Partial Hydrogenation of FAME on Trickle Bed Reactor using Nickel Catalyst

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INTRODUCTION

FAME (fatty acid methyl esters), also known as biodiesel, is a substitute for diesel fuel that can be used in engines without requiring modifications and has the advantage of producing cleaner emissions. It is defined as the products of the transesterification of vegetable oils and fats with methanol in the presence of an appropriate catalyst [1]. However, technical challenges remain in the application of biodiesel, such as low oxidative stability [2].

FAME synthesized from materials that contains higher unsaturated fatty acid composition has lower oxidative stability [3]. The oxidation of unsaturated FAME (fatty acid methyl ester) is an alternative fuel that is still limited in its application to engines because its low oxidation stability affects the quality of biodiesel storage. A solution to overcome this problem is the partial hydrogenation process in which polyunsaturated FAMEs react with hydrogen, and a catalyst breaks down unsaturated bonds which are oxidation determinants. The use of Ni/Al2O3 catalyst is more advantageous due to its lower cost and higher activity. In this research, partial hydrogenation was carried out in a trickle-bed reactor. The objective of the research is to investigate the effect of operating conditions on FAME conversion. The experimental result shows that the partial hydrogenation of polyunsaturated FAMEs in a trickle bed reactor broke down the polyunsaturated bonds (C19:2) of FAMEs into monounsaturated bonds (C19:1) and saturated bonds (C19:0). The conversion of polyunsaturated FAMEs reaches 8.93% under the inlet pressure of 0.7 MPa, the inlet temperature of 160°C, the hydrogen flowrate of 250 ml/min, and the biodiesel flowrate of 0.667 ml/min, and the catalyst size of 1.5 mm.

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**ABSTRACT**

**INTRODUCTION**

FAME (fatty acid methyl esters), also known as biodiesel, is a substitute for diesel fuel that can be used in engines without requiring modifications and has the advantage of producing cleaner emissions. It is defined as the products of the transesterification of vegetable oils and fats with methanol in the presence of an appropriate catalyst [1]. However, technical challenges remain in the application of biodiesel, such as low oxidative stability [2]. FAME synthesized from materials that contains higher unsaturated fatty acid composition has lower oxidative stability [3]. The oxidation of unsaturated FAME...
produces aldehydes, ketones, peroxides, and acids, which modify the properties of biodiesel and affect the combustion process [4]. Therefore, polyunsaturated FAME can be partially hydrogenated to increase their stability [5].

Partially hydrogenation catalysts are typically silica or alumina-supported nickel. This nickel catalyst has been used due to its financial cost, later supported nickel catalysts have been used more frequently because they are more active [6].

It is well known that reactant conversion and product selectivity after hydrogenation are influenced by the type of reactor. Liquid-phase hydrogenation in a batch-type reactor for partial hydrogenation was studied by the researchers [7]–[12]. When hydrogenation catalysts are used in the slurry stages of a batch-type reactor, a stirrer may speed up the process but shorten the catalyst's lifetime [13]. The use of catalysts in a batch-type reactor also causes issues with hydrogenated product filterability. The research on partial hydrogenation in a fixed-bed reactor, on the other hand, is limited in study on partial hydrogenation in a fixed-bed reactor. Gas and liquid phase reactants flow toward gravity in a trickle bed reactor through a bed of solid catalyst particles. The term “TRICKLE” refers to its operational characteristics, which include intermittent liquid flow in the form of films or droplets over the solid catalyst [14]. The benefits of trickle-bed reactors include a simpler separation process for the catalyst and products, as well as less mechanical damage to catalyst particles [15]. The partial hydrogenation of polyunsaturated FAMEs in a trickle bed reactor is investigated in this study.

**METHODS**

A commercial nickel-based catalyst (25% w.t Ni/Al₂O₃) was supplied by Tianjin Hutong Global Trade Co., Ltd. The biodiesel used in this work is 95.3% methyl linoleate (C19:2) and 4.7% methyl oleate (C19:1) was supplied by Jinan Boss Chemical Industry Co., Ltd. High purity hydrogen (99.97%) used as gases in the partial hydrogenation experiment supplied by PT. Energi Indogas Nusantara.

