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## RESEARCH ARTICLE

### BIO-GASOLINE SYNTHESIS BY CRACKING PROCESSES OF WASTE COOKING OIL

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#### ABSTRACT

The aim of this study is to evaluate the performance of both catalytic and thermal cracking processes in the thermochemical conversion of waste cooking oil into biofuel and explore the effect of ZSM-5 catalyst and cracking reactor temperature to products yield, biofuel calorific content and chemical composition.

**Key words:** Cracking, Waste Cooking Oil, Biofuel, Bio-Gasoline.

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#### INTRODUCTION

Nowadays, global need for renewable energy is growing larger and an intensive concern has been focused on its sustainability aspects such as environmental impact, and national's economic growth consideration. Environmental issues arising from the severe reliance on energy from fossil fuels have boosted research on fuel production engines using alternative energy sources (1). There are plenty natural resources which considered as prospective raw materials for biofuel production (2). Among these, triglyceride based compounds such as palm oil, fat, and others vegetable oil might become primary alternative resources for sustaining bio-energy production (3). Crude vegetable oils are the most significant in terms of global production (4). Palm oil commodity in Indonesia today has become one of the most prospective commodities in the world. According to Indonesia Ministry of Agriculture report, palm oil demand of Indonesia was over 2 million tons in 2015. Moreover, the annual palm oil production from Indonesia is approximately 32 million tons and from 8 years' period, the overall palm oil production tends to increase because of the higher demands (5). And consequently it will result in more waste cooking oil especially from household and industrial and it gives an opportunity to treat its wastes appropriately. Waste oil has many disposal problems like water and soil pollution,

human health concern and disturbance to the aquatic ecosystem (6). Hence, rather than disposing it and harming the environment, it can be used as an effective and cost efficient feedstock for biofuel production as it is readily available and not create competition with other users or have an adverse impact on the food supply chain (3). There are several ways that have been used to convert vegetable oil into biofuel, for example the transesterification reaction which produce biodiesel (3). However, using low quality cooking oil requires additional treatment due to its high free fatty acids and rancidity which can lead to poor quality of biodiesel (7). The free fatty acids (RCOOH) react with the alkaline catalyst and form soap, as a result of which part of the catalyst is neutralized and is no longer available for transesterification. The presence of soap may interfere with subsequent processing steps. Therefore, the FFA content should be smaller than 0.5 wt% and pretreatment like "degumming" process is sometimes necessary for FFA removal (8). Thus, it is necessary to find an alternative way to convert waste cooking oils into biofuel directly and it can be conducted via cracking process. The waste of cooking oil is suitable as biofuel feedstock to cracking process because it is composed of fatty acids such as 10-octadecenoic acid and hexadecanoic acid. This carbon chains can be cracked into hydrocarbons with shorter carbon chains that have conformity with the nature of fossil fuels. Gasoline production in petroleum refineries is mostly generated by the Fluid Catalytic Cracking (FCC) unit. This unit works by separating the feed chain into shorter length. This principle allows the use of different types of feed, provides that the feed has longer hydrocarbon chains than petrol.

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The development of vegetable oil cracking technology is backed by the depletion of oil reserves and the need to maintain the stability of energy supply from renewable raw materials (9). Catalytic cracking has more advantages than other triglyceride processing methods. First, it can produce various products such as gas, organic liquid product (OLP), water, and coke. However, large molecules existing in vegetable oils cannot easily penetrate deep into smaller 1-2 nm pores of the catalyst and therefore cracking effect is limited to the relatively small reaction sites at the catalyst surface. Larger pore's diameter within the catalyst is the most effective solution for the problem (10). Coke formation doesn't become a problem for uncatalyzed cracking process. OLP comprise oxygen compounds (aldehydes, ketones, and carboxylic acids) and hydrocarbons (normal paraffin, naphthenic, and olefin) that match the boiling point ranges of gasoline, kerosene, and diesel. Second, the reaction temperature is lower than that of pyrolysis, and large molecules are broken down into smaller compounds by dehydration, dehydrogenation, deoxygenation, and decarboxylation. Third, catalytic cracking offers a relatively lower cost route to energy consumption (3). Compared with transesterification, which converts triglycerides to biodiesel (methyl or ethyl esters of fatty acids), cracking has several advantages such as its low processing cost, and energy consumption for separation process. Catalytic cracking can produce more varied types of fuel such as gasoline and kerosene, among other products as well as diesel fuel. However, cracking process usually needs high processing temperature, and it becomes major consideration on its process safety. Moreover, higher energy consumption is also required to sustain its highly endothermic reaction (8).

