

## Kinetics of Biodiesel Production from Used Cooking Coconut Oil using Potassium Hydroxide

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### ABSTRACT

Kinetics of biodiesel production using homogeneous catalyst (potassium hydroxide [KOH]) was investigated. The reaction was performed in three-necked glass round-bottom flask, equipped with mechanical stirrer, a reflux double-coiled water condenser, a thermometer and a heating mantle. To investigate the optimum parameters influencing the production of biodiesel, the process was optimized by varying the molar ratio with 1:3–1:9, the amount of catalyst between 0.25 and 1.75 (wt. % of oil), temperature 40°C and 90°C and reaction time from 20 to 140 min. The reaction shows first-order kinetics with an average rate constant of  $5.20 \times 10^{-3}/\text{min}$  at 60°C. The Arrhenius constant and activation energy are found to be  $5.46 \times 10^{-3}/\text{min}$  and 36.8 KJ/mole. The catalytic constant  $K_{\text{cat(UCCO/KOH)}}$  for KOH is  $1.50 \times 10^{-3}$ . The entropy of activation and enthalpy of activation are  $-101.11\text{J/mole k}$  and  $-34.44\text{ KJ/mole}$ , respectively. The most probable mechanism has been proposed.

**Key words:** Activation energy, Biodiesel, First order, Kinetics, Used cooking coconut oil

### 1. INTRODUCTION

With increasing environmental concerns and continuously increasing global energy demand with fossil fuel, biodiesel is being considered as an effective renewable alternative to conventional fuels. Biodiesel has gained significant attention as an alternative fuel due to its renewable [1-4], biodegradable [5,6], sustainable [7], non-toxic [8] characteristics. Its resources are abundantly available [9], emits very less greenhouse gases [10-12] and sulfur oxides [13,14], lower emission of nitrogen oxides [15,16]. It is environmental friendly [17,18] and can be produced locally [19] with less pollution [20-22]. The production processes involved are generally safe and economically flexible [23,24]. In recent decades, biofuels have gained substantial attention owing to their diverse application [25-28]. Particularly in the field of the transport sector, where biodiesel is used as an alternative to conventional petroleum-based diesel [29] and has less pollutant after combustion. Biodiesel is commonly produced from vegetable oil, animal fats, and waste cooking oil through a transesterification process [30-36]. This process is simple and cheap, and in this chemical process triglycerides are converted to fatty acid alkyl ester and glycerol in the presence of a catalyst [37-38]. Recently, waste cooking oil has emerged as an attractive sustainable option as a source of raw material due to its low cost and added advantage of waste valorisation [39-45]. To improve biodiesel yield and process efficiency, optimization of process parameter and understanding of reaction kinetics and thermodynamics remain crucial. Therefore, the aim of the present study is to investigate the optimum parameter for biodiesel production using waste coconut cooking oil and evaluate important kinetics and thermodynamics parameter including rate constant, activation energy, catalytic constant, entropy of activation, to provide a comprehensive understanding of reaction behavior.

### 2. MATERIALS AND METHODS

#### 2.1. Materials

All the chemicals used in the present study were of analytical grade and purchased from various scientific supplier of Sadar, Nagpur city, Maharashtra, India, hundred percent pure coconut (Parachute) oil was purchased from local market of Tukum, Chandrapur city, Maharashtra, India. Household used cooking oil was used in the present study.

#### 2.2. Apparatus

Three vertical – neck flat bottom flask of half-liter capacity was used as a reaction vessel. One side of the neck was fitted with thermometer, while middle neck was fitted with double coiled reflux water condenser and the second side neck was left open to pour mixture.

#### 2.3. Preparation of Used Cooking Coconut Oil (UCCO)

Household UCCO was collected and heated above 100°C to remove the moisture content in the oil. It was then filtered with the help of sieve to remove the coarse particles and through masculine cloth to

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remove fine suspended food particles. Finally, oil was collected in the separate clean flask for further experiment.

#### 2.4. Preparation of Potassium Hydroxide (KOH) and Methanol Mixture

In required volume of methanol, previously weighed amount of KOH pellets were added in conical flask. The flask was covered with aluminum foil to avoid the evaporation of methanol and absorption of water by potassium methoxide. The mixture was shaking machine to completely dissolve the KOH pellets.