Fig. 1 depicts the experimental setup for partial hydrogenation of FAME. First, the Ni/Al₂O₃ catalyst (74.81 gram) was sieved to 1.50 mm and packed into the reactor. Once connected to the system, the reactor was pressurized to the required pressure. A high-pressure gas regulator controls the hydrogen pressure. A mass flow controller was used to regulate the different flowrates (150, 200, and 250 ml/min) of hydrogen gas. After that, the temperature was raised to 160°C and was monitored by a temperature controller. Before the experiment, the catalyst was reduced in flowing hydrogen at 250°C for 2 hours. Then a high-pressure pump was passed the feed FAME through the catalyst bed. Finally, for 80 minutes of reaction, the liquid products were collected every 20 minutes.

**Figure 1.** Experimental setup for partial hydrogenation of FAME
Trickle bed reactor design is shown in Fig. 2. This reactor is made from stainless steel with a diameter of 20.5 mm, length 380 mm, catalyst bed height 240 mm, and equipped with 80 mm of a furnace on the top of the reactor with 1 thermocouple as temperature controller and 3 thermocouples (T1, T2, and T3) as temperature indicator in the catalyst bed. Thermocouple T1 is placed 80 mm below the top of the catalyst bed, thermocouple T2 is placed 80 mm below thermocouple T1, and thermocouple T3 is placed 6.35 mm above from the bottom of the catalyst bed.

Before and after the partial hydrogenation procedure, the FAME composition was measured using a PerkinElmer gas chromatograph equipped with mass spectrometry (GC-MS). The parameters evaluated from the performance of the trickle bed reactor for partial hydrogenation were the amount of methyl linoleate conversion.

Methyl linoleate conversion is defined as a ratio between the number of moles of methyl linoleate reactant (\(C_{ML}\)) and the number of moles of methyl linoleate entering the reactor (\(C_{0ML}\)). The conversion equation can be seen in Eq. 1.

\[
\text{Conversion} = \frac{C_{ML} - C_{0ML}}{C_{ML}}
\]  

RESULT AND DISCUSSION

Effect of operating condition on FAME composition and methyl linoleate conversion

In order to study the effect of operating condition, partial hydrogenation of polyunsaturated FAMEs in a trickle bed reactor was investigated at various operating conditions: (a) the hydrogen pressure of 0.6 MPa, the hydrogen flowrate of 150 ml/min and the biodiesel feed flowrate of 4.825 ml/min, (b) the hydrogen pressure of 0.7 MPa, the hydrogen flowrate of 200 ml/min, and the biodiesel feed flowrate of 0.325 ml/min, and (c) the hydrogen pressure of 0.7 MPa, the hydrogen flowrate of 250 ml/min, and biodiesel feed flowrate of 0.667 ml/min. The effects of operating conditions on FAME composition are shown in Fig. 3.
Figure 3. Effect of reaction time of different FAME composition at various operating conditions: (a) 0.6 MPa, the hydrogen flowrate of 150 ml/min and the biodiesel flowrate of 4.825 ml/min, (b) 0.7 MPa, the hydrogen flowrate of 200 ml/min, and biodiesel feed flow rate 0.325 ml/min, and (c) 0.7 MPa, the hydrogen flowrate of 250 ml/min, and the biodiesel flowrate of 0.667 ml/min

Fig. 3a shows a graph of reaction time on FAME composition 1 (95.3% methyl linoleate and 4.7% methyl oleate), in the graph indicates that methyl linoleate was converted to methyl oleate at 20 minutes, and conversion fluctuates after 20 minutes. It is because the biodiesel feed flow rate is using high-pressure pump regulated with an inverter, a small flow rate makes the flow rate unstable, so it affects the conversion of methyl linoleate.

Fig. 3b shows a graph of reaction time on FAME composition 2 (95.2% methyl linoleate and 4.8% methyl oleate), in the graph shows that methyl linoleate was converted to methyl oleate and methyl stearate. Under this operating condition (b) the partial hydrogenation had higher conversion than on operating condition (a), which can be explained by an increase in hydrogen partial pressure and hydrogen flow rate that led to a greater concentration.
of hydrogen and caused the hydrogenation reaction to accelerate more faster [3].

