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Biorefinery Processes for Biomass Conversion to Liquid Fuel

Shuangning Xiu, Bo Zhang and Abolghasem Shahbazi
*Biological Engineering Program
School of Agriculture, NC A&T State University
U.S.A*

1. Introduction

The development of products derived from biomass is emerging as an important force component for economic development in the world. Rising oil prices and uncertainty over the security of existing fossil reserves, combined with concerns over global climate change, have created the need for new transportation fuels and for the manufacture of bioproducts to substitute for fossil-based materials.

The United States currently consumes more than 140 billion gallons of transportation fuels annually. Conversion of cellulosic biomass to biofuels offers major economic, environmental, and strategic benefits. DOE and USDA predict that the U.S. biomass resources could provide approximately 1.3 billion dry tons of feedstock for biofuels, which would meet about 40% of the annual U.S. fuel demand for transportation (Perlack et al., 2005). More recently, in January 2010, U.S. President Barack Obama delivered a request during his State of the Union speech for Congress to continue to invest in biofuels and renewable energy technology. Against this backdrop, biofuels have emerged as one of the most strategically important sustainable fuels given their potential to increase the security of supply, reduce vehicle emissions and provide a steady income for farmers.

Several biorefinery processes have been developed to produce biofuels and chemicals from the initial biomass feedstock. Of all the various forms energy can take, liquid fuels are among the most convenient in terms of storage and transportation and are conducive to the existing fuel distribution infrastructure. This chapter comprehensively reviews the state of the art, the use and drawbacks of biorefinery processes that are used to produce liquid fuels, specifically bioethanol and bio-oil. It also points out challenges to success with biofuels in the future.

2. Biorefinery concept

2.1 Biorefinery definition

A biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power, heat, and value-added chemicals from biomass. The biorefinery concept is analogous to today's petroleum refinery, which produces multiple fuels and products from petroleum (Smith & Consultancy, 2007).

The IEA Bioenergy Task 42 on Biorefineries has defined biorefining as the "sustainable processing of biomass into a spectrum of bio-based products (food, feed, chemicals,

materials) and bioenergy (biofuels, power and/or heat)." The biorefinery is not a single or fixed technology. It is collection of processes that utilize renewable biological or bio-based sources, or feedstocks, to produce an end product, or products, in a manner that is a zero-waste producing, and whereby each component from the process is converted or utilized in a manner to add value, and hence sustainability to the plant. Several different routes from feedstocks to products are being developed and demonstrated, and it is likely that multiple biorefinery designs will emerge in the future.

By producing multiple products, a biorefinery takes advantage of the various components in biomass and their intermediates, thereby maximizing the value derived from the biomass feedstock. A biorefinery could, for example, produce one or several low-volume, but high-value chemical or nutraceutical products and a low-value, but high-volume liquid transportation fuel such as biodiesel or bioethanol (see also alcohol fuel), while also generating electricity and process heat through combined heat and power (CHP) technology for its own use, and perhaps enough for sale of electricity to the local utility. In this scenario, the high-value products increase profitability, the high-volume fuel helps meet energy needs, and the power production helps to lower energy costs and reduce greenhouse gas emissions, as compared to traditional power plant facilities. Although some facilities exist that can be called biorefineries, the technology is not commonplace. Future biorefineries may play a major role in producing chemicals and materials that are traditionally produced from petroleum.

2.1 Two biorefinery platforms

Biomass can be converted to a wide range of useful forms of energy through several processes. As shown in Figure 1, there are two primary biorefinery platforms: sugar and thermochemical. Both platforms can produce chemicals and fuels including methanol, ethanol and polymers. The "sugar platform" is based on the breakdown of biomass into aqueous sugars using chemical and biological means. The fermentable sugars can be further processed to ethanol, aromatic hydrocarbons or liquid alkanes by fermentation, dehydration and aqueous-phase processing, respectively. The residues - mainly lignin - can be used for power generation (co-firing) or may be upgraded to produce other products (e.g., etherified gasoline). In the thermochemical platform, biomass is converted into synthesis gas through gasification, or into bio-oils through pyrolysis and hydrothermal conversion (HTC). Bio-oils can be further upgraded to liquid fuels such as methanol, gasoline and diesel fuel, and other chemicals.

3. Bioethanol production from lignocellulosic biomass

Ethanol is considered the next generation transportation fuel with the most potential, and significant quantities of ethanol are currently being produced from corn and sugar cane via a fermentation process. Utilizing lignocellulosic biomass as a feedstock is seen as the next step towards significantly expanding ethanol production capacity. However, technological barriers - including pretreatment, enzyme hydrolysis, saccharification of the cellulose and hemicellulose matrixes, and simultaneous fermentation of hexoses and pentoses - need to be addressed to efficiently convert lignocellulosic biomass into bioethanol. In addition to substantial technical challenges that still need to be overcome before lignocellulose-to-ethanol becomes commercially viable, any ethanol produced by fermentation has the inherent drawback of needing to be distilled from a mixture which contains 82% to 94% water. This section will review current developments towards resolving these technological challenges.

