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Combination of Cracking and Mixing Method to Improve Cedar Bio-oil Quality

（混合法と熱分解法を用いた杉由来のバイオオイルの品質向上に関する研究）

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ABSTRACT

Bio-oil produced by the pyrolysis of biomass is highly viscous and has a high water content, which makes it difficult to be used in engines. This research aims to develop a low cost and highly efficient upgrading of bio-oil produced from cedar for engine application. The commonly used upgrading methods are divided into two types; physical and chemical methods. In this research, both of the two types were discussed and compared with the combination of the both. The physical method employed in this research was mixing the bio-oil with biodiesel, and the mixed oil was tested in an engine. The chemical method employed in this study was the pyrolysis cracking. A two-unit reactor was the device for the pyrolysis cracking. The target product was the upgraded oil with higher combustion capability.

This thesis firstly studied the characteristics of the bio-oil derived from Japanese cedar blended with biodiesel, and their possible usage as a fuel for a diesel engine. The suitable mixing ratio, the optimum mixing condition and the possibility of driving an engine were discussed. The investigation included the elemental and compositional analysis, the heating value, the density, the viscosity, the water content, the carbon residue and the ash content. The blending ratios of bio-oil to biodiesel applied in the diesel engine are 1:9, 3:7 and 5:5. In the engine test, the 1:9 and 3:7 blends could be well utilized within a short time in the engine, but the 3:7 blend could not realize a long duration operation. The engine test was done based on the US EPA standard where the specific gas emissions were evaluated in addition to the full load performance.

Use of the pyrolysis cracking method in a bench-scale reactor with two heating units produced upgraded oil and saved the catalyst. The temperature of each unit was independently controlled using the temperature controllers respectively. The key point of this process is the use of different temperatures for each heating unit. In this way, the upgraded oil has equal quality as the one upgraded by other chemical methods. The catalyst is HZSM zeolite, which is commonly used in bio-oil crack upgrading. The bio-oil and the upgraded oil were characterized by measuring their elemental composition, water content and the chemical composition of their organic fraction. The model compounds were chosen to verify the reaction principle.

Both of the two methods were able to produce upgraded oil. By mixing it with bio-oil, the unexpected physical effects reduced. The mixing mixture at a low bio-oil/biodiesel mixing ratio can be applied in engine for hours, but the chemical defects have not been overcome. When using the pyrolysis cracking method, upgraded fuel has a certain improvement in the chemical properties, but a major drawback is the water content. This research is to study the possibility to mix the cracked oil with biodiesel to overcome the defects both in chemistry and physics. After the combination of the mixing and the cracking, a better upgraded oil was produced. The reaction conditions and the reaction principle was investigated as well.

Keyword: bio-oil upgrading, biodiesel, mixed fuel, cracked fuel, engine test, zeolite catalyst, fixed bed, two-stage reactors

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1.1 Background

Most researchers estimate the depletion time of fossil fuel is less than 50, 70 and 200 years for oil, gas and coal, respectively, if the world continues to consume fossil fuels at an unchanged rates.[1-1] Based on British Petroleum Statistical Review of World Energy 2016, it is about 115 years of coal production, and roughly 50 years of both oil and natural gas remaining. [1-2] It is noteworthy that oil will be depleted less than 50 years, earlier than the other types of fossil fuel.

To alleviate the energy crisis, considerable attention has been focused on the development of alternative fuels. Renewable biomass can be converted to biofuels and is a logical choice to replace fossil fuel.[1-3]

Biomass fuels include wood, short-rotation woody crops, agricultural wastes, short-rotation herbaceous crops, animal wastes and a host of other materials [1-4]. All biomass is produced by green plants converting sunlight into plant material through the photosynthesis. Unlike fossil fuel, biomass takes carbon out of the atmosphere while it is growing, and returns it when burned. This maintains a closed carbon cycle with no more increase in atmospheric CO_2 levels.

Biomass can be converted to various forms of energy by numerous technical processes, depending on the raw material characteristics and the type of energy desired. As a result, a wide variety of conversion schemes have been developed. Among various conversion technologies, the thermochemical conversion of biomass offers a convenient way to produce liquid fuels. [1-5]

The liquid products, known as bio-oils, have been regarded as promising candidates to replace petroleum fuels for power generation, heat or for extraction of valuable chemicals. A research on upgrading of bio-oil can alleviate the fossil energy crisis, especially the oil crisis.

Bio-oil is a dark brown liquid collected from conditions of the medium temperature pyrolysis of biomass(500 ℃), under the conditions of oxygen isolation[1-6]. It has a wide range of sources of raw materials. It is renewable, transportable and high energy density, and can be used as a potential liquid fuel, or chemical raw materials.

The composition and physico-chemical properties of bio-oil are affected by many factors such as the raw material type, the water content, the reactor type, the reaction temperature, the heating rate and the product collection method. However, bio-oil generally contains a variety of oxygen-containing compounds, such as acids, aldehydes, ketones, alcohols, phenol, which lead to high moisture and oxygen content. High viscosity, poor stability, low volatility and corrosive are the facts limiting the utilization of this oil. It cannot be directly used for vehicle fuel. In order to improve the quality of bio-oil for stable storage and transportation, and to expand the scope of use, it is necessary to change the nature of bio-oil so as to replace petroleum fuels. At present, the modification and upgrading of bio-oil have become one of the hot spots to research the application of biomass.

In order to use bio oil efficiently, two upgrading methods are discussed emphatically in this study: the mixing and the cracking. The investigation included the elemental and compositional analysis, the heating value, the density, the viscosity, the water content, the carbon residue and the ash content. The reaction principle and the optimization of experimental parameters were discussed.

1.2 Bio-oil

1.2.1 Production of bio-oil

Although biomass is a kind of fuel, its solid form makes it impractical for some applications, for example, as a transportation fuel. Converting solid biomass into a liquid fuel can greatly increase its applicability. Bio-oil is the liquid fuel resulting from biomass in a process known as the fast pyrolysis.[1-7]

Two main types of processes for production of bio-oils from biomass are the flash pyrolysis and the hydrothermal liquefaction. The flash pyrolysis involves the rapid thermal decomposition of organic compounds by heat in the absence of oxygen, which results in the production of charcoal, bio-oil and gaseous products. The hydrothermal liquefaction is also called the direct liquefaction, the hydrothermal upgrading/pyrolysis, the depolymerization and the solvolysis, which is conducted under elevated pressure and temperature to keep water in either liquid or supercritical state. The primary product of the hydrothermal liquefaction is bio-oil or bio-crude, and the main byproducts are the solid residue, bio-char and water containing soluble organic compounds. Both of the processes belong to the thermochemical technologies in which feedstocks organic compounds are converted into bio-oil 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 [1-8] .

1.2.2 Properties of bio-oil

The liquid product, bio-oil, is usually dark brown, free-flowing liquids having a distinctive smoky odor. The physical properties of bio-oils are described in several publications [1-9][1-10]. The different physical properties of bio-oils result from the chemical composition of the oils, which is significantly different from that of petroleum-derived oils. Bio-oil is a complex mixture of several hundreds of organic compounds, mainly including acids, alcohols, aldehydes, esters, ketones, phenols and lignin-derived oligomers. Some of these compounds are directly related to the undesirable properties of bio-oil. The potential of direct substitution of bio-oil for petroleum fuels and chemical feedstocks is limited due to their high viscosity, high water and ash contents, low heating value, instability and high corrosiveness. Consequently, upgrading of bio-oil is necessary to give a liquid product that can be used as a liquid fuel or chemical feedstocks in various applications. More details are listed in Table 1-1.

Table 1-1 Characteristics of general bio-oil[1-10]

Characteristic	Cause	Effects
Low pH	Organic acids from biopolymer degradation	Corrosion of vessels and pipework
Aging	Continuation of secondary reactions including polymerization	Slow increase in viscosity from secondary reactions such as condensation
		Potential phase separation
Alkali metals	slagging in furnac and agglomeration	Catalyst poisoning
	High ash feed	Deposition of solids in combustion
	Incomplete solids separation	Erosion and corrosion
		Slag formation
		Damage to turbines
Char	Incomplete char separation in process	Aging of oil
		Sedimentation
		Filter blockage
		Catalyst blockage
		Engine injector blockage
		Alkali metal poisoning
Chlorine	Contaminants in biomass feed	Catalyst poisoning in upgrading
Colour	Cracking of biopolymers and char	Discoloration of some products such as resins
Contamination of feed	Poor harvesting practice	Contaminants notably soil act as catalysts and can increase particulate carry over.
Distillability is poor	Reactive mixture of degradation products	Bio-oil can be distilled maximum 50% typically. Liquid begins to react below 100 ℃ and substantially decomposes

		above 100 ℃
High viscosity	Organic compounds of high viscosity are contained	Gives high pressure drop with increasing the equipment cost
		High pumping cost
		Poor atomisation
Low H:C ratio	Biomass has low H:C ratio	Upgrading of hydrocarbons is more difficult
Materials incompatibility	Phenolics and aromatics	Destruction of seals and gaskets
Miscibility with hydrocarbons is very low	Highly oxygenated nature of bio-oil	Will not mix with any hydrocarbons so integration into a refinery is more difficult
Nitrogen	Contaminants in biomass feed	Unpleasant smell
	High nitrogen feed such as proteins in wastes	Catalyst poisoning in upgrading
		NOx in combustion
Oxygen content is very high	Biomass composition	Poor stability
		Non-miscibility with hydrocarbons
Phase separation or In-homogeneity		Phase separation
	High feed water	Partial phase separation
	High ash in feed	Layering
	Poor char separation	Poor mixing
		Inconsistency in handling, storage and processing
Smell or odour	Aldehydes and other volatile organics, many from hemicellulose	While not toxic, the smell is often objectionable
Solids	See also Char	Sedimentation
	Particulates from reactor such as sand	Erosion and corrosion
	Particulates from feed contamination	Blockage
Structure	The unique structure is caused by the rapid de-polymerisation and rapid quenching of the vapours and aerosols	Susceptibility to aging such as viscosity increase and phase separation

Sulfur	Contaminants in biomass feed	Catalyst poisoning in upgrading
Temperature sensitivity	Incomplete reactions	Irreversible decomposition of liquid into two phases above 100 ℃
		Irreversible viscosity increase above 60 ℃
		Potential phase separation above 60 ℃
Toxicity	Biopolymer degradation products	Human toxicity is positive but small
		Eco-toxicity is negligible
Viscosity	Chemical composition of bio-oil.	Fairly high and variable with time
		Greater temperature influence than hydrocarbons
Water content	Pyrolysis reactions	Complex effect on viscosity and stability: Increased water lowers heating value, density, stability, and increase pH
	Feed water	Affects catalysts

Overall, bio-oils cannot be directly used as transportation fuels. Therefore, upgrading of bio-oil is needed to improve its properties for liquid fuel.

However, bio-oils have several environmental advantages over fossil fuels as a clean fuel. Bio-oils are CO_2/GHG neutral. Therefore, they can generate carbon dioxide credits. No SOx emissions are generated, because plant biomass contains insignificant amounts of sulfur. Therefore, bio-oil would not be subjected to SOx taxes. Bio-oil fuels also generate more than 50% lower NOx emissions than diesel oil in the gas turbine. [1-11]Renewable and locally produced bio-oil can be produced in countries with large volumes of organic wastes. Thus, bio-oils are cleaner and cause less pollution.

1.2.3 Uses of bio-oil

As a renewable liquid fuel, bio-oil can be readily stored and transported. It can serve as a substitute for fuel oil or diesel in many static applications including boilers, furnaces, engines and turbines for electricity generation. Alternatively, the crude oil could serve as a raw material for the production of adhesives, phenol-formaldehyde-type resins, wood flavors, etc. Different specialty chemicals are also possible to be produced from the bio-oils after further processing and separation. The following are some industrial uses of bio-oil:

(1) Combustion fuel for heat generation [1-12],

(2) Combustion in diesel engines/turbines for power generation [1-13][1-14],

(3) Use as a transportation fuel after upgrading[1-15][1-16],

(4) Production of anhydro-sugars like levoglucosan, which has potential for the manufacturing of pharmaceuticals, surfactants, biodegradable polymers[1-17],

(5) Use as liquid smoke and wood flavors [1-18],

(6) Production of chemicals and resins (e.g., agri-chemicals, fertilizers, acids and emission control agents)[1-19][1-20] ,

(7) Use for making adhesives [1-21] .

Bio-oils is a promising renewable energy source which have received extensive recognition around the world for their characteristics as combustion fuels used in boiler, engines or gas turbines and resources in chemical industries. Some problems affecting its industrial utilization and recommendations are described as follows:

(1) Poor oil quality.

Compared with heavy petroleum fuel oil, the bio-oils have several undesired properties for fuel applications such as high oxygen/water contents, high viscosity and corrosiveness. These undesired properties present many obstacles to use bio-oil as a substitute for petroleum-based fuel.

(2) High upgrading cost.

Over the years, various technologies have been developed for bio-oil upgrading, including the cracking, the hydrogenation, the supercritical fluids extraction, the solvent addition/esterification, the steam reforming and the emulsification. The emulsification appears to be the most practical approach due to simplicity. However, none of these bio-oil upgrading techniques have been commercialized due to low biofuel efficiency and their limitations.

1.2.4. Upgrading of bio-oil

Considering the above discussion on the properties of bio-oils, 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. The advantages and disadvantages of each technique are also described below.

(1) Cracking

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 cracking process in the refinery, in which the separation of oxygen elements occurs and thus the amount of hydrogen increases. Currently, the most widely used cracking processes are for the conversion of petroleum and petroleum products. However it also can be used to bio-oil. The cracking is a simple deoxidation process that is used for the purpose of improving the product quality without appreciable alteration of the boiling range. It also can be used for obtaining saturating olefins or for converting aromatics to naphthenes from bio-oil. Under the atmospheric pressure, usually at 500 ℃, anaerobic condition, the deoxidization and the cracking commence. The oxygen in bio-oils can be removed via the cracking.

The cracking 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.

(2) Hydrogenation

The hydrogenation is less popular than the cracking in the petroleum industry. It is a thermal process (>350 ℃) in which the hydrogenation accompanies the cracking process. 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. The wide range of products possible to be formed by the hydrogenation which is the results of combining catalytic cracking reactions with hydrogenation and the multiplicity of reactions that can occur. 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.

The hydrogenation 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.

(3) Supercritical fluids

A fluid is considered supercritical when its temperature and pressure go above its critical point. Supercritical fluids possess unique transport properties. They can effuse through solids like a gas and dissolve materials like a liquid. In particular, supercritical fluids have the ability to dissolve materials not normally soluble in either liquid or gaseous phases of the solvent, and hence to promote the gasification/liquefaction reactions. Supercritical fluids have been recently used to improve the oil yield and the 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 the 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 has been adopted. All these solvents have shown a significant effect on the bio-oil yield and the quality.

Although supercritical fluids 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.

(4) Solvent addition/esterification

Polar solvents such as methanol, ethanol and furfural have been used for many years to homogenize and to reduce viscosity of bio-oils [1--22], [1-23]. The immediate effects of adding these polar solvents are decreased viscosity and increased heating value. The increase in the 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[1-24] .

The chemical reactions that can occur between the bio-oil and methanol or ethanol are the esterification and the acetalization. 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 the 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.

(5) 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 the cracking, the dehydrogenation and the isomerisation[1-25]. 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.

The fast pyrolysis of biomass followed by the catalytic steam reforming and the shift conversion of specific fractions to obtain H_2 from bio-oil was presented as an effective way to upgrade bio-oils. Production of hydrogen by reforming bio-oil was investigated by NREL extensively, including the reactions in a fixed bed and a fluidized bed. Commercial nickel catalysts showed good activity in processing biomass derived liquids .

(6) Emulsification (emulsions)

One of the methods for 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 the emulsification with diesel oil has been investigated by many researchers. The main raw material in those researches is diesel. For example, a process for producing stable microemulsions, with 5 – 30% of bio-oil in diesel has been developed at Canmet Energy Technology Centre [1-26]. Those emulsions are less corrosive and show promising ignition characteristics.

Jiang and Ellis investigated the bio-oil emulsification with bio-diesel [1-27]. A stable bio-oil/bio-diesel 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 bio-diesel are with an octanol surfactant dosage of 4% by volume, an initial bio-oil/bio-diesel 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 of the acid number, the viscosity and the water content compared to the original bio-oil.

Overall, upgrading of bio-oil through the 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 the heating value, the cetane number and the corrosivity were still unsatisfied. Moreover, this process requires high energy for production. Design, production and testing of injectors and fuel pumps made from stainless steel or other materials are required.

Table 1-2 Comparison of upgrading methods

Upgrading methods	Advantages	Disadvantages
cracking/hydrofining	Cheaper route, commercialized already	High coking (8–25%) and poor quality of fuels obtained
hydrogenation/hydrogenolysis/catalytic cracking	Makes large quantities of light products	Need complicated equipment, excess cost, catalyst deactivation, reactor clogging
Sub- /super-critical fluid	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)	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
Steam reforming	Produces H_2 as a clean energy resource	Complicated, requires steady, dependable, fully developed reactors
Emulsification/emulsions	Simple, less corrosive	Requires high energy for production

1.3 Research objectives

1.3.1 Physical method

The physical method employed in this research was mixing the bio-oil with biodiesel, and the mixed oil was tested in an engine.

The emulsion of bio-oil has been studied for a long time but mainly concentrated in blending with diesel, methanol or ethanol, which are derived from fossil fuel, oil , gas and coal. [1-28] The bio-oils emulsified with biodiesel, renewable energy, were seldom reported. Jiang[1-29] and Alcala[1-30] described the phenomenon of emulsion conditions of pine wood bio-oil and vegetable biodiesel, but scarcely analyzed the causes of the emulsion. Garcia-Perez[1-31] researched the results of mixing bio-oil produced from oil mallee and pine and bio-diesel derived from canola vegetable oil. He did some analysis on causes, but did not cover any application. Furthermore, it should be pointed out that the effect of bio-oil and biodiesel feedstocks on the variation of bio-oil/biodiesel emulsion was remarkable. The emulsion in this experiment did not happen when using the above methods.

This research was carried out aiming at the real world adaption of the bio-oil in a diesel engine with the minimum cost. Considered from the practical point of view, the most convenient upgrading method, the emulsification, was studied. The bio-oil used in this research derived from the waste biomass, Japanese cedar, were produced in a pilot plant in Japan. In order to completely get rid of fossil fuel, biodiesel was chosen as another mixing material. The biodiesel used in this research was made from waste cooking oil. The determination of the possible blending requirement was the major scope rather than the optimization of the engine parameters. After completing the definition of the blend ratio, the continuous engine operation at the rated power point was conducted.

The engine operation points were picked up based on the US EPA standard and the specific gas emissions were evaluated in addition to full load performance.

The production of the bio-oil, the properties analysis of the raw bio-oils, the selection of the engine operation point and the definition of combustion phases are followed.

1.3.2 Chemical method

The chemical method employed in this study was the pyrolysis cracking. A two-unit reactor was the device for the pyrolysis cracking. The target product was the upgraded oil with a higher combustion capability.

The popular cracking methods are the fixed bed cracking, the moving bed cracking and the fluidized bed cracking[1-32][1-33]. The fixed bed cracking is chosen in this study for its simple equipment requirements.

Many types of catalysts have been studied in the literatures in order to investigate how far the catalyst can modify the bio-oil composition and the bio-oil quality. Most of these studies are focusing on the comparison of catalysts but not on the mechanism of catalysts. The control test without catalyst is considered unnecessary in these studies[1-34][1-35].

However, in this research, the effect of the commonly used catalyst HZSM-5 was discussed focusing on the comparison with the non-catalytic cracking. Most studies on the catalytic cracking of bio-oil are using only one heating reactor, where all components of bio-oil are in contact with the catalyst, including the components that tend to deactivate the catalyst. In this research, two heating units were employed so that the raw bio-oil was separated in the first heating unit and the cracking was done in the second heating unit. The components liable to deactivate the catalyst can be identified by changing the temperature in the first heating unit. In this way, the catalyst deactivation caused by different components were analyzed simultaneously, instead of treating the bio-oil as a whole[1-36], using model components separately[1-37] or analyzing the deactivated catalyst after the reaction[1-38].

Some researches reported that bio-oil component separation is difficult under the atmospheric pressure and side reactions tend to occur due to the poor heat stability of bio-oil[1-39][1-40]. But in this paper, side reactions did not significantly affect the experimental results by employing the two-stage heated reactors. Indeed, it is difficult to separate all components in bio-oil individually, but the components can be divided into 4 classes according to the chemical analysis, which was sufficient to explain the reaction mechanism of the deactivation. Different from the one heating unit process which is commonly used, the components in the upgraded bio-oil can be divided into 4 classes of organic components clearly by employing two heating units. By analyzing the reaction trend of these four classes of bio-oil components, the deactivation principle of the catalyst can be discussed without using model compounds. Previous studies generally considered that high molecular weight aromatic and aliphatic compounds are important reasons for the deactivation of catalysts[1-41][1-42], but in this research, the effects of phenols and naphthalenes on the catalyst were investigated to show the importance of their effects.

1.4 Bio-oil feedstocks

Bio-oil in this study was produced using the pilot-scale gasification plant shown in Figure 1.10 and Figure 1.11. The gasification reactor is an updraft gasifier. Air was supplied from the bottom of the reactor as a gasifying agent. The dried and crushed cedar wood was supplied into the reactor, the volatiles of the feedstock would be released as syngas, or called producer gas. The producer gas was cleaned by the tar removal process, which consists of two water coolers, two centrifuges and a char bed. After the tar removal process, the producer gas was introduced into a spark ignition gas engine. From the bottom of the gasifier, char was discharged by an agitator and a screw conveyor. In the first cooler, water and heavy tar contents in the producer gas were removed and the bio-oil was mainly recovered in the first centrifuge.

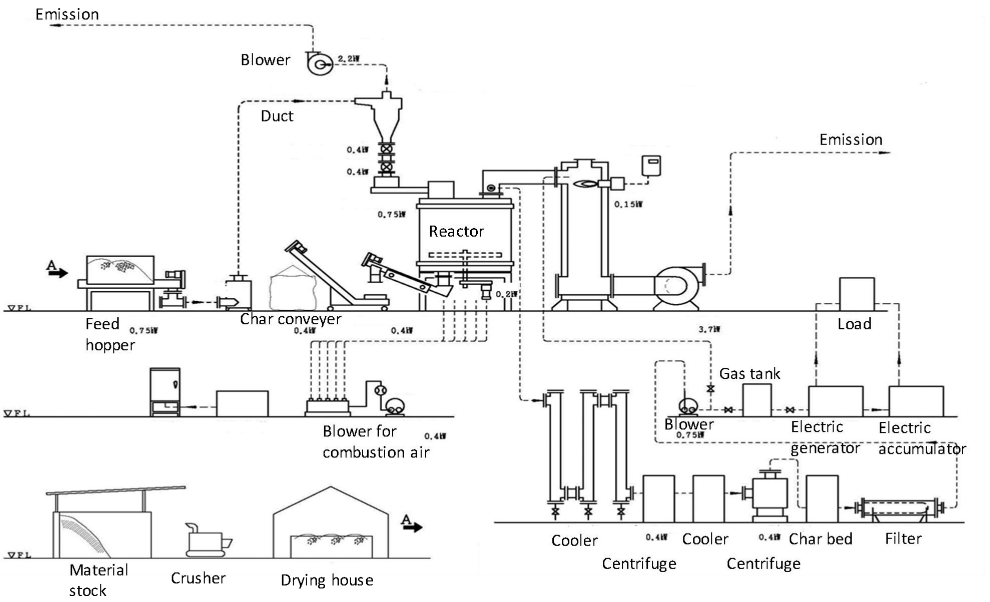

Figure 1-1 Process scheme of the pilot-scale gasification plant

Figure 1-2 Photo of the pilot-scale gasification plant

The mass balance of the bio-oil production is depicted in Figure 1-3. The bio-oil throughput which is available to run engines is around 4.5% of the total output volume and its maximum output is the synthetic gas by around 68.8%.

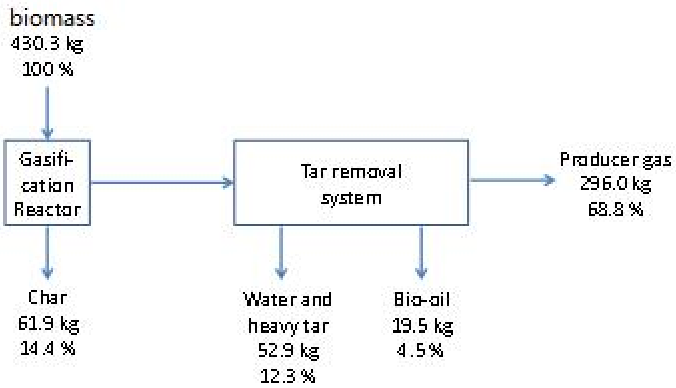

Figure 1-3 Mass balance of the bio-oil production

The raw bio-oil obtained from woody waste had a higher kinematic viscosity than diesel fuel as shown in Table 1-4 and many residues which were mainly composed of viable solid particles and highly dense liquid conglomerate. Those are some of the reasons to make its direct adaption to diesel engines difficult, due to unfavorable and unpredictable troubles in engine systems.

Table 1-3 Properties of the raw bio-oil compared with diesel

	Diesel[JIS2]	bio-oil
C（%）	85.04	57.5
H（%）	13.55	7.0
N（%）	0	0.2
S（%）	0	0
O（%）	0	35.5
Density [kg/cm^3] at 15 ℃	0.83	1.14
Kinematic viscosity [mm2/s] at 40 ℃	2.74	6.80
Water content [%wt/wt]	0	7.9
High Heat value [MJ/kg]	45	25.4

1.5 Thesis outline

The basic background of the bio-oil derived from biomass and the upgrading technology were introduced. The problems about the current situation of utilization and upgrading of bio-oil were discussed respectively. The upgrading methods chosen in the following research were the mixing and the cracking. The advantage and disadvantage of those methods were discussed. Cracking and mixing methods are discussed in the following chapters.

