Simulation of DMC Transesterification Reaction using ASPEN PLUS

Nur Amirah Mohd Ali[1,]*, Norashid Aziz[2]

[1,2] School of Chemical Engineering, Universiti Sains Malaysia, Engineering Campus, Seri Ampangan, 14300 Nibong Tebal, Seberang Perai Selatan, Penang, Malaysia

*Corresponding author: mira_ate@yahoo.com.my

Abstract: *Computer simulation has been widely used in chemical engineering processes and its implementation in biodiesel industry is very useful. In this study, a pilot plant scale of DMC transesterification reaction is simulated and validated using ASPEN PLUS software. The procedures for process simulation in ASPEN PLUS involved defining chemical components, selecting a thermodynamic model, determining plant capacity, choosing proper operating unit and setting up the input conditions such as flowrate, temperature, pressure and etc. In addition, the simulation results has successfully demonstrated the behavior of DMC transesterification reaction which has been carried out using sensitivity analysis block built in ASPEN PLUS. Based on the results, it was found that there are three main parameters that affecting production of PME i.e. amount of palm oil, molar ratio and temperature of reactor. These results obtained here can be further used for the optimization study.*

Keywords: Simulation; Pilot Plant; ASPEN PLUS; Biodiesel; Transesterification Reaction

1. INTRODUCTION

Simulation can save millions of dollars in predicting the performance of process alternative. The calculation of mass and energy balance can easily define in flowsheet simulator such as ASPEN PLUS, ChemCAD III, HYSIM, PRO II and SPEEDUP[1]. Moreover, the process conditions of the process can quickly define. Besides that, the basic simulations specifications, including the physical properties can be set up in shorten time. In addition, availability of model built-in package in simulator can practically help to describe accurate physical properties during simulation. After successfully simulate the process, scale up, optimization, control and dynamic calculation can be reveal well. Among those types of simulator, ASPEN PLUS has successfully demonstrated an excellent performance in chemical engineering process[2]. It is due to the availability of sophisticated built-in model block, the existence of powerful tool for simulation[3], the accessibility of excellent algorithm for optimization[4] and the capability approach of economic evaluation.

Lately, biodiesel become popular alternative sources of energy because the chemical properties were lessen of black smoke, carcinogenic fumes and sulphur[5]. Besides, the dependence on petroleum can be reduced by replacing it with renewable resources like vegetable oil and animal fat[6]. In addition to that, sustainable provisions of energy toward future generation can be assured. Recently, the variability of chemical process synthesis of biodiesel may facilitate to the best selection of chemical reaction depends on several conditions. For example, Malaysia and Indonesia are well known producer of palm oil. The utilization of palm oil in transesterification reaction will give better quality of biodiesel known as Palm Methyl Ester (PME). Due to that condition, Malaysia and Indonesia have a good chance to emphasize PME in international market. At the same time, it will offer an attractive business and operational opportunities which recommended for helping developing countries' economies to grow.

In 2010, a new reaction scheme of transesterification process was reported by Zhang et. al. and found it socially advantageous to arouse great attention in biodiesel industrial development. The reaction was involved a transesterification process between palm oil and Dimethyl Carbonate (DMC) at catalysis of heterogeneous base. The kinetic reaction was developed in experimental scale and the highest PME obtained is 96.2%[7]. The advantages of DMC transesterification reaction are i) it can produce valuable byproduct which is Gycerol Carbonate (GC), ii) it can enhance the mass transfer in the reaction, iii) it can easily shift the reaction equilibrium toward formation of PME, iv) it can accommodate safer chemical plant v) it can reduce energy consumption vi) it can lead to easy separation and finally vii) it can reduce the cost operation to buy a solvent.

