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Design of biodiesel production processes by base-catalyzed transesterification

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Abstract. A lot of efforts have been carried out to develop an alternative fuel for the current energy and environment questions. Biodiesel which is synthesized by transesterification of plant oils and animal fat is a real alternative fuel for its renewable and lower emissions. Currently, biodiesel production by the base-catalyzed transesterification of the vegetable oil and methanol is widely utilized in the world. This paper studies the design of biodiesel production with the glycerol phase separation processes, through installing a decanter between reactors and adding methanol and NaOH batch optimization operation to improve the biodiesel yield and the conversion rate of reactants. Simulation results show that biodiesel yield increased by 9.79% and triglyceride conversion rate increased by 6.99%.

Introduction

With the depletion of fossil fuels and global environmental degradation, the development of alternative fuels from renewable resources has received considerable attention. Biodiesel has become the foremost alternative fuel to those refined from petroleum products.

The most common way to produce biodiesel is by transesterification, which refers to a catalyzed chemical reaction involving vegetable oil and methanol to biodiesel and glycerol. The transesterification can be catalyzed through different methods: homogeneous alkali, homogeneous acid, supercritical alcohol with no catalyst and via heterogeneous catalysts[1].Currently, biodiesel production by the homogeneous base-catalyzed transesterification of the vegetable oil is widely utilized in the world. Transesterification is affected by four main factors: the molar ratio of methanol to oil, reaction temperature, reaction time and catalyst. Therefore, the design of the reactor system for the transesterification is very important. A low efficiency reactor system requires a higher feed ratio and separation cost [2]. Under the constraint of the reaction equilibrium, the reversible transesterification takes place only once called one-step reaction process. Correspondingly, the byproduct glycerol of the first reactor is removed from the product with help of the immiscible liquid–liquid separation and residues go on the second transesterifi-cation called two-step reaction process, which can be further conversion of raw materials.

The purpose of this work is to research the design of a biodiesel production process with phase separation in the reactor system. Based on the kinetic model of the homogeneous base-catalyzed transesterification of the refined vegetable oil and the liquid–liquid phase equilibrium of the product, the two-step reaction processes are designed. Finally, simulation analyzed the yield of biodiesel and conversion rate of triglyceride.

Biodiesel Reaction Kinetics Model

Biodiesel transesterification involved complex reaction kinetic mechanism .One molecule of triglycerides reacts with three molecules of methanol can result in the maximum production of three molecules methyl ester and one molecule glycerol. The reaction occurs as a sequence of three step

reversible reactions where triglycerides are converted to diglycerides, diglycerides to monoglycerides, and monogly-cerides to glycerol. The reaction steps are given by Eq. (1) .All reactions are carried out at atmospheric pressure.

$$
\begin{aligned}
&TG + 3CH_3OH \Leftrightarrow GL + 3RCOOCH_3 \\
&TG + CH_3OH \overset{k1,k2}{\Leftrightarrow} DG + R_1COOCH_3 \\
&DG + CH_3OH \overset{k3,k4}{\Leftrightarrow} MG + R_2COOCH_3 \\
&MG + CH_3OH \overset{k5,k6}{\Leftrightarrow} GL + R_3COOCH_3
\end{aligned}
\tag{1}
$$

The mathematical model for the production of biodiesel by one-step reactor is governed by the following Ordinary Differential Equations [3],

$$
\begin{aligned}
&\frac{dC_{TG}}{dt} = -k_1C_{TG}C_M + k_2C_{DG}C_{ME} \\
&\frac{dC_{DG}}{dt} = k_1C_{TG}C_M - k_2C_{DG}C_{ME} - k_3C_{DG}C_M + k_4C_{MG}C_{ME} \\
&\frac{dC_{MG}}{dt} = k_3C_{DG}C_M - k_4C_{MG}C_{ME} - k_5C_{MG}C_M + k_6C_{GL}C_{ME} \\
&\frac{dC_{ME}}{dt} = k_1C_{TG}C_M - k_2C_{DG}C_{ME} + k_3C_{DG}C_M - k_4C_{MG}C_{ME} + k_5C_{MG}C_M - k_6C_{GL}C_{ME} \\
&\frac{dC_M}{dt} = -\frac{dC_{ME}}{dt} \\
&\frac{dC_{GL}}{dt} = k_5C_{MG}C_M - k_6C_{GL}C_{ME}
\end{aligned}
\tag{2}
$$

Where $TG, DG, MG, RCOOCH_3, CH_3OH, GL$ are abbreviations of triglyceride, diglyceride, monoglyceride, methyl ester, methanol and glycerol respectively, and $C_{TG}, C_{DG}, C_{MG}, C_{ME}, C_M, C_{GL}$ are six components concentrations. The reaction rate constants k_i are expressed by $k_i = A_iTe^{-E_i/RT}$, which are reported in [4] at constant temperature 323K.The parameters are listed in Table 1.

