

Sequential Catalytic Conversion of Methyl Oleate Into Short Chain Alkane and Alkene Compounds

Donatus Setyawan Purwo Handoko^{1*}, Triyono²

¹FMIPA University of Jember

²FMIPA Gdjah Mada University, Yogyakarta

Corresponding Author: Donatus Setyawan Purwo Handoko

kreka_zeolit@yahoo.com

ARTICLE INFO

Keywords: Methyl 9-Octadecenoate, 1-Octadecanol

Received : 5 December

Revised : 22 January

Accepted: 23 February

©2024 Handoko, Triyono: This is an open-access article distributed under the terms of the [Creative Commons Atribusi 4.0 Internasional](https://creativecommons.org/licenses/by/4.0/).



ABSTRACT

Research on the conversion of methyl oleate (Methyl 9-octadecenoate) into shorter chain alkane compounds through the stages of methyl 9-octadecenoate into 1-octadecanol, 1-octadecanol into 1-octadecene and 1-octadecene into alkane compounds and short chain alkenes with a length of C₁₂ > have been done. The conversion process uses ZSiA and Ni/ZSiA catalysts which are placed in a fixed bed system reactor column and operated at temperatures of 400, 450 and 500 oC. ZSiA catalyst was made by washing natural zeolite with distilled water, soaking with 2 M HCl solution, adding 5% Na₂SiO₃ w/w, soaking with 2 M NH₄Cl solution, calcining at a temperature of 500 oC while flowing nitrogen gas for two hours at a flow rate of 20 milliliters per minute; oxidation during a two-hour oxygen flow rate of 20 milliliters per minute; and impregnation of Ni metal onto the catalyst sample's surface using Ni(NO₃)₂ 6H₂O metal 2% w/w. Subsequently, reduction was done for two hours while hydrogen gas was flowing at a rate of 20 mL per minute. The resultant catalyst was subjected to various analyses, including AAS analysis for metal cation content, gravimetric analysis for acidity, NOVA 1000 surface area analyzer for specific surface area, and X-ray diffractometer (XRD, Shimadzu-6000) analysis for crystallinity

INTRODUCTION

Fuel derived from petroleum, known as fossil fuel, is an energy source that cannot be renewed quickly. Worldwide the use of fuel derived from petroleum reaches 90% for transportation and industrial purposes. The continuous use of fuel derived from petroleum 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.

The use of fuel derived from petroleum produces many relatively dangerous pollutant compounds such as NO_x, SO_x, Pb, CO and particulate compounds. Compounds such as NO_x, SO_x can cause acid rain, resulting in damage to buildings and materials made of metal. Meanwhile, Pb and CO pollutants are toxic if they enter the human body through inhalation and food.

More than 20 countries in the world, including Indonesia, develop oil palm plantations. In fact, Indonesia, Malaysia, Nigeria and Papua New Guinea are the largest oil palm producing countries in the world. Apart from meeting the need for cooking oil, the development of oil palm plantations is also oriented towards its use as an alternative fuel source such as biodiesel.

The use of zeolite as an active metal carrier It is important to consider the characteristics of the natural zeolite, such as its acidity, high surface area, and porous structure, while producing metal/carrier system catalysts. When using natural zeolites as active metal carriers in the manufacture of catalysts, these characteristics are crucial.

Sang (2003) said that palm oil, a renewable biofuel source, can be cracked at atmospheric pressure at a temperature of 450 oC and at a WHSV of 2.5 h⁻¹ to produce biofuel in a fixed bed microreactor. The reaction uses microporous HZSM-5 catalyst, mesoporous MCM-41 and a composite of micromesoporous zeolite, to study the effect of catalyst pore size and acidity in producing biofuel. The products resulting from this process produce gas, organic liquid product (OLP), water and coke. This organic liquid product is composed of hydrocarbons compared to gasoline, kerosene and diesel fuel for its boiling point range. The maximum conversion of 99% palm oil to 48% gasoline by weight was obtained from a micromesoporous zeolite composite catalyst.

According to Twaiq (2003), catalytic cracking of palm oil to produce liquid hydrocarbon fuel has been studied in a fixed bed microreactor operated at atmospheric pressure, temperature 723 K and WHSV 2.5 h⁻¹ using mesoporous molecular sieve MCM-41. Mesoporous aluminosilicate with an S/Al ratio of up to 50 was synthesized using the hydrothermal method. Catalyst material with a crystal structure of MCM-41 with a mesoporous pore size with a surface area of between 550 to 1200 m²/g and has an average pore size of 1.8 to 2.8 nm. MCM-41 catalyst shows high activity for palm oil cracking. The MCM-41 material is selective for the formation of linear hydrocarbons, especially C13. The liquid product yield decreases with increasing catalyst surface area. Selectivity for gasoline increases while diesel selectivity decreases with conversion from palm oil.

Rajeshwer (2006), hydrogenation of short chain alkenes such as propene, butene, pentene and octene has been widely carried out. Hydrogenation generally uses catalysts such as Pd, Ni, Pt. Hydrogenation of straight chain

alkenes C10 to C13 (diolefins) with a Ni/ Al₂O₃ catalyst is a sequential reaction where hydrogenation of diolefins becomes mono olefins and further hydrogenation produces paraffins. Research on the hydrogenation of short chain alkenes has been widely carried out, but the hydrogenation of long chain alkenes is still very rarely carried out.

Yoon (1997), studied the hydrogenation reaction of 1,3-butadiene on the surface of platinum foil at a temperature of 300 to 375 K. The reaction was first order with respect to hydrogen and close to 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, but the reaction rate with Pt(100) catalyst shows a slower rate.

1. Palm Oil and Its Composition

Oil palm consists of four types or varieties based on shell thickness, namely *Macrocaraya*, *Dura*, *Tenera* and *Pisifera* types as in Table II.1. Palm oil producing countries other than Indonesia are Malaysia, Central America, Nigeria, Papua New Guinea (Ketaren, 1986).

Table 1. Shell Thickness of Various Types of Oil Palm

| Type | Shell thickness (mm) | description |
|-------------|----------------------|-------------|
| Macrocaraya | 5 | Very thick |
| Dura | 3 – 5 | Thick |
| Tenera | 2 – 3 | Currently |
| Pisifera | -- | Thin |

(Ketaren, 1986)

The content of water and impurities, the amount of free fatty acids, the peroxide value and bleaching power, the melting point, the amount of solid glycerides, the refining loss, the plasticity and spreadability, the transparent qualities, the amount of heavy metals, and the saponification value are all factors that affect the quality of palm oil seeds. (Ketaren, 1986). The primary constituents of palm oil are oleic acid and palmitic acid, which are made up of additional fatty acids (Table II.2). Triglyceride linkages are formed between these fatty acids and glycerol. Oleic acid is an unsaturated fatty acid with a carbon chain length of 18 and one double bond, whereas palmitic acid is a saturated fatty acid with a carbon chain length of 16. Another unsaturated fatty acid with a carbon chain length of is linolenic acid. 18 with three bonds twice. Generally speaking, palm oil has extremely little linolenic acid.

2. Ester

Esterification and transesterification reactions generally use either acid or base catalysts. The catalysts commonly used are sulfuric acid, NaOH, KOH (Fessenden and Fessenden, 1986).

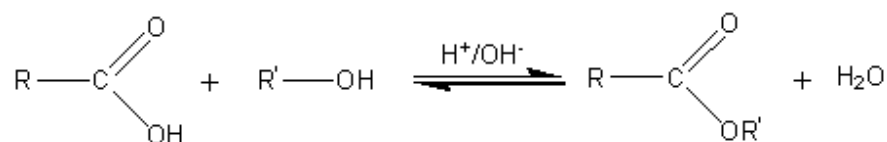


Figure 1. Fatty Acid Esterification Reaction with an Acid or Base Catalyst

The use of an acid catalyst in the esterification reaction can be directly added to the reaction system together with alcohol. When using a base catalyst, the base catalyst must first be reacted with alcohol to form an alkoxide, then the alkoxide will react with the fatty acid to form an ester.

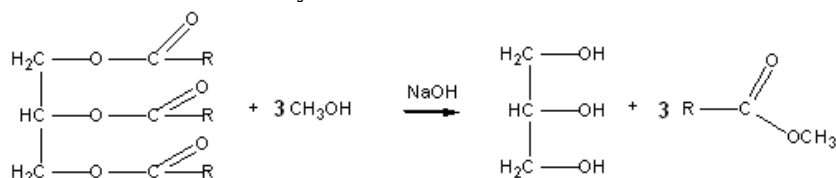


Figure 2. Triglyceride Transesterification Reaction with a Base Catalyst, NaOH (Fessenden and Fessenden, 1986)

The carboxylic acid group is inert to most reducing agents (such as hydrogen). This inertness can be reactivated by changing the carboxylic acid into an ester and then the ester is reduced using hydrogen and a catalyst to produce a pair of alcohols (Fessenden and Fessenden, 1986). The reduction of esters using hydrogen is called the ester hydrogenolysis process.

A reduction reaction that is relatively easy to carry out on a laboratory scale is the reduction of esters using LiAlH_4 , while the reduction of esters to alcohols involving hydrogen is widely used on an industrial scale, because this process involves very high hydrogen pressure, which is around 10 to 20 Mpa at a reaction temperature of 170 oC.

The reduction process of carboxylic acids is relatively difficult to carry out, but by using LiAlH_4 as a reducing agent, primary alcohol is produced very well.

3. Alcohol Dehydration

The alcohol elimination reaction at a temperature of 170 oC with the help of a homogeneous catalyst (H_2SO_4) produces alkene compounds (Fessenden and Fessenden, 1986), as in the figure below.

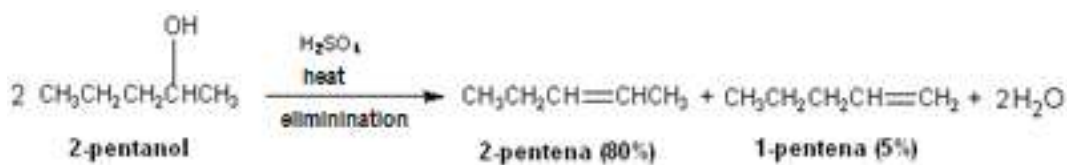


Figure 3. Alcohol Elimination Reaction

If an alcohol is reacted with sulfuric acid, a series of reactions will take place as in Figure 5. In general, primary alcohols produce sulfate esters at low temperatures, and produce ethers at medium temperatures and produce alkenes at high temperatures, although it cannot be avoided that the product obtained will be in mixed form. Tertiary alcohols and most secondary alcohols will produce alkene products (Fessenden and Fessenden, 1986).

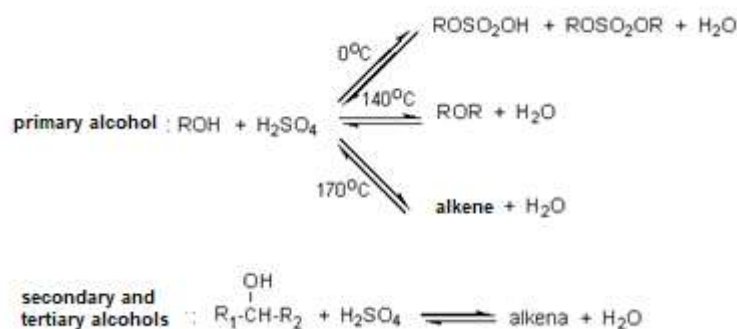


Figure 4. Reversible Reaction of Alcohol at Several Temperatures

Fatty alcohol is alcohol produced from the hydrogenation of fatty acid esters. In general, fatty alcohols come from saturated fatty acids. The boiling points and melting points in Table 2 tend to increase regularly with increasing chain length (number of carbon atoms). The longer the carbon chain, the lower the polarity of the hydroxyl group will be. Hexanol and octanol are slightly soluble in water, decanol and longer chain fatty alcohols are insoluble in water, but octadecanol and longer alcohols can, while being stored, absorb water vapor from the air. Table 2's melting and boiling temperatures show a consistent trend upward trend as chain length (or the number of carbon atoms) increases. The hydroxyl group's polarity decreases with length of the carbon chain; hence, the longer the carbon chain, the less polar the hydroxyl group. While octadecanol and longer alcohols can absorb water vapor from the air during storage, hexanol and octanol are marginally soluble in water, while decanol and fatty alcohols with longer chains are insoluble. For this reason, a very tightly closed container is needed for storage.

Table 2. Physical Properties of Several Fatty Alcohol Compounds (Fatty Alcohol)

| IUPAC name | Common name | Molecular formula | Mr (g/mol) | Hydroxyl number (mg KOH/g) | Mp (°C) | Bp (°C) (p.kPa) |
|----------------|------------------|-----------------------------------|------------|----------------------------|---------|-----------------|
| 1-Dodekanol | Lauril alkohol | C ₁₂ H ₂₆ O | 186,3 | 300 | 23 | 260 |
| 1-Tetradekanol | Miristil alkohol | C ₁₄ H ₃₀ O | 214,4 | 261 | 38 | 172 (2.67) |
| 1-Heksadekanol | Setil alkohol | C ₁₆ H ₃₄ O | 242,5 | 230 | 49 | 194 (2.67) |
| 1-Heptadekanol | Margaril alkohol | C ₁₇ H ₃₆ O | 256,5 | 218 | 54 | - |
| 1-Oktadekanol | Stearil alkohol | C ₁₈ H ₃₈ O | 270,5 | 207 | 58 | 214 (2.67) |

atm = 101,325 kPa), (Perry's, 1997)

4. Alkene Hydrogenation Reaction

The catalytic addition reaction by hydrogen to an alkene or alkyne is a reduction reaction of a π -bonded compound. This reaction is general for alkenes, alkynes and other compounds with π bonds. The hydrogenation reaction is exothermic, the reaction runs spontaneously but is very slow because the activation energy is very high.

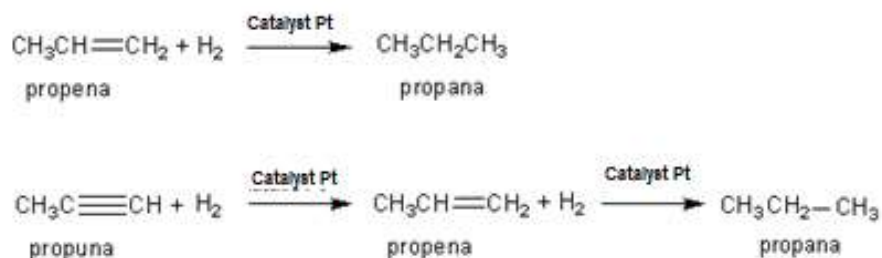


Figure 5. Addition Reaction with Hydrogen (Campbell, 1988)

Providing energy through heating cannot supply enough energy to bring many of these molecules to a transition complex state. The hydrogenation reaction of alkenes or alkynes will run quickly if a catalyst is added. For heterogeneous catalysts, the metals used as catalysts in the addition reaction of alkenes with hydrogen include: platinum, palladium, nickel, rhenium and copper.

