: Literature Review**

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*Technologies for Product Collection and Refining*

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## **Part 3: Literature Review**

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*Technologies for Product Collection and Refining*

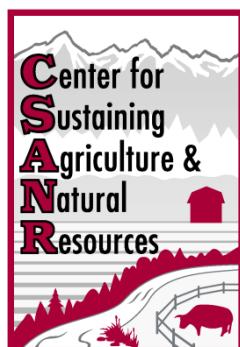
*by*

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Washington State University**



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This report is the third of a series of four reports available on the Department of Ecology's website at: [www.ecy.wa.gov/beyondwaste /organics](http://www.ecy.wa.gov/beyondwaste /organics). The reports are titled: Methods for Producing Biochar and Advanced Biofuels in Washington State. They are as follows:

- Part 1: Literature Review of Pyrolysis Reactors. This report reviews the technologies that have been developed for kilns, retorts and pyrolyzers. It can be found at:  
<http://www.ecy.wa.gov/biblio/1107017.html>.
- Part 2: Literature Review of the Biomass Supply Chain and Preprocessing Technologies. (From Field to Pyrolysis Reactor). This report reviews biomass sources, collection, and pretreatment. It can be found at: <http://www.ecy.wa.gov/biblio/1207033.html>.
- Part 3: Literature Review of Technologies for Product Collection and Refining. The report describes technologies and methods for bio-oil products recovery and characterization, biochar activation, bio-oil refining strategies and regulatory issues related with deployment of pyrolysis technologies. It can be found at: <http://www.ecy.wa.gov/biblio/1207034.html>.
- Part 4: Literature Review of Sustainability Goals, Business Models, and Economic Analyses. This report focuses on the criteria that need to be followed to integrate these technologies into sustainable business models. The last report presents sustainability criteria and several business models that could be used to build sustainable enterprises based on biomass pyrolysis technologies. It can be found at: <http://www.ecy.wa.gov/biblio/1207035.html>.

Some figures and photos in this report can be seen in color in the online file. Additional project reports supported by Organic Wastes to Fuel Technology sponsored by Ecology are also available on this web site. This report is also available at the Washington State University Extension Energy Program library of bioenergy information at [www.pacificbiomass.org](http://www.pacificbiomass.org).

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## **Beyond Waste Objectives**

Turning organic waste into resources, such as compost and bio-fuels, and the recovery of stable carbon and nutrients along with other products, promotes economic vitality in growing industries, and protects the environment. This creates robust markets and sustainable jobs in all sectors of the economy, and facilitates closed-loop materials management where a by-product from one process becomes feedstock for another with no waste generated.

## **Disclaimer**

The objective of this series of reviews is to describe existing technologies to create clean, non-polluting pyrolysis units for producing energy, fuels and valuable by-products. The Department of Ecology and Washington State University provide this publication to the public to help individuals interested in the develop of a biomass pyrolysis industry to identify suitable technologies for bio-oil condensers, pyrolysis vapor combustion, removal, cooling, briquetting, pelletization and activation of biochar and bio-oil refineries. This review also summarizes the analytical techniques needed to characterize bio-oils and biochars and the permits needed to implement a biomass pyrolysis industry in Washington State. Another major goal of this project is to identify what new technologies need to be developed or what hurdles need to be overcome to convert organic waste resources available in Washington State into valuable products. This review does not represent an endorsement of the processes described and is not intended to exclude any technology or company offering similar services, that due to time and space limitations was not cited.

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# Executive Summary

This is the third report of a serie named “Methods for Producing Biochar and Advanced Bio-fuels in Washington State”, which describes technologies and methods for products recovery, products characterization, biochar activation, bio-oil refining strategies and regulatory issues related with deployment of pyrolysis technologies.

The first section of this report describes technologies for the recovery of bio-oil, biochar, and for combusting pyrolysis vapors for heat production. Systems for bio-oil collection formed by one, two or multi-step condensers and for the combustion of pyrolysis vapors are described. Likewise this report describes some of the most common designs for biochar removal and cooling.

The second and third sections deal with methods to characterize pyrolysis oils and biochars. These methods are critical to ensure a good products quality. According to the International biochar initiative (<http://www.biochar-international.org/biochar>), “*biochar is a solid material obtained from the carbonization of biomass. Biochar may be added to soils with the intention to improve soil functions and to reduce emissions from biomass that otherwise naturally degrade to greenhouse gases. Biochar also has appreciable carbon sequestration value. These properties are measurable and verifiable in a characterization scheme, or in a carbon emission offset protocol*” . Thus, biochar characterization is critical for the commercialization of these products. The chemicals that could be obtained from bio-oil and the bio-oil refinery concepts that have been evaluated so far are discussed in the fifth section.

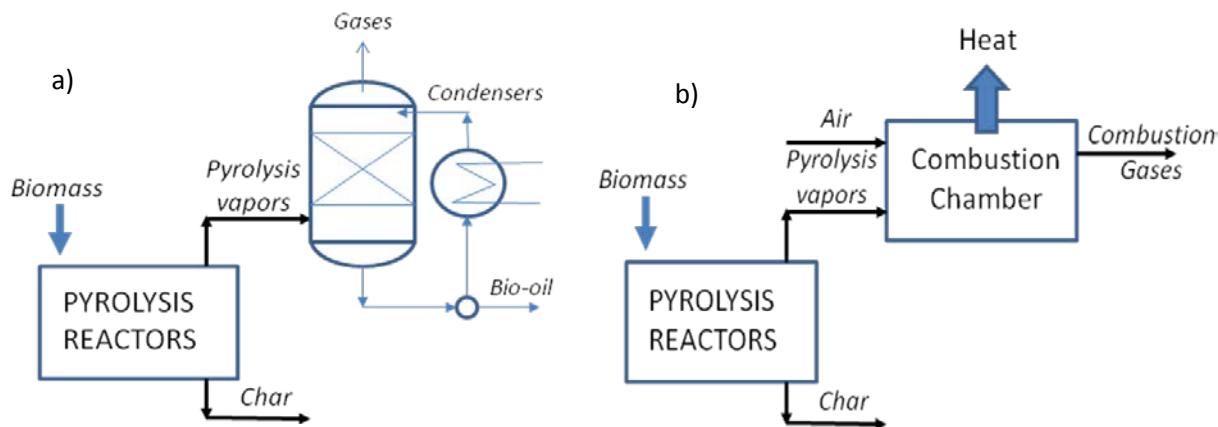
Options for using biochar in industrial applications (activated carbon and metallurgical application), household markets, and agricultural and silvicultural applications (soil amendment, fertilizers, and carbon sequestration) are also discussed in this section.

The final section deals with regulatory issues that need to be taken into account to deploy pyrolysis technologies. Material safety data sheets (MSDS) for the safe use, handling, storage and transportation of pyrolysis liquids and biochars as well as the environmental controls, permitting and Waste Streams are explained.

# 1. Introduction

This report is the third in a series of reports describing technologies needed to build an industry based on pyrolysis. The first report reviews the evolution of pyrolysis technologies and designs for slow and fast pyrolysis reactors. The second report discusses equipment needed to build the biomass supply chain (biomass harvest, densification and transport) and for biomass pre-processing (grinding, screening, and drying). This report describes designs to recover products (bio-oil condensers, incinerators with heat recovery, charcoal coolers and charcoal pelletizers) and for product utilization.

A pyrolysis unit typically consists of the equipment for biomass pre-processing, the pyrolysis reactor, and equipment for downstream processing. Most pyrolysis reactors can be classified as units that produce heat and biochar (using slow pyrolysis) or units that produce biochar and bio-oils (using fast pyrolysis) (Figure 1).



**Figure 1. Strategies for pyrolysis reactors: a) biochar and bio-oil production b) biochar and heat production.**

This report is intended to help those interested in developing a biomass pyrolysis industry identify suitable technologies for bio-oil condensers, pyrolysis vapor combustion, charcoal removal, cooling, briquetting, pelletization and activation, and bio-oil refineries. It also summarizes analytical techniques needed to characterize bio-oils and biochars and permits needed to implement a biomass pyrolysis industry in Washington State.

Methods to characterize bio-oil and biochar products, described in this report, are critical to identify techniques and instrumentation to control product quality. A review of the potential environmental impact of these technologies and potential health and safety issues associated with operating these systems is included to help prevent accidents, reduce the environmental impacts, and create a healthy working environment. The aim is to alert designers and operators to potential environmental issues so they can design a process that will meet or exceed standards.

As stated in the previous reports, pyrolysis technologies with oil recovery will not grow unless a market for bio-oil is developed. Thus, a review of the potential fuel, chemicals, and other materials that can be obtained from bio-oils is also presented. Although limited, the review of technologies for bio-oil refineries provides a general overview of existing options and concepts. Together, the information in these three reports is fundamental for selecting technologies to create a biomass economy based on pyrolysis in Washington State.

## 2. Products Recovery

This section describes downstream processing operations for the recovery of bio-oil, biochar, and heat including bio-oil condensation, combustion chambers and incinerators, and charcoal processing.

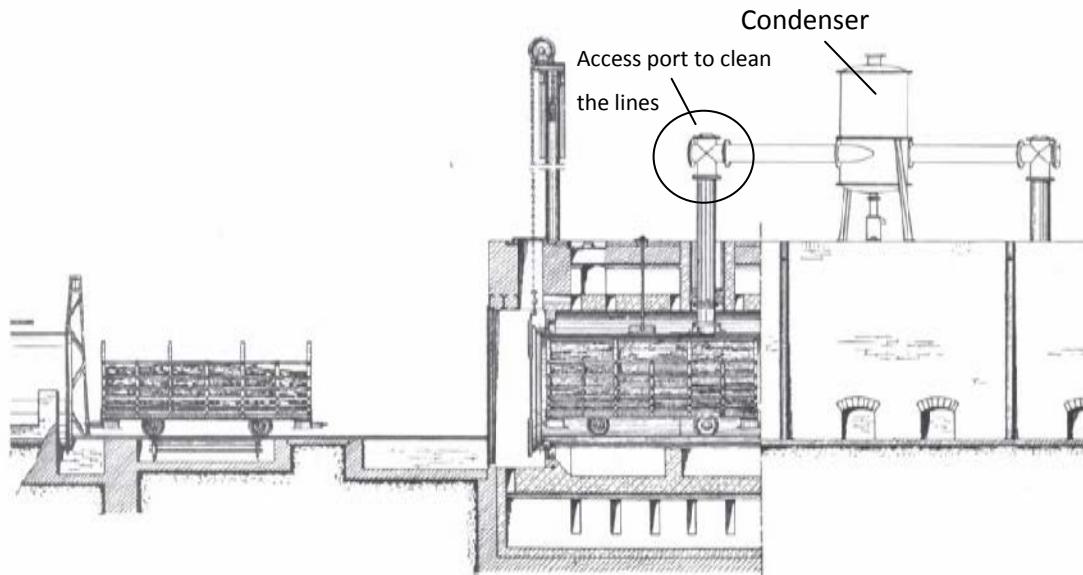
### 2.1. Bio-oil Condensation

A very important aspect of a pyrolysis plant is the bio-oil condensation process. Either single-phase or multi-phase pyrolysis oils may be collected during condensation depending on the feedstock, reactor and the condensation system employed. Although scrubbers and heat exchangers have been used by the petroleum and chemical industries for many years, the knowledge gained cannot be directly extrapolated to the design of bio-oil condensers due to the presence of acids and the low thermal stability of bio-oils. Fractional condensation systems were commonly used by the old wood distillation industry, however, few pyrolysis companies use fractional condensers to separate the water and acids from the pyrolysis oil. In fact, the modeling and performance of these systems is regaining interest in the academic community (Westerhof et al 2007, 2011).

The liquid collected from the fast pyrolysis of woody materials is typically a homogeneous liquid referred to as “bio-oil”. Meanwhile, the liquid collected from the slow pyrolysis of woody materials is formed by two separated phases sometimes called “decanted oil and pyroligneous acid/aqueous phase”. Lignin derived compounds are abundant in the decanted oil. Water and polar compounds in the pyroligneous acid mostly derives from cellulose and hemicelluloses. An important fraction of mono-phenols remains in the aqueous phase. The formation of tarry products (viscous black sticky oils) occurs when these mono-phenols continue to react with aldehydes which will gradually increase the yield of decanted oils (Bunbury 1926).

In order to minimize secondary reactions and maximize oil yields, pyrolysis vapors must be quenched and condensed very rapidly (Bridgewater and Brown, 2006). Condensers must be designed for easy cleaning because clogging and tarrying can occur both inside the pipes between the reactor and condenser or in the condenser itself (Bunbury 1926; Klar and Rule 1925). Condensation can be mitigated by keeping lines short and temperature over 420 °C (Klar and Rule 1925).

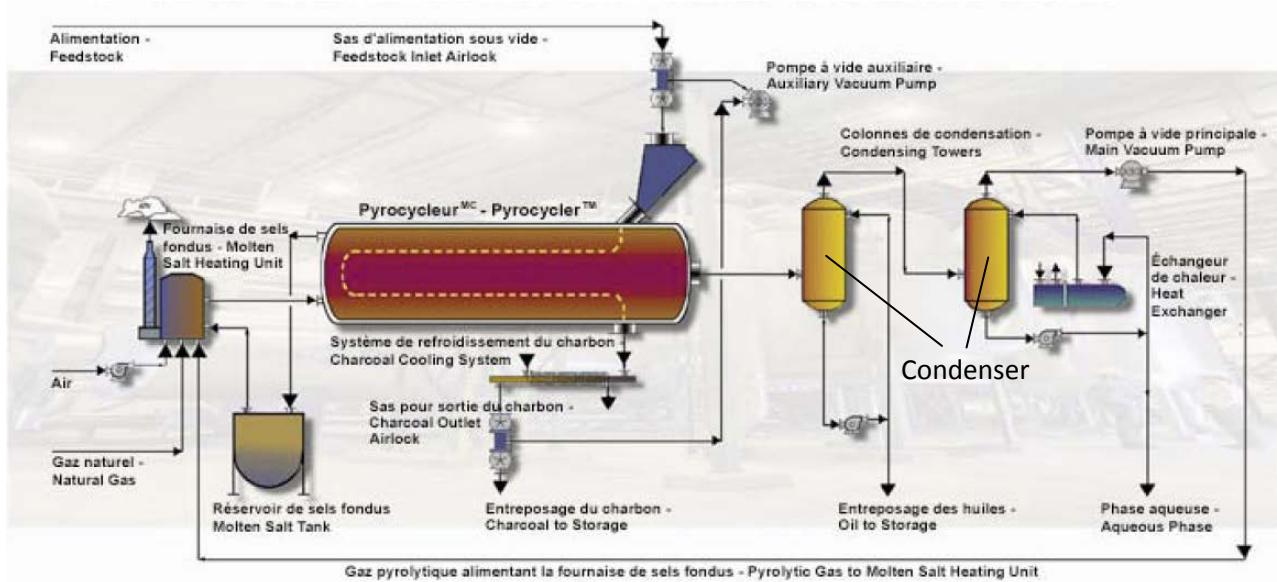
Figure 2 shows a configuration of a wagon reactor coupled with a Meyer condenser which typically collects decanted oil and pyrolygneous water. Access ports to clean the vapor lines connecting the reactor and the retort are important and should be taken into account when designing pyrolysis units.



**Figure 2. Cylindrical oven retort arrangement including a Meyer condenser (Source: Bunbury 1926).**

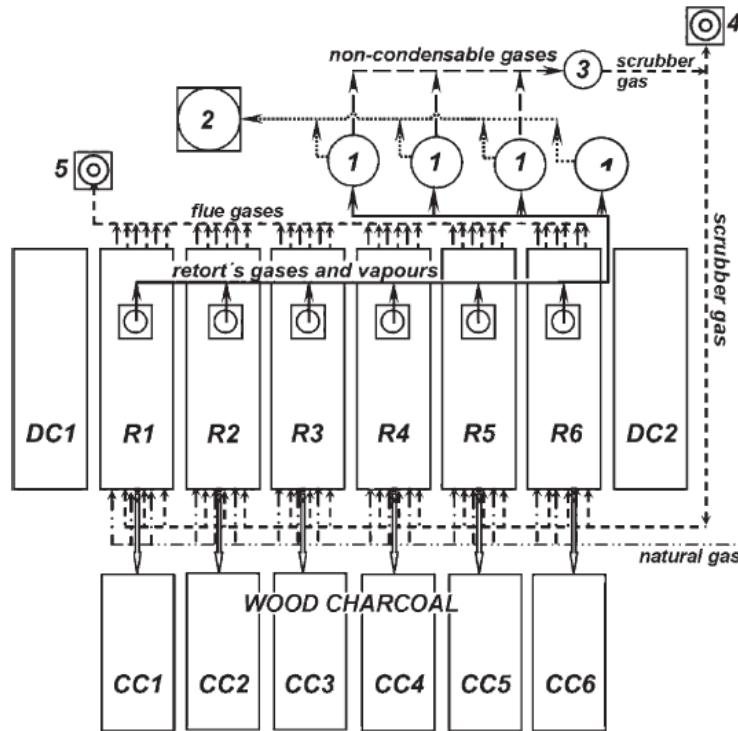
Liquids with distinctive chemical compositions can be produced using two or multi-step condensers. Lower water content and fewer light organic compounds are found in oils condensed at higher temperatures. As temperature in the first condenser increases (while maintaining the temperature of the second condenser at 25 °C), the liquid collected downstream will likely be in aqueous phase with high water content. Condensers of a vacuum pyrolysis plant (built at Jonquiere by the Pyrovac Institute in collaboration with Laval University) are shown in Figure 3.

This plant collects a stream rich in heavier molecules ( $C_{6+}$ ) and an aqueous phase rich in light organic compounds ( $C_1-C_4$  oxygenated molecules) and water. The acid content of bio-oils can drastically be reduced by carefully controlling the temperature of the first condenser (Westerhof et al. 2011). With the use of bio-oil hydrotreatment, the heavy fraction ( $C_{6+}$ ) enriched compounds can be transformed into transportation fuels. The old wood distillation industry targeted the fraction collected in the second condenser as it is rich in acids that were separated and commercialized as the final product of this technology.



**Figure 3. The Pyrocycling™ process using a two step condensation system (source: <http://newearth1.net/ecopyrotorrefaction.html>).**

A processing plant (Belišće, Croatia) with bio-oil condensers coupled with slow pyrolysis reactors is shown in Figure 4 (Thomas et al. 2009). With six water-cooled condensers and six retorts, this is a classic example of a batch system with condensers (Tomas et al. 2009). Due to the “violent phase of carbonization” (a drastic increase in the generation of pyrolysis vapors at around 350 °C), designing condensers for a batch system is a complex task. A greater surface area for cooling is required during this phase than for the remainder of the process. This can consequently increase the capital cost drastically without providing an adequate return. The most common approach to overcome this hurdle is a system where several reactors share a central condenser. This is done so that each reactor is at a different stage and only one of the connected reactors is undergoing violent carbonization. The effect of violent phase carbonization is not very important in this case (Klar and Rule 1925). This requires using long connecting pipes; therefore the pipes must contain a conveniently located access port for frequent cleaning. A major drawback to central condensation systems is keeping the operation of each individual pyrolysis reactor under observation and well synchronized (Klar and Rule 1925).



**Figure 4. Horizontal retort system for carbonization scheme in Belišæe, Croatia:** (R1-6) retorts, (DC1-2) pre-drying chambers, (CC1-6) charcoal cooling chambers, (1) water-cooled condensers, (2) pyrolygneous acid and tar vat, (3) scrubber for residual non-condensable wood gases, (4) scrubber gas stack, (5) flue gas stack. (Source: Tomas et al. 2009).

Bio-oil cooling can be conducted by direct or indirect heat exchangers (Klar and Rule 1925). Table 1 summarizes most bio-oil condensers that have been used in the petroleum industry. Each of the condensers listed in this table is described in more details in Appendix A. Rapid cooling of the volatile fraction can be achieved using direct contact condensers (e.g. spray towers). Using cold liquids such as bio-oils or auxiliary liquids (generally paraffin), vapors are cooled from 500-350 °C to near ambient temperature.

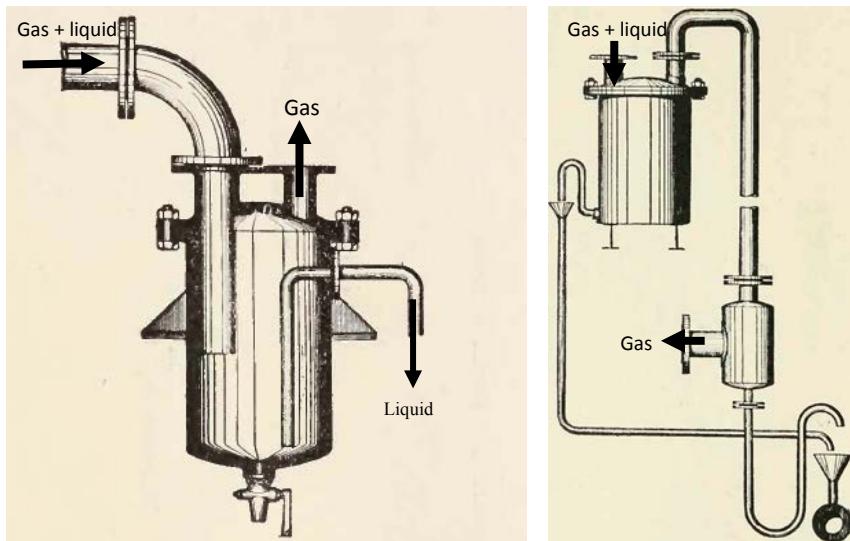
Direct coolers include single or fractional condensers (multi-step condensers). Fractional condensers result in two streams with well-defined boiling point distributions. The first step is operated between 40 and 90 °C and the second step is operated between 20 and 30 °C (Westerhof et al. 2011). Fractional condensers offer an inexpensive way to separate large bio-oil molecules (used for the precursors of transportation fuels) from small molecules which contribute to undesirable properties of bio-oils. Designs for direct contact condensers described in this section include the Meyer bubbling condenser, Barbet tab separator, and scrubbers.

**Table 1. Commonly used condensers in pyrolysis units.**

	Characteristics	References
<b>Direct Contact Condenser</b>		
Meyer condenser	Formed by a hot layer of condensed bio-oil through which vapors are bubbled. Gases ascend from the lower compartment through a perforated dome. Temperature is kept high enough to minimize condensation of water, prevent condensation of acetic acid and methyl alcohol, and to accelerate reactions of aldehydes and phenols which further produce tarry substances	Bunbury 1926
Barbet tab separator	Similar to the Meyer condenser but the pyrolysis vapors heat a lower compartment full of oil before bubbling through the plates	Bunbury 1926
Scrubbers	Pyrolysis vapors are put in contact with a liquid spray (an immiscible hydrocarbon, bio-oil or the aqueous phase). Since clogging in the first condensation tower is very intense, it is important to avoid packing. If the temperature in the first condenser is maintained at 80 °C, acetic acid can be almost completely removed	Bunbury 1926 Oasmaa et al. 2005, Westerhof et al. 2007, 2011 Klar and Rule 1925, San Miguel et al. 2011
Reactive Scrubbers	Scrubber in which a chemical reactant (typically an alcohol) is added as cooling liquid to stabilize bio-oil. Reactive species concentration is reduced.	Hilten et al. 2010
<b>Indirect Contact Heat Exchangers</b>		
Tube and shell	It is customary to first pass the pyrolytic gas and vapors through an easily cleanable section given the tendency of pyrolysis vapors to form incrustations during the condensation process. The most common design described in the literature suggests condensing the oils inside the tube while allowing the cooling water or air to circulate around the tubes. In order to facilitate cleaning and to avoid slagging etc., the length of the tubes in these exchangers should be limited keeping the cooling path relatively short.	Klar and Rule 1925; Bunbury et al. 1926; Veitch 1907
Coil Condenser	In coil condensers, the gaseous mixture passes through a single tube which, in order to afford an equal area of cooling, must be correspondingly longer. Rather than a coil wound into a spiral, the tube forming the coil is made up of a number of inclined and superimposed straight tubes connected by bends or elbows. The connecting elbows are located outside the water tank where they can be removed in order to clean the condensing tubes.	Klar and Rule 1925

Indirect cooling with water or air is also used in bio-oil condensation. The heat transfer area using air is typically 15 times larger than using water due to the difference in the heat transfer coefficient between air and water. Air cooling should be reserved for situations where obtaining clean cooling water is difficult (e.g. operating mobile units).

*Liquid gas separators:* These systems are used after the condensers. The condensate from the tubes is collected in the bottom chamber. An outlet in this chamber leads to the gas trap, or gas separator. The device used to separate the liquid condensed from the non-condensable gases in the old wood distillation industry is seen in Figure 5. These vessels were typically small (Bunbury 1926).

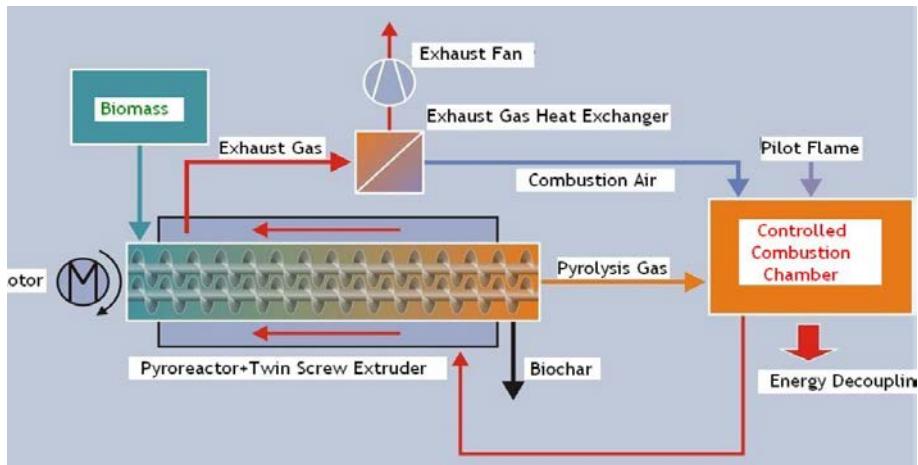


**Figure 5. Separation devices for the condensable fraction and pyrolysis gases (Source: (Klar and Rule 1925)).**

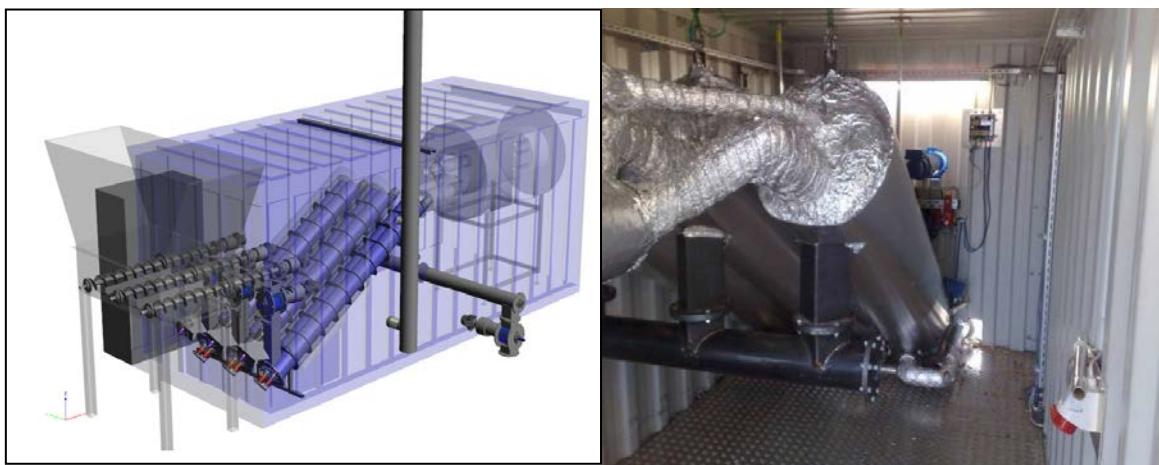
Other systems that may be added for downstream separation of pyrolysis products (aerosols) include: electrostatic precipitators (ESP), venturi scrubbers, or rotary demisters. Electrostatic precipitators have been used more often in the laboratory than in the industry despite their efficiency in aerosol removal (Bunbury 1926). Compared to the energy consumption of venturi scrubbers, which consume between 1.5 – 6 kWh/1000 m<sup>3</sup>, electrostatic precipitators are very efficient with energy consumption of 0.2 – 0.4 kWh/1000 m<sup>3</sup> (San Miguel et al. 2011).

## 2.2. Heat Recovery: Combustion Chambers and Incinerators

Given that condensation of bio-oils will not be economically viable until bio-oil refining installations are developed, currently, the most viable approach appears to be heat recovery through combustion of pyrolysis vapors to produce steam or electricity. Compared to traditional systems, heat recovery reduces the environmental impact of pyrolysis reactors and recovers the energy contained in pyrolysis vapors. A pyrolysis plant equipped with a heat recovery system is shown in Figures 6 and 7 and a continuous batch process system equipped with heat recovery where the gases and vapors are fed into the combustion chamber is shown in Figure 8.



**Figure 6. A green waste pyrolysis plant schematic diagram for the production of biochar (Weaver et al. 2010) (source: <http://ieabioenergy.com/DocSet.aspx?id=6735>).**



**Figure 7. Green waste pyrolysis plant (120 kg/h) with heat recovery (Weaver et al. 2010) (source: <http://ieabioenergy.com/DocSet.aspx?id=6735>).**

A centralized combustion system for pyrolysis vapors is advantageous when using batch pyrolysis reactors (Figure 8) (Murcia et al. 2008). The company CIRAD has been developing and installing afterburners for batch pyrolysis reactors since 1993. The system, called a CML process (Figure 8), is made up of a depollution system which incinerates waste gases without heat recovery and is linked to 12 production kilns. This system does not produce vapor or electricity from the energy contained in the pyrolysis vapors.



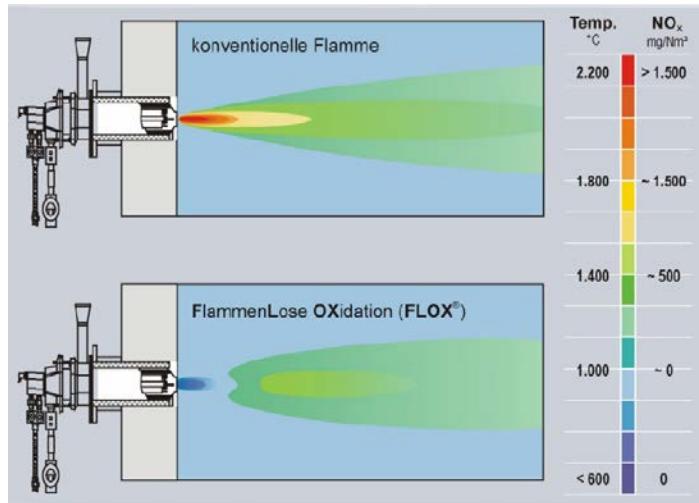
**Figure 8. Several batch pyrolysis reactors linked to an after burner known as a CML process (Source: [http://www.drveniugljen.hr/assets/files/prezentacije/06\\_Christian\\_Bedrossian.pdf](http://www.drveniugljen.hr/assets/files/prezentacije/06_Christian_Bedrossian.pdf)).**

The energy contained in pyrolysis vapors can be recovered by a system with heat recovery boilers (Figure 9) to produce hot gas, steam, or electricity. This can be done easily if the pyrolysis process is continuous.



**Figure 9. The steam produced by this auger pyrolysis unit with a thermal oxidizer can be used to generate electricity. (Source: <http://www.internationaltechcorp.org/IT-info.htm#convert>).**

Although little information on the combustion of pyrolysis vapors is found in the literature, Figure 10 shows one scheme with information on the temperature profile achieved in a thermal oxidizer chamber using pyrolysis vapors. Combustion of pyrolysis vapors (as is the case with the combustion of syngas) is expected to be much cleaner than the combustion of biomass itself but more studies are needed to characterize combustion gases derived from pyrolysis vapors.



