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Abstract. The purpose of this study is to analyze bio-oil composition produced from a low temperature pyrolysis of cooking oils under microwave irradiation. As the feedstock, waste cooking oil (WCO) and fresh cooking oil (FCO) were used. The sample was pyrolyzed at 400°C in a modified microwave reactor with an output power of 900 W. The feedstock was fed into the reactor at 2 ml/min for 60 min under nitrogen gas environment to ensure pyrolysis process. The results showed that the bio-oil compounds of both feedstocks were mainly composed of aliphatic hydrocarbons. Based on carbon number, bio-oil from WCO contained almost 70 wt.% of diesels fraction (C_{12}-C_{20}), slightly lower than FCO which is potential as fuel candidate for diesel engines.

Introduction

Security of energy supply and environmental issues have been a major concern in the world due to the use of fossil energy increases annually as the world population and economy increases [1]. One of the strategies to solve the problems is by developing renewable energy [2]. Development of renewable energy from natural resources from municipal liquid wastes such as fat and waste cooking oil that are considered as prospective raw materials for biofuels can be the main alternative energy source [1,3]. The abundant availability with low price of the material is the main reason to produce biofuels from waste cooking oil. For example, the amount of waste cooking oil generated from households in Indonesia can reach 2.9 million tons/year [4].

One of the thermochemical methods for converting waste cooking oil into alternative fuels is pyrolysis. This process can be applied for the production of liquid (bio-oil), solid (char), and gas by breaking the heavier hydrocarbon compounds into lighter ones at high temperature without or little present of oxygen [5]. Pyrolysis processes of materials can be performed by utilizing conventional heating or microwave heating [6]. On the one hand, conventional pyrolysis processes suffer from heat losses from heating source to the environment as the heat transfer of convection, conduction and radiation occurs from the reactor wall to the surface of the raw material inside the reactor. This mechanism makes conventional heating consumes more energy and requires a longer reaction time [7]. On the other hand, microwave heating is able to solve the limitation of conventional heating by the unique feature of volumetric heating of materials resulting in more rapid heating process, improve process yield, higher heating efficiency, and capable of being used to treat non-homogeneous wastes [6,8-9].

With regard to microwave application on processing of waste cooking oil, the literature showed that most of the studies mainly focused on the bio-oil production through microwave-assisted transesterification (MAT) [10]. There are only a few studies that pay attention to the use of microwave heating for pyrolysis of waste cooking oil. Study by Anis et al. [6] reports about the development of microwave reactor for pyrolysis of waste cooking oil in which amount and type of absorber material as well as microwave power are found as the main parameters affecting reactor temperature, heating rate, and thermal efficiency. Recent studies by Lam et. al. [8,11] provide an information regarding batch microwave pyrolysis of waste cooking oil to produce diesel-like fuel in which the sample with relatively homogeneous compounds is collected from a fried chicken restaurant. They found that pyrolysis temperature and type of absorber are the main parameters affecting composition and yields of bio-oil.

Based on the above description, microwave pyrolysis of cooking oils performed at relatively low temperature and continuous feeding process (instead of batch process) is important to be investigated. Thereby, this study is objected to investigate the bio-oil composition produced from a low temperature and continuous pyrolysis processes of waste and fresh cooking oils under microwave irradiation.

Materials and Methods

1.1. Materials

Waste cooking oil (WCO) and commercial/fresh cooking oil (FCO) were used as the feedstock in this work. WCO was obtained from some traditional food stalls in Semarang, Indonesia after being used several times for frying. The feedstocks were heated at 100±3°C for 30 min to remove moisture content [6]. After cooling, the solid particles were then separated using filter papers. Commercial particulate charcoal was also employed to absorb and convert microwave energy into heat. As a carrier gas and to ascertain the rightly pyrolysis condition, nitrogen gas (99.9%) was used.

