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Liquid Fuel Production via Catalytic Pyrolysis of Waste Oil

Malee Santikunaporn, Neera Wongtyanuwat, Channarong Asavatesanupap

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***Abstract*—**Pyrolysis of waste oil is an effective process to produce high quality liquid fuels. In this work, pyrolysis experiments of waste oil over Y zeolite were carried out in a semi-batch reactor under a flow of nitrogen at atmospheric pressure and at different reaction temperatures (350-450 ^{o}C). The products were gas, liquid fuel, and residue. Only liquid fuel was further characterized for its composition and properties by using gas chromatography, thermogravimetric analyzer, and bomb calorimeter. Experimental results indicated that the pyrolysis reaction temperature significantly affected both yield and composition distribution of pyrolysis oil. An increase in reaction temperature resulted in increased fuel yield, especially gasoline fraction. To obtain high amount of fuel, the optimal reaction temperature should be higher than 350 ^{o}C. A presence of Y zeolite in the system enhanced the cracking activity. In addition, the pyrolysis oil yield is proportional to the catalyst quantity.

***Keywords*—**Waste oil, pyrolysis oil, Y zeolite, gasoline, diesel.

I. Introduction

SHORTAGE in petroleum reserve has encouraged research around the world to develop novel source of renewable energy. For instance, vegetable oil has been converted to biodiesel, lignocellulosic material to bio-ethanol via fermentation, and animal mature to biogas by anaerobic digestion. As populations grow, a rise in demand for transportation fuel was forecasted to increase from 125 billion liters in 2015 to 202 billion liters in 2024 [1]. Pyrolysis is a process well-known for its ability to decompose biomass into valuable products under high temperature atmosphere and no oxygen. The process actually consists of many complicated mechanisms which convert lignocellulosic materials into bio-oil, gas and bio-char. A typical composition of biomass contained 40-45% cellulose, 25-30% hemicellulose, and 25-30% lignin [2]. Many different kinetic models were proposed for the breakdown of biomass molecular structure which was analyzed by thermogravimetric analysis (TGA). Approximately, 70% of the biomass is classified as volatile molecule was degraded as temperature rise to 700 ^{o}C, 20% fixed carbon was degraded between from 700 to 900 ^{o}C and 10% ash was removed at temperature higher than 900 ^{o}C [3].

Various different types of reactors are used to carry out pyrolysis reaction of biomass. An auger reactor consisting of a screw conveyor was used for pyrolysis reaction to convert red oak biomass at 600 ^{o}C to a 75% yield of bio-oil at a capacity of 1 kg/h [4]. A reduction in pyrolysis temperature to 450 ^{o}C using the same auger reactor has been shown to give roughly 56% bio-oil using 2-4 mm pine wood as a feedstock [5]. Another popular reactor used was a fixed-bed reactor, which was found to convert 1-2 mm empty fruit bunches to 45.75% bio-oil with low viscosity at 450 ^{o}C [6]. A novel rotating cone reactor was applied to convert 0.5 mm pine wood chips to 54.83% bio-oil at 550 ^{o}C and feed rate of 0.5 kg/h [7], other types of reactor for the pyrolysis process included fluidized bed, microwave reactor, and free fall reactor.

Catalysts are in some cases used to help to initiate the breakdown of solid materials such as municipal wastes and vehicle tyres. Recent research has shown that usage of catalyst including zeolite, alumina and calcium oxide caused an increase in formation of gaseous product. The yield of bio-oil was higher when non-catalytic pyrolysis was employed [8]. This is because catalyst such as zeolite provided high concentration of acidic surface which has been found to promote formation of carbocation and then resulted in the cleavage of the molecular structure [9]. Pyrolytic liquid oil usually contain alkyl-aromatics, long-chain hydrocarbon, and limonene.

The composition of bio-oil as analyzed by GC-MS was observed to be influenced by the types catalyst used for pyrolysis of tyres. Zeolite with higher Si/Al ratio and smaller pore size was investigated to produce lower content of aromatic compounds [10]. Alumina catalyst was observed to produce bio-oil with higher polar hydrocarbon and lower aliphatic hydrocarbon compared with bio-oil derived from silica catalyst [11].

In this work, the waste oil was converted to liquid products that can be used as liquid fuels, such as gasoline, jet-fuel and diesel, via catalytic pyrolysis reaction over Y zeolite catalyst. Reaction parameters studied were reaction temperature and catalyst quantity. Both product yields and composition distribution of liquid fuels were reported. Also, fuel properties were analyzed.

