



## Study of Reaction Kinetics on Biodiesel Production using In Situ Method without Catalyst

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### ABSTRACT

Biodiesel from rice bran using an uncatalyzed in-situ transesterification method in subcritical ethanol - water has been investigated. This study aims to determine the effect of the yield of biodiesel produced and to calculate the reaction kinetics that occur in the in situ process without a catalyst. This method is known to be economical because the experimental steps are reduced and environmentally friendly because we do not use a catalyst. In this experiment, CO<sub>2</sub> was used as a compressed gas and ethyl acetate as a co-solvent to increase yield. This reactor is equipped with a stirrer that uses a magnetic stirrer. Rice bran, a mixture of water, ethanol and ethyl acetate in a mole ratio of 1:10:9:2 is fed into the reactor, then injecting CO<sub>2</sub> gas to increase the pressure and to ensure the reaction takes place under subcritical conditions under operating pressure of 80 bar. Temperature (120 - 200°C) and reaction time (1 - 4 hours) were investigated to increase biodiesel. The highest yield of FAEE composition at 200°C for 3 hours was 91.264% with the results of calculating the kinetics of the transesterification reaction, the values of  $k_1$  and  $k_2$  were  $0.349 \cdot 10^{-3}$  and  $0.0045 \text{ mL}^3 \cdot \text{mmol}^{-3} \cdot \text{min}^{-1}$ . Meanwhile, in the esterification reaction, the values for  $k_1$  and  $k_2$  were 0.0194 and  $0.0579 \text{ mL}^3 \cdot \text{mmol}^{-3} \cdot \text{min}^{-1}$ .

**Keywords:** biodiesel, ethyl acetate, reaction kinetics, rice bran oil, yield

## 1. INTRODUCTION

Energy demands are increasing in line with the increasing human population and the development of an environmentally friendly mindset. Along with the increasing public concern for the environment and health, also given the increasing impact of diesel fuel, investigating alternative fuel sources has become important in this modern society, and biodiesel is considered a potential candidate to replace diesel according to Chuepeng et al.(Chuepeng et al. 2022). Biodiesel is one form of environmentally friendly and renewable fuel according to Jianbing Gao et al(Gao et al. 2022). Biodiesel burns cleaner than petroleum diesel fuel and it produces lesser carbon-derived gas emissions and PM according to Somporn et al(Katekaew et al. 2021) are characteristics of biodiesel as a specification of being environmentally friendly. Biodiesel is produced through a process called esterification reaction of free fatty acids with acid catalysts or triglyceride transesterification reactions with alcohol with basic catalysts according to Ergan et al(Temur Ergan, Yilmazer, and Bayramoğlu 2022). where the free fatty acid and triglycerides produce from animal oils or vegetable oils. Using animal oils and vegetable oils to make biodiesel is called renewable energy according to Knothe and Razon(Knothe and Razon 2017).

Biodiesel production increased from 1 billion to 18 billion liters in 2010. However, the current fall in oil prices in the range of 30-40 USD per barrel would be considered a temporary situation and could affect the total biodiesel production in the whole country and its policy development according to Indrawan et al(Indrawan et al. 2017). However, biodiesel still cannot be applied in large production. This is due to the large production costs. Biodiesel production has several aspects such as biodiesel purity, cost, composition, and yield according to Ergan et al(Temur Ergan et al. 2022).

The raw material production process is an important value in reducing the economic value of biodiesel production, which is around 70% according to Woo Go et al(Go et al. 2016). Rice bran is a raw material that has a low price according to Olagunju et al(Olagunju, Adelakun, and Olawoyin 2022). The low purchase price of raw materials with 15 – 23% oil quality according to Nguyen et al(Nguyen et al. 2019), and Chen et al(Chen et al. 2020) is an advantage in biodiesel production. The potential of Rice Brand Oil (RBO) production in Indonesia is estimated to reach 4.8-6 million tons annually if all rice bran is utilized to produce crude RBO according to Zulaikah et al(Zullaikah et al. 2021). Making biodiesel itself requires several characteristics of the material other than lipid content, namely FFA (Free Fatty Acid) levels and moisture content according to Choi et al(Choi et al. 2018)and Hoang et al(Hoang et al. 2021). So further research is needed to determine a good technology used in the production of biodiesel from rice bran. Which is 60-70% of the global production of Rice Brand Oil (RBO) used in non-food applications according to Zullaikah et al(Zullaikah et al. 2021). That is an advantage in biodiesel production.

The in situ method that has been developed is a method that can reduce production costs. In-situ is a method of reducing several steps in making biodiesel. The steps that are omitted in the in-situ method are the steps of extraction and manufacturing which are put together in one stage according to Woo Go A. et al(Go et al. 2016). So far, the use of catalysts in biodiesel production has experienced many obstacles, especially in the purification process.

The use of subcritical in-situ methods without catalysts is a good method for all types of raw materials. The main problem with the in-situ transesterification method is the reduction in water content in biomass according to Park et al(Park et al. 2015). Therefore renewable technology is needed to overcome this problem. Subcritical technology does not require both acidic and basic catalysts so raw materials with high FFA (Free Fatty Acid) content do not affect efficiency according to He H et al(He, Wang, and Zhu 2007). This uncatalyzed subcritical method uses CO<sub>2</sub> as a suppressor gas, in addition to the carbon dioxide-suppressing gas that is soluble in methanol, which can increase biodiesel selectivity according to Paudel et al(Paudel et al. 2015). So subcritical processes can be used in producing biodiesel from rice bran with even low specifications.

