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Pyrolysis of Lignocellulosic Biomass to Maximize Bio-oil Yield: An Overview

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Abstract

Pyrolysis is a process wherein organic materials are exposed to thermal treatment in the absence of an oxidizing agent, resulting in a solid (char), liquid (tar and bio-oil), and volatile gases (CO, CO_2, CH_4, and H_2). A low temperature, high heating rate, and short gas residence time will favour bio-oil production. Processing conditions can be altered to produce bio-oil at 65-80% of the original feedstock. Bio-oil can be utilized as a primary or secondary fuel source for boilers, heaters, turbines, engines, etc. However, additional research is required to find solutions to the corrosivity and poor storage characteristics of bio-oil. This paper reviews literature pertinent to bio-oil production via pyrolysis. Also, design considerations and conditions for optimization of bio-oil production are investigated.

Keywords. Biomass, bio-oil, lignocellulose, pyrolysis, pyrolytic-oil, tar.

INTRODUCTION

Biomass is any type of organic material that is available on a renewable or reoccurring basis, and includes such things as agricultural crops and waste, wood and wood wastes, animal wastes, aquatic plants, and organic fractions of municipal and industrial waste (BIOCAP and Pollution Probe, 2004). While there are innumerable materials that fall into the category of biomass, the vast majority possess a distinct chemical similarity. Cellulose, hemicellulose, and lignin (collectively known as lignocellulose) are structural polymers located in the cell wall of plants. The cell wall may comprise as much as 95% of the plant material, and consists primarily of polysaccharides (cellulose and hemicellulose), and in the case of woody plants, they also contain lignin (Goldstein, 1981). Cellulose comprises 40-60% dry weight of plant material, while hemicellulose and lignin make up 20-40% and 10-25% dry weight, respectively (United States Department of Energy, 2006). Therefore, the focus of processing biomass for chemicals and energy is usually directed towards extraction and conversion of lignocellulosic material.

Biomass feedstocks are available in two forms; namely, (1) residues or processing by-products, or (2) energy crops grown specifically for bioenergy or chemical production. The United States Department of Energy has proposed a model for processing biomass feedstocks and converting them to useable chemicals or fuels. Processing can either follow a "sugar platform", wherein lignocellulose is hydrolyzed and simple carbohydrates are used in further processing of products such as ethanol and lactic acid. The second route is the "thermochemical platform", where biomass undergoes pyrolysis or gasification to produce gases, liquids, or solids which are utilized for chemical and energy production.

Western Canada has the potential to become a leader in chemical and energy production from biomass feedstocks, mainly due to the abundance and diversity of renewable biological resources. A lignocellulose processing plant has been proposed for Nipawin, Saskatchewan, which plans to convert wood residue into fuel grade ethanol. The plant is projected to produce 75 million liters of biomass ethanol annually, making use of the 1.7 million cubic meters of residue produced annually from Saskatchewan boreal forest, and the 6 million cubic meters of stockpiled residue (Saskatchewan Eco Network, 2006). This project would fall into the "thermochemical platform" of the U.S. D.O.E. model. The feedstock will be gasified to produce syngas, which will then be converted to ethanol through the use of a catalyst.

This paper provides an overview of pyrolysis of lignocellulosic biomass (focusing on soft and hardwoods) and examines the potential alternative products produced during the process (solid, liquid, and gas). The design conditions and process parameters were evaluated in terms of maximizing the liquid (bio-oil) production from biomass pyrolysis.

DEFINITION

Pyrolysis is a process wherein organic materials are exposed to thermal treatment in the absence of an oxidizing agent, resulting in a solid (char), liquid (tar and bio-oil), and volatile gases (CO, CO_2, CH_4, and H_2). Pyrolysis is one step or set of reactions involved in the overall gasification process, however pyrolysis is utilized as a stand alone process depending on the products desired. Combustion, pyrolysis, and gasification are thermochemical processes whereby biomass feedstocks can be upgraded to chemicals and energy. By changing the operating conditions during pyrolysis, it is possible to modify the actual course of reactions and, thus, modify the final

product distribution; in particular, the kinetics of the process is influenced by the values of the main process parameters: temperature, solid residence time, composition of feedstock, particle size, and heating rate (Maschio et al., 1992). Pressure can also influence the reactions occurring during pyrolysis. In reference to wood pyrolysis, carbonation refers to the processes in which char is the principal product of interest; wood distillation is the process in which liquid is of interest; and destructive distillation is used when both char and liquid are targeted (Soltes and Elder, 1981).

