Green Chemistry

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/greenchem

Journal Name

Green Chemistry

Dynamic Article Links ►

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Kinetics of DBU-catalyzed transesterification for biodiesel in DBU/ethanol switchable-polarity solvent

Dongling Xue [a], Ying Mu[a], Yu Mao[a], Tiankui Yang* [a,b] and Zhilong Xiu* [a]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

The production of biodiesel from soybean oil and ethanol was investigated in switchable-polarity solvent (SPS) media of DBU and ethanol. The highest biodiesel yield catalyzed by DBU could reach 97.9% at optimized conditions, i.e. ethanol/oil molar ratio: 12:1, DBU/oil molar ratio: 2:1, reaction temperature: 70 ℃, reaction time: 2 h. According to the kinetic analysis, the reaction order of oil was estimated to be 0.7, the apparent activation energy was 16.763 kJ mo1^{-1},， the pre-exponential factor was 561.31 mol$^{0.3}$ mL$^{-0.3}$ min^{-1}) and the Arrhenius equation for the first time, which explain the high efficiency of DBU catalyst. The DBU-catalyzed transesterification in DBU/ethanol switchable-polarity solvent supplied an interesting alternative, which would be used to simplify the transesterification and separation into only one step.

1. Introduction

Biodiesel is chemically defined as the mono-alkyl-esters of long-chain-fatty-acids derived from renewable lipid sources. In fact, biodiesel is a variety of ester-based and oxygenated biofuel from renewable biological sources.[1] Fatty acid methyl esters (FAME) and fatty acid ethyl esters (FAEE) are two kinds of the most studied biodiesel, which are produced by methanol/ethanol and lipids, respectively, such as vegetable oils, animal fats, recycled cooking oils, greases and micro-algae oil, etc. Generally, methanol is preferred for transesterification because it is less expensive than other kinds of alcohols[1]. Meanwhile, ethanol is also a focus for concern because of its safety and security of sources and environment.

Nowadays there are many methods to produce biodiesel, nevertheless, transesterification between triglycerides and short chain alcohols is still the most common method. The transesterification can happen under both homogeneous catalysts (acid or base) and heterogeneous catalysts (solid acid, base and immobilized enzyme).[2] Also it can be carried out under some supercritical conditions.

Usually, it is easier to separate heterogeneous catalysts from biodiesel products, which is good for recycling of catalysts, reducing the negative environmental impact and process cost. However, heterogeneous acidic catalysts need higher reaction temperature and longer reaction time than regular reactions catalyzed by NaOH.[3-7] Moreover, some heterogeneous basic catalysts are wastage-prone and unfavourable for recycling in the reactions, and the reaction temperatures they catalyzed are also high.[8-9] Another kind of heterogeneous catalyst, i.e. immobilized enzyme, is limited on an industrial scale due to its high price, inactivation and long reaction time.[10-12] Additionally, supercritical reactions cannot avoid high energy consumption and maintenance costs.

Although homogeneous basic catalysts have much faster reaction rates than heterogeneous catalysts and homogeneous acidic catalysts in the transesterification of oils, it is difficult to separate regular homogeneous basic catalysts from glycerin layer.

Is there a new type catalyst that could avoid all the disadvantages above, and make a quick reaction and an easier separation? Actually, some researchers found a high potential catalyst – DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), which is a sort of amidine compounds used in organic synthesis as a non-nucleophilic basic catalyst. It is reported that transesterification occurred under catalyzing with DBU[13], which can form DBU/alcohol switchable-polarity solvent (SPS) and give excellent separation from decane (nonpolar liquid) with carbon dioxide[13-14]. And moreover, the interesting side-reaction presented a fairly good capacity of catalyzing transesterification by DBU. Additionally, the convenience of synthesizing DBU/alcohol PSP makes it promising to separate and reuse DBU catalyst[13-14]. However, DBU was reported to be not a good enough catalyst to get the highest yield of transesterification. Another organic soluble guanidine base, TBD (1,5,7-triazabicyclo[4,4,0]dec-5-ene) used for a variety of base-mediated organic transformations, showed much higher catalysis efficiency than DBU[15-16]. As an organic soluble base, TBD still cannot avoid the problem of what other homogeneous catalysts have to

