Topic: Conversion of Eucalyptus Wood Chip to Sugars and Chemicals: Development of Organosolv Fractionation, Hydrolysis and Depolymerization Processes

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ABSTRACT

This research focuses on the fractionation, hydrolysis and lignin depolymerization of woody eucalyptus. Fractionation of lignocellulosic biomass is a primary step for converting multi-structure biomass into biofuels and other industrial products in integrated biorefinery processes. Here, the effects of homogeneous and heterogeneous acid promoters (HNO_3-, HCl-, H_2SO_4-, and H_3PO_4-activated carbons) on a single-step aqueous organosolv fractionation of eucalyptus wood chips were studied and optimized. The optimized process contained 16.7% w/v biomass in a ternary mixture of methyl isobutyl ketone:methanol:water (25:42:33) with 5% AC-H_3PO_4 and incubated at 180 ºC for 60 min. Under these conditions, 41.2 wt.% cellulose was obtained in enriched solid pulp with the average glucan content of 75.9%. The majority of the hemicelluloses was hydrolysed into the aqueous-methanol phase, which contained 17.8 wt.% monomeric xylose and xylooligomers while 13.7 wt.% lignin was separated into the organic phase. The heterogeneous acid-promoter process is a potent alternative to corrosive homogeneous acids for lignocellulose fractionation in integrated biorefineries. Then, catalytic hydrolysis of woody eucalyptus with sulfonated carbon-based (SCB) catalysts prepared from three different carbon precursors (*i.e.* xylose, glucose, sucrose, and activated carbon) was studied under hot-compressed water (HCW). It was found that the reaction with sulfonated-sucrose shows the greatest performance, from which highest C_5 and C_6 sugar yields with less formation of unwanted by-products (*i.e.* furans, and 1,6-anhydroglucose (AHG)) were achieved at 200°C with 5 min reaction time. Furthermore, alkaline pretreatment and/or organosolv fractionation prior to the catalytic hydrolysis in the presence of SCB catalyst significantly improved the catalytic hydrolysis activity due to efficiently remove lignin, reduce hemicellulose and destroy the structure of cellulose. Apart from SCB catalysts, AC-H_3PO_4 (an acid promoter for organosolv fractionation) also showed great hydrolysis performance under HCW, from which high sugar yields with low unwanted by-product

formations can be achieved at 220°C with 5 min reaction time. The great benefit of AC-H_3PO_4 is its possible use for both organosolv fractionation (as acid promoter) and hydrothermal hydrolysis (as acid catalyst), which provides potential for combining fractionation and hydrolysis processes without intermediate material treatment required.

For the lignin proportion, organosolv lignin (OL) obtained from the fractionation was further purified and the solubility upgraded by the alkaline precipitation process (as called treated organosolv lignin; TOL). From the study, TOL was found to enhance higher solubility in organic solvents (*i.e.* tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), and methanol) than OL. Furthermore, the results of the compositional analysis revealed that OL contained small amounts of contaminations (*e.g.,* sugars, ash and sulfur), which came from the degradation of eucalyptus wood chips and H_2SO_4 during the fractionation. After alkaline precipitation treatment, most of these contaminations were efficiently removed without causing any significant structural change, as confirmed by XPS and solid-state NMR analyses. The results of molecular weight and TGA analyses indicated high molecular weight and high residue solid of OL and TOL, which probably specifies the presence of condensed lignin. Lastly, FTIR spectra proved the presence of base insoluble lignin (BIL) contaminants in OL and also confirmed that the alkaline re-precipitation process enables removal of these contaminants without causing significant structural change to the lignin. Then, the depolymerization of TOL was studied at several temperatures and solvent systems (water and methanol-water) with and without the presence of several mesostructured silica catalysts (*i.e.* SBA-15, MCM-41, ZrO_2-SBA-15 and ZrO_2-MCM-41) and phosphate-based catalysts (*i.e.* CoP_2O_6, and CaP_2O_6) The optimum conditions were observed at 300°C using water/methanol (50:50, wt/wt) as solvent in the presence of high acidity SBA-15, from which total syringol yield of 23 wt.% (7.2 wt.% in aqueous fraction and 15.8 wt.% in residual lignin) can be achieved. From GC/MS analysis, the main components in aqueous fraction from the reaction in the presence of SBA-15 included high proportion of syringol (72.1 wt.%) with slight formations of 1,2-benzenediol, benzaldehyde, and ethanone, whereas the main components extracted from residual lignin were syringol (17.2 wt.%) with other multi-compound mixture of polymeric phenolic compounds and high molecular weight of lignin. For the reaction catalyzed by phosphate based catalysts, the optimize condition can be achieved by using CaP_2O_6 at 300 ºC for 1 h with methanol/water mixture (50/50, wt/wt), from which total syringol yield of 16.7 wt.% can be obtained without char formation. The phenol

products mainly consisted of five phenols: syringol, 1,2-benzendiol, benzoic acid, benzaldehyde, and ethanone.

Keywords: Organosolv fractionation, Hydrolysis, Depolymerization, Hot compressed water, Phosphate based catalyst, Mesostructured silica