Non-catalytic reactions have also been carried out with CO<sub>2</sub> suppression gas and water. which reacted to H<sub>2</sub>CO<sub>3</sub>, 67.48% FAME was obtained and several reducing sugars were obtained in the Aqueous Phase at a temperature of 180°C according to Zullaikah et al(Zullaikah, Rahkadima, and Ju 2017). Biodiesel production is affected by temperature, pressure, material ratio, Free Fatty Acid (FFA) content, and time according to Zullaikah et al(Zullaikah et al. 2019). The influence of solvents and co-solvents in the formation of biodiesel is a factor that can increase production in subcritical conditions according to Najafabadi et al(Abedini Najafabadi, Vossoughi, and Pazuki 2015). The use of ethanol and ethyl acetate as solvents and co-solvents is used to increase the yield of biodiesel. Excess ethanol can increase the phospholipids extract while ethyl acetate can extract neutral lipids according to Lu et al(Lu, Wang, and Yuan 2015). In addition, ethyl acetate can convert lipids into FAEE according to Park et al(Park et al. 2017). Ethanol is a chemical that dissolves in water so it can inhibit the extraction and transesterification reactions. Ethyl acetate as a co-solvent function to separate the water phase and organic phase reactions. So it is expected to increase the extraction and transesterification reactions in biodiesel according to Zhang et al(Zhang et al. 2015).

Reaction kinetics is basic knowledge of a chemical reaction. which, is needed in expanding the scope of research that has been carried out. Information of reaction kinetic biodiesel production using in situ method without catalyst is insufficient. A study on the reaction kinetics of biodiesel production using microalgae as raw material has been carried out by (Nguyen et al. 2021). The transesterification reaction of used cooking oil biodiesel has also been studied by

(Haryanto et al. 2020). However, studies of the reaction kinetics of biodiesel production by in situ processes without a catalyst have never been studied. Therefore, This study aims to determine the effect of the yield of biodiesel produced and to see the reaction kinetics that occur in the in situ process without a catalyst. It is hoped that this calculation will add to the body of knowledge on the reaction kinetics that occurs in the biodiesel in situ production process without a catalyst.

## 2. METHODS

### 2.1 Materials

The raw material used in this study was the rice bran from Lamongan, Indonesia before the rice bran was used first to separate the impurities that were included in the rice bran. Rice bran oil has yields corresponding to range of 15 - 23% according to Nguyen et al (Nguyen et al. 2019), and Chen et al (Chen et al. 2020). With a high FFA (Free Fatty Acid) rate which has been analyzed using GC. Table 1 describes the composition of the rice bran oil we use.

**Table 1.** Rice Bran oil determined by using a gas chromatography (GC) analyzer.

Komponen	% Wt
FFA (Free Fatty Acid)	83.12
MG (Monogliseride)	2.05
DG (Digliseride)	2.25
TG (Trigliseride)	9.21
Others	3.37
Total	100.00

