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# High-Efficiency Separation of Bio-Oil

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## 1. Introduction

### 1.1. What is fast pyrolysis?

Biomass is a CO<sub>2</sub>-neutral energy source that has considerable reserve. It can replace fossil feedstock in the production of heat, electricity, transportation fuels, chemicals, and various materials. Liquid bio-fuels, which are considered to be substitutes for traditional petrol liquid fuels, can be produced from biomass in different ways, such as high-pressure liquefaction, hydrothermal pyrolysis, and fast pyrolysis.

Fast pyrolysis is a technology that can efficiently convert biomass feedstock into liquid biofuels. The liquid obtained from fast pyrolysis, which is also called crude bio-oil, may be used as burning oil in boilers or even as a transportation fuel after upgrading. Fast pyrolysis is a process in which lignocellulosic molecules of biomass are rapidly decomposed to short-chain molecules in the absence of oxygen. Under conditions of high heating rate, short residence time, and moderate pyrolysis temperature, pyrolysis vapor and some char are generated. After condensation of the pyrolysis vapor, liquid product can be collected in a yield of up to 70 wt% on a dry weight basis (Bridgwater et al., 1999; Lu et al., 2009). The obvious advantages of the process are as follows:

1. Low-grade biomass feedstock can be transformed into liquid biofuels with relatively higher heating value, thus making storage and transportation more convenient.
2. The by-products are char and gas, which can be used to provide the heat required in the process or be collected for sale.
3. For waste treatment, fast pyrolysis offers a method that can avoid hazards such as heavy metal elements in the char and reduce pollution of the environment.

Many researchers have focused on the techniques of fast pyrolysis, and various configurations of reactor have been developed to satisfy the requirements of high heating rate, moderate reaction temperature, and short vapor residence time for maximizing bio-oil production. During the past decades, many types of reactor have been designed to promote

the large-scale and commercial utilization of biomass fast pyrolysis, such as the fluidized bed reactor (Luo et al., 2004; Wang et al., 2002), the ablative reactor (Peacocke & Bridgwater, 1994), the rotating cone reactor (Muggen, 2010; Peacocke; Wagenaar, 1994) and Vacuum reactor (Bridgwater, 1999; Yang et al., 2001).

## 1.2. The composition and properties of bio-oil

The chemical composition of bio-oil is significantly different from that of petroleum fuels. It consists of different compounds derived from decomposition reactions of cellulose, hemicellulose, and lignin. The chemical composition of bio-oil varies depending on the type of biomass feedstock and the operating parameters. Generally speaking, bio-oil is a mixture of water and complex oxygen-rich organic compounds, including almost all such kinds of organic compounds, that is, alcohols, organic acids, ethers, esters, aldehydes, ketones, phenols, etc. Normally, the component distribution of bio-oil may be measured by GC-MS analysis.

Crude bio-oil derived from lignocellulose is a dark-brown, viscous, yet free-flowing liquid with a pungent odor. Crude bio-oil has an oxygen content of 30–50 wt%, resulting in instability and a low heating value (Oasmaa & C., 2001). The water content of bio-oil ranges from 15 to 50 wt%. The high water content of bio-oil derives from water in the feedstock and dehydration reactions during biomass pyrolysis (Bridgwater, 2012). Heating value is an important indicator for fuel oils. The heating value of bio-oil is usually lower than 20 MJ/kg, much lower than that of fuel oil. The high water content and oxygen content are two factors responsible for its low heating value. The density of bio-oil derived from fast pyrolysis is within the range 1100–1300 kg/m<sup>3</sup> (Adjaye et al., 1992). The pH value of bio-oil is usually in the range 2–3 owing to the presence of carboxylic acids such as formic acid and acetic acid. The strong acidity can corrode pipework and burner components. Measurements of the corrosiveness of bio-oil have shown that it can induce an apparent mass loss of carbon steel and the breakdown of a diesel engine burner (Wright et al., 2010).

Fresh bio-oil is a homogeneous liquid containing a certain amount of solid particles. After long-term storage, it may separate into two layers and heavy components may be deposited at the bottom. As mentioned above, the high content of oxygen and volatile organic compounds are conducive to the ageing problems of bio-oil. The aldol condensation of aldehydes and alcohols and self-aggregation of aldehydes to oligomers are two of the most likely reactions to take place. Coke and inorganic components in the bio-oil may also have a catalytic effect, thereby enhancing the ageing process (Rick & Vix, 1991).

## 1.3. The utilization of bio-oil

The oxygenated compounds in bio-oil can lead to several problems in its direct combustion, such as instability, low heating value, and high corrosiveness. Although higher water content can improve the flow properties and reduce NO<sub>x</sub> emissions in the fuel combustion process, it causes many more problems. It not only decreases the heating value of the fuel, but also increases the corrosion of the combustor and can result in flame-out. The low pH

value of bio-oil also aggravates corrosiveness problems, which may lead to higher storage and transportation costs. Many researchers have tested the combustion of bio-oil in gas boiler systems, diesel engines, and gas turbines (Czernik & Bridgwater, 2004).