In Chapter 2. Mixed fuel of bio-oil and biodiesel, to overcome the problems of high viscosity and high water content, which makes it difficult to be used in engines, a method of blending bio-oil with biodiesel was investigated in this chapter. This thesis studied the characteristics of the bio-oil derived from Japanese cedar blended with biodiesel, and their possible usage as a fuel for a diesel engine. The suitable mixing ratio, the optimum mixing condition and the possibility of driving an engine were discussed. The investigation included elemental and compositional analysis, the heating value, the density, the viscosity, the water content, the carbon residue and the ash content. The blending ratios of bio-oil to biodiesel applied in the diesel engine are 1:9, 3:7 and 5:5. In the engine test, the 1:9 and 3:7 blends could be well utilized within a short time in the engine, but the 3:7 blend could not realize a long duration operation. The engine test was done based on the US EPA standard where the specific gas emissions were evaluated in addition to the full load performance.

In Chapter 3. Cracking upgrading of bio-oil, the objective of this chapter is to find the optimum operating conditions to upgrade the bio-oil using the cracking method in a bench-scale reactor with two heating units. The temperature of each unit was independently controlled using the temperature controllers respectively. A constant stream of N_2 was fed from the top of the reactor for the continuous withdrawal of the products and maintenance of the inert atmosphere during pyrolysis. The liquid products were condensed in a glass receiver submerged in a cooling bath kept at 0° C. The gas products were collected in a gas bag. The key point of this process is the use of different temperatures for each heating unit. In this way, the upgraded oil has equal quality as the ones upgraded by other chemical methods and the zeolite catalyst can be reused. The bio-oil used in this chapter is the same as the one in the last chapter. The catalyst is HZSM zeolite, which is commonly used in bio-oil crack upgrading. The bio-oil and the upgraded oil were characterized by measuring their elemental composition, water content and the chemical composition of their organic fraction.

In Chapter 4. Combination of cracking and mixing method to improve the bio-oil quality, the liquid products collected from Chapter 3 was mixed with the biodiesel used in Chapter 2. The mixing method was the same as Chapter 2. The mixing ratios of 3:7 and 5:5 were tested. The results showed that the new mixtures were completely mixed stably at any mixing ratio. The mixed fuels stood for at least 1 month and no obvious layering was observed. The possible reason is that the polarity of the cracked oil is greatly reduced which lead to a harmony solution with biodiesel. Benzenes and phenols played an important role in this harmony solution. The combustion performance is measured by calculating the cetane index. The model compounds were chosen to verify the reaction principle. To investigate the range of improvement of the upgraded bio-oil by the combination of the mixing and the cracking methods compared with the individual mixing or cracking methods, the quantitative calculation were the main data to measure the fuels.

At last Chapter 5. Conclusions, This chapter summarizes the important concluding remarks of this thesis.

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Chapter 2
Mixed fuel of bio-oil and biodiesel

In this chapter, the mixing methods of bio-oil and biodiesel were tested. The objective is to improve the characteristics of bio-oil blended with biodiesel for the use in engine. The mixing temperature, the mixing time, the mixing ratio and the stirring speed are investigated for clarifying the suitable mixing parameters, optimizing the mixing conditions and demonstrating the possibility of engine operation.

2.1 Experimental methods

2.1.1 Sample preparation

The bio-oil produced from the pyrolysis of Japanese cedar was supplied by Meiwa Industry Co., Ltd., Japan. The pyrolysis produced in an updraft gasifier passed through a cooler to remove water and heavy tar and then was introduced to a centrifuge separator to recover misty light/medium tar (bio-oil). The biodiesel was produced from waste cooking oil by the transesterification method with KOH catalyst which was supplied from Best Trading.inc, Japan. In order to avoid usage of fossil fuel, biodiesel was chosen as the mixing material.

The effects of the initial bio-oil/biodiesel volume ratio, the stirring intensity, the mixing time and the temperature were examined. In this study, the stability of the mixture was characterized by the parameter “changed percentage”, defined as the proportion of bio-oil into biodiesel occupied in the initial bio-oil. Initial mixtures of bio-oil and biodiesel were prepared by adding 10, 20, 30, 40, 50 and 60% (by volume) bio-oil into biodiesel and mixed in a beaker with a stirrer. The experiment lasted until the mixture reached the stable state, which means the mixed liquid comes to a state of standing in the room temperature for more than 24 hours without appearance of the stratification or the precipitation. The mixing time needed was at least 10 hours. The color of samples were deeply dark and difficult to observe directly. For all of the mixtures after 30 hours stirring, a stratification happened after a few minutes and stopped after about 2 hours. Thus, after reaching the stable state, the upper and lower layers should be separated and weighed. The properties of the layers were then characterized by weight.

The experimental conditions are listed in Table 2-1.

Table 2-1 Mixing experimental parameters

Mixing temperature	25 °C, 40 °C, 60 °C
Mixing time	10 min, 20 min, 30 min 40 min, 50 min, 1 h, 5 h, 10 h, 15 h, 20 h, 25 h, 30 h
Stirring speed	600rpm, 800rpm, 1000 ppm
Percentage of bio-oil	10%, 20%, 30%, 40%, 50%, 60%

2.1.2 Indicators

Once the stirring stopped, a layer of darker color liquid with higher density started to settle at the bottom. The amount of the lower layer liquid after the blending always reduced compared to that before the blending. The lower layer after the blending had a higher viscosity and a darker color than the upper layer as shown in Figure 2-1.

After settled in the room temperature for 1 hour, the stratification stabilized and the mixture came to a steady state which means that the mixed liquid was capable of stabilizing in the room temperature for more than 24 hours without appearance of additional stratification and/or precipitation.

After reaching the steady state, the changed percentage (CP) of the lower layer by weight was used to evaluate the mixing result. It is defined as the following:

$$CP=(W_i-W_f)/(W_i)\times100\%$$

where CP: The changed percentage of the bio-oil;

W_i: Weight of the initial bio-oil (lower layer) before the blending;

W_f: Weight of the stabilized lower layer after the blending.

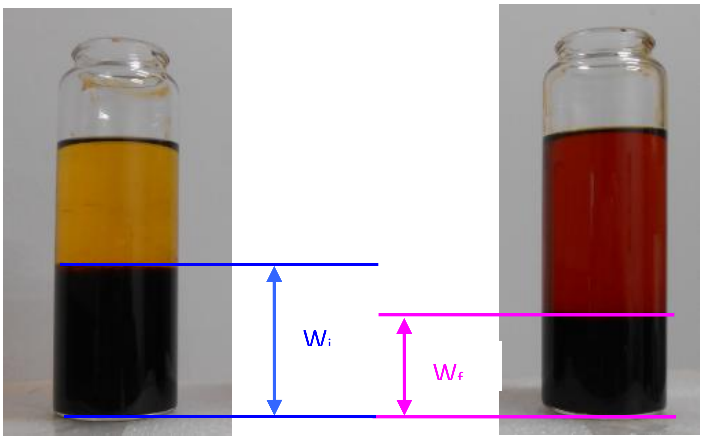

Figure 2-1. Mixtures before the blending (left side) and after the blending (right side).

2.2 Mixing Tests

2.2. 1 Effect of the mixing time and temperature

CP values were measured every ten minutes in the first hour and every five hours in the later 29 hours which is long enough for each mixtures to reach the maximum CP value. The CP values as functions of the mixing time, the initial bio-oil ratio and the mixing temperature are shown in Figures 2-2, 2-3 and 2-4.

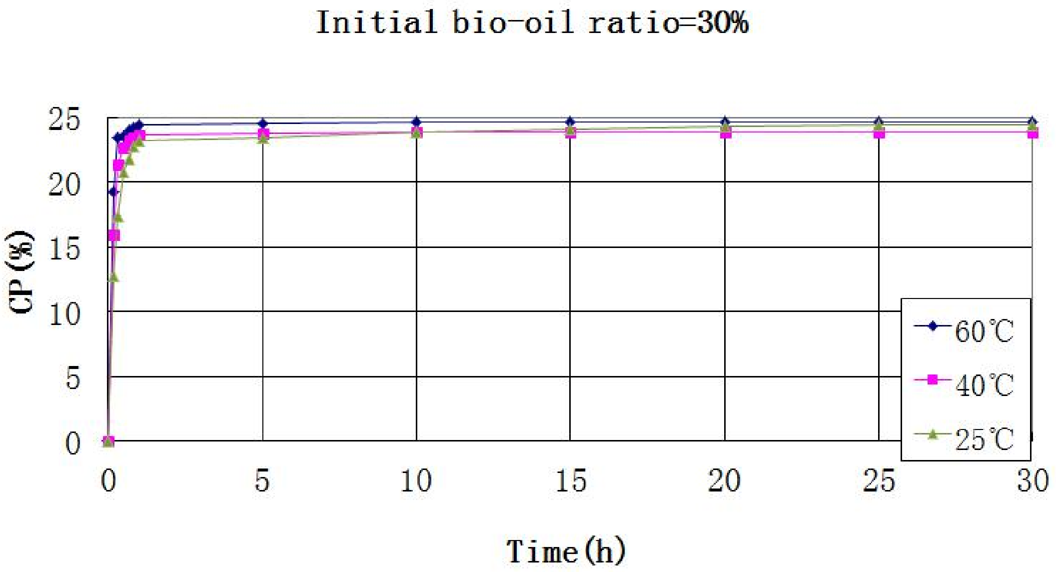

Figure 2-2. CP for 30% bio-oil content mixture at different mixing temperatures.

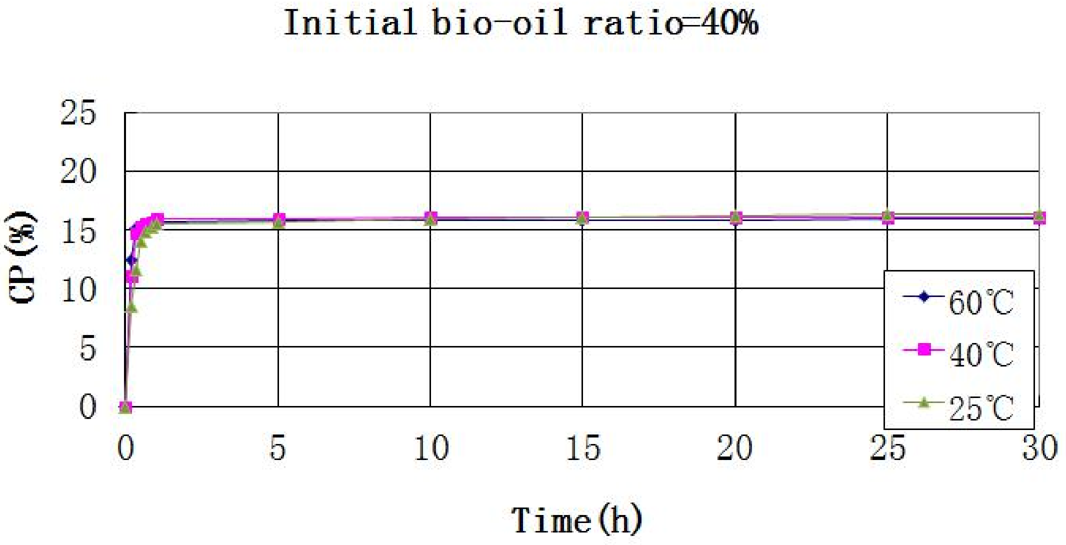

Figure 2-3. CP for 40% bio-oil content mixture at different mixing temperatures.

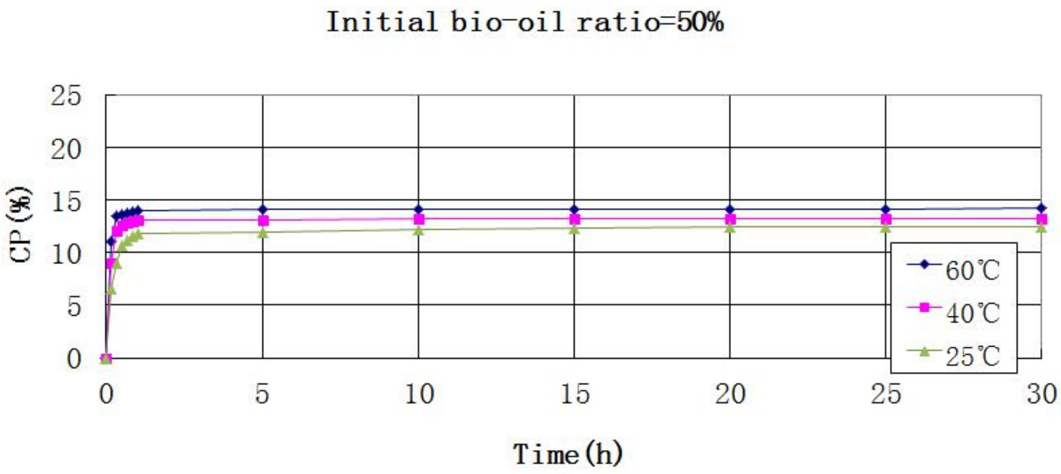

Figure 2-4. CP for 50% bio-oil content mixture at different mixing temperatures.

From Figures 2-2, 2-3 and 2-4, it can be seen that the mixing time for obtaining the maximum CP value was 25 hours at the mixing temperature of 25 °C regardless of the mixing ratio, but the mixing time needed for the maximum CP value decreased to 15 hours at the mixing temperatures of 40 and 60 °C. The major part of the mixing occurred in the first hour. For the later 20 hours, the increase of the CP value is less than 5%. By measuring every 10 minutes in the first hour, we can see that 95% of the maximum CP value was obtained in 20 minutes for the 40 and 60 °C mixtures, and 1 hour for the 25 °C mixtures. This clearly shows that the heating accelerates the mixing process but does not affect the maximum CP value so much. After separating the upper layer and the lower layer of the mixture when 95% of the maximum CP value was achieved, the stability of the two layers did not show much difference compared to mixtures which were blended for 30 hours. The separated liquids did not appear additional stratification and/or precipitation for at least 3 months.

Figure 2-5 shows that the CP value did not change significantly with the increase of the temperature. At the same mixing ratio, the CP values were almost the same. The physical and chemical properties of mixtures in higher temperatures also did not show any negative changes though some researchers pointed out that bio-oil should not be heated because it tends to coagulate the droplets, causing polymerization or destabilization [2-1].

Figures 2-2, 2-3, and 2-4 also show the same trend that at the same mixing temperature condition, the mixtures with lower initial bio-oil ratio always showed higher maximum CP values than the ones with higher bio-oil ratio. This phenomenon will be discussed in the section 2.2.2.

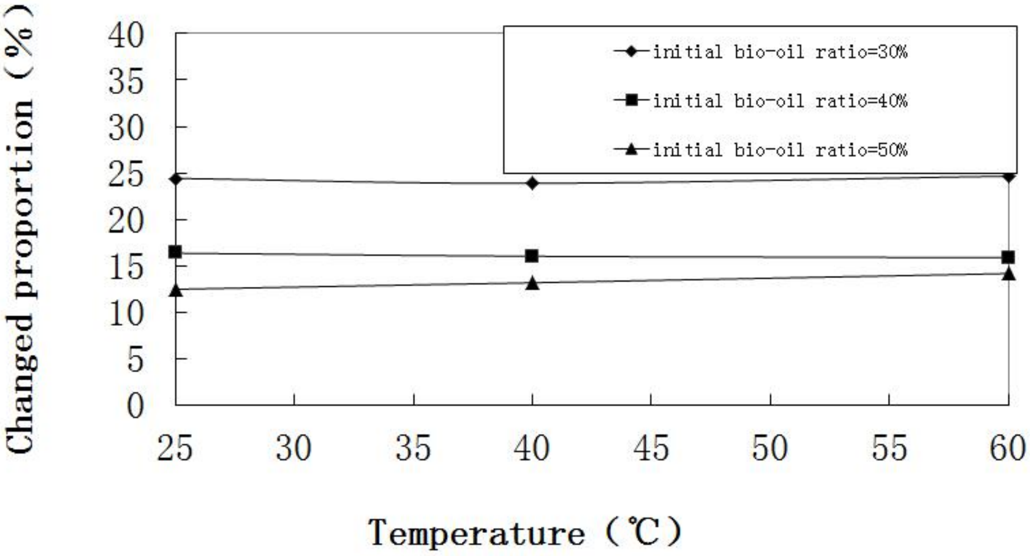

Figure 2-5. CP for all mixtures at different mixing temperatures.

2.2.2 *Effect of the mixing ratio*

Figure 2-6 shows the maximum CP value at various initial mixing ratios of bio-oil from 10% to 60%. The mixing temperature almost did not affect the curves. When the initial bio-oil mixing ratio was no more than 30%, the maximum CP values were closed to 25%, showing that the amount of bio-oil which could not be mixed into biodiesel was about 75% when the initial bio-oil mixing ratio was low. However, when the initial bio-oil mixing ratio was larger than 30%, the maximum CP value decreased gradually, and down to less than 10% when the initial bio-oil mixing ratio was 60%.

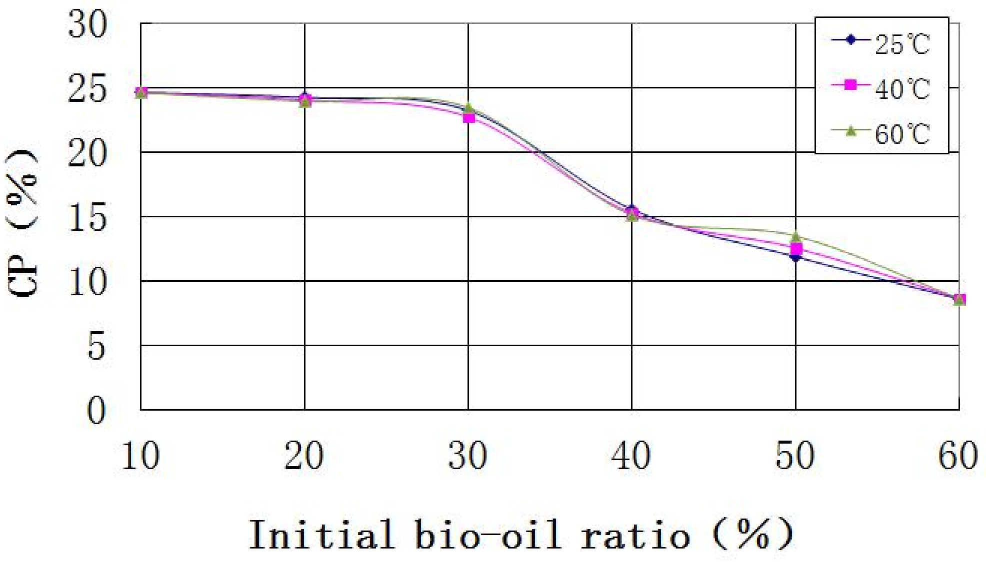

Figure 2-6. The maximum CP value at different initial bio-oil mixing ratios.

2.3 Main properties of raw and mixed fuels

The mixed fuels is dark brown, transparent, free flowing liquids with an acrid and smoky odor. These characteristics came from the complex compounds of the bio-oil. The complex compounds of the bio-oil are derived from the depolymerization of cellulose, hemicellulose and lignin. Chemically, it is comprised of a lot of water, more or less solid particles and hundreds of organic compounds that belong to acids, alcohols, ketones, aldehydes, phenols, ethers, esters, sugars compounds and multifunctional compounds [2-2]. Bio-oils are totally different from petroleum fuels in chemical compositions, which will result in the vast difference in the fuel properties between them. Based on the above facts, some main properties of the raw materials and mixture fuels were analyzed as follows.

2.3.1 Detection object

(1)Water

Water is the most abundant single component in bio-oils. It results from original moisture in feedstocks and the dehydration reactions during the pyrolysis process. The water contents depend on the initial moisture in feedstocks and the pyrolysis conditions. Some water in bio-oils is in the form of aldehyde hydrates, while much of it is probably hydrogen bonded to polar organic compounds. [2-3]

Bio-oils have limited solubility with water. The raw bio-oil used in this experiment, if some water added, would precipitate. After standing for a long time, the Turbid liquid separated into two parts, the upper part soluble in water and the lower part insoluble in water. The mixtures reached steady state also tended to separate into an aqueous phase and a heavier organic phase when water is added. Since the biodiesel is completely insoluble in water, it showed that the microemulsion structure of the bio-oil was destroyed with the increase of the water content. To maintain homogeneity, the water content should not be easily changed, which is determined by the chemical compositions of the bio-oil. Thus, water was a key factor in maintaining the stability of the bio-oil which would be discussed later in this chapter. Once this kind of phase separation takes place, it will undoubtedly bring great trouble to the utilization of bio-oils.

Water is also hard to be removed from bio-oils. The presence of water has both negative and positive effects on the storage and utilization of bio-oils. It lowers the heating values, and causes phase separation of bio-oils. It can be predicted that water content increases the ignition delay, and reduces the combustion rate and the flame temperature during the combustion process. In addition, it will lead to premature evaporation and subsequent injection difficulties during the preheating process. However, it helps to reduce the viscosity and facilitate the atomization in engine. It is beneficial for reducing pollutant emissions during combustion [2-4] for that water lowers and evens the temperature in chambers which was important for suppressing NOx formation. It also contributes to the microexplosion of droplets, which is beneficial for sufficient combustion.

(2)Oxygen Content

Bio-oils retain most of the original oxygen in the feedstocks. The oxygen content is determined mainly by the water content. Oxygen is present in almost all organic compounds in bio-oils. It is known to be the primary reason for the vast differences between bio-oils and petroleum fuels. These oxygenated compounds make bio-oils polar. This will be a defect for the utilization of bio-oils. The high oxygen content is responsible for the low heating value, corrosiveness and instability of bio-oils.

(3)Heating value

The lower heating value which is much lower than that of diesel is attributable to the high oxygen content. However, the density of bio-oils is about 1.2 g/ml compared with that of petroleum fuels, which is 0.8 – 1.0 g/ml. Therefore, the volumetric energy density of bio-oils can reach 50 – 60% of that of petroleum fuels.

(4)Viscosity

Viscosities of homogeneous bio-oils were measured as the kinematic viscosity by a glass viscometer. After the stratification of the mixture, the high viscosity part mainly remained in the lower layer, which let the viscosity of the upper layer closer to biodiesel.

(5)Stability

Bio-oils are not products of the thermodynamic equilibrium. Many components in them will take part in diverse reactions during storage. The instability of bio-oils can be described as a slow increase in the viscosity during storage or a fast increase in the viscosity by heating and the evaporation of volatile components and oxidation in air.[2-5]

(6)Aging

The chemical reactions may take place during ageing of bio-oils [2-6]. Bio-oil contains a lot of aldehyde. They can react with water to form hydrates; with alcohols to form hemiacetals, acetals and water; with phenolics to form resins and water; with proteins to form dimers; and with one another to form oligomers and resins. Moreover, acids can react with alcohols to form esters and water; mercaptans will react to form dimers; and olefins will polymerize to form oligomers and polymers. In addition, oxygen in air will oxidize bio-oils to form more acids and reactive peroxides that catalyze the polymerization of unsaturated compounds.

2.3.2 Detection method

The following characteristics were determined in this section: the elemental analysis of C, H, O, N and S, the moisture content, the ash content, the density, the high heating value (HHV), the cetane index, the kinetic viscosity and the chemical composition.

The ash content and the elemental analysis of C, H and N were determined by JM10 at 950 °C. The elemental analysis of O was determined by Vario micro cube at 1150 °C. The elemental analysis of S was determined by HSU-20+ICS-1100 after complete combustion. The moisture content was measured using the Karl Fischer method in accordance with the standards JIS K 2275. HHV was determined in accordance with the standards JIS K 2279. The kinetic viscosity was measured by an ostwald viscometer at 40 °C. The cetane index was calculated in accordance with the standards JIS K 2280-5. The ratio of the mixed bio-oil into the whole mixture was calculated as follow.

$R_{b/w}=(R_{bio\text{-}oil}\times CP)/[10-R_{bio\text{-}oil}\times(1-CP)]$

Where

$R_{b/w}$:The proportion of mixed bio-oil in the whole mixture;

$R_{bio\text{-}oil}$:The ratio using in mixing.

2.3.3 Detection result

Table 2-2. Main characteristics of the upper layer mixture compared with raw bio-oil and biodiesel (all mixtures were made at 40 °C with 30 hours mixing).

Bio-oil:Biodiesel	10:0	5:5	3:7	1:9	0:10
$R_{b/w}$(%)	100	2.7	9.1	11.5	0
C (%)	57.5	73.9	74.4	75.1	76.6
H (%)	7.0	11.1	11.1	12.0	12.6
N (%)	0.0	0.0	0.0	0.0	0.0
O (%)	35.5	14.9	14.4	12.8	10.8
S(mg/kg)	0.0	0.0	0.0	0.0	0.0
H_2O (%)	7.9	2.8	2.5	1.1	0.0
Ash (%)	0.0	0.0	0.0	0.0	0.0
Density (g/cm^3)	1.14	0.94	0.90	0.87	0.87
HHV (MJ/kg)	25.4	37.1	37.3	39.6	41.2
Cetane index	<20*	22.42	35.74	40.78	46.30
Kinetic viscosity (mm^2/s @ 40 °C)	6.80	4.82	4.51	3.91	3.80

*Cetane index of bio-oil was not suited to JIS K 2280-5 method for its high density.

Table 2-2 compares the main properties of the upper layer of the mixture (blended oil). This table shows substantial improvement of the oil quality when bio-oil was blended with biodiesel. An interesting observation is that the initial bio-oil mixing ratio did not strongly affect the properties of the blend oils. The density of the blend oils dropped compared with bio-oil. The kinematic viscosity of the blend oils drastically decreased and there also was a big drop in the oxygen and water contents. The HHV significantly increased to about 90% of that of biodiesel.