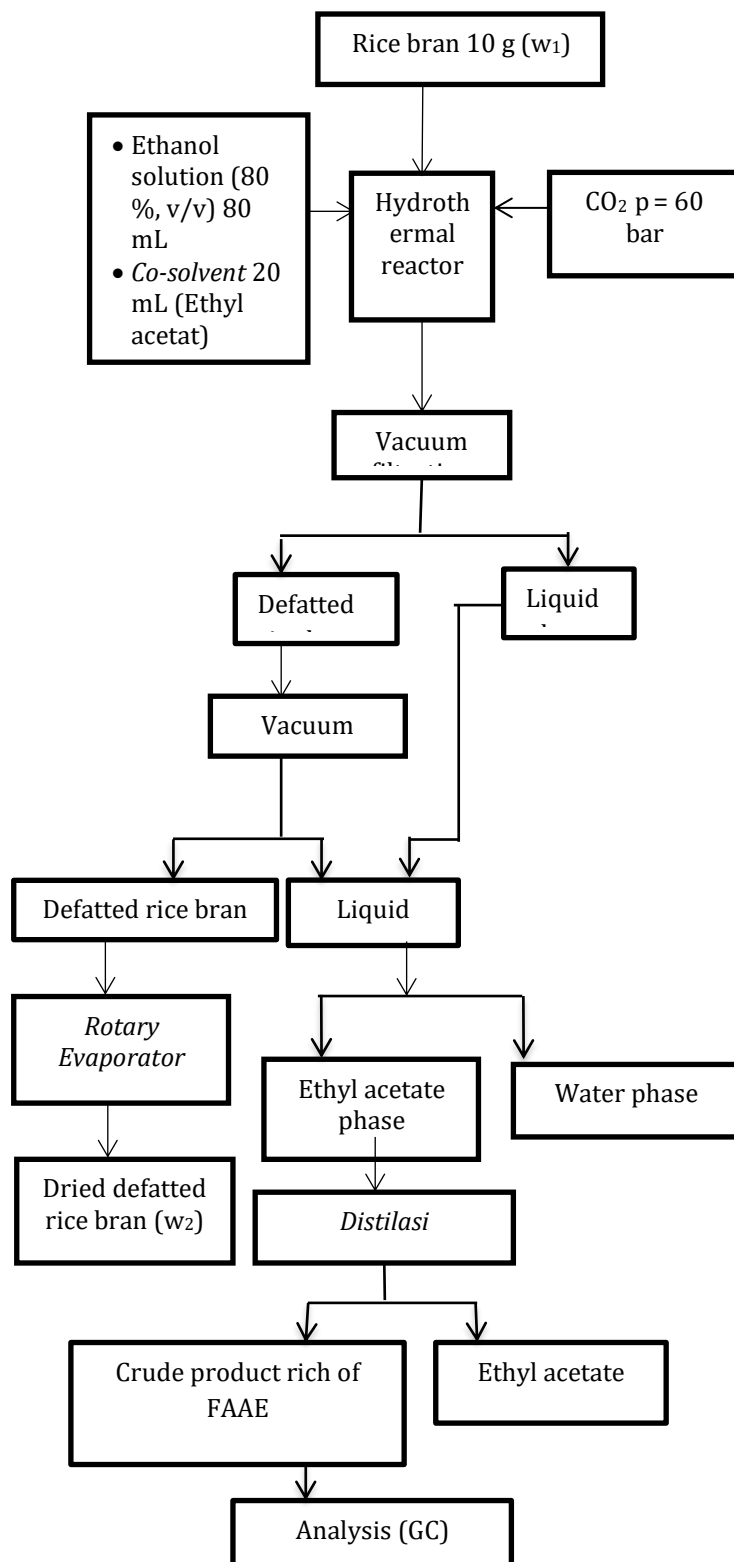
Source: laboratory analyzing

Other materials used are Ethyl acetate ( $\geq 98\%$ ) from Full Time (China), Ethanol absolute (99.9%) from Full Time. Suppressing gas, using CO<sub>2</sub>, was obtained from PT Aneka Gas (Surabaya, Indonesia). Analytical Grade from phenolphthalein (PP) indicator obtained from Cahaya Kimia (Surabaya, Indonesia) and Analytical Grade NaOH obtained from MERCK (Kenilwoth, NJ, USA). Other chemicals are analytical grade and obtained from commercial sources. Standards from Ethyl Levulinate, Ethyl Formate and Diethyl Ether come from Sigma Aldrich (St., Louis, MO, USA).

### 2.2 Maximum Biodiesel (FAEE) with Process (Acid Catalyzed Ethanolisys)

To obtain rice bran oil, we used a soxhletation procedure. By analyzing the FFA levels in the oil using the Rukunuddin et al (Rukunudin et al. 1998) procedure. The FFA (Free Fatty Acid) value of rice bran crude oil was  $51.8514 \pm 1.27\%$ . While using GC (Gas Chromatography) analysis the composition of rice bran oil is obtained which can be seen in the **Table 2**. Where the FFA level of rice bran oil is high. The high FFA (Free

fatty Acid) content made the acid catalyst chosen in this study, because according to Van Gerpen (Van Gerpen 2005), when the raw material contains above 5% FFA (Free Fatty Acid) and an alkaline catalyst is used in the transesterification process, soap will form which inhibits the separation of glycerol from biodiesel.



**Fig. 1.** Research Scheme

The conventional biodiesel production process uses the acid catalyzed ethanolisys method with the aim of

knowing the maximum FAEE (Fatty Acid Ethyl Esters) yield that can be produced. By using research procedure Lai et al (Lai et al. 2005) to obtain maximum biodiesel.

The maximum FAEE (Fatty Acid Ethyl Esters) calculation can be calculated as follows:

$$\text{Max FAEE Weight} = \frac{\% \text{FAEE Content}}{\text{Crude Biodiesel Weight}}$$

Table 2. Composition in Crude Rice Bran Oil

Komponen	Area	% Wt
FFA (Free fatty Acid)	3007267	83.12
MG (Monoglyceride)	74329.8	2.05
DG (Diglyceride)	81531.5	2.25
TG (Triglyceride)	333252.4	9.21
Others	121808.3	3.37
Total	3618189	100.00

Source: laboratory analyzing

### 2.3 In-Situ Method Without Catalyst In Ethanol - Subcritical Water Production

The process of making biodiesel using a cylindrical reactor made from stainless steel SS-136 and the inside is made of Teflon with OD = 10.8 cm; ID = 6 cm and reactor height 10.3 cm, with a volume capacity of 301.0514 mL and able to operate under a pressure of 120 bar with a maximum temperature of 260°C.

This reactor is equipped with a thermocouple connected to the controller and pressure gauge, a series of subcritical devices. This reactor is equipped with a stirrer using magnetic stirrer with a stirring speed of 400 rpm. Rice bran (10 gr), a mixture of water (16 mL), ethanol (64 mL) and ethyl acetate (20 mL) are put into the reactor then air purging is carried out inside the reactor by injecting 8 bar CO<sub>2</sub> gas for 10 seconds, besides it opens the valve release simultaneously, it aims to remove the air in the reactor through the valve release, then close the valve release again then reinject CO<sub>2</sub> gas to increase the pressure and to ensure the reaction occurs in subcritical conditions at operating pressure conditions of 80 bar. Then the heating process is carried out with various temperatures (120, 140, 160, 200°C.) And the reaction time used for (1, 2, 3 and 4 hours) with the addition of co-solvent (ethyl acetate, 20 mL). After the reaction process is finished in accordance with the temperature and reaction time used, the reaction is stopped and immediately cooled using ice water until the reactor temperature becomes 5-15°C.

Then open the valve release with the aim to reduce the reactor pressure to atmospheric pressure. The resulting product is a solid phase and a liquid phase which is then separated by a vacuum pump. The solid phase resulting from vacuum filtration extracted the remaining biodiesel content using 1:4 v/v ethanol. Then the liquid phase obtained is disarasi using ethyl acetate, so FAEE (Fatty Acid Ethyl Esters) and EL are more bound in the ethyl acetate phase than the water phase. After that the ethyl acetate phase is separated using

distillation to obtain crude biodiesel Fatty Acid Ethyl Esters (FAEE) which will then be carried out GC analysis.