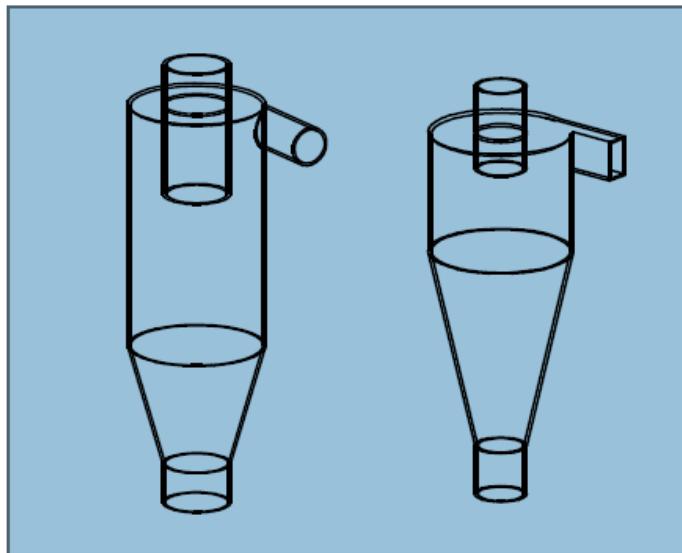
**Figure 10.** A flameless oxidation in the combustion chamber known as FLOX<sup>R</sup> (Weaver et al. 2010) (source: <http://ieabioenergy.com/DocSet.aspx?id=6735>).

## 2.3. Charcoal Removal and Cooling

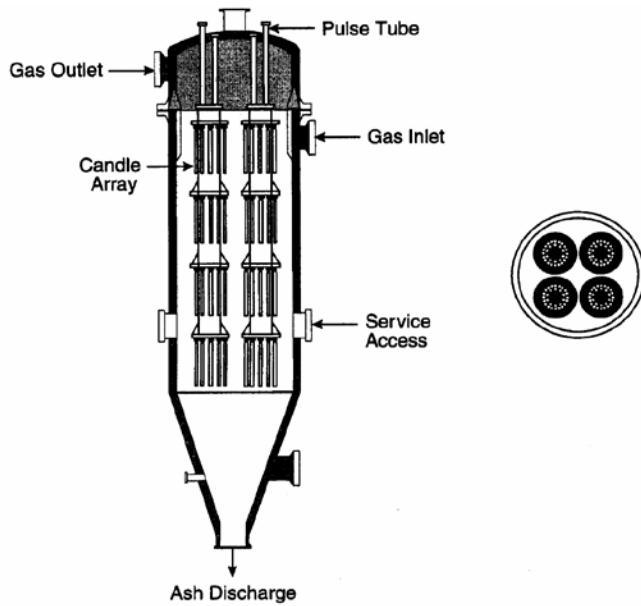
Systems for charcoal removal and cooling depend on the shape and size of the biochar produced and the design of the pyrolysis reactor. Biochar is produced in three different forms: small particles, chunks, or logs. In most ancient carbonization systems, char was allowed to cool inside the reactor and then was manually collected.

Cyclones (Figure 11) are typically used in fluidized and circulating bed pyrolysis reactors to separate the particles from the pyrolysis vapors. This is the simplest and cheapest equipment available, but only particles greater than 10 µm can be separated efficiently with this technology. However, due to attrition, fluidized bed reactors usually produce some amount of char fines (diameter smaller than 1 µm) which are difficult to separate by cyclones and find their way to the condensers (Di Benedetto and Salatino 1998; San Miguel et al. 2011; Scala and Chirone 2006).

*Hot filtration* is one of the most effective methods to remove particles from hot gases (Figure 12) (Ahmadi and Smith 2002; Dittler and Kasper 1999). Higher solid separation efficiencies (particularly with particles < 10 µm) can be achieved with ceramic filters. These systems require higher maintenance and operation costs and result in greater pressure drops. However, due to secondary reactions that take place between the vapor and the solid layer collected in the filter, the installation of hot gas filtration technologies reportedly reduces bio-oil yields (Ito et al. 1998; Schaill et al. 1996).

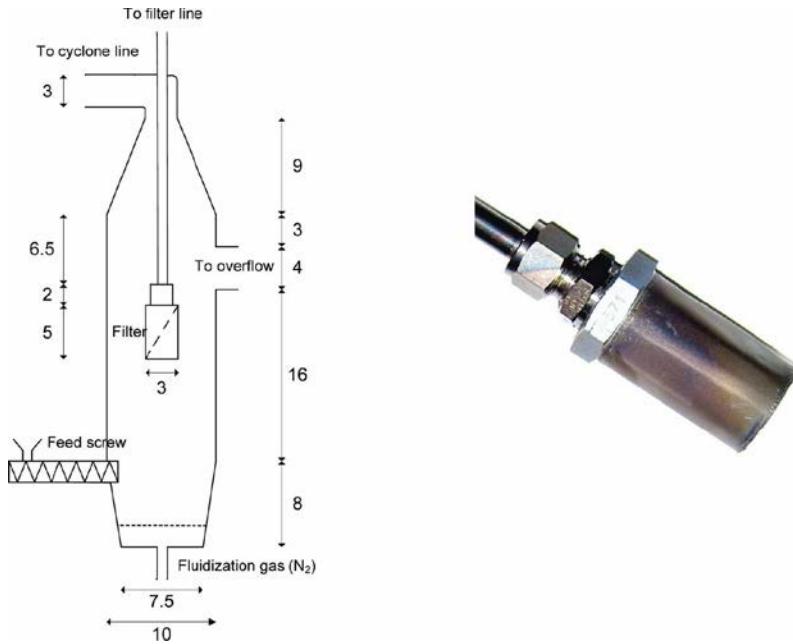


**Figure 11. Cyclones used to separate biochar (Source: San Miguel et al. 2011).**



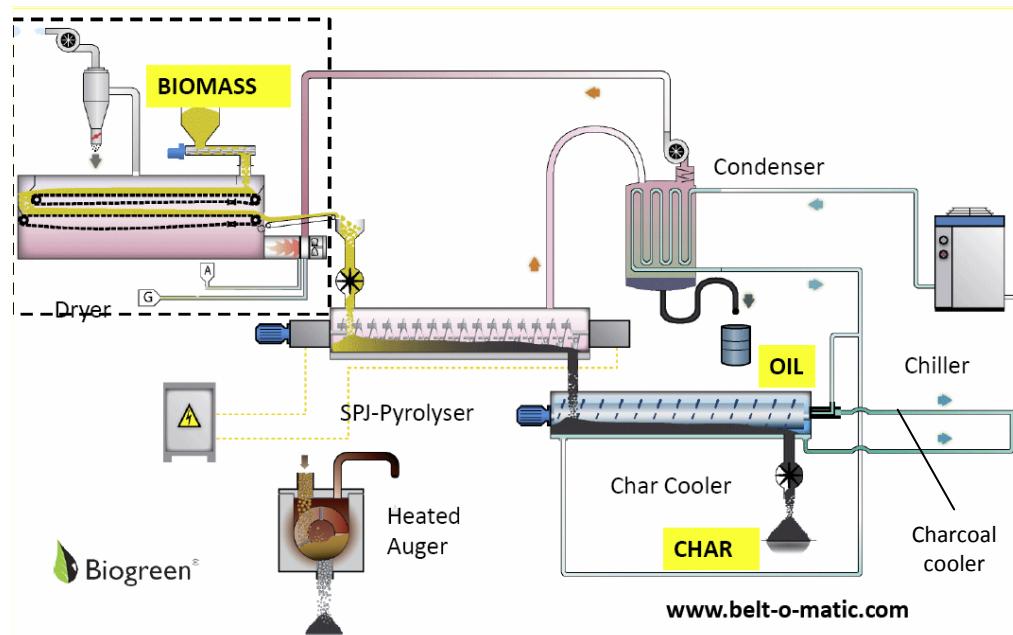
**Figure 12. Example of hot filter to remove particles from hot gases (Ahmadi and Smith 2002).**

Hoekstra et al. (2009) developed a filtration system for in-situ removal of char/ash from the pyrolysis vapors in a fluidized bed reactor (Figure 13). By integrating the filter with the fluidized bed, some of the problems associated with the increase in pressure drop in mesh filters over time are eliminated. Pores located on the outside surface of the filter retain the particles (char, sand). Even with a reused filter, good process stability concerning temperature and pressure drop across the hot gas vapor was achieved during a two-hour run. Apart from some deposits formed on the metal wire and small  $1 \mu\text{m}$  particles that slip through the filter, the inside of the filter remains clean (Hoekstra et al. 2009).



**Figure 13. Continuous bench scale reactor setup (Hoakstra et al. 2009).**

Separation of particles with diameters close to 1 mm in auger reactors and other moving bed reactors is conducted by gravity. An auger cooler coupled with the pyrolysis reactor cools the biochar in continuous systems using chips and powdery materials (Figure 14 and 15). This charcoal removal system can be used in combination with most pyrolysis reactors that handle chips and small particles (e.g. augers, multiple hearth kilns and rotary drums).



**Figure 14. Charcoal cooler for a continuous auger reactor (Miles 2010).**



Figure 15. Charcoal cooling system in vacuum pyrolysis plant (Source: Group Pyrovac).

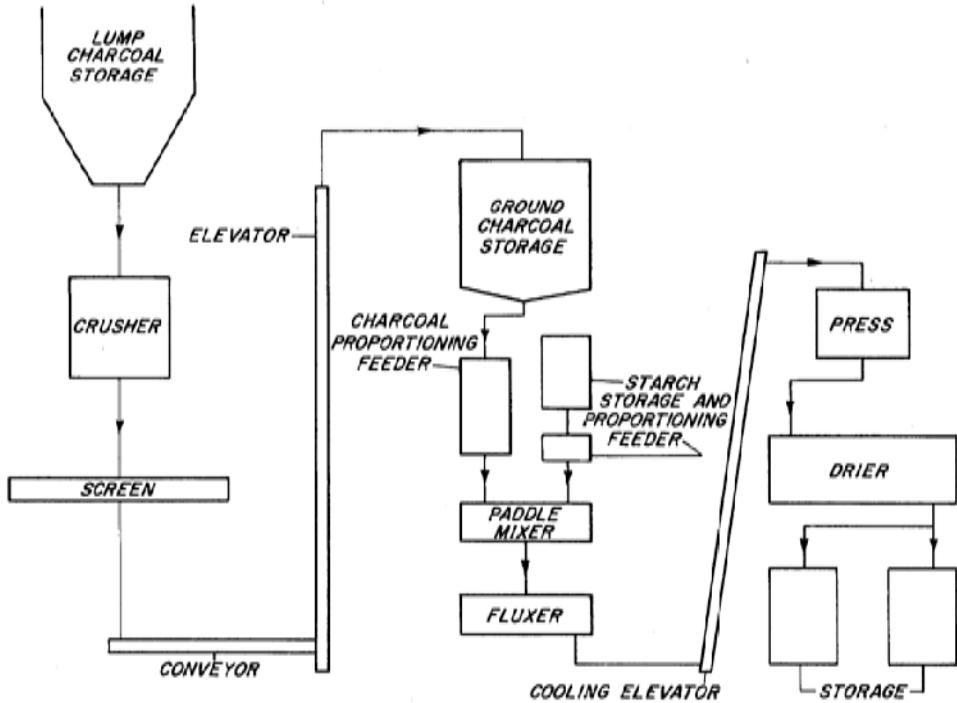
## 2.4. Charcoal Briquetting and Pelletization

Transportation of biochar must be done when it is in pellet or briquette form as it creates a safety and health hazard if it is transported in powdery form. A “briquette” is the material obtained by mixing powdered biochar with a binder. Biochar in the form of fines, binder, and filler are the raw materials for briquettes. The binder is made up of molasses, tar or starch. The most costly component of briquettes is the binder (typically starch). It must be able to resist bacterial attack and fermentation during storage. Filler is added to reduce costs and may also help control the burning rate of the briquette. Filler must cost less than biochar, be free of objectionable odor while burning, and must not be abrasive to the machinery.

Heated gases can be utilized for drying briquettes by simply attaching a briquetting unit to the carbonization plant. The steps shown in Figure 16 are typical of a 1 ton/hr briquetting plant and include the following dedicated equipment: hammer mill, paddle mixer, vertical fluxer, starch feeder or pump, briquette press with paddle feeder, bagging machine, boiler, conveyors and a building (Toole et al. 1961).<sup>1</sup>

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<sup>1</sup> Briquetting charcoal can be found in more detail at <http://www.fao.org/docrep/x5328e/x5328e0c.htm#Top OfPage> (date accessed: Nov. 13, 2010).



**Figure 16. Charcoal briquette commercial process manufacturing flow diagram (Toole et al. 1961).**

Emrich (1985) described equipment suitable for a medium size plant with a briquetting capacity of 1,000 to 5,000 tons/year (3-15 t of biochar per day or 12-60 t biomass/day). These plants include: 1) preparation, where the charcoal is accumulated and fed into a pulverizer by a precise feeder; 2) crushing, where a hammer mill is used to properly size the material; 3) mixing, which provides extra retention time to guarantee thorough blending with the binder, filler additives and etc.; 4) forming: where roller type presses are used and may be adjusted to different speeds and pressures; and 5) drying (Emrich 1985).

For heat and biochar production (typical application of slow pyrolysis processes) it is advantageous to pelletize or briquette the feedstock before pyrolysis. The shape and consistency of pellets and briquettes are partially conserved during pyrolysis. The use of binding agents, fillers and pelletizing biochar is expensive compared with making pellets at the front end. For fast pyrolysis to maximize oil production, small biomass particles must be pyrolysed and biochar pellets or briquettes produced afterward (Figure 16). The process shown in Figure 16 is used to produce biochar briquettes from lump charcoal produced from slow pyrolysis reactors.

### **3. Product Quality: Bio-Oil Characterization**

Quality assurance can be achieved by subcontracting a centralized lab (suitable for small pyrolysis plants) or in the plant's own laboratory (suitable for large pyrolysis plants) (Hess et al. 2006). Depending on the biomass composition, the pyrolysis process, and the condensation conditions, the liquid product (bio-oil) may be formed by two or more phases (Oasmaa and Peacocke 2001). Fast pyrolysis produces a single phase bio-oil, whereas slow pyrolysis produces a two phase bio-oil.

Oasmaa et al. (2009) published a review on bio-oil quality control and standards. Presently there are no recognized national or international standards for the specifications of bio-oil (Oasmaa and Peacocke 2001). However, the International Energy Association (IEA), Task 34 (2010 – 2012) addresses standards development within ASTM (Oasmaa et al 2009). Within the International Energy Association (IEA), the first set of standards was promulgated for bio-oil through the Pyrolysis Activity under Task XIII. The European biomass community is undergoing a lot of activity to develop protocols and standard methods for measuring properties of bio-oil. In order to provide credibility to measurements of final specifications and methods, an organization such as the American Society for Testing and Materials (ASTM) also needs to be involved. A pyrolysis oil standard initiative for bio-oils started in 2007 within D02 Petroleum Products and Lubricants Committee. End-use equipment manufacturers must also be involved in the establishment of specifications (Ringer et al. 2006).

#### **3.1. Biomass Composition**

The quality, quantity, properties, and chemical composition of biochar and bio-oil are dependent on raw materials, or biomass. Hence, insight into the biomass composition is very important for the outcome of biomass pyrolysis. Biomass composition is also important to develop tactics to favor reactions that give desirable product and limit reactions that produce undesirable outcomes. Biomass is composed primarily of cellulose, hemi-cellulose and lignin with a small fraction of light aliphatics and aromatics (extractives) and mineral matter (ash).

#### **3.2. Bio-oil Characterization**

Depending on the purpose of the analysis, bio-oils can be characterized and classified according to: their fuel properties, their physical appearance, their chemical composition, their solubility on targeted solvents, etc. In this section we will group the techniques used for bio-oil characterization into four main categories: fuel properties, chemical composition, solvent extraction and multiphase structure.

During fast pyrolysis, biomass generally is converted into the following: 8-15 wt. % small organic compounds (mostly, hydroxyacetaldehyde, acetol, acetic acid, formic acid and methanol); 5-10 wt. % mono phenols and furans; 6-15 wt. % hydrolysable sugars; 6-15 wt. % lignin oligomers; 10-15 wt. % water; and around 20 wt. % unknown fraction (likely products from cellulose and cross linked reactions, which may be the source of branched paraffins when the bio-oil is hydrotreated). The remaining biomass (15-25 wt. %) is either converted into gases or charcoal.

The yield of bio-oil is typically 60-75 wt. % of the original biomass. The bio-oil that is collected consists of the water, light fractions, mono phenols, furans, fermentable sugars, lignin oligomers and the unknown heavy fraction (likely cross linked sugars). Bio-oil generally exhibits viscosity of 35-53 cSt at 40 °C, contains a small amount of ash 0.04-0.24 wt. %, and is acidic (pH: 2.5-3.4). Bio-oils have complex multiphase systems due to the presence of char particles, waxy materials, aqueous droplets, and micelles formed from heavy compounds, (Garcia-Perez 2006; Elliott 2001; Frantini 2006; Kang et al. 2006).

### *3.2.1 Fuel and Physico-chemical properties of bio-oils*

Compared to petroleum fuel, bio-oil contains high oxygen content (45-50%) in the form of ester, ether, carbonyl, carboxyl and hydroxyl groups. The primary reason for the difference in properties and behavior between hydrocarbon fuels and biomass pyrolysis oil is the polar nature of bio-oils caused by the presence of oxygenated functional groups. The elemental composition of bio-oil (CHNSO content) is similar to that of the biomass from which it was derived (Mohan and Steele 2006). Table 2 presents properties and characteristics of wood-derived bio-oils.

**Table 2. Properties and characteristics of wood-derived crude bio-oil (Bridgwater 2003; Mohan et al. 2006).**

Property	Characteristics
Appearance	From almost black or dark red-brown to dark green
Miscibility	Water content from ~15 wt % to ~30 – 50 wt % before phase separation occurs. Miscible with polar solvents (methanol, acetone, etc.) but almost totally immiscible with petroleum-derived fuels.
Density	Approximately 1.2 kg/L (compared to ~0.85 kg/L for light fuel oil).
Viscosity	Viscosity varies from 25 cSt to 1000 cSt (measured at 40°C).
Distillation	Cannot be completely vaporized. Above 100 °C, rapidly reacts and eventually produces a solid residue ~50 wt % of the original liquid.
Stability	Chemically unstable. Store liquid at or below room temperature.

Fuel specifications establish a balance between engine requirements and the cost and availability of the fuel. An entire set of combustion characteristics must be fulfilled in order to label a substance as a fuel. The American Society for Testing and Materials (ASTM) typically serves as an international organization that develops and publishes voluntary consensus technical standards for a wide range of materials and methods. Oasmaa et al (2009) reviewed the status of the development of bio-oil standards within ASTM. A lack of specification for fuel applications is a handicap facing both producers and users of pyrolysis

oils. In-depth summaries of the potential for using biomass derived fuels on performance and durability of gas turbine systems and boilers is provided by Moses (1994), Diebold et al. (1999) and Drennan (1994), Oasmaa et al (2009). Accuracy of physical analysis is generally good with regard to homogeneous pyrolysis liquids. However, results for heterogeneous liquids may be inconsistent. Table 3 lists several methods to determine bio-oil physico-chemical properties.

### *3.2.2 Chemical Characterization*

Garcia-Perez et al. (2007) describe bio-oil composition in chemical families depending on the boiling point or the cracking temperature at which the compounds forming the family are evaporated. The very volatile compounds with boiling point below 100 °C (Family 1) are usually disregarded in most papers because the gas chromatography-mass spectroscopy (GC/MS) chromatograms are commonly recorded after solvent and water have been eluted to avoid damaging the MS detector. This family is formed mostly by hydroxyaceteldehyde, formic acid, and methanol and can be easily characterized by GC-FID using heavier solvents. Family 2 is formed by compounds with boiling points comparable to water (mostly acetic acid and acetol). The organics in this family can be quantified by GC/MS and the water by Karl Fischer titration. Family 3 is mainly formed by mono-phenols and mono-furans with boiling points between 100 and 200 °C. This fraction is typically quantified by GC/MS. Sugars are heavier and as such only the levoglucosan can be analysed by GC/MS without derivatization. The sugars in the oil (Family 4) can be classified in hydrolysable sugars and non-hydrolizable sugars. The hydrolysable sugars can be quantified by ion exchange chromatography after hydrolysis with sulfuric acid. The non-hydrolysable sugars are a large fraction which is currently poorly understood. Lignin oligomeric materials are typically quantified by cold water precipitation (Family 5). Up to now there is little agreement and standard techniques and method to characterize the chemical composition of bio-oils. Techniques to determine the chemical composition of bio-oils are summarized in Table 4.

**Table 3. Pyrolysis liquid analytical methods to quantify Fuel and Physical Properties**

Properties	Method/Standards	Range of values	References
Solids (char) content (wt. %)	Ethanol or methanol insolubles	0.01 – 3.0	Oasmaa and Peacocke (2001), San Miguel et al. (2011)
Particle size distribution	Microscopy + particle counter		Oasmaa and Peacocke (2001), Oasmaa et al. (1997)
Specific heat capacity (J/g K)	Differential Scanning Calorimetry	2.6 – 3.8 (25 – 70 °C)	Peacocke et al. (1994)
Conradson carbon residue content (wt. %)	ASTM D 189	14 – 23	Oasmaa and Peacocke (2001)
Ash content (wt. %)	EN 7, ASTM-482	0.01 – 0.20	Oasmaa et al (1997)
CHN content (wt. %)	ASTM D5291	C: 48 – 60 (Dry basis) H: 5.9 – 7.2 (Dry basis) N: 0 – 0.04 (Dry basis) O: 34 – 45 (Dry basis)	Oasmaa and Peacocke (2001)
Sulphur and chlorine content (ppm)	Capillary electrophoresis	S: 60 – 500 Cl: 3 – 75	Oasmaa and Peacocke (2001)
Alkali metals content	ICP, AAS	K + Na 5 – 500 ppm	Oasmaa and Peacocke (2001)
Density at 15 °C (kg/L)	ASTM D4052, ASTM D-369	1.11 – 1.30	Oasmaa and Peacocke (2001)
Kinematic Viscosity (20 – 60 °C) (cSt)	ASTM D 97	10 – 80 cSt @ 50 °C	Oasmaa and Peacocke (2001), Bridgewater 2003, Mohan et al 2006,
Dynamic Viscosity (mPa.s)	Rotational Viscometry		Oasmaa and Peacocke (2001), Leroy et al (1988), Oasmaa (1997), Garcia-Perez et al. (2006)
Pour Point (°C)	ASTM D97	-12 – 36	Li and Zhang (2003), Oasmaa et al (1997), Oasmaa and Peacocke (2001).
Heating value (HHV) (MJ/kg)	ASTM D4809, DIN 51900	16 – 19	Boucher et al (2000), Oasmaa and Peacocke (2001), Oasmaa 1997, Czernik and Bridgwater (2004)
Low Heating value (LHV) (MJ/kg)		13 – 18	Boucher et al (2000), Oasmaa and Peacocke (2001)
Ignition limit (°C)		110 – 120	
Flash point (°C)	ASTM D93, ASTM D 3828	40 – 110	Boucher et al 2000, Oasmaa and Peacocke (2001), Oasmaa et al. (1997)
Thermal conductivity		0.35 – 0.43	

Properties	Method/Standards	Range of values	References
(W/mK)			
pH	pH meter	2.0 – 3.7	Oasmaa and Peacocke (2001)
Thermal stability (Aging process)	FTIR method, following viscosity changes. Tests at 80 °C for 24 hours and at 40 °C for 1 week.		Scholze and Meier (2001), Oasmaa and Peacocke (2001), Oasmaa et al (1997, 2001, 2003), Polk & Phingbohipakkiya (1981), Czernik et al (1994), Oasmaa and Czernik (1999), Mohan and Steele 2006, Diebold et al. (1999).
Total Acid Number (TAN)	ASTM D664, D3339 ASTM D974, ASTM D664		Molte et al. (2010), Oasmaa et al (2010)
Distillation		Cannot be completely vaporized.	Bridgwater 2003, Mohan et al 2006

**Table 4. Quantification of Bio-oil Compounds, chemical families and functional groups**

Property, Fraction or Compound	Analytical Method or Standard	References
Macro chemical families	Deconvolution of DTG curves	Garcia-Perez et al. (2007)
Molecular weight distribution	GPC, MALDI-TOF-MS, LDI-TOF-MS, and Py-FIMS	Anderson et al (2000), Garcia-Perez et al (2006), Vuorinen et al (1998), Scholze et al. (2001), Hoekstra et al (2011), Bayarbach et al. (2006)
Water content	KF Titration (ASTM 203, 1744)	Garcia-Perez et al (2007), Oasmaa et al (1997), and Oasmaa and Peacocke (2001)
Mono phenols and furans	GC-MS	Ingram et al (2008), and Song et al. (2009)
Carboxylic, fatty and resin acids	GC/MS	Pakdel et al (1987, 1991, 1994), Branca et al. (2003) , Pimenta et al (1998)
Volatile fraction (classification of volatile fraction in chemical families)	2D-GC-TOF-MS	Fullana et al. (2005), Marsman et al (2008)
Lignin oligomers (pyrolytic lignin)	Cold water precipitation	Bayarbach and Meier (2009), Scholze and Meier (2001 a, b), Windt et al (2009), Bayarbach et al (2006), Scholze and Meier (2002).
Lignin oligomers of low molecular weight	Cold water precipitation followed by washing with $\text{CH}_2\text{Cl}_2$	Bayarbach and Meier (2009), Scholze and Meier (2001 a, b), Windt et al (2009), Bayarbach et al (2006), Scholze and Meier (2002).
Chemical structure of lignin oligomers	Titration with tri-sulfate, FTIR, SEC, MALDI-TOF-MS, LADO-TOF-MS, and Py-FIMS	Bayarbach et al (2006), Scholze and Meier (2001)
Methoxyl groups in pyrolytic lignin	Titration with trisulfate	Scholze and Meier (2001)
Hydrolyzable sugars soluble in water (mainly levoglucosan and cellobiosan)	Hydrolysis of water soluble fraction followed by ion exchange chromatography or HPLC.	Lian et al. (2010) and Mohan et al. (2006)
Total content of sugars	Brix determination (Anton Paar DMA 4500 hydrometer)	Oasmaa and Kuoppala (2008)
Elemental analysis (CHN-O)	ASTM D 5291	Anja Oasmaa and Peacocke (2001) and Acikgoz and Kockar (2009)
Overall functional groups	FTIR	Lievens et al (2011), Acikgoz et al (2009), Scholze and Meier (2001)

Property, Fraction or Compound	Analytical Method or Standard	References
<b>Carbonyl carbons, total aromatic carbons, carbohydrate-type carbons, methoxy- or hydroxyl-bound carbons: primary, secondary, tertiary and most quaternary alkyl carbons.</b>	<sup>13</sup> C-NMR	Ingram et al 2008, Mullen et al, 2009, Song et al. 2009
<b>Aliphatic protons, aliphatic hydroxyls, protons located alpha to ketone, aldehydes or carbonyl groups, methoxy, -CH<sub>2</sub>O-, - CHO-, CHO groups, phenolic –OH, nonconjugated olefinic protons, olefinic protons, and double bonds conjugated to carbonyls</b>	<sup>1</sup> H-NMR	Acikgoz and Kockar (2009) and Ingram et al. (2008)

Due to bio-oil's diverse chemical functionalities and wide range of molecular weights and boiling points, a combination of several analytical techniques is needed for global analysis of pyrolysis liquids including: GC-MS (volatile compounds), high performance liquid chromatography (HPLC), HPLC/electrospray MS (nonvolatile compounds), Fourier transform infrared (FTIR) spectroscopy, gel permeation chromatography (GPC) (molecular weight distributions), UV, UV-Fluorescence, nuclear magnetic resonance (NMR), thermogravimetry, and solvent extraction. Several of these techniques are discussed in Appendix C.<sup>2</sup>

### 3.2.3. Solvent extraction

*Solvent extraction* is another method used to characterize bio-oils (Mohan et al. 2006). Properly selecting solvents is the first step in developing a solvent extraction strategy. The degree of polarity significantly affects the solubility of pyrolysis liquids in solvents other than water (Oasmaa and Peacocke 2001). Alcohols, like ethanol and methanol, are good solvents for highly polar white wood and straw pyrolysis liquids. Hydrocarbons like hexane, diesel fuels and polyolefins do not dissolve with wood pyrolysis liquids but can be useful to adsorb extractive derived compounds such as fats, waxes, resins, terpenes, and essential oils. Table 5 shows several solvents used to extract bio-oil fractions and their polarity indices.

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<sup>2</sup> For further discussion of this topic see Diebold et al. 1999, Meier et al. 1999, and Oasmaa 1999.

**Table 5. Solvents used for pyrolysis oil fractionation (Source: Mohan et al. 2006).**

Solvent	Polarity Index	Applications
Pentane	0.0	Non polar to less polar compounds (e.g. hydrocarbons, olefins)
Benzene	3.0	Less to moderately polar compounds (e.g. phenols and oxygenated compounds)
Dichloromethane	3.4	Less to moderately polar compounds (e.g. phenols and oxygenated compounds)
Ethyl acetate	4.3	Polar compounds (e.g. ketones and aldehydes)
Methanol	6.6	Strongly polar compounds (e.g. sugars and acids)

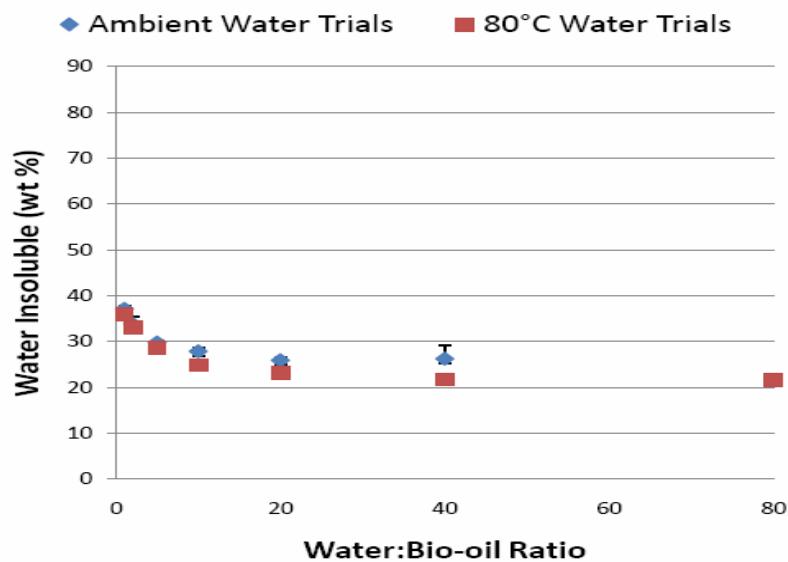
A scale of hydrophilicity (or water solubility, also an index related to polarity) of different bio-oil fractions proposed by Radlein et al. (1999) is presented in Table 6. The information in Tables 5 and 6 is very important to develop separation strategies. Diebold (2000) published an excellent analysis of phase co-solvency of bio-oil components and used the Hansen solubility parameters (total solubility, disperse solubility, polar solubility and hydrogen bonding solubility) to describe phase equilibrium in his analysis. The Hansen solubility parameters are used to predict the solubility of solutes and solvents (Diebold, 1999). The Hansen Solubility parameters (energy for dispersion bonds between molecules, energy for dipolar intermolecular force between molecules, the energy from hydrogen bonds) were developed by Charles Hansen to predict if one material will dissolve in another from a solution.

**Table 6. Pyrolysis liquid compound classes (Oasmaa and Peacocke 2001, Radlein et al. 1999).**

Compound class	Composition range (wt % of organic fraction)	Hydrophilicity (arbitrary scale 4 is highest)
C <sub>1</sub> compounds (formic acid, methanol, and formaldehyde)	5 – 10	4
C <sub>2</sub> -C <sub>4</sub> liner hydroxyl and oxo substituted aldehydes and ketones (acetol, hydroxyacetaldehyde, acetic acid)	15 – 35	4
C <sub>5</sub> -C <sub>6</sub> Hydroxyl, hydroxymethyl and/or oxo substituted furans, furanones, and pyranones	10 – 20	3
C <sub>6</sub> -C <sub>10</sub> Monomeric methoxy substituted phenols	6 – 15	2
Anhydrosugars, incl. anhydro-oligosaccharides (C <sub>6</sub> , C <sub>12</sub> ) (Levoglucosan and cellulobiosan)	6 – 10	4
C <sub>6</sub> -C <sub>30</sub> products of cellulose and hemicelluloses degradation reactions (cross linked sugars??)	20 – 40	Likely 3 – 4
Pyrolytic Lignin	15 – 30	1

Several solvent extraction techniques and their potential uses for bio-oil characterization are presented below.

