Topic: Liquid Hot Water (LHW) Pretreatment of Agricultural Residues and Evaluation of A Solvothermal Fractionation Process

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ABSTRACT

Several liquid biofuels and chemicals can be produced from biomass via the fermentation of sugars derived through the saccharification cellulose and hemicellulose components of the biomass. Pretreatment/fractionation of the biomass is an essential process that improves carbohydrate digestibility by enzymes. This project investigated the use of compressed liquid hot water (LHW) for the pretreatment of rice straw (RS), bagasse (BG), corn stover (CS) and empty palm fruit bunch (EPFB). The prime aim was to ascertain whether the pretreatment technology could process a feedstock that constitutes these residues. The study extended the investigation using homogeneous acids (H_2SO_4, HCl, H_3PO_4 and oxalic acid) and NaOH catalyst on the pretreatment of rice straw.

The pretreatment of compressed LHW on the agricultural residues was found to be effective in hemicellulose solubilization and the digestibility of the cellulose-enriched residues by enzymatic hydrolysis. Optimum processing conditions were 200°C with reaction times between 5 and 20 min. The maximum amounts of glucose and pentose present in the substrates were 408.8-482.7 mg/g and 81.1-174.0 mg/g respectively. Comparative analysis on the basis of severity factor showed susceptibility to LHW treatment was in the order BG > RS > CS > EPFB. Saccharification of the substrates gave maximum glucose yields of 75.7-82.3% and pentose yields of 27.4-42.4%. The inhibitory compounds furfural (0.77-2.35 mg/mL) and 5-hydroxy furfural (HMF, 0.32-0.67 mg/mL) were under the threshold for ethanolgens. Surface area and structural changes, and the removal of hemicellulose were parameters that impacted on the effectives of the biomass to enzymatic hydrolysis.

The presence of homogeneous acid catalysts (0.25 % w/v) or NaOH (0.25-1.0 w/v) effectively enhanced the enzymatic digestibility of the rice straw substrate at temperatures lower than LHW in the absence of a catalyst. Oxalic acid (0.25 %w/v) was found to be the best promoter at the optimum operating temperature of 160°C for 10 min, as it resulted in the highest glucose yield of 84.2% and the lowest formation of inhibitory furan compounds. This glucose yield is slightly higher than a value of 82.3% obtained from a

substrate that was derived by treatment with the alkali, NaOH (0.25, w/v) at 140°C for 10 min gave a glucose yield of 79.7% after enzymatic hydrolysis. The formation of HMF (0.02-0.26 mg/mL) and furfural (0.13-0.42 mg/mL) was lower than the concentration obtained with the acid-catalysed process. Sodium hydroxide was found to be a higher effective promoter for LHW at lower temperature. This could have been due to the higher acidity of water at increasing temperatures, which neutralized the alkali promoter in the reaction.

The clean fractionation (CF) process (i.e. a single-step fractionation) was studied as an alternative to obtain substrates for enzymatic hydrolysis for subsequent processing. This was conducted with a ternary mixture of water/ethanol/organic solvent that allowed the effective separation of cellulose, hemicellulose and lignin. The process allowed lignin to be recovered with high purity, thus providing the potential to produce high value products from lignin instead of burning it for it energy value. The organic solvents evaluated were methyl isobutyl ketone (MIBK), ethyl acetate (EA) and toluene (TOL), while H_2SO_4, HCL, and H_3PO_4 were the promoters examined. Methyl isobutyl ketone is the current choice of organic solvent used in the CF process. However, ethyl acetate was found low costs and toxicity.

Ethyl acetate was found to be a superior composite solvent to the conventional solvent MIBK by providing higher glucan and lignin yields. Glucan and xylan could be further solubilized and lignin recovery increased at higher temperature and acid concentration. The optimal fractionation conditions were found to be a water/ethanol/ethyl acetate (62.5%:25%:12.5%) mixture using 0.05 M H_2SO_4 at 160°C for 1 h, which gave the separation of a cellulose-enriched solid with 71.4 wt% glucan yield. The maximum of hemicellulose of 71.3 wt% was obtained as sugars, and dehydration products in the aqueous/alcohol phase were minimal. 84.9 wt% of lignin was recovered in the organic solvent phase with no cross-contamination of sugars.

Finally, microwave-assisted heating at 300 W for 1 h resulted in comparable glucan and lignin yields in the respective phases to conventional heating with the advantage of increased pentose yield and lower furan formation in the aqueous phase. The study provided a basis for efficient pretreatment/fractionation strategies for implementation in biorefineries using local agricultural feedstocks.

Keywords: Biorefinery, Enzymatic hydrolysis, Fractionation, Homogeneous catalyst, Lignocellulosic