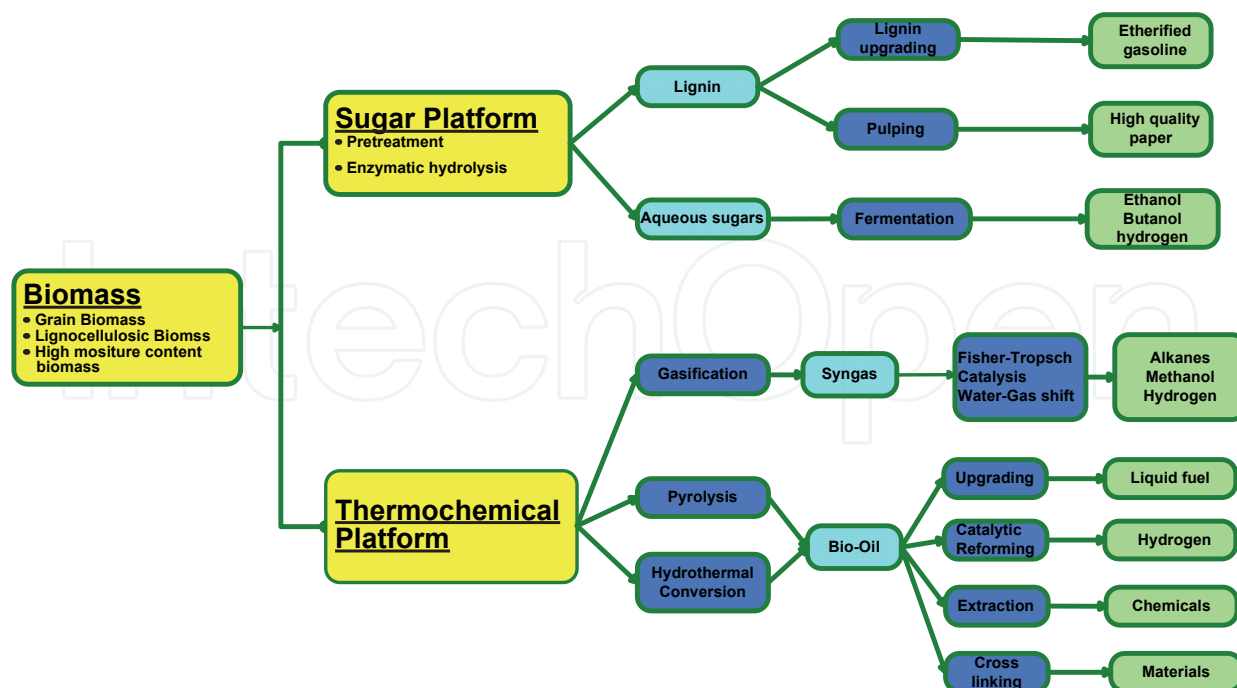


Fig. 1. Primary routes for biofuels conversion

3.1 Pretreatment

Pretreatment is required to break the crystalline structure of cellulosic biomass to make it more accessible to the enzymes, which can then attach to the cellulose and hydrolyze the carbohydrate polymers into fermentable sugars. The goal of pretreatment is to pre-extract hemicellulose, disrupt the lignin seal and liberate the cellulose from the plant cell wall matrix. Pretreatment is considered to be one of the most expensive processing steps in cellulosic ethanol processes, but it also has great potential to be improved and costs lowered through research and development (Lynd et al., 1996; Lee et al., 1994; Mosier et al., 2005).

Many pretreatment technologies have been developed and evaluated for various biomass materials. However, each pretreatment method has its own advantages and disadvantages, and one pretreatment approach does not fit all biomass feedstocks. Three widely used pretreatment technologies will be reviewed below.

3.1.1 Alkaline pretreatment

Removing lignin with alkaline chemicals such as dilute sodium hydroxide, aqueous ammonia and lime, has long been known to improve cellulose digestibility (Li et al., 2004). Among these alkaline reagents, sodium hydroxide (NaOH) has been widely used for pretreatment because its alkalinity is much higher than others, but it is also expensive, and the recovery process is complex. The following studies on various feedstocks illustrate this:

Untreated cattails contain 32.0% cellulose, 18.9% hemicellulose and 20.7% lignin. Zhang et al. (2010a) reported that 54.8% of cattail lignin and 43.7% of the hemicellulose were removed with a 4% NaOH solution. The glucose yield from 4% NaOH treated cattails was approximately 80% of the cellulose available.

Adding additional chemicals along with NaOH could improve pretreatment performance. Applying a NaOH and H₂O₂ solution helps in additional lignin removal through oxidative

action on lignin. Maximum overall sugar yield obtained from high lignin hybrid poplar was 80% with 5%NaOH / 5% H₂O₂ at 80°C (Gupta, 2008). Zhao et al. (2008) discovered that a NaOH-urea pretreatment, can slightly remove lignin, hemicelluloses, and cellulose in the lignocellulosic materials, disrupt the connections between hemicelluloses, cellulose, and lignin, and alter the structure of treated biomass to make cellulose more accessible to hydrolysis enzymes. The enzymatic hydrolysis efficiency of spruce also can be remarkably enhanced by a NaOH or NaOH/urea solution treatment. A glucose yield of up to 70% could be obtained at the cold temperature pretreatment of (-15°C) using 7% NaOH/12% urea solution, but only 20% and 24% glucose yields were obtained at temperatures of 238°C and 608°C, respectively.

Two theoretical approaches were used to study the enzyme kinetics of sodium hydroxide pretreated wheat straw, and describe the influence of enzyme concentrations of 6.25–75 g/L on the production of reducing sugars. The first approach used a modified Michaelis–Menten equation to determine the hydrolysis model and kinetic parameters (maximal velocity, V_{max} , and half-saturation constant, K_e). The second, the Chrastil approach, was applied to study all the time values from the rate of product formation, taking into account that in a heterogeneous system, these reactions are diffusion limited and the time curves depend strongly on the heterogeneous rate-limiting structures of the enzyme system.

3.1.2 Hot-water pretreatment

Hot water pretreatment is often called autohydrolysis. The major advantages of this method are less expense, lower corrosion to equipment and less xylose degradation and hence fewer byproducts with inhibitory compounds in the extracts (Huang et al. 2008). Hot water under pressure can penetrate the cell structure of biomass, hydrate cellulose, and remove hemicellulose.

Hot water pretreatment could effectively improve the enzymatic digestibility of biomass cellulose. At optimal conditions, 90% of the cellulose from corn stover pretreated in hot-water can be hydrolyzed to glucose (Mosier et al., 2003). When cattails were pretreated at 463K for 15 min, 100% of the hemicellulose was removed and 21.5% of the cellulose was dissolved in the water phase. The process could be further optimized to improve its efficiency (Zhang et al. 2010b).

The pretreatment process of bagasse was studied over a temperature range of 170-203°C, and a time range of 1-46 min. A yield of 80% conversion was achieved, and hydrolysis inhibitors were detected (Laser et al., 2002). Hot water pretreatment also was reported to improve enzymatic digestibility of switchgrass, resulting in 80% glucose yield (Kim et al., 2008). The optimal hot-water pretreatment conditions for hybrid poplar of 15% solids (wt/vol) were 200°C at 10 min, which resulted in the highest fermentable sugar yield of between 54% and 67% (Kim et al., 2008).

3.1.3 Dilute-acid pretreatment

The use of acid hydrolysis for the conversion of cellulose to glucose is a process that has been studied for the last 100 years. Dilute acid (0.5-1.0% sulfuric acid) pretreatment at moderate temperatures (140-190°C) can effectively remove and recover most of the hemicellulose as dissolved sugars. Furthermore lignin is disrupted and partially dissolved, increasing cellulose susceptibility to enzymes (Yang and Wyman, 2004). Under this method, glucose yields from cellulose increase with hemicellulose removal to almost 100% (Knappert

et al., 1981). Dilute acid hydrolysis consists of two chemical reactions. One reaction converts cellulosic materials to sugar and the other converts sugars into other chemicals, many of which inhibit the growth of downstream fermentation microbes. The same conditions that cause the first reaction to occur simultaneously cause over-degradation of sugars and lignin, creating inhibitory compounds such as organic acids, furans, and phenols.

Partial cellulose may be degraded as oligomers or monomers during the acid pretreatment process. Sugar (glucose and xylose) yields were often reported for the pretreatment and enzyme hydrolysis stage separately, and as the total for both stages. Lloyd and Wyman (2005) reported that up to 92% of the total sugars originally available in corn stover could be recovered via coupled dilute acid pretreatment and enzymatic hydrolysis. Conditions achieving maximum individual sugar yields were often not the same as those that maximized the total sugar yields, demonstrating the importance of clearly defining pretreatment goals when optimizing the process.

Dilute-sulfuric acid pretreatment of cattails was studied using a Dionex accelerated solvent extractor (ASE) at varying acid concentrations of 0.1 to 1%, treatment temperatures of 140 to 180 °C, and residence times of 5 to 10 min. The yield of extractable products obtained from the pretreatment process increased as the final temperature, treatment time, or acid concentration increased. The highest glucose yield from the pretreatment was 55.4% of the cellulose at 180°C for 15 min with 1% sulfuric acid. The highest glucose yield from the enzyme hydrolysis stage (82.2% of the cellulose) and the highest total glucose yield for both the pretreatment and enzyme hydrolysis stages (97.1% of the cellulose) were reached at a temperature of 180°C, a sulfuric acid concentration of 0.5%, and a time of 5 min.