Fresh bio-oil from different feedstocks can generally achieve stable combustion in a boiler system. One problem, however, is the difficulty of ignition. The high water content of bio-oil not only decreases its heating value, but also consumes a large amount of latent heat of vaporization (Bridgwater & Cottam, 1992). Thus, the direct ignition of bio-oil in a cold furnace is not easy, and an external energy source is needed for ignition and pre-heating of the furnace. The combustion of bio-oil in diesel engines is more challenging. Its long ignition delay time, short burn duration, and lower peak heat release have limited its combustion properties (Vitolo & Ghetti, 1994). Experiments employing bio-oil in gas turbines have proved largely unsuccessful. The high viscosity and high ash content of bio-oil result in severe blocking and attrition problems in the injection system. Moreover, acid in the bio-oil is harmful to the mechanical components of the gas turbine.

Even though many combustion tests of bio-oil have shown its combustion performances to be inferior to those of fossil fuels, the environmental advantages of bio-oil utilization cannot be ignored. Comparative tests have shown that the SO<sub>2</sub> emissions from bio-oil combustion are much lower than those from fossil fuel combustion.

Bio-oil is a mixture of many organic chemicals, such as acetic acid, turpentine, methanol, etc. Many compounds in bio-oil are important chemicals, such as phenols used in the resins industry, volatile organic acids used to produce de-icers, levoglucosan, hydroxyacetaldehyde, and some agents applied in the pharmaceutical, synthetic fiber, and fertilizer industries, as well as flavoring agents for food products (Radlein, 1999). Besides, bio-oil can also be used in a process that converts traditional lime into bio-lime (Dynamotive Corporation, 1995).

## **2. Separation of bio-oil for upgrading or refinement**

### **2.1. The importance of separation technology**

Bio-oil cannot be directly applied as a high-grade fuel because of its inferior properties, such as high water and oxygen contents, acidity, and low heating value. Thus, it is necessary to upgrade bio-oil to produce a high-grade liquid fuel that can be used in engines (Bridgwater, 1996; Czernik & Bridgwater, 2004; Mortensen et al., 2011).

In view of its molecular structure and functional groups, and using existing chemical processes for reference, such as hydrodesulfurization, catalytic cracking, and natural gas steam reforming, several generic bio-oil upgrading technologies have been developed, including hydrogenation, cracking, esterification, emulsification, and steam reforming.

Components with unsaturated bonds, such as aldehydes, ketones, and alkenyl compounds, influence the storage stability of bio-oil, and hydrogenation could be used to improve its overall saturation (Yao et al., 2008). Hydrogenation can achieve a degree of deoxygenation

of about 80%, and transform bio-oil into high-quality liquid fuel (Venderbosch et al., 2010; Wildschut et al., 2009). This process requires a high pressure of hydrogen, which increases both the complexity and cost of the operation. Alcohol hydroxyl, carbonyl, and carboxyl groups were easily hydrodeoxygenated, and phenol hydroxyl and ether groups were also reactive, while furans, having a cyclic structure, were more difficult to convert (Furimsky, 2000). After the separation of bio-oil, the components with alcohol hydroxyl, carbonyl, carboxyl, phenol hydroxyl, and ether groups can be efficiently hydrodeoxygenated at a low hydrogen pressure, while the hydrodeoxygenation of more complex components, such as ethers and furans, may be achieved by developing special catalysts.

Catalytic cracking of bio-oil refers to the reaction whereby oxygen is removed in the form of CO, CO<sub>2</sub>, and H<sub>2</sub>O, in the presence of a solid acid catalyst, such as zeolite, yielding a hydrocarbon-rich high-grade liquid fuel. In the process of cracking, oxygenated compounds in bio-oil are thought to undergo initial deoxygenation to form light olefins, which are then cyclized to form aromatics or undergo some other reactions to produce hydrocarbons (Adjaye & Bakhshi, 1995a). Since bio-oil has a relatively low H/C ratio, and dehydration is accompanied by the loss of hydrogen, the H/C ratio of the final product is generally low, and carbon deposits with large aromatic structures tend to be formed, which can lead to deactivation of the catalyst (Guo et al., 2009a). The cracking of crude bio-oil is always terminated in a short time, with a coke yield of about 20% (Adjaye & Bakhshi, 1995b; Vitolo et al., 1999). Alcohols, ketones, and carboxylic acids are efficiently converted into aromatic hydrocarbons, while aldehydes tend to condense to form carbon deposits (Gayubo et al., 2004b). Phenols also show low reactivity and coking occurs readily (Gayubo et al., 2004a). Besides, some thermally sensitive compounds, such as pyrolytic lignin, might undergo aggregation to form a precipitate, which would block the reactor and lead to deactivation of the catalyst. Consequently, efforts have been made to avoid this phenomenon by separating these compounds through thermal pre-treatment (Valle et al., 2010). Therefore, to maintain the stability and high performance of the cracking process, it is necessary to obtain fractions suitable for cracking by separation of bio-oil, to achieve the partial conversion of bio-oil into hydrocarbon fuels.

Bio-oil has a high content of carboxylic acids, so catalytic esterification is used to neutralize these acids. Both solid acid and base catalysts display high activity for the conversion of carboxylic acids into the corresponding esters, and the heating value of the upgraded oil is thereby increased markedly (Zhang et al., 2006). Since this method is more suitable for the transformation of carboxylic acids, which constitute a relatively small proportion of crude bio-oil, an ester fuel with a high heating value can be expected to be produced from the esterification of a fraction enriched with carboxylic acids obtained from the separation.