Figure 5 from Wu (2005) depicts the collision mechanism in the platinum catalyst surface ethene hydrogenation reaction. The two ethene molecules physisorb with hydrogen on the catalyst surface to start the ethene hydrogenation reaction step. The energy for the reaction (E_{reaction}) will be readily exceeded due to the effective collision of the two reactants, allowing products to develop on the catalyst's surface before the products desorb from it.

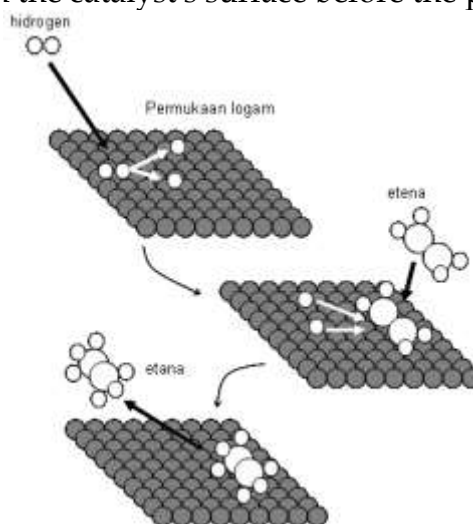


Figure 6. Catalytic Reaction of Ethene with Hydrogen on the Surface of a Platinum Catalyst (Wu, 2005)

LITERATURE REVIEW

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).

METHODOLOGY

1. Research Materials and Tools

Wonosari natural zeolite from PT Prima Zeolita, materials from E.Merck and quality p.a., and 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% were the research materials utilized. Additional materials include pH paper and gases such as oxygen, nitrogen, and hydrogen (P.T. Samator Gas). A set of fixed bed reactors, thermocouples, thermometers, ovens, hot plates, laboratory glassware, atomic absorption spectroscopy (AAS, Varian FS 220), GC-MS (Shimadzu QP-2010S), surface area analyzer NOVA 1000 (Quantachrome Nova Win2 version 2.2), and X-ray diffractometer (XRD, Shimadzu-6000) are among the equipment needed for the research.

2. Research Procedure

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.

3. Ni/ZSiA Catalyst Preparation

100 mesh zeolite is passed through distilled water and then rinsed while being stirred. followed by a 30-minute soak in 2% HF, three rounds of distilled water washing, and three hours of oven drying at 120 oC. To create a Z catalyst, it was then oxidized with oxygen for two hours at 500 oC and then calcined with nitrogen for two hours at 500 oC with a gas flow rate of 20 mL/minute (Handoko, 2001). After that, the Z catalyst was stirred for 20 to 30 minutes in a 2 M HCl solution with a zeolite: HCl solution ratio of 1:1 (v/v) (Zhang, 1999). The zeolite samples came next. were cleaned with distilled water until pH = 6, dried in an oven for three hours at 120 oC, and then underwent two hours of oxidation using oxygen gas flowing at a rate of 20 mL/minute at 500 oC and two hours of calcination using nitrogen gas flowing at the same rate for two hours at 500 oC. The Z catalyst was then placed in a beaker with distilled water dissolved in it, and 5% (w/w) of Na-Silicate (Na₂SiO₃) was added. The mixture was then heated for 24 hours at a temperature between 80 and 90 degrees Celsius while being stirred with a magnetic stirrer. Following the sample's cooling, oxidation with oxygen gas was carried out at a temperature of 500. in order to produce a ZSi catalyst. This process started with calcination with nitrogen gas at a temperature of 500 oC for two hours with a gas flow rate of 20 mL/minute.

1. Ni/ZSiA Catalyst Preparation

After cooling the ZSi catalyst, a 2 M NH_4Cl solution was added to the beaker in a 1:1 (v/v) ratio. The mixture was then heated once again for 4 hours at 90 °C using a magnetic stirrer (Zhang, 1999). The ZSiA catalyst was then obtained by cooling and continuing the oxidation process with oxygen gas at 500 °C for two hours at a gas flow rate of 20 mL/minute. The calcination process was then carried out with nitrogen gas at 500 °C for two hours at a gas flow rate of 20 mL/minute. Using the wet impregnation process, Ni metal (2% (w/w)) was impregnated onto the ZSiA catalyst surface. 9.91 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ salt was dissolved in 100 mL of distilled water, and 100 g of sample (ZSiA catalyst) was added after the mixture was homogenized. After that, it is heated to between 80 and 90 degrees Celsius (at 1 atmosphere pressure) and stirred to allow the water component to gently evaporate. To obtain a Ni/ZSiA catalyst, the sample is first heated to 120°C for two hours, and then it is reduced to 500°C for two hours with hydrogen gas flowing at 20 mL/minute, and oxygen gas is added at 20 mL/minute during this time (Handoko, 2001). This process continues until the water component has evaporated. Metal content at every treatment step AAS was used for analysis, the gravimetric method for acidity, the XRD method for crystallinity, and the BET method for surface area.

2. Preparation of Methyl 9-Octadecenoate

A two-neck flask holding 100 mL of oleic acid was filled with a mixture of 24 mL of methanol and 2.96 mL of sulfuric acid. The combination was refluxed for four hours at sixty degrees Celsius, and the reflux results were stored until the next day. Next, a separating funnel is used to separate the water layer from the organic layer (ester layer). After neutralizing the ester layer with distilled water, anhydrous Na_2SO_4 was used to dry it. After being heated to between 100 and 120 °C in an open container, the resultant methyl 9-octadecenoate was subjected to GC-MS analysis.

3. Hydrogenation Reaction of Methyl 9-Octadecenoate with ZSiA Catalyst
ZSiA catalyst was heated to 400 °C in a fixed bed reactor column after being divided into three weight groups of 5 g, 10 g, and 15 g. The next step involves passing 10 g of feed chemical (methyl 9-octadecenoate) through the catalyst at a flow rate of 20, 40, or 60 mL/minute. Thirty minutes are spent on the procedure. The products were subjected to GC-MS analysis.

1. Research Materials and Tools

Wonosari natural zeolite from PT Prima Zeolita, materials from E. Merck and quality p.a., and oleic acid (91.59%), 1-octadecanol 95%, 1-octadecene 90%, HCl 37% (v/v), HF 40% (v/v), NH_4Cl , Na_2SiO_3 , $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 97% were the research materials utilized. Additional materials include pH paper and gases such as oxygen, nitrogen, and hydrogen (P.T. Samator Gas). A set of fixed bed reactors, thermocouples, thermometers, ovens, hot plates, laboratory glassware, atomic absorption spectroscopy (AAS, Varian FS 220), GC-MS (Shimadzu QP-2010S), surface area analyzer NOVA 1000 (Quantachrome Nova Win2 version 2.2), and X-ray diffractometer (XRD, Shimadzu-6000) are among the equipment needed for the research.

4. Research Procedure

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.

5. Ni/ZSiA Catalyst Preparation

100 mesh zeolite is passed through distilled water and then rinsed while being stirred. followed by a 30-minute soak in 2% HF, three rounds of distilled water washing, and three hours of oven drying at 120 oC. To create a Z catalyst, it was then oxidized with oxygen for two hours at 500 oC and then calcined with nitrogen for two hours at 500 oC with a gas flow rate of 20 mL/minute (Handoko, 2001). After that, the Z catalyst was stirred for 20 to 30 minutes in a 2 M HCl solution with a zeolite: HCl solution ratio of 1:1 (v/v) (Zhang, 1999). The zeolite samples came next. were cleaned with distilled water until pH = 6, dried in an oven for three hours at 120 oC, and then underwent two hours of oxidation using oxygen gas flowing at a rate of 20 mL/minute at 500 oC and two hours of calcination using nitrogen gas flowing at the same rate for two hours at 500 oC. The Z catalyst was then placed in a beaker with distilled water dissolved in it, and 5% (w/w) of Na-Silicate (Na_2SiO_3) was added. The mixture was then heated for 24 hours at a temperature between 80 and 90 degrees Celsius while being stirred with a magnetic stirrer. Following the sample's cooling, oxidation with oxygen gas was carried out at a temperature of 500. in order to produce a ZSi catalyst. This process started with calcination with nitrogen gas at a temperature of 500 oC for two hours with a gas flow rate of 20 mL/minute.

1. Ni/ZSiA Catalyst preparation

After cooling the ZSi catalyst, a 2 M NH_4Cl solution was added to the beaker in a 1:1 (v/v) ratio. The mixture was then heated once again for 4 hours at 90 oC using a magnetic stirrer (Zhang, 1999). The ZSiA catalyst was then obtained by cooling and continuing the oxidation process with oxygen gas at 500 oC for two hours at a gas flow rate of 20 mL/minute. The calcination process was then carried out with nitrogen gas at 500 oC for two hours at a gas flow rate of 20 mL/minute. Using the wet impregnation process, Ni metal (2% (w/w)) was impregnated onto the ZSiA catalyst surface. 9.91 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ salt was dissolved in 100 mL of distilled water, and 100 g of sample (ZSiA catalyst) was added after the mixture was homogenized. After that, it is heated to between 80 and 90 degrees Celsius (at 1 atmosphere pressure) and stirred to allow the water component to gently evaporate. To obtain a Ni/ZSiA catalyst, the sample is first heated to 120°C for two hours, and then it is reduced to 500°C for two hours with hydrogen gas flowing at 20 mL/minute, and oxygen gas is added at 20 mL/minute during this time (Handoko, 2001). This process continues until the water component has evaporated. Metal content at every treatment step AAS was used for analysis, the gravimetric method for acidity, the XRD method for crystallinity, and the BET method for surface area.

2. Preparation of Methyl 9-octadecenoate

A two-neck flask holding 100 mL of oleic acid was filled with a mixture of 24 mL of methanol and 2.96 mL of sulfuric acid. The combination was refluxed for four hours at sixty degrees Celsius, and the reflux results were stored until the next day. Next, a separating funnel is used to separate the water layer from the organic layer (ester layer). After neutralizing the ester layer with distilled water, anhydrous Na₂SO₄ was used to dry it. After being heated to between 100 and 120 °C in an open container, the resultant methyl 9-octadecenoate was subjected to GC-MS analysis.

- ## 3. Hydrogenation Reaction of Methyl 9-octadecenoate With ZSiA Catalyst
- ZSiA catalyst was heated to 400 °C in a fixed bed reactor column after being divided into three weight groups of 5 g, 10 g, and 15 g. The next step involves passing 10 g of feed chemical (methyl 9-octadecenoate) through the catalyst at a flow rate of 20, 40, or 60 mL/minute. Thirty minutes are spent on the procedure. The products were subjected to GC-MS analysis.

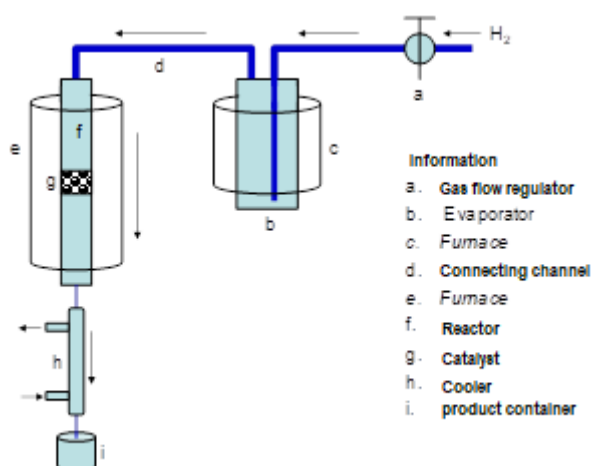


Figure 7. Fixed Bed Reactor

4. Catalytic Hydrogenation Reaction of 1-Octadecanol with ZSiA Catalyst

In an evaporator column, ten grams of the compound—pure 1-octadecanol, 95%—were evaporated at a temperature between 300 and 400 °C. The reactor was then heated to 400, 450, and 500 °C after being filled with 10 g of ZSiA catalyst. In order to force steam out of the feed and interact with the catalyst in the reactor column, hydrogen at flow rates of 20, 40, and 60 mL/minute is passed through the evaporator column. The products were subjected to GC-MS analysis.

5. Hydrocracking Reaction of 1-Octadecene with Ni/ZSiA Catalyst

A total of 10 g of pure 1-octadecene sample (90% content) was placed in the evaporator column and 10 g of the Ni/ZSiA catalyst was placed in the fixed bed reactor column. Next, the reactor column is heated first, so that it reaches the desired catalytic reaction temperature (400, 450 or 500 °C). After the reactor temperature is reached, the evaporator column is immediately heated until evaporation occurs, hydrogen is flowed at a certain speed (10, 20, 30 and 40 mL/minute). The vapor of the octadecene compound along with hydrogen will flow past the surface of the catalyst.

The resulting reaction product (Organic Liquid Product, OLP) was stored in a sample bottle for up to 30 minutes and the reaction product was analyzed using GC-MS.

RESULT AND DISCUSSION

1. Catalyst Characterization Results

1. Catalyst Crystallinity

Harber (1991) states that the surface area, Si/Al ratio, acidity, cation concentration, and crystallinity of zeolite material are necessary for its use as a catalyst. The pore radius, pore volume, and acidity of the zeolite are intimately linked to these characteristics. The ability of the crystal lattice to hold its shape is indicated by the zeolite crystallinity. A substance must meet certain criteria in order to be utilized as a catalyst, including having crystalline characteristics and stability. The Z catalyst exhibits crystalline characteristics, and it is anticipated that ion exchange and the creation of Bronsted acid sites will take place following treatment with sodium silicate (Si enrichment) and acid (HF, HCl, NH₄Cl) (ZSiA catalyst). Therapy utilizing As seen in Figure 10, the ZSiA catalyst's surface still exhibits crystalline characteristics when Ni metal is impregnated into it.