#### 2.5. Optimum Parameters

The purpose of optimum parameters is to determine the best combination of oil to methanol ratio, amount of catalyst, reaction time, and temperature to produce the highest yield of biodiesel. Oil to methanol ratio was varied from 1:3 to 1:9. The amount of catalyst was varied using KOH of 0.25–1.75 g of weight percent of oil for each of the molar ratios. Optimization of temperature was done at a range of 40°C–90°C and reaction time of 20–140 min, and corresponding volume of the biodiesel produced was recorded after purification for each of the variations.

#### 2.6. Washing of Biodiesel

The biodiesel was purified by adding distilled water with a volume ratio of 1:1 water and biodiesel. Then the mixture was stirred for 10 min. The hydrated layer was drained off to get clear biodiesel.

#### 2.7. Determination of Biodiesel Yield Percentage

Biodiesel yield was determined using the equation;

$$\text{Percentage biodiesel yield} = \frac{\text{Volume of biodiesel produced}}{\text{Volume of oil}} \times 100\%$$

#### 2.8. Kinetic Measurement

At pre-determined optimum conditions, 100g of UCCO was taken in three neck flat round bottom flask. Previously stirred 1.25 g of KOH and 28.22 g of methanol (1:6) were added in the reaction flask containing used coconut oil. The reaction mixture was refluxed at 70°C and stirred at 600 rpm. Simultaneously stop – watch was started, and the reaction mixture was withdrawn at 20–100 min of time intervals. Aliquots of reaction mixture were cooled at each instant, and the volume of biodiesel generated was measured. From the volume of biodiesel produced, the weight of biodiesel was evaluated. Once the weight of biodiesel produced is known, the amount of used coconut oil reacted and unreacted can be calculated.

#### 2.9. Order of Reaction

The amount of used coconut oil (a-x) unreacted at various time intervals of the reaction was determined at optimum conditions. Using this data order of reaction was determined as below;

- A plot of the logarithm of ratio of the initial amount of used coconut oil to the amount of used coconut oil unreacted against time was plotted
- A plot of the logarithm of used coconut oil unreacted against time was plotted.

The order of reaction was confirmed by various methods. Further, the average reaction rate constant, activation energy, Arrhenius constant, and catalytic constant. Activation entropy and activation enthalpy were evaluated.

### 3. RESULTS AND DISCUSSION

#### 3.1. Optimum Parameter

##### 3.1.1. Oil to methanol ratio

The most important parameter affecting the biodiesel yield is oil to methanol ratio. The results show that as the oil-to-methanol ratio increases from 1:3 to 1:6, the percentage yield of biodiesel increases from 47.5% to 80%. Further increases in the ratio from 1:6 to 1:9, the percentage yield decreases, from 80% to 57.5% [Table 1].

##### 3.1.2. Amount of catalyst

Production of biodiesel is affected by the amount of catalyst. In the present study, KOH is used as a catalyst. Increasing the amount of KOH from 0.25g to 1.25% (w/w), the percentage yield of biodiesel increases from 50% to 80%, while above 1.25% (w/w) yield decreases from 80% to 60% as shown in Table 1.

##### 3.1.3. Temperature

The reaction temperature was varied from 40 to 70°C. It was observed that the yield of biodiesel increases from 55% to 80%, and increases in temperature beyond 70°C resulted in decreases in biodiesel yield to 60%. This is due to vaporization of methanol [Table 1].

##### 3.1.4. Reaction time

The reaction time of biodiesel production was varied between 20 and 140 min at intervals of 20 min. It is found that when time increases from 200 to 100 min, the percentage yield of biodiesel increases to 80%. Further increase in reaction time from 100 to 140 min decreases the yield of biodiesel to 70% [Table 1].

##### 3.1.5. Order of reaction

At optimum condition, biodiesel produced at each time interval was determined. From the weight of biodiesel, the weight of reacted and unreacted UCCO (a-x) was calculated. The successive difference in unreacted used coconut oil (a-x) was evaluated. It is observed that successive difference in weight of unreacted used coconut oil is not constant. It indicates that the reaction is not a zero-order reaction. The difference in the values of the logarithm of unreacted UCCO is almost constant. Hence biodiesel production using used coking coconut oil is first order reaction [Table 2].

##### 3.1.6. Kinetics of biodiesel production

The kinetic study was undertaken on the basis of volume of biodiesel produced; from the volume, weight of biodiesel produced at various time intervals of reaction was determined. The kinetics of biodiesel production can be represented as;

$$-\frac{[\text{UCCO}]}{dt} = [\text{UCCO}][\text{Methanol}]$$

Where [UCCO] = Used cooking coconut oil.

