

Production of Furfural and Hydroxymethylfurfural by Autohydrolysis and Catalyzed Hydrolysis of wood: A Potential *in situ* Board Resin



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OUTLINE



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Motivation



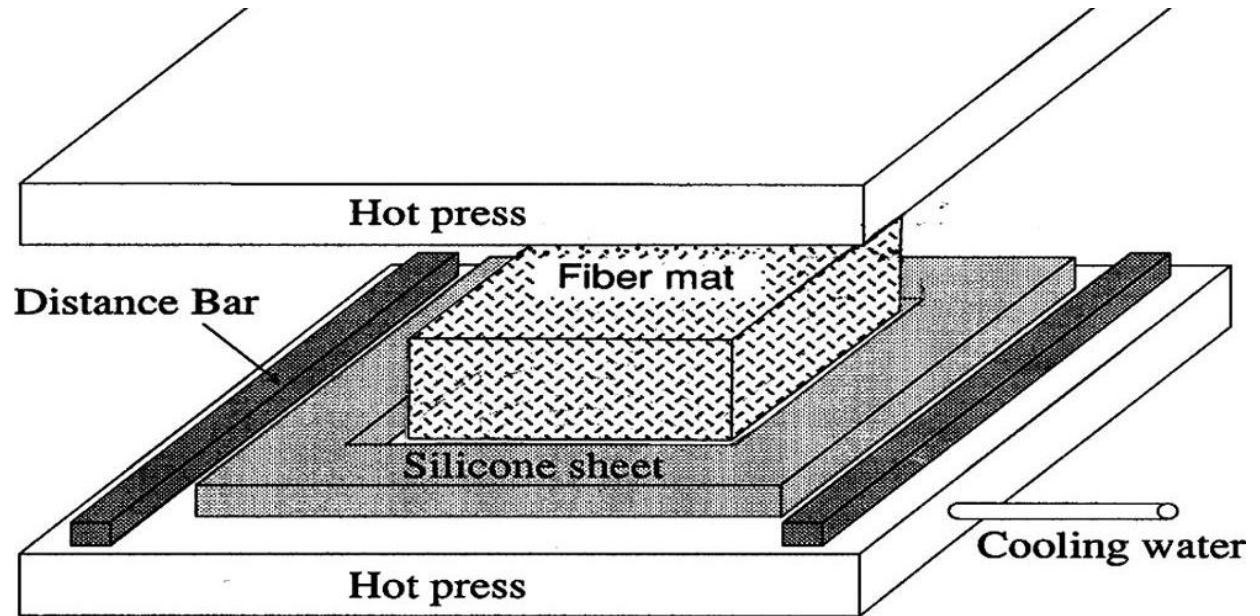
- Using a closed press system, Rowell and McSweeney (2008) formed self-bonding fiberboards from moist aspen fiber by pressing at 200°C for either 4 or 8 min.
- Static bending tests on the fiberboard specimens showed an improved modulus of rupture, and no change in modulus of elasticity compared to control specimens pressed in an open press system.
- Analysis of volatile compounds collected from the closed press after pressing for 50 minutes showed a peak in the concentration of furfural 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?

Conditions

Temp : 200 C

Time: 4 or 8 min

FMC: 15%



Closed press system

Objectives



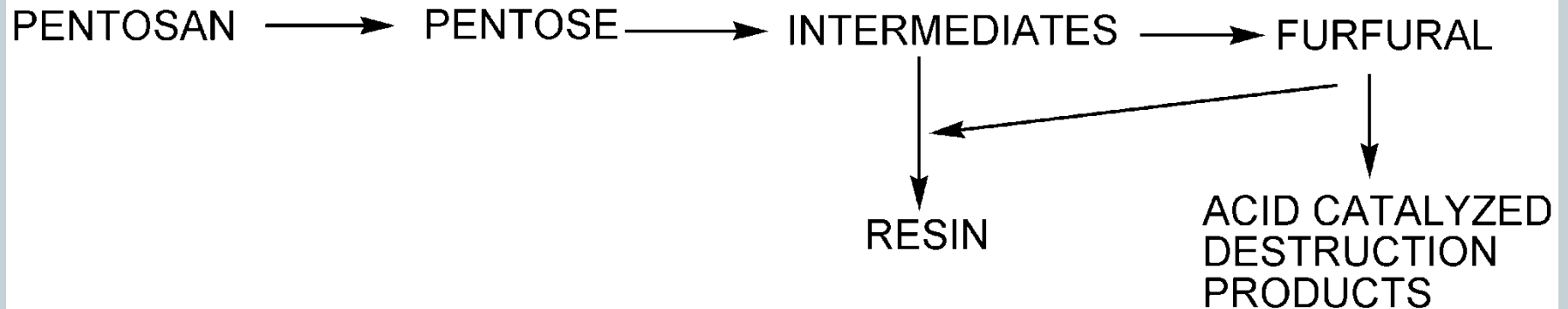
- To explore reaction conditions that affect formation of furans from thermal degradation of wood hemicelluloses in the presence of moisture.
- To study the effect of adding a Lewis acid catalyst on furan yields.

