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## ARTICLE

# Esterification of free fatty acids with supercritical methanol for biodiesel production and related kinetic study

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Tianwei Jin<sup>a</sup>, Bin Wang<sup>a</sup>, Jinhui Zeng<sup>b</sup>, Chun Yang<sup>c</sup>, Yuqi Wang<sup>d</sup>, Tao Fang<sup>a,\*</sup>

Non-catalytic esterification of free fatty acids (oleic acid) with methanol for biodiesel production was studied in the reaction temperature range of 220~280 °C. In order to optimize the reaction conditions, the influence of the process parameters on biodiesel yield was studied with response surface methodology (RSM). It was found that biodiesel yield decreases at an exorbitant temperature. So a reaction temperature not higher than 260 °C is appropriate. And at the temperature of 260 °C with the methanol to oleic acid molar ratio of 20/1 and the reaction time of 60 min, biodiesel yield can reach about 95%. In addition, a simplified approach to implementing a kinetic model for the esterification reaction was developed, the experimental results were found to fit a first-order kinetic law and the kinetic parameters were analyzed and discussed. The rate constant of esterification in supercritical methanol increases significantly in comparison to that of subcritical conditions, and the apparent activation energy is higher than that of subcritical conditions.

## 1. Introduction

Energy resource is a crucial factor that affects the world's politics and economy. Fossil fuels, as the main resource, are unsustainable, and make a tremendous contribution to the environmental problems. Made from animals and plant oil, biodiesel has its properties as sustainable and eco-friendly which makes it a promising alternative to fossil fuels. Research on biodiesel has become a hotspot.

Traditional way of producing biodiesel is a transesterification reaction of animal and vegetable fats and oils in the presence of a catalyst. Through the transesterification process, the large, branched molecular structure of bio-oil was changed to be smaller straight-chain which was required in regular diesel combustion engines.<sup>1</sup> The disadvantages of conventional process include aspects of environmental pollution, production efficiency and feedstock flexibility. For an alkali-catalyzed transesterification, the water and free fatty acids contents of the feedstock are strictly limited.<sup>2</sup> Besides, the catalysts in products generally lead to some difficult separation process which may cause environmental pollution if misconducted. Intensive studies have been conducted to overcome the shortcomings of alkali-catalyst transesterification. The Supercritical methanol process was initially introduced in 2001,<sup>3</sup> its advantages include high efficiency, no catalysts and being less restricted by the moisture and FFAs contents in the feedstock.<sup>4</sup> But this method requires a severe reaction condition with high temperature and high pressure, which brings a serious economic problem and safe management issue.<sup>5</sup> A catalyst-free two-step supercritical methanol process was developed

as an improvement.<sup>6</sup> By separating the transesterification reaction into hydrolysis of oils to fatty acids in subcritical water and subsequent methyl esterification of fatty acids to their methyl esters in supercritical methanol, more moderate reaction condition (270 °C/7-20MPa) can be accepted.<sup>7</sup> And high-quality biodiesel can be produced with low glycerol content.

As to the second step of the two-step supercritical process, waste acid from other production processes can also be used for producing biodiesel with supercritical methanol. As shown by Yujaroen et al.,<sup>8</sup> the esterification of palm fatty acid distillate (PFAD) in supercritical methanol gave FAMES production a yield of 95% at 300 °C with the PFAD to methanol molar ratio of 1/6 and the reaction time of 30 min. As shown by Alenezi et al.,<sup>9</sup> to the non-catalyst esterification of free fatty acids with supercritical methanol at 10MPa, at 270 °C and 290 °C, the yield of FAMES reached 93% and 97% in 30 min, respectively; while the yield reached 97% in only 5 min when the temperature was 320 °C.

So far, few data in literature have been reported regarding non-catalytic esterification reactions. In this work, we aim to discuss how the factors affect the yield of biodiesel and find the optimized operating condition through the method of response surface analysis. In addition, on the basis of experimental data, a simplified first-order kinetic model was built to describe the esterification of free fatty acids in supercritical methanol.

