Performance of KOH as a catalyst for Trans-esterification of Jatropha Curcas Oil

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ABSTRACT
Jatropha curcas is one of promising raw materials for biodiesel in the world particularly in Aceh, Indonesia. In this study, Jatropha curcas oil was extracted from fruits to produce methyl ester via the trans-esterification of Jatropha curcas oil by using KOH catalyst. The performance of KOH catalyst was verified by conducting the kinetics experiments at the atmospheric pressure with molar ratio of 1:12, 1:14 and 1:16 of the oil to methanol, the reaction temperature in the range of 30-60^{o}C, and with the catalyst in the range of 0.75-1.5% (weight). The effect of operating parameters was investigated. The result showed that the optimum oil (methyl ester) yield was achieved for the molar ratio of 1:16, with the catalyst concentration of 1.5%. The rate constant of trans-esterification increased with the increase in the reaction temperature. Using the Arrhenius equation, the activation energy, *Ea* = 28.8 kJ moL^{-1} was obtained at the reaction temperature of 60^{o}C. The biodiesel produced was fairly met with the ASTM, where in the density (at 15^oC gr/ml), flash point, kinematic viscosity (at 40^oC) and cetane index were 0.99, 190 ^oF, 5.30 and 49, respectively.

***Keywords* - Kinetics, Jatropha curcas, trans-esterification, biodiesel**

I. INTRODUCTION
Due to increasing world crude oil price, decreasing the crude oil sources and environmental concerns, Indonesia government has supported the development of alternative domestic energy sources in particular the renewable energy material. Raw material of palm oil for biodiesel is largely available in Indonesia especialy Aceh. However, other raw materials have been investigated to anticipate the increase of palm oil need as cooking oil. Among others, Jatropha curcas which needs rainfall at least 250 mm per year can easily grow all over the islands in Indonesia. Indeed, it is one of the promising raw materials for biodiesel.
A number of researches have been conducted to investigate the production of biodiesel from Jatropha curcas, and to determine the environmental impact. Preuksakorn and Gheewala stated that the properties of Jatropha methyl ester (JME) produced via trans-esterification using Methanol, Sodium methoxide, NaOH catalyst and 10% HCl [1]. The JME properties meet the Australian fuel standard [2].

Using the same catalyst, Jha et al. investigated the kinetics of trans-esterification on Jatropha curcas oil to butyl ester at atmospheric pressure with a molar ratio of 1:21 of the Jatropha curcas oil to butanol, and found the best reaction temperature of 105^{o}C [3]. Meanwhile, Sayyar et al. concluded that the extraction yield of oil from Jatropha seed using n-hexane and petroleum as the solvents depends on type of solvents, temperature, solvent to solid ratio, processing time and particle size of the meals. The optimum condition was found at the temperature of around 68^{o}C and 8 h reaction time with the solid to n-hexane solvent ratio of 1:6 and the particle size of (0.5-0.75 mm).
The kinetics study highlighted the Activation energy of 8.022 kJ moL^{-1} [4]. From the lab scale, Kywe and Oo produced biodiesel from Jatropha curcas oil by using the optimal sodium hydroxide catalyst concentration of 1%, reaction temperature of 65^{o}C, 1 h reaction time and molar ratio of the oil to methanol 1:6, and the yield was 92%. Interestingly, at the room temperature, the yield was 90% for potassium hydroxide catalyst with 5 h reaction time and molar ratio of 1:8 [5]. In the resent publication, kinetics and thermodynamics of oil extraction from Jatropha curcas in aqueus hexane solution containing HCl, H_2SO_4, and H_3PO_4 was addressed, in which the first reaction order kinetics was found by differential method. The Activation energy *Ea* of 26.676 $kJmoL^{-1}$ was obtained for the concentration HCl of 15% (weight) [6].

Even if the synthesis techniques of biodiesel from Jatropha curcas oil have been proposed in the recent publications, the performance of KOH catalyst for the trans-esterification of Jatropha curcas oil has not been verified yet. Therefore, the objective of this study is to investigate the performance of KOH catalyst for trans-esterification of Jatropa curcas oil to produce biodiesel in particular obtaining the optimum condition. The kinetics experiments were conducted at the atmospheric pressure with molar ratio of 1:12, 1:14 and 1:16 of the oil to methanol, the reaction temperature in the range of 30-60^{o}C, and with the catalyst in the range of 0.75-1.5% (weight). The range of all parameters was set within the smallest and the highest value in the previous studies and titration.

