Research Article

Effects of Ion Exchange Process on Catalyst Activity and Plasma-Assisted Reactor Toward Cracking of Palm Oil into Biofuels

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Abstract

Biofuels can be produced through a conventional catalytic cracking system and/or a hybrid catalytic-plasma cracking system. This paper was focused on studying effect of Na^+ ion exchange to HY-Zeolite catalyst on catalyst performance to convert palm oil into biofuels over a conventional continuous fixed bed catalytic cracking reactor and comparing the catalytic cracking performance when carried out in a continuous hybrid catalytic-plasma reactor. The catalysts were characterized by X-ray Diffraction (XRD) and Bruneuer-Emmet-Teller (BET) surface area methods. The biofuels product were analyzed using Gas Chromatography-Mass Spectrometry (GC-MS) to determine the hydrocarbons composition of biofuels product. From the results, ion exchange process of Na^+ into HY-Zeolite catalyst decreases the catalyst activity due to decreasing the number of active sites caused by blocking of Na^+ ion. The selectivity to gasoline ranges achieved 34.25% with 99.11% total conversion when using HY catalyst over conventional continuous fixed bed reactor system. Unfortunately, the selectivity to gasoline ranges decreased to 13.96% and the total conversion decrease slightly to 98.06% when using NaY-Zeolite catalyst. As comparison when the cracking reaction was carried out in a hybrid catalytic-plasma reactor using a spent residual catalytic cracking (RCC) catalyst, the high energetics electron from plasma can improve the reactor performance, where the conversion and yield were increased and the selectivity to lower ranges of hydrocarbons was increased. However, the last results were potential to be intensively studied with respect to relation between reactor temperature and plasma-assisted catalytic reactor parameters. Copyright © 2019 BCREC Group. All rights reserved

Keywords: catalytic-cracking; palm oil; hybrid catalytic-plasma reactor; biofuels

1. Introduction

The rapid increase in population, industrial development, and population mobility in Indonesia have led to an increase in national energy consumption. However, petroleum production continues to decline. These issues encourage efforts to find alternative renewable fuels as a supply of petroleum-based energy substitutes, namely by developing renewable resource-based environmentally friendly fuels derived from vegetable oils. One of them is the conversion of palm oil into biofuels product. Biofuels are a

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liquid or gas fuels produced from the utilization of biomass and vegetable oils, i.e. biodiesel, bio-ethanol, biogasoline, and biokerosene [1]. Bio-fuels can be produced from vegetable oils, such as: palm oil [2,3] or other vegetables. Although the processing cost of the biofuels is not competitive yet due to the price of vegetable oils source, the renewable energy aspect is more important.

Interestingly, the biofuels can be obtained by cracking vegetable oils by using thermal, catalytic, or even by plasma-assisted cracking. Thermal cracking generally requires relatively higher temperatures to break down heavy hydrocarbons into lighter hydrocarbons. The thermal cracking process requires temperatures between 500-850 ºC [4]. Catalytic cracking is carried out at relatively lower temperatures compared to reactions in thermal cracking [5]. Some of the benefits of catalytic cracking in compared to thermal cracking is lower temperature required and the products can be in the form of gas, organic liquid products (OLP), water, and coke [6], as well as operational costs are cheaper, and are more flexible to various types of vegetable oils [7]. Basically, the catalytic cracking process begins with the formation of carbenium ions in presence of the most acid catalysts [8]. The carbenium ions are formed due to the addition of H^+ ions from Brönsted acid sites into the reactant structures. The most of catalytic cracking processes were carried out using these acid catalysts [9]. However, some alkaline catalysts have also been studied for catalytic cracking process, i.e. Na_2CO_3 [10-12], CaO [9,13], and MgO [9].

The temperature required for the catalytic cracking process is around 450 ºC, lower than the pyrolysis process or the thermal cracking which requires higher temperatures between 500-850 ºC [4]. Li *et al.* [14] have conducted catalytic cracking experiments with cottonseed oil as the raw material and have examined the effect of temperature on the yield of biogasoline and biodiesel. The temperature range used was between 400-500 ºC and the largest yield obtained at 426.2 ºC. Tamunaidu and Bhatia [3] and Mancio *et al.* [12] has carried out a process of catalytic cracking to produce biogasoline from crude palm oil (CPO) at a temperature of 450 ºC and atmospheric pressure. Ahmad *et al.* [15] also said that the yield of gasoline, kerosene, and the largest biodiesel from the catalytic cracking process with edible and non-edible oil raw materials occurred in the temperature range 350-550 °C and atmospheric pressure.

