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Reactive distillation for biodiesel production from soybean oil

Lida Simasatitkul, Pimpatthar Siricharnsakunchai, Yaneeporn Patcharavorachot, Suttichai Assabumrungrat, and Amornchai Arpornwichanop†

Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand
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Abstract−Biodiesel, which is regarded as a promising alternative to a conventional petroleum-based diesel fuel, can be produced from transesterification of vegetable oils and alcohol in conventional batch and continuous reactors. Since the transesterification is an equilibrium-limited reaction, a large excess of reactants is usually used to increase the production of biodiesel, thereby requiring more expensive separation of unreacted raw materials. This study proposed the use of a reactive distillation for transesterification of soybean oil and methanol catalyzed by sodium hydroxide to produce biodiesel. The simulation results showed that a suitable configuration of the reactive distillation column consists of three reactive stages. The optimal conditions for the reactive distillation operation are at the molar feed ratio of methanol and oil at 4.5 : 1, reflux ratio of 3, and reboiler duty of 1.6×10^7 kJ h^{-1}. Methanol and soybean oil should be fed into the column at the first stage. The effect of important operating and design parameters on the performance of reactive distillation was also presented.

Key words: Reactive Distillation, Biodiesel Production, Soybean Oil, Transesterification, Simulation

INTRODUCTION

Biodiesel as an alternative fuel has been presently receiving much attention due to the limited availability of conventional petroleum diesel and environmental concerns. It can be directly used to replace petroleum diesel without modifying diesel engines since their properties, e.g., specific gravity, cetane number, viscosity, cloud point, and flash point, are similar [1]. In general, biodiesel is derived from a transesterification reaction of triglycerides in vegetable oils or animal fats with alcohol (i.e., methanol and ethanol) under the presence of catalysts [2-4].

Various types of catalyst, which includes alkali and acid-based catalysts in both heterogeneous and homogeneous forms, and numerous feedstock based on available local vegetable oils can be employed for biodiesel production. As a result, there are a number of researches concerning the production of biodiesel from different vegetable oils and alcohols. An analysis of the effect of important operating conditions such as temperature, feed molar ratio, and type of catalyst, on the efficiency of a biodiesel production system is also the main topic of interest. For example, Narvaez et al. [5] investigated the kinetics of the transesterification of palm oil with methanol catalyzed by sodium hydroxide in a batch stirred reactor. Sharma et al. [6] studied the effect of key reaction parameters on the synthesis of biodiesel from various crude vegetable oils and determined optimal conditions for maximizing the biodiesel yield.

It has been known that the transesterification of vegetable oils to fatty acid ester as a biodiesel is an equilibrium-limited reaction. A large excess of alcohol over a stoichiometric ratio is usually employed in conventional reactors to achieve a high degree of the conversion of vegetable oils, thereby requiring the expensive separation of unreacted reactants from the biodiesel product [7]. As a consequence, potentially alternative processes to overcome such a difficulty should be explored. When considering the characteristics of the transesterification reaction, the use of reactive distillation, a multifunctional reactor combining chemical reaction and distillation in a single column, is a promising way. The simultaneous separation and reaction inside the column allow the equilibrium-limited reaction to take place more completely and reduce the separation cost of unreacted reactants [8-10]. Although a number of investigations have been reported on the implementation of a reactive distillation to biodiesel production, most of them focus on the utilization of free fatty acid extracted from vegetable oils as a reactant for an esterification process [11,12]. Matallana et al. [13] studied the production of biodiesel from lauric acid and 2-ethyl hexanol by using the reactive distillation. Kumar and Mahajani [12] applied the reactive distillation for the esterification of lactic acid with n-butanol catalyzed by Amberlyst-15. To date, few studies on reactive distillations have been performed for the transesterification of vegetable oils [7]. Recently, Silva et al. [14] preliminarily studied the synthesis of biodiesel from transesterification of soybean oil with ethanol by using reactive distillation. The effect of operating conditions such as catalyst concentration and ratio of ethanol and oil on the performance of biodiesel production was only studied without considering the impact of design parameters.

The aim of this work is concentrated on the analysis of a reactive distillation for biodiesel production from the transesterification of soybean oil with methanol. Pure soybean oil is considered to be a suitable feedstock due to its low content of free fatty acid (less than 0.3%), and thus a pretreatment of feedstock by removal of free fatty acid is unnecessary. A residue curve map is used as a tool to analyze a reactive distillation operation. Furthermore, the effect of various operating and design parameters on the performance of the reactive distillation for biodiesel production is investigated.

