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# 3<sup>rd</sup> iSNPiNSA



International Seminar on New Paradigm  
and Innovation on Natural Sciences  
and its Application



Developing Innovation  
and Application of  
Applied Sciences  
for Sustainable  
Development

PROCEEDINGS



Diponegoro University  
2013

**The 3<sup>rd</sup> International  
Seminar on  
New Paradigm and Innovation  
on Natural Sciences and its  
Application 2013**



***“Developing Innovation and Application of  
Applied Sciences for Sustainable Development”***

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# PREFACE

Good Morning Ladies and Gentlement

On behalf of the Organizing Committee, i would like to warmly welcome you to the 3rd Internasi3nal Seminar on New paradigm and Innovation on Natural Sciences and Its Application (ISNPINSA). This seminar has been successfully conducted since 2011 and therefore becoming an annual event since then. The theme of ISNPINSA this year is Developing Innovation and Its Application of Applied Sciences for Sustainable Development.

The aims of this seminar are to facilitate brain storming and state of the art information in field of sciences and mathematic; to increase innovation of technology that can be applied in industries; to contribute in formulating strategy to increase the role of science for the community; and to stimulate collaboration between industries, researchers and government to increase community welfare.

We divided the parallel session in this seminar into specific topic that can accommodate the field range from chemistry, physics, biology, mathematics and the science related to them. By inviting the speakers from academics and industries, we hope that this event can be a bridge between researchers, scientists and industries in order to foster developing innovation and its application to support sustainable development.

In closing, I wish to express my gratitude to all speakers, presenters and participants in this seminar. I hope that we can have a fruitful and productive discussion, brain storming and presentation that can increase and develop our understanding in sciences. I take this opportunity to thank the organizing committee for this seminar and the Faculty of Science and Mathematics for the necessary funding. The various sponsors are also thanked for their kind hospitality.

Thank you

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# Kinetics Study for Biodiesel Production from Rubber Seeds (*Hevea Brasiliensis*) by in Situ Esterification Method

Widayat<sup>a,b</sup>, Agam Duma Kalista Wibowo<sup>a</sup>, Hadiyanto<sup>a,b</sup>

<sup>a</sup>Chemical Engineering, Diponegoro University Jl. H. Prof. Sudarto, SH, Semarang, Indonesia 50275  
Phone 024-7460058 Fax. 024-7480675

<sup>b</sup>C-Biore : Center of Biomass and Renewable Energy

## ABSTRACT

Until now there's no research about kinetic models for biodiesel production process by in situ especially for biodiesel production from rubber seeds. Biodiesel is a methyl esters or ethyl fatty acids which made from vegetable oils (edible and nonedible) or animal fats. The purpose of this research was to study the suitable kinetic models for biodiesel production by in situ method with target as environmentally friendly alternative fuel from nonedible materials. This research focused on the determination of kinetic model based on esterification reaction for biodiesel production process from rubber seeds using  $H_2SO_4$  0.25% (v/v) catalyst concentration, ratio of raw material to methanol (1:3) for 2 hours at 60°C. Kinetics model that represent the process of biodiesel production is:

$$\frac{dC_{FA}}{dt} = -k_f \cdot C_{FA}$$

with, esterification reaction rate constants is 0.002/minute.

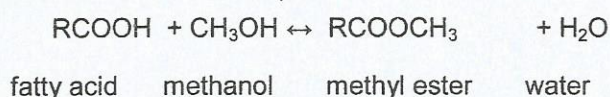
**Keywords:** Biodiesel, rubber seed, in situ, esterification, kinetics model.

## 1. INTRODUCTION

Since fossil fuels increase greenhouse gas emissions and cause global warming, the use of alternative resources like biofuels are more pronounced every day. For example, European Community has decided to replace at least 5.75% of the yearly consumed fossil fuels by biofuels, by the year 2010. The use of these biofuels does not contribute to the growth of greenhouse gases [1]. As an alternative to fossil fuels, biofuels must be technically feasible, economically competitive, environmentally acceptable, and readily available [2]. Regarding these properties, biodiesel has been widely recognized as a promising biofuel. On the other hand, biodiesel is usually more expensive than petroleum-based diesel fuel when it is produced from vegetable oils or animal fats [3].