The evaluation indicators of renewable fuels typically include the cetane number/the cetane index, the viscosity and HHV. Compared to biodiesel which is available for engine, the cetane index of the 1:9 upper layer mixtures was only a little low. The cetane index of 3:7 upper layer mixtures was lower than 1:9 mixtures but still more than 35. These two types of mixtures were certainly can be applied to medium-speed diesel engine. The viscosity of three types of mixture was more closed to biodiesel than to bio-oil. Lower water content ensured that the loss of HHV was not too much. HHV of the three types were half higher than the bio-oil and only 10% lower than the biodiesel. Overall, when the bio-oil mixing ratio was up to 30%, the performance of the main characteristic of mixtures decreased but not much compared to the biodiesel. The mixtures were suitable for medium-speed diesel engine and the 1:9 ratio mixtures were even suitable in high-speed diesel engine for its cetane index was closed to 40.

In this chapter, a comparison of the main features of the bio-oil, the biodiesel and their mixtures was carried out. Because the lower layer of mixtures are impossible to be used, unless otherwise specified, the mixtures discussed in this chapters refers to biodiesel-rich upper layer. Some of their physical and chemical characteristics were tested in this chapter. The main components were determined by GC-MS, the analysis of the mixed fuels was based on the chemical nature of the main components.

2.4 Compositional Analysis

The raw bio-oil obtained from woody biomass had a higher kinematic viscosity than diesel fuel as shown in Table 2-2. The complexity of the bio-oil itself results in the difficulty to analyze and characterize. Gas chromatography-mass spectrometry (GC-MS) is the technique most widely used in the analyses of the composition.

A Rxi®-5Sil MS Colum was used in the GC and helium was selected as the carrier gas. The oven heating profile was set at an increase of 4 °C/min from 40 to 300 C, with the initial temperature and the final temperature maintained for 10 min. The initial injection temperature was 300°C. The full analysis took 84 min.

The major components of one kind of the crude bio-oil based on the GC-MS analyses are shown in Table 2-3. From the ion current shown in Figures 2-7 and 2-8, the totally different components of bio-oil and biodiesel were clearly shown. The peaks of the boi-oil mainly appeared in the first 45 min, which means the gasification temperatures of the main compositions was lower than 180 ℃ while those of biodiesel were higher than 180℃. Judging from the two figures, the bio-oil contains hundreds of ingredients, but no dominant component in it while the substances, the retention times of which are at 55 min and 49 min, dominates the biodiesel.

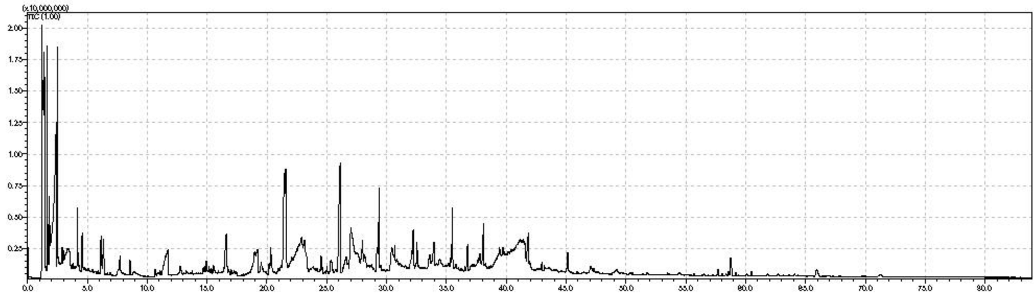

Figure 2-7 Ion current of bio-oil

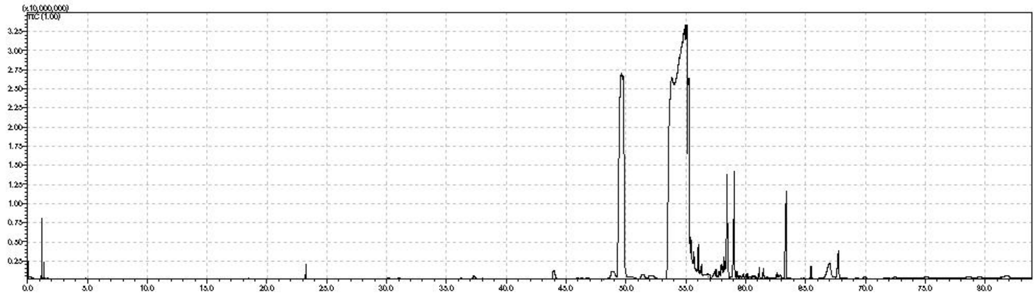

Figure 2-8 Ion current of biodiesel

Table 2-3 Main components of bio-oil

Serial number	Retention time(min)	Area（%）	Name
1	41.18	7.85	.beta.-D-Glucopyranose, 1,6-anhydro-
2	2.398	4.59	Acetic acid
3	21.575	3.89	Phenol, 2-methoxy-
4	22.9	3.51	Hexanal
5	27.036	2.68	Catechol
6	26.124	2.56	Creosol
7	2.532	2.2	2-Propanone, 1-hydroxy-
8	1.217	2.17	Methyl Alcohol
9	39.443	2.17	2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-
10	35.505	1.99	Phenol, 2-methoxy-4-(1-propenyl)-, (Z)-
11	29.381	1.9	Phenol, 4-ethyl-2-methoxy-
12	1.401	1.67	Water
13	30.457	1.66	1,2-Benzenediol, 3-methyl-
14	1.351	1.62	Acetone
15	1.256	1.55	Methyl formate
16	32.222	1.49	Phenol, 2-methoxy-3-(2-propenyl)-

17	23.144	1.42	Maltol
18	16.594	1.39	Phenol
19	11.724	1.36	2(5H)-Furanone
20	37.77	1.28	2(3H)-Naphthalenone,4,4a,5,6,7,8-hexahydro-4a-methyl-
21	3.337	1.17	.+/-.-Tetrahydro-3-furanmethanol
22	26.64	1.14	2,6-Dimethyl-octa-2,6-dien-1-ol
23	18.989	1.13	2-Cyclopenten-1-one, 2,3-dimethyl-
24	39.733	1.12	4-Ethoxy-3-anisaldehyde
25	33.947	1.07	Vanillin
26	27.533	1.05	5-Hydroxymethyldihydrofuran-2-one
27	38.103	1.05	2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-

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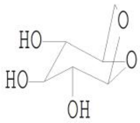

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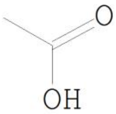

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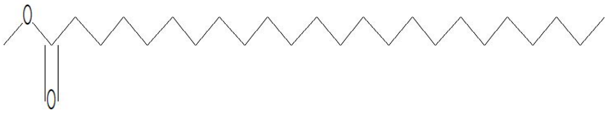

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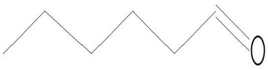

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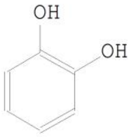

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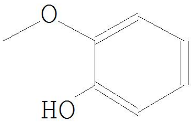

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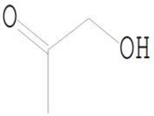

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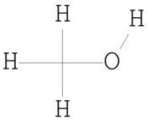

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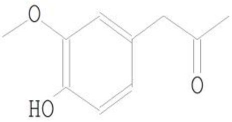

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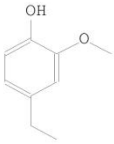

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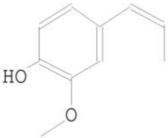

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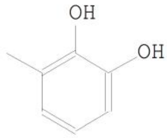

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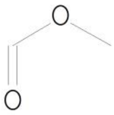

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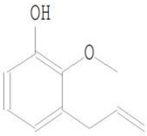

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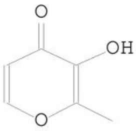

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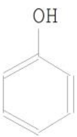

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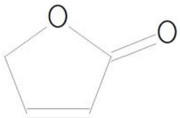

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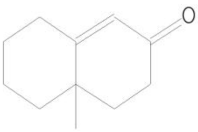

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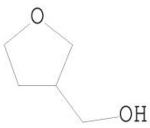

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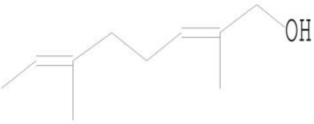

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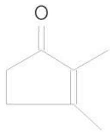

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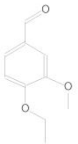

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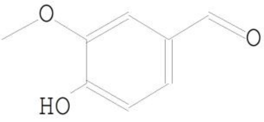

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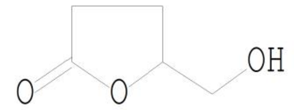

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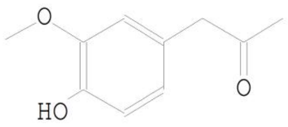

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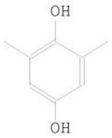

Figure 2-9 Chemical structures of main components in the bio-oil
(serial number 1 to 27)

From Table 2-3, we can see clearly that no component accounts for the vast majority in the bio-oil， and all of the substances above account for only 55% of the total area of the peaks. The retention time of these peaks were mainly detected in the first 45 minutes.

From the chemical structures of these components shown in Figure 2-9, the oxygen content should be high and the hydrocarbon content is relatively low. High contents of ketone, acid and phenol reduce the energy density and the stability of bio-oil. This will be a defect for the utilization of bio-oils as discussed in section 3.1.2.

Table 2-4 Main components of the biodiesel

Serial number	Retention time(min)	Area（%）	Name
28	54.895	30.59	9-Octadecenoic acid, methyl ester, (E)-
29	53.815	16.98	9,12-Octadecadienoic acid (Z,Z)-, methyl ester
30	49.611	10.84	Hexadecanoic acid, methyl ester
31	55.078	8.88	Methyl stearate
32	58.462	2.03	cis-11-Eicosenoic acid, methyl ester
33	59.057	1.84	Methyl 18-methylnonadecanoate
34	49.676	1.63	2-Methylheptanoic acid
35	49.77	1.62	Pentanoic acid, 2-methyl-
36	63.385	1.59	Docosanoic acid, methyl ester
37	49.822	1.39	Tridecanoic acid, methyl ester
38	66.989	1.05	9-Octadecenoic acid, 1,2,3-propanetriyl ester, (E,E,E)-
39	49.805	0.9	Pentadecanoic acid, 14-methyl-, methyl ester

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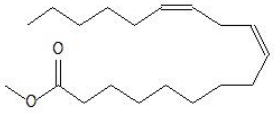

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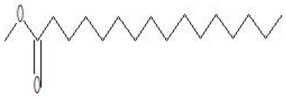

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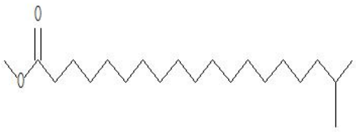

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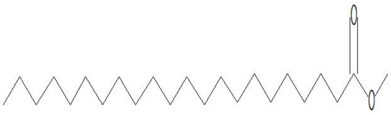

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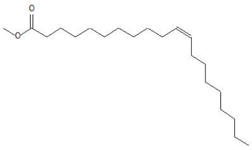

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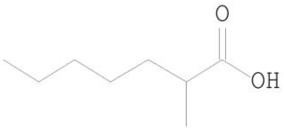

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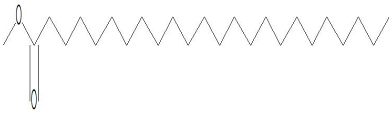

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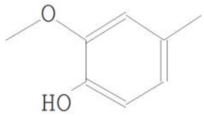

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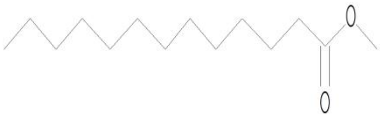

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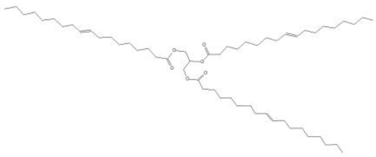

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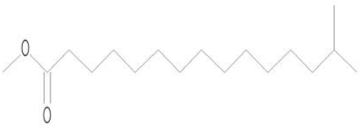

Figure 2-10 Chemical structures of main components in the biodiesel (serial number 28 to 39)

Table 2-4 shows the main components of the biodiesel we utilized and Figure 2-10 shows the chemical structures of these main components. The main components of the biodiesel are long chain fatty acids. Octadecene methyl and methyl hexadecanoate dominate the main properties of the biodiesel. The retention time of their peaks were mainly detected after 45 minutes.

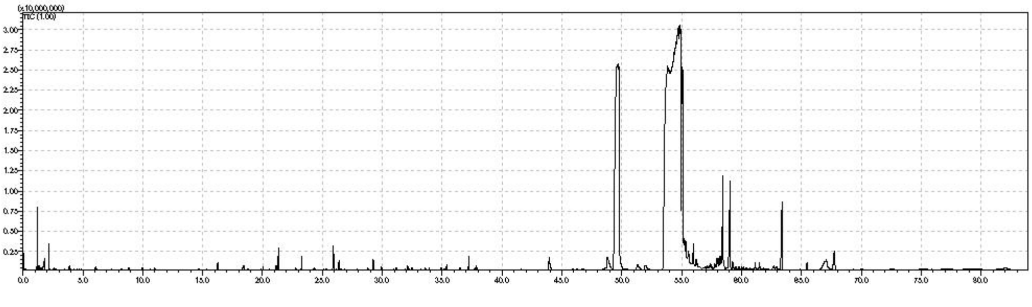

Figure 2-11 Ion current of 1:9 mixture

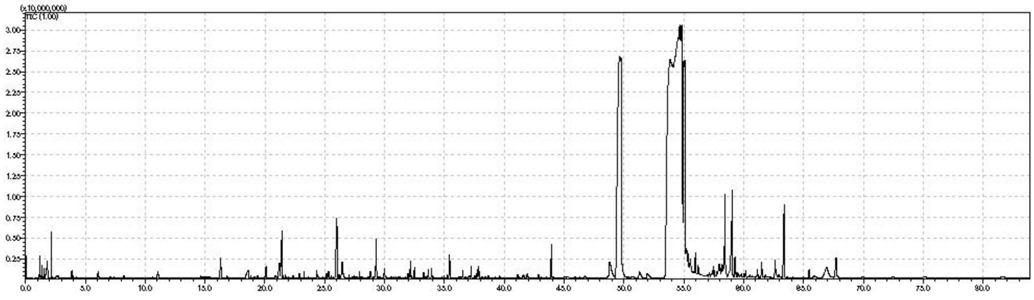

Figure 2-12 Ion current of 3:7 mixture

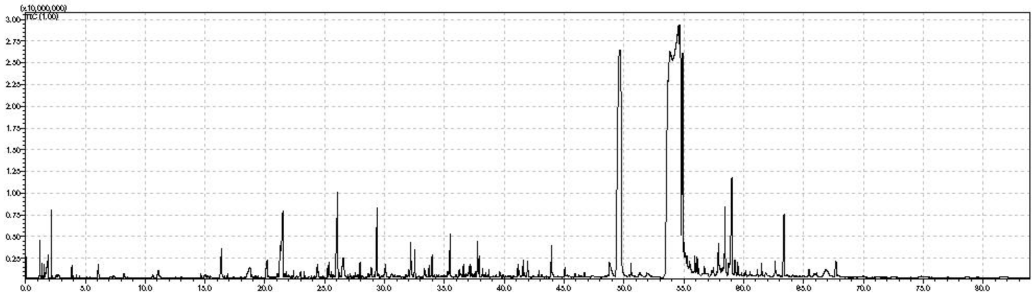

Figure 2-13Ion current of 5:5 mixture

As shown in Figures 2-11, 2-12 and 2-13, with the increase of the ratio of the bio-oil, the components of the bio-oil (the peak time before 45 minutes) was increasing. The most obvious ones are 2-methoxy-Phenol (Retention Time=21.435min)，Creosol (Retention Time=25.996min)， 4-ethyl-2-methoxy-Phenol (Retention Time = 29.299min)，2-methoxy-4-(1-propenyl)-(Z)-Phenol (Retention Time =33.945 min), 1-(4-hydroxy-3-methoxyphenyl)-2-Propanone (Retention Time = 39.370 min)and Methyl tetradecanoate (Retention Time = 43.953min). Phenol, ketone, ester with simple structures seemed easier to be emulsified in the mixtures. Moreover, a lot of short carbon chain acid, alcohol and ester exists in the mixture, such as formic acid, acetic acid, acetone, methanol and so on, the retention time of which concentrated in the first 5 minutes.

The composition of the lower layer of the mixtures were also analyzed as shown in Figure 2-14 and Table 2-5. At the beginning, the highest peak is methanol. Because the lower layer appears as waxy solid, the samples were dissolved in methanol. Some substances abound in the raw bio-oil were not detected in the mixed liquid, the retention time of which were between 20 minutes to 40 minutes. These substances are mainly long chain organics with a carbon ring.

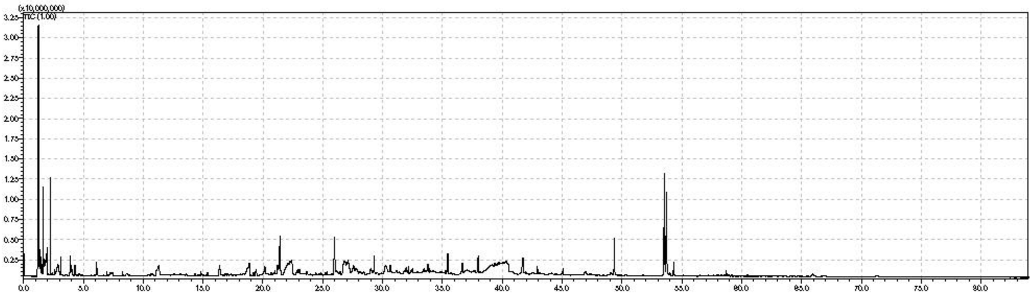

Figure 2-14 Ion current of the pyrolytic lignin-rich lower layer of the mixture

Table 2-5 Main components of the pyrolytic lignin-rich lower layer

Retention time(min)	Area（%）	Name
53.567	9.72	9,12-Octadecadienoic acid (Z,Z)-, methyl ester
40.333	6.57	.beta.-D-Glucopyranose, 1,6-anhydro-
39.37	4.97	2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-
21.435	3.14	Phenol, 2-methoxy-
25.996	2.53	Creosol
22.412	2.39	Cyclopropyl carbinol
26.861	2.3	Catechol
22.095	2.27	Pentanoic acid, 4-oxo-
27.121	2.14	2H-Pyran, tetrahydro-2-[(tetrahydro-2-furanyl)methoxy]-
18.86	1.99	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-
1.988	1.89	Acetic acid
2.243	1.83	2-Propanone, 1-hydroxy-
49.22	1.72	1-Heptanol, 2,4-dimethyl-, (R,R)-(+)-
41.734	1.65	Homovanillic acid
11.337	1.51	2(5H)-Furanone
30.286	1.51	1,2-Benzenediol, 3-methyl-
37.064	1.27	.alpha.-D-Glucopyranose, 4-O-.beta.-D-galactopyranosyl-
39.677	1.24	4-Ethoxy-3-anisaldehyde
1.613	1.16	Acetaldehyde, hydroxy-
31.995	1.12	Phenol, 2,6-dimethoxy-
23.068	1.11	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-
27.781	1	2-Deoxy-D-galactose

Table 2-6 compares the upper parts of the mixtures at different mixing ratios. Octadecene methyl and methyl hexadecanoate dominate the main properties of three kinds of mixed fuels. Their main ingredients were nearly the same as biodiesel, regardless of the mixing ratios. That is why the bio-oil could not dominate the composition of the mixtures. The properties of the upper layers, such as the proportion of elements, the water content and the viscosity were rightly closer to those of biodiesel, especially closer to the properties of octadecene methyl and methyl hexadecanoate.

Table 2-6 Main components of different mixing ratio mixtures

Bio-oil/biodiesel=1:9		
Retention time(min)	Area（%）	Name
54.876	31.59	9-Octadecenoic acid, methyl ester, (E)-
53.838	20.78	9,12-Octadecadienoic acid (Z,Z)-, methyl ester
49.622	16.31	Hexadecanoic acid, methyl ester
55.016	10.76	Methyl stearate
58.453	2.04	cis-11-Eicosenoic acid, methyl ester
59.049	1.78	Methyl 18-methylnonadecanoate
63.393	1.16	Docosanoic acid, methyl ester
67.098	0.78	9-Octadecenoic acid, 1,2,3-propanetriyl ester, (E,E,E)-
48.814	0.66	9-Hexadecenoic acid, methyl ester, (Z)-
67.758	0.49	Tetracosanoic acid, methyl ester
Bio-oil/biodiesel=3:7		
Retention time(min)	Area（%）	Name
54.635	29.87	9-Octadecenoic acid, methyl ester, (E)-
53.854	18.7	9,12-Octadecadienoic acid (Z,Z)-, methyl ester
49.624	15.25	Hexadecanoic acid, methyl ester
55.016	8.76	Methyl stearate
59.041	1.87	Methyl 18-methylnonadecanoate
58.459	1.71	cis-11-Eicosenoic acid, methyl ester
63.389	1.18	Docosanoic acid, methyl ester
26.01	1	Creosol
21.43	0.84	Phenol, 2-methoxy-
66.946	0.76	9-Octadecenoic acid, 1,2,3-propanetriyl ester, (E,E,E)-
Bio-oil/biodiesel=5:5		
Retention time(min)	Area（%）	Name
54.692	29.26	9-Octadecenoic acid, methyl ester, (E)-

53.858	17.94	9,12-Octadecadienoic acid (Z,Z)-, methyl ester
49.66	12.9	Hexadecanoic acid, methyl ester
54.92	8.04	Methyl stearate
59.011	2.42	Methyl 18-methylnonadecanoate
21.499	2.28	Phenol, 2-methoxy-
26.08	1.95	Creosol
58.456	1.33	cis-11-Eicosenoic acid, methyl ester
29.366	1.14	Phenol, 4-ethyl-2-methoxy-
63.368	0.92	Docosanoic acid, methyl ester

The stable and high quality blend oils were able to be produced by mixing the bio-oil and the biodiesel without any additives as an upper layer of the stratified mixture. The mixing process needed a long time exceeding 10 hours for each mixture to achieve the maximum CP (changed proportion of bio-oil)) value while 95% of the maximum CP value could be achieved in the first hour of mixing. Heating contributed to accelerate the mixing process but did not affect the maximum CP value. By reducing the initial bio-oil mixing ratio, the maximum CP value of 25% by weight of the bio-oil was achieved.

The upper layer mixture showed desirable properties in regards to the viscosity, the water content and the oxygen content compared to the raw bio-oil. The analysis of the upper layer mixtures (blend oils) discovered no components accounting for the vast majority in the bio-oil. Most of the components in the bio-oil contained the oxygen element. Long carbon chain fatty acid esters dominated the main properties of the biodiesel. Phenol, ketone, ester with simple structures are easier to be emulsified or resolved in the upper layer mixture. Methyl octadecene and methyl hexadecanoate dominate the main properties of the upper layer mixed fuels. The main ingredients of the blend oils were nearly the same as the biodiesel, regardless of the mixing ratios. Compared with the biodiesel which can be used in the internal combustion engines, the blend oils showed similar characteristics on the centane index, HHV and the viscosity. The application of these blend oils in an internal combustion engine should be tested in the next step.

2.5 Principle analysis

Compounds in bio-oil are of different sizes and natures. There are highly polar components (water, acids and alcohols), less polar components (esters, ethers and phenolics) in it. These components are not completely mutual soluble. Thus, the bio-oil can be considered as microemulsions. Water and water soluble molecules form the continuous phase. Water insoluble materials are dispersed as micelles in the bio-oils. Some multipolar compounds act as emulsifiers to stabilize the structures.

It can be considered that both the solution and the emulsification occurred in the mixing process. The complexity of the blending reaction is that the bio-oil itself is an emulsified liquid. Hundreds of compounds in the bio-oil are of different properties. There are both high polar components (water, acids and alcohols) and low polar components (esters, ethers and phenolics) in it. These components are not completely mutual soluble. If water will be added, the precipitation happens immediately. It proves that water insoluble molecules form the continuous phase of the emulsified liquid. Water and water soluble materials are dispersed as micelles in the bio-oil. Some multipolar compounds act as emulsifiers to stabilize the structures.

After mixed with biodiesel, the main structures of the bio-oil changed into a biodiesel-based structure since the main components in the upper mixture were coming from the biodiesel. Material which was dissolved in the biodiesel or could react with the biodiesel formed a new continuous phase in which very little moisture was contained. With the increase of the ratio of the bio-oil, the components in the bio-oil emulsified or dissolved was increasing. The most obvious examples are 2-methoxy-Phenol ， Creosol ， 4-ethyl-2-methoxy-Phenol ， 2-methoxy-4-(1-propenyl)-(Z)-Phenol, 1-(4-hydroxy-3-methoxyphenyl)-2-Propanone and Methyl tetradecanoate. Phenol, ketone and ester with simple structures are also easy to be emulsified in the mixtures, such as formic acid, acetic acid, acetone, methanol and so on. Plenty of long chain organics which contain a carbon ring was not soluble in the fatty acid. A portion of the biodiesel was also detected in the lower layer. It means that the two phases are partially miscible emulsion. That is why the stratification started when the stirring was stopped.

The mixed proportion from the bio-oil into the upper layer increased as the initial bio-oil mixing ratio decreased and the limit was 25%. Water and other substances of high polarity mainly remained in the lower layer. These high polarity substances were much easier to resolve into high polarity liquid, bio-oil, than resolved or emulsified into the upper layer, which was mainly low polarity substances, biodiesel.

2.6 Engine test

The fuel mixtures with different mixing ratios (bio-oil/biodiesel=1:9,3:7,5:5), with 5% methanol addition, stirred at 800rpm under 40℃, within 20 hours mixing were used for the engine performance test in this chapter. All of the mixtures reached the stable state and no deterioration occurred in one month. The full load performance, the exhaust emission and the specific fuel consumption were investigated from the view point of the compatibility to diesel based on the US EPA regulation mode. Through the evaluation, the acceptable blending ratio will be discussed.