*Water Separation:* By simply adding water to bio-oil it can easily be separated into water soluble and organic fractions (Oasmaa and Peacocke 2001). The heavy, mainly lignin-derived fraction (but also containing water and some sugars) separates out from the aqueous fraction during phase separation. Phase separation typically occurs by adding water until the liquid is about 25 wt. % water (Peacocke et al. 1994). Carbohydrate-derived compounds (light compounds, hydrolysable sugars and cross linked sugars) are abundant in the water-soluble fraction. Brown et al. (2009) studied the effect of water temperature and water/bio-oil ratio on yield of decanted oil proving that the fraction of decanted oil obtained was dependant on the water/bio-oil ratio (Figure 17). Usually 25 – 30 wt. % of the whole bio-oil is comprised of the “lignin-rich” fraction (or decanted oil).



**Figure 17. The amount of decanted oil is affected by temperature and the water/bio-oil ratio (Brown et al. 2009).**

A phase diagram for a pyrolysis liquid/water system can be used to estimate the content of water and organics in the decanted oil and aqueous phases (Figure 18) (Oasmaa and Czernik 1999).

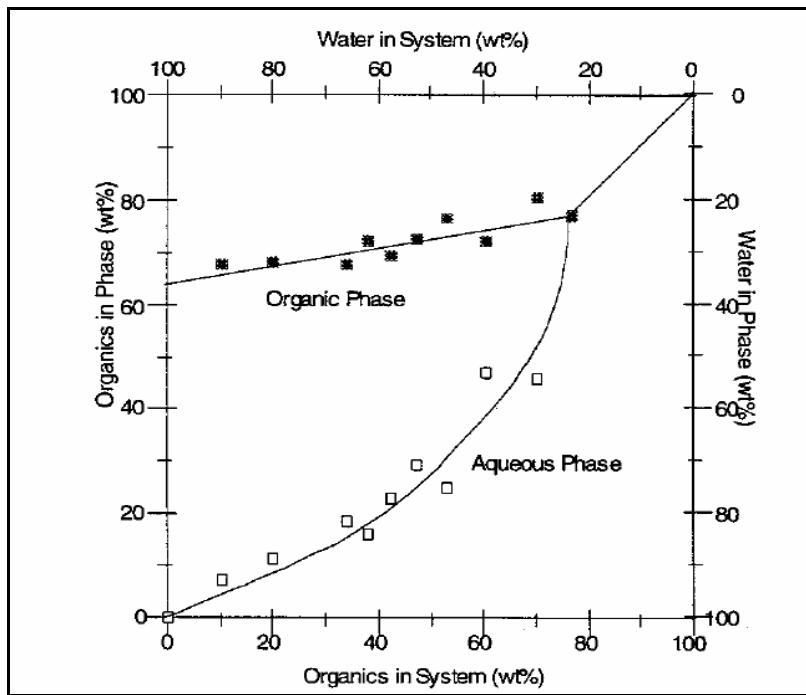
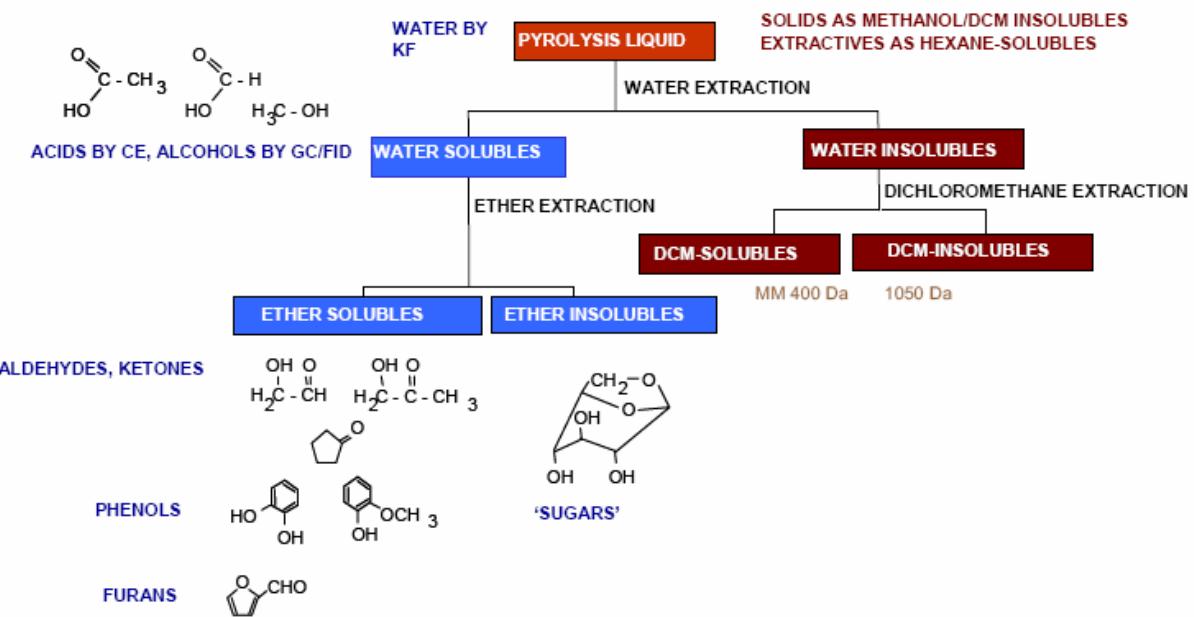


Figure 18. Phase diagram of biomass pyrolysis oil/water (Oasmaa and Czernik 1999).

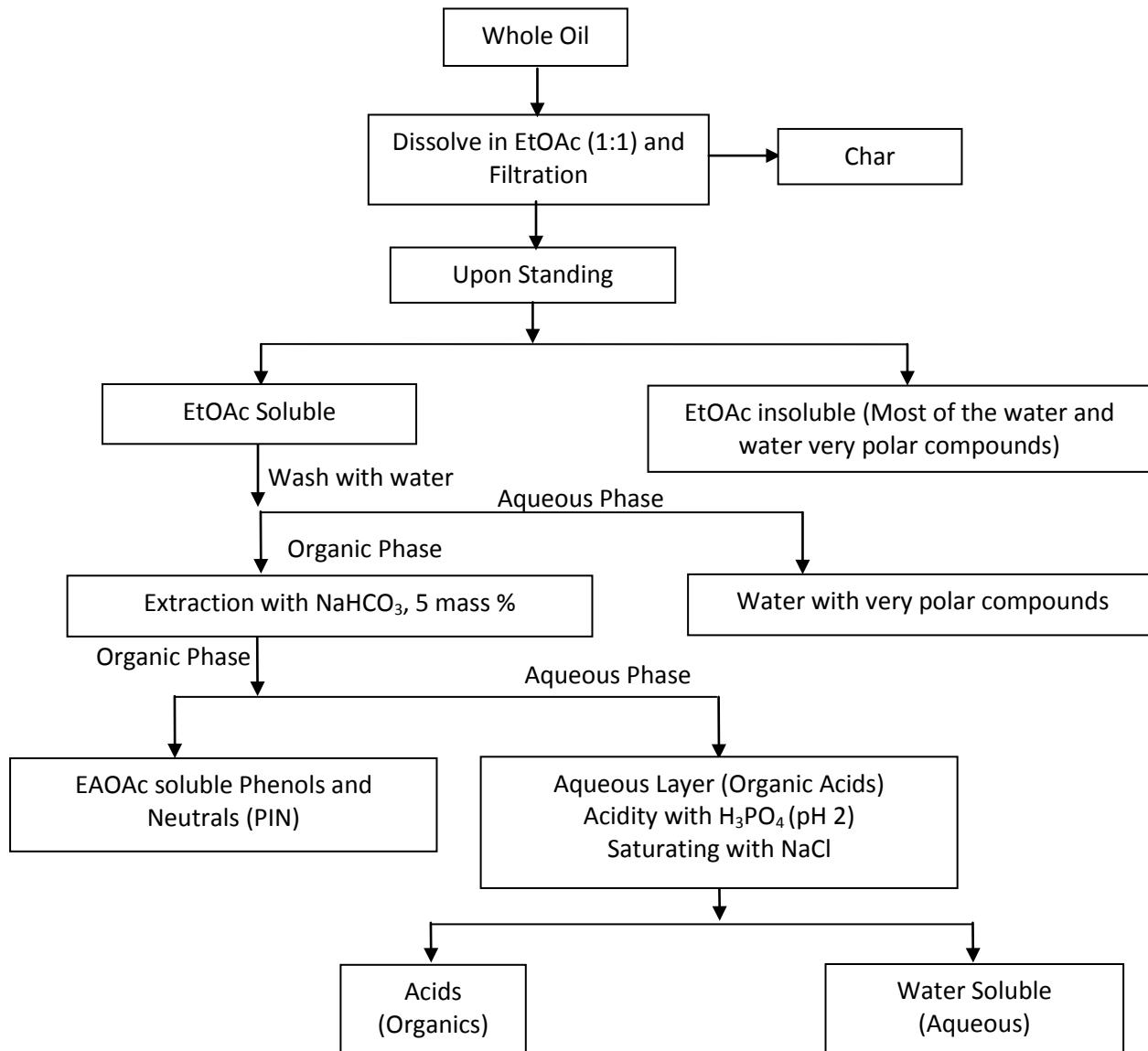
Song et al. (2009) explored the use of aqueous salt solutions for bio-oil extraction. The use of salts is an effective method to improve the separation of bio-oil. Ethyl acetate can be used to further extract the water soluble fraction. Silipa et al. (1998) proposed a scheme for the separation of bio-oils using water precipitation followed by the extraction of the water soluble fraction with ethyl acetate and the washing of the water insoluble fraction with dichloromethane (Figure 19).



**Figure 19. The separation and characterization of biomass-based flash pyrolysis bio-oil using solvent fractionation (Source: Spila et al. 1998, <http://www.biocoup.com/index.php?id=144>).**

If the bio-oil contains large amounts of wood extractives, it is recommended to use an extraction with n-hexane (Garcia-Perez et al. 2007, Sipila et al. 1998). The use of ethyl acetate was developed for the extraction of mono and oligo-phenols. A fractionation method developed by National Renewable Energy Lab (NREL) is shown in Figure 20 (Chum et al. 1989).

**Fractional distillation:** Fractional distillation of bio-oil is impossible due to the presence of oligomeric sugars (hydrolyzable and cross-linked) and lignin derivatives. Due to this fact, bio-oil differs from most grades of petroleum. The chemical composition of the oils obtained from vacuum distillation was characterized by Schirmer et al. (1984). The distillation characteristics of the fresh bio-oil, studied by Adjaye et al. (1992), showed that using 174 Pa at 200 °C produced the maximum amount of organic distillate. Aromatic, aliphatic and naphthenic hydrocarbons, as well as oxygenated compounds such as furans, alcohols, acids, ethers, aldehydes, ketones and phenols made up this distillate fraction (Adjaye et al. 1992).



**Figure 20. Bio-oil fractionation method developed by NREL (Chum et al. 1989).**

### 3.2.4. Multiphase structure of bio-oils

Liquid products of pyrolysis may be formed by two or more phases depending on the composition of the feedstock, and pyrolysis and condensation conditions (Oasmaa and Peacocke 2001). While slow pyrolysis of woody biomass usually results in a two phase bio-oil (decanted oil and pyroligneous water), fast pyrolysis of the same feedstock typically results in a single phase bio-oil. An extra phase (called the upper layer or extractive rich layer) is the result of the presence of extractive in the feedstock (Garcia-Perez et al. 2006, Oasmaa et al. 2003, Oasmaa and Peacocke 2001). Table 7 summarizes studies on the multiphase structure of bio-oils.

**Table 7. Multi-phase structure of bio-oils**

Property, Fraction or Compound	Method	References
Structure (phases) in the micrometer scale	Optical microscopy with polarized and non-polarized light	Garcia-Perez et al (2006), Oasmaa et al 2003, Oasmaa and Peacocke (2001)
Effect of temperatures on bio-oil structural features	Microscopic analyses conducted on hot stages	Ba et al (2004), Garcia-Perez et al (2006), Oasmaa et al (2003)
Melting of waxy materials (derived from extractives)	Optical Microscopy with polarized light, CPM, NIR scattering technique, rheology and DSC	Garcia-Perez et al. (2006), Paso et al (2009), Nolte et al (2010)
Nano-structure (pyrolytic lignins)	Dynamic rheometers (oscillatory frequency sweep), SANS	Garcia-Perez et al (2006), Frantini et al (2006), Nolte et al. (2010)

The distinction between the continuous medium and the dispersed phase in bio-oils is not obvious due to the fact that they are multiphase and viscous colloidal systems. The multiphase complex structure of pyrolysis oils derived from biomass can be attributed to the presence of micelles formed of heavy compounds in a matrix of holocellulose-derived compounds and water, char particles, aqueous droplets, droplets of a different nature, and waxy materials (Garcia-Perez et al. 2006).

## 4. Product Quality: Biochar Characterization

The industrial charcoal producer cannot do without analytical work, whereas the traditional charcoal maker will rarely engage themselves with it (Emrich 1985). Depending on the results of the analytical tests, the charcoal or a charcoal derivative may or may not be regarded as a quality product. While small pyrolysis units are likely to sub-contract the analysis of the biochar produced to other centralized laboratories, large pyrolysis units are likely to analyze their own products. Fortunately, expensive and extremely sophisticated equipment is not required to perform many of these analytical procedures (Emrich et al. 1985).

Charcoal makers differentiate between charcoal fines, charcoal dust, lump charcoal, activated carbon, pellets, extrudates and charcoal briquettes (Emrich 1985). Depending on the final application, industrial or household market, the quality parameters that need to be tested will vary. Each market requires understanding of consumer or industrial user habits, packing styles and specifications.

Depending on the final use of the biochar as either a household fuel or for an industrial application, the quality properties may vary. Several industrial uses include: the iron and steel industries (blast iron, furnaces, ferro-silica, metal hardening and the non-ferrous metal industry), the chemical industry (manufacturing of carbon disulphide, sodium cyanide and carbides), the activated carbon and filter industry (water purification, dechlorination, gas purification, solvent recovery, waste-waste treatment and cigarette filters), as a soil amendment (horticulture), as a poultry and animal feed, as a pigment for paints and printing, the cement industry and as a gas generator (for cars and electric power). The environmental, agricultural and silvicultural applications of biochars such as carbon storage to prevent CO<sub>2</sub> emissions are gaining growing interest. Each of these applications will require a specific set of characteristics.

In general, if charcoal is used as a cooking fuel only, it does not matter whether hard or softwoods are utilized (Emrich 1985). A lighter charcoal with higher attrition and abrasion characteristics (a biochar that decomposes more easily) is produced from softwoods. These characteristics make it undesirable for several industrial applications as a reductant for activated carbon and a blast furnace. By using agglomeration with special binders, an adequate industrial charcoal can be made from softwood since these binders have the capacity to reinforce the formed char (Emrich 1985). Common techniques used to analyze biochar are discussed in the following section.<sup>3</sup>

According to the International Biochar Initiative, <http://www.biochar-international.org/biochar>, "biochar is a solid material obtained from the carbonization of biomass. Biochar may be added to soils with the

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<sup>3</sup> For more information about these analytical techniques see Marsh and Rodriguez-Reinoso 2006 and Emrich 1985.

*intention to improve soil functions and to reduce emissions from biomass that would otherwise naturally degrade to greenhouse gases. Biochar also has appreciable carbon sequestration value. These properties are measured and verifiable in a characterization scheme*”. This section is devoted to describe bio-char characterization schemes.

## 4.1 General Biochar Properties

Some charcoal producers check char quality using physical observation and other simple techniques. The main criteria used to evaluate biochar quality are appearance, size and density. Table 8 summarizes some of the most important properties used to characterize biochars. Appendix D describes biochar properties in more detail including bulk chemical composition, surface chemical composition, and porosity.

**Table 8. General properties of biochar.**

Property	Methods/Standards	References
<b>Specific weight</b>	ASTM D 854-10 (for soils), ASTM D6111-09 (for Plastic lumber), ASTM D2395-07ae1 (for wood)	Emrich 1985
<b>Secreening analysis</b>	<b>Sieving</b>	<b>Emrich 1985</b>
<b>Friability tests</b>	<b>ASTM D440-07 (Test method of drop Shatter test for coal). ASTM D 441-07 (for Tumbler Test for Coal)</b>	<b>Emrich 1985, Speight 2005</b>
<b>Caloric value (Kcal/kg)</b>	<b>ASTM D5865-11a (for Coal and Coke)</b>	<b>Emrich 1985</b>
<b>Breakthrough curves</b>	<b>Solid phase extraction</b>	<b>Marsh and Rodriguez-Reinoso 2006, Agyei et al. 2002</b>
<b>Biochar reactivity</b>	<b>Thermogravimetric Analysis (TGA)</b>	<b>Quyn et al 2003, Li et al 2006, Assadullah et al 2010</b>
<b>Proximate analysis</b>	<b>ASTM D7582-10e1, ASTM D 5142 (For coal and coke)</b>	<b>Emrich 1985, Toole 1971, Lehman and Joseph 2009</b>
<b>Sulfur content</b>	<b>ASTM D4239 (For coal and coke)/calorimetric combustion</b>	<b>Emrich 1985</b>
<b>Phosphorus content</b>	<b>NA</b>	<b>Emrich 1985</b>
<b>Alkyl carbon composition</b>	<b>Cross Polarization/Spin-Lattice Relaxation Time/Total Sideband Suppression (CP/T1-TOSS)-NMR</b>	<b>Brewer et al. 2009</b>
<b>Cation exchange capacity</b>	<b>ASTM D7503-10 (Inorganic fine-grained soils)</b>	<b>Duquette 2008, Silber et al 2010</b>
<b>Anion-exchange Capacity</b>		<b>Valdes et al 2022</b>
<b>Chemical Analysis (Moisture, ash and, volatile</b>	<b>ASTM D 1762-84(2007) (wood charcoal)</b>	<b>Lehman and Joseph 2009</b>

matter)		
Ash chemical composition	ASTM D 6349 (coal and coke)	Asadullah et al. 2010
Structural features of biochar	Raman spectroscopy	Li et al 2006, Assadullah et al. 2010, Brewer et al. 2009

#### 4.1.1. Surface chemical composition and pore characterization

Many characteristics of biochar depend on its surface properties, summarized in Table 9.

**Table 9. Surface properties and methods to characterize the composition of biochar.**

Property	Method	References
pH at point of zero charge (pHpzc)		Noh et al 1989, 1990
Content of lactone, carboxyl, phenolic, and carbonyl groups	Chemical Boehm titration	Boehm et al 1964, 1966, Goertzen et al. 2010, Marsh and Rodriguez-Reinoso 2006, Valdes et al 2002, Lehman and Josepg 2009
Functional groups on the surface	X-ray photoelectron spectroscopy (XPS)	Marsh and Rodriguez-Reinoso 2006, Scudiero 2011, Boehm 2002
Functional groups on the surface	Temperature programmed desorption (TPD)	Marsh and Rodriguez-Reinoso 2006
Surface oxygen complexes	Adsorption with N <sub>2</sub> , SO <sub>2</sub> , CH <sub>3</sub> OH, and H <sub>2</sub> O	March and Rodriguez-Reinoso 2006
Functional groups on the surface	Enthalpies of adsorption	March and Rodriguez-Reinoso 2006
Surface area (open and close cavities)	Small Angle X-Ray Scattering (SAXS)	Marsh and Rodriguez-Reinoso 2006
Surface area and pore size distribution	Brunauer-Emmett-Teller (BET) equation	Marsh and Rodriguez-Reinoso 2006
Mesoporosity (2-50 nm)	Capillary condensation	Marsh and Rodriguez-Reinoso 2006
Large mesoporosity	Mercury porosimetry	Marsh and Rodriguez-Reinoso 2006

The international biochar Initiative (IBI) has published recently guidelines for standardized Product definition and for testing Bio-char that going to be used in soil ([http://www.biochar-international.org/sites/default/files/Guidelines\\_for\\_Biochar\\_That\\_Is\\_Used\\_in\\_Soil\\_Final.pdf](http://www.biochar-international.org/sites/default/files/Guidelines_for_Biochar_That_Is_Used_in_Soil_Final.pdf)). This guideline is intended to establish a common definitions, testing and measurement methods for bio-char to

be used as a soil amendment and will serve as the basis for an IBI certification program to catalyze the commercialization of bio-char as a soil amendment. This guideline considers the existence of three categories of tests requirements depending on the conditions the bio-char was produced.

IBI requieres all bio-chars to be tested for *Test Category A* (Basic Utility Properties) which includes the most basic properties describing the performance biochar for use in soil: Moisture, Organic Carbon, H:C<sub>org</sub>, Total Ash, Total Nitrogen, pH, Electrical Conductivity, Liming, Particle size distribution. *Test Category B* is also required for all biochars is related with toxicant assessments and include: Earthworm Avoidance, Germination Inhibition Assay, Polycyclic Aromatic Hydrocarbons (PAHs), Dioxin/Furan (PCCD/F), polychlorinated biphenyls, Arsenic, Cadmium, Chromium, Cobalt, Copper, Lead, Molybdenum, Mercury, Nickel, Selenium, Zinc, Boron, Chlorine, Sodium. Test Category C is optional for all biochar materials and includes: Mineral N (ammonium and nitrate), total phosphorous & potassium (P&P), Available P, Volatile Matter, Total Surface Area, External Surface Area. The Guidelines proposed by IBI also contains information for the bio-char sampling method and the preferred product labeling and documentation.

The Biochar standards proposed by the International Bio-char Initiative ([http://www.biochar-international.org/sites/default/files/Guidelines\\_for\\_Biochar\\_That\\_Is\\_Used\\_in\\_Soil\\_Final.pdf](http://www.biochar-international.org/sites/default/files/Guidelines_for_Biochar_That_Is_Used_in_Soil_Final.pdf)) grade biochar according to its carbon content into: Class 1biochar contains 60 % carbon or more; Class 2 biochar has been between 30 and 60% carbon; and Class 3 biochar has between between 10% and 30% carbon. A critical review on the effect of bio-char on soil properties was published by Verheijen et al. (2010) ([http://eusoils.jrc.ec.europa.eu/ESDB\\_Archive/eusoils\\_docs/other/EUR24099.pdf](http://eusoils.jrc.ec.europa.eu/ESDB_Archive/eusoils_docs/other/EUR24099.pdf))

## **4.2 Potential Pollutants (Polyaromatic hydrocarbons and dioxins compounds) in Biochar**

The presence of toxic compounds and contaminats in biochar depends on the nature of the feedstock and the pyrolysis conditions employed. Therefore, biochar must be sampled and analyzed for potential toxic compounds. The International Biochar Initiative has established Guidelines the testing of potential pollutants in biochar .While some potential pollutants (Arsenic, Cadmium, Chromium, Cobalt, Copper, Lead, Molybdenum, Mercury, Nickel, Selenium, Zinc, Boron, Chlorine and Sodium) are present in the feedstock processed other polycyclic Aromatic Hydrocarbons (PAHs) and Dioxin/Furan (PCCD/F) could be formed during the pyrolysis process. A detailed explanation for the need to measure PAHs and Dioxins/Furans (PCCD/F) can be found elsewhere ([http://www.biochar-international.org/sites/default/files/IBI\\_White\\_Paper-Implications\\_of\\_Potential\\_Dioxin\\_in\\_Biochar.pdf](http://www.biochar-international.org/sites/default/files/IBI_White_Paper-Implications_of_Potential_Dioxin_in_Biochar.pdf)). A full risk

assessment for PAHs, heavy metals and dioxins is required to relate contaminant toxicity to bio-char type (Verheijen et al. 2010)

In this section we discuss only the mechanism of polycyclic aromatic and dioxin formation. A review of the mechanism responsible for the formation of these two pollutants during pyrolysis can be found elsewhere (Garcia-Perez and Metcalf 2008). The authors were not able to find any reference to the presence of leachable polycyclic aromatic hydrocarbons (PAHs) or dioxins in chars produced from the fast pyrolysis of woody biomass, but the literature in this field is limited. More research is needed to confirm the absence of these pollutants in bio-oils. Small amounts of PAHs have been reported in bio-oils, and some PAHs may be found in biochar if pyrolysis vapors containing small amounts of PAHs come in contact and condense on the surface of the biochar at relatively low temperatures. These small amounts of PAHs are a result of a complex set of poly-condensation reactions in solid phase leading to the formation of unstable polycyclic aromatic moieties in chars. Biochars produced at temperatures over 500 °C from clean feedstocks and that are not in contact with pyrolysis vapors at temperatures at which they can condense on the surface should not contain measurable concentrations of leachable PAHs.

Although dioxins form during the incineration of municipal solid wastes they are not likely to form during pyrolysis with feedstocks with low contents of chlorines. The main two mechanisms thought to explain the formation of dioxins during thermochemical conversion are pyrosynthesis (or precursor mechanism) and de novo synthesis (Garcia-Perez and Metcalf 2008). Pyrosynthesis supposes that the dioxins are formed by the polycondensation of precursors (e.g. polychlorophenols, polychlorobenzenes). This mechanism occurs in the gas phase at temperatures between 300 and 600 °C. De novo synthesis involves the presence of carbon in the solid phase. O<sub>2</sub> is also essential for the de novo-formation which occurs between 200 and 400 °C. Few studies about PHA, dioxin, and furan contaminants on biochar have been found; therefore more work is needed to be done in this topic.

The concentration of the total and bioavailable concentrations of toxic PHAs and dioxins was measured by Hale et al. (2012) for 50 biochars produced via slow pyrolysis between 250 and 900 °C, using various production methods and feedstocks. Total PHA concentrations for bio-chars produced by slow pyrolysis ranged from 0.07 µg/g to 3.27 µg/g which is below existing environmental quality standards for PHAs in soils. Bio-chars produced by fast pyrolysis and gasification exhibited higher concentrations of PHAs (between 0.3 µg/g and 45 µg/g). The bio-available compounds are those that are able to cross an organism's cellular membrane. In the case of bio-chars produced by slow pyrolysis systems it ranged from 0.17 ng/L to 10 ng/L, far lower than the concentrations reported in clean urban sediments. Gasification produced bio-chars exhibited higher bioavailable concentration (162+/- 71 ng/L). Very low concentrations of dioxins (up to 92 pg/g) were detected and bioavailable concentrations were below detection limits.

# 5. Products From Bio-Oil and Biochar

This section describes products that can be obtained from bio-oils and biochar.<sup>4</sup>

## 5.1. Bio-oil Products

Crude bio-oil can be used as feedstock for producing fuels, chemicals, and materials. Although bio-oil has been successfully tested in engines, turbines, and boilers and has been upgraded to high-quality hydrocarbon fuels, it cannot be considered a commercial commodity due to lack of standards that ensure consistent performance and lack of companies to process crude materials into final products with established markets.<sup>5</sup>

By taking advantage of bio-oil's most abundant functional groups (carbonyl, carboxyl and phenolics) it is possible to develop useful products. Table 10 shows the content of some of the most important functional groups in bio-oils.

**Table 10. Content of the most important chemical groups in bio-oils (Radlein 2005)**

Feedstock	Moles Functional Groups / kg Organic Liquid				
	Carbonyl	Carboxyl	Hydroxyl	Phenolic	Methoxyl
Maple	2.1	5.7	0.92	2.8	2.1
Wheat Straw	1.4	5.3	1.4	3.0	1.1
Poplar-Aspen	2.1	6.2	0.8	2.8	1.6
Peat Moss	1.2	3.0	1.3	1.8	0.7

## 5.2. Energy from Bio-oils

This section summarizes strategies to produce energy, fuels and bio-products from bio-oils.

*Heat and electricity:* Energy production from bio-oil has been in development for the last twenty years. The heating value of bio-oil is 40 – 50% lower than that of fossil fuel. This is mainly due to the large number of oxygenated compounds and water. Although significant differences in ignition, viscosity, energy content, stability, pH, and emission levels have been observed, bio-oil is similar to light fuel oils in its combustion characteristics. Combustion tests have shown that fast pyrolysis oils could be used in industrial boiler applications in which heavy and light fuel oils are currently used (<http://www.btgworld.com>).

<sup>4</sup> This report does not review the syngas products because most syngas is used as a heat source in the pyrolysis unit. Spath and Dayton (2003) published an excellent review of technologies for syngas utilization.

<sup>5</sup> For further reviews on potential products from bio-oil see Czernik and Bridgwater 2004 and Radlein 1999.

The oil remaining after the production of food flavoring (liquid smoke) at Red Arrow has been combusted for many years. In order for pyrolysis oils to be burned in boilers and burners without clogging nozzles, certain limitations regarding viscosity and the content of solids must not be exceeded. One of the main problems is to keep the nozzles operational after they are shut down. Because bio-oil has to be heated before spraying it, small scale boilers without systems to preheat the fuel cannot use bio-oils as fuel. In contrast many diesel engines and heavy fuel boilers have preheating systems to heat the oil to 150 °C (Scholze 2002).

Several studies have shown bio-oil to fuel slow speed diesel engines (Czernik and Bridgwater 2004, Moses 1994, Oasmaa et al 2001, Oasmaa and Czernik 1999, Van de Kamp 2000, Venderbosch and van Helden 2001). Dual fuels or bio-fuels with alcohol added perform best in higher speed engines. Some damage to the injectors and fuel pumps were observed on the tests with diesel emulsions up to 50 percent bio-oil (<http://www.forestprod.org/biomass09steele.pdf>). Oils produced by Dynamotive were tested by the Orenda Aerospace Corporation (<http://www.forestprod.org/biomass09steele.pdf>). Tests with pure bio-oils with fuel modes proved successful, but some problems were reported concerning deposits in the combustion chamber and on the blades.

It is possible to fuel a Stirling engine with combined heat and power application using bio-oil. A 25 kW Stirling CHP unit supplied with a modified FLOX (flameless oxidation) burner that included an air pressure atomizer was fueled with bio-oil by ZSW (Germany). Burning bio-oil in such a burner proved to be functional without noticeable residues and with emissions below German standards. Thermal and electrical efficiencies were between 50 and 60% (<http://www.forestprod.org/biomass09steele.pdf>). The Metso/Fortum/UPM/VTT consortium is targeting heat and power production (Buttler et al 2011, Lehto et al 2010)

Major hurdles preventing commercialization of pyrolysis oils as fuels, despite the fact that they have successfully been combusted, include a lack of bio-oil quality standards, the intrinsic limitation of pyrolysis units to maintain bio-oil quality while the quality of the feedstock changes, and the lack of commercial energy systems (turbines, boilers, diesel engines) designed to use these oils as regular fuels (<http://www.btgworld.com>). Pre-heating bio-oil, altering the fuel pump, the linings and the injection system, or blending with other fuels are strategies that can make bio-oil use effective (Mohan et al. 2006). Chiaramonti et al. 2006 published an excellent review of the hurdles and challenges of using bio-oils as fuel for power generation. Some of the most common alternatives used to improve the fuel quality of bio-oils (up-grading) for energy production are listed in Table 11.

**Table 11. Bio-oil up-grading strategies**

<b>Up-grading strategy</b>	<b>References</b>
Production of micro-emulsions	Chiaramonti et al 2003 a, b, Ikura et al 1998, Jiang and Ellis 2009, 2010, Qi et al 2007
Extraction of fractions with bio-diesel	Garcia-Perez et al 2007, 2010
Blending with solvents	Boucher et al 2000, Chiaramonti et al. 2007, Diebold 2000, San Miguel et al 2011, Nguyen and Honnery 2008
Acetilization and esterification	Junming et al 2008, Gunawan et al. 2012, Li et al. 2011 , Miao and Shanks 2009, Moens et al 2009, Peng et al 2009, Radlein et al 2005, Wang et al 2010 a, b
Calcium enriched bio-oil (CEB)	Czernik and Bridgwater 2004, Sotirchos and Smith 2003

### 5.3. Chemical Products and Transportation Fuels

The production of transportation bio-fuels and chemicals from bio-oil is critical to improve the economic viability of biomass pyrolysis conversion pathways. Table 12 and 13 summarize potential chemical products and transportation fuels that can be obtained from bio-oils. For a more detailed description of fuels and chemicals than can be produced from bio-oils see Appendix E.