When switchgrass was pretreated for 60 min with 1.5% acid, the highest glucan conversion yield of 91.8% was obtained (Yang et al. 2009).

3.2 Enzyme hydrolysis

After pretreatment, hydrolysis converts the carbohydrate polymers into monomeric sugars. Although a variety of process configurations have been studied for conversion of cellulosic biomass into ethanol, enzymatic hydrolysis of cellulose provides opportunities to improve the technology so that biomass ethanol is competitive with other liquid fuels (Wyman, 1999). Novozymes (www.novozymes.com) and Genencor (www.genencor.com) are two companies leading research & development for advanced cellulosic ethanol enzymes. In early 2010, Novozymes said its new Cellic® CTec2 enzymes enable the biofuel industry to produce cellulosic ethanol at a price below US\$ 2.00 per gallon for the initial commercial-scale plants that are scheduled to be in operation in 2011. This cost is on par with gasoline and conventional ethanol at current US market prices. According to Novozymes, the new enzyme can be used on different types of feedstock including corn cobs and stalks, wheat straw, sugarcane bagasse, and woodchips. The enzyme is designed to break down cellulose in biomass into sugars that can be fermented into ethanol. Genencor, a division of Danisco also introduced its enzyme Accellerase®, which is designed to do the same thing.

The selection of the enzymes needs to match the pretreatment technologies and the feedstock used, as well as the process. For example, if a dilute acid pretreatment is used, most of the hemicellulose is degraded, so hemicellulases is unnecessary. However, if an alkaline or hot-water pretreatment is used, the hemicellulose still needs to be hydrolyzed and hemicellulases will be needed.

The cellulose portion of the biomass is another difficulty. In order to efficiently break it down, a mixture of several enzymes with different activities is required. This mixture includes three basic types of enzymes.

1. Endoglucanases break bonds between adjacent sugar molecules in a cellulose chain, fragmenting the chain into shorter lengths. Endoglucanases act randomly along the cellulose chain, although they prefer amorphous regions where the chains are less crystalline.
2. Cellobiohydrolases attack cellulose chains from the ends of the chain. This exo- or processive action releases mainly cellobiose (glucose dimer). Because endoglucanases create new ends for cellobiohydrolases to act upon, the two classes of enzymes interact synergistically.
3. β -glucosidases break down short glucose chains, such as cellobiose, to release glucose. β -glucosidases are important as they act on cellobiose, which inhibits the action of the other cellulases as it builds up the hydrolysis reactor.

3.3 Fermentation for bioethanol production

Saccharomyces cerevisiae (baker's yeast) has been used for industrial ethanol production from hexoses (C6 sugars) for a thousand years. However, a significant amount of pentoses (C5 sugars) derived from the hemicellulose portion of the lignocellulosic biomass is present in the hydrolysate from the pretreatment process. Modern biotechnologies enable fermenting microorganisms to use both C5 and C6 sugars available from the hydrolysate. This further increases the economic competitiveness of ethanol production and other bio-products from cellulosic biomass.

Recently, microorganisms for cellulosic ethanol production, such as *Saccharomyces cerevisiae*, *Zymomonas mobilis* and *Escherichia coli*, have been genetically engineered using metabolic engineering approaches. Lau et al. (2010) compared the fermentation performance of *Escherichia coli* KO11, *Saccharomyces cerevisiae* 424A(LNH-ST) and *Zymomonas mobilis* AX101 for cellulosic ethanol production. Three microorganisms resulted in a metabolic yield, final concentration and rate greater than 0.42 g/g consumed sugars, 40 g/L and 0.7 g/L/h (0-48 h), respectively. They concluded that *Saccharomyces cerevisiae* 424A(LNH-ST) is the most promising strain for industrial production because of its ability to ferment both glucose and xylose.

Vasan et al (2011) introduced an *Enterobacter cloacae* cellulase gene into *Zymomonas mobilis* strain and 0.134 filter paper activity unit (FPU)/ml units of cellulase activity was observed with the recombinant bacterium. When using carboxymethyl cellulose and 4% NaOH pretreated bagasse as substrates, the recombinant strain produced 5.5% and 4% (V/V) ethanol respectively, which was three times higher than the amount obtained with the original *E. cloacae* isolate.

In 2010, Purdue University scientists improved a strain of yeast that can produce more biofuel from cellulosic plant material by fermenting all five types of the plant's sugars: galactose, manose, glucose, xylose and arabinose. Arabinose makes up about 10 percent of the sugars contained in cellulosic biomass (Casey et al., 2010).

3.4 Closing remarks

Ethanol provides the first model for biofuel commercialization. However, in order to make the cellulosic ethanol process economically viable, both government subsidies and scientific

R&D are still required. And it is generally accepted that ethanol alone is not going to provide a long-term solution to meet society's energy needs (Hill et al., 2006). It suffers from a somewhat low energy density, inability to be transported through pipelines and fairly high cost for extraction from fermentation broths. This is opening the door to developing many other molecules as replacements for ethanol and thus, discovering new fuel molecules to be produced via microbial biotechnology.

4. Bio-oil production from lignocellulosic biomass and high moisture content biomass

Bioethanol is only one of the products that may be extracted from lignocellulosic feedstocks. Other forms of energy and a full range of value-added bioproducts may be produced from biomass by thermochemical means. Thermochemical conversion processes include pyrolysis, hydrothermal conversion and gasification. The major product of pyrolysis and hydrothermal conversion, known as "bio-oil" or "biocrude", can be used as a boiler fuel or as fuel in combustion engines. Alternatively, the bio-oil can serve as a raw material for the production of chemicals and biomaterials. One of the major technical obstacles to large scale thermochemical conversion of biomass into bio-oil is its poor oil quality and low biofuel production rate. This section intensively reviewed current technologies used to produce bio-oil and technologies development towards improving the bio-oil yield and quality.

4.1 Current processes for conversion of biomass to bio-oils

Two main types of processes for production of bio-oils from biomass are flash pyrolysis and hydrothermal conversion, as shown in Fig.1. Both of the processes belong to the thermochemical platform in which feedstock organic compounds are converted into liquid products. An advantage of the thermochemical process is that it is relatively simple, usually requiring only one reactor, thus having a low capital cost. However, this process is non-selective, producing a wide range of products including a large amount of char (Huber & Dumesic, 2006).

The characteristic and technique feasibility of the two thermochemical processes for bio-oil production are compared in table 1. Flash pyrolysis is characterized by a short gas residence time (~1s), atmospheric pressure, a relatively high temperature (450-500 °C). Furthermore, feedstock drying is necessary. Hydrothermal processing (also referred to in the literature as liquefaction, hydrothermal pyrolysis, depolymerisation, solvolysis and direct liquefaction), is usually performed at lower temperatures (300-400 °C), longer residence times (0.2-1.0 hr.), and relatively high operating pressure (5-20 Mpa). Contrary to flash pyrolysis and gasification processes, drying the feedstock is not needed in the hydrothermal process, which makes it especially suitable for naturally wet biomass. However, a reducing gas and/or a catalyst is often included in the process in order to increase the oil yield and quality.