The emulsion fuel obtained from bio-oil and diesel is homogeneous and stable, and can be burned in existing engines. Research on the production of emulsions from crude bio-oil and diesel suggested that the emulsion produced was more stable than crude bio-oil. Subsequent tests of these emulsions in different diesel engines showed that because of the presence of carboxylic acids, the injector nozzle was corroded, and this corrosion was accelerated by the high-velocity turbulent flow in the spray channels (Chiaramonti et al., 2003a; Chiaramonti et

al., 2003b). Besides corrosion, the high water content of bio-oil will lower the heating value of the emulsion as a fuel, and some high molecular weight components such as sugar oligomers and pyrolytic lignin will increase the density and reduce the volatility of the emulsion. Thus, it is beneficial to study the emulsification of the separated fractions that contain less water and fewer high molecular weight components.

Catalytic steam reforming of bio-oil is also an important upgrading technology for converting it into hydrogen. Research on the steam reforming of acetic acid and ethanol is now comparatively mature, with high conversion of reactants, hydrogen yields, and stability of the catalysts (Hu & Lu, 2007). However, some oxygenated compounds in bio-oil show inferior reforming behavior. Phenol cannot be completely converted even at a high steam-to-carbon ratio, while m-cresol and glucose not only show low reactivity, but are also easily coked (Constantinou et al., 2009; Hu & Lu, 2009). To improve the reforming process, some further investigations of steam reforming based on other separating methods are needed.

Therefore, it is necessary to combine crude bio-oil utilization with the current upgrading technologies. Taking advantage of efficient bio-oil separation to achieve the enrichment of compounds in the same family or the components that are suitable for the same upgrading method is a significant strategy for the future utilization of high-grade bio-oil.

## 2.2. Conventional separation technologies

The efficient separation of bio-oil establishes a solid foundation for its upgrading. Currently, conventional methods for bio-oil separation include column chromatography, solvent extraction, and distillation.

### 2.2.1. Solvent extraction

The solvents for extraction include water, ethyl acetate, paraffins, ethers, ketones, and alkaline solutions. In recent years, some special solvents, such as supercritical CO<sub>2</sub>, have also been used for extraction or other research. By selecting appropriate solvents for extraction of the desired products, good separation of bio-oil can be achieved.

Some researchers have used non-polar solvents for the primary separation of bio-oil, such as toluene and n-hexane, and then proceeded to extract the solvent-insoluble fraction with water; finally, the water-soluble and water-insoluble fractions were further extracted with diethyl ether and dichloromethane, respectively (Garcia-Perez et al., 2007; Oasmaa et al., 2003). A lot of organic solvents are consumed during the process. Considering the cost of these solvents and the difficulty of the recovery process, the operating costs are unacceptable, which hinders its industrialization.

Supercritical fluid extraction is based on the different dissolving abilities of supercritical solvents under different conditions. Supercritical fluid extraction at low temperatures contributes to preventing undesirable reactions of thermally sensitive components. Researchers usually use CO<sub>2</sub> as the supercritical solvent. In a supercritical CO<sub>2</sub> extraction,



compounds of low polarity (aldehydes, ketones, phenols, etc.) are selectively extracted, while acids and water remain in the residue phase (Cui et al., 2010).

### 2.2.2. Column chromatography

The principle of column chromatography is that substances are separated based on their different adsorption capabilities on a stationary phase. In general, highly polar molecules are easily adsorbed on a stationary phase, while weakly polar molecules are not. Thus, the process of column chromatography involves adsorption, desorption, re-adsorption, and re-desorption. Silica gel is commonly used as the stationary phase, and an eluent is selected according to the polarity of the components. Paraffin eluents, such as hexane and pentane, are used to separate aliphatic compounds. Aromatic compounds are usually eluted with benzene or toluene. Some other polar compounds are obtained by elution with methanol or other polar solvents (Ertas & Alma, 2010; Onay et al., 2006; Putun et al., 1999).

### 2.2.3. Distillation

Distillation is a common separating technology in the chemical industry. This method separates the components successively according to their different volatilities, and it is essential for the separation of liquid mixtures. Atmospheric pressure distillation, vacuum distillation, steam distillation, and some other types of distillation have been applied in bio-oil separation.

Due to its complex composition, the boiling of bio-oil starts below 100 °C under atmospheric pressure, and then the distillation continues up to 250–280 °C, whereupon 35–50% of residue is left (Czernik & Bridgwater, 2004).

The thermal sensitivity of bio-oil limits the operating temperature of distillation. In view of the unsatisfactory results obtained by atmospheric pressure distillation, researchers have employed vacuum distillation to lower the boiling points of components, and bio-oil could thereby be separated at a low temperature. Characterization of the distilled organic fraction showed that it had a much better quality than the crude bio-oil, containing little water and fewer oxygenated compounds, and having a higher heating value.

Steam distillation is performed by introducing steam into the distilling vessel, to heat the bio-oil and decrease its viscosity, and finally the volatile components are expelled by the steam. In a study combining steam distillation with reduced pressure distillation, bio-oil was first steam distilled to recover 14.9% of a volatile fraction. The recovered fraction was then further distilled by reduced pressure distillation to recover 16 sub-fractions (Murwanashyaka et al., 2001). In this process, a syringol-containing fraction was separated and syringol with a purity of 92.3% was obtained.