Therefore, most of researchers used temperature ranges of 400-550 ºC in their conventional reactor (batch or fixed bed reactor) in order to make sure activity of the catalysts.

Another study, implementation of cracking technology using plasma role without catalysts was carried out at a high voltage of about 6-7 kV with a frequency of 6-18 kHz [16]. Following researchers reported the results of their study on cracking of heavy hydrocarbons using plasma treatment without catalyst. Khani *et al.* [17] studied plasma cracking to n-hexa-decane hydrocarbons in a batch dielectric-barrier discharge (DBD) reactor with an AC power supply without catalyst. Prieto *et al.* [18] focused on plasma cracking process on heavy oils to produce hydrocarbons and hydrogen gases. Matsui *et al.* [19] also discussed a batch plasma reactor to reform liquid phase hydrocarbon fuels into the gas phase and solid at room temperature. It is very interesting to investigate the synergistic roles of high energetic electrons from plasma and catalytic activity within the plasma-assisted reactor [20].

With respect to potential of alkali-based catalyst for cracking process on batch reactor, more investigations of the effect of Na when supported on zeolite (HY or ZSM5) for catalytic cracking of vegetable oil over continuous fixed bed reactor are purposed in this study. In term of comparing performance of reactor, this study is also purposed to compare between a conventional continuous fixed bed reactor and a continuous hybrid catalytic-plasma reactor for the catalytic cracking process to produce biofuels from palm oil by utilization of spent residual catalytic cracking catalyst.

2. Materials and Method

2.1 Catalysts Preparation and Materials of Research

Commercial refined palm oil was purchased from the local market to used as raw material. The NaY-Zeolite catalyst was prepared by ion exchange process adopted the method of Alwash *et al.* [21]. The dried HY-Zeolite (Zeolyst International) was soaked while stirring in 1 M of NaCl (Merck) at 80 ºC for 4 h in such a way that mole ratio of HY-Zeolite to sodium chloride was 1:80. The slurry was then filtered and washed with distilled deionized water to remove the excess NaCl. In order to achieve a complete exchange of sodium into the zeolite, the procedure was repeated twice. The sample was then dried overnight at 80 ºC in an oven (Memmert) and then calcined in a box

furnace (NEY VULCAN 3-550) at 550 ºC for 5 h. The catalyst was then pelleted and crushed into the desired size. Another catalyst used over a hybrid catalytic-plasma reactor was a used residual catalytic cracking (RCC) from petrochemical company in Indonesia. The used RCC catalyst was pretreated by washing it by distilled water at 60 ºC. Thus, the catalyst was dried overnight at 110 ºC in an oven (Memmert) and calcined at 500 ºC for 3 hours in a furnace (Ney Vulcan 3-550). The resulted powder was pelleted and crushed into the desired size. The other catalyst is a commercial original HY Zeolite from Zeolyst International. The catalyst was dried at 110 ºC for 24 hours in an oven (Memmert) and calcined at 550 °C for 5 hours in a box furnace (Ney Vulcan 3-550). The HY catalyst was pelleted and crushed into the desired size.

2.2 Catalyst and Reactors Performance Testing

The catalysts (Na-based Zeolite Y and spent residual catalytic cracking) were tested using two different reactor configurations, i.e. a continuous fixed bed reactor (Figure 1) and a continuous hybrid catalytic-plasma reactor (Figure 2). From Figure 1, the fixed bed reactor was fabricated from stainless steel tube with a diameter of 1 inch which placed inside the split electric heater. The reactor temperature was measured and controlled using a digital temperature controller. Catalyst was put inside the fixed bed reactor which was supported by glass wool. From Figure 2, the hybrid plasma-catalytic reactor was equipped with a split electric furnace and a temperature controller to adjust the reactor temperature. The catalysts were put inside the tubular glass reactor within discharge zone. High voltage power supply with a power up to 250 watt (high voltage of up to 50 kV DC) was used to provide the high voltage on the reactor electrodes. The discharge voltage was measured by a digital oscilloscope (Tektronix TBS 1052B-EDU 50 MHz 1 GS/s) through a High Voltage Probe (x1000).