†To whom correspondence should be addressed.
E-mail: Amornchai.A@chula.ac.th

SIMULATION OF REACTIVE DISTILLATION FOR BIODIESEL PRODUCTION

Biodiesel is normally produced by a transesterification process of vegetable oils with methanol. The transesterification reaction consists of three-step reactions in series as shown below:

$$\begin{aligned} TG + CH_3OH &\underset{k_2}{\overset{k_1}{\longrightarrow}} DG + RCOOCH_3 \\ DG + CH_3OH &\underset{k_4}{\overset{k_3}{\longrightarrow}} MG + RCOOCH_3 \\ MG + CH_3OH &\underset{k_6}{\overset{k_5}{\longrightarrow}} GL + RCOOCH_3 \end{aligned} \quad (1)$$

From the above reaction scheme, triglyceride (TG), a major component in vegetable oils, reacts with methanol in the presence of catalyst to produce methyl esters ($RCOOCH_3$) as a biodiesel product and diglyceride (DG), monoglyceride (MG), and finally glycerol (GL) as a by-product. All the reactions are reversible and can be catalyzed by either alkali or acid catalysts; however, the alkali catalyst is preferable due to a higher reaction rate.

1. Kinetic Model of Soybean Oil

As mentioned earlier, the transesterification of triglyceride in vegetable oils and alcohol involves three reversible reactions (Eq. (1)). Kinetic expressions and rate constants for each reaction are necessary information for process simulations. This work was focused on the production of biodiesel from the transesterification of soybean oil and methanol with sodium hydroxide catalyst. Trilinolein, a major component in soybean oil, was represented as the triglyceride whereas dilinolein and monolinolein were referred to as the intermediate reactants. Methyl linoleate (methyl ester) was considered to be a major biodiesel product. The kinetic studies by Noureddini and Zhu [15] showed that the transesterification is a homogeneous liquid-phase and equilibrium-limited reaction and the kinetic parameters can be explained by the Arrhenius law. The rate expressions of each reaction are shown as follows:

$$\begin{aligned} r_{TG} &= -k_1[TG][A] + k_2[DG][A] \\ r_{DG} &= k_1[TG][A] - k_2[DG][E] - k_3[DG][A] + k_4[MG][E] \\ r_{MG} &= k_3[DG][A] - k4[MG][A] - k_5[MG][A] + k_6[GL][E] \\ r_E &= k_1[TG][A] - k_2[DG][E] + k_3[DG][A] \\ &\quad - k_4[MG][E] + k_5[MG][A] - k_6[GL][E] \\ r_{GL} &= k_5[MG][A] - k_6[GL][E] \end{aligned} \quad (2)$$

where TG, DG, MG, GL, A, and E denote the triglyceride, diglyceride, monoglyceride, glycerol, methanol, and methyl ester (biodiesel), respectively, and k_i is the rate constant of reaction i.

Table 1 shows the reaction constants of the transesterification reaction of soybean oil and methanol [15].

Table 1. Values of kinetic constant for transesterification of soybean oil and methanol

Rate constant	k_0 (L mol^{-1} s^{-1})	E_a (cal mol^{-1})
k_1	3.9×10^{7}	13,145
k_2	5.78×10^{5}	9,932
k_3	5.906×10^{12}	19,860
k_4	9.888×10^{9}	14,639
k_5	5.335×10^{3}	6,421
k_6	2.1×10^{4}	9,588

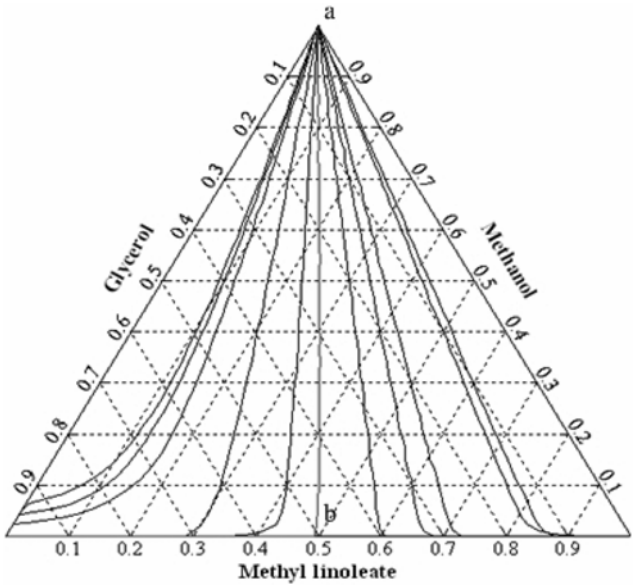

Fig. 1. Residue curve map for a ternary system in biodiesel production.

2. Phase Equilibrium

Fig. 1 shows the residue curve map of the tertiary system consisting of methanol, glycerol, methyl linoleate, in biodiesel production. There is a binary azeotrope (methyl linoleate and glycerol) at 229 °C. As glycerol and biodiesel can be decomposed at 150 °C and 250 °C, respectively, the reactive distillation should not be operated at higher reboiler temperatures. In addition, the composition of the products obtained from the transesterification reaction trends to be in the right-hand side of the distillation region (line ab in Fig. 1). Since the reactive distillation column cannot be operated across a distillation boundary, pure glycerol cannot be obtained. From Fig. 1, the binary azeotrope does not affect the separation because it is saddle node, and thus the distillate product stream of a reactive distillation is pure methanol while the bottom stream comprises methyl linoleate and glycerol.

