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Heat treatment of wet wood fiber: A study of the effect of reaction conditions on the formation of furfurals

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Abstract
Furan monomers are produced when wood is heated at high temperatures. To understand the process conditions for production of furfural (FF) and hydroxymethylfurfural (HMF) from wood, samples of milled aspen wood were subjected to autohydrolyzis by microwave heating in a sealed Teflon reactor. The experiments were designed to simulate temperature and pressure variables of a fiberboard press and their effect on production of furans from the hemicelluloses that have the potential for promoting self-bonding of the wood fibers. The effect of a Lewis acid catalyst, $AlCl_3 \cdot 6H_2O$ on the formation of FF and HMF was also studied. The hydrolysates were analyzed for the liberated wood sugars and dehydration products, FF and HMF. The FF and HMF yields under autohydrolyzis conditions increased with increase in severity factor, CS. Under catalyzed hydrolyzis conditions, the FF yield decreased, while the HMF yield increased with increase in severity factor. Under catalyzed hydrolyzis conditions the FF yield decreased presumably due to degradation reactions including resin formation. The increase in HMF yield with increasing severity factor was most likely due to hydrolyzis of glucan from cellulose. These results suggest that FF and resin yields could be enhanced with the addition of a Lewis acid catalyst to the wood particles, but that process variables need to be controlled in order to avoid or minimize degradation of the wood cellulose.

Keywords: *Aspen, autohydrolyzis, catalyzed hydrolyzis, Lewis acid catalyst, hemicelluloses, furfural, hydroxymethylfurfural.*

Introduction

Recent studies have demonstrated the ability of hardwood to self-catalyze the hydrolyzis of wood in a sealed reactor, given sufficient heat and time (Garrote *et al.* 2001, 2007, Garrote and Parajo 2002, Mittal *et al.* 2009a, 2009b). This example can be termed autohydrolyzis because the hydronium ions needed to catalyze hydrolyzis of the hemicellulose are provided by the wood itself – from acetyl groups that are released from the hemicellulose polymer when it is heated in the presence of moisture (Conner and Lorenz 1986). The major carbohydrate product of the autohydrolyzis reaction is xylose and its oligomers, with relatively minor amounts of the other pentoses and hexoses. Under certain conditions of heat, pressure, time, and an acid catalyst, some of the liberated sugars undergo dehydration to form furfural (FF) from the pentoses and hydroxymethylfurfural (HMF) from the hexoses. The FF and HMF having alpha-substituted aldehyde groups can be expected to participate in typical aldehyde condensation reactions. The yields of FF and HMF can be reduced by side reactions, such as decomposition and intra- and inter-molecular condensation reactions (Figure 1, Norton 1947, Harris *et al.* 1960).

The transformation of the hemicelluloses to furans under experimental reactor conditions may also have implications for the physical properties of boards made under high temperature and pressure with moist wood particles. The wood particles contained in the heated board press may also be expected to undergo autohydrolyzis reactions similar to those described in the previous paragraph. It is well known that the hemicelluloses are much less stable to heat

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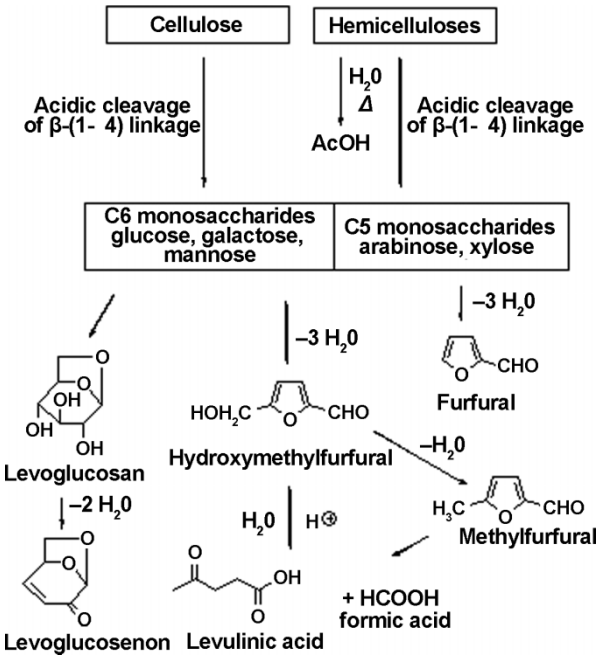