Before reaction, the reactor was flushed by nitrogen flow (100 cm^3/min) for 15 minutes. The reactor was heated up to a certain temperature based on the reactor temperature variable in the experimental design. During the process, vapour product (cracked substance) was flowed through a condenser in order to condense the vapour product to form the collected liquid fuel. The liquid fuel product was stored in a flask and analyzed using a gas chromatography-mass spectrometry (GC-MS) (SHIMADZU QP2010S equipped with a DB-1 column).

2.3 Catalysts Characterization

The catalysts were characterized using X-Ray Diffraction (XRD) (Shimadzu XRD-7000) method to determine the crystal structure, while the catalysts surface area was determined by Bruneuer-Emmett-Teller (BET) surface area method (ChemBET PULSAR
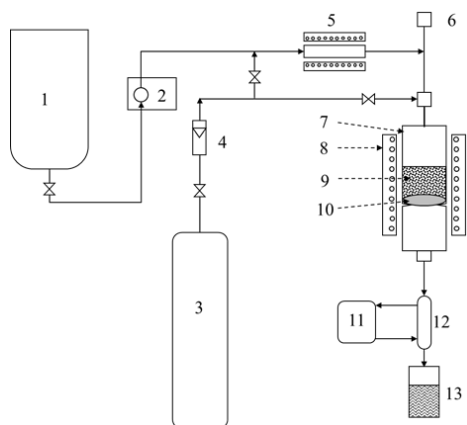

Figure 1. Catalytic conventional reactor used for catalytic conversion of palm oil to biofuels: (1) Palm oil tank, (2) Peristaltic pump, (3) Nitrogen tank (N_2), (4) Rotameter, (5) Electric preheater, (6) Thermocouple, (7) Fixed-bed reactor, (8) Electric heater, (9) Catalyst bed, (10) Glass wool, (11) Chiller, (12) Condensor, (13) Product collector.
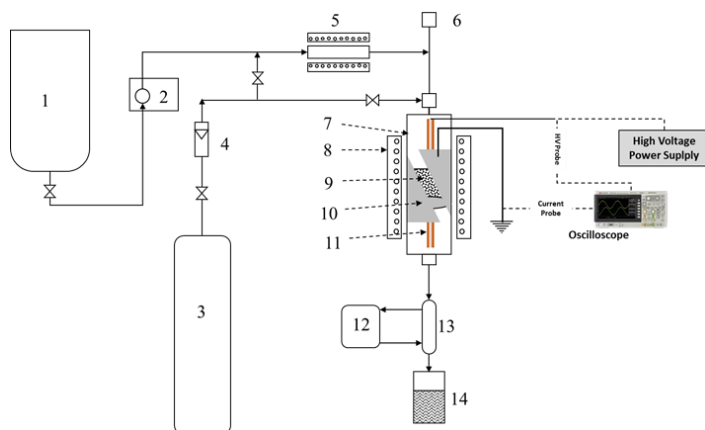
Figure 2. Hybrid catalytic-plasma reactor system used in the catalytic conversion of palm oil to biofuels: (1) Palm oil tank, (2) Peristaltic pump, (3) Nitrogen tank (N_2), (4) Rotameter, (5) Electric preheater, (6) Thermocouple, (7) Reactor, (8) Electric heater, (9) Catalyst bed, (10) Ground electrode, (11) High voltage electrode, (12) Chiller, (13) Condensor, (14) Product collector.

Quantachrome). In the XRD analysis, a Cu-Kα radiation (k = 1.54 Å) was operated at 30 mA and 30 kV. The diffraction patterns were generated at 2θ angle ranges of 10° to 90° with a scanning speed of 4°.min⁻¹ at ambient temperature.