II. Materials and Methods

A. Materials

Waste oil collected from small industries was used as a feed stock in this work. Before using waste oil, small particles in the oil were removed by filtering in a centrifuge at a speed of 3,000 rpm for 30 min and boiled to remove moisture for 20 min. A Y zeolite was used as catalyst for testing the pyrolysis

Channarong Asavatesanupap is with the Department of Mechanical Engineering, Faculty of Engineering, Thammasat University, Pathumthani, Thailand (corresponding author, phone: 662-564-3001 ext. 3211; fax: 662-564-3028; e-mail: acharnna@engr.tu.ac.th).

Malee Santikunaporn and Neera Wongtyanuwat are with the Department of Chemical Engineering, Faculty of Engineering, Thammasat University, Pathumthani, Thailand (e-mail: smalee@engr.tu.ac.th, neera.vtv@hotmail.com).

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activity. All catalysts were calcined at the suitable temperature and time before use.

B. Catalytic Pyrolysis Reaction

The catalytic reaction was conducted in a semi-batch reactor at temperatures between 350-450 °C under atmospheric pressure with a flow of nitrogen gas. The 1-L round bottom glass reactor was heated and stirred by the heating mantle. The top of the reactor was connected with a condenser at 25 °C. The schematic experiment was set up as shown in Fig. 1. Waste oil and catalyst was put inside the reactor at a ratio of 10:1. Before each run, the nitrogen gas was fed into the reactor to remove an oxygen and kept at a constant flow of 80 mL/min. Products obtained from the reaction were cooled with a condenser at 25 °C and collected in a trap for liquid and in a gas-sampling bag for gas.

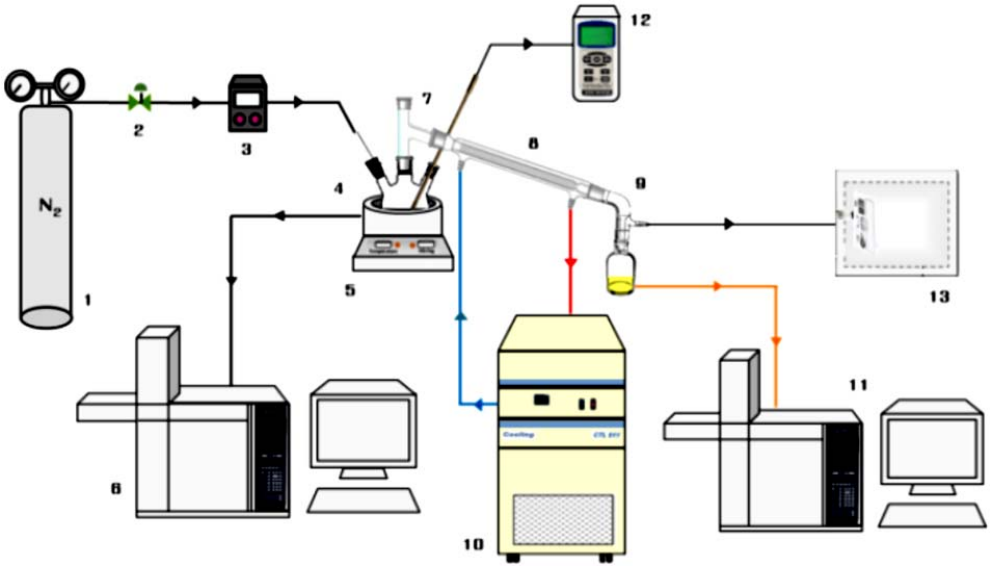


Fig. 1 Schematic diagram of the catalytic pyrolysis system: (1) N_2 tank, (2) Flow controller, (3) Flow meter, (4) glass reactor, (5) stirring heating mantle, (6) Simdis GC, (7) Three-way adapter, (8) Liebig condenser, (9) Vacuum bent adapter, (10) Cooling, (11) GC, (12) Data logger and (13) Gas-sampling bag

C. Products

Three main parts were kept after the reaction: a gas-phase product, a liquid-phase product or pyrolysis oil and a char residue. Pyrolysis oil was further analyzed by using a simulated distillation gas chromatography for carbon distribution, a bomb calorimeter for a heating value. Liquid products were categorized into four groups which were (1) gasoline (2) jet fuel (3) diesel and (4) long residue by the boiling temperature as shown in Table I.

