# Conversion Of Methyl Oleate Compounds Into 1-Octadecanol Compounds Through Catalytic Cracking With Ni/Zeolite Catalyst

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## Abstract

*Research has been carried out on the cracking of methyl oleate (methyl 9-octadecenoate) compounds into 1-octadecanol compounds with Ni/zeolite catalysts and fixed bed reactors at temperatures of 400 oC to 500 oC. First, the conversion of methyl oleate to methyl octadecanoate was carried out, then the conversion was carried out to 1-octadecanol. The preparation of methyl octadecanoate is by reacting methanol with NaOH to produce a methoxide compound, then the methoxide compound is reacted with methyl oleate to produce methyl 9-octadecanoate. Furthermore, methyl 9-octadenoate was converted to 1-octadecanol compound with a fixed bed reactor and Ni/zeolite catalyst.*

*The yield obtained from the conversion of 10 grams of methyl 9-octadenoate to 1-octadecanol with a fixed bed reactor and Ni/zeolite catalyst was 10 grams.*

***Keywords** : methyl oleate, 1-octadecanol, Ni/zeolite, Fixed bed reactor*

## I. Introduction

The methyl 9-octadecenoate compound with a boiling point of 351.4 ℃ before being processed using a catalyst was analyzed using GC-MS. The GC-MS chromatogram of the standard methyl 9-octadecenoate is presented in Figure 1 and the names of the compounds after analysis with GCMS are presented in Table 1.
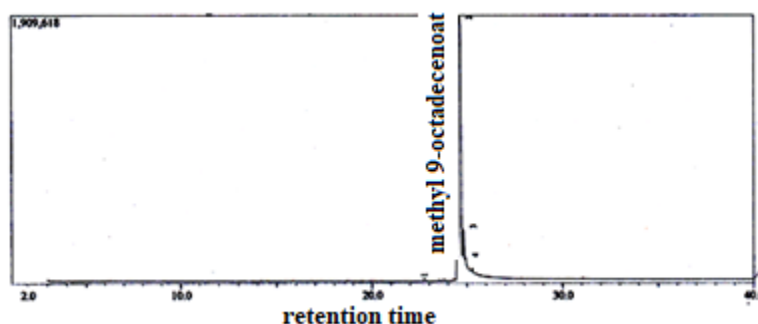


**Figure 1. GC-MS chromatogram of a standard methyl 9-octadecenoate compound**

GC-MS chromatogram of methyl 9-octadecenoate samples showed 4 dominant compounds. The most dominant peak was the peak with a retention time (tR) of 24.61 minutes (methyl 9-octadecenoate) with a relative concentration of 91.59%, a retention time of 24.81 minutes (methyl octadecanoate) with a relative concentration of 5.50% and a retention time of 24.81 minutes (methyl octadecanoate) with a relative concentration of 5.50% and retention 24.91 minutes (methyl 9.12-octadekadienoate) with a relative concentration of 2.51%.

**Table 1. The content of methyl ester as a result of initial 9-octadenoic acid esterification (estimated from Shimadzu GC-MS QP2010 library data)**

| Compound | tR (minutes) | Amount (%) |
|---|---|---|
| Methyl 9-octadecenoate | 24,61 | 91,59 |

| Methyl octadecanoate | 24,81 | 5,50 |
| Methyl 9,12-octadekadienoate | 24,91 | 2,51 |
| amount | | 99,60 |