Figure 1. Possible reaction mechanism of cellulose and hemicelluloses decomposition at high temperatures.

and undergo thermal degradation more rapidly than cellulose (Stamm 1964). It is also known that the hemicellulose component of wood is an amorphous polymer that lacks the crystalline regions found in cellulose, which are more resistant to water penetration. Therefore, the partial removal of hemicelluloses would be expected to improve resistance of the wood to water swell and thus increase board stability. Under certain reaction conditions, the furans produced by the wood or similar lignocellulosic material may be expected to condense to form an *in situ* resin, which could be a substitute or partial replacement for added board resins (Norimoto 1994, Boonstra *et al.* 1998, Dwianto *et al.* 1998, Laemsak and Okuma 2000).

Using a closed press system, Rowell and McSweeny (2008) formed self-bonding fiberboards from aspen fiber that had been sprayed with water to bring the fiber moisture content to 15%. The moist fibers were pressed at 200°C for either 4 or 8 min to form fiberboards with a specific gravity of either 0.64 or 1.0. Static bending tests on specimens prepared from these fiberboards showed an improved modulus of rupture and no change in modulus of elasticity compared to control specimens pressed in an open press system. In a separate experiment, where the press time was extended to 50 min, analysis of volatile compounds collected from the closed press showed a peak in the concentration of FF collected at 20 min. These results raised several questions. What is the fate of the furans produced from the thermal degradation of the wood hemicelluloses in the closed press system? Is it possible that they undergo condensation reactions to form bonding resins? If so, is such a resin produced in sufficient amounts to promote self-bonding of the fibers? What are the conditions for optimizing *in situ* formation of such a resin?

The primary objective of this study was to explore reaction conditions that affect formation of furans from thermal degradation of wood hemicelluloses in the presence of moisture. The secondary objective was to study the effect of adding a Lewis acid catalyst on furan yields. To produce measurable amounts of the target compounds at the lower temperature available to our test equipment, the length of heating was considerably longer than press times used in the closed press system. In addition to depolymerization of the hemicelluloses into pentosans and hexosans, the nascent pentoses such as arabinose and xylose would be converted to FF. In addition, we expected that hexoses would also undergo direct dehydration to HMF.

Materials and methods

Wood sample preparation

Small chips (approximately 1.27 cm by 2.54 cm) of aspen wood were processed in a Wiley mill to pass through a 1-mm mesh size screen attached to the mill. Using a shaker apparatus loaded with a 30-mesh sieve attached to a 40-mesh sieve, the milled wood was screened through the two sieves. The fraction captured on the 40-mesh sieve was used in these experiments. This fraction was air-dried for approximately 3 days. After air drying, its moisture content was determined in triplicate by weighing each replicate before and after oven-drying at 105°C for 4.5 h.

Autohydrolyzis

A series of autohydrolyzis reactions, from 10 to 100 min in duration, were conducted in a microwave oven, with each sample contained in a CEM Advanced Composite Vessel reactor (CEM Corp., Matthews, NC, USA). Five grams (on an oven-dried basis) of the air-dried, milled wood sample was mixed with 30 ml of de-ionized water in the 100-ml Teflon (DuPont, Wilmington, DE, USA) vessel of the unassembled reactor. A threaded cap and coupling were then added to complete the assembled reactor, which was placed on a turntable in a CEM MDS-2000 microwave oven. The oven was programmable for power level, time, temperature, and pressure within the vessel. Temperature was measured in the sample by means of an infra-red sensor

contained within a quartz tube projecting into the vessel and its contents. Both pressure and temperature readings were continuously available and were recorded as needed during the course of each reaction. Prior to heating, the assembled reactor containing the sample was pressurized to 0.55 MPa with nitrogen, and the reactor valve closed and then examined for leaks around its fittings. The reactor valve was then slowly opened to release pressure prior to connection to the microwave oven pressure sensing tube. Heating for all runs was at full power and set-point temperatures were reached in approximately 2 min. After each heating run, the reactor valve was closed and the sealed reactor with residual pressure was cooled in a water bath for approximately 45 min in order to condense the FF vapor into the liquid. After cooling to lower than room temperature, the contents of the reactor were filtered under suction on Ahlstrom 909 filter paper (Ahlstrom, Helsinki, Finland) and the residue was air-dried. The pH of the filtrate (liquor) captured in the vacuum flask was recorded. The liquor was stored frozen until required for analysis.