Catalyst addition has two main advantages both to increase the rate of reaction and actively selective toward particular products (2). Several studies have reported that the temperature required for catalytic cracking (450°C) was usually lower than that of pyrolysis (500-850°C) (3). A range of studies have investigated the catalytic cracking of palm oil using different catalyst at 450°C and 1-5 atm in laboratory-scale reactors. The resulting products have resembled gasoline, kerosene, and diesel fuel, with the dominant yield of gasoline (3). Previous study has showed that ZSM-5 catalyst promotes the formation of aromatic and aliphatic hydrocarbons through deoxygenation process acid fraction. The amount of aromatic compounds in liquid products increased in the presence of ZSM-5 catalyst. The aromatic compound has an advantage in increasing the octane number of gasoline even though it should be limited due to environmental regulation (11).

## MATERIALS AND METHODS

**Waste Cooking Oil:** Waste cooking oil was collected from nearby food stalls. Waste cooking oil then filtered through a coarse sieve to remove its solid content. Filtration process is conducted twice to ensure no solid contained. Then waste cooking oil is stored in container at room temperature and the composition was determined using Gas-Solid Chromatography.

**Catalyst preparation:** Catalyst ZSM-5 which obtained from Wish Chemicals Yueyang Factory, China in powder form must be made in granular form to facilitate the process of calcination and cracking. Granulation was done manually by adding the adhesive agent in the form of kaolin (5 wt. %) to form pellets of the same size 0.3 x 0.5 cm. Furthermore, catalyst was

activated in the furnace with a heating temperature of 450°C and followed by calcination by flowing nitrogen gas for 30 minutes. After being activated and calcinated, the catalyst was cooled and its characteristic was analyzed.

**Thermal Cracking:** 40 mL waste cooking oil was taken using measuring cylinders. Before being taken from its container, waste cooking oil was shaken to ensure that it is well-mixed. Both preheaters 1 and 2 were set in 430°C then the reactor was set in 450, 500, and 550°C for each running session. The preheater and reactor were also equipped with a temperature control device to ensure that the temperature remained constant. The product of cracking process was cooled in 3 stages double pipe condenser which aims to transform gas into organic liquid product.

**Catalytic cracking reaction:** The experiments were carried out in the temperature range of 450-550°C in a stainless steel tubular reactor (1 cm internal diameter) filled with catalysts with the length of 1 cm and equipped with 2 stages preheater to ensure that the oil enters the reactor in the vapor phase. The reactor and preheaters were also equipped with a temperature control device to ensure the temperature remained constant.

The overall process was conducted in semi-batch operation mode. The oil flow rate was about 2 ml/minute. For the first 20 minutes, waste cooking oil was supplied to the preheater gradually. Then, the system was maintained with gasses flow to the condenser continuously for about 2 hours. White colored vapor which contain several types of hydrocarbon were tend to condenses when it reached the end of the condenser as organic liquid product (Figure 1).

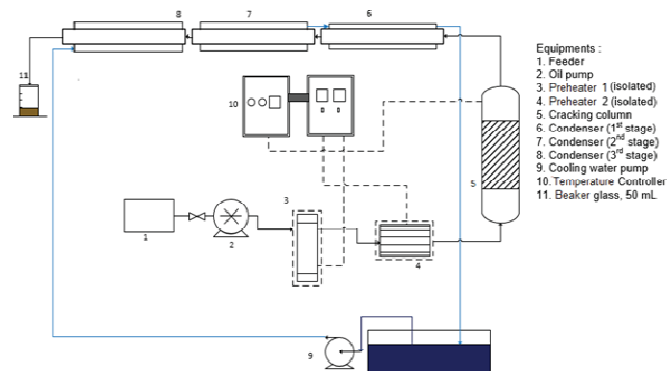


Figure 1. The equipment scheme of cracking process

**Product Analysis:** The cracking product consists of organic liquid product (OLP), water, gas, and coke. The organic liquid product contains a large number of components of liquid hydrocarbons (11). The OLP was analyzed using GC and GC-MS and grouped into 3 categories based on the number of atom carbon: C<sub>5</sub>-C<sub>11</sub>, C<sub>12</sub>-C<sub>15</sub>, and C<sub>16</sub>-C<sub>20</sub> that then was arranged into categories based on the organic compounds such as paraffin, olefin, aromatic, cyclo-paraffin, acid, and alcohol.