Background



- Wood carbohydrates consist of cellulose, hemicelluloses and pectins.
- Hemicelluloses are heteropolysaccharides made up of pentosans and hexosans.
- As long ago as 1948, Dunlop proposed that under high temperature hydrolysis conditions pentosans are converted to furfural in two or more steps

Schematic for conversion of pentosan to furfural and other byproducts.



Dunlop, A.P. (1948) Industrial and engineering chemistry, 40(2)



Materials:

Aspen

P. tremuloides





Sample preparation:

1-inch x ½-inch chips were milled in a Wiley mill and sized in a stack of sieves.

Fraction captured on the 40-mesh screen was used in this study



Milling →



Microwave reactor:

S/L : 1/6

Temp: 190 C and
200 C

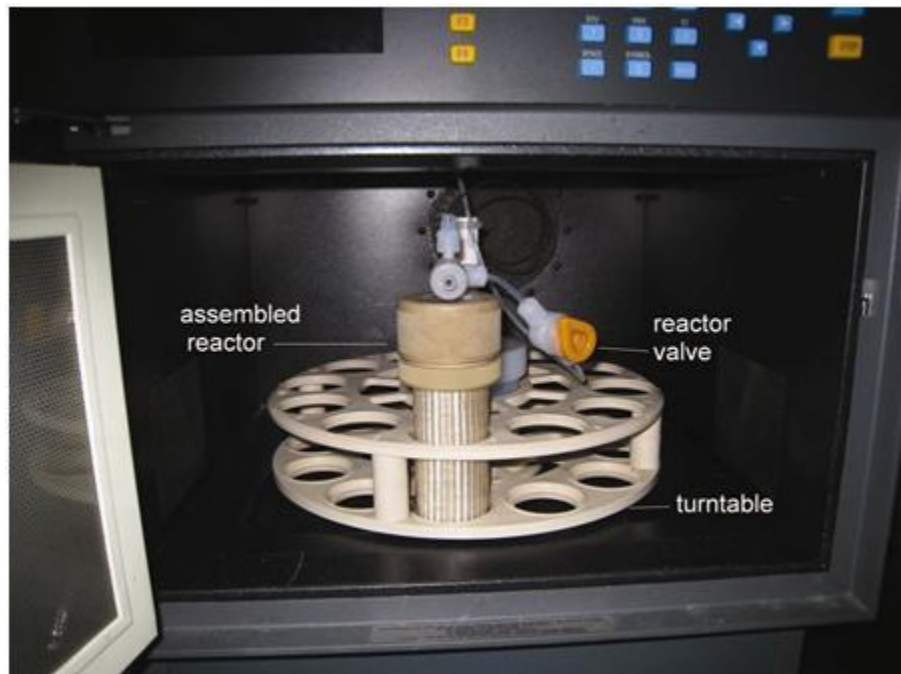
Pressure:

145-190 psi

180-200 psi

Time: 10 – 100
min

Catalyst:
 $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$



Analytical Procedures



Sample	Analyte	Method
Hydrolysis liquors	Furfural (FF) and hydroxymethylfurfural (HMF)	HPLC with diode array detector
Hydrolysis liquors	Sugars	HPLC with pulse amperometric detection
Starting milled wood	Sugars and lignin	HPLC with pulse amperometric detection
Posthydrolysis residues	Sugars and lignin	HPLC with pulse amperometric detection

