

Mechanism of catalytic conversion of palm oil (methyl oleate) to short fraction compounds (biogasoline) sequentially

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Abstract

Research has been carried out on the catalytic conversion of palm oil (methyl oleate) into short fraction compounds (biogasoline). The process is carried out with a fixed bed reactor in which a catalyst has been placed and operated at a temperature of between 400 oC to 500 oC for 30 minutes. Firstly, convert methyl oleate into 1-octadecanol with a Ni/zeolite zeolite catalyst. Next, 1-octadecanol is converted to 1-octadecene. Then the conversion of 1-octadecene to octadecane continues and then continues with the cracking reaction of octadecane into short fraction compounds. Compound analysis using GCMS. The analysis results show that the conversion of methyl oleate to 1-octadecane is 87.21%, the conversion of 1-octadecanol to 1-octadecene is 20.21%, while the conversion of 1-octadecene to octadecane and short fraction compounds is 15.29%.

Keywords: methyl oleate, biogasoline, short fraction, 1-octadecene

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I. Introduction

The energy and fuel crisis has occurred since the end of 1970, so that in the early 1980s people began to think about the possibility of exhausting fuel reserves originating from petroleum (fossil fuel). Many studies are exploratory in nature to obtain alternative renewable fuel sources (renewable resources fuel) (Knothe et al., 1997).

Yoon (1997), studied the hydrogenation reaction of 1,3-butadiene on the surface of platinum foil, single crystals of Pt (100), Pt (111), Pt (755) at temperatures of 300 to 375 K. The reaction is first order with respect to hydrogen and approaches zero order with respect to 1,3-butadiene. The product composition is relatively constant in the early stages of the reaction and does not depend on the surface structure of the platinum. If the reaction temperature is increased, the reaction rate will increase. Hydrogenation of 1,3-butadiene with Pt (111), Pt (755) single crystal and Pt foil catalysts at room temperature shows almost the same reaction rate, however the reaction rate with the Pt(100) catalyst shows a slower rate.

Su (1998), studied the dehydrogenation and hydrogenation of cyclohexene on the Pt surface. An increase in temperature on the Pt surface will cause the hydrogenation reaction rate to decrease and increase the dehydrogenation reaction rate. At a temperature of 300 to 400 K, the hydrogenation reaction of cyclohexene occurs to cyclohexane and the dehydrogenation reaction forms benzene.

Petroleum, known as fossil fuel, is an energy source that cannot be renewed quickly. Worldwide the use of petroleum reaches 90% for transportation and industrial purposes, meanwhile, Indonesia is one of the countries that is very rich in natural oil and gas resources. Continuous petroleum exploration results in increasingly depleting petroleum reserves. Some petroleum fractions that are widely used by humans are gasoline (gasoline) and diesel (diesel fuel), which are used as motor vehicle fuel or engine fuel in industry. Most of the country's foreign exchange is generated from the oil and gas sector, especially petroleum.

II. Methodology

1. Research Materials and Tools

The research materials used were: Wonosari natural zeolite from PT Prima Zeolita, materials from E.Merck and quality p.a. consisting of: oleic acid (91.59 %), 1-octadecanol 95 %, 1-octadecene 90 %, HCl 37 % (v/v), HF 40 % (v/v), NH₄Cl, Na₂SiO₃, Ni(NO₃)₂·6H₂O 97 %. Other materials such as: oxygen, nitrogen and hydrogen gas (P.T. Samator Gas), pH paper.

The equipment required for the research is: a set of fixed bed reactors, thermocouples, thermometers, ovens, hot-plates, laboratory glassware, analytical balance (Mettler RE 200), atomic absorption spectroscopy (AAS, Varian FS 220), GC- MS (Shimadzu QP-2010S), surface area analyzer NOVA 1000 (Quantachrome Nova Win2 version 2.2), X-ray diffractometer (XRD, Shimadzu-6000).

2. Research Procedures

This research procedure is divided into several stages such as catalyst preparation, making methyl 9-octadecenoate, hydrogenation of methyl 9-octadecenoate with a ZSiA catalyst, catalytic hydrogenation of 1-octadecanol with a ZSiA catalyst, hydrocracking of 1-octadecene with a Ni/ZsiA catalyst.

