



Formic acid reinforced autohydrolysis of wheat straw for high yield production of monosugars and minimal lignin precipitation

Ömer Özyürek^{a,b,*}, Adriaan van Heiningen^b

^a Forest Product Engineering, Faculty of Forestry, Duzce University, 81620, Duzce, Turkey

^b University of Maine, Department of Chemical and Biological Engineering, Orono, ME, USA

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ABSTRACT

Wheat straw was pretreated at 150 °C for 100 min at a liquor-to-straw ratio of 6 L/kg (oven dry basis) straw using aqueous formic acid (FA) concentrations ranging from 0 to 15 g/L. The results showed excellent sugar and lignin mass balances for pretreatment, and precipitated lignin in the hydrolysate obtained at 15 g/L of FA decreased to 0.31 g/100 g straw compared to autohydrolysis (no FA) of 0.94 g/100 g straw. The average molecular weight of precipitated lignin decreased from 1970 g/mole for autohydrolysis to 710 g/mole at 15 g/L of FA. The monomeric sugar yield during pretreatment improved from 3.83 g/100 g for autohydrolysis to 23.5 g/100 g at 15 g/L FA.

1. Introduction

Wheat straw is an abundantly available agricultural residue in the world at 355 million tons (Sarkar et al., 2012). Presently much of the wheat straw is burnt or left in the field after harvesting. Burning straw has traditionally been done and creates large amounts of air pollutants (Li et al., 2008) and causes health problems. Similar to other biomass, wheat straw consists of cellulose (33–40% w/w), hemicelluloses (20–25% w/w) and lignin (15–20% w/w) and a small amount of extractives and mostly silica-containing ash (Prasad et al., 2007). The variation in composition depends on the wheat species, soil, climate conditions, etc. (Utne and Hegbom, 1992). With a significant carbohydrate content of about 70% w/w, wheat straw is a potential cheap and abundant feedstock for production of fermentable sugars. However, a cost-efficient pretreatment technology and low enzymatic charge is required for competitive sugar production (\leq \$0.30/kg) at industrial scale.

Autohydrolysis would be a cost-effective process because only water/steam is needed. Unfortunately, the formation of “sticky lignin” precipitates in the hydrolysate leads to severe plugging in the hydrolysis reactor and downstream equipment in a continuous process (Gutsch et al., 2012). This is at least part of the reason why the hydrolysate in the industrial prehydrolysis-Kraft process is combined with kraft spent liquor rather than used for the production of sugars and chemicals. The explanation for the formation of precipitated lignin in the hydrolysate is condensation of lignin fragments dissolved by acid hydrolysis. The structure and quantity of precipitated lignin in

autohydrolysate were studied by Leschinsky et al. (2009). These studies showed that exposure of hardwood prehydrolysate to 170 °C led to formation of highly condensed precipitates. In recent work (Yasukawa et al., 2014; van Heiningen et al., 2017) it was found that the presence of formic acid at relatively low concentrations (5–20 g/L) during hot water (160 °C) treatment of mixed hardwood chips significantly reduced the amount of lignin precipitates in the pre-hydrolysate. In addition, the formic acid reinforced hydrolysate contained much more monomeric hemicellulose sugars than that without formic acid supplementation. The explanation for the reduced lignin condensation/precipitation is that formyl cations generated by protonation of formic acid react with dissolved lignin by aromatic substitution. The resulting electron withdrawing formyl group on the aromatic ring reduces its reactivity towards further condensation. Thus the net result is a decrease in the amount and average molecular weight of the precipitated lignin particles formed during prehydrolysis. In the present study, we quantified the effect of low formic acid concentrations during pretreatment of wheat straw on hemicellulose dissolution and lignin precipitate formation. In addition to FA 1 g/L sulfuric acid (SA) was added to determine the effect of higher acidity on formic acid reinforced autohydrolysis.

2. Materials and methods

2.1. Materials

Wheat straw samples locally obtained in the State of Maine, US,

* Corresponding author at: Forest Product Engineering, Faculty of Forestry, Duzce University, 81620, Duzce, Turkey.
E-mail address: omerozyurek@duzce.edu.tr (Ö. Özyürek).

were cut to a suitable size fraction (1–2 cm) using a grinder Munson Mill. The chopped material was air dried at room temperature. The moisture content was determined according to the TAPPI (T 412 om-11) test method and the material was sealed in plastic bags and stored at room temperature before formic acid reinforced autohydrolysis.

2.2. Pre-hydrolysis of wheat straw

The prehydrolysis of 15 g (o.d. basis) wheat straw was performed at 150 °C, for 100 min (includes heat-up time) in a polyethylene glycol (PEG) bath laboratory reactor with 8 rotating digesters. The required amount of water, formic acid (FA) and sulfuric acid (SA) at different concentrations taking into account the moisture content of the wheat straw were added to the 220 mL stainless steel pressure vessels to obtain different liquor-to-straw (L/S) ratios L/kg. The equivalent heat-up time of the content of the vessels was about 8 min. The vessels were submerged in the PEG bath and exposed to a rotating motion to ensure uniform mixing between the straw and liquor. The used FA concentrations accounting for dilution by straw moisture are 0 (Control), 2, 5, 10, and 15 g/L. Another variable was the L/S ratio which was studied at control (0 g/L FA) and 10 g/L FA and 4, 6, 8, and 10 L/kg. The final L/S ratio was selected as 6 L/kg based on these experiments. Finally, at a FA concentration of 15 g/L and L/S ratio of 6 L/kg, 1 g/L SA was added to determine the effect of higher acidity on FA assisted prehydrolysis because it was proposed by van Heiningen et al. (2017) that formyl cations generated by protonation of formic acid with additional sulfuric acid would further minimize lignin condensation and thus its precipitation. All prehydrolysis experiments were performed in duplicate. After the prehydrolysis time of 100 min was reached, the vessels were immersed into ice-water to stop the prehydrolysis reaction. The prehydrolysate liquor and residual solids were collected by filtration using a 200 mesh nylon filter and the liquid part weighed and stored at –20 °C for later analysis. The pre-treated solid residues were stored in a zip locked plastic bag and placed in a refrigerator at 4 °C for further testing.