As the amount of methanol is in excess equation can be written as;

$$-\frac{[\text{UCCO}]}{dt} = K'[\text{UCCO}]$$

**Table 1:** Optimum parameters for biodiesel production from used cooking coconut oil

S. No.	Parameters	Optimum value
1.	Oil to methanol ratio	1:6
2.	Amount of catalyst	1.25 g% (w/w)
3.	Temperature	70°C
4.	Reaction time	100 min

**Table 2:** Biodiesel production from used cooking coconut oil: order of reaction

Time/ min	Pure coconut oil reacted/g	Pure coconut oil unreacted (a-x)/g	ln (a-x)	Difference in ln (a-x)
00	--	100	4.6052	---
20	12.874	87.126	4.4673	0.1379
40	24.139	75.861	4.3289	0.1384
60	33.546	66.454	4.1965	0.1324
80	41.778	58.222	4.0642	0.1323
100	49.515	50.485	3.9217	0.1425

Difference in ln (a-x) is almost constant

Taking integral and logarithm –

$$\ln \frac{[\text{UCCO}]_0}{[\text{UCCO}]_t} = k't$$

Were,

$[\text{UCCO}]_0$  = initial weight of UCCO at zero time.

$[\text{UCCO}]_t$  = weight of UCCO remains unreacted at time,

After simplifying,

$$k' = \frac{2.303}{t} \log \frac{[\text{UCCO}]_0}{[\text{UCCO}]_t}$$

Using this equation, observed rate constants were determined at each time interval. The mean of the observed rate constant gives the average rate constant, k. The average rate constant for biodiesel production from UCCO using KOH was found to be  $5.20 \times 10^{-3}/\text{min}$  at  $70^\circ\text{C}$ .

### 3.1.7. Effect of oil to methanol ratio on average rate constant

Oil to methanol ratio is an important parameter in the production of biodiesel. Hence, the average rate constant was determined at various oil to methanol ratio ranging from 1:3 to 1:6. The average rate constant for biodiesel production from UCCO using KOH increases from  $2.10 \times 10^{-3}/\text{min}$  to  $5.20 \times 10^{-3}/\text{min}$  by changing the oil-to-methanol ratio from 1:3 to 1:6.

### 3.1.8. Effect of amount of catalyst on average rate constant

Biodiesel production is greatly governed by the presence of catalyst and its quantity. Hence, kinetics of biodiesel production is greatly affected by the presence of catalyst. The average rate constant varies from  $3.0 \times 10^{-3}/\text{min}$  to  $5.20 \times 10^{-3}/\text{min}$  by changing the amount of catalyst from 0.25 g to 1.25 g (w/w).

### 3.1.9. Catalytic constant, $K_{cat} (\text{UCCO}/\text{KOH})$

The average rate constant was determined at various amount of catalyst (KOH) ranging 0.25 g to 1.25 g % (w/w). The average rate constant was plotted against the amount of catalyst. The slope of the plot gives the catalytic constant. The value of  $K_{cat} (\text{UCCO}/\text{KOH})$  is found to be  $2.20 \times 10^{-3}$  [Table 3 and Figure 1].

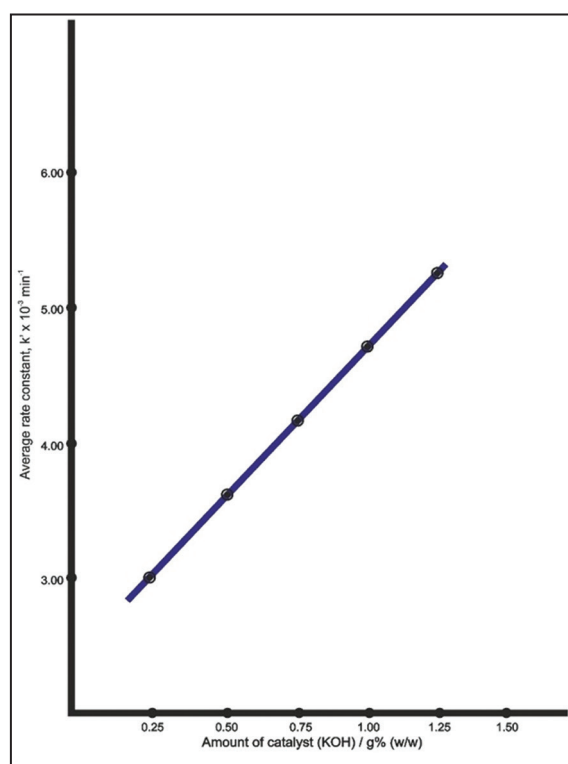
### 3.1.10. Effects of temperature on average rate constant

