Ball Milling: Effective Pretreatment Leading to A Clean Cellulosic Sugar Conversion

Eileen Wu[1], Rodney Seals[2], Jinxue Jiang[3], Yalan Liu[3], Huinan Liu[3], Jinwu Wang[3], Michael Wolcott[3]

1. Department of Chemical Engineering, University of California at Berkeley, 2. Department of Chemical Engineering, University of Arkansas at Fayetteville, 3. Composite Materials and Engineering Center, Washington State University

Background

Corn ethanol is predominately produced by the dry milling process, in which the entire corn kernel is ground into fine powder referred as meal. The meal is then made slurry, gelatinized, liquefied, and saccharified to dextrose, a simple sugar for consequent fermentation into ethanol . Analogous to sugar production from the dry milling corn ethanol process, we conceived a process to produce pilot scale cellulosic sugars including ball-milling Douglas-fir wood into very fine powder, slurry formation, liquefaction/viscosity reduction by extrusion, and saccharification. Slurry can be formed by direct steam injection or just mixing with deionized water. Between slurry formation and liquefaction steps, a dilute acid, alkali or hydrothermal treatment can be inserted to improve substrate digestibility or reduce the degree of milling requirements and energy consumption.

Objectives

The goal of this investigation was to study the effect of post ball milling treatments on final sugar yields, costs, and purity of cellulosic sugars.

Methods

Douglas-fir wood chips (13.3%) were hammer milled passing through a 1/16 inch screen, then Wiley milled to pass through 20 mesh, and further planetary ball milled (PQ-N2 Planetary Ball Mill, Across International) for 60 minutes. High solid hydrolysis at 15 wt% consistence with 5.5% CTec2/HTec2 enzyme products per dried wood powder were conducted in 1000 ml shake flasks with 700 grams solution. After hydrolysis, a simple vacuum filtration was used to separate hydrolysate from the lignin-rich solid residuals. In order to compare the effect of hot water, dilute alkali (0.5% NaOH), and dilute acid (0.5% H_2SO_4) on sugar yield, three preparations were autoclaved for 3 hours at 121°C (Table 1). The pH values were measured before and after hydrolysis and controlled by sodium hydroxide and sodium citrate buffer.

Table 1 Post milling treatment conditions and the control (blank)

Blank	H_2O	NaOH	H_2SO_4
Ball milled, 35.4 mm; 15% solid; Enzymatic hydrolyzed, 5.5% enzymes/dry wood and vacuum filter separated	Ball milled, 35.4 mm; Autoclaved at 121°C for 3h, 15% solid; Enzymatic hydrolyzed, 5.5% enzymes/dry wood and vacuum filter separated	Ball milled, 35.4 mm; Autoclaved at 121 °C for 3h, 15% solid, 0.5% NaOH; Enzymatic hydrolyzed, 5.5% enzymes/dry wood and vacuum filter separated	Ball milled, 35.4 mm; Autoclaved at 121 °C for 3h, 15% solid, 0.5% H_2SO_4; Enzymatic hydrolyzed, 5.5% enzymes/dry wood and vacuum filter separated