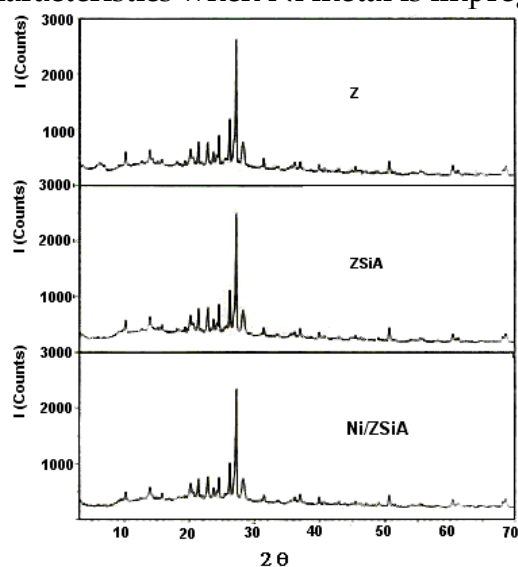


Figure 8. Diffractogram of Z, ZSiA, Ni/ZSiA Catalysts

Table 3 indicates that quartz, clinoptilolite, and mordenite are among the various forms of natural zeolite that are utilized as a carrier for the active metal Ni (ZSiA). This was demonstrated by comparing the natural zeolite sample with the normal natural zeolite's XRD diffractogram pattern, as reported by Treacy and Higgins (2001).

Table 3. Identification of the Position of the Diffraction Angle (2θ) in the XRD Diffractogram of Catalysts Made with Standard Natural Zeolites

| Types of zeolites | 2θ | |
|-----------------------|--|--|
| | Natural zeolite samples | Natural zeolite according to Treacy and Higgins (2001) |
| <i>Mordenite</i> | 6,54; 13,81; 18,03; 24,42; 25,64; 25,99; 27,00; 35,58; 36,90; 39,83; 45,33; 47,91; dan 48,70 | 6,51; 13,83; 18,19; 24,43; 25,63; 26,04; 27,09; 35,61; 36,87; 39,82; 45,28; 47,97; dan 48,70 |
| <i>Clinoptilolite</i> | 19,19; 20,40; 22,38; 25,32; 25,99; 28,08; 29,81; 36,22; 45,34; dan 48,92 | 19,10; 20,40; 22,36; 25,35; 26,04; 28,15; 29,79; 36,19; 45,38; dan 48,92 |
| <i>Quartz</i> | 20,86; dan 26,70 | 20,86; dan 26,65 |

Table V.2 illustrates how the resultant catalyst's intensity rose from Z to ZSiA. This is because of the addition of Na₂SiO₃, the activation procedure using HCl and NH₄Cl solutions, and the heating at 500 oC. The crystallinity increased as a result of this circumstance, going from 300, 1429, and 259 to 342, 1560, and 284.

Table 4. Intensity Diffractogram with the Largest Peak from the Resulting Catalyst

| 2θ (degrees) | d (Å) | Type | Intensity (counts) | | |
|------------------------|----------|-----------------------|--------------------|------|---------|
| | | | Z | ZSiA | Ni/ZSiA |
| 24,39 | 2,26 | <i>Mordenite</i> | 300 | 342 | 264 |
| 25,99 | 2,99 | <i>Clinoptilolite</i> | 472 | - | - |
| 26,70 | 3,18 | <i>Quartz</i> | 270 | 200 | 164 |
| 27,00 | 3,30 | <i>Mordenite</i> | 1429 | 1560 | 1411 |
| 28,08 | 3,34 | <i>Clinoptilolite</i> | 259 | 284 | 253 |
| 29,82 | 3,43 | <i>Clinoptilolite</i> | 192 | - | - |
| 39,83 | 3,65 | <i>Mordenite</i> | 161 | 95 | 105 |

2. Metal Content in the Resulting Catalyst

As seen in Figure 11, the Ca and Fe metal content decreased during the calcination treatment and Si enrichment of the zeolite up to the acid treatment. There was a slight but not particularly noticeable rise in the Ca and Fe concentration on the Ni/ZSiA catalyst.

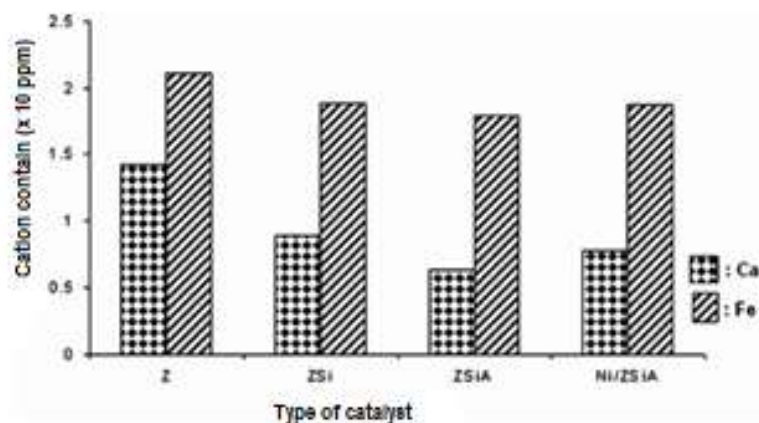


Figure 9. Ca and Fe Metal Content of Various Types of Catalysts, Z: Zeolite Catalyst, ZSi: Zeolite Catalyst Enriched with Si (Na_2SiO_3), ZSiA: ZSi Catalyst Treated with Acid, Ni/ZSiA: ZSiA Catalyst Impregnated with Ni Metal

The performance of the resulting catalyst may be hampered by the uncontrolled presence of metals including Ca, Fe, Na, and Mg (Harber, 1991). Before being used as a carrier for Ni metal in the metal/bearing system catalyst preparation, zeolite is acid treated to reduce or eliminate the presence of metals such as Ca, Fe, Na, and Mg that are not desired as catalysts (Lestari, 2010). This is done in order to allow the maximum quantitative amount of Ni metal to be impregnated. Using ion exchange methods, 2 M HCl is the acid used to prepare the metal/bearing system catalyst, which seeks to dissolve the metals in the zeolite and create Bronsted acid sites. (1980, Satterfield). Figure 12 shows an illustration of the exchange of metal ions, M^+ with H^+ .

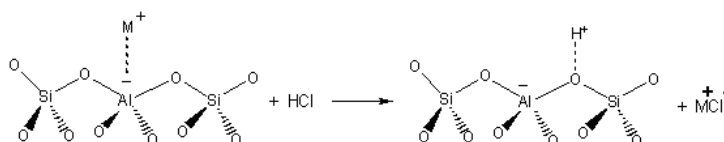


Figure 10. Exchange of M^+ ions (Metal ions) with H^+ ions in Zeolite

The study's findings demonstrate that, as shown in Figure 12, acid treatment with 2 M HCl led to a decrease in the zeolite's Ca and Fe metal content by ion exchange. An indication of a decline in other impurity metals, such as Mg, K, Na, and Fe, was the zeolite's declining Ca and Fe metal concentration in this investigation.

3. Acidity of Resulting Catalyst

It is clear from Figure 13 why acid treatment causes an increase in acidity after Na_2SiO_3 treatment. The creation of Bronsted acid sites on the zeolite surface by ion exchange is indicated by the increase in acidity. Ni metal impregnated with $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ salt exhibits a reduction in acidity. The presence of Ni metal is probably what caused the transition from a Bronsted acid site to a Lewis acid site, and the acid strength of the Bronsted acid site is higher than that of the Lewis acid site.

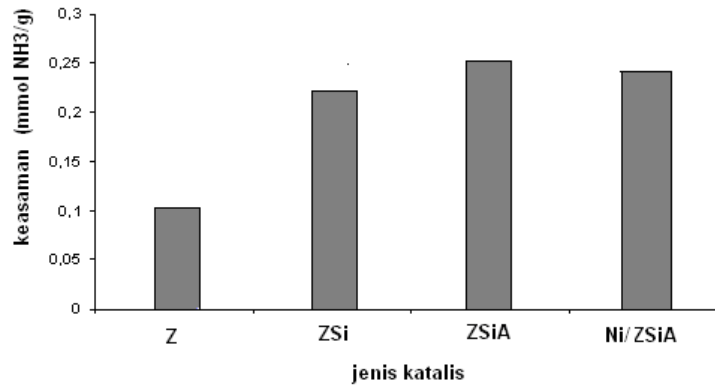


Figure 11. Acidity of Some Resulting Catalysts

Z : Zeolite Catalyst,
 ZSi: Zeolite Catalyst Enrichment with Si,
 ZSiA: ZSi Catalyst Treated with Acid,
 Ni/ZSiA: ZSiA Catalyst Impregnated with Ni Meta

As per Satterfield (1980) and Van Santen (1995), the number of moles of base (ammonia) absorbed by Bronsted acid sites and Lewis acid sites per gram on the catalyst surface is the catalyst's acidity, or acid quantity. Satterfield (1980) states that the higher the catalyst acidity, the more ammonia base that can be adsorbed on the catalyst surface

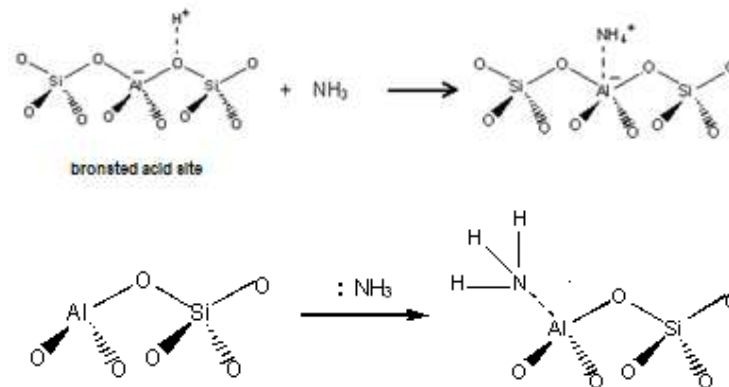


Figure 12. Chemisorption of Ammonia on the Zeolite Surface in Determining Catalyst Acidity

Decaionization and dealumination increase the thermal stability of zeolite in its employment as a catalyst at high temperatures, whilst the acid strength of a catalyst is explained as the catalyst's surface's capacity to adsorb reactants (organic compounds). Acid (HF, HCl, and NH₄Cl) is applied to the zeolite, which serves as a catalyst and a carrier for Ni metal. The release of metals from the zeolite surface, including Na, Ca, Fe, K, and Mg, as well as dealumination processes, which include the release of Al from the zeolite framework, are affected by this acid treatment. Satterfield (1982) asserts that the acidity of the catalyst directly correlates with its activity in catalytic reactions involving organic compound reactants. Specifically, a catalyst's capacity to change reactant molecules into products by forming carbonium ions as bridges during isomerization, cracking, and polymerization processes. The acid site is situated

on either the Lewis or Bronsted acid sites. Acid treatment (HF, HCl, and NH₄Cl) can raise the acidity of the zeolite catalyst.

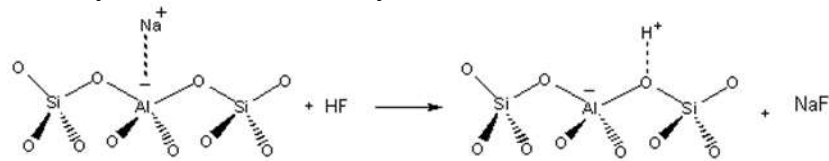


Figure 13. Exchange of Metal Ions (Na⁺) when Treating Zeolite with 2 M HF

The quantitative rise in ammonia chemisorption on the catalyst surface characterizes the increase in acidity. Increasingly acidic catalysts are particularly helpful when hydrocracking events are used to split lengthy hydrocarbon chains into shorter ones (Satterfield, 1982)

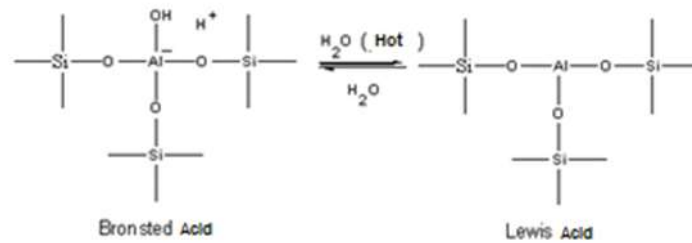


Figure 14. Equilibrium of Bronsted Acid Sites and Lewis Acid Sites (Satterfield, 1982)

The increase in acidity is characterized by a quantitative rise in ammonia chemisorption on the catalyst surface. Catalysts that are getting more and more acidic are very useful when hydrocracking events are employed to break long hydrocarbon chains into shorter ones (Satterfield, 1982).

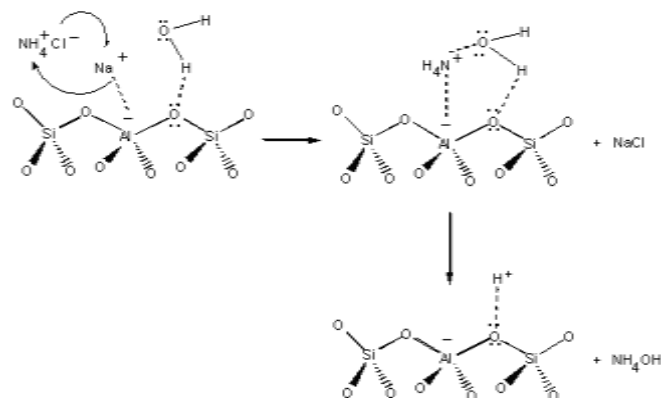


Figure 15. Formation of Bronsted Acid Sites

The existence of Lewis and Bronsted acid sites, which are in equilibrium, determines the acidity of zeolite as a catalyst. The carbon chain in the adsorbed bond will be broken by the acid site's interaction with the electron cloud in the carbon chain bond.

Si/Al Ratio and Catalyst Dealumination Results

As seen in Figure V.10 (19), an increase in the Si/Al ratio represents the release of Al within the framework (Al framework) into Al outside the framework. When acid is treated with HF or HCl in the zeolite, the Al framework also becomes Al outside the framework because the presence of Al in the zeolite framework carries a negative charge that is stabilized by the presence of metal ions such as Na⁺, Ca²⁺, K⁺, Mg²⁺, Fe³⁺, or H⁺ ions. has an immediate effect on lowering the zeolite's metal ion content. In order to create the Ni/ZSiA catalyst, Figure V.9 (18) depicts an increase in the Si/Al ratio during the treatment stage with HF, Na₂SiO₃, HCl, and NH₄Cl. However, this increase is not really important. The acid treatment with HF 2 M, HCl 2 M, and NH₄Cl 2 M is what caused the increase in the Si/Al ratio. The zeolite becomes increasingly non-polar as the Si/Al ratio rises, and the more non-polar the zeolite is, the easier it will interact with chemicals. inert (Twaiq, 2003). It is often appropriate to utilize zeolite with a comparatively higher Si/Al ratio as a catalyst in the hydrogenation reaction of methyl 9-octadecenoate, 1-octadecanol, and 1-octadecene.

