

## Esterification of Free Fatty Acid with High Chain Alcohol for Biodiesel Production Using Semi-Batch Reactive Distillation

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### Abstract

The esterification of oleic acid with 2-ethylhexanol in presence of sulfuric acid as homogeneous catalyst was investigated in this work to produce 2-ethylhexyl oleate (biodiesel) by using semi batch reactive distillation. The effect of reaction temperature (100 to 130°C), 2-ethylhexanol:oleic acid molar ratio (1:1 to 1:3) and catalysts concentration (0.2 to 1wt%) were studied. Higher conversion of 97% was achieved with operating conditions of reaction temperature of 130°C, molar ratio of free fatty acid to alcohol of 1:2 and catalyst concentration of 1wt%. A simulation was adopted from basic principles of the reactive distillation using MATLAB to describe the process. Good agreement was achieved.

**Key Words:** Biodiesel, Reactive distillation, Esterification, Homogeneous catalyst

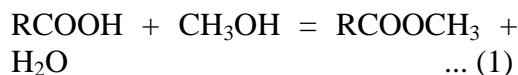
### Introduction

Sustainable energy management is a major concern of the modern society. The increasing energy demand makes the implementation of sustainable fuels a crucial issue worldwide [1,2]. Biodiesel has become increasingly attractive because it is made from renewable sources and combines high performance with environmental benefits [3–5]. Unlike petroleum diesel that contains hydrocarbons, biodiesel consists of a mixture of monoalkyl esters of long-chain fatty acids.

Biodiesel has several advantages over petroleum diesel: it is safe, renewable, nontoxic and biodegradable; it contains no sulfur that effected lubricity prolongates the diesel engine life [2,5]. Biodiesel not only has a higher cetane number than petroleum diesel but also has a higher

flash point, meaning better and safer performance and it generates less hydrocarbons, fewer carbon dioxide and fewer particles than petroleum diesel. Biodiesel can be blended with any amounts of petroleum diesel and defined by a “B” followed by the vol % of biodiesel [4]. The conventional biodiesel production process based on the use of alkaline catalyst, such as sodium hydroxide or sodium methoxide, for transesterification of triglyceride posed serious separation problem. The presence of water and/or free fatty acids (FFA) in the reaction system leads to saponification [6-8]. A homogeneous acid catalyst, such as sulfuric acid or hydrochloric acid can also be used [9,10], which does not produce soap and increase the fuel production. Meher *et.al.* suggested an alternative way to solve the FFA

problem by using an acid catalyst. The esterification of FFA by methanol can be carried out before the transesterification of oil as shown in Eq. 1 [11]. Thus, valuable FFAs can be completely converted to biodiesel without being wasted.



There are five primary ways for making biodiesel: (i) direct use and blending of vegetable oil (ii) use of microemulsions with short-chain alcohols (iii) thermal cracking (pyrolysis) of vegetable oils (iv) transesterification of triglycerides catalyzed by bases, acids, or enzymes and (v) esterification of fatty acids with alcohols, using acid catalysts ( $\text{H}_2\text{SO}_4$ ) or solid acids.

Usually, an alcohol excess is used for driving the reaction equilibrium towards the product side. This alcohol excess must be recovered in order to reutilize it and furthermore purify the biodiesel. The alcohol recovery process is generally carried out by distillation process, thus, the energy consumption, operating costs, equipment number and the production time increase.

Reactive distillation (RD) is the process in which chemical reaction and separation are carried out simultaneously within a fractional distillation apparatus. It may be advantageous for liquid-phase reaction systems when the reaction must be carried out with a large excess of one or more of the reactants, when a reaction can be driven to completion by removal of one or more of the products as they are formed, or when the product recovery or by-product recycle scheme is complicated or made infeasible by azeotrope formation [12]. By continuous separation of products from reactants while the reaction is in

progress, the reaction can proceed to a much higher level of conversion than without separation [13].

The aim of this work is the study of the production of biodiesel by esterification of oleic acid with 2-ethylhexanol in a reactive distillation column. The esterification of oleic acid using sulfuric acid as a catalyst has been investigated at different process conditions: temperature, oleic acid: 2-ethylhexanol ratio, sulfuric acid concentrations.