## 2. Materials and methods

### 2.1 Materials

**Table 1 Factors and levels of the response surface method**

| Symbols | Variables                 | Low level | Central level | High level |
|---------|---------------------------|-----------|---------------|------------|
| $x_1$   | Reaction temperature (°C) | 240.00    | 260.00        | 280.00     |
| $x_2$   | Reaction time (min)       | 20.00     | 40.00         | 60.00      |
| $x_3$   | Molar ratio (mol/mol)     | 1.00      | 10.50         | 20.00      |

Methanol 99% was purchased from Fuyu Fine Chemical Co. Ltd., Tianjin, China. Oleic acid 98% was provided by Fuchen Chemicals Co. Ltd., Tianjin, China. The standard chemicals of methyl oleate and methyl palmitate (with the purities of 99.99% and 99.99%, respectively) were obtained from Nu-Chek Co. Ltd., USA.

## 2.2 Esterification in supercritical methanol

A batch type reactor was applied to study the esterification reaction in supercritical methanol. This experiment system consists of an electric furnace, three 10 ml steel reactors made by GH2132 (the maximum allowable reaction temperature and pressure are 650 °C and 50 MPa, respectively) for three parallel reactions and a temperature controller, as shown in Fig.1 and Fig.2. There are two thermocouples; one was inserted at the location of the furnace while the other one was inserted into the hollow type crew of a reactor. And a pressure sensor was used to monitor the pressure in the reactor. Prior to the experiment, the furnace temperature was controlled between 240 and 300 °C, and the corresponding reaction temperature was 220 and 280 °C, because there is about a 20 °C difference between the reaction temperature and the furnace temperature. The three reactors were firstly charged with the mixture of methanol and oleic acid with the preset molar ratio, respectively. After the furnace temperature reached the set point and remained stable for 5 minutes, three reactors were placed into the furnace. After a period of reaction (10~60 min), the reactors were removed from the heater and placed in a water bath to stop the reaction. The reaction products were discharged and washed with hot water several times to remove the unreacted methanol and water produced during the reaction. Finally, the FAMES obtained were drawn for gas chromatography analysis.

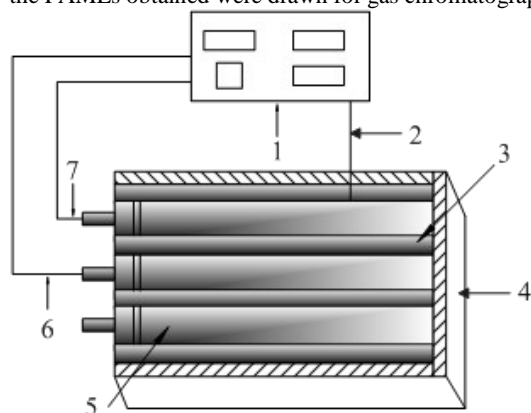


Fig.1 Batch reactor with a vibrator

1—temperature control instrument ; 2, 7—thermocouple ; 3—electrically heated panel ; 4—the furnace with a vibrator ; 5—reaction vessel ; 6—pressure sensor

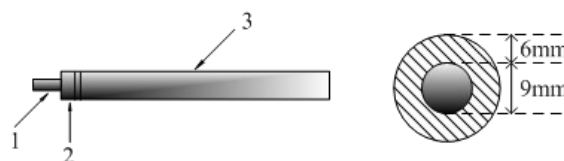


Fig.2 Reaction vessel

1— hollow type screw ; 2—vessel head ; 3—vessel body

## 2.3 Product analysis

Analysis of FAMES in the products was carried out by gas chromatography (GC, Purkinje General Instrument Co., Ltd., Beijing) with a flame ionization detector (300 °C). The GC consists of a column (DB-5, 30 m, 0.32 mm ID, 0.25 μm, Agilent Technologies, Inc., USA). And the parameters for oven temperature were programmed to increase from 150 °C to 230 °C (with holding time of 10 min) at the ramping rate of 10 °C min<sup>-1</sup>, and then increase to 280 °C (with holding time of 5 min) at the ramping rate of 10 °C min<sup>-1</sup>. The samples were prepared by adding about 0.05 ml of oil to 4 ml of n-hexane. The sample mixture weighted was injected into the GC and identified with the ISO 660:1983 standards.<sup>10</sup> The yield of FAMES was calculated by the following Eq. (1):

$$y, \% = \frac{W_{\text{FAMES}}}{W_{\text{oil}}} \times 100\% \quad (1)$$

where  $W_{\text{FAMES}}$  and  $W_{\text{oil}}$  are the mass amounts of the obtained FAMES and the oil in the sample, respectively. The yield was calculated with a value of 100 for the assumed theoretical maximum concentration as being the ratio of the actual yield and theoretical yield of the product.