1.2. Experimental apparatus

A schematic diagram of the pyrolysis experimental apparatus is shown in figure 1. A continuous microwave-assisted pyrolysis system was performed for treating WCO and FCO. The system consisted of a modified microwave reactor, cooling and controlling systems. The microwave oven has a frequency of 2.45 GHz and a maximum output power of about 900 W. A three-neck quartz glass reactor of 1000 ml was used as a reactor and put vertically inside the microwave cavity. Two K-type thermocouples were installed inside the reactor and microwave cavity for measuring the temperatures. A temperature controller was applied to control the pyrolysis reaction temperature. A double tube condenser with mixture of water and ice as a cooling fluid was used to condense vaporize pyrolysis product. To collect bio-oil product, a liquid collector of 500 ml glass bottle was used.

The pyrolysis of WCO and FCO was carried out at a fix temperature of 400ºC. In each experiment, the reactor was filled with 300 grams of charcoal as microwave absorber, which was then heated to pyrolysis temperature process. After the specified pyrolysis temperature has been reached, the sample of WCO or FCO was injected into the reactor at a fix flow rate of 2 ml/min for 60 min. In this study, nitrogen gas flow rate was set at 100 ml/min.

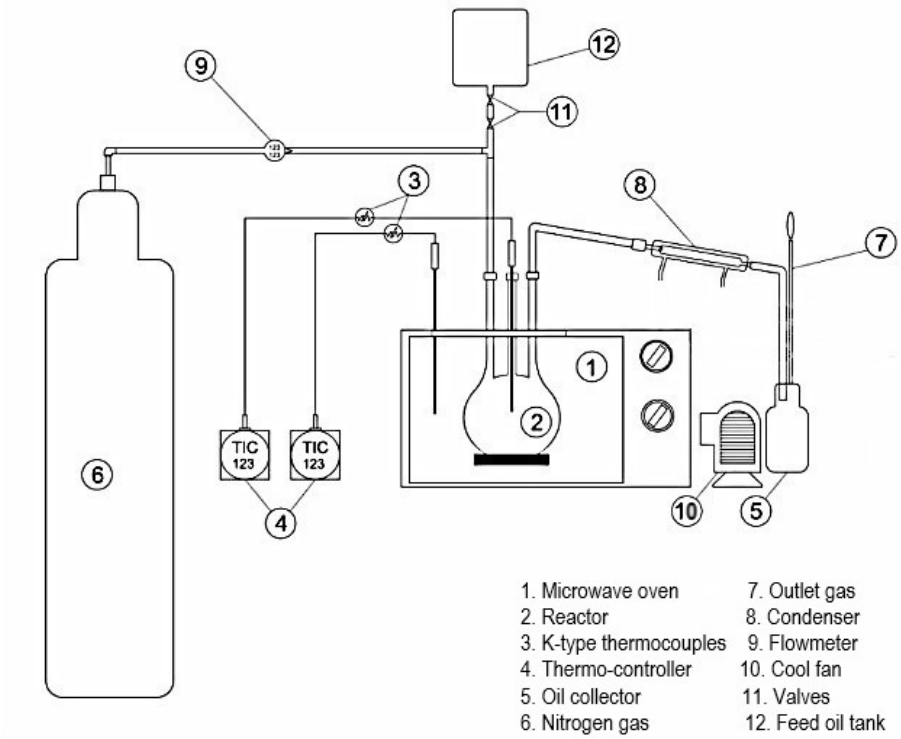

Figure 1. Schematic diagram of the microwave pyrolysis experimental apparatus.

1.3. Analytical Method

Composition of the bio-oil products was analyzed by using a Perkin Elmer GC Clarus 680 MS Clarus SQ 8T. The oven temperature was programmed at 60°C for 5 min, ramp at 5°C/min to 280°C and hold at 280°C for 5 min. Maximum temperature of oven was set at about 300°C. Total runtime of analyzed samples was about 54 min. Injector split ratio was set at 42.2:1. Helium was used as carrier gas with 0.8 ml/min of flow rate. The sample was filtered by using a filter paper before injected into the GC at one microliter. Three samples were taken to obtain the average.

Results and Discussion

The GC-MS chromatograms of bio-oils produced from pyrolysis of WCO and FCO at a temperature of 400°C are shown in figures 2 and 3, respectively. NIST MS 2.0 software was applied for characteristic peaks identification on the compound spectra. At a pyrolysis temperature reaction applied in this work, the chemical compositions of bio-oils from WCO and FCO were found to be different as the feedstocks are also thought to have different compounds.