### 2.4 Analyses of FAEE (Fatty Acid Ethyl Esters)

Analysis of FFA (Free Fatty Acid), MG (Monoglyceride), DG (Diglyceride) and TG (Triglyceride) on Crude Rice Bran Oil (CRBO) as well as FFA, MG, DG, TG in the CBD (Crude Biodiesel) of the reactor were analyzed using Shimadzu GC-2010 Plus type gas chromatography (Kyoto, Japan) with a flame ionization detector (FID). The column used was DB-5HT (5% -phenyl) -methylpolysiloxane non-polar column (15 m × 0.32 mm i.d., 0.1 mm film thickness; Agilent Tech. Palo Alto, California). The temperature of the injector is set at 80°C and the detector temperature flame ionization detector (FID) is set at 365 °C. The temperature of the column starts at 80 °C with being held for 5 minutes, then increased to 100°C with an increase of 5°C / minute and maintained for 5 minutes. Then, the temperature is raised to 305 °C with an increase of 15 °C / minute without holding time. After that the temperature is raised to 335 °C with an increase of 5°C / minute which is then maintained for 5 minutes. Then proceed with an increase in temperature up to 365°C with an increase of 15 °C / minute and maintained for 10 minutes. Split ratio used is equal to 1:50 with carrier gas in the form of nitrogen gas (N<sub>2</sub>). Then, 20 mg of Crude Rice Bran Oil (CRBO) and Crude Biodiesel (CBD) oil samples were dissolved in 1 mL ethyl acetate each with a boiling point of 77.1°C, then 1 µL of CRBO and CBD samples were injected into GC respectively. As for the experimental sample, 1 µL of the sample is directly injected into the GC. The calculation of % Free Fatty Acid (FFA), Monoglyceride (MG), Diglyceride (DG), triglyceride (TG) and Fatty Acid Ethyl Ester (FAEE) on Crude Biodiesel (CBD) is based on the percent of area of each existing peak, and peaks with areas under 10,000 are considered impurities. After obtaining %FFA, MG, DG, TG and %FAEE are calculated, then calculate the mass of FAEE based on the following formula:

$$\text{Yield FAEE (\%)} = \frac{\text{FAEE mass obtained (gr)}}{\text{maximum FAEE mass (gr)}} \times 100\%$$

## 3. RESULTS AND DISCUSSION

### 3.1 Acid Catalyzed Ethanolisys

In this study, the acid-ethanolysis process was also carried out, in which the crude rice bran oil (CRBO) produced from the extraction was then converted into biodiesel using an acid catalyst (H<sub>2</sub>SO<sub>4</sub>). The purpose of acid-ethanolysis is to determine the maximum yield of fatty acid ethyl esters (FAEE) that can be produced. From the acid-ethanolysis process, Crude biodiesel (CBD) was produced with a yield of 88.19 ± 0.27% and a FAEE yield of 88.11%. The composition of Crude Biodiesel (CBD) resulting from acid ethanolysis can be seen in **Table 3**.

**Table 3** Maximum Biodiesel Composition

Komponen	Area	% wt
<b>FFA (Free Fatty Acid)</b>	158651.6	4.46
<b>FAEE (Fatty Acid Ethyl Ester)</b>	3130848	88.11
<b>MG (Monogliseride)</b>	88769.9	2.50
<b>DG (Digliseride)</b>	30157.3	0.85
<b>TG (Trigliseride)</b>	22924.8	0.65
<b>Others</b>	122175.1	3.44
<b>Total</b>	3553526	100.00

Source: laboratory analyzing

It can be seen from **Table 2** and **Table 3** that the components from CRBO (Crude Rice Bran Oil) have been converted into Biodiesel Fatty Acid Ethyl Ester (FAEE). FFA converted by 94.16%, TG by 92.9%, DG by 62%. Meanwhile, MG rose from 2.25 to 2.50%. This is due to the hydrolysis of Triglyceride compounds in Crude rice bran oil (CRBO) into diglycerides indirectly forming FAEE which can occur due to a lack of additional volume of ethanol or a lack of time for acid ethanolysis. Meanwhile, the increase in the content of other components in Crude Biodiesel (CBD) can occur due to the formation of other substances such as glycerol as a by-product of the formation of fatty acid ethyl esters (FAEE) according to Atadashi et al (Atadashi et al. 2012).

### 3.2 Effect of Temperature

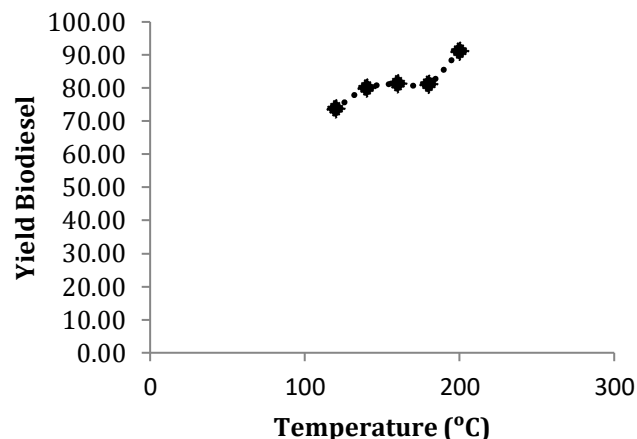
In this study temperature 120 - 200°C was used. In the study according to Im et al (Im, Kim, and Lee 2015) it has been carried out on making biodiesel at a temperature of 125°C. In addition, based on research Zullaikah et al (Zullaikah et al. 2017) obtained the best biodiesel yield at a temperature and a duration of 200°C and 3 hours. By establishing the use of ethyl acetate as a fixed variable. Because the transesterification reaction is an endothermic reaction, the yield usually increases with increasing temperature according to Habaki et al (Habaki, Hayashi, and Egashira 2014). Temperature is the main factor influencing extract efficiency and selectivity in extraction with subcritics. Temperature affects the physical properties of the water and also determines the strength of the analyte in the decomposition / hydrolysis process.