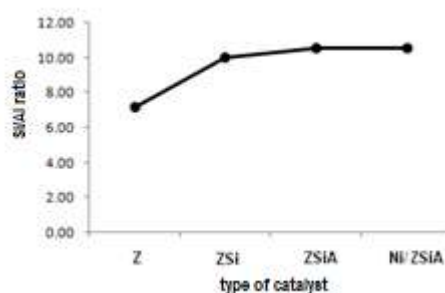


Figure 16. Si/Al Ratio of Various Types of Catalysts, Z: Zeolite Catalyst, ZSi: Zeolite Catalyst Enriched with Si, ZSiA: ZSi Catalyst Treated with Acid, Ni/ZSiA: ZSiA Catalyst Impregnated with Ni Metal

Figure 16 shows a modest (0.19%) but non-significant drop in the Si/Al ratio on the Ni/ZSiA catalyst type. It is probable that the Si and Al contents of the Ni(NO₃)₂·6H₂O salt do not change much during the impregnation of Ni metal, resulting in a reasonably stable Si/Al ratio for Ni/ZSiA. The Si/Al ratio rises by 40.17% upon the addition of Si metal from the Z catalyst type, converting it to ZSi. More dealumination in the zeolite structure makes the zeolite more non-polar, and non-polar zeolite tends to favor reactants or feeds with non-polar interactions, like methyl 9-octadecenoate, 1-Octadecene and 1-Octadecanol. Zeolite's handling as a catalyst carrier is typically tailored to the kind of feed utilized, taking the feed's polarity into consideration. Augustine (1995) states that raising the Si/Al ratio will affect the acidity and thermal stability of the zeolite, which will allow hydrogenation processes at high temperatures.

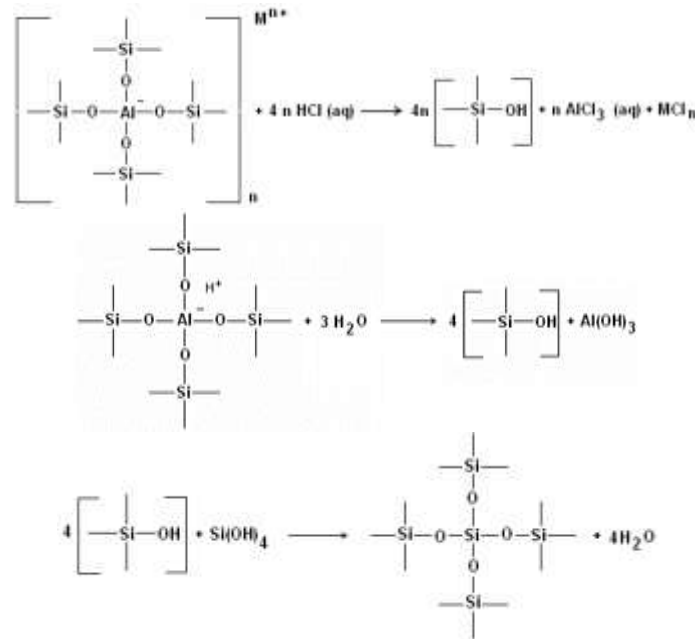


Figure 17. Al Framework Release (Dealumination) in the Zeolite Framework

A catalyst's comparatively high Si/Al ratio makes it ideal for non-polar feedstocks or reactants, according to Twaiq (2003). Low Si/Al catalysts are generally better able to interact with polar reactants. Thermal stability is increased when the Si/Al ratio rises, according to Satterfield (1982). In the meantime, Harber (1991) stated that the activity of a zeolite catalyst is contingent upon several factors, including acidity, surface area, total pore volume, and crystallinity, in addition to the catalyst's Si/Al ratio. Dealumination and hydrothermal processes can raise the Si/Al ratio, which will enhance the thermal stability of the zeolite framework, according to Augustine (1995) and Satterfield (1980). This circumstance can be explained by the fact that the zeolite ring through the Si-O-Al- bond forms a ring with a specific pore diameter that was initially covered by impurities and becomes more open due to the dissolution of the impurities before being treated with acid (HF, Na₂SiO₃, HCl, and NH₄Cl). As demonstrated in Figure 20, the zeolite ring has a more open and comparatively shorter pore diameter following a dealumination event brought on by acid treatment.

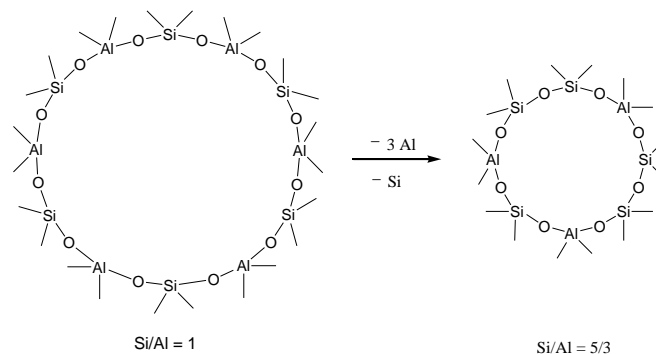


Figure 18. The Release of Al Results in an Increase in the Si/Al Ratio and is Followed by a Decrease in the Zeolite Pore Diameter

Trisunaryanti (1996) states that the concentration of Na^+ , Ca^{2+} , Fe^{3+} , and Mg^{2+} metal ions can be reduced by acid treatment with HF, HCl, and NH_4Cl . While Ni metal was impregnated from $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ salt, there was a minor drop in the Si/Al ratio. The impregnation of Ni metal from the $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ salt was the cause of this drop; a minor amount of Si was liberated from the zeolite framework, resulting in a slight decrease in the Si/Al ratio. As a result, the Si/Al catalyst ratio comparatively increases from Z to ZSiA and Ni/ZSiA catalyst types, indicating that the catalyst is becoming more non-polar and thus more appropriate for the feed employed in the catalytic reaction, specifically methyl 9-octadecenoate, 1-octadecanol, and 1-octadecene.

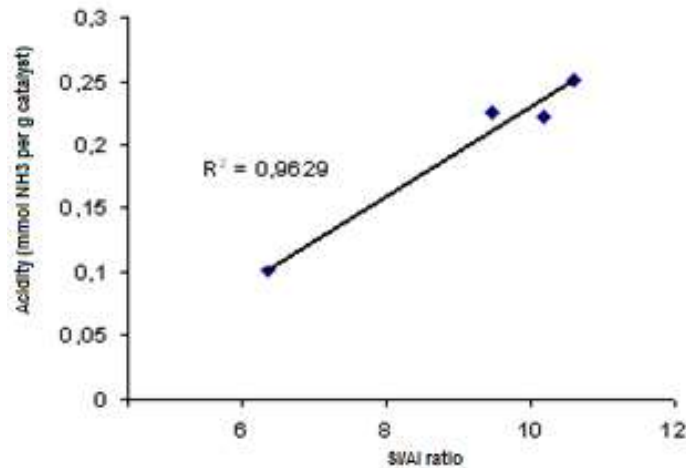


Figure 19. Relationship Between Acidity and Catalyst Si/Al ratio

Hubungan antara keasaman dengan rasio Si/Al seperti Gambar 21. adalah linier. Semakin tinggi rasio Si/Al maka zeolit semakin asam dan semakin bersifat non polar. Zeolit yang semakin asam memiliki indikator semakin banyak ion H^+ yang terbentuk pada permukaan zeolit. Ion H^+ pada permukaan zeolit, yang berarti situs asam Bronsted yang semakin banyak maka kemampuan dalam mengadsorpsi basa amoniak semakin banyak pula.

1. Catalyst Surface Area

The size of the (active) surface within a certain area per weight of catalyst is estimated by a solid's specific surface area. This surface area is supposed to be able to adsorb reactants, causing reactants to collide with the catalyst surface and producing reaction products. It is believed that more products will be created when a catalyst has a higher specific surface area since this increases the number of active surfaces that can interact with the reactants. According to the study's findings, zeolite's specific surface area somewhat reduced following its impregnation with Ni metal. The fact that there is a tiny quantity of buildup but a relatively even impregnation of Ni metal can explain this condition at the pore opening or a portion of the zeolite surface, causing a small decrease in the zeolite's surface area as measured by the BET technique. According to the findings of the AAS analysis, the Ni metal content in the Ni/ZSiA catalyst was 1.06% rather than the desired 2.00%. The success rate of nickel metal impregnation into zeolite samples is thus 53.00%.

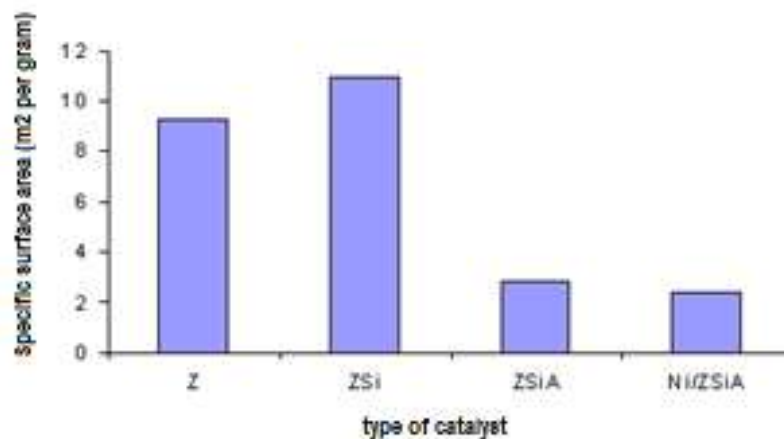


Figure 20. Specific Surface Area of Various Types of Catalysts, Z: Zeolite Catalyst, ZSi: Zeolite Catalyst Enriched with Si, ZSiA: ZSi Catalyst Treated with Acid, Ni/ZSiA: ZSiA Catalyst Impregnated with Ni Metal

It is clear from the study findings displayed in Figure 22 why the catalyst's surface area rises after being treated with Na_2SiO_3 . In the meantime, the catalyst's specific surface area significantly decreases as a result of acid treatment. Damage to the zeolite framework during dealumination may be the reason for the decrease in catalyst surface area, and dealumination-related contaminants may block the catalyst's pores (Figure 23). Because of this, the adsorbed nitrogen gas is unable to penetrate the catalyst's pores during the examination using the BET method, allowing only the catalyst's outer and partially interior surfaces to be observed.

6. Catalyst Pore Size Distribution Frequency

Catalyst pores are classified as follows by Augustine (1995): micropores (less than 0.5 nm), mesopores (1.0 – 3.0 nm), and macropores (more than 5.0 nm). According to Figure 23, the mesoporous region is where the catalyst pores are typically found. The mega pore area has comparatively few pores. The zeolite treated with acid, Na_2SiO_3 , and Ni metal impregnation showed a significant increase in the number of pore sizes in the range of 10 to 20 angstroms, which can be explained by the frequency analysis of the pore size distribution using the NOVA surface analyzer equipment (BET method). The 10 to 20 angstrom region's zeolite pores demonstrate a notable rise in the the range of pore diameters between the Z, ZSi, ZSiA, and Ni/ZSiA catalyst types. The range of 21 to 50 angstroms is also where the number of pore sizes increases; the bigger the pore size, the less the number of pore sizes increases.

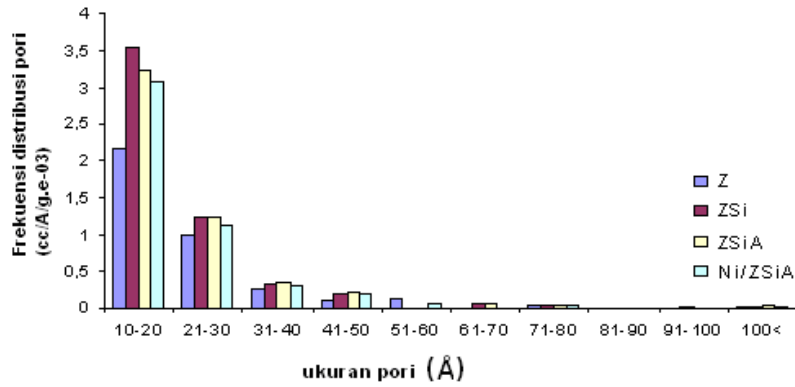


Figure 21. Frequency of Pore Distribution of Various Types of Catalysts, Z: Zeolite Catalyst, ZSi: Zeolite Catalyst Enriched with Si, ZSiA: ZSi Catalyst Treated with Acid, Ni/ZSiA: ZSiA Catalyst Impregnated with Ni Metal

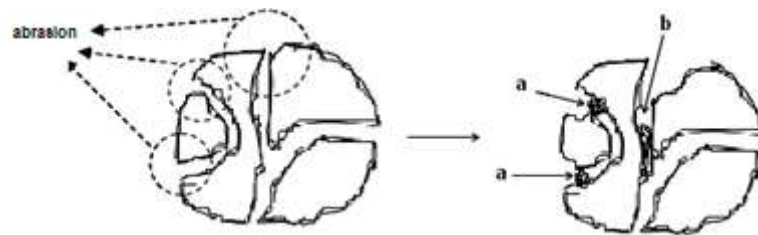


Figure 22. Abrasion in the Pore Mouth Area Causes Closure of (a) the Pore Mouth and (b) the Inner Pore Channel

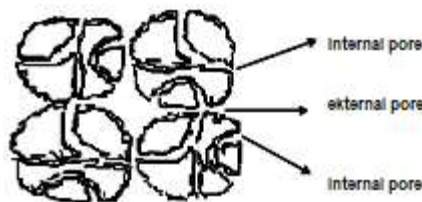


Figure 23. The Existence of Internal and External Pores in Zeolite

When using zeolite as a catalyst, its pores are very helpful in facilitating the adsorption process, particularly physisorption, which brings reactants closer to the catalyst's active sites. Cleaning the zeolite pores in order to maximize the adsorption capacity of the zeolite on the feed is one of the attempts made in this research to boost the activity of zeolite as a catalyst.

When using zeolite as a catalyst, its pores are very helpful in facilitating the adsorption process, particularly physisorption, which brings reactants closer to the catalyst's active sites. Cleaning the zeolite pores in order to maximize the adsorption capacity of the zeolite on the feed is one of the attempts made in this research to boost the activity of zeolite as a catalyst.

2. Catalytic Conversion of Methyl 9-octadecenoate to 1-octadecanol with ZSiA catalyst

1. Catalytic Hydrogenation of Methyl 9-octadecenoate

Before being processed using a catalyst, the methyl 9-octadecenoate compound with a boiling point of 351.4 oC was analyzed using GC-MS. The following is a GCMS image of the compound Methyl 9-octadecenoate.