## 2.4 Design of experiments

In this study, the optimization of the esterification reaction of free fatty acid in supercritical methanol has been carried out with three important variables which include reaction temperature ( $x_1$ ), reaction time ( $x_2$ ), methanol to oleic acid molar ratio ( $x_3$ ). The effects of these variables on the yield of biodiesel were studied with the method of the Box-Behnken Design by the software of Design Expert V8.0.5. The range of each variable was obtained by the single factor experiment. Table 1 summarizes the range and levels of the three variables investigated in this study.

## 3. Results and discussion

### 3.1 Single Factor Experiment

Fig.3 shows the influence of reaction temperature on the yield of FAMES, where the raw material methanol / acid molar ratio is 6:1 and the reaction time is 1 h.

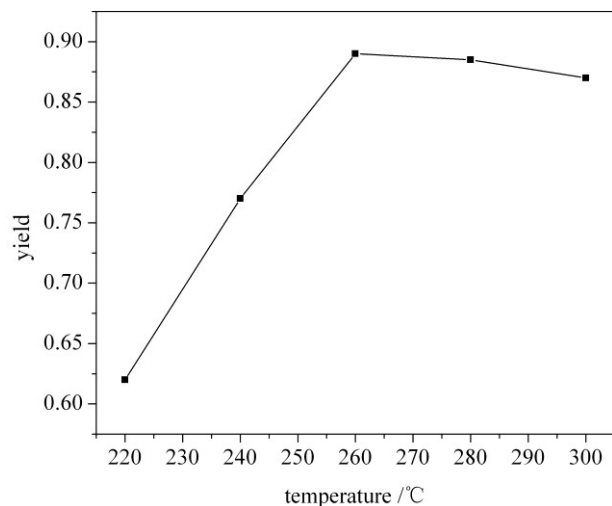


Fig. 3 Effect of temperature on esterification

At 220 °C, the yield of FAMES is low, as just reaching 62% after reacting for 1h. The yield of FAMES would increase with temperature increasing, for instance at 260 °C, the yield of FAMES could reach 89% after 1h; while in the same reaction time, when the reaction temperature is further increased, the yield of fatty acid remains substantially constant. If the temperature is too high and surpasses a certain value, the yield of FAMES would slightly decrease. Imahara et al.<sup>11</sup> found that when the temperature exceeds 350 °C, the unsaturated FAMES are serious degradation and isomerization. In order to get higher yields, the operating temperature for supercritical methyl esterification should be below 300 °C.

Ratio of raw materials is another key factor for the supercritical esterification. In the stoichiometric equation, the molar ratio of oil to methanol is 1:1, but in order to get a higher yield of FAMES, methanol in non-catalyzed methyl ester of oleic acid need to drastically excess.

Figure 4 shows the influence of methanol to oleic acid molar ratio on the yield of FAMES at 260 °C, 1 h reaction conditions, in the range of 1/1 to 40/1. It was found that when the methanol / acid molar ratio is 1/1, the yield was 75%; as the methanol / acid molar ratio risen up to 20:1, the yield of FAMES significantly increased to 87%; within a certain range, increase of the proportion of methanol has positive influence on the yield of FAMES, but a large excess of methanol would lead to a decreasing of yield of FAMES, for instance when the methanol to oleic molar ratio is 40/1, the yield dropped to 86%, because the excess of methanol makes a corresponding decrease in the concentration of oleic acid, the combined effect of the concentration change of reactants is not conducive for the balance of esterification moved in the positive direction.

Figure 5 is the variation of yield of FAMES with the reaction time at 260 °C, methanol to acid molar ratio of 6:1. The results showed that the yield of FAMES increases with reaction time; when the reaction time is 20 min, the yield is only 62%; after 60 min, the yield of FAMES increases to 87.5%, and in a longer reaction time, the yield of FAMES remain unchanged at 88%, under the condition of 260 °C, methanol of acid molar ratio of 6:1.

### 3.2 Development of regression model equation

The results obtained in the experiments are summarized in Table 2. As shown in the table, the biodiesel yield ranged from 53% to 93%, depending on different the conditions of the experiments.