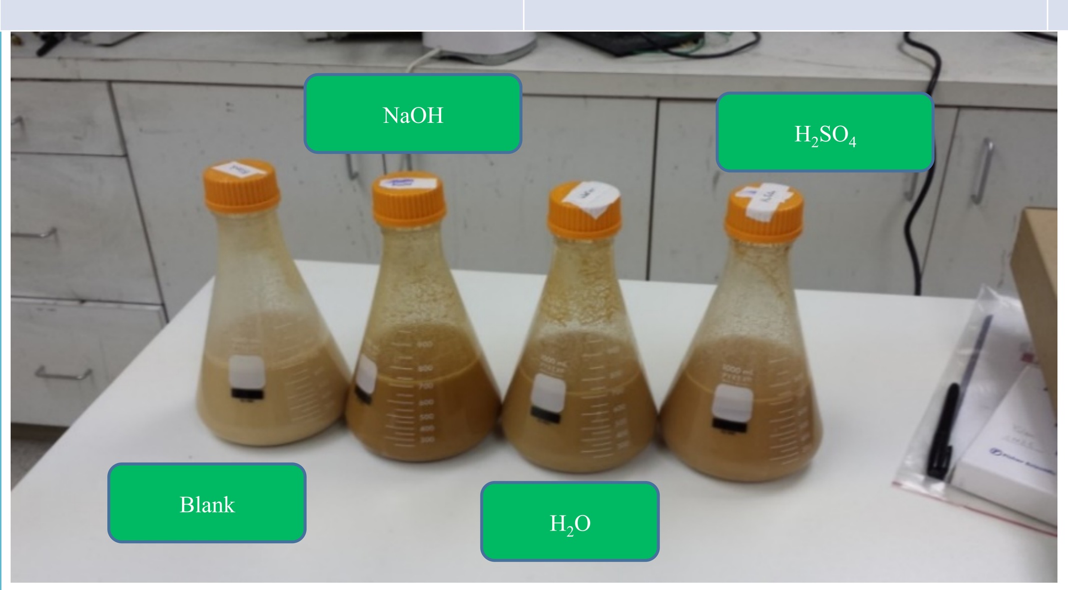

Fig. 1 Appearance of the slurry before vacuum filter separation

Fig. 2 Wet lignin residues after vacuum filtration; moisture is around 250% dry based.

Acknowledgement

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Results

Fig. 3 Change of the size of the wood after 60 minutes of ball milling for the feed of 20 mesh. The total specific energy consumption was 21.9 MJ/kg wood, and the net energy used was 6.3 MJ/kg wood. D_10 means 10% volume cumulative distribution particle size.

	Glucan %	Xylan/Mannan %	Galactan %	Arabinan %	Lignin %
Douglas-fir	45.5	16.5	2.7	1.3	28.9

Table 2 Wood composition of Douglas-fir (obtained by two-step acid hydrolysis)

Table 3 Enzymatic hydrolysis yields of ball milled wood powders of the control and autoclaved with 5.5% enzymes per dry milled wood. Soluble lignin content in hydrolysates was measured using absorbance at 205 nm

	Glucose Yield (%)	Xylose/Mannose Yield (%)	Total Sugar Yield (%)	Soluble Lignin (%)	Glucose (g/L)	Xylose/ Mannose (g/ L)	Total Sugar (g/L)
Blank	64.9	25.9	54.3	0.91	45.6	6.8	52.4
H_2O	59.4	31.2	51.7	0.98	41.7	8.2	50.0
NaOH	44.9	35.7	42.4	1.22	31.6	9.4	40.9
H_2SO_4	48.0	86.2	58.4	0.43	33.8	22.7	56.4

