Reactive Extraction Processing of Spirulina-Platensis Microalgae to Produce Biodiesel: Kinetics Study

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Abstract – Reactive extraction processing of microalgae to produce biodiesel is a part of the solution for the global problems that confronting the world nowadays. In this research, the kinetics of reactive extraction of Spirulina-platensis microalgae has been studied in the temperature range (27-65°C), alcohol-to-oil molar ratio of 3714:1 in the time interval (2-10h). The process was developed to obtain maximum biodiesel yield of 84.7%. Results concluded that the reaction is a pseudo first order with activation energy of 37.762 kJ/gmol and Arrhenius factor of 1.89E+05 h⁻¹. The reaction rate constants are ranged from 0.041 h⁻¹ at 27°C to 0.218 h⁻¹ at 65°C. In addition, this study provides an overview on the kinetic investigations studied before on various oilseeds.

Index Terms –Biodiesel, Kinetics, Microalgae, Reactive Extraction.

I. INTRODUCTION

Nowadays, energy and emissions of green house gases become the most important global problems confronting the world [1]-[2]. Since more than 80% of the world's energy needs are supplied from fossil fuels[1]-[3]. The problem is that the population growth is not covered by domestic crude oil production and its derivatives, and the formation of these fuels requires millions of years, hence the petrol fuels are non-renewable[3]-[4]. Also, change of the petroleum prices leads to global and international conflicts especially in the developing countries. In addition, the emission profile of the green house gases according to the international energy agency (IEA) rose by one billion metric tons over last year to reach now 34.83 billion metric tons and, in the last 30 years carbon dioxide emissions have risen by 80% [5]. These problems could be decreased by using biodiesel instead of petro-diesel fuel [1]-[6].

Biodiesel has become more attractive fuel in many countries; as it can be made from wide range of sustainable biomass, such as vegetable oils (edible or non-edible), used fryer oil, waste streams, agricultural residues, microalgae (e.g. Chlorella vulgaris and Spirulina-Platensis) and tallow [7]. It is a renewable and environmental friendly energy resource [8]. Biodiesel has an established market in Europe, as it is already commercially produced and used with existing distribution and storage infrastructure. Using microalgae as a promising biomass feedstock to produce biodiesel has several advantages over production from terrestrial plant crops[9]-[11]. Microalgae are fast growing photosynthetic microorganisms that reproduce themselves every 2 or 3 weeks, and can be cultivated in saline water, or wastewater(1m² of wastewater is required to produce 800 g of dry algae). Microalgae can be used for carbon dioxide mitigation(1 kg of algal biomass requiring about 1.8 kg of CO₂) and can produce lipids at up to 77 wt% of total biomass [1],[12]. In addition, microalgae as a fuel source do not conflict with the food crisis; since it is not main food source [8]. So, biodiesel production from microalgae is considered a part of the solution for the global problems.

Several studies have been published on the extraction of microalgae oil and it's conversion to biodiesel using base catalysts [13]-[15] or acid catalysts [16]-[19]. Basically, most of the previous studies require microalgae oil extraction by mechanical or chemical methods. However, this step can be eliminated by transesterification of the biomass lipids directly to fatty acid alkyl esters, a process known as reactive extraction " or in situ transesterification"[20]-[26]. Consequently, success of using microalgae to produce biodiesel commercially is an important factor for developing countries sustainable development; the increase of energy security and positive economic effects would be performed. However, firstly, the production technology must be developed. The most recent method for biodiesel production is batch transesterification processes; however, generally, continuous processes give lower production cost and more uniform product quality than batch processes [3],[23]. In order to
design an efficient continuous reactor for biodiesel production from microalgae oil, a suitable kinetics mechanism and reaction rate constants must be found [27]-[29].