Components in oil from plants may have nonpolar or polar properties and are thermally labile. To extract nonpolar components from plants, an increase in temperature up to 200°C may be needed according to Budrat and Shotipruk (Budrat and Shotipruk 2009). So it can be seen in **Fig. 2**. the higher the temperature, the higher the Biodiesel yield Fatty Acid Ethyl Ester (FAEE) obtained. It can be seen from **Fig. 3**. that at 4 hours the FFA converted to Biodiesel (FAEE) tends to decrease compared to the 3 hour time of 91.264%.

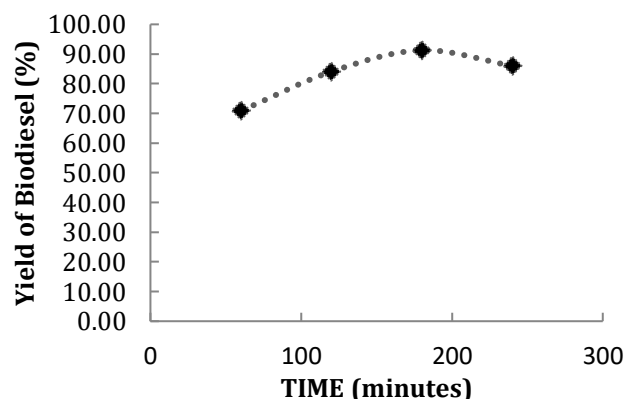
### 3.3 Effect of Time

In this study, time variables of 1, 2, 3 and 4 hours were used. The effect of time on Biodiesel yield Fatty

Acid Ethyl Ester (FAEE) is shown in **Fig. 3**. Oil recovery produced 91.81% with the largest yield of 91.264%.



**Fig. 2.** Effect of Biodiesel Content (FAEE) on the P Condition: 80 bar, 80% ethanol-water concentration and time 180 minutes with CO<sub>2</sub> suppressor gas.



**Fig. 3.** Biodiesel yield (FAEE) with respect to P: 80 bar, 80% ethanol-water concentration and 200 °C temperature with CO<sub>2</sub> suppressor gas.

Based on **Fig. 3**. states that the longer the reaction time, the higher the yield obtained. Seen at 3 hours, the yield was 91.264%. Established research that has been done at 3 hours has the greatest yield value that can be seen in **Figure 3**. As research has been done by Zullaikah et al (Zullaikah et al. 2017) that at 3 hours obtained biodiesel with the best yield. As we know that time is a factor in the kinetics of reactions. Therefore, the longer the time, the greater the yield obtained. However, it is different with the research that has been done. At 4 hours there was a decrease in yield along with the composition of Biodiesel Fatty Acid Ethyl Ester (FAEE). The length of reaction time can lead to polymerization and degradation of unsaturated oleic and linoleic fatty acids according to Zullaikah et al (Zullaikah et al. 2017). Seen at high temperatures the color of biodiesel looks darker compared to lower temperatures. In addition, at 3 hours the reaction has experienced equilibrium. It can be seen from **Figure 3** that at 4 hours the Free Fatty Acid (FFA) converted to Biodiesel Fatty Acid Ethyl Ester (FAEE) tends to go down compared to the 3 hour time of 91.264%.

### 3.4 Biodiesel Reaction Kinetics (FAEE) in In - situ Without Catalysts

Rice bran oil has two types of lipids, namely Free Fatty Acid (FFA) and Triglyceride (TG). These two types of lipids have different kinetic reactions in producing Fatty Acid Ethyl Esters (FAEE). Therefore the reaction kinetics are evaluated from both transesterification reactions with TG lipids and esterification with FFA lipids.

#### 3.4.1 Kinetics of the Transesterification reaction

Based on the analysis of the reaction content in the subcritical reactor the kinetics of the reaction results are obtained. Calculation of the kinetics of this transesterification reaction uses quantitative analysis results of gas chromatography and the full calculation is displayed in the appendix. In determining the kinetics of this transesterification reaction the integral method is used.