2.6.1 Materials and methods

According to the methodology of the blending which was described in the Chapter 2, the bio-oil which was derived from Japanese cedar was mixed with the biodiesel. The blend fraction of the bio-oil to the biodiesel was 50%, 30% and 10% in volume.

As shown in Table 2-7, the density of the blend oils slightly dropped but still out of the standards of diesel fuel (JIS K2204 2007, 0.86 in max.) (China GB19147 2009, 0.81-0.85). The kinematic viscosity of the blend oils were close to the maximum number (ASTM975, 4.1 in max. for No. 2-D) (EN590 2013, 4.5 in max.). There was a bit drop in the oxygen content but the water content decreased in half of the raw bio-oil. The heating value was recovered up to 77% of that of the diesel even with 50% fraction of the raw bio-oil whose heating value was half of that of the diesel.

Table 2-7 Properties of the tested fuels

	Bio-oil	5:5	3:7	1:9	BDF	Diesel
C(%)	57.5	73.9	74.4	75.1	76.6	85.04
H(%)	7.0	11.1	11.1	12.0	12.6	13.55
N(%)	0.0	0.0	0.0	0.0	0.0	0
O(%)	35.5	14.9	14.4	12.8	10.8	0
S(mg/kg)	0.0	0.0	0.0	0.0	0.0	0
H_2O(%)	7.9	2.8	2.5	1.1	7.9	0
Ash(%)	0.0	0.0	0.0	0.0	0.0	0
Density (g/cm^3)	1.14	0.94	0.90	0.87	0.85	0.83
HHV (MJ/kg)	25.4	37.1	37.3	39.6	41.2	45
Kinetic viscosity (mm^2/s@40℃)	6.80	4.82	4.51	3.91	6.80	2.744

For the engine test, a single cylinder direct fuel injection diesel engine was used and Table 2-8 shows the engine specification [2-7][2-8]. Figure 2-15 shows the experimental equipment for the engine test. It is consisted of a diesel engine, measurement devices and a dynamometer which controls the engine operation at a certain constant engine load and speed. The in-cylinder pressure data were instantaneously measured by a crystal pressure transducer (KISTLER 6053B). The total hydrocarbon (THC) and the smoke concentration in the exhaust gas were measured by the HFID (HORIBA MEXA-1170HFID) and by the opacity type smoke meter (HORIBA MEXA-600S), respectively. CO, CO_2, NOx and SO_2 emissions were measured by a NDIR type exhaust gas analyzer (Iwatadengyo Co., Ltd FAST-3100). The intake air temperature and the exhaust gas temperature were measured by a K-type thermocouple with the diameter of 1.0 mm. The fuel consumption was measured by using the electric weighing instruments. All measurement data were continuously processed at the same time in the data collection unit (KEYENCE NR-HA08 and NR-TH08) and a personal computer.

Table 2-8 Test engine specification

Engine specification	
Cylinder number	1
Bore × Stroke	70mm × 57mm
Displacement volume	219cm^3
Compression ratio	20.6
Aspiration type	Natural
Rated power	3kW/3600rpm
Combustion chamber	Re-entrant
Injection pressure	20MPa
Injection timing	17.5 ± 0.5 deg. BTDC
Number of injection hole	4
Diameter of injection hole	0.22mm
Diesel fuel spray angle	95 deg

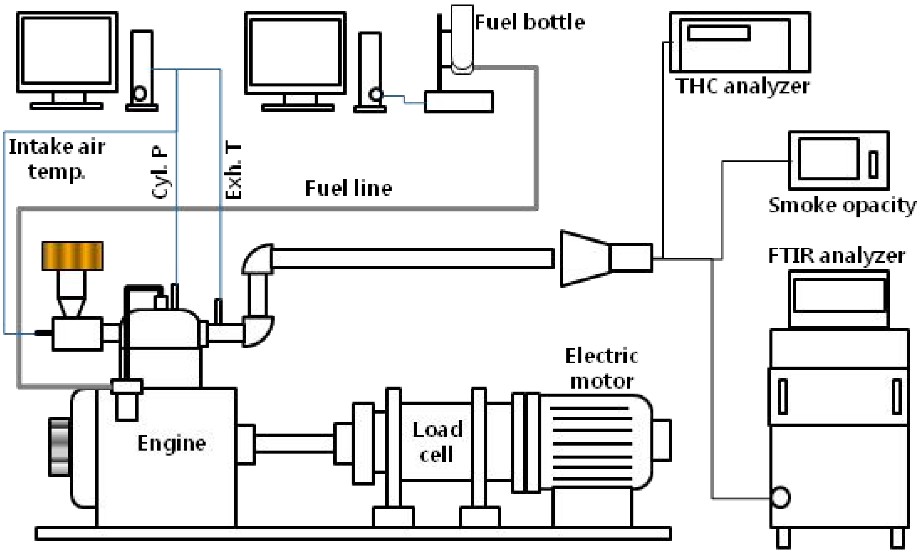

Figure 2-15 Experimental apparatus

The engine speed and the torque were specified in Table 2-9. The Letter “I” means that engine speed is 2450rpm while “R” is for the 3500rpm. The number behind “I” or “R” means the percentage of the load at the rated speed. For example, “I100” means the full load at 2450rpm. The standard diesel should perform 7.3 Nm and 1.87kW at I100 according to the EPA regulation.

Table 2-9 Specified operation point of engine test

Operation point	Engine speed	Torque	Power
-	rpm	Nm	kW
Idle	1500	0	0
I50	2450	3.65	0.94
I75		5.47	1.40
I100		7.3	1.87
R10	3500	0.86	0.32
R50		4.3	1.58
R75		6.45	2.36
R100		8.6	3.15

2.6.2 Full load performance

Figure 2-16 shows the maximum reachable torque for all the test fuels. The full load performance was evaluated upon the EPA regulation. The red lines are torque 8.6 Nm for R100 and 7.3 Nm for I100. The maximum reachable torques of the blended fuels were marked using black circles. The maximum reachable torques of the fuels of different ratios of bio-oil showed not much gap to the red lines except for the standard deviation of the engine torque went slightly worse for the 50% blend in the case of 2450rpm, but the engine was stably operated even for the this case.

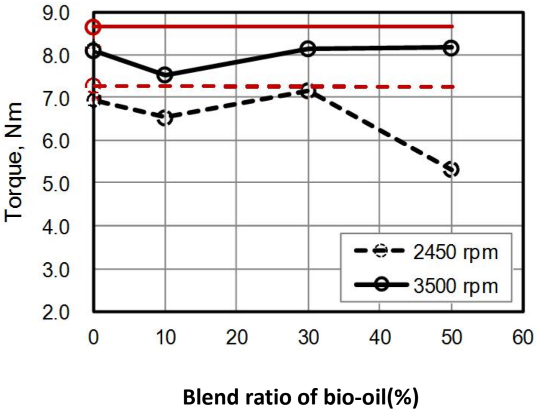

Figure 2-16 The maximum reachable torque

For more detail investigation, Figures 2-17 and 2-18 show the cylinder pressure and the rate of the heat release. By comparison, it is found that the performance and the cycle time of the maximum heat release cylinder were almost the same.

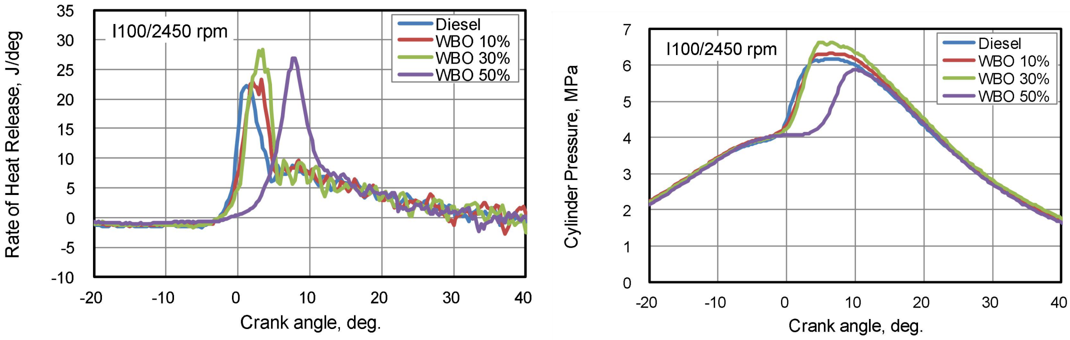

Figure 2-17 The cylinder pressure and the rate of heat release at I100, 2450rpm

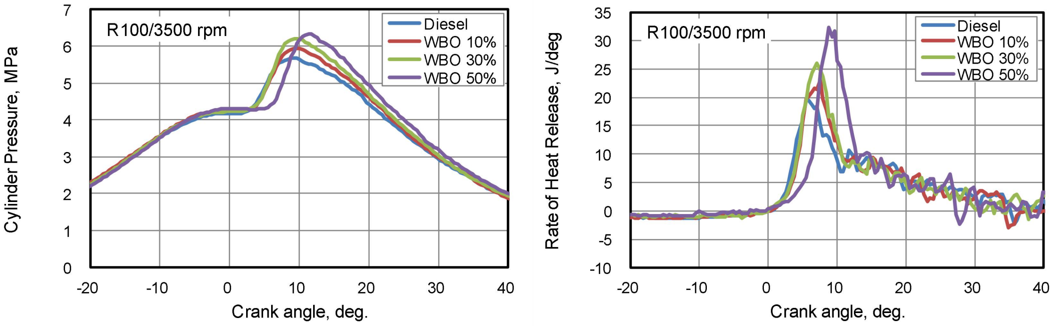

Figure 2-18 The cylinder pressure and the rate of heat release at R100, 3500rpm

As shown in Figure 2-19, the ignition timing was slightly delayed with the increase of the blend ratio up to 30%, and for the 50% blend, the ignition delay became more significant. It means that the higher the blend ratio is, the longer the time is required.

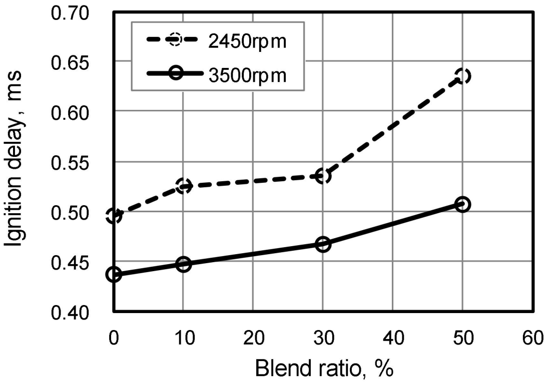

Figure 2-19 Ignition delay

To conclude, the full load power was almost the same even with the increase of the blend ratio. With the rise of the blend ratio, the heating value per unit mass decreases. But the total amount of the heat release per single combustion was compensated by the increased injection amount due to the increased injection rate driven by the higher density.

2.6.3 NOx emission

In Figure 2-20, NOx emission is plotted in the forms of the concentration at 2450rpm and at 3500rpm. With the rise of the blend ratio, the NOx emission decreased for the case of 2450rpm and this tendency was clearest for R10. NOx is formed by the reaction between oxygen and nitrogen in air. Its formation is related to the combustion temperature and hydrocarbon radicals during combustion. The higher the temperature and content of radicals are, the higher the emission of NOx is. It can be inferred that, with the increase of the mixing ratio (bio-oil/biodiesel), the combustion temperature and the heat generation decreased. Thus, the amount of hydrocarbon radicals reduced.

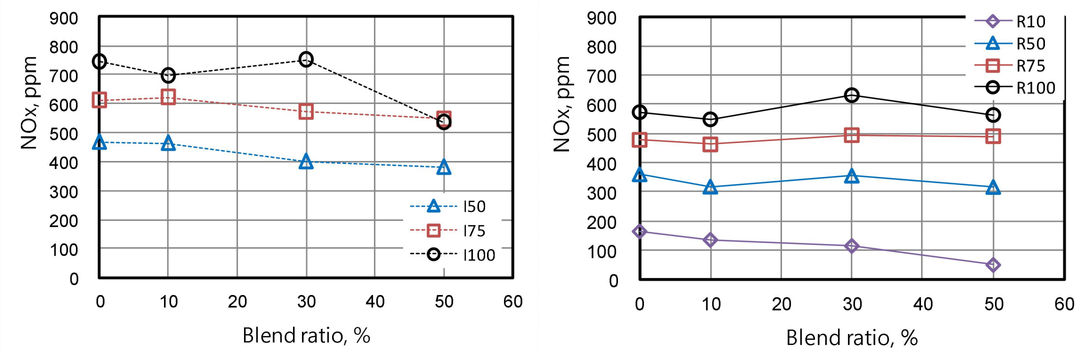

Figure 2-20 NOx emission as a function of the blend ratio

(left at 2450rpm, right at 3500rpm)

2.6.4 Smoke emission

The smoke emission was measured by the form of the opacity(%), and the results are illustrated in Figure 2-21. In the case of the 10% blend, the number of smoke is too much high and might be erroneous when the measurement was carried out. The smoke opacity generally became higher for both engine speeds by the increase of the blend ratio. The smoke opacity for R50 in the 50% blend was 100%. The viscosity of the bio-oil is higher than that of the diesel and thus lead to the poorer atomization. This surely resulted in the worsen smoke emission. On the other hand, from the analysis of the chemical structure, the organic material containing carbon-ring contain more carbon atoms and branched chain, constituting stable structure difficult to be completely combusted into CO_2. The black smoke thereby is generated.

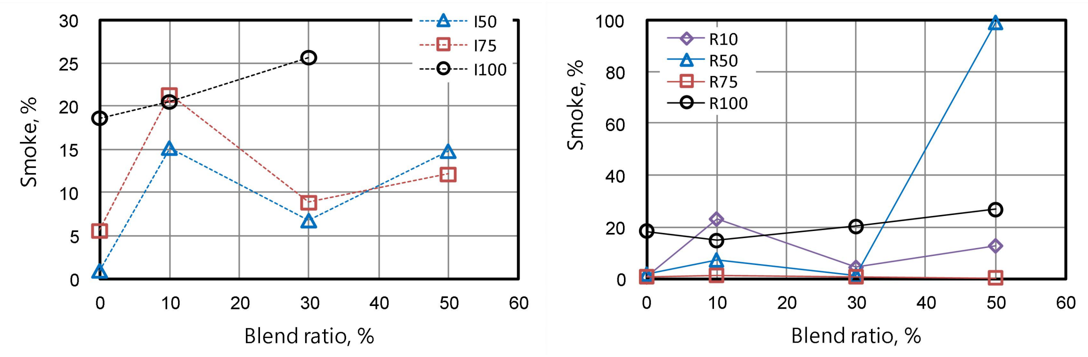

Figure 2-21 Smoke emission as a function of the blend ratio

(left at 2450rpm, right at 3500rpm)

2.6.5 CO emission

Figure 2-22 shows the CO emission as a function of the blend ratio. The increase of the blend ratio resulted in the higher CO emission for both engine speeds. Especially, in R10, the CO emission turned out double higher for the 30% blend than that for diesel and around 4 times higher for the 50% blend due to the misfire which was led by the enlarged ignition delay. The smoke shown in 4.2.3 proved that the fuel was not completely combusted due to the high physical stability of the bio-oil in the combustion physics. This will undoubtedly increase the THC emissions.

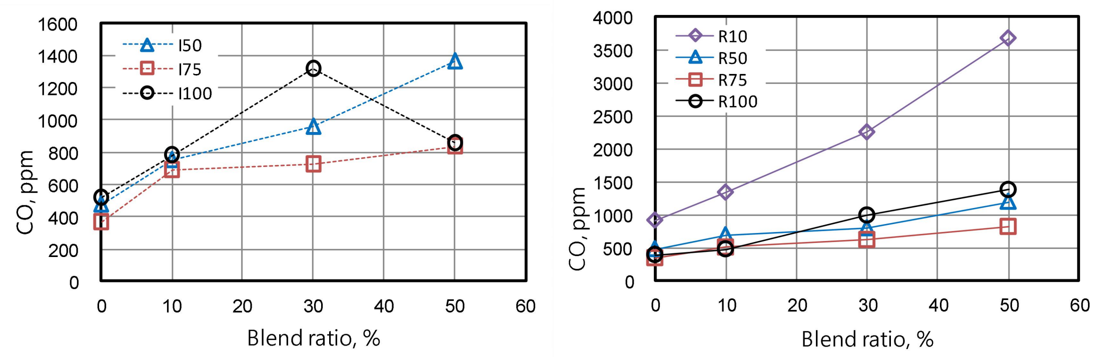

Figure 2-22 CO emission as a function of the blend ratio

（left at 2450rpm, right at 3500rpm ）

2.6.6 THC emission

The THC emission is depicted in Figure 2-23. The THC emission increased with the increase of the blend ratio up to 30% at 2450rpm. At 3500rpm, the THC emission was higher for the blend oil in the range of low loads. At R10, the THC emission of the 50% blend drastically increased around double magnitude and the engine was not possible to keep its stable operation by the intermittent misfire. It is because that the ignition timing was too much delayed by the heavier blending and thus it made the firing difficult. The poorer spray condition might be one reason.

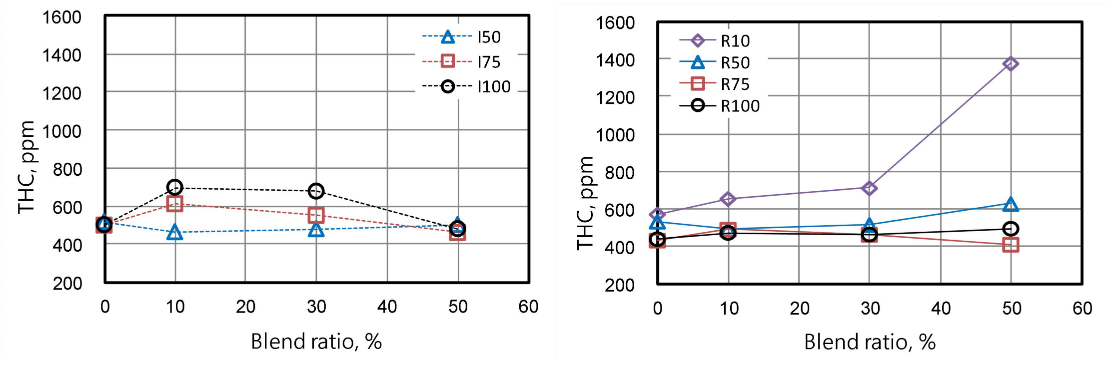

Figure 2-23 THC emission as a function of the blend ratio

(left at 2450rpm, right at 3500rpm)

2.6.7 Exhaust emissions of EPA mode

As shown in Figure 2-24, the EPA mode exhaust emissions were evaluated with regard to C1-8 mode for the non-road mobile vehicle and D2-5 mode for the gen-sets. The red line is EPA Tier 1 standard set by EPA. In the case of C1-8 mode, the NOx+THC emission was placed around the regulation limit and slightly increased with the increase of the blend ratio and this was caused by the increase of the THC emission. The NOx+THC emission of D-5 mode for the biodiesel was lower than those of the 10% and 30% blends and went slightly over the limit. As shown in Figure 2-20, the NOx emission of the fuel without bio-oil addition was higher than those of the 10% and 30% blends. However, NOx+THC emission of the 50% blend in D5-mode became worse than the diesel due to the explosive THC emission caused by CO emission due to incomplete combustion depicted in Figure 2-21 and 2-22

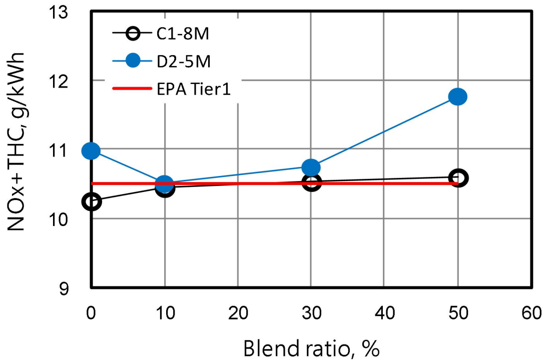

Figure 2-24 NOx+THC emission as a function of the blend ratio

Figure 2-25 illustrates the result of the CO and PM (caused by smoke) emissions.

The CO emission result positioned around the regulation limitation for the both mode of diesel and for the C1-8 mode of the 10% blend. The specific CO emissions of R10 and I10 were difficult to meet the regulation and this CO emission increase appeared more significant with the increase of the blend ratio. Up to the 30% blend ratio, the PM emission was below the limitation for both modes. But because of the much worsen performance at R10, the PM emission of the 50% blend went far over the limitation.

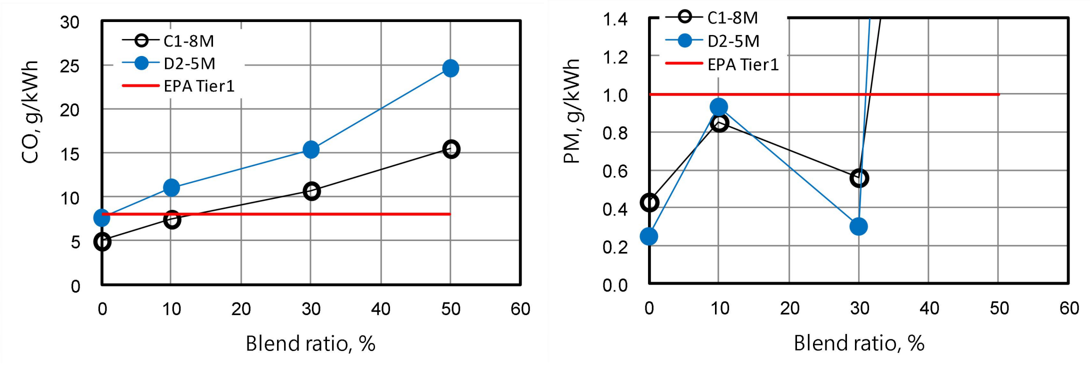

Figure 2-25 CO (left) and PM (right) emission

2.6.8 Eight hours test

For the 50% blending ratio, the maximum engine power at 3500rpm was compatible to the diesel. Nevertheless, all the exhaust emissions went far over the limitations. Therefore, the present bio-oil can be utilized in a diesel engine up to around 30% blend ratio with the biodiesel.

The engine operational test carried out during 8 hours continuously at the rated engine full output performance. For the 30% blend, about 0.5kW went down soon after 30 minutes and was kept constant but decreased again after 7 hours. Since the first half hour operation, the combustion was not happened for a certain time in seconds. The cylinder pressure rise by the combustion was not happened and the cylinder pressure was the same as that of the motoring because the engine was motored in force by the electric motor. In addition to that, the indication of the fuel metering was not changed. There might be some problem in the fuel delivery pump and hence failure to feed the fuel into the injector. But since several seconds, the injection of the fuel was recovered and the combustion occurred normally. The recovery might be introduced by the forced motoring by the electric motor. Due to the reversibility, the test was kept to go through the 8 hours.

The failure mode intermittently and irregularly happened as shown in Figure 2-26. The duration of the failure and the interval randomly dispersed from 1 second to 40 seconds and 2 times to 5 times in 1 hour, respectively.

After finishing all the tests, the remainder of the 30% blend oil in the fuel delivery system was flushed with the diesel fuel via running by the electric motor but the injection was not happened.

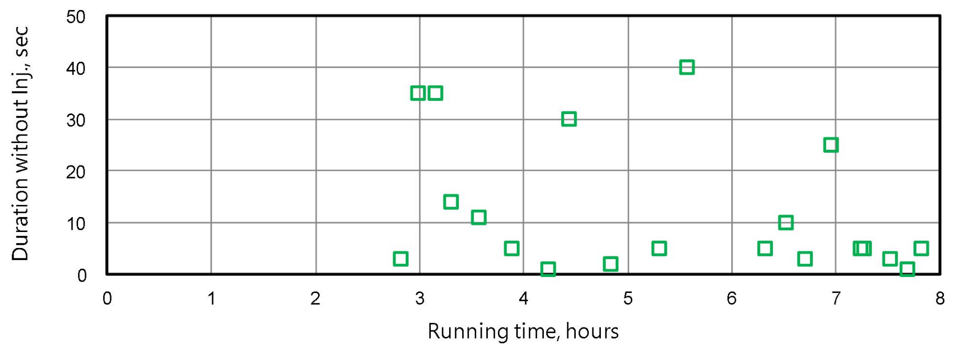

Figure2-26 Time history of the duration without injection

Figure 2-27 shows that the viscous material blocked the nozzle tip. It is neither like the raw materials, bio-oil and biodiesel, nor like the upper layer of the mixture. It is more likely the lower layer of the mixture after storing for a long time from the outlook. Thus, the failure of the 8 hours test is thought to be due to the polymerization of the bio-oil which was unstable when heated, even to 30℃. The main components changed when heated, and the bio-oil phase would separate. The interaction, such as the esterification reaction between hydroxyl and carboxyl, the etherification reaction between hydroxyl and carbonyl, the polymerization among the unsaturated bonds, should have happened. A direct result of these reactions is the increase of the average molecular weight and the water content. The viscosity should increase along with the increase of the molecular weight.