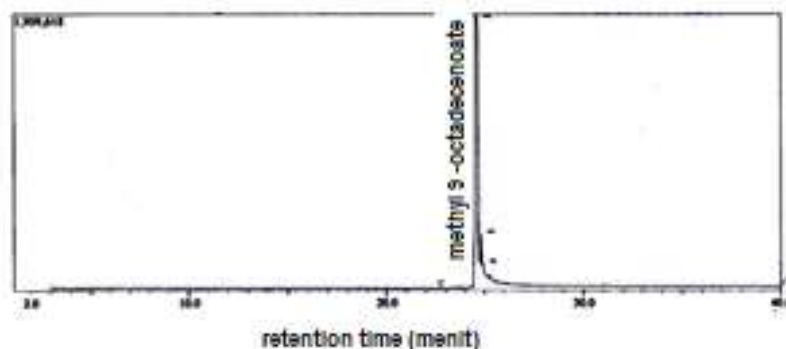


Figure 24. GC-MS Chromatogram of Standard Methyl 9-Octadecenoate Compound

Four main chemicals were identified in the methyl 9-octadecenoate sample's GC-MS chromatogram. The peak that has the highest retention time (tR) is methyl 9-octadecenoate, which has a relative concentration of 91.59%. The peak with the lowest retention time (tR) is methyl octadecanoate, which has a relative concentration of 5.50%, and the peak with the highest retention time (tR) is methyl 9,12-octadecadienoate, which has a relative concentration of 2.51%.

Table 5. Methyl Ester Content Resulting from the Initial Esterification of 9-Octadecenoic Acid (Estimated by Shimadzu QP2010 GC-MS Library Data)

| Compound | tR (m) | Amount (%) |
|------------------------------|--------|------------|
| Methyl 9-octadecenoate | 24,61 | 91,59 |
| Methyl octadecanoate | 24,81 | 5,50 |
| Methyl 9,12-octadecadienoate | 24,91 | 2,51 |
| Amount | | 99,60 |

A fixed bed system reactor used for thermal cracking at 400 oC produced findings identical to those of the original component. methyl 9-octadecenoate thermal cracking GC-MS chromatogram. According to the thermal process results, methyl 9-octadecenoate accounted for 90.93%, indicating its relative dominance. 34.50% of the 1-octadecanol chemical was produced by the catalytic cracking method with a ZSiA catalyst in a fixed bed system reactor that was run at 400 oC, 60 mL/minute of hydrogen flow rate, and 5 g of catalyst weight. Up to 59.11% of the methyl 9-octadecenoate molecule was produced during the remaining catalytic step. This procedure yielded a 36.86% yield.

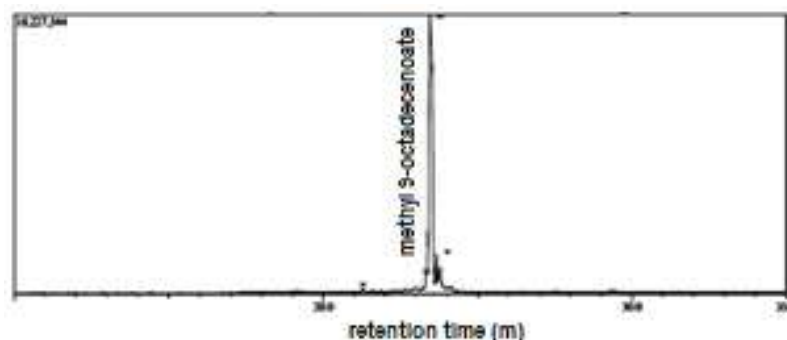


Figure 25. GC-MS Chromatogram of Thermal Cracking Results at 400 oC

The catalytic reaction using the ZSiA catalyst operated with a fixed bed reactor at a temperature of 400 oC and a hydrogen flow rate of 100 mL/minute and a catalyst amount of 5 g apparently did not produce 1-octadecanol product due to the hydrogen flow rate being too fast. When the hydrogen flow rate was reduced to 80 mL/minute and the catalyst weight was 5 g, it turned out that 1-octadecanol product was still not produced. A carrier gas (hydrogen) flow rate that is too fast indicates that the hydrogen contact time with the catalyst is too short resulting in no interaction between the catalyst surface and the compound being fed. Likewise, at a hydrogen flow rate of 80 mL/minute, the interaction between hydrogen and the catalyst surface is still too fast.

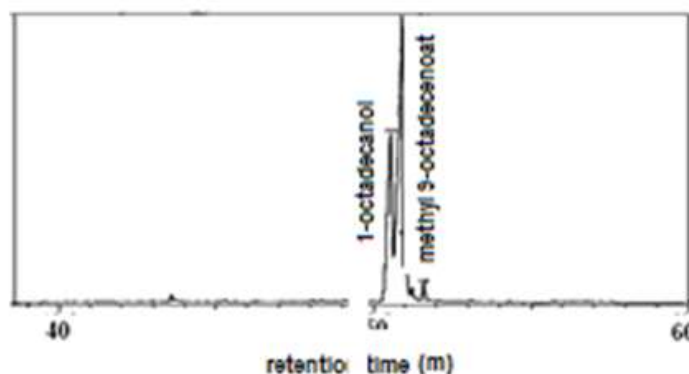


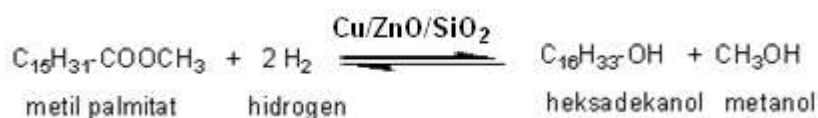
Figure 26. GC-MS Chromatogram of the Catalytic Hydrogenation Product of Methyl 9-Octadecenoate at a Temperature of 400 oC for 60 Minutes with a Hydrogen Flow Rate of 60 mL/minute

Based on Figure 26, the compound 1-octadecanol at a pressure of 760 mmHg has a boiling point of 336 oC and methyl 9-octadecenoate at a pressure of 760 mmHg has a boiling point of 351.4 oC. Based on the difference in boiling point and the semipolar column, 1-octadecanol comes out of the column first compared to methyl 9-octadecenoate.

Table 6. Several Products Resulting from the Catalytic Hydrogenation of Methyl 9-octadecenoate with a 5 gram ZSiA Catalyst and an H₂ Flow Rate of 60 mL/minute (Estimated Shimadzu QP2010 GC-MS Library Data)

| Compound name | tR (menit) | Amount (%) |
|----------------------|---------------|------------|
| 1-oktadekanol | 50,62 | 34,50 |
| Metil 9-oktadekenoat | 50,95 | 59,11 |
| Amount | | 93,61 |

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 beds 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.

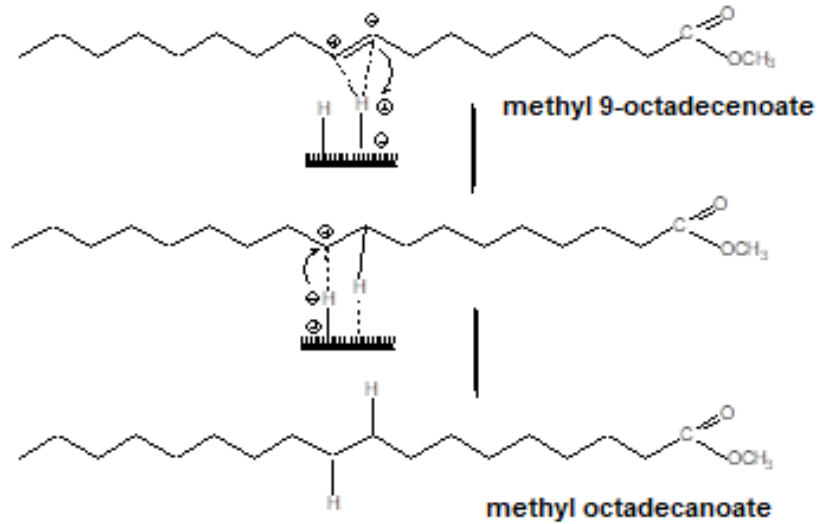
Table 7. Some Products Result from Thermal Cracking of 9-Methyl Octadecenoate

| | |
|--------------|--------|
| 7 | 0,301 |
| C14 FAME | 1,166 |
| C16 FAME (0) | 41,214 |
| C16 FAME (1) | 0,030 |
| C18 FAME (0) | 3,655 |
| C18 FAME (1) | 38,914 |
| C18 FAME (2) | 12,176 |

The results of research carried out in the laboratory produced 34.50% of the 1-octadecanol compound at a temperature of 400 oC and a hydrogen flow rate of 60 mL/minute and 5 g of catalyst. This situation is caused by the reaction system being very different from research conducted by Zhilong (2007) and Brands (2002). Some of the differences in these reaction systems are:

1. The research does not use supercritical conditions with very high pressures (9 and 15 MPa).
2. Do not use propane or butane solvents in the reaction system.

Up to 34.50% of the initial 91.59% methyl 9-octadecenoate was transformed into 1-octadecanol. It is believed that there are two steps in the reaction process of methyl 9-octadecenoate to 1-octadecanol in this reaction system. First, methyl 9-octadecenoate is adsorbed on the catalyst surface via the Bronsted acid site interacting with the double bond at C number 9. The double bond then opens (an addition reaction takes place) in accordance with the reaction mechanism described by Horiuti-Polanyi in Campbell (1988).



According to the process below, the second step involves reducing ester groups to alcohol groups to produce 1-octadecanol (Fessenden and Fessenden, 1986). The feed might go through both phases as it goes past the cataly

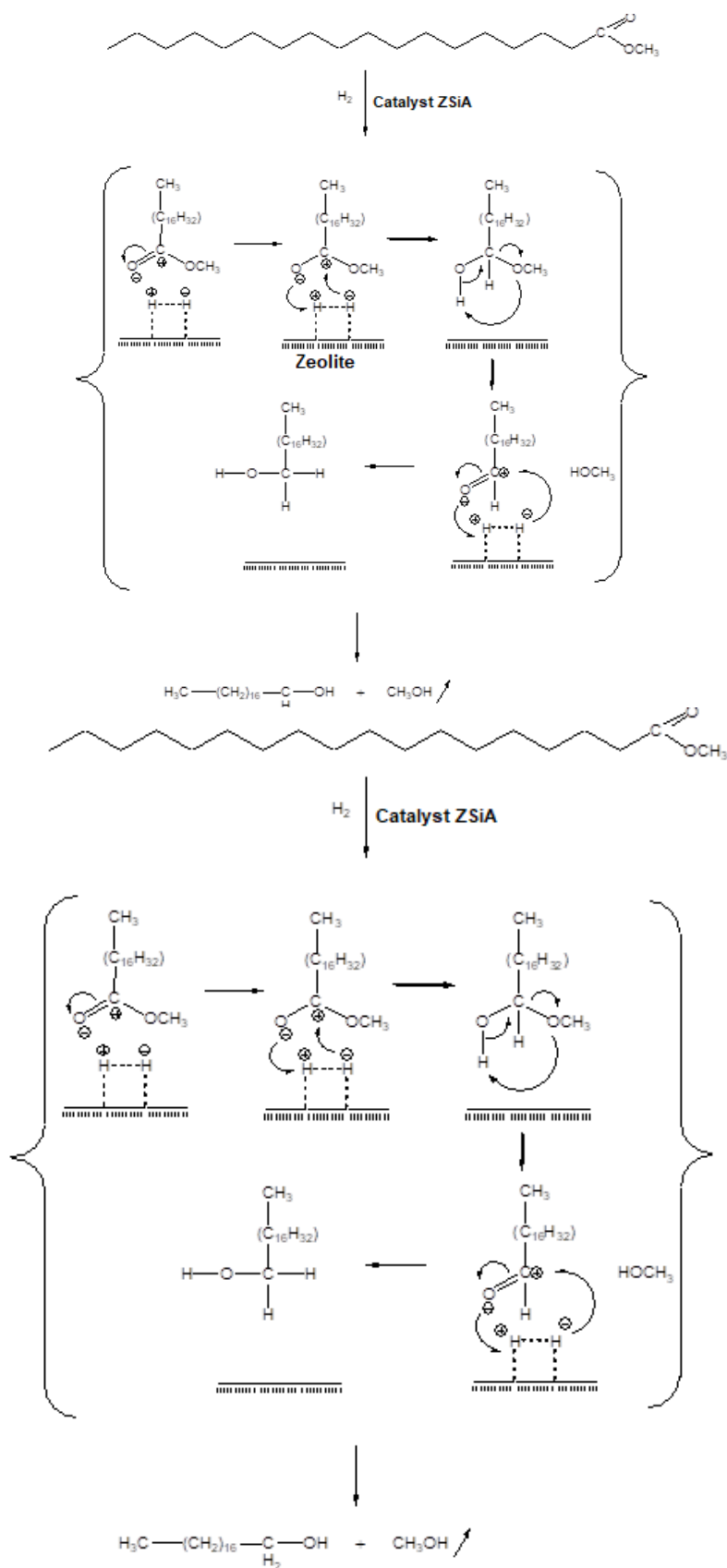


Figure 27. Reduction of Methyl-9-Octadecanoate To 1- Octadecanol

2. Growth of 1-octadecanol Products on Variations in Catalyst Weight and Hydrogen Flow Rate

Catalytic hydrogenation of methyl 9-octadecenoate was carried out by placing 5 g of methyl 9-octadecenoate into an evaporator equipped with a flow of hydrogen gas as a carrier gas with varying flow rates of 20, 40 and 60 mL/minute. A number of ZSiA catalysts weighing 5, 10 and 15 g were placed in a fixed bed reactor column which was heated to a temperature of 400 oC for 30 minutes. The product was collected in a bottle, then the product resulting from the catalytic hydrogenation reaction was analyzed by GC-MS and presented in Figure 30.