This method is done by first guessing the reaction order to get the general reaction rate equation through mathematical integration and the use of assumptions that are appropriate to the reaction conditions. Furthermore, a plot between concentration versus time is made in the form of a straight line equation. And if a straight-line equation is obtained that satisfies the reaction rate equation it is considered to meet the data fitting. The reactions are reviewed as follows:

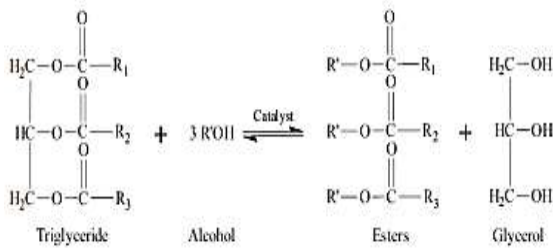
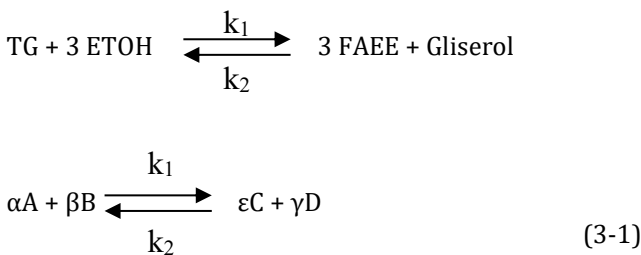


Fig. 3. Transesterification reactions according to Pereira et al.,(Pereira et al. 2014)

The reaction is simplified as follows :



Kinetic data analysis is performed using research data from the reactor batch (table 4). Assumptions taken in the kinetic analysis are as follows:

1. The reaction kinetics equation is based on elementary and reversible reactions.

2. Research using excess ethanol (1: 10 molar ratio, rice bran to ethanol), so that  $C_B \sim C_{B0}$ .
3. Equation of reaction rates based on triglycerides as reactant limiting.

Table 4. Research Data

Time	FAEE	TG	FFA
0	83.115	9.210	83.12
60	79.385	0	14.545
120	85.418	0.000	8.515
180	78.985	2.461	5.951
240	75.138	2.738	18.153

Source: laboratory analyzing

The general equation of reaction rate in equation (3-1) using the first assumption: (Octave Levenspiel 1999)

$$(-r_A) = -\frac{dC_A}{dt} = k_1 C_A^\alpha C_B^\beta - k_2 C_C^\varepsilon C_D^\gamma \quad (3-2)$$

Apply the second assumption until equation (3-2) becomes:

$$(-r_A) = -\frac{dC_A}{dt} = k_1 C_A C_B^3 - k_2 C_C^3 C_D \quad (3-3)$$

$$(-r_A) = -\frac{dC_A}{dt} = k_1 C_A C_{B0}^3 - k_2 C_C^3 C_D \quad (3-4)$$

Where  $k_1 C_{B0}^3 = K_1^*$  then equation (3-4) becomes

$$(-r_A) = -\frac{dC_A}{dt} = K_1^* C_A - k_2 C_C^3 C_D \quad (3-5)$$

And based on the same stockhiometrics:

$$C_A = C_{A0} (1 - x_A)$$

$$C_B = C_{B0} - C_{A0} \cdot 3x_A = C_{A0} (M - 3x_A) ; \text{ where } M = C_{B0}/C_{A0}$$

$$C_C = C_{C0} + C_{A0} \cdot 3x_A ; \text{ where } C_{C0} = 0, \text{ so } C_C = C_{A0} \cdot 3x_A$$

$$C_D = C_{D0} + C_{A0} \cdot x_A ; \text{ where } C_{D0} = 0, \text{ so } C_D = C_{A0} \cdot x_A$$

So the equations (3-5) become:

$$C_{A0} \frac{dx_A}{dt} = K_1^* C_{A0} (1 - x_A) - k_2 (C_{A0} \cdot 3x_A)^3 C_{A0} x_A \quad (3-6)$$

$$C_{A0} \frac{dx_A}{dt} = K_1^* C_{A0} (1 - x_A) - 27k_2 (C_{A0} x_A)^4 \quad (3-7)$$

$$\frac{dx_A}{dt} = K_1^* (1 - x_A) - 27k_2 C_{A0}^3 x_A^4 \quad (3-8)$$

Where is the unit for  $k_1$ ,  $K_1^*$  and  $k_2$  sequencely :  $\text{mL}^3 \cdot \text{mol}^{-3} \cdot \text{min}^{-1}$  ;  $\text{min}^{-1}$  ; and  $\text{mL}^3 \cdot \text{mol}^{-3} \cdot \text{min}^{-1}$ . When equilibrium is reached, the following equation applies:

$$k_1 C_{Ae} C_{Be}^3 = k_2 C_{Ce}^3 C_{De} \quad (3-9)$$

$$Ke = \frac{k_1}{k_2} = \frac{C_{Ce}^3 C_{De}}{C_{Ae} C_{Be}^3} = \frac{(C_{A0}^3 x_{Ae})^3 C_{A0} x_{Ae}}{C_{A0} (1-x_{Ae}) C_{A0}^3 (M-3x_{Ae})^3}$$

$$Ke = \frac{k_1}{k_2} = \frac{27x_{Ae}^4}{(1-x_{Ae})(M-3x_{Ae})^3} \quad (3-10)$$

Substituting equation (3-10) to equation (3-8), is obtained by the following equation:

$$\frac{dx_A}{dt} = K_1^*(1-x_A) - 27\frac{k_1}{Ke}C_{A0}^3x_A^4 = K_1^*(1-x_A) - 27\frac{K_1^*C_{A0}^3}{KeC_{B0}^3}x_A^4 \quad (3-11)$$

$$\frac{dx_A}{dt} = K_1^* \left[ (1-x_A) - \frac{27x_A^4}{KeM^3} \right] \quad (3-12)$$

With  $\left[ (1-x_A) - \frac{27x_A^4}{KeM^3} \right]$  is denoted as B until equation (3-12) becomes simpler to:

$$\begin{aligned} \frac{dx_A}{dt} &= K_1^* \cdot B \\ \frac{dx_A}{B} &= K_1^* \cdot dt \\ \frac{dx_A}{B} &= K_1^* \cdot \Delta t \end{aligned} \quad (3-13)$$

Equation (3-13) is solved by plotting 1 / B vs xA graphs and then by trapezoidal method computing the area of the graph which is the value  $\frac{dx_A}{B}$ . With the known value of the area known, the value  $K_1^*$ ,  $k_1$  and  $k_2$  can be known.