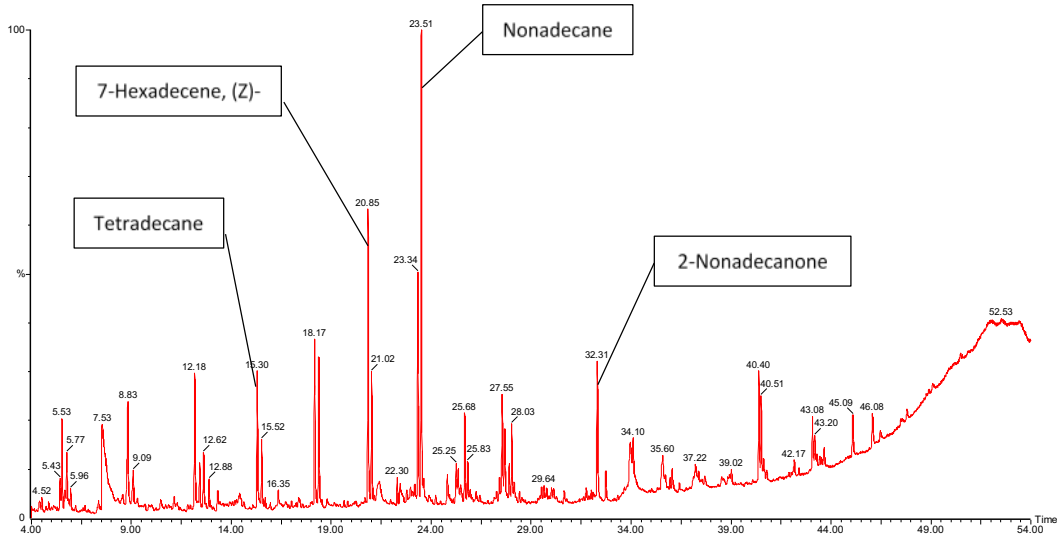

Figure 2. GC-MS chromatogram of bio-oil from WCO produced at 400°C.

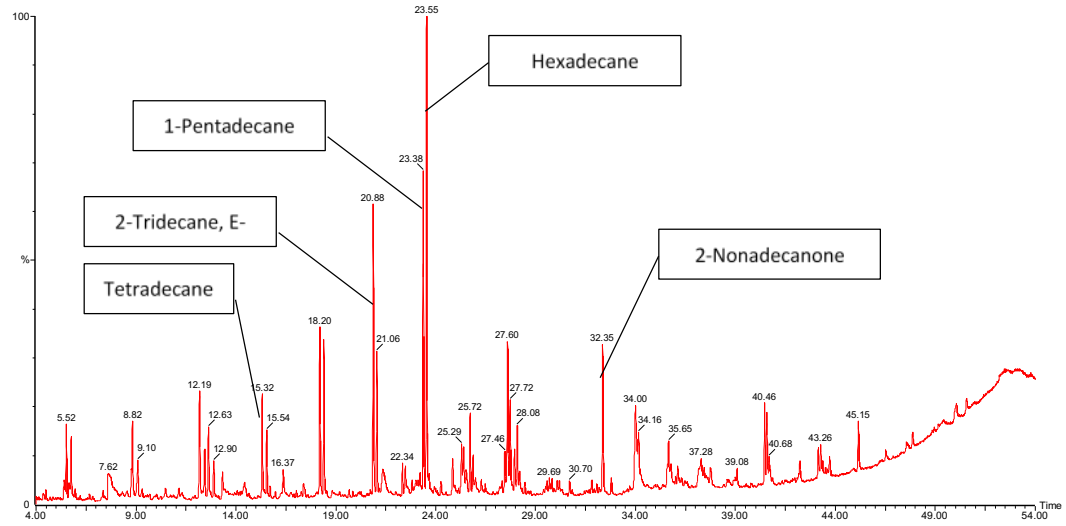

Figure 3. GC-MS chromatogram of bio-oil from FCO produced at 400°C.

