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# Preparation and Characterization of Bio-Oil from Biomass

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## 1. Introduction

Bio-oil is a kind of liquid fuel made from biomass materials such as agricultural crops, algal biomass, municipal wastes, and agricultural and forestry by-products via thermo-chemical processes (Demirbas, 2007). As one kind of new inexpensive, clean and green bio-energies, bio-oil is considered as an attractive option instead of conventional fuel in the aspect of reducing environmental pollution.

Currently, biomass crops are distributed abroad in the world and the amount is very large, including woody and herbaceous crops growing in temperate and subtropical regions (Ragauskas, et al., 2006). The annual production is about 2740 Quads (1 Quad = 1016Btu), which is about 8 times the total annual world energy consumption (C. Xu & Lad, 2007). Though, the biomass resource is abundant in the world, the efficiency of utilization is very low. With energy crisis and fuel tension, it is more important to develop new technology in order to use biomass resource efficiently. In addition, biomass resources can also cause less NO<sub>x</sub> and SO<sub>x</sub> emission due to the less content of nitrogen and sulfur (Sun, et al., 2010).

In recent years, the research on bio-oil has been paid more attention due to the property of sustainable, carbon neutral, and easy to store and transport. Thus, a series of methods are developed to prepare and upgrade bio-oil including fast pyrolysis, liquefaction, gasification, hydrotreatment, and so on. In addition, the characterization of bio-oil is also being focused and got more achievements.

Herein, several selected features concerning the bio-oil are surveyed. In the first part, the preparation of bio-oil is reviewed. The second part will focus on the characterization of bio-oil from biomass.

## 2. Preparation of bio-oil

Biomass can be converted to bio-oil by the way of fast pyrolysis, liquefaction and gasification processes, and it can also be further obtained high-quality products with the help of upgrading and separation processes. The product properties are different through these approaches, which attribute to the differences in technology as well as equipment.

### 2.1 Fast pyrolysis

Pyrolysis is defined as a thermo-chemical process of the decomposition to smaller molecules by thermal energy (Demirbas, 2007). Fast pyrolysis is a high temperature process in which

the feedstock is rapidly heated in the absence of oxygen, vaporises and condenses to a dark brown mobile liquid (A. V. Bridgwater & Peacocke, 2000; Q. Zhang, et al., 2006).

The biomass fast pyrolysis is attractive because the biomass can be readily converted into liquid products. These liquids, such as crude bio-oil, have advantages in transport, storage, combustion, retrofitting, and flexibility in production and marketing (Demirbas, 2009).

### 2.1.1 Raw materials

Biomass raw materials are marked by their tremendous diversity, which include forest products wastes, agricultural residues, organic fractions of municipal solid wastes, paper, cardboard, plastic, food waste, green waste, and other waste (Demirbas, 2009). Nowadays, a lot of materials have been used in the scientific research as raw materials, such as wood leaf (Zabaniotou & Karabelas, 1999), wood industry residues (Garcia-Perez, et al., 2007), rice husks and sawdust (Zheng, et al., 2006), corn stalks (Yi, et al., 2000), and so on.

In the stage of raw materials preparation, drying is usually essential because of the existence of water in the feedstock, which will transfer into liquid product finally. High content of water will reduce the heat value of bio-oil and affect its storage stability. In general, we can make use of by-product gas to dry the feedstock in order to reduce energy consumption (Brammer & Bridgwater, 1999; A. V. Bridgwater & Peacocke, 2000).

### 2.1.2 Reactors configuration

At present, a variety of reactor configurations have been studied by many organisations, a summary list is shown in Table 1.

Reactor type	Organisation
Fluid bed	Aston University, VTT, NERL, Hamburg university, Oldenberg University, INETI, Dynamotive, etc.
Ablative	NERL, Aston University, ZSW-Stuttgart University
Circulating fluid bed	CRES, CPERI
Entrained flow	GTRI, Egemin
Rotating cone	Twente University, BTG/Schelde/Kara
Transported bed	Ensyn, (at ENEL, Red Arrow, VTT)
Vacuum moving bed	Laval University/Pyrovac

Table 1. Fast pyrolysis reactor types and locations (A. V. Bridgwater & Peacocke, 2000)

However, in all the configurations, fluid bed has been most extensively researched and obtains the huge achievement, which resulting from their ease of operation and ready scale-up. A representational fluid bed fast pyrolysis system is shown in Figure 1. The reactor configurations mainly contain a hopper, two screw feeders, an electric heater, a fluidized-bed reactor, two cyclones, a condenser, and an oil pump, as well as some thermocouples and pressure meters (Zheng, et al., 2006). In the experiment process, the raw materials are fed to the hopper at a certain rate and the hot vapour produced will be quickly cooled into liquid product in the condenser.

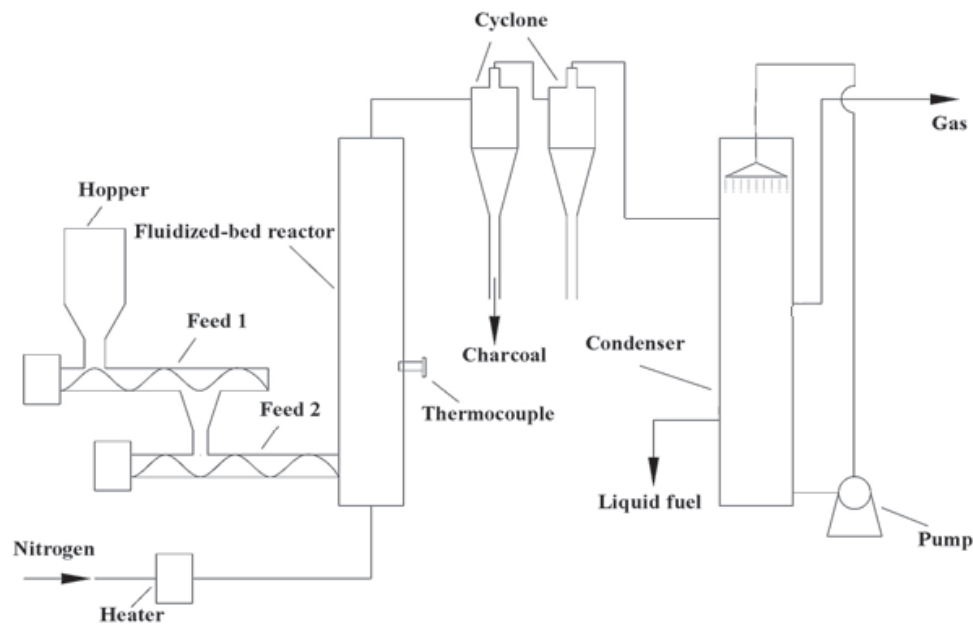


Fig. 1. The experimental device (Zheng, et al., 2006)

As a kind of most popular and ideal configuration, we have reason to believe that fluid bed will achieve greater developments in performance and cost reduction in the near future (A. V. Bridgwater & Peacocke, 2000).

### 2.1.3 Temperature of reaction

Fast pyrolysis is a high temperature process, thus temperature has tremendous effect to the yield of liquid. The correlation between them is shown in Figure 2 for typical products from fast pyrolysis of wood (Toft, 1996). In the lower temperature, the liquid yield is low due to the less sufficient pyrolysis reaction, which will produce high content of char at the same time. Likewise, the excessive temperature will also lead to liquid yield decreased resulting from the increase of gas product.