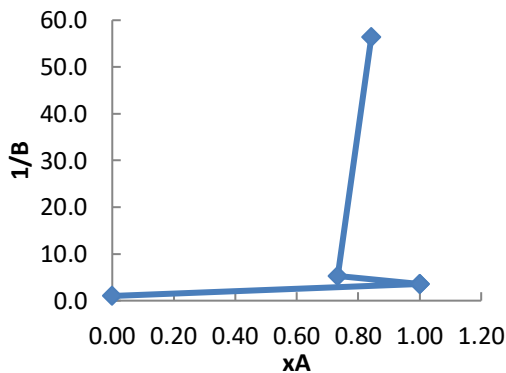
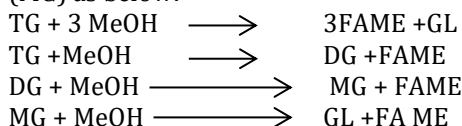


Fig. 4. 1 / B relationship of TG conversion to braking transesterification rice at 200°C.

From the calculation of the surface area of the graph in Figure 4.11 by using the trapezoidal method we obtained  $k_1 = 0.349 \cdot 10^{-3} \text{ mL}^3 \cdot \text{mmol}^{-3} \cdot \text{min}^{-1}$  and  $k_2 = 0.0045 \text{ mL}^3 \cdot \text{mmol}^{-3} \cdot \text{min}^{-1}$  (Octave Levenspiel 1999). From these results the price constant of the reaction speed left ( $k_2$ ) is greater than that of the product ( $k_1$ ). Thus in the in situ transesterification reaction, the Fatty Acid Ethyl Ester (FAEE) decomposition reaction (left reaction) runs faster than the formation reaction (product direction) (Octave Levenspiel 1999).

This is because the Triglyceride (TG) conversion reaction turns into Diglyceride (DG) and Monoglyceride (MG) as below:



(Ergan et Al.,2022).

Based on the above reaction stages, Triglycerides (TG) were subsequently converted to Diglycerides (DG), Monoglycerides (MG) and Glycerol. At each reaction stage, a biodiesel / methyl ester molecule is formed for each reacting alcohol molecule according to Ergan et Al. (Temur Ergan et al. 2022).

Triglycerides as a limiting reactant are arranged on a glycerol chain with 3 groups of fatty acids. Thus in the reaction, the hydrolysis of triglycerides will first occur by the acid catalyst to cut off each of the fatty acids until they produce free fatty acids, diglycerides and monodiglycerides. Furthermore, these free fatty acids react to form the appropriate esters according to Morrison et al. (Morrison et al. 1975).

### 3.4.2 Kinetics of the Esterification reaction

The reactions are reviewed as follows:

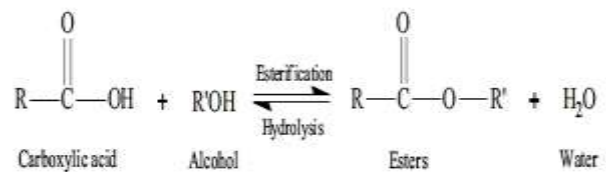
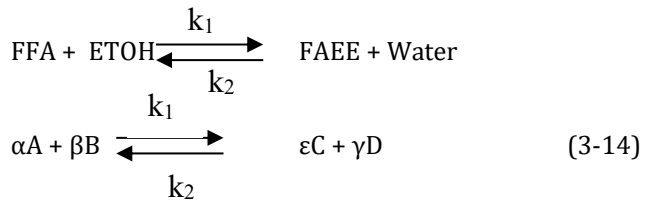


Fig. 5. Esterification Reaction according to Pereira et al. (Pereira et al. 2014)

The reaction is simplified as follows:



Analyses of kinetic data were performed using research data from batch reactors (table 1). The assumptions made in the kinetic analysis are as follows:

1. Equation of reaction kinetics based on elementary and reversible reactions.
2. Research using excess ethanol (1: 10 molar ratio, rice bran against ethanol), up to  $C_{B0} \sim C_{B0}$ .
3. Equation of reaction rate based on triglycerides as limiting reactants (Octave Levenspiel 1999).

General equation of reaction rate in equation (4-14) using first assumption :

$$(-r_A) = -\frac{dC_A}{dt} = k_1 C_A C_B - k_2 C_C C_D \quad (3-15)$$

Where  $k_1 C_{B0}^3 = K_1^*$  so the equation (3-15) become

$$(-r_A) = -\frac{dC_A}{dt} = K_1^* C_A - k_2 C_C C_D \quad (3-16)$$

And based on the stochastic equivalent:

$$C_A = C_{A0} (1 - x_A)$$

$$C_B = C_{B0} - C_{A0} \cdot x_A = C_{A0} (M - x_A); \text{ where } M = C_{B0}/C_{A0}$$

$$C_C = C_{C0} + C_{A0} \cdot x_A; \text{ where } C_{C0} = 0, \text{ so } C_C = C_{A0} \cdot x_A$$

$C_D = C_{D0} + C_{A0} \cdot x_A$ ; where  $C_{D0} = 0$ , so  $C_D = C_{A0} \cdot x_A$

So the equation (3-16) become :

$$C_{A0} \frac{dx_A}{dt} = K_1^* C_{A0} (1 - x_A) - k_2 (C_{A0} x_A) C_{A0} x_A \quad (3-17)$$

$$C_{A0} \frac{dx_A}{dt} = K_1^* C_{A0} (1 - x_A) - k_2 (C_{A0} x_A)^2 \quad (3-18)$$

$$\frac{dx_A}{dt} = K_1^* (1 - x_A) - k_2 C_{A0} x_A^2 \quad (3-19)$$

Where the unit for  $k_1$ ,  $K_1^*$  and  $k_2$  sequencely :  $\text{mL}^3 \cdot \text{mol}^{-3} \cdot \text{min}^{-1}$ ;  $\text{min}^{-1}$ ; dan  $\text{mL}^3 \cdot \text{mol}^{-3} \cdot \text{min}^{-1}$ .