---

[a] *School of Life Science and Biotechnology,Dalian University of Technology, Linggong Road 2, Dalian 116024, Liaoning Province, People's Republic of China. Fax: 86 411 84706369; Tel: 86 411 84706369; E-mail: zhlxiu@dlut.edu.cn*
[b] *Wilmar (Shanghai) Biotechnology Research & Development Centre Co., Ltd, Shanghai 200137, People's Republic of China. Fax: 86 21 58487667; Tel: 86 18621569666; E-mail: yangtiankui@wilmar-intl.com* *tkyang@dlut.edu.cn*

face above. Some technologies of TBD immobilization which try to make easier separation and reuse of it need longer time to achieve higher transesterification conversion than that catalyzed by homogeneous TBD [17-18].

In this study, DBU played a dual role as catalyst and solvent. When DBU was added, the reaction system of oil and ethanol was transformed into homogeneous from heterogeneous, compared with the circumstance without DBU, because not only can DBU dissolve oil, but it can also dissolve ethanol. Therefore, the kinetics of DBU-catalyzed transesterification will be studied to understand how the PSP works on the premise of high yield so as to reduce the pressure of product separation and catalyst recycle in the future. We optimized the conditions for biodiesel using DBU as catalyst at first, and then examined the kinetics of DBU-catalyzed transesterification of soybean oil and ethanol. The reaction rate constants (*k*) at four temperature levels were determined and the apparent activation energy (E_a) was first shown. And these kinetic parameters might be helpful for elucidating the reaction mechanism of biodiesel formation with DBU in the further research To our knowledge, there is no published report on the kinetics of DBU-catalyzed transesterification in DBU/ethanol switchable-polarity solvent.

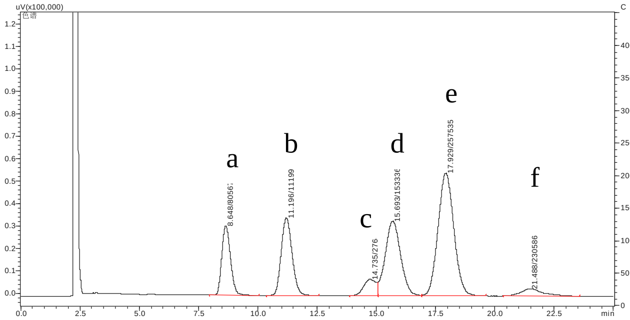

Fig. 1. Chromatogram for biodiesel produced from soybean oil and ethanol under the catalysis of DBU.

a. C16:0, ethyl palmitate; b. C17:0, methyl heptadecanoate (internal standard substance); c. C18: 0, ethyl stearate; d. C18: 1, ethyl oleate; e. C18: 2, ethyl linoleate; f. C18:3, ethyl linolenate.

Reaction conditions: molar ratio of ethanol and soybean oil: 12:1; molar ratio of DBU and soybean oil: 2:1; 70 ℃, 2h

2. Experimental

2.1 Materials

Soybean oil was purchased from a local supermarket. DBU (99%) was purchased from Aladdin Chemistry Co. Ltd. To test the chemical properties and parameters of the oil, ethanol (95%, v/v), potassium hydroxide, hydrochloric acid, and diethyl ether were procured from Sinopharm Chemical Reagent Co., Ltd. For GC analysis, the internal standard methyl heptadecanoate was obtained from Aladdin Chemistry Co. Ltd. The standards of ethyl palmitate, ethyl stearate, ethyl oleate, ethyl linoleate, and ethyl linolenate were procured from J&K Scientific Ltd.

2.2 Transesterification of soybean oil with ethanol by DBU catalyst

A refluxing reaction system consisted of a 250 mL four-neck glass flask with a magnetic stirrer, a water-cooled condenser, and a thermometer was used for the transesterification of soybean oil with ethanol. Typically, soybean oil (44.000 g, 0.05 mol) and ethanol (27.642 g, 0.60 mol) were displaced into the flask at a predetermined temperature. To the stirred solution, DBU (15.224 g, 0.10 mol) was added to initiate the reaction. Because of the presence of DBU, the sharp-cut two-phase system was transformed into the only-one-phase homogeneous solution which was clear and transparent. Preliminary studies were conducted to evaluate the reproducibility of the biodiesel yield. Average results for three repetitive tests were obtained.