The reaction mechanisms of the two processes are different, which have been studied by many investigators (Demirbaş, 2000a; Minowa et al., 1998). The hydrothermal process occurred in aqueous medium which involves complex sequences of reactions including solvolysis, dehydration, decarboxylation, and hydrogenation of functional groups, etc. (Chornet and Overend, 1985). The decomposition of cellulose was studied by Minowa et al. (1998). The effects of adding a sodium carbonate catalyst, a reduced nickel catalyst, and no

catalyst addition in the decomposition of cellulose in hot-compressed water were investigated. They found that hydrolysis can play an important role in forming glucose/oligomer, which can quickly decompose into non-glucose aqueous products, oil, char and gases (Fig. 2). Without a catalyst, char and gases were produced through oil as intermediates. However, in the presence of an alkali catalyst, char production was inhibited because the oil intermediates were stabilized, resulting in oil production. Reduced nickel was found to catalyze the steam reforming reaction of aqueous products as intermediates and the methanation reaction. Typical yields of liquid products for hydrothermal conversion processes were in the range of 20-60%, depending on many factors including substrate type, temperature, pressure, residence time, type of solvents, and catalysts employed (Xu and Etcheverry, 2008).

Methods	Treatment condition/ requirement	Reaction mechanism /process description	Technique Feasibility	
			Pros.	Cons.
Flash/Fast Pyrolysis	Relatively high temperature (450-500 °C); a short residence time (~1s); atmosphere pressure; drying necessary	The light small molecules are converted to oily products through homogeneous reactions in the gas phase	High oil yield up to 80% on dry feed; lower capital cost; Commercialized already	Poor quality of fuels obtained
Hydrothermal Processing (HTU)/ liquefaction /hydrothermal pyrolysis	Lower temperature (300-400 °C); longer residence time (0.2-1.0 hr.); High pressure (5-20 Mpa); drying unnecessary	Occurs in aqueous medium which involves complex sequences of reactions	Better quality of fuels obtained (High PTU, low moisture content)	Relatively low oil yield (20-60%); Need high pressure equip, thus higher capital cost

Table 1. Comparison of two typical thermochemical processes for bio-oil production

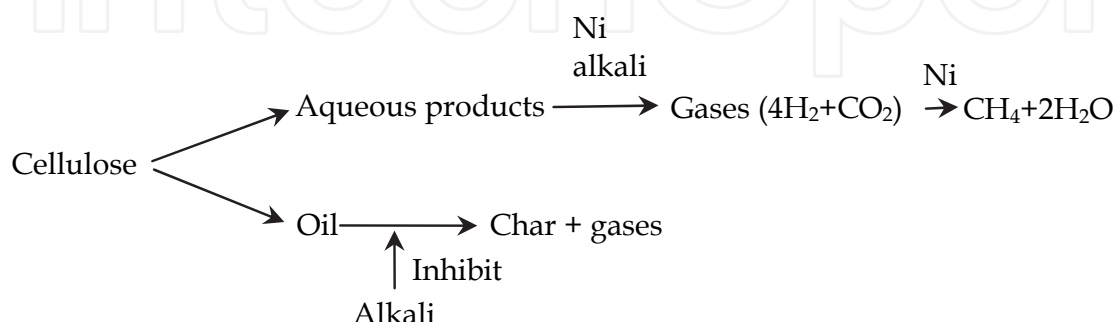


Fig. 2. Reaction pathway for the hydrothermal processing of cellulose

With flash pyrolysis, the light small molecules are converted to oily products through homogeneous reactions in the gas phase. The principle of the biomass flash pyrolysis process is shown in Fig.3. Biomass is rapidly heated in the absence of air, vaporizes, and quickly condenses to bio-oil. The main product, bio-oil, is obtained in yields of up to 80% wt on dry feed, together with the by-product char and gas (Bridgewater and Peacocke, 2000).

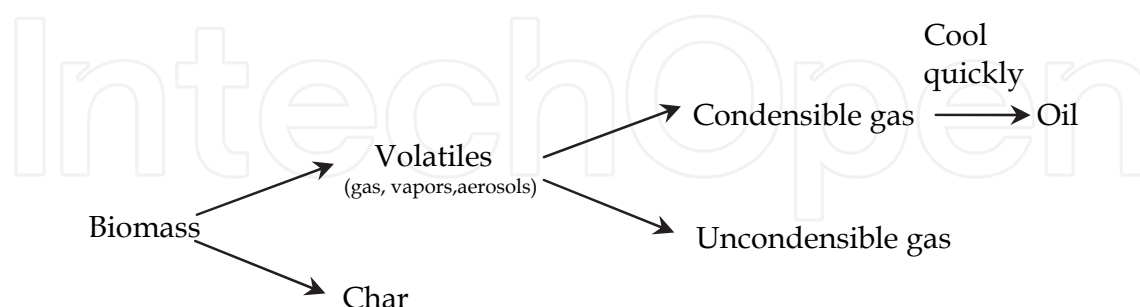


Fig. 3. Reaction pathway for the biomass flash pyrolysis process

4.2 Related research development of flash pyrolysis and hydrothermal process

Flash pyrolysis for the production of liquids has developed considerably since the first experiments in the late 1970s. Several pyrolysis reactors and processes have been investigated and developed to the point where fast pyrolysis is now an accepted, feasible and viable route to renewable liquid fuels, chemicals and derived products. Since the 1990s, several research organizations have successfully established large-scale fast pyrolysis plants. Bridgewater and Peacocke (2000) have intensively reviewed the key features of fast pyrolysis and the resultant liquid product, and described the major reaction systems and processes that have been developed over the last 20 years.

Unlike flash pyrolysis, technological developments in the area of hydrothermal conversion present new ways to turn wastes to fuel. Hydrothermal processing was initially developed for turning coal into liquid fuels, but recently, the technique has been applied to a number of feedstocks, including woody biomass, agricultural residues, and organic wastes (e.g., animal wastes, municipal solid wastes (MSW), and sewage sludge). Table 2 summarizes representative literature data of hydrothermal processing of common types of biomass and the most influential operating parameters. As can be seen from Table 2, organic waste materials are more favourable than woody biomass and agricultural residues for hydrothermal processing, owing to their higher oil yield and the higher heating value of their bio-oil products.

This earlier work was very promising, showing that hydrothermal technology can be used as an efficient method to treat different types of biomass and produce a liquid biofuel. In particular, hydrothermal conversion processes present a unique approach to mitigate the environmental and economic problems related to disposing of large volumes of organic wastes. It not only reduces the pollutants, but also produces useful energy in the form of liquid fuel. Compared with flash pyrolysis, hydrothermal conversion is at an early developmental stage, and the reaction mechanisms and kinetics are not yet fully understood.