Catalyzed hydrolyzis

To investigate the effect of a Lewis acid catalyst on the yields of FF and HMF, the same procedure as in autohydrolyzis was followed, except that instead of the de-ionized water, a solution of the Lewis acid catalyst, $AlCl_3 \cdot 6H_2O$ was added to the wood particles. The catalyst level was 1% (w/w) relative to wood, and reaction conditions were 200°C, for 10, 20, 30, and 40 min.

Analytical procedures

Samples of starting milled wood (untreated wood) and residues from the autohydrolyzis and catalyzed reactions were analyzed for sugars and lignin contents. This was accomplished by a 72% (v/v) sulfuric acid primary acid hydrolyzis, of the polymeric mass to oligomers, followed by a 4% (v/v) sulfuric acid secondary acid hydrolyzis step to the sugar monomers. The sugars were analyzed by a Dionex Ion Chromatograph (Dionex, Sunnyvale, CA, USA) with a pulsed amperometric detector (PAD) and Carbo Pac Pa-1 column (Dionex, Sunnyvale, CA, USA). The remaining lignin was determined as Klason.

The autohydrolyzis and catalyzed hydrolyzis reaction liquors were analyzed by taking an aliquot that was filtered through a 0.45-μm nylon syringe filter. The filtrates were analyzed for furans with an Agilent 1100 Series LC/MS equipped with a Diode Array Detector (DAD). The UV signal was monitored at 280 nm for peak quantitation. Separation was obtained on a Zorbax Eclipse XDB-C8 analytical column (Agilent Technologies, Santa Clara, CA, USA) using mobile phase of 80:20, 0.005 M H_2SO_4/acetonitrile (ACN).

Secondary hydrolyzis

The filtrates were also analyzed for sugars after a 4% sulfuric acid hydrolyzis, to liberate sugar monomers from oligomers.

Combined severity factor

The combined severity factor, CS, which is a single reaction coordinate that combines the time, temperature, and pH of the hydrolyzis reaction, was calculated according the equation of Chum *et al.* (1990):

$$\mathrm{CS} = \log(t) + T_r - T_b/14.75 - \mathrm{pH}$$

where t is residence time (min), T_r is the reaction temperature (°C), and T_b is a reference temperature (100°C). (Overend and Chornet 1987), and pH is the measured pH of the hydrolysate.

Results and discussion

As shown in Figure 2, the pH of the hydrolysates decreased with increase in hydrolyzis time. The lowest pH that the autohydrolyzis liquors reached was approximately 2.8. This decrease in pH was probably due to accumulation of acetic acid released

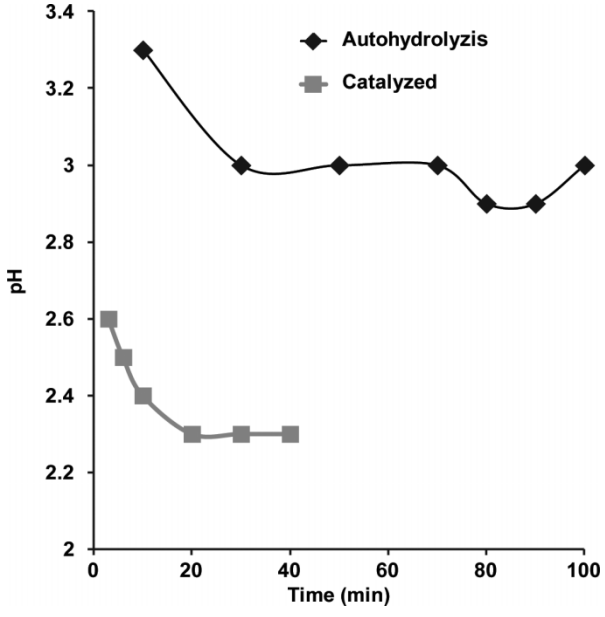

Figure 2. pH values of noncatalyzed and catalyzed hydrolysates produced at 200°C.

from hydrolyzis of acetyl esters. The most likely source of the esters is from the major hardwood xylan, O-acetyl-(4-O-methylglucurono)-xylan (Teleman *et al.* 2000). The reactions with the Lewis acid catalyst $AlCl_3 \cdot 6H_2O$ produced liquors with lower pH than those without the catalyst. The pH of the liquors from catalyzed hydrolyzis was well below that of an equivalent aqueous aluminum chloride solution. It was not clear whether the lower pH was due to release of additional acetyl groups promoted by the Lewis acid catalyst. Another possible contribution to acidity may be due to the capacity of trivalent aluminum ions to displace hydrogen ions from the wood fiber surface by cation exchange mechanism.

