ABSTRACT

Lignocellulosic biomass has been identified as a suitable feedstock for the production of fuels and chemicals. This is required due to the high utilization of fossil fuels which has increased the production of carbon dioxide and had a direct impact on the economic, environmental, political, and life quality of population. Therefore, the current thesis work aims at to dissolve the lignocellulosic biomass and its derived components namely cellulose, hemicellulose, disaccharides and monosaccharides in suitable ionic liquids (ILs). Precise experimental data and reliable theoretical models are basic requirements for the better understanding the dissolution process. In order to evaluate the potential ILs, COSMO-RS model has been used to screen the vast number of ILs for the solvation of cellulose, hemicellulose and simple sugars. Based on the infinite dilution activity coefficients (IDAC) of the components in IL, the selected anions and cations were then visualized by observing their interactions with cellulose, hemicellulose and simple sugars using interaction energies, natural bonding orbital (NBO) analysis and molecular dynamics (MD) simulations. The experimentally obtained solid-liquid equilibria (SLE) values of monosaccharide and disaccharides were then compared with COSMO-RS predicted values. The solubility of monosaccharides and disaccharides in ILs were found to increase with increasing temperature. In addition, the NRTL and UNIQUAC models were successfully correlated with experimental data with a maximum deviation of 5%.

The dissolution order of cellulose and hemicellulose in ILs was primarily determined by the evaluation of hydrogen bonds between the oxygen atom of anion and hydroxyl proton of cellulose/hemicellulose. From this discernible fact, the anion of the IL was observed to play a leading role in the dissolution process as compared to the cation in the solvation process. Eventually, acetate $[OAc]^{-}$ anion and 1-ethyl-3-methylimidazolium $[Emim]^{+}$ cation were found to be good candidates for the dissolution of cellulose and hemicellulose. Furthermore, two categories of cosolvents namely protic and aprotic solvents have been selected in order enhance the cellulose dissolution IL. From MD simulations results, aprotic solvents were found to be a best cosolvent for the enhancement of cellulose dissolution in IL. This was further confirmed by the measurement of solid-liquid equilibria with cellulose. The regenerated cellulose powder was then characterized by Fourier transform spectroscopy (FTIR), X-ray diffraction (XRD) and thermal gravimetric analysis (TGA).

Pretreatment of lignocellulosic biomass is an essential step in a commercial biorefinery. Therefore, the current thesis also investigates the efficiency of two pretreatment pathways of biomass, namely ionic liquid and dilute acid (H_2SO_4) hydrolysis. Both the processes are compared in terms of their composition and enzymatic saccharification efficacy. For the IL process, bamboo was dissolved in [Emim][OAc] at different temperatures (90 °C, 110 °C, 130 °C, and 150 °C) for 3 h. The crystallinity index, thermal decomposition temperature, hemicellulose and lignin content of bamboo found to decrease during [Emim][OAc] pretreatment. The enzymatic hydrolysis rate for IL pretreated biomass was 4.7 times higher than that of the dilute acid. This was primarily attributed to the difference in the crystallinity and delignification in IL process. To improve the enzymatic hydrolysis efficiency of bamboo, combined pretreatment (dilute acid + ionic liquid) process was also employed and compared with IL pretreated cellulose and bamboo samples. The results of the study revealed that IL pretreatment may offer unique advantages compared to dilute acid pretreatment process for bamboo which can produce high sugar yields with IL pretreatment.