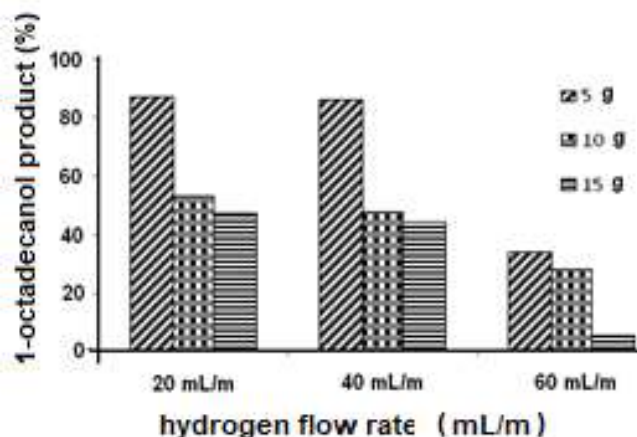
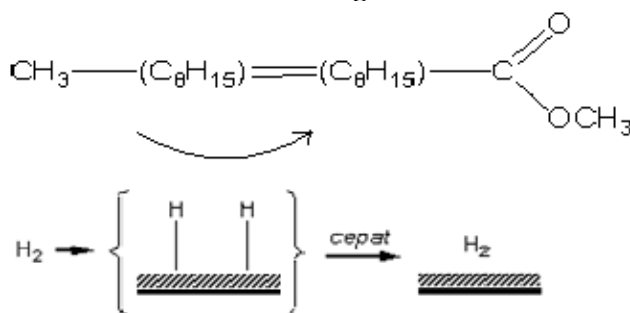


Figure 28. Obtaining 1-Octadecanol Product from Variations in Hydrogen Flow Rate and Catalyst Weight Variations at a Temperature of 400 oC

Based on Figure 30, it can be explained that the catalytic hydrogenation reaction of methyl 9-octadecenoate at a temperature of 400 oC using a ZSiA catalyst shows that the product of the 1-octadecanol compound decreases with increasing hydrogen flow rate and increasing catalyst weight from 5, 10 and 15 g. The increase in catalyst weight and increase in hydrogen gas flow rate shows that the interaction between the catalyst surface and hydrogen shows a dominant influence, so that the interaction between methyl 9-octadecenoate and hydrogen on the catalyst surface occurs in a relatively short time. The shorter the interaction of hydrogen with methyl 9-octadecenoate causes the interaction between hydrogen and methyl 9-octadecenoate to become weaker and the probability of the product 1-octadecenoate also becoming smaller.



This situation causes a quantitatively greater hydrogen flow rate, indicating that less 1-octadecanol is produced. In this reaction, the rate of hydrogen dissociative adsorption is the rate determining step, the more hydrogen is adsorbed, the greater the probability of the reaction occurring.

As the weight of the catalyst increases (5, 10 and 15 grams), the amount of 1-octadecanol compound produced decreases. This decrease is due to the greater the number of catalysts, the higher the catalyst density, so that the path through which the feed (methyl 9-octadecenoate) passes becomes increasingly obstructed due to the density of the catalyst placed in the column. Density can be illustrated as a mean free path with the external pore diameter changing relatively when a small amount of catalyst is added compared to when a larger amount of catalyst is added. This situation is likely that the product is blocked in the catalyst, so that the product produced from the catalytic hydrogenation process of methyl 9-octadecenoate, the greater the amount of catalyst added, the less product produced.

With a larger amount of catalyst (dy) compared to a smaller amount of catalyst (dx) and at a constant hydrogen flow rate, the catalytic hydrogenation reaction of methyl 9-octadecenoate produces less 1-octadecanol product. This situation is likely caused by the increasing number of catalysts (dy) in a fixed reactor diameter and the amount of reactant (R) being supplied remains the same, causing the movement of reactants to become relatively slower or inhibited ($dR/dy < dR/dx$) as illustrated in Figure 31 This situation is likely to cause the interaction of the reactants to take a relatively long time, causing the reactants or reaction products to be adsorbed too strongly so that they can contaminate or poison the surface of the catalyst.

Adsorption that is too strong can be caused by the increasing number of catalysts in a fixed reactor diameter causing the catalyst density to increase. When the catalyst density increases because the number of catalysts is relatively large and the number of reactants remains constant, relatively fewer reaction products are produced

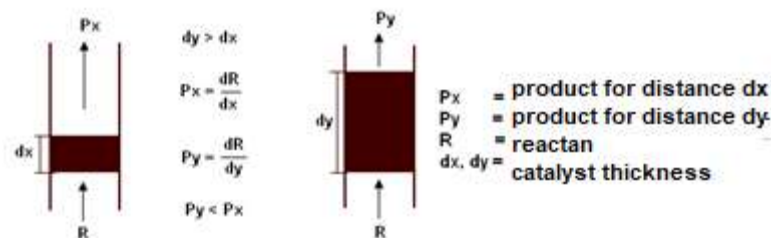


Figure 29. The Relationship Between the Amount of 1-octadecanol Product and the Amount of ZSiA Catalyst Used

According to Satterfield (1982), space time yield (STY) is defined as the amount of product per unit time and per unit reactor volume. In a fixed reactor volume unit, the greater the unit of time given, the less product produced per unit of time (STY).

$$STY \text{ (space time yield)} = \frac{\sum \text{product}}{\text{time} \cdot \text{volume of reactor}}$$

Obtaining products from the catalytic hydrogenation process of methyl 9-octadecenoate, the more catalyst is given, the resulting product is relatively small. The greater the hydrogen flow rate given to the reaction system, the less product produced. The contact time of the catalyst with the methyl 9-octadecenoate compound is too fast and even though the amount of catalyst added is greater, the product produced is quantitatively less.

3. Catalytic Hydrogenation Reaction of 1-octadecanol

The 1-octadecanol compound was hydrogenated in a fixed bed system reactor using 10 g of ZSiA catalyst and 10 g of pure 1-octadecanol compound as the reactant weight at 400 oC. The physical characteristics of pure 1-octadecanol compound are as follows: it is a solid with the chemical formula C₁₈H₃₈O, a content of 95%, a boiling point of 336 oC, a density of 0.81 g/mL, and a melting point of 58 oC. Prior to utilizing the ZSiA catalyst for the catalytic hydrogenation procedure, GC-MS analysis was performed on the standard 1-octadecanol molecule. Using GC-MS equipment, the analysis's findings demonstrated that the substance 1-octadecanol was found at a retention time of 23.33 minutes and is as seen in Figure 32.

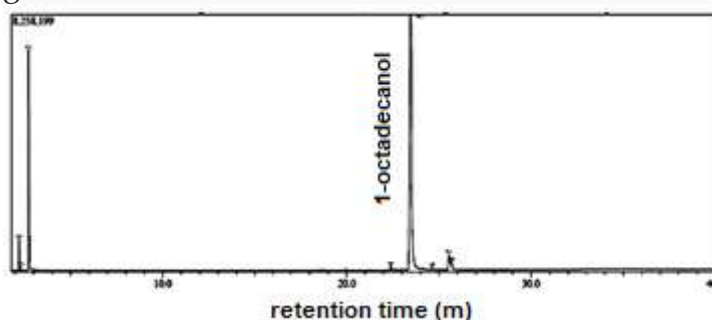


Figure 30. GCMS Chromatogram of the Compound 1-Octadecanol

Figure 32's GC-MS chromatogram demonstrates that the yield of the 1-octadecanol that was found was 70.65%. This is because the amount of 1-octadecanol calculated was reduced by the solvent percentages of 1.75% (1) of diethyl ether and 23.11% (3) of chloroform. If the solvent is not included in the calculation or is not visible in the GCMS analysis, the percentage of 1-octadecanol can reach 95%. Many compounds with chains shorter than C:18 were generated as thermal products at 400 oC from 1-octadecanol. The conversion of the 1-octadecanol molecule is relatively substantial, i.e., larger than 50%, or the percentage of compounds having a chain length shorter than C:18 is relatively large.

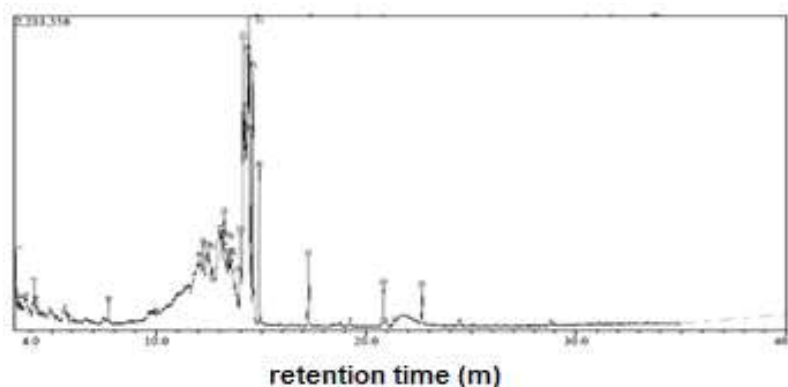


Figure 31. Thermal Process GCMS Chromatogram of 1-Octadecanol

Figure 33 displays the GC-MS chromatogram of the 1-octadecanol compound's thermal cracking results. Table 6 displays the results of thermal cracking of the 1-octadecanol complex. The compound 9-octadecene (12.60%) is the predominant product.

Table 8. 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)

| Compound Name | SI | tr (m) | amount (%) |
|---------------|----|--------|------------|
| 4-dodecene | 96 | 3,28 | 1,50 |
| 5-tetradecene | 95 | 4,18 | 0,83 |
| Pentadecane | 96 | 7,72 | 0,62 |
| Hexadecane | 95 | 12,23 | 0,51 |
| 7-hexadecene | 95 | 14,01 | 3,88 |
| 1-octadecene | 97 | 14,14 | 12,60 |
| 3-octadecene | 96 | 14,34 | 9,45 |
| 5-octadecene | 97 | 14,67 | 8,68 |
| Octadecane | 96 | 22,65 | 1,13 |
| Amount | | | 39,20 |

Numerous product chemicals are seen in the GC-MS chromatogram obtained from the analysis of the byproduct of the catalytic hydrogenation reaction of 1-octadecanol with the ZSiA catalyst. As indicated in Table 7, the result of catalytically hydrogenating 1-octadecanol with a ZSiA catalyst at 400 oC yields alkane and alkene compounds up to C18, which reaches 49.60% of the chain length. and with a relative concentration of 20.21%, 1-octadecene is the predominant chemical generated

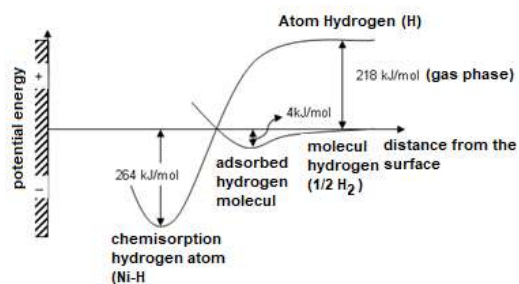


Figure 32. Energy Potential Diagram (Campbell, 1988)

The quantity of hydrogen on the catalyst surface decreases quantitatively as a result of less pressure-induced adsorption of hydrogen, which is less than ideal. This lowers the likelihood of collisions between the adsorbed hydrogen and the 1-octadecanol functional group, resulting in 49.60% of the alkane and alkene products. If the collision process begins with physisorption and progresses through chemisorption, it can happen more readily..

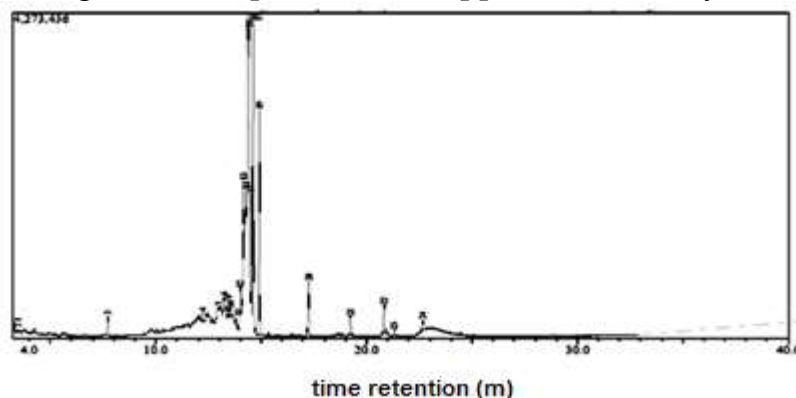


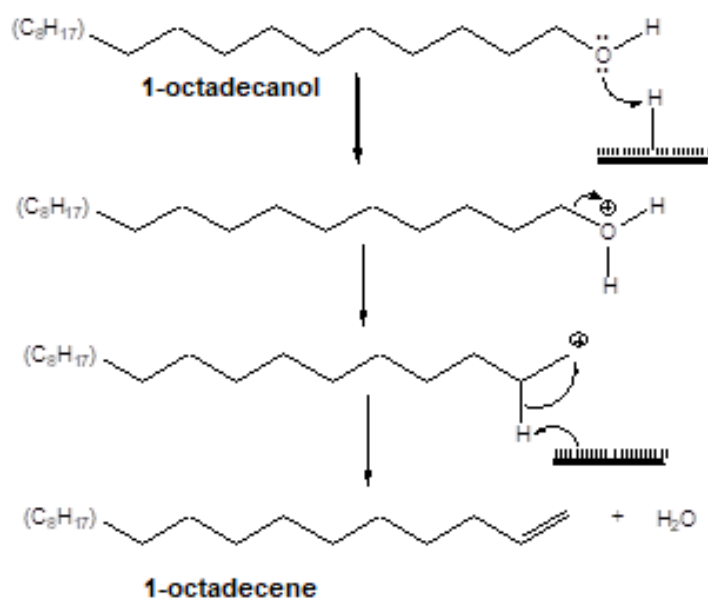
Figure 33. GC-MS Chromatogram of the Hydrogenation Reaction of 1-Octadecanol with ZSiA Catalyst at a Temperature of 400 oC

Alkene compounds are typically produced via the catalytic reactions of alcohol compounds at rather high temperatures, according to Groggins (1952). Campbell (1988) states that alkane compounds are produced via catalytic hydrogenation of alkene molecules using the "Horiuti-Polanyi" mechanism. Many alkene and alkane compounds are generated in the catalytic hydrogenation reaction of 1-octadecanol with a ZSiA catalyst at 400 oC.