**Table 12. Chemicals that can be obtained from bio-oils.**

<b>Chemical</b>	<b>Note</b>	<b>Reference</b>
Acetic Acid	World Production: 7 million tons/year, potential price: 0.6 \$/kg	Patel et al. 2006, Rasrendra et al. 2010
Adhesives	Phenol substitute for the production of adhesives for the production of wood panels (plywood, MDF, particle board and OSB)	Czernik and Bridgwater 2004, Effendi et al. 2008, Mohan et al. 2006
Aldehydes and ketones	Separation of aldehydes and ketones have been investigated by bio-coupling	Vitasari et al. 2010,
Alkylaromatics	Conversion using zeolites	Resasco et al 2010
Antioxidants	Antioxidant properties of lignin derived compounds	Garcia-Perez et al 2010
Asphalt paving substitution	Production of asphalt emulsions	Mullaney et al. 2002
Bio-carbon electrodes	Production of electrodes, calcinations at 1000 °C and graphitization at 2700 °C.	Coutinho et al. 2000
Coal dust suppression	The current product used to coat coal piles is a plasticizer that is bio-degradable and does not contaminate ground water	Mullaney et al 2002
Fertilizer	Amides, imines and Mannich reaction products, are produced from the reaction of bio-oil functional groups (carbonyl, carboxyl, hydroxyl, phenolic and methoxyl) with ammonia, urea, and other amino compounds and can function as slow release organic fertilizers	Radlein et al. 2005
Food additives	Commercialized by Red Arrow Products and RTI. A new method for the separation of glycoaldehyde from pyrolysis oil via physical extraction has been reported by researchers from the Eindhoven University of Technology	Czernik and Bridgwater 2004, Mohan et al. 2006, Vitasari et al 2010
Glucose	Can be obtained by hydrolyzing hydrolyzable sugars (levoglucosan, cellobiosan)	Lian et al. 2010, Patel et al. 2006

Chemical	Note	Reference
5-hydroxymethyl furfural (HMF)	Attractive building block for further derivatization	Patel et al. 2006
Levoglucosan	By using demineralized cellulose, high yields of levoglucosan (up to 46 wt. %) and levoglucosenone (up to 24 wt. %) can be generated	Czernik and Bridgwater 2004, Radlein et al (1999)
Methanol	Can be produced from the distillation of pyroligneous water	Emrich 1985
Pesticides	Significant activity against two bacteria and the Colorado potato beetle were shown using bio-oil derived from dried coffee grounds	Bedmutha et al. 2011, Booker et al. 2010
Impermeabilizer	Black residue of tar distillation commercialized to impermeabilize ships	Emrich 1985
Road de-icer	Calcium salts of carboxylic acids	Czernik and Bridgwater 2004
Surfactants	More than 10 commercial grades are used for ore flotation	Emrich 1985
Wood preservatives	Bio-oils can act as insecticides and fungicides due to some of the terpenoid and phenolic compounds present	Czernik and Bridgwater 2004, Mohan et al. 2008

**Table 13. High value fuels derived from bio-oils.**

Fuel	References
Hydrogen production	Bleeker et al 2010, Czernik et al. 1999, Davidian et al. 2007, Galdamez et al. 2005, Medrano et al. 2010, Rioche et al. 2005, Takanabe et al. 2004, Wang et al. 1997, 1999, Wang et al. 1997, 1998)
Synthesis gas	van Rossum et al. 2007, Mohan et al. 2006
Ethanol	Bennett et al 2009, Lian et al 2010, Miyafiji et al 2005, Olson and Freel 2007, Patel et al. 2006, Prosen et al. 1993, Shafizadeh and Stevenson 1982.
Hydrotreatment to Produce hydrocarbons	Adjaye et al. 1996, Baker and Elliott 1993, Bui et al. 2009, Christensen et al 2011, De Miguel-Mercader 2010, Elliott and Baker 1989, Elliott et al. 2009, 2010, French et al. 2009, 2010 and 2011, Furimisky 2000, Hogendoorn and de Miguel Mercader 2010, Maggi and Delmon 1997, Mahfud 2007, Oasmaa et al 2010, Senol et al 2005, Tang et al 2009, Vanderbosch et al. 2010, Wildschut et al. 2009 and 2010, Wilson and Williams 2003, Wright et al. 2010

## 5.4. Bio-oil Refineries

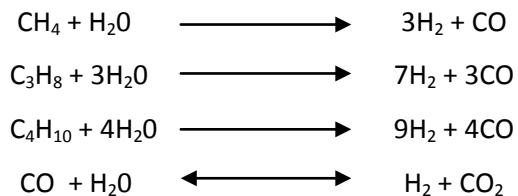
Integrating pyrolysis technologies into bio-refinery concepts to fully utilize all bio-oil fractions is a primary challenge facing the thermochemical conversion industry and scientific community. Although bio-oil up-grading is currently limited to laboratory and pilot plant studies, rapid developments in this area are occurring (Buttler et al 2011). To improve the economic viability of bio-oil refineries, the combined production of drop-in fuels for large markets and high-value products for niche markets is needed. The integration of these new dimensions into the existing infrastructure (e.g. the pulp and paper industry or petroleum refineries) is another important consideration for enhancing the economic viability of pyrolysis technologies.

The old wood distillation industry usually delivered crude products (pyroligneous acid and tars) to specialized distilleries. The rectification and separation of methanol, acetone and acetic acid in the old

wood distillation industry was often performed separately to the carbonization itself (Emrich et al. 1985). The new bio-oil refineries could also make use of similar concepts. In this section we discuss several bio-refinery concepts. An excellent review on recent laboratory and commercial developments in fast pyrolysis and up-grading has been recently published by Buttler et al (2011).

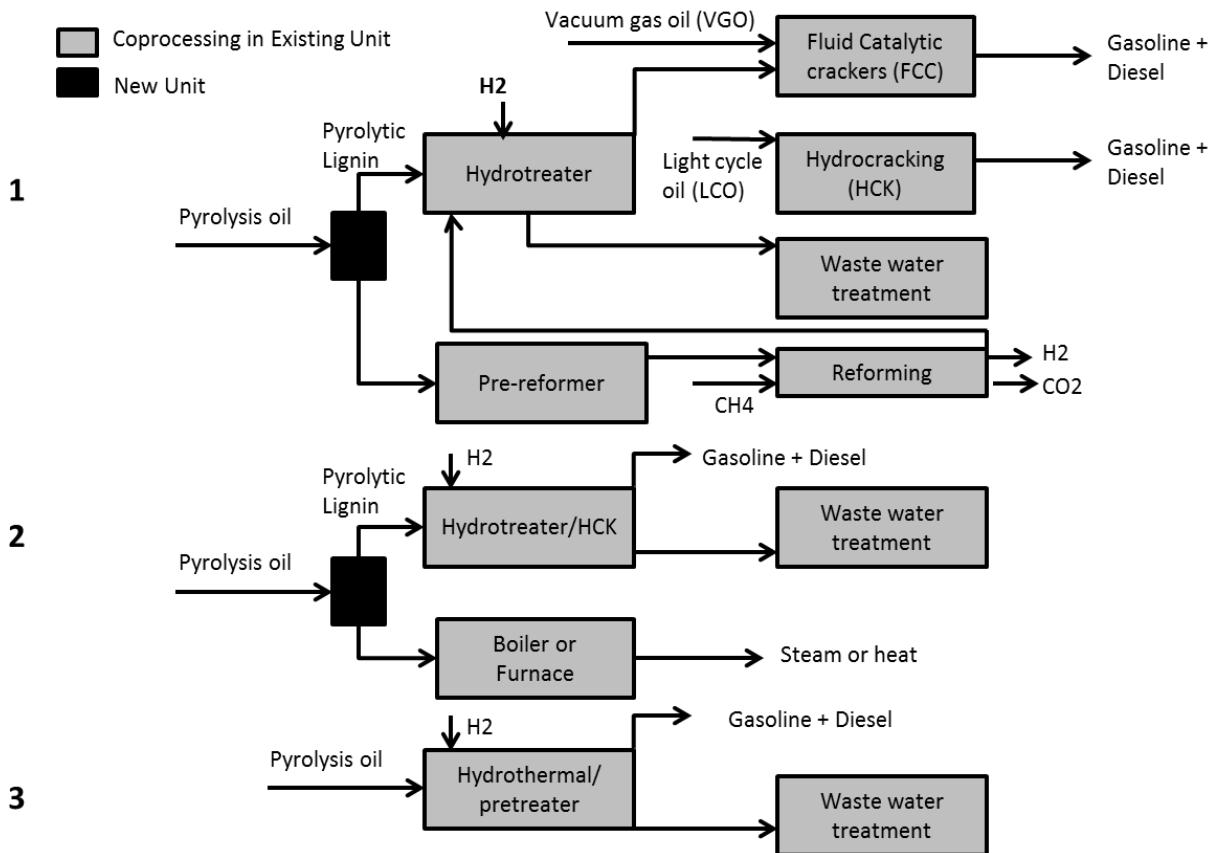
#### **5.4.1 Bio-oil Refinery Schemes Based on Hydrotreatment**

One of the main challenges to utilize bio-oils as a feedstock to produce hydrocarbon like biofuels is their high oxygen content (~46%). To produce green gasoline or diesel oxygen has to be removed from bio-oil typically with hydrogen in a process known as hydrotreatment. Although, there are different ways to produce the hydrogen needed for the hydrotreatment step (partial oxidation of residual oils, gasification of coal, and water electrolysis), steam reforming of gases like methane, ethane and propane is by far the most commonly used method. According to Jones et al (2009) 16% of the cost of the hydrotreated bio-oil will be associated to the natural gas used to produce the hydrogen needed for the hydrotreatment step. During steam reforming the C1-C4 hydrocarbons are heated at temperatures over 800 °C and mixed with water vapor (steam) in a presence of a Ni based catalyst to produce hydrogen, CO and CO<sub>2</sub> as shown in the following chemicals reactions:



The CO not converted in the steam reformed is then converted at lower temperatures in a Water Shift reactor. The CO<sub>2</sub> in the gas stream is then removed by adsorption or absorption. The purified hydrogen produced is then compressed and used in the hydrotreatment step.

Marinangeli et al. (2005) studied several options for using whole crude pyrolysis oil and its two fractions (pyrolytic lignin (decanted oil) and the water soluble phase) to produce transportation fuels. Decanted oil can be converted into gasoline with lower H<sub>2</sub> consumption using mild hydrotreating followed by hydrocracking (bio-oil molecules are catalytically broken into smaller molecules in the range of gasoline and kerosene) (Marinangeli et al. 2005). Three bio-oil refinery schemes evaluated by Marinangeli et al. (2005) are shown in Figure 21.



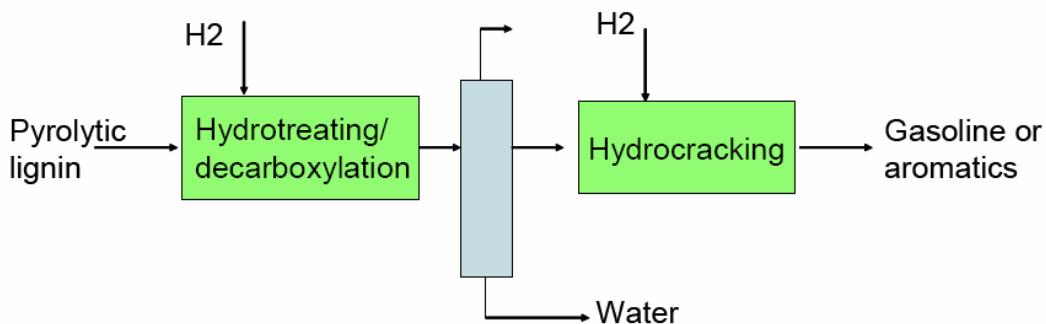
**Figure 21. Processing routes for pyrolysis oil (Adapted from: Marinangeli 2005).**

In the first scheme, the water-soluble phase of pyrolysis oils is considered suitable for generating hydrogen. Steam reforming of the water-soluble portion of pyrolysis oil can provide most or all of the hydrogen used in a bio-oil refinery (Marinangeli et al. 2005). Removing oxygen from decanted oil (rich in lignin derived compounds) naturally generates materials in the gasoline boiling range because of the molecular structure of this phase. The decanted phase has less oxygen and as such requires less hydrogen than pyrolysis oil (Marinangeli et al. 2005).

The second scheme assumes that the aqueous phase is used to produce heat and steam. Thus, the hydrogen consumed for the hydrotreatment of the decanted oil is generated through the use of conventional means.

The third scheme considers that no hydrogen will be produced from the bio-oil and that the whole bio-oil will be hydro-thermally treated. The fact that large quantities of hydrogen are required to generate water during hydrotreatment, due to the high levels of oxygen (46%) in pyrolysis oil, is the main drawback with this concept (Marinangeli et al. 2005). Although the hydrotreatment of decanted oil can be conducted in a single step, the hydrotreatment of the whole bio-oil has to be conducted in two steps. The main purpose of the first hydrotreatment step is to stabilize aldehyde groups and/or reduce the oxygen content and the total acid number (TAN). Transportation fuel is produced in the second hydrocracking step (Holmgren et al.

2008). A scheme in which water is separated after the first hydrotreatment step is described in Figure 22. The main disadvantage here is that some pyrolytic sugars are lost in the water phase due to solubility.



**Figure 22. Hydrotreating/hydrocracking of pyrolytic lignin process flow (Marinangeli et al. 2005).**

Hydrogen consumption and product yield from bio-oil hydroprocessing is shown in Table 14 (Holmgren et al. 2008). About 41 wt. % of the bio-oil is converted into products in the naphtha and diesel range (Holmgren et al. 2008).

**Table 14. Estimated consumption of hydrogen and yield of diesel and naphtha obtained from pyrolysis oil hydrotreatment (wt. %) (Holmgren et al. 2008).**

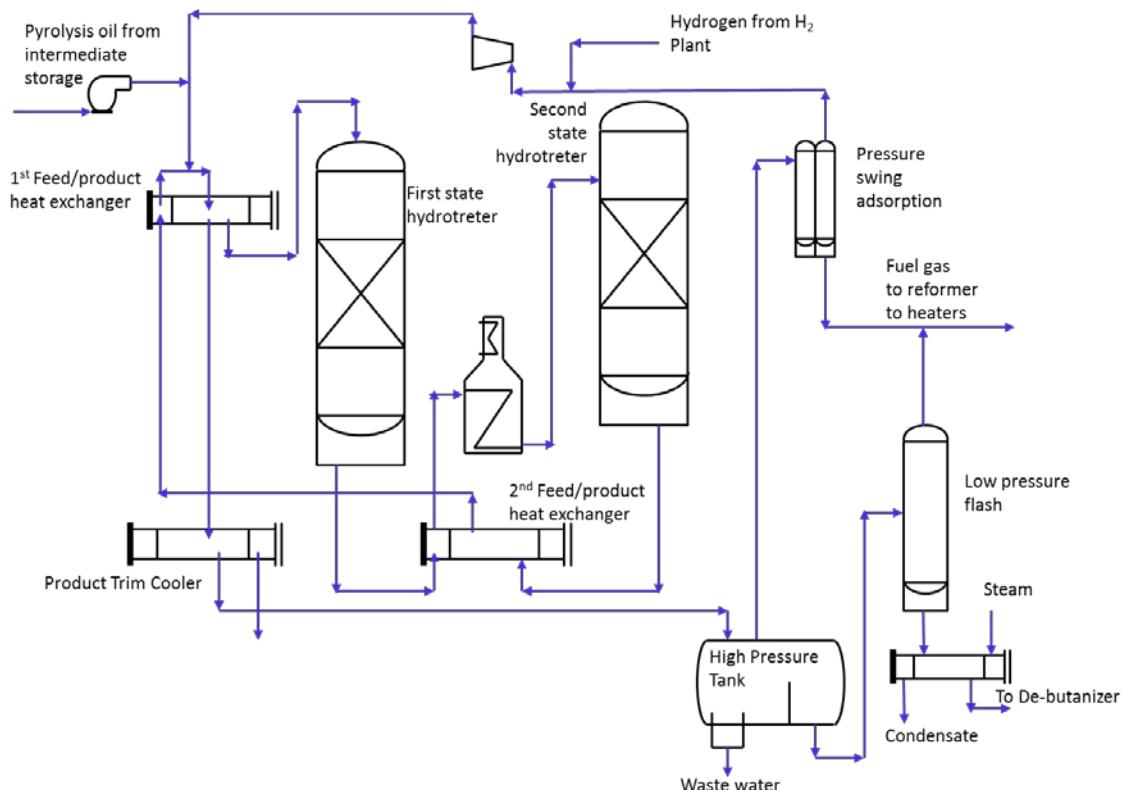
Feed	Wt. %
H <sub>2</sub>	3-4.5
<b>Products</b>	
Naphtha range	21
Diesel range	21
Water, CO <sub>2</sub> , more volatile compounds (lights)	60

The composition of multiple samples of the gasoline range product from bio-oil hydroprocessing is compared to gasoline composition in Table 15. Based on pyrolysis oil, carbon recovery is about 50% (Holmgren et al. 2008). Clearly, the content of paraffins and iso-paraffins is much lower in hydrotreated bio-oil than in commercial gasoline. Naphthene content is considerably higher. The source of paraffins and iso-paraffins is not well known, but naphthene is produced from lignin derived intermediates.

**Table 15. Gasoline cut of a hydroprocessed bio-oil (wt. %) composition (Holmgreen et al. 2008).**

Hydroprocessed Bio-oil (from mixed wood)			Gasoline
	Min.	Max.	
Parafins	5.2	9.5	44.2
Iso-paraffins	16.7	24.9	35
Olefins	0.6	0.9	4.1
Naphthene	39.6	55.0	7
Aromatic	9.9	34.6	38
Oxygenate		0.8	

Jones et al. (2009) describe several refining pathways and presents mass and energy balances of several concepts for a 2,000 dry metric tons/day plant to process hybrid poplar chips. An important parameter influencing the economic viability of a bio-oil refinery is the possibility of co-locating the plant with an existing refinery (Jones et al. 2009). A detailed overview of the two-step stabilization section and preheater are shown in Figure 23.<sup>6</sup>



**Figure 23. Pyrolysis stabilization flow diagram (Adapted from: Jones et al. 2009).**

The concept of distributed pyrolysis units followed by hydrotreatment in a centralized refinery is being pursued by Evergent ([www.envergenttech.com](http://www.envergenttech.com)). This is a joint venture between Ensyn's Rapid Thermal Preprocessing (RTP) and UOP Hydroprocessing Technologies (Buttler et al. 2011). The first 1 ton/day demonstration unit able to produce 4 barrels per day of gasoline, diesel and jet fuel is expected to be operational in 2014 at the Tesoro Corporation refinery in Kapolei Hawaii (Elliot et al. 2010, Gross 2010). There are plans to build other 9 new systems in Malasia (Buttler et al. 2011, Tan 2010). Dynamotive ([www.dynamotive.com](http://www.dynamotive.com)) and IFP are also pursuing an association to produce transportation fuels via hydrotreatment (Buttler et al. 2011, Radlein et al 2010).

<sup>6</sup> For further details see Jones et al. 2009.

#### 5.4.2 Alternative Bio-oil Refinery Concepts

The concepts described in the previous section target the production of fuel with limited emphasis on high-value bio-products. High-value bio-oil products are critical to enhance the economic viability of a rural bio-oil refinery. Schemes that integrate the production of high-value chemicals with bio-fuels production are discussed here.

The bio-refinery concept employed by the old wood distillation industry produced biochar, tars, acetone and wood naphtha (Figure 24). Slow pyrolysis technologies were the basis for this industry. The separation of decanted tar and dissolved tar is shown in Figure 24. While decanted tars are lignin products, dissolved tars are presumably products derived from the carbohydrate fraction (Hawley and Calderwood 1925). As explained in the previous section, advanced hydrotreatment methods now allow production of transportation fuels from these tars.

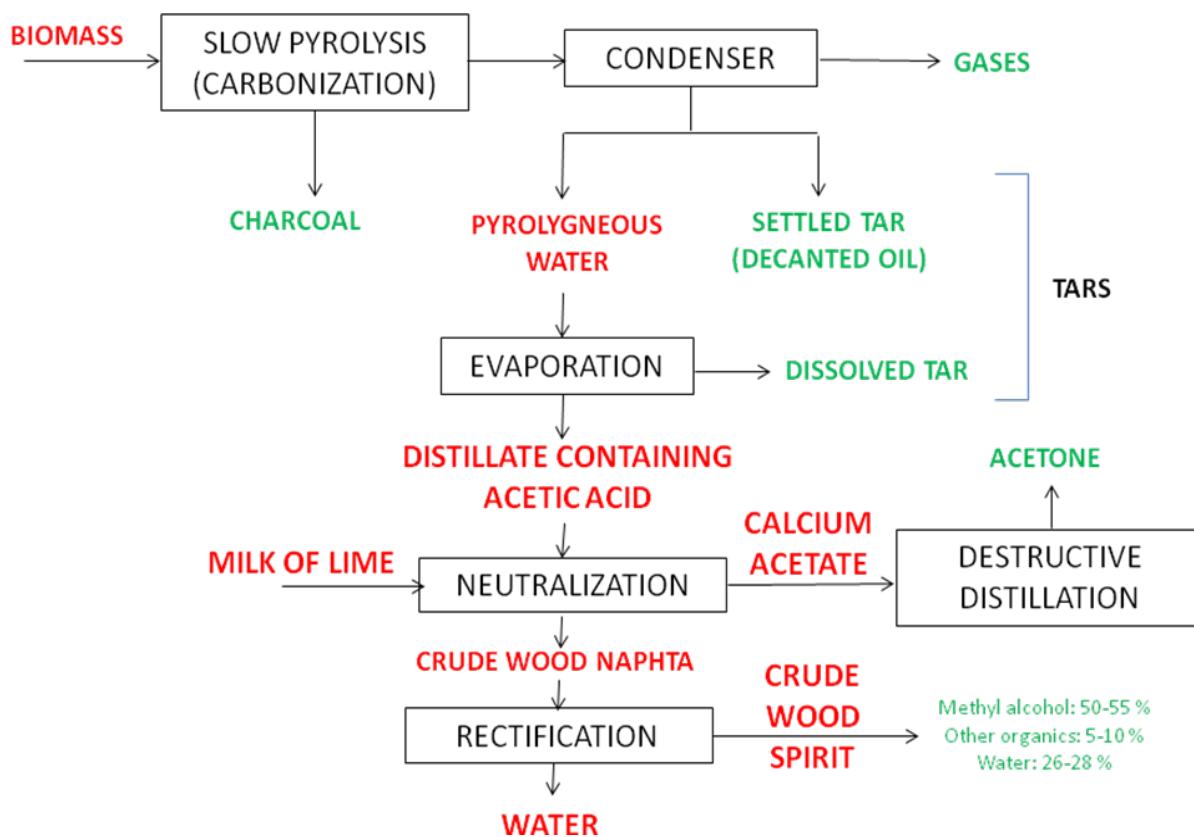


Figure 24. Old wood distillation industry's bio-refinery concept (Klar and Rule 1925).

After the separation of the crude wood spirit (Figure 24) the pyroligneous acid is distilled in copper vessels and a limewash is used to collect the acetic acid and water vapors. Using drums at a temperature no higher than 180 °C, the precipitated lime acetate is dry-evaporated. This crude acetate contains 80% calcium acetate by weight and is also known as grey acetate (Emrich 1985). An acetic acid at 85% can be obtained by decomposing grey acetate with sulfuric acid. An alternative method can be used to obtain

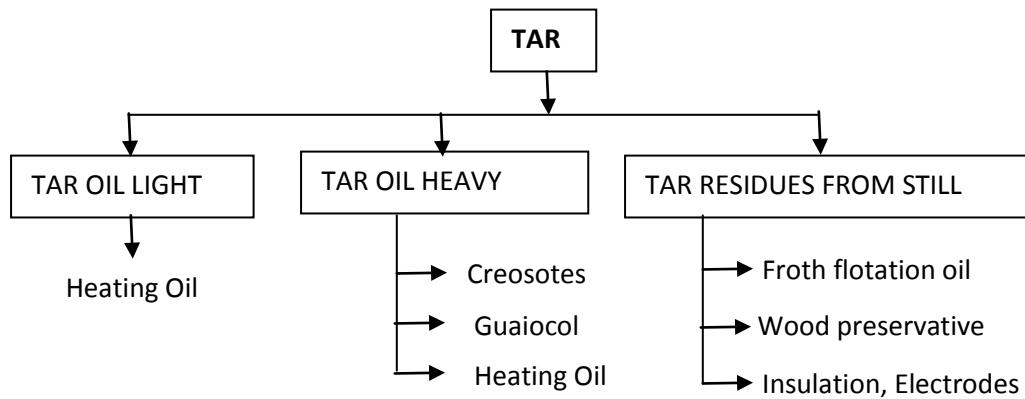
acetone which includes heating grey acetate to 400-500 °C. Rectification (Figure 24) can be used to purify the crude acetone (Emrich et al. 1985). Passing the pyroligneous acid over catalysts at 500 °C is another alternative to obtain acetone.

Direct recovery of acetic acid by distillation is another process used to refine the aqueous phase (Emrich 1985). The first step is distillation of the pyroligneous acid from a weak acid solution. Toluene ( $C_7H_8$ ) is used by several companies during the distillation process to draw off the moisture. The two stage process is slightly more sophisticated. Upon distillation in the first step, the solution is diluted with xylene which combines with water to form a binary mixture with a very low boiling point. Once the concentration of acetic acid is obtained from the first stage, it is then distilled again with benzene to form a fresh mixture (Emrich 1985).

The des Products Chemiques de Clamancy and Lambotte Brother plant developed a slightly different method (Emrich 1985). This method eliminates moisture with the distillation of an azeotrope formed with butyl acetate, or using a tar reactor with a counter-current of circulating butyl acetate through which a fraction of the wood spirit is passed (Emrich 1985).

The acetic acid ether method is used by a plant belonging to the Deutsche Gold und Silber Scheidenanstalt, to extract acetic acid. A ten meter tower with a counter current of acetic ether introduced from the bottom is then used as the extraction tower. The pyroligneous acid obtained from the wood spirit is introduced into the top of this tower. In order to ensure good contact, the tower is fitted with rassings rings (Emrich 1985). The run-off water at the bottom of the tower contains some dissolved ether which can be collected through rectification. From the top, a mixture of ether and acetic acid with little tar is released. Using rectification, the collected ether can be recycled back into the extraction tower. Vacuum distillation is then used to separate the crude acetic acid from any remaining tar. An acetic acid of 95% is the result (Emrich 1985).

*Tar processing:* Tar is obtained at different locations in the plant throughout the entire process and kept separate in tanks (Emrich et al. 1985). A large quantity of tar can be secured from the settling of pyrolysis oil before the process even begins. Commercial uses of tar obtained from pyrolysis are shown in Figure 25.

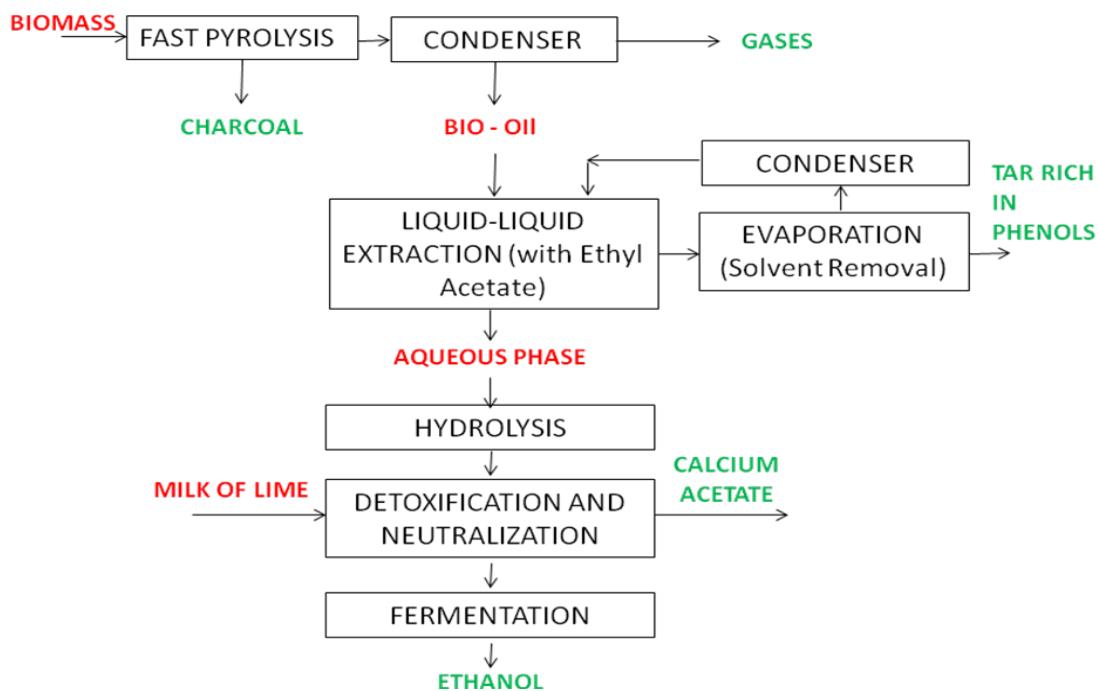


**Figure 25. Commercial products from recovered pyrolytic tar (Emrich 1985).**

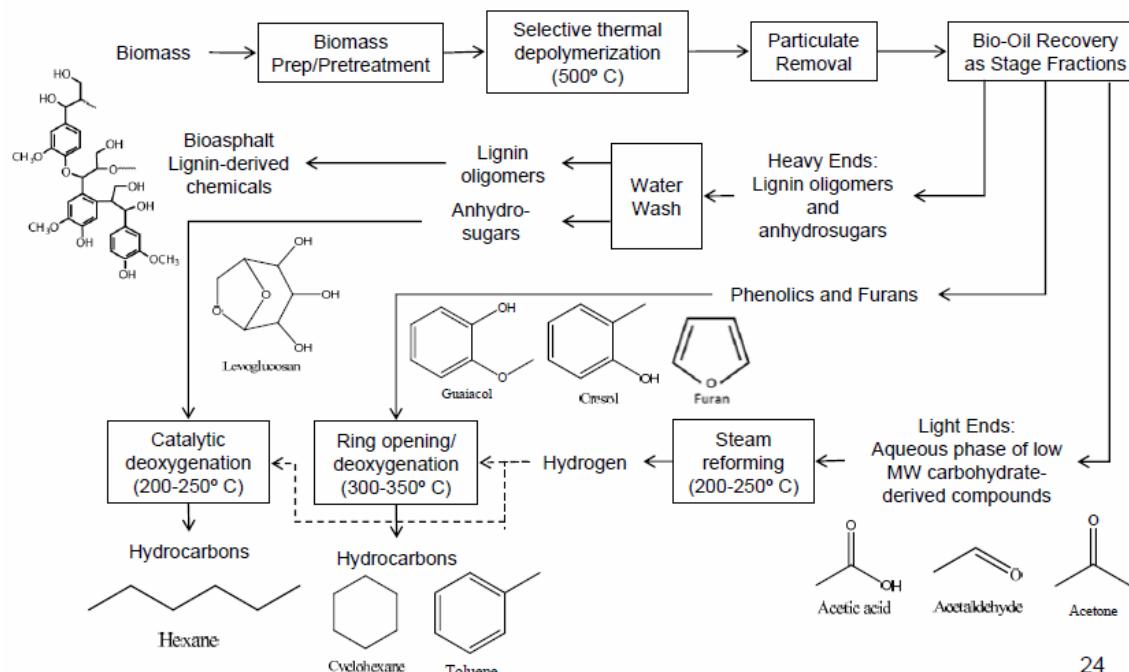
By distilling the tar, the content of waste, wood spirits, and light oils can be separated. Most of the moisture, acetic acid, wood spirit, and light oils are given off when the tar is heated to 140 °C. Direct introduction of steam further heats the tar until no more acetic acid is carried off. A tar free of moisture and acid that still contains heavy oils is the retort residue. An open fire retort similar to those used in distilling coal tar can be used to separate the creosote. Since tar tends to froth, preliminary heating should be done with care. After completion of the first distilling step at around 110 °C, the temperature should be raised to 250 – 260 °C before resuming distillation. Different vessels are used to collect the oils which are respectively lighter and heavier than water. Once the operation is completed at a temperature of 260 °C, the residue of tar distillation (pyrolytic pitch) remains (Emrich 1985). This pitch has a dark brown or black color. Four different grades of tar, marketed by their softening points, are typically supplied by charcoal plants (Emrich 1985).