2.3 Kinetics experiment

Kinetics experiments were performed in the above reaction system with a sampling port. The molar ratio of ethanol to soybean oil and the catalyst amount were fixed under the optimal condition (ethanol/oil molar ratio: 12:1; DBU/oil molar ratio: 2:1). The total reaction volume was considered as constant during transesterification because the volume of samples withdrawn was less than 1% of the total volume. The sample of 0.1 mL was withdrawn from the mixed reaction system at intervals and then put into an ice chamber of -20 ℃ to stop the reaction immediately. A solution with a known amount of methyl heptadecanoate (served as internal standard) was prepared preliminarily. Samples for GC analysis were prepared by adding exactly 0.1 mL of the withdrawn of reaction mixture and 0.2 mL of the internal standard solution (19.54 mg/mL) and diluted to 10 mL with n-hexane.

2.4 Analysis of samples

Samples prepared as described above were analyzed by a Shimadzu GC2014 Gas Chromatograph System equipped with a capillary column (PEG-20w; 0.25 mm * 30 m, 0.1 μm film thickness) and a FID detector. The samples were injected at an oven temperature of 195 ℃ (held for 20 min). Nitrogen was used as carrier gas. The temperature of the injector and detector was set at 220 ℃ and 260 ℃, respectively. The sample injection volume was 1 μL, and split ratio was 20:1. Compared with the standards, the components in the biodiesel were determined by GC in the range of 8-24 min as shown in Fig. 1.

The concentration of FAEEs was quantified by internal standard method using methyl heptadecanoate as the internal standard. The yield of FAEEs was calculated by the following equation:

$$Yield(\%) = \frac{m_{actual}}{m_{theoretical}} \times 100\% = \frac{\frac{m_{MH}}{n} \times (1-n)}{C_{FAEEs} \times a \times b} \times 100\% \qquad (1)$$

Where m_{actual} and $m_{theoretical}$ are the actual and theoretical mass of FAEEs, respectively; m_{MH} is the mass of methyl heptadecanoate per μL of GC sample, which is constant in the samples; *n* is the mass fraction of methyl heptadecanoate of a sample, which could be acquired by GC; C_{FAEEs} is the mass concentration of FAEEs when the oil totally converts to FAEEs in the system; *a* is the multiple of FAEE which is going to dilute; *b* is the volume of the GC sample.

3. Kinetic model

The overall transesterification reaction of soybean oil and ethanol was described as Fig. 2.

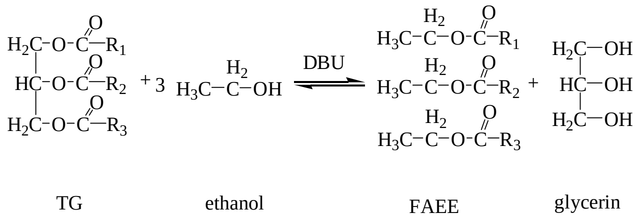

Fig. 2 The overall reaction of soybean oil and ethanol with DBU

The kinetic model is proposed on basis of the three major assumptions: (1) The glyceride mass transfer rate towards the catalyst active sites can influence the overall process rate in the initial reaction period; (2) Ethanol was enormously excess compared with soybean oil and could shift the reaction equilibrium towards the formation of FAEEs (12:1 in this study); (3) the reverse reaction could be negligible and the change of its concentration during the course of transesterification was ignored. The following rate equations were considered:

$$\upsilon = k c_{TG}^{\alpha} c_{EtOH}^{\beta} = -\frac{d c_{TG}}{dt} = k_1 c_{TG}^{\alpha} \qquad (2)$$

$$k_1 = k\ c_{EtOH}^{\beta} \qquad (3)$$

Where k is the reaction rate constant; C_{TG} is the concentration of oil in the reaction system; C_{EtOH} is the concentration of ethanol; k_1 is apparent reaction rate constant; α, β are the partial reaction orders for oil and ethanol, respectively. The concentration of soybean oil in terms of fractional conversion as:

$$c_{TG} = c_{TG0}(1-x) \qquad (4)$$

Where C_{TG0} is the initial concentration of oil; C_{TG} is the concentration of oil at time t; and x is the conversion of oil.