Table 1 VALUES OF RATE CONSTANT (L/MOL MIN)

Rate constant	k_1	k_2	k_3	k_4	k_5	k_6
values	0.050	0.110	0.215	1.228	0.242	0.007

Affection Factors of Transesterification Reaction

The transesterification is a relatively complex process, Many researchers recognized that one of the main factors affecting the yield of biodiesel is the molar ratio of methanol to triglyceride. Theoretically, an excess of methanol used in biodiesel production benefits transesterification chemical equilibrium to the positive direction move and a higher methanol triglyceride ratio can result in a greater ester conversion in a shorter time. In addition, the molar ratio is associated with the type of catalyst used and the molar ratio of methanol to triglycerides in most researches is 6:1, with the use of an alkali catalyst.

Temperature influences the reaction and yield of the biodiesel product clearly. A higher reaction temperature can decrease the viscosities of oils and result in an increased reaction rate, and a shortened reaction time. But when the reaction temperature increases beyond the optimal level, the yield of the biodiesel product decreases because a higher reaction temperature accelerates the saponification reaction of triglycerides [5]. The reaction temperature must be less than the boiling point of methanol in order to ensure that the methanol will not leak out through vaporization. Depending on the oil used, the optimal temperature ranges between 323K and 333K.

Reaction time is one of the factors affecting the yield of biodiesel. At the beginning, the reaction is slow due to the mixing and dispersion of methanol into the oil. After a while, the reaction proceeds very fast. Excess reaction time will lead to a reduction in the product yield due to the backward reaction of transesterification, resulting in a loss of esters as well as causing more fatty acids to form soaps [6]. Normally, the yield reaches a maximum within 90 min and then remains relatively constant with a further increase in the reaction time.

The catalyst also plays an important role since its concentration can affect the yield of the biodiesel product.As the catalyst concentration increases the conversion of triglyceride and the yield of biodiesel increase. Eevera et al. [7] found that the yield reaches an optimal value when the catalyst concentration reaches 1.5 wt% and then decreases a little with a further increase in catalyst concentration.

Design of Two-Step Transesterification Reaction

One-step reaction is difficult to achieve a high conversion rate [8]. Base on the analysis of previous factors affecting the yield of biodiesel of one-step reactor, two series of isothermal continuous stirred tank reactors system are established. Including two CSTR and a decanter mainly, Glycerol phase in the first transesterification reactor is separated from biodiesel in the decanter1 due to immiscibility between methyl ester and glycerol. The biodiesel phase, containing biodiesel, unreacted methanol and raw material oil, enters the second reactor to react with additional catalyst NaOH. The glycerol phase and the second transesterification product are fed into the subsequent separation process for further separation. The two-step transesterification reaction system is shown in Fig.1.

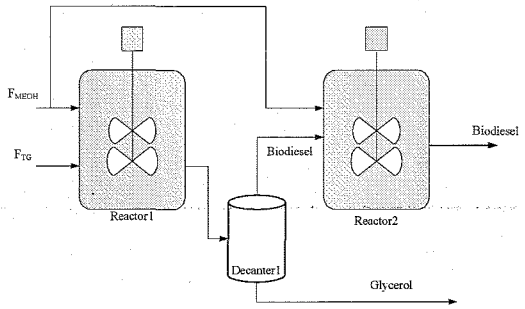

Figure 1. Two-step transesterification reaction system

As Stiefel and Dassori[9] mentioned, the feed ratio can be reduced if the process is designed with multiple reactors in series with decanters in between, because most of the glycerol in the reactor effluent is removed before the mixture is fed to the next reactor. So in order to improve the biodiesel yield and feed conversion, reduce the separation difficulty and the production cost, the reasonable and effective operation steps are necessary. In this paper, for two-step transesterification, using batch, reasonable adding methanol method is beneficial. Design steps are as follows:

(1) Adding methanol in batches, takes feed ratio of methanol to oil equal to 6 and split ratio of methanol feed to the first reactor to total methanol feed equal to 0.6.
(2) Separating materials continuously between two CSTR, taking into account the effect of temperature on the separation, takes separation temperature is around about 323 K and reaction pressure is set to 1 atm.
(3) In order to ensure the concentration of catalyst NaOH has little effect on the reaction rate, takes the amount of NaOH into the first reactor is 1wt%(by weight of oil) and 0.2wt% complement into the second reactor.
(4) Separated from the upper level of liquid directly into the second reactor, the lower liquid is extracted refined glycerol.

Simulation and Analysis

To compare the effect of the removal of the glycerol phase, both one-step and two-step transesterification process are programmed by Matlab software, the set of ODEs are integrated using the Runge-Kutta Fehlberg (RKF) method.

Fig.2 and Fig.3 respectively show the concentration of reactant and products during continuous transesterification of vegetable oil at 323K and a residence time of 60 min for one-step reaction. The concentration of TG (triglyceride) decreases from initial value 0.8351mol/l to 0.0931mol/l at the end of the continuous run, and the concentration of methyl ester increases from 0 to 2.0950mol/l at the end of the continuous run. However, after 30 min, there are no significant changes in these values. This situation also happens with the rest of the components which no further changes occur after reaching the balance point. This indicates that a residence time of 30 min is suitable to complete the one-step reaction. According to these parameters and reaction conditions of the front, the yield of biodiesel can be expressed as the percent of ME/ (3*TG), the conversion rate of TG is expressed as the percent of (TG0-TG)/TG0.Results from Fig.4 shows that the yield of biodiesel is 83.62%, and the conservation of TG is 88.85% for one-step reaction. The transesterification achieve almost 80% after 10min and approaches the reaction equilibrium after 30min.