3. Reactive Distillation for Biodiesel Production

The production of biodiesel from the transesterification of soybean oil with methanol in a reactive distillation was investigated in this study. Due to its low content of free fatty acid (less than 0.3 wt%), soybean oil can be directly used as the feedstock for biodiesel production without requiring a pretreatment unit. Simulations of the reactive distillation were performed by using HYSYS commercial software to analyze the effect of key operating and design parameters on its performance for biodiesel production. A rigorous equilibrium stage model and UNIQUAC model for describing thermodynamic properties and phase equilibriums were used. Methyl linoleate (biodiesel) was taken as the product of the transesterification reaction, whereas glycerol was considered to be the by-product. The following conditions were determined as the standard case study: the column was operated at atmospheric pressure and the pressure drop was negligible, soybean oil (trilinolein) and methanol were fed at the first stage of a reactive section, and total condenser and a stage efficiency of 100% were assumed.

Fig. 2 shows the configuration of the reactive distillation column used in this study. The column contains a total of 22 stages (includ-

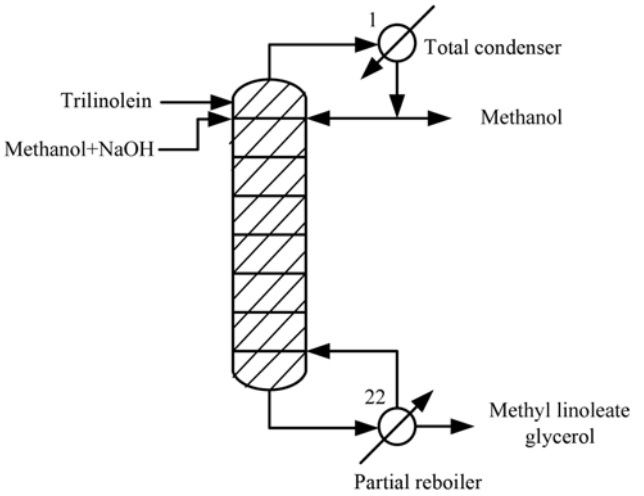

Fig. 2. Schematic diagram of reactive distillation for biodiesel production.

ing a condenser and a reboiler). Methyl linoleate and glycerol are produced in a reactive zone where the transesterification of trilinolein and methanol occurs. Since sodium hydroxide was used as a homogeneous catalyst, the reaction was assumed to occur over all the stages of the reactive distillation column.

To determine the performance of reactive distillation, the conversion of trilinolein in soybean oil and the yield of methyl linoleate as defined by Eqs. (3)-(4) was considered.

$$\text{Conversion} = \frac{F_{trilinolein,0} - F_{trilinoleion}}{F_{trilinolein,0}} \times 100\% \quad (3)$$

$$\text{Yield} = \frac{F_{methyl\ linoleate}}{3 \times F_{trilinolein,0}} \times 100\% \quad (4)$$

where $F_{trilinolein,0}$, $F_{trilinolein}$, and $F_{methyl\ linoleate}$ are the molar flow rates of trilinolein in feed and outlet streams, and methyl linoleate, respectively.

SIMULATION RESULTS

1. Standard Condition

At the standard condition, the feed streams consisting of trilinolein and methanol at the flow rates of 50 and 300 kmol/h, respectively, are separately fed to a reactive distillation column at the first stage. The column is operated at pressure of 1 atm with the reflux ratio of 3, feed temperature of 50 °C, and the reboiler duty of 1.2×10^7 kJ/h. Figs. 3(a) and 3(b) show, respectively, the composition and temperature profiles within the column under the standard condition. There is a large amount of methanol at the top of the column, whereas less trilinolein, dilinolein and monolinolein are observed. The bottom products consist of mostly methyl linoleate (biodiesel product) and slightly glycerol as a by-product. Under the standard condition, the conversion of trilinolein is 99% and the purity of methyl linoleate is 81%. The unreacted methanol, the lowest-boiling point substance, is withdrawn from the reactive distillation column as a distillate stream, whereas a mixture of methyl linoleate and glycerol is removed as a bottom stream as earlier stated in Section 2.2. The phase separation of methyl linoleate and glycerol in the product stream was not observed. It is noted that under low operating temperatures, glycerol cannot be separated from biodiesel product. To separate glycerol from biodiesel in the reactive distillation column, a higher temperature operation is required; however, this can result in a decreased amount of methanol in the reaction section, thus decreasing the conversion of trilinolein. In addition, this would make glycerol decompose.

