Journal of Engineering Science, Vol. 11, 17–26, 2015

Simulation and Economic Analysis of Biodiesel Production using Supercritical Methanol

Dipesh Shikchand Patle, Phung Eng Wei and Zainal Ahmad*

School of Chemical Engineering, Universiti Sains Malaysia, Engineering Campus, 14300 Nibong Tebal, Pulau Pinang, Malaysia

*Corresponding author: chzahmad@eng.usm.my

Abstract: *There is an increasing interest towards the use of vegetable oils (palm oil in Malaysia) in the much sought eco-friendly biodiesel production. This study focuses on the biodiesel production using supercritical methanol. The main highlights of this process include the un-necessity of catalyst and the insensitivity to the presence of free fatty acids and water in the feedstock. In this study, steady state simulation and sensitivity analysis of biodiesel production using supercritical methanol are performed. In the subsequent part, cost analysis is done using the Aspen Process Economic Analyzer. The feed oil is found to be the main contributor to the total manufacturing cost.*

Keywords: Steady state simulator, biodiesel production, FAME, Aspen Process Economic Analyzer, supercritical methanol

1. INTRODUCTION

The demand for energy is increasing exponentially, and because conventional energy resources are limited, researchers are always seeking alternative energy sources.[1] Biodiesel is a fuel derived from vegetable oil or animal fat, which consists of long-chain alkyl esters. The typical process for biodiesel production includes trans-esterification, which involves the use of short chains of aliphatic alcohol such as methanol or ethanol.[2,3] Biodiesel offers many advantages over petro-diesel such as renewability, sustainability and biodegradability. Biodiesel also possesses a higher flash point than petroleum diesel, which makes it less volatile and more convenient for transportation and handling. Moreover, the dramatic increase in the price of petroleum due to finite sources of fossil fuels as well as environmental concerns have led researchers to search for alternative energy sources, and in particular, sources of biodiesel.[4] Additionally, biodiesel has a more favourable combustion profile than petro-diesel due to the lower emission of hazardous gases, such as carbon dioxide and carbon monoxide.[5]

A number of studies have focused on the production of biodiesel via trans-esterification of vegetable oil with alcohol under different operating conditions.[2,3] This reaction can be performed in the presence of acidic or basic catalysts. However, there are drawbacks of using acidic/basic catalysts. First, alkali-catalysed processes are very sensitive to the presence of free fatty acids (FFAs) and water. Second, acid-catalysed processes require a long reaction time. Additionally, these processes require additional steps to separate the products and the catalyst, which ultimately increases both capital and operating cost. To overcome these challenges, here the authors propose the production of biodiesel from vegetable oils via non-catalytic trans-esterification with methanol under supercritical conditions.[6,7] Supercritical methanol forms a single phase in methanol/oil mixtures. Additionally, the reaction time is comparatively shorter. Therefore, the reaction occurs without a catalyst, and the separation of the products is much easier and more environmentally friendly. However, the reaction requires a temperature of 350°C–400°C and pressures of up to 45–54 MPa. These extreme conditions lead to increased energy consumption.

A steady state simulator is required to investigate the feasibility of this process and to study the effect of various process parameters. Additionally, techno-economic analysis is important to determine the overall capital and production cost of the plant. Therefore, this study aims at the development of the process and its validation including a sensitivity analysis and cost analysis. The results are validated with data reported in the literature, followed by a sensitivity analysis, where the effect of the number of tubes and tube diameter is determined. Subsequently, a cost analysis is performed using the Aspen Process Economic Analyzer. The most dominant factors contributing to the total cost of production are determined.

2. SUPERCRITICAL METHANOL PROCESS FOR BIODIESEL PRODUCTION

One of the main processes in biodiesel production is trans-esterification, where a triglyceride is converted to an alkyl-ester by reacting with light alcohols. Methanol is generally used due to its low cost. The chemical reaction involved in trans-esterification can be represented as shown below:

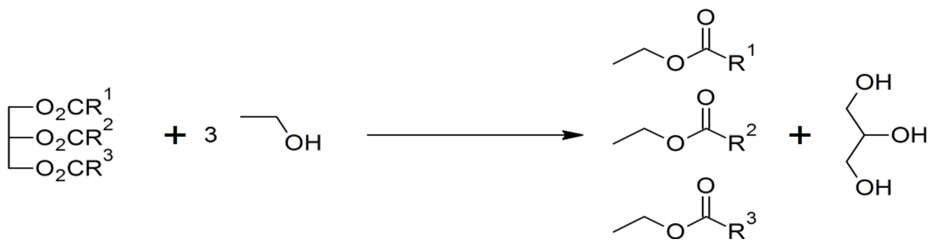

Figure 1: Chemical reaction for the trans-esterification of a triglyceride with methanol to form a mixture of fatty esters and glycerine (source: U.S. Department of Energy).