2.3. Analytical methods

Before analysis the wheat straw samples were ground in a Wiley Laboratory Mill outfitted with a 0.5 mm screen. The moisture content was determined according to the TAPPI (T 212 om-06) test method, and the material was sealed in zip locked plastic bags and stored at room temperature. The ash (TAPPI T 211 om-12) content and the acetone solubility were examined according to method (TAPPI T 204 cm-07). The prehydrolysis yield determined by gravimetric measurements was calculated from the dry weight of the prehydrolysed straw and the weight of initial straw.

The sugar content of wheat straw and pretreated solids was determined using high performance anion exchange chromatography (HPAEC) with pulsed amperometric detection (PAD) (Dionex ICS-3000, CarboPac PA20 column). The wheat straw and pretreated solid residues were subjected to a two-step sulfuric acid hydrolysis (72 and 4%). The total sugar content of the pre-hydrolysate was determined by HPAEC-PAD after 4% sulfuric acid hydrolysis. The oligosaccharides content in the prehydrolysate was determined by subtraction of the mono sugar content in the fresh liquor (i.e. no sulfuric acid hydrolysis) from the corresponding total sugar content measured after 4% sulfuric acid hydrolysis. Laboratory Analytical Procedures (LAP) from the National Renewable Energy Laboratory (NREL) were used to determine the lignin (acid insoluble and soluble) contents of the samples (Sluiter et al., 2011). The acid-insoluble lignin was obtained by weighing the solids (dry basis) remaining after the two-step sulfuric acid hydrolysis. The ash content of the Klason lignin was determined and the Klason lignin content was reported on an ash-free basis. The acid-soluble lignin was analyzed by UV-vis analysis at a wavelength of 320 nm against blank 4% sulfuric acid with an absorptivity of 30 L/g cm.

Hemicellulose components or degradation products in the wheat straw, pretreated solids and prehydrolysate liquor such as acetyl groups (or acetic acid), formic acid, HMF and furfural were determined by HPLC using a refractive index detector and BIO-RAD Aminex HPX-87H column. 5 mM sulfuric acid was used as mobile phase. Flow rate and column temperature were 0.6 mL/min and 60 °C, respectively. The acetyl group (AcG) content in the original straw and prehydrolysis residual solids was calculated based on the amount of acetic acid.

Uronic anhydride (UA) content of the original straw was determined using the chromophoric group analysis after a two-step acid hydrolysis treatment of the secondary hydrolysate according to the method developed by Scott (1979). Dimethylphenol was used as standard, and the content of UA was calculated from the difference in UV absorption at 400 and 450 nm 4-O-methyl glucuronic anhydride was calculated from uronic anhydride content using the formula (4-O-methyl glucuronic anhydride = UA × (190/176))

The amount of precipitate in the pre-hydrolysate liquor was determined after centrifugation at 14000g for 15 min at room temperature. After removal of the supernatant, the precipitate was subjected to vacuum drying at room temperature and its weight determined. The molecular weight of the precipitates was measured by SEC with UV and RI detectors using DMSO/0.5% w/w LiBr as eluent at flow rate of 0.5 mL min⁻¹ at 60 °C. The lignin fractions were dissolved without derivatization at room temperature in the SEC eluent and filtered through a 0.45 µm PTFE syringe filter prior to injection. Standard calibration was performed using pullulan standards of molecular weight range 342–3.44 × 10⁵ g mol⁻¹.

3. Results and discussion

3.1. Chemical composition of wheat straw

The chemical composition of the wheat straw used in this study are given in Table 1. As shown in Table 1, wheat straw mostly consists of glucan and xylan, 40.5 and 22.9% respectively, for a total carbohydrate content (sum of glucan, xylan, arabinan, mannan + acetyl groups (1.48%) and 4-O-methyl glucuronic anhydride (1.82%)) of 70.1% on oven dry basis of wheat straw. This value is important because a cheap and abundant raw material with high carbohydrate content is required as potential feedstock for production of fermentable sugars. All identified components of wheat straw add up to 98.6%, which is an indication of the good accuracy of the chemical analyses. The main part of glucan originates from cellulose and xylan represents most of the hemicelluloses. The total amount of carbohydrates is slightly higher than that reported in literature for wheat straw. Although the total lignin content (24.1%) was similar, the ash content (3.02%) was lower than the literature reported results (Ertas et al., 2014; Mustajoki et al., 2010). Slight differences in the values could be due to the growth environment, growing season, growing location, soil conditions, analysis

Table 1
Chemical composition of wheat straw on oven dry basis.

Component	g/100 g od straw
Arabinan	2.17 ± 0.01 ^a
Galactan	0.64 ± 0.02
Glucan	40.5 ± 0.41
Xylan	22.9 ± 0.06
Mannan	0.62 ± 0.01
Acetyl groups (AcG)	1.48 ± 0.02
4-O-methyl glucuronic anhydride	1.82 ± 0.03
Acid soluble lignin (ASL)	0.81 ± 0.09
Klason lignin (KL)	23.3 ± 0.01
Ash	3.02 ± 0.03
Extractives	1.30 ± 0.05
Total	98.6 ± 0.74

^a The range and average of duplicate measurement is reported.

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