The basic phenomena that take place during pyrolysis are: a) heat transfer from a heat source, leading to an increase in temperature inside the fuel; b) initiation of pyrolysis reactions due to this increased temperature, leading to the release of volatiles and the formation of char; c) outflow of volatiles, resulting in heat transfer between the hot volatiles and cooler unpyrolyzed fuel; d) condensation of some of the volatiles in the cooler parts of the fuel to produce tar; and e) autocatalytic secondary pyrolysis reactions due to these interactions (Babu and Chaurasia, 2003a). Therefore, the pyrolysis of biomass can be broken down into two overall processes: i) physical heat transfer, and ii) chemical reactions. It is important to note the secondary reactions which result from the interaction of volatiles and gases with the char, to form secondary products. These secondary volatiles, gases, and char may be undesirable, and their production is affected by gas/volatile retention time in the reaction zone.

In a study examining the pyrolysis characteristics of rice straw, cotton stalk, and pine sawdust, Chen et al. (2003a) noted that the general pyrolysis of biomass can be divided into three phases:

1. Moisture evaporation, corresponding to temperatures < 130°C.

2. Main devolatilization, corresponding to temperatures < 450°C.

3. Continuous slight devolatilization, corresponding to temperatures > 450°C.

The authors also stated that biomass officially starts to pyrolyze at a temperature of 200°C, releasing volatiles. It was noted that the main devolatilization is due to the decomposition of cellulose and hemicellulose, while the continuous slight devolatilization is due to lignin and the remaining cellulose and hemicellulose. The hemicelluloses break down first at temperatures of 197 to 257°C (470 to 530 K), cellulose follows in the temperature range of 237 to 347°C (510 to 620 K), and lignin is the last component to pyrolyze at temperatures of 277 to 497°C (550 to 770 K) (Demirbaş and Gönenç, 2002). Soltes and Elder (1981) summarized the effect of the main process parameters on pyrolysis products:

1. If the purpose is to maximize the yield of liquid products, a low temperature, high heating rate, short gas residence time process would be required.

2. For high char production, a low temperature, low heating rate process would be chosen.

3. If the purpose is to maximize the yield of fuel gas resulting from pyrolysis, a high temperature, low heating rate, long gas residence time process would be preferred.

The heating rate is affected by the particle size of the material to be pyrolyzed.

Depending on the operating conditions, the pyrolysis processes can be divided into three sub-classes: conventional pyrolysis, fast pyrolysis, and flash pyrolysis (Maschio et al., 1992); the operating conditions for each can be found in Table 1.

Table 1. Operating conditions of conventional, fast, and flash pyrolysis (Maschio et al., 1992).

	Conventional pyrolysis	Fast pyrolysis	Flash pyrolysis
Operating temperature (^{o}C)	300-700	600-1000	800-1000
Heating rate (^{o}C/s)	0.1-1	10-200	≥ 1000
Solid residence time (s)	600-6000	0.5-5	< 0.5
Particle size (mm)	5-50	< 1	Dust

PYROLYSIS PROCESS DESIGN

As previously mentioned, to maximize the yield of the liquid products, a low temperature, high heating rate, short gas residence time process would be required. Therefore, liquid production would be favored with fast and flash pyrolysis processes at moderate temperatures. Bridgewater and Peacocke (2000) provided an overview of the fast pyrolysis process for producing bio-oil from biomass. Fast pyrolysis design considerations provided in the study are listed in Table 2.

Table 2. Key fast pyrolysis design features (Bridgwater and Peacocke, 2000).