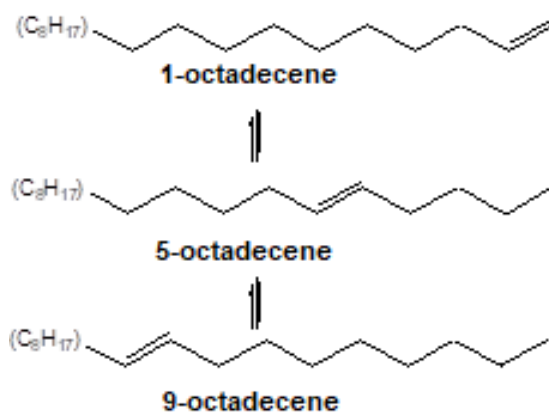
Table 9. The Product of the Catalytic Hydrogenation Reaction of 1-octadecanol Compounds Becomes Alkane and Alkene Compounds with a Chain Length < C18 at a Temperature of 400 oC (Estimated by Shimadzu GC-MS QP2010 Library Data)

| Compound name | t_R (m) | Amount (%) |
|---------------|-----------|------------|
| 5-dodecene | 3,28 | 0,23 |
| Heptadecane | 7,73 | 0,80 |
| Pentadecane | 12,23 | 0,30 |
| 7-hexadecene | 14,01 | 3,29 |
| 9-octadecene | 14,15 | 10,40 |
| 1-octadecene | 14,38 | 20,21 |
| 5-octadecene | 14,63 | 14,37 |
| Amount | | 49,60 |

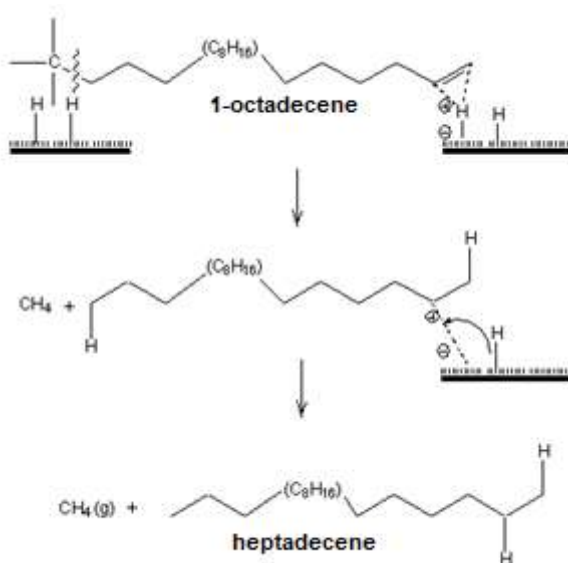
When 1-octadecanol was hydrogenated using a ZSiA catalyst in a fixed bed reactor at 400 oC, 49.60% of the alkane and alkene products with a chain length less than C18 were generated. It is believed that there are two primary steps in the catalytic hydrogenation mechanism of 1-octadecanol: the reduction of the alcohol group to an alkene and the breaking of the alkene bond to create shorter chain alkanes and alkenes. The following is the mechanism:



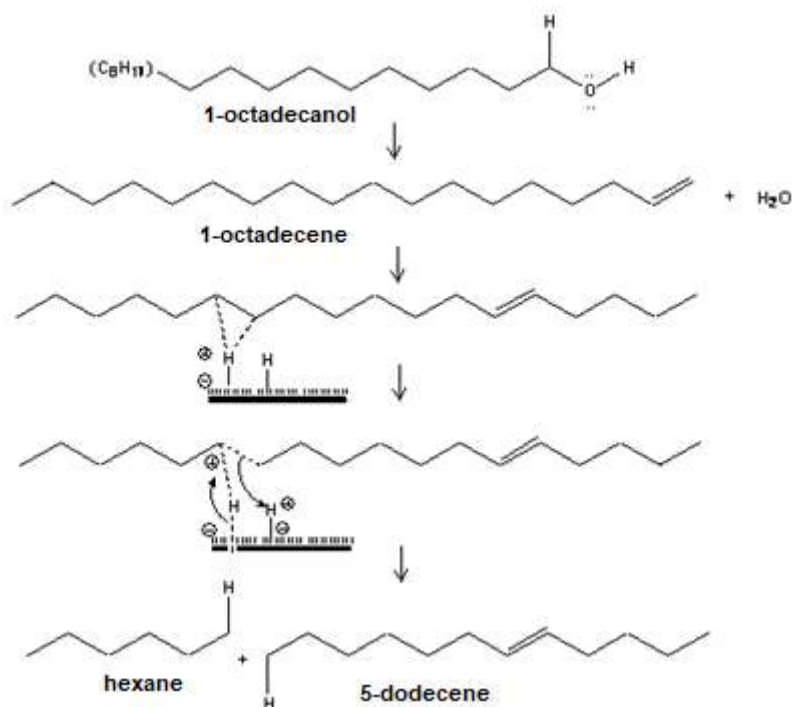
According to Campbell (1988), the 1-octadecene compound then forms its isomers, namely 5-octadecene and 9-octadecene with relative concentrations of 14.37 and 10.40%.



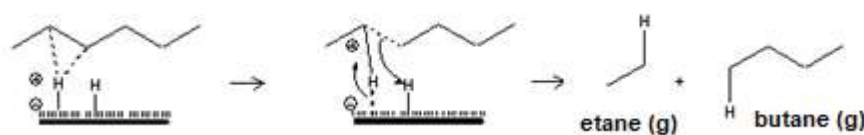
Furthermore, the compounds 1-octadecene, 5-octadecene and 9-octadecene undergo further cracking to form shorter alkane and alkene compounds.



The mechanism of the compound 1-octadecanol to 5-dodecene is thought to follow several stages as follows: dehydration of alcohol, shift of double bonds, breaking of bonds to 5-dodecene and hexane, breaking (hydrogenation) of hexane into smaller compounds (ethane and butane) in the phase gas.



Then hexane decomposes into gaseous compounds or volatile compounds as follows



4. Catalytic Hydrocracking of 1-octadecene with Ni/ZSiA Catalyst

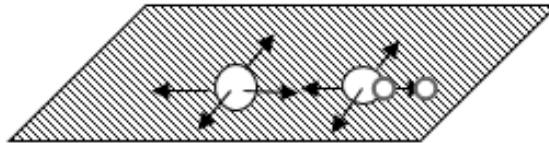
1. Obtaining catalytic hydrocracking reaction products of 1-octadecene with Ni/ZSiA catalyst

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 dissociation of hydrogen adsorption on the Ni surface as a catalyst is illustrated as in Figure 34, namely (1) physical adsorption or physisorption, (2) transition state, (3)) chemical adsorption (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.



Reactants that have been adsorbed on the surface of a solid can experience a "migration" event, namely the movement of molecules in one dimensional plane. Molecules that migrate (in a fixed adsorbed position) are very likely to collide with other molecules.



Thus, the more reactant molecules are adsorbed on the surface of the catalyst solid, the greater the probability of collisions occurring and producing reaction products. Collisions (encounters) between reactant molecules have less energy but occur between active reactant molecules so a lower activation energy is required.

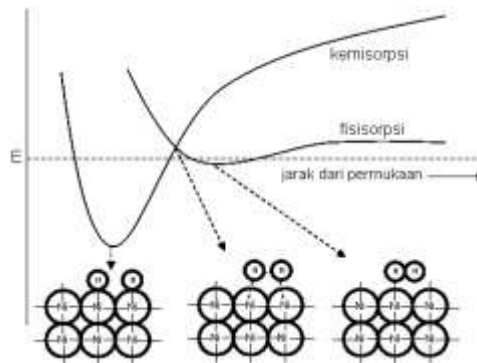


Figure 33. Schematic Illustration of the Hydrogen Adsorption Process on the Ni Catalyst Surface (Bartholomew, 2006)

The adsorption process, both physisorption and chemisorption, of the reactants 1-octadecene and hydrogen reaches an optimum state at a hydrogen flow rate of 10 mL/minute and a temperature of 450 oC. Thus, based on the Horiuty-Polanyi mechanism, the interaction between hydrogen and the double bonds in the 1-octadecene compound on the surface of the catalyst can take place and then the collision takes place effectively. After the addition reaction (opening of double bonds) in the 1-octadecene compound takes place, it is possible for a long chain bond breaking reaction to become a shorter chain.

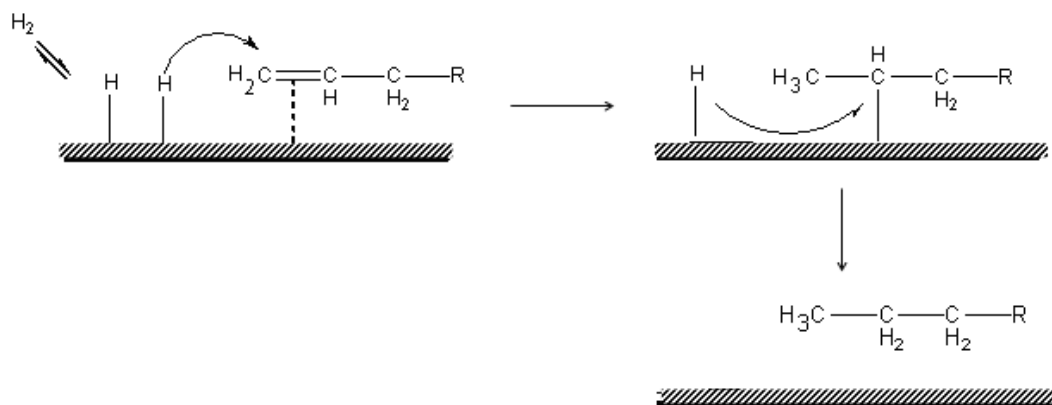


Figure 34. The Hydrogenation Mechanism of 1-Octadecene in Opening the Double Bond is Based on the "Horiuti-Polanyi"

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 35. In the hydrogenation process on the catalyst surface based on Figure V.25a above, the hydrogen flow rate is 10 mL/minute both at temperatures of 400, 450 and 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.

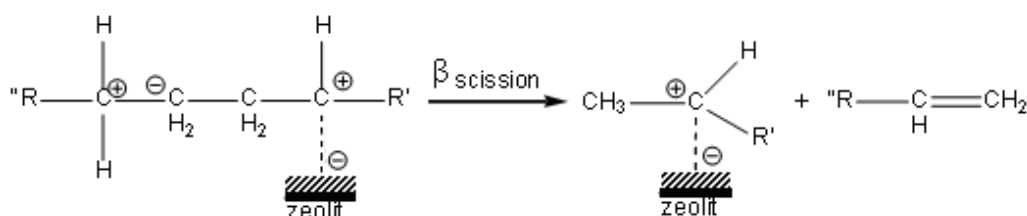


Figure 35. The Interaction of Alkanes on the Catalyst Surface Results in Shorter Chain Alkene Compounds (Campbell, 1988)

The likelihood of an effective collision between the adsorbed hydrogen and the adsorbed 1-octadecene compound on the catalyst surface will increase during the dissociation and migration process. From a kinetic perspective, it makes sense that an increase in the amount of hydrogen adsorbed on the catalyst surface would result in a higher reaction rate constant.

Based on the research findings, it was discovered that when compared to a hydrogen flow rate of 10 mL/minute at a temperature of 400 and 500 oC, namely 4.78 and 9.13%, a temperature of 450 oC had a yield of 19.51%, which is the ideal condition. There are several factors that influence the activity of a catalyst such as: physical and chemical properties of the catalyst (internal factors), such as acidity, specific surface area, Si/Al ratio and metal content (Harber, 1991). the type of reactant fed and the type of carrier gas supplied (Augustine, 1995). environmental conditions such as pressure and reaction temperature (Gasser, 1987). At a higher temperature and constant pressure, the number of reactants (species) that is adsorbed decreases.

According to Gates (1979), the cracking reaction of long carbon chain compounds is endothermic and is preferred at high temperatures. Cracking of long chain hydrocarbons can produce the following compound products: olefins and paraffins (shorter chains), alkyl aromatics through dealkylation and cyclohexane.

The results of GC-MS analysis of the catalytic hydrocracking reaction products of 1-octadecene using the Ni/ZSiA catalyst were grouped into 4, namely: shorter chain alkane compound products (<C12), short chain alkene compound products (<C12), compound products alkanes with bond lengths C13 to C17 and alkene compound products with bond lengths C13 to C17.

Table 10. Alkane Compound Product < C12 from the Catalytic Hydrocracking Reaction of 1-octadecene with a Ni/ZSiA Catalyst at a Temperature of 450 oC, Hydrogen Flow Rate 10 mL/minute, Reaction Time 30 Minutes (Estimated by Shimadzu QP2010 GC-MS Library Data)

| No. | Compound name | retensi (m) | Amount (%) |
|--------|---------------|-------------|------------|
| 1 | dekane | 4,41 | 0,49 |
| 2 | undekane | 6,49 | 1,32 |
| 3 | dodekane | 11,90 | 11,56 |
| Amount | | | 13,37 |

Based on the type of catalytic hydrocracking reaction product of the 1-octadecene compound using a fixed bed system reactor in Table 7, in general the breaking of long carbon chain bonds begins with the opening of double bonds based on the "Horiuti-Polanyi" mechanism which can be depicted as Figure 35.

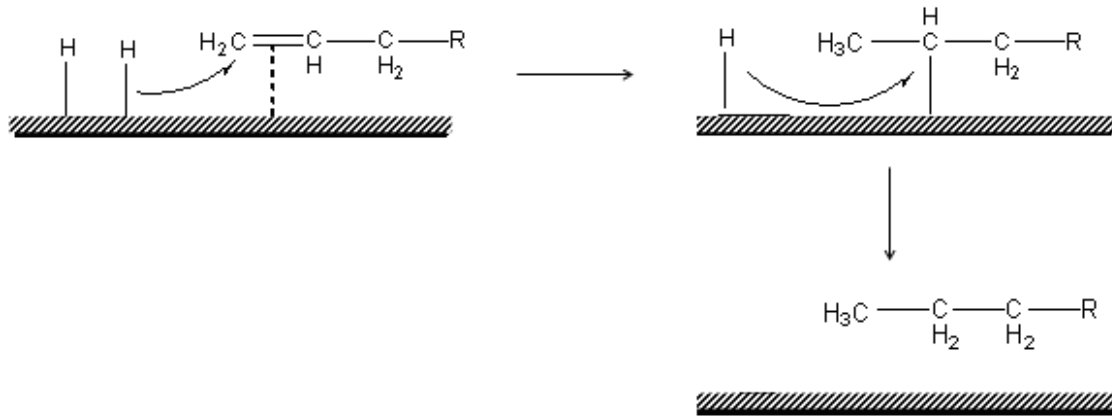
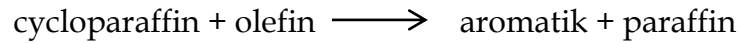


Figure 35. Mechanism of Addition Reactions on the Surface of the Catalyst in the Formation of Long Chain Alkane Compounds

According to Gates (1979), secondary reactions can occur after the initial cracking stage has taken place. Some of the secondary reactions that occur are:

1. Hydrogen transfer reaction



Isomerization



Disproportionation of lighter molecular weight olefins

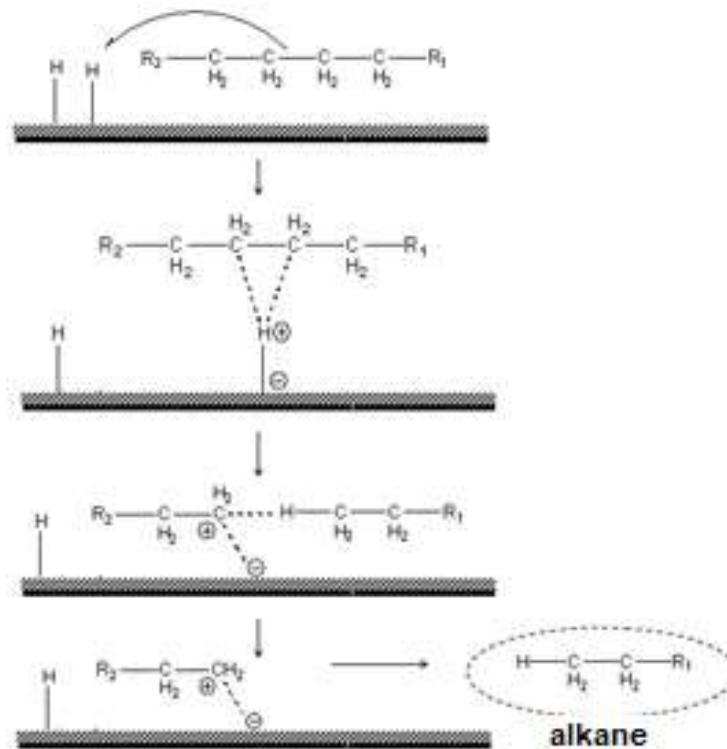


Figure 38. The Mechanism of the Cracking Reaction on the Catalyst Surface to form short Chain Alkane Compounds

According to the feed flow, the breakdown of alkane compounds produced by the interaction between the top layer's catalyst surface and the lower layer's catalyst surface can occur again (Figure V.32). Shorter alkane molecules as well as other types of compounds like cyclic, aromatic, or isomeric forms may arise from this interaction.