Due to above reasons, DMC based reaction has great potential towards sustainability of energy sources especially in transportation sector. Statistically, the demand of PME keep increasingly in advanced, due to increment number of transportation. Higher demand of PME might require a scale up of the process to industrial scale, which would be 10,000 times greater than laboratory scale. Changing the scale of reaction could lead to differences in mass profile. In practice, scale up can be categorize under some circumstances depend on the quality of the product that be produced. It can be miniplant, pilot plant, demonstration plant and commercial plant. As mentioned, the production of PME is indispensible in biodiesel industry and hence a commercial plant is the best plant to be built. Before going to commercial plant, it is necessary to test the plant at pilot scale because it was hardly to design the full scale reactor directly. In this study, the overview of pilot scale for DMC based reaction is done using ASPEN PLUS. This study is purposely to check the technological feasibility of the process and to serve a number of functions. The function of a pilot plant was summarizing as below[8]:

1. To produce material for evaluation and introduction into the market
2. To define effluent problems and test methods of their solution
3. To check the feasibility of using batch operation
4. To check effect of built-up impurities and other long-term effect

5. To check whether the process can be "scaled-up" or not
6. To check materials of construction
7. To obtained design information for difficult unit operations
8. To check that no important factors have been overlooked or misinterpreted
9. To obtain the confidence of those allocating the capital by showing that the process is technically and economically feasible.

2. METHODOLOGY

Simulation model for DMC transesterification reaction is developed by using ASPEN PLUS. The procedure involved defining chemical components, selecting a thermodynamic model, determining plant capacity, choosing proper operating units and setting up input conditions. The major input conditions that need to be specified are flowrate of reactant, temperature and pressure. For DMC transesterification reaction, the components properties such as DMC and GC are mostly available in ASPEN component library. Otherwise, palm oil and palm methyl ester were defined as triolein and methyl oleate respectively due to property similarity of the components [9, 10]. On the other hand, the selection of the right physical property methods is required to successfully simulate the reaction. There are four factors that need to be considered in choosing property methods; 1) the nature of the properties of interest, 2) the composition of the mixture, 3) the temperature and pressure range and 4) the availability of parameters. Based on Fig. 1 and consideration of all factors, the suitable property methods for this reaction are non-random two-liquid (NRTL) and universal quasi-chemical (UNIQUAC) model. After that, specifications of reaction kinetics are made by using available data from Zhang et. al. and the types of reaction kinetic stipulate is POWERLAW. Details information was summaries in Table 1.

Table 1 Kinetic Values

Reaction Name	DMC Transesterification Reaction
Reaction Type	POWERLAW → Kinetics
Reaction Stoichiometry	TRIOL-01 + 2 DIMET-01 → 3 METHY-01 + 1:3-D-01
Reacting Phase	Liquid
Kinetic Model	Pseudo First-Order Reaction
Power Law Kinetics Expression	K: 2.1×10^{-7} sec^{-1} E: 18.153 kcal/mol [Ci] basis: Molarity

