Study on Kinetics of Transesterification of Biodiesel in Zanthoxylum bungeanum seed Oil Ethyl Ester

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Abstract. Zanthoxylum bungeanum seed oil (ZSO) was the by-product of the zanthoxylum industry, and was a kind of cheap and abundant source in china, which can be great potential of use as a feedstock for biodiesel production in terms of reducing the producing cost. Kinetics of Transesterification of Biodiesel from Zanthoxylum bungeanum seed Oil Ethyl Ester using Sodium ethoxide as an alkaline catalyst was studied in this paper. The results showed that the progression of transesterification was grade 1.5, the reaction activation energy was 17.876kJ·mol-1 and the pre-exponential factor was 0.8521L/(mol·min). The contrast between experimental value and predicted value displayed the dynamics model had a good veracity, and can be applied for predicting reaction rate of progress.

Biodiesel is usually produced by transesterification of vegetable oils or animal fats[1]. The transesterification reaction is a chemical reaction of triglyceride and a short chain alcohol under the action of a catalyst to produce a fatty ester monoester[2-4]. Studies on the transesterification kinetics of biodiesel from palm oil, cottonseed oil, soybean oil, rapeseed oil, and tung oil have been reported[5-8]. Kinetic studies of transesterification of *ZSO* with methanol to prepare biodiesel are also available on literature[9]. It is generally believed that fatty acid alkyl esters are prepared by transesterification, using different short chain alcohols or selecting different lipids, and the kinetic model and parameters of the transesterification reaction are also different[10, 11]. At present, there is no report on the reaction kinetics of the transesterification of *ZSO* with bioethanol.

In this paper, Kinetics involved in the process of biodiesel production and its stability have been critically studied. The research could provided a substantial and theoretic foundation for biodiesel production of *ZSO* ethyl ester.

1 Experimental

1.1 Materials and reagents

ZSO was provided by a local company located in Hancheng, Shaanxi Province, China. This is a high yield area for Z. bungeanum Maxin. Eethanol, Sodium ethoxide, change-color-silica gel and other chemicals were of analytical reagent grade. The pretreated ZSO used in this experiment, with the acid value and the saponification value of 1.56 mg KOH/g and 189.3 KOH/g,

was adapted for biodiesel preparation while alkali was as catalyst.

1.2 Measurement of biodiesel conversion rate

The conversion rate of biodiesel was calculated by measuring the conversion rate of glycerin. Glyceric spectrophotometer method was improved in the experiment based on the research by Yan jie[12]. The method adopted was proved well at veracity and credibility[13].

1.3 The Kinetics of Biodiesel Production from ZSO by Transesterification

In this paper, the reaction kinetics of preparation of biodiesel from *ZSO* ethyl ester by alkali-catalyzed transesterification was studied for the first time. A macro-reaction kinetics model was established and relevant kinetic parameters were calculated to lay a theoretical foundation for the production and application of *ZSO* ethyl ester biodiesel.

In order to simplify the kinetic model for the preparation of biodiesel from *ZSO*, it is assumed here that the transesterification reaction is completed in one step, and the reaction equation is simplified as follows.

Triglyceride(A) + 3ethanol →

3 Fatty acid ethyl ester(FAEE) + Glycerol
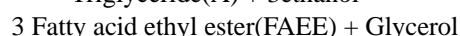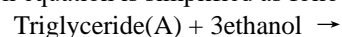
When the absolute amount of absolute ethanol in one of the reactants is excessive, the positive reaction rate is much greater than the reverse reaction, and its influence on the reaction can be ignored. Therefore, the transesterification reaction kinetic equation can be expressed as (1):

$$-\frac{dc_A}{dt} = k_A c_A^\alpha c_B^\beta \qquad (1)$$

$$\text{or} \qquad -\frac{dc_B}{dt} = k_B c_A^\alpha c_B^\beta \qquad (2)$$

When there is a far excess of ethanol, it can be considered that the concentration remains substantially unchanged during the reaction. Formula (2) can be converted to:

$$-\frac{dc_A}{dt} = \frac{\Delta c_A}{\Delta t} = k_1 c_A^\alpha \qquad (3)$$

Where $k_1 = k_A c_B^\beta$, $\Delta c_A = c_{A,0} \times y$ (y is the conversion rate of ZSO biodiesel). $\ln\frac{\Delta c_A}{\Delta t} = \ln k_1 + \alpha \ln c_A$ would be obtained by taking logarithm both sides of equation (3). Drawing figure by the relation of $\ln\frac{\Delta c_A}{\Delta t}$ and $\ln c_A$, you can get a straight line. The slope of the straight line is the desired α.

The reaction rate constant k_A of different temperature can be calculated by changing the reaction temperature.

In the same way, when the ZSO is much excessive, β and the rate constant k_B at different reaction temperatures can be found.

According as Arrhenius equation $\ln k = -\frac{E_a}{RT} + \ln A$, a beeline can be drew by using of the relation on $\ln k$ and $\frac{1}{T}$, activation energies E_a would be gained by the linear slope, frequency factor(or pre-exponential factor called) can be acquired by the linear intercept.

2 Results and discussion

For getting partial progression α of transesterification on ZSO, two times, three times, four times, five times and six times of excessive ethanol respectively were used in the reaction, namely the ethanol-to-oil molar ratio of 9:1, 12:1, 15:1, 18:1, and 21:1 adopted. The reaction condition was at catalyst amount of 1.7%, reaction time 120min, reaction temperature of 45℃, 55℃, 65℃, and 75℃ fixed respectively. Spectrophotometric was adopted to determine biodiesel conversion of under different conditions, and the relationship between $ln(\Delta c/\Delta t)$ and lnc under different temperature conditions could be obtained, the results showed as Fig. 1.
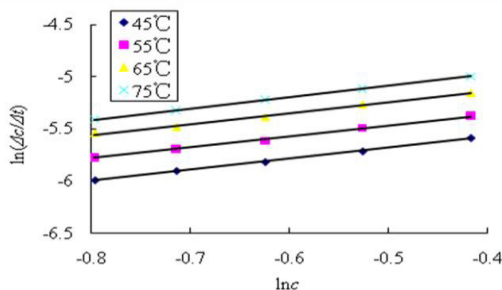
Fig. 1. The relation between $ln(\Delta c/\Delta t)$ and lnc under different temperature

For getting partial progression β of transesterification on ZSO, the ZSO molar ratio added into reaction system

was excessive for two times, three times, four times, five times and six times to ethanol when the partial progression of ethanol was calculated, such as the ethanol-to-ZSO molar ratio of 3:3, 3:4, 3:5, 3:6, and 3:7 employed. The other reaction condition were respectively at 1.7% catalyst amount, reaction time of 120min, and reaction temperature fixed separately of 45℃, 55℃, 65℃ and 75℃. The relationship between $ln(\Delta c/\Delta t)$ and lnc under different temperature conditions could be obtained, the result of experiment was showed as Fig. 2.
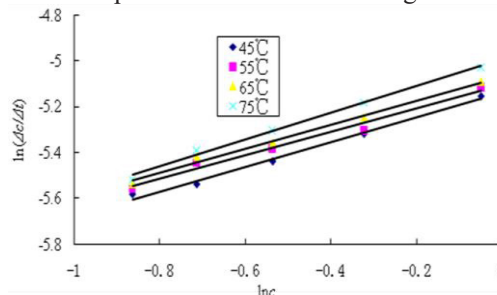
Fig. 2. The relation between $ln(\Delta c/\Delta t)$ and lnc under different temperature

According to Fig.1 and Fig.2, the reaction order α and β corresponding to ZSO and ethanol respectively, and the reaction rate constants k_1 and k_2 can be obtained at different temperatures. The results are shown in Table 1 and 2. From the table, we can see that the linear correlation of the fitted linear equations are good, and the reaction rate constants increase with the increase of temperature. The reaction grades under different temperature conditions were averaged to obtain a reaction grade of 1.5 for the preparation of ZSO ethyl ester biodiesel by alkali-catalyzed transesterification.

