Preliminary Modified Biodiesel Production by Coupling Reactive distillation with a Steam Reformer via Aspen Plus®

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Abstract. The conventional two-step biodiesel production process (esterification step followed by a transesterification step) from crude palm oil (CPO) has been carried out for years. However, the production cost from this process still cannot compete with fossil diesel. To reduce the capital and operating cost, the process should be modified by replacing both the reactor and the distillation column of the transesterification step with reactive distillation. In addition, glycerol, a by-product of the process, could convert to $\text{H}_2$, a high value-added product, via a steam reformer to help reduce the biodiesel production cost. The energetic and economic possibility of the modified biodiesel production process was studied and simulated via Aspen Plus software in this work. The biodiesel production capacity from CPO (15 wt.% FFA) of ca.1,000 kg/hr employed from previous researches was considerably basis. The conventional and modified processes in terms of process utility and biodiesel production cost were compared. The simulation results show that the biodiesel cost from the modified process decreased by 40.85% compared to the conventional ones, because of the reduction of capital cost and selling $\text{H}_2$. The result preliminarily confirmed that the modified biodiesel process was promising due to energy saving and economic concern.

Keywords: Biodiesel; Reactive distillation; Steam reformer; Simulation; Production cost

1. Introduction

Recently, as one of the developing countries, Thailand consumes a lot of crude oil every year [1]. The top policy has been reducing imports of fossil fuel from abroad by seeking renewable and sustainable energy resources within the country. Biodiesel (FAME) from palm oil has been continuously supported by the government for the past 20 years [2]. Biodiesel is generally produced from the transesterification of crude palm oil (CPO) or palm stearin with short-chain alcohol (methanol or ethanol) involving homogeneous catalyst (KOH or NaOH) under appropriate temperatures and stirring rates, as shown in the equation below, [3]. The chemical equation also shows that glycerol is presented as a by-product waste. In 2014, there were about 3.5×10^6 m³/day of glycerol waste produced from the biodiesel production process [4].

\[
\begin{align*}
\text{O} & \quad \text{O} & \quad \text{O} \\
\text{R}_1 & \quad \text{R}_2 & \quad \text{R}_3 \\
\text{(triglycerides)} & \quad \text{(methanol)} \\
& + 3 \text{CH}_3\text{OH} & \text{KOH} & \quad \text{CH}_3\text{O} & \quad \text{R}_1 \\
& & & \quad \text{OH} & \quad \text{OH} \\
& & & \quad \text{CH}_3\text{O} & \quad \text{R}_2 \\
& & & \quad \text{OH} \\
& & & \quad \text{CH}_3\text{O} & \quad \text{R}_3 \\
& & & \quad \text{OH} & \quad \text{OH} \\
\end{align*}
\]

(glycerol) (FAME)
Hydrogen (H₂) is an important feedstock for several kinds of manufacturing such as crude oil refinery and the chemicals sectors, however, it is also considered as clean energy for the future including heating and transportation [5]. Although the most of H₂ production is from a steam reforming of the crude oil refinery, the H₂ can also be alternatively produced from steam reforming of bio-oxygenated fuels such as methanol, ethanol, ethylene glycol, acetic acid, glycerol and so on [6]. The idea of using steam reforming process in converting glycerol waste to H₂ production should be beneficial in both renewable energy and waste disposal.

Several inexpensive raw materials such as waste cooking oil (WCO) or CPO used for biodiesel production lately has increased because of commercial competition with fossil diesel. However, the problem of such a low-cost feedstock is a high content of free fatty acid (FFA) that usually affects the impurity of biodiesel products. Then, the two-step acid-alkali biodiesel process (described by Zhang et al. [7]) has been used to produce biodiesel as the conventional method. Nevertheless, the conventional process still suffers from economic and environmental problems due to using a large amount of homogeneous catalysts [8]. To solve this problem, reactive distillation (RD) with heterogeneous catalyst integrating reaction and distillation into one unit is recently purposed as an alternate approach to reduce investment and operation costs [9].

The aim of this study is energetic and economic analysis of the modified biodiesel production process with a reactive distillation column and steam reforming unit via Aspen Plus® as a simulator.