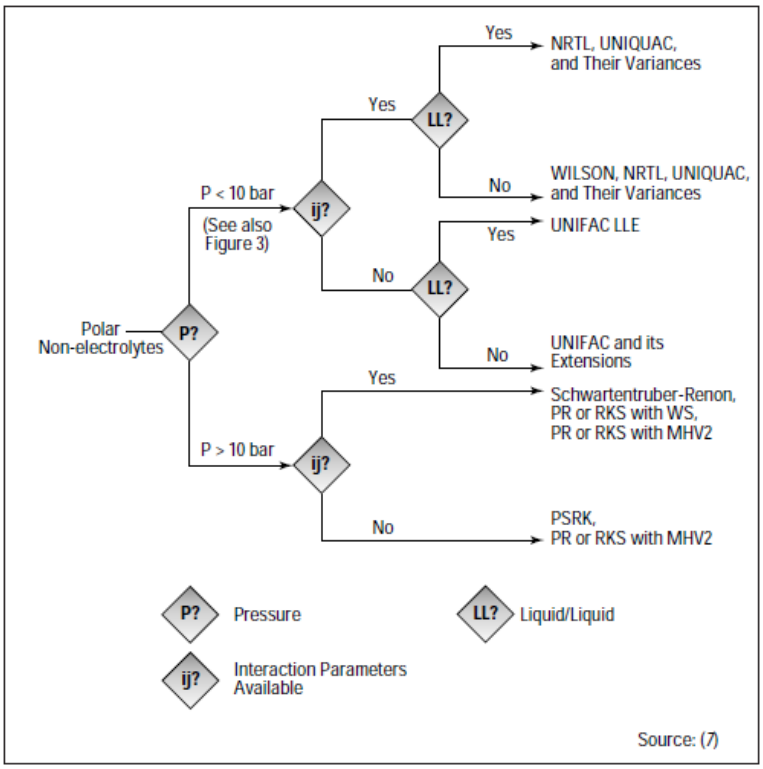

Fig. 1: Options for polar and nonelectrolyte components.

3. RESULTS AND DISCUSSION

In this section, the result obtained has been scaled up to pilot scale, by factor of 660. The volume of batch reactor after scale up was estimated around 200 L. The different in term of mass and concentration of PME can be seen on Figure 3.1 and Figure 3.2. Based on Figure 3.1, the mass of PME produced for laboratory scale is too small which is 77.27 g. As for pilot scale, the mass of PME is large which approximately 51.06 kg. A big gap in the mass of PME between laboratory scale with pilot scale does not affect the concentration of PME as shown in Figure 3.2. This is happen because the volume for both scale are differ. In pilot scale, the larger mass of PME produce is divided by a larger volume of mixture could give the similar concentration as laboratory scale. Therefore, it is proved that the pilot scale developed is 100% matched and in agreement with experimental results.

