Prediction of crude palm oil solubility in hot compressed water using thermodynamic model prediction

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Abstract. The solubility of crude palm oil in hot compressed water was predicted using thermodynamic model prediction. The solubility data was used to understand the phase equilibria in the separation process. In this study, the modified UNIFAC method was used. The solubility prediction using the modified UNIFAC involves several parts that are; pseudo TAG structure development, GC parameter determination and solubility calculation. Pseudo TAG structure was developed based on the crude palm oil composition analyzed using GC-FID. No solubility of CPO in HCW was obtained through this method. Meanwhile, the solubility of HCW in CPO increases from 8.76 to 13.38 mole (%) from the temperatures of 120 to 180°C respectively. The solubility prediction using this method is beneficial due to the less experimental data and inexpensive.

1. Introduction

Phase equilibria is an important perspective that needs to be explored in order to understand the separation process. From this phase equilibria, the distribution of the component can be explained in term of solubility. The efficiency of the process also can be evaluated by comparing the solubility obtained from the experimental data. Phase equilibria is developed from the compounds solubility in the solvent which can be obtained from binary experimental route or thermodynamic model prediction. Generally, there are many experimental routes to obtain phase equilibria data in order to understand the phase behaviour for liquids [1]. The experimental routes includes the static, recirculation and continuous flow methods. Among that, the static method offers the most accurate data compared to the others. However, this method is difficult, expensive, time consuming and is unattainable for the thermo labile compound [2,3]. Therefore, the predictive molecular thermodynamic model is a more preferable method for this purpose. It is a computational method for the phase equilibria prediction which helps researcher to develop the system without or less experimental input. This is beneficial especially for the high pressure process [3] and high molecular weight solute such as triglyceride (TAG). Phase equilibria prediction for systems containing hot compressed water (HCW) is very limited with less than 10 publications found in the literature [4,5,6]. This method includes the empirical model, Hansen solubility parameter, Universal Quasi Chemical Functional Group Activity Coefficient (UNIFAC) and COSMO-RS methods [5,6]. Syed Jaapar et al. (2015) had applied COSMO-RS method to predict the solubility of 6-gingerol and 6-shogaol in HCW with or without the addition of ethanol as entrainer [6]. In their study, the predictive capability of the method had been
validated based on selected hydrocarbons 72 which have similar functional groups with the solute of interest due to the limited experimental solubility data of the compound and obtained AAD not more than 0.2648 [6]. Fornari et al. (2008) applied various versions of UNIFAC model and proposed a modified A-UNIFAC model with temperature dependent associating energy to predict the solubility of polycyclic aromatic hydrocarbon (PAH) in HCW [4]. An average reduction of absolute average standard deviation (AASD) is obtained from 27.7 to 6.1% by the introduction of temperature dependent associating energy in the A-UNIFAC model [4]. However, the study also found that the optimized modified UNIFAC (Dortmund) model had provided the best representation of PAH solubility in HCW compared with UNIFAC, A-UNIFAC and modified A-UNIFAC [4]. Carr et al. (2010) also utilized the modified UNIFAC proposed by Fornari et al. (2008) with some modification on carboxylic acid-water and aromatic hydrocarbon-water interaction parameters to predict the naproxen solubility in HCW between 130 to 170 °C and obtained an average deviation of 6% [5]. Therefore, in this study the modified UNIFAC model are used to predict the solubility of crude palm oil (CPO) in hot compressed water (HCW).

2. Methodology

In order to predict the solubility of crude palm oil (CPO) in hot compressed water (HCW), the modified UNIFAC model was used [8]. The characterization of the component to represent the CPO is one of the important criteria in the solubility prediction since that CPO consist up to 14 different type of triglyceride (TAG). In this study, pseudo-TAG structure was used as proposed by Espinosa et al (2002). The methods show a good performance history and easier method in comparison with the multicomponent system approach. The solubility prediction using the modified UNIFAC involves several parts that are; pseudo TAG structure development to represent CPO, GC parameter determination and solubility calculation as summarized in Figure 1.

2.1. Analysis of CPO using Gas Chromatography -Flame Ionization Detector (GC-FID)

The overall CPO analysis including FFA, MAG, DAG and TAG was conducted using GC-FID (Agilent technologies, USA) based on the AOCS method Cd 11b-91. This analysis was conducted at Sime Darby Research Sdn Bhd, Carey Island, Selangor, Malaysia. In this method, an overall composition of CPO was screened based on the carbon number and composition of fatty acid consist in CPO was identified and used to develop the pseudo-TAG structure for CPO.