Furans analysis

The FF yield as a function of time during hydrolyzis in the absence and presence of a Lewis acid catalyst, $AlCl_3 \cdot 6H_2O$ is shown in Figure 3. In the absence of the Lewis acid catalyst, the FF yield appeared to reach a plateau after 55 min of reaction, and in the presence of the catalyst it started from approximately 2.5% at 10 min, and declined to approximately 2.0% after 40 min. For the non-catalyzed reaction, the maximum FF yield was calculated to be 3.5% of the weight of wood fiber after approximately 55 min at 200°C. It would appear that beyond 60 min the FF yield is limited by degradation into other by-products. This behavior in FF yield at long reaction times appears to be consistent with early studies of the kinetics of FF formation and decay in acidic solutions of pentose (Dunlop 1948, Williams and Dunlop 1948, Root *et al.* 1959). In those studies, degradation of FF was influenced by FF and hydrogen ion concentrations. Therefore, the rate of degradation of FF would be expected to increase at the long reaction times where more FF had been formed. In the presence of the Lewis acid catalyst the maximum FF yield occurred at 10 min, the shortest time that could be measured in these experiments, and it was estimated to be 2.5% of the weight of the wood. Apparently, the lower pH of the Lewis acid catalyzed reactions compared with autohydrolyzis reactions, resulted in a higher rate of FF degradation.

Dunlop (1948) first proposed that in the conversion of pentosans to FF, not all of the pentosans that are hydrolyzed to pentose will be converted to FF. During the process of dehydration of the pentose to FF, some of the FF is lost when a resin is formed by condensation reactions of intermediates, or of intermediates with the nascent FF, or by self-condensation of the nascent FF. The nascent FF can also undergo acid-catalyzed degradation reactions such as auto-oxidation and condensation with lignin or other components of the lignocellulose.

Figure 4 shows the HMF yield during hydrolyzis in the absence and presence of a Lewis acid catalyst. In the presence of a Lewis acid catalyst, the HMF yield reached a maximum of approximately 1.75% of the weight of wood after 30 min of reaction, and declined to approximately 1.2% after 50 min. However in the absence of the catalyst, the HMF yield

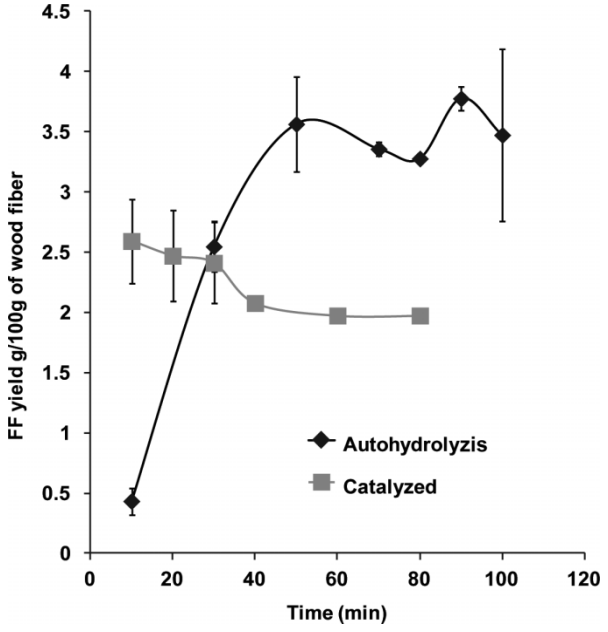

Figure 3. Furfural (FF) yield in noncatalyzed and catalyzed hydrolysates conducted at 200°C; error bars represent standard deviation of duplicate measurements.