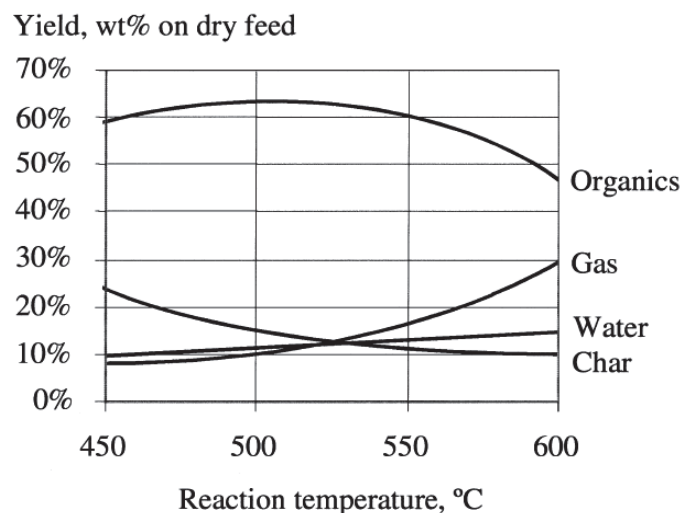


Fig. 2. Typical yields of organic liquid, reaction water, gas and char from fast pyrolysis of wood, wt% on dry feed basis (Toft, 1996)

In order to achieve high liquid yield, the pyrolysis reaction temperature is better to be controlled around 500°C in the vapour phase for most forms of woody biomass (A. V. Bridgwater, et al., 1999b). Of course, different crops may have different maxima yield at different temperatures.

#### 2.1.4 Vapour residence time

Vapour residence time is also important to the liquid yield of pyrolysis reaction. Very short residence times will lead to the incomplete depolymerisation of the lignin, while prolonged residence times can cause further cracking of the primary products (A. V. Bridgwater, et al., 1999b). Too long or short residence time will reduce the organic yield, so it is necessary to select a suitable residence time. In general, the typically vapour residence time is about 1 s.

#### 2.1.5 Liquids collection

The collection of liquids has been a major difficulty in the preparation of fast pyrolysis processes, because the nature of the liquid product is mostly in the form of mist or fume rather than a true vapour, which increases the collection problems (A. V. Bridgwater, et al., 1999b). Furthermore, it is important to choose appropriate condenser and optimum cooling rate; otherwise, some vapour products will take place polymerization and decomposition to produce bitumen (lead to blockage of condenser) and uncondensable gas if cooling time delay. In order to achieve good heat-exchange effect, it is necessary to let the product vapours contact fully with the condensed fluid. Thus, it is regarded as a good method to cool vapour product effectively by using well-sprayed liquid scrub in the bottom of the liquids collection equipment (Zheng, et al., 2006). At present, electrostatic precipitators is widely used by many researchers due to its effectiveness to the liquids collection. However, a kind of very effective method and equipment has not yet to be found by now.

### 2.2 Liquefaction

Liquefaction is considered as a promising technology to convert biomass to liquefied products through a complex sequence of physical and chemical reactions. In liquefaction process, macromolecular substances are decomposed into small molecules in the condition of heating and the presence of catalyst (Demirbas, 2000a; Demirbas, 2009).

Pyrolysis and liquefaction are both thermo-chemical conversion, but the operating conditions are different as shown in Table 2 (Demirbas, 2000a). Moreover, as two kinds of different transformation method, there are also lots of differences between the liquefaction (Eager, et al., 1983; Hsu & Hixson, 1981) and pyrolysis (Adjaye, et al., 1992; Alen, 1991; Maschio, et al., 1992) mechanisms of biomass.

Process	Temperature(K)	Pressure(MPa)	Drying
Liquefaction	525-600	5-20	Unnecessary
Pyrolysis	650-800	0.5-0.1	Necessary

Table 2. Comparison of liquefaction and pyrolysis (Demirbas, 2000a)

#### 2.2.1 Direct liquefaction

Liquefaction can be divided in two categories, direct liquefaction and indirect liquefaction. Direct liquefaction refers to rapid pyrolysis to produce liquid tars and oils and/or condensable organic vapours, while indirect liquefaction is a kind of condensing process of gas to produce liquid products in the present of catalysts (Demirbas, 2009). In the process of

liquefaction, there are lots of reactions occurred such as cracking, hydrogenation, hydrolysis and dehydration, and so on.

The direct liquefaction of *Cunninghamia lanceolata* in water was investigated, and the maximum heavy oil yield can reach 24% (Qu, et al., 2003). Similar yield of oil (25–34%) are achieved by other researchers through the experiment on the liquefaction of various wood in an autoclave (Demirbas, 2000b). The results show that there are no obvious correlations between the raw materials and bio-oil yields.

### 2.2.2 Sub/supercritical liquefaction

Supercritical liquefaction is a thermo-chemical process for the conversion of biomass to bio-oil in the presence of supercritical solvents as reaction medium. At present, water, as reaction medium, is attracting widely attention in the aspect of various biomass conversions due to a series of advantages compared with other organic solvents (Sun, et al., 2010). On one hand, water is an economic and environmental friendly solvent, because it will eliminate the costly pretreatment or drying process of wet raw materials and not produce pollution. On the other hand, water possess suitable critical temperature (374°C) and critical pressure (22MPa), and it has a strong solubility for organic compounds derived from biomass in the supercritical condition (C. Xu & Lad, 2007).

There are lots of research works on the aspect of biomass liquefaction in the condition of supercritical condition. For instance, a variety of lignocellulosic materials' conversion at around 350°C in the presence of CO and NaCO<sub>3</sub> at Pittsburgh Energy Technology Center (PETC) (Appell, et al., 1971), woody biomass (Jack pine sawdust) liquefaction in the supercritical water without and with catalysts (alkaline earth and iron ions) at temperatures of 280–380°C (C. Xu & Lad, 2007), paulownias liquefaction in hot compressed water in a stainless steel autoclave in the conditions of temperature range of 280–360°C, and so on. In general, the yields of liquid through supercritical liquefaction are in the range of 30–50%, which is depend on temperature, pressure, catalysts, etc.

### 2.2.3 Catalyst

In the process of liquefaction, it is essential to use catalyst in order to achieve higher liquid yield and better quality products. In generally, the common catalysts are used in liquefaction process are alkali salts, such as Na<sub>2</sub>CO<sub>3</sub> and KOH, and so on. (Duan & Savage, 2010; Minowa, et al., 1995; Zhou, et al., 2010)

The researcher in university of Michigan produced bio-oils from microalga in the presence of six different heterogeneous catalysts (Pd/C, Pt/C, Ru/C, Ni/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, CoMo/  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (sulfided), and zeolite) (Duan & Savage, 2010). The bio-oils produced are much lower in oxygen than the original algal biomass feedstock, and their heating values are higher than those of typical petroleum heavy crudes. Moreover, the effects of more catalysts are investigated on the liquefaction, such as Fe, NaCO<sub>3</sub> (Sun, et al., 2010), Ca(OH)<sub>2</sub>, Ba(OH)<sub>2</sub>, FeSO<sub>4</sub> (C. Xu & Lad, 2007), and so on. In summary, the presence of catalyst can decompose macromolecules (including cellulose and hemicellulose) into smaller materials, which will form all kinds of compound through a series of chemical reactions.

### 2.2.4 Reaction pressure

Hydrogen pressure plays a significant role in the liquefaction of biomass, especially in the condition with extension of reaction times. Yan et al. discuss the effect of hydrogen pressure



to the yield of liquid. The results show that the dependence on  $H_2$  pressure is weak at the early stage of reaction, but the following stage increase the demand to the hydrogen due to the formation of bio-oil accompany with the decomposition reaction of preasphaltene and asphaltene (Yan, et al., 1999).

In addition, the presence of either the hydrogen or the higher pressure in the reaction system will suppress the formation of gas and increase the bio-oil yield. Liquefaction in a high-pressure  $H_2$  environment also led to bio-oil with an increased H content and H/C ratio (Duan & Savage, 2010), which is beneficial to the increase of its heating value in the process of combustion.

### 2.2.5 Reaction temperature

The yield of bio-oil is depended on the reaction temperature due to differences of reaction type in different temperature periods. Figure 3. reveal the study results on the liquefaction of *Cunninghamia lanceolata* (Qu, et al., 2003). It is clear that the yield of heavy oil increases firstly and then decreases as the increasing reaction temperature, and reaches the maximum value at around  $320^\circ\text{C}$ . The reason might be the competition of hydrolysis and repolymerization. Hydrolysis cause biomass decomposition and then forms small molecule compounds, which rearrange through condensation, cyclization and polymerization to form new compounds. In general, the maximum oil yield is obtained in the temperature range of 525-600K at experimental conditions.