Average rate constants were determined at optimum conditions and various temperatures ranging from  $40^\circ\text{C}$  to  $70^\circ\text{C}$ . The average rate constant changes from  $1.50 \times 10^{-3}/\text{min}$  to  $5.20 \times 10^{-3}/\text{min}$  as shown in Table 4.

**Table 3:** Kinetics of biodiesel production from used cooking coconut oil: catalytic constant

Amount of catalyst (KOH)/g % (w/w)	Average rate constant $k' \times 10^{-3}/\text{min}$
0.25	3.00
0.50	3.54
0.75	4.10
1.00	4.64
1.25	5.20

KOH: Potassium hydroxide. Catalytic constant,  
 $K_{cat} (\text{UCCO}/\text{KOH}) = 2.20 \times 10^{-3}$

**Figure 1:** Kinetics of biodiesel production from used cooking coconut oil; catalytic constant.

### 3.1.11. Activation energy and Arrhenius constant

Activation Energy,  $E_a$ , and Arrhenius constant,  $A$  were determined using Arrhenius equation [46]:

$$K = A \cdot e^{-E_a/RT}$$

where,  $K$  is the average rate constant,  $A$  is the Arrhenius constant,  $E_a$  is the activation energy,  $R$  is the gas constant, and  $T$  is the temperature in kelvin. Taking the logarithm of above equation-

$$\ln k = \ln A - E_a/RT$$

This is the equation of a straight line of the form  $y = mx + c$ . Arrhenius plot was plotted between  $\ln k$  and  $1/T$ . From the slope of the plot, the activation energy was evaluated and found to be  $36.8 \text{ kJ/mole}$  [Table 4 and Figure 2]. Arrhenius constant, was determined  $A = 5.52 \times 10^{-3}/\text{min}$  was determined from the intercept of the plot.

**Table 4:** Kinetics of biodiesel production from used cooking coconut oil: Energy of activation

Amount of used cooking coconut oil : 100 g  
 Oil to methanol ratio : 1:6  
 Amount of catalyst (KOH) : 1.25 g% (w/w)  
 Reaction time : 100 min

Temperature t/°C	Average rate constant, k'×10 <sup>-3</sup> /min	1/T/10 <sup>-3</sup> /k	ln k'
40	313	3.19	-6.50
50	323	3.09	-6.06
60	333	3.00	-5.66
70	343	2.91	-5.26

Slope of the plot of ln k' versus 1/T=-4428.57; Activation energy, Ea=36.8 KJ/mole; Arrhenius constant, A=5.52×10<sup>-3</sup>/min

3.1.12. Thermodynamic parameters

Entropy of activation, ΔS‡ and enthalpy of activation, ΔH‡, were determined using the straight-line equation of Polanyi and Eyring [47, 48];

$$\ln \frac{k}{T} = \frac{\Delta H^\ddagger}{R} \cdot \frac{1}{T} + \ln \frac{K_b}{h} + \frac{\Delta S^\ddagger}{R}$$

Were,

k = Average rate constant

K<sub>b</sub>= Boltzmann constant

T = Temperature in kelvin

h = Plank's constant

ΔS‡ = Entropy of activation

ΔH‡ = Enthalpy of activation

R = Gas constant

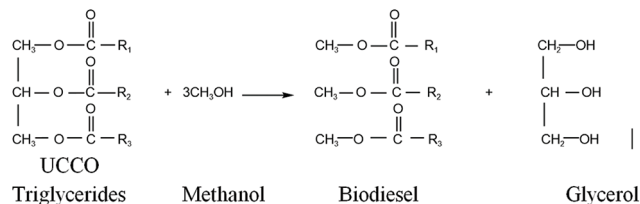
A plot of ln  $\frac{k}{T}$  against  $\frac{1}{T}$  gives the straight line with slope  $\frac{\Delta H^\ddagger}{R}$  and

intercept  $\ln \frac{K_b}{h} + \frac{\Delta S^\ddagger}{R}$ . From this plot ΔS‡ and ΔH‡ can be determined.