II. MATERIAL AND METHOD
RAW MATERIAL AND PREPARATION
Jatropha curcas fruits were picked by hand from the plants located at Syiah Kuala University. The fruits were blended, and the oil was filtered to separate the waste and oil. The oil was preheated at the temperature of 35 ^{o}C to remove the water content which can affect the reaction rate of trans-esterification and create the saponification [7]. The oil was then titrated to find the range of KOH catalyst concentration applied [8].

TRANS-ESTERIFICATION OF JATROPHA CURCAS OIL

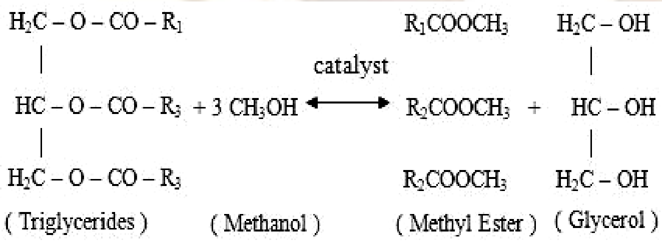
To produce methyl ester via the trans-esterification of Jatropha curcas oil, the trans-esterification reaction was taken place in a glass reactor equipped with reflux condenser, a mechanical stirrer, a thermometer and sample port. The reactor was submerged with a temperature controlled water bath.

The first kinetics experiment was conducted at the atmospheric pressure with molar ratio of 1:12 of the oil to methanol with the KOH catalyst concentration of 0.75% (weight), stirred at 200 rpm, and the reaction temperature of 30^oC. The oil was firstly put in the reactor. The catalyst and methanol were placed in a sealed volumetric flask, and the mixture was stirred using a magnetic stirrer for 15 minutes. Then, the mixture was put in the reactor and stirred for 40 minutes to let the trans-esterification reaction occurs. The samples were taken at the reaction time of 3, 6, 10, 20 and 40 minutes and the composition was analysed by using a gas liquid chromatography (GLC). When the reaction completed, the mixture was placed in an extraction flask and settled for 12-24 hours to separate methyl ester and glycerol. Methyl ester was washed using distilled water in a sealed volumetric flask and stirred for 15 minutes. The excess solvent was separated using rotary vacuum evaporator. Methyl ester was analysed to find the characteristics of density, flash point, kinematic viscosity and cetane index by using American Society for Testing and Materials [9].

The experiment was repeated for the conditions; 1:14 and 1:16 of the oil to methanol molar ratio, the reaction temperature in the range of 30^oC, 40^oC, 50^oC and 60^oC with KOH catalyst concentration of 0.75%, 1%, 1.25% and 1.5% (weight).

III. RESULTS AND DISCUSSION

The trans-esterification reaction to produce biodiesel of methyl ester from Jatropha curcas oil of triglycerides by using KOH catalyst is expressed as follows [10]:



The reaction rate is faster at the beginning reaction time than the end reaction time. At the beginning reaction time, triglycerides is transformed to diglycerides following with monoglycerides. At the end of reaction time, monoglycerides is then transformed to be three moles of methyl ester and glycerol.

EFFECT OF KOH CATALYST CONCENTRATION

The effect of KOH catalyst concentration on the percent methyl ester yield is clearly shown in Figs. 1, 2 and 3, as the results of kinetics experiments. Fig. 1 represents the reaction temperature (^oC) versus the percent (weight) methyl ester yield for the molar ratio of 1:12 of the oil to methanol with the KOH catalyst concentrations of 0.75, 1, 1.25, and 1.5 % (weight). As can be seen in Fig. 1, the methyl ester yield for the KOH catalyst concentration of 1.5 % is much higher than the methyl ester yield for the KOH catalyst concentration of 0.75 % at the reaction temperature from 30^oC to 60^oC.