2. Methodology

2.1 The conventional biodiesel production process

As Zhang et al. [7] described, CPO (with 15wt% FFA) is simultaneously fed into the esterification reactor with methanol and sulfuric acid (H₂SO₄). The FFA in CPO reacts with methanol with H₂SO₄ as an acid catalyst) to produce biodiesel and water as shown in the chemical equation below. After depletion of FFA, triglycerides and biodiesel are continuously passed to the transesterification unit with alkali catalyst (NaOH) and yield biodiesel and glycerol. Excess methanol is recycled to the transesterification reactor for cost reduction and process efficiency. The product mixture is separated into the organic phase (high content of FAME) and the aqueous phase (high content of glycerol) by water extraction in the washing column. Finally, Biodiesel and glycerol are further purified by distillation. The conventional biodiesel process is shown in Figure 1.

\[
R_1\text{-COOH} + \text{CH}_3\text{OH} \xrightarrow{\text{H}_2\text{SO}_4} \text{CH}_3\text{O}C=O \xrightarrow{\text{R}_1} + \text{H}_2\text{O}
\]

(FFA) (methanol) (FAME) (water)

Figure 1 The 2-step acid-alkali biodiesel production process for high FFA feedstock [7]
2.2 the modified biodiesel production process

2.2.1 Components and Thermodynamic method, the modified biodiesel production used in this study is presented in Figure 2. The Aspen Plus® tool was used for simulation of this process. Regarding the CPO as raw material which is high content of triolein (C$_{57}$H$_{104}$O$_6$) and tripalmitin (C$_{51}$H$_{98}$O$_6$) (approximately 80 wt.%), both of them were represented in this simulation. Accordingly, methyl oleate (C$_{19}$H$_{36}$O$_2$) and methyl palmitate (C$_{17}$H$_{34}$O$_2$) were taken as FAME products and their properties were available in the library of the Aspen tool. Due to the high polar components present in this process such as methanol and glycerol, the UNIF-DMD and NRTL thermodynamic/activity models were used to estimate the activity coefficients in the liquid phase. The CPO was fed approximately 1167 kg/hr at 25 °C, 1 atm based on 1,000 kg/hr biodiesel capacity rates.

2.2.2 Esterification reactor, it was described and modeled by Zhang et al. [7], the RStoic in the model palette was operated at the mild condition (70°C and 4 atm).

2.2.3 Washing column was modeled to remove remaining H$_2$SO$_4$ and other polar chemicals by using water washing. This unit might be a different part of Zhang et al. [7], but this simulation was used because of the lower price of water than using other chemicals for neutralization.

2.2.4 Transesterification reactor, the RadFrac palette was modified to reactive distillation. From the optimization to the highest purity of products, the column (19 theoretical stages with a reflux ratio of 2 at atmospheric pressure) was carried out simultaneously with a packed bed of CaO catalyst in the middle. The kinetic model used in this study was the pseudo-first-order because of the high amount of methanol (molar ratio of methanol-to-CPO = 9:1), and all kinetic parameters were followed by the work of Lee et al. [10]

2.2.5 Reforming reactor was modeled by the RGibbs palette, since the lack of kinetic information of glycerol steam reforming. RGibbs block calculates chemical and phase equilibrium by the minimizing of Gibbs free energy method. The reforming reactor was operated at 1 atm and 500-900°C to study the effects of temperature on H$_2$ yield.

Main reactions occurring in steam reforming process of glycerol was selected as follow;

\[
\begin{align*}
C_3H_6O_3 + 3H_2O & \leftrightarrow 7H_2 + 3CO_2 \quad \Delta H_f^{298} = 128 \text{ kJ/mol}^{-1} \\
CO + H_2O & \leftrightarrow CO_2 + H_2 \quad \Delta H_f^{298} = -41.1 \text{ kJ/mol}^{-1}
\end{align*}
\]
\[\begin{align*}
CO + 3H_2 & \leftrightarrow CH_4 + H_2O \quad \Delta H_r^{298} = -206 \text{ kJ mol}^{-1} \quad (3) \\
CO_2 + 4H_2 & \leftrightarrow CH_4 + 2H_2O \quad \Delta H_r^{298} = -165 \text{ kJ mol}^{-1} \quad (4) \\
2CO & \leftrightarrow CO_2 + C \quad \Delta H_r^{298} = -172.4 \text{ kJ mol}^{-1} \quad (5) \\
CO + H_2 & \leftrightarrow C + H_2O \quad \Delta H_r^{298} = -131.3 \text{ kJ mol}^{-1} \quad (6) \\
CH_4 & \leftrightarrow C + 2H_2 \quad \Delta H_r^{298} = 74.8 \text{ kJ mol}^{-1} \quad (7)
\end{align*}\]