Because of the complexity of the product resulting from cracking processes, to calculate the selectivity of a particular product is using the percentage of each peak area to the total peak area of the compound obtained from the chromatogram (12). The equipment used on this analysis was GC-MS QP2010S SHIMADZU with AGILENT HP1MS Column, and Helium as the gas carrier.

## RESULTS AND DISCUSSION

The Effect of Temperature and ZSM-5 Catalyst to Products Yield: The raw material used in this research is waste cooking oil that contains long chain carboxylic acid components comprise 10-octadecenoic acid, hexadecanoic acid, 9,12-hexadecadienoic acid, and several other fatty acids. Its density was 0.8974 gm/mL. Generally, waste cooking oil has higher heating value than palm oil because of heating effect when it used for frying. Even though, the heating value of waste cooking oil resulted from calorimeter bomb test was 10,002.986 cal/gr. But it does not mean that waste cooking oil can be used directly as a fuel. Its boiling point has to be lowered by cracking process, so becomes lighter fraction as combustion reaction takes place mainly at vapor phase (8). It is a straightforward relation that the process temperature becomes higher as the load of cooling system getting higher. Both thermal and catalytic cracking process performances have appreciable different liquid products yields for different process temperatures. (FIGURE 2) reveals that increasing temperature of cracking will tend to decrease liquid product yield. This is due to the need of cooling system load getting higher to reach the product's dew point temperature. The formation of non-condensable gases affects the liquid product yield. Besides, in each product of thermal cracking, there were approximately 5-15% water which produced and for catalytic cracking 5-10%. The presence of water, various oxygenated compounds and acids reduces the stability as well as fuel quality. It is well known that the formation of water is a product of biomass pyrolysis. Usually, water is generated due to the dehydration reaction which occurs at the initial stage of biomass pyrolysis. This also depends on the initial moisture content and the oxygen content of the biomass feed (13). Carbonylation reaction and hydrogen oxidation also took place as a consequence of not completely anaerob process. The result of thermal and catalytic cracking at various temperatures is listed in (TABLE 1).

Table 1. Product of thermal and catalytic cracking processes.

Cracking	Temperature	Residue	Product
	(°C)	(gram)	(mL)
Thermal	450	22.20	8.25
	500	21.80	8.00
	550	19.61	6.85
Catalytic	450	15.17	6.90
	500	3.34	4.95
	550	3.54	2.60

(Table 1) shows that the higher process temperature, the lower liquid product yield. Non-condensable gases such as methane, ethane, etc were mainly formed when high temperature process resulted in lower liquid product recovery. (Figure 2) shows a relationship between liquid product recovery and process temperature for both thermal and catalytic cracking processes.

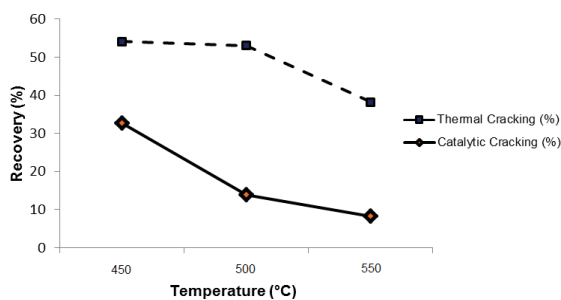


Figure 2. The relationship between recovery and cracking temperature

**The Effect of Both Catalyst and Temperature to Organic Liquid Product (OLP) Caloric Value:** Caloric value is the energy content of a material per mass that is exhausted when the fuel is completely burned. Calorimeter bomb has been used by many researchers to analyze material caloric values for various applications. Caloric value becomes important property for a material which directly related to further usage as a type of fuel (14). The heating value of several products and commercial fuels listed in (TABLE 2).

Table 2. Heating value of several fuels

No	Fuels	Heatingvalue, cal/g
1	Premium	10509.00
2	Pertamax	10575.00
3	Pertamax plus	10622.00
4	Biosolar	10546.00
5	Solar dex	10755.00
6	Waste cooking oil	10002.99
7	Therm 450°C	10582.33
8	Therm 500°C	10623.74
9	Therm 550°C	10342.64
10	Catal 450°C	10880.48
11	Catal 500°C	10760.62