However, biodiesel has not been commercialized massively around the world because of the high price of raw materials (fresh vegetable oil), resulting in high price of biodiesel which contrast with diesel fuel from petroleum. One of the low cost raw materials is rubber seeds which nonedible materials. With regard to plant rubber, rubber seeds are not yet widely used especially in Indonesia whereas the oil level is high enough around 40-50% [4]. Utilization of rubber seeds as a raw material for biodiesel production is quite potential in Indonesia.

Biodiesel production involves esterification and transesterification reaction. Esterification is the conversion of free fatty acids to esters. Commonly suitable catalyst has strong acids characteristic such as sulfuric acid, organic sulphuric acid or strong acid cation exchanger resin are used by industry [5]. Esterification reaction is shown as follow:



The free fatty acid content of unrefined rubber seed oil was about 17%, i.e. acid value of 34 [4] so that acid esterification process can be used for oils that FFA content is higher than 3% [6]. Esterification is reversible reaction where free fatty acid/FFA is converted to alkyl ester via acid catalyst (HCl or H<sub>2</sub>SO<sub>4</sub> commonly). When free fatty acid in the oils is high such as used frying oil, simultaneous esterification followed by transesterification reaction via acid catalysts can potentially get almost complete biodiesel conversion. Esterification process follows the same reaction mechanism as transesterification acid catalyst [7].

To get the oils by conventional methods, seed is pressed by mechanical process or extracted with chemical solvents. After that the oil is pretreatment by degumming process. This process requires high production costs. Biodiesel production is made also from rubber seed oil by using two-stage esterification followed by transesterification reactions [4], [8]. This process still has the same weakness as the pretreatment process of oil. To overcome this shortcoming, the (trans)esterification process by in situ methods to be one alternative.

Biodiesel production process can reduce production costs if using in situ (trans)esterification. In this process, the cost of extraction with solvents and oil purification can be removed so that biodiesel production becomes simpler [9]. The first in situ transesterification was introduced by Harrington & Evans [10-11] from sunflower seeds.

Another approach to produce monoesters from high-acidity oils is in situ esterification, i.e., simultaneous oil extraction and acidic esterification or alcoholysis. In this process, alcohol acts as an extraction solvent for oil components and as a reagent to esterify these components [12-13]. By using this process the production cost of biofuels may be further reduced since the oil extraction step in the conventional process will be omitted as well. For example on research by Ozgul & Turkay was done in situ esterification from rice bran [14] and developed further until the last in situ transesterification from castor seeds [9].

## 2. KINETICS MODEL

Biodiesel production process by in situ involves two processes running simultaneously. It is extraction and (trans)esterification process in one reactor, but in this study only represented by esterification reaction, therefore can be made kinetics model by combining extraction rate and esterification reaction rate.

### 2.1. Kinetics model of extraction rate

The extraction process takes place in two stages. The first stage, most of the dissolved substances is extracted rapidly because of scrubbing and dissolving caused by the thrust of fresh solvent and then on the next process will be slowly by external diffusion of remaining dissolved substances in the solution [15].

According to Yang et al., [16], the extraction process can be modeled as order 1 and order 2. Order 1 mechanism model consider the order 1 rate law so that this research only use order 1 kinetics model based on the existing equation which dissolving of oil in solid material into the solution can be expressed in the following formula:

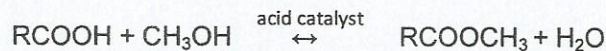
$$\frac{dC_t}{dt} = k(C_s - C_t) \quad (1)$$

Equation (1) was modified based on the concentration of FFA (%) as follow:

$$\frac{dC_{FA}}{dt} = k(C_{FA,s} - C_{FA}) \quad (2)$$

### 2.2. Kinetics model of reaction rate

Research study of reaction kinetics is represented by esterification reaction as follow:



Assuming order 1 reaction then reaction rate:

$$-\frac{dC_{FA}}{dt} = k_f \cdot C_{FA} \cdot C_{MeOH} - k_r \cdot C_{FAME} \cdot C_{H_2O} \quad (3)$$

Reaction condition is aimed to remove water from reaction system and to add methanol in excess, therefore we can ignore the reverse reaction (the reaction to the left) so that the equation becomes:

$$-\frac{dC_{FA}}{dt} = k_f \cdot C_{FA} \cdot C_{MeOH} \quad (4)$$

In addition, with the excess methanol is added into the reaction system as expressed by Joelianingsih et al. [17].  $C_{MeOH}$  can be considered stable and the equation (3) can be written as:

$$\frac{dC_{FA}}{dt} = -k_f \cdot C_{FA} \quad (5)$$

Based on the assumption, this esterification reaction is order 1 reaction. So that the reaction rate constant unit is ( $k_f$ ) (1/time) [18].

### 2.3. Kinetics model of extraction-reaction rate

Kinetics model of extraction-esterification reaction is made by combining the kinetics model of extraction rate at Equation (2) with kinetics model of esterification reaction rate at Equation (1) becomes:

$$\frac{dC_{FA}}{dt} = -k_f \cdot C_{FA} + k_{FA,s} \cdot C_{FA,s} - C_{FA} \quad (6)$$

The extraction rate constant ( $k$ ) and the esterification reaction rate constant ( $k_f$ ) can be obtained by using MATLAB 7.0.1 from above equations.

Thus, this research aims to determine the kinetic model that suitable for biodiesel production from rubber seeds by in situ method so that it will be known extraction rate constants ( $k$ ) and esterification reaction rate constant ( $k_f$ ).

## 3. METHODOLOGY

### 3.1. Materials

Rubber seeds were procured from rubber plantation Kendal Indonesia. Methanol (technical),  $\text{H}_2\text{SO}_4$  catalyst was used pro analysis (Merck, Germany).

### 3.2. Experimental procedure

Rubber seeds were peeled and the kernels were crushed, macerated and dried in an oven at  $55^\circ\text{C}$  for 2 hours. One hundred grams kernels were inserted into a flask assembled by a mixer/stirrer (see figure 1). Then methanol which has been mixed with a catalyst is added and stirred as well as heated at  $60^\circ\text{C}$  for 2 hours at atmospheric pressure. 5 mL of biodiesel blend products were taken every 15 minutes (for 2 hours) to analyze the acid value.

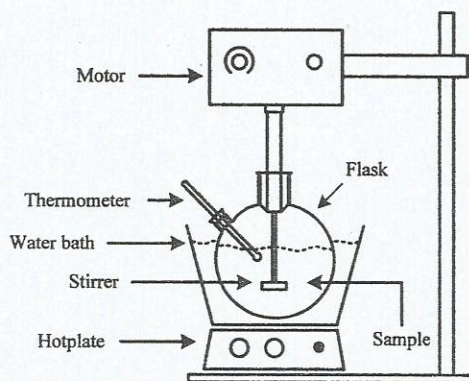


Figure 1. Experimental tool set

### 3.3. Computation Methods

The parameters in 2, 5 and 6 equations obtained with numerical solution. Computation was done with MATLAB Software. The equations are a Ordinary Differential Equations (ODEs) that solution with Runge Kutta 4<sup>th</sup> methods. So, the parameters in kinetic models obtained with optimization methods with fmins function and ODE45 function. Optimization method use Hooke-Jeeves method.

## 4. RESULTS AND DISCUSSION

Before doing the research, first the raw material of rubber seed kernel was done proximate analysis such as moisture content, ash content, protein and fat/oil content. The analysis results were obtained the following data.