Figure 1 shows that a triglyceride contains 3 separate ester functional groups and can react with 3 moles of methanol to form fatty acid methyl esters (FAME), i.e., biodiesel and glycerol. A catalyst is not necessary for this reaction to occur when using supercritical methanol. Freedman et al.[8] discussed the results of a parametric study of trans-esterification reaction variables, such as temperature, molar ratio of alcohol to oil, type of catalyst and the degree of oil refinement. Those authors presented the relationship between the rate of the reaction and the alcohol-to-oil ratio. Additionally, Freedman et al.[8] compared two types of feedstock, namely, crude vegetable oil and refined vegetable oil. Recently, the trans-esterification of triglycerides with supercritical methanol to produce biodiesel is being given much attention.

Saka dan Kusdiana[4] reported that the supercritical methanol process requires a very high methanol to oil ratio (42:1) and a very high operating temperature and pressure of 350°C and 43 MPa, respectively. They used the rapeseed oil as feedstock to study biodiesel production using the supercritical alcohol method. Morais et al.[9] investigated the environmental impact-based biodiesel production processes, namely, conventional alkali-catalysed processes, acid-catalysed processes and the supercritical methanol process. Life cycle assessment (LCA) was used to determine the potential environmental impact of each process. This study showed that the supercritical process has a higher environmental impact because it requires a higher amount of methanol to undergo the supercritical trans-esterification reaction.

Cao et al.[10] found a way to decrease the operating temperature and pressure of the supercritical methanol process by introducing propane as the co-solvent in the reaction. Propane decreases the critical point of methanol, which promotes the supercritical condition at a lower temperature. The optimum conditions reported are 280°C, 12.8 MPa, an alcohol to oil molar ratio of 24:1 and a propane to oil molar ratio of 0.05:1. They reported that 98% of oils were converted to biodiesel within a duration of 10 min. Kasteren and Nisworo[11] further accessed the applicability of the supercritical process through an economic analysis and reported that the process can compete with the conventional alkali- and acid-catalysed processes. Demirbas[6,7] reviewed the production of biodiesels and suggested that by increasing the reaction temperature, especially to supercritical conditions, the yield of the FAME could increase.

Supercritical fluid has received much attention due to its unique properties.[4] Under these conditions, the molecules in the substance have a high kinetic energy like a gas and have a high density like a liquid. Therefore, the chemical reactivity of a chemical substance can be enhanced, as the dielectric constant of the supercritical fluid is lower than that of the liquid.[4] Methanol in a supercritical state can dissolve well in many types of non-polar organic substances, such as oils or fats, which subsequently supports the use and implementation of supercritical methanol in biodiesel production. On the other hand, the ionic products of supercritical methanol are increased by increasing the pressure.[12]

3. SIMULATION OF THE PROCESS

The plant capacity is considered to be 10,000 tons of biodiesel per annum. A combination of UNIQUAC and the Redlich-Kwong (RK-ASPEN) thermodynamic model is used as the UNIQUAC model cannot be used at high pressure and high temperature.[13] The Redlich-Kwong EOS model is also suitable when highly polar components are present.[2,3] The distillation columns and other separation processes are operated at lower pressure, but the reactors are operated at high pressure. Some components, which are not directly available in the Aspen Plus, are represented by other similar components chosen from the Aspen database. For instance, triolein ($C_{57}H_{104}O_6$) was selected to represent the palm oil feedstock and oleic acid methyl ester ($C_{19}H_{36}O_2$). This assumption is reasonable, as oleic acid is the major component in rapeseed oil, palm oil and peanut oil.[2,11] A vacuum is applied in the distillation columns for methanol recovery and product purification in order to avoid the product. Figure 2 presents a schematic of the process of biodiesel production using supercritical methanol modified from Sandra et al.[13]

Table 1: Design and operating parameters.