Eq. (2) can be rewritten according to Eq. (4).

$$\upsilon = -\frac{d c_{TG}}{dt} = -\frac{d[c_{TG0}(1-x)]}{dt} = c_{TG0}\frac{dx}{dt} = k_1 c_{TG}^{\alpha} \qquad (5)$$

By integrating, it gives:

$$\frac{dx}{dt} = \frac{k_1}{c_{TG0}}[c_{TG0}(1-x)]^{\alpha} \qquad (6)$$

$$\ln(\frac{dx}{dt}) = \alpha \ln[c_{TG0}(1-x)] + \ln\left(\frac{k_1}{c_{TG0}}\right) \qquad (7)$$

The rate constant k_1 can be obtained by a linear fitting of Eq. (7). Then the apparent activation energy for the transesterification reaction could be calculated using the natural logarithm of Arrhenius equation as Eq. (8).

$$\ln k_1 = -\frac{E_a}{RT} + \ln A \qquad (8)$$

where E_a is the apparent activation energy, R is the gas constant, T is temperature in Kelvin, and A is the pre-exponential factor.

4. Results and discussion

The transesterification of soybean oil with ethanol needs activation by a catalyst to achieve a high yield. During transesterification in DBU/ethanol SPS, DBU was used as the homogeneous catalyst. All the reactions were carried out by refluxing systems, in which higher yield could be obtained. The effects of main reaction conditions on the yield of FAEEs were explored in the coming experiments. And the kinetic parameters were then determined on basis of reaction data obtained under the optimal conditions.

4.1 Effect of molar ratio of ethanol to oil on the yield of FAEEs

The molar ratio of ethanol to soybean oil is one of the most important variables affecting the FAEEs yield. It is evident that the transesterification of 1 mole soybean oil needs three moles of ethanol at least theoretically. Ethanol used in the reaction system was in enormous excess compared with soybean oil in order to drive the reaction equilibrium towards the formation of FAEEs because the transesterification is reversible. As what it is shown in Fig. 3, the FAEEs yield increased with increasing of the molar ratio of ethanol to soybean oil over the range from 3:1 to 25:1. The highest yield (80.1%) was achieved at the molar ratio of 25:1 for 1 h. There was little increase of the yield from the molar ratio 12:1 to 25:1 in contrast to the increasing moles of ethanol. This phenomenon means excessive ethanol can not increase the yield of FAEE because of its dilution, which could reduce the opportunities and frequency of collision between DBU and oil. The transesterification retains approximate equilibrium from 12:1 to 25:1. Therefore, the optimal molar ratio of ethanol and oil was to be 12:1.

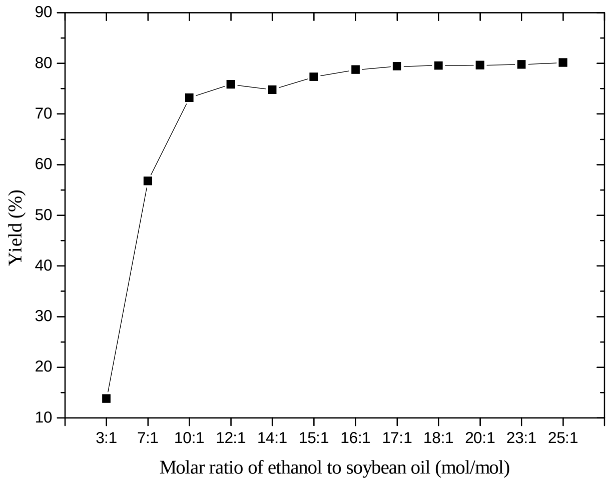

Fig. 3 Effect of ethanol/oil molar ratio on the yield of FAEEs. Reaction conditions: catalyst amount: 20% DBU (based on the oil weight); reaction time: 1 h

4.2 Effect of molar ratio of DBU to oil on the yield of FAEEs

The effect of the molar ratio of DBU to soybean oil on the FAEEs yield was investigated within the range of 0.3:1–5.0:1 and the results are shown in Fig. 4. It was found that the cut-off point of FAEEs yield is at the molar ratio of 2.0:1 for DBU to soybean oil. It is known that the catalytic activity was quite influenced by alkalinity and the amount of base. Distinctly, more DBU amount is conducive to FAEEs production. The yield of FAEEs increased rapidly with increasing of the molar ratio of DBU to oil from 0.3:1 to 2.0:1, which could be attributed to the effect of more basic amount. However, the FAEEs yield declined abruptly when the catalyst amount was above 2.0:1, indicating that too much catalyst played a negative role in the transesterification, because too much catalyst would reduce the relative content of reactants. Based on the effective collision theory, the dilution effect would offset the positive effect of more catalyst, resulting in decrease of conversion. In order to avoid this problem and reduce the costs, the optimum molar ratio of DBU to soybean oil was chosen to be 2.0:1.