2.4 Calculation of Conversion, Selectivity, and Yield

Composition of palm oil feed and biofuels product were identified by Gas Chromatography-Mass Spectrometry (GC-MS) to determine the content of compounds. Indentification and composition of biofuels product was done using Gas Chromatography-Mass Spectrometry (GC-MS) (QP2010S SHIMADZU, DB-1 column). On the GC-MS, the samples were analyzed at 50 °C oven temperature (hold for 5 min) and ramped 10 °C.min⁻¹ to 260 °C and held for 33 min. The conversion, yield, and selectivity were calculated from the steady-state mass balance using the following equations.

$$m_{feed} = m_{gas} + m_{coke} + m_{OLP} + m_{unreacted\,palm\,oil} \qquad (1)$$

$$Conversion\,(\%wt) = \frac{m_{feed} - m_{unreacted\,palm\,oil}}{m_{feed}} \times 100\% \qquad (2)$$

$$Yield\,of\,OLP\,(\%wt) = \frac{m_{OLP}}{m_{feed}} \times 100\% \qquad (3)$$

$$Yield\,of\,gas\,(\%wt) = \frac{m_{gas}}{m_{feed}} \times 100\% \qquad (4)$$

$$Yield\,of\,coke\,(\%wt) = \frac{m_{coke}}{m_{feed}} \times 100\% \qquad (5)$$

$$Selectivity\,of\,gasoline\,ranges\,(\%wt) = \frac{m_{gasoline(C_5-C_{12})}}{m_{feed} - m_{unreacted\,palm\,oil}} \times 100\% \qquad (6)$$

$$Selectivity\,of\,kerosene\,ranges\,(\%wt) = \frac{m_{kerosene(C_{13}-C_{14})}}{m_{feed} - m_{unreacted\,palm\,oil}} \times 100\% \qquad (7)$$

$$Selectivity\,of\,diesel\,ranges\,(\%wt) = \frac{m_{diesel(C_{15}-C_{18})}}{m_{feed} - m_{unreacted\,palm\,oil}} \times 100\% \qquad (8)$$
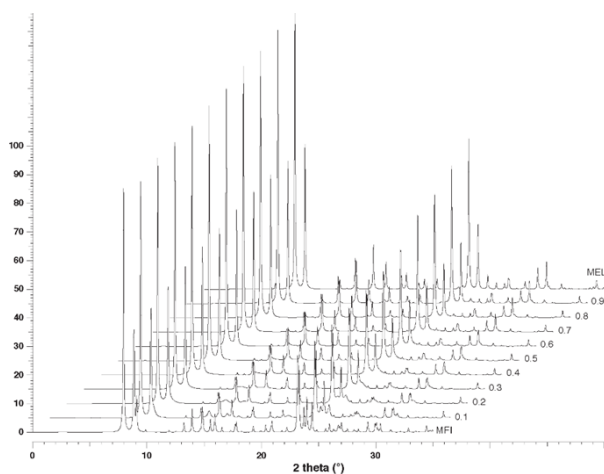
Where m_{feed} is equal to mass of palm oil fed to the reactor, m_{gas} is mass of gas product, m_{coke} is mass of coke, m_{olp} is mass of OLP, and $m_{unreacted\,palm\,oil}$ is mass of unreacted palm oil.

3. Results and Discussion

3.1 Catalysts Characterization

3.1.1 XRD analysis

Based on the XRD analysis, the spent RCC catalyst has the high peak intensity at 2θ of 13.53°; 22.29°; 25.78°; 27.74°; 31.07°; 45.99° which is similar to the ZSM-5 peaks (Figure 3) from collection of XRD peaks of zeolite [22]. However, slight different structure of the spent RCC catalyst may be due to modification from the ZSM-5 by manufacturer and changed during previous usage.

Based on the XRD patterns (Figure 4), it can be suggested that the structure of zeolite HY and NaY is identical indicating that the exchange of Na into H atom on HY zeolite was not significantly change the crystal structure, but it reduces crystallinity of the HY catalyst [23]. The XRD intensity of NaY catalyst is smaller than HY catalyst which due to slight decreasing its crystallinity. Therefore, the addition of Na⁺ ion into the HY zeolite by ion exchange method results in a decrease in crystallinity of the catalyst, but it did not significantly change the crystal structure.