Figure 2-27 Nozzle tip : right (before the test) and left (after the test)

2.6.9 Four hours test

The 10% blending mixture was used in a four hours engine test. The maximum engine power at 3500rpm was compatible to the diesel. The engine kept running for four hours without interruption, which meant that the blockage did not occur and the 10% mixture can be applied in the engine at least 4 hours. The emission was listed in Figure 2-28

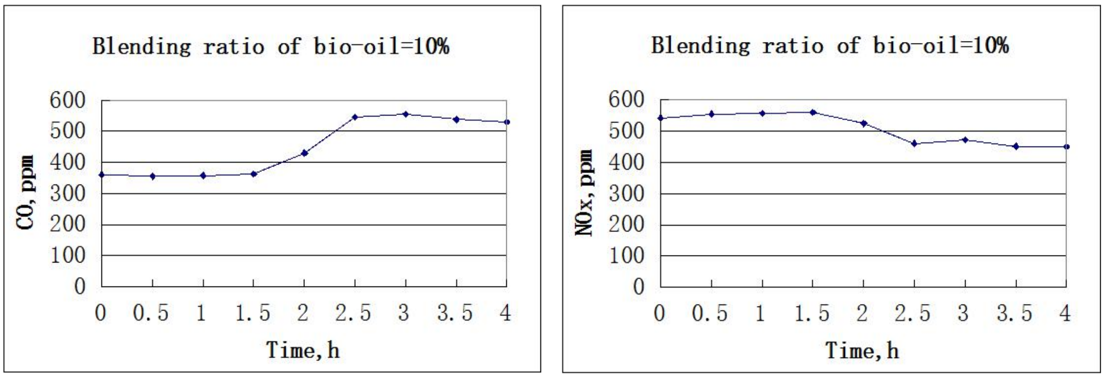

Figure 2-28 CO (left) and NOx (right) emission of 4 hours engine operation

It is clearly shown that the emission of CO increased while NOx decreased along with time. Since CO and NOx come from the incomplete combustion, it should be considered that the incomplete combustion is increasing. The combustion efficiency was declining with time. Regardless of the mixing ratio, some hazardous substances are included in the mixture, which is the limit of the blended fuel. The bio-oil can not perform beyond its own combustion performance.

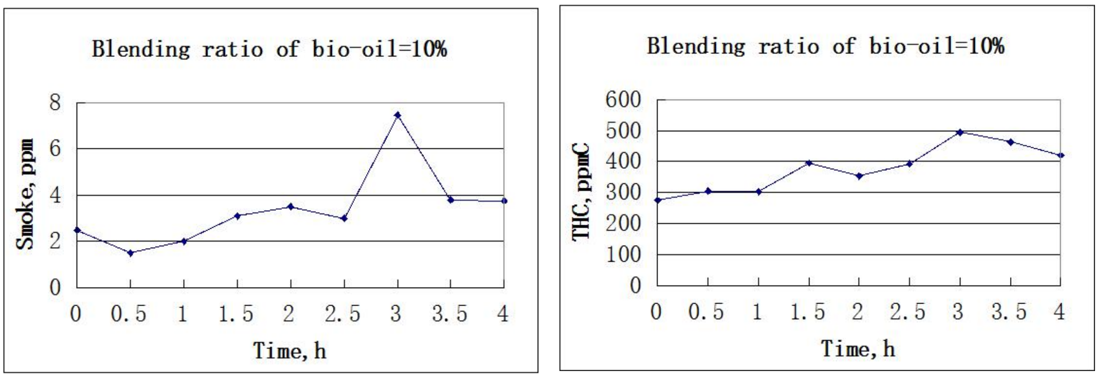

Figure 2-29 Smoke (left) and THC (right) emission of 4 hours engine operation

In Figure 2-29, the smoke and THC emissions showed the same increasing tendency accompanied with the combustion efficiency. Changes in the smoke emissions were unstable especially when it came to 3h .In general, the blended fuel does not reduce the molecular weight of macromolecules and does not alter the chemical structure of the oxygen-containing substance. The oxygen-containing substance and macromolecules will certainly reduce the combustion efficiency, no matter how low the percentage they are. This adverse effect will be accumulated with time and eventually results in non-lasting combustion in engine.

However, four hours is a smooth running, showing that blended fuels significantly improve the quality of bio-oil itself. If the long time combustion is needed, a fundamental means of upgrading should be considered.

2.7 Summary

A stable bio-oil/biodiesel emulsion was produced without additives. The stable and high quality blend oils were able to be produced by mixing bio-oil and biodiesel without any additives as an upper layer of the stratified mixture. The mixing process needed a long time exceeding 10 hours for each mixture to achieve the maximum CP (changed proportion of bio-oil) value while 95% of the maximum CP value could be achieved in the first hour of mixing. Heating contributed to accelerate the mixing process but did not affect the maximum CP value. By reducing the initial bio-oil mixing ratio, the maximum CP value of 25% by weight of the bio-oil was achieved.

The upper layer mixture showed desirable properties in regards to the viscosity, the water content and the oxygen content compared to the raw bio-oil. The analysis of the upper layer mixtures (blend oils) discovered no components accounting for the vast majority in the bio-oil. Most of the components in the bio-oil contained the oxygen element. Long carbon chain fatty acid esters dominated the main properties of biodiesel. Phenol, ketone, ester with simple structures are easier to be emulsified or resolved in the upper layer mixture. Methyl octadecene and methyl hexadecanoate dominate the main properties of the upper layer mixed fuels. The main ingredients of the blend oils were nearly the same as biodiesel, regardless of the mixing ratios. Compared with biodiesel which can be used in internal combustion engines, the blend oils showed similar characteristics on the centane index, HHV and the viscosity. The application of these blend oils in the internal combustion engine should be tested in the next step.

When mixing with the biodiesel, the main structure of the bio-oil changed into a biodiesel-based structure. The material which was dissolved into the biodiesel or can react with the biodiesel replaced the water formed in the continuous phase. With the increase of the ratio of the bio-oil, the compositions of the bio-oil in mixed fuels were increasing. The components dissolved into the biodiesel was mainly short carbon chain acid, alcohol and ester. Phenol, ketone and ester with simple structures seemed to be emulsified in the mixtures easily. Plenty of long chain organics which contains a carbon ring was not soluble in the fatty acid. The biodiesel dominated traits of the mixtures since its content dominated the most components in the mixture fuels.

Up to 30% blending ratio of the bio-oil with the bio-diesel, the engine operation was compatible to the diesel. It resulted that almost identical full load engine output was achieved, the NO+THC and PM emissions were positioned around the EPA Tier1 standard. It should be careful of the increase of the kinematic viscosity by adding the raw bio-oil because it may affect the spray condition in negative direction resulting in higher exhaust emissions like smoke.

For 8 hours continuous operation in the engine, the fuel injection system was encountered with the irreversible failure after finishing the 8 hours operation and it is confirmed by the impossibility of the fuel injection with the diesel fuel. The fuel injection stop was occurred frequently and it intermittently observed through the whole test duration. It is thought to be due to the polymerization and other reactions of the bio-oil when heated in the engine for a long time.

For 4 hours test of 10% blending ratio mixture, though the combustion efficiency is declining, the continuous operation was successful. It also proved that blended fuel has its limits and cannot overcome the chemical disadvantages from the bio-oil. A chemical upgrading should be studied in the next work.

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Chapter 3

Cracking upgrading of bio-oil

The objective of this research is to explore the possibility to upgrade distilled bio-oil in bench-scale fixed bed reactors with two heating units using the cracking method. The catalyst is HZSM-5 zeolite, which is commonly used in bio-oil upgrading by the cracking. The result showed that by using two heating units, even without catalyst, the upgrading was achieved well. The catalytic cracking promoted the deoxygenation rate and further improved the quality of the upgraded oil compared with the non-catalytic cracking case. By separating two heating units with different operating temperatures, the catalytic effect and the deactivation of the catalyst was clarified. The raw bio-oil and the upgraded oil were characterized by measuring their element content, water content and the chemical composition of its organic fraction.

3.1. Characteristic and objective of cracking

In order to use bio-oil as a liquid fuel, the cracking method was discussed in this chapter. The catalytic cracking method is mainly in the medium temperature and the atmospheric pressure by adding catalysts for bio-oil upgrade. The macromolecules contained in the bio-oil crack into small molecules, the oxygen element is removed in the form of CO_2, CO and H_2O. However, CO_2 is a more ideal form of deoxidation, because it removes more oxygen than CO and easier to separate from the liquid than H_2O. Williams et al. [3-1] proposed that the catalytic cracking should be carried out mainly through the following two ways: (1) Zeolite molecular sieves catalyze the cracking of bio-oil into alkanes, and then aromatize the alkanes; (2) the oxygenates in the bio-oil are directly deoxygenated to aromatic compounds. Currently, as the catalytic cracking catalysts, acidic catalysts such as HZSM-5, NaZSM-5, Y-type molecular sieves and aluminum phosphate molecular sieves are mainly used. The HZSM-5 catalyst has a good catalytic effect, which has good selectivity and activity. By the strong acid sites located in the cross-channel, only the simple structure of the molecule, for exmple, linear chain alkanes, can enter the pores and react with each other to form C1-C10 hydrocarbons and CO_2, CO and H_2O. However, the cyclic and branched hydrocarbons are trapped on the catalyst surface.

The biggest problem of the catalytic cracking process is the inactivation of the catalyst caused by coking problems. Many literatures have been devoted to this deactivation of the molecular sieve catalysts. It is reported that the coking mainly occurs on the surface of the zeolite catalyst, and thus blocks the pore and the acid sites in the catalyst. Guo et al [3-2] analyzed the coke precursors on the catalyst surface. They found that after the deactivation of HZSM-5, low boiling point compounds with short-chain or more branched saturated alkanes were attached to the surface of the catalyst, while the coke precursors inside the catalyst were aromatics (mainly PAHs). The catalyst deactivation occurred from the inside to the outside. In order to maintain the activity of the catalyst, they used tetralin as a solvent, mixed with bio-oil at a ratio of 1: 1 to lower the viscosity of the bio-oil and improve the stability and maintain the life of the catalyst. It is reported that the inactivation can be avoided with this additive.

However, in this thesis, no additive was used for the purpose to realize the cracking with a lowest cost. The popular cracking methods are the fixed bed cracking, the moving bed cracking and the fluidized bed cracking[21,22]. The fixed bed cracking is chosen in this study for its simple equipment requirements.

Many types of catalysts have been studied in the literatures in order to investigate how far the catalyst can modify the bio-oil composition and the bio-oil quality. Most of these studies are focusing on the comparison of catalysts but not on the mechanism of the catalysts. The control test without catalyst is considered unnecessary in these studies[3-1][3-2][3-3][3-4][3-5][3-6][3-7]. However, in this chapter, the effect of the commonly used catalyst HZSM-5 was discussed focusing on the comparison with the non-catalytic cracking. Most studies on the catalytic cracking of bio-oil are using only one heating reactor, where all components of bio-oil are in contact with the catalyst, including the components that tend to deactivate the catalyst. In this chapter, two heating units were employed so that the raw bio-oil was separated in the first heating unit and the cracking was done in the second heating unit. The components liable to deactivate the catalyst can be identified by changing the temperature in the first heating unit. In this way, the catalyst deactivation caused by different components were analyzed simultaneously, instead of treating the bio-oil as a whole[3-4][3-8], using the model components separately[3-9] or analyzing the deactivated catalyst after the reaction[3-10].

Some researches reported that bio-oil component separation is difficult under the atmospheric pressure and side reactions tend to occur due to the poor heat stability of bio-oil[3-11][3-12]. But in this chapter, side reactions did not significantly affect the experimental results by employing the two-stage heated reactors. Indeed, it is difficult to separate all components in bio-oil individually, but the components can be divided into 4 classes according to the chemical analysis, which was sufficient to explain the reaction mechanism of the deactivation. Different from the one heating unit process which is commonly used, the components in the upgraded bio-oil can be divided into 4 classes of organic components clearly by employing two heating units. By analyzing the reaction trend of these four classes of bio-oil components, the deactivation principle of the catalyst can be discussed without using model compounds. Previous studies generally considered that high molecular weight aromatic and aliphatic compounds are important reasons for deactivation of catalysts[3-13][3-14], but in this research, the effects of phenols and naphthalenes on the catalyst were investigated to show the importance of their effects.

3.2. Materials and methods

3.2.1. Bio-oil

The bio-oil was produced from the pyrolysis of Japanese cedar as mentioned in the above chapter. The pyrolysis gas produced in an updraft gasifier passed through a cooler to remove water and heavy tar and then was introduced to a centrifuge separator to recover the bio-oil [3-15].

The elemental content and properties of the bio-oil used in this experiment are listed in Table 3-1.

Table 3-1 The element analysis and properties of the raw bio-oil

C (%)	57.5
H (%)	7.0
N (%)	0.0
O (%)	35.5
S(mg/kg)	0.0
H_2O (%)	8.3
Ash (%)	0.0
Density (g/cm^3)	1.14
HHV (MJ/kg)	23.1
Cetane index	＜20
Kinetic viscosity (mm^2/s @ 50 °C)	12.7

*Cetane index of bio-oil was unable to measure accurately for its high density.

3.2.2. Catalytic materials

The HZSM-5 catalyst used in the experiment was provided by Tosoh corporation. Prior to the experiments, the catalytic materials were calcined at 500 °C for 3 h and stored in a desiccator. Its properties are listed in Table 3-2.

Table 3-2 Properties of the catalyst

Pore size (Å)	5.8

SiO_2/Al_2O_3 (mol/mol)	40
Specific surface area (m^2/g)	330
Crystal size (µm)	2 × 4
Particle size (µm)	10
NH_3-TPD (mmol/g)	1.3

3.2.3. Experimental set-up

The schematic diagram of the experimental set-up is shown in Figure 3-1. The raw bio-oil was firstly introduced into the first heating unit and then introduced into the second heating unit with or without packing of the catalyst. As a carrier gas, N2 gas was fed at the flow rate of 10mL/min from the top of the first heating unit for the continuous withdrawal of the products and the maintenance of the inert atmosphere during the cracking. The product flowing out from the bottom of the second heating unit was in gaseous form, and was condensed in a glass receiver submerged in an ice-water bath. Non-condensable gases were collected in a gas bag. A filter was placed between the ice-water bath receiver and the gas bag for recovering condensable vapor which might leak from the condenser.

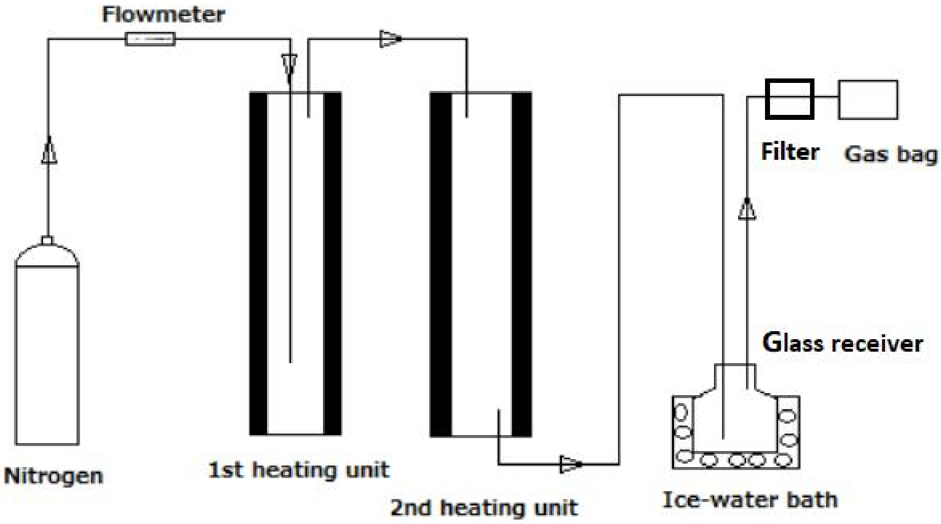

Figure 3-1. Schematic diagram of the experimental set-up.

3.2.4. Experimental procedure and product collection

Initially, the second heating unit was filled with 10g catalyst (the catalytic cracking) or no catalyst (the non-catalytic cracking), while the first heating unit was filled with 30g of the raw bio-oil. The first heating unit was heated to a specified temperature after the second heating unit was heated to 500 °C for 60 minutes.

The liquid products were collected and quantitatively measured in the pre-weighted glass receiver. The non-condensable gas products were collected and measured by difference. The amount of the solid residue left in the first heating unit was measured by weighing the first heating unit before and after the experiment. The solid products consisted of the coke left in the first heating unit and the coke on the catalyst weighed by the difference. The amount of condensable vapors recovered in the filter was also weighed by the difference and the weight was added to the liquid products yield.

3.2.5. Analysis methods

The following characteristics were determined: the elemental analysis of C, H, O, the moisture content, the ash content, the density, the high heating value (HHV), the cetane index, the kinetic viscosity and the chemical composition.

The ash content and the elemental analysis of C, H were determined by JM10 at 950 °C. The elemental analysis of O was determined by Vario micro cube at 1150 °m. The moisture content was measured using the Karl Fischer method in accordance with the standards JIS K 2275. HHV was determined in accordance with the standards JIS K 2279. The kinetic viscosity was measured by the ostwald viscometer at 40 °C. The cetane index was calculated in accordance with the standards JIS K 2280-5.

GC-MS is the technique used in the analyses of the product oil composition. A Rxi®-5Sil MS Column was used in the GC and helium was selected as the carrier gas. The oven heating profile was set at an increase of 5 °C /min from 30 to 280 °C.

3.3 Results and discussion

3.3.1. Effect of the catalyst

In order to investigate the effect of the zeolite catalyst, the cracking with catalyst in the second heating unit was compared with the non-catalytic cracking. In each run, after the second heating unit was heated to 500 °C and kept for 10 min, the first heating unit was heated to 500 °C and kept for 1 h. After 1 h run, No more liquid or gas product could be observed. The yield was listed in the Table 3-3.

Table 3-3. Product yield distribution by weight

	Liquid	solid	gas
With catalyst	61.3% (water:organic=16.6:44.7)	19.8%	18.8%
Without catalyst	75.7% (water:organic=16.8:58.9)	18.3%	14.4%

As shown in Table 3-3, the gas product in the case without the catalyst was less than the one in the case with the catalyst while the liquid product was more.

The upgraded oil in the liquid product was the target in this experiment. The collected liquid product was divided into two layers： the water layer and the organic layer. The element analysis data of the two layers are listed in Table 3-4

Table 3-4 Element analysis of the liquid product

Element content by weight	Without catalyst		With catalyst	
	Water layer	Organic layer	Water layer	Organic layer
C(%)	21.85	67.91	10.11	73.47
H(%)	9.35	7.83	9.73	7.22
O(%)	68.70	24.07	79.93	19.03

Obviously, some organic matter is soluble in the water layer. That is why C element was also detected in the water layer.

Though in the non-catalytic cracking, the organic liquid product was more than in the case of the catalytic cracking, the C content was lower and the O content was higher, which means that the heating value of the organic liquid product was lower than the catalytic cracked bio-oil.

Compared with the raw bio-oil properties listed in Table 3-1, the C content increased by 10% and the O content decreased by 11% in the non-catalytic cracking, while the C content increased by 16% and the O content decreased by 16% in the case of the catalytic cracking. The cracking was achieved without the catalyst, while the zeolite promoted the rate of the deoxygenation by 50%.

The possible reason for this promotion was the adsorption and the acidic sites of the zeolite. The adsorption on the surface of the zeolite extended the cracking reaction time of oxygen-containing molecules and the acidic sites contributed to enhance the deoxygenation reaction[3-16][3-17]. Other physical properties of the raw bio-oil and the organic liquid products are listed in Table 3-5.

Table 3-5 Physical properties comparison of the organic liquid and the raw bio-oil

	Bio-oil	Organic liquid from catalytic cracking	Organic liquid from non-catalyst cracking
Density (g/cm^3)	1.14	1.02	1.03
Kinetic viscosity (mm^2/s@50 °C)	12.7	4.72	4.85
Water content(%)	8.3	8.0	8.2
Cetane index	＜20	38.26	37.54
HHV(MJ/kg)	23.1	31.8	29.9

Significant improvement in the physical properties was observed after the cracking regardless of the usage of the catalyst. A further improvement was obtained by using the catalyst.

In order to analyze the phenomenon in more details, GC-MS was employed to identify the chemical compositions of the raw bio-oil and the organic liquid. The result of the raw bio-oil is shown in Figure 3-2.

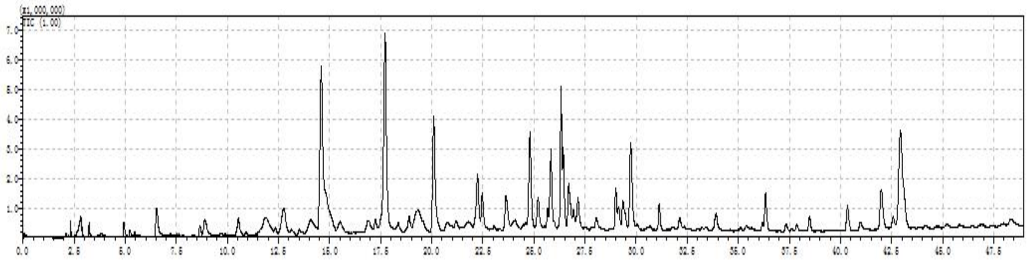

Figure 3-2 Ion current of the raw bio-oil

Though hundreds of organics were detected, if picking out the highest 20 peaks, the area of these 20 peaks accounted for 90% of the total area. These 20 organics are listed in Table 3-6.

Table 3-6 The main chemical compositions of the raw bio-oil

Name	Retention time(min)	Area(%)
1-Hydroxy-2-butanone	4.9	1.96
Propanal	5.2	1.26
3,5-Dimethylpyrazole	6.5	1.98
2(5H)-Furanone	8.9	2.36
1,2-Cyclopentanedione, 3-methyl-	12.7	3.90
Phenol, 2-methoxy-	14.6	18.09
2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-	15.5	1.37
Phenol, 2,4-dimethyl-	16.9	1.55
Creosol	17.7	17.07
Phenol, 4-ethyl-2-methoxy-	20.1	12.98
Phenol, 2-methoxy-3-(2-propenyl)-	22.2	2.31
Phenol, 2-methoxy-4-propyl-	22.5	4.51
trans-Isoeugenol	24.8	5.93
Naphthalene, 1,2,4a,5,6,8a-hexahydro-4,7-dimethyl-1-(1-methylethyl)-	25.8	1.98
Naphthalene, 1,2,4a,5,8,8a-hexahydro-4,7-dimethyl-1-(1-methylethyl)-, [1S-(1.alpha.,4a.beta.,8a.alpha.)]-	26.3	3.70
Di-epi-.alpha.-cedrene-(I)	29.0	1.44
2-Naphthalenemethanol, decahydro-.alpha.,.alpha.,4a-trimethyl-8-methylene-, [2R-(2.alpha.,4a.alpha.,8a.beta.)]-	29.7	2.35
Kaur-15-ene, (5.alpha.,9.alpha.,10.beta.)-	36.3	1.10
Naphthalene, decahydro-1,1,4a-trimethyl-6-methylene-5-(3-methyl-2,4	42.0	1.05

-pentadienyl)-, [4aS-(4a.alpha.,5.alpha.,8a.beta.)]-		
Ferruginol	42.9	2.54

The main components could be divided into 4 classes. The first one is oxygen-containing small molecules with the retention time from 2.5 to 10 min, the main components of which are kinds of ketone, furan and imidazole. The second class is phenols with the retention time of 10 to 25min, whose main components are guaiacol and its homologues. The third class with the retention time from 25 to 30min are naphthalenes, which mainly contained naphthalene and naphthol. The fourth one was the materials whose retention time were later than 30min, mainly containing long-chain aliphatic macromolecular and polycyclic macromolecular structural substances. The area proportions of these four classes are listed in Table 3-7.

Table 3-7 Component classification of the bio-oil

	1st class	2nd class	3rd class	4th class
Rage of retention time(min)	2.5~10	10~25	25~30	＞30
Area（%）	8.2%	74.0%	10.8%	7.0%

Figure 3-3 showed the GC-MS result of the organic liquid products. Two high peaks came out at the retention time of 5.1 min and 7.8 min after the cracking. According to the data base, these two were toluene and xylene, which were most likely the product of the phenolic deoxygenation.

In the catalytic cracking, the phenols peak and the naphthalenes peak deceased more evidently than in the non-catalytic cracking, along with more product of toluene and xylene than the non-catalytic cracking. Therefore， more phenolic deoxygenation happened when the catalyst was used for the cracking. Considering the high thermal stability of benzene ring and naphthalenic ring[3-18][3-19], the decrease of naphthalenes shall be interpreted as coking on the catalyst.

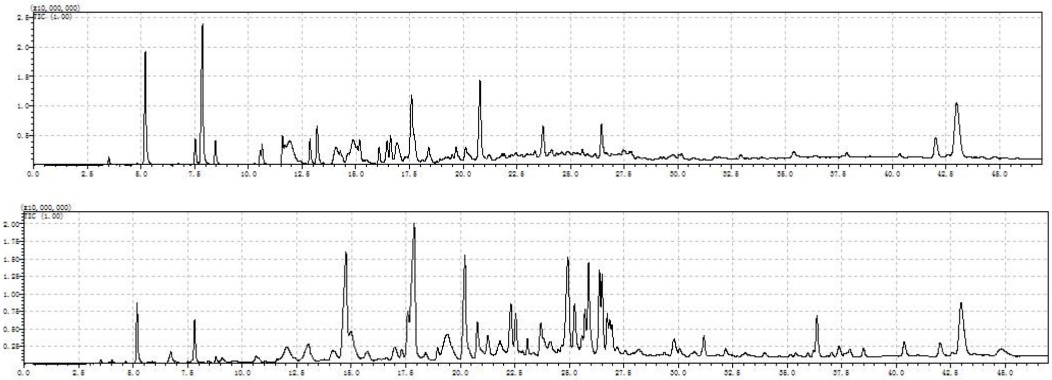

Figure 3-3 Ion current of the organic liquid of the catalytic cracking (above) and the non-catalytic cracking (below)

In summary of the above data, the most likely reactions in the second heater unit are the phenolic deoxygenation and the naphthalene coking on the catalyst. In the non-catalytic cracking, the phenols and naphthalenes were directly condensed in the ice-water bath receiver without contact with the catalyst. In order to verify this speculation, different temperatures in the first heating unit were tested in the following section.

3.3.2 Catalytic test at different temperatures in the first heating unit

In order to confirm the reaction of the 4 component classes, after the second unit was heated to 500 °C, the first heating unit was heated to 510°C, 550°C and 600°C. The heating time was 15min, 18min, 21min respectively, and then holding the temperature until 1 hour. The operation condition was listed in Table 3-8.