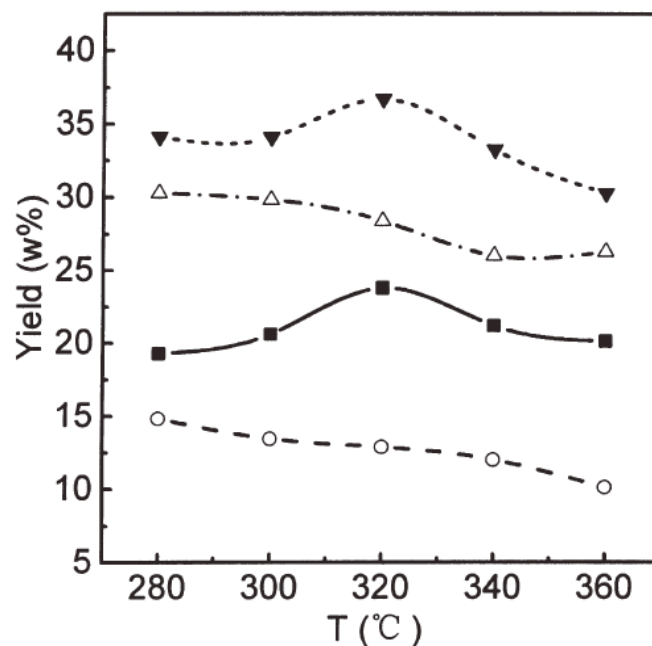


Fig. 3. Effect of reaction temperature on liquefaction of *Cunninghamia lanceolata*. ■ heavy oil yield; ○ Organics Dissolved yield; △ residue yield; ▼ total yield. (Qu, et al., 2003)

### 2.2.6 Solvent

Bio-oil obtained from liquefaction process is a kind of a very viscous liquid resulting in many problems in the stage of production and storage (Demirbas, 2000a). Therefore, in order to reduce the viscous, it's necessary to add some solvent during the process of

liquefaction, such as ethyl acetate, methanol and alcohol due to their high solubility and lower price.

In some conditions, the solvent can play the role of hydrogen-donor solvent in the process of liquefaction. This kind of solvent not only reduce the viscous of products but also increase the yield of liquid, that's because the presence of hydrogen-donor solvent will induce strong destruction of molecular structure of sawdust (Yan, et al., 1999). In summary, it is very important to select a proper solvent for liquefaction of biomass.

### 2.3 Upgrading and separation

As a renewable energy source, biomass can be convert to bio-oil and has some advantages compared with conventional fossil fuel. Unfortunately, the application range for such oils is limited because of the high acidity (pH~2.5), high viscosity, low volatility, corrosiveness, immiscibility with fossil fuels, thermal instability, tendency to polymerise under exposure to air and the presence of oxygen in a variety of chemical functionalities (Gandarias, et al., 2008; Wildschut, et al., 2009; Q. Zhang, et al., 2007). Hence, upgrading and separation of the oils is required for most applications. The recent upgrading techniques are described as follows.

#### 2.3.1 Catalytic hydrogenation

The catalytic hydrogenation is performed in hydrogen providing solvents activated by the catalysts of Co-Mo, Ni-Mo and their oxides or loaded on  $Al_2O_3$  under pressurized conditions of hydrogen and/or CO. For catalytic hydrogenation, it's important to select a catalyst with higher activity. There's actually been studies show that the Ni-Mo catalyst presented a higher activity than the Ni-W catalyst for the phenol HDO reactions in all the temperature (Gandarias, et al., 2008). Moreover, Senol et al. investigated the elimination of oxygen from carboxylic groups with model compounds in order to understand the reaction mechanism of oxygen-containing functional groups, and obtained three primary paths of producing hydrocarbons through aliphatic methyl esters (Senol, et al., 2005).

In order to improve the properties of pyrolysis liquids and achieve higher liquid yield, A two-stage hydrotreatment process was proposed (Elliott, 2007; Furimsky, 2000). The first stage is to remove the oxygen containing compounds which readily undergo polymerization at high temperature condition. In the second stage, the primary reactants will further convert to other products.

Hydrotreatment is an effective way to convert unsaturated compounds into some more stable ones, but it requires more severe conditions such as higher temperature and hydrogen pressure. Although hydrogenation of bio-oil has made huge progresses, more stable catalysts maybe the largest challenge to make production of the commercial fuels from the bio-oil more attractive.

#### 2.3.2 Catalytic cracking

Catalytic cracking is that oxygen containing bio-oils are catalytically decomposed to hydrocarbons with the removal of oxygen as  $H_2O$ ,  $CO_2$  or CO. Guo et al. investigated the catalytic cracking of bio-oil in a tubular fixed-bed reactor with HZSM-5 as catalyst. The results show that the yield of organic distillate is about 45%, and that the amount of oxygenated compounds in the bio-oil reduce greatly (Guo, et al., 2003). Moreover, seven mesoporous catalysts were compared in converting the pyrolysis vapours of spruce wood



for improving bio-oil properties (Adam, et al., 2006). The experiment results confirmed the advantageous of catalyst usage, and the Al-SBA-15 catalyst performs more balanced among all the catalysts tested.

Catalytic cracking can convert macromolecule oxygenated substances to lighter fractions (Adjaye & Bakhshi, 1995; S. Zhang, et al., 2005). Furthermore, it is considered as a promising method and has drawn wide attention due to the price advantage.

### 2.3.3 Steam reforming

At present, catalytic steam reforming of bio-oils is a technically to produce hydrogen, which is extremely valuable for the chemical industry. The steam reforming of aqueous fraction from bio-oil is studied at the condition of high temperature (825 and 875°C) using a fixed-bed micro-reactor (Garcia, et al., 2000). The results show that catalytic efficiency is depend on the water-gas shift activity of catalysts. National Renewable Energy Laboratory (NREL) demonstrated reforming of bio-oil in a bench-scale fluidized bed system using several commercial and custom-made catalysts, and hydrogen yield was around 70% (Czernik, et al., 2007). Besides, some researchers also studied the effect of noble metal-based catalysts for the steam reforming of bio-oil and achieve good results (Rioche, et al., 2005).

A major advantage of producing hydrogen from bio-oil through steam reforming is that bio-oil is much easier and less expensive than other materials.

### 2.3.4 Emulsification

To combine bio-oil with diesel fuel directly can be carried out through emulsification method by the aid of surfactant. This is a relatively short-term way to use bio-oil. The ratio range of bio-oil/diesel emulsification is very wide, and the viscosity of emulsion is acceptable (D. Chiaramonti, et al., 2003). Zheng studied the emulsification of bio-oil/diesel and obtained many kinds of homogeneous emulsions (Zheng, 2007). The physical properties of emulsions are shown in Table 3, which shows the emulsions have higher heat value, lower pH and lower viscosity compared with bio-oil.

	25% Bio-oil +74% diesel +1% emulsifier	50% Bio-oil +49% diesel +1% emulsifier	75% Bio-oil +24% diesel +1% emulsifier
<b>Viscosity</b>	73	129	192
<b>pH</b>	2.7	2.5	2.2
<b>LHV(MJ/kg)</b>	34.55	29.1	23.65

Table 3. Properties of emulsions (Zheng, 2007)

It is therefore possible to consider bio-oil emulsification as a possible approach to the wide use of these oils reducing the investment in technologies. Nevertheless, high cost and energy consumption input are needed in the transformations. Moreover, the dominant factor is that the corrosion was accelerated by the high velocity turbulent flow in the spray channels in the experiment process.