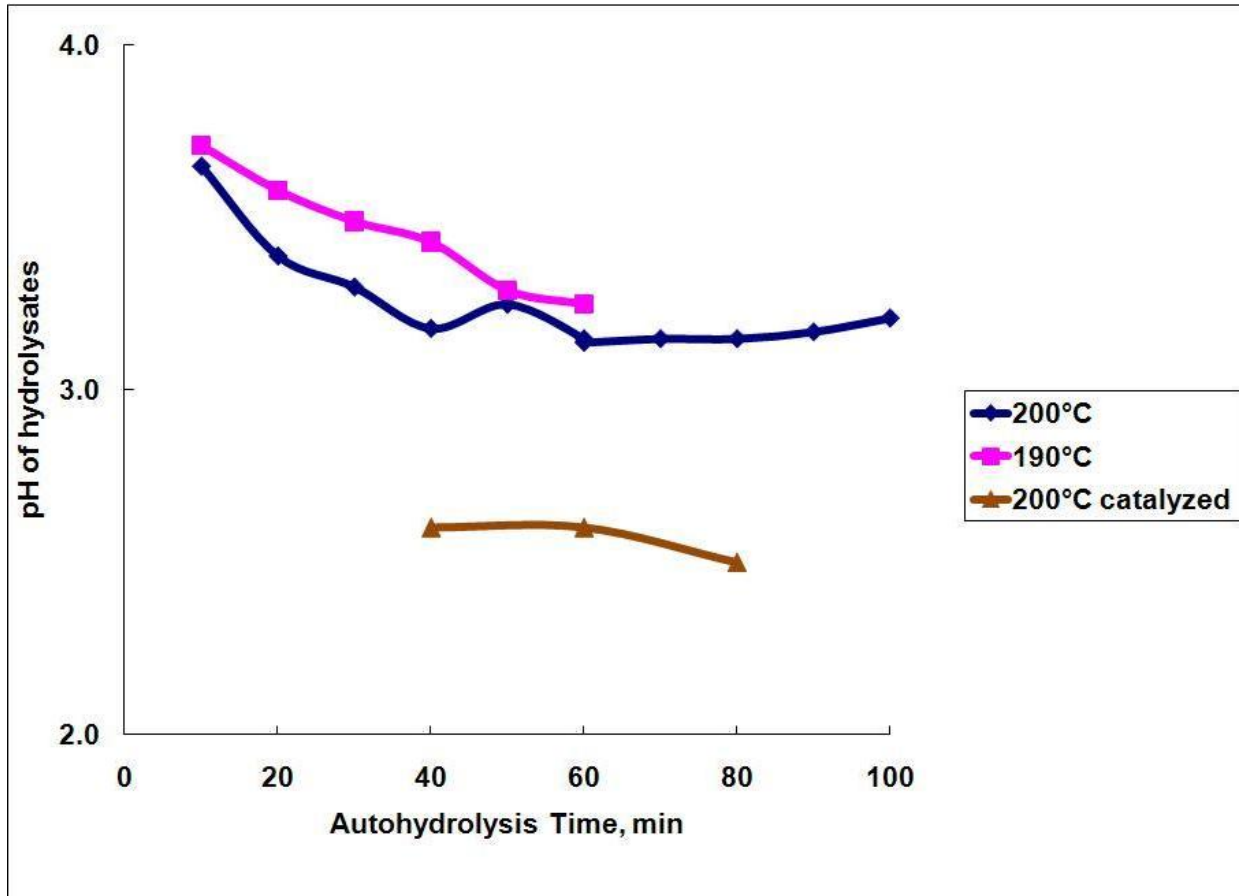
Results and Discussion



- pH of hydrolysates
- Furfural (FF) yield in autohydrolysis liquors
- Hydroxymethylfurfural (HMF) yield in autohydrolysis liquors
- Changes in carbohydrate and lignin contents of residues after autohydrolysis
- Sugar and pentosan content of secondary hydrolysates of primary autohydrolysates

pH of hydrolysates generally decreased with increasing severity of reaction conditions (higher temperature and longer hydrolysis time)

