CHAPTER VII

CONCLUSIONS AND RECOMMENDATION

7.1. Conclusions

7.1.1. Effects of co-solvents on the production of biodiesel from PKO in SCM

The reaction of co-solvent with other reactants (vegetable oil and methanol) did not occur at supercritical conditions. However, the addition of liquid co-solvents did not allow the reaction to be completed at milder conditions due to the critical properties of the co-solvents, which are close to those of methanol. The addition of co-solvents (THF and hexane) in this process did not show either negative or positive effects on methyl esters content, thus THF and hexane are appropriate co-solvents for reduced viscosity of PKO in the scale-up reactor.

7.1.2. Effects of additional parameters and scale-up reactor optimization

The transesterification of PKO in SCM achieves equilibrium after 30 min reaction time in a 250-mL reactor and less than 10 min in a 5.5-mL reactor. The methyl esters content from crude vegetable oil was slightly lower than that of refined vegetable oil, plausibly because of the lower triglyceride content. The delayed and deficient quenching time had no significant effect on ME content for biodiesel production with SCM in both 5.5-mL batch and continuous reactor.

For scale-up reactor optimization, the optimal conditions (ME content over 96.5 %) located with temperature range of 310 to 330 °C, pressure range of 17.5 to 18.5 MPa and methanol to oil molar ratio of 35:1 to 40:1. However, the actual highest ME content of approximately 93 % was observed from the scale-up reactor probably due to the optimal range in the regression model was narrower than the controllable range of the operating parameters.

7.1.3. Residence time estimation method

The simple compressible flow model as a tool for residence time estimation was successfully derived and checked within 280 to 350 °C, 20 to 35 MPa and 12:1 to 42:1 methanol to oil molar ratio. The PR-MHV2-UNIQUAC thermodynamic model with adjusted binary interaction coefficients was employed to evaluate the development of the compressibility factor during reaction progress along the reactor. Although the thermodynamic model fitting of VLE from literatures had maximum relative error of approximately 10 % for glycerol + methanol VLE, the simple compressible flow model was proven to be adequate at temperature below 320 °C.

Nevertheless, it prediction was over-estimated values due to the interfering of thermal degradation reaction at temperature over 320 °C, that were not taken into account in this model.

In addition, the simple compressible flow model demonstrated that the chemical kinetics of biodiesel production with SCM was retarded by the development of the compressibility factor along the reactor, especially at low methanol to oil molar ratio. In conclusion, the residence time can be estimated by integration of molar volume of reaction mixture which calculated by the PR-MHV2-UNIQUAC thermodynamic model.

7.2. Recommendation

In this work the continuous production of biodiesel with SCM in a tubular reactor was explored. Some issues have arisen from this exploration and warrant further researches as following aspects:

7.1.1. Thermal degradation of unsaturated fatty acids (UFA) in SCM

Since thermal degradation reaction of UFA plays an important role on biodiesel production in SCM, but the details of this reaction especially in SCM are limited. Furthermore, thermal degradation of UFA in SCM under high pressure is somewhat difference from the degradation at atmospheric pressure or pyrolysis. Even though thermal degradation reaction can avoid by keep operating temperature in range of 270 – 300 °C or use the gradual heating technique to maintain the maximum ME content, but these approaches reduce the rate of transesterification and the simplicity of process which are strong points of biodiesel production with SCM. On the other hand, thermal degradation of UFA has been reported to improve the fuel properties of biodiesel, except the ME content, that is produced from SCM process at temperature over 400 °C. Therefore, the additional studies on thermal degradation of UFA in SCM are interesting to improve the biodiesel production with SCM process.

7.1.2. Mixing intensity of a tubular reactor for biodiesel production with SCM

Effect of mixing intensity for biodiesel production with SCM has been not came to full attention in either batch or continuous studies, whereas it affect on ME content as mention in Section 2.4.2.5. For instance, the better mixing intensity allows the reaction complete shortly in batch reactor at constant temperature. Consequently, a tubular reactor performance for biodiesel production with SCM might be enhanced by assisting of some mixing equipment such as pre-mixing tank or static mixers.

7.1.3. Residence time distribution in a tubular reactor for biodiesel production with SCM

The effect of compressibility changes on ME content in biodiesel production with SCM has been successfully discovered in this work, while dispersion effect which generally influences the efficiency of a tubular reactor did not take into account. The dispersion effect can be determined experimentally by residence time distribution measurement. However, the residence time distribution measurement requires more precise equipments such as real-time temperature, pressure, flow rate and tracer monitoring system. Thus, further researches on residence time distribution in a tubular reactor could perform the batter understanding on the biodiesel production with SCM.