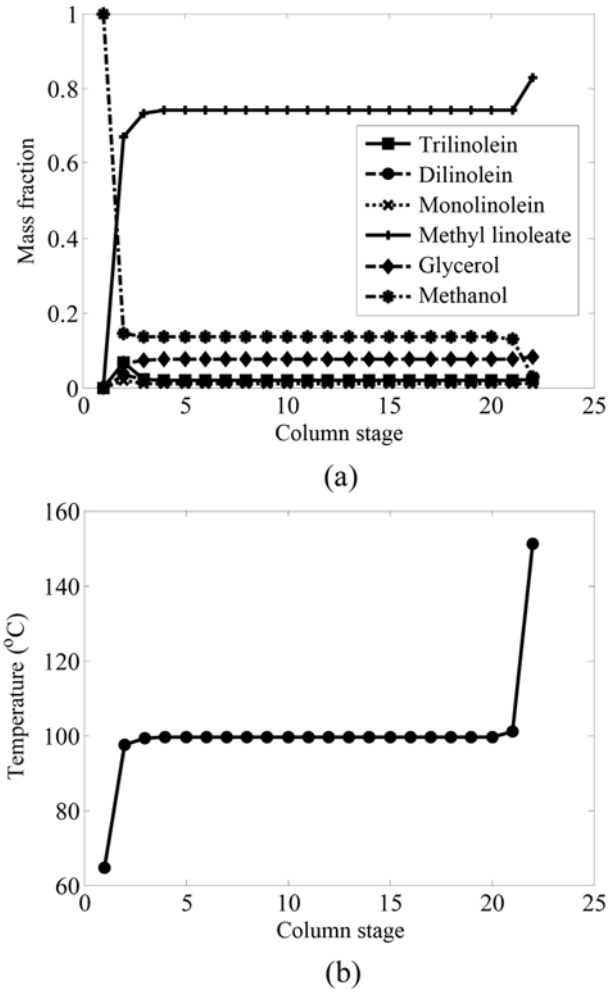

Fig. 3. (a) Composition and (b) temperature profiles in reactive distillation for biodiesel production at standard condition.

2. Effect of Feed Ratio of Methanol and Oil

The molar feed ratio of methanol and oil (trilinolein) is one of the key parameters on the performance of the reactive distillation. Fig. 4 shows the effect of molar feed ratio of methanol to oil on the conversion of trilinolein and the yield and purity of methyl linoleate. The simulation results demonstrate that the conversion of trilinolein and the yield of methyl linoleate increase with increasing feed molar ratio. The purity of methyl linoleate shows a decreasing trend at a higher ratio of methanol and oil due to the dilution effect of unreacted methanol. It is found that the feed streams of methanol and oil at the ratio of 4.5 is an optimal condition in terms of the product yield and purity. Fig. 4 also compares the performance of the reactive distillation with that of a conventional continuous reactor operated at 100 °C. It is clearly indicated that at the same feed ratio, the implementation of the reactive distillation to produce biodiesel gives

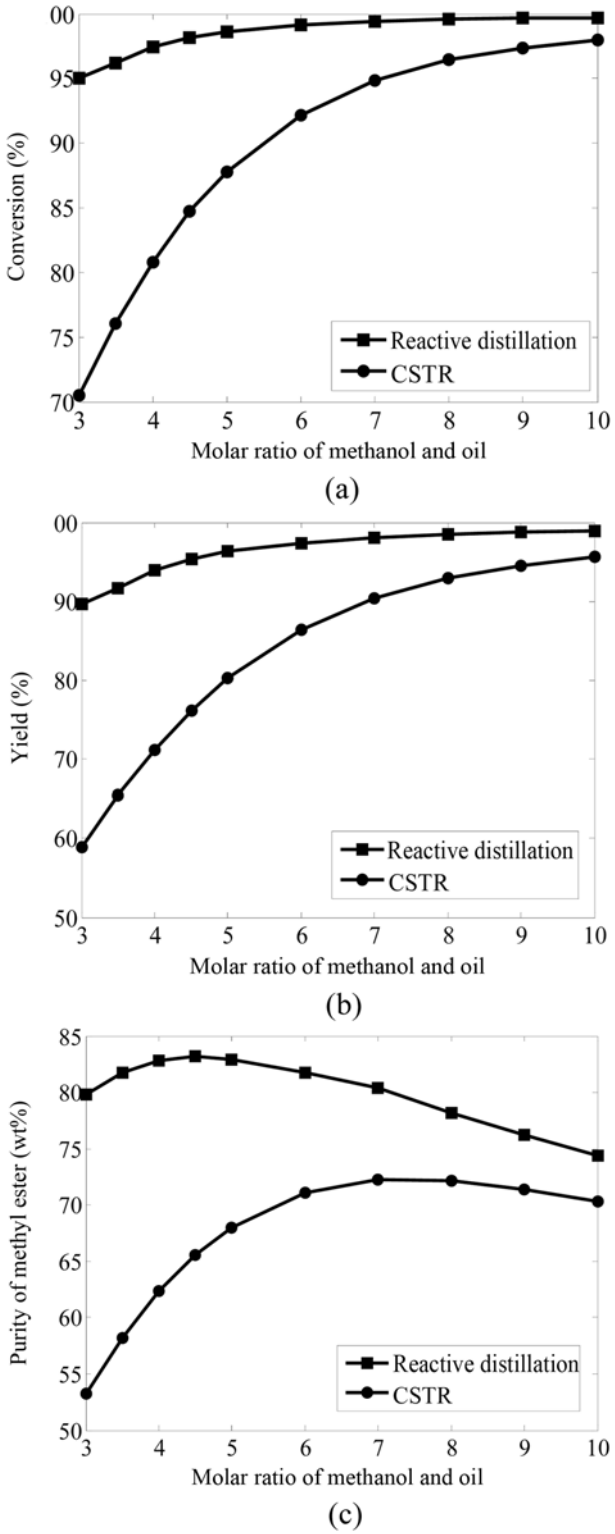

Fig. 4. Effect of molar feed ratio of methanol and oil on (a) conversion of trilinolein, (b) yield of methyl ester, and (c) purity of methyl ester.

a better performance because the removal of methyl linoleate and glycerol promotes the transesterification reaction.