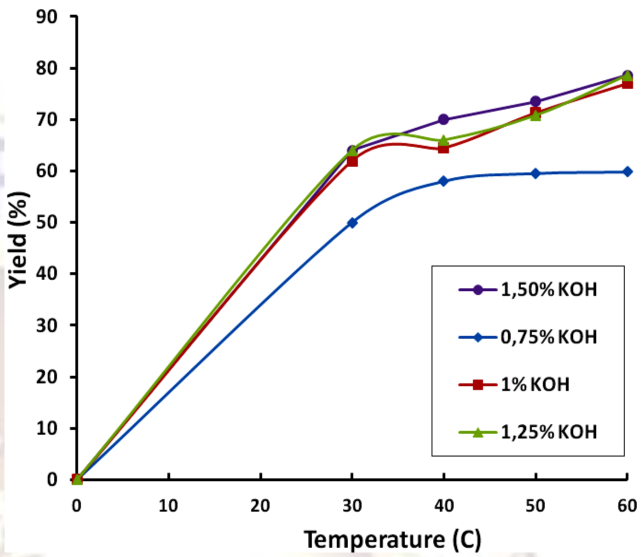


Fig. 1. The methyl ester yield versus the reaction temperature for the molar ratio of 1:12 of the oil to methanol with the KOH catalyst concentrations of 0.75, 1, 1.25, and 1.5 % (weight)

For examples, the methyl ester is approximately 79.5% and 70.2% for the KOH catalyst concentration of 1.5 % at the reaction temperature of 60^oC and 40^oC, respectively (see the top curve in Fig. 1). At the same reaction temperature, it is approximately 60.3% and 57.9%, respectively for the KOH catalyst concentration of 0.75 % (see the bottom curve in Fig. 1).

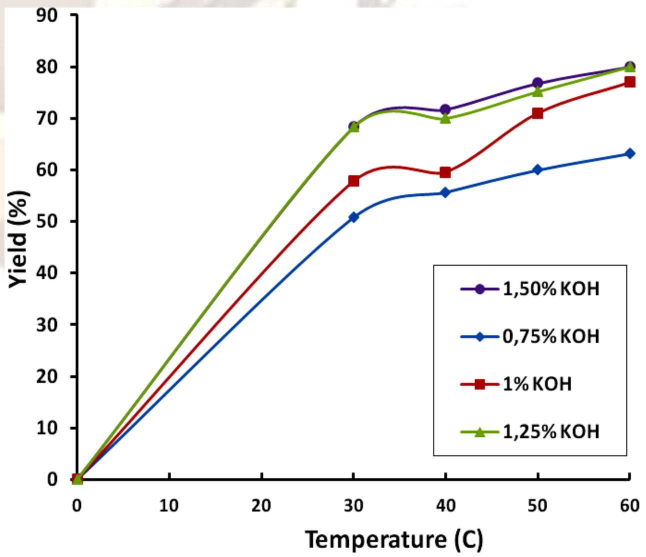


Fig. 2. The methyl ester yield versus the reaction temperature for the molar ratio of 1:14 of the oil to methanol with the KOH catalyst concentrations of 0.75, 1, 1.25, and 1.5 % (weight)

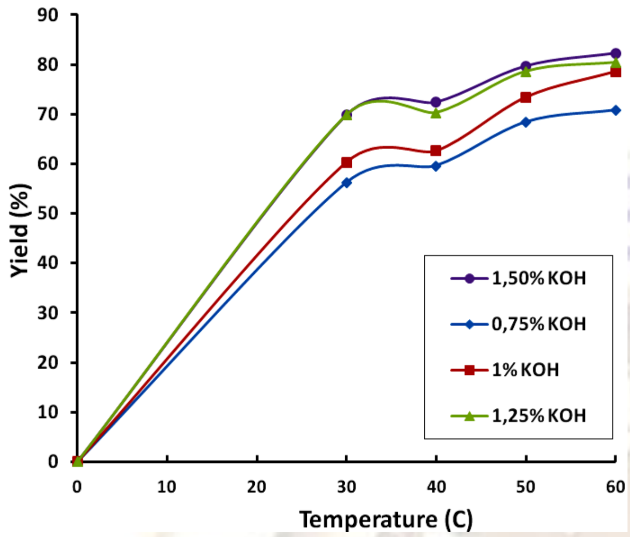


Fig. 3. The methyl ester yield versus the reaction temperature for the molar ratio of 1:16 of the oil to methanol with the KOH catalyst concentrations of 0.75, 1, 1.25, and 1.5 % (weight)

The methyl ester yield for the KOH catalyst concentration of 1.5 % is still higher than the methyl ester yield for the KOH catalyst concentrations of 1% and 1.25% even if the plots are likely very close one another. For example, the methyl ester yield for the KOH catalyst concentration of 1.5 % is approximately 79.5%, and it is approximately 78.5% and 77% for the KOH catalyst concentrations of 1.25% and 1%, respectively as shown by the plots at the reaction temperature of 60^{o}C in Fig. 1.