The values of entropy of activation and enthalpy of activation are found as -109.11 J mole K and -34.44 KJ/mole, respectively [Table 5 and Figure 3].

4. MOST PROBABLE MECHANISM

Biodiesel production from UCCO consists of the reaction of one mole of UCCO (triglycerides) and three moles of methanol to produce three moles of biodiesel and one mole of glycerol.



Step 1: Formation of methoxide and protonated KOH takes place by mixing methyl alcohol and KOH;



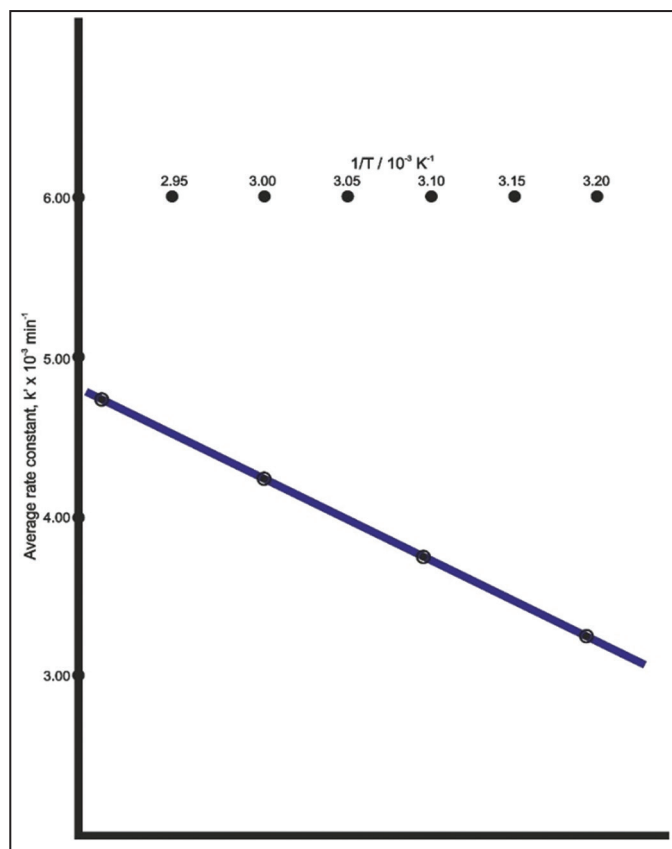
Methoxide anion acts as a nucleophile and attacks the carbonyl group of triglycerides molecule. After the exchange of ions, there is the formation of one molecule of biodiesel and diglycerides.

**Table 5:** Kinetics of biodiesel production from used cooking coconut oil: Thermodynamic parameter

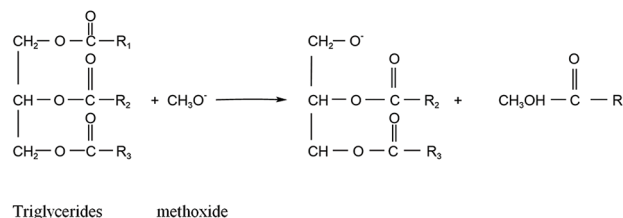
Amount of used cooking coconut oil : 100 g  
 Oil to methanol ratio : 1:6  
 Amount of catalyst (KOH) : 1.25 g% (w/w)  
 Reaction time : 100 min<sup>-1</sup>

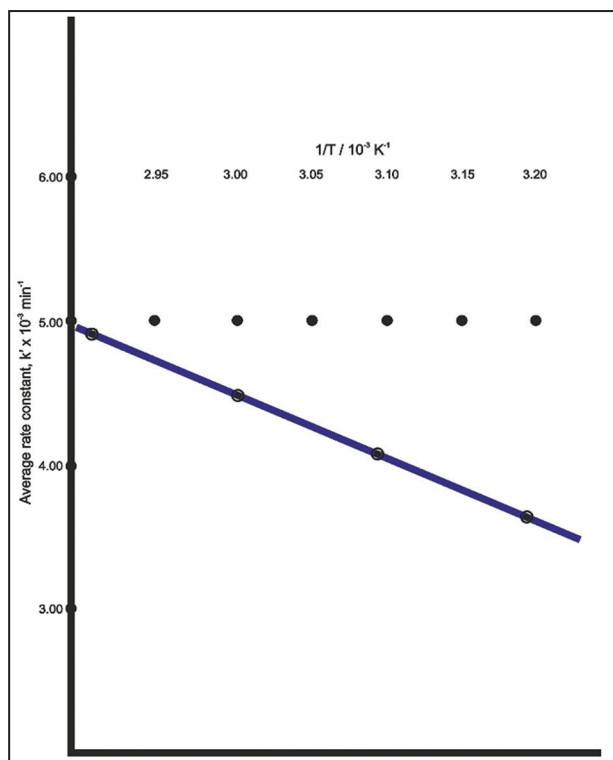
Temperature t/°C	1/T/10 <sup>-3</sup> /k	Average rate constant, k'×10 <sup>-3</sup> /min	k'/T	ln k'/T
40	313	3.19	1.50	4.79
50	323	3.09	2.33	7.21
60	333	3.00	3.48	10.43
70	343	2.91	5.20	15.16