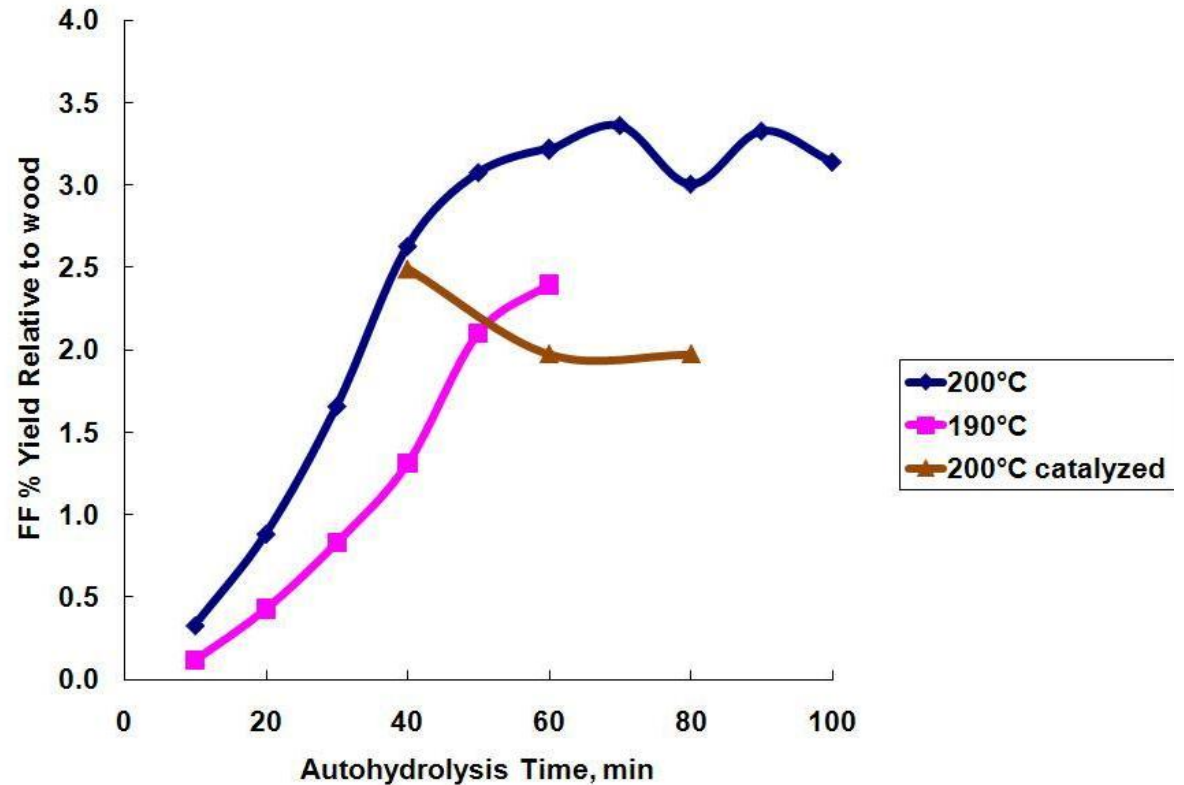
Lewis acid catalyst produced liquors with pH well below that of the non-catalyzed reactions



pH values of hydrolysates produced under different reaction conditions

FF yield reached a plateau at about 70 min at 200 C

In the presence of the Lewis acid catalyst, FF yield declined with time



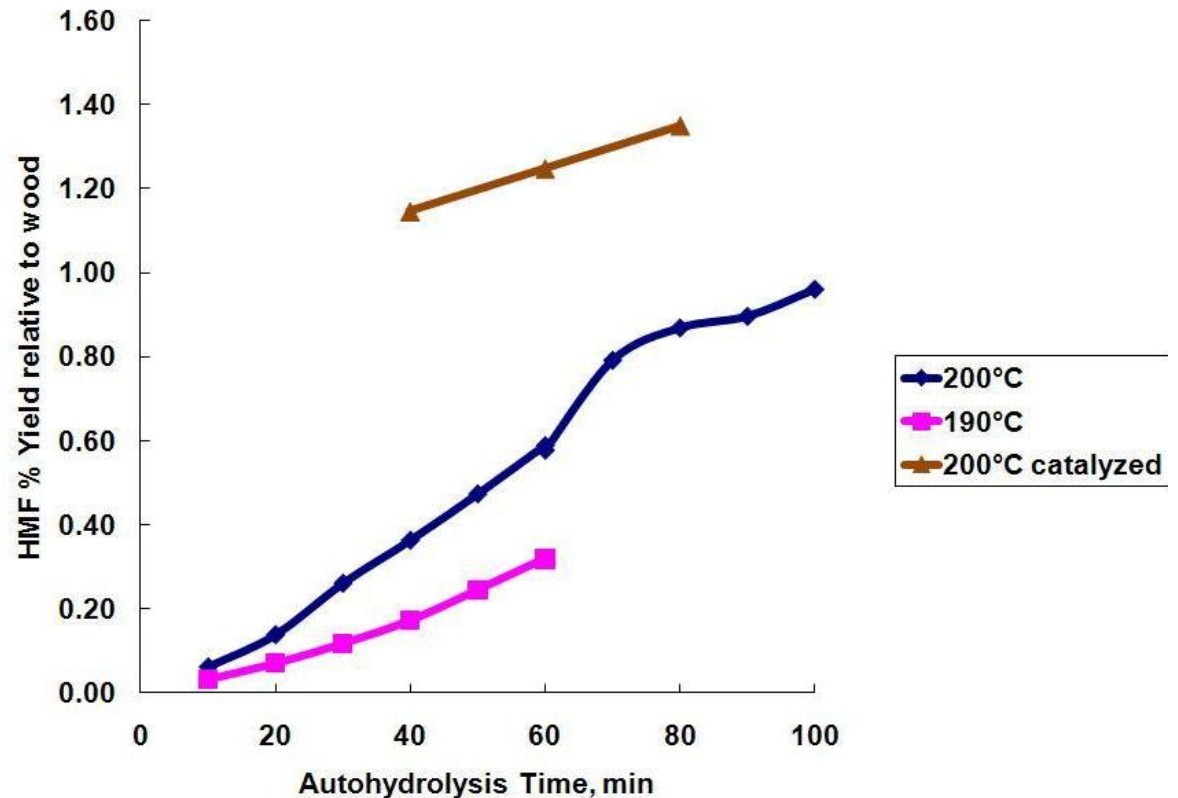
Furfural yield in autohydrolysis liquors produced under different reaction conditions