2.1. Ni/ZSiA Catalyst Preparation

Zeolite with a passing size of 100 mesh is soaked in distilled water and washed while stirring. Then soaked in 2% HF for 30 minutes, then washed with distilled water, repeated 3 times, then dried in the oven at a temperature of 120 oC for 3 hours. Next, it was oxidized with oxygen at a temperature of 500 oC for 2 hours and calcined with nitrogen at a temperature of 500 oC for 2 hours with a gas flow rate of 20 mL/minute to obtain a Z catalyst (Handoko, 2001).

Next, the Z catalyst was washed using a 2 M HCl solution with a ratio of zeolite: HCl solution = 1: 2 (v/v) while stirring for 20 to 30 minutes (Zhang, 1999). Next, the zeolite samples were washed using distilled water until pH = 6 and dried in an oven at a temperature of 120 oC for 3 hours and continued with oxidation using oxygen gas at a flow rate of 20 mL/minute at a temperature of 500 oC for 2 hours and calcination with nitrogen gas at a rate of flow 20 mL/minute at a temperature of 500 oC for 2 hours. Then to the Z catalyst in a beaker, 5% (w/w) of Na-Silicate (Na₂SiO₃) was added which was dissolved in distilled water and then heated at a temperature between 80 oC to 90 oC for 24 hours while stirring using a magnetic stirrer. Then the sample was cooled and continued with oxidation with oxygen gas at a temperature of 500 oC for 2 hours with a gas flow rate of 20 mL/minute and continued with calcination with nitrogen gas at a temperature of 500 oC for 2 hours with a gas flow rate of 20 mL/minute to obtain a ZSi catalyst.

The ZSi catalyst was cooled and a 2 M NH₄Cl solution was added to the beaker with a ratio of 1: 2 (v/v) and the mixture was heated again at a temperature of 90 oC for 4 hours with a magnetic stirrer (Zhang, 1999). Then cooled and continued with the oxidation process using oxygen gas at a temperature of 500 oC for 2 hours with a gas flow rate of 20 mL/minute and continued with calcination with nitrogen gas at a temperature of 500 oC for 2 hours with a gas flow rate of 20 mL/minute to obtain the ZSiA catalyst. .

Impregnation of Ni metal (Ni 2% (w/w)) on the surface of the ZSiA catalyst was carried out using the wet impregnation method. 9.91 g of Ni(NO₃)₂·6H₂O salt was dissolved in 100 mL of distilled water while stirring until homogeneous, then 100 g of sample (ZSiA catalyst) was added. Then it is heated and evaporated at a temperature of 80 oC to 90 oC (at 1 atm) while stirring so that the water component will slowly evaporate. After the water component has evaporated, the sample is placed in an oven at a temperature of 120oC for 2 hours and continued with the oxidation process with oxygen gas at a temperature of 500oC for 2 hours with a gas flow rate of 20 mL/minute and reduction at a temperature of 500oC with hydrogen gas flowing at 20 mL/minute to obtain a Ni/ZSiA catalyst (Handoko, 2001).

Each stage of treatment is analyzed for metal content using AAS, acidity using the gravimetric method, crystallinity using XRD and surface area using the BET method.

2.2 Preparation of Methyl 9-octadecenoate (methyl oleate)

A total of 24 mL of methanol was mixed with 2.96 mL of sulfuric acid then added to a two-neck flask containing 100 mL of oleic acid. The mixture was refluxed for 4 hours at a temperature of 60 OC and the reflux results were left overnight. Next, the organic layer (ester layer) is separated from the water layer using a separating funnel. The ester layer was washed with distilled water until neutral and dried with anhydrous Na₂SO₄. The resulting methyl 9-octadecenoate was heated in an open container at a temperature of 100-120 OC and then analyzed by GC-MS.

