CHAPTER 5 CONCLUSIONS

5.1 Conclusions

A modelling approach to predict the solubility of biomolecules in supercritical carbon dioxide with cosolvents was presented. The Constantinou-Gani and Joback group contribution methods were used to estimate solute pure component properties and the LKP and MMM equations of state to determine solute solubilities. The ternary solute-SCF-cosolvent systems were modelled as pseudo binary systems with the SCF-cosolvent binary pair being modelled as a single pseu do component using Kay's mixing rules to estimate the pseudo component properties. Twenty-one (21) systems consisting of polar and nonpolar solutes and cosolvents were tested over a range of temperatures, pressures and cosolvent concentrations. The AI was found to be a very useful indicator of which equation of state is the most appropriate. When the AI was $\leq$ 0.3 the MMM EOS resulted in a much better prediction of the measure solubility otherwise the use of the LKP equation of state was better. When the so-called AI criterion was followed, the AARD ranged from 0.5% to 25.5% with an average of 10.0% however, when the AI criterion was not followed the error ranged from 9.6% to 99% with an average of 69.0%. Finally, Kay's mixing rules were shown to be appropriate to estimate solvent properties in the ternary mixture. The results and investigations of this work may be helpful in applying EOS models, suitable for predicting solid-gas equilibrium in cases where experimental data are not available. In future work, we aim to expand the present model to multi-component of solutes including other mixing rules for more precise results.

The shrinking core model with appropriate solubility equations and transport properties was applied to predict the behaviour of dynamic supercritical fluid of isoflavones from soybean, using aqueous methanol as the cosolvent, in a packed bed. The transport steps involved in extraction are pore diffusion, mass transfer at the solid-fluid interface, and axial dispersive transport in the fluids. Prior knowledge about estimated solubility for isoflavones in the fluids from equations of state and calculated physical properties from group contribution methods and available correlations were used. Even though, the experimental solubility data was not available but a reliable computer technique, based on interval analysis, was applied to identify the correct phase equilibrium. The kinetic data depended on five main factors: pressure, temperature, fluid flow rate, cosolvent

concentration, and particle size was compared with the model prediction. Supercritical seed-isoflavones extraction processes can be effectively described with the mathematical model presented in this paper. The model was validated by experimental data. The results of this validation show a good agreement (AARD = 6.54 %) between the experimental data and the simulations. To investigate the contribution of each parameter involved in the model, transport parameters such as Q, ρ_m, μ_m, k_f, D_e, D_L, and C_{sat} were varied. The model shows that the axial dispersion coefficient does not affect the results of the simulations and hence the axial dispersion phenomenon could be removed from the model. In term of sensitivity, the following descending ranking can be suggested: the film mass transfer coefficient, the solubility, the effective diffusion coefficient, and the supercritical fluid flow rate. The present model could be used as a tool for operational optimization and scaling up of $SCCO_2$ extraction process. The extractor configuration was investigated using the analysis of residence times. It was showed that the process with two extractors connected in series had advantages over other configurations.

5.2 Recommendations

The following recommendations are made for possible future study.

1. The accuracy of solubility predictions were based especially on the physical properties estimated using group contribution methods. Some of the results were less satisfactory for complex and multifunctional solids. Solid solubility is limited by the availability of group contribution parameters between some special groups and the gas. New group contribution methods developed from bunch of data with heavy biomolecules or complex compounds would solve this problem.

2. Sublimation pressure and solid molar volume must also be taken to consideration for improving the estimation. Their affect significantly to the predicting solubilities as mentioned before in Equation 3.7.