% distribution

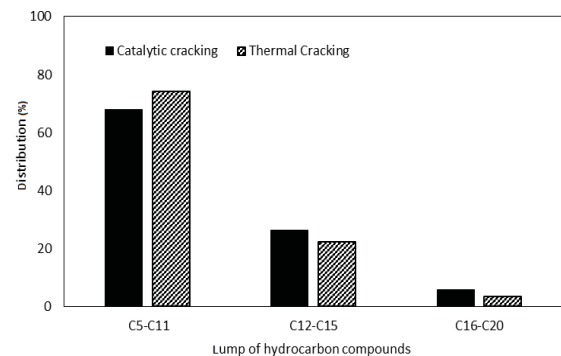


Figure 3. The relationship between % distribution and lump of hydrocarbon compounds

Caloric value of products from catalytic and thermal cracking processes shows their characteristic. The product of catalytic cracking process tends to have higher heating value than the product of thermal cracking because the addition of catalyst in cracking process produce aromatic compounds which have high octane number. High octane number of compounds tends to support combustion reaction, prevent knocking which result in higher heating value (14). (Table 2) reveals that the heating value of cracking products tend to increase in the product of lower process temperature except its decreasing from 500°C to 450°C in thermal cracking processes. The caloric value of thermal and cracking products appreciably similar to standard fuels marketed in Indonesia. The highest caloric value was at temperature of 450°C from catalytic process and the lowest caloric value at 550°C from cracking process without catalyst.

### The Effect of Catalyst on Type of Product Compounds:

The organic liquid products derived from thermal and catalytic cracking were analyzed using GC-MS and the results are shown in (TABLE 3). It can be observed from this table that the liquid product is composed of various groups of organic compounds such as paraffin, olefins, aromatic, cyclic compounds, alcohol and carboxylic acid which are generally classified as bio-gasoline (C<sub>5</sub>-C<sub>11</sub>), bio-kerosene (C<sub>12</sub>-C<sub>15</sub>), and biodiesel (C<sub>16</sub>-C<sub>20</sub>) depending on the lump of carbon atoms. From the result of GC-MS analysis showed that there is an increase in the group of C<sub>5</sub>-C<sub>11</sub> in the catalytic cracking due to

the secondary reaction is more dominant, so the liquid products consist of hydrocarbon compound with shorter carbon chain. With catalyst, the oxygenated compounds which come from thermal cracking diffuse into the pores of catalysts and reacts with protons in the active site through several reaction pathways include dehydration, decarboxylation, decarbonylation, and oligomerization (11). The result shows that the ZSM-5 catalyst promotes the formation of aromatic hydrocarbons through deoxygenated process of acid fraction. The amount of aromatic compound increase in the presence of ZSM-5 catalyst from 0 to 34.60%. The increasing number of aromatic compounds shows that the ZSM-5 facilitates the reaction of aromatization. Besides, olefin content of the product decreases in the presence of ZSM-5 catalyst from 32.41 to 11.51% for bio-gasoline fraction and from 7.46 to 3.78% for bio-kerosene fraction. With the use of catalyst, paraffin content of the product decreases from 38.61 to 20.12% for bio-gasoline fraction and increases from 14.89 to 22.01% for bio-kerosene fraction. The relationship between % distribution and lump of hydrocarbon compounds is shown in (FIGURE 3). Overall (C<sub>16</sub>-C<sub>20</sub>) content of both cracking products is below 6%. Bio-kerosene contents are increase as ZSM-5 catalyst introduced to the process. Overall, the products contain 74.13% bio-gasoline for thermal cracking process, and 67.81% for catalytic cracking process. Thus, bio-gasoline content from thermal cracking process is higher than catalytic cracking process.

## Conclusion

In this study, both thermal and catalytic cracking processes were conducted in order to convert waste cooking oil into bio-gasoline. Several parameters might affect process performance which resulted in different product's yield and specification. Cracking temperature variation gave appreciable effect on yield and product's caloric values. Higher cracking temperature encouraged non-condensable gases formation so that bio-gasoline obtained becomes lower and resulted in higher cooling load to attain gas's dew point temperature. The percentage recovery of organic liquid product from the cracking process varies from the lowest yield of 8.31% to the optimal yield of 54.08%. Heating values of bio-gasolines were various because of the different cracking temperature and introduced catalyst. The highest caloric content attained by the product of catalytic cracking at 450°C with its caloric value of 10,880.48 cal/g, becomes comparable with several standard fuels.

Catalytic activity of ZSM-5 showed that the catalyst improved the selectivity of hydrocarbon compounds by decreasing the undesirable oxygenated compounds and promoted the formation of aromatic and aliphatic hydrocarbons. Catalytic cracking process with ZSM-5 catalyst results in lower bio-gasoline content.

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