Due to its thermal sensitivity, it is difficult to efficiently separate bio-oil by conventional distillation methods. Molecular distillation seems to offer a potential means of realizing bio-oil separation, because it has the advantages of low operating temperature, short heating time, and high separation efficiency.

### 2.3. Molecular distillation

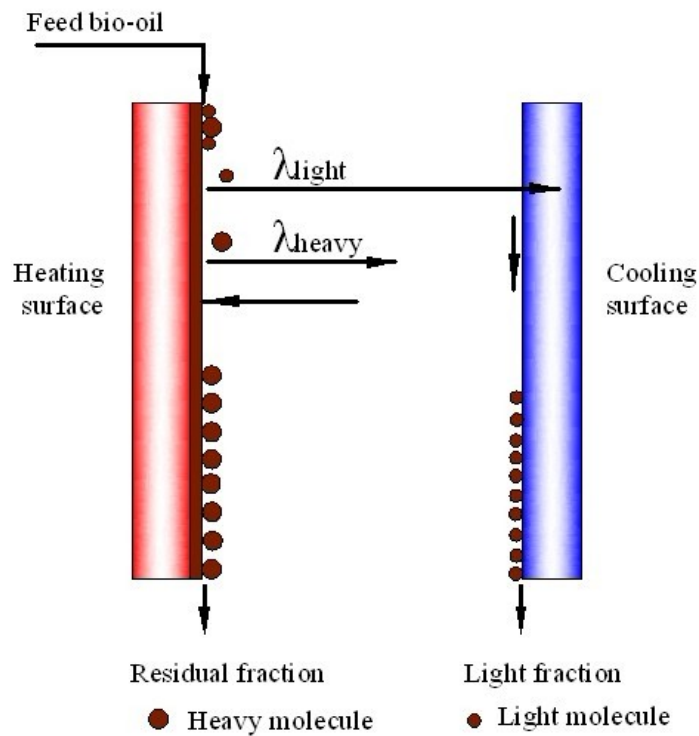
There are forces between molecules, which can be either repulsive or attractive depending on intermolecular spacing. When molecules are close together, the repulsive force is dominant. When molecules are not very close to each other, the forces acting between them are attractive in nature, and there should be no intermolecular forces if the distance between molecules is very large. Since the distances between gas molecules are large, the intermolecular forces are negligible, except when molecules collide with each other. The distance between collisions with another molecule is called its free path.

The mean free path of an ideal gas molecule can be described by Eq. (1):

$$\lambda_m = \frac{k}{\sqrt{2}\pi} \frac{T}{d^2 p} \quad (1)$$

Where  $T$  (°C) is the local temperature;  $\lambda_m$  (m) refers to the mean free path;  $d$  (m) is the effective diameter of the molecule;  $P$  (Pa) is the local pressure; and  $k$  is the Boltzmann constant.

As is apparent from Eq. (1), the molecular mean free path is inversely proportional to the pressure and the square of the effective molecular diameter. Under certain conditions, that is, if the temperature and pressure are fixed, the mean free path is a function of the effective molecular diameter. Apparently, a smaller molecule has a shorter mean free path than a larger molecule. Furthermore, molecular mean free path will increase with increasing temperature or decreasing pressure.



**Figure 1.** Schematic representation of molecular distillation.



Molecules will move more rapidly when the liquid mixture is heated. Surface molecules will overcome intermolecular forces and escape as gas molecules when they obtain sufficient energy. With an increased amount of gas molecules above the liquid surface, some molecules will return to the surface. Under certain conditions, the molecular motion will achieve dynamic equilibrium, which is manifested as equilibrium on a macroscopic scale.

Traditional distillation technology separates components by differences in their boiling points. However, molecular distillation (or short-path distillation) is quite different and precisely relies on the various mean free paths of different substances. As shown in Fig. 1, the distance between the cooling and heating surfaces is less than the mean free path for a light molecule, but greater than that for a heavy molecule. Therefore, the light molecules escaping from the heating surface can easily reach the cooling surface and be condensed. The dynamic balance is thereby broken, and the light molecules are continuously released from the liquid phase. On the contrary, the heavy molecules are not released and return to the liquid phase. In this way, the light and heavy molecules are effectively separated.

Molecular distillation technology has been widely used in the chemical, pharmaceutical, and foodstuff industries, as well as in scientific research to concentrate and purify organic chemicals. It is a feasible process for the separation of thermally unstable materials, taking into account that it only takes a few seconds to complete the separation process. Bio-oil is a complex mixture of many compounds with a wide range of boiling points. It is thermally sensitive and easily undergoes reactions such as decomposition, polymerization, and oxygenation. Additionally, most of the compounds are present in low concentrations. Molecular distillation is not limited by these unfavorable properties and is suitable for the separation of bio-oil to facilitate analysis and quantification of its constituent compounds.