TABLE I
LIQUID PRODUCTS CATEGORIES

Composition	Number of C atoms	Boiling Point (°C)
Gasoline	C7-C10	140-180
Jet fuel	C11-C14	180-250
Diesel	C15-C20	250-350
Long Residue	>C20	350-500

III. Result and Discussion

Waste oil used in this experiment was a dark brown color with high viscosity as shown in Fig. 2. The composition of waste oil was determined by using a simulated distillation gas chromatography. The results are presented in Table II. The composition of waste oil was mostly long residue about 97.7 wt.%. This can be said that waste oil has a high potential feed for liquid fuels production via cracking processes.

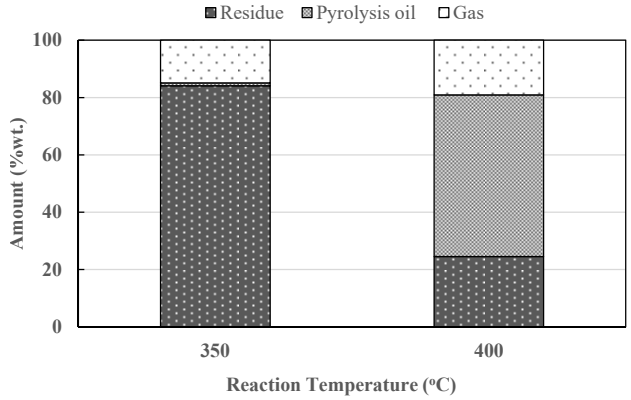


Fig. 2 Waste oil used as a feed

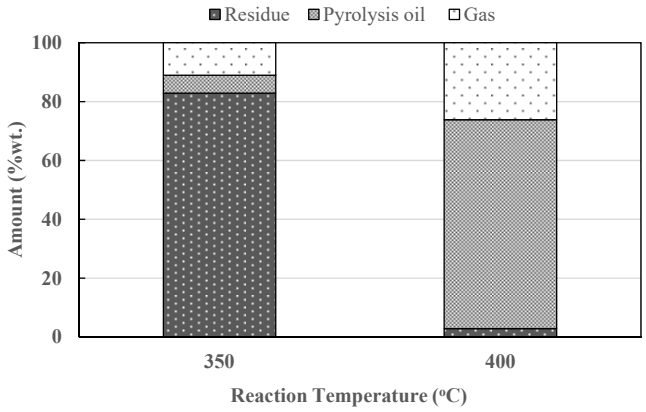
TABLE II
FEED COMPOSITION AND PROPERTIES

Name	**Value**
Properties	
Density	890 kg/m^3
Viscosity @40 °C	77.3 cSt
Composition	**Amount (wt.%)**
Gasoline	1.0
Kerosene	0.3
Diesel	1.0
Long Residue	*97.7*

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(a) No catalyst



(b) Y zeolite

Fig. 3 Product yields from catalytic pyrolysis with and without catalyst at different reaction temperatures

A. Effect of Reaction Temperature

In this part, the pyrolysis reactions of waste oil were carried out in a semi-batch reactor with and without catalyst at two different temperatures (350 and 400 °C) under a N_2 flow at atmospheric pressure. A Y-zeolite was chosen to study the effect of reaction temperature. The product yields of each experiment are shown in Fig. 3. The results showed that the cracking activity was improved when increasing the reaction temperature. The temperature for thermal cracking of waste oil should be higher than 350 °C due to low yields of pyrolysis oil. An increase in reaction temperature from 350 to 400 °C resulted in a dramatic increase in yields of pyrolysis oil. However, a high yield of pyrolysis oil (71 wt.%) were obtained over Y zeolite with a small residue (2.8 wt.%) left inside the reactor at 400 °C. Pyrolysis oils obtained at 300 °C were not further determined for their compositions due to low yields.

Fig. 4 shows comparison of compositions of pyrolysis oils obtained from the pyrolysis reaction at 400 °C with and without Y zeolite catalyst. The composition of pyrolysis oil was altered when having Y zeolite in the system. A dramatic increase in gasoline from 12 to 26 wt.% and jet-fuel from 30 to 35 wt.% was found over Y zeolite. However, almost one-half of diesel yield was decreased. It can be said that both reaction temperature and a presence of catalyst affect the cracking activity of waste oil.

