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Organic Liquid Products from Cracking of Used Cooking Oils with Commercial Catalysts

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Catalytic cracking is widely used in biofuel production from natural fats and vegetable oils. Used cooking oils are one of the major wastes from food processing in Thailand. They are interesting raw materials to produce biofuel. This study focused on catalytic cracking of used cooking oils over two commercial (Z and Y zeolite) catalysts to generate light organic liquid products. The cracking reactor used was based on a fixed bed reactor setup. Temperature of reaction (400 °C) was controlled by a digital controller and a thermo-couple connected to the reactor. The liquid products obtained were subsequently analysed by gas chromatography and mass spectrometry. The maximum liquid yield of 82.5 % was obtained. From the chemical analysis, the organic liquid products were found to contain three (gasoline-, kerosene-, and diesel-like) groups with the carbon number between C_7 – C_{11}, C_{12} – C_{15}, and C_{16} – C_{21}.

1. Introduction

One of the main causes of the global warming is from colossal energy consumption by mankind. CO_2 emissions from fossil fuel combustion and related industrial processes are up to 78 % of the increase in total greenhouse gas released (Adua et al., 2019). Fossil fuels are derived from the decomposition of buried dead organisms. Duration of the fuel formation from this natural processing took millions of years. In a recent situation, fossil fuels are important energy resources for everyday life of people and used for country development. They are non-renewable. In Thailand, a 2018 report of energy consumption by the Thai Department of Alternative Energy Development and Efficiency showed that the growing demand of petroleum and coal/lignite product was at 4.9 % from the energy consumption in the previous year. Similar to many countries, fossil fuels are used for the main energy consumption. It caused a lot of problems of pollutant emissions which released into the atmosphere such as CO, CO_2, nitrogen oxides (NOx), and sulfur-containing residues that are motivating factors of global warming and greenhouse effect (Crabbe et al., 2001). From these reasons, renewable energy offers an attractive option to replace fossil fuels.

Biofuels from natural fats and vegetable oils can decrease emissions from transportation (Tamunaidu and Bhatia, 2007). Animal fats (Tippayawong and Singkham, 2015) and vegetable oils (Tippayawong and Sittisun, 2012) are interesting raw materials for biofuels. Food production tended to increase in similar fashion to the growth in population. Hence there are a lot of food processing wastes available. Used cooking oils are one of the major wastes from food processing in Thailand. Used cooking oils lost nutrition after used in food processing. It has more disease depreciation chemicals such as atherogenesis, Alzheimer's disease, cancer's disease, and protein modification (Cao et al., 2019). Although it is considered worthless for further food process, biofuel production from waste cooking oils is promising.

There are many ways to upgrade used cooking oils. The most important uses of waste cooking oil is transferring it to biodiesel (Emara Ismaail et al., 2018). For examples, the transesterification reaction is a common method of manufacturing biodiesel. It changes triglyceride to esters and glyceride (Tamunaidu and Bhatia, 2007). Pyrolysis that cracks oil molecules at temperatures typically between 300 and 600 °C (Khuenkaeo and Tippayawong, 2019) and high pressure without the catalyst (Khuenkaeo and Tippayawong, 2018). Biomass, which is long-chain hydrocarbon, is heated with low oxygen. Hydrocarbon bonds are broken at high temperature and pressure and turn into liquid fuel but lower volume and quality than other processes. The general product from pyrolysis has a lot of water and oxygen content (Prasertpong and Tippayawong,

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2019) and instability (Maher and Bressler, 2007). Then, the hydrocracking method is normally facilitated by rearranging and breaking hydrocarbon chains with high performance catalyst at high pressure hydrogen. Both conditions cause high expenses. Catalytic cracking is widely used in the refining industry (Jaroenkhasemmeesuk et al., 2018). This process improves chemical composition by increasing the reaction rate and reduces energy consumption. After cracking reaction, transformed triglycerides into fatty acids and converted to the organic liquid product. A catalyst for using in this method is developed with increased productivity, high selectivity, longevity, and decreased production cost. It proves that the catalytic cracking process allows many advantages in comparison to other processes (Ong and Bhatia, 2010).

