Oxalic acid pretreatment of rice straw particles and loblolly pine chips: Release of hemicellulosic carbohydrates

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ABSTRACT: This study was conducted to evaluate the effect of oxalic acid (OA) pretreatment on carbohydrates released from rice straw particles and wood chips. The results showed that OA treatment accelerated carbohydrates extraction from rice straw particles and wood chips. OA pretreatment dramatically increased the amount of carbohydrates extracted, up to 24 times for wood chips and 2.3 times for rice straw particles. Sugars released from the OA-treated rice straw particles and wood chips increased with increasing treatment temperature and duration. OA treatment also improved the primary physical properties of rice straw particleboard and wooden medium density fiberboard (MDF), except for the mechanical strength of MDF. Carbohydrates extracted from rice straw particles and wood chips could be a potential sustainable resource for biofuel or biobased chemicals.

Application: Mills potentially could use OA pretreatment to extract carbohydrates from rice straw particles and wood chips to produce biofuel or biobased chemicals, and could use the process to improve the physical properties of rice straw particleboard and wood MDF (except for the mechanical strength).

With recently renewed interest in ethanol production of cellulosic material, the pulp and paper industry proposed the concept of “Value Prior to Pulping” (VPP) to compensate for energy-intensive refining processes [1-6]. Instead of converting all of the woody biomass into a single product, specific hemicelluloses are either partially or completely extracted through a prehydrolysis process. In this way, a raw material is obtained for bioethanol or other chemical feedstocks. The remaining solid (cellulose, residual hemicellulose, and lignin) is then the raw material for pulp or fiber products [7].

Early studies indicated that oxalic acid (OA) or its derivatives are suitable for pretreatment of wood chips to reduce energy consumption and improve medium density fiberboard (MDF) performance [8-10]. Essential steps in the pretreatment include heating wood chips with atmospheric steam, impregnating the chips with OA and/or its chemical derivatives, and heating the system for an effective extraction of the carbohydrates [10-12]. This pretreatment of wood chips significantly reduces the energy demand in the thermomechanical refining process and does not adversely affect the paper product; even handsheet strength and paper brightness are increased under optimized condition [10]. Similar results at lower temperatures have been reported for poplar (black cottonwood; *Populus trichocarpa*) [13]. Increasing the amount of chemicals, reaction duration, and temperature improved carbohydrates removal. Pulp and paper research organizations throughout the world are conducting various forms of VPP research work [7]. A large number of wood and agriculture residues also are used to make composites panels in the wood industry each year. However, only limited research on this subject has been reported so far.

In our previous research, we investigated the effects of OA and steam treatment on the physical properties of rice straw and wood-based composites panels [12]. As a continuation from the earlier work, the main objective of this study was to evaluate the pretreatment effect on carbohydrate released from rice straw particles and wood chips.

MATERIAL AND METHODS

Rice straw (Calrose M-206), obtained from Sacramento Valley in California, USA, was approximately 1 m tall at harvest and cut above the water line, leaving the lower third as stubble in the field. This rice was harvested with a conventional straw walker combine rather than a rotary, which optimizes straw quality by retaining much longer sections of stalks for bailing. The average moisture content of the straw was about 8.1%. For the experiments, the rice straw was broken down into particles in a hammer mill, in which a perforated metal plate with an opening of 19.05 mm (3/4 in.) was used. Commercial loblolly pine (*Pinus taeda*) wood chips were stored frozen in plastic bags. The initial moisture content of the wood chips was about 65% before pretreatment.

