

Modelling of Methyl Stearate Biodiesel Production by Reactive Distillation

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Abstract: Methyl stearate is a biodiesel having cetane number much higher than the petrodieseland other biodiesels. The stearic acid is found in a numerous vegetable oilswhich can be converted to methyl stearate biodiesel by reactive distillation of stearic acid with methanol. In this work, different ways of increasing the yield of methyl stearate biodiesel have been studied using Aspen HYSYS. The yield of methyl stearate biodiesel is found to be in direct proportion to both temperature and pressure. At low temperature, high yield can be achieved by increasing the operating pressure. While performing reactive distillation at low pressure, increasing temperature favors high yield. A tray by tray analysis has been presented for understanding of the distillation behavior. A model has been developed for application of a wide range of temperatures and pressures.

Keywords: Aspen HYSYS, Methyl stearate biodiesel, Modeling, Reactive distillation, Stearic acid

I. INTRODUCTION

Currently, most of the energy requirements are fulfilled by fossil fuels however these resources are limited and inadequate for meeting the future energy requirements. So the quest of finding the renewable resources is increasing day by day [1]. Biodiesel is considered as an important renewable resource which can directly be used as a substitute petroleum diesel without any alteration in the engine because much of their properties such as viscosity, specific gravity, cloud point, cetane number and flash point are quite similar [2–4]. Usually, diesel fuels with cetane number from 40 to 55 are used in the diesel engines, although premium diesel fuels may have cetane number as high as 60 [5]. Freedman and Bagby have reported cetane numbers for methyl stearate as 75.6 [6], Klopfenstein reported as 86.9 [7] and Gerpen predicted value of cetane number of methyl stearate as 78.6 [8]. The higher value of cetane number of methyl stearate is an indication of better combustion in comparison to the fossil diesel fuel. Thus it can be blended with diesel having low cetane number to enhance the combustion efficiency.

Several methods have been used for the production of methyl stearate biodiesel [9,10]. In recent years, biodiesel production has been studied by reactive distillation of alcohol and fatty acids [11]. One of the advantages of reactive distillation is that both chemical reaction and separation processes are performed in a single unit. Another advantage is its frequent use when reaction equilibrium limits the conversion [12]. Reactive distillation has scopes for the avoidance of azeotropes' and difficult separations [13,14]. He et al [15] has reported that reactive distillation reactor was very effective in trans-esterifying of alkyl esters to biodiesel. Kapilakarn et al showed that the production cost of biodiesel is lower when it is carried out with a reactive distillation column [16]. Several simulations have been performed for making industrial plants more efficient using reactive distillation [3,10,17,18]. The researchers have studied the effect of reflux ratio, reboiler duty and feed ratio on the production of methyl stearate biodiesel using reactive distillation [19]. The dynamic Simulink model of Houge [20] accounts for general behavior of the reactive biodiesel process, and there are some aspects like chemical equilibrium, temperature in the column, yield, and conversion which require validation by comparing to published data and results. Moreover, no researcher has discussed the effect of varying temperature and pressure on the performance of the process through simulation. Also in the previous simulation studies, no model has been presented for determining the methyl stearate biodiesel production at various temperature and pressure. The present work aims to simulate a reactive distillation plant on various temperatures and pressures for maximizing the yield of methyl stearate biodiesel production with the aid of Aspen HYSYS. The simulations have been performed with equal proportion of reactants while a constant reflux ratio of 3 has been employed. A tray by tray analysis has been presented to understand the performance of the column better. Finally a model has been developed for a wide range of temperatures and pressures.

II. Material and Methods

The simulation was performed using Aspen HYSYS V8.4. Fig. 1 shows the process schematic for methyl stearate biodiesel production. The HYSYS Databank was used for the components selection. The components selected were stearic acid, methanol, water, and methyl stearate. Wilson package was selected as

fluid package while UNIFAC VLE was used for the purpose of coefficient estimation. The type of reaction selected was equilibrium having Gibbs free energy as K_{eq} source.

