Valorization of pretreatment wastes from hydrolyzed biomass by slow pyrolysis

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ABSTRACT

Lignocellulosic biomasses are significant storehouse of renewable carbon and are currently deployed in the production of biofuel ethanol. The complex nature of cellulose, hemicelluloses and lignin makes it indispensable to hydrolyze the lignocellulosic feedstock to produce fermentable sugars. Dilute-acid hydrolysis is one of the widely used pretreatments that recover most of the hemicellulose as dissolved sugars and increases glucose yields from cellulose. The hydrolysis residue, a major by-product of biomass hydrolysis, is rich in recalcitrant carbon as most of the cellulosic and hemicellulosic components are released in the hydrolysate during dilute acid and enzymatic pretreatments. The current use of hydrolysis residues is found in power plants for power generation through combustion. Since these residues are carbon-rich materials their effective utilization in the production of value-added compounds through pyrolysis and gasification has a tendency to balance the high cost related in the industrial production of ethanol.

The hydrolysis residues differ in their composition than the untreated biomass, hence it is significant to explore their pyrolytic behavior in order to provide practical insights for industrial application. As a result of pyrolysis, the hydrolysis residues are thermally depolymerized and decomposed into bio-oil, biochar and gas. The yield and composition of pyrolysis products depend on the composition of feedstock and operating conditions for pyrolysis which include temperature, heating rate, residence time and pressure. Slow pyrolysis that has a long residence time and slow-heating rate primary yields biochar and pyrolysis gas unlike fast pyrolysis that occurs at a higher heating rate with a short residence time and generates mostly bio-oils.

In this work, the conversion of hydrolysis residues from forestry (pinewood) and herbaceous (timothy grass, wheat straw) biomass to liquid, gaseous and solid products was studied through slow pyrolysis at 700°C (heating rate of 5°C/min) for 4 h. Specific to the pyrolysis products (biochar, bio-oil and pyro-gas), different analytical characterizations were employed to understand their chemical properties. The structural and compositional features of biochars were characterized using Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), themogravimetric and differential thermogravimetric analysis (TG-DTA), X-ray diffraction (XRD), pH, electrical conductivity and BET surface area. The elemental composition of the bio-chars was assessed using CHNS (carbon-hydrogen-nitrogen-sulphur) and ICP (inductively coupled plasma) analysis. The bio-oils were characterized using CHNS for elemental content, bomb colorimeter for calorific value, FTIR for the functional groups, NMR (nuclear magnetic resonance) and GC-MS (gas chromatography-mass spectrometry) for compositional analysis. The composition of pyrolysis gases was accessed through GC-MS.

As a result of slow pyrolysis, pinewood residues had a high yield of biochar (41.7 wt%) and bio-oil (22.3 wt%), whereas high yield of pyro-gas (28.8 wt%) was found in case of timothy grass residues. Biochars from herbaceous residues presented relatively high amount of alkaline metals (from ICP) as well as Ca and Na containing peaks in their XRD patterns. Calorific values were high for biochar from pinewood residues (30.7 MJ/kg) and bio-oil from timothy grass residues (28.9 MJ/kg). This was because of high lignin content in pinewood biomass. Wheat straw and timothy grass biochar were significantly alkaline in nature compared to pinewood biochar which provide insights for their use as soil amendments in reducing soil acidity. Pinewood biochar was found to be thermally stable with a high calorific value and having stronger C–C bonds than C–H and C–O bonds which suggest its potential to sequester carbon in soil for a longer time. The presence of O–H, C–O and C–H stretching vibrations in the bio-oils indicated the presence of aliphatics, aromatics, polyaromatics, carboxylic acids and its derivatives. This research explores different pyrolytic behavior of hydrolysis residues (a major wastes from biorefining industries) in order to provide practical insights for their industrial applications.