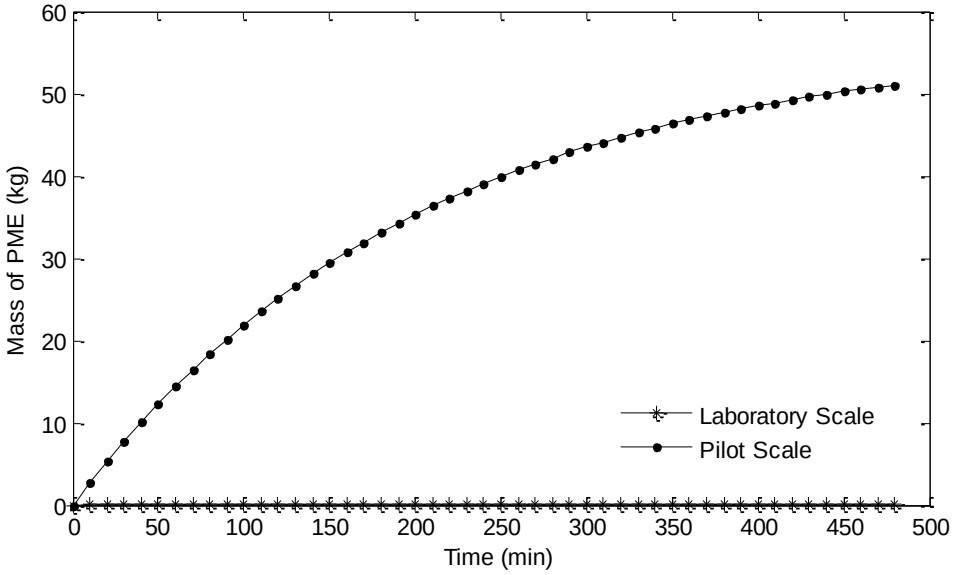

Fig. 2 Mass of PME vs Time

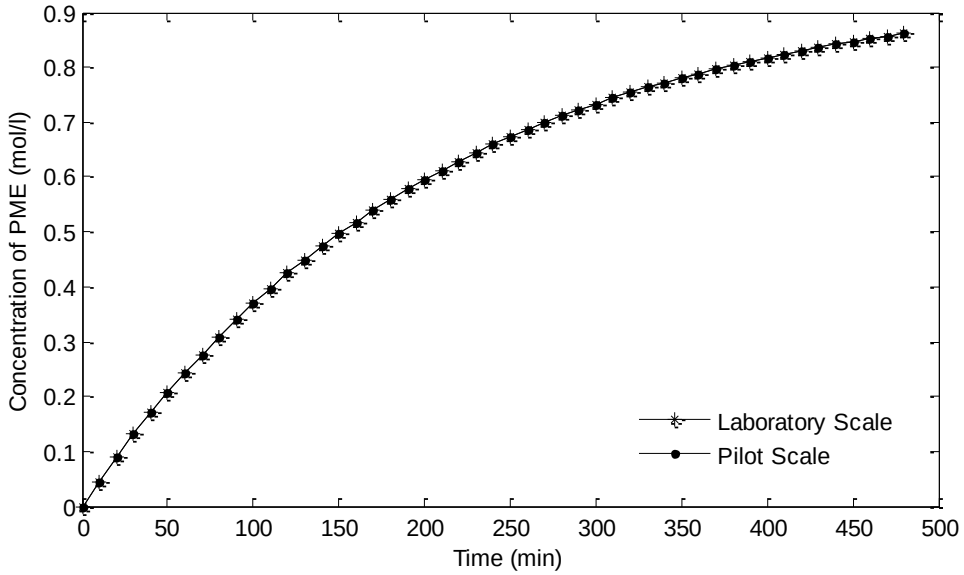

Fig 3. Concentration of PME vs Time

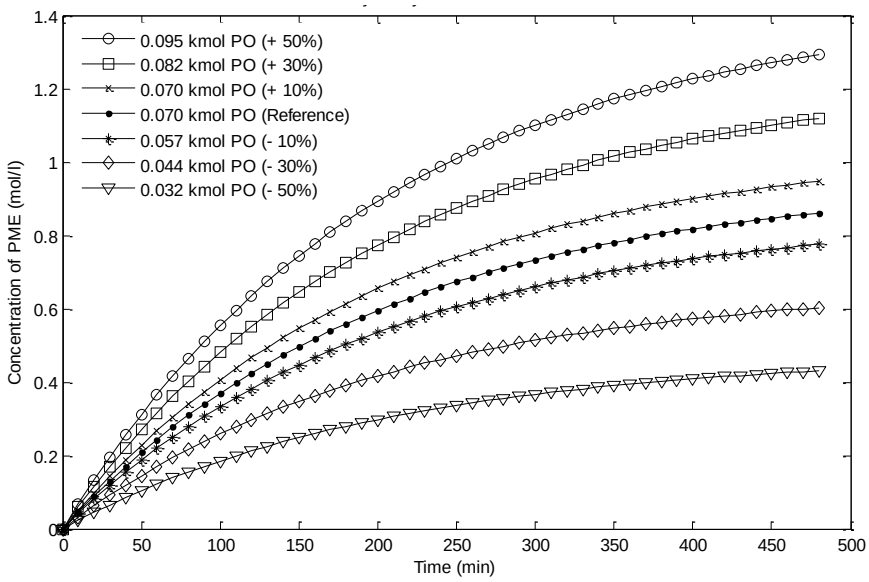

Fig 4. Sensitivity Analysis of Amount of Palm Oil

Figure 3.3 shows the different amount of palm oil used for DMC transesterification reaction. As results, the concentration of PME gives significant change toward this variable. As seen from figure, the concentration of PME was increase when the amount of palm oil increased and vice versa. Moreover, the reaction does not reach equilibrium at 480 min which means that the reaction can produce higher concentration of PME after 480 min.

