

The effect of H-USY catalyst in catalytic cracking of waste cooking oil to produce biofuel

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Abstract

The crisis in petroleum is caused by the diminishing supply of petroleum resources from nature. This phenomenon encourages researchers to continue to look for processes and methods to produce energy from other resources. One of these ways is to produce energy that can be utilized from waste, including converting waste cooking oil into biofuel. This method not only could provide a source of renewable energy, but also help resolve the issue of household waste. The process used to produce biofuel from waste cooking oil is by catalytic cracking, where waste cooking oil after pretreatment is converted into biofuel in the flow reactor with H-USY catalyst. In this research, the reaction temperatures used are 400 °C, 450 °C, 500 °C and 550 °C and reaction times are 30, 45 and 60 minutes with the mass ratio of the amount of waste cooking oil to the amount of catalyst used is 40:1 (w/w). The highest yield of liquid biofuel product was obtained at 60.98%. The use of H-USY catalyst shows that the distribution of components contained in biofuel are 28.02% of diesel products (C₁₇-C₂₀), 23.96% of gasoline (C₆-C₁₂) and 7.78% of Heavy oil (C₂₀ >) in catalytic cracking of waste cooking oil with a reaction time of 45 minutes at a temperature of 450 °C.

Keywords: biofuel, catalytic cracking, H-USY, waste cooking oil

Abstrak (Indonesian)

Krisis minyak bumi yang disebabkan oleh semakin berkurangnya pasokan sumber minyak bumi dari alam, hal ini mendorong para peneliti untuk terus mencari cara menghasilkan energi yang berasal dari sumber lainnya, salah satu caranya adalah menghasilkan sumber energi yang bisa dimanfaatkan dari limbah diantaranya adalah mengubah minyak jelantah menjadi *biofuel*, selain dapat menghasilkan energi dari sumber yang dapat diperbaharukan dan juga dapat membantu menanggulangi limbah rumah tangga. Proses untuk menghasilkan biofuel dari minyak jelantah adalah dengan proses *catalytic cracking* dimana minyak jelantah **setelah melalui proses pretreatment** dirubah menjadi bahan bakar biofuel didalam *flow reactor* dengan bantuan katalis H-USY. Pada penelitian ini **temperatur reaksi yang digunakan** adalah 400 °C, 450 °C, 500 °C dan 550 °C dan waktu reaksi **adalah** 30, 45 dan 60 menit dengan rasio massa jumlah minyak jelantah terhadap jumlah katalis adalah 40:1 (w/w). Hasil *yield* tertinggi dari produk *biofuel* diperoleh adalah 60,98%. Penggunaan katalis H-USY menunjukkan bahwa distribusi komponen yang terkandung dalam produk adalah 28,02% diesel (C₁₇-C₂₀), 23,96% bensin (C₆-C₁₂) dan 7,78% minyak berat (C₂₀>) dalam perengkahan katalitik minyak jelantah dengan waktu reaksi 45 menit pada suhu reaksi 450 °C.

Kata Kunci: *biofuel*, *catalytic cracking*, H-USY, minyak jelantah

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INTRODUCTION

Demands for petroleum fuel worldwide in the past year has experienced a significant increase, not only in developed countries but also in developing countries like Indonesia. The reality is as reported in the 2018 Indonesian Energy Outlook, if it is assumed that there is no discovery of new resources, based on the R/P (Reserve/Production) 2018 ratio, then petroleum will run out in 9 years, natural gas in 42 years, and coal in 68 years [1].

One alternative energy that is being developed both in Indonesia and elsewhere is biofuel. The term biofuel refers to solid (bio-char), liquids (ethanol and biodiesel), or gases (biogas, biohydrogen and biosynthetic gas) which are mostly produced from biomass [2]. Waste cooking oil is one of the potential biodiesel feedstock to be utilized in Indonesia along with microalgae [3], *Jatropha curcas L.* seed oil [4], and *reutalis trisperma* [5]. This can be seen from the production of waste cooking oil in Indonesia which can reach 4,000,000 tons/year [6].