3.1.2 BET surface area analysis

Table 1 represents that surface area of the NaY catalyst is lower than the HY zeolite catalyst. This fact indicates that the ion exchange process of Na⁺ ion into the HY zeolite reduces its surface area which due to pore blocking by
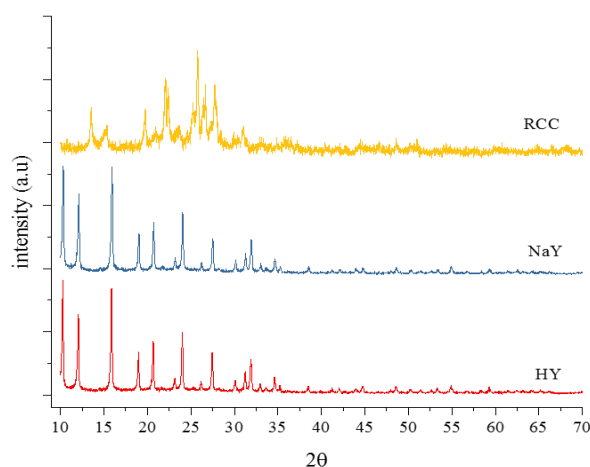

Figure 3. XRD pattern of standard ZSM-5 from reference [22]

Figure 4. XRD patterns of RCC, NaY, and HY catalyst.

Na. As reported previously that ion exchange of Na+ into the HY zeolite did not significantly change the crystal structure, but it reduces the crystallinity of the HY catalyst which in turn reduces the catalyst surface area [23].

3.2 Effect of Ion Exchange of Na+ to HY-Zeolite Catalyst on Catalytic Cracking Process Performance over a Continuous Fixed Bed Reactor

In this cracking process, refined palm oil, where the fatty acids composition of the raw material is presented in Table 2, was used as raw material to be cracked to become lower carbon chains hydrocarbons. Meanwhile, Figure 5 shows the molecular structure of palmitic acid and oleic acid in the refined palm oil used in this study based on GC-MS analysis. Palmitic acid is a saturated fatty because it has no double bond, while oleic acid is an unsaturated fatty acid due to has one double bond [24]. Wijanarko *et al.* [25] who studied biogasoline production from palm oil trough catalytic cracking with Y-alumina catalyst said that the most dominant content of palm oil that cracked catalytically was palmitic acid and oleic acid. The more palmitic acid and oleic acid content, the higher the biogasoline product. Because of the more unsaturated fatty acid content in the catalytic cracking process, the more hydrogen gas should be used in the hydrocracking process to break the double bonds [26].

Based on Table 3, palm oil conversions on the catalytic cracking process over a continuous fixed bed reactor using HY and NaY catalysts were 99.11% and 98.06%, respectively. Decreasing the conversion slightly was indicated by lower catalyst surface area and crystallinity of NaY than HY (Figure 4, Table 1). Previous researchers said that activity of catalyst to convert the vegetable oils into biofuels product was dependent on catalyst activities due to contribution of the surface area of catalyst [27]. Catalysts with the large surface area can reduce the mass transfer limitations. Furthermore, Sriningsih *et al.* [28] also said that the catalyst surface area can increase the catalyst activity on the cracking process. However, yield of organic liquid product (OLP) produced on the catalytic cracking process using the NaY catalyst was 94.36% which was higher than that when using HY catalyst of 91.99% which may be due to decreasing catalyst surface area (Table 1). These were in accordance with the statement explained by Seo *et al.* [29] that the use of catalysts with larger surface area enhances the gas production and decreases the

(a)

(b)
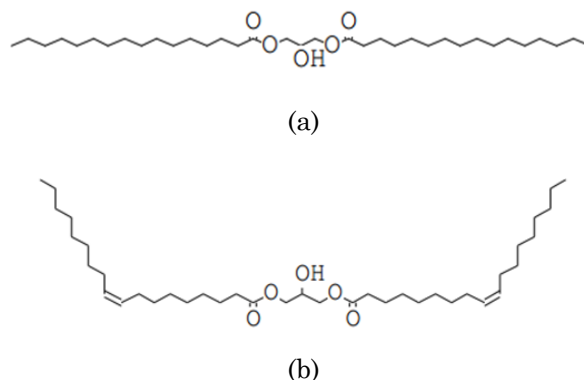
Figure 5. Molecular structure of palmitic acid (a) and oleic acid (b).