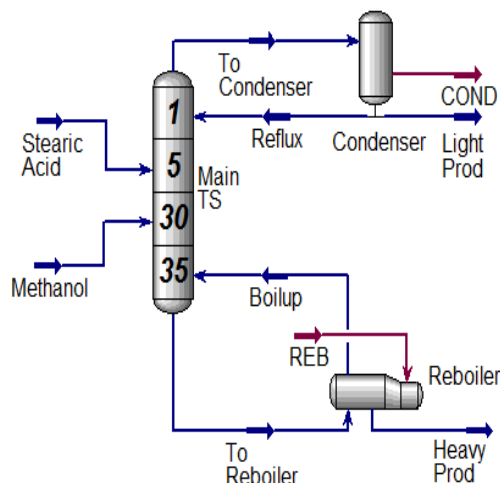
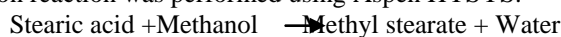


Fig. 1 Process schematic of Aspen HYSYS model for methyl stearate biodiesel production

The following esterification reaction was performed using Aspen HYSYS:



The column consisted of 35 stages; the feed consisted of stearic acid entered at 5th stage while methanol entered at 30th stage. The “Light Prod” stream as shown in Fig. 1 consisted mainly of water produced by the esterification reaction with some unconverted methanol. The “Heavy Prod” stream mainly comprised of the desired product i.e. methyl stearate. Total condenser was selected as condenser type while reboiler was of kettle type. The value of reflux ratio was set at 3.0. The column was divided into five main sections, viz, condenser section, rectification section, reaction section, stripping section and reboiler section. The reaction section covered the major proportion of the height of column (stage 5 – 30). Sparse Continuation Solver was used as it is readily used for reactive distillation [19]. For column convergence, two specs were selected i.e. distillate rate and reflux ratio to make the degree of freedom zero. Both reactants were introduced in equal proportion. The pressure of the column was varied from 1 bar to 10 bar to study the effects of pressure on the formation of desired product. The methanol feed was introduced in the vapor phase at a constant temperature of 140°C while the temperature of stearic acid feed was varied over a wide range to investigate the effects of temperature on the column performance.

III. Results and Discussion

The summary of the results have been shown in Table 1, which represents the simulation results performed at various temperature and pressure at a reflux ratio of 3.0. The effects of different operating conditions are discussed below.

3.1. Effects of operating pressure

Fig. 2 illustrates the effect of pressure on the production of methyl stearate biodiesel. The formation of methyl stearate biodiesel is in direct proportion to the column pressure at all temperatures though it is not linear as is evidenced by Table 1, which shows that the mole fraction of methyl stearate at 1.5 bar is 0.748 while at 10 bar, it is found to be 0.997 at the same value of temperature. It is also clear that the pressure dependence is more at low pressures as the mole fraction has been increased by 0.169 from 1.5 bar to 4 bar while there is an increase in mole fraction of only 0.080 from 4 bar to 10 bar at the same temperature.