The reactor configuration and pretreatment procedure have been described previously [12]. The concentration of the OA solution for pretreatment was 0.33%. Temperatures of 100°C, 120°C, 140°C, and 160°C were used for pretreatment at periods of 5 min and 10 min. For the positive control, rice straw particles were processed with hot water (160°C) for 10 min without chemicals. After pretreatments, the pressure in the digester was released and the rice straw particles were flooded with 70°C hot water, which was circulated for 30 min to rinse the hemicellulosic sugar from the treated rice straw. The pretreatment procedure for wood chips was the same as that for rice straw particles, but the wood chips were only treated at the three higher temperatures (120°C, 140°C, and 160°C) for 10 min. Following the pretreatments, the extracted rice straw particles and wood chips and the hemicelluloses extracts were collected and weighted. The rice straw particles and wood chips mass and moisture content were measured before and after pretreatment. The extracted wood chips (OA-treated chips and positive control samples) and raw control chips (without OA or steam pretreatment) were processed separately through the thermomechanical refiner to produce MDF fibers. We used a laboratory pressurized refiner (Sprout-Bauer model 1210P; Andritz, Graz, Austria) with 300 mm diameter plates, D2B505 plate pattern, and 0.1778 mm (0.007 in.) refiner gap. The wood fibers and rice straw particles were dried at 103(±2)°C to 2%-3% moisture content in a tray dryer, and then the dried rice straw particles were hammer-milled again, using a perforated metal plate with opening size of 6.35 mm (1/4 in.). The dried wood fibers and hammer-milled rice straw particles were bagged before wood-based MDF and rice straw particleboard fabrication.

A high performance liquid chromatography system equipped with an integrated amperometric detector was used to analyze the carbohydrates in the aqueous extracts, according to the method described by Shuai et al. [14]. Internal bonding (IB), modulus of elasticity (MOE), modulus of rupture (MOR), linear expansion (LE), water absorption (WA) and thickness swelling (TS) of rice straw particleboard and wood MDF panels were tested in accordance with ASTM D 1037-06a - "Standard test methods for evaluating properties of wood-base fiber and particle panel materials."

RESULTS AND DISCUSSION

Carbohydrates extracted from rice straw particles potentially could be a sustainable resource for biofuel or biobased chemical feedstocks. Therefore, the effect of pretreatment conditions on carbohydrate extraction has been investigated in this study. **Table I** shows the quantities of carbohydrates extracted from rice straw particles. The main carbohydrates extracted from rice straw were glucose, mannose, and arabinose. Generally, more total carbohydrates were extracted from the OA-treated rice straw particles than from the positive control sample (steam-treated without OA solution). OA treatment at 160°C for 10 min led, for example, to 2.3 times more carbohydrate extraction compared to the positive control. This result clearly demonstrated that the addition of OA in hot water accelerated the carbohydrates extraction of rice straw particles. During OA pretreatment, the amount of sugars released from rice straws was dependent on treatment temperature and duration. When the pretreatment temperature increased from 100°C to 160°C, the amount of abstracted sugar increased 82%

Sample ID	Content (g kg^{-1} o.d. rice straw)					Total Carbohydrate (g kg^{-1} o.d. rice straw)
	Arabinose	Galactose	Glucose	Xylose	Mannose	
PC	0.74	0.36	4.73	0.07	3.36	9.26
100/5	0.33	0.30	5.90	0.01	3.42	9.96
120/5	1.38	0.28	5.61	0.09	2.16	9.53
140/5	3.41	0.22	5.76	1.76	3.05	14.19
160/5	2.74	0.30	8.24	0.62	6.20	18.10
100/10	0.51	0.44	5.67	1.75	2.29	10.66
120/10	2.36	0.21	4.99	1.29	2.80	11.65
140/10	2.70	0.16	6.99	1.36	4.00	15.21
160/10	2.78	0.73	10.26	0.56	6.94	21.26

I. Carbohydrate types and amounts extracted from rice straw particles. Samples are identified as positive control (PC) and by pretreatment temperature (°C)/duration (min).

Sample ID	Content (g kg^{-1} o.d. wood chips)					Total Carbohydrate (g kg^{-1} o.d. wood chips)
	Arabinose	Galactose	Glucose	Xylose	Mannose	
PC	0.63	0.36	0.18	nd	nd	1.17
120/10	3.53	1.1	0.49	0.49	0.48	6.09
140/10	4.87	3.78	2.57	4.27	8.38	23.88
160/10	4.38	5.25	4.75	4.83	9.45	28.66

II. The content of the carbohydrates extracted from wood chips. Samples are identified as PC and by pretreatment temperature (°C)/duration (min).