Pretreatment	
Feed drying	Essential to ~10%
Particle size	Small particles needed; costly
Washing and additives	For chemicals production
Reactor	
Reactor configuration	Many configurations, but no best design
Heat supply	High heat transfer rate needed
Heat transfer	Gas-solid and/or solid-solid
Heating rates	Wood conductivity limits heating rate
Reaction temperature	500°C maximizes liquids from wood
Product conditioning and collection	
Vapour residence time	Critical for chemicals, less for fuels
Secondary cracking	Reduces yields
Char separation	Difficult from vapour or liquid
Ash separation	More difficult than char separation
Liquids collection	Difficult. Quench and EP seem best

Pretreatment

Transportation and storage of biomass feedstocks pose some feasibility problems with respect to using biomass in processes such as pyrolysis. The solution is then to densify the material in the form of pellets, briquettes, or wafers (to name a few) in order to improve the materials' handling characteristics. Prior to densification, the material is typically conditioned to a moisture content around 10% for optimal compression (depending on the feedstock). This corresponds with the biomass moisture content required by pyrolysis, as reported by Table 2 by Bridgwater and Peacocke (2000). Depending on the pyrolysis reactor, the material may have to be milled, as the densified (or raw) product may be too large for efficient pyrolysis in the reactor. This is due to the fact that the particle sizes of the densified (or raw) material are generally much larger than that recommended for fast pyrolysis, and will therefore reduce the feedstock heating rate significantly. The raw biomass is sometimes rinsed (i.e. with water) to remove alkali that can cause corrosion of equipment in contact with bio-oil, even at very low concentrations (Sandvig et al., 2004).

Reactor

The goal of most fast pyrolysis systems is to inject heat into the biomass particle quickly and collect the condensables from the exiting stream quickly and efficiently to maximize liquid yield (Sandvig et al., 2004). The process conditions and desired final product will dictate the selection of an appropriate reaction vessel. The most common pyrolysis systems employ the following types of reactor: rotary kiln, moving-bed with concurrent or countercurrent flow (in conventional pyrolysis), entrained bed, fluidized bed, circulating fluid bed, transporting bed, vacuum moving bed, multiple hearth, or fixed-bed tubular reactor (Bridgwater and Peacocke, 2000; Demirbaş and Gönenç, 2002). Other reactor types include rotating cone and vortex. Fluid beds and circulating fluid beds are the most popular reactor configurations due to ease of operation and ready scale-up (Bridgwater and Peacocke, 2000). However, if the biomass feedstock of interest has a particle size >1 mm, then these reactor configurations may be unable to produce the solid heating rate necessary for fast pyrolysis; resulting in a less than optimum bio-oil yield. To overcome this problem, a relatively new type of reactor known as an ablative reactor, has been developed. Larger particles (i.e. wood chips) are pressed to the heated surface of the reactor. On the hot surface of the wood a liquid film arises which is removed by friction, allowing possible pyrolysis of new layers. The pyrolysis of the thin liquid layer left on the heated surface is then easily completed (Meier and Faix, 1999). The reaction is initially transient, but quickly becomes steady state. This process appears to allow fast pyrolysis of larger particles.

An advantage of the ablative reactor is that it generally does not require an inert gas to flush the oxygen from the reaction site. The pyrolysis reaction takes place between the particle and the reactor wall. However, pressure must be applied to the biomass, forcing it against the reactor wall. Therefore, the rate of pyrolysis is dictated by the heat supplied to the reactor wall, rather than conduction through the biomass particles.

Ablative pyrolysis differs from and has the following advantages over most other pyrolysis processes (Centre Relais Innovation, 2006):

1. The mode of heat transfer is radically different in that the heat is transferred through a reacting liquid film rather than through a gas phase. This gives much more intensive reactors with higher specific throughputs and potentially lower costs.

2. Inert or recycle gas is not required as in most other reactors, which leads to lower volume systems and hence, lower costs.

3. Much larger particles of wood (biomass) can be used such as whole tree chips rather than finer particles required in all other processes in order to achieve high heating rates.