### 2.3.5 Distillation

A large amount of water from the raw material is unavoidable in the bio-oil even if it is dry material. The existence of water is bad for the upgrading of the bio-oil, thus water should be

removed from the bio-oil. The water in the bio-oil can be removed through azeotropic distillation with toluene (Baker & Elliott, 1988). In addition, the light and weight fractions can also be separated by distillation such as molecular distillation, and the obtained light fraction can be used as the material for upgrading process (Yao, et al., 2008).

### 2.3.6 Extraction

Bio-oil is a complex mixture, which nearly involves hundreds of compounds, mainly including acids, alcohols, aldehydes, esters, ketones, sugars, phenols, phenol derivatives, and so on. The oil fractions can be separated by the way of water extraction and obtain water-insoluble and water-soluble fractions, which can be separated further (Sipila, et al., 1998). The whole process is shown in Figure 4.

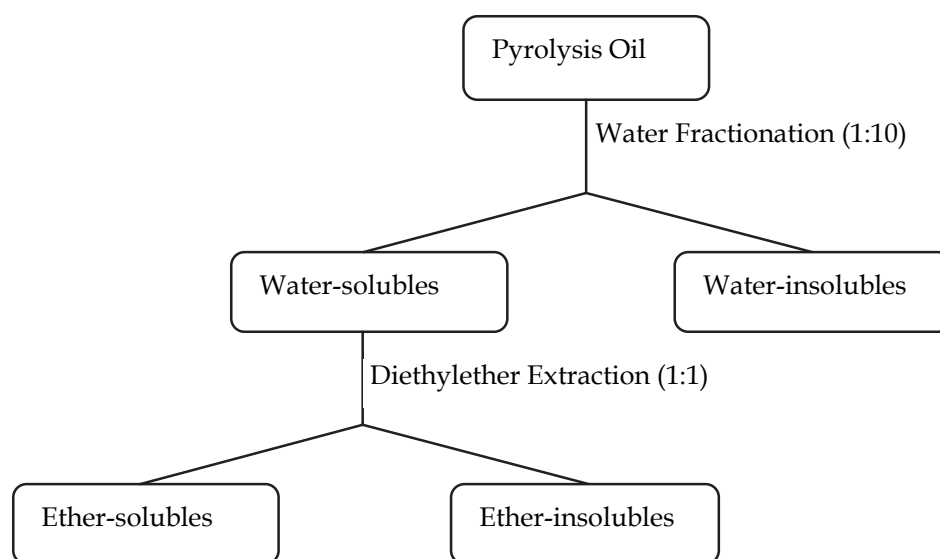


Fig. 4. Fractionation scheme of bio-oil (Sipila, et al., 1998)

There are many substances that can be extracted from bio-oil, including a range of flavourings and essences for the food industry (A. V. Bridgwater, et al., 1999b).

### 2.3.7 Column chromatography

The composition of the bio-oil is complex and a lot of material properties are similar among them. Thus, it is unrealistic to separate all kinds of fractions by conventional methods such as distillation and extraction. Nevertheless, column chromatography, as a new separation technology, can satisfy the high sensitivity requirement needed by the bio-oil separation. For instance, phthalate esters, which is considered as toxic material to human and being wife, can be separated from bio-oil by the way of column chromatography (Zeng, et al., 2011).

## 3. Characterization of bio-oil

As well known, the material property depends on its structure and constitute. Bio-oil has poor properties due to the complexity of composition, which causes the limitation of application range. In order to understand the properties and composition of bio-oil so as to use effectively, it's necessary to carry on characterization to bio-oil.

### 3.1 Physiochemical properties

The bio-oil from biomass is typically a dark-brown liquid with a pungent odour, and the physiochemical properties of the bio-oil are different from conventional fossil fuels. The mainly physiochemical properties contain components, heating value, water content, density, flash point, and so on.

#### 3.1.1 Components

The components of bio-oil are complicated, comprising mainly water, acids, alcohols, aldehydes, esters, ketones, sugars, phenols, phenol derivatives, lignin-derived substances, and so on. The complexity of the bio-oil itself results in the difficult to analyze and characterize (Wildschut, 2009). Gas chromatography-mass spectrometry (GC-MS) has been the technique most widely used in the analyses of the component (Sipila, et al., 1998). The major components of one kind of crude bio-oil based on the GC-MS analyses are shown in Table 4.

Main components	RT/min	Area w/%
formaldehyde	1.42	3.14
aldehyde	1.51	6.52
hydroxyacetaldehyde	1.61	3.14
hydroxypropanone	1.72	2.70
butyric acid	1.82	0.96
acetic acid	2.07	29.76
glyceraldehyde	2.6	3.54
3,4-dihydroxy-dihydro-furan-2-one	2.77	3.27
2,2-dimethoxy-ethanol	2.86	6.83
furfural	3.13	6.56
2,5-dimethoxy-tetrahydro-furan	3.5	3.47
4-hydroxy-butyric acid	4.27	0.43
5H-furan-2-one	4.51	0.74
2,3-dimethyl-cyclohexanol	4.76	1.31
3-methyl-5H-furan-2-one	5.19	0.38
corylon	6.15	1.18
phenol	6.59	1.57
o-cresol	6.8	1.12
m-cresol	7	1.46
2-methoxy-6-methyl-phenol	7.79	1.78
3,4-dimethyl-phenol	8.99	1.14
4-ethyl-phenol	9.7	1.31
3-(2-hydroxy-phenyl)-acrylic acid	10.1	1.53
catechol	10.81	3.53
3-methyl-catechol	11.9	1.36
vanillin	12.7	0.24
4-ethyl-catechol	12.86	0.71
levoglucosan	14.73	9.95
2,3,4-trimethoxy-benzaldehyde	15.5	0.20
3-(4-hydroxy-2-methoxy-phenyl)-propenal	15.8	0.15

Table 4. Components of crude biomass oil (Hu, et al., 2011a)

### 3.1.2 Heating Value

The standard measurement of the energy content of a fuel is its heating value (HV). HV is divided into lower heating value (LHV) and higher heating value (HHV) depending on the water produced through hydrogen in vapour or liquid phase. Heating value can be determined by the oxygen-bomb calorimeter method (Demirbas, 2009).

The heating value of the pyrolysis oils is affected by the composition of the oil (Sipila, et al., 1998). At present, HHV of bio-oil can be determined directly according to DIN 51900 by the oxygen-bomb calorimeter. In addition, the HHV of the bio-oil is also calculated using the following formula (Milne, et al., 1990).

$$\text{HHV} = 338.2 \times C + 1442.8 \times \left( H - \frac{O}{8} \right) \quad (\text{MJ/kg}) \quad (1)$$

The LHV can be determined by the HHV and the total weight percent of hydrogen (from elemental analysis) in the bio-oil according to the formula (Oasmaa, et al., 1997) as shown below.

$$\text{LHV} = \text{HHV} - 218.3 \times H\% \text{ (wt\%)} \quad (\text{KJ/kg}) \quad (2)$$

Bio-oil is of a lower heating value (15 - 20 MJ/kg), compared to the conventional fossil oil (41 - 43 MJ/kg) (A.V. Bridgwater, et al., 1999a; Wildschut, et al., 2009). That is to say that the energy density of bio-oil is only about half of the fossil oil, which is attributed to the higher water and oxygen contents. In order to improve the heating value of bio-oil so that it can be used in the engine, it is necessary to reduce the contents of water and oxygen by the way of upgrading, as described above.

### 3.1.3 Water content

The water content in the bio-oil is analyzed by Karl-Fischer titration according to ASTM D 1744. The sample solvent is a mixture of chloroform and methanol (3:1 v/v) (Sipila, et al., 1998), because this solvent can dissolve almost all of the component of bio-oil. In the process of experiment, a small amount of bio-oil (0.03-0.05g) was added to an isolated glass chamber containing Karl Fischer solvent. The titrations were carried out using the Karl Fischer titrant (Wildschut, et al., 2009).