Thermal cracking at 400 ºC using a fixed bed reactor system did not show any different results from the initial components. The GC-MS chromatogram of thermal cracking of methyl 9-octadecenoate is shown in Figure 2. The results of the thermal process showed that 90.93% was methyl 9-octadecenoate which was relatively dominant. The catalytic cracking process with a Ni/Zeolite catalyst using a fixed bed system reactor operated at a temperature of 400 oC and a hydrogen flow rate of 60 mL/minute and a catalyst weight of 5 g produced 34.50% 1-octadecanol as shown in Figure 2. 59.11% was obtained from the catalytic process of methyl 9-octadecenoate compound. The yield of the process results is 36.86%.
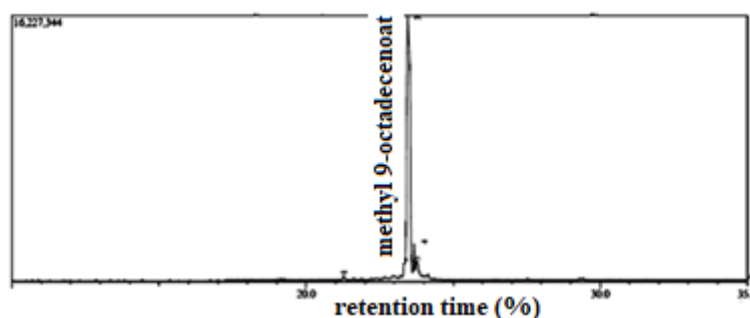


**Figure 2. GC-MS chromatogram of thermal cracking from methyl octadecenoate result at 400 ºC.**

The catalytic reaction using a Ni/zeolite 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 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/min and the catalyst weight was 5 g, 1-octadecanol was still not produced. The flow rate of carrier gas (hydrogen) that is too fast indicates that the contact time of hydrogen with the catalyst is too short resulting in no interaction between the surface of the catalyst 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.
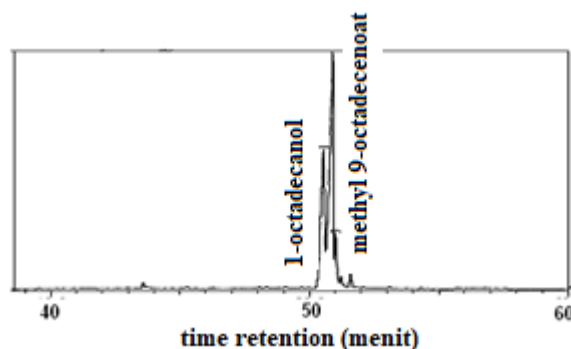


**Figure 3. GC-MS chromatogram of the catalytic hydrogenation product of methyl 9-octadecenoate at 400 ºC for 60 minutes at a hydrogen flow rate of 60 mL/minute**

Based on Figure 3, the compound 1-octadecanol at a pressure of 760 mmHg has a boiling point of 336 oC and methyl 9-octadecanol at a pressure of 760 mmHg has a boiling point of 351.4 oC. Based on the difference in boiling points and the column being semipolar, 1-octadecanol left the column earlier than methyl 9-octadecenoate.

**Table 2. Some of the catalytic hydrogenation products of methyl 9-octadecenoate with 5 grams of Ni/zeolite catalyst and a flow rate of H₂ of 60 mL/minute (estimated from Shimadzu GC-MS QP2010 library data)**

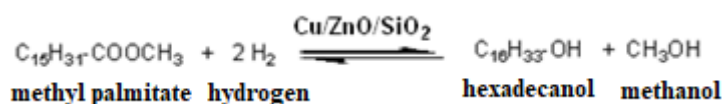| Compound name | tR (minute) | Amount (%) |
| --- | --- | --- |
| 1-octadecanol | 50,62 | 34,50 |
| Methyl 9-octadecenoate | 50,95 | 59,11 |

| Amount | 93,61 |
|--------|-------|

1. The results of research conducted in the laboratory produced 34.50% 1-octadecanol at a temperature of 400 °C and a flow rate of 60 mL/minute of hydrogen and 5 g of catalyst. This situation is due to the fact that the reaction system is very different from the research conducted by Zhilong (2007) and Brands (2002). Some of the differences in these reaction systems are:
2. The research did not use supercritical conditions with very high pressures (9 and 15 MPa).
3. Do not use propane or butane solvents in the reaction system.