### 3. High-efficiency separation of bio-oil at Zhejiang University

#### 3.1. A molecular distillation apparatus

Fig. 2 shows a KDL-5 wiped-film molecular distillation apparatus used for bio-oil separation research at Zhejiang University, which was manufactured by UIC Corporation in Germany. It consists of four main units, namely a feeding unit, an evaporation unit, a condensation unit, and a reduced pressure unit. The feeding unit mainly comprises a graduated dosing funnel with a double jacket, which is filled with heat-transfer oil to control the temperature and to ensure free flowing of the feedstock. The evaporation unit comprises a cylindrical evaporator with a surface area of 0.048 m<sup>2</sup>, encased in a double jacket containing heat-transfer oil to maintain good temperature homogeneity. It is worth noting that all of the temperatures of these sections are independent. The condensation unit has two cold traps. The first cold trap (or internal condenser) is located in the center of evaporator, and condenses the volatile compounds reaching the cooling surface. There is another cold trap to prevent uncondensed volatile organic compounds from entering the pump. In the reduced pressure unit, the condensation temperature is usually set at −25 °C. The evaporation temperature ranges from room temperature to 250 °C, while the operating pressure can be as low as 5 Pa.



**Figure 2.** KDL-5 molecular distillation apparatus.

The bio-oil used at Zhejiang University was produced from a bench-scale fluidized bed fast pyrolysis reactor (Wang et al., 2008). Crude bio-oil often contains some solid particles, which would abrade the evaporator surface and block the orifice of the dosing funnel, so it is necessary to perform some pre-treatments. Centrifugation and filtration are usually used to remove the solid particles, and traditional reduced pressure distillation can also be used to remove water and volatile compounds. The pre-treated bio-oil is placed in the funnel and then the separation process starts. The volatile components released from the thin liquid film are condensed by the internal condenser to form the distilled fraction, while the heavy compounds that are not vaporized flow along the evaporator surface and are collected as the residual fraction.

Because of the short residence time of the feed material at the evaporation temperature, this gentle distillation process only puts a low thermal load on the materials to be distilled. It is therefore appropriate for the separation of bio-oil, which is thermally unstable.

## 3.2. Single separation process under different operating conditions

### 3.2.1. Physical characteristics of samples

Bio-oil used in the single separation process was produced by the pyrolysis of Mongolian pine sawdust (Wang et al., 2008). Wang et al. (Guo et al., 2009b; Wang et al., 2009) carried out experimental research on molecular separation of the bio-oil, which was pre-treated by centrifugation and filtration to remove solid particles. Molecular distillation of the bio-oil at

50, 70, 100, and 130 °C, respectively, was investigated under a fixed pressure of 60 Pa. Under all of the tested conditions, the light fraction collected by the second condenser placed before vacuum pump was designated as LF, the middle fraction condensed by the internal condenser as MF, and the heavy fraction as HF.

The color of the distilled fractions becomes lighter while the residual fractions become darker. Under the four conditions, water was concentrated in the LFs, which had water contents of about 70 wt%. The LFs could not be burned because of their high water contents. The pH values of the LFs were in the range 2.13–2.17 as a result of their carboxylic acid contents. On the other hand, the HFs had the highest heating values and the lowest water contents, resulting in good ignitability but inferior fluidity. At a distillation temperature of 70 °C, the water content of the MF was as low as 2 wt%. The total mass of the bio-oil distillation fractions amounted to more than 97% of the bio-oil feed. With increasing temperature, the yield of the LF increased without any coking or polymerization problem. Water and volatile carboxylic acids were evaporated from the feedstock in the temperature range 50–130 °C under low pressure, and more carboxylic acids escaped from the liquid at higher temperature. However, on further increasing the temperature, this phenomenon was not so pronounced, due to more and more molecules of higher boiling point also being distilled. The yield of the distilled fraction increased with increasing distillation temperature. However, too high temperature may lead to decomposition of some chemical compounds in the crude bio-oil. Hence, there must be an optimum temperature to realize reasonable separation.

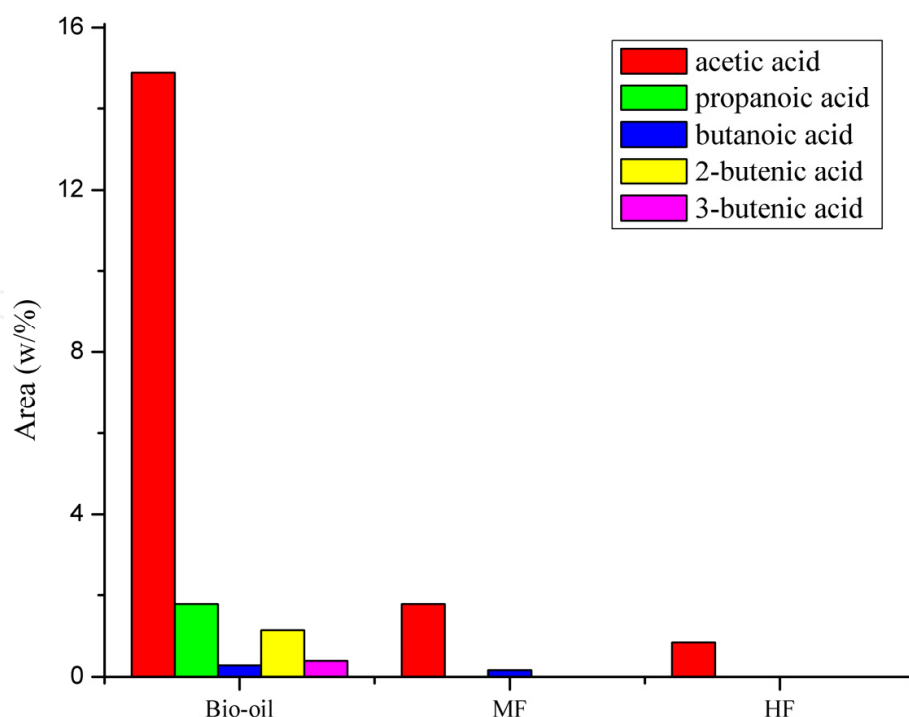
### *3.2.2. Distribution of acidic compounds in bio-oil fractions*