3. Effect of Feed Temperature

The effect of feed temperatures on the performance of the reactive distillation in terms of the conversion of trilinolein and yield of methyl linoleate is studied. Fig. 5 indicates that when the feed temperature is increased from 25 ºC to 90 ºC, the conversion of trilinolein and the yield of methyl linoleate are slightly decreased. An increase in feed temperatures decreases the amount of methanol in the reaction section of the column. This causes the reductions of trilinolein conversion and methyl linoleate yield in the reactive distillation. Since the feed temperature slightly affects the reactive distillation performance, the subsequent studies will be performed using the feed temperature of 25 ºC.

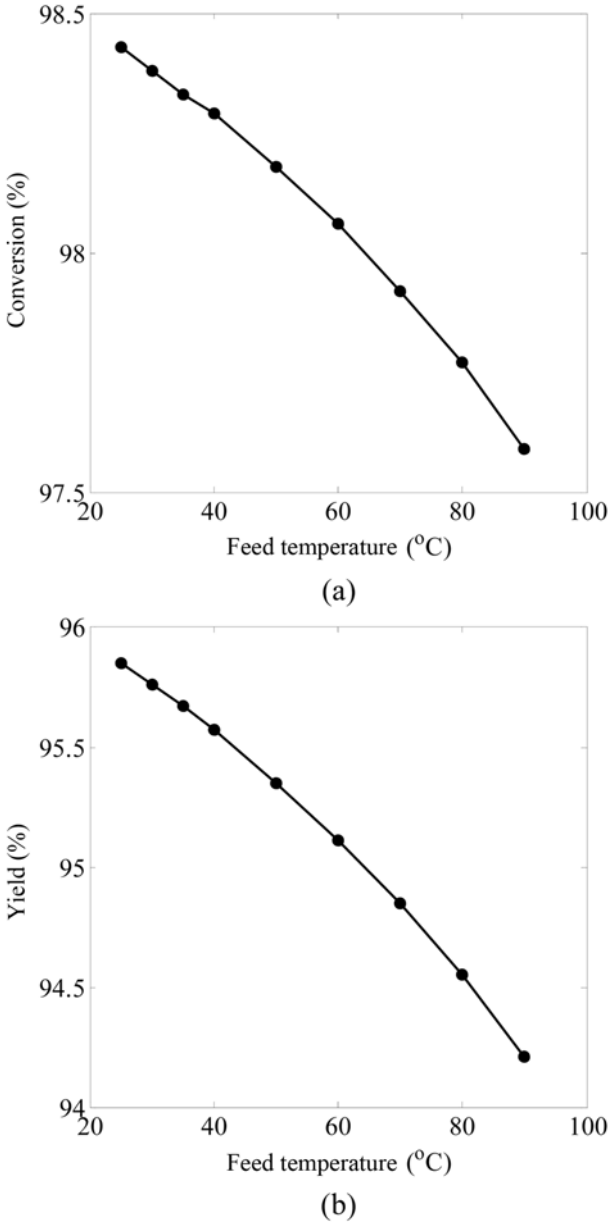

Fig. 5. Effect of feed temperature on (a) conversion of trilinolein and (b) yield of methyl ester.

4. Effect of Reboiler Heat Duty

The effect of reboiler heat duty on the performance of reactive distillation is shown in Fig. 6. Increased reboiler duty improves the conversion of trilinolein and the yield of methyl linoleate as the temperature in the reaction section increases. However, the performance

of reactive distillation for biodiesel production is degraded at high reboiler duty (>2×10^7 kJ/h). This is due to the large amount of methanol in the distillate stream being removed from the column. The result also shows that the reboiler duty increases the reboiler temperature (Fig. 6(a)). Fig. 6(c) shows an increase in the purity of biodiesel product with the increased reboiler duty since trilinolein highly reacts with methanol to produce methyl linoleate. Although the operation of reactive distillation at the reboiler duty of 2×10^7 kJ/h gives the highest trilinolein conversion, a high reboiler temperature may cause the decomposition of glycerol and biodiesel products. As a result, a suitable reboiler duty of the reactive distillation is 1.6×10^7 kJ/h.