Use of organic solvents is another method to separate fast pyrolysis bio-oil. In Figure 26, lignin derived tars are extracted with ethyl acetate. Separating the phenolic fraction from the lignin and sugars that are derived from the cellulose with solvent extraction is the first step. This solvent extraction step results in pyrolytic sugars in aqueous phase (levoglucosan and cellobiosan). These pyrolytic sugars are then hydrolyzed to mono-sugars, detoxified (removing most of the acids and phenols), neutralized to an appropriate pH, and finally, fermented to produce ethanol. It is important to reduce the tendency of the phenolic fraction to form coke during combustion or hydrotreatment by the separation and full utilization of the sugars (Garcia-Perez et al. 2009). The advantage of this method is that the energy needed to concentrate products from the water soluble fraction is minimized since the aqueous phase is not very diluted with water. A disadvantage of this method is the use of organic solvents, which must be recycled.

Brown (2010) proposed a bio-oil refinery concept with three condensation steps to produce heavy lignin oligomers and sugars, mono-phenols and a light fraction rich in C<sub>1</sub>-C<sub>4</sub> oxygenated molecules. By adding water into the fraction rich in sugars, sugars and lignin oligomers can be separated. Aliphatic compounds are then produced by hydrotreating the sugars (Figure 27).



**Figure 26. Alternative concept for the production of ethanol and tar rich in phenols in a bio-refinery (Garcia-Perez et al. 2009).**



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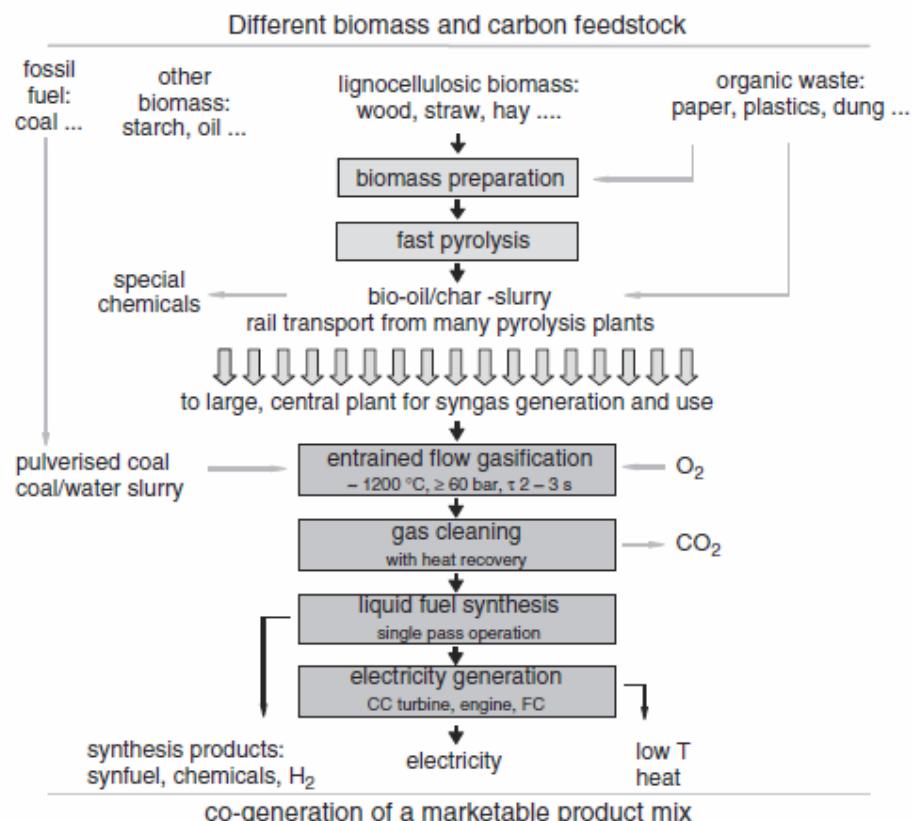
**Figure 27. Strategy for up-grading bio-oil (Brown 2010).**

Bio-oil gasification and further conversion of syngas to produce valuable products is another concept of interest (Figure 28) (Henrich et al. 2009). Extensive studies have explored the production of syngas from

pyrolysis oil (van Rossum et al. 2007, Wright et al. 2008). An estimate of the material and energy balances for the total process is presented by Henrich et al. (2009). The Bioliq concept proposed by KIT (Germany) consisting in the production of a bioslurry followed by its gasification is being tested in 12 tons per day a demonstration plant commissioned in 2008 (Henrich 2007, Dahmen 2010).

The esterification and acetylation of bio-oils has been used as the main concept for the bio-oil refinery concept proposed by Radlein (2005) (Figure 29). This concept has been studied expetnsively by other researchers (Gunawan et al. 2012, Li et al 2011, Moens et al 2009, Peng et al 2009).

An integrative overview of the options studied by Biomass Technology Group (BTG) to process pyrolysis oils is shown in Figure 30. This figure integrates several technologies described in previous sections.



**Figure 28. Simplified scheme which uses bio-oil/biochar slurries to produce Fischer-Tropsch (FT) syngas (Henrich et al. 2009).**

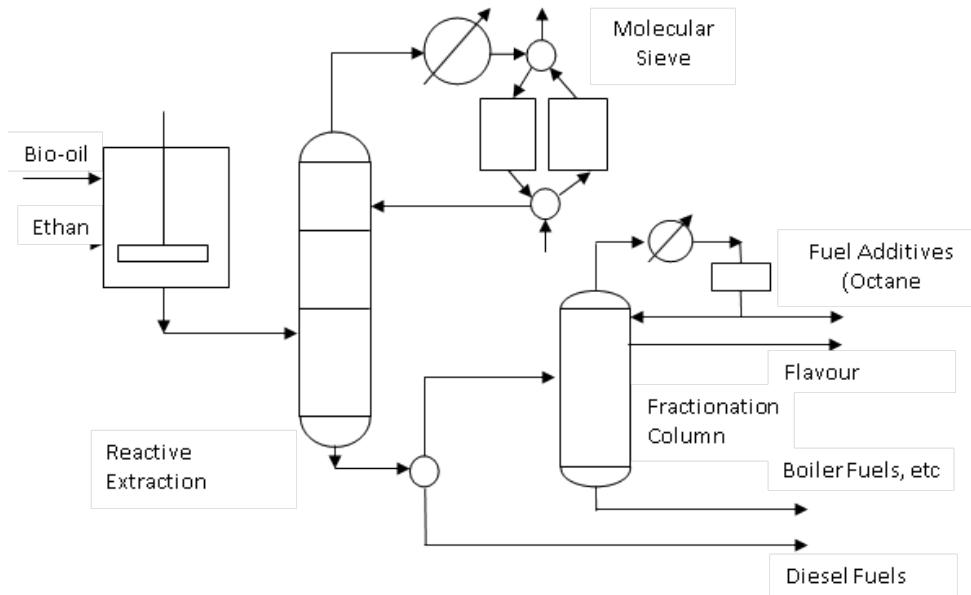


Figure 29. Bio-oil refinery concept based on the acetylation of esterified bio-oil (Radlein 2005).

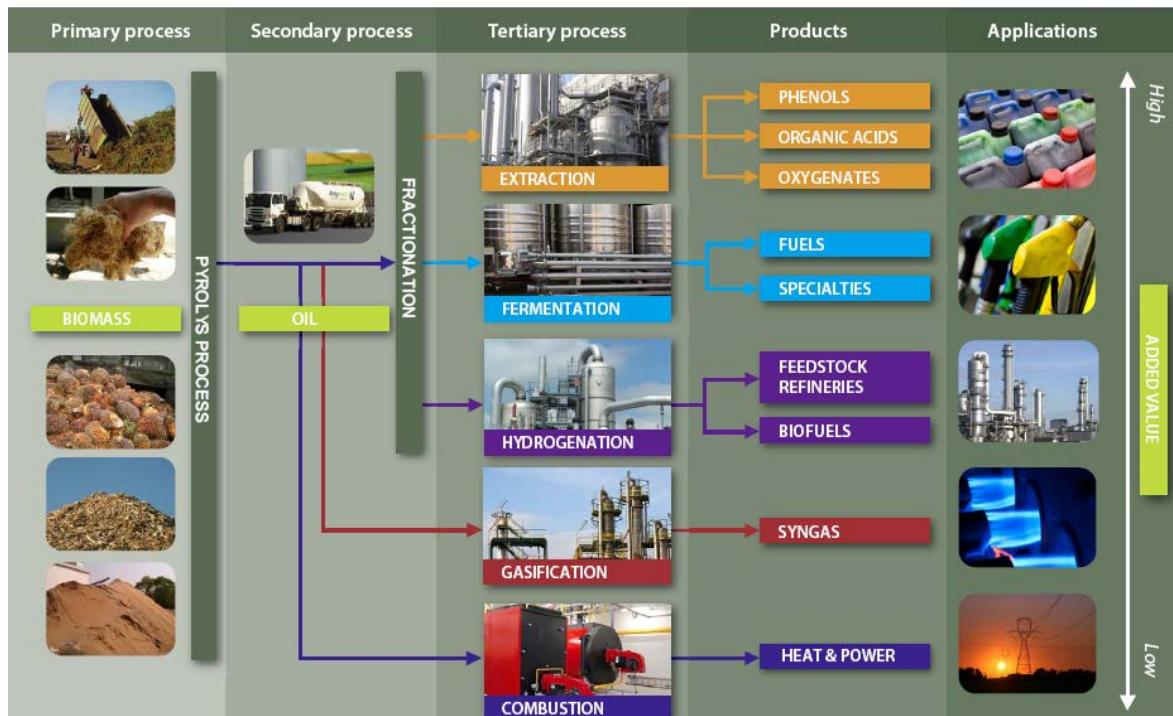


Figure 30. Bio-refinery vision of BTG (source: <http://www.btgworld.com/index.php?id=23&rid=8&r=rd>).

## 5.5. Biochar Products

Today there are two main markets for biochar utilization: industrial applications (activated carbon and metallurgical applications) and household markets. The development of environmental, agricultural and silvicultural applications of biochars also may open new markets. Each market is associated with

different tactics, individual specifications, packing styles and marketing habits. New markets for biochar products (e.g. carbon sequestration), will inevitably require specialized producers (Emrich 1985, Toole 1961). This section provides a comprehensive overview of products that can be produced from biochar<sup>7</sup>.

### *5.5.1 Household Fuel*

The use of biochar for cooking is common in many developing countries. Cooking with biochar in industrialized countries has developed specifically for patios, gardens, beaches, camp sites and public spaces.<sup>8</sup> Lump biochar is a preferred cooking fuel in developing nations and users are aware of significant differences in cooking time and calorific values of different chars (Emrich 1985, Kambewa et al. 2007). Biochar briquettes were introduced into the United States in 1955. Export specifications of biochar for cooking are shown in Table 16 (Emrich 1985).

**Table 16. Specifications for biochar export (Emrich 1985).**

Properties	Lump biochar	Briquettes	
		Without energy extender	With energy extender
Ashes (wt. %)	3 – 4	Max. 8	Max. 25
Moisture (wt. %)	Less than 5	5	5
Carbon (wt. %)	80 – 82	70-75	60-65
Volatiles (wt. %)	10 – 15	10-15	10-15
Binder (wt. %)	-	Max 8	Max. 8
Calorific Value (kcal/kg)	6,800 – 7,200	6,000	5,200

### *5.5.2 Activated Carbon - Activating Biochar*

Activated carbon refers to many types of carbon that have been treated to increase its adsorptive properties. Because the adsorptive properties of existing activated carbon are based on the surface area of their carbonaceous matrices, activated carbon tends to be produced from feedstocks with low ash content (example wood, coconut shells and hard coal). The high ash content of some biomasses makes it difficult to achieve very high surface area, but may confer some interesting characteristics to biochars for environmental applications. Activated carbon is used in liquid and gas phase adsorption processes and is available in either a powder or granular (extruded) form. Adsorption onto activated carbon is often considered the most economical for the removal of organic compounds and metals from diluted aqueous solutions. US-EPA has stated that activated carbon adsorption is one the best available environmental control technologies (Marsh and Rodriguez-Reinoso 2006, Derbyshire et al 2001). Although biochar can be obtained from any biomass, producing activated carbon that is capable of performing with the efficiency required for industrial applications does not happen easily (Marsh and Rodriguez-Reinoso 2006). Commercial activated carbon on the market today is the result of intensive research and

<sup>7</sup> Further information and detail is provided by Marsh and Rodriguez-Reinoso 2006 and Emrich 1985.

<sup>8</sup> Using charcoal as fuel and its efficiency is described by the Food and Agriculture Organization (FAO 1987).

development to optimize various applications. Activated biochar may find new markets for numerous applications in the ecosystem if materials with acceptable sorption properties could be produced at a fraction of current activated carbon production cost using waste lignocellulosic materials as feedstocks.

The usability of wood biochar for activated carbon depends on the ash content and its availability in uniform and unvarying quality. Biochar made from coconut shells, hardwood species, sawdust and wood waste (with the exception of bark), can produce exceptionally good activated carbon (Emrich 1985). In order to adsorb molecules of different sizes, activated carbon must have a large volume of micropores with the appropriate pore size distribution. An adequate proportion of mesopores is also necessary to facilitate access to the micropores (Marsh and Rodriguez-Reinoso 2006).

In addition to a thorough physico-chemical characterization, the activated carbon producer should test the biochar to determine the adsorption capacity of the finished product before commercializing the material. The molasses index, the methylene blue value and isotherms of benzene are tests developed by the industry to evaluate the quality of activated carbons. Similar tests must be developed for biochar designed for environmental applications to guarantee the products capacity to adsorb common pollutants. Nowadays there are ongoing research processes to identify the applications of biochars according to their specific characteristics. However, there is not yet a rapid screening technique to relate the biochar characteristics with a particular use (<http://www.anzbiochar.org/publications.html#publications>).

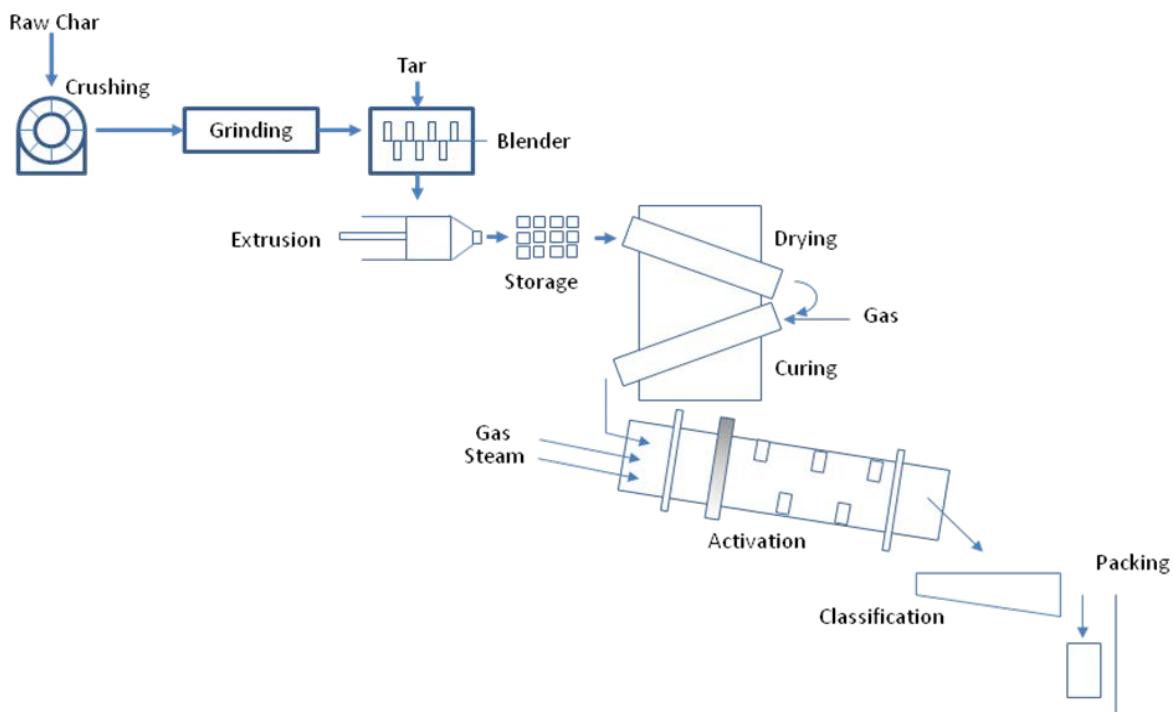
Industrial applications that may use activated carbon include liquid and gas phase applications. *Liquid phase applications* include municipal wastewater and industrial wastewater treatment plants, swimming pools, tropical centers, fish tanks, and drinking water. Also included in this list is the purification of oils, fats, winery tanks, beverages, and tank cleaning in insecticide and pesticide spraying operations. *Gas/vapor phase applications* include purification of exhaust emissions, recirculated air purification, solvent recovery in printing machinery and processes where high volatile matter is continuously being released. It also can be used to prevent offensive odors. Table 17 shows some applications of activated carbon in different industrial processes.

Adsorption capacity and surface area of activated carbon are interrelated. However, surface area is only one factor to measure the adsorptive capacity for a specific purpose. Activated carbon with large total surface areas and with micropores may be ineffective in adsorbing larger color forming compounds from solutions, while they may be effective in removing small odor-causing impurities from gases. This explains a large number of shapes, grades and types of activated carbon on the market (Emrich 1985). Chemical and physical means are used to conduct biochar activation.

**Table 17. Uses of activated carbon (Source: from information from Marsh and Rodriguez-Reinoso 2006)**

Applications	Industrial examples	Main Compunds
<b>Liquid-phase adsorption</b>		
Adsorption of inorganic solutes from aqueous solution	Heavy metals removal from wastewater treatment systems.	Mercury, chromium, molybdenum, cobalt, nickel, copper, cadmium, lead, uranium, gold, arsenic, barium, iron and vanadium.
Adsorption of organic solutes from aqueous solutions	Drinking water, wastewater treatment, food and beverage, pharmaceutical and chemical industries.	Phenols, natural organic matter (NOM), aniline, nitrobenzene, benzoic acid, and pesticides.
<b>Gas-phase applications</b>		
Gas purification	Chemical industry, reduction of pollutants, protection against poison gases, odor control, etc.	H <sub>2</sub> S, SO <sub>x</sub> , NO <sub>x</sub> , volatile organic compounds (VOC).
Separation of gas mixtures	Air separation, treatment of landfill gas, purification of natural gas, tertiary oil recovery	Nitrogen from oxygen, CO <sub>2</sub> from landfill gas, CO <sub>2</sub> from natural gas, CO <sub>2</sub> /CH <sub>4</sub> from effluent gas on tertiary oil recovery.
Methane storage	Storage of natural gas adsorbed on activated carbon.	CH <sub>4</sub>
Solvent Recovery	Paint, petrochemical, printing, rubber, synthetic fiber, adhesives, metal fabrication, solvent manufacturing, and coating industries.	Acetone, benzene, ethanol, ethyl ether, pentane, methylene chloride, tetrahydrofuran, toluene, xylene, chlorinated hydrocarbons and aromatics.
<b>Liquid-phase applications</b>		
Water treatment	Removal of pollutants organic compounds: i) natural organic matter (NOM), ii) synthetic organic compounds, iii) by-products of chemical water treatment.	i) Residues of the metabolism of living things, ii) oil, benzene and toluene, phenols and chlorophenols, trichloromethane and carbon tetrachloride, detergents, pesticides, dyes, surfactants, etc. iii) trihalomethanes with chlorine (CHCl <sub>3</sub> , CHBrCl <sub>2</sub> , CHBr <sub>2</sub> Cl and, CHBr <sub>3</sub> ).
Chemical and pharmaceutical	i) Control product quality, iii) removal of toxic chemicals, iii) extraction of pharmaceuticals in processes involving fermentation iv) filters for dialysis of poisons and drugs, felts for wounds, etc.	Recovery of antibiotics, vitamins, and steroids.
Adsorption of dyes	Wastewater treatment of the dyes industry.	Acid, basic, reactive, direct, disperse, sulfur and metallic dyes.
<b>Porous carbons in catalytic processes</b>		
Carbon-supported catalysts	Platinum, palladium and iron supported on activated carbon.	Catalytic hydrogenation of α, β-unsaturated aldehydes to give unsaturade alcohols, hydrogenations of crotonaldehyde, CO hydrogenation etc.
Catalysis by carbon surfaces	i) Production of phosgene (carbonyl chloride), ii) reactions involving hydrogen, iii) reactions involving oxygen, and iv) reactions involving halogen.	i) Formation of phosgene by combination of carbon monoxide and chlorine ii) RX + H <sub>2</sub> → RX (X = Cl, Br), iii) NO + (1/2)O <sub>2</sub> → NO <sub>2</sub> iv) SO <sub>2</sub> + Cl <sub>2</sub> → SO <sub>2</sub> Cl <sub>2</sub>

*Physical activation (thermal steam activation):* Thermal activation is a process of selective gasification (removal) of individual carbon atoms. The weakest carbon atoms can be removed from within porous carbon by using gasification or water vapor (at 700-1,000 °C). Carbon with varying porosities can be produced in presence of carbon dioxide and steam (Marsh and Rodriguez-Reinoso 2006). Powdered carbon is often extruded in presses before activation, with the aid of coking binders. The extruded product is carbonized at only moderate temperatures. It is activated by water vapor in a rotary furnace or in a fluidized bed (Emrich 1985). The art of the processor lies in conducting the activation process in such a way that combustion of the carbon does not take place from outside of the grains (Emrich 1985). Figure 31 shows an activation plan for the production of activated carbon pellets (Emrich 1985).



**Figure 31. Activated carbon plan for manufacturing pellets or granular activated carbon (Emrich 1985).**

*Chemical activation:* Three common methods of chemical activation involve zinc chloride, phosphoric acid, and potassium hydroxide. The mechanisms for these activations are all different. Zinc chloride promotes the extraction of water molecules from the lignocellulosic structures of parent materials. Phosphoric acid combines chemically within the lignocellulosic structures. Potassium hydroxide effect, follows a more complex mechanism. It involves disintegration (explosively) of a structure following intercalation as well as some gasification by the oxygen of the hydroxide group (Marsh and Rodriguez-Reinoso 2006).

*Activation strategies for environmental applications:* The market for activated carbon for industrial and household use is not large enough for the amount of biochar that could be produced from the waste materials generated in Washington State. However, if we could get substantially the same result with

“activated biochar” at a fraction of the cost of activated carbon, the market for ecological and environmental applications may grow dramatically. In the case of environmental applications regeneration is not likely to occur. In order to reduce costs biochars should be produced from materials with higher ash content with lower value on energy markets. The minerals contained in the biochar “ash” (Fe, Mn, Alkalines) can have a profound impact on the ability of biochar to “cleanup” some pollutants in waste gas and liquids perhaps at much lower costs than activated carbon.

Researchers at Washington State University are currently studying the development of biochars to remove nutrients (P and N) from Anaerobic digesters. Dairies in Washington State produce over 1.5 million tons of manure annually accounting for 18,900 tons of phosphorous that is concentrated in lagoons prior to land application. Annual land applications have led to concerns of environmental degradation caused by  $\text{NO}_3$  leaching and P runoff. These applications may deliver  $> 600 \text{ kg N ha}^{-1} \text{ y}^{-1}$  and  $160 \text{ kg P ha}^{-1} \text{ y}^{-1}$  exceeding the needs of crops, resulting in leaching to groundwater or runoff losses to waterways. The land disposal of manure from dairy operations has led to excess phosphorous accumulation causing an extreme risk to the environmental quality of the Pacific Northwest (PNW) region. One method for nutrient management and reclamation of nutrients on dairy farms is the use of anaerobic digesters for the production of methane gas and electricity production. After digestion, the effluent flowing from the digester is a combination of nutrients and undigested fiber while the liquid effluent remains high in P and N. Ideally the excess P and N within the effluent stream could be recovered as a fertilizer and exported off farm. The design of biochars with simultaneous buffering and nutrient adsorption capacity should be further investigated.

Carboxylic acid groups on the surface of biochar are essential for improving the biochar's nutrient holding capacity, as well as polarizing the surface which may also increase water retention of the material. A high proportion of carboxyl acids as well as other acidic oxygen groups may also provide biochar many of the desirable properties of humic acid which is an important degradation product of soil organic matter. The relatively high concentration of acidic groups can allow the formation of chelates with metal ions and help to bind positively charged ions to the surface of the carbon. When the surface density of carboxylic acid groups is very high, chelates with metal ions can almost completely immobilize potentially toxic metal compounds. The results obtained by Valdes (2002) indicate that total acidic groups on activated carbons can reach at least  $2 \text{ meq g}^{-1}$  with half the acidic groups being carboxyl groups. Smith (2011) showed that biochar ozonation could be an excellent approach to generate acidic functional groups on biochar surface and enhance its capacity to remove nitrogen from waste streams. The author (Smith 2011) proved that the pH at zero charge of ozonated biochars is considerably reduced when the biochar is oxidized. The acidic nature of oxidized biochars means that they may be well suited for retention of basic ions such as ammonia or other cation compounds (Kastner, 2009). Chiang et al. (2002) has shown a

strong correlation between the quantity of ammonia adsorbed by the oxidized carbon and the concentration of acid groups on the surface.

The adsorption of phosphate ions will depend mostly on the concentration and accessibility of cations found in the ash. Effects of metal ion concentrations in fly ash have been the subject of significant research (Lu, et al., 2009; Agyei et al., 2000; 2002; Namasivayam and Sangeetha 2004; Oguz, 2005; Xue et al., 2009). The use of fly ash has been considered for its potential to remove phosphate compounds from waste water. The biochar ash composition plays an important role in the adsorption or precipitation of suspended phosphates (Xue et al 2009), in basic solutions ( $\text{pH} > 7$ ) biochar ash with high content of calcite is effective in phosphate removal (Lu et al 2009), in acidic conditions, biochar ash rich in aluminum and iron induces precipitation of phosphates (Oguz 2005). The application of this information to biochars for the removal of relatively low concentration phosphates is of interest, because of the desire to develop an adsorbent capable of removing both nitrogen and phosphorous compounds from waste streams. The addition of appropriate metal ions to the structure of the biomass should aid in creating additional basic sites on the char surface which will become positively charged in solution and attract anions to the surface.

Streubel et al. (2011) studied the role untreated and freshly produced biochar can have on nutrient adsorption by allowing AD effluent to be filtered through the char-media for 15 days. Results showed that the char sequestered an average of 381 mg/L P from the AD effluent as a coating on the biochar. There was an increase of total (1.9 g kg<sup>-1</sup>), Olsen (763 mg kg<sup>-1</sup>), and water extractable P (914 mg kg<sup>-1</sup>) bound to the biochar accounting for a recovery of 32% of the P in the AD effluent. While the study was completed with untreated biochar, it is possible to design biochars with modified surface acidity/area, and cation/anion exchange capacities and with a different ash composition to further enhance nutrient removals from AD effluents.

### *5.5.3 Industrial Applications*

Due to increased environmental regulation and diversification of the chemical industry, applications of biochar for the industrial market have multiplied. Industrial applications of biochar include gas generation (for cars, electric power), fuel for the cement industry, iron and steel industry, metallurgy (blast iron furnaces, ferro-silica, metal hardening, non-ferrous metal industry) and the chemical industry (e.g. manufacturing carbon disulphide, sodium cyanide, carbides) (Emrich 1985).

Wood charcoal (biochar) was universally used as a reductant when iron was first made by man. During the eighteenth century, metallurgical coke was introduced as an alternative. Today, the largest biochar based pig-iron industry in the world is located in Brazil (Pelaez-Samaniego et al. 2008). Biochar provides strong reducing properties. Metal extraction is facilitated when carbon is heated with ores containing

metal, oxides, and sulfides and the carbon readily combines with oxygen and sulphur. Hardwood species (eucalyptus) makes up most of the biochar used in blast furnaces. Despite the fact that biochar is generally acknowledged to be as good, if not better, than coke, it is challenging to obtain adequate supplies of biochar to feed large iron and steel industry, which are needed to achieve competitive steel prices (Emrich 1985).

Properties that need to be accounted for in order to provide continued use of biochar in metallurgical applications include: 1) relatively few and un-reactive inorganic impurities, 2) specific pore structure with large surface area, 3) almost smokeless, 4) low sulfur content, 5) good reduction ability and 6) a high carbon to ash ratio (Emrich 1985).

#### *5.5.4 Carbon Sequestration and Soil Fertility*

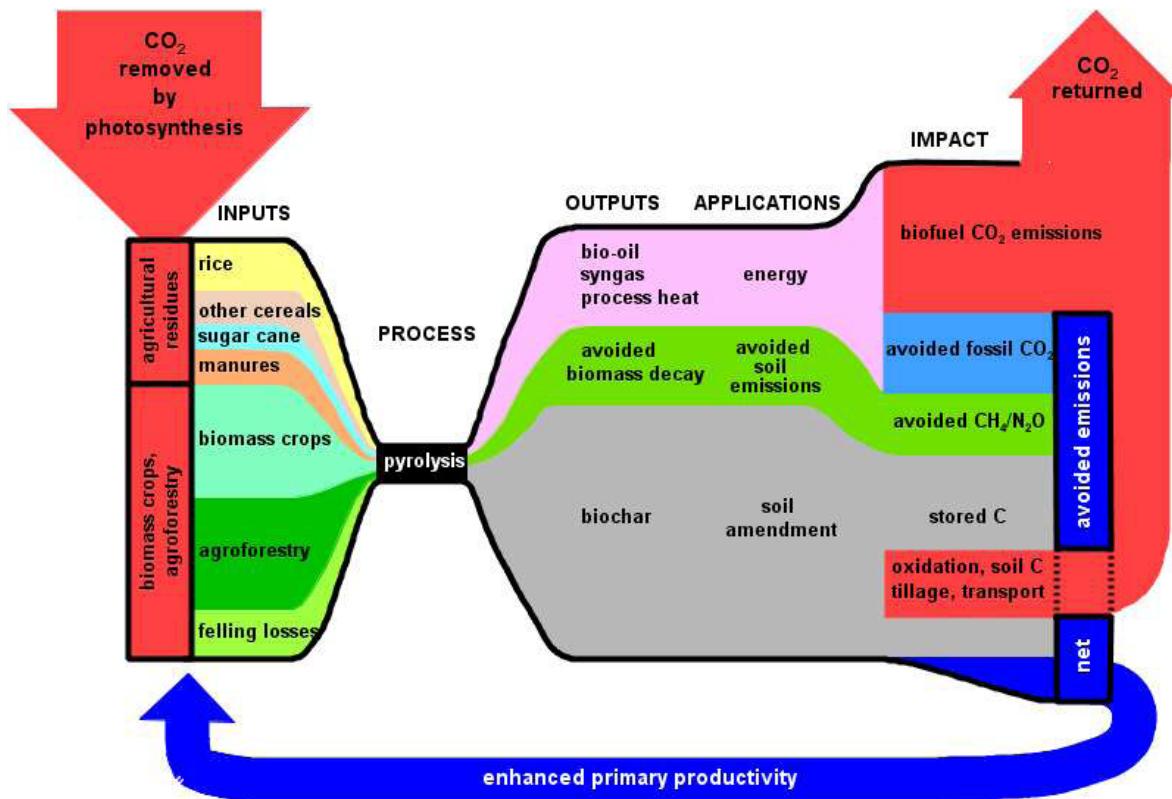
Public interest in the potential of biochar to sequester carbon and enhance soil fertility is growing (Lehmann and Stephen 2009). Using biochar to enhance soil fertility is a market that could utilize a vast majority of the organic waste generated in the state (Granaststein et al 2009, Garcia-Perez and Smith 2011). The main obstacle for this application is that the price for carbon sequestration with biochar is not high enough to justify its production (Garcia-Perez et al. 2010). To increase the economic viability of using biochars as soil amendments, functionalized biochars that can provide more than one environmental function (e.g. increased water holding capacity, improved fertilizer efficiency, sorption of pesticides) and consequently receive higher prices. Benefits from engineered biochars in agriculture include: 1) Improved water holding capacity at the root zone; 2) Improved fertilizer holding capacity at the root zone and 3) improved soil health. Multiple benefits can improve the value of the biochar product. In addition, markets for activated carbon can also provide improved off-take value.