The high content of carboxylic acids in bio-oil is one of the main reasons for its corrosiveness, which damages storage tanks, boilers, and gas turbines. As a consequence, detailed research on the separation of acidic compounds has been carried out under the condition of distillation at 50 °C.

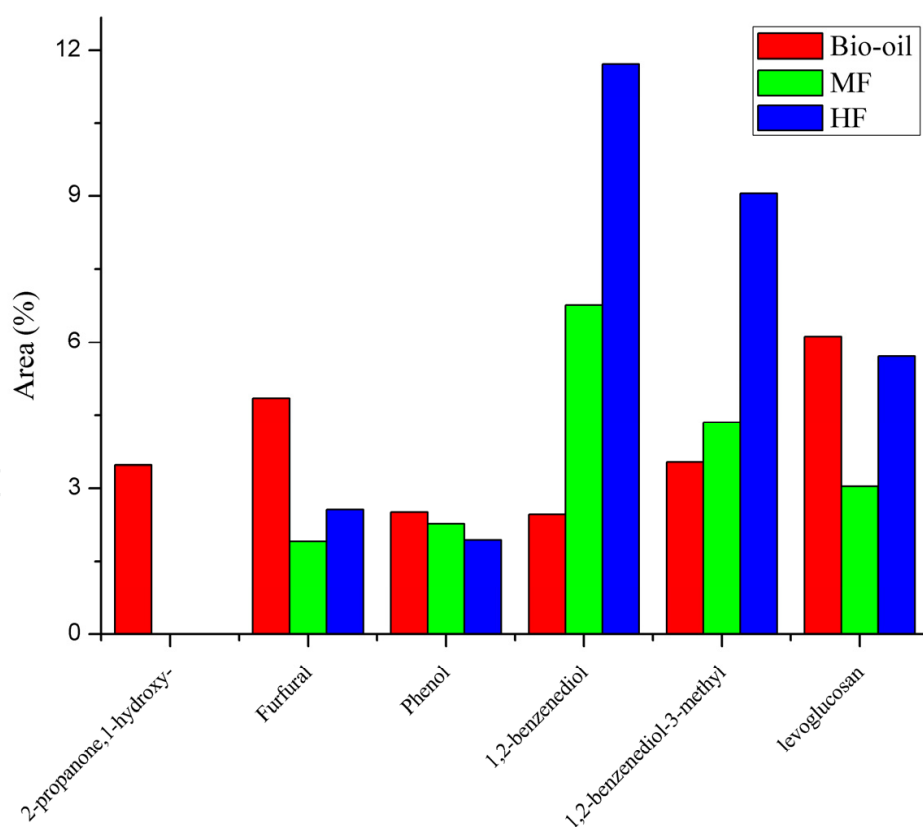
The carboxylic acid content in the refined bio-oil was used to estimate the separation efficiency. Guo et al. (2009b) chose five major acids in bio-oil and studied their separation characteristics. As shown in Fig. 3, the amount of acetic acid, the most abundant acid in bio-oil, was reduced to 1.9 wt% and 0.96 wt% in the MF and HF, respectively. The results indicated that acidic compounds could be effectively separated from the crude bio-oil by means of molecular distillation technology. The LF, which was rich in water and carboxylic acids, was valuable for further catalytic esterification of bio-oil acidic compounds. Both MF and HF could be further upgraded to produce high-quality fuels.

### *3.2.3. Distribution characteristics of several chemicals in three fractions*

Fig. 4 illustrates the distributions of selected compounds in bio-oil, MF, and HF. Six chemicals were selected as being representative of ketones, aldehydes, phenols, and sugars, respectively. 1-Hydroxy-2-propanone, the most abundant ketone in bio-oil, could not be detected in the MF or HF after separation, indicating that it was extremely enriched in the



**Figure 3.** Contents of acidic compounds in three samples obtained at 50 °C (Guo et al., 2009b).



**Figure 4.** Distributions of selected compounds obtained at 50 °C in three fractions.

LF. The content of furfural in the HF was just a little higher than that in the MF, but much lower than that in bio-oil. The distributions of these two compounds reflected the

enrichment of small ketone and aldehyde molecules in the LF. Phenol appeared to be difficult to separate as there were similar distributions in bio-oil, MF, and HF. In contrast, compounds of higher molecular weight tended to be enriched in the MF and HF. For example, 1,2-benzenediol and 3-methyl-1,2-benzenediol were more abundant in the MF and HF than in the bio-oil before separation. In particular, the relative content of 1,2-benzenediol amounted to 11.73 wt% in HF, about five times higher than that in bio-oil (2.45 wt%).