Raw Materials	Reactor Capacity	Temp. (°C)	Pressure (Mpa)	Time (min)	Oil Yield (%)	Heating Value(MJ/kg)	Reference
a) Woods							
Beech	--	277-377	--	25	13.8-28.4	27.6-31.3	Demirbaş, et al., 2005a
Spruce	--	277-377	--	25	13.8-25.8	28.3-33.9	Demirbaş, et al., 2005b
Sawdust	0.2 L	280	N/A		7.2	--	Karagöz et al., 2005
b) Agricultural residues							
Corn stalk	0.3 L	300	10 Mpa	30	28.3 on organic basis	29.7	Minowa et al., 1998
Rice husk	0.3 L	300	10 Mpa	30	28.8 on organic basis	30.8	Minowa et al., 1998
Rice straw	1.0 L	260-350	6-18 Mpa	3-5	13.0-38.35	27.6-35.8	Yuan et al., 2007
c) organic wastes							
Swine manure	1-L autoclave	260-340		0-90	14.9-24.2	36.1	Xiu et al., 2010a
Swine manure	Continuous mode	285-305	9-12	40-80	2.8-53.3	25.2-33.1	Ocfemia et al., 2006
Dairy manure	Batch/continuous mode	250-380	10-34	--	50	--	Appell, et al., 1980
Sewage sludge	5 t/d	300	10	--	48	37-39	Itoh, et al., 1994
Garbage	0.3 L autoclave	250-340	6-18	6-120	27.6	36	Minowa, et al., 1995
Sewage sludge	0.3 L autoclave	150-300	--	0-180	44.5	35.7	Suzuki, et al., 1990
Sewage sludge	4.2L microwave	250-350	8-20	--	30.7	36.4	Bohlmann, et al., 1999
MSW	autoclave	260-340	13-34	--	32	46	Gharieb, et al., 1995
MSW	autoclave	295-450	--	20-90	35-63.3	--	Kranich et al., 1984
Sewage sludge	20 kg/hr.	300-360	10-18	5-20	--	30-35	Goudriaan et al., 2000

Table 2. Overview of literature on hydrothermal processing of common types of biomass

4.3 Properties of bio-oils

The differences in processing conditions result in significant differences in the product yield and product composition of bio-oils. Recently, Lu et al. (2009) intensively reviewed the fuel properties fast pyrolysis oils and discusses how these properties affect the utilization of bio-oils. In general, bio-oils are complex mixtures of volatile hydrocarbons, alcohols, organic acids, aldehydes, ketones, ethers, furans, phenols and other non-volatile compounds. The unstable fragments in bio-oil could rearrange through condensation, cyclization, and polymerization to form new compounds, such as aromatics. Table 3 describes selected properties of bio-oils produced from hydrothermal liquefaction of swine manure and pyrolysis of wood. For comparison purposes, the characteristics of heavy petroleum fuel oil were also presented in Table 3.

Properties		Liquefied bio-oil from swine manure(xiu et al., 2010a)	Pyrolysis bio-oil from wood pyrolysis (Zhang et al., 2007)	Heavy petroleum fuel oil (Oasmaa et al., 1999)
Moisture content (wt%)		2.37	15-30	0.1
PH		--	2.5	-
Specific gravity		1	1.2	0.94
Elemental composition (wt%)	C	72.58	54-58	85
	H	9.76	5.5-7.0	11
	O	13.19	35-40	1.0
	N	4.47	0-0.2	0.3
Ash		0.78	0-0.2	0.1
HHV(MJ/kg)		36.05	16-19	40
Viscosity(at 50 0C)(cP)		843	40-100	180
Solids (wt%)		--	0.2-1	1
Distillation residue (wt%)		63	Up to 50	1

Table 3. Comparison of selected properties of bio-oils produced by hydrothermal liquefaction of swine manure and pyrolysis of wood and heavy fuel oil

As shown in Table 3, liquefied oils have much lower oxygen and moisture contents, and consequently much higher energy value, as compared to oils from fast pyrolysis. The corresponding HHV of liquefied oil from swine manure is 36.05 MJ/kg, which about 90% of that of heavy fuel oil (40 MJ/kg). The properties of bio-oil from both processes are significantly different from heavy petroleum fuel oil. Compared with heavy petroleum fuel oil, the bio-oils have the following undesired properties for fuel applications: high viscosity, high water and ash contents, high oxygen content and low heating value.

Pyrolysis oil is acidic in nature, polar and not miscible with conventional crude oil. In addition, it is unstable, as some (re)polymerization of organic matter in the oil causes an increase in viscosity over time. Overall, bio-oils can not be directly used as transportation fuels due to their high viscosity, high water and ash contents, low heating value, instability and high corrosiveness. Therefore, bio-oil has to be upgraded before it can be used as an engine fuel.

4.4 Typical bio-oil upgrading technologies and their limitation

Considering the above discussion on the properties, it is obvious that the fuel quality of bio-oils is inferior to that of petroleum-based fuels. There have been intensive studies on bio-oil

upgrading research and various technologies have been developed for bio-oil upgrading. Table 4 summarizes current techniques in bio-oil upgrading. The characteristics, as well as recent progress, advantages, and disadvantages of each technique are also described as follows:

Upgrading methods	Treatment condition/requirement	Reaction mechanism /process description	Technique Feasibility	
			Pros.	Cons.
Hydrotreating /hydrofining	Mild conditions, (~500°C /low pressure) chemical needed: H ₂ /CO, catalyst (e.g., CoMo, HDS, NiMo, HZSM-5)	Hydrogenation without simultaneous cracking (eliminating N, O and S as NH ₃ , H ₂ O and H ₂ S)	Cheaper route, Commercialized already	high coking (8-25%) and poor quality of fuels obtained
Hydro-cracking /hydrogenolysis /catalytic cracking	Severe conditions, (>350 °C, 100~2000 Psi), chemical needed: H ₂ /CO or H ₂ donor solvents, catalyst (e.g., Ni/ Al ₂ O ₃ -TiO ₂)	Hydrogenation with simultaneous cracking Destructive(resulting in low molecular product)	Makes large quantities of light products	Need complicated equipment, excess cost, catalyst deactivation, reactor clogging
Supercritical fluid	Mild conditions, organic solvents needed such as alcohol, acetone, ethyl acetate, glycerol	Promotes the reaction by its unique transport properties: gas-like diffusivity and liquid-like density, thus dissolved materials not soluble in either liquid or gaseous phase of solvent	Higher oil yield, better fuel quality (lower oxygen content, lower viscosity)	Solvent is expensive
Solvent addition (direct add solvent or esterification of the oil with alcohol and acid catalysts)	Mild conditions, polar solvents needed such as water, methanol, ethanol, and furfural	Reduces oil viscosity by three mechanisms: (1) physical dilution (2) molecular dilution or by changing the oil microstructure; (3) chemical reactions like esterification and acetalization	The most practical approach (simplicity, the low cost of some solvents and their beneficial effects on the oil properties)	Mechanisms involved in adding solvent are not quite understand yet
Emulsification /Emulsions	Mild conditions, need surfactant (e.g. CANMET)	Combines with diesel directly. Bio-oil is miscible with diesel fuels with the aid of surfactants	Simple, less corrosive	Requires high energy for production
Steam Reforming	High temperature(800-900 °C), need catalyst (e.g. Ni)	Catalytic steam reforming + water-gas shift	Produces H ₂ as a clean energy resource	Complicated, requires steady, dependable, fully developed reactors
Chemical extracted from the bio-oils	Mild conditions	Solvent extraction, distillation, or chemical modification	Extract valuable chemicals	Low cost separation and refining techniques still needed

Table 4. Brief description, treatment condition, and technical feasibility of the current techniques used for upgrading bio-oil

4.4.1 Hydrotreating

It is generally recognized that the higher the hydrogen content of a petroleum product, especially the fuel products, the better the quality. This knowledge has stimulated the use of a hydrogen-adding process in the refinery, which is called hydrogenation. Currently, the most widely used hydrogenation processes for the conversion of petroleum and petroleum products is hydrotreating.