The West Coast has a range of distinctly different approaches to carbon sequestration: 1) British Columbia has a carbon tax ([http://www.fin.gov.bc.ca/tbs/tp/climate/carbon\\_tax.htm](http://www.fin.gov.bc.ca/tbs/tp/climate/carbon_tax.htm)); 2) California has a cap & trade system (<http://www.arb.ca.gov/cc/capandtrade/capandtrade.htm>) ; 3) Oregon has The Climate Trust (<http://www.climatetrust.org/>) ; and 4) Washington has an emission inventory and reporting law (RCW 70.94.151) and greenhouse gas reduction limits (RCW 70.235.020). In the last few years, voluntary markets for renewable energy in US have been growing due to its greenhouse gas (GHG) benefits (Bird et al., 2008). Emerging carbon regulation efforts had focused on the Regional Greenhouse Gas Initiative in the Northeast, the Western Climate Initiative, and the Midwestern Greenhouse Gas Reduction Accordto add to the current voluntary markets for renewable energy (Bird et al., 2008, Funk 2009,). A more recent state and province effort is called North America 2050: A Partnership for Progress (<http://na2050.org/>). Working groups have been organised, however, terrestrial carbon sequestration (turning farms from a source to a sink) is not a focus of this effort.

The economics of carbon sequestration through biochar (if biochar is approved for carbon storage payments) could improve dramatically if it is inserted into a mandatory carbon cap with associated markets or carbon cap and tax. Today, the value (based on its calorific content) of crude biochar without additional treatment is approximately \$66 per ton. If biochars are engineered to improve soil fertility, over those obtained with untreated biochar, higher prices may be obtained. The economic value of biochar could also be increased by its ability to adsorb nitrogen and phosphorous from waste water streams and by increasing its cation/anion exchange capacity. Development of strategies to improve the capabilities of biochars to adsorb nitrogen and phosphorous from waste streams is an area of intense study (Smith 2011). The potential use of biochars, used to remove nutrients from waste streams, as a soil amendment and improving fertilizer efficiency is receiving growing attention (Lehmann and Joseph, 2009).

Studies of the Terra Preta soils in the Amazon basin provide much of the knowledge regarding the potential benefits of biochar as a soil amendment (Lehman et al. 2009). As the evidence suggests, these soils provide long lasting carbon storage and improve crop production due to the biochar-like materials that have substantially altered the physical and chemical properties of these soils. Krug and Hollinger (2003) stated that deep and extremely fertile soils in some areas of the Illinois Plain were developed under anthropogenic conditions where char from natural and man made fires improved the soil organic carbon. Downie et al., (2011) reported some places with Terra Preta in Australia with a significant better nutrients content and cation exchange capacity compared with adjacent soils. They claimed that the existence of these kinds of soils in temperate climates would help in both storing C and using biochar. On the other hand, scientists in Japan have been researching biochar for years in temperate climate soils. They stated that the effects of biochar in crops is related mainly to soil infertility and the presence of nitrogen-fixing bacteria and symbiotic organisms that thrive in char amended soils (Ogawa and Okimori 2010). Ogawa and Okimori (2010) observe that biochar effects are more evident in infertile tropical soils.

The least fertile soils can benefit the most from the addition of biochar. According to Ammonette (2010), sustainable biochar technologies can offset up to 130 Gt CO<sub>2</sub>-C eq emissions worldwide during the first century of adoption. With regard to biomass type, global soil fertility, and carbon intensity of fuel offset, biochar offers a 22% advantage over the combustion of biomass. The three most important variables that affect the impact of biochar uses are the recalcitrance of biochar, the carbon intensity of the fuel being offset, and the biochar yield during pyrolysis (Amonette 2010, Woolf et al. 2010). Maximum avoided emissions by the production of biochar and heat, as estimated by Woolf et al. (2010) and Amonette (2010), could range from 1.0 to 1.8 GT CO<sub>2</sub> Ceq yr-1. For 100 years, the cumulative avoided emissions range from 66 to 130 GT CO<sub>2</sub> – Ceq. The impact that slow pyrolysis technologies with heat recovery could have on carbon cycling (production of heat and biochar) are illustrated in Figure 32.



**Figure 32. Sustainable biochar production concept with the use of biochar to enhance soil fertility and sequester carbon (Amonette et al. 2010, Woolf et al. 2010).**

Producing value-added biochars that can substantially enhance soil fertility as well as carbon storage is critical since payment for carbon storage alone is unlikely to fully recover production costs.

### 5.5.5 Biochar Gasification

Small gasifiers able to utilize biochar and wood as fuel to operate vehicles, boats, trains, and small electric generators<sup>9</sup> were developed during World War II. By the end of the war about 90% of the vehicles in Sweden were powered by gasifiers and there were more than 700,000 wood gas generators (FAO 1986). Updraft and downdraft gasifiers are the two main concepts used to operate these engines. Hot gases that are usually laden with dust and contain up to 1 wt. % of tar and particulates are produced by a downdraft gasifier. If the dust is not properly removed, costly problems with maintenance, repairs, and reliability can occur. Improper removal of these syngas contaminants is the main cause of gasifier engine system failure. The gas is very dirty during initial start up and must be burned in the gasifier until the system is fully functional.

<sup>9</sup> Designs of wood gas generators are found elsewhere ([http://www.windward.org/notes/notes63/wal63\\_b.htm](http://www.windward.org/notes/notes63/wal63_b.htm), [http://journeytoforever.org/biofuel\\_woodgas.html](http://journeytoforever.org/biofuel_woodgas.html), <http://www.scribd.com/doc/31422608/Wood-Gas-as-Fuel-1>).

These gasifiers can also be coupled with Diesel Engines to produce Electricity. Replacement of up to 70% of petroleum derived fuel with producer gas for operating stationary engines appears to be a worthwhile investment, especially for isolated areas (SERI 1988). However, given the convenience of liquid fuels, many users prefer to pay more despite the very clear advantages of replacing imported petroleum with producer gas.

# **6. Regulatory Issues of Current Pyrolysis Technologies**

## **6.1. Health and Safety of Handling Bio-oils**

A better understanding of health and safety issues associated with bio-oil exposure is necessary to develop safe working practices (Ringer et al. 2006). Although Diebold (1999) published a review of bio-oil toxicity, the health risks posed by fast pyrolysis liquids have not been clearly elucidated. Nonetheless, a limited degree of mutagenicity and teratogenicity is associated with fast pyrolysis liquids depending on the source, chemical composition, and dosage (Diebold 1999, Oasmaa and Peacocke 2001).

### *Material and Safety Data Sheets (MSDS) for Bio-oils*

For the safe use, handling, storage and transportation of fast pyrolysis liquids, material and safety data sheets are essential.<sup>10</sup> But due to high variability in properties and limited development in commercial systems, there is no universally accepted MSDS for bio-oils. Private producers have developed MSDS for pyrolysis liquids (e.g. Ensyn, Dynamotive, BTG and Fortum). An MSDS which suitable for inclusion with samples for shipment was prepared at Aston University (UK) (Oasmaa and Peacocke 2001).

Czernick prepared an MSDS with the IEA Bio-energy Pyrolysis Activity Group (Bridgwater et al. 1999). Adequate safety equipment and facilities (e.g. protective clothing, chemical resistant gloves, safety glasses or goggles and a well ventilated environment) are required when working with pyrolysis liquids.

It is likely that fast pyrolysis liquids will be classified as a “dangerous” or a “hazardous” substance for transportation, and appropriate national and international regulations must be met. Since pyrolysis liquids are not approved on the UN carriage list (UN 1999), its own classification UN 1993 Flammable Liquid, N.O.S., (Fast Pyrolysis Liquid), 3, 1°(a), 2°(a), 1 must be provided (Table 18). Figure 33 shows packing labels that should be used for domestic and international shipments.

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<sup>10</sup> Several bio-oil MSDS sheets can be found at: (1) [http://www.pyne.co.uk/Resources/user/docs/CIRAD\\_MSDS-Final.pdf](http://www.pyne.co.uk/Resources/user/docs/CIRAD_MSDS-Final.pdf) and (2) <http://www.unh.edu/p2/biooil/bounhif.pdf>.

**Table 18. Package label information (Oasmaa and Peacocke 2001).**

UN Symbol	Substance ID Number	Name of substance	Hazard Identification Number	Label Model Number	Class and Item Number
	1993	Flammable liquid (Fast Pyrolysis liquid)	33	3 6.1 11	3 1°(a), 2°(a), 2° (b), 3° (b), 5° (c)



Class 3 Flammable liquid  
Label 3



Class 6 Toxic substances  
Label 6.1

**Figure 33. Fast pyrolysis packaging labels that should be used on all shipments nationally and internationally (Oasmaa and Peacocke 2001).**

CIRAD-FORET, as part of the BIOTOX project, provided a very detailed study on the transport, storage, and handling of biomass derived fast pyrolysis oils in order to comply with all international modes of transport (Conversion and Resource Evaluation Ltd. 2006).<sup>11</sup> CIRAD also published a detailed description of bio-oil toxicity, safe handling and transportation (Blin 2005).

## 6.2. Health and Safety of Handling Biochar

Although biochar is a very stable substance once it has cooled, precautions are necessary to prevent spontaneous combustion (from absorption of oxygen) during storage. Biochar fines should be removed before it is stored (Toole 1961, FAO 1985). Although spontaneous combustion is always a possibility, “hot biochar” (material still burning after the cooling cycle) is a much more frequent cause of fires during the storage process. To prevent “hot biochar” from reaching the storage area, the char may need to sit in an open dry area for 24 hours before it can be stored (Toole 1961).

<sup>11</sup> A detailed report by Conversion and Resource Evaluation Ltd. (2006) on storage and handling regulations for pyrolysis liquids in the European Union is found at:

<http://www.pyne.co.uk/Resources/user/docs/TRANSPORT%20STORAGE%20AND%20HANDLING%20OF%20BIOMASS%20DERIVED%20FAST%20PYROLYSIS%20LIQUIDS.pdf>.

Biochar is listed as a flammable solid and an oxidizing material because it can cause fires through friction, spontaneous chemical changes, absorption of moisture, or as a result of the heat retained from the manufacturing process (Toole 1961). The most important regulations for the storage, transport, and distribution of charcoal are described by in detail by FAO (1987). The US Department of Transportation Pipeline and Hazardous Materials Safety Administration (PHMSA) have established rules for the transportation of charcoal (49 CFR 172.101- Hazardous Materials Table).<sup>12</sup> Several MSDS for modified charcoals, activated carbons and biochars are also available.<sup>13</sup>

Granatstein et al. (2009) studied the likelihood that reactions leading to the formation of dioxins, chlorinated furans, and polycyclic aromatic hydrocarbons could occur during biomass pyrolysis at temperatures between 350 and 600 °C. Although the literature is limited, available data for polycyclic aromatic hydrocarbons (PAHs) and dioxins/furans indicate no human health or environmental hazard from biochar (Garcia-Perez 2008). Garcia-Perez (2008) concluded that it is possible to produce biochar with concentrations of PAHs and dioxins/furans several times lower than current clean up levels required under the Model Toxic Control Act, Chapter 70.105D RCW. Concentrations of dioxins measured in the biochar were close to those reported for background levels in Washington soils. Additional studies of biochar produced with other technologies and feedstocks are needed.

### **6.3. Environmental Controls, Permitting and Waste Streams**

One of the goals of this review is to identify or develop designs that do not emit toxic air pollutants or that are well below the minimal levels according to Chapter 173-460-150 Washington Administrative Code (WAC). Emissions are an indication of incomplete or unoptimized designs since the design objective is to use all the materials produced from the process (zero waste). Facilities emitting below minimal levels are not be required to obtain an air permit, while a facility that can only achieve Acceptable Source Impact Levels (ASILs) will need to go through an air emission permit process. Achieving ASIL standards is only possible in systems that utilize the pyrolysis vapors to produce heat or other valuable products. Old carbonization technology is not likely to receive permits to operate in the state.

A detailed description of the permits required by Washington State has been compiled in a Permit Hanbook (Commonly required Environmental Permits, Licenses and Approvals for Washington State)

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<sup>12</sup> The 49 CFR 172.101- Hazardous Materials Table is available at <http://www.phmsa.dot.gov/about/agency>.

<sup>13</sup> <http://www.packervision.com/Data/Products/Data-Sheets/-1694906429.pdf>,  
[http://www.unitexchemical.com/MSDS\\_CURR/UPLXCHARCATALYST5066\\_MSDS.pdf](http://www.unitexchemical.com/MSDS_CURR/UPLXCHARCATALYST5066_MSDS.pdf),  
<http://www.thecloroxcompany.com/products/msds/charcoalproducts/kingsfordcharcoalbriquets.pdf>,  
[http://www.buyactivatedcharcoal.com/activated\\_carbon\\_msds](http://www.buyactivatedcharcoal.com/activated_carbon_msds),  
<http://www.iluka.com/uploads/documents/Datasheets/Iluka%20Char%20MSDS%20Nov%2006%20Aust.pdf>

(<http://www.ecy.wa.gov/pubs/9029.pdf>). Refer to this publication and contact local, state and federal agencies to identify all required permits.

Prior to construction of any new or modified emission source, all facilities must complete a Notice of Construction (NOC) application in order to evaluate the need for an ongoing air permit.<sup>14</sup> A simple NOC review may include review of steady state air dispersion modeling, if needed. A moderately complex NOC review may include a health risk assessment of emission exposure. Fee reductions are available for small businesses, extreme hardship, and pollution prevention initiatives. More information on this permit can be found elsewhere (<http://www.ecy.wa.gov/pubs/9029.pdf>)

Air pollution in Washington State is based on federal, state, and local laws and regulations (<http://www.ecy.wa.gov/pubs/9029.pdf>). Ecology enforces air quality regulations in counties without air pollution control agencies. Local clean air agencies, which implement and enforce most state regulations, may be more stringent than those of the state. Large, new energy related projects (oil refineries, pipelines, and power plants) are under the jurisdiction of the Washington State Energy Facility Site Evaluation Council (EFSEC).

Annual registration fees are assessed to operating permit sources that emit above exemptions listed for Criteria Pollutants 173-400-102(5) WAC or the toxic air pollutants specified in WAC 173-460-150 WAC. Most fee eligible facilities (> 90%) pay a periodic registration fee of \$400 as stated in 173-455-040(3a) WAC. Higher fees may be assessed for criteria emissions above threshold, which qualifies a facility for annual registration. See 173-400-102 WAC for what qualifies for periodic versus annual registration. Annual registration fees are based on several factors as outlined in 173-455-040(3b) WAC.

Grant et al. (2006) describe permits needed for a lignocellulosic biomass feedstock assembly system for wheat and barley straw in Idaho Falls, ID.<sup>15</sup> In Idaho, there are three main categories of air permits: minor source, major source and permit of significant deterioration (PSD), listed in order of increased complexity. Dust generated during biomass grinding and from the unloading and transfer of the ground biomass material from truck to storage to the pyrolysis reactor should be carefully evaluated. According to Idaho regulations, these operations are considered a minor source if less than 100 tons are generated per year (Grant et al. 2006). In Idaho, air permits may not be required for small field grinding operations (Grant et al. 2006). Truck unloading operations will require a baghouse to control particulates (Grant et al.

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<sup>14</sup> The NOC application form is available at <http://www.ecy.wa.gov/biblio/ecy07002.html>. Fees for reviewing the NOC (\$1,250 to \$18,000) depend on the complexity of the work as listed in 173-441-120 WAC at <http://apps.leg.wa.gov/WAC/default.aspx?cite=173-455-120>. Review fees are subject to change in July 2011.

<sup>15</sup> A report as detailed the one by Grant et al. (2006) could not be found for Washington State, however, the conditions in Washington are similar to those in Idaho; and pyrolysis industries may operate across borders.

2006). Total particle emissions will stay below 100 tons per year and the operations will receive “minor source status” (Grant et al. 2006).

In Washington there are two main categories of permits: minor sources and major sources and many categories within the minor source. Applicants file a Notice of Construction application and Ecology determines where the project fits (minor source or major source) based on potential emissions the applicant is proposing.

Permitting an industrial operation of this type addresses four major areas, or waste streams 1) particulate air pollution, 2) storm water runoff, 3) fuel leaks and 4) laboratory chemical waste (Grant et al. 2006). A Stormwater Pollution Prevention Control (SPPC) plan is required for mobile and centralized pyrolysis plants and may be required if a central pyrolysis plant or rural bio-oil refinery has truck refueling capabilities on site of a capacity over 10,000 gallons above ground (Grant et al. 2006). The fueling system must have a secondary containment design for storm water runoff protection (Grant et al. 2006). A detailed list of all the permits, required in Idaho is reported by Grant et al. (2006).

## 7. Conclusion

Because of the diversity of situations in which pyrolysis can be applied (e.g. feedstocks, scale, mobile or stationary units) and the diversity of products that can be obtained from this technology (e.g. second generation bio-fuels, chemicals, biochar, activated charcoal and heat), it is very difficult to identify a single technology that can be used across all potential conditions. Thus, in order to accelerate the growth of this industry, development of concepts for pyrolysis units that are easily adapted for different applications and conditions is critical. Sustainability must be addressed as a design goal not as a design obstacle. The environmental, social and economic benefits of this new technology must be maximized.

### *Reactors*

The pyrolysis reactor is just one of many components necessary to obtain valuable products from biomass resources in Washington. Pyrolysis reactors can be used based on two main business models: (1) production of biochar and heat and (2) the production of bio-oil. Promising designs for larger reactors (>100 ton/day) include moving beds, rotary drums, fluidized beds and circulating beds whereas, ablative and auger reactors are suitable for smaller pyrolysis units (10-100 ton/day). Although fluidized bed and circulating bed reactors result in very high yields of oil, the use of large volumes of sand and carrier gas is a limitation to these designs.

### *Preprocessing*

The composition of the biomass at the gate can be controlled by the supply chain chosen.

Particle size and moisture content of the biomass are controlled by preprocessing strategies. The current literature provides enough information to propose rational biomass handling and preprocessing schemes.

### *Light Compounds*

An excellent way to capture the content of light compounds (acetic acid and acetol) is with the use of fractional condensers. Using this technology, C1-C4 molecules are separated from the precursors of transportation fuels. These C1-C4 molecules can be further processed for other outcomes through advanced biorefineries. New products must also be developed using these C1-C4 small organic molecules that are collected.

### *Heat Recovery*

Recovering the energy of volatiles and reducing the environmental impact of pyrolysis technologies can be done with heat recovery boilers coupled with the pyrolysis reactors. The energy contained in the volatiles typically is not recovered by most combustion chambers used to reduce environmental impacts of pyrolysis reactors. It is necessary to design and build components for heat recovery in order to enhance economic viability.

### *Biorefining and bio-products*

Biorefining is simply integrating technologies to convert each bio-oil fraction into valuable products. Development of high-value products should complement two main bio-oil refinery concepts: bio-oil hydrotreatment and bio-oil gasification followed by F-T synthesis. The main hurdle to producing advanced fuels from bio-oils is a lack of rural refineries to convert crude bio-oil into stabilized oil compatible with existing petroleum refineries and high value products. Current bio-oil hydrotreatment concepts consume too much hydrogen and do not result in the development of high-value products.

### *Biochar*

The economic viability of slow and fast pyrolysis technologies could be improved with the development of biochar with known and consistent attributes, and engineered biochars (as part of a strategy to obtain smart carbon and nitrogen products) to enhance soil fertility, store carbon, and play a useful environmental function. One of the most effective tools to reduce atmospheric carbon concentrations is the use of biochar to sequester carbon. Activated biochar can be used with a wide range of applications, from environmental to industrial uses.

### *Quality*

A standard set of analytical methods and procedures are necessary to control feedstock and product (bio-oil and biochar) quality. For small operations, a central analytical lab is a key component of quality control.

### *Regulation*

Pyrolysis and bio-oil refineries must comply with environmental regulations and obtain appropriate permits. Handling and transporting bio-oil and biochar must follow well-defined procedures.

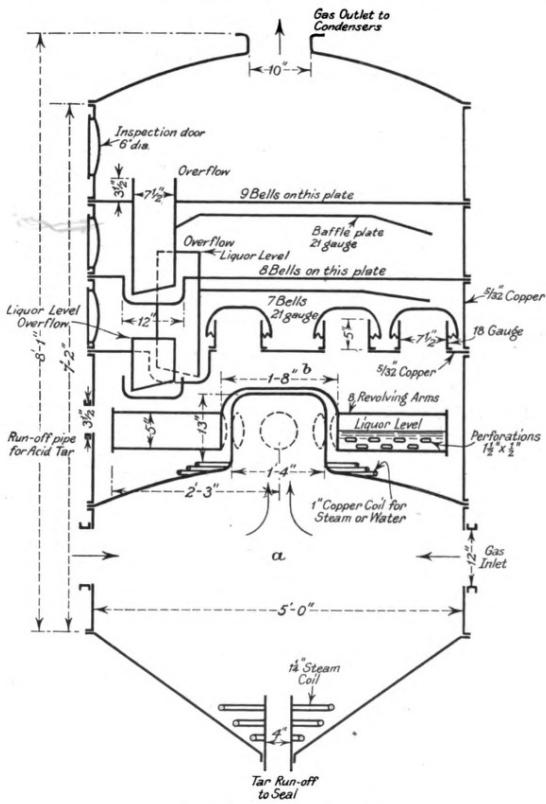
# Appendix A: Bio-Oil Condensers

## Direct contact condensers

Rapid cooling of the volatile fraction can be achieved using direct contact condensers (e.g. spray towers). Using cold liquids such as bio-oils or auxiliary liquids (generally paraffin), vapors are cooled from 500–350 °C to near ambient temperature.

Direct coolers include single or fractional condensers (multi-step condensers). Fractional condensers result in two streams with well-defined boiling point distributions. The first step is operated between 40 and 90 °C and the second step is operated between 20 and 30 °C (Westerhof et al. 2011). Fractional condensers offer an inexpensive way to separate large bio-oil molecules (used for the precursors of transportation fuels) from small molecules which contribute to undesirable properties of bio-oils. Designs for direct contact condensers described in this section include the Meyer bubbling condenser, Barbet tab separator, and scrubbers.

*Bubbling condensers:* A Meyer bubbling condenser (Figure A1) operates using a hot layer of condensed bio-oil through which vapors are bubbled. Temperature is kept high enough to minimize condensation of water, prevent condensation of acetic acid and methyl alcohol, and to accelerate reactions of aldehydes and phenols which further produce tarry substances (Bunbury 1926).

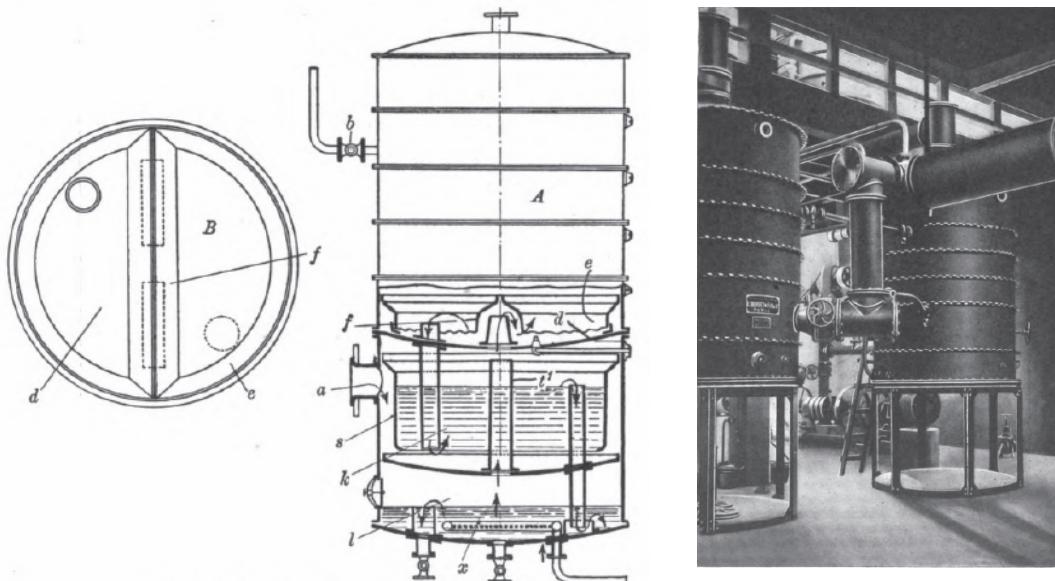


**Figure A1. Meyer bubbling condenser (Source: Bunbury 1926).**

Gases ascend from the lower compartment through a perforated dome. They then enter a second compartment consisting of a series of pipes, or extended arms, from an inverted dome or cup. A series of small perforations or slots are cut near the lower portions of one side of these arms. Gases emerging through these perforations induce a revolving motion of the arms. Another steam or water coil surrounding the base of the dome regulates the temperature of this compartment. The highest boiling constituents of the tar condense in this compartment. The tar is filled to a height level with the center line of the revolving arms. An overflow pipe located at this level conducts the bio-oil to a storage vat. Vapors then travel upward through three plates forming the base of the other three components (Bunbury 1926). The high flow rate of inert gases is a major hurdle for using these condensers with fluidized beds reactors.

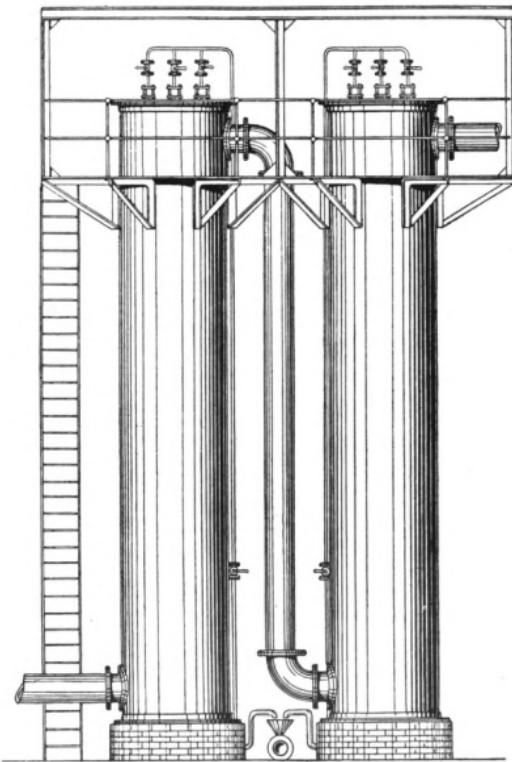
A bath of tarry liquor lies on the base plate of each compartment. The various high boiling constituents of the tar are condensed in different compartments. Those with the highest boiling points are condensed in the second compartment, those with the lowest are condensed in the top compartment, and those with intermediate boiling points are condensed in the third and fourth compartments. Entrained liquid particles become trapped within the second compartment and coalesce in the tar layer. An outlet located in the center of the top of the separator allows the uncondensed vapors and gases to escape.

The Barbet tab separator is seen in Figure A. Though similar to the Meyer condenser, the Barbet tab separator has several differences in its construction and layout (Figure A2). To allow for cleaning without disrupting distillation operations, condensers should be installed in pairs. Bunbury (1926) describes this condenser in further detail.



**Figure A2. Barbet tab separator section (left) and a pair of Barbet tar separators (right) (Source: Bunbury 1926).**

*Scrubbers:* Scrubbers (empty or packed towers) were used in the old wood distillation industry as the main condensers separating the heavy bio-oil fractions, or as scrubbing towers used to clean the produced gases (similar to those used in gas purification). Since clogging in the first condensation tower is very intense, it is important to avoid packing. Passing water or pyroligneous liquor helps remove acetic acid, methyl alcohol, and acetone (Figure A3) (Bunbury 1926).



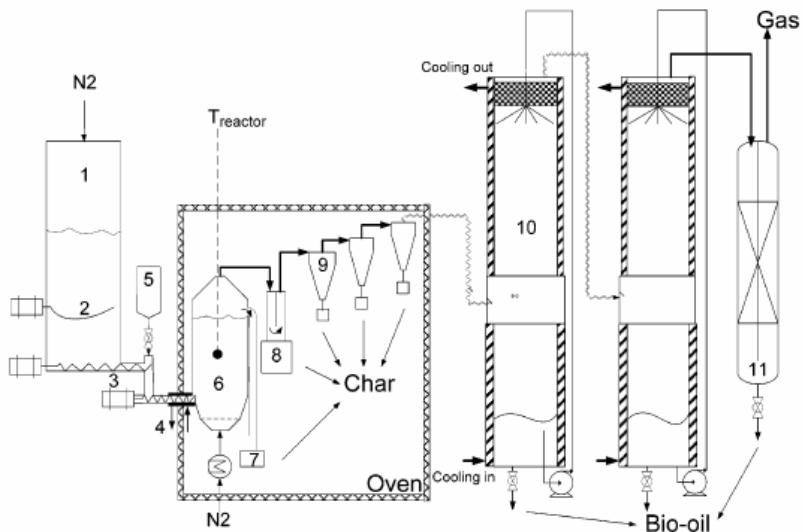
**Figure A3. Scrubbing towers designed to recover the volatile gases leaving the condensers (Bunbury 1926).**

Empty scrubbers are once again gaining popularity as the main condensation step since they are difficult to clog and tend to achieve good liquid separations. Westerhof et al. (2011) studied the use of these scrubbers as the main condensation device for pyrolysis plants as well as the use of hydrocarbons or fuels as cooling liquids. In order to ensure the generation of small droplets in the nozzle, mineral oil viscosity should be lower than pyrolysis oil viscosity (San Miguel et al. 2011). Figure A4 shows two step scrubbers to recover heavy oil and light oil/aqueous phases from a vacuum pyrolysis plant built in Jonquiere, Quebec.



**Figure A4. A Pyrocycling™ system containing a two step condensation process**

Oasmaa et al. (2005) and Westerhof et al. (2007, 2011) studied the effect of two step condensers on the separation of light molecules and water from the precursors of transportation fuels. This research demonstrates that the behavior of these condensers can be well explained by considering phase equilibrium. If the temperature in the first condenser is maintained at 80 °C, acetic acid can be almost completely removed. An equilibrium model proposed by Westerhof et al. (2007, 2011) describes the behavior of these condensers. Figure A5 shows a scheme of the system used to conduct these studies (Westerhof et al. 2007). The Thermochemical Conversion group at Iowa State University working under Robert Brown is also working on development of a fractional condenser (<http://www.cset.iastate.edu/research-projects/pyrolysis-process-development-unit.html>).



**Figure A5. A fluidized bed pyrolysis reactor connected to a two step condenser (scrubbers) at bench scale :**  
**(1) biomass hopper (2) mechanical stirrer (3) feeding system (4) cooling jacket (5) sand storage hopper (6)**  
**fluidized bed reactor (7) overflow tube + collecting vessel (8) knock-out vessel (9) cyclones (10)**  
**countercurrent spray condensers (11) intensive cooler (Westerhof et al. 2007).**

If the temperature in the second condenser is not kept low enough, non-condensable gases may carry considerable amounts of light C<sub>1</sub>-C<sub>4</sub> compounds (known as wood-naphtha in the old wood distillation industry) (Klar and Rule 1925). In this case, additional water scrubbers may be required to clean the gases and extract components of pyroligneous acid (Klar and Rule 1925).