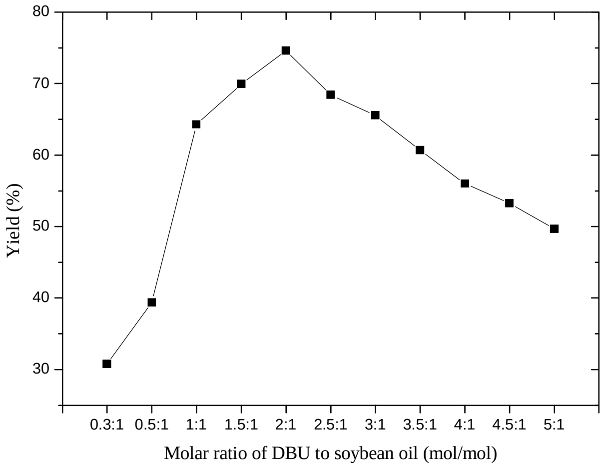

Fig. 4 Effect of the molar ratio of catalyst to soybean oil on the yield of FAEEs. Reaction conditions: molar ratio of ethanol and soybean oil: 9:1; reaction time: 1 h

4.3 Effect of reaction time on the yield of FAEEs

The effect of reaction time on the yield of FAEEs was studied under the catalysis of DBU. And as the results shown in Fig. 5, the reaction time increased in degrees within the range from 30 min to 210 min. It is observed that the FAEEs yield increased rapidly within the duration from 30 min to 150 min, and then remained relatively constant. The optimum reaction time was 120 min, at which the highest FAEEs yield reached 97.9%.

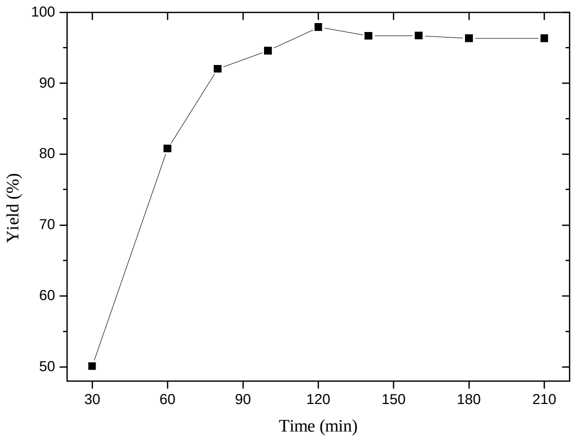

Fig. 5 Effect of reaction time on the yield of FAEEs. Reaction conditions: molar ratio of ethanol and soybean oil: 12:1; molar ratio of DBU and soybean oil: 2:1)

4.4 Determination of the kinetic parameters

The transesterification of soybean oil and ethanol was carried out at the temperature of 55, 60, 65, and 70 ℃, respectively, under the optimal conditions, i.e. ethanol/oil molar ratio of 12:1 and DBU/oil molar ratio of 2.0:1. As shown in Fig. 6, the maximum temperature studied was chosen to be 70 ℃, because the volatilization of ethanol over its boiling point of 78.4 ℃ may decrease the actual amount of ethanol involved in the transesterification. A typical time course of FAEEs profile is shown in Fig. 5, the formation of FAEEs was rather fast in the initial stage of the reaction, then increased and finally reached the equilibrium. On account of little fluctuations in the concentration of FAEEs during the equilibrium, we studied the reaction kinetics in the first stage from 0 min to the point with a zero slope. Nonlinear fitting was carried out by cubic polynomial equation through origin.