Catalytic cracking of used cooking oils is favorable as it is cost effective and simple in converting used cooking oils to hydrocarbon biofuels which may have similar chemical properties to conventional petroleum fuels. Zeolite based catalysts are among the most common catalysts used in catalytic cracking reactions. There are several types of zeolite based catalysts including ZSM-5, H-Y, H-mordenite etc. that were applied to cracking of vegetable oils (Zhao et al., 2017). The use of ZSM-5 and Y-Re-16 catalysts may be useful in catalytic cracking of used cooking oils. ZSM-5, a popular choice for fluid catalytic cracking (Benavides et al., 2017), was widely studied to increase the yields of light biofuel in the organic liquid product, while Y-Re-16 was used to improve conversion rate. Both ZSM-5 and Y-Re-16 catalysts were used to upgrade biomass pyrolysis oil (Jaroenkhasemmeesuk et al., 2017), but few works were reported on upgrading used cooking oils. Most related research focused on cracking reactions in a fixed bed reactor setup. To the authors' knowledge, catalytic cracking of used cooking oil with Y-Re-16 catalyst and experimental investigation under a flow reactor setup remained relatively rare.

In this study, biofuel production from cracking of used cooking oil was considered, where the effect of ZSM-5 and Y-Re-16 catalysts on cracking performance in a flow reactor at 400 °C was investigated.

2. Materials and methods

2.1 Raw materials

Used cooking oils are domestic waste which are not suitable to reuse in cooking again (Teixeira et al., 2018). In this study, they were obtained from a restaurant in Chiang Mai University. After collection, they were filtered by high quality filter paper with 125 mm-diameter, washed with water, and heated at 105 °C for 30 min to remove water. The ZSM-5 and Y-Re-16 catalysts were obtained from a commercial supplier. Prior to the experiments, they were calcined at 350 °C for 4 h, with similar procedure to Jaroenkhasemmeesuk et al. (2017). They were kept in a desiccator with silica gel to avoid the moisture content. Both catalyst characteristics are shown in Table 1.

Table 1: ZSM-5 and Y-Re-16 characteristics.

Appearance	ZSM-5, solid	Y-Re-16, solid
SiO_2/Al_2O_3 molar ratio	38	> 5
Shape	Cylinder (pelletized)	Pellet
Dimension	Ø 2 mm, 2-10 mm long	Ø 2-3 mm, 10-20 mm long
Pore volume	≥ 0.25 cm^3/g	0.30-0.50 cm^3/g
BET surface area	≥ 250 m^2/g	≥ 620 m^2/g

2.2 Experimental setup

Catalytic cracking involves breaking up large hydrocarbon molecules into smaller ones by using catalysts at elevated temperature and pressure. The diagram of the fixed bed reactor system used in this work is shown in Figure 1. The cracking experiment include a heating mantle for evaporating the used cooking oil in a 1000 mL flask connected to the fixed bed reactor (made of stainless steel,70 mm in diameter, thickness of 5 mm, length of 150 mm). It was heated by a two-band heater (total 2.0 kW). There was a socket for supporting the catalyst at the middle of the reactor and a thermocouple installed on the top for measuring and controlling the temperature inside the reactor. There were two condensers used which was a coil condenser (counter flow of 40 °C water) and a dry ice condenser trap (-35 °C dry ice mixed with acetone at the middle). All catalytic cracking experiments were carried out using a low vacuum pump as a driving force. The average evaporating rate of used cooking oil was 1g per min and the gas hourly space velocity was 0.166 h^{-1}.

