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KINETIC MODEL OF ALGAL BIODIESEL PRODUCTION UNDER SUPERCRITICAL METHANOLYSIS

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ABSTRACT

A model for the supercritical trans-esterification reaction of algae is developed to study the effect of the operating parameters on the process kinetics. A well-mixed batch reactor equation was used to express the lab scale reactor. The model is based on experimental data described in a previous study. The experimental work were designed to study the effect of reaction time between 5-50 min; reaction temperatures of 423-573K, and methanol to dry algae volume/weight (vol./wt.) ratios of 12:1-40:1. The fitting of the data indicated that the reaction is a forward first order reaction in terms of triglycerides. Two parameters were introduced to consider the effect of methanol to algae ratio and reaction time. The activation energy is 9.91 kJ/mol. Excellent fitting between the experimental results and model prediction is observed. The model shows that the optimum methanol to algae ratio and reaction time were 26 and 27 min. respectively. The triglyceride at the model optimum conditions at 600K is almost completely converted to biodiesel.

Keywords: kinetic model, reaction kinetics, algal biodiesel, supercritical trans-esterification.

1. INTRODUCTION

Biodiesel is prepared via transesterification reaction between oil and alcohol in the presence of an acid or base catalyst [1, 2]. The overall alcoholysis process is a sequence of three reversible consecutive reactions [3]:

$$TG + R'OH \leftrightarrow DG + R'COOR_1 \quad (1)$$

$$TG + R'OH \leftrightarrow MG + R'COOR_2 \quad (2)$$

$$MG + R'OH \leftrightarrow GL + R'COOR_3 \quad (3)$$

Where

TG = Triglycerides
DG = Diglycerides
MG = Monoglycerides
R' OH = Alcohol
GL = Glycerol
R'COOR = Alkyl esters

The most important factors affecting in the alcoholysis reaction are; the type and concentration of catalyst, type of alcohol, molar ratio of alcohol to oil, reaction temperature, residence time, presence of free fatty acids and moisture.

The biodiesel production under supercritical conditions is a catalyst-free chemical reaction between triglycerides and low molecular weight alcohols, such as methanol and ethanol, at a temperature and pressure over the critical point of the mixture. At supercritical conditions, the reactive mixture is homogenous avoiding the mass transfer limitations present in the alkali process due to the liquid-liquid partial miscibility of alcohols and triglycerides [4]. The kinetics of supercritical transesterification is divided into three regions, slow (<553K), transition (553K-603KºC) and fast (>603ºC) regions. The transesterification reaction usually follows the first-order rate law with respect to the triglyceride concentration alone especially in the slow and transition regions [5-7]. The most frequently used alcohol in biodiesel production is methanol. The kinetics of methanolysis was a subject different study [8-13].

In this study, a kinetic model of supercritical methanolysis reaction in a batch reactor is developed using an experimental data of our previous study [14]. The main goal of the present study is to validate the proposed model for optimizing the operating conditions of methanolysis reaction, and to investigate the reaction kinetics.

2. EXPERIMENTAL WORK

The supercritical methanolysis were carried out in a stainless steel PARR batch reactor of 500 ml capacity, assembled with a thermocouple thermometer and a pressure gauge. The experimental protocol for one-step supercritical methanol process is as follows: 10g of dry algae was subjected to a non-catalytic supercritical methanol process in the 500 mL PARR reactor under a matrix of conditions: reaction times of 5, 10, 20, 30, 40 and 50 min; reaction temperatures of 423-573K, and methanol to dry algae volume/weight (vol. /wt.) ratios of 12:1, 20:1, 30:1and 40:1. The pressure inside the reactor varied according to the process temperature. After the reaction was completed, the reactor was subjected to sudden cooling. The reaction mixture was collected and filtrated to separate the algal cells.

3. MATHEMATICAL MODELLING

The model is developed to reflect the total conversion of triglyceride in algae to fatty methyl esters (FAME) in a batch reactor, and to study the effect of reaction time and methanol to algae ratio on the non-catalytic reaction (thermal) operation. The reaction can be written as follows [15]:

$$1\ mol\ Triglyceride + 3\ mol\ Methanol \rightarrow 3\ mol\ FAME + 1\ mol\ Glycerol \quad (4)$$

The proposed model is developed according to the following assumptions[15]:

- The rate constant is a function of temperature and independent of concentrations.
- Production of intermediate species is negligible.
- The reaction takes place in the liquid phase.
- The reaction occurs according to the above chemical equation, which eliminate the necessity of considering a multiple step reaction mechanisms.