Sample ID	IB (MPa)	MOE (MPa)	MOR (MPa)	TS (%)	WA (%)	LE (%)
RC	0.16(0.02)	1437(192)	7.01(0.93)	67.91(1.57)	125(3.58)	0.41(0.02)
100/5	0.26(0.02)	1609(220)	8.03(0.71)	52.52(2.12)	107(3.13)	0.38(0.03)
120/5	0.27(0.03)	1518(79)	7.70(1.31)	50.41(2.26)	102(5.35)	0.34(0.05)
140/5	0.26(0.03)	1649(72)	8.10(0.57)	45.56(0.15)	101(9.10)	0.30(0.02)
160/5	0.27(0.04)	1671(116)	8.65(0.78)	46.47(1.82)	100(3.99)	0.29(0.02)
100/10	0.20(0.04)	1505(135)	7.53(0.49)	54.45(1.02)	112(4.06)	0.39(0.04)
120/10	0.23(0.04)	1450(26)	7.33(0.15)	51.31(1.13)	105(8.17)	0.36(0.06)
140/10	0.19(0.03)	1434(120)	7.47(0.74)	49.41(3.74)	109(3.72)	0.35(0.04)
160/10	0.21(0.04)	1547(84)	7.97(0.81)	47.33(3.25)	102(8.77)	0.33(0.02)
* Data in parentheses are standard deviation.						

III. The primary physical properties of oxalic acid (OA)-treated particleboards and raw control (RC). Samples are identified by pretreatment temperature (°C)/duration (min).

and 99% for the two pretreatment durations of 5 min and 10 min. These increases probably resulted from enhanced degradation of hemicellulose within rice straw particles as treatment temperature and duration increased. The amount of xylose extracted from rice straw was expected to be more; however, most of the xylose extracted at those temperatures is oligomeric xylose, which was not measured.

The main carbohydrates extracted from the wood chips were arabinose, galactose, glucose, xylose, and mannose. **Table II** shows the carbohydrate quantities extracted from loblolly pine chips. As expected, the total weight of carbohydrates extracted from the OA-treated pine also was much more than that from the positive control sample processed with hot water without chemicals. The OA treatment at 160°C for 10 min led, for example, to 24 times more carbohydrate extraction compared to the positive control. These results demonstrate that the amount of extracted carbohydrates can be increased dramatically by the addition of OA in hot water. The same result was observed in our other studies using rice straw particles as experimental lignocellulosic material. Also in this context the temperature played a pivotal role: a temperature increase from 120°C to 140°C entailed 3.7 times more carbohydrate extraction. The predominant carbohydrate removed from the positive control samples and the OA-treated samples at 120°C was arabinose. However, chips treated with OA solution at 140°C and 160°C released mainly mannose. Kenealy et al. [15] observed the same effect by treating spruce, aspen, maple, and southern yellow pine with diluted OA solution before refining [15].

Results of the experiments also showed that the total carbohydrates extracted from wood chips is much lower than that from rice straw particles when the chips are OA-treated below 120°C or steam-treated without chemicals. The experimental result was consistent with expectations, but opposite when the OA pretreatment temperature exceeds 140°C. The reason for this is not yet clear, but we speculated that the geometries greatly influenced the amount of sugar extracted from rice straw and wood chips when the pretreatment temperature was below 140°C. The carbohydrates could be extracted easily from rice straw particles because of their smaller dimension and looser structure compared with wood chips at lower pretreatment temperature. More hemicellulose can be degraded and converted into sugar for both rice straw and wood chips with increasing the OA pretreatment temperature. However, the increase in chemical reaction rate between rice straw and oxalic acid is much lower than that between wood chips and oxalic acid. Oxalic acid could not effectively penetrate the rice straw surface because of the hydrophobic wax and a high amount of inorganic silica on the outer surface of rice straw. The rate of chemical reaction between oxalic acid and materials, instead of geometries of material, influenced how much sugars were released from rice straw and wood chips at higher pretreatment temperature (i.e., above 140°C). Therefore, more hemicellulose converted from the degradation of hemicellulose could be extracted from wood chips than from rice straw particles at higher OA pretreatment temperatures. We also noticed that the amount of galactose, arabinose, and xylose extracted from wood chips seems much too high for treatments at 140°C and 160°C for 10 min (Table II). Measurement errors also might have affected results.