## **Experimental Section**

### **Materials**

Oleic acid (98%) was supplied from Thomas baker, india. This acid is unsaturated fatty acid that jatropa oil which is inedible oil contains 44.8% of it. 2-ethylhexanol alcohol (99% from GC analysis) was maintained from ministry of science and technology as industrial alcohol. Since this alcohol is typically a waste alcohol from the manufacturing of butanol, this process makes sense from an economic viewpoint. Sulfuric acid as catalyst, ethanol and phenolphthalein for titration.

### **Reaction Procedure**

The reaction was carried out in a lab scale reactive distillation column that consists of a 250 ml flask equipped with oil bath to set up a constant reaction temperature, magnetic stirrer, condenser, and column distillation. The feed is charge into the flask in the bottom of the rectifying column that also used as a reactor and reboiler. Esterification of fatty acid is a reversible reaction and water is formed. Removal of water can drive the reaction equilibrium to the completion and therefore increase the conversion. The best solution is working at temperatures above  $100^\circ\text{C}$ , in a system with continuous water

removal. By removing water as by-product, the equilibrium is shifted towards ester formation. The ester (biodiesel) will always be separated in the bottom of the reactive distillation column. Water is present as side product and typically is removed as top product due to its lower boiling point. 5 ml of diluted solution was taken for the determination of unreacted acid. This was titrated against 0.1 KOH solution using phenolphthalein as indicator and 2 ml ethanol for dilution. Difference between the fresh acid reading and reading for reaction mixture was used for finding out the % yield of ester.

$$\text{Acid value} = \frac{V \cdot N \cdot \text{mwt}}{m_{\text{sample}}} \quad \dots (2)$$

$$X\% = \left(1 - \frac{[\text{Acid}]_{\text{initial}}}{[\text{Acid}]_{\text{final}}}\right) \times 100 \quad \dots (3)$$

And the amount of catalyst used is normalized to the total amount of reactants:

In these equations, V, N and m.wt is volume, concentration and molecular weight of KOH, m is weigh of sample. X [%] is the conversion of the fatty acid,  $[\text{Acid}]_{\text{initial}}$  and  $[\text{Acid}]_{\text{final}}$  are the molar concentrations of fatty acid before and after reaction,  $W_{\text{cat}}$  [%] is the weight percent of catalyst used in reaction and  $M_{\text{cat}}$ ,  $M_{\text{acid}}$  and  $M_{\text{alcohol}}$  are the amounts of catalyst, acid and alcohol, respectively.

### Simulation Process

To develop a mathematical model of reactive distillation for biodiesel production, mass balance as well as the thermodynamic equilibrium equations on each tray is written. The stages are counted from top to bottom as shown in Fig. (1).

The model is valid under the following assumptions:

- I. All the plates are equilibrium stages.
- II. Vapor phase is an ideal gas mixture.
- III. The reaction takes place only in the reboiler, therefore, rate of reaction just added for reboiler equation.
- IV. Constant operating pressure
- V. Vapor phase hold up is assumed to be negligible as compared to the liquid phase hold up on each stage.
- VI. The column was considered isothermal (temperature for all stages is the same) therefore energy balance not established.

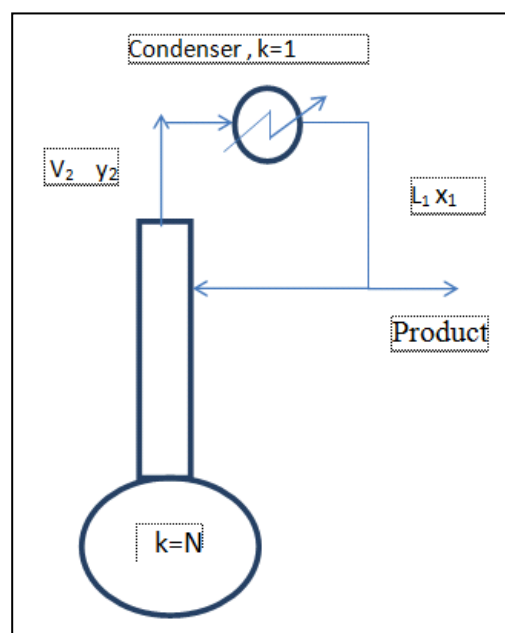


Fig. 1, Scheme of semi-batch distillation column

The column was simulated assuming 4 stages including the reboiler. The feed was introduced at the reboiler and the reaction took place in reboiler. The simulation was carried out by solving the system simultaneously using MATLAB program.