Overall, all the curve of the methyl ester yield for the KOH catalyst concentrations of 1.5 % is on the upper plots than the ones for the lower the KOH catalyst concentrations in the reaction temperature range of 30-60^{o}C with the molar ratio of 1:12, 1:14 and 1:16 of the oil to methanol, as can be observed from Figs. 1, 2 and 3, respectively. In other words, the higher KOH concentration applied in the trans-esterification of Jatropha curcas oil to biodiesel results in the higher biodiesel yield. However, the optimum KOH concentration would be approximately 1.5%, as can be seen from the Figs. where the yield for 1.25% KOH is almost the same as the yield for 1.5% KOH.

EFFECT OF OIL TO METHANOL RATIO

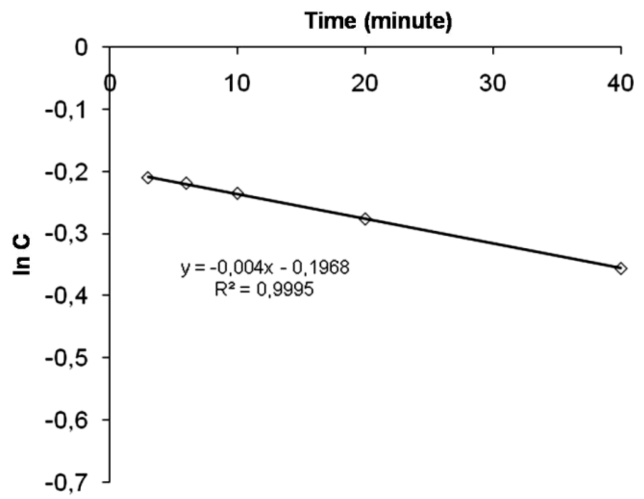
The effect of molar ratio of Jatropha curcas oil to methyl ester can be highlighted from Figs. 1, 2 and 3. By increasing the molar ratio of the oil to methanol, the methyl ester yield increases at the same KOH catalyst concentration and reaction temperature. As can be observed from 1 and 2, by increasing the molar ratio of the oil to methanol from 1:12 to 1:14, the methyl ester yield increases from approximately 70.8% to 80.5%, respectively for the reaction temperature of 60^{o}C and the KOH catalyst concentration of 1.5%.

The effect of increasing the molar ratio of oil to methanol on the methyl ester yield because the more methanol molar is available, the more trans-esterification of the oil to methyl ester can be possibly taken place in the reactor. This creates the more methyl ester yield. Other examples can be highlighted from Figs. 2 and 3. The methyl ester yield increases from approximately 80.5% to 82.5% for the increase in the molar ratio of the oil to methanol from 1:14 to 1:16, respectively for the reaction temperature of 60^{o}C and the KOH catalyst concentration of 1.5%. For the KOH catalyst concentration of 1%, it increases from approximately 74.5% to 78.4%, respectively for the molar ratio of the oil to methanol from 1:14 to 1:16 for the reaction temperature of 60^{o}C (see Figs. 2 and 3). The similar effect of increasing the molar ratio of the oil to methanol on the methyl ester yield is viewed in the range temperature of 30, 40, 50 and 60 ^{o}C for the KOH catalyst concentrations of 0.75% and 1.25%.