Table 3-8 Operation condition

	Heating time	Holding time	Setting temperature of the First unit
Partial distillation(PD) operation	15min	45min	510℃
Further distillation(FD) operation	18min	42min	550℃
Complete distillation(CD) operation	21min	39min	600℃

The three operation conditions were called partial distillation(PD) operation, further distillation(FD) operation, complete distillation(CD) operation respectively. For each operation, the experiments were repeated three times without changing the catalyst in the second heating unit, but replacing the residue in the first unit with new bio-oil.

Figure 3-4 shows the analysis results of three runs at CD operation. It was clear that 3 big peaks came out before 10 min, which referred to small molecule, the target product. The second peak and the third peak were higher than the first one. The height of the three peaks was the highest in the first run, and the height decreased in the second run without changing the catalyst. It proved that the activity of the catalyst decreased. When it came to the third run, these three peaks further reduced, as the activity of the catalyst further decreased. In order to see the change clearly, the components of these 3 runs were shown in Tables 3-9, 3-10 and 3-11.

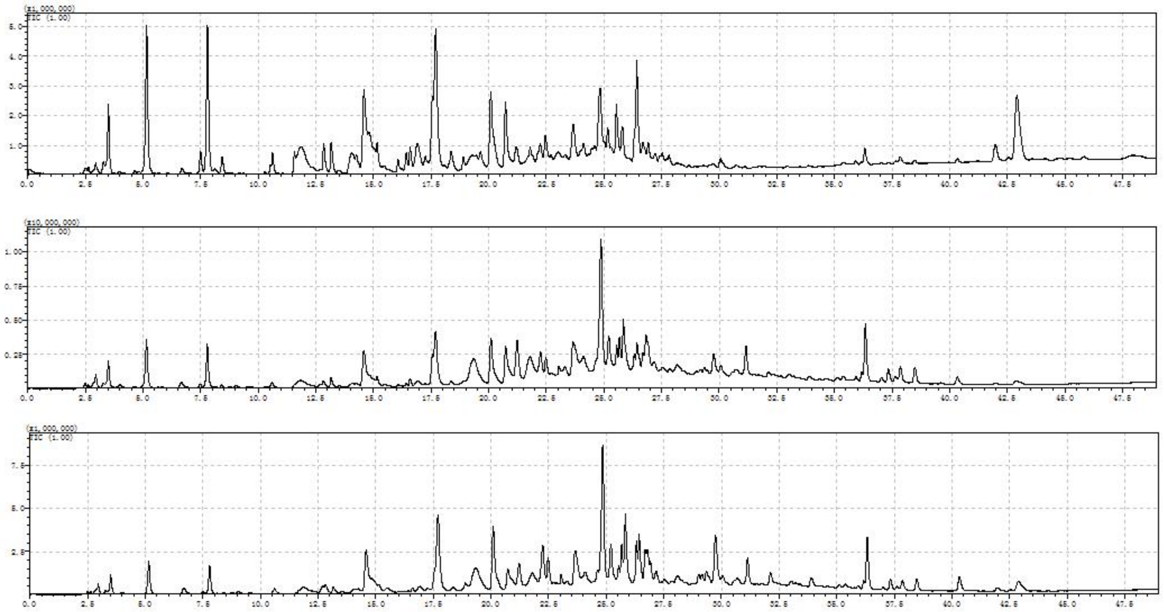

Figure 3-4 Comparison of consecutive tests for CD operation

(First run: above, Second run: middle, Third run:below)

Table 3-9 Main components of the liquid product in the first cracking run for CD operation

Name	Area%	Retention time（min）
Cyclopropane, 1,1-dimethyl-	0.43	2.54
Furan, 2-methyl-	0.50	2.95
1,3-Cyclohexadiene	0.61	3.28
Benzene	5.88	3.50
Toluene	13.59	5.15
2-Cyclopenten-1-one	0.58	6.70
Ethylbenzene	1.73	7.49
p-Xylene	10.44	7.80
Phenol	0.32	8.12
o-Xylene	0.76	8.44
Benzene, 1-ethyl-2-methyl-	1.45	10.62
Mesitylene	1.31	11.57
Phenol	2.70	11.85
Indane	1.40	12.84
1H-Indene, 1-chloro-2,3-dihydro-	1.99	13.17
Phenol, 2-methyl-	1.75	14.07
1H-Indene, 2,3-dihydro-2-methyl-	0.42	14.26

Phenol, 2-methoxy-	7.09	14.58
Phenol, 3-methyl-	4.04	14.83
Benzofuran, 2-methyl-	1.48	15.16
1H-Indene, 2,3-dihydro-5-methyl-	0.54	16.06
2-Methylindene	0.72	16.42
2-Methylindene	1.09	16.59
Phenol, 3,4-dimethyl-	2.70	16.91
2-Methoxy-5-methylphenol	0.75	17.27
Creosol	8.83	17.70
2,3-Dimethoxytoluene	0.65	18.90
Catechol	0.35	19.31
1H-Indene, 1,3-dimethyl-	0.97	19.66
Phenol, 4-ethyl-2-methoxy-	2.79	20.09
Naphthalene, 1-methyl-	3.37	20.72
Phenol, 2-methoxy-4-propyl-	2.09	22.47
Naphthalene, 1-ethyl-	0.24	23.34
Phenol, 2-methoxy-4-(1-propenyl)-, (Z)-	1.72	24.80
Naphthalene, 1,2,4a,5,8,8a-hexahydro-4,7-dimethyl-1-(1-methylethyl)-, (1.alpha.,4a.beta.,8a.alpha.)-(.+/-.)-	1.20	25.54
Naphthalene, 1,2,3,4-tetrahydro-1,6-dimethyl-4-(1-methylethyl)-, (1S-cis)-	5.62	26.43
Cadala-1(10),3,8-triene	0.67	26.92
(-)-Aristolene	0.16	27.23
Cadina-1(10),6,8-triene	0.65	27.81
Naphthalene, 1,6-dimethyl-4-(1-methylethyl)-	0.36	30.06
Kaur-15-ene, (5.alpha.,9.alpha.,10.beta.)-	0.34	36.33
7-Isopropyl-1,1,4a-trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene	0.20	37.88
1,3,6,10-Cyclotetradecatetraene, 3,7,11-trimethyl-14-(1-methylethyl)-, [S-(E,Z,E,E)]-	0.05	38.49
Naphthalene, decahydro-1,1,4a-trimethyl-6-methylene-5-(3-methyl-2,4-pentadienyl)-, [4aS-(4a.alpha.,5.alpha.,8a.beta.)]-	0.36	41.97

Table 3-10 Main components of the liquid product in the second cracking run for CD operation

Name	Area%	Retention time（min）
Furan, 2-methyl-	1.11	2.95
Benzene	3.94	3.49
Toluene	7.96	5.14
Benzene, 1,3-dimethyl-	5.07	7.79
1H-Indene, 1-chloro-2,3-dihydro-	1.05	13.15
Phenol, 2-methoxy-	5.64	14.58
2-Methylindene	0.62	16.58
Naphthalene	5.09	17.55
2-Methoxy-5-methylphenol	6.10	17.69
Catechol	5.55	19.35
Phenol, 4-ethyl-2-methoxy-	7.59	20.10
4-Hydroxy-2-methylacetophenone	4.67	21.24
Phenol, 2-methoxy-3-(2-propenyl)-	1.14	22.25
Phenol, 2-methoxy-4-propyl-	2.99	22.49
Cyclohexane, 1-ethenyl-1-methyl-2,4-bis(1-methylethenyl)-, [1S-(1.alpha.,2.beta.,4.beta.)]-	0.16	23.05
Phenol, 2-methoxy-4-(1-propenyl)-, (Z)-	2.07	23.64
trans-Isoeugenol	10.58	24.88
1H-Cycloprop[e]azulene, 1a,2,3,4,4a,5,6,7b-octahydro-1,1,4,7-tetramethyl-, [1aR-(1a.alpha.,4.alpha.,4a.beta.,7b.alpha.)]-	0.84	25.22
Naphthalene, 1,2,3,4-tetrahydro-1,6-dimethyl-4-(1-methylethyl)-, (1S-cis)-	2.38	26.43
2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-	9.45	26.85
2-Naphthalenemethanol, decahydro-.alpha.,.alpha.,4a-trimethyl-8-methylene-, [2R-(2.alpha.,4a.alpha.,8a.beta.)]-	0.76	29.76
Naphthalene, 1,6-dimethyl-4-(1-methylethyl)-	0.50	30.06
3,7,11-Trimethyl-dodeca-2,4,6,10-tetraenal	1.71	31.17
Kaur-15-ene, (5.alpha.,9.alpha.,10.beta.)-	0.10	35.94
Kaur-15-ene, (5.alpha.,9.alpha.,10.beta.)-	2.36	36.35
Kaur-16-ene, (8.beta.,13.beta.)-	0.18	37.36
7-Isopropyl-1,1,4a-trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene	0.74	37.85
Bicyclo[9.3.1]pentadeca-3,7-dien-12-ol, 4,8,12,15,15-pentamethyl-, [1R-(1R*,3E,7E,11R*,12R*)]-	0.14	40.35

Table 3-11 Main components of the liquid product in the third cracking run for CD operation

Name	Area%	Retention time （min）
Furan, 2-methyl-	0.77	2.96
Benzene	2.74	3.50
Toluene	4.80	5.16
Benzene, 1,3-dimethyl-	3.20	7.79
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	1.57	12.72
Indane	0.29	12.83
Phenol, 2-methoxy-	6.59	14.58
Creosol	8.60	17.72
Catechol	9.11	19.32
Phenol, 4-ethyl-2-methoxy-	10.08	20.09
Naphthalene, 1-methyl-	1.47	20.72
4-Hydroxy-2-methylacetophenone	2.66	21.21
Eugenol	2.16	22.25
Phenol, 2-methoxy-4-propyl-	4.54	22.48
Cyclohexane, 1-ethenyl-1-methyl-2,4-bis(1-methylethenyl)-, [1S-(1.alpha.,2.beta.,4.beta.)]-	0.23	23.05
Phenol, 2-methoxy-4-(1-propenyl)-, (Z)-	1.96	23.63
trans-Isoeugenol	10.59	24.85
Naphthalene, decahydro-4a-methyl-1-methylene-7-(1-methylethenyl)-, [4aR-(4a.alpha.,7.alpha.,8a.beta.)]-	0.58	25.67
.alpha.-Guaiene	1.38	25.84
Naphthalene, 1,2,3,5,6,8a-hexahydro-4,7-dimethyl-1-(1-methylethyl)-, (1S-cis)-	1.56	26.31
Naphthalene, 1,2,3,4-tetrahydro-1,6-dimethyl-4-(1-methylethyl)-, (1S-cis)-	3.46	26.43
Naphthalene, 1,2,3,4,4a,7-hexahydro-1,6-dimethyl-4-(1-methylethyl)-	1.33	26.69
2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-	7.54	26.78
Cyclohexanemethanol, 4-ethenyl-.alpha.,.alpha.,4-trimethyl-3-(1-methylethenyl)-, [1R-(1.alpha.,3.alpha.,4.beta.)]-	0.24	27.17
Di-epi-.alpha.-cedrene-(I)	0.44	29.01
cubedol	0.50	29.34
Naphthalene, 1,6-dimethyl-4-(1-methylethyl)-	0.45	30.06
Phenylacetylformic acid, 4-hydroxy-3-methoxy-	0.81	30.56

Phenol, 2,6-dimethoxy-4-(2-propenyl)-	0.50	30.70
3,7,11-Trimethyl-dodeca-2,4,6,10-tetraenal	1.46	31.14
Kaur-15-ene, (5.alpha.,9.alpha.,10.beta.)-	2.02	36.33
1,3,6,10-Cyclotetradecatetraene, 3,7,11-trimethyl-14-(1-methylethyl)-, [S-(E,Z,E,E)]-	0.32	38.47
1,3,6,10-Cyclotetradecatetraene, 3,7,11-trimethyl-14-(1-methylethyl)-, [S-(E,Z,E,E)]-	0.27	40.34
Ferruginol	0.43	42.88

In above three Tables 3-9,3-10 and 3-11, it is shown clearly that the three high peaks before 10 min were benzene, toluene and xylene, which may originated from the cleavage or the polymerization. The cleavage was from 2-methoxy-Phenol (retention time=14.6), Creosol (retention time=17.7), 4-ethyl-2-methoxy-Phenol (retention time=20.1) of the bio-oil as shown in Figure 3-2. The percentage of these phenols decreased sharply.

Table 3-12 Comparison of the six peaks area percentage

Name	Retention time (min)	Raw bio-oil	first run	Second run	Third run
Benzen	3.5	not detected	5.9%	3.9%	2.7%
Toluene	5.1	not detected	13.6%	8.0%	4.8%
Xylene	7.8	not detected	10.4%	5.1%	3.2%
2-methoxy-Phenol	14.6	18.1%	7.1%	5.6%	6.6%
Creosol	17.7	17.1%	8.8%	6.1%	8.6%
4-ethyl-2-methoxy-5-Phenol	20.1	13.0%	2.8%	7.6%	10.1%

Table 3-12 listed the comparation of these six peaks area percentage. The deoxidation or the decomposition products of 2-methoxy-Phenol, Creosol and ethyl-2-methoxy-Phenol happened to be benzen, toluene and xylene. The main reaction took place here should be the deoxidation and the dealkylation. The principle will be discussed in the later part of this chapter.

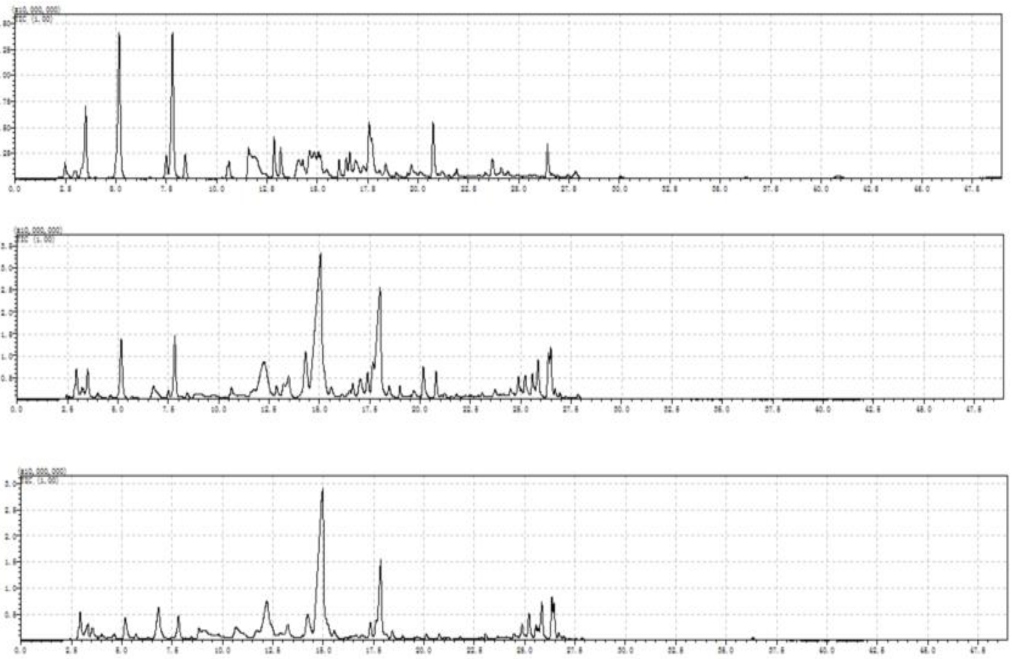

Figure 3-5 Comparison of consecutive tests for FD operation

(First run: above, Second run: middle, Third run:below)

Figure 3-5 showed the result for FD operation. The same trend as CD operation was observed. Three high peaks came out before 10 min, which referred to benzene, toluene and xylene. The toluene peak and the xylene peak were higher than the benzene peak. The height of the three peaks was highest in the first run, and the height decreased in the second run without changing the catalyst. It proved that the activity of the catalyst decreased. When it came to the third run, these three peaks further reduced, as the activity of the catalyst further decreased. The components of these 3 runs were shown in Table 3-13, 3-14 and 3-15.

Table 3-13 Main components of the liquid product in the first cracking run for FD operation

Name	Area%	Retention time (min)
Cyclobutane, methoxy-	1.26	2.46
Furan, 2-methyl-	0.33	2.95
Acetic acid	1.29	3.03
Benzene	9.85	3.50
Toluene	19.90	5.16
Ethylbenzene	1.92	7.50
p-Xylene	13.39	7.81

Benzene, 1,3-dimethyl-	1.29	8.45
Benzene, 1-ethyl-2-methyl-	1.52	10.62
Mesitylene	2.25	11.57
Phenol	4.57	11.90
2-Phenyl-[1,3]dioxolane-4,5-dicarboxylic acid, dimethyl ester	0.11	12.42
Indane	2.84	12.85
1H-Indene, 1-chloro-2,3-dihydro-	2.35	13.18
Phenol, 2-methyl-	2.79	14.07
Benzene, 1-ethenyl-3-ethyl-	0.55	14.27
Phenol, 3-methyl-	3.18	14.88
Benzofuran, 2-methyl-	1.39	15.17
Phenol, 2,6-dimethyl-	0.50	15.47
1H-Indene, 2,3-dihydro-5-methyl-	1.05	16.08
2-Methylindene	0.94	16.43
2-Methylindene	1.31	16.60
Phenol, 3,4-dimethyl-	1.87	16.91
2-Methoxy-5-methylphenol	0.70	17.27
1H-Indene, 2,3-dihydro-4,7-dimethyl-	0.23	17.38
Naphthalene	6.19	17.57
Creosol	2.37	17.71
1H-Indazole, 5,7-dimethyl-	0.27	18.08
Benzofuran, 4,7-dimethyl-	0.93	18.39
2,3-Dimethoxytoluene	0.32	18.90
1H-Indene, 1,3-dimethyl-	0.20	19.48
1H-Indene, 1,3-dimethyl-	1.00	19.66
Naphthalene, 1-methyl-	0.21	19.88
Phenol, 4-ethyl-2-methoxy-	0.54	20.09
Naphthalene, 1-methyl-	4.03	20.74
2,5,6-Trimethylbenzimidazole	0.14	21.00
Naphthalene, 1-methyl-	0.26	21.17
2,5,6-Trimethylbenzimidazole	0.07	21.51
Naphthalene, 1,2,3,4-tetrahydro-2,7-dimethyl-	0.27	21.92
Naphthalene, 2-ethyl-	0.28	23.34
Naphthalene, 2,6-dimethyl-	1.14	23.70
Naphthalene, 2,6-dimethyl-	0.52	24.12
Benzene, (1,1-dimethyldecyl)-	0.51	24.46
Naphthalene, 1,2,3,4-tetrahydro-1,6-dimethyl-4-(1-methylethyl)-, (1S-cis)-	2.99	26.42
Naphthalene, 1,2,3,4-tetrahydro-1,6-dimethyl-4-(1-methylethyl)-, (1S-cis)-	0.30	26.65

Table 3-14 Main components of the liquid product in the second cracking run
for FD operation

Name	Area%	Retention time (min)
1-Pentene, 5-methoxy-	0.52	2.46
Methyl vinyl ketone	1.55	2.85
Furan, 2-methyl-	2.66	2.94
Urea	3.06	3.22
Benzene	4.67	3.50
Furan, 2,5-dimethyl-	0.51	4.00
Spiro[2,4]hepta-4,6-diene	0.20	4.63
Toluene	9.60	5.16
3-Cyclopentene-1-acetaldehyde, 2-oxo-	2.36	6.77
Ethylbenzene	0.95	7.50
p-Xylene	7.24	7.82
1,3,5,7-Cyclooctatetraene	0.34	8.44
Benzene, 1-ethyl-3-methyl-	1.12	10.63
6-Bromohexanoic acid, 3-phenylpropyl ester	1.03	11.72
Phenol	8.80	12.27
Indane	1.07	12.87
1H-Indene, 1-chloro-2,3-dihydro-	1.37	13.21
1,2-Cyclopentanedione, 3-methyl-	2.52	13.48
Phenol, 2-methyl-	5.83	14.32
Phenol, 2-methoxy-	2.73	15.01
Phenol, 2,6-dimethyl-	0.63	15.59
Benzene, 1-methyl-2-(2-propenyl)-	0.25	16.12
2-Methylindene	0.96	16.67
Phenol, 2,4-dimethyl-	2.53	17.04
2-Methoxy-5-methylphenol	2.26	17.39
Creosol	17.38	18.02
Benzofuran, 4,7-dimethyl-	1.04	18.47
2,3-Dimethoxytoluene	0.75	19.00
Naphthalene, 1,2-dihydro-6-methyl-	0.56	19.72
Phenol, 4-ethyl-2-methoxy-	3.76	20.17
Naphthalene, 1-methyl-	2.23	20.80
.alpha.-Guaiene	0.17	23.04
Naphthalene, 2-ethyl-	0.08	23.36
Naphthalene, 2,6-dimethyl-	0.44	23.72
Benzene, (1,1-dimethyldecyl)-	1.03	24.48
Naphthalene, 1,2,4a,5,8,8a-hexahydro-4,7-dimethyl-1-(1-methylet	0.47	24.88

hyl)-, (1.alpha.,4a.beta.,8a.alpha.)-(.+/-.)-		
Naphthalene, 1,2,4a,5,8,8a-hexahydro-4,7-dimethyl-1-(1-methylethyl)-, (1.alpha.,4a.beta.,8a.alpha.)-(.+/-.)-	0.98	25.57
.alpha.-Muurolene	1.33	25.87
Naphthalene, 1,2,3,4-tetrahydro-1,6-dimethyl-4-(1-methylethyl)-, (1S-cis)-	3.83	26.48
Isoledene	0.09	27.24
Cadina-1(10),6,8-triene	0.39	27.84

Table 3-15 Main components of the liquid product in the third cracking run for FD operation

Name	Area%	Retention time (min)
Furan, 2-methyl-	3.38	2.93
Acetic acid	9.27	3.33
Furan, 2,5-dimethyl-	0.74	4.00
Toluene	4.51	5.16
Cyclopentanone	1.19	5.69
Furfural	0.32	6.31
1H-Imidazole, 4,5-dimethyl-	4.71	6.84
Benzene, 1,3-dimethyl-	3.65	7.81
Cyclopentene, 1-ethenyl-3-methylene-	0.24	8.45
2-Cyclopenten-1-one, 2-methyl-	2.70	8.84
2-Cyclopenten-1-one, 3,4-dimethyl-	0.32	9.80
3-Furancarboxylic acid, methyl ester	0.74	11.03
Phenol	23.99	12.20
Phenol, 2-methyl-	5.96	14.23
Phenol, 2,6-dimethyl-	1.01	15.55
2-Methylindene	0.52	16.64
2-Methoxy-5-methylphenol	2.39	17.34
Creosol	12.33	17.85
Benzofuran, 4,7-dimethyl-	1.27	18.43
2,3-Dimethoxytoluene	0.41	18.93
Phenol, 4-ethyl-2-methoxy-	1.11	20.11
Naphthalene, 1-methyl-	0.81	20.76
Benzene, (1,1-dimethyldecyl)-	1.05	24.47
1H-Cycloprop[e]azulene, 1a,2,3,4,4a,5,6,7b-octahydro-1,1,4,7-tetramethyl-, [1aR-(1a.alpha.,4.alpha.,4a.beta.,7b.alpha.)]-	0.44	24.86
Cyclohexene, 6-ethenyl-6-methyl-1-(1-methylethyl)-3-(1-methylethylidene)-, (S)-	0.97	25.55
.alpha.-Muurolene	1.91	25.86
Naphthalene, 1,2,3,5,6,8a-hexahydro-4,7-dimethyl-1-(1-methylethyl)-, (1S-cis)-	2.25	26.35
Naphthalene, 1,2,3,4,4a,7-hexahydro-1,6-dimethyl-4-(1-methylethyl)-	0.35	26.70
Cadina-1(10),6,8-triene	0.21	27.82
Kaur-15-ene, (5.alpha.,9.alpha.,10.beta.)-	0.16	36.32

The difference of the FD run campared with the CD run is that the amounts of naphthalene and macromolecules were not so much. Table 3-16 listed the area percentage whose retention time was later than 25 min. Table 3-16 listed the difference.

Table 3-16 Area percentage of naphthalene and macromolecules in FD operation **and the** CD operation

	FD	CD
First run	5.8%	15.0%
Second run	9.0%	40.5%
Third run	7.6%	41.4%

As the temperature and heating time increased, more macromolecules and naphthalenes was distilled off from the first heating unit. That was the reason why, in the CD condition, the detected amounts of macromolecules and naphthalenes were higher than in the FD condition. The macromolecules and naphthalenes was harmful as stated in Chapter 1. The catalyst lost its activity and the cracking of macromolecules and naphthalenes reduced, resulting in an increasing trend with the run times increasing in CD condition. There was a slight decline in the third run at FD condition. This may be due to the coking on the catalyst. The detail of the reaction will be discussed in the later part of this chapter. Figure 3-6 listed the reaction result for PD operation

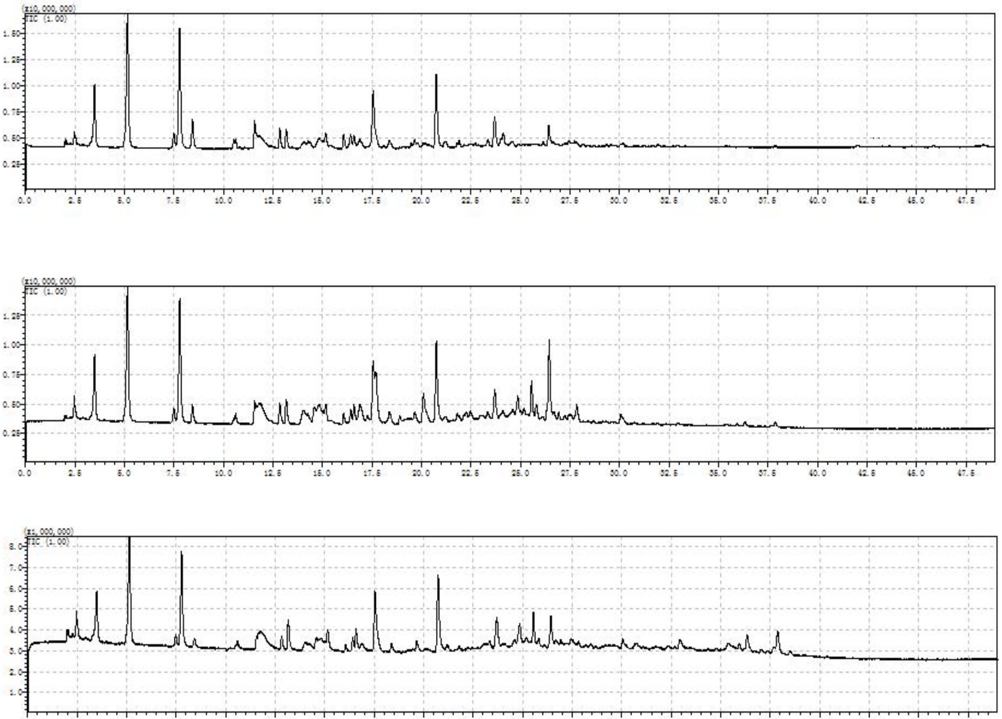

Figure 3-6 Comparison of consecutive tests for PD operation

(First run: above, Second run: middle, Third run:below)

No obvious changes were observed from the first run to the third run. The data was listed in Tables 3-17, 3-18 and 3-19.