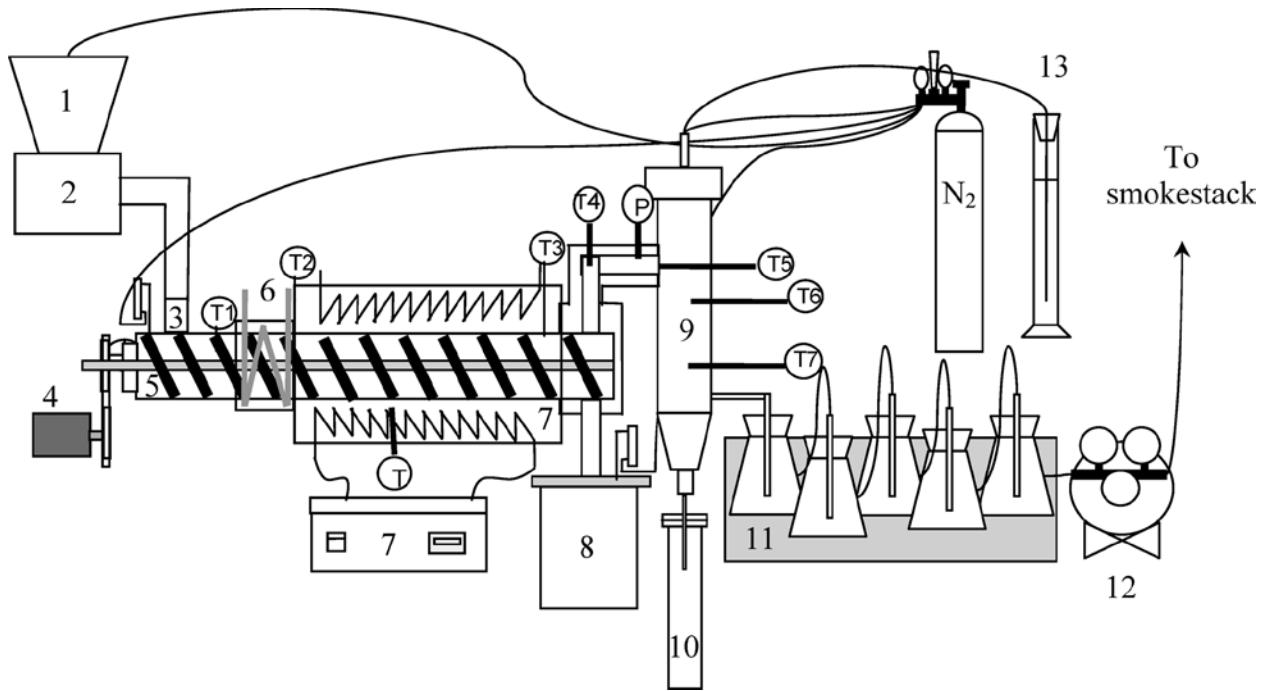
Figure A6 shows one of the condensers at a pilot plant in Spain consisting of two 90° full-cone nozzles and a woven wire mesh demister which efficiently recovers entrained mineral droplets of oil (San Miguel et al. 2011).



**Figure A6. Condenser of pyrolysis vapors (San Miguel et al. 2011).**

Milosavljevic et al. (1997) reported general design methods for scrubbers. Another bio-oil collection system that has been used, with little information provided in the literature, is a venturi scrubber. Several general methods for the design of these venturi scrubbers can be located elsewhere (Goncalves et al. 2003, Gamisans et al. 2002, Allen and van Santen 1996).

Researchers at the University of Georgia developed an on-line esterification system (coupled with an auger pyrolysis reactor) to improve bio-oil quality (Figure A7) (Hilten et al. 2010). Reactive species concentration are reduced with a simple reactive condensation technique in which esterification is performed on the bio-oils using ethanol. This method results in a reduction in water, acids and viscosity of the oils produced (Hilten et al. 2010).



**Figure A7. Esterification of bio-oils during condensation in a continuous auger reactor (Hilten et al. 2010).**

### Indirect contact heat exchangers

Indirect cooling with water or air is also used for bio-oil condensation. The heat transfer area when using air is typically 15 times larger than when using water due to the difference in the heat transfer coefficient between air and water. Air cooling should be reserved for situations where obtaining clean cooling water is difficult (e.g. operating mobile units).

*Tube and shell heat exchangers* and coils are some of the most commonly used heat exchangers reported in the literature (Klar and Rule 1925; Veitch 1907). The old wood distillation industry used a variety of different indirect heat exchanger designs (e.g. tube and shell exchangers like those shown in Figures A8, A9, A10) (Klar and Rule 1925; Veitch 1907). It is customary to first pass the pyrolytic gas and vapors through an easily cleanable section given the tendency of pyrolysis vapors to form incrustations during the condensation process. The most common design described in the literature suggests condensing the oils inside the tube while allowing the cooling water or air to circulate around the tubes (Klar and Rule 1925). In order to facilitate cleaning and to avoid slagging etc., the length of the tubes in these exchangers should be limited keeping the cooling path relatively short. These types of condensers usually operate on the counter current mode (Bunbury et al. 1926).

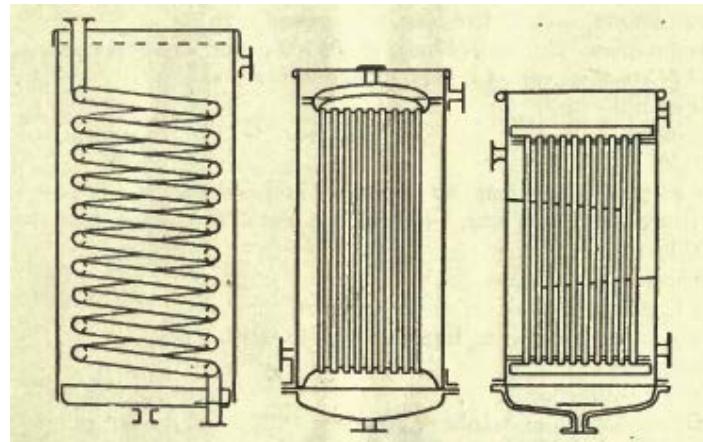


Figure A8. Several condenser variations (tube and shell, and coil) (Source: Veitch 1907).

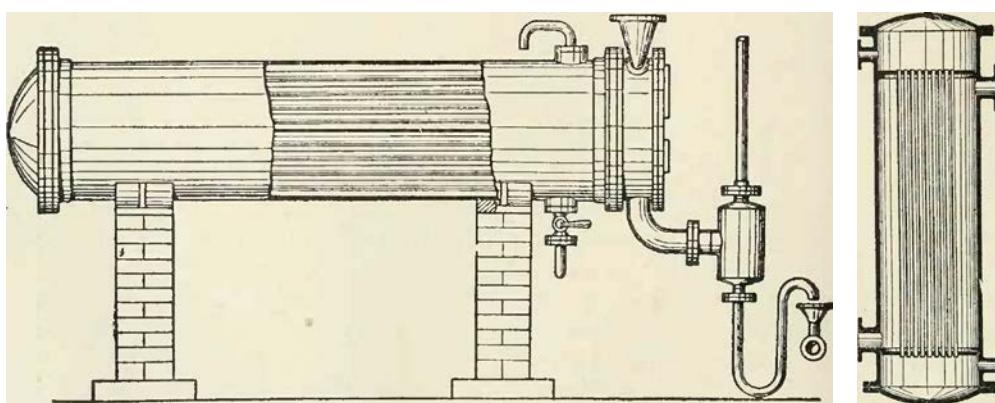


Figure A9. Tubular horizontal and vertical condensers (Source: Klar and Rule 1925).

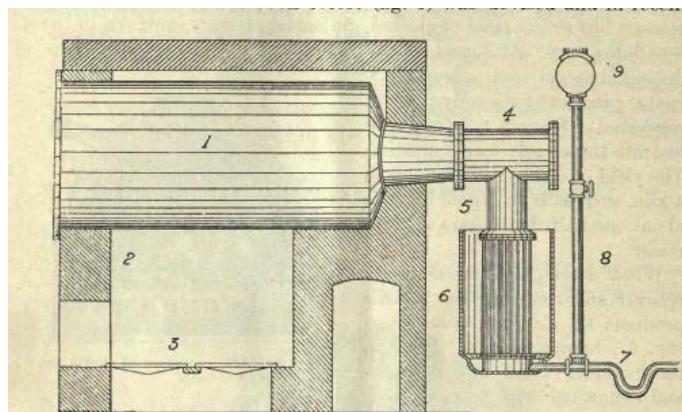
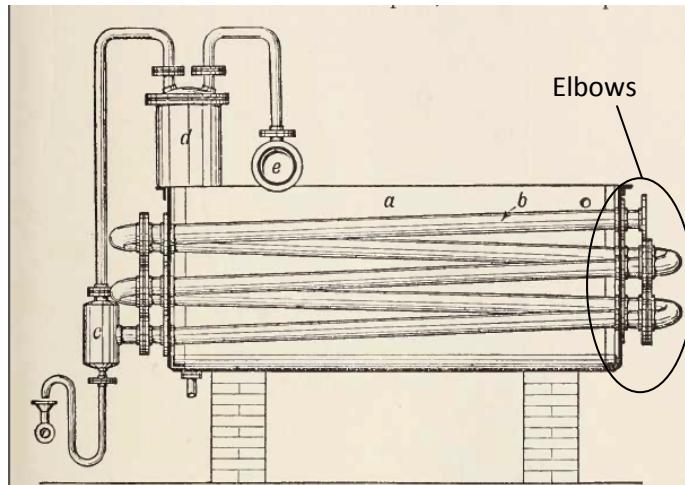


Figure A10. Round retort reactor system equipped with condenser (tube and shell): 1, retort; 2, fire walls; 3, grate; 4, neck; 5, pipe to condenser; 6, condenser; 7, trapped delivery pipe; 8, gas pipe; 9, gas main. (Source: Veitch 1907).

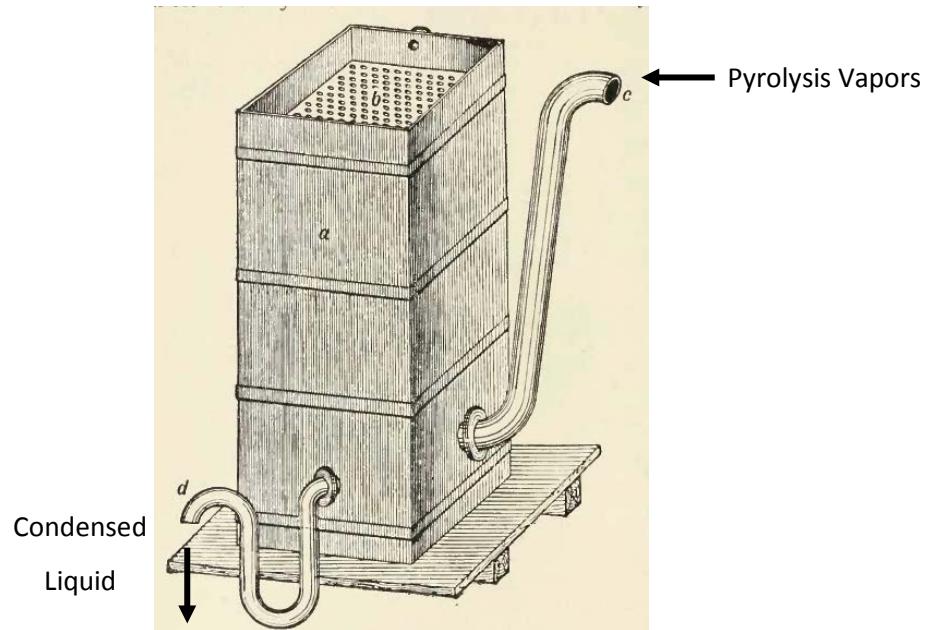
*Coil condensers:* In coil condensers, the gaseous mixture passes through a single tube which, in order to afford an equal area of cooling, must be correspondingly longer. Rather than a coil wound into a spiral, the tube forming the coil is made up of a number of inclined and superimposed straight tubes connected

by bends or elbows (Figure 15) (Klar and Rule 1925). The connecting elbows are located outside the water tank where they can be removed in order to clean the condensing tubes. Several coils arranged in a vertical plane within a single large tank of water may be used if a greater capacity is required. These coils are connected in parallel at one end to the main vapor delivery pipe and at the other to the corresponding outlet pipe.



**Figure A11. Coil condenser with straight tubes and elbows located outside the water tank: a) water tank; b) copper condenser tube; c) gas separator; d) hydraulic seal; e) gas-main (Klar and Rule 1925).**

*Wooden condensers* consist of several closely fitted rectangular wooden tanks with two perforated wooden partitions between which extend the copper condenser tubes (Figure 16). Similar to tubes of a locomotive boiler, the tubes on these condensers are fitted into perforations with the aid of a tube expander. The mixture of gas and vapor circulates through round tubes after entering the condenser immediately above the lower tube plate. The gas and vapor then enters an adjacent condenser after escaping through an outlet beneath the upper tube plate (Klar and Rule 1925). Though cheap to construct, this type of condenser should only be used if the pyrolysis vapors have been cooled enough by passing through a long connecting pipe so that deposition of tar and coke within the condenser itself is not possible (Klar and Rule 1925).



**Figure A12. American tubular condenser with wood vapor chamber and copper cooling tubes (a: wooden tank; b: wooden tube plate; c: vapor inlet-pipe; d: condensed liquor outlet pipe. (Source: Klar and Rule 1925).**

## Appendix B: Bio-Oil Characterization

*Calorific value:* The amount of heat produced when fuel is burned completely is known as the heat of combustion. For every fuel there are two values for heat of combustion: the net, lower heating value (LHV) or gross, higher heating value (HHV) heat of combustion (Oasmaa et al. 1997). A calorimetric bomb [ASTM D4809 – 09a] is typically used to measure the gross calorific value (Boucher et al. 2000, Oasmaa and Peacocke 2001). Only 40-45 wt % of that exhibited by hydrocarbon fuels comprises the lower heating value (LHV) of bio-oils (Czernik and Bridgwater 2004). Due to the high oxygen content, the presence of water and the higher bio-oil density, the LHV of bio-oils, on a volume basis, is 60% of the heating value of hydrocarbon oils.

*Density* can be measured using ASTM D4052 or ASTM D369 (Boucher et al. 2000, Oasmaa and Peacocke 2001)). As water content increases, density of wood pyrolysis liquids typically decreases (Oasmaa and Peacocke 2001).

*Flash point* (°C) is the lowest temperature at which the vapor above the sample is ignited by the test flame. It can be measured using ASTM D93 (Oasmaa and Peacocke 2001) or the tag closed tester (Fischer-Tag) (ASTM D3828) (Boucher et al. 2000). Flash point is quite important for fuel handling. The flash point of a fuel is of no significance to the performance of an engine, despite its importance from a safety standpoint (Oasmaa et al. 1997).

*Pour point* is the lowest temperature at which pyrolysis oil can be pumped or at which movement is still noticeable. ASTM D97 is used to determine this (Li and Zhang 2003, Oasmaa et al. 1997, Oasmaa and Peacocke 2001).

*Clouding point* is the temperature at which the waxes in the pyrolysis oil precipitate. The paraffin constituents of bio-oil precipitate as a wax under low-temperature conditions. Malfunctioning or stalling of an engine can be caused by settling of the wax which blocks fuel lines and filters. ASTM D2500 describes the cloud point which is determined by the temperature at which a cloud of wax crystals first appears in a liquid when it is cooled. Rheological studies, microscopy analyses with polarized light, and differential scanning calorimetry (DSC) can also be used to determine a liquid's clouding point (Garcia-Perez et al. 2006; Oasmaa et al. 1997).

*Char content:* In addition to actual solids, solids measured as insoluble material in some specific solvents contain heavy organic material not dissolved in the solvent (sometimes waxes). Another solvent that can be used is methanol-dichloromethane (Oasmaa and Peacocke 2001; San Miguel et al. 2011). Depending on the pyrolysis technology employed and the efficiency of the solid separation devices (ceramic filters or

cyclones), solid contents can range between 0.05 and 0.5 wt. % (Oasmaa and Peacocke 2001, San Miguel et al. 2011).

*Char particle size distribution:* To provide an efficient atomization of the fuel, solids should be smaller than the tolerances in the injection needles, which are already small (Oasmaa et al. 1997). Two optical methods used to measure biochar particle size distribution, an image analyzer and a particle counter, were developed by VTT Technical Research of Finland. The prior method diluted the sample in ethanol (1:500) then let it through a particle counter that would detect particles larger than 5 µm (Oasmaa et al. 1997).

*Viscosity:* *Kinematic viscosity* of standard fuels, which can be measured using ASTM D445, is determined using a fixed volume of liquid flowing under gravity though a calibrated capillary at a closely controlled temperature measured as a function of time. One of the most common devices used to measure kinematic viscosity is the Cannon-Fenske (Oasmaa et al. 1997). A device used to measure *dynamic viscosity* is the rotaviscorometer (e.g. BrookField viscometer, model LV-DVI+, and TA Instruments) (Ingram et al. 2008). When conducting studies at high temperatures it is important to take into account the evaporation of light compounds (Oasmaa et al. 1997). At high strains, bio-oil behaves as a Newtonian fluid (Leroy et al. 1988), which means that when increasing the shear rate, the viscosity will remain constant (Oasmaa et al. 1997). Despite this, it will tend to show elastic properties at very low strains (Garcia-Perez et al. 2006).

*Thermal conductivity:* Bio-oil thermal conductivity is important for process design. Thermal conductivity can be measured using comparative and absolute methods (Jamieson et al. 1975, Peacocke et al. 1994, Oasmaa and Peacocke 2001).

*Specific heat:* Differential scanning calorimetry (DSC) or a test-ring can be used to measure the specific heat capacity of pyrolysis liquids (Peacocke et al. 1994)

*Conradson carbon residue* is a measurement of the material left over once all volatile components have been vaporized in the absence of air. A specified weight of sample is placed in a crucible and then subjected to destructive distillation (Oasmaa et al. 1997). Conradson carbon residue is a good indication of bio-oil susceptibility to carbonization. It can be measured using ASTM D189.

*Ash content:* To measure the ash content, the solid residue obtained by the Conradson carbon residue is ignited and burned in a crucible at 775°C, cooled, and weighed (ASTM D482). During ashing, the alkaline contents may partially evaporate. The possible evaporation may not be important for total ash as the ash and alkaline contents of wood pyrolysis liquids are usually low (Oasmaa et al. 1997).

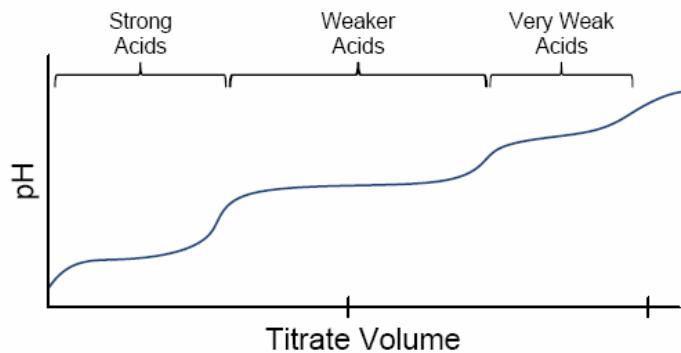
*Metals:* The content of metals in the ash is determined after digesting it in mineral acids (mixture of nitric and hydrochloric acids at a 2:1 ratio). The ash is typically digested with Inductively Coupled Plasma

Atomic Emission Spectrometry (ICP-AES) or Atomic Absorption Spectroscopy (AA) is then used to analyze the aqueous solution (Oasmaa et al. 1997).

**Total Acid Number (TAN):** The TAN method can be used to measure the acidity of pyrolysis oils and their products of hydrotreating using ASTM D664, ASTM D3339 or ASTM D974 (Oasmaa et al. 2010). The amount of potassium hydroxide (KOH) in milligrams needed to neutralize the acids in 1 g of oil is known as the TAN (Nolte et al. 2010, Oasmaa et al. 2010). Strong acids (i.e. mineral acids), weak acids (i.e. carboxylic acids) and very weak acids (i.e. phenols and substituted phenols) are included in pyrolysis oils. For higher TAN values than ASTM D3339 is specified for, ASTM D664 is typically used.

A mixture of toluene, isopropyl alcohol and water is used to prepare a sample. A burette is then used to titrate potassium hydroxide into the solution. While the KOH is titrated into the solution, the potentiometer output is monitored. The buffer potential is considered the TAN if the inflection is indistinguishable. A plot of pH vs. titrate volumes and the inflection points for weak and strong acids is seen in Figure B1 (Brown et al. 2009).

### **Acid number titration curve illustrating the location of different strength acids**



**Figure B1. Total acid number determination (Brown et al. 2009).**

**Thermal stability (aging):** Pyrolysis liquids are not stable like conventional petroleum fuels due to the high amount of compounds containing reactive oxygen and low boiling volatiles (Oasmaa and Peacocke 2001). The loss of light compounds by evaporation and the reactions leading to increases in bio-oil molecular weight are the main causes for bio-oil aging (Oasmaa et al. 1997, Oasmaa and Kuoppala 2003, Oasmaa and Peacocke 2001). The main causes of bio-oil polymerization are the polymerization of double-bonded compounds (Polk & Phingbodhipakkiya 1981) and the formation of water as the byproduct of etherification and esterification that occurs between hydroxyl, carbonyl and carboxyl group components (Czernik et al. 1994, Oasmaa and Czernik 1999, Oasmaa and Peacocke 2001). In order to quickly compare the stability of different pyrolysis liquids, a simple test (Oasmaa and Peacocke 2001)

was developed (Oasmaa et al. 1997). In this test, increased viscosity is measured while the pyrolysis liquid is kept at a fixed temperature for a certain amount of time in a closed container. Oasmaa and Peacocke (2001) recommend using the stability test for the internal comparison of pyrolysis liquids that have similar initial viscosities. The results should be excluded if the weight loss is > 0.1 wt % (Ba et al. 2004, Diebold and Czernik 1997, Mohan and Steele 2006, Oasmaa et al. 2003, Oasmaa et al. 2004). Diebold et al. (1999) published an excellent review on the chemical and physical mechanisms of the storage stability of fast pyrolysis bio-oils.

# **Appendix C: Techniques to Analyse the Chemical Composition of Bio-Oils**

## **Overall molecular weight and boiling point distribution**

*Thermogravimetric analysis:* Heating rates of 10 °C/min in nitrogen are typically the conditions used for the thermogravimetric analysis (TGA) of bio-oil. A new approach based on the thermogravimetric behavior of pyrolysis oils to estimate the chemical composition of these bio-oils in terms of macro-chemical families was proposed by Garcia-Perez et al. (2007). By applying curve-fitting procedures, the DTG curves were interpreted in the terms of macro-families. Although this technique does not allow a very precise quantification of bio-oil composition, it is useful for comparing bio-oils (Garcia-Perez et al. 2007).

*Molecular weight distribution:* One of the few analytical techniques available to study the overall molecular weight distribution of pyrolysis oil is gel permeation chromatography (GPC) (Anderson et al. 2000, Garcia-Perez 2006, Vuorinen et al. 1998). Depending on the size of the molecules and hydrodynamic volumes, the speed of penetration may vary. Smaller molecules fit inside the pores while the larger molecules are able to move faster. The GPC system is typically used with differential refractometer detectors (Scholze et al. 2001b). However, it has been recently proven that substantial errors in the prediction of the molecular weight can arise due to the conversion of the elutriation volume to molecular weight (Hoekstra et al. 2011). The response of the compounds is not independent of the nature of the molecules studied.

As standard for quantification in most bio-oil GPC analyses reported in the literature, tetrahydrofuran (THF) is extensively used as an eluent and polystyrene. However, several limitations arise with the use of THF to characterize the molar mass distribution of bio-oils. For example, some poly-sugars and high molar mass compounds are partially or totally insoluble in THF. On the other hand, dimethyl-formamide (DMF) is reported to be one of the more effective organic solvents used to dissolve lignins over a wide range of molar masses. Sugars and polar heavy compounds can also be used with DMF (Garcia-Perez et al. 2007). Estimating the molecular weight distribution of oils using other techniques includes: MALDI-TOF-MS, LDI-TOF-MS and Py-FIMS (Bayarbach et al. 2006).

## **Composition of individual species and groups of compounds**

*Water content:* Pyrolysis liquids contain low boiling (below 100 °C) water soluble compounds, and hence conventional drying methods cannot be used to quantify water (Oasmaa and Peacocke 2001). The water content of pyrolysis liquids is typically measured by Karl Fischer (KF) Titration [ASTM E203] ( Garcia-

Perez et al. 2007, Oasmaa et al. 1997). KF volumetric or coulometric titrations are typically used. The coulometric titration is developed for analyzing trace amounts of water. The volumetric titration is suitable for measurements of water in a wider range of concentration (from parts per million to pure water) (Oasmaa and Peacocke 2001). Oasmaa and Peacocke (2001) provide a detailed description of the reactions during KF water titration.

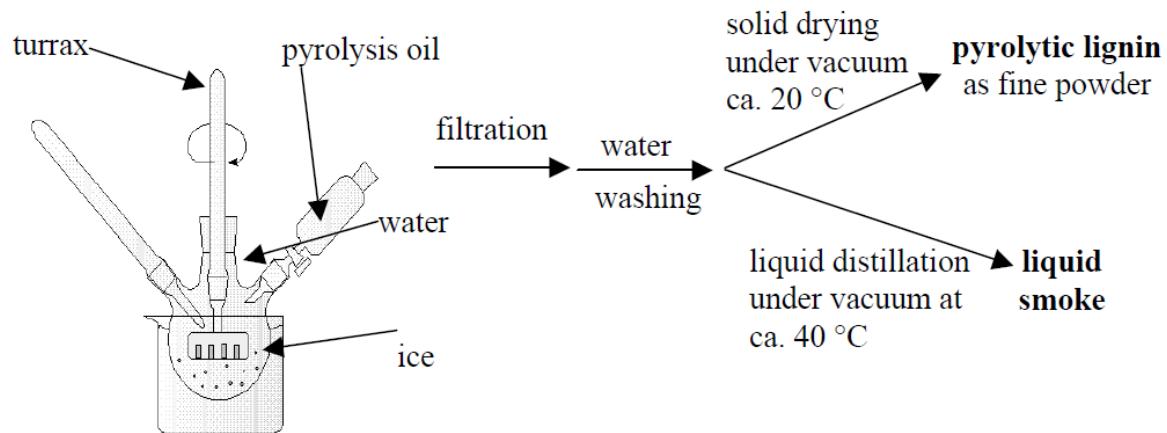
*Gas chromatography-flame ionization detector (GC-FID):* Head space GC-FID analyses can be used to analyze the light compounds (C1-C4).

*Gas chromatography-mass spectroscopy (GC-MS):* GC-MS is perhaps one of the most common techniques to characterize bio-oils. This technique is very useful for quantifying the content of phenols and furans, which account for around 10-15 wt. % (Ingram et al. 2008, Song et al. 2009). GC/MS has also been used to quantify carboxylic, fatty, and resin acids in bio-oils (Pakdel et al. 1994, Pakdel and Roy 1987). Computer matching of the mass spectra with a library (NIST) is used to identify the peaks in the GC/MS chromatogram (Branca et al. 2003). The internal standard method is typically used to quantify the compounds. Some of the most common compounds used as standards include flouranthene and naphthalene. Calibration lines are typically prepared by the injection of several standard solutions for each of the quantified compounds. The concentration range should be chosen by using successive approximations until it becomes considerably slim and contains the quantified value (Branca et al. 2003, Pakdel and Roy 1991, Pimenta et al. 1998).

*Two-dimensional gas chromatography with time-of-flight mass spectrometric analyses (2D-GC-TOF-MS):* This technique is relatively new (Marsman et al. 2008) and has been used to classify bio-oil volatile fractions into chemical families. The classifications of the volatile fraction of bio-oils is as follows: (a) analytes with carboxylic group, (b) compounds with C=O, (c) cyclic oxygen containing component, (d) all methoxy - phenolic derivatives, (e) all glycosides as derivatives of glucose (intramolecular anhydrides), (f) hydroxy-benzene derivatives (excluding methoxy phenols), (g) alkyl substituted benzenes and (h) aliphatic and cyclic hydrocarbons (Fullana et al. 2005, Marsman et al. 2008).

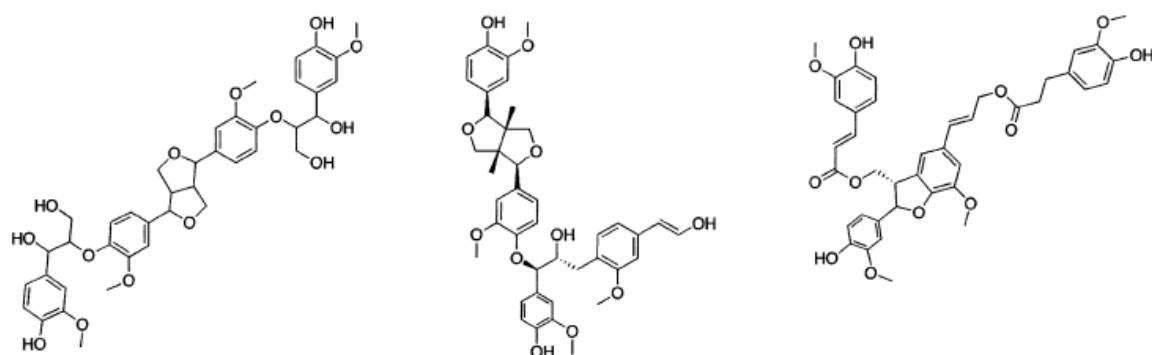
*Lignin oligomers (also known as pyrolytic lignin):* Typically, the cold water precipitation method is used to analyze the content of lignin derived oligomers (Bayarbach and Meier 2009; Scholze and Meier 2001a, b; Windt et al. 2009). More than 50% of the lignin present in biomass is depolymerized, vaporized and appears in the liquid product solution when biomass undergoes rapid pyrolysis (Piskorz 1989). By slowly adding pyrolysis oil to cold water, this fraction can be separated from the crude pyrolysis oil (Scholze and Meier 2001). By adding 60 ml of the oil via droplets to 1000 ml of ice-cooled water at a rate of ca. 1.0 ml/min while stirring the liquid with an ultra turrax (oil to water ratio must be at lease 1:10 and the turrax speed must be 6000 r.p.m) the pyrolytic lignin can be obtained. Figure C1 depicts a schematic diagram of

the experimental setup proposed by Scholze et al. (2001a). Pyrolytic lignin is precipitated after slowly adding the pyrolysis oil to the water. The solution is then filtered and the pyrolytic lignin, that is still wet, is dried in a vacuum at 298 K (Scholze et al. 2001a, 2002).



**Figure C1. A schematic diagram of the setup used to produce pyrolytic lignin and liquid smoke (Source: Scholze et al. 2001a).**

Several methods have been used to study the composition of pyrolytic lignin (FTIR, SEC, MALDI-TOF-MS, LADI-TOF-MS, and Py-FIMS) (Bayarbach et al. 2006, Scholze and Meier 2001a). Scholze and Meier (2001a) described the method used to determine the content of methoxyl groups in pyrolytic lignin by titration with trisulfate (Scholze and Meier 2001a). A general composition assigned to the pyrolytic lignin can be seen in Figure C2.



**Figure C2. Tetrameric units of g-lignin (Frantini et al. 2006).**

Further separation of the water insoluble fraction with CH<sub>2</sub>Cl<sub>2</sub> will result in a fraction soluble in CH<sub>2</sub>Cl<sub>2</sub> (also known as low molecular weight lignin oligomers) and an insoluble fraction (also known as high molecular weight lignin oligomers).

*Hydrolyzable sugars:* Ion exchange chromatography or high performance liquid chromatography (HPLC) can be used to analyze the hydrolyzable sugars soluble in the water soluble fraction (Lian et al. 2010, Mohan et al. 2006). Levoglucosan and cellobiosan are the main hydrolyzable sugars. Following the same method to separate lignin oligomers, the sugars soluble in water can be separated from the lignin oligomers. Using sulfuric acid, the sugars are then hydrolyzed and analyzed with the appropriate method (IEC, HPLC).