Hydrotreating (HDT) is a nondestructive, or simple hydrogenation process that is used for the purpose of improving product quality without appreciable alteration of the boiling range. It has become the most common process in modern petroleum refineries. Bio-crude may also be processed by a conventional refinery and potentially augmented with petroleum crude. The oxygen in bio-oils can be removed via hydrotreating. The catalysts commonly used for hydrotreating are sulphide CoMo/Al₂O₃, NiMo/Al₂O₃ systems. (Nava et al., 2009).

Hydrotreating requires mild conditions, while the yield of bio-oil is relatively low. The process also produces a large amount of char, coke, and tar, which will result in catalyst deactivation and reactor clogging.

4.4.2 Hydro-cracking

Hydro-cracking is less popular than the hydrotreating in the petroleum industry.

Hydro-cracking is a thermal process (>350 °C, >660°F) in which hydrogenation accompanies cracking. Relatively high pressure (100 to 2000 Psi) is employed, and the overall result is usually a change in the character or quality of the end products (Ancheyta and Speight, 2007). This process is performed by dual-function catalysts, in which silica-alumina (or zeolite) catalysts provide the cracking function, and platinum and tungsten oxide catalyze the reactions, or nickel provides the hydrogenation function. Alumina is by far the most widely used support

Hydro-cracking is an effective way to make a large amount of light product, but it requires more severe conditions such as higher temperature and hydrogen pressure to deal with acids, which is not economical and energy efficient.

4.4.3 Supercritical fluids (SCFs)

A fluid is considered supercritical when its temperature and pressure go above its critical point. SCFs possess unique transport properties. They can effuse through solids like a gas and dissolve materials like a liquid. In particular, SCFs have the ability to dissolve materials not normally soluble in either liquid or gaseous phase of the solvent, and hence to promote the gasification/liquefaction reactions (Xu and Etcheverry, 2008).

SCFs have been recently used to improve oil yield and quality and have demonstrated a great potential for producing bio-oil or bio-crude with much higher caloric values and lower viscosity. Water is the cheapest and most commonly used supercritical fluid in hydrothermal processing, but utilizing water as the solvent for liquefaction of biomass has the following drawbacks: 1) lower yields of the water-insoluble oil product; 2) it yields a bio-oil that is very viscous, with a high oxygen content. To enhance the oil yields and qualities the utilization of organic solvents such as ethanol (Xu and Etcheverry, 2008; Xiu, et al., 2010b), ethyl acetate (Demirbas, 2000a), acetone (Heitz et al., 1994; Liu and Zhang, 2008), 2-propanol (Ogi et al., 1994), 1,4-dioxane (Bao et al., 2008; Mazaheri et al., 2010; Cemek and Kucuk, 2001), methanol (Minami and Ska, 2003,2005; Yang et al., 2009) and butanol (Ogi et al., 1993) has been adopted. All these solvents have shown a significant effect on bio-oil

yield and quality. Minami and Ska (2003, 2005) have reported that 90% of beech wood was successfully decomposed in supercritical methanol. The above motioned supercritical organic solvent fluids are predominately used in hydrothermal treatment processing to improve the bio-oil yield and quality. However, it was also used to upgrade pyrolysis bio-oil. For example, Tang et al. (2009) reported that supercritical ethanol ($T = 243.1^{\circ}\text{C}$, $P_c = 6.37$ MPa) can upgrade lignin-derived oligomers in pyrolysis oil, and thus reduce the tar or coke. Although SCFs can be produced at relatively lower temperature and the process is environmentally friendly, these organic solvents are too expensive to make it economically feasible on a large scale. Recently, researchers have been trying to test less expensive organic solvent as a substitute for SCFs. Crude glycerol, the low-value by-product of biodiesel production, has shown very promising results for being using as an SCF solvent. Glycerol has been used as an organic solvent for biomass delignification (Demirbaş, 2008; Demirbaş and Celik, 2005a; Küçük, 2005), bio-oil separation (Li et al., 2009) and to significantly improve the performance of liquefaction in the conversion of biomass into bio-oil (Demirbaş, 2000b; Xiu et al., 2010c; Gan et al., 2010). Xiu et al. found that cross-reactions between swine manure and crude glycerol significantly affected the hydrothermal process, and that the use of crude glycerol dramatically increased bio-oil yield from 23.9% to 70.92% (Xiu et al., 2010c, Fig.4). In addition, they discovered that the free fatty acid in the crude glycerol is the key component that leads to enhancement of the oil yield (Fig.5). Moreover, the oil quality was also improved, having a lower density and viscosity.

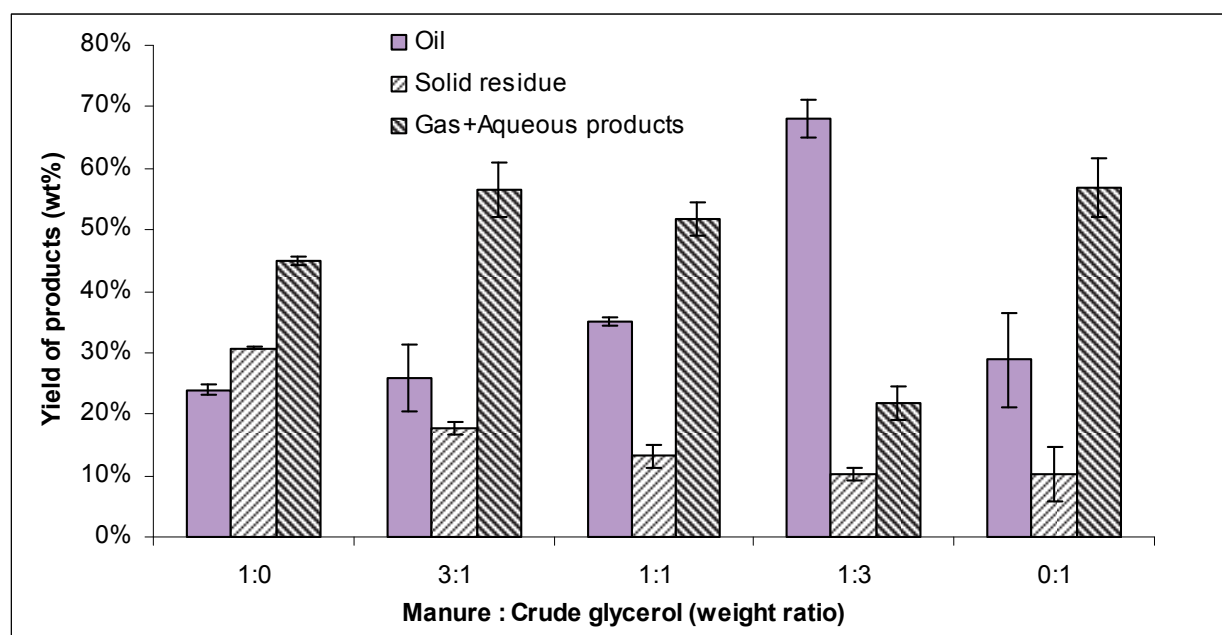


Fig. 4. Effect of swine manure to crude glycerol ratio (weight ratio) on the products yield in hydrothermal pyrolysis of swine manure. (Xiu et al., 2010c)