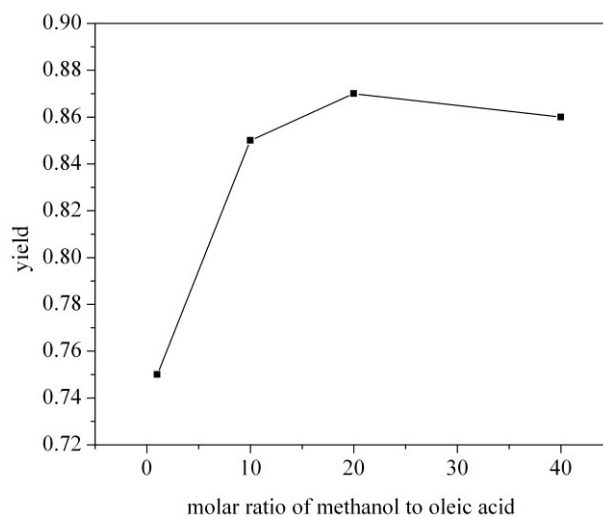


Fig. 4 Effect of methanol to oleic acid molar ratio on esterification

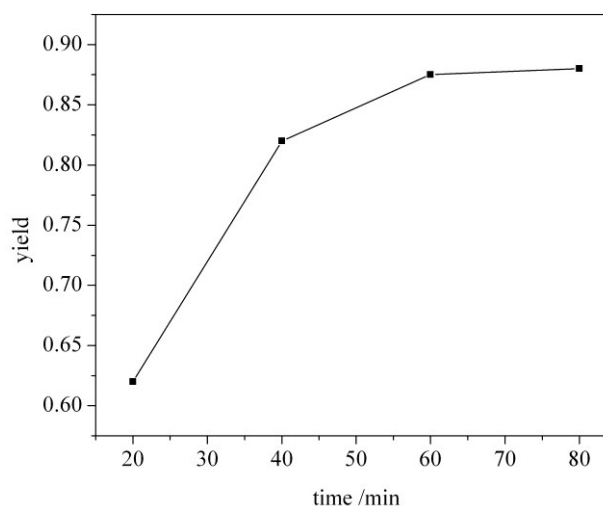


Fig. 5 Effect of reaction time on esterification

These results can be fitted into a second order regression model equation by Design Expert software V8.0.5, as given in Eq. (2):

$$y = 0.87 + 0.060x_1 + 0.094x_2 + 0.026x_3 - 0.072x_1x_2 - 0.053x_1x_3 + 0.070x_2x_3 - 0.017x_1^2 - 0.080x_2^2 - 0.035x_3^2 \quad (2)$$

the positive signs in front of the terms indicate the synergistic effects while the negative signs indicate the antagonistic effects. According to the equation, the three process variables have linear and quadratic effects on the yield of biodiesel. The model was found to have the correlation value ( $R^2$ ) of 0.9258, which means that 92.58% of the total variation in the results was attributed to the independent variables investigated in this study.

Table 3 shows the statistical analysis based on analysis of variance (ANOVA) for the response surface quadratic model. The value of  $P > F$  for the model is less than 0.05, which indicating it is a significant model. Besides, the  $P$ -value of 0.0086 indicates that there are only 0.86% of chance that an  $F$ -value larger than 'model  $F$ -value' could occur, due to the disturbance in the experiments. Apart from that, the 'Lack of Fit  $F$ -value' of 0.5532, greater than 0.05, implies that Lack of Fit is not significant relative to pure error.

**Table 2 Design of the response surface method and the corresponding results**

| Design points | Process variables                          |                                 |                                    |                 |
|---------------|--|---------------------------------|------------------------------------|-----------------|
|               | Reaction temperature<br>$T/^\circ\text{C}$ | Reaction time<br>$t/\text{min}$ | Methanol to oleic acid molar ratio | Biodiesel yield |
| 1             | 280.00                                     | 40.00                           | 1.00                               | 0.93            |
| 2             | 240.00                                     | 40.00                           | 20.00                              | 0.81            |
| 3             | 260.00                                     | 20.00                           | 1.00                               | 0.72            |
| 4             | 260.00                                     | 60.00                           | 1.00                               | 0.71            |
| 5             | 240.00                                     | 60.00                           | 10.50                              | 0.92            |
| 6             | 260.00                                     | 40.00                           | 10.50                              | 0.87            |
| 7             | 260.00                                     | 40.00                           | 10.50                              | 0.87            |
| 8             | 260.00                                     | 60.00                           | 20.00                              | 0.93            |
| 9             | 240.00                                     | 40.00                           | 1.00                               | 0.68            |
| 10            | 280.00                                     | 60.00                           | 10.50                              | 0.87            |
| 11            | 280.00                                     | 20.00                           | 10.50                              | 0.77            |
| 12            | 260.00                                     | 20.00                           | 20.00                              | 0.66            |
| 13            | 280.00                                     | 40.00                           | 20.00                              | 0.85            |
| 14            | 260.00                                     | 40.00                           | 10.50                              | 0.87            |
| 15            | 240.00                                     | 20.00                           | 10.50                              | 0.53            |