Table 1. Proximate analysis results of rubber seeds compared to other researcher

Component	Composition (%)	
	A	B
Water content	7.78	7.6
Ash content	4.19	3.1
Protein content	21.69	21.7
Fat/oil content	26.85	39

Note: wet basis

A = my own research results

B = Stosic & Kaykay, [19] referenced from Aritonang, (1986)

Research results were obtained water content 7.78%, while compared with Stosic and Kaykay, [19] the result of water content is not too different, so that in biodiesel production is necessary to dry the raw material because the presence of water can disrupt the process of biodiesel production. After drying process (55°C, 2 hours), water level was decreased from 7.78% to 4.04%. From Table 1 ash and protein content are 4.19% and 21.69% respectively, and those results are not too different if compared with Stosic and Kaykay, [19]. Drying the raw material will not change the composition of rubber seed significantly. According to Andayani, [20] the protein content after drying the rubber seed was not very different, yet the presence of water in raw material causes the protein to be decreased at 13.85% (dry basis) and 12.62% (wet basis). Whereas oil content was 26.85% lower than that expressed by Ketaren, [21] which was about 40-50% and Stosic & Kaykay, [19] was 39%, this was because the low quality of rubber seeds. The high content of oil, protein, and water in kernel caused

rubber seeds damaged easily. The damage can be caused by the activity of the enzymes and microorganisms contained in the seeds. According to Ketaren [21], lipase enzyme is one type of enzyme which active in the harvested grain. The action of this enzyme will encourage decomposition of triacylglycerol into fatty acids and glycerol. This process is called hydrolysis process. Hydrolysis can occur while oil is still in the harvested seed, during processing and storing. To reduce hydrolysis or damage in the oil, usually kernels are dried before extracted. In addition, according to Andayani, [20] the drying process to rubber seed kernel will not lower the oil content but it can increase the yield of oil. This is because the affinity of oil with surface materials will be reduced and causes clotting proteins in the cell wall and cause damage to the cell wall so that the wall would be easily damaged. This causes the cell walls easily penetrated by oil or fat so that the oil will easily come out. Andayani, [20] dried rubber seed kernel at 70°C for 2 hours. The result could increase the yield of oil 10.14% whereas in this research, rubber seed kernels were dried at 55°C for 2 hours so that the expected result of oil yield will not be different.

#### 4.1. Kinetics model of extraction-reaction rate

Kinetics model of biodiesel production process by in situ include first order extraction rate and first order esterification reaction rate kinetics model because the extraction and the reaction process run simultaneously in same reactor.

In this study, the reaction kinetics modeling based on esterification reactions only (H<sub>2</sub>SO<sub>4</sub> 0.25%, ratio of raw material to methanol 1:3 w/v) this refers to research results by Widayat., et al, [22] and also because it is assumed that the most dominant process is esterification reaction due to the high content of FFA from rubber seeds in biodiesel production process. The assumption to analyze the kinetics model of esterification reaction rate is [18]:

- a. Excess of methanol addition and water removal from the system reaction so that the reverse reaction is ignored (the reaction to the left is ignored). With excess methanol, methanol is not the limiting reactant.
- b. Concentration of methanol can be considered constant.

Kinetic model of extraction-esterification reactions rate was supposed from combination between kinetic model of extraction and esterification reaction rate which the equation is shown as follow:

$$\frac{dC_{FA}}{dt} = -k_f \cdot C_{FA} + k_{FA,S} \cdot C_{FA,S} \quad (7)$$

Prior to prove the equations model above, first it will be discussed the kinetics model from each equation by assuming:

- 1) Only influenced by esterification reactions while the extraction process do not affect significantly ( $k = 0$ ).
  - 2) Only influenced by extraction process while the esterification reactions do not affect significantly ( $k_f = 0$ ).
  - 3) Either extraction process and esterification reaction are affect significantly ( $k_f \neq 0, k \neq 0$ ).
- Therefore, it will be discussed one by one in order to prove each assumption above.

- 1) Only influenced by esterification reactions

If it is assumed that only influenced by esterification reaction while the extraction process do not affect significantly ( $k = 0$ ), thus the equation  $k(C_{FA,S} - C_{FA}) = 0$ , so that the first order of esterification reaction kinetics model is shown as follows:

$$\frac{dC_{FA}}{dt} = -k_f \cdot C_{FA} \quad (8)$$

Above equation can be solved by MATLAB 7.0.1 which resulting the esterification reaction rate constants ( $k_f$ ) was 0.002/minute and sum of square error (SSE) was 0.051. The graph is shown in Figure 2. We can compare between the blue line is the calculation result data by MATLAB 7.0.1 and the green star is experimental result data. The graph shows that the concentration of FFA decreases because the FFA is converted into biodiesel.