3. Cracking tools

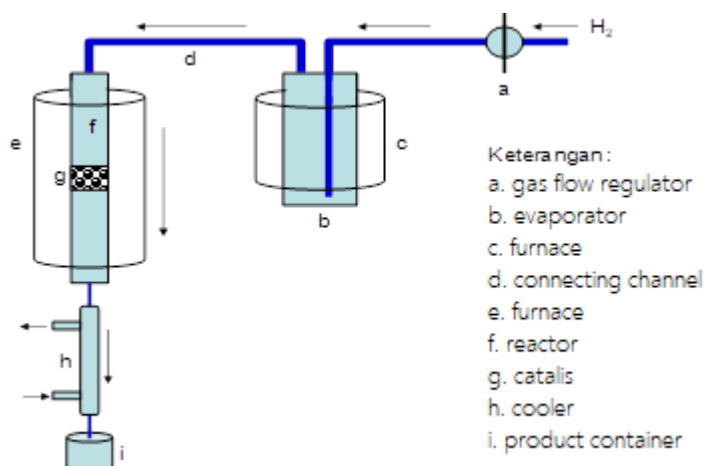


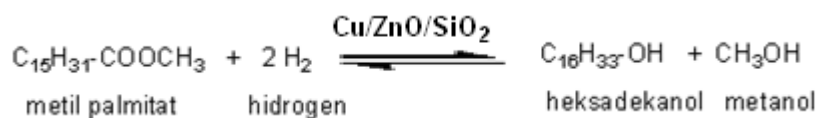
Figure 1. A set of cracking tools

III. Results and Discussion

1. Conversion of methyl 9-octadecenoate to 1-octadecanol

Methyl 9-octadecenoate which was initially 91.59% was converted into 1-octadecanol as much as 34.50%. The reaction mechanism of methyl 9-octadecenoate to 1-octadecanol in this reaction system is thought to follow two stages. The first stage is the adsorption of methyl 9-octadecenoate on the catalyst surface through the interaction of the Bronsted acid site with the double bond at C number 9 and the opening of the double bond (addition reaction) occurs in accordance with the reaction mechanism according to Horiuti-Polanyi in Campbell (1988).

According to Brands (2002), hydrogenation of methyl palmitate produces hexadecanol and methanol. Hydrogenation of methyl palmitate was carried out using a fixed bed system reactor operated at a temperature of 473 K (200 oC) with a hydrogen pressure of 9 MPa and a Cu/ZnO/SiO₂ catalyst and using butane solvent in a supercritical state. The results of this reaction produce 98.60% hexadecanol and 0.5% hexadecane.



The research results of Zhilong (2007) stated that the conversion process of fatty acid methyl ester (FAME) into fatty alcohol (FA) with a chain length of C16 – C18 in a batch system reactor reached greater than 95%. The hydrogenation reaction in FAME was carried out in a downflow fixed bed reactor with an internal diameter of 17 mm and a length of 0.6 m and the amount of CuO/Cr₂O₃ catalyst used was 15 g.

In this research, FAME catalytic hydrogenation was carried out at a pressure of 15 MPa and a temperature of 240 oC using propane and carbon dioxide as solvents in a supercritical state in a fixed bed reactor.