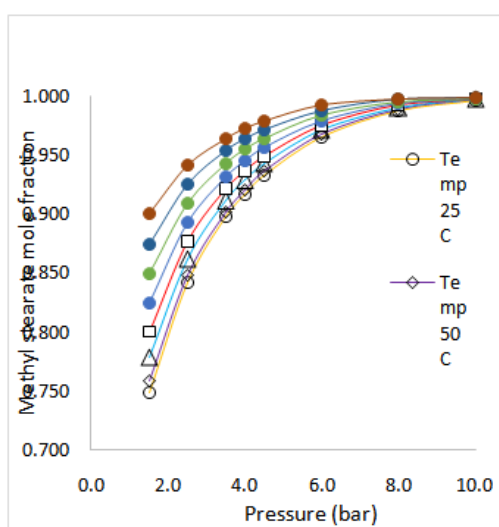


Fig. 2 Effect of pressure on the production of Methyl stearate biodiesel

3.2. Effects of feed temperature

Fig. 3 illustrates the effects of temperature on the production of methyl stearate biodiesel. The figure shows that the formation of methyl stearate increases by increasing the feed temperature. Table 1 shows that at an operating pressure of 1.5 bar, the mole fraction of methyl stearate is found to be 0.748 at 25°C, which is increased to 0.901 at 350°C. It is also clear that the temperature has almost same effect throughout the temperature range as the mole fraction has been increased by 0.077 from 50°C to 200°C while there is an increase in mole fraction of 0.066 from 200°C to 350°C at the same operating pressure. Shinde et al [22] also found that higher temperature favors better reactor performance. Kusmiyati and Sugiharto [23] have reported a higher conversion of oleic acid and methanol to biodiesel at higher temperature.

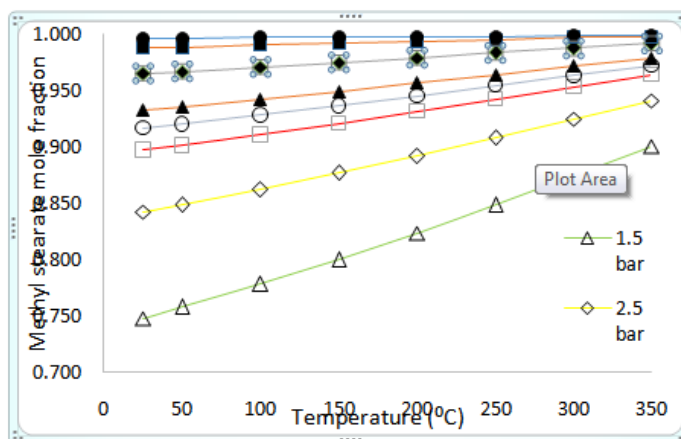


Fig.3 Effect of temperature on the production of Methyl stearate biodiesel

3.3. Tray by tray analysis at optimum condition

A number of optimum conditions exists for operating the column depending on the utility costs. If for an industry, the cost of electricity is very low compared to the cost of natural gas, then a possible optimum condition would be operating the column at high pressure and low temperature e.g., 10 bar and 25°C. If an industry has heating sources readily available within the plant or the cost of energy from fuel combustion is lower in comparison with the compression cost then operating at high temperature (350°C) and low pressure (2.5 bar) would be the optimum solution. Fig. 4 represents tray by tray analysis of the column at one of the optimum set of conditions i.e., 10 bar and 25°C. The figure shows that the mole fraction of methyl stearate increases from stage 5 (where the stearic acid has been introduced) to down the column while stearic acid has

been consumed in the same stages. Water is only found at the top of the column with a mole fraction of 0.96 while methanol is found in a very low quantity at the rectification section and at the Light Prod. Further it is clear from the figure that the bottom contains no amount of water and methanol in the bottom section only contains the desired product i.e. methyl stearate with trace amount of unconverted stearic acid. It is also shown from the figure that methanol is consumed more in the process than stearic acid because its mole fraction is almost zero in nearly all stages of the column. In addition, the reactants mole fraction were found to be negligible in the Heavy Prod. stream and Light Prod. stream, which indicates that the reactants had almost completely consumed in the process.