It could be noted that when the oil sample has longer carbon chain, many numbers of compounds will produce during decomposition. Based on figures 2 and 3, bio-oil produced from WCO contained a smaller number of compounds compared to that of FCO. In this work, the number of identified main compounds produced from WCO was 16 compounds. Among them, tetradecane, 7-hexadecene, (Z)-, and nonadecane were found to be the most dominant compound in bio-oil which occupied 10.13%, 18.87%, and 15.64%, respectively. In the meantime, at the same temperature of 400°C, there were 19 identified main compounds from bio-oil chromatogram produced from the decomposition of FCO sample. At this condition, tetradecane, 1-pentadecene, and hexadecane were found to be the most major compound in bio-oil which occupied 11.66%, 10.58%, and 14.72%, respectively. These results indicated that WCO feedstock has hydrocarbons chains relatively shorter than FCO feedstock. It is possibly due to breaking of hydrocarbons chains by several frying process.

GC-MS analysis proved that the bio-oils produced from microwave pyrolysis of WCO and FCO at temperature of 400°C mainly consisted of three groups of hydrocarbon compounds including alkanes,

alkenes, and cycloalkanes. Table 1 shows the bio-oils product composition with regard to hydrocarbon compounds group.

Table 1. Chemical compounds of the bio-oils product.

	WCO (%)	FCO (%)
Aliphatic		
Alkanes	55.50	50.42
Cycloalkanes	4.78	4.13
Alkenes	39.72	45.45
Aromatic	-	-
Sum	**100**	**100**

It could be observed from the table that both bio-oils product totally composed of aliphatic hydrocarbons. The highest number of aliphatic hydrocarbons were alkanes and alkenes. In this study, the aliphatic hydrocarbons also contained a small number of cycloalkanes. WCO was thermally cracked into liquid hydrocarbons of alkanes from nonane (C_9H_{20}) to nonadecane ($C_{19}H_{40}$) as the higher compounds' concentration in the bio-oil. Alkene consists of compounds with shorter hydrocarbon chains compared to alkanes with the C_9-C_{16} domain compound. The most important compounds in alkene were 3-tetradecene, (Z)- ($C_{14}H_{28}$) and 7-hexadecene, (Z)- ($C_{16}H_{32}$) compounds with 5.23 wt.% and 18.87 wt.%, respectively. For FCO decomposition case, it was found that the composition of bio-oil has a longer carbon chain than that of WCO. The content of the alkanes consisted of nonane (C_9H_{20}) to octadecane ($C_{26}H_{54}$), while alkene consisted of 1-nonene (C_9H_{18}) to 1-docosene ($C_{22}H_{44}$) compounds.

Table 2 shows the fuel fraction of bio-oils product that was evaluated based on the number of carbon atom. As can be seen from the table, bio-oil from WCO had higher content of gasoline fraction. This proved that bio-oil produced from pyrolysis of WCO was dominated by shorter carbons chains. In the meantime, bio-oil from FCO was mainly composed of kerosene and diesel fractions, indicating a relatively longer carbon chains of the bio-oil compounds.

Table 2. Fuel fraction in the bio-oils product.

Carbon component	WCO (%)	FCO (%)	Fuel Fraction
C_5- C_{12}	24.43	17.61	Gasoline
C_{10}- C_{16}	64.52	81.03	Kerosene
C_{12}- C_{20}	69.69	81.26	Diesel
> C_{20}	-	4.53	Heavy fuel

The high number of aliphatic hydrocarbons in the bio-oil indicated the potential to be utilized as fuel and as chemical raw materials [11]. This was found in the high content of kerosene and diesel fractions in the bio-oil from both WCO and FCO raw materials. Nevertheless, there was still quite a bit content of heavy fuel fraction in the bio-oil from FCO.

Conclusions

Bio-oil composition produced from a relatively low temperature pyrolysis of WCO dan FCO under microwave irradiation has been successfully investigated. The bio-oil compounds of both feedstocks were totally composed of aliphatic hydrocarbons. Most of bio-oils compounds were alkenes and alkanes aliphatic hydrocarbons. The results also showed that bio-oils from WCO tended to have lighter hydrocarbon compounds (C_9-C_{19}) indicated also by the high content of gasoline fraction. Whereas bio-oils from FCO composed of relatively higher hydrocarbon compounds (C_9-C_{26}) that were dominated by kerosene and diesel fractions. This finding is essential to be followed up further to study the parameters for bio-fuel production.

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