Stream/Block in Figure 1	Parameters (unit)	Value
Stream 101	Fresh methanol (kg h^{-1})	1948
Stream 102	Waste palm oil feed (kg h^{-1})	1282
Heater F-101	Temperature and Pressure in (K and bars, respectively)	573.15 and 20
Distillation Column T-301	Reflux ratio and theoretical stages, respectively	2 and 4
Distillation Column T-301	Temperature and pressure for condenser (K and MPa, respectively)	301.45 and 0.002
Distillation Column T-301	Temperature and pressure for reboiler (K and MPa, respectively)	373.85 and 0.003
Distillation Column T-401	Reflux ratio and theoretical stages, respectively	2 and 5
Distillation Column T-401	Temperature and pressure for condenser (K and MPa, respectively)	593.35 and 0.001
Distillation Column T-401	Temperature and pressure for reboiler (K and MPa, respectively)	571.95 and 0.002
Distillation Column T-501	Reflux ratio and theoretical stages, respectively	2 and 5
Reactor R-100	Temperature and pressure in (K and bars, respectively)	573.15 and 20
Reactor R-100	Methanol to oil molar ratio	42:1
Reactor R-100	Assumed conversion of FFA (%)	95
Reactor R-100	Assumed conversion (%)	95

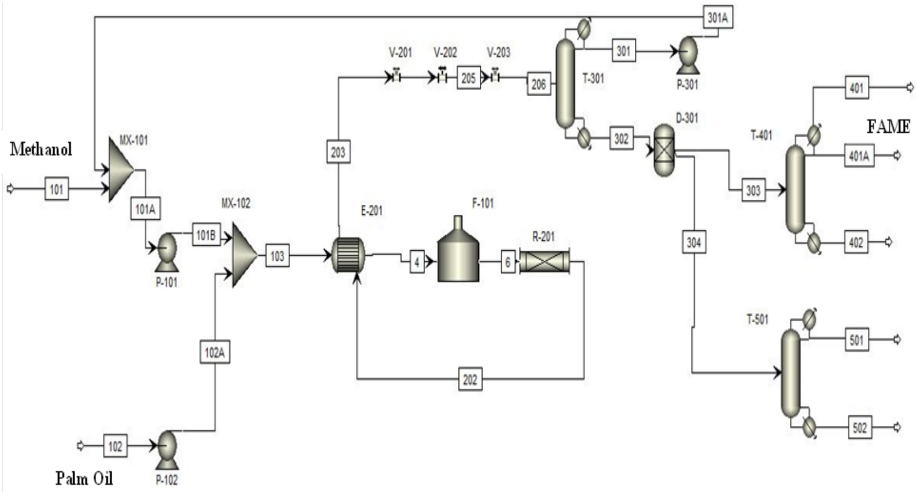

Figure 2: Plant simulation for biodiesel production by using the supercritical methanol method.

4. RESULTS AND DISCUSSION

4.1 Comparison of Steady State Results

Table 2 presents the comparison of the results of the present simulation and the results reported in the literature. It can be observed that the results presented here are in good agreement with those reported by Sandra et al.[13] Figure 3 presents the distribution of various costs in the biodiesel production. It can be clearly observed that the cost of feed oil is the major contributor to the total cost of biodiesel production. Any small deviations may be due to changes made in the process (Figure 2).

Table 2: Comparison of simulation results.

Parameters	Results of present simulation	Results reported by Sandra et al.[13]
Biodiesel (kg h^{-1})	1209.5	1212.2
Glycerol (kg h^{-1})	122.1	120.4
Purity of FAME (mass %)	97.2	99.8
Purity of glycerol (mass %)	99.5	99.7
Reactor conversion (%)	91	97

4.2 Sensitivity Analysis

Figure 3 presents the variation of biodiesel (i.e., FAME) with the number of tubes in the plug flow reactor. It can be clearly seen that FAME production increases with an increase in the number of tubes. However, there is not much change after 18 tubes. Additionally, FAME increases with the increase in the diameter of each tube in the reactor as can be seen in Figure 4. There was no significant change when considering tube diameters beyond 0.35 ft because at this point, most of the oil is already converted to biodiesel. Increases in the number of tubes or the diameter of tubes may lead to increased capital investment. However, the cost analysis of these variables was not investigated in this study.

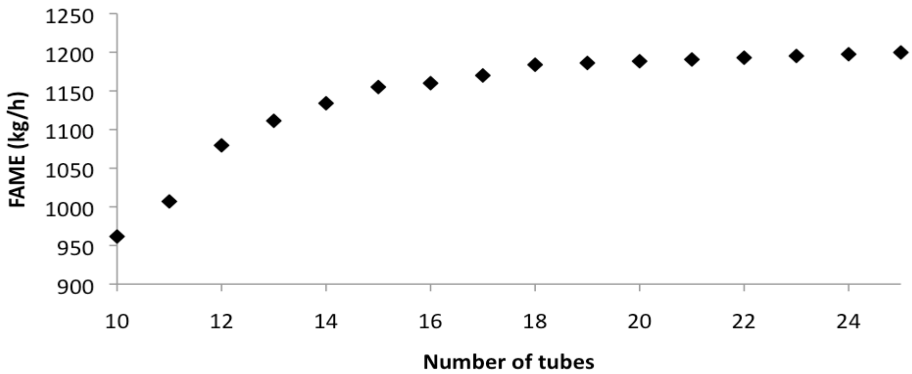

Figure 3: Effect of the number of tubes in the reactor on FAME production.