3.1. Mathematical model

The general equation for a batch reactor can be written as:

$$\frac{dx}{dt} = \frac{(-rA) * V}{NA_o} \quad (5)$$

Where

x = Conversion is calculated as:

$$x = \frac{Mass\ of\ FAME\ produced}{Mass\ of\ algae\ used * fraction\ of\ oil\ in\ algae} \quad (6)$$

FAME = Fatty methyl esters.

t = Time in minutes

V = Reactor volume in m^3

NA_o = Initial number of moles of FAMEs used in the reaction

$-rA$ = Reaction rate in mol/min /m^3

$$-rA = k * \frac{NA}{V} \quad (7)$$

Where

k = Reaction rate constant in min^{-1}, which can be written in a modified Arrhenius equation:

$$k = 2.2602 \times T^{-0.3478} \times \exp\left(-\frac{9.91 * 10^3}{R \times T}\right) \quad (8)$$

T = Temperature in K

R = Universal gas constant =8.314 J/mol/K

NA = Number of moles of FAME present in the reactor

Two dimensionless parameters were fitted to account for the effect of reaction time and methanol to algae ratio. Those two parameters are k_1 and k_2, developed by fitting the reaction time and methanol to algae ratio to the experimental data, multiplied by the rate to account for the effect of total reaction time and methanol to algae ratio on the conversion respectively. Each parameter is fitted to a polynomial as shown below:

$$k_1 = -5.4 * 10^{-5} \times \exp\left(-\frac{t}{7.758}\right) + 1.18 * 10^{-5} \times t^{0.33} - 6.4 * 10^{-5} \times t^{0.045} + 1.65 * 10^{-4} \times t^{-0.4021} \quad (9)$$

$$k_2 = 7.15 * 10^5 \times r^{0.19} - 8.48 * 10^{-6} \times r^{6.3447} - 7.87 * 10^5 \times r^{0.547} \quad (10)$$

Where

r = Methanol to algae ratio

k_1 = A dimensionless parameter to account for the effect of varying the reaction time

k_2 = A dimensionless parameter to account for the effect of methanol to algae ratio

3.2. Process kinetics

The fitting results have shown that the best fitting was achieved when the reaction is assumed a first order in triglycerides as shown in Equation (4) [15]. A forward reaction is ideally represents the experimental data under study [8]. The presence of excess methanol and the reaction time had an effect on the reaction rate and the conversion of triglycerides. The kinetic rate equation did not reflect the reaction time or the methanol to algae ratio effect on the process. Equations 6 and 7 were developed to consider the effect of the reaction time and methanol to algae ratio respectively.

3.3. Parameters estimation

The model parameters were fitted according to the experimental results, three parameters were fitted namely: k, k_1, and k_2. The fitting process was achieved using the fitting tool box in Matlab. Unfortunately, there is no data in literature for methanolysis reaction using oil from algae. Feyzi *et al*. [15] estimated the activation energy at79.8 kJ/mol of sunflower oil methanolysis; however the experimental conditions were totally different from the experimental conditionsused to develop this model. Feyzi *et al*. [15] conducted their experiments over a narrow temperature range 322-332 K using catalytic methanolysis ($Cs_xH_{3-x}PW_{12}O_{40}$/Fe-SiO_2nanocatalyst). The pressure is not mentioned in the article [15]. While as mentioned in the experimental section, in our case the temperature was varied between 423-673K. The process was simply a thermal conversion without using catalyst. The reaction was conducted under supercritical conditions which imply high temperature/pressure operation. The activation energy in this case is estimated to be 9.91 kJ/mol as shown in Equation (8). The reaction rate constant is expressed in modified Arrhenius equation (Equation 8).

Madras *et al*. [16] studied the methanolysis reaction of sunflower oil between 200-400ºC under a pressure of 200 atm. Madras *et al*. [16] estimated the activation energy at 2 kJ/mol under supercritical

CO_2without catalyst. For soybean oil, He *et al*. [5] estimated the activation energy at 56 kJ/mol for methanolysis under supercritical conditions. The pressure was varied between 0.8-3.5 atm. and the temperature was varied between 210-280ºC without catalyst.

3.4. Model validation and prediction

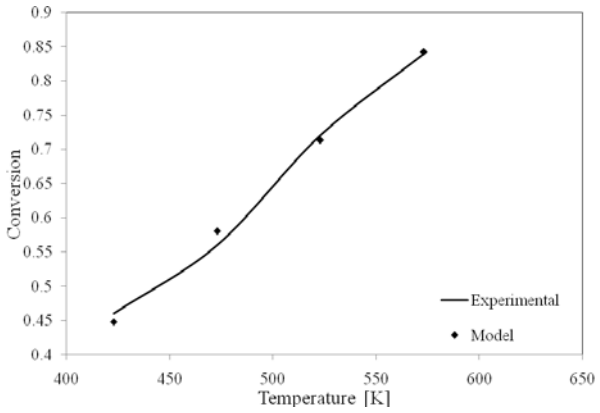

Figure-1. A comparison between the experimental results and the model prediction at different temperatures using a methanol to algae ratio of 12 and a reaction time of 30 min.