The determination of phase composition can be made by solution of material balance equations. The solution of material balance equations are derived for condenser, the column stages and reboiler as follow:-

- For Condenser ( $k=1, i=1-4$ )

$$\frac{dx_{1(i)}}{dt} = \frac{V_{(1)}y_{2(i)} - L_{(1)}x_{1(i)}}{H_{(1)}} \quad \dots (5)$$

- For Column ( $k=2,3$  and  $i=1-4$ )

$$\frac{dx_{k(i)}}{dt} = \frac{V}{M_{in}} (y_{k+1(i)} - y_{k(i)}) + \frac{L}{M_{in}} (x_{k-1(i)} - x_{k(i)}) \quad \dots (6)$$

- For Reboiler ( $k=N$  and  $i=1-4$ )

$$\frac{dx_{N(i)}}{dt} = \frac{(L_{(k)}x_{N-1(i)} - V_{(k)}y_{N(i)})}{H_{(k)}} + \text{Rate} \dots (7)$$

Where

H is holdup, K is stage, i is component  
Equilibrium ratio ( $k=2$  to N)

$$y_{k(i)} = \frac{\alpha_i x_{k(i)}}{\sum_{j=1}^i \alpha_j x_{k(j)}} \quad \dots (8)$$

Where

$\alpha_i$  is the relative volatility  
x is composition of liquid phase  
y is composition of vapor phase

The UNIQUAC model was applied to consider the nonideal liquid-phase behavior. The degree of deviation from ideality in liquid phase is represented by  $\gamma_i$  (activity coefficient). It was employed for the vapor-liquid equilibrium (VLE) calculations in MATLAB.

Activity coefficient consists of two terms, residual and combinatorial

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad \dots (9)$$

$$\ln \gamma_i^C = 1 - J_i + \ln J_i - 5q_i \left( 1 - \frac{J_i}{L_i} + \ln \frac{J_i}{L_i} \right) \quad \dots (10)$$

$$\ln \gamma_i^R = q_i \left[ 1 - \sum_k (\theta_k \frac{\beta_{ik}}{S_k} - e_{ki} \ln \frac{\beta_{ik}}{S_k}) \right] \quad \dots (11)$$

## Results and Discussion

### 1- Effect of Mixing Speed

Fig. (2) illustrates the relationship between conversion of oleic acid with time at different mixing speeds (500-900 rpm) using a homogeneous catalyst of concentration of 1wt%, reaction temperature of 130°C and oleic acid:2-ethylhexanol molar ratio of 1:1.

The results obtained here, showed that the conversion increased from 91.78 to 96.55% for mixing speed of 500 to 650 rpm respectively, then decreasing to 93.97% for mixing speed of 900 rpm. When the speed is higher than the desired one which gave high conversion, there was a negative effect because of the formation of very small droplet that behave as rigid drop, causing the molecules inside the drop could not move and transferred from center of drop to surface to be converted, therefore the reaction and conversion took place only on the surface which gave lower value.

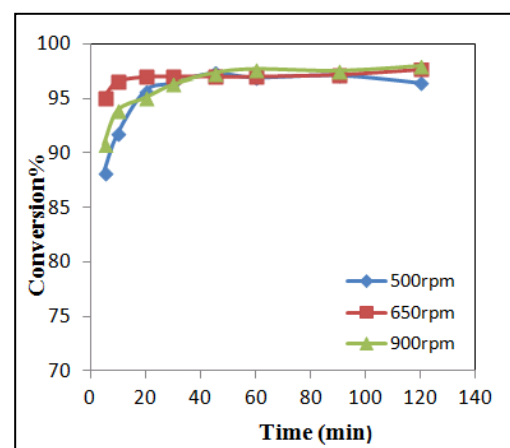


Fig. 2, Effect of mixing speed on conversion of oleic acid

**[Operating conditions:** molar ratio of free fatty acid: alcohol was 1:1, reaction temperature 130°C and concentration of sulfuric acid 1wt%]

## 2- Effect of Molar Ratio of Alcohol to Free Fatty Acid

The most important parameter effect biodiesel production is molar ratio of alcohol to oil. For batch studies of conventional process the alcohol to oil ratio of feed has considered as an important factor for determining equilibrium constant and excess of alcohol used to shift the reaction to equilibrium. On contrast, reactive distillation used to overcome this problem since it reduce the need of excess alcohol and reduce the time by continuous removing of water instead of adding excess reactant.