Table 1. Surface area of catalysts by BET characterization method

Catalysts	Surface Area (m²/g)
HY-Zeolite	814.087
NaY-Zeolite	727.037

Table 2. Palm oil composition by GC-MS analysis

Name	Fatty Acids	Molecular Formula	Chemical Formula	Composition (%wt)
2-hydroxy-1,3-propanediyl Hexadecanoic acid	Palmitic Acid	$C_{35}H_{68}O_5$	C16:0	44.53
2-hydroxy-1,3-propanediyl 9-Octadecenoic acid	Oleic Acid	$C_{39}H_{72}O_5$	C18:1	41.91
2-hydroxy-1,3-propanediyl Octadecanoic acid	Stearic Acid	$C_{39}H_{76}O_5$	C18:0	1.80
2,6,10,14,18-Pentamethyl-2,6,10,14,18-eicosapentaene	-	$C_{25}H_{42}$	-	6.44
Bicyclo[10.1.0]tridec-1-ene	-	$C_{13}H_{22}$	-	5.32

liquid products because they tend to produce the shorter chain hydrocarbons as the products. Therefore, addition of Na into the HY catalyst using the ion exchange method affect on reducing the catalyst surface area causes the decreasing of catalyst activity to convert the palm oil into biofuel through a catalytic cracking process. Otherwise, based on several studies from the literature, the presence of Na can inhibit the secondary cracking, so it can enhance the number of long-chain hydrocarbon products so that, the yield of gasoline (short-chain hydrocarbon) decrease.

Most components of the catalytic cracking products were organic liquid product (OLP) according to the GC-MS analysis. The compositions were gasoline (34.25%), kerosene (31.13%), and diesel (9.34%) (Table 3) when using HY catalyst, and gasoline (13.96%), kerosene (19.68%), and diesel (49.21%) when using NaY catalyst. It suggests that the NaY catalyst can produce more long-chain hydrocarbons range than HY catalyst. The higher content of long-chain hydrocarbons in the liquid product of the catalytic cracking using NaY catalyst is

due to the role of Na in the catalyst. Inline with results of Konwer *et al.* [30], Dandik & Aksoy [10], and Idem *et al.* [9] that the catalytic cracking of vegetable oils using Na_2CO_3 catalyst occurs through the formation of fatty acid salts and then decompose at high temperatures into shorter chain hydrocarbons. In addition, they explained that the fatty acid salts are formed due to the fusion between triglycerides and Na^+ ions present in the catalyst. Idem *et al.* [9] said that the use of catalysts with group IA and IIA metals can inhibit the secondary cracking so they can reduce the formation of gas products and the number of longer chain hydrocarbon products increases. Therefore, the content of longer chain hydrocarbons in the liquid fuels product from the catalytic cracking using NaY catalyst is higher than that when using HY catalyst.

3.3 Comparison Conventional Fixed Bed Reactor and Hybrid Catalytic-Plasma Reactor for Catalytic Cracking Reaction

With respect to compare the catalytic cracking performance over a conventional continuous flow fixed bed reactor and a continuous flow hybrid catalytic-plasma reactor, the conversion over later reactor system shows better performance. Catalytic cracking of palm oil over the hybrid catalytic-plasma reactor was carried out at 375 ºC using the pretreated-spent RCC catalyst. This performance was compared with that over the conventional catalytic fixed bed reactor at 400 °C using the same catalyst which is presented in Table 4. From this table, conversion of palm oil over the conventional catalytic reactor at 400 ºC is 79.29% lower than that over the hybrid catalytic-plasma reactor (95.79%) even at lower temperature (375 °C). However, the gasoline product was not produced in this research which may be due to low reaction temperature so that the

Table 3. Performance of palm oil cracking using HY and NaY catalysts over a conventional continuous fixed bed reactor

Parameters	Catalyst	
	HY	NaY
Conversion	99.11%	98.06%
Yield OLP	91.99%	94.36%
Selectivity gasoline (C_5 - C_{12})	34.25%	13.96%
Selectivity kerosene (C_{13} - C_{14})	31.13%	19.68%
Selectivity diesel (C_{15} - C_{18})	9.34%	47.88%
Yield gas	5.08%	1.88%
Yield coke	2.05%	1.82%

Table 4. Comparison of palm oil catalytic cracking performance by using a continuous flow conventional fixed bed reactor and a continuous flow hybrid catalytic-plasma reactor.