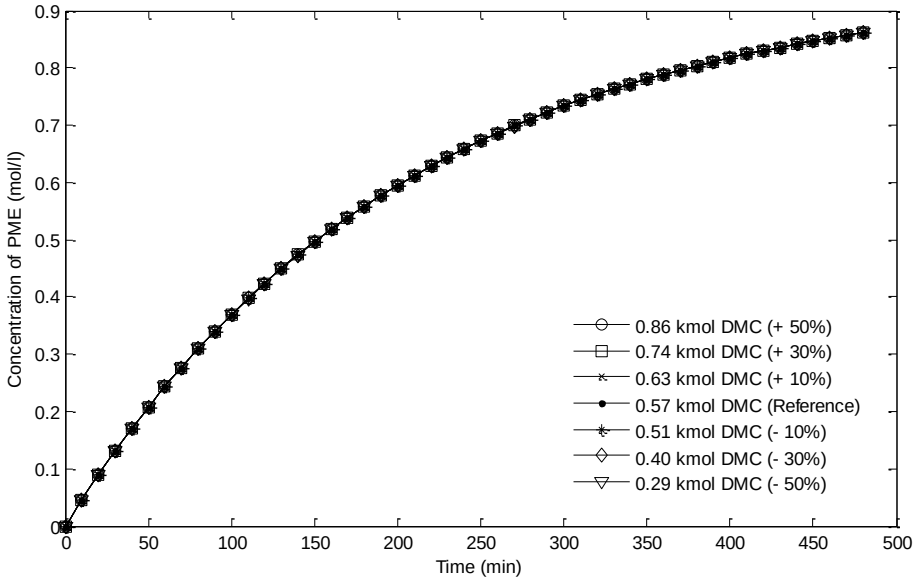

Fig 5. Sensitivity Analysis of Amount of DMC

Further analysis was performed toward amount of DMC. Figure 3.4 shows that, the PME concentration does not vary when the amount of DMC is varied. Therefore, amount of DMC can

be disregarded from this reaction because it apparently does not give any impact on concentration of PME.

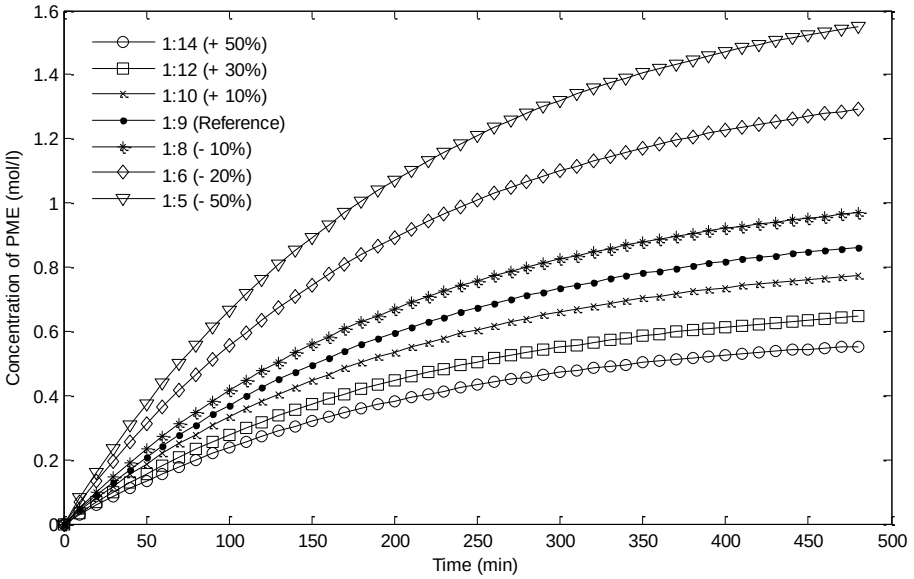

Fig 6. Sensitivity Analysis of Amount of Molar Ratio

As can be seen in Figure 3.5, the sensitivity of molar ratio shows significant change on production of PME. It is observed that, the PME concentration was decrease when the molar ratio is increase. It happens because, at higher molar ratio, the amount of palm oil that has been utilized is smaller and too much excess of DMC present on the reaction might cause reverse reaction to occurred. Due to that condition, molar ratio is one of the important variables that need to be considered.