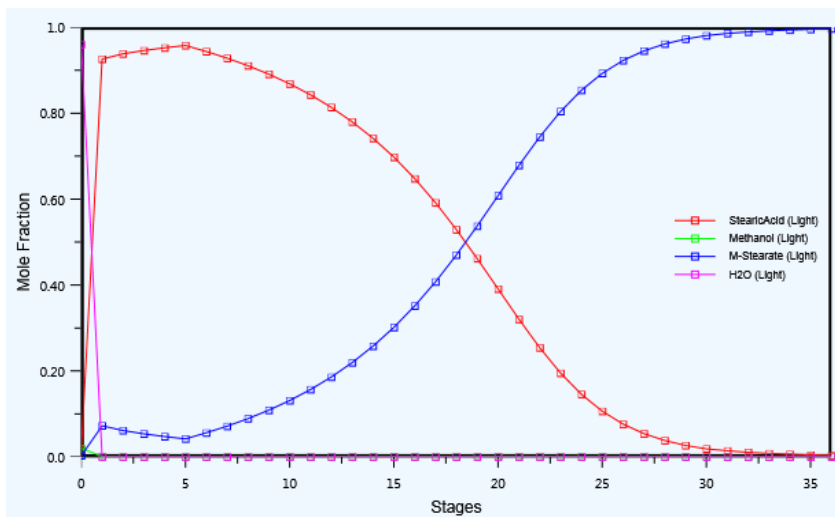


Fig. 4 Mole fraction profiles of the components at 10 bar and 25⁰C

Table 1. Mole fraction of Methyl stearate at various temperature and pressure

	25 ⁰ C	50 ⁰ C	100 ⁰ C	150 ⁰ C	200 ⁰ C	250 ⁰ C	300 ⁰ C	350 ⁰ C
1.5 bar	0.748	0.758	0.778	0.800	0.824	0.849	0.875	0.901
2.5 bar	0.842	0.849	0.862	0.877	0.892	0.908	0.925	0.941
3.5 bar	0.897	0.902	0.911	0.921	0.932	0.943	0.954	0.964
4.0 bar	0.917	0.921	0.928	0.937	0.945	0.955	0.964	0.972
4.5 bar	0.933	0.936	0.942	0.949	0.957	0.964	0.972	0.979
6.0 bar	0.965	0.967	0.971	0.975	0.979	0.984	0.988	0.992
8.0 bar	0.988	0.989	0.990	0.992	0.994	0.995	0.997	0.998
10.0 bar	0.997	0.997	0.997	0.998	0.998	0.998	0.999	0.999

3.4. Mathematical modeling

The modeling was performed with the aid of Microsoft Excel Trend line option. Various trend lines were selected and the best fit equations have been selected. We have modeled the simulations at two extreme conditions both for constant temperature and constant pressure. At constant temperature, the two extreme simulated temperatures are 25⁰C and 350⁰C; for which the best fit models are as follows:

At 25⁰C:
 $y = -0.0001x^4 + 0.0034x^3 - 0.0381x^2 + 0.2066x + 0.5137$; $R^2 = 0.9998$

At 350°C:

$$y = -5E-05x^4 + 0.0014x^3 - 0.0157x^2 + 0.0869x + 0.8016; \quad R^2 = 0.9996$$

Where, x is pressure (applicable range: 1.5 bar to 10 bar) and y is mole fraction of methyl stearate. Similarly keeping the distillation at constant pressure, the two extreme simulated pressures are 1.5 bar and 10bar; for which the developed models are:

At 1.5 bar:

$$y = -5E-10x^3 + 5E-07x^2 + 0.0003x + 0.7395; \quad R^2 = 0.9999$$

At 10 bar:

$$y = 1E-10x^3 - 7E-08x^2 + 2E-05x + 0.9962; \quad R^2 = 0.9419$$

Where, x is temperature (applicable range: 25°C to 250°C) and y is mole fraction of methyl stearate. It is clear from the R² values that the models developed are perfectly in agreement with our simulated results.

IV. CONCLUSIONS

From the simulation results, it was found that at low temperature reactive distillation, the mole fraction of methyl stearate biodiesel can be increased by increasing the operating pressure. However the trend showed that at low values of temperature, there was more increase in the formation of biodiesel on increasing pressure. While performing the reactive distillation at low pressure, the mole fraction of methyl stearate biodiesel can be increased by increasing the temperature of stearic acid feed. In addition, at low values of pressure, the mole fraction of methyl stearate increases more rapidly with the increase in temperature. The model developed can be used for simulating the process data within the limits mentioned above. However, more experimental studies are required to validate the simulation results presented in this work.

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