#### *3.2.4. Statistical method to evaluate the separation of bio-oil*

As the composition of the bio-oil and the effects of the operating conditions on the distribution of each fraction are both complicated, Wang et al. (2009) put forward a statistical method to directly evaluate the separation level of bio-oil by molecular distillation. The separation coefficients of four groups, “Complete Isolation”, “Nonvaporization”, “Enrichment”, and “Even Distribution”, were calculated from the ratios of relative peak of a single component with respect to total components. The results showed that “Complete Isolation” had the largest percentage, followed by “Even Distribution”, “Non-vaporization”, and “Enrichment” which contained only small parts. Meanwhile, the temperature had a significant effect on the distributions of the compounds.

### **3.3. Multiple molecular distillation for bio-oil separation**

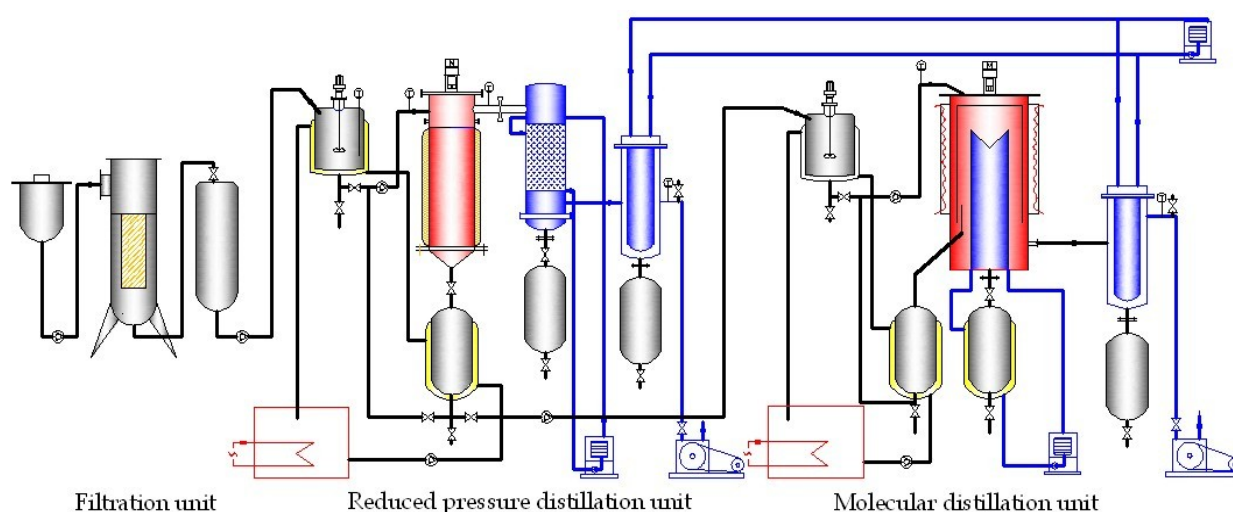
Based on the above single distillation experiments, a multiple molecular distillation experiment was carried out to further evaluate the separation characteristics of bio-oil (Guo et al., 2010b). The feed bio-oil, which was pre-treated by centrifugation, filtration, and vacuum distillation, was firstly distilled at 80 °C and 1600 Pa to obtain the distilled fraction 1 (DF-1) and the residual fraction 1 (RF-1). A part of RF-1 was then further distilled at 340 Pa to obtain DF-2 and RF-2 fractions. In the multiple distillation process, the distilled fraction yield of each distillation process was about 26 wt%. The amounts of water in RF-1 and RF-2 were greatly reduced. The RFs from the two processes had higher heating values than the feed bio-oil or DFs. The acid content was 11.37 wt% in the feed bio-oil, while it was 17.36 wt% for DF-1, nearly four times higher than that in RF-1 (4.56 wt%). In the second process, the acid content of RF-2 was further reduced to 1.38 wt%. The content of monophenols in RF-1 was 36.24 wt%, about twice that in DF-1 (18.02 wt%). Sugars showed non-distillable character in the two distillation processes, and no amounts could be detected in the DF.

In order to gain a deeper insight into the bio-oil distillation properties, Guo (Guo et al., 2010b) proposed a separation factor to evaluate the separation characteristics. The separation factors of acetic acid and 1-hydroxy-2-propanone were approximately 0.9, implying that they could be mostly distilled off. 2-Methoxyphenol, phenol, 2(5H)-furanone, and 2-methoxy-4-methylphenol, the separation factors of which ranged from 0.61 to 0.74, proved to be difficult to separate effectively. Higher molecular weight compounds, such as 3-methoxy-1,2-benzenediol, 4-methoxy-1,2-benzenediol, and 1,2-benzenediol, were very difficult to distil, having separation factors close to zero.



### 3.4. The joint distillation system at Zhejiang University

Based on the operation experiences gained with the KDL5 molecular distillation apparatus, a larger-scale joint reduced pressure and molecular distillation set-up was established in the State Key Laboratory of Clean Energy Utilization, Zhejiang University. The flow diagram of this joint distillation system is illustrated in Fig. 5. The processing capacities of the reduced pressure distillation and molecular distillation units were both 8–10 kg/h, and they could be run at temperatures up to 300 °C and pressures down to 50 Pa. The reduced pressure distillation unit could be operated separately to remove the water from bio-oil as well as to obtain bio-oil fractions. When these two units were assigned to run together, the pre-treated bio-oil from the first reduced pressure distillation unit could be pumped directly into the molecular distillation unit.