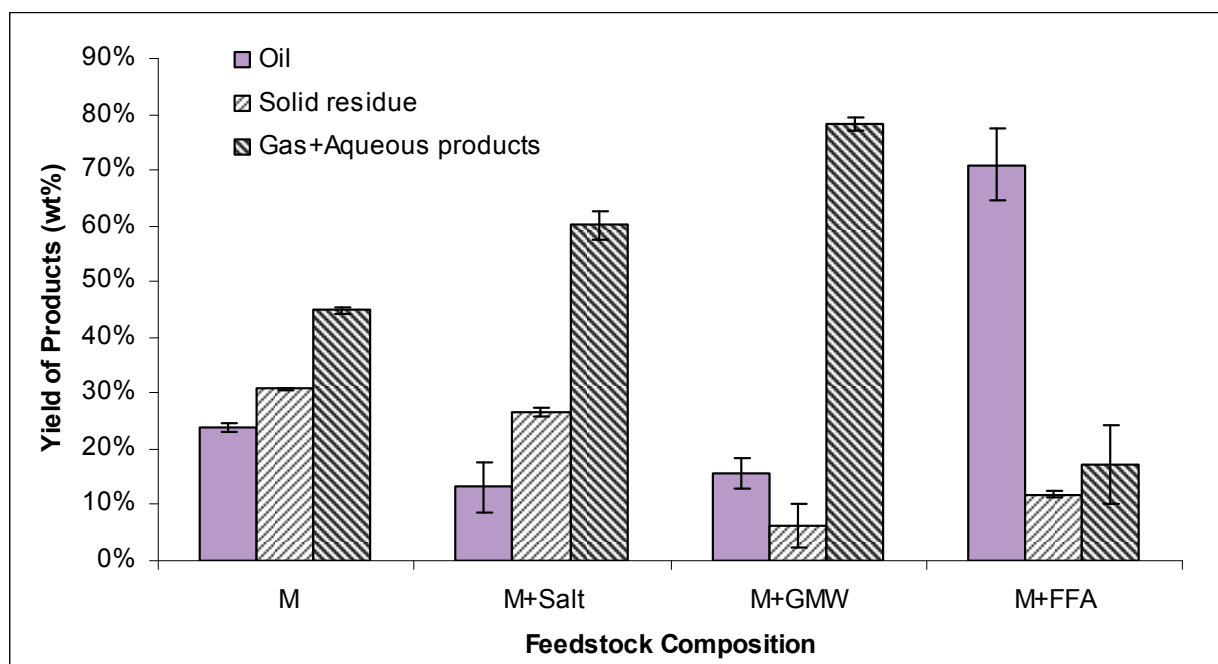


Fig. 5. Effect of crude glycerol fractionated components on the products yield in hydrothermal pyrolysis of swine manure. (Xiu et al., 2010c). M-manure; GMW-glycerol, methanol and water; FFA-free fatty acids.

4.4.4 Solvent addition / etherification

Polar solvents such as methanol, ethanol, and furfural have been used for many years to homogenize and to reduce viscosity of biomass oils (Radlein et al., 1996; Diebold and Czernik, 1997; Oasmaa, 2004; Boucher et al., 2000). The immediate effects of adding these polar solvents are decreased viscosity and increased heating value. The increase in heating value for bio-oils mixed with solvents occurs because the solvent has a higher heating value than that of most bio-oils. The solvent addition reduces the oil viscosity due to the following three mechanisms: (1) physical dilution without affecting the chemical reaction rates; (2) reducing the reaction rate by molecular dilution or by changing the oil microstructure; (3) chemical reactions between the solvent and the oil components that prevent further chain growth (Oasmaa and Czernik, 1999).

Most studies have directly added solvents after pyrolysis, which works well to decrease the viscosity and increase stability and heating value. However, several recent studies showed that reacting the oil with alcohol (e.g., ethanol) and acid catalysts (e.g., acetic acid) at mild conditions by using reactive distillation, resulted in a better bio-oil quality (Mahfud et al., 2007; Xu et al., 2008; Tang et al., 2008; Oasmaa, et al., 2004; Xu and Etcheverry, 2008). This process is referred to as catalytic etherification or etherification treatment in the literature (Xiong et al., 2009; Wang et al., 2010; Hilten et al., 2010; Yu et al., 2009).

The chemical reactions that can occur between the bio-oil and methanol or ethanol are esterification and acetalization (Fig.6). In such a case, the reactive molecules of bio-oil like organic acids and aldehydes are converted by the reactions with alcohols to esters and acetals, respectively. Thus, in addition to the decrease in viscosity and in the aging rate, they also lead to other desirable changes, such as reduced acidity, improved volatility and heating value, and better miscibility with diesel fuels.

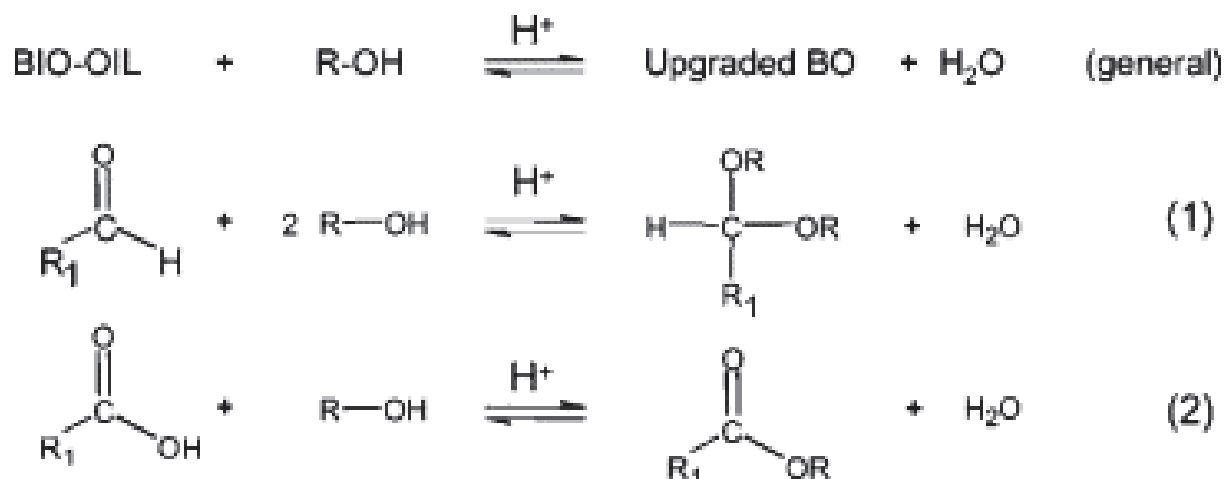


Fig. 6. Reactions involved in bio-oil alcoholysis: (1) acetalization, (2) esterification. (Mahfud et al., 2007)

Most environmental catalysts applied in bio-oil upgrading are heterogeneous catalysts. Solid acid catalysts, solid base catalysts (Zhang et al., 2006), ionic liquid catalysts (Xiong et al., 2009), HZSM-5, and aluminum silicate catalysts were investigated for esterification of bio-oils (Peng et al., 2008, 2009).