Table 3-17 Main components of the liquid product in the first cracking run for PD operation

Name	Area%	Retention time (min)
Acetone	0.85	2.46
Benzene	9.52	3.49
Toluene	20.87	5.16
Ethylbenzene	1.63	7.49
Benzene, 1,3-dimethyl-	15.06	7.79
o-Xylene	2.66	8.44
Benzene, 1-ethyl-2-methyl-	0.85	10.53
Benzene, 1-ethyl-4-methyl-	1.04	10.62
Mesitylene	2.79	11.57
Phenol	1.92	11.85
Indane	1.94	12.84
Indene	2.09	13.17
Phenol, 2-methyl-	1.41	14.04
Indan, 1-methyl-	0.32	14.27
Phenol, 3-methyl-	2.10	14.82
1H-Indazole, 7-methyl-	0.16	15.04
Benzofuran, 2-methyl-	1.53	15.16
1H-Indene, 2,3-dihydro-5-methyl-	1.17	16.07
Benzene, (1-methyl-2-cyclopropen-1-yl)-	1.01	16.42
2-Methylindene	1.01	16.59
Phenol, 2,5-dimethyl-	1.25	16.89
Naphthalene	9.76	17.56
1H-Indene, 1,3-dimethyl-	0.34	19.47
1H-Indene, 1,3-dimethyl-	0.74	19.65
Naphthalene, 1-methyl-	7.75	20.74
Naphthalene, 1,2,3,4-tetrahydro-2,7-dimethyl-	0.29	21.90
Naphthalene, 2-ethyl-	0.66	23.34
Naphthalene, 2,6-dimethyl-	2.64	23.69
Naphthalene, 1,7-dimethyl-	0.39	24.01
Naphthalene, 2,6-dimethyl-	1.14	24.12
Naphthalene, 2-(1-methylethyl)-	0.41	26.14

Naphthalene, 1,2,3,4-tetrahydro-1,6-dimethyl-4-(1-methylethyl)-, (1S-cis)-	1.47	26.42
Cadina-1(10),6,8-triene	0.31	27.73
Azulene, 1,4-dimethyl-7-(1-methylethyl)-	0.38	30.16

Table 3-18 Main components of the liquid product in the second cracking run for PD operation

Name	Area%	Retention time (min)
Acetone	1.41	2.46
Benzene	7.88	3.49
Toluene	16.36	5.15
Ethylbenzene	1.23	7.49
p-Xylene	11.88	7.79
o-Xylene	1.10	8.44
Benzene, 1-ethyl-2-methyl-	0.95	10.61
Mesitylene	1.85	11.57
Benzofuran	1.21	11.67
Phenol	6.01	11.87
Indane	1.52	12.84
Indene	2.19	13.17
Benzene, 1-methyl-2-(2-propenyl)-	0.29	14.26
Phenol, 2-methoxy-	1.90	14.58
2-Propenal, 3-phenyl-	0.23	15.04
Benzofuran, 2-methyl-	1.51	15.17
1H-Indene, 2,3-dihydro-5-methyl-	0.74	16.07
Benzene, (1-methyl-2-cyclopropen-1-yl)-	0.78	16.43
2-Methylindene	1.15	16.59
Phenol, 2,4-dimethyl-	2.29	16.91
2-Methoxy-5-methylphenol	0.53	17.27
Naphthalene	8.05	17.56
2-Methoxy-5-methylphenol	3.33	17.70
2,3-Dimethoxytoluene	0.56	18.91
1H-Indene, 1,3-dimethyl-	0.82	19.66
Phenol, 4-ethyl-2-methoxy-	3.13	20.10
Naphthalene, 1-methyl-	6.29	20.75
1H-3a,7-Methanoazulene, 2,3,6,7,8,8a-hexahydro-1,4,9,9-tetramethyl-, (1.alpha.,3a.alpha.,7.alpha.,8a.beta.)-	0.12	21.81
Ethanone, 1-(2-hydroxy-4-methoxyphenyl)-	0.71	22.26
Naphthalene, 2-ethyl-	0.42	23.35
Naphthalene, 2,3-dimethyl-	1.89	23.70

Naphthalene, 1,5-dimethyl-	0.41	24.14
Naphthalene, 1,2,4a,5,8,8a-hexahydro-4,7-dimethyl-1-(1-methylethyl)-, [1S-(1.alpha.,4a.beta.,8a.alpha.)]-	0.17	25.18
Naphthalene, 1,2,4a,5,8,8a-hexahydro-4,7-dimethyl-1-(1-methylethyl)-, (1.alpha.,4a.beta.,8a.alpha.)-(.+/-.)-	1.06	25.55
Naphthalene, 1,2,4a,5,8,8a-hexahydro-4,7-dimethyl-1-(1-methylethyl)-, [1S-(1.alpha.,4a.beta.,8a.alpha.)]-	0.39	25.78
Naphthalene, 1,2,3,4-tetrahydro-1,6-dimethyl-4-(1-methylethyl)-, (1S-cis)-	6.30	26.44
Cadala-1(10),3,8-triene	0.48	26.92
Cadina-1(10),6,8-triene	1.05	27.84
Naphthalene, 1,6-dimethyl-4-(1-methylethyl)-	0.48	30.06

Table 3-19 Main components of the liquid product in the third cracking run for PD operation

Name	Area%	Retention time (min)
Acetone	1.74	2.46
Benzene	8.79	3.48
Toluene	17.39	5.14
Benzene, 1,3-dimethyl-	10.97	7.78
o-Xylene	0.40	8.42
Nickel tetracarbonyl	0.38	10.20
Benzene, 1-ethyl-4-methyl-	1.15	10.59
Mesitylene	1.24	11.55
Phenol	2.26	11.81
Indane	1.37	12.83
Indene	3.37	13.16
Phenol, 2-methyl-	1.70	14.04
1-Phenyl-1-butene	0.22	14.26
Phenol, 2-methoxy-	1.72	14.56
Benzofuran, 2-methyl-	2.23	15.15
1H-Indene, 2,3-dihydro-5-methyl-	0.58	16.06
2-Methylindene	0.88	16.42
2-Methylindene	1.69	16.58
Naphthalene	11.31	17.55
Benzofuran, 4,7-dimethyl-	0.79	18.37
1H-Indene, 1,3-dimethyl-	1.11	19.65
Naphthalene, 1-methyl-	8.52	20.72
Benzofuran, 2-methyl-	0.53	23.00
Naphthalene, 2,6-dimethyl-	2.42	23.68
Naphthalene, 1,2,4a,5,8,8a-hexahydro-4,7-dimethyl-1-(1-methylethyl)-, (1.alpha.,4a.beta.,8a.alpha.)-(.+/-.)-	1.17	25.54
Naphthalene, 1,2,3,4-tetrahydro-1,6-dimethyl-4-(1-methylethyl)-, (1S-cis)-	3.05	26.42
Anthracene	1.86	32.93
Kaur-15-ene, (5.alpha.,9.alpha.,10.beta.)-	0.54	36.33
7-Isopropyl-1,1,4a-trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene	1.00	37.88

It should be noticed that the area percentage does not equal to the content percentage. However, the trend of change can be confirmed by comparing the same components from different runs. Although slightly difference existed, the main component contents such as benzenes and phenols were similar. It meant that the activity of the catalyst still maintained and functioned after three consecutive runs. Therefore, a low separation temperature was helpful to maintain the catalyst activity. Naphthalene and macromolecules contents were low, which mainly remained in the first heating unit at the low separation temperature. It proved that naphthalene and macromolecules were big important influencing factors for the catalyst.

The chemical composition of the products after three runs is compared in the following Figure 3-7.

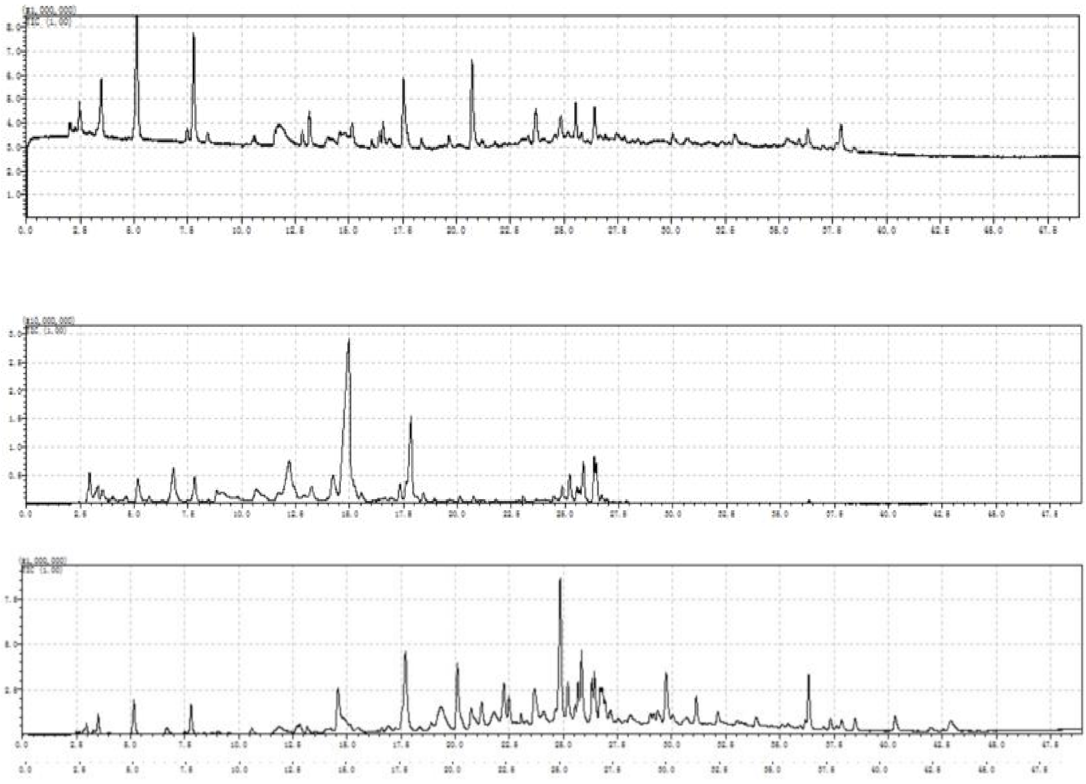

Figure 3-7 Comparison of the composition of the components after three times of consecutive tests at different temperatures

(PD:above, FD: middle, CD:below)

Figure 3-7 showed that the content of small molecules was the highest in PD condition after the consecutive runs. To see it more clearly, the chemical composition is divided into four classes and listed in Table 3-20.

Table 3-20 The area percentage in GC-MS of 4 component classes in the organic liquid from different operation condition

	1st class	2nd class	3rd class	4th class
PD				
First run	52.0%	40.0%	8.0%	0.0%
Second run	44.8%	43.9%	10.8%	0.0%
Third run	48%	41%	7%	0.5%
FD				
First run	49.2%	45.0%	5.8%	0.0%
Second run	33.7%	57.3%	9.0%	0.0%
Third run	37.0%	55.5%	7.6%	0.02%
CD				
First run	34.8%	50.2%	13.6%	1.4%
Second run	18.1%	40.4%	33.4%	7.1%
Third run	11.5%	47.1%	33.1%	8.3%

The main ingredients of ” 1st class” were small molecules and benzenes, of “2nd class” were phenols, of “3rd class” were naphthalenes, and of “4th class” were macromolecule including long chain molecules and polycyclic aromatic hydrocarbons. In summary, in the first run of each operation condition, the yield of small molecules was higher than in the second and the third runs. The yield of phenols in the first run was lower than in the second and the third runs at the operation condition PD and FD. It can be concluded that at the first run of each operation condition, the catalyst has the highest activity to convert phenols to toluene and xylene. When the catalyst was reused without regeneration, the activity decreased and more phenols were collected in the condenser than in the first run.

When in the PD run， the distilled ingredients from the first heating unit were mainly some small molecule components including the oxygen-containing heterocyclic compounds, ketones and benzenes. From the first run to the third run, the yield of each class did not change significantly, which shows that the deactivation was not serious. Small molecule components was not the main reason for the catalyst deactivation.

When in the FD run, more phenols were distilled from the first heating unit. That is why the yield of phenols was higher than the one at CD runs. After the first run in FD condition, a significant decrease in the small molecule components was observed, accompanied by the increase in the yield of phenols. The yields of naphthalene and macromolecules in FD condition were in low level, similar as in the case of PD. This proved that phenols were important cause of the catalyst deactivation.

When in the CD run, a big amount of naphthalenes and macromolecules are distilled from the first heating unit. A serious decline happened in the yield percentage of the small molecules from the first run to the second run. A further decline was observed at the third run. It clearly showed that naphthalenes and macromolecules coked on the catalyst, resulting in a serious catalyst inactivation. A test result about the components separated from the first unit was listed in Table

3-21.

Table 3-21 Table A5 Components area percentage of oil and liquid yield after the 1st heating unit in the CD operation

Heating time	Yield of liquid	1st class	2nd class	3rd class	4th class
0-15min	41%	37.4%	57.56%	4.22%	0%
15-18min	17%	19.1%	74.2%	5.06%	1.65%
15-21min	20%	5.47%	77.33%	13.45%	4.44%
21-60min	6%	*	*	*	*

*After standing in the room temperature for one day, the product liquid converted to state like tar and thus can not be analyzed in GC-MS

Though the first class components in the collected liquid was 37%, 19% and 5.5%, the content of benzenes was limited(<5%). There is a large amount of aldehyde, acid and ester in it.

Moreover, it should not be considered that the naphthalenes and macromolecules collected in the ice-water bath came from the distillation only. Part of them should be the product of the polymerization reaction in the heating process.

Small molecules, whose main components were toluene and xylene, did not contain oxygen. This class of product should be the target product because of the higher heating value. A low separation temperature should be used to avoid the contact of naphthalenes and macromolecules with the catalyst.

3.3.3 Yield and property

The yield of the product from the first run in each temperature was listed in Table 3-22. in the CD operation condition, all feedstocks were converted to water, liquid, coke(on catalyst or in the first heating unit) and gas, but in the FD and PD operation condition, some liquid feedstocks remained in the first heating unit after the cracking. A portion of the liquid remained in the first reactor was observed as shown in Table 3-22. This part was considered as high-boiling-point substances and was not distilled from the first heating unit. This liquid part was also called “feedstocks remain” and was treated as unreacted feedstocks. Though side reaction was considered as happened in the first unit, but it was not the subject for discussion in this study.

Table 3-22 The product yield in the weight percentage(%)

	Water	Oil	coke on catalyst	gas	Feedstocks remain
CD	16.6	44.7	4.1	18.8	15.7
FD	14.1	40.2	2.98	16.2	26.5
PD	12.7	35.1	0.12	12.1	40.0

The coke on the catalyst at each temperature was only a little, though the color of the catalyst turned from white to black. This shows that very little amount of coke on the catalyst will also have a significant impact on the activity.

As shown in Table 3-22, the amount of remained Feedstocks was big when condition came to PD. These ingredients were mainly considered to be naphthalene and macromolecules. However, the oil product did not decline much because these unreacted ingredients, if heated to the reaction temperature, would mainly be converted into coke and gas.

The coke on the catalyst detected in FD and CD condition was very little, less than 3% compared to the 100% raw bio-oil. But if compared with each other, the amount of CD coke on the catalyst was 33 times higher than the PD coke and 1.3 times higher than the FD coke. This proved that a low separation temperature greatly improved the coking problem on the catalyst.

The oil product in PD condition seems to be the best result. Table 3-23 listed the properties compared with the bio-oil and the oil product from the CD condition.

Table 3-23 Comparison of modified oil properties

	bio-oil	CD	PD
viscosity(mm2/s@50°C)	12.7	4.8	4.8
Density (g/cm^3)	1.14	1.05	1.03
Cetane index	＜20	38.3	40.2
Times of catalyst reused		1	4*

* The catalyst can be continuously used at least four times

The properties of the upgraded oils were highly improved campared with the raw bio-oil. Although little difference performed between the CD and PD group, the catalyst usable at least 4 times was the largest advantage of the PD group, and the oil product did not reduce significantly.

3.3.4 Main reaction

The formation of benzenes were considered to be related to both of the cracking and the polymerization reactions. In this section, acetic acid is used as a representative of oxygen acids to describe the polymerization reactions to benzenes while the guaiacol is selected as a representative of deoxidation cracking.

Bio-oil has high acidity and high content of organic acids, of which acetic acid content should be detected in the product, but actually not. Based on the study of Gayubo AG[3-20], it is considered that the deoxygenation pathway of acid is the decarboxylation and the dehydration. It can be presumed that acetic acid firstly removes H_2O and CO_2 to generate acetone, then the acetone is decarboxylated to ethylene, and then aromatization of ethylene resulted in aromatic compounds. In addition, according to the carbenium reaction mechanism, the HZSM-5 catalyst provides proton conjugation with oxygen in the acetic acid to form alkenes and carbocations and removed H_2O. The alkenes form hexacycloalkanes on the catalyst surface and then are dehydrogenated to form the aromatic hydrocarbon. Various carbenium ions cleavaged at the α-bond and the β-bond to form double bond olefins. Olefins formed a stable benzene ring structure and more stable chain hydrocarbons, while phenol and ketones were formed from the oxygen containing olefins. The cracking mechanism is shown in Figure 3-8.

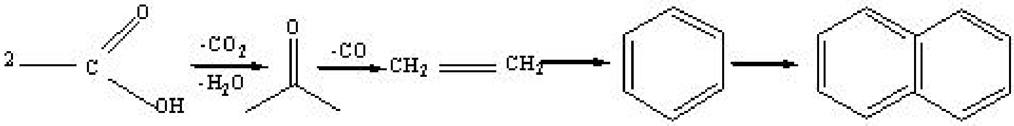

Figure 3-8 Reaction pathway of acetic acid

In the previous part of this chapter, it was found that the biggest change of the cracking came from the oxygen-containing phenols and benzenes. It indicated that the deoxidation, the methyl fragmentation and the isomerization occurred on phenols. It can be inferred that the mechanism of the catalytic cracking of oxygen-containing phenols may be: the HZSM-5 catalyst provides strong acid protons, combined with the methoxy on the benzene ring, which removed the oxygen and formed the carbon positive ions and the stable phenol substance. If keeping heating phenol on the catalyst, multiple aromatization reactions would happen and finally PAHs generated resulting in the coking on the catalyst as shown in Figure 3-9

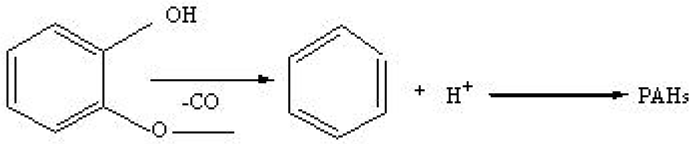

Figure 3-9 Reaction pathway of oxygen-containing phenols

3.4 Summary.

The bio-oil can be upgraded in a process with two heating unit with or without the zeolite catalyst. The main reaction of the cracking is the deoxygenation of phenols. The zeolite catalyst contributes to promote the deoxygenation rate. However, utilization of zeolite catalyst results in a decrease of the liquid product yield. As a liquid fuel, the properties of the catalytic cracked oil were better than the non-catalytic cracked oil. The hundreds of components in the raw bio-oil can be divided into 4 classes, the main ingredients of which were benzenes and small molecules, phenols, naphthalenes and macromolecules. Small molecules are not the main cause of the catalyst deactivation. Phenols slightly deactivate the catalyst. The contact of naphthalenes and macromolecules with zeolite is a big problem causing the deactivation. A lower separation temperature and shorter heating time in the first heating unit helps to alleviate the inactivation reaction.

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Chapter 4

Combination of cracking and mixing method to improve the bio-oil quality

In this chapter, the objective is to convert the bio-oil into engine fuels. As stated in the last three chapter, the bio-oil cannot be used in engines directly due to its high viscosity and low heating value. By mixing it with the biodiesel, the unexpected physical effects reduced. The mixing mixture at a low bio-oil/biodiesel mixing ratio can be applied in the engine for hours. But the chemical defects have not yet been overcome. When using the cracking method, the upgraded fuel has a certain improvement on the chemical properties, but a major drawback in the physical properties is the water content. This chapter is to study the possibility to mix the cracked oil with the biodiesel to overcome the defects both in the chemical and physical properties.

4.1. Methods and materials

The materials used for mixing are the biodiesel and the cracked bio-oil.

4.1.1 Biodiesel

The biodiesel was made from waste cooking oil by the transesterification method with KOH catalyst which was supplied from Best Trading.inc, Japan. The properties were listed in Table 4-1.

Table 4-1 Properties of the biodiesel

C (%)	76.6
H (%)	12.6
N (%)	0.0
O (%)	10.8
S(mg/kg)	0.0
H_2O (%)	0.0
Ash (%)	0.0

Density (g/cm^3)	0.87
HHV (MJ/kg)	41.2
Cetane index	46.30
Kinetic viscosity (mm^2/s @ 40 °C)	3.80

As shown in Table 4-2, the main components in the biodiesel was long-chain fatty acid esters, which includes Octadecanoic acid methyl ester and Hexadecanoic acid methyl ester.

Table 4-2 Main components of the biodiesel

Serial number	Retention time(min)	Area （%）	Name
28	54.895	30.59	9-Octadecenoic acid, methyl ester, (E)-
29	53.815	16.98	9,12-Octadecadienoic acid (Z,Z)-, methyl ester
30	49.611	10.84	Hexadecanoic acid, methyl ester
31	55.078	8.88	Methyl stearate
32	58.462	2.03	cis-11-Eicosenoic acid, methyl ester
33	59.057	1.84	Methyl 18-methylnonadecanoate
34	49.676	1.63	2-Methylheptanoic acid
35	49.77	1.62	Pentanoic acid, 2-methyl-
36	63.385	1.59	Docosanoic acid, methyl ester
37	49.822	1.39	Tridecanoic acid, methyl ester
38	66.989	1.05	9-Octadecenoic acid, 1,2,3-propanetriyl ester, (E,E,E)-
39	49.805	0.9	Pentadecanoic acid, 14-methyl-, methyl ester

The nature of the biodiesel is dominated by long-chain fatty acids ester. Normally, long-chain molecules are non-polar molecules. When mixed with water, the biodiesel is not dissolved in water, no matter with the mixing time and the temperature.[4-1]

When mixed with bio-oil directly, some part of the bio-oil dissolved in the biodiesel while some part not. It is considered that the dissolved part is the non-polar molecules. As analyzed in Chapters 2 and 3, the main components of the bio-oil were oxygen-containing small molecules, phenols and naphthalene. The insoluble part of the bio-oil should be the oxygen-containing molecules, which were polar in most cases. The oxygen-free ingredients were limited in the bio-oil. Without the chemical upgrading, the incomplete mixing problem cannot be improved. [4-2][4-3]

4.1.2 Cracked oil

The cracked oil was produced from the bio-oil cracking stated in Chapter 3. The bio-oil was the same sample as in Chapters 2 and 3, which was made from the pyrolysis of Japanese cedar.

The cracked oil was produced in fixed bed reactors with two heating units as described in Chapter 3. The first heating unit was used as a separator. Some part of the components was distilled and then introduced into the second reactor. The HZSM-5 catalyst was filled in the second reactor. The amount of the catalyst is one third of the raw bio-oil. The zeolite was provided by Tosoh corporation as shown in Chapter 3. The cracking process was also the same as shown in Chapter 3.

In this chapter, the cracked oil samples were obtained from different cracking condition: CD, FD and PD as descripted in Chapter 3. In each operation condition, the cracking was done three times. The experiments were repeated three times without changing the catalyst in the second heating unit, but replacing the residue in the first unit with new bio-oil.

The samples are listed in Table 4-3. The main components of the samples were divided into 4 classes as described in Chapter 3.

Table 4-3 Cracked oil samples and the bio-oil
(the main area percentage in GC-MS of 4 component classes)

	1st class	2nd class	3rd class	4th class
Main components	Small molecules and Benzenes	Phenols	Naphthalenes	Macromolecules
Bio-oil	8.2%	74.0%	10.8%	7.0%
PD				
First run	52.0%	40.0%	8.0%	0.0%
Second run	44.8%	43.9%	10.8%	0.0%
Third run	48%	41%	7%	0.5%
FD				
First run	49.2%	45.0%	5.8%	0.0%
Second run	33.7%	57.3%	9.0%	0.0%
Third run	37.0%	55.5%	7.6%	0.02%
CD				
First run	34.8%	50.2%	13.6%	1.4%
Second run	18.1%	40.4%	33.4%	7.1%
Third run	11.5%	47.1%	33.1%	8.3%

The properties needed to be improved was the water content, which limited the combustion capability. The water content of each sample was around 8%, which was not much changed compared with the raw bio-oil. The water contents of the first run samples at different temperatures are listed in Table 4-4. In this table, not significant trend on the water content is observed. The more detailed discussion will be conducted after the mixing tests.