HMF yield continued to increase up to the maximum reaction time of 100 min

Without the catalyst the HMF yield reached 1%

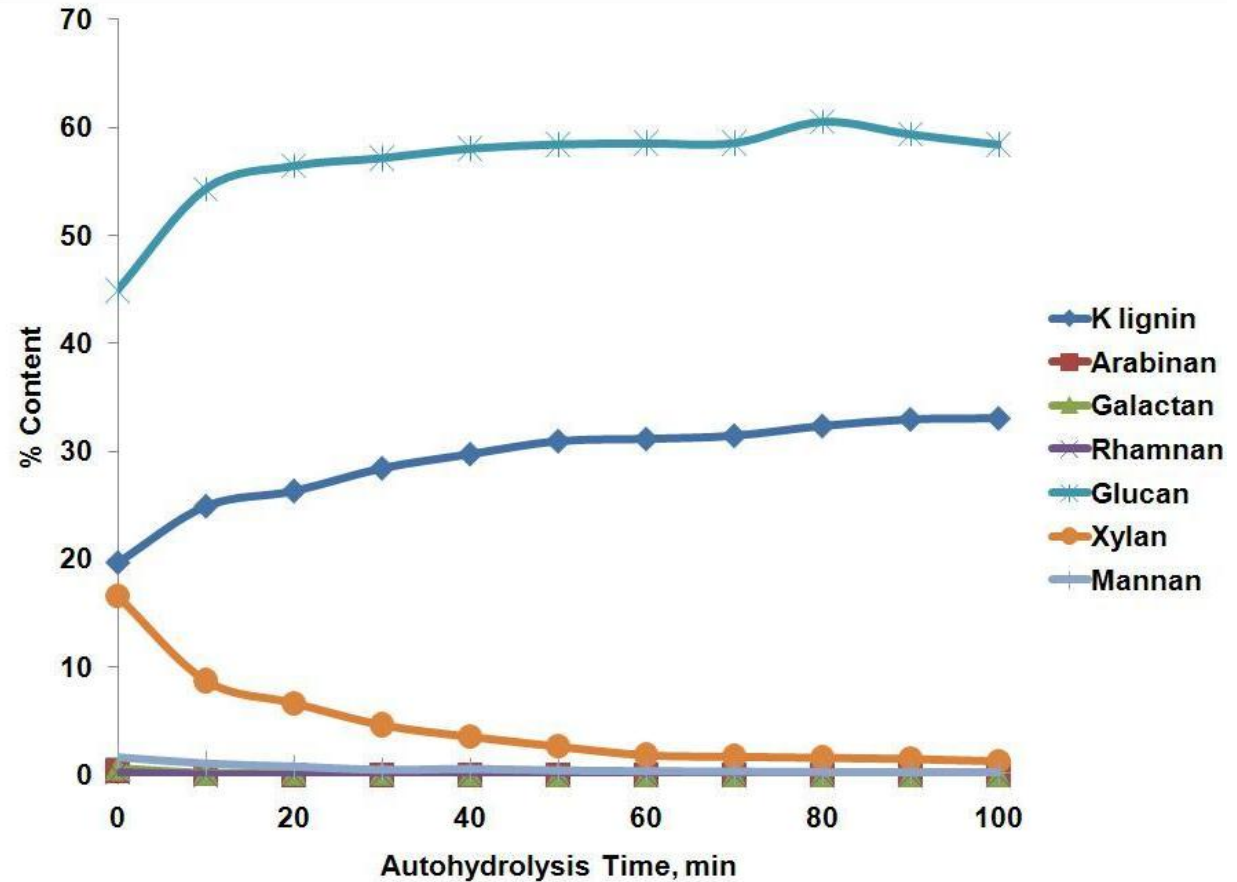
With the catalyst the HMF yield reached 1.4%