Based on Table 1 and Table 2, methyl 9-octadenoate which was initially 91.59% converted to 1-octadecanol as much as 34.50%. The reaction mechanism of methyl 9-octadenoate to 1-octadecanol in this reaction system is thought to follow two stages. The first step is the adsorption of methyl 9-octadenoate on the surface of the catalyst 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 according to the reaction mechanism according to Horiuti-Polanyi in Campbell (1988).

The second step is the reduction of the ester group into an alcohol group (Fessenden and Fessenden, 1986), so that 1-octadecanol is produced. Both of these steps can occur when the feed interacts with the catalyst.

According to Brands (2002), the hydrogenation of methyl palmitate produces hexadecanol and methanol. The hydrogenation of methyl palmitate was carried out using a fixed bed reactor system which was 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 as a solvent in a supercritical state. The results of the reaction produce 98.60% hexadecanol and 0.5% hexadecane.

$$C_{15}H_{31}\text{-}COOCH_3 + 2H_2 \xrightleftharpoons{Cu/ZnO/SiO_2} C_{16}H_{33}\text{-}OH + CH_3OH$$

methyl palmitate   hydrogen                                    hexadecanol   methanol

The results of Zhilong's research (2007), stated that the process of converting fatty acid methyl ester (FAME) into long-chain alcohols with chain lengths 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.

## II.     Methodology

Ni/zeolite catalyst with weight variations of 5, 10 and 15 g was placed in a fixed bed reactor column and then heated to a temperature of 400 °C. Furthermore, hydrogen with a flow rate of 20, 40, 60 mL/minute was flowed through 10 g of the feed compound (methyl 9-octadecenoate) so that it passed through the catalyst. The process is carried out for 30 minutes. The products obtained were analyzed by GC-MS.
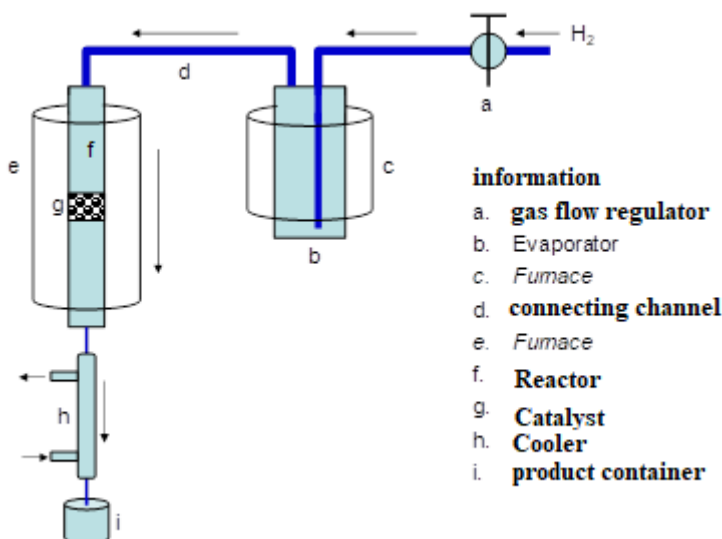


**information**
a. gas flow regulator
b. Evaporator
c. Furnace
d. connecting channel
e. Furnace
f. Reactor
g. Catalyst
h. Cooler
i. product container