Take $1/T$ as abscissa and lnk_A as ordinate drawing, a straight line can be obtained, as shown in Fig. 3. Apparent activation energy E_a=17.876kJ • mol^{-1}, would be obtained from the slope of the regression equation; The apparent frequency factor A=e$^{-0.16}$=0.8521L/(mol· min) could be found by the intercept, which is consistent with the conclusions of literature[14, 15]. Therefore, the kinetic equation at the reaction temperature of 75°C can be expressed as r_A=1.602×10$^{-3}c_A^{1.0916}c_B^{0.5368}$.
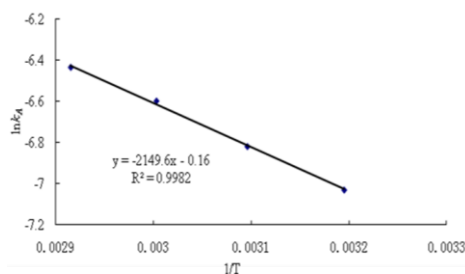
Fig. 3. Relationship between temperature and transesteri-fication reaction rate constants

Integrating the equation $-\frac{dc_A}{dt} = k_1 c_A^\alpha$, and the formula (4) can be obtained:

$$y = \frac{k_1 c_A^{\alpha} t}{c_{A,0}}$$

$$(4)$$

According to formula (4), the theoretical conversion rate of *ZSO* ethyl ester biodiesel at different reaction temperatures and reaction times can be predicted and

verified by experiments, the results are shown in Fig. 4. As can be seen from the figure, the actual measurement values are in good agreement with the predicted values, indicating that the macro-kinetic model is accurate and reliable.

Table 1. Reaction order and rate constants of *ZSO* under different temperature conditions

Temperature /℃	α	k_1 (L/mol)$^{1/2}$/min	k_A L/(mol·min)	R^2
45	1.0522	0.005764	0.0008851	0.9988
55	1.0536	0.007130	0.001092	0.9966
65	1.0550	0.008909	0.001361	0.9940
75	1.0916	0.01119	0.001602	0.9980

Table 2. Reaction order and rate constant of ethanol under different temperature conditions

Temperature/℃	β	k_2 (L/mol)$^{1/2}$/min	k_B L/(mol·min)	R^2
45	0.5356	0.005858	0.005980	0.9918
55	0.5112	0.009977	0.01018	0.9801
65	0.4726	0.01292	0.01316	0.9938
75	0.5368	0.01569	0.01602	0.9986
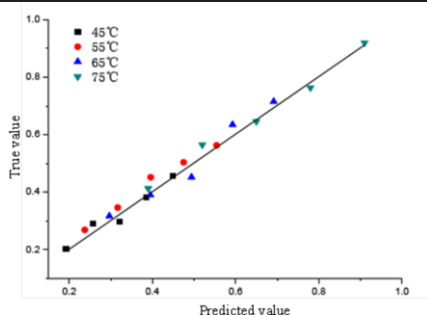
Fig. 4. Relationship between actual measured values and predicted values

3 Conclusion

The kinetic study on the preparation of biodiesel from *ZSO* by alkali-catalyzed transesterification showed that the transesterification reaction order of *ZSO* and ethanol was 1.5, and the activation energy of reaction was 17.876 kJ·mol^{-1}, and the pre-exponential factor was 0.8521L/(mol·min). The kinetic equation in 75℃ is $r_A = 1.602 \times 10^{-3} c_A^{1.0916} c_B^{0.5368}$. The contrast between experimental value and predicted value displayed the dynamics model had a good veracity, and can be applied for predicting reaction rate of progress.

Acknowledgement

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