For oleic acid and 2-ethylhexanol using homogeneous catalyst ( $H_2SO_4$ ), Fig.(3) shows the effect of molar ratio of 2-ethylhexanol: oleic acid on the conversion of oleic acid at a constant temperature of  $130^\circ C$ , concentration of sulfuric acid of 1wt% and mixing speed of 650 rpm. It can be clearly seen the activity profile, when the molar ratio increased from 1 to 2 the conversion was found to increase from 78% to 97% after 20 min reaction time while for further increase in 2-ethylhexanol ratio to 3, the conversion decrease to reach 93.40% after 2 h reaction time.

As the alcohol to acid molar ratio varies to reach three orders of magnitude, dehydration to ethers is a potentially unwanted side reactions, the formation of alkene which cause decrease in conversion were occurred. Also further increasing in alcohol led to disturbing the stoichiometric of alcohol to acid and accordingly decreases in reaction rate. As well as the molar ratio of alcohol to acid increased, the catalyst was diluted by excess of alcohols this also led to decreased conversion.

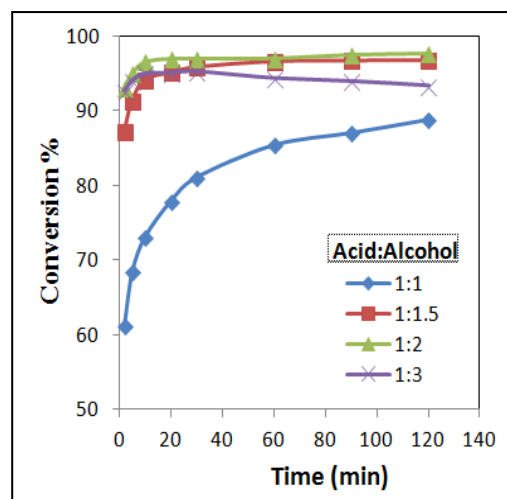


Fig. 3, Effect of Acid:Alcohol molar ratio on oleic acid conversion

**[Operating conditions:** reaction temperature  $130^\circ C$ , concentration of homogeneous catalyst 1wt% ( $H_2SO_4$ ) and mixing speed 650 rpm]

## 3- Effect of Reaction Temperature

Fig. (4) illustrates the variation of conversion with time at different reaction temperatures of 100, 110 120 and  $130^\circ C$  to enhance the separation of water.

It has been observed as the temperature increase, the conversion increase from 93.34% at  $100^\circ C$  to reach 96.55% at  $130^\circ C$  after 10 min reaction time with constant molar ratio of oleic acid:2-ethylhexanol of 1:2 and catalyst amount of 1wt%.

Since the esterification reaction is endothermic, increasing the reaction temperature led to increasing conversion. The high temperature cause increase in activity of molecules which mean more molecules have more energy, therefore the probability of molecules to react increased.

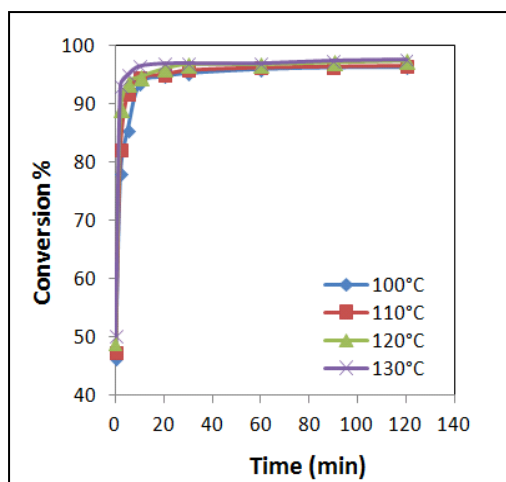


Fig. 4, Effect of temperature on oleic acid conversion

#### 4- Effect of Catalyst Concentration

The amounts of catalyst also play a role on the conversion of the esterification reaction but less effect than temperature and molar ratio. The varying amount of catalysts was studied in this work at the following reaction conditions: ratio of alcohol to fatty acid 2:1, temperature 130°C and mixing speed of 650 rpm during 120 min of reaction time.