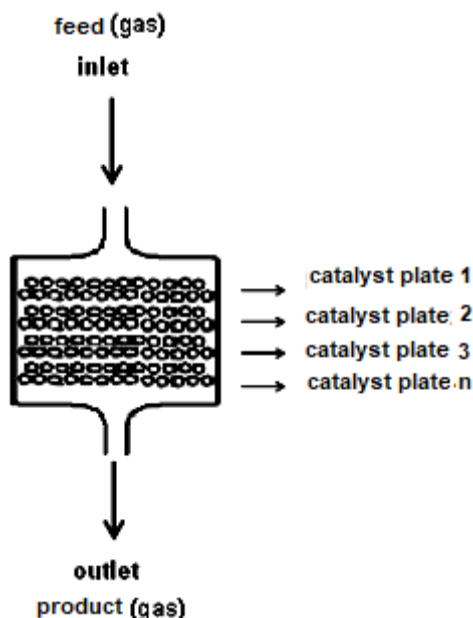


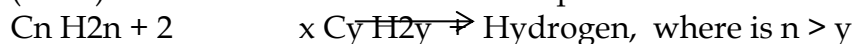
Figure 39. Catalyst Arrangement in the Reactor

At a fixed reactor diameter, the more catalyst used in the 1-octadecene hydrocracking catalytic process, the more often or longer the feed experiences interaction with the catalyst surface. This situation will support the interaction process between the compound being fed (reactant) and the catalyst surface, thus supporting the breaking of bonds, thereby obtaining shorter compounds. Shorter alkene compound products can also be formed alongside shorter alkane compound products.

Table 11. Alkene Compound Product < C12 from the Catalytic Hydrocracking reaction of 1-octadecene with a Ni/ZSiA Catalyst at a Temperature of 450 oC, Hydrogen flow rate 10 mL/m, Reaction Time 30 Minutes (Estimated by Shimadzu QP2010 GC-MS Library Data)

| No. | compound name | retensi (m) | Amount (%) |
|-----|---------------|-------------|------------|
| 1 | 1-undekena | 4,28 | 0,95 |
| 2 | 1-dodekena | 6,29 | 0,67 |
| 3 | 4-dodekena | 11,54 | 0,30 |

Based on the table above, it can be concluded that the process of catalytically breaking the long chain bonds of the 1-octadecene compound produces the majority of alkane compound products with shorter chain lengths (<C12) and reaches 13.37% of the total products obtained.



According to Campbell (1988), the breaking of long chain saturated bonds on the surface of an acid catalyst is generally followed by the formation of double bonds with shorter chain lengths which is called dehydrogenation.

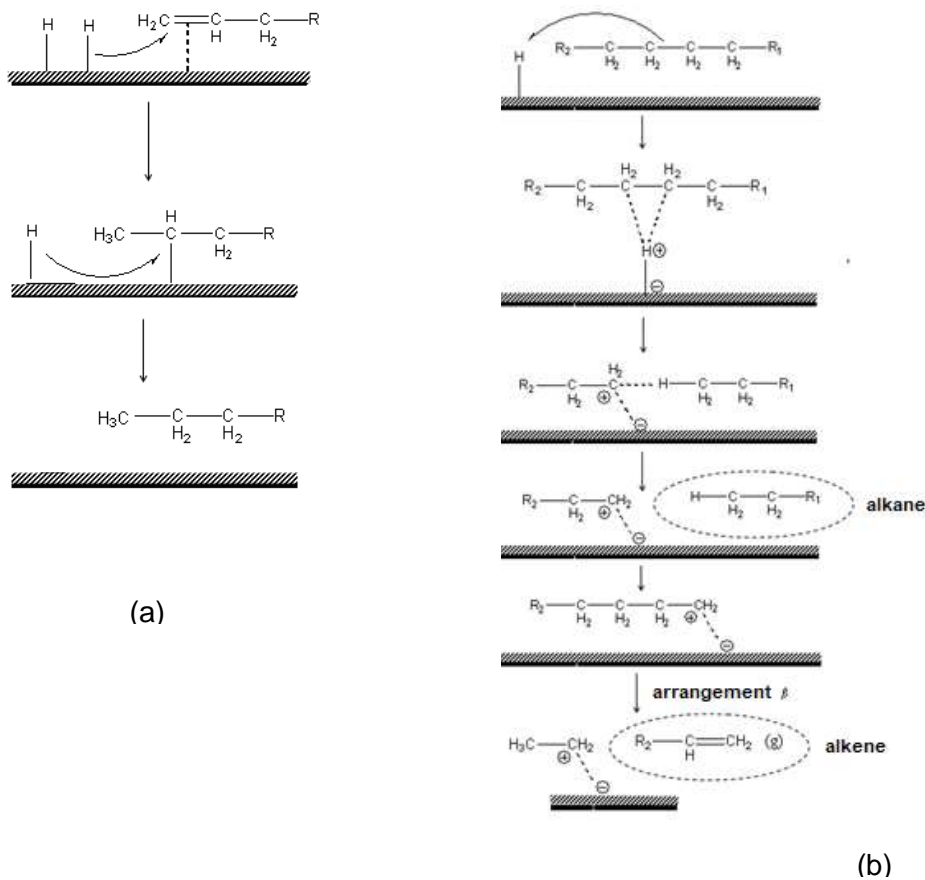


Figure 40. The Competition Mechanism for the Formation of Alkane and Alkene Products on the Catalyst Surface Begins with the Opening of Double Bonds and is Followed by the Breaking of Saturated Bonds

Based on the table above, relatively more alkene products are produced from the 1-octadecene catalytic hydrocracking process compared to alkane products. This situation predicts that the opportunity for interaction between the feed and hydrogen as a reactant is less dominant, so that after the opening of the double bond occurs according to the mechanism according to Horiuti-Polanyi on the surface of the catalyst of the 1-octadecene compound, this is followed by the breaking of the saturated chain bonds and a chain alkene compound is produced. shorter and fewer short chain alkanes.

Based on the description of Figure 36, it can be explained that the cracking reaction event of the 1-octadecene compound with unsaturated long chain bonds will produce a dominant alkene product, while the alkane product that occurs will partially experience a dehydrogenation event to form short chain alkene compounds.

The catalytic hydrocracking reaction of 1-octadecene compound also produces cyclic compound products. According to Gates (1979), cyclization products from cracking reactions can form from olefins to naphtha (naphthenes), where the reaction equilibrium constant at 420 oC is relatively large.



Figure 41. Formation of Saturated Cyclic Compounds (Naphthane) from Alkane Compounds on the Catalyst Surface

According to Gates (1978), the mechanism for the formation of cyclic compounds can generally be explained as in Figure 37. After obtaining good alkane compounds from the interaction of 1-octadecene compounds from the surface of the Ni/ZSiA catalyst in the first catalyst layer, it is predicted that further interactions will occur between the compounds. alkane with the next catalyst surface to obtain a cyclic compound.

Table 11. Product of C13 to C17 Alkane Compounds from the Catalytic Hydrocracking Reaction of 1-octadecene with a Ni/ZSiA Catalyst at a Temperature of 450 oC, Hydrogen Flow Rate of 10 mL/minute, Reaction Time of 30 minutes (Estimated by Shimadzu QP2010 GC-MS Library Data)

| No. | Compound name | t (m) | Amount (%) |
|--------|---------------|-------|------------|
| 1 | Tridekane | 6,49 | 1,32 |
| 2 | Tetradekane | 11,9 | 11,58 |
| 3 | Heksadekanae | 16,84 | 1,89 |
| Amount | | | 14,79 |

The product of the catalytic hydrocracking reaction is the 1-octadecene compound, in addition to alkane, alkene and silkis compounds, there are also compounds in the form of isomers.

Table 12. Product of Alkene Compounds C13 to C17 from the Catalytic Hydrocracking Reaction of 1-octadecene with a Ni/ZSiA Catalyst at a Temperature of 450 oC, Hydrogen Flow Rate 10 mL/minute, Reaction Time 30 Minutes (Estimated by Shimadzu QP2010 GC-MS Library Data)

| No. | Compound name | t (m) | Amount (%) |
|--------|---------------|-------|------------|
| 1 | 1-tetradekene | 8,88 | 1,22 |
| 2 | 7-tetradekene | 9,25 | 0,16 |
| 3 | 7-pentadekene | 11,46 | 0,67 |
| 4 | 1-pentadekene | 12,24 | 0,33 |
| 5 | 1-heksadekene | 16,26 | 0,84 |
| Amount | | | 3,22 |

Based on Table 9. The catalytic results of hydrocracking of 1-octadecene produced 1-hexadecene. This situation can be explained according to the following mechanism,

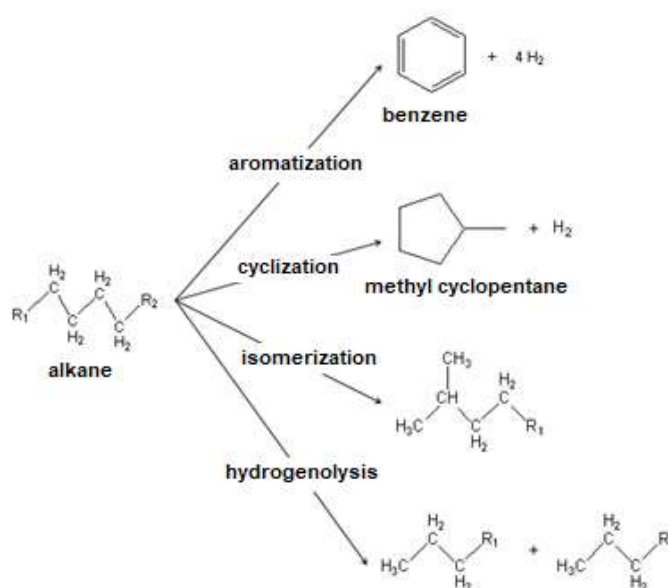
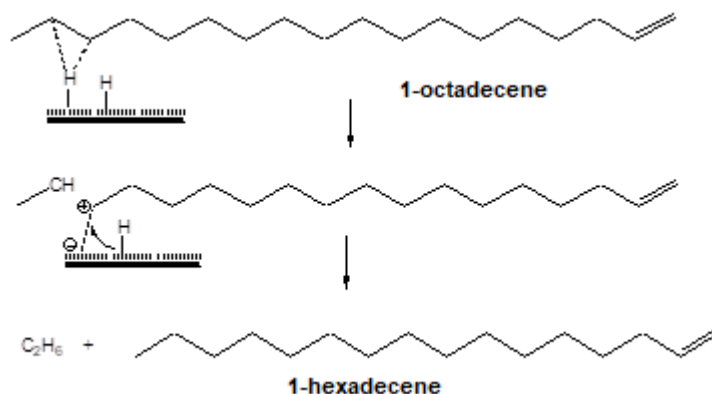


Figure 43. Several Types of Compound Products Resulting from Bond Breaking of a Long Chain Alkane (Campbell, 1988)

According to Campbell (1988), breaking the bonds of long chain compounds using a catalyst can produce several groups of compounds as follows: short chain alkanes and alkenes (from hydrogenolysis), cyclic compounds, isomerization forms, aromatization.

KESIMPULAN DAN REKOMENDASI

Natural zeolite undergoes an increase in acidity due to the release of Ca and Fe metals that are contained in it after acid treatment. In addition, dealumination activities caused by acid treatment of natural zeolite raise the zeolite's Si/Al ratio. The principal product of catalytic hydrogenation of methyl 9-octadecenoate with ZSiA catalyst is 1-octadecanol. When the catalyst weight increased from 5 to 15 g and the hydrogen gas flow rate increased from 20 to 60 mL/min, the 1-octadecanol product quantitatively reduced. With a maximum concentration of 87.21% and a lowest concentration of 5.22%, 1-octadecanol is the principal result of the catalytic hydrogenation of the methyl 9-octadecenoate molecule using ZSiA catalyst. Using the ZSiA catalyst, the catalytic hydrogenation of 1-octadecanol to 1-octadecene has a propensity to rise as reaction system temperatures rise from 400, 450, and 500 oC and hydrogen flow rates rise from 20, 40, and 60 mL/min. The primary byproduct of the catalytic hydrogenation of 1-octadecanol to 1-octadecene was 20.21%, followed by 14.37% for 5-octadecene and 10.40% for 9-octadecene. Maximum alkane and alkene products < C₁₂ (15.29%) were obtained from the catalytic hydrocracking of 1-octadecene with a Ni/ZSiA catalyst at 450 oC when the hydrogen flow rate was 10 mL/minute. This was followed by 500 and 400 oC when the hydrogen flow rate was 10 mL/minute.

DAFTAR PUSTAKA

Augustine, R.L., 1996, *Heterogeneous Catalysis for Chemist*, Marcel Dekker Inc., New York.

Bartholomew, C. H. and Farrauto, R.J., 2006, *Fundamentals of Industrial Catalytic Processes*, 2nd edition, John Wiley and Sons Inc., New Jersey.

Brands, D.S., Poels, E.K., Dimian, A.C. and Blik, A., 2002, *Solvent-Based Fatty Alcohol Synthesis Using Supercritical Butane : Flowsheet Analysis and Proses Design*, J. Am. Chem, Vol 79 (1).

Campbell, I. M., 1988, *Catalysts at Surfaces*, Chapman and Hall Ltd., New York.

Fessenden, R.J. and Fessenden, J.S., 1986, *Organic Chemistry*, 3rd edition, Wadsworth, California.

Satterfield, C.N., 1980, *Heterogenous Catalysis in Practices*, McGraw-Hill Book Co., New York.