Process design of continuous biodiesel production by reactive distillation: Comparison between homogeneous and heterogeneous catalysts

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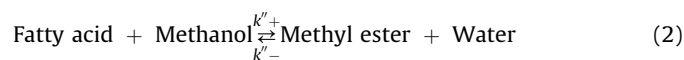[c] Engineering Department, Lancaster University, Lancaster, LA1 4YR, United Kingdom

ABSTRACT

Biodiesel production by reactive distillation processing is an attractive option to overcome the thermodynamic limitations inherently associated with conventional processes. Process simulations of transesterification of soybean oil and methanol were performed using the commercial package Aspen Plus®. Four different continuous processes were designed and simulated by using homogeneous alkali-based catalysts and heterogeneous acid-based catalysts in both conventional reactor/distillation and reactive distillation. Effects of important operating and design parameters on performance of each process were analyzed and optimum conditions were determined. The proposed homogeneous alkali-catalyzed RD for biodiesel production did not only eliminate the requirement of separation and purification of the products but also improved the biodiesel yield at reduced methanol in the feed and at lower energy consumption in comparison with the conventional approach of sequential reaction and distillation. It was demonstrated that the heterogeneous magnesium methoxide, instead of homogeneous catalyst, offered significant benefits such as reaching less number of unit operations, reducing energy consumption, and not requiring neutralization, waste water disposal or salt waste processing. The energy requirement of the reactive distillation process catalyzed by magnesium methoxide was about 153 kWh/t biodiesel or 139.2 kWh/t biodiesel with an allocated purity of 98 wt% to glycerol by-product.

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1. Introduction

The increasing energy demand, rising world fuel prices and concerns about global warming are making alternative sustainable sources of energy more attractive. Biodiesel, a renewable energy derived from vegetable oils and animal fats, presents competitive properties of lubricity, biodegradability and particulate emissions [1]. Biodiesel is a mono alkyl ester of fatty acid which is produced by either transesterification of triglycerides with alcohol (usually used methanol) to fatty acid alkyl ester (biodiesel) and glycerol (by-product), or esterification of fatty acid (FA) with alcohol to fatty acid alkyl ester (biodiesel) and water (by-product). Both trans-esterification and esterification reactions are expressed by equations 1 and 2, respectively.

$$\text{Triglyceride } + \text{ 3Methanol} \underset{k'_-}{\overset{k'_+}{\rightleftharpoons}} \text{3Methyl ester } + \text{ Glycerol} \qquad (1)$$

$$\text{Fatty acid } + \text{ Methanol} \underset{k''_-}{\overset{k''_+}{\rightleftharpoons}} \text{Methyl ester } + \text{ Water} \qquad (2)$$

In general, the manufacturing technology of biodiesel production relies on homogeneous catalysts and operates under batch or continuous modes. However, these techniques suffer from catalyst separation from product, leading to further downstream purification and methyl ester recovery [2–5]. Heterogeneous catalysts would be of interest as substitute to homogeneous catalysts [6].

The mechanism of transesterification includes three reversible steps, requiring a large excess of alcohol over a stoichiometric ratio to achieve high conversions of the triglycerides or the fatty acids, and thus, underlying more reactant consumption and product recycles.

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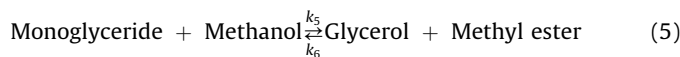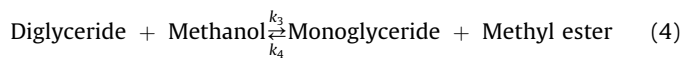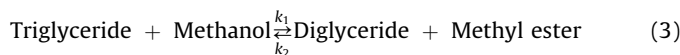 E-mail address: Suttichai.A@chula.ac.th (S. Assabumrungrat).

An interesting way to overcome the two aforementioned limitations is by intensifying both reaction and downstream separation through the reactive distillation (RD) process for the biodiesel production [7–16]. Reactive distillation is a unit operation in which the chemical reaction and the product separation occur simultaneously in one unit. The chemical equilibrium would be shifted forward the products without excessive use of reactants or downstream separation. The success of the RD process for biodiesel production has been illustrated via the esterification of fatty acids [8,16–18]. Limited studies on RD for transesterification have been revealed, and they mostly focused on homogeneous catalyst [14,15]. The study using a heterogeneous catalyst in RD for transesterification is still scarce and no comparative study on both types of catalysts to authors' knowledge has been carried out on process efficiency.

In this study, the process of transesterification using different types of catalyst; i.e., homogeneous and heterogeneous catalysts, by reactive distillation is investigated, and process efficiency is compared. Process simulations of transesterification of soybean oil and methanol are performed using the modular package Aspen Plus® (AspenTech) and effects of important operating and design parameters on performance of the RD process are analyzed.