4. The mode of heat transfer leads to a higher-quality product.

Both contact and radiant ablative pyrolysis processes are available. Lédé (2003) noted that contact ablative pyrolysis can be carried out with a hot moving or fixed disk, or a hot rotating cylinder. A study by Helleur and co-workers (2001) briefly describes an ablative reactor that was utilized to pyrolyze used tires. The reactor is a long coiled stainless steel tube that is able to provide very high heat and mass transfer ratios.

Bridgwater (1999) provided a schematic (Figure 1) of a typical fast pyrolysis process. Although the diagram is intended to depict a fluid bed reactor, the general process has commonalities with most other pyrolysis reactors.
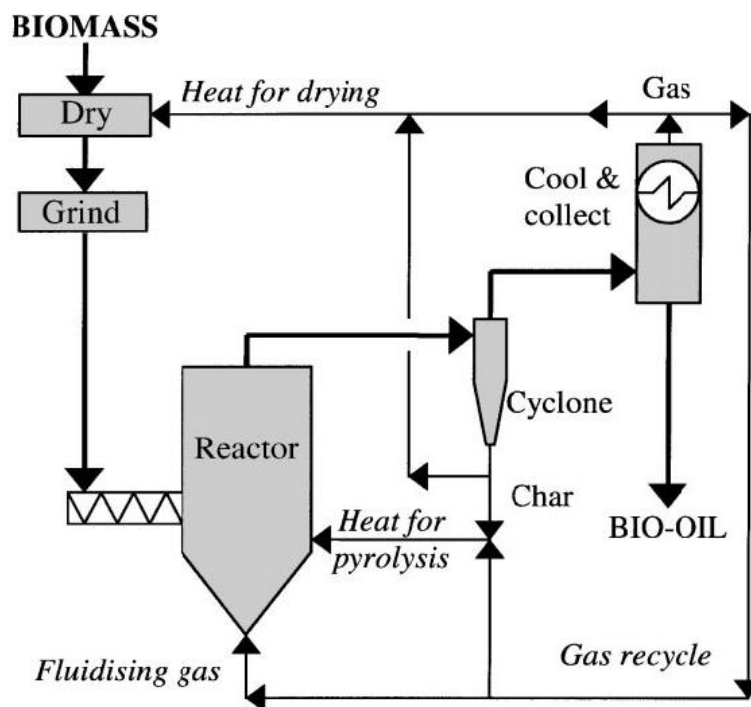

Figure 1. Schematic of a fluid bed fast pyrolysis process (Bridgwater, 1999).

Product Conditioning and Collection

The pyrolysis process produces char and vapours. Condensing the vapours will yield the liquid product, and the non-condensable vapours are the pyrolytic gases. Therefore, methods of collecting and handling the pyrolysis products are required. Bridgwater (1999) reviewed the collection and handling of the pyrolysis vapours. It was explained that the vapours are not true vapours, but are described as a combination of true vapours, micron-sized droplets, and polar molecules bonded with water vapour molecules. Therefore, pyrolytic vapours must strike a

surface to be collected, even when cooled past the dew point temperature. Bridgwater (1999) stated that as of seven years prior to his study there was no optimal collection method; and that collection requirements may be different between feedstocks and reactor configurations. Common collection methods include electrostatic precipitators, quenching/contact with a cooled liquid (larger scale), shell-in-tube condensers, and fiber filters (Bridgwater, 1999; Sandvig et al., 2004).

Soltes and Elder (1981) noted that char yield from softwood pyrolysis is generally higher (than hardwoods), and the yields of acetic acid and methanol (produced after further processing) are higher for softwoods as well. It was explained that condensing pyrolysis vapours produced a tar and an aqueous layer called pyroligneous acid. By processing the pyroligneous acid, one can produce methanol and acetic acid if chemical production is of interest.

In literature, it has been reported that a 65-80% liquid yield is expected with fast pyrolysis. However, this may be an overestimate because some water still remains in the liquid portion of the final product (D. Soveran, Manager, Energy Branch, Production and Process Engineering Section, Saskatchewan Research Council). Upgrading pyrolytic bio-oils is required before they can be considered acceptable as a regular fuel; and mainly consists of oxygen removal, as oxygen is the major constituent contributing to the poor storage and usage characteristics of bio-oil (Vitolo et al., 1999). Vitolo et al. (1999) explains that there are two proposed methods for oxygen removal from bio-oils:

1. Catalytic hydrotreating with hydrogen or hydrogen and carbon monoxide under pressure and/or in the presence of hydrogen donor solvents.

