

Abstract

Depleting fossil fuels and the increasing energy demand has necessitated the move to alternative renewable forms of energy. Lignocellulosic biomass is a renewable and sustainable source for highly valuable bio-based chemicals and material production in a biorefinery system. The effective fractionation of the main components of lignocellulosic biomass (cellulose, hemicellulose and lignin) into usable forms is a crucial step in unlocking an economically viable, high-value product producing biorefinery. The main concern associated with the conversion of lignocellulose is overcoming biomass recalcitrance using pretreatment while still maintaining a green, cost-effective and energy efficient process. Over the last decade, molten hydrate salts have been used for isolated cellulose dissolution, however very few studies have been done to check their ability in lignocellulosic biomass pretreatment.

The aim of the study was to compare seven molten hydrate salt solvent systems including unary, binary and ternary mixtures of $\text{ZnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ and Urea for the effective pretreatment of corncob in terms of physicochemical properties and pretreatment efficiencies and to optimise these efficiencies. The molten salt hydrate pretreatment systems used in this study are aimed at fractionating the corn cobs biomass into a solid fraction which mostly contains cellulose and lignin as the major components, while the liquid fraction contains hemicellulose as the main component.

The pretreatment experiments were carried out at 70 °C for 60 minutes at a biomass: solvent ratio of 1:10. Physicochemical change after pretreatment was checked by FTIR, XRD and SEM. The most efficient solvent mixture was identified by gravimetric analysis for its ability to fractionate the biomass into a cellulose and lignin rich solid fraction and a hemicellulose-rich liquid fraction. The effect of solvent pretreatment operating variables (temperature, time and solvent concentration) was investigated to maximize cellulose recovery, hemicellulose recovery in the liquid fraction and lignin recovery from the biomass by response surface methodology (RSM) approach using a central composite design (CCD).

Physicochemical analysis showed a decrease in crystallinity and an increase in surface area after the pretreatment in all the MHS solvents tested. This work has successfully shown the use of $\text{ZnCl}_2 \cdot 4\text{H}_2\text{O}$ / Urea, to pre-treat and fractionate corn cob with high recovery of cellulose (100%), low recovery of hemicellulose (42%) and lignin (44%) when compared to the other proposed systems. Through the RSM approach, optimum pretreatment conditions obtained

were: 90 min, 120 °C and concentration of 71.32%/28.68 (w/w) $\text{ZnCl}_2 \cdot 4\text{H}_2\text{O}$ / Urea. At these conditions, the predicted recovery for cellulose, hemicellulose and lignin 99.03%, 27.18% and 72.43% respectively with a desirability of 0.902. The actual recovery was 91%, 29% and 68% for cellulose, hemicellulose and lignin respectively at the same conditions.

For a better understanding of the dissolution kinetics and thermodynamics of cellulose, hemicellulose and lignin dissolution in $\text{ZnCl}_2 \cdot 4\text{H}_2\text{O}$ / Urea solvent system, a kinetic study was carried out. The results reveal the dissolution to be a 1st order kinetics and the obtained activation energy for cellulose, hemicellulose and lignin dissolution were 14.10 $\text{kJ} \cdot \text{mol}^{-1}$, 11.29 $\text{kJ} \cdot \text{mol}^{-1}$ and 7.606 $\text{kJ} \cdot \text{mol}^{-1}$, respectively. The positive values for ΔH and ΔG indicate that the dissolution process for all three components are endothermic and endergonic. The less negative ΔS for hemicellulose dissolution (-0.190; -0.195 $\text{kJ} \cdot \text{mol}^{-1}$) showed that the process of dissolution of hemicellulose occurred more rapidly and produced more stable products. It was concluded that $\text{ZnCl}_2 \cdot 4\text{H}_2\text{O}$ / Urea pretreatment provided a potential way to fractionate lignocellulosic biomass which can improve the effective utilization of all feedstock fractions.