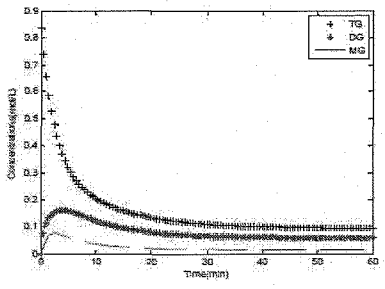

Figure 2. Concentration profiles of TG, DG, MG for one-step reaction

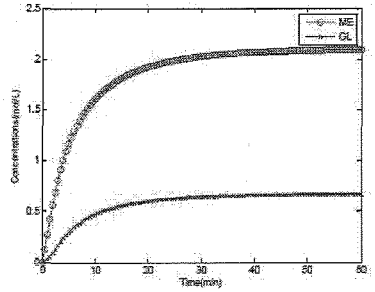

Figure 3. Concentration profiles of ME, GL for one-step reaction

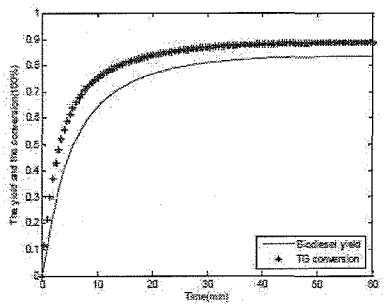

Figure 4. The biodiesel yield and TG conversion profiles for one-step reaction

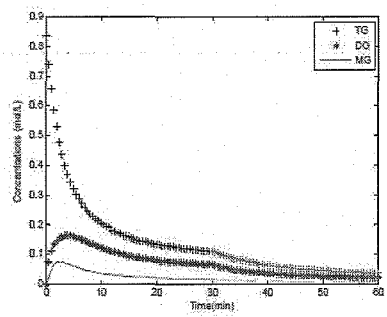

Figure 5. Concentration profiles of TG, DG, MG for two-step reaction

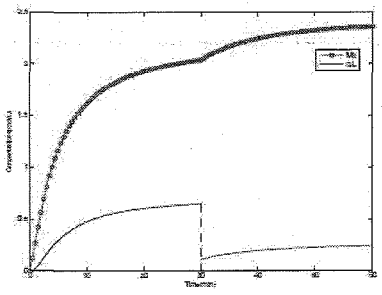

Figure 6. Concentration profiles of ME, GL for two-step reaction

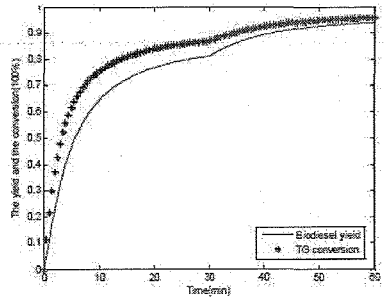

Figure 7. The biodiesel yield and TG conversion profiles for two-step reaction

Fig.5 and Fig.6 respectively present the concentration profile of six components for two-step reaction based on previous design strategy. The purpose of these figures are to show the reaction precedes of two-step reaction strategy which increased the biodiesel concentration from 2.0950mol/l to 2.3548mol/l, decreased the TG concentration from 0.0931mol/l to 0.0348mol/l. Concentration values are list in Table 2 when reaction approach the equilibrium end 60min of two methods.

Fig.7 shows the yield of biodiesel and the conversion rate of TG during continuous transesterification of vegetable oil at 323K and a residence time of 60 min for two-step reaction, the yield of biodiesel is 93.41%, and the conservation of TG is 95.84%. Two-step reaction increases the biodiesel yield by 9.79%, TG conversion rate increased by 6.99%. Through comparative analysis of two cases, for two-step reaction with glycerol phase split, adding methanol and NaOH batch optimization operation strategy, yield and conversion rate have increased significantly.

TABLE 2 CONCENTRATION OF SIX COMPONENT AT TIME END (MOL/L)

Component	TG	DG	MG	ME	M	GL
One-step reaction	0.0931	0.0584	0.0142	2.0950	2.9156	0.6694
Two-step reaction	0.0348	0.0219	0.0056	2.3548	3.5962	0.2411

Conclusion

In this work, the design of biodiesel production with the glycerol phase separation processes are researched, through installing a decanter between reactors and adding methanol and NaOH batch optimization operation strategy to improve the biodiesel yield and the conversion rate of reactants. Taking feed ratio of methanol to TG equal to 6, split ratio of methanol feed to the first reactor to total methanol feed equal to 0.6, and takes separation temperature is around about 323 K and reaction pressure is set to 1 atm. Through simulation comparative analysis of two cases, results show that two-step reaction increase the biodiesel yield by 9.79%, TG conversion rate increased by 6.99%, yield and conversion rate have increased significantly.

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