**Table 3 ANOVA for response surface quadratic model**

| Source      | Sum of squares | Degree of freedom | Mean square | F-value | Prof>F |                 |
|-------------|----------------|-------------------|-------------|---------|--------|-----------------|
| Model       | 0.18           | 9                 | 0.020       | 10.86   | 0.0086 | significant     |
| x1          | 0.029          | 1                 | 0.029       | 15.36   | 0.0112 |                 |
| x2          | 0.070          | 1                 | 0.070       | 37.50   | 0.0017 |                 |
| x3          | 5.513E-0003    | 1                 | 5.513E-0003 | 2.94    | 0.1471 |                 |
| x1x2        | 0.021          | 1                 | 0.021       | 11.21   | 0.0204 |                 |
| x1x3        | 0.011          | 1                 | 0.011       | 5.88    | 0.0598 |                 |
| x2x3        | 0.020          | 1                 | 0.020       | 10.45   | 0.0231 |                 |
| x12         | 1.131E-003     | 1                 | 1.131E-003  | 0.60    | 0.4725 |                 |
| x22         | 0.024          | 1                 | 0.024       | 12.60   | 0.0164 |                 |
| x32         | 4.523E-003     | 1                 | 4.523E-003  | 2.41    | 0.1811 |                 |
| Residual    | 9.375E-003     | 5                 | 1.875E-003  |         |        |                 |
| Lack of Fit | 9.375E-003     | 3                 | 3.125E-003  | 0.94    | 0.5532 | Not significant |
| Pure Error  | 0.000          | 2                 | 3.333E-003  |         |        |                 |
| Cor Total   | 0.19           | 14                |             |         |        |                 |
| R-Squared   | 95.13%         |                   |             |         |        |                 |

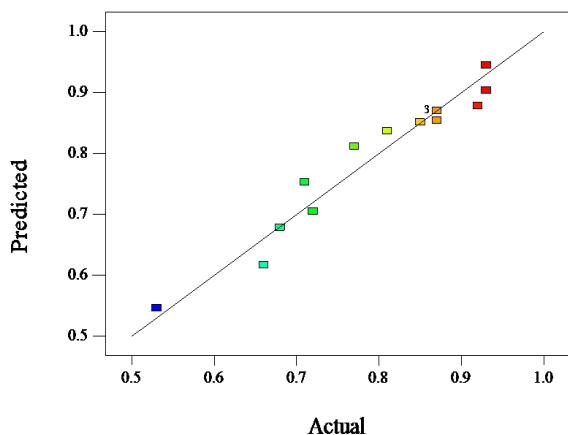


Fig.6 Predicted yields versus actual yields of FAMES

Fig.6 shows a plot of experimental yields of FAMES versus theoretical yields of FAMES and the R-squared value is 95.13%.

### 3.3 Interactions between process variables

The results in Table 3 show that interactions between variables have significant effects on the yield of biodiesel. Therefore, investigating these interactions is significant and important for a comprehensive optimization study. Fig.7 – Fig.9 show the influence of interactions between different variables on the yield of biodiesel in three dimensional surface responses, respectively.