2.2 Calculation of solubility

From the analysis of TAG composition using GC-FID, the pseudo TAG structure was developed using the equations 1, 2 and 3 as shown in Figure 1 to represent the CPO. This pseudo structure was splitted based on its structural group to predetermine the GC parameter [8]. The GC parameter would be uses to calculate the ln γ as shown in Figure 1. The γ would be used to calculate the mole fraction of the CPO in HCW phases or vice versa using equation 4.

\[ (x_iy'_i) = (x_iy_i) \]

(4)

where \( x_i \) is mole fraction of component \( i \), \( y'_i \) is activity coefficient and superscripts ‘ and “ is mean phase 1 and phase 2 or in this study ; HCW phase and CPO phase. Then, calculated \( x_i \) was used to constructed the phase diagram for the system containing HCW and CPO. The ICAS 13.1 software (CAPEC, Dermark) was uses to calculate this solubility.
Figure 1: Calculation of TAG solubility in HCW using modified UNIFAC

\[(\text{CH}_2\text{COO})_2\text{CHCOO}(\text{CH} = \text{CH})_n(\text{CH}_3)_m(\text{CH}_2)_n(\text{CH}_3)\]  

\[n = \sum_{t=1}^{N} n_t x_t \quad (2)
\]

\[m = \sum_{t=1}^{N} m_t x_t \quad (3)
\]

\[X_m = \frac{\Sigma_i v_m^{(i)} x_i}{\Sigma_i \Sigma_n v_n^{(i)} x_i} \quad r_i = \frac{\Sigma_k v_k^{(i)} R_k}{\Sigma_i \Sigma_n v_n^{(i)} x_i} \quad (1)
\]

\[q_i = \frac{v_k^{(i)} Q_k}{\Sigma_j v_j^{(i)} x_j} \quad \Theta_m = \frac{Q_m X_m}{\Sigma_i Q_i X_i} \quad \psi_{nm} = \exp \left( - \frac{a_{nm} + b_{nm} T + c_{nm} T^2}{T} \right)
\]

\[V_i' = \frac{r_i^{3/4}}{\sum_j r_j^{3/4} x_j} \quad F_i = \frac{q_i}{\Sigma j r_j x_j}
\]

\[\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (4)
\]

\[\ln \gamma_i^C = 1 - V_i' + \ln V_i' - 5 q_i \left( 1 - \frac{V_i}{F_i} + \ln \frac{V_i}{F_i} \right)
\]

\[\ln \gamma_i^R = \sum_i v_k^{(i)} (\ln \Gamma_k - \ln \Gamma_k^{(i)})
\]

\[\ln \Gamma_k = Q_k \left[ 1 - ln \left( \sum_m (\theta_m \psi_{mk}) \right) - \sum_m \theta_m \psi_{km} \right]
\]
3 Result and discussion

3.1 Analysis of fatty acid using GC-FID

The fatty acid composition of CPO obtained from HCWE process is tabulated in Table 1. As shown in Table 1, the HCWE CPO consist a slightly higher saturated fatty acids at 50.630.15% in comparison with commercial CPO at 49.91% [9]. However, the compositions are still in the range of the Malaysian CPO (Corley and Tinker, 2003b).

3.2 Calculation and pseudo TAG structure development for crude palm oil (CPO)

Table 1 is shows the calculation of m for CH=CH functional group and n for CH₂ functional group using fatty acid composition in CPO corresponding to the simple TAGs. For example, P(C16:0) represent Tripalmitin (PPP) TAGs.

| Fatty acid | x_i | n | m |
|------------|-----|---|---|
| La (C12:0) | 0.03 | 30 | 0 |
| M(C14:0)   | 1.59 | 36 | 0 |
| P (C16:0)  | 44.89 | 42 | 0 |
| S (C18:0)  | 4.12 | 48 | 0 |
| Ar (C20:0) | 0.15 | 54 | 0 |
| Pi (C16:1) | 0.87 | 36 | 3 |
| O (C18:1)  | 37.16 | 42 | 3 |
| L (C18:2)  | 11.55 | 36 | 6 |
| Li (C18:3) | 0.35 | 30 | 9 |

From Table 1, the values of 35.5~36 and 1.9~2 were obtained for n and m respectively. Therefore, the Pseudo-TAG molecule to represent CPO is [(CH2COO)2CHCOO](CH = CH)2(CH2)3(CH3)3. The van der Waals sphere representation for this molecule is shown in figure 2.

Figure 2: Pseudo-TAG structure to represent the crude palm oil
3.3 Solubility of crude palm oil (CPO) in hot compressed water (HCW)

The predicted solubility of CPO in HCW and HCW in CPO is shown in Figure 3. This solubility was calculated between the temperatures of 60 to 180°C. Water was set as liquid phase at all conditions. No solubility of CPO in HCW was obtained though the this method represent as one solubility line in Figure 3. This indicated that CPO was completely insoluble in the HCW from the temperature of 120 to 180°C. CPO which mainly consist of TAGs is known insoluble compounds with water due to higher hydrophobic chain length of the acid [10]. Meanwhile, the solubility of HCW in CPO increases from 8.76 to 13.38 mole (%) from the temperatures of 120 to 180°C respectively. This data was slightly lower by about 1.7 folds in comparison with binary experimental data as tabulated in Figure 3 [11]. This showing that the solubility is irrelevant to effect the quality of the CPO due to its lower concentration for less than 0.15% (w/w) and the hydrolysis during the process can be ignored.

4 Conclusion

This paper shows that the thermodynamic model prediction can be used to predict the solubility of CPO in hot compressed water with less experimental data. The experimental measurement of solubility was very difficult and expensive for hot compressed water system. This data is important the understanding of the mass transfer mechanism in separation process.

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