**Figure 4. Fixed bed reactor**

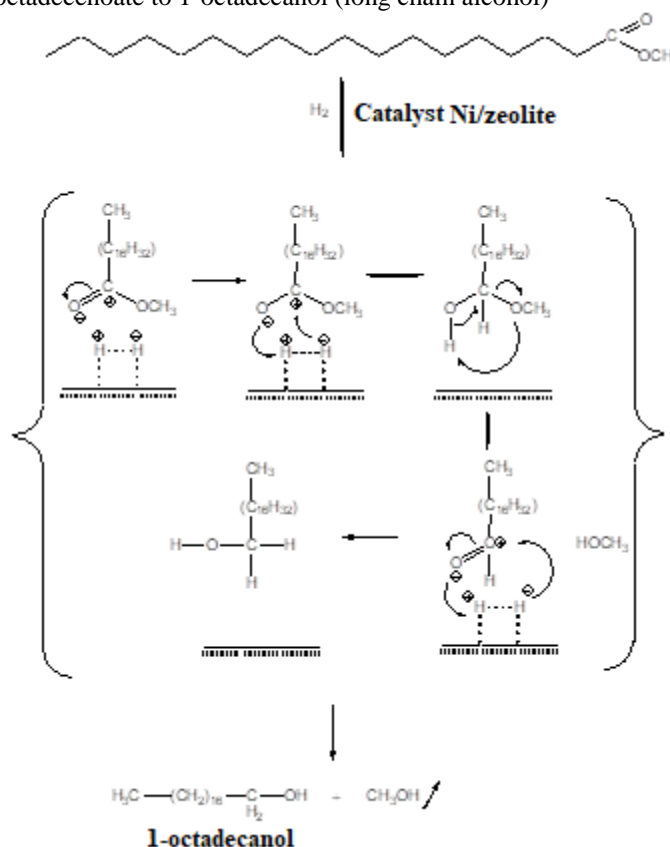## III.     Results and Discussion

Catalytic hydrogenation of methyl 9-octadenoate

The catalytic hydrogenation reaction of methyl 9-octadenoate to produce 1-octadecanol follows the following mechanical steps:

Opening of the double bond, from methyl 9-octadenoate to methyl octadecanoate



**methyl 9-octadecenoate**

**methyl octadecanoate**
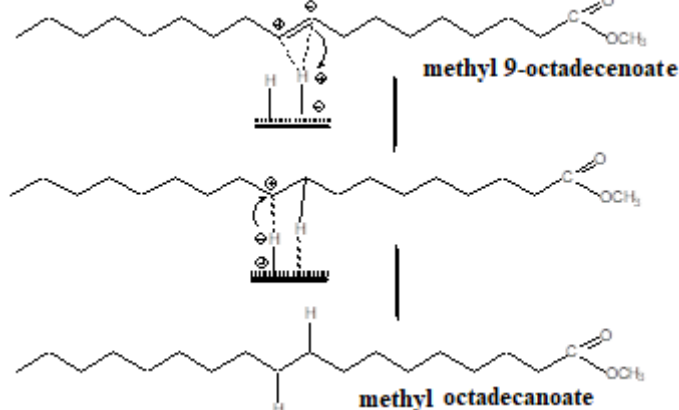
Change from methyl 9-octadecenoate to 1-octadecanol (long chain alcohol)



$H_2$ **Catalyst Ni/zeolite**

**1-octadecanol**

## IV.     Product Growth of 1-octadecanol on Variation of Catalyst Weight and Hydrogen Flow Rate

The catalytic hydrogenation of methyl 9-octadenoate was carried out by placing 5 g of methyl 9-octadenoate into an evaporator equipped with a flow of hydrogen gas as the carrier gas with various flow rates of 20, 40 and 60 mL/minute. A number of Ni/zeolite catalyst 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 is collected in a bottle container, then the product resulting from the catalytic hydrogenation reaction is analyzed by GC-MS and is presented in Figure 5 below,
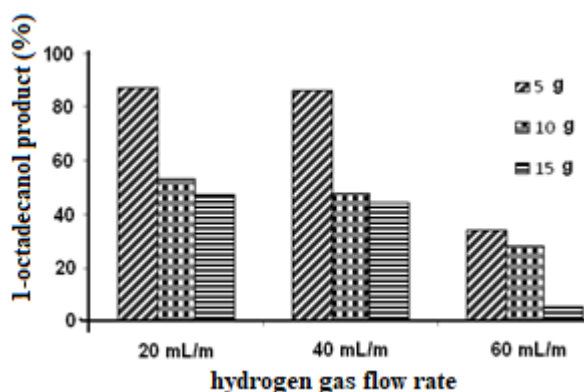
**Figure 5. Product yield of 1-octadecanol at various hydrogen flow rates and catalyst weight variations at 400 oC.**