*Total content of sugars:* A relatively small fraction of the products of cellulose and hemicellulose produced during pyrolysis make up the hydrolyzable sugars. Since cross linked sugars do not yield monosugars when hydrolyzed, they are difficult to analyze. Oasmaa and Kuoppala (2008) characterized the water soluble fraction (obtained from the water precipitation method) following the classic Brix determination. Commercially, the Brix method is used for the quantification of sugar content in wine and grapes. For the determination of Brix at 20 °C, a piece of equipment called the Anton Paar DMA 4500 can be used. A hydrometer, which indicates a liquid's specific gravity (the density of a liquid in relation to that of pure water), is used to determine the sugar content. Every 1 g of sugar per 100 g of grape juice determines the degree of Brix (°Br) (Oasmaa and Kuoppala 2008). A bio-oil content of cross-linked sugars 20 wt. % higher than those of the hydrolysable sugars was obtained by the authors. The solid residue obtained after the water was evaporated from the water soluble fraction correlated very well with the Brix calculated (Oasmaa and Kuoppala 2008).

## Overall composition

*Elemental analysis:* ASTM D5291 guides the determination of the mass content of carbon, hydrogen, nitrogen and oxygen (CHN-O) (Oasmaa and Peacocke 2001, Acikgoz and Kockar 2009). Carbon, hydrogen and nitrogen are simultaneously determined as gaseous products (carbon dioxide, water vapor and nitrogen) in this method. Most equipment does not directly measure oxygen quantity. The difference is used in these cases to calculate the oxygen content (Oasmaa et al. 1997).

*Overall functional groups:* Several very useful techniques to identify bio-oil functional groups include Fourier Transform Infrared (FTIR) spectroscopy and nuclear magnetic resonance (NMR). Until recently these technologies have been limited to quantitative analysis of bio-oils.

*Carbon 13-NMR:* These analyses commonly use solutions of 10-20 wt % bio-oil (Ingram et al. 2008). Due to their large chemical shift regions, the <sup>13</sup>C NMR spectra are particularly instructive (Ingram et al. 2008, Mullen et al. 2009, Song et al. 2009). The integrated <sup>13</sup>C spectra can be divided into five general chemical shift ranges for analysis: 215-163 ppm (carbonyl carbons), 163-110 ppm (total aromatic carbons), 110-84 ppm (carbohydrate-type carbons), 84-54 ppm (methoxy- or hydroxy-bound carbons),

and 54-1 ppm (primary, secondary, tertiary, and most quaternary alkyl carbons). A further subdivision of the aromatic region consists of: 125-112 ppm (guaiacyl carbons) and 112-110 ppm (syringyl carbons). Also, a further subdivision of the alkyl region consists of 34-24 ppm (mostly secondary and tertiary carbons) and 24-6 ppm (most primary and some secondary carbons). The facilitation of more precise measurements that allow for accurate integrations as a fraction of the total carbons present is the result of the areas selected on the integral curves being flat at each of the preceding breaks.

*Hydrogen-1 NMR:* The  $^1\text{H}$  NMR spectra are made up of aliphatic protons that occur between 0.0 and 1.6 ppm as well as others that are found from 1.6 to 2.2 ppm along with aliphatic hydroxyls, protons located alpha to ketone, aldehydes or carboxyl groups, and benzylic protons that occur from 2.2 to 3.0 ppm. A substantial amount of aliphatic protons that are consistent with the  $^{13}\text{C}$  NMR spectra are found in bio-oils (Acikgoz and Kockar 2009, Ingram et al. 2008). From 3.0 to 4.2 ppm, methoxy,  $-\text{CH}_2\text{O}-$ , and  $-\text{CHO}$  functionality appear. From 4.2 to 6.4 ppm, further  $-\text{CHO}$  groups, phenolic  $-\text{OH}$ , and nonconjugated olefinic protons are seen. From 6.4 to 6.8 ppm as well as at lower fields (6.8 to 8.0 ppm) where the bulk of the aromatic protons occur, olefinic protons on double bonds conjugated to carbonyls are found. From 8.0 to 10.0 ppm, lower field aromatic protons and aldehyde protons are found. A considerable overlap of various types of proton resonances occurs when the  $^1\text{H}$  chemical shift range is compressed relative to that of  $^{13}\text{C}$ . (Ingram et al. 2008). Quantification is very difficult given the complications resulting from the wide chemical shift range over which hydroxyl protons overlap the chemical shift ranges. Direct comparison of the  $^1\text{H}$  NMR spectra of bio-oils is possible (Ingram et al. 2008).

*Fourier transform infrared spectroscopy (FTIR):* The study of bio-oil composition has also been done with FTIR (Acikgoz et al. 2009). The change of oxygen content mainly affects the intensity of carbonyl adsorption bands as indicated by FTIR data. Elucidating the aging processes of pyrolysis oil can be done quickly with the FTIR method (Scholze and Meier 2001).

# Appendix D: Biochar Properties

## General Properties

*Specific weight* refers to charcoal density which depends on the density of the raw material (Emrich 1985).

*Hardness* is a very important coefficient for industrial charcoal because it defines resistance to disintegration. In some countries, standard scales have been imposed (Emrich 1985).

*Screening analysis:* A standardized set of screens with varying mesh sizes are used to analyze the distribution of grain sizes of charcoal fines and charcoal powder (Emrich 1985).

*Friability tests* indicate the extent to which biochar will break into smaller pieces when subjected to repeated handling (Emrich 1985). A tumbler test can be used to evaluate the friability of the biochar (Emrich 1985).

*Heating or calorific value* is determined with a calorimetric bomb. It depends on the content of fixed carbon and can only be reduced by high ash content. Heating values are generally comparable to bituminous coal (6,500-7,200 kcal/kg) (Emrich et al. 1985).

*Breakthrough curves* simulate the performance of carbon when it is used to remove pollutants from a liquid or gaseous stream. The breakthrough curve plots the duration of the test against the concentration of the adsorbate in the effluent stream, a mixture of air or liquid and the adsorptive. As long as the bed of carbon has the capacity to adsorb, this process will continue. The breakthrough curve is S-shaped, symmetrical and is described in terms of its midpoint, steepness and shape.<sup>16</sup>

*Biochar reactivity* indicates resistance to oxidization in the presence of oxygen in steam and is measured at 370 °C using a thermogravimetric analyzer (Li et al. 2006, Assadullah et al. 2010).

## Bulk Chemical Composition

Bulk chemical composition describes the composition of the material apart from the surface. In many applications (e.g. during combustion) the behavior of biochar is mainly related to its bulk properties.

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<sup>16</sup> More information on this method is provided by Marsh and Rodriguez-Reinoso (2006).

*Proximate analyses* of biochar can be determined using ASTM D7582 – 10 or ASTM D1762-07 (Emrich 1985). Biochar fixed carbon should be 74-81 wt. % (Toole 1961). For the industrial charcoal consumer, the volatile content should not exceed 30% (Emrich 1985).

*Ash composition:* The concentration of sodium, potassium, magnesium and calcium present in the biomass is determined using atomic absorption spectroscopy. Once the ashing process is complete (see the method for proximate analysis), the ash is dissolved in mineral acids and the solutions are analyzed by atomic absorption.

*Elemental analysis* (of C, H, N and O) is determined using the combustion method.

*Sulfur and phosphorous content* can be determined with the calorimetric combustion of the biochar with the addition of dilute sodium hydroxide (Emrich 1985). Sulfur and phosphorous content below 0.05% and 0.03% respectively are desired (Emrich et al. 1985).

*Solid state  $^{13}\text{C}$  NMR:* A good sensitivity by  $^{13}\text{C}$  CP/TOSS NMR can be used to obtain a quantitative char composition, in particular alkyl carbon composition. The bridgehead carbon can be used to estimate the aromaticity of the biochar (Brewer et al. 2009).

*FTIR/Raman spectroscopy* can determine structural features of biochar (Li et al. 2006). In order to reduce thermal emission, the biochar sample is mixed and ground with spectroscopic grade potassium bromide (KBr). During the acquisition of a Raman spectrum, the char sample is protected from the produced heat because KBr is an excellent heat dissipating medium. Ten Gaussian bands can be fitted to a Raman spectra in the range of 800-1800  $\text{cm}^{-1}$ . Assadullah et al. (2010) and Li et al. (2006) described the assignments of these bands.

*FTIR-PAS:* Fourier transform infrared (FTIR) coupled with a photoacoustic detector can be used to investigate surface functionality (Brewer et al. 2009).

## Surface Chemical Composition

*pH at point of zero charge (pHpzc)* determines the pH at which electrical charge density on a surface is zero. Varying concentrations of char are placed in contact with solutions of varying pH (3-11). The pH<sub>pzc</sub> value is obtained as the concentration of the biochar is increased and each curve approaches an asymptotic pH value.

*Chemical (Boehm) titration* is based on the principle that oxygen groups on carbon surfaces have different acidities and can be neutralized by bases of different strengths (Goertzen et al. 2010). Carbon is suspended for a few hours in solutions of sodium carbonate (to determine lactone and lactol rings),

sodium ethoxide in ethanol solution (to measure carbonyl groups), sodium bicarbonate (to determine carboxylic acids and anhydrides) or sodium hydroxide (to determine phenols). The neutralization caused by surface groups is then determined by comparing the solution with a blank solution (Marsh and Rodriguez-Reinoso 2006). The content of lactone, carboxyl, phenolic and carbonyl groups, as well as the content of the basic groups on the surfaces of biochar can be determined using this method.

*X-ray photoelectron spectroscopy (XPS)* analysis can be used to quantify the chemical composition of biochar surfaces. When x-ray radiation excites the core electrons of surface atoms, electrons are emitted, each with characteristic kinetic energy which is then analyzed in the spectrometer to provide a spectrum (Marsh and Rodriguez-Reinoso 2006).

*Temperature programmed desorption (TPD)* requires programmed heating of suitably oxidized carbon in vacuum or in flow of helium. This method also requires a facility (mass spectrometer) to quantitatively measure the gases evolved, usually water, carbon dioxide and carbon monoxide (the latter desorbing at the highest of temperatures) (Marsh and Rodriguez-Reinoso 2006). The decomposition of carboxyl type groups produces carbon dioxide while the decomposition of carbonyl and ether oxygen produces carbon monoxide (Marsh and Rodriguez-Reinoso 2006).

*Surface oxygen complexes:* The nature and amount of oxygen surface groups are extremely important for the adsorption of polar molecules with high polarity. Marsh and Rodriguez-Reinoso (2006) described the use of adsorbents to assess the effects of surface oxygen groups within microporosity using the adsorption of gases with different polarities. Using Dubinin-Radushkevich (DR ) equation plots for analyses, the adsorptive molecules typically used are N<sub>2</sub>, SO<sub>2</sub>, CH<sub>3</sub>OH, and H<sub>2</sub>O (polarities 0, 1.6, 1.7, 1.8, respectively). For non-polar molecules (e.g. N<sub>2</sub>) adsorption is mainly influenced by pore structure (March and Rodriguez-Reinoso 2006).

*Enthalpies of adsorption:* Physical adsorption (also referred to as physisorption) of gases is an exothermic process with enthalpy changes in the region of < 50 kJ/mol of adsorbed adsorbate and is considered to be reversible. Chemisorption is when an adsorbed layer is irreversibly bonded to the surface chemically. The formation of chemisorbed layers has enthalpies of around 400 kJ/mol (Marsh and Rodriguez-Reinoso 2006). The heat evolved can be measured using calorimetric methods (Marsh and Rodriguez-Reinoso 2006).

## **Characterization of Porosity**

*Small Angle X-Ray Scattering (SAXS):* The surface areas calculated from the scattering at interfaces are always the highest reported of the several methods. The scattering at the surfaces of what was termed “closed porosity” is now understood to be the cause of this (Marsh and Rodriguez-Reinoso 2006).

Dimensions of scattering are within the range of 1-200 nm (Marsh and Rodriguez-Reinoso 2006).

Scattering from the open porosity can be removed from closed porosity by prior filling with deuterated benzene ( $C_6D_6$ ) leaving only scattering from closed porosity, which facilitates interpretations of these scattering curves. Therefore, the carbon porosity can be studied in total as well as in parts (Marsh and Rodriguez-Reinoso 2006).

*Microporosity:* The most suitable method to elucidate porosity of biochars through the use of molecules with the same dimensions as the pore entrance. Measuring the extent of the adsorption of gases using automatic volumetric methods suitable for most solids with surface areas  $> 1 \text{ m}^2/\text{g}$  is commonly used. In 1937, Emmett and Brunauer originally used the volumetric method (Marsh and Rodriguez-Reinoso 2006). The extent of adsorption and the porous networks into which the adsorption process has occurred is provided by a visual inspection of isotherm shapes (Marsh and Rodriguez-Reinoso 2006). The Brunauer-Emmett-Teller (BET) equation predicts monolayer coverage rather than surface area. A convenient way to indicate adsorption capacity of a porous solid is to use the term surface area (Marsh and Rodriguez-Reinoso 2006).

*Mesoporosity* refers to porosity with an entrance dimension of 2 -50 nm. The way that nitrogen is adsorbed into porosity is the basis of such a definition. Capillary condensation is the filling of the porosity. The definition (2-50 nm) is arbitrary because it is a function of the adsorbate and the transitions in pore filling mechanisms are dependent on the size of the adsorbate molecule. However, these definitions must suffice as nitrogen is dominantly the characterizing adsorptive. Mesoporosity role is as a transport pore (a means of passage) to permit rapid access to the retaining microporosity of the adsorbate of the system (Marsh and Rodriguez-Reinoso 2006).

*Mercury porosimetry:* For the characterization of the larger mesoporosity, mercury porosity is an alternate technique. The physical phenomenon of mercury porosity is that mercury has a contact angle with solids of about  $140^\circ$  and does not wet the surfaces of solids; hence, in order to push mercury into tubes, an applied force is required. Noting the amount of mercury that must enter the sample and the pressure that has to be applied, a mercury porosimeter is a high pressure piece of equipment that is fitted with the ability to apply pressure to mercury. For the use on meso- and macroporous carbons and graphitic materials having open porosity, such instruments are commercially available (Marsh and Rodriguez-Reinoso 2006).

# Appendix E: Fuels and Chemicals from Bio-Oils

## Chemical Products and Transportation Fuels

In this section we review the potential of bio-oil to produce chemical products and transportation fuels.

*Acetic acid* can be produced by biomass pyrolysis.<sup>17</sup> More than  $7 \times 10^6$  t/a acetic acid is produced annually (Patel et al. 2006). Also, it is one of the more important C2 building blocks (Patel et al. 2006). The carbonylation of methanol synthesizes the bulk amount (65%). Fermentation with microorganisms only produces 190,000 t which are used for food purposes. The largest acetic acid uses are in the form of vinyl acetate ( $4.1 \times 10^6$  t/year), ethyl acetate (1 million t/year), peeracetic acid (18,000 t/year), acetic anhydride (1 to  $2 \times 10^6$  t/year), chloroacetic acid (370,000 t/year), and acetate salts (Patel et al. 2006). The fact that the market price of acetic acid (0.6 USD/kg, 2009 level) is significantly higher than pyrolysis oil price estimates (0.18 – 0.38 USD/kg) means that the separation and commercialization of acetic acid likely will continue to increase the economic attractiveness of the pyrolysis oil value chain (Rasrendra et al. 2010). A process based in solvent extraction for acetic acid recovery from the aqueous phase produced by pyrolysis was commercially established in the 1930s and 1960s (Rasrendra et al. 2010). The separation of organic acids, particularly acetic acid from the aqueous stream of phase of splitted pyrolysis oil using a long chain aliphatic tertiary amine was reported by Rasrendra et al. (2010). By adjusting the process conditions and selecting the proper amine and dilute combination, acid recovery was optimized. An acetic acid recovery of 48% was obtained using the reactive extraction process successfully demonstrated in a continuous contactor-separator (CCS) device (Rasrendra et al. 2010).

*Adhesives:* The manufacture of wood panels such as plywood, MDF, particle board and OSB employs renewable phenolic resins from bio-oils.<sup>18</sup> Resins are prepared by utilizing either the phenolic enriched fraction obtained after fractional condensation, further processing such as solvent extraction, or by utilizing the whole liquid product. None of the phenolic fractions produced allow 100% substitution of the phenol content of the resins without impacting effectiveness, compared to commercial formulations based petroleum-derived phenol. High-quality resins can be produced from the replacement of 30-50% of the phenol with pyrolytic lignin in novolak and resole formations despite the fact that lignin is less

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<sup>17</sup> One of the main goals of the old wood distillation industry was to produce acetic acid. The process to produce acetic acid by pyrolysis is discussed elsewhere (Bates 1922, Dumesny and Noyer 1908, Klark 1925, Veitch 1907).

<sup>18</sup> Effendi et al. (2008) published a review of the production of renewable phenolic resins from bio-oils.

reactive than phenol. Further research is required to meet quality requirements and develop a low cost renewable resin. Areas of concern include the variability of renewable resin properties, odor, and wood panel press times; the potential for increased emissions of volatile organic compounds; and the lack of reactive sites compared to phenol (Czernik and Bridgwater 2004, Effendi et al. 2008, Mohan et al. 2006).

*Aldehydes and ketones:* Since conventional techniques are unfeasible, the reactive extraction with an aqueous bisulphite solution seems to be a promising method to isolate carbonyl compounds (Vitasari et al. 2010, <http://www.biocoup.com/index.php?id=144>). Identifying and purifying carbonyl compounds have been achieved by this reaction for a long time. Since bisulphite selectively reacts to carbonyl compounds, the purification step can be done with this forward reaction. The crystallized aldehyde-bisulphite salt is then separated from the mixture. The equilibrium from the recovery is then shifted to the left so the allowing the pure compound to be obtained.

*Alkyloaromatics:* The catalytic conversion of small oxygenates from bio-oil into alkyl aromatics on zeolites is being studied by researchers at the University of Oklahoma (Resasco et al. 2010).

*Antioxidants:* Bio-oil is a very good source of antioxidants due to the presence of lignin derived compounds (Garcia-Perez et al. 2010)

*Asphalt paving substitution:* The possibility of using bio-oil as a substitute for petroleum products in asphalt emulsions has been explored by several research groups (Mullaney et al. 2002).

*Bio-carbon electrodes:* The production of graphite-like materials from pyrolytic pitch has been studied by Cautinho et al. (2000). Bio-pitch is used to compress together ground solid charcoal. The green, pre-molded electrode has a 120 mm length and a diameter of 25 mm. It is cured using a treatment involving an increasing temperature. Following the curing step, the electrode then undergoes calcinations at 1000 °C, followed by graphitization at 2700 °C. The bio-oil derived electrode has comparable properties to the ordinary electrodes (Cautinho et al. 2000).

*Coal dust suppression:* Another possible market for bio-oil is coal dust suppression. The current product used to coat coal piles is a plasticizer that is bio-degradable and does not contaminate ground water (Mullaney et al. 2002).

*Fertilizers:* Amides, imines and Mannich reaction products, are produced from the reaction of bio-oil functional groups (carbonyl, carboxyl, hydroxyl, phenolic and methoxyl) with ammonia, urea, and other amino compounds and can function as slow release organic fertilizers (Radlein 2005, <http://www.pyne.co.uk/Resources/user/PYNE%20Newsletters/Pynews%2005.pdf>). Fertilizers with 10% nitrogen, produced with this method, have a lower leachability compared to mineral fertilizers and will result in less pollution of the groundwater. Additionally, it contains humic type matter (lignin) making it a

good soil conditioning material. Typical fertilizer with controlled release sells for around \$250-1250/ton (Redlein et 2005) (bio-oil prices: \$180-380/ton).

*Food additives:* Smoking to preserve food has become less and less important over the course of the last 50 years and today fish and meat are typically smoked only for flavoring reasons. Glucoaldehyde, glyceraldehydes, pruvaldehyde, dihydroxyacetone, acetone, and diacetyl are effective browning agents (Mohan et al. 2006). An application that has been commercial for over 10 years uses the water-soluble part of fast pyrolysis bio-oil as browning agent. Both phenolic compounds that provide the smoky flavors and the low-molecular-weight aldehydes that are effective meat browning agents (especially glycolaldehyde) are included in the aqueous extract of bio-oil. Methods for the isolation of glycolaldehyde based on crystallization have been patented by Red Arrow Products and RTI. This particular compound is susceptible to decomposition at temperatures higher than 100 °C. If glucose is used instead of wood as the feedstock for fast pyrolysis, the production of glycolaldehyde becomes more attractive (Czernik and Bridgwater 2004). A new method for the separation of glycoaldehyde from pyrolysis oil via physical extraction has been reported by researchers from the Eindhoven University of Technology (Vitasari et al. 2010). Reactive extraction with the use of tertiary amines for separating acid compounds is incorporated in the conceptual design.

*Glucose* can be obtained by hydrolyzing hydrolyzable sugars (levoglucosan, cellobiosan) (Lian et al. 2010). Glucose is an important compound for C<sub>6</sub> building blocks (Patel et al. 2006).

*5-hydroxymethyl furfural (HMF)* is an attractive building block for further derivatization since it possesses particular molecular features and functionalities including a hydroxymethyl group which can be subjected to etherification oxidation and an aldehyde group making the introduction of various C-C bonds possible. Synthesis of linear polymers from the disfunctionalized furan opens up a large industrial group of aromatics. Oxidative alkoxylation from dihydrofuran derivatives allows for the conversion to dihydrofuran derivatives. Heterocycles such as pyrrol, pyridoxines or pyridines can then be synthesized (Patel et al. 2006). Studies on the production and separation of HMF from pyrolysis oils are limited.

*Levoglucosan*<sup>19</sup>: By using demineralized cellulose, high yields of levoglucosan (1,6-anhydro-*a*-D-glucopyranose) (up to 46 wt. %) and levoglucosenone (up to 24 wt. %) (6,8-dioxabicyclo[3.2.1.]oct-2-en-4-one) can be generated (Czernik and Bridgwater 2004). Considerably lower yields (< 10%) of levoglucosan are produced from the pyrolysis of lignocellulosic materials. The efficient isolation of levoglucosan from the pyrolytic liquids is one of the main difficulties involved in its production. Due to the high production price of levoglucosan from lignocellulosic materials, it is unlikely to see extensive

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<sup>19</sup> Radlein (1999) published a review on the production and potential applications of levoglucosan.

use in the near future despite its potential for the manufacturing of pharmaceuticals, surfactants, biodegradable polymers, and others (Czernik and Bridgwater 2004). Glucose used to obtain other products (ethanol, lipids and bio-plastics) can be produced with the easy conversion of levoglucosan and other hydrolyzable sugars.

*Methanol*<sup>20</sup> can be produced from the distillation of the pyroligneous water. The product obtained is typically dark-yellow in color and contains small quantities of acetic, butyric and propionic acids (Emrich 1985).

*Pesticides:* The University of Western Ontario has a very active program in the development of pesticides. Significant activity against two bacteria (*Streptomyces scabies* and *Clavibacter michiganensis* subsp. *michiganensis*) and the Colorado potato beetle (*Leptinotarsa decemlineata*) were shown using bio-oil derived from dried coffee grounds (Bedmutha et al. 2011, Booker et al. 2010). Converting tobacco leaves to natural pesticides in the form of bio-oil can be done since tobacco's pesticide properties are well-known (Booker et al. 2010).

*Pyrolytic pitch* is a dark brown or black residue of tar distillation commercialized to impermeabilize ships. Charcoal plants normally supply four different grades which are marked by their softening points (Emrich 1985).

*Road de-icers:* The production of calcium salts or carboxylic acids that can be used as environmentally friendly road de-icers is a potential application of the formic, acetic and propionic acids present in the water soluble fraction of bio-oil. Other volatile components (such as aldehydes and esters) in such a distillate can either react with lime or will be evaporated during the recovery of solid calcium salts. Though not currently economic, the scale-up of the production de-icers is technically feasible. Calcium chloride is known to have deleterious effects on plants, but it is a common de-icer because it is less expensive (<http://www.forestprod.org/biomass09steele.pdf>).

*Surfactants:* Oils for the production of surfactants are recovered at various stages of tar distillation and during raw acetic acid refining. They range from transparent to dark brown and have a characteristic smell. More than 10 commercial grades are known and made according to specifications, classified by specific weight, viscosity, calorific value and boiling point. They are widely used in the flotation process

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<sup>20</sup> The current price of methanol is between \$380 and 400/ton (\$1.14 – 1.19/gal) (source: <http://www.icis.com/v2/chemicals/9076034/methanol/pricing.html>: accessed June 27, 2011). Although relatively low, the price of methanol is higher than crude bio-oil commercialization price (around: \$ 0.83 /gallon).

for the separation and beneficiation of ores (Emrich 1985). The price of flotation agents is \$400-2,300 /ton higher than the \$180-380/ton that can be obtained with crude bio-oils.

*Wood preservative:* Bio-oils can act as insecticides and fungicides due to some of the terpenoid and phenolic compounds present in bio-oils (Czernik and Bridgwater 2004). Impregnating wood with bio-oil can protect it from fungi (Czernik and Bridgwater 2004). The synergistic fungicidal properties of bio-oils as a potential substitute for creosote have been demonstrated by several researchers (<http://www.forestprod.org/biomass09steele.pdf>). Pentachlorophenol has been proven to be 10 times more effective with bio-oil (Mohan et al. 2008). Studies of whole bio-oils and their lignin-rich fractions as potential environmentally friendly wood preservatives have been performed with hopes to replace the metal-based CCA and copper systems that have raised environmental concerns (Mohan et al. 2008). In order to provide decay resistance, the prevention of leaching is critically important for both raw bio-oils and their fractions. Mohan et al. (2008) have had some success in initial tests of a polymerization chemical to prevent leaching (Mohan et al. 2008).

*Production of hydrogen:* There are currently no commercial biomass processes for direct hydrogen production ( Bleeker 2010, Medrano et al. 2010).<sup>21</sup> However, there are extensive investigations on the production of hydrogen from steam reforming of bio-oil (Czernik et al. 1999, Davidian et al. 2007, Galdamez et al. 2005, Medrano et al. 2010, Qi et al. 2007, Rioche et al. 2005, Takanabe et al. 2004, Wang et al. 1997, 1998, 2007). Catalysts that show good activity in the reforming of bio-oils include: nickel, NiAl, coprecipitated Ni-Al promoted with lanthanum, Pt/ZnO<sub>2</sub>, Pt, and Rh supported on ceria-zirconia catalysts. Commercialized catalysts developed for applications in fixed beds are susceptible to attrition in fluidized beds. A fluidizable catalyst with both high activity and mechanical strength at the conditions of the steam performing process needs to be developed. In order to recover catalyst activity, the coke that is formed must be combusted. The hydrogen can then be used for electricity production in Fuel cells and is a critical reagent for hydrotreatment.

*Production of synthesis gas:* Roughly 2% of the world's energy consumption is represented by synthesis gas (syngas). Syngas is a very important product for many processes. Various grades of syngas (essentially hydrogen and carbon monoxide) can be produced via gasification. Due to low ash content, pyrolysis oils potentially can be gasified in the 1000-1250 °C range (Van Rossum et al. 2007). Van Rossum et al. (2007) studied the production of synthesis gas/high-Btu gaseous fuel from the pyrolysis of biomass-derived oil (e.g., bio-oil). Bio-oil to gas conversions as high as 83 wt. % have been reported (Van Rossum et al., 2007). Product gas compositions include: syngas, 16-36 mol %; CH<sub>4</sub>, 19-27 mol %; and C<sub>2</sub>H<sub>4</sub>, 21-31 mol % (Mohan et al. 2006).

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<sup>21</sup> Padro and Putsche (1999) published an excellent survey on the economics of hydrogen technologies.

*Production of ethanol:* Ethanol is an interesting platform chemical since fermentation is already used to produce it from biomass in bulk quantities. The world ethanol production was estimated at 40 billion liters in 2003 (Patel et al. 2006). The three major uses for ethanol are: fuel and fuel additive (69%), as a solvent and a building block for chemical synthesis (21%), and as an ingredient of alcoholic drinks and a disinfectant and a preserving agent in the food industry (10%) (Patel et al. 2006). The production of ethanol from the fermentation of pyrolytic sugars is described in several papers (Lian et al. 2010, Bennett et al. 2009, Miyafiji et al. 2005, Olson and Freel 2007, Prosen et al. 1993, Shafizadeh and Stevenson 1982).

*Production of hydrocarbons via bio-oil hydrotreatment:* One of the most promising areas to fully utilize bio-oils is the production of drop-in fuels using hydrotreatment. The process of hydrotreatment is usually performed in the presence of catalysts, under high hydrogen pressure, and at a high temperature (Adjaye et al. 1992, Maggi and Delmon 1997). A special two-stage method was patented by Pacific Northwest National Labs (PNNL) (Baker and Elliott 1993, Elliott and Baker 1989). Typical conditions for hydrotreatment include: the use of a cobalt-molybdenum catalyst, temperatures from 300-400 °C, a pressure of 7-10 MPa and a hydrogen rich environment (about 95%). Hydrocracking which follows the hydrotreatment step, breaks down heavy molecules into shorter chains. Conditions for this process are more severe than for hydrotreating with a nickel-molybdenum catalyst, temperature ranging from 400-500 °C, and pressure from 10-14 MPa (Wright et al. 2010). These hydrocarbons can be direct substitutes for jet fuel, diesel, and gasoline.

Early work on bio-oil hydrotreatment was conducted at PNNL using catalysts in petroleum processing technologies (sulfided NiMo/Al<sub>2</sub>O<sub>3</sub> and CoMo/Al<sub>2</sub>O<sub>3</sub> catalysts) (Elliott et al. 2010) resulting in a hydrocarbon rich product with high hydrogen consumption. A bench scale reactor configuration with two fixed bed reactors operating at a hydrogen pressure of 21 MPa was used for the first studies on the hydrotreatment of pyrolytic oils (Elliott et al. 2010). A down-flow operation (trickle bed) was used with both of these reactors. The first reactor, or the stabilization reactor, was operated using low temperature (150-200 °C). Deep hydrodeoxygenation reactions took place in the second reactor which was operated at much higher temperatures (300-400 °C).

Elliott (2010) reported that 121 gallons of hydrocarbons/ton of dry wood can be obtained using the hydrotreatment of bio-oil. This is equivalent to four barrels of hydrocarbons per ton of biomass, which means a 34% yield of hydrocarbon. An overall efficiency up to 61% can be achieved with the pyrolysis-hydrotreatment process. Heat and power are the products of most of the remaining energy (Elliott 2010, French et al. 2009, Vanderbosch et al. 2010).

During the stabilization step at a temperature of 250 °C and in the presence of H<sub>2</sub> and catalyst, parallel reactions take place including: decarboxylation (limited CO<sub>2</sub> production), re-polymerization (water production), and hydrotreating (Vanderbosch et al. 2010). The cellulose-derived fraction of the oil needs to be transformed, preferably into alcohols with a “mild hydrogenation” step. Subsequently, this allows for further hydrogenation and dehydration (Vanderbosch et al. 2010). For the hydrotreatment of bio-oils, noble metal catalysts (Rhthenium (Ru)/Carbon (C), Ru/Titanium Oxide (TiO<sub>2</sub>), Ru/Aluminium oxide (Al<sub>2</sub>O<sub>3</sub>), Platinum (Pt)/C, and Palladium (Pd)/C) have also been studied along with the sulfided NiMo/Al<sub>2</sub>O<sub>3</sub> and CoMo/ Al<sub>2</sub>O<sub>3</sub> catalysis (Baldwing et al. 2009, Mahfud 2007, Wildschut et al. 2009 and 2010, Wilson and Williams 2003).

Despite the consensus that bio-oil must be stabilized (sugars must be hydrogenated into alcohols) before it can be co-fed into an existing petroleum refinery, the level of deoxygenation of the pyrolysis oils for successful co-processing in refining remains unclear. Baldwin et al. (2009) recommend that the oxygen content must be reduced to less than 7 wt. % before the oil can be considered stabilized and ready to be co-processed in an existing petroleum refinery. The oil is almost completely miscible with petroleum at these oxygen levels. Stabilized oil with higher oxygen content has been shown by De Miguel-Mercader (2010) to have low acidity, good volatility, and good miscibility. This oil can also be hydrocracked without the formation of coke (Hogendoorn and de Miguel Mercader 2010).

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