The application of the simple kinetic models, with the study of effects of the solid particle sizes, nature of the solvent (or alcohol), temperature and solvent-to-solids ratios on the kinetics of extraction and transesterification processes had been previously investigated more times on different oilseeds[30]-[33]. A study of the kinetics of in-situ transesterification of Spirulina-Platensis microalgae will provide parameters that can be used to predict the extent of the reaction at any time under particular conditions. Among several kinetic studies published on transesterification of simple esters, only a few were concerned with the transesterification of vegetable oil fatty esters, such as those by [34]-[36]. But, although methyl esters from microalgae oil have been produced on a bench scale and pilot scale in several countries; to our knowledge, there are no published reports on its kinetics.

The objectives of this work were to evaluate a first-order kinetics mechanism and to find out the reaction rate constants for in-situ transesterification of Spirulina-Platensis microalgae with methanol when conc. H$_2$SO$_4$ was used as a catalyst. A reaction condition focused on the reported optimum conditions for the in-situ transesterification process of Spirulina-Platensis microalgae at atmospheric pressure; 3714:1 molar ratio of alcohol to oil, temperature 65 °C, continuous agitation at 650 rpm and catalyst concentration 100% wt of oil [1]. In addition, as the energetic aspect of the reactive extraction of microalgae is of a fundamental importance, the parameters of Arrhenius equation are obtained. Also, this investigation includes a review on the previous kinetics studies that published on the transesterification of different oilseeds. The obtained result can be used to predict a conversion yield of microalgae reactive extraction in continuous reactors efficiently.

II. PREVIOUS KINETIC STUDIES ON TRANSESTERIFICATION OF ESTERS

Meziane S, Kadi H and Lamrous O [37] studied the kinetics and thermodynamics aspect of oil extraction from olive cake by using ethanol 96% for solvent-to-solids ratios (3-5 ml solvent/g solids), temperatures (20-50°C) and contact time (0-60 min) at constant agitation of 800 rpm. They explained the kinetic study by the model of [38] and their results produced by this model were found to be in good agreement with the experimental data. This model is based on two stages for the oil extraction. The first step corresponds to a simple washing of the oil from the particle surface. In the second step, the extraction is controlled by two mechanisms: slow diffusion from broken cells and very slow diffusion from intact cells [39],[40]. In this investigation, the extractions were performed in an isothermal cylindrical reactor of 600 ml equipped with a mechanical agitator, and the solid-liquid separation was performed by vacuum filtration in a Buchner funnel and then the miscella was distilled under reduced pressure by rotary-evaporator apparatus. The yield of oil in the extract was found to be increased with increasing the studied parameters. The predominant mechanism in the extraction was proved to be the washing of the oil occurring on the particle surface. The values of the activation energy were 8.56 kJ mol$^{-1}$ for the washing stage, 9.88 kJ mol$^{-1}$ for the first stage of diffusion and 17.55 kJ mol$^{-1}$ for the second stage of diffusion by changing temperature from 20 to 50 °C. Further, the results obtained from thermodynamic study of extraction process by Meziane S, Kadi H and Lamrous O [37] gave positive values of enthalpy and entropy changes and negative values of change in free energy.