2. Cracking catalysts (zeolites, silica-alumina, and molecular sieves) at atmospheric pressure.

Literature is available pertaining to the upgrading of pyrolytic bio-oil (Adam et al., 2005; Vitolo et al., 1999; Vitolo et al., 2001), however, this topic is beyond the scope of this review.

PRODUCT UTILIZATION AND COMPOSITION

All three by-products (solid, liquid, and gas) of biomass pyrolysis find utilization in various applications. The charcoal can be used as solid fuel, as a raw material in the metallurgical industry (i.e. iron ore smelting), and also as a substitute for activated carbon (Maschio et al., 1992).

Gases resulting from pyrolysis can be collected and used as supplemental fuel for heating the pyrolysis reactor. Numerous other applications are available for gas resulting from biomass pyrolysis. For example, Chen et al. (2003b) determined that the hydrogen concentration of pyrolytic gas can be enhanced by the addition of catalysts. The hydrogen gas can then be used as clean fuel for heat generation and transportation. Pyrolysis gas, compared with conventional gasification gas, is more advantageous, as it is higher in heating value and, consequently, can be applied well to the downstream gas turbine or other combustion engines for power generation or used as a substitute for civil gas for cooking (Chen et al., 2003c).

As opposed to gasification, in which all structural identity is lost in the formation of simple molecules, pyrolysis offers high yields of liquid products that retain some of the integrity of the monomeric units present in the original polymers (Soltes and Elder, 1981). Ganesh and Banerjee (2001) stated that a potential use of biomass pyrolysis is to target the liquid fuels, mainly

pyrolytic oils, for use in gas turbines. Chemical extraction and flavouring for the food industry are also potential markets and uses for pyrolytic bio-oil (Sandvig et al., 2004). In Table 3, Bridgewater and co-workers (2002) provide a comparison between pyrolysis liquid, diesel, and heavy fuel oil. The authors also provided a flowchart highlighting the various applications of pyrolysis liquid (Figure 2). It is important to note that the properties of bio-oil can vary greatly depending on the process conditions and initial biomass feedstock. Sandvig and co-workers (2004) report that pyrolytic oil is a mixture of oxygenated hydrocarbons and water; specifically, bio-oil is made up of the following constituents: 20-25% water, 25-30% water-insoluble pyrolytic lignin, 5-12% organic acids, 5-10% non-polar hydrocarbons, 5-10% anhydrosugars, and 10-25% other oxygenated compounds.

Table 3. Comparison between pyrolysis liquid, diesel, and heavy fuel oil (Bridgwater et al., 2002).

	Pyrolysis liquid	Diesel	Heavy fuel oil
Density (kg/m^3 @ 15°C)	1220	854	963
Typical composition			
%C	48.5	86.3	86.1
%H	6.4	12.8	11.8
%O	42.5	-	-
%S	-	0.9	2.1
Viscosity (cSt at 50°C)	13	2.5	351
Flash point ($^{\circ}$C)	66	70	100
Pour point ($^{\circ}$C)	-27	-20	21
Ash (%wt)	0.13	<0.01	0.03
Sulphur (%wt)	0	0.15	2.5
Water (%wt)	20.5	0.1	0.1
LHV (MJ/kg)	17.5	42.9	40.7
Acidity (pH)	3	-	-

Characterization of pyrolysis bio-oils is difficult due to their complex chemical composition. In terms of quality control, Adam and co-workers (2005) used the aldehyde and organic acid yields to evaluate the quality of the pyrolysis bio-oil resulting from their study. They explained that the presence of aldehydes resulted in reactions causing instability. Organic acids will lower the pH of the bio-oil, increasing the corrosivity.