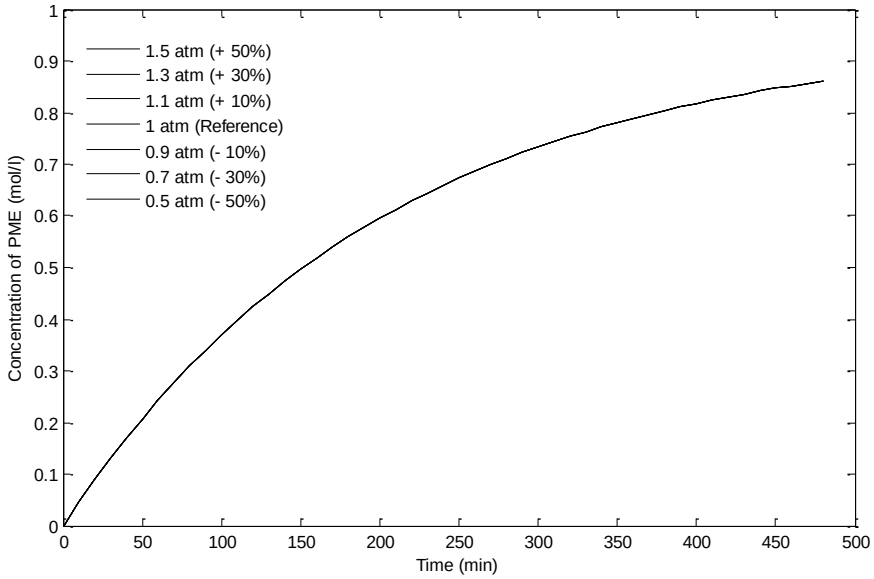

Fig 7. Sensitivity Analysis of Amount of Reactor Pressure

Figure 3.6 represent the respond of PME concentration at different reactor pressure. The results obtained are similar with Figure 3.4. It shows insignificant change toward concentration of PME and the maximum generalization of PME is 0.86 mol/l.

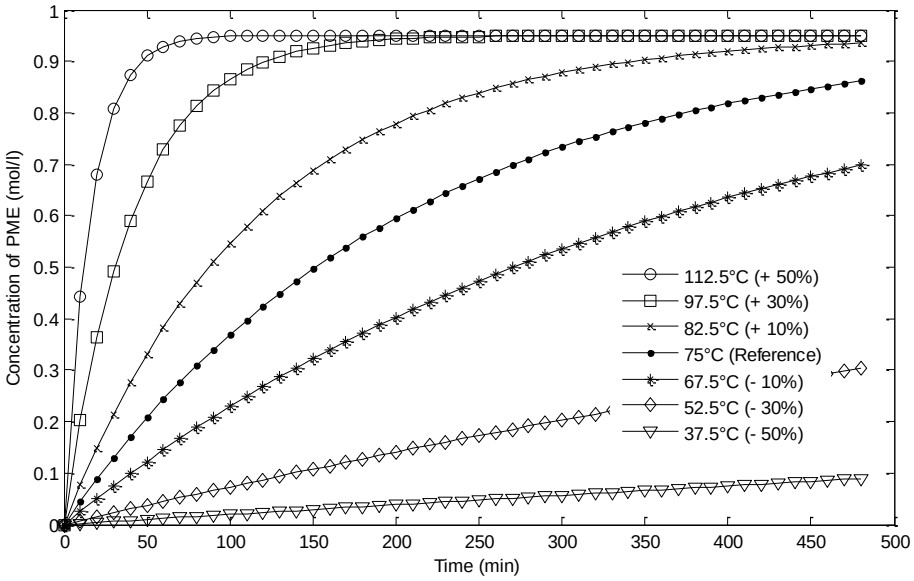

Fig 8. Sensitivity Analysis of Amount of Temperature of Reactor

Figure 3.7 illustrate the performance of PME production at different temperature of reactor. At 37.5^{o}C, the concentration of PME was the lowest. Meanwhile, at 112.5^{o}C, the concentration of PME was the highest and reaches steady state within 220 min. Therefore, changes in reactor temperature give significant impact on productivity of PME and reaction time.