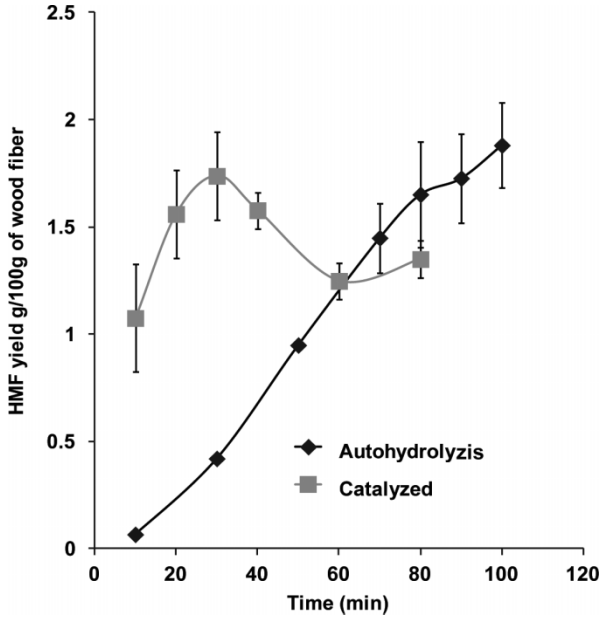

Figure 4. Hydroxymethylfurfural (HMF) yield in noncatalyzed and catalyzed hydrolysates at 200°C; error bars represent standard deviation of duplicate measurements.

continued to increase out to the maximum hydrolyzis time of 100 min. HMF may have been produced at low enough levels that degradation or condensation reactions occurred at a lower rate than the rate of its formation. HMF conversion to levulinic acid and other degradation or condensation products is a first-order reaction; therefore, the rate of loss of HMF is dependent on its concentration (McKibbins *et al.* 1962, Efremov *et al.* 1998).

Residue analyzes

Figure 5a summarizes changes in carbohydrate and lignin contents of residues after autohydrolyzis at 200°C. Long autohydrolyzis times resulted in decreased contents of xylan and mannan in the residues. It should be noted that the levels of lignin and glucan of the autohydrolyzed samples were greater than those of the non-autohydrolyzed samples. This was due primarily to the mass losses of extractives, hemicelluloses, and soluble lignin in autohydrolyzed samples. Autohydrolyzis times that were greater than 80 min showed slight declines in glucan levels, indicating onset of possible degradation.

In the presence of a Lewis acid catalyst, carbohydrate and lignin contents of residues after hydrolyzis at 200°C were determined only for the 40-, 60-, and 80-min time intervals. As shown in Figure 5b, the levels of arabinan, galactan, rhamnan, xylan, and mannan had declined to approximately 0. However, the glucan levels showed a slight decline that was indicative of earlier onset of possible degradation compared with autohydrolyzis.

Sugar analyzes

Figure 6 summarizes sugar analyzes of the autohydrolyzis and catalyzed hydrolyzis liquors, respectively. Prior to analysis, the primary hydrolyzis liquors were subjected to acid hydrolyzis to liberate monomers from oligomers. The pentosan and xylose contents in these hydrolysates generally decreased with increase in time as they were being converted to FF. It should be noted that xylose and FF mass recovery in the hydrolysates accounted for only a small fraction of the mass loss of the pentosans (arabinan, xylan, and mannan) primarily responsible for production of xylose and ultimately FF. This appears to be consistent with the hypothesis that some of the FF produced from the pentosans was bound to hydrolyzis reaction intermediates and lignin fragments or was degraded to succindialdehyde, which could condense to a resin (Marcusson 1921, Dunlop 1948).