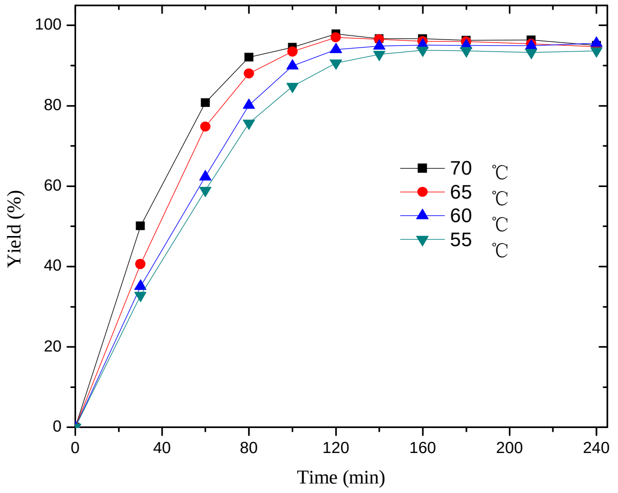

Fig. 6 Typical concentration–time profile for FAEEs at different temperatures. Reaction conditions: ethanol/oil molar ratio l: 12:1; DBU/oil molar ratio: 2.0:1

The apparent order of the reaction *α*, the rate constants k_1, and its corresponding correlation coefficient are listed in Table 1. The apparent activation energy for the transesterification reaction was calculated using the Arrhenius equation, when the reaction rate constants at four different temperatures were determined. As shown in Fig. 7, there exhibited good linearity between lnk_1 and 1/*T* over the temperature range of 55-70 ℃. The apparent activation energy (E_a) obtained was 16.76 kJ mo1^{-1} and the pre-exponential factor (*A*) was 561.31 mol$^{0.3}$ mL$^{-0.3}$ min^{-1}. Thus, the natural logarithm of Arrhenius equation about the reaction rate and the reaction temperature (55-70 ℃) could be written as:

$$\ln k_1 = 6.33 - 2016.16 / T \tag{9}$$

Therefore, because Arrhenius equation is

$$k_1 = A e^{-\frac{E_a}{RT}} \tag{10}$$

The kinetic equation of the overall transesterification was shown below:

$$\upsilon = 561.31 e^{-\frac{16.76}{RT}} c_{TG}^{0.7} \qquad (11)$$

According to Freedman's research, the energy activation of base catalyzed transesterification of oil was usually in the range of 33.6-84 kJ mol^{-1} [19]. It is obviously that the apparent activation energy of DBU-catalyzed transesterification in our study is fairly lower than Freedman's result, which infers the transesterification is more easily to carry out under the catalysis of DBU than regular base catalyst. Further research is needed to study the catalytic cycling performance of DBU in PSP system.

Table 1 Reaction rate constants for the transesterification of soybean oil and ethanol at different temperatures

T（K）	$1/T$（1/K）	k_1	$\ln k_1$	α	R^2
328.15	3.05×10^{-3}	1.17	0.15	0.74	0.999
333.15	3.00×10^{-3}	1.26	0.23	0.73	0.999
338.15	2.96×10^{-3}	1.43	0.36	0.69	0.999
343.15	2.91×10^{-3}	1.48	0.40	0.65	0.999

.

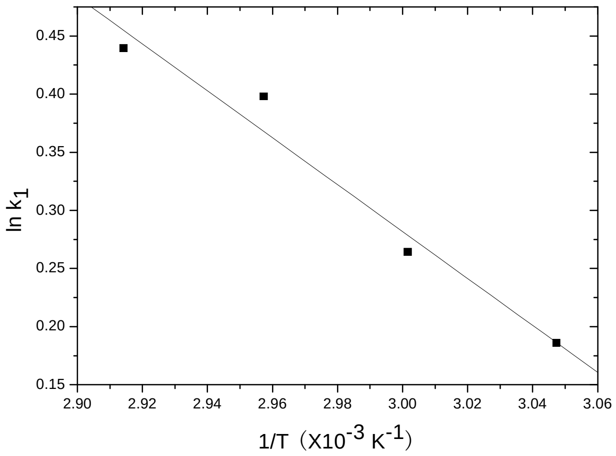

Fig. 7 Prediction of ln$k$ as a function of 1/T for the transesterification reaction of soybean oil with ethanol. Reaction conditions: molar ratio of ethanol and soybean oil: 12:1; molar ratio of DBU and soybean oil: 2:1

5. Conclusions

In this study, DBU was identified as an effective homogeneous catalyst for the transesterification of soybean oil and ethanol in SPS system composed of ethanol and DBU. The effects of reaction conditions (ethanol/oil molar ratio, catalyst amount and time) on FAEEs yield were studied and we optimized the reaction conditions for providing valuable experimental data for promising industrial application. Kinetics of this DBU-catalyzed transesterification reaction was investigated at four different temperatures. The kinetic equation of transesterification was presented. The apparent activation energy (E_a) and the pre-exponential factor (A) were reported for the first time.