**Figure 5.** Schematic diagram of the joint distillation system.

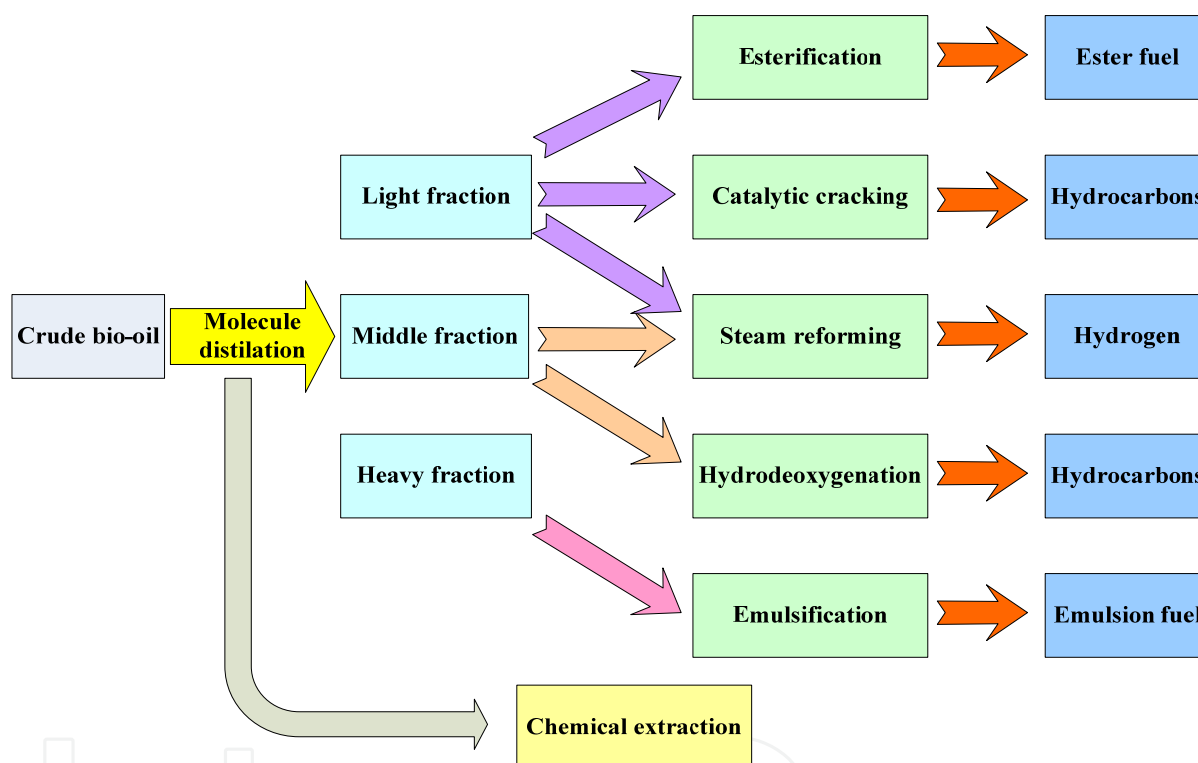
### 3.5. Further research on the distilled fractions

Based on the molecular distillation results, a scheme of the process combining molecular distillation separation with bio-oil upgrading is proposed. The light fraction rich in carboxylic acids and other light components could be used for esterification, catalytic cracking, and steam reforming, to produce ester fuel, hydrocarbons, and hydrogen, respectively. For the middle fraction, steam reforming at high temperature or hydrodeoxygenation at high pressure could efficiently convert this fraction into hydrogen or hydrocarbons. The heavy fraction, which consisted mainly of pyrolytic lignin and sugar oligomers, could be emulsified with diesel to obtain emulsion fuel with a relatively high heating value. On the other hand, the extraction of some valuable chemicals can benefit the overall economy of this process.

Recently, some further research has been performed, aiming at investigating some characteristics of the distilled fractions and devising more promising upgrading methods. Thermal decomposition processes and the pyrolysis products of crude bio-oil and distilled fractions were investigated by means of TG-FTIR by Guo (Guo et al., 2010a). The light



fraction (LF) was completely evaporated at 30–150 °C, with the maximum weight loss rate at about 100 °C due to the volatilization of water and compounds of lower boiling point. The middle fraction (MF) and heavy fraction (HF) contained more lignin-derived compounds, and these decomposed continuously over a wide temperature range of 30–600 °C, leaving a final residue yield of 25–30%. Upgrading of the distilled fraction rich in carboxylic acids and ketones was carried out by Guo (Guo et al., 2011). Carboxylic acids accounted for 18.39% of the initial fraction, with acetic acid being the most abundant. After upgrading, the carboxylic acid content decreased to 2.70%, with a conversion yield of 85.3%. The content of esters in the upgraded fraction increased dramatically from 0.72% to 31.1%. The conversion of corrosive carboxylic acids into neutral esters reduced the corrosivity of the bio-oil fraction.



**Figure 6.** A scheme of the process combining molecular distillation separation with bio-oil upgrading.

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