The acquired parameters to discuss further were mole fraction \(y\) and yield of important gaseous products. These parameters can be determined by the equation below:

\[
y_{H_2} = \frac{N_{H_2}^{\text{out}} \text{(kmol hr}^{-1})}{\sum N_{\text{prod}}^{\text{out}} \text{(kmol hr}^{-1})}
\quad (8)
\]

\[
H_2 \text{ yield } (\%) = \frac{N_{H_2}^{\text{out}} \text{(kmol hr}^{-1})}{7 \times N_{\text{Gly}}^{\text{in}} \text{(kmol hr}^{-1})} \times 100\%
\quad (9)
\]

\[
CO_2 \text{ yield } (\%) = \frac{N_{CO_2}^{\text{out}} \text{(kmol hr}^{-1})}{3 \times N_{\text{Gly}}^{\text{in}} \text{(kmol hr}^{-1})} \times 100\%
\quad (10)
\]

3 Results and discussion

3.1 Reactive distillation

Figure 3 displays the composition profile of the optimum stage for the reactive distillation column. In this study, methanol was fed into the column at stage 14 and triglycerides were fed at stage 7. It shows that the reaction occurs within stage 7 to 14, while each component simultaneously separates in stage 1-6 and 15-19, respectively. Moreover, using the RD, it could completely separate methanol from FAME and glycerol, then there is no need to install any washing columns or purifier columns downstream anymore.

Comparing with the conventional system, the energy consumption of RD is 1731.73 Mhr\(^{-1}\) which is only 47.53 % of the conventional distillation columns. The result implies that the utility cost of the modified process is lower than the conventional process.

![Figure 3 Composition profiles in the reactive distillation](image_url)
3.2 Steam reforming reactor

3.2.1 Temperature effects

The equilibrium yields of H\textsubscript{2} and CO\textsubscript{2} for the reformer unit at the reaction temperature in the range of 500-900 °C (W/G = 1:1) is shown in figure 4. The graph shows that the H\textsubscript{2} yield rapidly increases with reaction temperature increase, and achieving the highest value (60%) at 800°C. While the trend of CO\textsubscript{2} yield is in the opposite direction. The result indicates that the glycerol steam reforming (GSR) reaction (equation 1) is the largest endothermic compared to the other reactions. However, the GSR reaction may reach the equilibrium at a temperature around 800-900°C because of the effects of several side reactions.

Figure 4 Equilibrium yield of H\textsubscript{2} and CO\textsubscript{2} at several reaction temperature, atmospheric pressure and the water to glycerol molar ratio (W/G) = 1:1

Figure 5 Effects of W/G on the H\textsubscript{2} yield at several reaction temperature
3.2.2 Water to glycerol feed Molar ratio (W/G)
Generally, the water/glycerol molar ratio is the most important parameter in the design process for the \( \text{H}_2 \) production from steam reforming because H-atom in water (or steam) is the important resource of \( \text{H}_2 \) gas as followed by equation (1). Figure 5 is the evidence to support that \( \text{H}_2 \) production is enhanced by W/G increase and the maximum at around 10. However, at each value of W/G, the highest \( \text{H}_2 \) yield achieves at the reaction temperature 650-800°C.

3.3 Biodiesel Cost
In this section, the biodiesel production cost is comparable between the conventional process and modified process which is shown in figures 6 and 7, respectively. There are four scenarios that are used to calculate the biodiesel production cost, and the results are shown in figure 6. This can be seen that the biodiesel cost from the conventional process is 0.71 $/l at the biodiesel production capacity 1,000 kg hr\(^{-1}\). This is rather closed to 0.52 $/l from Haas et al.’s work [11]. Figure 6 shows that the modified process can reduce biodiesel cost to 40.8% compared to the conventional one. This result is explained by the modified process has no biodiesel and glycerol purification column (see figure 2). Moreover, without both columns, the utility cost is also reduced to 38% as shown in Figure 7.

![Figure 6 Biodiesel cost in several scenarios](image)

![Figure 7 Utility usage in the conventional process and modified process.](image)
Conclusions
In this paper, the convention biodiesel production process for low quality raw materials was modified by using the reactive distillation and H₂ production unit. Both processes were simulated by the process simulation software with the same biodiesel production rate at 1,000 kg/hr⁻¹. The simulation results show that the reactive distillation has higher efficiency of separating methanol from the other products with lower installation cost by cutting downstream purification units. In this case, the steam reforming was proposed to be the H₂ production unit. The results show that the optimum conditions for the highest H₂ production rate were S/G molar ratio = 10, and 650°C at 1 atm. Moreover, the modified process could reduce the production cost to 40.8% comparing to the conventional one. Then these preliminary results show that this modified process can be valuable to both of energy saving and economic concern.

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