Fig. 3c shows a graph of reaction time on FAME composition 3 (91.4% methyl linoleate, 7.2% methyl oleate and 1.4% methyl stearate), it shows methyl linoleate was converted to methyl oleate (cis-methyl oleate and trans- methyl oleate) and methyl stearate. The increase of trans- methyl oleate composition with reaction time, indicating that some unreacted cis-methyl oleate is changed into trans-methyl oleate at this pressure and temperature. This result is consistent with the work done by Laverdura et al. [16]. They discovered that simultaneous hydrogenation and cis-trans isomerization of C=C bonds occur during the hydrogenation of vegetable oil or FAMEs.

The three graphs show that the composition of methyl linoleate (C19:2) was reduced while the composition of methyl oleate (C19:1) and methyl stearate (C19:0) was raised. According to these results, partial hydrogenation reaction has been occurred, the polyunsaturated FAMEs bond (C19:2) has been breakdown into a monounsaturated bond (C19:1) and a saturated bond (C19:0). The partial hydrogenation reaction converted the polyunsaturated bond (C19:2) on the FAME component into a monounsaturated bond (C19:1) and a saturated bond (C19:0). It also shows that the best conversion of polyunsaturated FAMEs is on 20 minutes of reaction time. The conversion gets lower along with increasing time. It is because of the temperature decreases along with increasing time as seen in Fig. 3d. The Arrhenius equation can be used to explain this.

\[ k = A \times \exp\left(-\frac{E_a}{RT}\right) \]  

(2)

where \( k \) represents the reaction rate constants, \( A \) represents the pre-exponential factor, \( E_a \) represents the reaction activation energy, \( R \) represents the universal gas constant, and \( T \) represents the temperature [13]. The reaction rate is influenced by the temperature function. A decrease in temperature will reduce the reaction rate so that the conversion will decrease.

![Figure 4. Methyl linoleate (C19:2) conversion at various operating conditions: (a) 0.6 MPa, the hydrogen flowrate of 150 ml/min and the biodiesel flowrate of 4.825 ml/min, (b) 0.7 MPa, the hydrogen flowrate of 200 ml/min, and biodiesel feed flow rate 0.325 ml/min, and (c) 0.7 MPa, the hydrogen flowrate of 250 ml/min, and the biodiesel flowrate of 0.667 ml/min](image)

**Effect of temperature profile on methyl linoleate conversion**

The effect of temperature profile on methyl linoleate was investigated on the best conversion methyl linoleate, whereas operating condition: 0.7 MPa, the hydrogen flowrate of 250 ml/min and the biodiesel flowrate of 0.667 ml/min.
Figure 5. Temperature profile on operating condition: 0.7 MPa, the hydrogen flowrate of 250 ml/min and the biodiesel flowrate of 0.667 ml/min

Fig. 5 shows the temperature profile on methyl linoleate conversion, the longer the reaction time the temperature decreases, this corresponds to Fig. 3bc which shows that after 20 minutes the conversion of methyl linoleate decreases. According to Zhang et al., the hydrogenation is an exothermic reaction [17], this result is contrary to the data obtained, this is because of the heat generated by the reaction coming out of the system since the catalyst bed in the reactor is not insulated so that the temperature in the reactor will decrease which also causes the conversion to decrease.

CONCLUSION
In a trickle bed reactor, partial hydrogenation of FAMEs was investigated. The partial hydrogenation of FAME in a trickle bed reactor resulted in the breakdown of the polyunsaturated FAMEs bond (C19:2) on FAMEs into a monounsaturated bond (C19:1) and a saturated bond (C19:0). The conversion of polyunsaturated FAMEs reaches 8.93% under the operating condition: the inlet temperature of 160°C, the hydrogen pressure of 0.7 MPa, the hydrogen flowrate of 250 ml/min, and biodiesel feed flowrate of 0.667 ml/min. This research can still be developed, the future research direction for this research is to add an insulator to the catalyst bed in the reactor so the temperature can be maintained inside the reactor.

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