The existence of water in the bio-oil is unavoidable, which is due to moisture in the raw material. In general, the water content of bio-oil is usually in the range of 30-35 wt% (Radlein, 2002), and it is hard to remove from bio-oil resulting from the certain solubility of bio-oil and water. The existence of water has both negative and positive effects on the storage and utilization of bio-oils. On the one hand, it will lessen heating values in combustion, and may cause phase separation in storage. On the other hand, it is beneficial to reduce viscosity and facilitate atomization (Lu, et al., 2009).

### 3.1.4 Oxygen content

The elemental compositions of the oils (C, H, O and N) can be determined using a CHN-S analyzer according to ASTM D 5373-93. The oxygen content will be calculated by difference (Wildschut, et al., 2009).

The oxygen content of the bio-oil varies in the range of 35-40% (Oasmaa & Czernik, 1999). The presence of high oxygen content is regarded as the biggest differences between bio-oil and

fossil oil, that's because it lead some bad properties, such as corrosiveness, viscosity, low energy density, thermal instability, and so on (Elliott, et al., 2009). Of course, a certain amount of oxygen in the fuel is beneficial to improve combustion sufficiency. However, it is imperative to removal of oxygen in the bio-oil through hydrodeoxygenation (HDO) and reduction of the oxygen content below 10 wt% by a catalytic hydrotreatment reactions is possible under severe conditions (Wildschut, et al., 2009).

### 3.1.5 Density

Density can be measured at 15°C using picnometer by ASTM D 4052 (Sipila, et al., 1998). The density of bio-oil is usually in the range of 1.1-1.3kg/m<sup>3</sup>, which is depending on the raw materials and pyrolysis conditions. The density of bio-oil is larger than the gasoline and diesel because of the presence of a large number of water and macromolecule such as cellulose, hemicelluloses, oligomeric phenolic compounds (Oasmaa & Czernik, 1999), and so on.

### 3.1.6 Ash

Ash is the residue of bio-oil after its combustion, and the ash can be determined according to ASTM D 482. The ash of bio-oil is usually vary in 0.004-0.03 wt% (Oasmaa & Czernik, 1999), which is also relevant to the raw materials and reaction conditions. In general, the ash content is higher for the straw oil than for other oils due to their originally higher amounts in straw than in wood (Sipila, et al., 1998).

The presence of ash in bio-oil can cause erosion, corrosion and kicking problems in the engines and the valves (Q. Zhang, et al., 2007). However, there is no effective way to reduce the content of ash by now.

### 3.1.7 Mechanical impurities

The mechanical impurities are measure as ethanol insolubles retained by a filter after several washings and vacuum-drying (Sipila, et al., 1998). Generally, the presence of mechanical impurities cannot avoid in the preparation process of the bio-oil. Mechanical impurities mainly contain pyrolysis char, fine sand, materials used in the reactor, and precipitates formed during storage (Oasmaa & Czernik, 1999).

The content of mechanical impurities in different oils are usually varies in 0.01 to 3 wt% with the particle sizes of 1-200 μm (Oasmaa, et al., 1997). The presence of mechanical impurities is harmful to the storage and combustion of bio-oil, resulting in agglomerate and viscosity increases (Lu, et al., 2009). The most economical and efficient method to reduce the content of mechanical impurities would be filtration.

### 3.1.8 Flash point

The flash point of a volatile liquid is the lowest temperature at which it can vaporize to form an ignitable mixture in air. Flash point is measured using a flash-point analyzer according to ASTM D 93. The test temperature is usually employ increase of 5.5°C/min in the range of 30-80°C (Wildschut, et al., 2009).

Flash point is influenced by the raw materials and preparation method, because of these will result in the differences in composition and content of the bio-oil from biomass. In general, the bio-oils from hardwood have a high flash point due to the low contents of methanol and evaporation residue of ether soluble (Sipila, et al., 1998).



### 3.1.9 pH

The bio-oil has amount of diluted water and volatile acids, such as acetic and formic acid, which results in the low pH values varied in 2-3. The presence of acids in the bio-oil is the main reason to account for the property of corrosion to materials in the storage and application processes. Therefore, it requires upgrading to fulfil the requirement of fuels before application through upgrading processes.

### 3.2 Combustion property

Combustion is the oxidation of the fuel at elevated temperatures, and accompanied by the production of heat and conversion of chemical species.

As a kind of clean and renewable energy, bio-oil has a potential to be used as a conventional fossil fuel substitute. However, the usage of bio-oil has been limited due to some problems during its use in standard equipment constructed for combustion petroleum-derived fuels (Czernik & Bridgwater, 2004). Bio-oil has the low heating values (leading low flame temperature) (Demirbas, 2005) and high water content, which is harmful for ignition. Furthermore, organic acids in the bio-oil are highly corrosive to common construction materials. In addition, the present of solid, high viscosity, coking are also the primary challenge in the process of combustion (Yaman, 2004). Of course, bio-oil has some important advantages such as effectively volatility and combustibility. In the combustion applications, biomass has been fired directly either alone or along with a primary fuel such as diesel, methanol, ethanol, and so on (Demirbas, 2004).

The combustion properties of the bio-oil can be tested by the biomass fuels combustion system, which consists of a droplet generator, a laminar flow reactor, and a video imaging system (Wornat, et al., 1994). The device can observe the combustion behaviors of bio-oil droplets directly. The tests can be performed both a fibre-suspended single droplet and a stream of freefalling mono-dispersed droplets (Lu, et al., 2009).

In the present chapter, we will introduce the combustion property of the bio-oil in standard equipment such as boilers, diesel engines, and gas turbines.

#### 3.2.1 Combustion in boiler

Boiler is a common device used for generate heat and power through burning fuels such as wood, coal, oil, and natural gas. The source of combustion materials for boiler is widespread, but the fuel combustion efficiency is usually less than engines and turbines. It is suitable for bio-oil used in boiler instead of conventional fossil fuel and coal, etc (Czernik & Bridgwater, 2004). Though it is difficult to ignite for bio-oil due to the high content of water, it can burn steadily once ignited, and the observed flame lengths with pyrolysis oils are similar to those of conventional fuel oils (Shaddix & Hardesty, 1999).

The ignition of bio-oil is the key to the combustion in boiler. Some modifications of the existing burner and boiler are better effective method to improve its ignitability and combustion stability. The boiler can be designed in a dual fuel mode, hence the bio-oil can be co-fired with petroleum fuel at different ratios (Gust, 1997).

Emissions of  $\text{NO}_x$  and  $\text{SO}_x$  from boilers firing bio-oil are lower than those from residual fuel oil, but emissions of particulate (soot, carbonaceous cenospheres, and ash) are higher from bio-oil resulting from the high content of ash and incomplete combustion of the oil. Generally, Emissions of  $\text{NO}_x$  and carbon monoxide (CO) from combustion of bio-oil vary in 140-300ppm and 30-50ppm respectively, which are all at acceptable levels (Shaddix & Hardesty, 1999).



### 3.2.2 Combustion in diesel engine

The diesel engine has the highest thermal efficiency (up to 45%) of any regular internal or external combustion engine due to its very high compression ratio, of course it report a high demand for the fuel quality.

VTT (Technical Research Centre of Finland) investigated the combustion performance of bio-oil in the diesel engine (4.8kW, single-cylinder, high-speed) (Solantausta, et al., 1994). The results showed that bio-oil was not suitable for a conventional diesel engine and produced many problems because of the specific properties. For one thing, bio-oil could not auto-ignition without additives (nitrated alcohol) and it also needs a pilot injection system. For another thing, an amount of coke formed in the process of combustion of bio-oil, which resulting in the periodic clogging of the fuel injector. In addition, severe material wear occurred, which is considered as difficult to avert.

A detailed investigation ignition delay and combustion behavior has been carried out by MIT by comparing with the performance of two bio-oils and No.2 diesel fuel in a direct injection engine (Shihadeh & Hochgreb, 2000). The bio-oil exhibited longer ignition delays due to the relatively slow chemistry process to the diesel fuel.