Slope of the plot ln k'/T=-4142.86; Intercept of the plot=-11.04

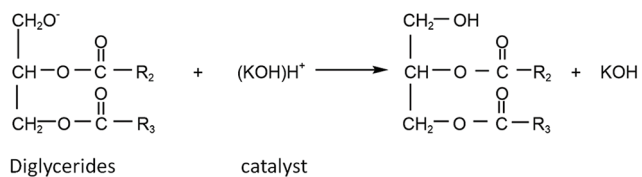


**Figure 2:** Kinetics of biodiesel production from used cooking coconut oil: Energy of activation.

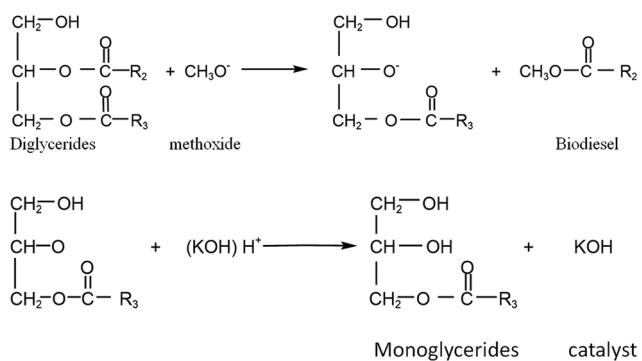




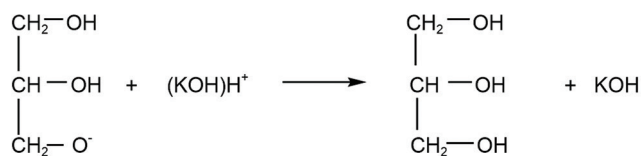
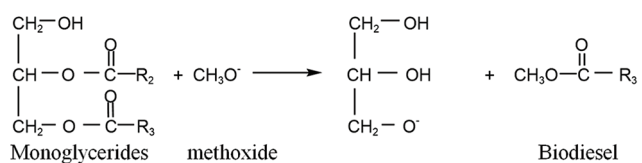
**Figure 3:** Kinetics of the biodiesel production from used cooking coconut oil; thermodynamic parameters.



Step 2: Above sequence is repeated for diglycerides to give monoglycerides



Step 3: Sequence is repeated for monoglycerides to glycerol



[where R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are carbon chains of fatty acid]

**5. CONCLUSION**

UCCO is an important, cheap, and readily available source for biodiesel production. The optimum parameters for biodiesel production are oil to methanol ratio (1:6), Amount of catalyst (1.25% w/w), temperature (70°C), and reaction time (100 min). Biodiesel production shows a pseudo first order kinetics. The average rate constant is 5.20 × 10<sup>-3</sup>/min at 70°C. The catalytic constant for KOH as a catalyst is found to be K cat (UCCO/KOH) = 1.50 × 10<sup>-3</sup>, which shows that KOH results in rapid conversion of UCCO into biodiesel. The activation energy and Arrhenius constant are 36.8 KJ/mole and 5.46 × 10<sup>-3</sup>, respectively, while entropy of activation and enthalpy of activation are ΔS<sup>‡</sup> = -109.11 J mole K and ΔH<sup>‡</sup> = -34.44 KJ/mole, respectively. On the basis of kinetic and thermodynamic parameters, the most probable mechanism has been proposed.

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**7. CONFLICTS OF INTEREST**

The author declares that they have no conflicts of interest.

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