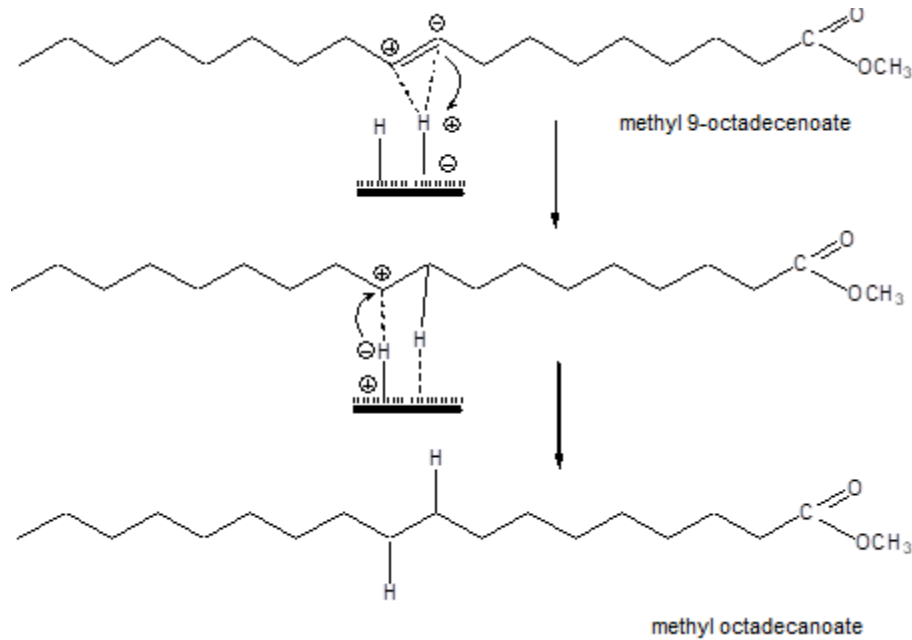


Figure 2. Opening of the double bond in methyl 9-octadecanoate to become methyl octadecanoate

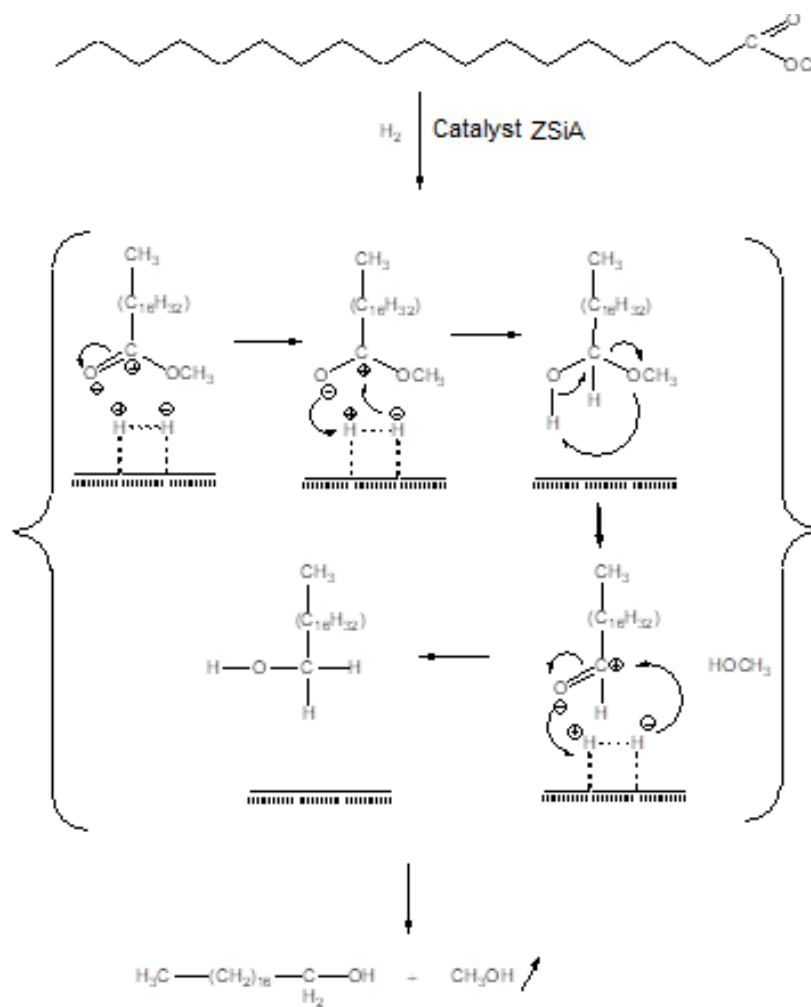


Figure 3. Conversion of methyl octadecanoate to 1-octadecanol

2. Conversion of 1-octadecanol to 1-octadecene

The next stage is the conversion of 1-octadecanol to 1-octadecene, based on the results. The conversion process of 1-octadecanol to 1-octadecene is shown in Figure 4 below.