2.3 Experimental procedure

The schematic of the experimental procedure is shown in Figure 2. About 100 g of the used cooking oil was loaded into the 1000 mL flask sitting on the hot plate. About 12.5 g of the catalyst were loaded and positioned at the middle of the cracking reactor. The reactor was then heated to 400 °C. Then, the hot plate was switched on and the oil was vaporized into gas phase. The oil vapour was sucked into the cracking reactor and reacted with the catalyst. The gas product was then passed to the two condensing units and cooled to 40 °C and -35 °C. The OLP was collected at room temperature and weighed. The remaining solid residue in the flask was also weighed. The difference was determined as the mass of the non-condensible gas. The product yields were calculated as a ratio between the mass of the products and the mass of the original oil used in each experiment, determined according to Eq (1) as;

$$\text{Product yield } (\% \text{ w/w}) = \frac{m_p}{m_i} . 100 \tag{1}$$

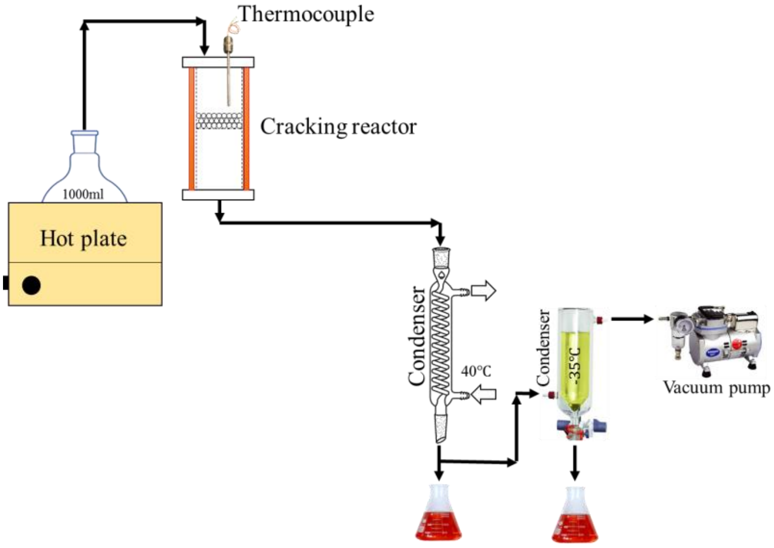

Figure 1: Schematic of the fixed bed reactor setup.

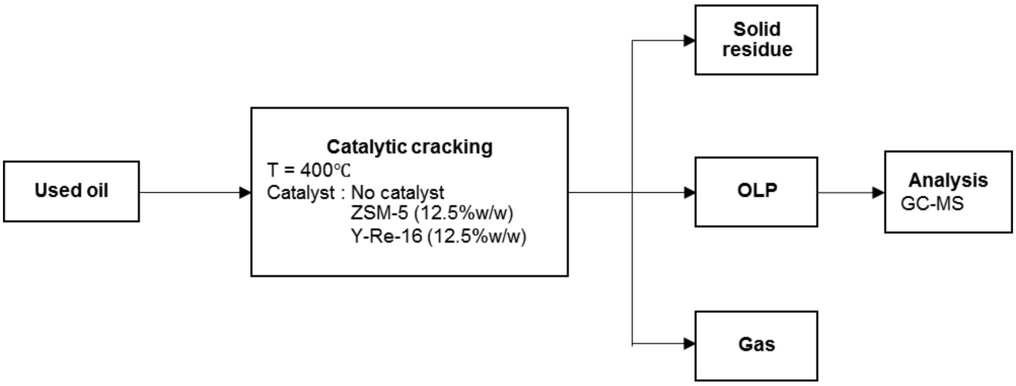

Figure 2: Schematic of the experimental procedure.