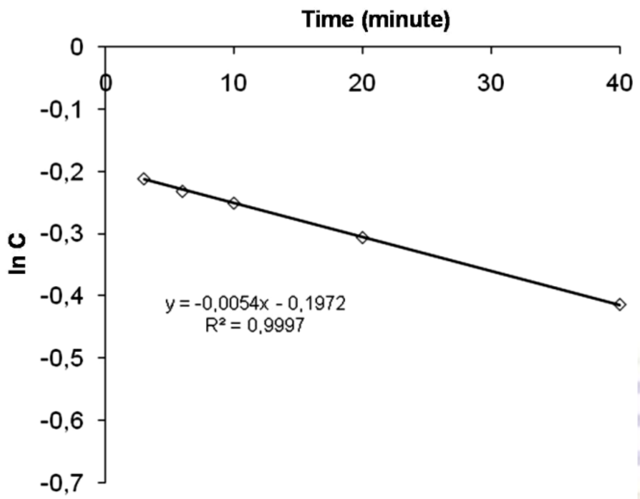
PERFORMANCE OF KOH CATALYST

Figs. 1, 2 and 3 show the effect of reaction temperature on the methyl ester yield from trans-esterification of Jatropha curcas oil. It was noticeably shown that increasing the trans-esterification reaction temperature increases the methyl ester yield. The reaction rate constant was also expected increased by increasing the reaction temperature, and it was observed in the kinetics experiments. The reaction rate constant at the reaction temperature of 30^{o}C, 40^{o}C, 50^{o}C and 60^{o}C were obtained by sampling and analysing the methyl ester concentration at the reaction time of 3, 6, 10, 20 and 40 minutes.

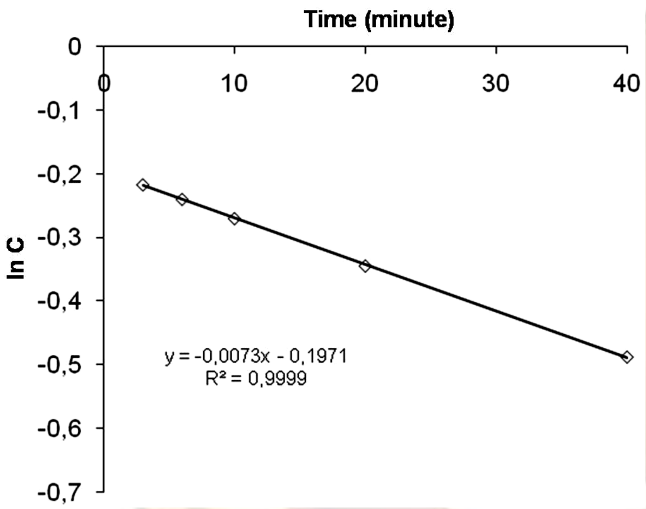
The results of kinetics experiments with the oil to methanol molar ratio of 1:16, the KOH catalyst concentration of 1.5% (weight) was chosen to obtain the rate constant because this operation condition gave the optimal yield of methyl ester.



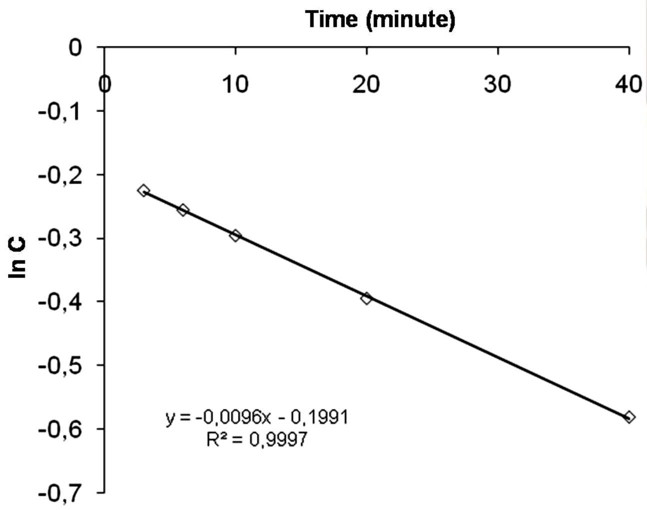
(a)



(b)



(c)



(d)

Fig. 4. The reaction time versus ln C (C is the methyl ester concentration for trans-esterification of Jatropha curcas oil to methyl ester with the oil to methanol molar ratio of 1:16, the KOH catalyst concentration of 1.5% for the reaction temperature; (a) 30°C, (b) 40°C, (c) 50°C and (d) 60°C

As can be seen in Fig. 4.a, the slope of straight line of reaction time versus ln C (C is the methyl ester concentration), which is 0.004 minute^{-1}, represents the reaction rate constant at the reaction temperature of 30°C. Meanwhile, the reaction rate constant for the reaction temperature of 40°C, 50°C and 60°C is approximately 0.0054 minute^{-1}, 0.0073 minute^{-1} and 0.0096 minute^{-1}, as shown in Figs. 4.b, 4.c and 4.d, respectively.