Pyrolysis liquid is characterized by poor long-term stability which is occurs by an increase in viscosity and molecular weight of the oils (Meier and Faix, 1999). Czernik and Bridgwater (2004) reviewed the state of the art in the area of combustion of bio-oil in boilers, diesel engines, gas turbines, Stirling engines, and upgrading to potential transport fuel. The authors noted that the

properties of bio-oil pose some problems with respect to its use as fuel, which include: poor volatility, difficult ignition (resulting from low heating value and high water content), high viscosity, coking (thermally unstable compounds), and corrosiveness (acids). Therefore, additional research is required to overcome the negative properties of this fuel. Bio-oil is a dark brown liquid that is free flowing, has a pungent smoky odour, and a density of approximately 1200 kg/m^3 (Sandvig et al., 2004).
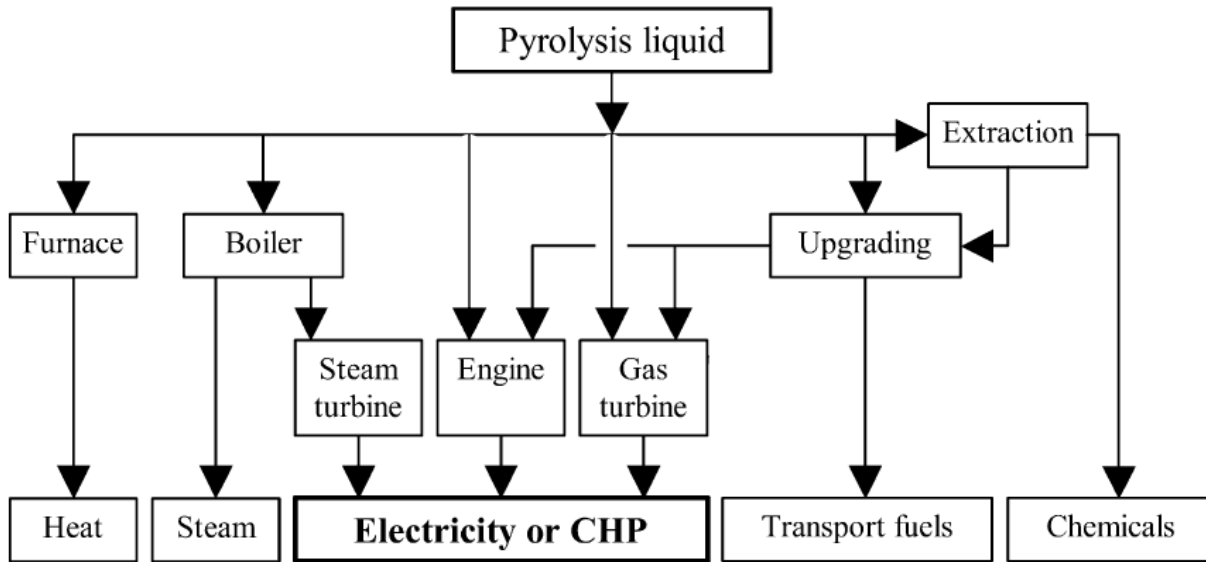

Figure 2. Potential applications of pyrolysis liquid (Bridgwater et al., 2002).

There appears to be some variability in the literature in terms of the terminology pertaining to the pyrolytic liquid. Commonly, tar, pyrolysis liquid, and oil or bio-oil are used to describe all or a portion of the pyrolytic liquid, however, all of these terms apply to a condensable portion of the vapours generated via biomass pyrolysis. Oasmaa et al. (2003) described that forestry residue pyrolysis liquid separates immediately after condensation to a polar, liquid bottom phase (80-90 wt %) and a hydrophobic viscous top phase (10-20 wt %). The following terminology was used:

Pyrolysis Liquid. Liquid product obtained from fast heating of biomass in the absence of air. Synonyms are pyrolysis oil and bio-oil.

Forestry Residue Liquid. The bottom phase, which comprises majority (80-90 wt %) of the product liquid.

Top Phase of Forestry Residue Liquid. The top phase of forestry residue liquid is the extractive rich fraction of product (10-20 wt %) that separates out of the product liquid during condensation.

Water Insolubles. The water insoluble fraction of pyrolysis liquid is composed of degraded lignin, extractives, and solids (char).