2.4 GC-MS analysis

Gas chromatography and mass spectrometry (GC/MS) is one of the popular analytical platforms. GC-MS can be applied to solve a wide range of problems such as analysis of biological samples. It is the analysis method for smaller molecules such as fatty acid, aromatics, alcohols, and benzenes. This analysis is used by the US National Institute of Standards and Technology to develop the definitive methods standard reference. In this study, the chemical composition of the OLP was determined by GC-MS. The GC/MS instrument used was an Agilent Technology model 7890A GC equipped with DB5-MS capillary column (30 m × 0.25 mm × 0.25 μm) and an Agilent Technology MS model 5975C. The condition of GC/MS operating was at inlet temperature of 230 °C; solvent delay of 4 min; oven temperature programmed from 45 °C for 5 min, then increased to 280 °C at 10 °C/min and hold for 10 min at 280 °C; injection volume of 0.5 μl; detector temperature of 280 °C; total runtime of 39 min (Prasertpong et al., 2017).

3. Results and discussion

The physical appearances of the original used cooking oils and the OLPs from cracking with no catalyst, with the ZSM-5 or Y-Re-16 catalysts are shown and compared in Figure 3. The OLP resulted from cracking with the Y-Re-16 catalyst appeared to have darker colour than the rest.

The mass yields of the liquid products from the experiments are summarized in Table 2. It can be seen that the maximum OLP yield of more than 81 % was obtained from the thermal cracking at 400 °C with no catalyst. And the lowest OLP yield obtained was about 76 % of the original raw material via catalytic cracking with the Y zeolite catalyst at 400 °C. The yield of the OLP from using the Z zeolite catalyst was slightly higher. While the remaining residues in the flask from evaporation were the same as expected, the use of zeolite catalysts appeared to generate more non-condensible gas component, in comparison with the no catalyst case. This implied that the ZSM-5 or Y-Re-16 may be able crack the used cooking oil to much lighter products, hence the mass of the resulting OLP was lightly less. It was reported that in a fluid catalytic cracking of bio-oil with the Y-zeolite, high coke and low liquid yields were obtained (Mante et al., 2014).

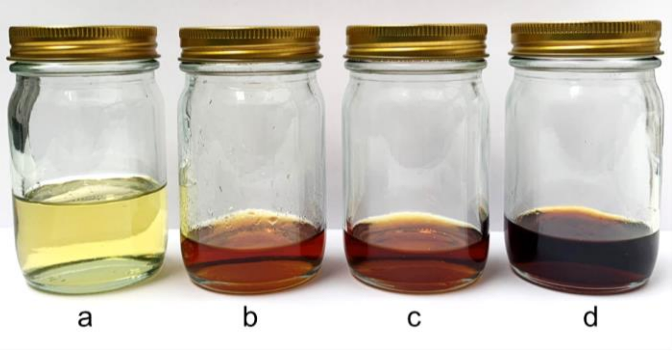

Figure 3: (*a*) *Used cooking oil;* (*b*) *the OLP by thermal cracking;* (*c*) *the OLP by catalytic cracking with ZSM-5; and* (*d*) *the OLP by catalytic cracking with Y-Re-16*.

The OLPs from catalytic and thermal cracking of the used cooking oil should be analysed further for chemical composition. The ingredients of the OLPs were also summarized in Table 3. From the analysis results, it was shown that the main components of the OLPs included complicated compounds such as – gasoline (C_7-C_{11}) (Gandidi et al., 2018), kerosene (C_{12}-C_{15}), and diesel (C_{16}-C_{21}) (Khammasan and Tippayawong, 2018).

From the peak areas of considered hydrocarbon components, the most percentages found for gasoline, kerosene, and diesel were 17.42, 18.40, and 67.57 by thermal cracking, catalytic cracking with the Y zeolite, and catalytic cracking with the Z zeolite. It seemed that each case preferred different components. It should be noted that the tests were done at only 400 °C, so higher temperatures may be considered next time. For future works, mixing of the catalysts between ZSM-5 and Y-Re-16 may be useful in generating good quality OLPs from used cooking oils. This is because using mixed catalysts may help refine the main compositions of the product by combining different catalysts that may be able to provide desirable components. The future study may be performed involving optimization of process variables.