Fig.7 shows the effects of reaction time and reaction temperature on biodiesel yield with a methanol to oleic acid molar ratio of 10.5/1. At a low reaction temperature of 240 °C, biodiesel yield is significantly affected by reaction time. However, at higher reaction temperature, the relevancy of reaction time to the augmentation of yield is not so enormous. At 240 °C, the yield reaches 85% after about 50 min while it would take less than 30 min to achieve the same yield at 280 °C. Higher temperature induces faster reaction rate over lower temperature. However, it is found that with a relatively long reaction time, the yield of biodiesel at a higher temperature of 280 °C would be lower than that at a lower temperature of 240 °C. It mostly due to the instability of FAMES that it may decompose while treated at a high temperature for a long time. The probable degradation of oleic

**Table 4 Kinetic parameters at 220–280 °C**

| Temperature<br>T / °C | Rate constants k<br>/ min <sup>-1</sup> | Pre-exponential factor A<br>/ min <sup>-1</sup> | Apparent Activation<br>energy<br>Ea/ kJ mol <sup>-1</sup> |
|-----------------------|---|---|---|
| 220                   | 0.0256                                  | 0.18  | 7.91  |
| 240                   | 0.0276                                  |   |   |
| 250                   | 0.0517                                  |   |   |
| 260                   | 0.0569                                  |   |   |
| 270                   | 0.0648                                  | 8.16  | 21.98   |
| 280                   | 0.0671                                  |   |   |

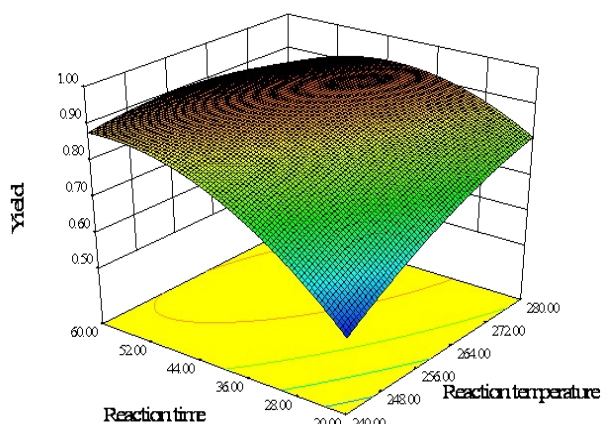


Fig.7 Effects of reaction time and temperature on biodiesel yield when the M/O molar ratio is 10.5/1

acid methyl ester at a high temperature is considered as another cause for this phenomenon.<sup>12</sup> Hence, the reaction temperature for the esterification of free fatty acid in supercritical methanol should be restricted within a certain range.

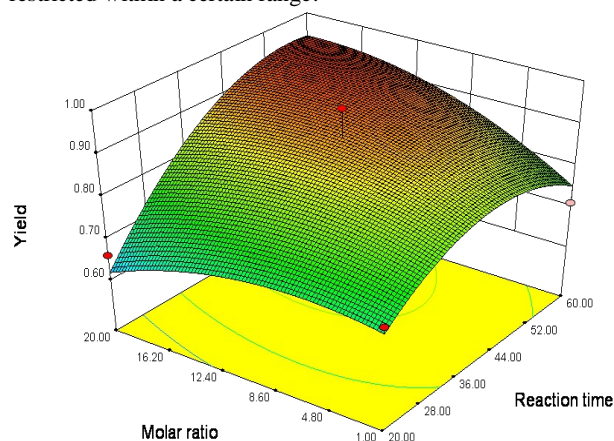


Fig.8 Effects of reaction time and molar ratio on biodiesel yield under 260 °C

Fig.8 represents the effect of interaction between the reaction time and the molar ratio of methanol to oleic acid on biodiesel yield at the constant reaction temperature of 260 °C. Within the beginning period of the reaction, the yield of biodiesel is only marginally affected by the increment in molar ratio. However, in a long time reaction, the effect of molar ratio becomes significant.

The effect of the reaction temperature and the methanol to oleic acid molar ratio on biodiesel yield in constant reaction time of 40 min is

shown in Fig.9. It is found that at a relatively lower temperature of 240 °C, the biodiesel yield increases marginally with molar ratio, because an increase in the proportion of methanol can favorably shifts the equilibrium. However, at 280 °C, the biodiesel yield slightly decreases when the molar ratio increases to a certain extent. It may be due to the decomposition of FAMES at a high temperature and this effect becomes significant when the concentration of free fatty acid reduces too much. In addition, because of the limitation of reaction equilibrium and difficulties in separating excessive methanol from biodiesel, the molar ratio should not be too large.