Darnoko D and Cheryan M [34] studied the kinetics of base-catalyzed transesterification of palm oil in a batch reactor with methanol at 6:1 molar ratio of alcohol-to-oil, in the presence of KOH (1% wt.) through temperature range from 50°C to 65°C. They perform their investigation in a 1-L three-necked agitated flask equipped with a reflux condenser. The reactor was immersed in a constant-controlled temperature. At the start, the reactor was filled with 500 g refined, bleached and deodorized palm oil, and potassium hydroxide as a catalyst was dissolved with known amount in the required quantity of methanol and heated separately to the desired temperature. At various times, samples were withdrawn quickly from the reactor with a Pasteur pipet and analyzed for TG, DG, MG, total methyl esters, and glycerol content by gel permeation chromatography [41]. The composition of the methyl esters was analyzed by gas chromatography [34],[42]. The authors reported that, the rate of transesterification in a batch reactor increased with temperature up to 60° C. The conversion of triglycerides (-TG), diglycerides (-DG) and monoglycerides (-MG) appeared to be a pseudo second order up to 30 mins of reaction time. Reaction rate constants for TG, DG and MG hydrolysis reactions were calculated to be 0.018 -0.191 (wt % . min$^{-1}$) and the activation energies were: 14.7, 14.2 and 6.4 kcal/mol for the TG, DG and MG hydrolysis reactions respectively.
Theerayut Leevijit et al.[30] studied also the transesterification of palm oil with methanol (methanol-to-oil molar ratio 6:1) in the presence of NaOH (1% wt.) as a catalyst in a well-mixed batch reactor at 60°C, these conditions were reported as an optimum reaction conditions in[37]. During the reaction, samples were collected and analyzed by thin layer chromatography/flame ionization detector (TLC/FID) to determine the weight percentages of reaction compositions on glycerol free basis. The authors reported that the effect of mass transfer could be observed that it was eliminated; thus, the obtained reaction rate was a true intrinsic rate of a homogeneous reaction. The experimental mole concentrations were calibrated and fitted to a mathematical model of second-order kinetics without shunt reaction. To quantify the weight percentage of methyl esters in the product during the reaction, the authors were used two standards: the correlation coefficient (R²) and the mean relative deviation (MRD). The R² was 0.9936 and the MRD was 1.835%. Moreover, Cheng Sit Foon, Choo Yuen May and Ma Ah Nga[33] studied the kinetics of base-catalyzed transesterification of palm oil based on molar ratio of oil to methanol of 1:10, 0.125 mole/kg oil sodium hydroxide concentrations at 60.5 °C. They reported that the best kinetics mechanism appeared to be a pseudo second-order.

M. Berrios, J. Siles, M.A. Martin and A. Martin [32] studied the kinetics of the esterification of free fatty acids (FFA) in sunflower oil with methanol in the presence of sulphuric acid at concentrations of 5 and 10 wt% relative to free acids as catalyst and methanol/oleic acid mole ratios from 10:1 to 80:1. The acid value of the samples were ranged from 5 to 7 mg KOH/g oil, which is slightly higher than the levels typically found in frying oils. The authors studied the influence of temperature on the esterification rate was studied at a fixed methanol/oleic acid ratio of 60:1, the two catalyst concentrations and 30, 40, 50 and 60 °C. The experimental set-up used was identical with that previously employed by[43] batch stirring reactor of 2 lit capacity with magnetic stirring and heating system maintained at the required temperature’s. Berrios, J. Siles, M.A. Martin and A. Martin [32] suggest their kinetic model based on that the catalyzed chemical reaction is the controlling step which occurred in the liquid phase; and the methanol/oleic acid mole ratio used was high enough for the methanol concentration to remain constant throughout the process. Their experimental results were found to fit a first-order kinetic law for the forward reaction and a second-order one for the reverse reaction [44]-[46]. The energy of activation for the forward reaction decreased with increasing catalyst concentration from 50745 to 44559 J/mol. In this investigation, the authors reported that the free fatty acids (FFA) in sunflower oil can be effectively removed by esterification with methanol, using a 5% sulphuric acid concentration relative to FFA, a methanol/oleic acid mole ratio of 60:1, a temperature of 60 °C and agitation at a speed of 250 rpm or higher. Also, this study provided a final acid value for the oil lower than 1 mg KOH/g oil within 120 min. based on the optimum operating conditions.