References

1 A. Demirbas, Biofuels: Securing the plant's future energy needs, Springer: New York, 2009.

2 N. U. Soriano Jr., R. Venditti, D. and S. Argyropoulos, *Fuel*, 2009, 88, 560–565.

3 C. M. Garcia, S.Teixeira, L. L. Marciniuk and U. Schuchardt, *Bioresource Technology*, 2008, 99, 6608-6613.

4 A. A. Kiss, F. Omota, A. C. Dimian and G. Rothenber, Topics in Catalysis. 2006, 11, 141-150.

5 Y. M. Park, J. Y. Lee, S. H. Chung, I. S. Park, S. Y. Lee, D. K. Kim, J. S. Lee and K. Y. Lee, *Bioresource Technology*, 2010, 101, S59-S61.

6 H. F. Guo,P. Yan, X. Y. Hao and Z. Z. Wang, *Materials Chemistry and Physics*, 2008, 112, 1065-1068.

7 H. Noureddini and D. Zhu, *JAOCS.*, 1997, 11, 1457-1463

8 M. L. Granados, M. D. Z. Poves, D. M. Alonso, R. Mariscal, F. C. Galisteo, R. M, J. Santamaria and J. L. G. Fierro, *Applied Catalysis B: Environmental*, 2007, 73, 317-326.

9 M. L. Granados, D. M. Alonso, A. C. Alba-Rubio, R. Mariscal, M. Ojeda and P. Brettes, *Energy & Fuels*, 2009, 23, 2259-2263.

10 S. F. A. Halim and A. H. Kamaruddin, *Process Biochemistry*, 2008, 43, 1436-1439.

11 M. Kalantari, M. Kazemeini and A. Arpanaei, Biochemical *Engineering Journal*, 2013, 79, 267-273.

12 C. H. Liu, C. C. Huang, Y. W. Wang, D. J. Lee and J. S. Chang, *Applied Energy*, 2012, 100, 41-46.

13 L.Phan, H. Brown, J. White, A. Hodgson and P. G. Jessop, *Green Chem.*, 2009, 11: 53-59.

14 P. G. Jessop, D. J. Heldebrant, X. W. Li, C. A. Eckert and C. L. Liotta, *Nature*, 2005,8, 1102.

15 U. Schuchardt, R. Sercheli and R. M. Vargas, *Journal of Brazilian Chemical Society*, 1998, 9, 1199-1210.

16 D. Fabbri, V. Bevoni, M. Notari and F. Rivetti, *Fuel*, 2007, 86, 690-697.

17 R. Sercheli, R. M. Vargas and U. Schuchardt, *JAOCS.*, 1999, 10, 1207-1210.

18 P. T. Nguyen, B. Nohair, N. Mighri and S. Kaliaguine, *Microporous and Mesoporous Materials*, 2013, 180, 293–300.

19 B. Freedman, R. O. Butterfield and E. H. Pryde, *JAOCS.*, 1986, 10, 1375-1380

Kinetics of DBU-catalyzed transesterification for biodiesel in DBU/ethanol switchable-polarity solvent

Abstract：

The production of biodiesel from soybean oil and ethanol was investigated in switchable-polarity solvent (SPS) media of DBU and ethanol. The highest biodiesel yield catalyzed by DBU could reach 97.9% at optimized conditions, i.e. ethanol/oil molar ratio: 12:1, DBU/oil molar ratio: 2:1, reaction temperature: 70 ℃, reaction time: 2 h. According to the kinetic analysis, the reaction order of oil was estimated to be 0.7, the apparent activation energy was 16.763 kJ mo1^{-1},， the pre-exponential factor was 561.31 mol$^{0.3}$ mL$^{-0.3}$ min^{-1}) and the Arrhenius equation for the first time, which explain the high efficiency of DBU catalyst. The DBU-catalyzed transesterification in DBU/ethanol switchable-polarity solvent supplied an interesting alternative, which would be used to simplify the transesterification and separation into only one step.