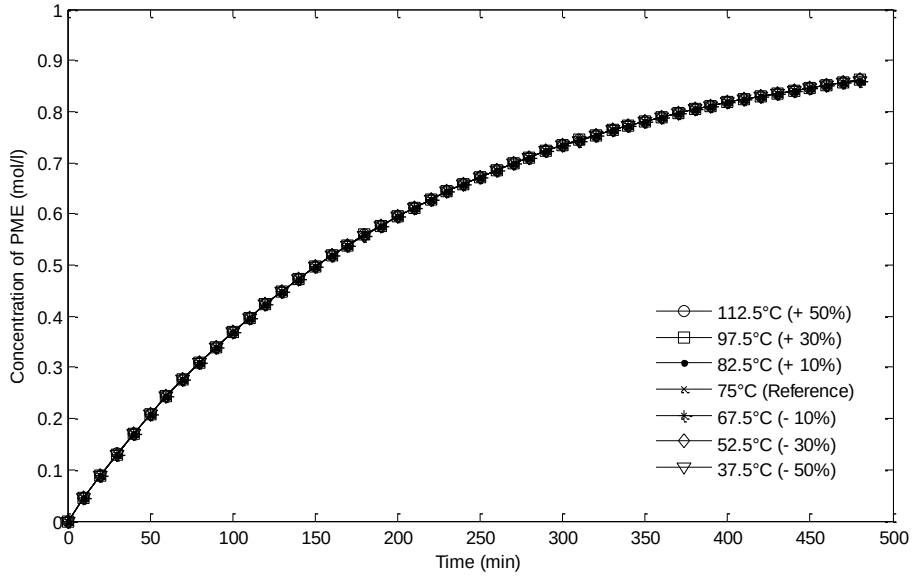

Fig 9. Sensitivity Analysis of Amount of Temperature of Stream

Finally, the sensitivity analysis evaluation is based on temperature of inlet stream. Based on Figure 3.8, the results obtained from Aspen Plus give that the maximum concentration of PME produce was 0.86 mol/l. It also reported that, the amount of PME does not change when the temperature of stream being change. Therefore, this parameter can be ignored.