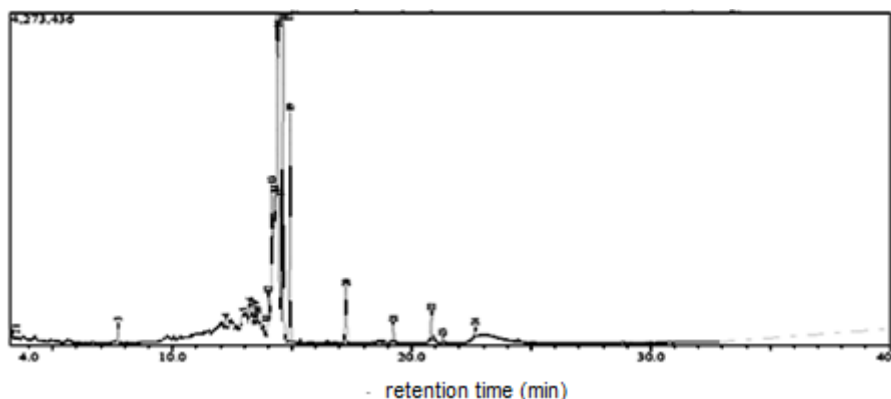


Figure 4. GC-MS chromatogram of the hydrogenation reaction of 1-octadecanol with a ZSiA catalyst at a temperature of 400 °C

Based on Figure 4, the GCMS results can be tabulated as in Table 1 below, The most dominant product is 1-octadecene with an amount of 12.60%

Table 1. Alkane and alkene products with a chain length < C18 from the thermal cracking reaction of 1-octadecanol at a temperature of 400 oC (estimated by GCMS QP2010 Shimadzu library data)

Nama Senyawa	SI	t _R (menit)	Jumlah (%)
4-dodecene	96	3,28	1,50
5-tetradecene	95	4,18	0,83
Pentadecane	96	7,72	0,62
Heksadecane	95	12,23	0,51
7-heksadecene	95	14,01	3,88
1-oktadecene	97	14,14	12,60
3-oktadecene	96	14,34	9,45
5-oktadecene	97	14,67	8,68
Oktadecane	96	22,65	1,13
amount			39,20

The reaction mechanism that can be written is as follows:

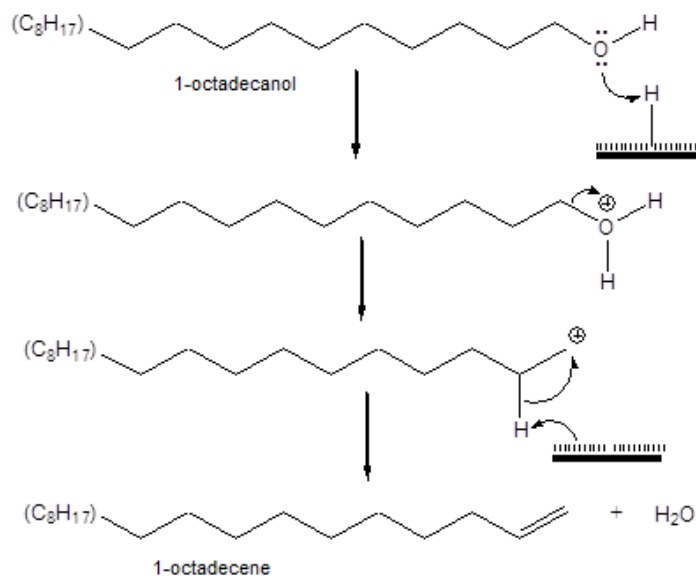


Figure 5. Mechanism of formation of 1-octadecene

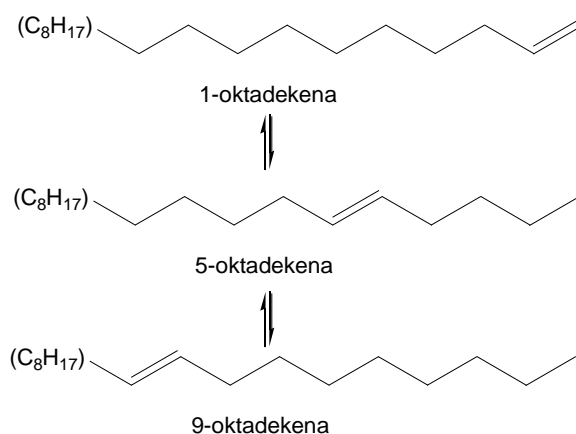


Figure 6. Isomerization of the 1-octadecene compound

Meanwhile, the mechanism of change from 1-octadecanol to hexane and 5-dodecene compounds is as follows:

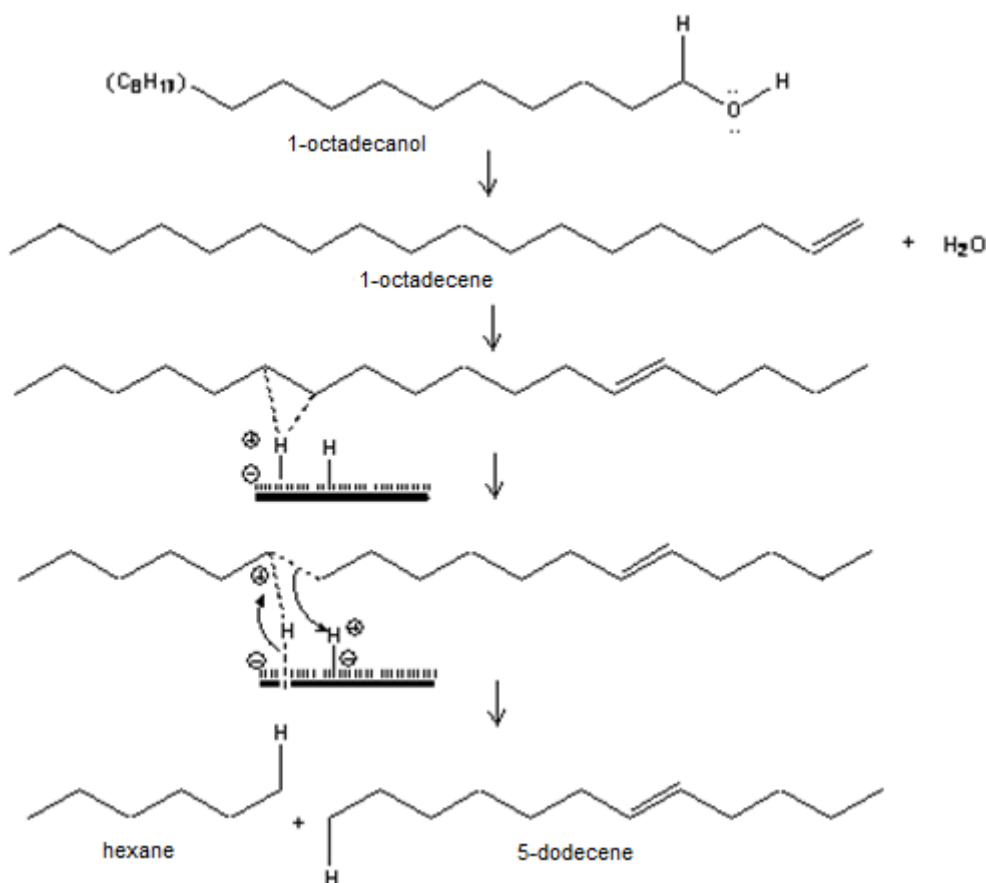


Figure 7. Changes from 1-octadecanol to hexane and 5dodecene compounds

The mechanism by which hexane compounds become gaseous compounds, namely ethane and butane, is as follows:

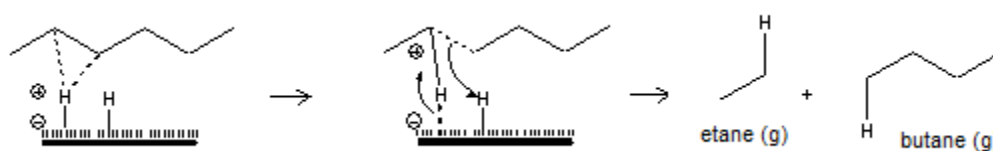


Figure 8. Change of hexane to ethane and butane

The yield of alkane and alkene products with a chain length < C12 from the catalytic hydrocracking reaction of 1-octadecene compounds at varying temperatures and hydrogen flow rates was determined over a period of 30 minutes from 10 g of catalyst and 10 g of feed. At a hydrogen gas flow rate of 10 mL/minute and a reaction temperature of 450 oC, the largest number of reaction products was obtained, so it can be concluded that the effect of a flow rate of 10 mL/minute in each temperature region showed maximum results.