In recently, more researches about the combustion of bio-oil have been reported, including erosion-corrosion problems to standard materials in UK (A. V. Bridgwater, et al., 2002), selection of optimum operating characteristics (A. V. Bridgwater, et al., 2002; Leech, 1997; Ormrod & Webster, 2000), tests on emulsions of bio-oil in diesel fuel used in different engines (Baglioni, et al., 2001; D. Chiaramonti, et al., 2003), and so on.

### 3.2.3 Combustion in gas turbine

A gas turbine, also called a combustion turbine, is a rotary engine that produces energy via the flowing combustion gas. Gas turbine is widely used in various aspects, most important of which are driving electric power generators and providing power to aircraft (Czernik & Bridgwater, 2004).

Combustion of bio-oil in has been demonstrated in a 2.5 MWe industrial gas turbine (J69-T-29) at Teledyne CAE (USA) as early as 1980s (Kasper, et al., 1983). The combustion system of the J69 consists of an annular combustor and a centrifugal fuel injector rotating as shaft speed. The test results show that the combustion efficiency of the bio-oil in this gas turbine is over 99%.

The first industrial application of bio-oil in gas turbines combustion was carried out in the year of 1995 (Andrews, et al., 1997; Andrews & Patnaik, 1996). The researchers used a 2.5MWe class-GT2500 turbine engine, which was designed and built by Mashproekt in Ukraine. The fuel of GT2500 turbine is diesel oil rather than its standard fuel (kerosene), and the gas turbine a "silo" type combustion chamber, which can be modified more easily. The results about atomization tests show that both water and bio-oil can generate a wider cone angle than diesel oil, this is because diesel oil has lower viscosity and surface tension and the interaction between primary and secondary flows (David Chiaramonti, et al., 2007).

### 3.3 Corrosion property

Bio-oil obtained by the fast pyrolysis of straw is an acidic fuel with pH of 3.4–3.5. It contains a large amount of organic acids, phenol and water. For this reason, biomass oils will strongly corrode aluminium, mild steel and nickel based materials, whereas stainless steel, cobalt based materials, brass and various plastics are much more resistant (Oasmaa, et al., 1997).

The corrosion extent of the metal can be determined by the weight increase and variations on the metal surface, which can be analyzed by optical micrography and X-ray photoelectron spectroscopy (XPS). Generally, the corrosion performance of metals are sensitive to materials, temperature condition and bio-oil property. The corrosion in bio-oil of four kinds of metals used frequently in engines (including iron, lead, steel and copper) is studied at different temperatures and for different test durations using a simulation corrosion evaluation apparatus (Figure 5) for internal combustion engine fuel (Hu, et al., 2011b). The results of mass variation rates of four metals at different temperature are summarised in Table 5.

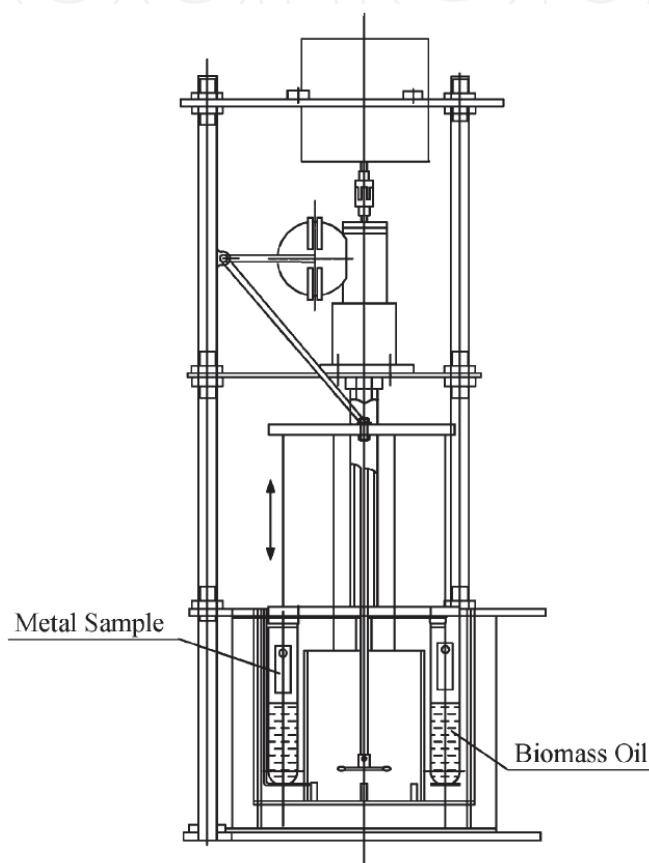


Fig. 5. Schematic diagram of corrosion test apparatus, metal strip was dipped intermittently with frequency of 15 per min (Hu, et al., 2011b)

Metal	25°C		40°C		55°C	
	5h	10h	5h	10h	5h	10h
Iron	10.25	19.89	11.15	21.64	11.81	25.60
Lead	7.53	11.23	16.70	17.28	20.35	25.10
Steel	3.27	8.41	6.11	12.43	7.60	12.91
Copper	0.67	1.56	0.78	1.57	1.19	2.19

Table 5. Weight increase of metals at different temperatures and during different exposure times, g/m<sup>2</sup> (Hu, et al., 2011b)

### 3.3.1 Cu strip

Corrosion information can be obtained from the weight increase of the metal strips when immersed in the biomass oil. Study shows that the weight increase for copper was the smallest compared with the other metals, which indicated its best anticorrosive ability (Hu, et al., 2011b). The chemisorption of oxygen and other gases in the atmosphere will initially increase the weight of the strips. Furthermore, after contacting with biomass oil, some corrosion products, such as  $\text{Cu}_2\text{O}$  and  $\text{CuO}$ , are formed on the surface of the metals. These cannot be removed washed by physical methods and result in an increase in weight of the samples. In the case of copper, these corrosion layers do not prevent the underlying metals from further corrosion. However, the corrosion of copper will become slow because of its noble character (Darmstadt, et al., 2004).

### 3.3.2 Stainless steel

Stainless steel has anti-corrosion ability like Cu strip due to the presence of Cr, which is the mainly anti-corrosion element in the stainless steel. For AISI 1045 steel, the corrosion volumes increased with corrosion time and temperatures. After corrosion, layers of oxide and/or hydroxide are formed on the metal surface. X-ray photoelectron spectroscopy (XPS) results show the presence of  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$ , which are mainly corrosion products. However, these layers cannot protect the metal from further oxidation (Hu, et al., 2011b). For austenitic steel (SS 316), it is not causes corrosion in the experiment condition, which is mainly attribute to the formation of chromium oxide layer that prevents further oxidation (Darmstadt, et al., 2004). Consequently, the stainless steel can be taken into consideration in the selection of construction materials for pyrolysis units and diesel engine.

### 3.3.3 Lead

The bio-oil corrosiveness to lead is especially severe compared with stainless steel and copper. A significant weight variation was found for lead, which increased with temperature. When lead comes into contact with bio-oil, oxide and/or hydroxide layers are formed on the metal surface. The chief components in this layer are  $\text{PbO}$  and  $\text{Pb}(\text{OH})_2$ . However, this layer did not protect the underlying metal against further oxidation though the oxide layer is relatively thick (Hu, et al., 2011b).

### 3.3.4 Iron

Bio-oil is very corrosive to iron compared with stainless steel, which is essentially noncorrosive. There is a oxide layer as the same as stainless steel even the same components ( $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$ ). However, XPS results show that the corrosion product on the steel surface was thicker than on iron (no signal for metallic iron from the substrate). Likewise, the layer cannot protect the metal from further oxidation (Hu, et al., 2011b).

## 3.4 Tribological performance

As a new type energy fuel, bio-oil is mainly used for combustion heating equipment such as industrial furnace, gas turbine, diesel engine, and so on. However, bio-oil will be able to lead higher friction and wear to the oil pipeline and nozzle in the process of injection, which has very serious effect to the stable combustion even safety performance (Wang, et al., 2008). Therefore, it is necessary to learn about bio-oil tribological properties and its mechanism.