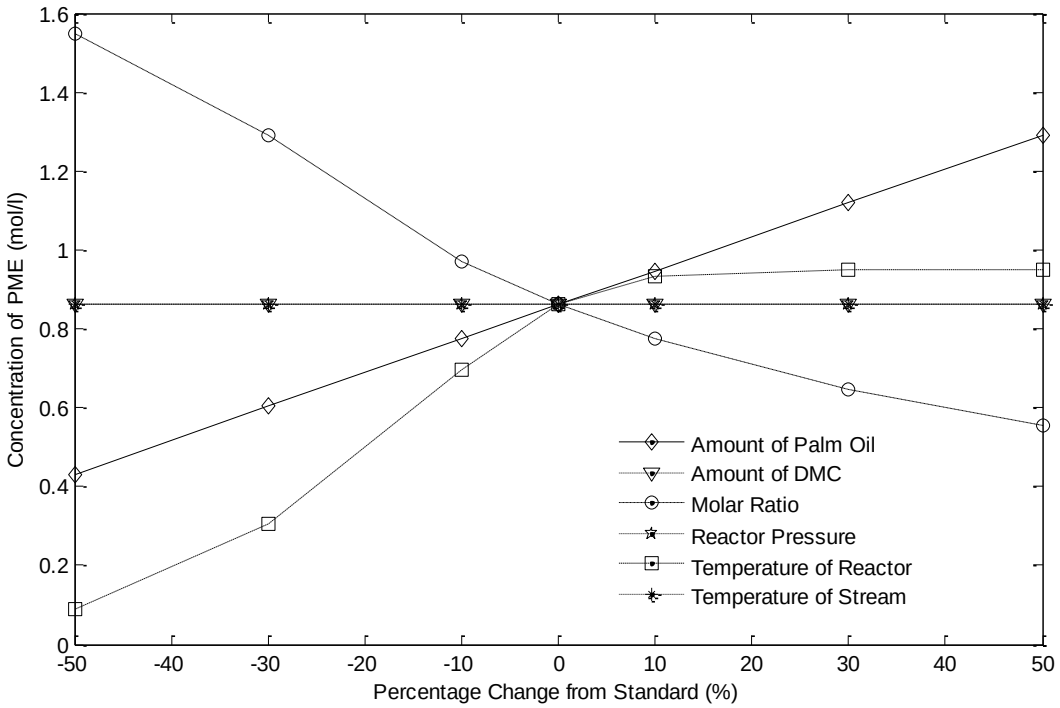

Fig 10. Concentration of PME vs Percentage Change from Standard

Figure 3.9 show a summary for all parameter studied by using a spider diagram approach. This diagram can easily display the level of single activity done in sensitivity analysis. The changes parameters were demonstrated in percentage form (±50%, ±30% and ±10%). Based on the figures, the parameters that give significant change on concentration of PME are amount of palm oil, molar ratio and temperature of reactor. On the other hand, the amount of DMC, reactor pressure and temperature of inlet stream show insignificant changes toward concentration of PME. Finally, this diagram was useful to determine parameters that would results in positive or negative of objective function in optimization.

4. CONCLUSION

In this work, DMC transesterification reaction was modeled to pilot scale by using ASPEN PLUS. The model developed is in good contract with experimental results. A simulation study for pilot scale of DMC transesterification showed that the quality of PME produced was the same as experimental results but the amount of PME produced was larger. Additionally, a sensitivity analysis study was prepared in this work by considering six common parameters which are amount of palm oil, amount of DMC, molar ratio, reactor pressure, temperature of

reactor, and temperature of stream. Among those parameters, amount of palm oil, molar ratio and temperature of reactor were significantly affected the concentration of PME, while others are not. Overall, improvements of DMC transesterification reaction can be done in future, since the behavior of the process has been revealed in this paper.

5. ACKNOWLEDGEMENTS

Financial support from Ministry of Higher Education (MOHE), Malaysia through the MyMaster scholarship to the first author and Universiti Sains Malaysia through RU grant are greatly acknowledged.

6. REFERENCES

1. Process Simulation Program, 1979. A comprehensive flowsheeting tool for chemical engineers. *Computer of Chemical Engineering*, 3, 329.
2. Radu M. I. and Anton A. K., 2013. Optimal design, dynamics and control of a reactive DWC for biodiesel production, *Chemical Engineering Research and Design*.
3. Smejkal Q. and Soos M., 2002. Comparison of computer simulation of reactive distillation using ASPEN PLUS and HYSYS software, *Chemical Engineering and Processing*, 41, 413–418.
4. Zhao M., Li Y., and Sun S., 2011. Analysis and optimization of two-column cryogenic process for argon recovery from hydrogen-depleted ammonia purge gas, *Chemical Engineering Research and Design*, 89, 863-878.
5. S. Jansri, S.B. Ratanawilai, M.L. Allen and G. Prateepchaikul, "Kinetics of methyl ester production from mixed crude palm oil by using acid-alkali catalyst," *J. Fuel Process. Technol.*, vol. 92, pp. 1543-1548, 2011.
6. J.V. Gerpen, "Biodiesel Processing and Production," *J. Fuel Process. Technol,*. vol. 86, pp. 1097-1107, 2005.
7. L. Zhang, B. Sheng, Z. Xin, Q. Liu and S. Sun, "Kinetics of transesterification of palm oil and dimethyl carbonate for biodiesel production at the catalysis of heterogeneous base catalyst," *J. Bioresource Technol.*, vol. 101, pp. 8144-8150, 2010.
8. Zlokarnik, M., Ger. Chem. Eng 7 (1984), 150-159 : Scale-Up in Process Engineering.
9. Y. Zhang, M.A. Dube, D.D. McLean and M. Kates, "Biodiesel production from waste cooking oil: 1. Process design and technological assessment," *J. Bioresource Technol.*, vol. 89, pp. 1-16, 2003.
10. Y. Zhang, M.A. Dube, D.D. McLean and M. Kates, "Biodiesel production from waste cooking oil: 2. Economic assessment and sensitivity analysis," *J. Bioresource Technol.*, vol. 90, pp. 229-240, 2003.