The results are displayed in Fig.(5) and shows that reaction was highly depend on presence of catalyst which accelerate the reaction. it gave 59.13% after 120 min. Conversely, in the presence of acid catalysts, a different results were observed. Therefore the conversion increased to reach 86% and 97% when the reaction catalyzed by 0.2wt% and 1wt% sulfuric acid respectively after 60 min. The increase in catalyst concentration considerably shortened the time needed to reach the reaction equilibrium. This in agreement with **Kusmiyati and Sugiharto A., 2010**, who studied the effect of concentration of sulfuric acid on esterification of oleic acid with methanol and showed that further adding of catalyst amount above 1wt% did not lead the conversion to increase significantly [14]. Since sulfuric acid absorbs some of the water formed by

reacting with it to form solvated ions, thus reducing the amount of free water in the system therefore the best concentration achieved was 1wt%.

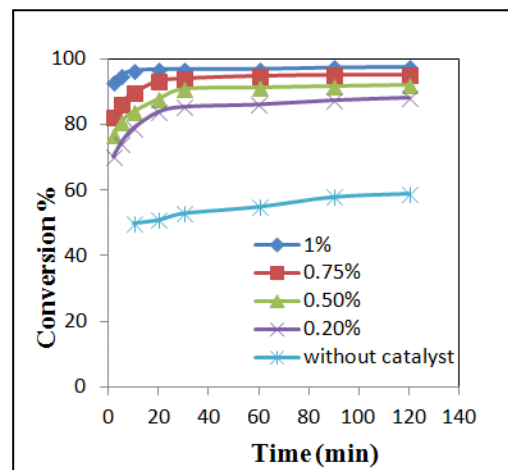


Fig. 5, Effect of homogeneous catalyst concentration on oleic acid conversion

**[Operating conditions:** reaction temperature 130°C, molar ratio of 2-ethylhexanol:oleic acid 2:1 and mixing speed 650 rpm]

#### Testing of Biodiesel Obtained from Oleic Acid

Biodiesel obtained from oleic acid was analyzed by ASTM (American Standard for Testing Material). Table (1) shows biodiesel from this experiment

Table 1, Petroleum diesel vs. biodiesel

Fuel properties	Biodiesel [15]	Diesel [15]	Recent work[16]
Flash point °C	100–170	60–80	100
Kinematic viscosity (mm/s)@40°C	1.9–6.0	1.3–4.1	5.9562
Density g/ml @30°C	0.88	0.85	0.859
Pour point °C	-15 to 10	-35 to -15	-10
Cloud point °C	-3 to 12	-15 to 5	-7
Boiling point °C	182-338	188-343	198
Carbon residue%			0.136

### Simulation Results

The predicted results from the simulation model of batch reactive distillation could be utilized to speculate the composition of reactants and products to compare them with experimental work.

Figs. (6) to (8) displaying the composition change with time for oleic acid with homogeneous catalyst at various conditions of temperature and molar ratio of alcohol to FFA with constant concentration of catalyst (1wt %).

There are simple differences between theoretical and experimental results.

The main deviation due to non ideality of a system which ignored in the experiment but considered for theoretical study.

Fig. (6) shows a decrease in mole fraction of oleic acid with time, which approached nearly zero within 5 min, this is due to the fact that is converted to biodiesel after the reaction reached its suitable conditions.