Based on Figure 5, it can be explained that the catalytic hydrogenation reaction of methyl 9-octadenoate at a temperature of 400 oC using a Ni/Zeolite catalyst showed that the product of the 1-octadecanol compound decreased with increasing hydrogen flow rate and increasing catalyst weight from 5, 10 and 15 g. The increase in the weight of the catalyst and the increase in the flow rate of hydrogen gas shows that the interaction between the catalyst surface and hydrogen shows a dominant influence, so that the interaction between methyl 9-octadenoate and hydrogen on the catalyst surface occurs in a relatively short time. The shorter the interaction between hydrogen and methyl 9-octadenoate, the weaker the interaction between hydrogen and methyl 9-octadenoate and the smaller the probability of the occurrence of 1-octadecanol.
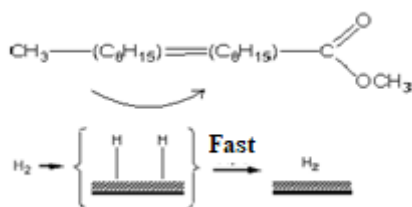


This situation causes a quantitative increase in the flow rate of hydrogen, indicating that less 1-octadecanol is produced. In this reaction, the dissociative adsorption rate of hydrogen is the rate determining step, the more hydrogen is adsorbed, the greater the probability of the reaction occurring.

As the catalyst weight increased (5, 10 and 15 grams) the amount of 1-octadecanol produced decreased. This decrease was caused by the increasing amount of catalyst, the higher the catalyst density, so that the path through which the feed (methyl 9-octadenoate) was increasingly hampered due to the density of the catalyst placed in the column. Density can be illustrated as the mean free path with a relatively changing external pore diameter when a small amount of catalyst is added to when a larger amount of catalyst is added. In this situation, it is possible that the product is inhibited in the catalyst, so that the product resulting from the catalytic hydrogenation process of 9-octadenoate methyl methyl is that the greater the amount of catalyst added, the less product will be produced.

At a higher amount of catalyst (dy) compared to a small amount of catalyst (dx) and at a constant hydrogen flow rate, the catalytic hydrogenation reaction of 9-octadenoate methyl produces less 1-octadecanol product. This situation is probably caused by the increasing number of catalysts (dy) in a fixed reactor diameter and the constant amount of reactants (R) flowing which causes the movement of the reactants to be relatively slower or inhibited ($dR/dy < dR/dx$) as illustrated in Figure 6. This situation is likely to cause the interaction of the reactants to be relatively longer, causing the reactants or reaction products to be adsorbed too strongly so that they can contaminate or poison the catalyst surface.

Adsorption that is too strong can be caused by the increasing amount of catalyst in a fixed reactor diameter causing the catalyst density to increase. At the increasing catalyst density because the amount of catalyst is relatively large and the number of reactants is constant, the resulting reaction product is relatively less.
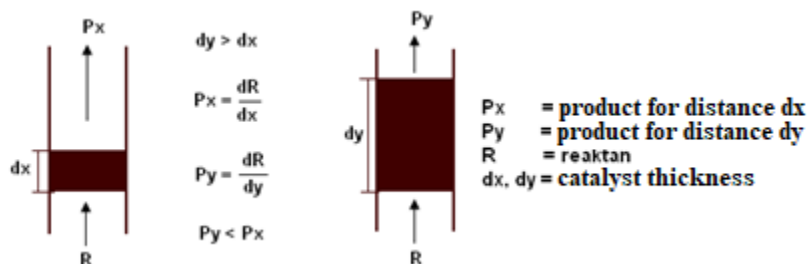
**Figure 6. The relationship between the amount of 1-octadecanol product and the amount of ZSiA catalyst used.**

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

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

The product obtained from the catalytic hydrogenation process of methyl 9-octadenoate, the more catalysts given, the relatively small amount of product is produced. The greater the flow rate of hydrogen supplied to the reaction system, the less product will be produced. The contact time of the catalyst with the methyl 9-octadenoate compound was too fast and even though the amount of catalyst added increased, the resulting product decreased quantitatively.