Pankaj Tiwari, Rajeev Kumar and Sanjeev Garg [47] studied the kinetics, modeling and simulation of alkali-catalyzed transesterification of Linseed and Jatropha curcas oils. Experiments were carried out in a 2.0 lit batch reactor with 9:1 methanol-to-oil molar ratio, and 1%wt. catalyst concentration at 60°C; to generate kinetic data and a reversible kinetic model was developed. The equilibrium conversions were achieved in less than 45 minutes for the two oils. K. Ramezani, S. Rowshanzamir, and M.H. Eikani [31], Agra IB, Warnijati S and Wiratni [17] studied the kinetics of base-catalyzed transesterification of Castor oil with methanol at 8:1 molar ratio of alcohol to oil, and 0.5 wt% acid catalyst concentration at 65 °C. They reported that the best kinetics mechanism appeared to be a pseudo first-order.

III. EXPERIMENTAL WORK

A. Materials

The raw material used in this study was dried biomass of Spirulina-Platensis microalgae which was supplied from the Soils Water and Environment Res. Inst., Agriculture Research Center (ARC), Giza, Egypt. The culture conditions were identical with that previously mentioned [48]. Total lipids content of Spirulina-Platensis microalgae and its acid value were estimated to be 0.1095g/g biomass and 37.4 mg KOH/g Oil, respectively. Methanol (99.9% purity) as a reacting alcohol, and concentrated Sulphuric acid (98% purity) as a catalyst for the reactive extraction process were used in this study. All solvents and reagents were of analytical reagent grade and were obtained from commercial sources.

B. Transesterification reaction procedure

The experimental set-up used was identical with that previously illustrated [1], batch stirring reactor of 1 lit of capacity, and heating system consisted of a jacketed reactor through which water from a thermo stated system at the required temperature was circulated. Constant concentration of sulphuric acid (100%wt/wt.oil), 80 ml alcohol
volume and continuous stirring at 650 rpm were used in this study. These conditions were published as optimum conditions for the in-situ transesterification of *Spirulina-platensis* microalgae [1]. The acid-methanol solution was prepared freshly by mixing predetermined amounts of sulphuric acid and methanol. H₂SO₄ was dissolved with continuous stirring on a magnetic stirrer for 5 min. The solution was prepared freshly in order to maintain the catalyst activity. Dried microalgae of 15 gm was added carefully to catalyst/alcohol mixture and blended on low setting for several minutes. At this point, the simultaneous extraction and transesterification reaction has been initiated; where the catalyst/alcohol solution attacked the triglyceride (oil) in the microalgae biomass and cleaved off a fatty acid chain. The vessels containing the reaction mixtures were then heated and maintained at the temperatures of interest for specified periods. The major reactive extraction processes and performed product purification steps are summarized in Fig. 1.

**C. Method of analysis**

Fatty acids composition of the extracted oilgae sample was determined using gas chromatographic analysis of the oil ethyl esters. Modification of the oil to its ethyl esters was made using 2 % H₂SO₄ as catalyst in the presence of dry ethyl alcohol in excess. The chromatographic analysis was made using Hewlett Packard Model 6890 Chromatograph. A capillary column 30 m length and 530 μm inner diameter, packed with Apiezon® was used. Detector temperature, injection temperature and the column temperature were 280 °C, 300 °C and 100 to 240 °C at 15 °C/min, respectively.

**Fig. 1 Experimental set-up of reactive extraction process for biodiesel production from *Spirulina-Platensis* microalgae**
IV. RESULTS AND DISCUSSION

A. Calculation of biodiesel yield

From the experimental procedure that published in [1], the amount of collected biodiesel is difficult to be measured; since it mixed with the unreacted glycerides; however, by knowing the weight of the obtained co-product glycerol, the yield of the biodiesel can be predicated from the balanced equation of the transesterification reaction that shown in Fig. 2.