Considering the simplicity, the low cost of some solvents such as methanol and their beneficial effects on the oil, this method seems to be the most practical approach for bio-oil quality upgrading.

4.4.5 Emulsification (emulsions)

One of the methods in using bio-oil as a combustion fuel in transportation or boilers is to produce an emulsion with other fuel sources. Pyrolysis oils are not miscible with hydrocarbon fuels, but with the aid of surfactants they can be emulsified with diesel oil. Upgrading of bio-oil through emulsification with diesel oil has been investigated by many researchers (Chiaromonti et al., 2003a, b; Ikura et al., 2003; Jiang & Ellis, 2010; Garcia-Perez et al., 2010).

A process for producing stable microemulsions, with 5-30% of bio-oil in diesel has been developed at CANMET Energy Technology Centre (Oasmaa & Czernik, 1999; Ikura, et al., 1998). Those emulsions are less corrosive and show promising ignition characteristics.

Jiang and Ellis (2010) investigated the bio-oil emulsification with biodiesel while leaving the pyrolytic lignin phase behind. A stable bio-oil/biodiesel emulsion was produced using octanol as an emulsifier. The effects of several process variables on the mixture stability were also examined. They found that the optimal conditions for obtaining a stable mixture between bio-oil and biodiesel are with an octanol surfactant dosage of 4% by volume, an initial bio-oil/biodiesel ratio of 4:6 by volume, a stirring intensity of 1200 rpm, a mixing time of 15 min, and an emulsifying temperature of 30 °C. Various properties of the emulsion have shown more desirable values in acid number, viscosity, and water content compared to the original bio-oil. The reduction in viscosity and corrosiveness of the emulsion was also reported by Ikura et al (1998).

Chiaromonti et al. (2003b) tested the emulsions from biomass pyrolysis liquid and diesel in engines. Their results suggest that corrosion accelerated by the high velocity turbulent flow in the spray channels is the dominant problem. A stainless steel nozzle has been built and successfully tested. Long term validation however, is still needed.

More recently, He et al. (2010) used a novel high-pressure homogenization (HPH) technique to improve the physicochemical properties and storage stability of switchgrass bio-oil. Compared with the conventional emulsification method, which consists of mixing bio-oil with diesel oil, the HPH technique improved the original properties of bio-oil by decreasing the viscosity and improving its stability in storage. However, the heating value, water content, density, PH value, or ash content did not change.

Overall, upgrading of bio-oil through emulsification with diesel oil is relatively simple. It provides a short-term approach to the use of bio-oil in diesel engines. The emulsions showed promising ignition characteristics, but fuel properties such as heating value, cetane and corrosivity were still unsatisfied. Moreover, this process required high energy for production. Design, production and testing of injectors and fuel pumps made from stainless steel or other materials are required.

4.4.6 Steam reforming

The term "reforming" was originally used to describe the thermal conversion of petroleum fractions to more volatile products with higher octane numbers, and represented the total effect of many simultaneous reactions such as cracking, dehydrogenation and isomerisation (Yaman, 2004). Reforming also refers to the conversion of hydrocarbon gases and vaporized organic compounds to hydrogen containing gases such as synthesis gas, which is a mixture of carbon monoxide and hydrogen. Synthesis gas can be produced from natural gas, for example, by such processes as reforming in the presence of steam (steam reforming) (Klass, 1998).

Fast pyrolysis of biomass followed by catalytic steam reforming and shift conversion of specific fractions to obtain H₂ from bio-oil was presented as an effective way to upgrade biomass pyrolysis oils. Production of hydrogen from reforming bio-oil was investigated by NREL extensively, including the reactions in a fixed bed and a fluidized bed (Wang et al., 1997,1998; Czernik et al., 2007). Commercial nickel catalysts showed good activity in processing biomass derived liquids (Ekaterini & Lemonidou, 2008).

4.4.7 Chemicals extracted from the bio-oils

There are many substances that can be extracted from bio-oil, such as phenols used in the resins industry, volatile organic acids, nitrogen heterocycles and n-alkanes (Ross et al., 2010; Gallivan and Matschei, 1980). Most recently, Cao et al. (2010) extracted triacetoneamine (TAA) in a bio-oil from fast pyrolysis of sewage sludge with a high yield (27.9%) and high purity (80.4%) using acetone as the absorption solvent. Hydrothermal bio-oil contains up to 50 wt % asphalt, which makes it a good candidate for the asphalt industry. Recently, Fini and her colleagues fractionated and chemically modified the bio-oil into an effective asphalt bio-binder, which has remarkable potential to replace or augment petroleum-based road asphalt (Fini et al, 2010).

The only current commercially important application of bio-oil chemicals is that of wood flavor or liquid smoke (Mohan et al., 2006). Commercialization of special chemicals from bio-oils requires more devotion to developing reliable low cost separation and refining techniques.

4.5 Closing remarks

Flash pyrolysis processes are so far the only commercially practiced technology for production of bio-oil or bio-crude from biomass. However, pyrolysis oils consist of high

oxygen/water contents and hence only about half the caloric value of petroleum (20-25 MJ/kg. In addition, they are strongly acidic and corrosive. Hydrothermal liquefaction with a suitable solvent (water or organics) is superior to pyrolysis. It can potentially produce liquid oils with much higher caloric values. In particular, liquefaction to produce bio-oil from organic wastes is a promising way to not only create value, but also reduce pollutants associated with sludge. There are intensive studies on bio-oil upgrading and several techniques have been developed.

Solvent addition (esterification) appears to be the most practical approach due to simplicity, the low cost of some solvents and their beneficial effects on the oil properties. However, none of these bio-oil upgrading techniques has been commercialized due to low biofuel efficiency and their limitations. Therefore, novel refinery processes are needed to systematically upgrade bio-oils into transportation fuels that have desirable qualities, while producing other value-added co-products to make the economics work.

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This book aspires to be a comprehensive summary of current biofuels issues and thereby contribute to the understanding of this important topic. Readers will find themes including biofuels development efforts, their implications for the food industry, current and future biofuels crops, the successful Brazilian ethanol program, insights of the first, second, third and fourth biofuel generations, advanced biofuel production techniques, related waste treatment, emissions and environmental impacts, water consumption, produced allergens and toxins. Additionally, the biofuel policy discussion is expected to be continuing in the foreseeable future and the reading of the biofuels features dealt with in this book, are recommended for anyone interested in understanding this diverse and developing theme.

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University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
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InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

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