When equilibrium is reached, the following equation applies:

$$k_1 C_{Ae} C_{Be} = k_2 C_{Ce} C_{De} \quad (3-20)$$

$$K_e = \frac{k_1}{k_2} = \frac{C_{Ce} C_{De}}{C_{Ae} C_{Be}} = \frac{(C_{A0} - x_{Ae}) C_{A0} x_{Ae}}{C_{A0} (1 - x_{Ae}) C_{A0} (M - 3x_{Ae})}$$

$$K_e = \frac{k_1}{k_2} = \frac{x_{Ae}^2}{(1 - x_{Ae})(M - 3x_{Ae})} \quad (3-21)$$

Substituting equation (3-20) to equation (3 - 21), is obtained by the following equation

$$\frac{dx_A}{dt} = K_1^* (1 - x_A) - \frac{k_1}{K_e} C_{A0} x_A^2 = K_1^* (1 - x_A) - 27 \frac{K_1^* C_{A0}}{K_e C_{B0}} x_A^2 \quad (3-22)$$

$$\frac{dx_A}{dt} = K_1^* \left[ (1 - x_A) - \frac{1}{K_e M} x_A^2 \right] \quad (3-23)$$

With  $\left[ (1 - x_A) - \frac{1}{K_e M} x_A^2 \right]$  is denoted as B until equations (3-23) are simplified into :

$$\frac{dx_A}{dt} = K_1^* \cdot B$$

$$\frac{dx_A}{B} = K_1^* \cdot dt \quad (3-24)$$

$$\frac{dx_A}{B} = K_1^* \cdot \Delta t$$

Equation (3-24) is solved by plotting  $1/B$  vs  $x_A$  graphs and then by trapezoidal method computing the area of the graph which is the value  $\frac{dx_A}{B}$ . With the known values of area known, the values of  $K_1^*$ ,  $k_1$  and  $k_2$  are known.

From the calculation of the surface area of the graph in figure 10 using the trapezoidal method we obtained  $k_1 = 0.0194 \text{ mL}^3 \cdot \text{mmol}^{-3} \cdot \text{min}^{-1}$  and  $k_2 = 0.0579 \text{ mL}^3 \cdot \text{mmol}^{-3} \cdot \text{min}^{-1}$ . From these results the price constant of the reaction speed left ( $k_2$ ) is greater than that of the product ( $k_1$ ). Thus in the in situ transesterification reaction, the FAEE decomposition reaction (left reaction) runs faster than the formation reaction (product direction) (Octave Levenspiel 1999). This is in line with the research that in the relatively long time biodiesel was not optimally obtained. However, at 3 hours FAEE is optimally formed.

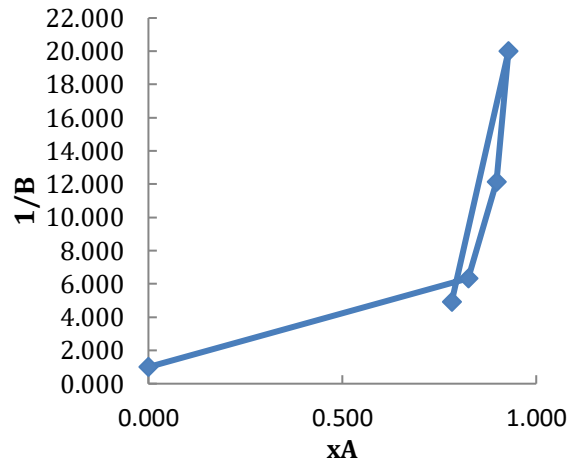


Fig. 6.  $1/B$  relationship of FFA conversion to braking transesterification rice at 200°C.

#### 4. CONCLUSION

The conclusions drawn from this study are:

1. At 3 hours, % Recovery FAEE is 91.264%. With 3 hours, it is the equilibrium time for making Fatty Acid Ethy Ester (FAEE) with subcritical in-situ. While at 4 hours it was 86.026%, 2 hours was 84.083% and 1 hour was 70.608%.
2. The higher the temperature, the higher the FAEE content that is formed. The highest % recovery FAEE at a temperature of 200°C was 91.264%. Whereas at a temperature of 180°C it was 54.547%, 160°C was 63.180%, 140°C was 32.738% and 120°C was 17.415%.
3. Based on the kinetics of the transesterification reaction, the values for  $k_1$  and  $k_2$  were  $0.349 \cdot 10^{-3}$  and  $0.0045 \text{ mL}^3 \cdot \text{mmol}^{-3} \cdot \text{min}^{-1}$ . While the esterification reaction obtained  $k_1$  and  $k_2$  values of 0.0194 and  $0.0579 \text{ mL}^3 \cdot \text{mmol}^{-3} \cdot \text{min}^{-1}$ .

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