The extracted microalgae oil sample contained the following major fatty acids: mystic (22.67%), palmitic (49.58%), palmitoleic (2.75%), stearic (5.56%), linoleic (7.41%) and eicosic (4.36%); all were determined by gas chromatography. Based on these constituents, the average molecular weight of the Spirulina-platensis oil was calculated to be 845.19 g/mol [1]. From the balanced transesterification reaction (Fig. 2), it has been shown that the chemical structure of fatty acid methyl esters is increased by four hydrogen atoms over that of microalgae oil, so its molecular weight will be 849.19 g/mol. Since the transesterification product is three moles of fatty acid methyl esters, therefore the biodiesel average molecular weight is equal to 283 g/mol. Biodiesel yield can be calculated from (1) based on its molecular weight and the glycerol weight.

\[
\text{Biodiesel Yield} \% = \frac{\text{Biodiesel weight}}{\text{Microalgae oil weight}} \times 100 \quad (1)
\]

B. Effect of temperature and time on the reactive extraction process

To investigate the influence of reaction time and temperature, a methanol volume of 80 ml was used since it was found that no appreciable differences in the equilibrium FAME conversion were obtained with the use of higher alcohol volumes [2]. Reactions were carried out at different temperatures of 27°C up to 65°C as shown in Table 1, using methanol-to-oil molar ratio of 37:1, catalyst concentration of 100% (wt./wt. oil) and continuous stirring at 650 rpm.

As mentioned above, the percentage yield of the produced FAME was calculated based on the total amount of co-product glycerol obtained, concerning experimental and analytical error to be ±5%. The progress of the microalgae oil to biodiesel conversion process at different temperature levels is shown in Fig. 3. For the samples investigated at room temperature (no process heating), asymptotic FAME conversion value was not reached within the time boundaries of this study.

Within the investigated experimental conditions, equilibrium conversions of FAME were observed to reach similar asymptotic values after a reaction time of 8 and 10 h for temperatures of 50 and 65°C. Although faster conversion rates could be observed by use of reaction temperatures greater than the boiling point of the reacting methanol (e.g. 90 °C), the process heating and pressure requirements may inhibit the use of such temperature levels. The use of a reaction temperature of 65°C may therefore prove more beneficial, if we consider the total energy consumption and operation cost of the whole biodiesel conversion system.

Table 1 Effect of reaction temperatures and time on biodiesel yield

<table>
<thead>
<tr>
<th>Time, hr</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>27 °C</td>
</tr>
<tr>
<td>2</td>
<td>1.35</td>
</tr>
<tr>
<td>4</td>
<td>10.62</td>
</tr>
<tr>
<td>8</td>
<td>30.22</td>
</tr>
<tr>
<td>10</td>
<td>34.71</td>
</tr>
</tbody>
</table>
Temperature has detectable effect on the ultimate conversion to ester. However, higher temperatures improve the initial miscibility of the reacting species, leading to a significant reduction in the time required to reach maximum conversion, as observed in Fig. 3. The optimum temperature was 65°C for 8 h. At lower temperatures of 27°C, the process was incomplete and no FAMEs were observed.

C. Kinetics study
In this research, the kinetics of reactive extraction "in-situ transesterification" process has been studied at temperatures (27-65°C) for time intervals (2-10 h), while the other operating parameters were fixed: alcohol-to-oil molar ratio of 3714:1, catalyst concentration of 100% (wt/wt.oil) and stirring rate at 650 rpm. These conditions had been provided a maximum recommended level of FAME yield (84.7%) from *Spirulina-Platensis* microalgae [1]. In addition, decreased the surface tension and facilitated their separation from glycerin [46]. The data used for the kinetics study are summarized in Table 2.

Transesterification reaction consists of a series of reversible steps in which the oils (represented as triglycerides) are sequentially converted to di- and mono-glycerides, and eventually to glycerol, with one mole of fatty acid alkyl esters (RCOOR₁) liberated at each step as shown in (2), (3) and (4) below:

\[
\text{Triglyceride} + R\text{R}_1\text{OH} \leftrightarrow \text{diglyceride} + \text{RCOOR}_1 \quad (2)
\]
\[
\text{Diglyceride} + R\text{R}_1\text{OH} \leftrightarrow \text{monoglyceride} + \text{RCOOR}_1 \quad (3)
\]
\[
\text{Monoglyceride} + R\text{R}_1\text{OH} \leftrightarrow \text{glycerol} + \text{RCOOR}_1 \quad (4)
\]