According to Page (1987) and Bartholomew (2006), the meaning of adsorption is divided into 3, namely (1) physical adsorption or physisorption, (2) transition state, (3) chemical adsorption. Through physisorption, the feed or reactant will approach the surface of the catalyst and be adsorbed on the solid surface of the catalyst so that it experiences further interaction with the active site of the catalyst, namely the Bronsted acid site and the Lewis acid site, which is hereinafter called chemisorption.

3. Conversion of 1-octadecene into short chain alkane and alkene compounds

According to Campbell (1988), the product of breaking long chain bonds can be alkanes or short chain alkenes as shown in the mechanism in Figure 8. In the hydrogenation process on the catalyst surface based on Figure 7 above, a hydrogen flow rate of 10 mL/minute is good at temperatures of 400, 450 or 500 oC show maximum results. At a hydrogen flow rate of 10 mL/minute, hydrogen adsorption onto the catalyst surface was very good compared to higher hydrogen flow rates. At a hydrogen flow rate of 10 mL/minute, relatively more hydrogen is adsorbed on the catalyst surface quantitatively compared to a faster hydrogen flow rate, so it is possible for the hydrogen to be in a condensed state and undergo dissociation and migration. The relatively fast migration of hydrogen makes it possible for the probability of collisions to occur with 1-octadecene molecules and the resulting reaction product to be <C12 to be greater.

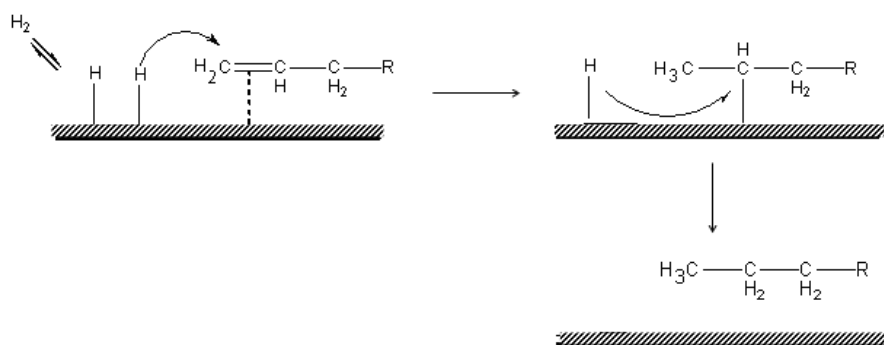


Figure 9. Hydrogenation of long chain alkene compounds into short chain alkene compounds

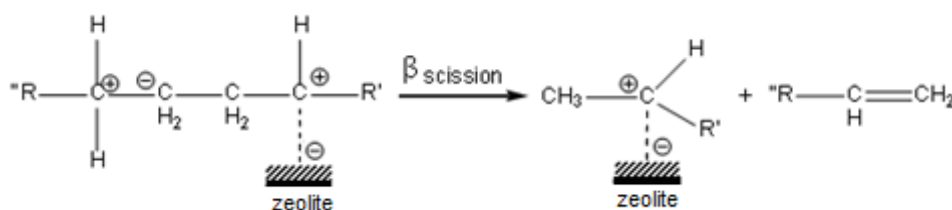


Figure 10. Breaking down long chain alkane compounds into short chain alkane and alkene compounds



Figure 11. Breaking down hexane compounds into ethane and butane

IV. CONCLUSION

Based on observations of research results, it can be concluded that methyl oleate can be converted into short chain alkane compounds through sequential stages, namely:

1. Methyl oleate (Methyl 9-octadecenoate) becomes 1-octadecanol as much as 34.50%,
2. 1-octadecanol becomes 1-octadecene as much as 12.60%,
3. 1-octadecene becomes octadecane and short chain alkane and alkene compounds are as much as 90%

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