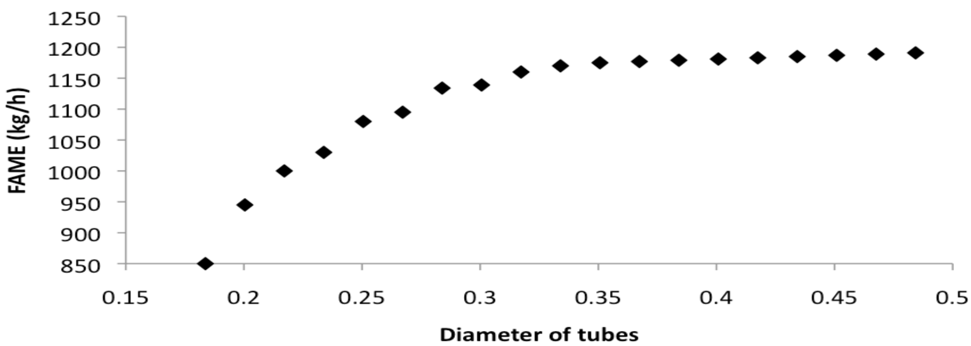

Figure 4: Effect of the diameter of each tube in the reactor on FAME production.

4.3 Economic Analysis of the Process

Table 3 presents the total capital cost, total manufacturing cost, raw materials cost and total utility cost associated with the concern process when assuming that the plant will be built and function in Malaysia. The estimated costs are given in U.S. dollars. The costs of methanol ($408.23 per ton), oil ($718.47 per ton), biodiesel ($1.464 per kg) and glycerol ($2 per kg) are considered. The plant is assumed to have 330 operating days per year. Figure 5 shows the distribution of various costs. Fifty six per cent of the total cost is contributed by the cost of feed oil. The second biggest contribution (27%) is steam, which is required to maintain high operating conditions in the unit operations.

Table 3: Economic analysis of the process.

Item	Value
Total capital cost (USD)	10.62×10^6
Total operating cost (USD per annum)	1.76×10^7
Total utility cost (USD per annum)	4.27×10^6

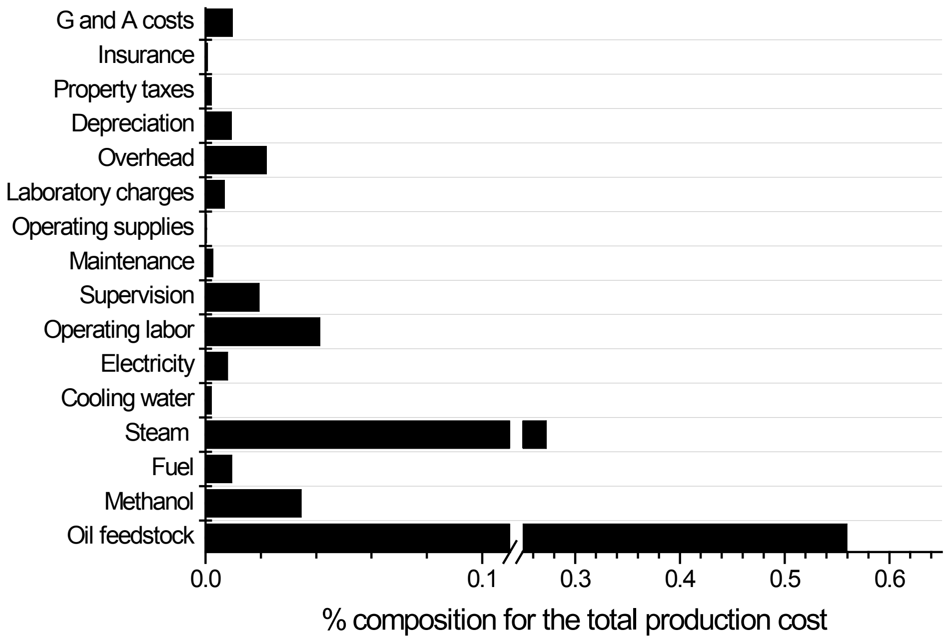

Figure 5: Percentage composition for the total production cost.