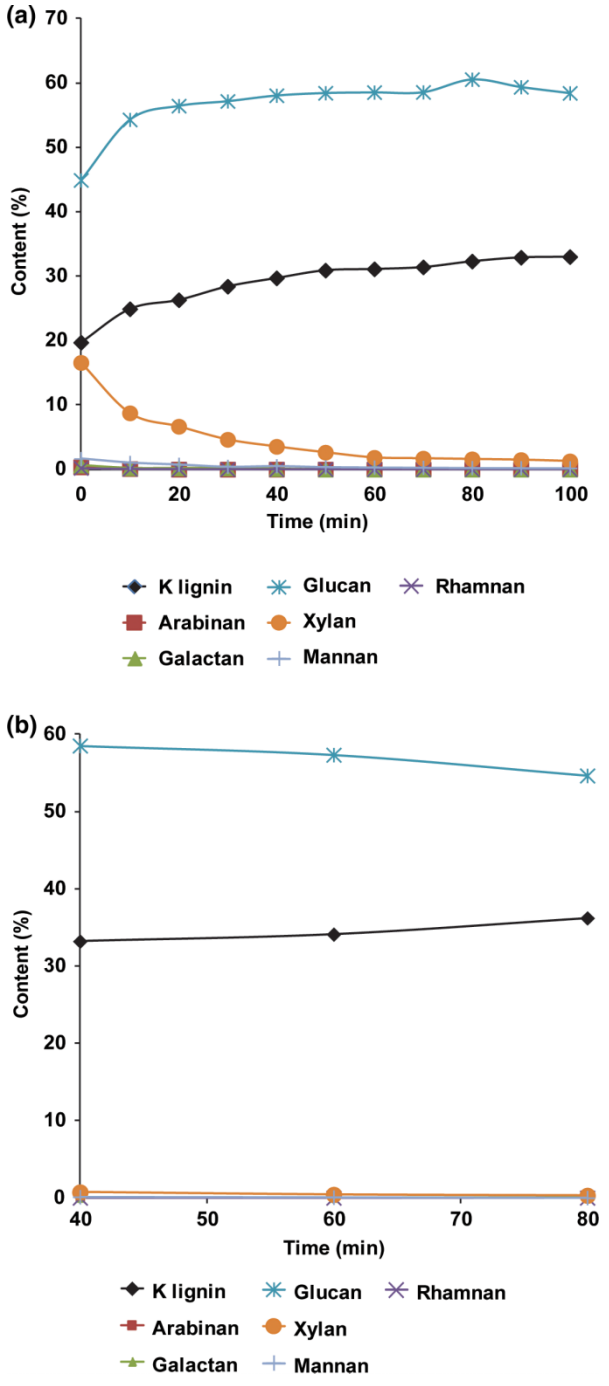

Figure 5. Changes in carbohydrate and lignin contents of residues after (a) autohydrolyzis and (b) catalyzed hydrolyzis at 200°C.

Effect of CS on FF and HMF production

As shown in Figure 7a, under autohydrolyzis conditions, the rate of FF formation was approximately 1.68 times higher compared with the rate of HMF formation, and the yields of both FF and HMF increased with increase in CS. However, under catalyzed hydrolyzis conditions, the FF yield decreased, while the HMF yield increased with increase in CS (Figure 7b). The rate of FF degradation

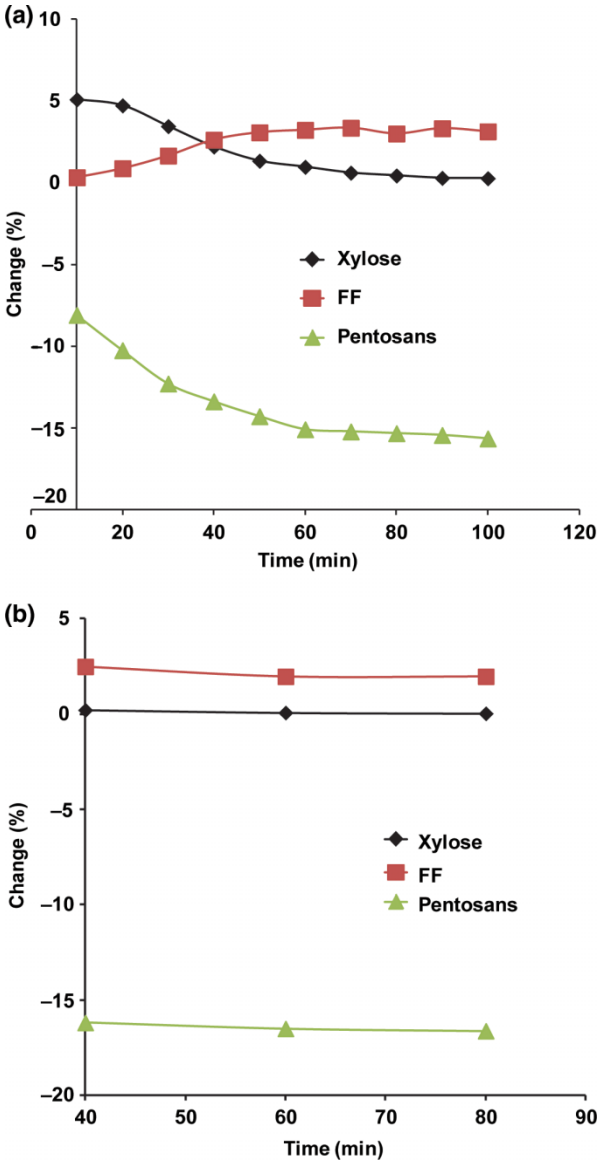

Figure 6. Percent change in sugar and pentosan content of secondary hydrolysates from primary (a) autohydrolysates and (b) catalyzed hydrolysates produced at 200°C.