Table III shows the effect of OA pretreatment on the primary physical properties of urea formaldehyde-bonded rice straw particleboards. OA treatment significantly improved the mechanical properties and dimensional stability of rice straw particleboards, especially for internal bonding strength. Pretreatment time had a negative effect on performance of OA-treated rice straw particleboard panels, whereas the effect of temperature on the performance of OA-treated rice straw panels was not significant. **Table IV** shows that OA treatment before wood chip refining resulted in better wooden MDF dimensional stability. However, OA pretreatment had a slight negative effect on MDF mechanical strength. Hemicelluloses are more water-soluble and more hydrophilic than cellulose and lignin. The improvement of dimensional stability is mainly attributable to the partial removal of hemicelluloses by the

Sample ID	IB (MPa)	MOE (MPa)	MOR (MPa)	TS (%)	WA (%)	LE (%)
RC	0.40(0.08)	1563(192)	14.80(2.57)	26.99(2.14)	101.62(10.63)	0.24(0.01)
120/10	0.26(0.05)	1304(180)	12.22(1.73)	24.22(0.78)	93.77(7.56)	0.42(0.03)
140/10	0.25(0.04)	1377(215)	13.57(1.76)	23.85(0.34)	94.63(5.58)	0.40(0.03)
160/10	0.26(0.04)	1487(93)	15.11(0.70)	20.58(2.63)	83.99(9.04)	0.35(0.04)
* Data in parentheses are standard deviation.						

IV. The primary physical properties of OA-treated medium density fiberboard (MDF) panels and RC. Samples are identified by pretreatment temperature (°C)/duration (min).

OA pretreatment. Paraffin waxes are currently used in the panel industry to delay water absorption. Physical-chemical treatments, such as OA treatment before refining, could have the same effect, i.e., decrease the hygroscopicity of wood fibers and rice straw particles, and improve the dimensional stability of panels in the longer term.

CONCLUSIONS

The results of this study showed that OA treatment before refining accelerated carbohydrates extraction from rice straw particles and wood chips. The main components of extracted solutions were glucose, mannose, and arabinose for rice straw particles, and arabinose, galactose, glucose, xylose, and mannose for wood chips. The amount of extracted carbohydrates could be increased up to 24 times for wood chips and 2.3 times for rice straw particles by the addition of OA in pretreatment. The sugars released from the OA-treated rice straw particles and wood chips increased with increasing treatment temperature and time. OA treatment improved the primary physical properties of rice straw particleboard and wooden MDF, except for the mechanical strength of MDF. The OA process described in this paper shows promising potential for increasing profitability by using extracted carbohydrates for biofuel or biobased chemicals. **TJ**

ABOUT THE AUTHORS

The search for clean and renewable energy has become one of the main challenges for human beings. Ethanol production from cellulosic material could be a good energy option.

In previous research, scientists tried to convert all of the woody biomass into a single product (bioethanol), but that process is very difficult and uneconomical. In our study, specific hemicelluloses were partially extracted through a prehydrolysis process. In this way, a raw material was obtained for bioethanol, and the remaining solid (cellulose, residual hemicellulose, and lignin) could be the raw material for panel products.

The most difficult aspect of this research was to analyze the chemical component of the extracted solution. The chemical component was measured by an expert at the University of Wisconsin.

By using oxalic acid (OA) pretreatment, the amount of extracted carbohydrates dramatically increased, up to 24 times for wood chips and 2.3 times for rice straw particles. The OA process showed a promising potential for increasing profitability by using extracted carbohydrates for biofuel or biobased chemicals. At the same time, OA treatment improved the primary physical properties of rice straw particleboard and MDF from wood (except for the mechanical strength of MDF).

Some panel factories could benefit from the information in this study. An MDF factory, for example, could pre-treat wood chips before refining to compensate for the energy intensive refining process.

Our next step is to optimize the conditions at the pilot-scale for carbohydrate release from wood chips and rice straw supplied by our industrial partners, while maintaining the enhanced water adsorption and composite strength characteristics for a commercial application.

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