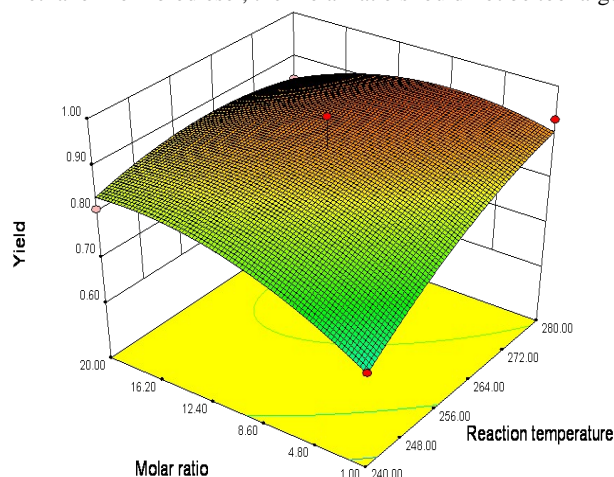


Fig.9 Effects of reaction temperature and molar ratio on biodiesel yield in 40min

According to these analysis conclusions and the optimized result with response surface methodology, the yield of fatty acid methyl esters would be 95.8% with the temperature of 260 °C, the methanol to oleic acid molar ratio of 20/1 and the reaction time of 60 min. While the average yield of three parallel tests can reach 94.6% under the same condition, very close to the predicted value.

### 3.4 Kinetics parameters of the process

The influence of temperature on biodiesel yield from 220 °C to 280 °C is shown in Fig.10. The reaction was carried out with a fixed methanol to oleic acid molar ratio of 7/1 and with a vibration frequency of 3Hz. The experimental data obtained are shown by the symbols. Between 220 and 240 °C, as below the critical temperature of methanol, the maximum yield achieved was about 60 % in 40 min. When the temperature is between 250 and 280 °C surpassing the critical point, the biodiesel yield could reach about 90% in 40 min. It was observed that increasing the reaction temperature had a favorable influence on biodiesel yield.

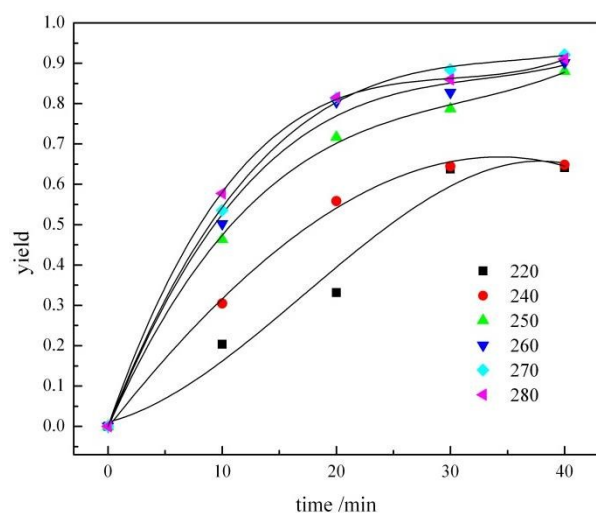
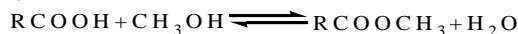


Fig.10 Effect of reaction time on biodiesel yield at 220~280 °C ( $P=8\sim 15\text{MPa}$ )

Non-catalytic methyl esterification is a one-step reaction where FFAs reacts with methanol to form FAME and byproduct water, according to the reaction formula



As shown by Minami and Saka,<sup>7</sup> the esterification reaction in the supercritical methanol could be modeled as a second-order reversible reaction and they introduced a new concept of auto-catalytic esterification. In that approach, the FFAs act as reactant and acid catalyst. The authors did not mention the application of their model and the values of respective rate constants, nor the fit degree of the model to the experimental data in that work. A simplified model was introduced by Sendzikiene et al.<sup>13</sup> hypothesizing a first-order irreversible reaction to explain the acid catalyzed esterification. In this study, a simplified model for the irreversible esterification reaction of FFAs with supercritical methanol was developed. Due to the high molar ratio, the reverse reaction was ignored, and the concentration of methanol can be regarded as invariant. Considering only the forward reaction and assuming the whole reaction as a first-order reaction, the apparent rate constant of the reaction ( $k$ ) can be given by the following equation:

$$r_A = -\frac{dc_A}{dt} = kc_A \quad (3)$$

where  $c_A$  is the concentration of FFAs and can be described as  $c_{A0}(1-x)$ ,  $c_{A0}$  is the initial concentration of FFAs, and  $x$  is the initial concentration of FFAs, and  $x$  is the percent conversion of FFAs that is equal to the biodiesel yield in this reaction.