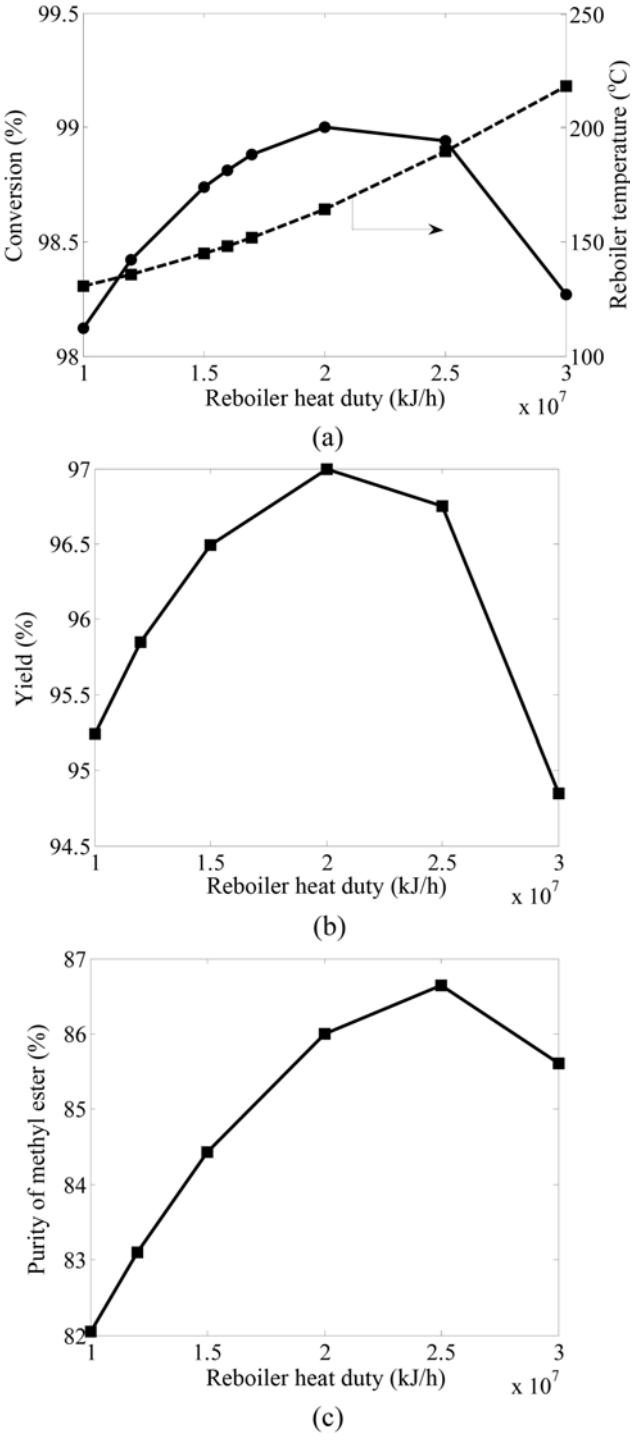

Fig. 6. Effect of reboiler duty on (a) conversion of trilinolein, (b) yield of methyl ester, and (c) purity of methyl ester at different reflux ratios (methanol to trilinolein molar ratio of 4.5 : 1, 20 reactive stages, feed location at the first stage of the column).

5. Effect of a Number of Reactive Stages

In this study, sodium hydroxide is considered as a homogeneous catalyst for the production of biodiesel from soybean oil. It is mixed with methanol before being fed into the reactive distillation column to react with trilinolein. As a result, the amount of catalyst is independent of a number of reactive stages in the column. Fig. 7 demonstrates the effect of changing the number of reactive stages on the reactive distillation performance when the feed ratio of methanol and trilinolein is 4.5 : 1. It is noted that the transesterification reaction is carried out at all the stages of the column. The results indicate that adding more reactive trays improves the system performance. Increasing the reactive stages causes trilinolein and metha-

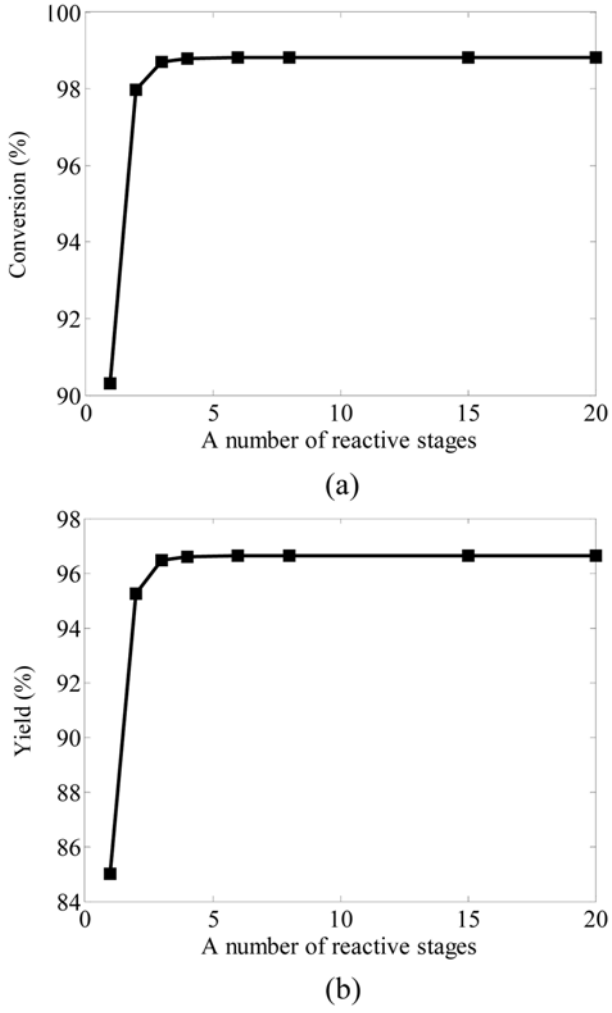

Fig. 7. Effect of a number of reactive stages on (a) conversion of trilinolein and (b) yield of methyl ester (methanol to trilinolein molar ratio of 4.5 : 1, reflux ratio of 3, reboiler duty of 1.6×10^7 kJ h^{-1}).