2. Methodology

Owing to non-ideal behavior of reaction mixture, Dortmund modified UNIFAC model, which has been demonstrated to agree well with the reaction mixture [19–21], was employed to predict relevant phase equilibrium properties. The predictive UNIFAC model was selected because of the lack of literature data on interaction parameters between reaction mixture, which are required for phase equilibrium models (i.e., UNIQUAC, NRTL, etc.). Kuramochi et al. [22] carried out experimental investigation on the vapor/liquid equilibrium (VLE) and liquid/liquid equilibrium (LLE) of a number of binary and ternary of mixtures, including the VLE of methanol–biodiesel and methanol–glycerol mixtures, the LLE of water–biodiesel, methanol–biodiesel–glycerol and methanol–water–biodiesel mixtures and compared the results with those predicted by several models derived from the UNIFAC approach. They reported that the Dortmund modified UNIFAC model was the most appropriate one to represent the models of VLE and LLE of the methanol–soybean biodiesel and methanol–glycerol mixtures. Moreover, Dortmund modified UNIFAC allows prediction of solubility of water in biodiesel, which is of importance for the design of a purification process for water-washed biodiesel [22]. The rigorous continuous stirred tank reactor (CSTR) model in Aspen Plus was employed for the conventional process. The RD column was simulated using the RADFRAC module of Aspen Plus, which relies on the equilibrium stage model. The RADFAC model has been extensively used in RD and model is based on assumption that the vapor from the stage below and liquid from the stage above are brought into intimate and well-mixed contact on the stage. The vapor and liquid streams leaving the stage are assumed to be in equilibrium with each other and the overall reactive distillation process is modeled as a sequence of these equilibrium stages. The model includes equations of acronym MESH, which are four equations of the mass balance which includes the kinetic models of the reactions involved, the equilibrium between phases, the summation of compositions to unity and the heat balance. The RADRAC model does not require the need to set details about the packing and the size of the column, leading to assume preliminary values of stage efficiency. Details about the model were reported in our previous study [23]. The stages including the condenser, were assumed to be operated at total efficiency. Three relevant steps in the transesterification were assumed to take place, as illustrated by Eqs. (3)–(5).

$$\text{Triglyceride} + \text{Methanol} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \text{Diglyceride} + \text{Methyl ester} \quad (3)$$

$$\text{Diglyceride} + \text{Methanol} \underset{k_4}{\overset{k_3}{\rightleftarrows}} \text{Monoglyceride} + \text{Methyl ester} \quad (4)$$

$$\text{Monoglyceride} + \text{Methanol} \underset{k_6}{\overset{k_5}{\rightleftarrows}} \text{Glycerol} + \text{Methyl ester} \quad (5)$$

Trilinolein, a major component in the soybean oil and methanol were employed as feedstock for biodiesel production. The kinetic models proposed by Noureddini and Zhu [24] and Huang et al. [25] using sodium hydroxide and magnesium methoxide catalysts, respectively, were employed. The rate expressions of transesterification catalyzed by sodium hydroxide are shown as follows:

$$r_{TG} = -k_1[TG][A] + k_2[DG][E]$$
$$r_{DG} = k_1[TG][A] - k_2[DG][E] - k_3[DG][A] + k_4[MG][E]$$
$$r_{MG} = k_3[DG][A] - k_4[MG][E] - k_5[MG][A] + k_6[GL][E]$$
$$r_{GL} = k_5[MG][A] - k_6[GL][E]$$
$$r_E = k_1[TG][A] - k_2[DG][E] + k_3[DG][A] - k_4[MG][E] + k_5[MG][A] - k_6[GL][E]$$

where k_i is the rate constant of reaction i, and [TG], [DG], [MG], [GL], [A] and [E] are molar concentration of triglyceride, diglyceride, monoglyceride, glycerol, methanol, and methyl ester (biodiesel), respectively. The expressions of the rate constants and the activation energy are summarized in Table S1.

In case of heterogeneous catalyst, Huang et al. [25] proposed the kinetic of the overall transesterification with soybean oil and methanol using magnesium methoxide as follows.

$$r_E = [k^+ C_{TG} C_A - k^- C_E C_{GL}]$$

where TG, A, E and GL denote the triglyceride, methanol, methyl ester (biodiesel) and glycerol, respectively, and k^+ and k^- are the rate constant. The rate constants and the activation energy catalyzed by magnesium methoxide are summarized in Table S2.

A standard purity of biodiesel of 96.5% was set and the yield of biodiesel was defined by Eq. (6).

$$\text{yield} = \frac{F_P}{3 \times F_0} \times 100\% \quad (6)$$

where F_0 is the molar flow rate of triglyceride in the feed stream and F_P is the molar flow rate of biodiesel in the product stream.

3. Results and discussion

3.1. Model validations

Model validations of kinetic parameters of the reaction catalyzed by sodium hydroxide homogeneous base catalyst and magnesium methoxide solid base catalyst performed in a batch reactor are shown in Fig. 1a and b, respectively. The kinetic parameters were subsequently employed to validate the reactive distillation model along with the experimental data reported by He [26]. Using similar operating conditions (vis. oil feed flow rate = 63.7 g/min, methanol feed flow rate = 9.24 g/min, number of trays of 20 and total reflux mode, feed stage: top tray), the profile of triglyceride conversion with respect to the cumulative residence time is shown in Fig. 1c. A deviation between the model and experimental data of the relative root mean square deviation as low values as 0.19, showing a good agreement of the model presented herein.