### 3.4.1 Friction efficiency

Generally, the four-ball tribometer is used to study the tribological performances of bio-oil to obtain friction coefficient, and the wear scar diameter can be measured by digital microscope. Xu et al. studied the tribological performance and explained the lubrication mechanism of the straw based bio-fuel by four-ball tribometer at 1450rpm (Y. Xu, et al., 2007). The experimental results showed that the extreme pressure of the bio-fuel was up to 392 N, and the extreme pressure of diesel oil was 333 N. These results indicated that the straw based bio-oil has a potential lubrication performance than the diesel oil.

The friction coefficient of straw-based bio-oil under different loads suggested that it increased with load (Figure 6), which may be result from the real contact surface distortion increased with the load. The frictional coefficient of bio-oil are varied in 0.08 and 0.11 between 196N and 294N. The wear scar diameter on the ball surface increased with load slowly in 30min (Figure 7).

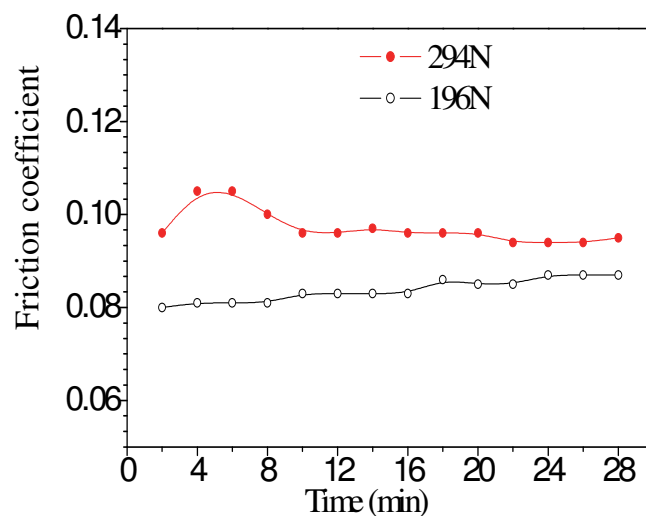


Fig. 6. Variations of friction coefficient of bio-fuel with test duration under different loads (Y. Xu, et al., 2007)

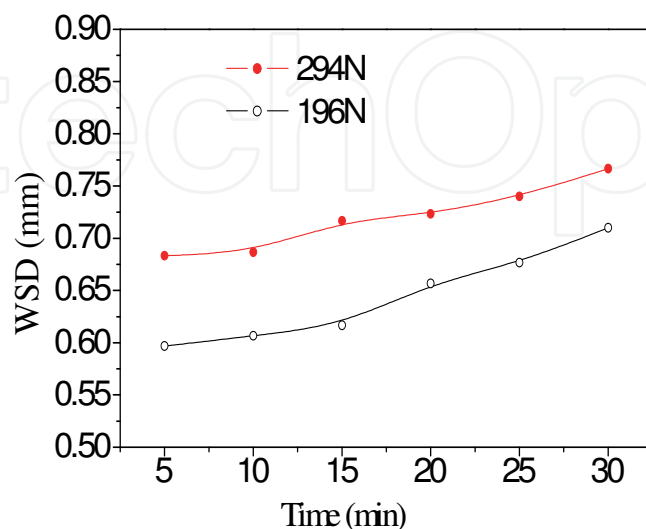


Fig. 7. Variations of wear scar diameter of bio-fuel with test (Y. Xu, et al., 2007)

### 3.4.2 Wear volume/weight

The weight loss of bio-oil during the process of use can be analyzed by thermo-gravimetric analyze (TGA). In case of used bio-fuel, its weight loss reduced 11% when the temperature was over 530°C compared with that of fresh bio-oil, because some compounds in bio-oil may reacted during the friction process(Figure 8). (Y. Xu, et al., 2007)

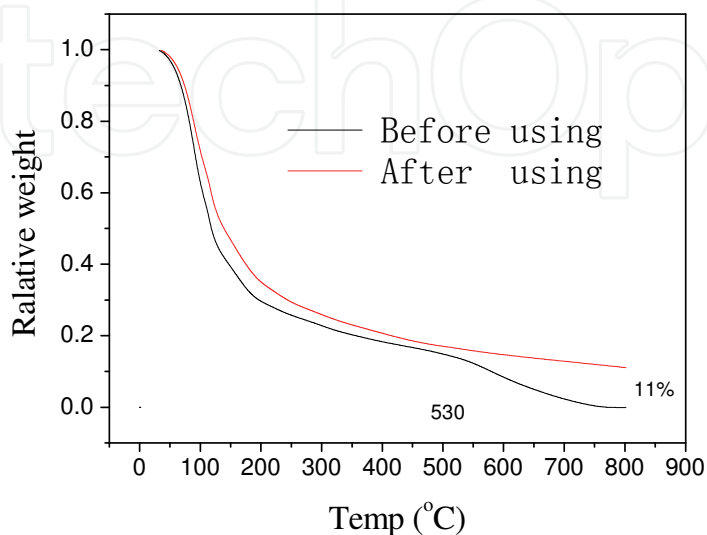


Fig. 8. TGA curves of bio-fuel before and after (Y. Xu, et al., 2007)

### 3.4.3 Lubricity

As well known, the alternative fuel from biomass cannot be used well in internal combustion engine because of the serious lubrication (Y. Xu, et al., 2007). However, using emulsion technology to mixing bio-oil with diesel is one of the most convenient approaches to use bio-oil reasonable (Ikura, et al., 2003; Qi, et al., 2008).

Xu et al. investigated the lubricity of the bio-oil/diesel emulsion by high frequency reciprocating test rig (Figure 9) (Y. Xu, et al., 2010; Y. Xu, et al., 2009). Table 6 showed that the average friction coefficient of the emulsified bio-oil was 0.130, which was lower than commercial diesel number zero (0.164). This result indicated that the emulsified bio-oil had better lubricity properties than commercial diesel number zero.

Item	Diesel	Emulsified bio-oil
Average friction coefficient	0.164	0.130
Corrected wear scar diameter/ $\mu\text{m}$	226	284

Table 6. Comparison of friction coefficient and wear resistance between emulsified bio-oil and diesel (Y. Xu, et al., 2010)

The lubrication mechanism of emulsified bio-oil could be attributed to the polar groups and oxygenic compounds. The interaction between them caused the tiny liquid drops deposit on the surface of friction, which generated frictional chemical reaction and led to the better boundary lubrication. However, the existence of oxygen might accelerate the corrosion wear on the rubbing surface.

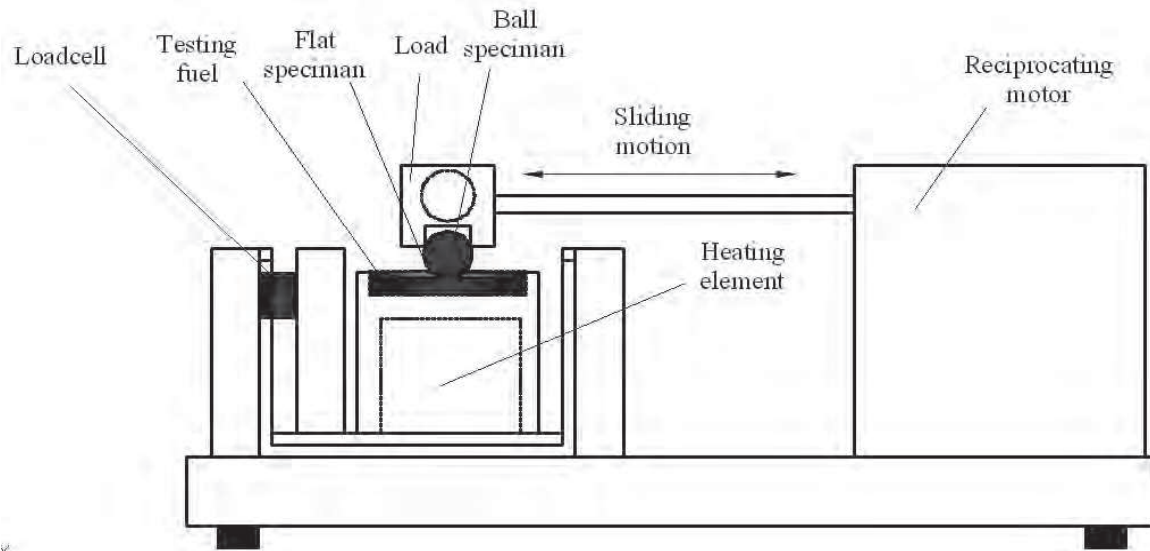


Fig. 9. Schematic diagram of lubricity test by high frequency reciprocating test rig (Y. Xu, et al., 2010)

Hu et al. studied the tribological performance of distilled biomass oil from rice straw by pyrolysis process in a four-ball tribometer. The results showed that the refined biomass oil had certain anti-wear and friction-reducing properties (Hu, et al., 2008b).