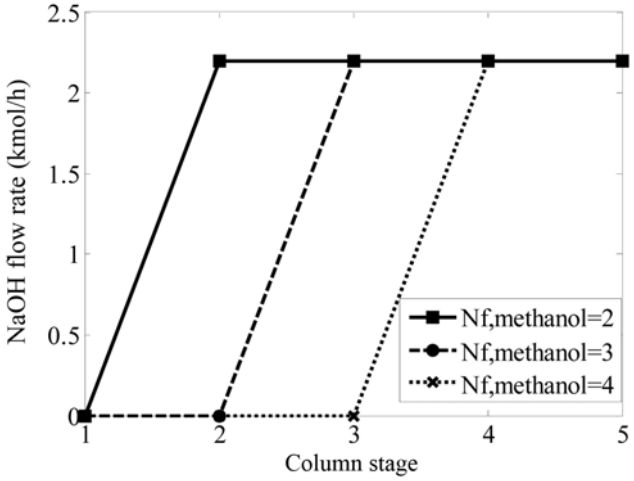

Fig. 8. Profile of NaOH at different feed locations of methanol when a number of the reactive stages are 3.

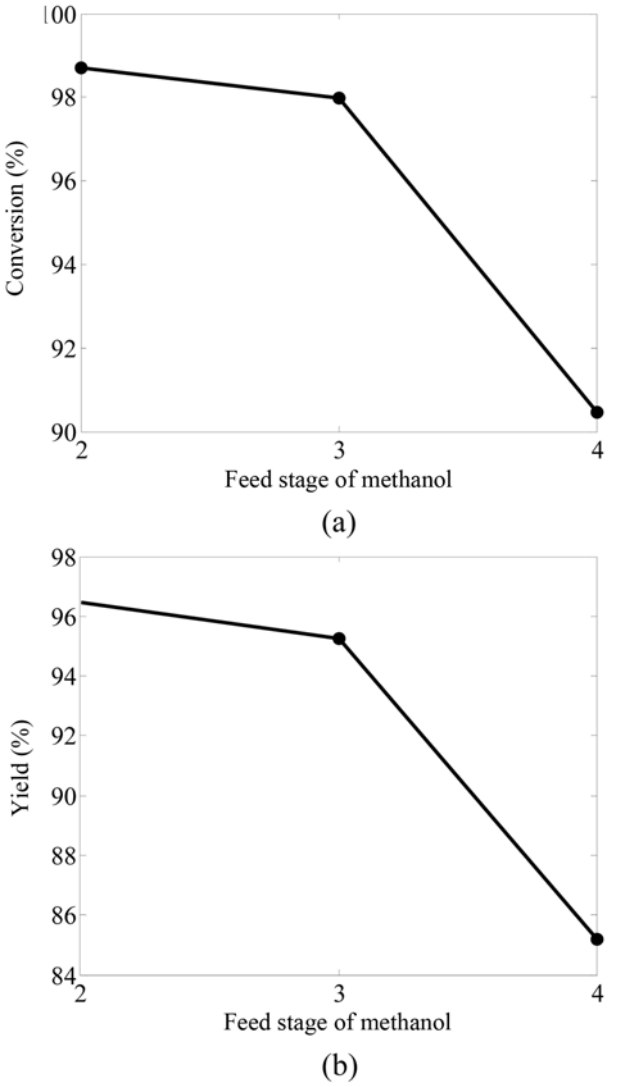

Fig. 9. Effect of feed location of methanol on (a) conversion of trilinolein and (b) yield of methyl ester (molar ratio of 4.5 : 1, reflux ratio of 3, reboiler duty of 1.6×10^7 kJ/h).

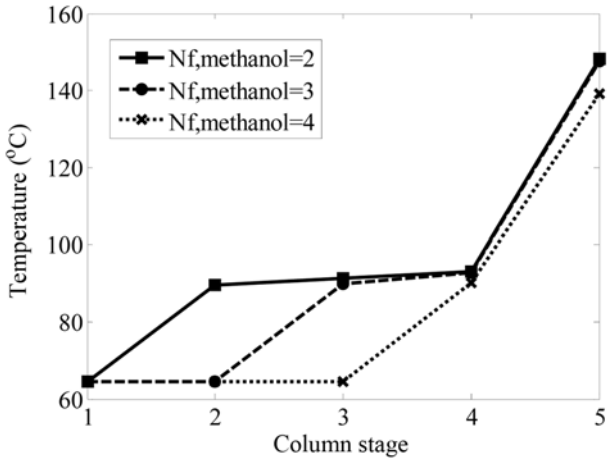

Fig. 10. Temperature profiles at different feed locations of methanol.

nol to have more contacting area, thereby enhancing the conversion of trilinolein. It is noticed that the performance of the reactive distillation is slightly improved when a number of the reactive stages are higher than 3.