Waste cooking oil contains fatty acids, mostly palmitic acid (21.47%) and oleic acid (28.64%) [7]. These fatty acids can be converted into other forms with economic value to not pollute the environment into biodiesel fuel with an esterification process. In addition to the esterification process, waste cooking oil can be converted into biofuel by catalytic cracking process using catalysts with high selectivity to fuel that can be utilized by people.

There are several common methods for converting vegetable oil into biofuels: trans-esterification, hydrocracking, hydrothermal, and catalytic cracking. Trans-esterification is the process of exchanging groups of organic esters with solvent organic groups such as methanol and ethanol. However, trans-esterification products are biodiesel which have oxidative stability and lower storage, higher production costs than petroleum-based fuels [8]. The Catalytic cracking process uses an easy and inexpensive method to convert vegetable oils into biofuels that are similar to petroleum-based fuels. During catalytic cracking, oxygen atoms can be removed in the form of H₂O, CO, and CO₂ under various complex chemical reactions. Production costs can be reduced and product yields can be increased through the development of catalysts with good selectivity and long service life.

Ultra stable Y (USY) zeolite is widely used for various chemical reactions, not only as a catalyst but also as a support, due to its excellent thermal stability and shape-selective properties [9,10]. USY has been used as a catalyst in catalytic cracking reactions of

Jatropha Curcas L. seed oil [4], rubber seed oil [11], polyethylene [12], soybean oil [13] and waste cooking oil [14]. The products obtained had compositions similar to those of gasoline. The acidic site of USY serves as an active site for hydrogenation and dehydrogenation reactions so that a combination of metals with USY zeolite carriers will produce a multifunctional catalyst [15].

Li et al [14] studied the process of producing liquid hydrocarbon fuels with raw materials from waste cooking oil using catalytic cracking with USY zeolite catalyst, at 100 minutes reaction time, reaction temperature 430 °C and USY catalyst ratio with waste cooking oil is 1:30, the results of liquid product is 64%.

The effect of H-USY catalyst, reaction temperature and reaction time in catalytic cracking of waste cooking oil on yield biofuel and the composition of the products will be discussed in this paper.

MATERIALS AND METHODS

Materials

Waste cooking oil in this study was collected from household waste and USY Catalyst Commercial was obtained from Sigma-Aldrich Pte Ltd, Singapore.

Methods

The USY catalyst was first calcined at 550 °C for 5 hours in an oxygen-flowed reactor to become H-USY before use as the catalysts in this research. The catalytic cracking mass ratio of waste cooking oil to H-USY catalyst was 40:1 (w/w). The raw material was first put into a 1 atm pressure reactor for preheating. This reactor has a diameter of 4.5 cm with a length of 60 cm and has an injection port with a length of 19 cm on the left and right side which also functions as the reactor cover.

The main reactor, where the reaction of catalytic cracking occurred, has a diameter of 7.5 cm with a reactor height of 60 cm and an injection port of 10 cm length at the top and 30 cm at the bottom.

Firstly, the reactor filled with catalyst was heated to the target temperature 400 °C, 450 °C, 500 °C, or 550 °C then the waste cooking oil was injected into the reactor and reacted for 30, 45, or 60 minutes. The condensable gas product from catalytic cracking was condensed into the liquid product in the cooling system product reservoir and the incondensable gas was accommodated in the gas sampling bag.

After the experiment, the residual left in the reactor and condensed liquid biofuel products were weighed, and the gas conversion is calculated by

subtracting the initial weight with the residue and liquid formed in the final product.

RESULTS AND DISCUSSION

Effect of Reaction Temperature and Reaction Time on the Distribution of Catalytic Cracking Products.

Figure 1 shows the effect of the reaction temperature and reaction time on the composition of the catalytic cracking final product. Figure 1 shows the relative yield of liquid and gaseous product as well as the unreacted residue. The operating temperature of catalytic cracking used in this research starts from 450-550 °C, this is because the boiling point of waste cooking oil itself is 375 °C and to break large molecules into compounds with smaller molecules, higher temperature is needed as an energy source for the cracking process.