Hydroxymethylfurfural yield in autohydrolysis liquors produced under different reaction conditions

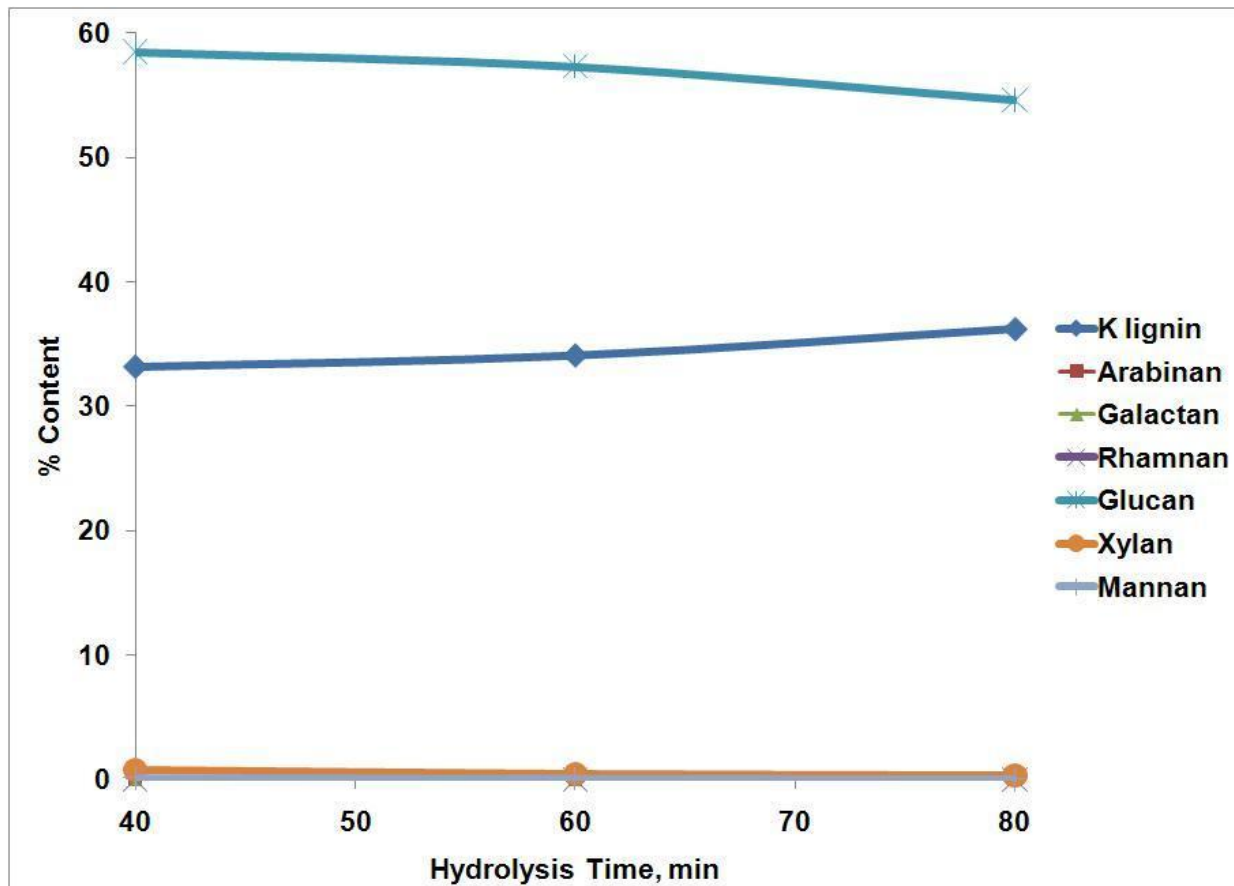
Arabinan, Galactan, Rhamnan and Mannan decreased to zero much earlier than Xylan