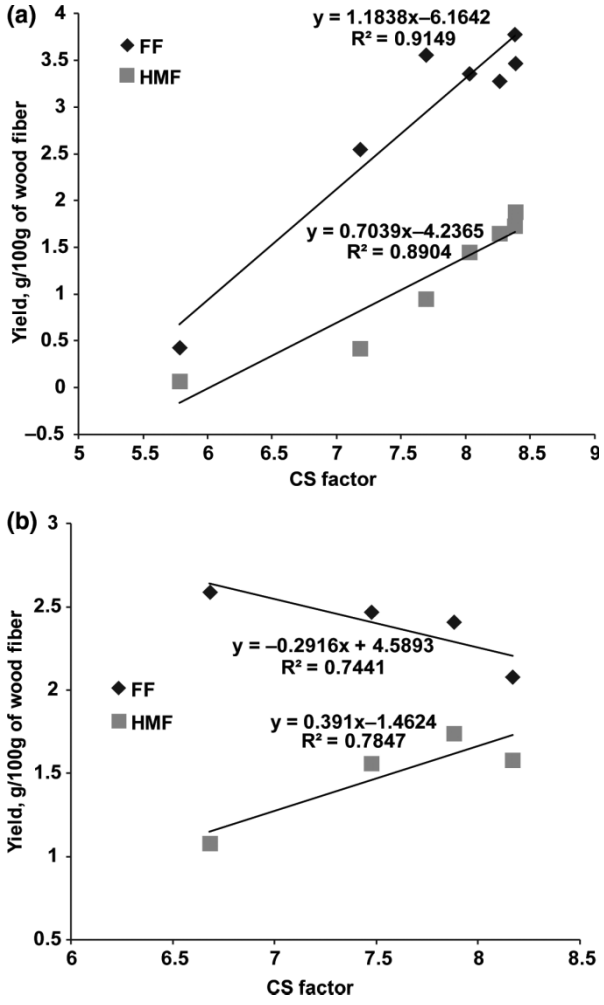

Figure 7. Yield of FF and HMF as a function of CS factor in (a) autohydrolyzis and (b) Lewis acid hydrolyzis of wood fiber.

was approximately 0.75 times lower compared with the rate of HMF formation. Evidently, the Lewis acid catalyst promoted both the conversion of the nascent FF into condensation by-products, and the degradation of hexosans to HMF.

Conclusions

This study demonstrated that under autohydrolyzis conditions approximately 3.5% and 1.75% of FF and HMF, respectively, could be produced in a microwave-heated, pressurized apparatus. However in the presence of a Lewis acid-catalyst, production of FF decreased from approximately 2.6% to 1.8%, and that of HMF decreased from approximately 1.7% to 1.3%. The objective of this study was to simulate autohydrolyzis or catalyzed hydrolyzis reactions that are likely to take place in a board-making press with moist lignocellulosic particles or injection of steam.

Under autohydrolyzis conditions, the rate of FF formation was higher than that of HMF formation, and production of both FF and HMF increased with increase in CS. However, in the presence of the Lewis acid catalyst, $AlCl_3.6H_20$, production of FF decreased with increase in CS. It is reasonable to conclude that under these conditions FF was converted into formic acid and condensation polymers of succindialdehyde (Williams and Dunlop 1948). Such polymers could potentially contribute to *in situ* resin formation or cross-linkages between fibers.

Hydroxymethylfurfural (HMF) unlike FF did not decrease with increase in CS in the presence of a Lewis acid catalyst. It is possible that degradation reactions were minor, at these low HMF levels, relative to the rate of HMF formation. Also it is

possible that in the presence of the Lewis acid catalyst, there was an increased level of glucans that contributed to the formation of HMF. Such an increase could conceivably originate from cellulose breakdown at high CS values. Cellulose breakdown could be detrimental to the mechanical properties of a self-bonded particle board.

Further research is needed to determine (1) the rate of hemicellulose degradation; (2) the contribution of the other hemicellulose sugars to the formation of FF and HF in the early stages of degradation; (3) if any HMF comes from cellulose; and (4) the role of lignin in self-bonding of wood fiber. Finally, physical testing of boards made with incorporated Lewis acid catalyst could be compared with those without the catalyst in order to assess the effect of the catalyst on strength and water absorption properties.

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