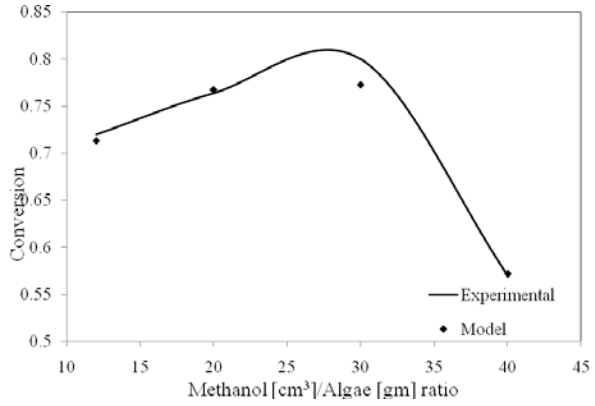

Figure-2. A comparison between the experimental results and the model prediction at different methanol to algae ratios at temperature 250ºC for 30 mins.

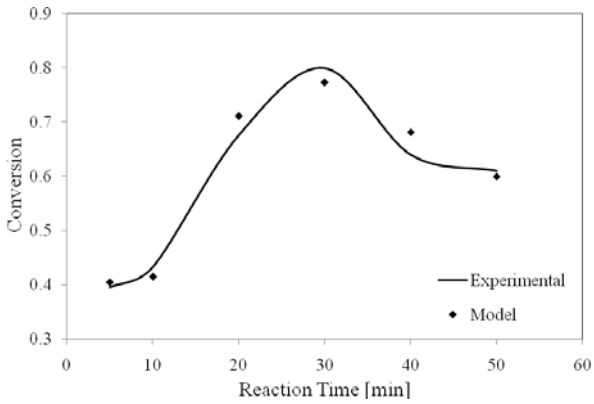

Figure-3. A comparison between the experimental results and the model prediction at different reaction times using a temperature of 250ºC and a methanol to algae ratio of 30.

Figures 1, 2, and 3 show a comparison between the experimental results and model prediction under different reaction conditions. Excellent fitting of the model to the experimental data is observed. To check the prediction power of the model, an experiment was repeated for three times at 573K using 30 methanol to algae ratio for 30 minutes. The average conversion was 0.94; the experiment was not used to fit the model. The model showed a conversion of 0.92 under those operating conditions.

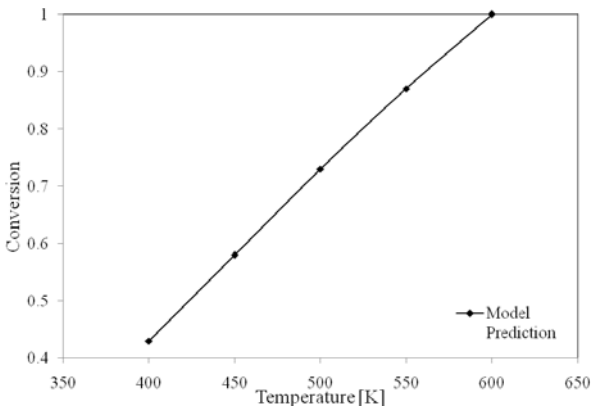

Figure-4. Conversion as a function of reaction temperature as calculated from the proposed model under optimum conditions of methanol to algae ratio and a reaction time (26 and 27 mins. respectively).

4. RESULTS AND DISCUSSIONS

The statistical analysis of the model parameters is performed to further investigate the model validity. A summary of the results is shown in Table-1. The analysis shown in Table-1 demonstrates the adequacy of the model to represent the data. The critical F tabulated value is 2.66, while observed F is equal to 304. The Fisher (F) test indicates that the model is adequate to represent the data, having observed F more than one hundred times critical F indicates a better adequacy than just having F observed just slightly higher than F critical. The correlation

coefficient R^2, which is a measure of the good fit between the model and experimental data, is 0.98; indicating excellent fit.

Table-1. Statistical analysis for the proposed model parameters.

$F_{observed}$	**304**
Number of samples	14
$F_{critical}$ (0.05,3,11)	2.66
R^2	0.98

After validating the model, the model was used to optimize the operating conditions. The optimum methanol to algae ratio is26 while the optimum reaction time is 27 min. The experimental results have shown that the optimum methanol to algae ratio and the reaction time are 30 and 30 mins respectively [14]. Under the model optimum conditions, the conversion is almost unity at 600K as shown in Figure-4.

5. CONCLUSIONS

A model for the methanolysis reaction of algae is developed to study the effect of the operating parameters on the process kinetics. The fitting of the data indicated that the reaction is a forward first order reaction in terms of triglycerides. Two parameters were introduced to consider the effect of methanol to algae ratio and reaction time. The activation energy is 9.91 kJ/mol. Excellent fitting between the experimental results and model prediction is observed. The model shows that the optimum methanol to algae ratio and reaction time were 26 and 27 min respectively. The experimental results have shown that the optimum methanol to algae ratio and the reaction time are 30 and 30 mins respectively. The triglyceride is almost completely converted to bio diesel at 600K at the model optimum conditions within the experimental operating conditions in this study.

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