Table 2: *Mass yields of the products from catalytic cracking at 400 °C.*

	Temperature (°C)	Catalyst (% w/w)	Remaining residue (%)	OLP (%)	Gas (%)
No catalyst	400	0	9.51	81.53	8.65
ZSM-5	400	12.5	9.95	77.14	10.23
Y-Re-16	400	12.5	9.94	75.70	11.52

From Table 3, the chemical composition of the OLPs which have the number of carbon in the chain over 21 appeared in the OLPs from thermal cracking and catalytic cracking over Y-Re-16. It seemed that the ability to break the hydrocarbon chain by the thermal cracking and catalytic cracking with Y-Re-16 were lower than that by the catalytic cracking with ZSM-5. The composition analysis of the OLPs obtained from the catalytic cracking with ZSM-5 shows that all products were within the range of gasoline, kerosene, and diesel groups.

Table 3: Composition of organic liquid products from cracking of used cooking oil.

Components	% area of thermal cracking at 400 °C	% area of catalytic cracking with ZSM-5	% area of catalytic cracking with Y-Re-16
Gasoline			
8-Tetraoxatetrasilocane (C_8)	0.53	-	1.13
Xylene (C_8)	-	1.88	-
Heptadecene (C_8)	3.23	-	-
Cyclopropane (C_9)	0.56	-	-
Nonanoic acid (C_9)	1.05	0.52	1.62
Decanoic acid (C_{10})	9.32	0.89	10.05
Spirodecane (C_{10})	2.12	-	-
n-Undecene (C_{11})	0.61	1.82	1.28
2-Tetradecene (C_7)	-	9.45	-
2-Methylethylbenzene (C_9)	-	0.91	-
2-Methylindane (C_{10})	-	0.53	-
Hemimellitene (C_9)	-	0.82	-
Kerosene			
n-Dodecene (C_{12})	0.51	1.23	1.48
9-Tetradecadiene (C_{12})	0.51	-	-
1-Tridecene (C_{13})	0.82	1.63	1.03
n-Tridecane (C_{13})	0.64	0.91	1.1
n-Tetradecene (C_{14})	1.49	-	1.71
n-Tetradecane (C_{14})	0.55	1.66	1.05
Tetradecanoic acid (C_{14})	1.04	-	0.66
13-Tetradecadiene (C_{14})	3.8	5.16	4.38
n-Pentadecene (C_{15})	0.66	0.84	-
n-Pentadecane (C_{15})	2.48	0.87	5.93
Myristic acid (C_{14})	-	-	-
Cyclohexane (C_{15})	-	-	1.06
Diesel			
1-Hexadecene (C_{16})	0.41	-	0.62
2-Heptadecanone (C_{16})	0.55	0.5	0.83
n-Hexadecanoic acid (C_{16})	40.19	0.64	37.78
n-Heptadecene (C_{17})	1.6	5.69	3.68
n-Heptadecane (C_{17})	0.4	1.01	-
9-Octadecene (C_{18})	0.64	0.63	0.76
cis-Vaccenic acid (C_{18})	10.01	9.37	1.69
n-Octadecanoic acid (C_{18})	1.76	1.8	8.22
1-Nonadecene (C_{19})	8.11	44.2	7.12
10-Heneicosene (C_{21})	2.4	3.73	4.8
Oleic acid (C_{21})	0.68	-	-
Others			
1-Docasanol (C_{22})	0.43	-	0.44
Cyclotetracosane (C_{24})	0.56	-	-

4. Conclusions

The catalytic cracking of used cooking oil with different catalysts can produce different main composition of organic liquid products, which are gasoline, kerosene, and diesel. This experiment was tested at only temperature 400 °C. The result may change, depending on the temperature because the temperature is important factor for catalytic cracking process. Increasing of temperature reaction of thermal cracking significant effect to decreasing of yield of OLP. For future study, temperature and percent of loading and mixture catalyst are variable factors in experiment, which is going to analyse maximum yield and hydrocarbon composition.

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