Parameters	Reactor Configuration	
	Conventional Catalytic Fixed Bed (T = 400 ºC)	Hybrid Catalytic-Plasma (T = 375 ºC)
Conversion of palm oil	79.29 %	95.79 %
Yield of Organic Liquid Product (OLP)	75.27 %	92.75 %
Selectivity of kerosene (C_{13} - C_{14})	1.51 %	18.15 %
Selectivity of diesel (C_{15}-C_{18})	14.27 %	9.55 %

catalyst did not actively work at the lower temperature. The reaction temperature should be in the range of 400-500 °C. From the comparison, the increasing of palm oil conversion, biofuels yield, and selectivity to short-chain hydrocarbons product indicates a significant role of plasma. These facts confirm that the plasma affects the reaction performance through the collisions of high energetic electrons, flowed from high voltage electrode to ground electrode, with electrons pair from covalent bonds of the reactant molecules [31] which in turn break the bonds or at least excite the electron pairs of the covalent bonds. Plasma is an active species containing electrons, atoms and molecules that are excited and ionized, radical groups, photons and neutral particles where the electrons have much higher energy [32], so that the activation energy needed during the reactions on the catalyst surface can be reduced [33-36].

If the high energetic electrons from plasma collides with reactant molecules, there will be a breakdown of the chemical bonds that also produce additional high energetic electrons as [34-36]. The produced high energetic electrons were accelerated when passing through a high voltage electric field within the discharge zone. The increase in internal energy in the reactant molecules due to the collisions with high energetic electrons affects the activation energy for the occurrence of chemical reactions through the phenomena of excitation, dissociation, or others [35]. To control the amount of energy of the flowed electrons and to distribute the electrons to the entire surface of electrode, a dielectric like barrier (glass made), which in turn enhance the contact between reactant molecules and the electrons [35].

Usage of the spent RCC catalyst within discharge one of the hybrid catalytic-plasma reactors is aimed to reduce the activation energy or controlling the reaction direction [37]. The catalyst placed in the discharge zone is also purposed to increase the contact area and the contact time between high energetic electrons and the reactant molecules. This excitation of the electron pair of the reactant molecule from the ground to the outermost energy level reduce the energy required for cracking the reactant molecules so that the termination of the bond chain becomes easier [39]. In the hybrid catalytic-plasma process, the active species (high-energy electrons, metastable compounds, and free radicals) were not only formed around the plasma discharge zone but also formed inside the catalyst pore due to the direct contact between the plasma and catalyst [40]. The formation of active species, such as: free radicals and metastable compounds, increases the reaction between reactants adsorbed on the catalyst surface and other active species formed in the discharge gap and the pores of the catalyst which subsequently enhance formation of biofuels due to intimate cracking mechanism [40]. Thus, the catalyst duty becomes lower due to the assistance of excitation of covalent electron pairs by plasma [38].

4. Conclusions

Ion exchange process of Na^+ into HY zeolite catalyst decreases the catalyst activity towards cracking process due to lowering catalyst surface area and crystallinity. Over the conventional continuous flow catalytic fixed bed reactor, the selectivity of gasoline range hydrocarbons reaches 34.25% and 13.96% when using HY and NaY catalysts, respectively, while the palm oil conversion achieves 99.11% and 98.06%, when using HY and NaY catalysts, respectively. In addition, from comparison of reactor performance between a continuous flow hybrid catalytic-plasma reactor and a conventional continuous flow fixed bed reactor using a spent residual catalytic cracking (RCC) catalyst, the hybrid catalytic-plasma reactor showed significant improvement especially on the palm oil conversion and liquid fuels yield although at lower reaction temperature. The plasma role on the catalytic cracking of palm oil also led to lowering ranges of carbon chain of the hydrocarbons product. This improvement was due to the role of high energetic electrons from plasma introduction which exciting electron pairs of covalent bond of reactant molecules. Therefore, combination of appropriate catalyst and plasma role is potential to be more investigated in the catalytic cracking process of palm oil.

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