Table 4-4 The water content comparison

Bio-oil	7.9%
PD cracked oil	8.0%
FD cracked oil	8.5%
CD cracked oil	8.3%

4.1.3 Mixing setup

The effects of the initial cracked-oil/biodiesel volume ratio, the stirring intensity, the mixing time and the temperature were examined. In this study, the stability of the mixture was characterized by the parameter "changed percentage", as defined in Chapter 2. When mixing finished, if the mixed liquid was capable of stabilizing in the room temperature for more than 24 hours without appearance of additional stratification and/or precipitation, CP should be calculated as follow:

$$CP=(W_i-W_f)/(W_i)\times 100\%$$

where CP: The changed percentage of the sample oil;

W_i: Weight of the initial sample before the blending;

W_f: Weight of the layer insoluble in biodiesel after the blending.

The Initial mixtures of the cracked oil and the biodiesel were prepared by adding 10, 30 and 50% (by volume) cracked oil into the biodiesel and mixed in a beaker with a stirrer. The experimental conditions are listed in Table 4-5.

Table 4-5 Mixing experimental parameters

Mixing temperature	25 °C, 40 °C
Mixing time	10 min, 20 min, 30 min, 40 min, 50 min 60 min
Stirring speed	0ppm, 600rpm, 800rpm
Percentage of sample oil	30%, 50%

4.2 Mixing result

CP values were measured every ten minutes in the first hour. The CP value of the cracked oil was compared with the CP value of the bio-oil/biodiesel mixture. The results were obtained at different temperatures with different mixing ratios as shown in Figures 4-1,4-2, 4-3 and 4-4.

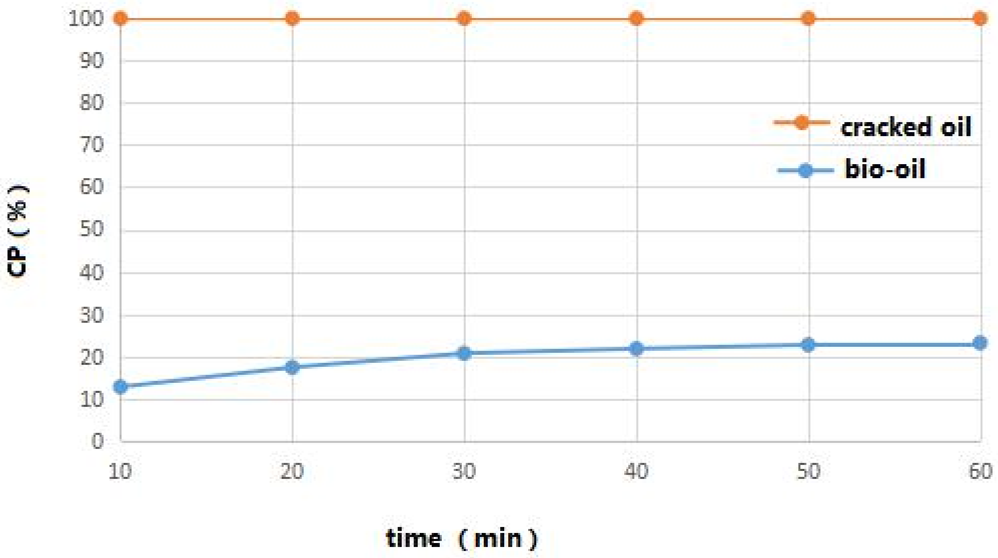

Figure 4-1 The mixing result at 25℃(Ratio of cracked oil/biodiesel=3:7)

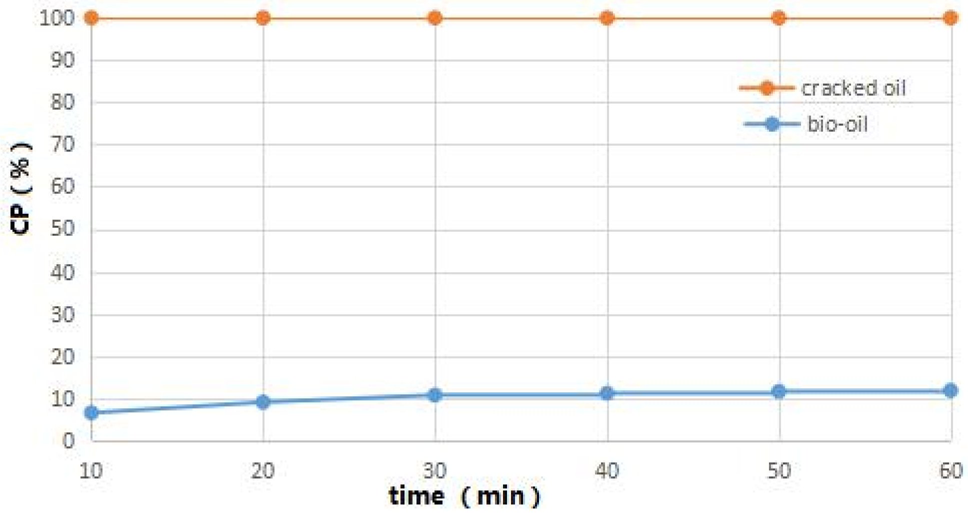

Figure 4-2 The mixing result at 25 ℃(Ratio of cracked oil/biodiesel=5:5)

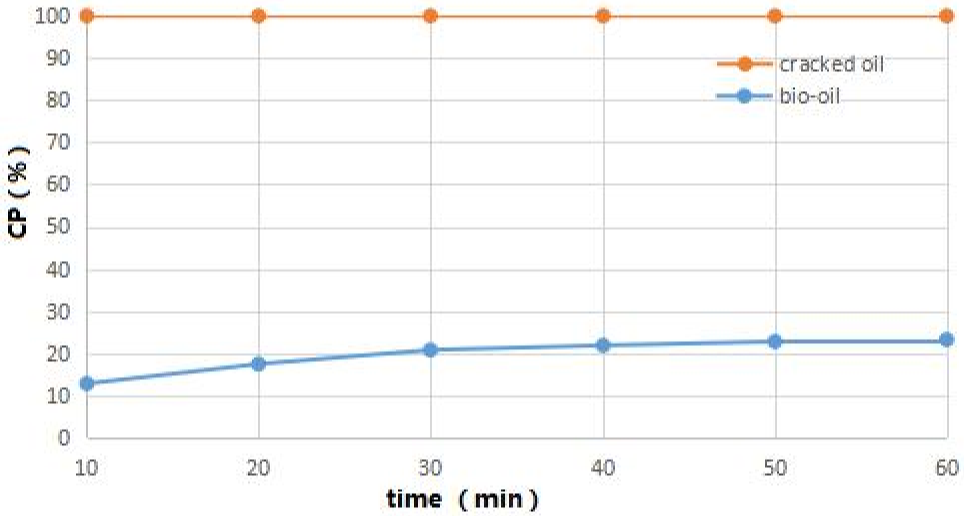

Figure 4-3 The mixing result at 40 ℃ (Ratio of cracked oil/biodiesel=3:7)

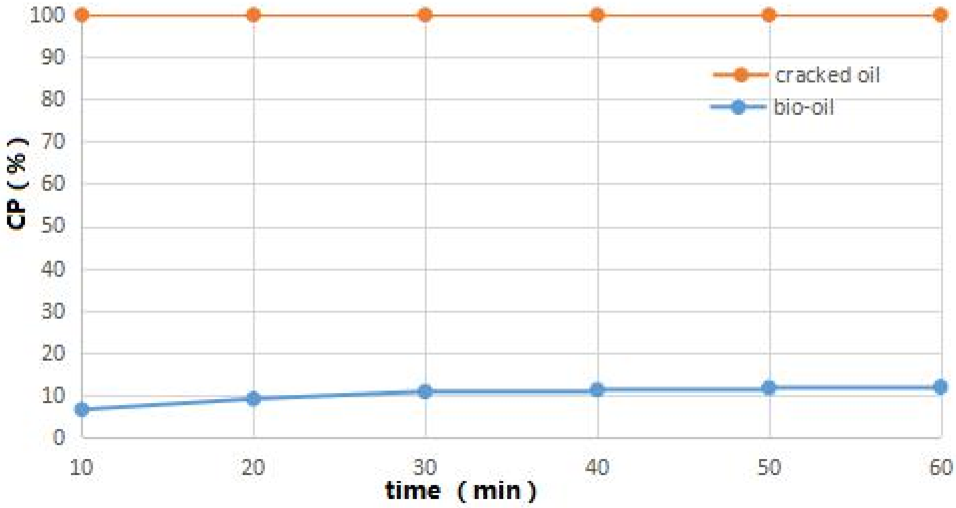

Figure 4-4 The mixing result at 40 ℃ (Ratio of cracked oil/biodiesel=5:5)

In Figures 4-1, 4-2, 4-3 and 4-4, the line marked with the cracked oil referred to all 9 types of the cracked oil produced in Chapter 3. Because all of them showed the same tendency, always being 100% CP value, only one straight line was painted on the top of the figures. It means the cracked oil can be perfectly mixed with biodiesel and formed a harmonious state without any stratification and precipitation. The stability was confirmed as well. The harmonious state last more than 6 months and no stratification or precipitation was observed.

To compared with the bio-oil/biodiesel mixture, the CP value of which was drawn in the same figures. The highest CP value was the mixture with the ratio of oil/biodiesel=30% at 40 ° C. The value was no more than 25%. To reach this value, 50 min stirring was needed. The harmonious state did not happen in the bio-oil/biodiesel mixtures because a stratification was observed after the stirring finished.

The stirring speed was analyzed. The harmonious state occurred even when the stirring speed was 0 at 25° C or 40° C. It can be considered that the cracked oil can be mixed with biodiesel harmonious at any conditions. The cracked oil contains water, but is soluble in biodiesel , so it should be a mixed material of both polar and non-polar ones.

4.3 Mixing principle

Figure 4-5 shows the photo of the mixture of the cracked oil mixed with the biodiesel. The harmonious state did show the stratification or the precipitation, but it is not transparent. This is an emulsion of both polar water and the non-polar biodiesel.

Figure 4-5 The harmonious state of CD cracked oil/biodiesel=5:5 mixture(left) and 3:7 mixture(right)

In view of the fact that the color of the mixture is dark, an additional mixture CD cracked oil/biodiesel=1:50 was made and standing in room temperature for 2 weeks as shown in Figure 4-6. The solution is transparent, without obvious precipitation or stratification.

Figure 4-6 The harmonious state of CD cracked oil/biodiesel=1:50

The main ingredients of the cracked oil obtained from the operation condition FD and PD were benzenes and phenols as shown in Table 4-3. Unlike the bio-oil, whose main ingredient was phenols (area percentage>70% in the GC-MS detection) and almost no benzenes existed in it, benzenes took nearly the half content in the cracked oil obtained from the FD and PD runs. The benzenes are mainly deoxygenated products, whose polarity were lower than phenols.[4-4] The polarity of oxygen-containing small molecule such as acetic acid, through the deoxygenation and the polymerization, were significantly reduced. Meanwhile, the phenols still existed after cracking in a large amount, taking 40~50% area percentage in the GC-MS detection. These phenols provide polarity groups, and phenol and benzene are miscible, so a stable mixture is formed in the polar order of H_2O>phenols>benzenes>biodiesel.

To prove this inference, benzene and guaiacol (2-methoxy-Phenol) were selected as the representative of benzenes and phenols to simulate the mixing process.

Figure 4-6 shows the solubility of each material in the biodiesel.

Figure 4-6 Mixing results of benzene(left), guaiacol(middle),water(right) with biodiesel

Benzene and guaiacol immediately dissolved in the biodiesel. Water was absolutely insoluble in the biodiesel.

Figure 4-7 shows the mixing result of benzene and guaiacol in water. A stratification was seen obviously. Benzene was on the top of the water layer and guaiacol sinks to the bottom

Figure 4-7 Mixing results of benzene(left) and guaiacol(right) with water

Benzene and guaiacol are miscible, but if water was mixed in, the result was shown in Figure 4-8.

Figure 4-8 Mixing results of benzene-guaiacol-water
(Before shocking: left, After shocking: middle, Standing for 1 hour: right)

The three phases in Figure 4-8 were immiscible at the first place. After slight shock for 5 seconds, the mixture became to be an emulsion which was opaque. It proved when benzene mixed with guaiacol, the mixture has a certain degree of emulsifying capacity with water. After standing in the room temperature for 1 hour, the stratification was observed. However, at the same time, there is a certain degree of emulsification maintained. The mixture did not return to the original transparent state.

All types of three phases mixing results are shown in Table 4-6.

Table 4-6 Three phases mixing results after standing for 1 hour

benzene	○	○	○	×
guaiacol	○	○	×	○
biodiesel	○	×	○	○
water	×	○	○	○
Result				

○ mixed in
× not mixed in

Except for the benzene-guaiacol-biodiesel phases, all mixtures showed the stratification. In the benzene-biodiesel-water and guaiacol-biodiesel-water phases, the water layer at the bottom is transparent. It can be considered as the emulsification effect of water was weaker than benzene-guaiacol-water phases， because not so many organic molecules can be dispersed in the water layer. It seemed that benzene-guaiacol was a key factor which could enhance the emulsification effect. By comparing benzene-biodiesel-water and guaiacol-biodiesel-water, it can be seen that without guaiacol in, the benzene-biodiesel-water phases were completely transparent. This phenomenon implies that after benzene dissolved in the biodiesel, the organic layer was separated from water. So the guaiacol played the most important role in the emulsification system.

Figure 4-9 showed the result of all materials mixed together.

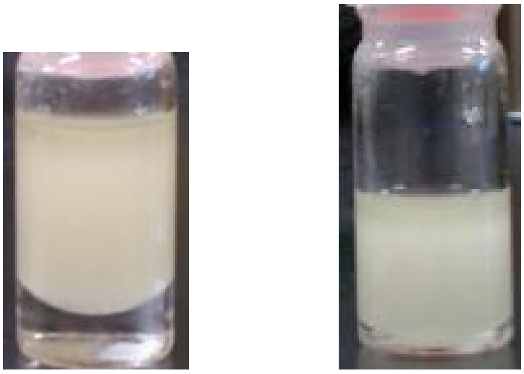

Figure 4-9 Mixing results of benzene-guaiacol-biodiesel-water
equal volume mixing（left） 5% volume of water in (right)

After standing in the room temperature for 1 hour, the equal volume mixture of benzene-guaiacol-biodiesel-water also separated into the water layer and the organic layer, but if we reduce the amount of water, the four phases mixture can be kept in the harmonious state.

In summary, benzene-guaiacol mixture can be used as an emulsifier between water and biodiesel. Guaiacol alone is also effective as an emulsifier in the biodiesel, but as good as use of benzene-guaiacol. If adjusting the mixing ratio properly, the mixtures could be kept in the harmonious state.

The actual cracked bio-oil composition is more complicated. Benzenes include benzene, toluene, ethylbenzene and so on. Phenols include phenol, cresol, ethylphenol, methoxyphenol, guaiacol and so on. Other ingredients scattered in it and formed the harmonious state. Although the proper ratio of each component in the harmonious state is not the target in this study, a research on the formation of phenols and benzenes should be a key to solve complex structure problems of the bio-oil.

In addition, using two heating units to separate some macromolecules components should also be an important factor because the cracked oil obtained from the second and third runs of CD operation could also be completely mixed into the biodiesel. Some components not soluble in the biodiesel were separated from the catalytic cracking and remained in the first unit. But it is difficult to find the model compounds of macromolecules to simulate the mixing experiment.

4.4 Fuel characteristics comparison

The target of Chapter 4 is to improve the physical characteristics of the cracked oils. Since all cracked oils can be mixed with the biodiesel completely, the physical characteristics can be calculated directly.

Table 4-7 compares the mixed fuels obtained from the separation temperature of CD and PD. The yield of the cracked oil obtained from the CD run was the highest, but the catalyst could be reused at least 4 times when in the PD run. The cost should be lower than the runs at higher heating temperatures and longer heating time.

For the balance of using more bio-oil and to ensure the fuel quality, the mixing ratio 5:5 was selected in the comparison.

Table 4-7 Fuel characteristics comparison between the mixed cracked fuels

	CD cracked oil/ biodiesel=5:5	PD cracked oil/ biodiesel=5:5
C (%)	75.04	74.42
H (%)	9.91	12.1
N (%)	0	0
O (%)	14.91	13.40
S(mg/kg)	0	0
H_2O (%)	4.15	4.00
Ash (%)	0	0
Density (g/cm^3)	0.96	0.95
HHV (MJ/kg)	37.0	40.9
Cetane index	42.30	43.15
Kinetic viscosity (mm^2/s @ 40 °C)	4.3	4.3

The water content halved successfully when the mixed state maintained stably. No big difference was observed between the CD run and the PD run. Considering the cost of the catalyst, the PD run samples should be a suitable choice.

Table 4-8 compared the yield of cracking method and the combination method. When the mixing ratio is 3:7, the product oil is more than the product oil from 5:5 ratio, but the consumption of biodiesel increases.

Table 4-8 Yield of upgraded oil from cracking method and the combination

	Raw Bio-oil (%)	Upgraded oil (%)
Cracking		
CD run	100	44.7
FD run	100	41.2
PD run	100	35.1
Combination		
CD cracked oil/biodiesel=3:7	100	149.0
CD C cracked oil/biodiesel=5:5	100	89.4
FD cracked oil/biodiesel=3:7	100	137.3
FD cracked oil/biodiesel=5:5	100	82.4
PD cracked oil/biodiesel=3:7	100	117.0
PD cracked oil/biodiesel=5:5	100	70.2

In Table 4-9, the mixed cracked oil obtained from the PD run was compared with the other oils made in Chapter 2. The best oil is the oil of the ratio of bio-oil/Biodiesel=1:9.

Table 4-9 **Fuel characteristics comparison between the mixed cracked fuel and the mixed fuel**

	Bio-oil/ Biodiesel=1:9	PD cracked oil/biodiesel=1:9
C (%)	75.1	76.4
H (%)	12.0	12.55
N (%)	0	0
O (%)	12.8	11.4
S(mg/kg)	0	0
H_2O (%)	1.1	0.8
Ash (%)	0	0
Density (g/cm^3)	0.87	0.89
HHV (MJ/kg)	39.6	41.05
Cetane index	40.78	45.69

Kinetic viscosity (mm^2/s @ 40 °C)	3.91	3.9
Biodiesel consumption	90%	90%
bio-oil consumption	10%	28.5%
Biodiesel/bio-oil consumption	9	3.15

In Table 4-9, the mixed fuel of bio-oil/biodiesel=1:9 is better in regards to the oxygen content, the water content, the density and viscosity, while the cracked oil/biodiesel=1:9 has a little advantages in the C, H contents, the cetane index and HHV. Overall, the two fuels are comparable in the performance, but considering the feedstocks consumption, the mixed fuel of bio-oil/biodiesel=1:9 consumes 9 times more biodiesel than the bio-oil. The bio-oil recovery rate is low, but the biodiesel consumption is too much. The fuel of cracked oil/biodiesel=1:9 consumes biodiesel of 3.15 times in weight of the bio-oil. The utilization rate of the bio-oil is higher. In view of that the raw material is waste pruned wood, it should be better if consuming more bio-oil and get better fuels. Moreover, the oxygen-containing small molecule, the multi-ring material, and the macromoleculesion, which are harmful for engines, are limited in the cracked oil. The cracked oil mixed with the biodiesel could be a better choice for expanding the utilization of the bio-oil.

4.5 Summary

The cracked oil, no matter in what condition it is produced, is capable of mixing with biodiesel at any mixing ratio. The mixing reduces the water content of the cracked oil. The reason why the complete mixing was successful should be ascribed to the ratio of benzene-phenol phases. Phenol plays the most important role as an emulsifier, but if no benzene or biodiesel mixed in the phases, the complete mixing could not be realized. The water content in the mixture is an unfavorable factor, because the benzene-phenol-biodiesel phases are unable to mix under the excess water content. The upper limit of mixed water could be around 8%. PD cracked oil/biodiesel=5:5 has advantages in the catalyst saving, the biodiesel saving and the utilization rate of the bio-oil. Based on the calculated data, it is more suitable for application to fuel.

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Chapter 5
Conclusions

In order to use bio-oil efficiently, two upgrading methods are discussed emphatically in this study: the mixing and the cracking. An ideal upgraded bio-oil should be adapted for stable combustion. The mixing and the cracking are selected as the simplest ways to realize this target. The upgrading can be carried out in the atmospheric pressure. No additive was applied in the experiments.

5.1 Conclusion of the mixing experiment

Biodiesel is selected as the other agent for mixing experiment because this biodiesel is produced from waste cooking oil, not from fossil energy. This helps to ease the energy crisis. The bio-oil is mixed with the biodiesel in different ratios. A stable bio-oil/biodiesel mixture was produced after standing in the room temperature and was applied in the engine. The mixing ratio is the most important fact affecting the mixed result. Nearly 25% bio-oil could be mixed into the biodiesel when the mixing ratio of bio-oil/biodiesel was lower than 3:7. When the mixing ratio of bio-oil/biodiesel got higher, the percentage of the bio-oil mixable into the biodiesel became less. 10 hours are needed for each mixture to finish the mixing, although most part of the dissolve and the emulsification occurred in the first mixing hour. A higher temperature speeded up the reaction process, but did not affect the mixing result obviously. The upper layer mixture showed desirable properties in regards to the viscosity, the water content and the oxygen content compared to the raw bio-oil. The analysis of the upper layer mixtures discovered long carbon chain fatty acid esters dominating the main properties of the upper layer of the mixture.

The application of these blend oils are tested in EPA model for an engine operation. Up to 30% blending ratio of the bio-oil with the bio-diesel, the engine operation was compatible to the diesel. It resulted that almost identical full load engine output was achieved and the NO+THC and PM emissions were positioned around the EPA Tier1 standard. It should be careful on the increase of the kinematic viscosity by adding the raw bio-oil because it may affect the spray condition in the negative direction resulting in higher exhaust emissions like smoke. For 8 hours continuous operation of the engine, the fuel injection system was encountered with the irreversible failure after finishing the 8 hours operation and it is confirmed by the impossibility of the fuel injection with the diesel fuel. The fuel injection was stopped frequently and it intermittently observed through the whole test duration. It is thought to be due to the polymerization and other reactions of the bio-oil when heated in the engine for a long time. For 4 hours test of the 10% blending ratio mixture, though the combustion efficiency was declining, the continuous operation was successful. It also proved that the blended fuel has its limits and cannot overcome chemical disadvantages coming from the bio-oil. A chemical upgrading should be studied in the next work.

5.2 Conclusion of the cracking experiment

The pyrolytic cracking method is selected for the chemical upgrading of the bio-oil. Two heating unit with or without the zeolite catalyst was tested in various conditions. The idea was to separate some undesirable components from the raw bio-oil. The main means of the separation is the distillation. Small molecules (acid, alcohol and ketones), benzenes and phenols were distilled in the first heating unit at a relatively low temperature and introduced into the second heating unit. With the catalyst in, the upgraded oil yield was reduced, but the decomposition rate increased. The oxygen content is lower than the upgraded oil produced from the non-catalyst cracking process. The yield of oil from the catalytic cracking was 6% lower than the non-catalytic run, but the oxygen content in the product oil was 5% higher than the non-catalytic run. Considering that the total oxygen content in the catalytically cracked oil was only 19%, the catalyst promoted the rate of the deoxygenation by 50%. For getting a higher quality oil, the catalytic cracking was chosen for the next step, although the cost will be higher than the non-catalytic run.

The hundreds of components in the raw bio-oil and the products were divided into 4 classes: small molecules, phenols, naphthalenes and macromolecules. Comparing the results at different separation temperatures, it proved that the main reaction of the cracking was the deoxygenation of phenols. The main components remained in the first unit were high-boiling macromolecules which are harmful to the catalyst. Compared with the traditional one reactor cracking, the catalyst could be avoided with the contact with these hazardous substances. CD, FD, PD three operation conditions were tested. When the separation temperature went high(CD), a large amount of naphthalenes and macromolecules were distilled in the first heating unit. The loss of the catalyst activity happened obviously. When the lower(FD and PD), the loss of the activity also happened but the degree of the inactivation reduced. The largest increased composition of the product was benzenes, including benzene, toluene and xylene. These benzenes were correspond to the deoxygenation and the dealkylation products of phenols, including methylphenol, methoxyphenol and ethyl phenol. The macromolecule cleavage and the small molecule polymerization were also the reactions happened in the second heating unit, but was not the main reaction.

The fuel performance improved significantly. The difference between the first runs of each separation temperature was small. Considering the catalyst cost, the low separation temperature is suitable for promotion and in-depth study

5.3 Conclusion of the combination experiment

The cracked oil product, no matter in what condition it was produced, was capable of mixing with the biodiesel at any mixing ratios. It directly proved that the chemical properties of the bio-oil have been greatly improved. Benzenes and phenols constituted the main components of the cracked oil and it formed a balance system between the polar and the non-polar molecules. Using the model compounds of benzene and guaiacol, it proved that phenols in the harmonious state played the most important role in forming the harmonious mixture. Without the addition of benzene and biodiesel, it could not form the harmonious state.

The water content in the mixture was an unfavorable factor, where the benzene-phenol-biodiesel phases were unable to mix under the excess water. The upper limit of the mixed water could be around 8%. The PD cracked oil/biodiesel=5:5 has advantages in the catalyst saving, the biodiesel saving and the utilization rate of the bio-oil. Based on the calculated data, it is more suitable for application as a fuel.

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