6. Effect of Feed Location of Methanol

The location of a feed stream is an important design parameter having an effect on a reactive distillation performance. In general, a lighter reactant should be fed on the bottom stage of the reactive zone, whereas a heavier reactant is fed on the top stage of the reactive zone. However, for transesterification reaction of soybean oil and methanol, both the reactants are introduced to the column at the first reactive stage. Fig. 8 shows the distribution of sodium hydroxide within the column at different feed locations of methanol when the total number of reactive stages is 3. It is found that no catalyst exists above the feed stage of methanol. Therefore, moving the feed stage of methanol down to the bottom of the reactive distillation column decreases the conversion of trilinolein and the yield of methyl linoleate as shown in Fig. 9. Although a higher amount of methanol is observed at the upper stage of methanol feed location, the transesterification is less pronounced due to the absence of catalyst. Fig. 10 shows the profiles of the column temperature when methanol is fed to the column at different stages. The results show that introducing methanol at the top of the reactive distillation column can increase column temperatures, thus increasing the transesterification reaction.

From simulation studies, it is found that for biodiesel production from soybean oil, a suitable configuration of the reactive distillation column consists of only three reactive stages. The optimal conditions for the operation of the reactive distillation are at the molar feed ratio of methanol and oil at 4.5 : 1, reflux ratio of 3, and reboiler duty of 1.6×10^7 kJ h^{-1}. Methanol and soybean oil should be fed into the column at the first stage of the reactive distillation column. Fig. 11 shows the typical composition and temperature profiles of the reactive distillation at the optimal designed conditions. It can be seen that the compositions of the distillate product consist of only methanol, while the bottom product consists of mainly methyl linoleate.

CONCLUSIONS

We investigated the use of a reactive distillation for biodiesel pro-

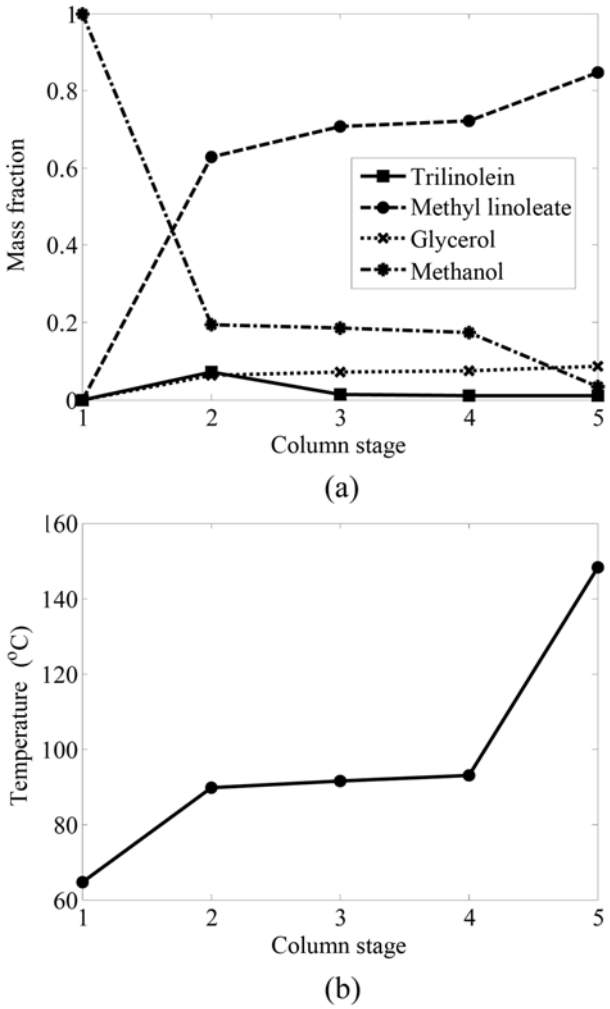

Fig. 11. (a) Composition and (b) temperature profiles in reactive distillation column (feed temperature of 25 °C, molar ratio of 4.5 : 1, reflux ratio of 3, reboiler duty of 1.6×10^7 kJ/h, reactive stage=3 and feed location of soybean oil and methanol at the first stage).

duction from transesterification of soybean oil (represented by trilinolein) and methanol catalyzed by sodium hydroxide. Effects of operating and design parameters of the reactive distillation, i.e., feed molar ratio, feed location, a number of reactive stages, on biodiesel production were analyzed to determine a suitable reactive distillation configuration. The results showed that increases in the molar feed ratio of methanol and oil and the reboiler duty enhance the performance of the reactive distillation in terms of the conversion of trilinolein, whereas the effect of feed temperature shows an opposite trend. The increased reactive stage also improves the performance of reactive distillation. To achieve a high conversion of trilinolein, soybean oil and methanol should be introduced at the first stage of column.

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