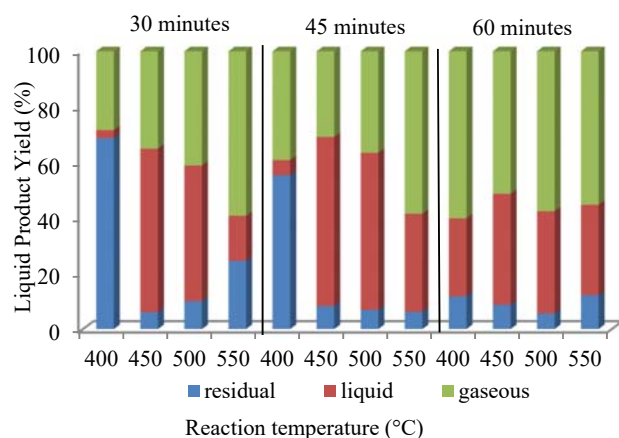


Figure 1. The Effect of reaction temperature and reaction time on the yield of catalytic cracking products

In Figure 1 above, it can be seen that the gas yield obtained increased at higher reaction temperature and with a reaction time of 30 minutes. The least gas yield is obtained at a reaction temperature of 400 °C at 30 minutes reaction time with a value of 28.31% and the largest gas composition was also obtained at a reaction temperature of 400 °C but the reaction time was 60 minutes with a value of 59.95%. This is because the reaction time would accommodate a longer time for waste cooking oil to be converted as a gas product but, as shown in the figure 1 above, the residual was also the highest at 400 °C, especially in 30 and 40 minutes reaction times which are 68.76% and 55.45%. This residual fraction is the raw material left unconverted into a gas or liquid product because the temperature and the reaction time didn't provide the necessary conditions for the catalytic cracking process.

The gas produced in the catalytic cracking process can be formed due to the de-oxygenation and catalytic cracking reactions of the second stage in the form of CO, CO₂ and H₂O or it can also be caused by further cracking of organic liquid products formed into light hydrocarbon gases such as methane, ethane, olefin and others [16].

The Effect of Reaction Temperature against Yield Liquid Product

The effect of reaction temperature on biofuel yield in the catalytic cracking process of waste cooking oil using H-USY catalyst can be seen in the Figure 2.

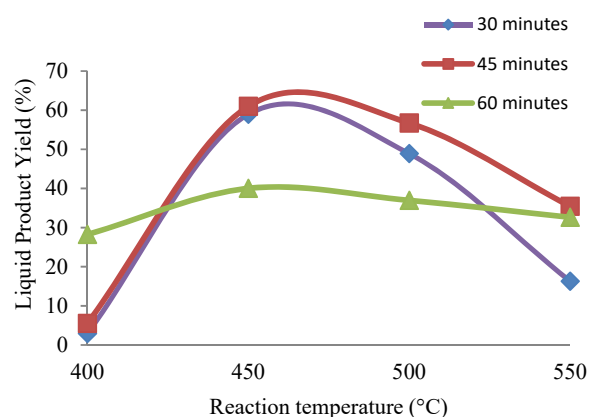


Figure 2. The effect of reaction time on the yield of liquid product at 400-550 °C reaction temperature.

From the figure 2 it can be seen that at a temperature of 400 °C the yield of the biofuel produced is relatively less than the other temperatures used in this research except for the 60 minutes reaction time which results in a higher biofuel yield of 40.03% compared to the yield at 550 °C reaction temperature at 30 minutes reaction time which is 16.28% of liquid product.

At 450 °C reaction temperature the biofuel yield obtained is the highest for 45 minutes reaction time which is 60.98% and then decreases again at temperature of 500 °C and 550 °C which are 56.71% and 35.43%, respectively. The catalytic cracking process using the H-USY catalyst follows the pattern where the smallest percent yield is obtained at the lowest temperature of 400 °C and increases sharply at a temperature of 450 °C and decrease gradually for each addition of 50 °C reaction temperature.

The decrease of the production of the liquid product as the reaction temperature increase was due to conversion into light hydrocarbon gases with short carbon chains, such as methane, ethane and others.

The Effect of Reaction Time against Yield Liquid Product

The effect of reaction time on biofuel yield in the catalytic cracking process of waste cooking oil using H-USY catalyst can be seen in the Figure 3.