PROCESS KINETICS AND MODELING

Although detailed mathematical modeling of pyrolysis reactions and kinetics is beyond the scope of this paper, models exist which pattern the reaction kinetics (Várhegyi et al., 1997; Babu and Chaurasia, 2003a; Gómez et al., 2004; Radmanesh et al., 2006), heat transfer (Liliedahl and Sjöström, 1998), heat transfer and reaction kinetics (Babu and Chaurasia, 2003b), and simultaneous heat, mass, and momentum transfer along with chemical kinetics (Babu and Chaurasia, 2004). Modeling of the pyrolysis process is very complex due to the simultaneous heat and mass transfer, along with the associated chemical kinetics of the heterogeneous primary and secondary reactions.

ECONOMICS

Brammer and co-workers (2006) investigated the opportunities for pyrolytic bio-oil in the European heat and power markets. A major finding was that the implementation of bio-oil heat and power generation systems will depend on a number of factors including: application, scale, and location as it applies to economic and logistical factors. Therefore, the cost to produce biomass has the potential to vary greatly depending on the geographic area. In determining bio-oil production costs (Table 4), Brammer and co-authors assumed that all production parameters were constant except for the following: biomass annual availability, biomass cost (transport and handling included), biomass lower heating value, biomass initial moisture, real interest rate for capital, cost of electricity, and labour rate.

The study by Brammer and co-workers (2006) found that in six of the countries, using bio-oil is economically competitive with conventional fuels in at least one application (heat, combined heat and power (CHP), and electricity). In the rest of the countries, none of the applications utilizing bio-oil were competitive with the current conventional fuels.

Table 4. Bio-oil production costs for selected European countries as of August 2002 (Brammer et al., 2006).

Country	Feedstock	Bio-oil Cost ($/MWh)
Austria		
	Wood (sawmill residues)	44
Belgium		
	Wood (industry by-product)	45
Denmark		
	Wood (hardwood forestry residues)	56
	Wood (industry by-product)	48
	Wood (softwood forestry residues)	52
Finland		
	Wood (forestry residues)	37
France		
	Wood (forestry residues)	44
Germany		
	Wood (industry by-product)	102

Greece		
	Wood (forestry residues)	44
	Cereal straw	51
	Cotton stalks	42
	Olive tree prunings	40
Ireland		
	Wood (forestry residues)	51
	Wood (sawmill residues)	52
	Wood (tree cuttings)	52
Italy		
	Wood (industry by-product)	21
Netherlands		
	Wood (industry by-product)	34
	Dried grass	38
Norway		
	Wood (forestry residues)	55
	Wood (industry by-product)	58
Portugal		
	Wood (forestry residues)	40
Spain		
	Wood (fruit tree prunings)	42
	Orujillo	23
	Thistle	59
UK		
	Wood (forestry residues)	45

CONCLUSIONS

Following an overview of pyrolysis of biomass for the purpose of bio-oil production, the following conclusions were drawn:

1. It is evident that precise prediction of the composition and abundance of end-products from the pyrolysis of wood residue (or any other biomass feedstock) is nearly unattainable.

2. The kinetics of the pyrolysis process are influenced by the process parameters such as temperature, solid residence time, composition of feedstock, particle size, heating rate, and pressure. It would also be wise to add reactor configuration (design) to this list as well.

3. A low temperature (500°C), high heating rate, short gas residence time process is required to maximize liquid (bio-oil) yield from biomass pyrolysis.

4. An ablative reactor design is able to produce the high heating rates required for large particles

5. Additional research is required to improve the storage, handling, and usage of bio-oil, as its corrosiveness and increasing viscosity pose some problems.

6. The cost to produce bio-oil varies between geographic regions due to factors such as biomass annual availability, biomass cost, biomass lower heating value, biomass initial moisture, real

interest rate for capital, cost of electricity, and labour rate (to name a few). Therefore, the cost to produce bio-oil may not be competitive with conventional fuels.

7. Technology for bio-oil production via pyrolysis is acceptable for commercial application. However, detailed knowledge of the biomass feedstock and desired product is required in order for an efficient design to be achieved.

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