In this work, R was a linear chain of 14–20 carbon atoms containing a variable number of unsaturations depending on the particular origin of the raw material, and R₁ was a methyl radical. Transesterification reaction is not elementary, and it is a reversible reaction, but some simplifications can be assumed to predict a simple kinetic model only for the beginning time of the reaction. This reaction is heterogeneous; methanol is only sparsely soluble in microalgae oil; so it requires agitation in order to avoid mass transfer taking control over the process [1],[29].

![Influences of reaction temperatures and time on biodiesel yield](image-url)
The kinetic model used in this investigation relied on the following assumptions:
(a) The transesterification reaction was considered and the hydrolysis reaction of triglyceride considered being negligible
(b) The transesterification reaction was a reversible heterogeneous process the rate of which under the operating conditions used was controlled by that of the chemical reaction; where the extraction time of microalgae oil is small (1 h) compared to the time of its transesterification to biodiesel, 8 or 10 h and can be neglected [1].
(c) The rate of the non-catalyzed reaction was negligible relative to the catalyzed reaction [29].
(d) The chemical reaction occurred in the oil phase.
(e) The methanol/oilgae mole ratio used was high enough for the methanol concentration; to remain constant throughout the process and to shift the reaction in forward direction, thus the reverse reaction was ignored [27],[28].

Under these conditions, the reaction was assumed to be irreversible pseudo-homogeneous, first-order, and hence to conform to the following kinetic law (5):

\[ r = -\frac{d[TG]}{dt} = k'[TG] \]  

(5)

Where, \( k' = k[ML]_0 \), \([ML]_0\) is the initial alcohol concentration, and \( k \) is the specific rate constant.

**Table 2 Data required for kinetics investigation**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature range (°C)</td>
<td>27 - 65</td>
<td>Assume that the reaction medium is immiscible, so the total volume of the reaction components is the sum of the individual volumes, which equals to 82.5 ml.</td>
</tr>
<tr>
<td>Catalyst type</td>
<td>H₂SO₄</td>
<td></td>
</tr>
<tr>
<td>Catalyst conc. (%wt of oil)</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Catalyst vol. (ml)</td>
<td>0.82</td>
<td></td>
</tr>
<tr>
<td>Mixing intensity (rpm)</td>
<td>650</td>
<td></td>
</tr>
<tr>
<td>Time interval (hr)</td>
<td>2 - 10</td>
<td></td>
</tr>
<tr>
<td>Alcohol/oil molar ratio</td>
<td>3714</td>
<td></td>
</tr>
<tr>
<td>Total vol. of reaction medium (ml)</td>
<td>82.50161</td>
<td></td>
</tr>
<tr>
<td>Microalgae</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oil content (%)</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Biomass weight, g</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>Oil weight, g</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>Density (g/ml)</td>
<td>0.892</td>
<td></td>
</tr>
<tr>
<td>Volume (ml)</td>
<td>1.681614</td>
<td></td>
</tr>
<tr>
<td>Mol. Wt.</td>
<td>845.19</td>
<td></td>
</tr>
<tr>
<td>Initial moles, mol</td>
<td>0.001775</td>
<td></td>
</tr>
<tr>
<td>Initial oilgae conc. [TG,0] (mol/lit)</td>
<td>0.021512</td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vol. (ml)</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>Density (g/ml)</td>
<td>7.91</td>
<td></td>
</tr>
<tr>
<td>Mass (g)</td>
<td>632.8</td>
<td></td>
</tr>
<tr>
<td>Mol.wt. (g/mol)</td>
<td>32</td>
<td></td>
</tr>
<tr>
<td>No. of moles</td>
<td>19.775</td>
<td></td>
</tr>
<tr>
<td>Initial alcohol conc. [ML,0] (mol/lit)</td>
<td>239.6923</td>
<td></td>
</tr>
</tbody>
</table>
By integrating (5) it gives,

$$\ln[TG, t] - \ln[TG, 0] = k' t$$  \hspace{1cm} (6)