By integrating, it gives

$$-\ln(1-x) = kt \quad (4)$$

so the rate constant  $k$  can be obtained by a linear fit of the equation 4. By fitting the experimental data at different temperatures, a good linear relation between  $-\ln(1-x)$  and  $t$  was found and it supported the hypothesis that the reaction is a first-order reaction. The rate constants at different reaction temperatures are listed in Table 4. With the apparent rate constants at different temperatures determined, the apparent activation energy for the esterification reaction was calculated using the Arrhenius formula below:

$$k = Ae^{-\frac{E_a}{RT}} \quad (5)$$

where  $A$  is the factor of frequency, and  $E_a$  is the energy of activation. The formula could be deduced as

$$\ln k = -\frac{E_a}{RT} + \ln A \quad (6)$$

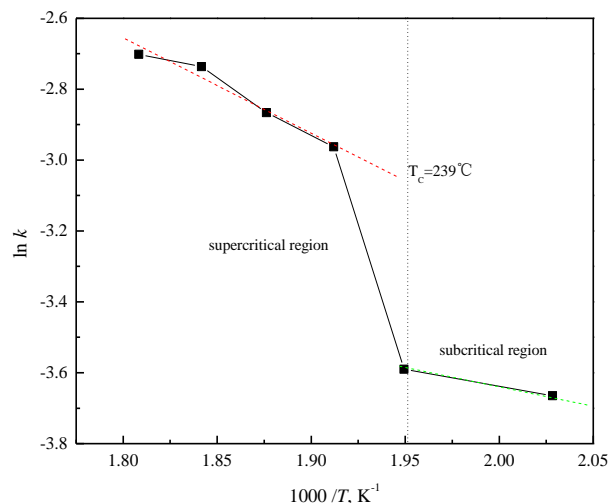


Fig.11 Arrhenius plot for esterification reaction

The relation of  $\ln k$  and  $1000/T$  is shown in Fig.11. It can be found that  $\ln k$  is non-linear with  $1000/T$  over the temperature range of 220~280 °C. However, in the supercritical temperature region (above 240 °C), good linearity is observed. And the rate constants increase drastically near the critical temperature point, mainly due to the considerable changes in the physical properties of methanol. The properties of the fluid are very sensitive to the change of reaction temperature and pressure near the critical point.

The apparent activation energy in the supercritical methanol is 21.98 kJ mol<sup>-1</sup>, which is much larger than that in the subcritical state. Thus, the kinetic model for the esterification of oleic acid with supercritical methanol was expressed as:

$$r_A = -\frac{dc_A}{dt} = 8.16e^{-\frac{2.198 \times 10^4}{RT}} \cdot c_A \quad (7)$$

## 4. Conclusions

Through the response surface optimization, the optimal operating conditions are obtained; under this condition the experimental methyl ester yield is 94.6%, which agree the predictive value well. A simplified irreversible first order reaction kinetic model was built. The results showed that the reaction rate of the esterification reaction will have a substantial increase when the reaction condition changes from subcritical state to supercritical state. It is because when the methanol is in the supercritical state, the reaction system becomes homogeneous; the reaction is significantly accelerated as the obstacle between two reactants disappears.

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<sup>a</sup> School of Chemical Engineering and Technology, Xi'an Jiaotong University, Xi'an, China

<sup>b</sup> Department of Chemical and Biological Engineering, Zhejiang University, Hangzhou, China

<sup>c</sup> The First affiliate hospital, Xi'an Jiaotong University, Xi'an, China

<sup>d</sup> School of chemical engineering, Northwest University, Xi'an, China

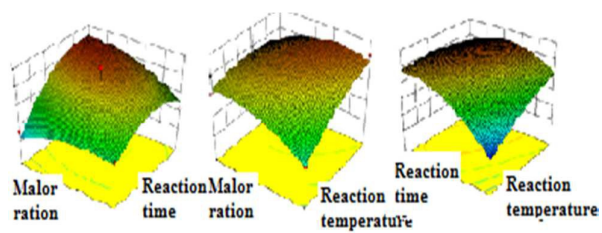
\* Corresponding Arthur. E-mail: taofang@mail.xjtu.edu.cn.

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## Table of contents



The interaction of raw material ration, reaction temperature and reaction time on the esterification reaction of free fatty acids, and a kinetic analysis of it.