### 3.5 Biodegradability

As the production expanding constantly, bio-oil also caused environmental problems like as fossil fuels. In production, transportation, storage and application processes, bio-oil will destroy local ecological environment if it emissions into the soil and water as a result of the accident or improper management (Hu, et al., 2008a).

Generally, the methods which control oil pollution can be divided into three kinds: physical, chemical, and biological; the former two methods are very expensive and treatment is not completely or cause secondary pollution. However, biological method is economic, efficient and the final product is carbon dioxide and water, without any secondary pollution (Fu, et al., 2009). A mass of research indicate that biological degradation plays an important role in the purification of the oil pollution, but the microbial degradation ability itself restricts the oil pollutant further degradation (Pelletier, et al., 2004).

#### 3.5.1 Degradation properties in soil

The degradation rate of the bio-oil in the soil is responsive to microorganism, temperature, oil content, pH, etc (Hu, et al., 2008a). Hu et al. gained a strain of bio-oil degrading mold (a kind of *Aspergill versicoir*, named as EL5) through enrichment, separation and purification from sludge collected from a paper mill. The yield of CO<sub>2</sub> was taken as degradation test index. The results showed that the degradation speed of bio-oil was positively correlated to the temperature and negatively correlated to substrate concentration. The degradation rate of the bio-oil in the soil can reach 40% in the suitable temperature (30°C) and neutral pH, compared with only 6% under the same conditions without degrading mold (Hu, et al., 2008a).



### 3.5.2 Degradation properties in aquatic environment

As the degradation of bio-oil in the soil, the degradation rate of the bio-oil in the aquatic environment is also responsive to microorganism, temperature, oil content, pH, etc. During the acclimation, the biodegradation process of bio-oil is accorded approximately with the first-order reaction by the way of Sturm method which is described by measuring CO<sub>2</sub> volume from the microbes' production (Fu, et al., 2009). A schematic diagram of biodegradation experiment is shown in Figure 10. The whole device was carried out under aerobic conditions. The biodegradation ability could be improved in aqueous culture under neutral and acidic conditions. The optimal temperature for biodegradation of bio-oil is 40°C. The optimal inocula content for the biodegradation of bio-oil was 16%.

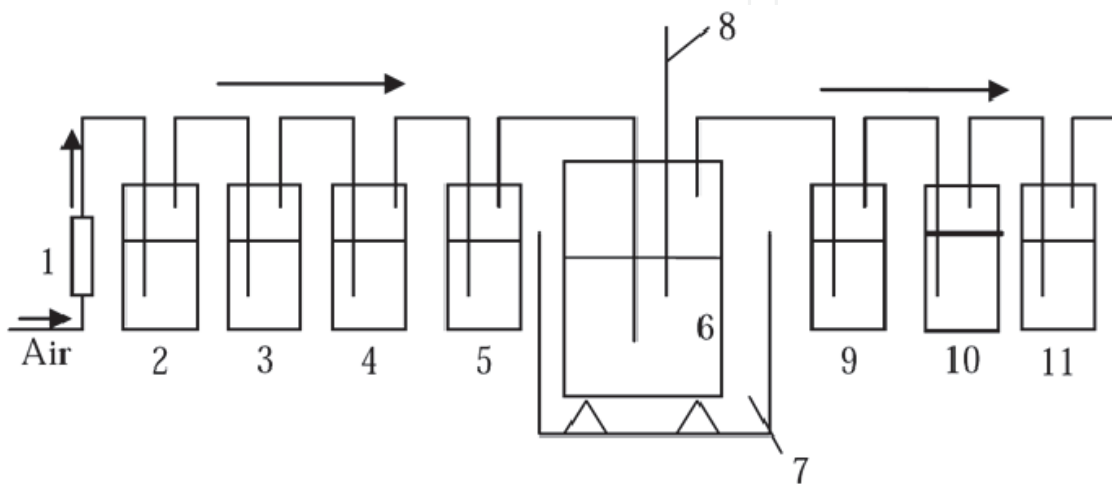


Fig. 10. Schematic diagram of biodegradation experiment

Notes: 1. Flow meter; 2-4. Three bottles for absorbing CO<sub>2</sub> from atmosphere; 5. Bottle for testing the absorbency; 6. Bioreactor; 7. Constant temperature water bath; 8. Thermometer; 9-11. Three bottles for absorbing CO<sub>2</sub> from biodegradation (Fu, et al., 2009)

Blin investigated the biodegradation properties of various pyrolysis oils and EN 590 diesel sample in the Modified Sturm (OECD 301B). The results showed that various bio-oils degraded 41-50% after 28 days, whereas the diesel only has 24% biodegradation. The biodegradation model of bio-oil can be very well described by a first-order kinetic equation (Blin, et al., 2007).

## 4. Conclusions

This chapter reviewed the preparation methods and characterization of the bio-oil. The bio-oil showed the promising prospects as an alternative renewable energy sources to replace the fossil fuel. However, the bio-oil has high acid value, high oxygen, and low heating values compared with the commercial diesel fuel. It is urgent to investigate the thermochemical conversion mechanism of the biomass. What's more, the more effective upgrading methods should be carried out the raw bio-oil because of these disadvantages. The properties such as basic physiochemical property, combustion, corrosion, lubricity and biodegradability of the bio-oil from biomass were also discussed. Furthermore, the chemical components and the quality standard of the bio-oil was needed to be established as soon as possible in order to accelerate the development and application of the bio-oil.

## 5. Acknowledgements

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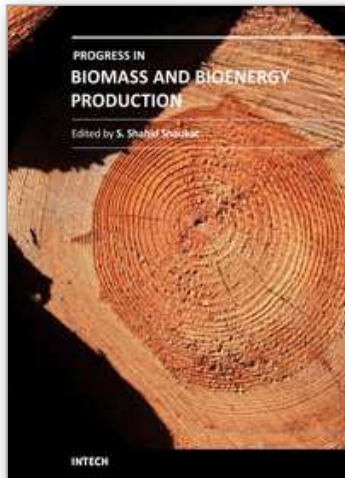


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## **Progress in Biomass and Bioenergy Production**

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Alternative energy sources have become a hot topic in recent years. The supply of fossil fuel, which provides about 95 percent of total energy demand today, will eventually run out in a few decades. By contrast, biomass and biofuel have the potential to become one of the major global primary energy source along with other alternate energy sources in the years to come. A wide variety of biomass conversion options with different performance characteristics exists. The goal of this book is to provide the readers with current state of art about biomass and bioenergy production and some other environmental technologies such as Wastewater treatment, Biosorption and Bio-economics. Organized around providing recent methodology, current state of modelling and techniques of parameter estimation in gasification process are presented at length. As such, this volume can be used by undergraduate and graduate students as a reference book and by the researchers and environmental engineers for reviewing the current state of knowledge on biomass and bioenergy production, biosorption and wastewater treatment.

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