4.4 Energy Analysis

Table 4 shows the energy spent in each unit operation. The distillation column for methanol recovery (T-301) consumes (1.573 MW) maximum energy out of an overall energy consumption. This accounts for more than 50% of the total energy consumption. High energy consumption in T-301 is due to the high methanol to oil ratio in the reactor, which has to be recovered and recycled to satisfy economic and environmental concerns. Additionally, heaters contribute to a significant amount of energy consumption (1.155 MW), as heating is required to maintain required operating conditions in the reactor. However, 0.523 MW is recovered using heat exchangers, which leads to the total energy consumption of 2.643 MW.

Table 4: Energy spent in each unit operation.

Unit operation	Energy spent (kW)
Pumps	7.04
Heaters	1155
Methanol recovery	1573
Biodiesel production	421
Glycerol purification	9.90
Salt removing (Evaporator)	–
Heat recovery	523
Total	2643

5. CONCLUSION

Here, the authors perform and validate the steady state simulation of biodiesel production using the supercritical methanol method. A sensitivity analysis of the simulated biodiesel process is also performed. Increasing the number of tubes in the reactor was found to increase biodiesel production. In addition, increasing the diameter of each tube in the reactor had a significant impact on biodiesel production. Economic analysis was performed using the Aspen Process Economic Analyzer. These results showed that the main factor contributing to the total production cost of biodiesel is the oil feedstock, which accounts for 56% of the total manufacturing cost. The maximum level of energy consumption was observed in the methanol recovering distillation column. This model can be used as a guide for the preliminary understanding of this process and also as a reference for more sophisticated models for plant design and the specification of process equipment.

6. ACKNOWLEDGEMENT

The authors would like to acknowledge the financial support received from the Universiti Sains Malaysia through the Research University (RU) grant 1001/PJKIMIA/814155.

7. REFERENCES

1. Wolfram, C., Shelef, O. & Gertler, P. J. (2012). How will energy demand develop in the developing world? Working paper, National Bureau of Economic Research, Massachusetts, U.S. Retrieved 15 May 2013, http://www.nber.org/papers/w17747.
2. Zhang, Y. et al. (2003). Biodiesel production from waste cooking oil: 1. Process design and technological assessment. *Biores. Technol.*, 89(1), 1–16.
3. Zhang, Y. et al. (2003). Biodiesel production from waste cooking oil: 2. Economic assessment and sensitivity analysis. *Biores. Technol.*, 90(3), 229–240.
4. Saka, S. & Kusdiana, D. (2001). Biodiesel fuel from rapeseed oil as prepared in supercritical methanol. *Fuel*, 80(2), 225–231.
5. Mahajan, A., Ahluwalia, A. S. & Mahajan, P. (2011). Properties of biodiesel produced from various oilseeds. *Int. J. Res. Environ. Sci. Technol.*, 1(4), 26–29.
6. Demirbas, A. (2009). Biodiesel from waste cooking oil via base-catalytic and supercritical methanol transesterification. *Energ. Convers. Manage.*, 50(4), 923–927.
7. Demirbas, A. (2009). Production of biodiesel fuels from linseed oil using methanol and ethanol in non-catalytic SCF conditions. *Biomass Bioenergy*, 33(1), 113–118.
8. Freedman, B., Pryde, E. H. & Mounts, T. L. (1984). Variables affecting the yields of fatty esters from transesterified vegetable oils. *J. Am. Oil Chem. Soc.*, 61, 1638–1643.
9. Morais, S. et al. (2010). Simulation and life cycle assessment of process design alternatives for biodiesel production from waste vegetable oils. *J. Cleaner Prod.*, 18(3), 1251–1259.
10. Cao, W., Han, H. & Zhang, J. (2005). Preparation of biodiesel from soybean oil using supercritical methanol and co-solvent. *Fuel*, 84(4), 347–351.
11. Kasteren, J. M. N. V. & Nisworo, A. P. (2007). A process model to estimate the cost of industrial scale biodiesel production from waste cooking oil by supercritical transesterification. *Resour. Conserv. Recycl.*, 50(4), 442–458.
12. Holzapfel, W. (1969). Effect of pressure and temperature on the conductivity and ionic dissociation of water up to 100 kbar and 1000°C. *J. Chem. Phys.*, 50, 4424–4428.
13. Sandra, G., Ivana, L. & Skala, D. (2009). Biodiesel synthesis at high pressure and temperature: Analysis of energy consumption on industrial scale. *Biores. Technol.*, 100, 6347–6354.