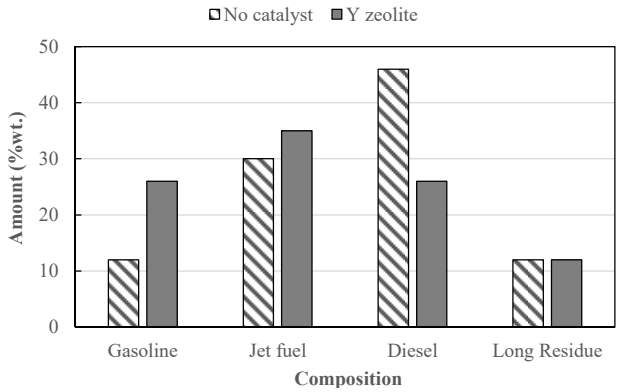


Fig. 4 Composition of pyrolysis oils obtained from the pyrolysis reaction over Y zeolite catalyst and no catalyst at 400 °C

B. Effect of Catalyst Quantity

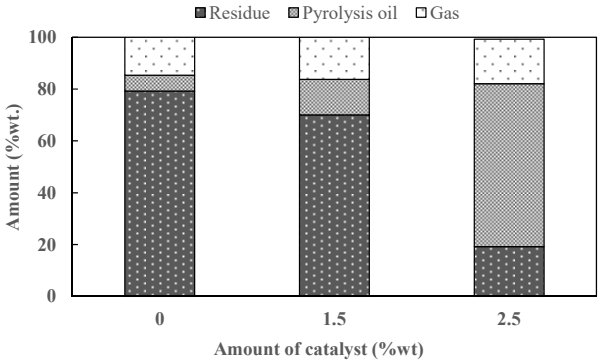


Fig. 5 Product yields from pyrolysis reaction over Y zeolite at various amount at 375 °C

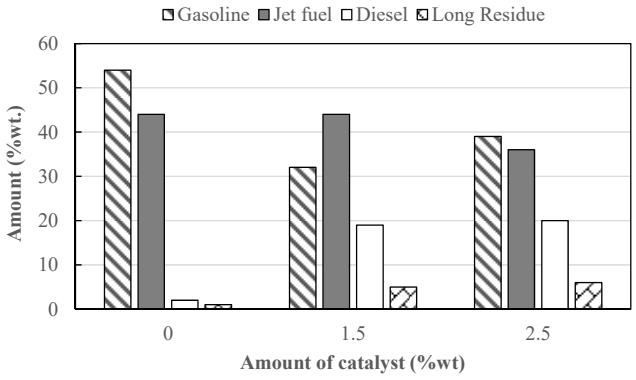


Fig. 6 Composition of pyrolysis oils obtained from the pyrolysis reaction over various amount of Y zeolite catalyst at 375 °C

In this section, effect of catalyst quantity on product yields was determined over three various amounts of Y zeolite (0, 1.5 and 2.5 wt.%) at a constant temperature of 375 °C and a constant atmospheric pressure under a N_2 flow. At 375 °C, pyrolysis oil was found to be only 6.2 wt.% without catalyst as shown in Fig. 5. However, the amount of pyrolysis oil was doubled when having 1.5 wt.% of Y zeolite. By addition of Y zeolite from 1.5 to 2.5 wt.%, the yield of pyrolysis oil was increased more than 4.5 times (from 13.7 to 62.9 wt.%). It can

be concluded that the amount of Y zeolite significantly affects yield of products, and the amount of catalyst is proportional to the yield of pyrolysis oil.

The composition of pyrolysis oil over various amounts of Y zeolite was presented in Fig. 6. An increase in amount of Y zeolite from 1.5 to 2.5 wt.% resulted in increasing amount of gasoline from 32 to 39 wt.%. The figure showed that yield of liquid fuels slightly depended on the amount of catalyst.

C. Product Properties

After the reaction, liquid products were collected and analyzed in terms of its properties such as viscosity, density and heating value. Properties of pyrolysis oil were presented in Table III.

TABLE III
PROPERTIES OF PYROLYSIS OIL

Name	*Value*
Color	Yellow
Density	794 kg/m^3
Viscosity @40 ºC	1.3 cSt
Heating value	44.8 MJ/kg

For Table III, physical properties of pyrolysis oil differed from waste oil. The color of pyrolysis oil is pale yellow, while waste oil is dark brown. From the density and viscosity of pyrolysis oil, it can be indicated that pyrolysis oil is lighter than waste oil. In addition, its heating value is 44.8 MJ/kg which is in both gasoline and diesel range.

IV. CONCLUSION

Waste oil has a high potential for fuel production via pyrolysis process. The amount and composition of pyrolysis oil depend on the reaction conditions such as temperature and catalyst. The suitable reaction temperature for fuel production should be higher than 350 ºC. An increasing catalyst quantity can produce high yield of pyrolysis oil at lower reaction temperature.

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