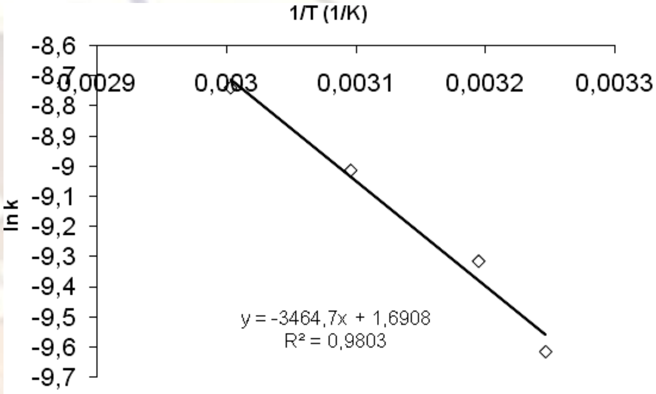


Fig. 5. The presentation of 1/T versus ln k for trans-esterification of Jatropha curcas oil to methyl ester with the oil to methanol molar ratio of 1:16, the KOH catalyst concentration of 1.5% at the reaction temperature of 60°C

The trans-esterification reaction is a first order process expressed by Equation (1), the Arrhenius equation where the reaction rate constant increases with increasing the reaction temperature.

$$k = Ae^{-Ea/RT} \quad (1)$$

where k is the trans-esterification reaction rate constant, A denotes as the Arrhenius constant or frequency factor, Ea represents the trans-esterification activation energy, R is the universal gas constant, T is the reaction temperature. The activation energy can be worked out by plotting ln k versus $1/T$ by which the slope of the straight line is the activation energy terms of $-Ea/R$, and the intercept is the Arrhenius constant terms of ln A. As can be seen in Fig. 5, the Arrhenius constant is approximately 5.42, and the activation energy is approximately 28.8 kJ moL^{-1}.

PROPERTI OF JATROPHA CURCAS BIODIESEL

The property of methyl ester as the Jatropha curcas biodiesel in this study was determined by American Society for Testing and Materials (ASTM). The density, flash point, kinematic viscosity and cetane index was termined by D.1298 method, D.93 method, D.445 method and D.976 method of ASTM, respectively [9]. A comparison of the property of Jatropha curcas biodiesel produced in this research and ASTM-based biodiesel is listed in Table 1.

Table 1. A comparison of the property of Jatropha curcas biodiesel and the ASTM-based biodiesel

No	Property	Jatropha curcas Biodiesel	Biodiesel Standard (ASTM)
1	Density at 15°C gr/ml	0,9914	0,87 – 0,89
2	Flash Point P.M, CC, °F	190	>100
3	Kinematic viscosity at 40°C	5,30	3,5 – 5
4	Cetane index	49	≥ 48

As shown in Table 1, the Jatropha curcas biodiesel density is a bit higher than the ASTM-based biodiesel. The flash point of Jatropha curcas biodiesel is far above the ASTM-based biodiesel reflecting involatile nature of the Jatropha curcas biodiesel. Meanwhile, the kinematic viscosity of Jatropha curcas biodiesel is exceed the ASTM, but it is still close the ASTM maximum of 5. The cetane index would be acceptable by the ASTM because it is 49 being very close to 48 based on the ASTM.

IV. CONCLUSIONS

The performance of KOH catalyst for trans-esterification of Jatropha curcas oil to methyl ester was verified. The kinetics experiments were performed with molar ratio of 1:12, 1:14 and 1:16 of the oil to methanol, the reaction temperature in the range of 30-60^{o}C, and with the catalyst concentration in the range of 0.75-1.5% (weigh) at the atmospheric pressure.
The results showed the effect of operating parameters, and it was found that the optimum oil (methyl ester) yield was achieved for the molar ratio of 1:16 with the catalyst concentration of 1.5%. By increasing the reaction temperature, the rate constant of trans-esterification increased. The activation energy was obtained at the reaction temperature of 60^{o}C, and the value was 28.8 kJ moL^{-1}. The property of Jatropha curcas biodiesel produced in this research was close with the biodiesel based on the ASTM.

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