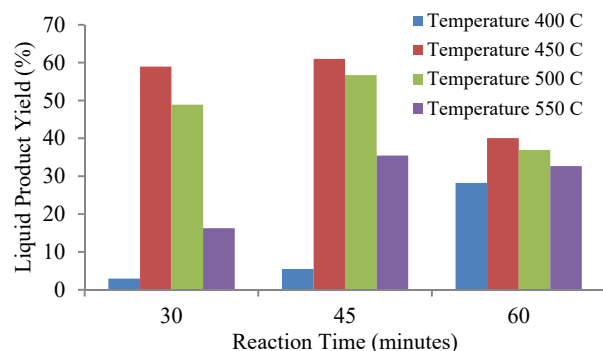


Figure 3. The effect of reaction time on the yield of liquid product

From the Figure 3, it can be observed that a reaction time of 30 minutes results in a smaller percent yield than the reaction time of 45 minutes and yield decreased again for 60 minutes reaction time. Reaction time of 45 minutes results in the highest yield of liquid biofuel products which is equal to 60.98% at a reaction temperature of 450 °C, but at a reaction time of 60 minutes all the yield of liquid biofuel products is relatively decreased so it can be concluded that the increase of reaction time reduces the liquid biofuel production in catalytic cracking using H-USY catalyst and the optimal reaction time for catalytic cracking using the H-USY catalyst is at 45 minutes reaction time in reaction temperature of 450 °C.

From the Figure 3 above the yield of liquid biofuel products tends to decrease with the increasing of reaction time. This phenomenon can be caused by the reduction of catalyst performance over time because one of the main problems associated with the performance of acid zeolite catalysts is the loss of activity and selectivity of forms over time [17].

Distribution of Liquid Product Compositions at 450 °C Reaction Temperature in Various Reaction Times

Two samples were taken with the best yield of liquid biofuel product in catalytic cracking at a reaction temperature of 450 °C and reaction times of 30 and 45 minutes. These samples were then tested for Gas chromatography–mass spectrometry (GC-MS) to determine the content of the components in

the biofuel. The results obtained are presented in the figure 4.

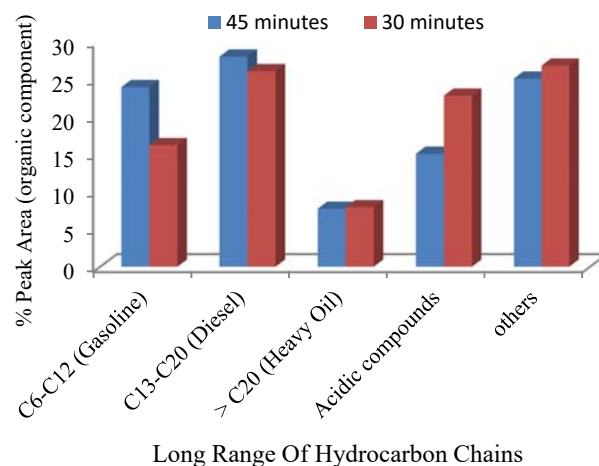


Figure 4. The effect of reaction time and reaction temperature on liquid product composition distribution of catalytic cracking

From the figure 4 of the above analysis it can be seen that catalytic cracking using H-USY catalyst produces biofuels that have the highest level of C₆-C₁₂ (gasoline) with 23.96% peak area at 45 minutes reaction time while 30 minutes reaction time produces 16.26% peak area of gasoline components. The catalytic cracking for 45 minutes reaction time also contains more long-range hydrocarbons such as C₁₇-C₂₀ (diesel) with 28.02% peak area and with 30 minutes reaction time of catalytic cracking. The result showed that the biofuel product contained the hydrocarbon with C₁₇-C₂₀ (diesel) carbon chain which is 26.08% peak area.

CONCLUSION

The catalytic cracking of waste cooking oil using the H-USY catalyst showed the best results with the highest yield percentage which is 60.98% at the optimum reaction temperature of 450 °C and a reaction time of 45 minutes. The highest distribution of components contained in biofuel, namely diesel products (C₁₇-C₂₀) were 28.02% peak area in catalytic cracking of waste cooking oil also with a reaction time of 45 minutes at a temperature of 450 °C.

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