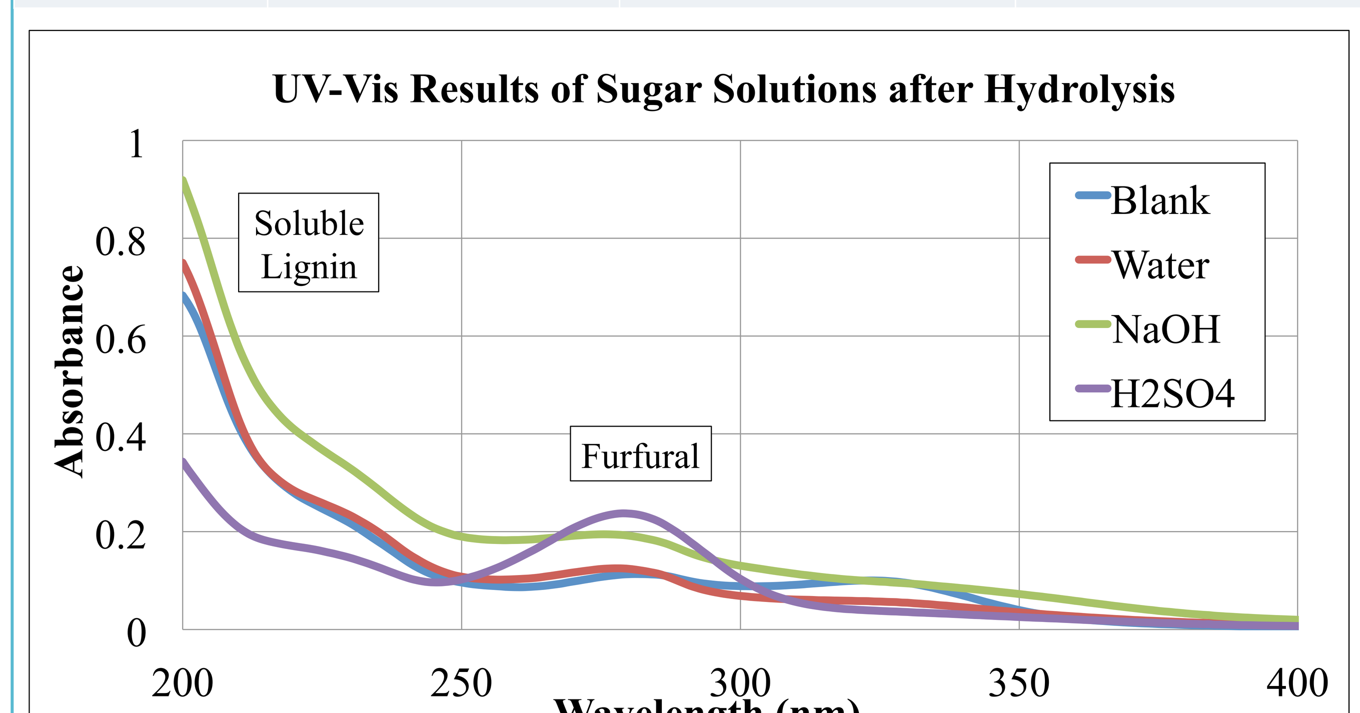

Fig. 4 Peaks at 280 nm indicated the formation of furfural, while peaks at 205 nm and 240 nm indicated presence of soluble lignin.

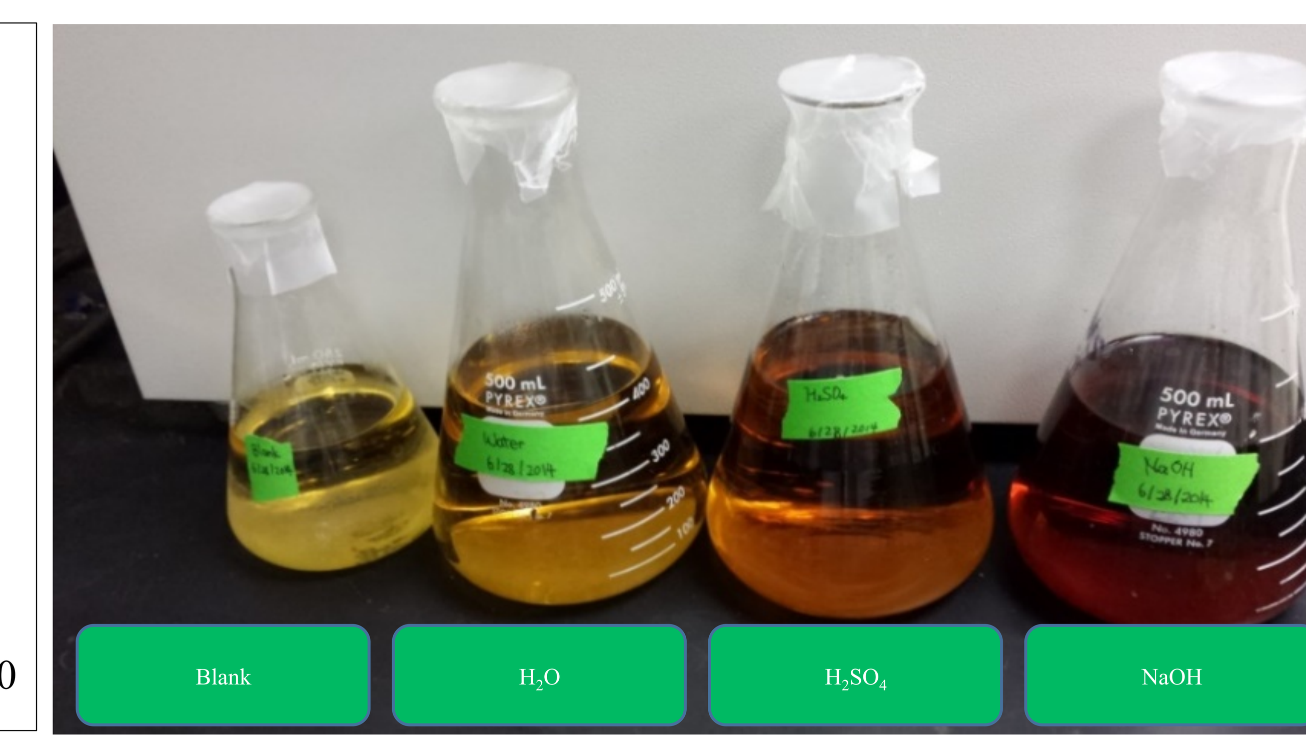

Fig. 5 Color difference of cellulosic sugars after enzymatic hydrolysis and filtration.

Conclusion

Fig. 5 was an image of aqueous cellulosic sugars (hydrolysates) obtained by three post milling treatments of wood powers and the control demonstrating the advantage of the sole mechanical pretreatment, i.e. cleaner cellulosic sugars and less impurities as indicated by the color (Figs. 4 & 5). Sole mechanical pretreatment (Blank) is much lighter in color than those by alkaline (NaOH), acid (H_2SO_4), and hot water (Water) treatments. The post milling treatments could enhance xylose/ mannose yields (in particular, the dilute acid treatment). However, the cellulosic sugars obtained from the sole mechanical pretreatment contained less impurities (aromatics and furans) than those obtained by alkaline, acid and hot water treatments.