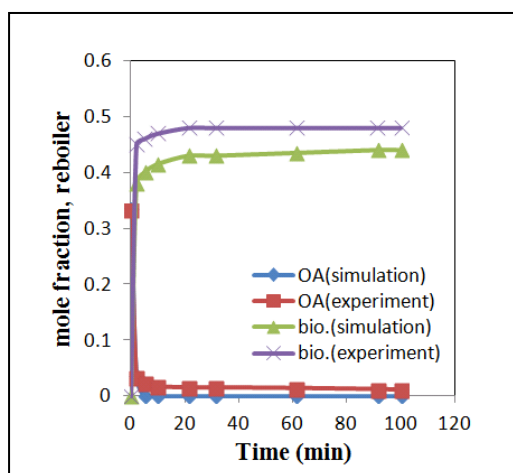


Fig. 6, mole fraction of oleic acid and its biodiesel

[**Operating conditions:** molar ratio alcohol: acid was 2:1, reaction temperature 130°C and concentration of homogeneous catalyst wt 1% ( $H_2SO_4$ )]

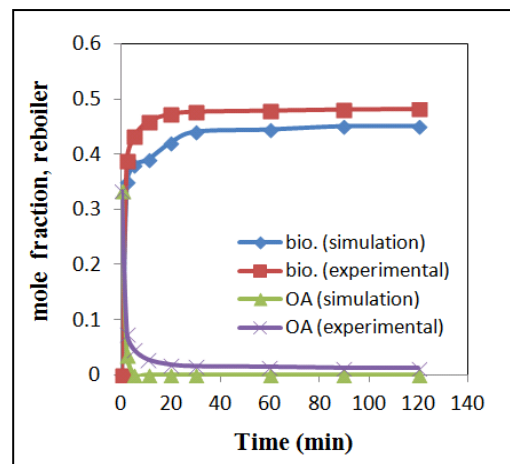


Fig. 7, mole fraction of oleic acid and its biodiesel

[**Operating conditions:** molar ratio of alcohol:acid was 2:1, reaction temperature 100°C and concentration of homogeneous catalyst 1wt% ( $H_2SO_4$ )]

This result was in a good agreement with experimental results as shown in the figure. While for biodiesel, the mole fraction in still increased for both experiment and simulation, but simulation gave lower fraction as a result of water presence. At temperature 100°C at the same ratio of alcohol: acid of (2:1) very good agreement shown in Fig. (7). Composition for theoretical and experimental reaches 0.45 and 0.48 biodiesel, respectively after 120 min.

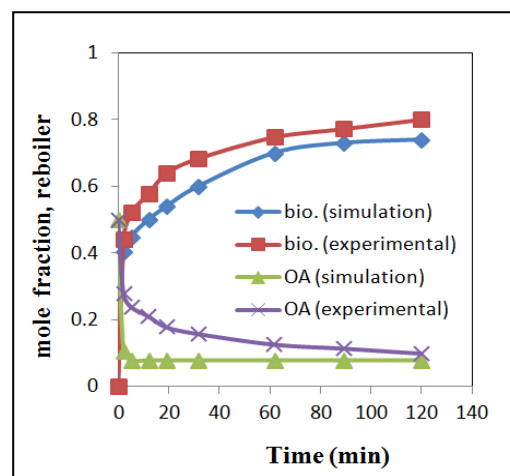


Fig. 8, mole fraction of oleic acid and its biodiesel

**[Operating conditions:** molar ratio alcohol:acid was 1:1, reaction temperature 130°C and concentration of homogeneous catalyst 1wt% (H<sub>2</sub>SO<sub>4</sub>)]

### Conclusions

- 1- The influence of various parameters reaction was studied and shown that the best conditions for biodiesel production were molar ratio of 1:2, temperature 130°C and catalyst amount of 1wt% which give higher conversion 96.55% after very short time of 10 min reaction.
- 2- Reversible reaction not occurs because of continuous removal of water during reaction and shifts it to equilibrium. Stoichiometric ratio is enough to give high conversion, since it reach 88.91% at time 2 h while reached 97.68% for ratio 1:2 at the same time and may be obtain higher conversion for low ratio if we use high temperature but cannot rise temperature because sulfuric acid is dangerous and cause crackling when added to mixture therefore we prefer high ratio and low temperature when using sulfuric acid as catalyst.
- 3- The most parameter effect on esterification is molar ratio then temperature while amount of catalyst has very small effect on biodiesel production.

### Nomenclature

C: concentration of KOH solution, mole/l.

mwt.: molecular weight of KOH, g/mole.

V: volume of KOH solution, ml.

M: weight of sample, g.

X: conversion, dimensionless.

$\gamma_i^C$ : Combinational term for activity coefficient

$\gamma_i^R$ : Residual term for activity coefficient

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