Where $[TG, 0]$ is the initial concentration of TG "microalgae oil", $[TG, t]$ is the concentration of TG at time $t$. The rate constant $k'$ can be obtained by a linear fitting of (6) for 1st order reaction through origin. Calculations of the concentration of unreacted fatty acids during in-situ transesterification process as a function of time are based on the data mentioned previously in Fig. 3 and illustrated in Table 2.

The experimental data were fitted, and a graph of $\ln[TG, t] - \ln[TG, 0]$ versus time $t$ at different temperatures was plotted in Fig. 4. It shows the linear correlation which suggest that the in-situ transesterification reaction is a pseudo first order. The reaction rate constants $k$ at different temperatures was estimated as shown in Table 3.

The influence of temperature on the specific reaction rate was determined by fitting the predicated $K$ values to the well-known Arrhenius formula (7). Using plots of $\ln K$ as a function of the reciprocal temperature, both the frequency factor and the apparent activation energy required to initiate the reactive extraction could be obtained, as shown in Fig. 5.

$$K = K_0 \cdot \exp\left(\frac{-E_a}{RT}\right)$$  \hspace{1cm} (7)

Reforming of the above equation to get (8):

$$\ln(K) = \ln(K_0) - \frac{E_a}{RT}$$  \hspace{1cm} (8)

where $E_a$ is the activation energy, $R$ is the universal gas constant, $T$ is the temperature in Kelvin, and $k_0$ is the pre-exponential factor (or frequency factor).

![Fig. 4 Prediction of $\{\ln[TG, 0] - \ln[TG, t]\}$ as a function of reaction time $t$ at different temperatures.](image-url)
Table 3 Reaction rate constant for the 1st order reactive extraction of microalgae with methanol at different temperature

<table>
<thead>
<tr>
<th>Temperature(°C)</th>
<th>k' (hr⁻¹)</th>
<th>k (hr⁻¹)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>27</td>
<td>0.041</td>
<td>2.073 x 10⁻³</td>
<td>0.945</td>
</tr>
<tr>
<td>40</td>
<td>0.111</td>
<td>5.613 x 10⁻³</td>
<td>0.952</td>
</tr>
<tr>
<td>50</td>
<td>0.195</td>
<td>9.86 x 10⁻³</td>
<td>0.973</td>
</tr>
<tr>
<td>65</td>
<td>0.218</td>
<td>11.024 x 10⁻³</td>
<td>0.942</td>
</tr>
</tbody>
</table>

In the reactive extraction process, the extraction rate increases with increase in reaction temperature, and at higher temperature, the rate of reaction is higher. Thus reaction rate increases with subsequent increase in extraction rate. The rate constants k and its corresponding correlation coefficient at different temperature are illustrated in Table 3. The rate constants for the formation of FAME ranged from 0.041 to 0.218 hr⁻¹. The activation energy for the reactive extraction of *Spirulina-Platensis* is microalgae is 37.762 kJ mol⁻¹ and Arrhenius constant is 1.89E+05 hr⁻¹ with correlation coefficient of 98.5%.

V. CONCLUSIONS

Reactive extraction processing of *Spirulina-Platensis* microalgae is a promising technology to produce biodiesel. The kinetics study reported that the reaction is a pseudo first order with a reaction rate constant ranged from 0.041 to 0.218 hr⁻¹ when the temperature is changed from 27°C to 65°C; as the reaction rate is higher when the temperature increased. The activation energy is 37.762 kJ mol⁻¹ and Arrhenius constant is 1.89E+05 hr⁻¹ were estimated with accuracy greater than 98.5%. Hence, this study may help the researchers in the biodiesel production reactor design when developed in the future.
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