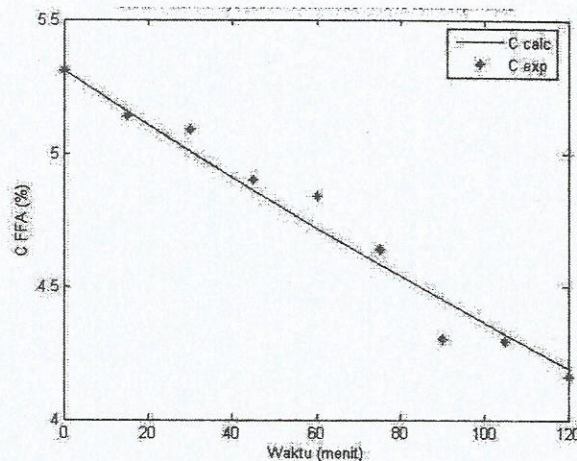


Figure 2. Graph of esterification reaction rate kinetics vs time(SSE = 0.051)

2) Only influenced by extraction process.

If it is assumed that only influenced by extraction process while esterification reaction do not affect significantly ( $k_f = 0$ ) thus  $-k_f \cdot C_{FA} = 0$ , so that the first order of extraction rate kinetics model which based on the concentration of FFA (%) is shown as follows:

$$\frac{dC_{FA}}{dt} = k(C_{FA,s} - C_{FA}) \quad (9)$$

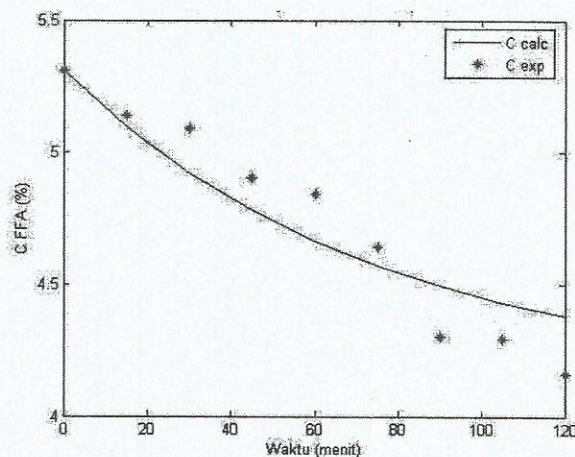


Figure 3. Graph of extraction rate kinetics vs time (SSE = 0.1871).

For  $C_{FA,s} = 4.16\%$ , Equation (9) can be solved by MATLAB 7.0.1 and obtained the graph as in Figure 3 which resulting the extraction rate constants ( $k$ ) was 0.0138/min, SSE was 0.1871.

3) Either extraction process and esterification reaction are affect significantly.

If assume either extraction process and esterification reaction are affect significantly, the kinetics model with  $C_{FA,s} = 4.16\%$  is shown as follow:

$$\frac{dC_{FA}}{dt} = -k_f \cdot C_{FA} + k(C_{FA,s} - C_{FA}) \quad (10)$$

Using MATLAB 7.0.1 the esterification reaction rate constants ( $k_f$ ) was 0.0020/minute, the extraction rate constants ( $k$ ) is 0.0001/minute and SSE was 0.051. The graph is shown as follow:

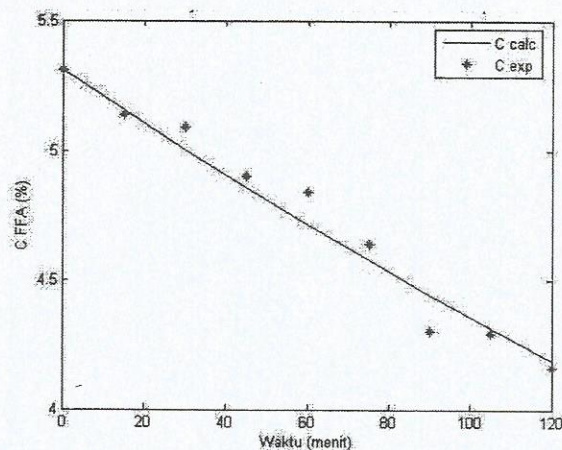


Figure 4. Graph of extraction-esterification reaction rate kinetics vs time ( $C_{FA,s} = 4,16\%$ ,  $SSE = 0.051$ )

While compared with  $C_{FA,s} = 3\%$ , hence its graph is:

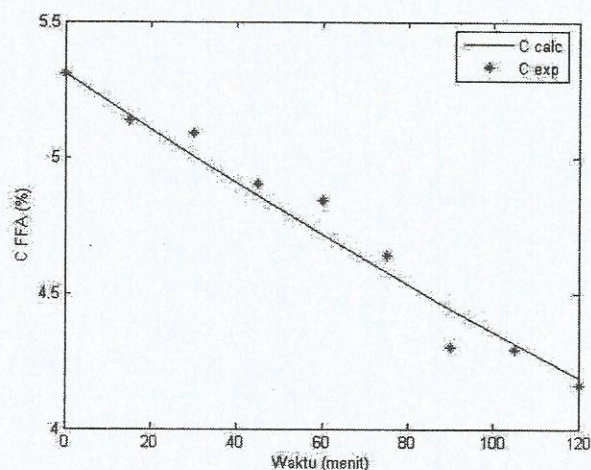


Figure 4. Graph of extraction-esterification reaction rate kinetics vs time ( $C_{FA,s} = 3\%$ ,  $SSE = 0.051$ )

Using MATLAB 7.0.1 the esterification reaction rate constants ( $k_f$ ) was 0.0020/minute, the extraction rate constants ( $k$ ) was 0.0001/minute and SSE was 0.051. From Figure 5 and 6, it was shown that the difference of  $C_{FA,s}$  would obtained the same constants and SSE.

Based on the assumptions, it can be summarized as follows:

Table 2. Comparison of rate constants and SSE from each assumption

Assumption (the influential)	Rate constants (1/minute)	SSE
(1)	$k_f = 0.002$	0.051
(2)	$k = 0.0138$	0.1871
(3) $C_{FA,s} = 4,16\%$	$k_f = 0.002$ . $k = 0.0001$	0.051
(4) $C_{FA,s} = 3\%$	$k_f = 0.002$ . $k = 0.0001$	0.051

Based on Table 2 above it can be concluded that the suitable kinetics model are kinetics model of esterification reaction and joining model between extraction process and esterification reaction because those model have the smallest SSE while compared to the others. Kinetics model of esterification reaction solely can also be justified because of the simplest equation. The most dominant process or quickly between the extraction process and esterification reaction is the esterification reaction, because the esterification reaction rate constants is higher than that the extraction rate constants.

## CONCLUSION

time, with

the suitable kinetics models are the kinetics model of esterification reaction and or kinetics model of extraction-esterification reaction, with the dominant process is esterification reaction. But the simplest kinetics model can be represented by the kinetics model of esterification reaction rates as follow:

$$\frac{dC_{FA}}{dt} = -k_f \cdot C_{FA}$$

with the esterification reaction rate constants ( $k_f$ ) was 0.0020/minute.

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## NOMENCLATURE

$C_s$  = Concentration of oil at saturation conditions (g/L)

$C_t$  = Concentration of oil at t minute (g/L)

$k$  = Extraction rate constants

$C_{FA}$  = Concentration of free fatty acid at t minute

$C_{FAME}$  = Concentration of fatty acid methyl ester

$C_{MeOH}$  = Concentration of methanol

$C_{H_2O}$  = Concentration of water

$k_f$  = Esterification reaction rate constants (to the right)

$k_r$  = Esterification reaction rate constants (to the left)

$C_{FA,s}$  = Concentration of fatty acid at the end (%)

$t$  = Time (menit)

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