According to Page (1987) and Bartholomew (2006), the dissociation of hydrogen adsorption on the surface of Ni as a catalyst is illustrated in Figure 7, namely (1) physical adsorption or physisorption, (2) transition state, (3) chemical adsorption. Through physisorption, the feed or reactants will approach the surface of the catalyst and be adsorbed on the solid surface of the catalyst so that they experience further interactions with the active sites of the catalyst, namely Bronsted acid sites and Lewis acid sites, hereinafter referred to as chemisorption (Figure 7).
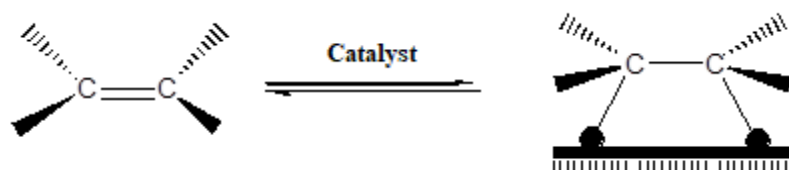


The reactants that have been adsorbed on the surface of the solid can experience "migration" events, namely the movement of molecules in one dimensional plane. Migrating molecules (in a fixed position being adsorbed) are very likely to collide with other molecules.
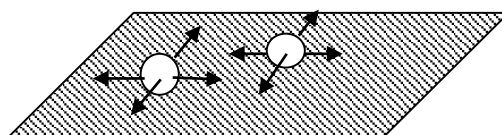


Thus, the more reactant molecules are adsorbed on the solid surface of the catalyst, the greater the probability of collisions occurring and producing reaction products. Collisions (encounter = meeting) between these reactant molecules are of lower energy but occur between active reactant molecules so that a lower activation energy is required.
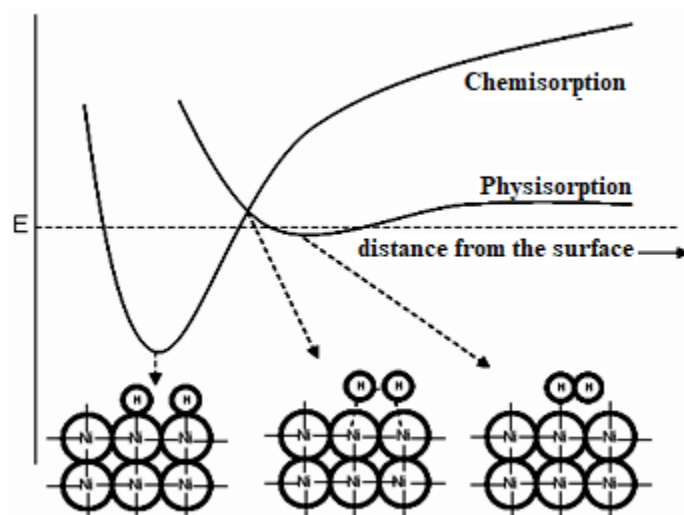
**Figure 7. Schematic illustration of the hydrogen adsorption process on the Ni catalyst surface (Bartholomew, 2006)**

## V. Conclusion

The catalytic hydrogenation of methyl 9-octadenoate with Ni/zeolite catalyst resulted in 1-octadecanol as the main product. The 1-octadecanol product decreased quantitatively with increasing hydrogen gas flow rate from 20 to 60 mL/min and increasing catalyst weight from 5 to 15 g. The main product of the catalytic hydrogenation of methyl 9-octadenoate with Ni/zeolite catalyst is 1-octadecanol with a maximum concentration of 87.21% and a minimum concentration of 5.22%.

## GLOSSARY OF TERM

| Synbol | Difinition | Unit |
|---|---|---|
| ZSiA | Zeolite Impregnation Si and Acid Treatment | |
| GCMS | Gas Chromatography and Mass Spectroscopy | |
| STY | Space Time Yield | |
| FAME | Fatty Acid Methyl Ester | |

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