Glucan and K lignin remained relatively constant



Changes in carbohydrate and lignin contents of residues after autohydrolysis at 200 C

Lewis acid catalyzed hydrolysis for times longer than 40 min showed a slight decline in glucan levels

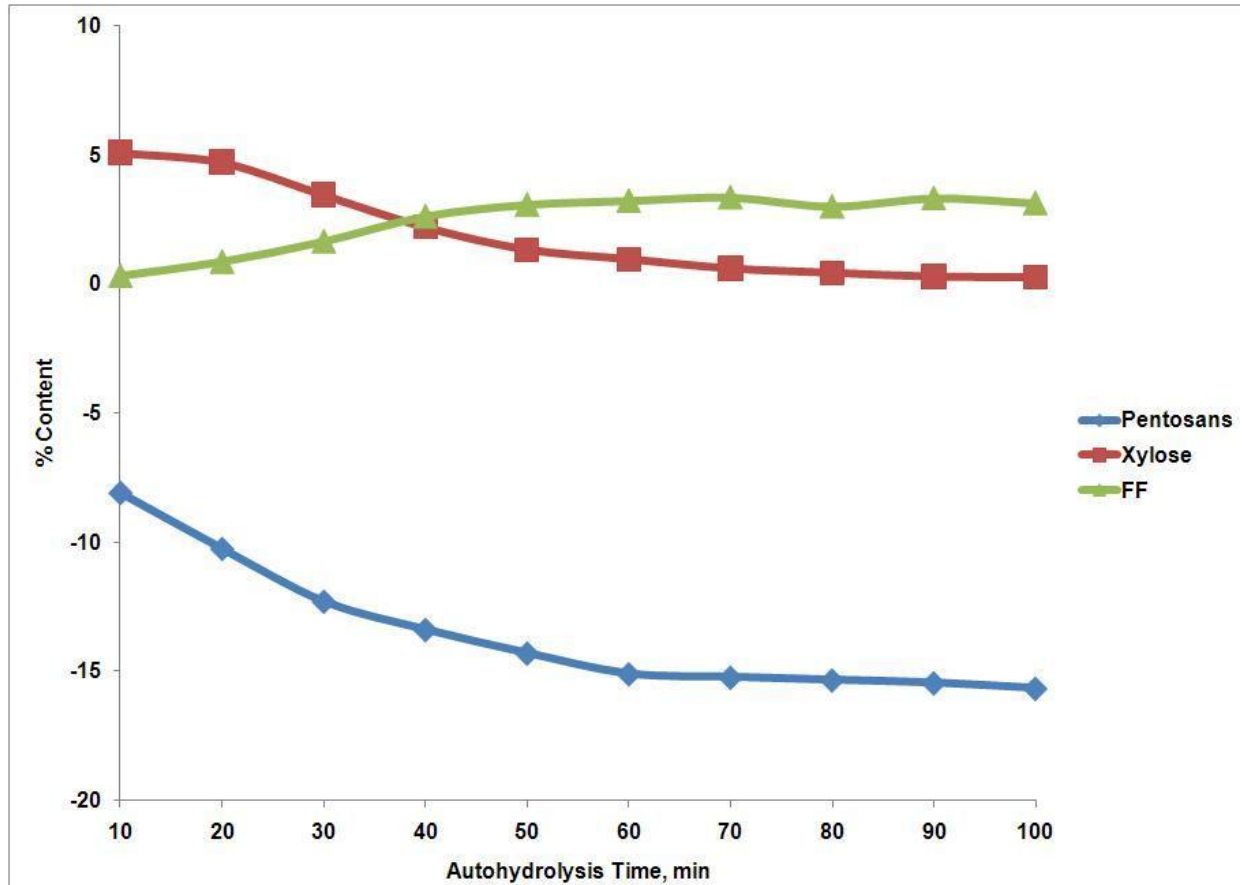


Changes in carbohydrate and lignin contents of residues after autohydrolysis at 200 C in the presence of a catalyst



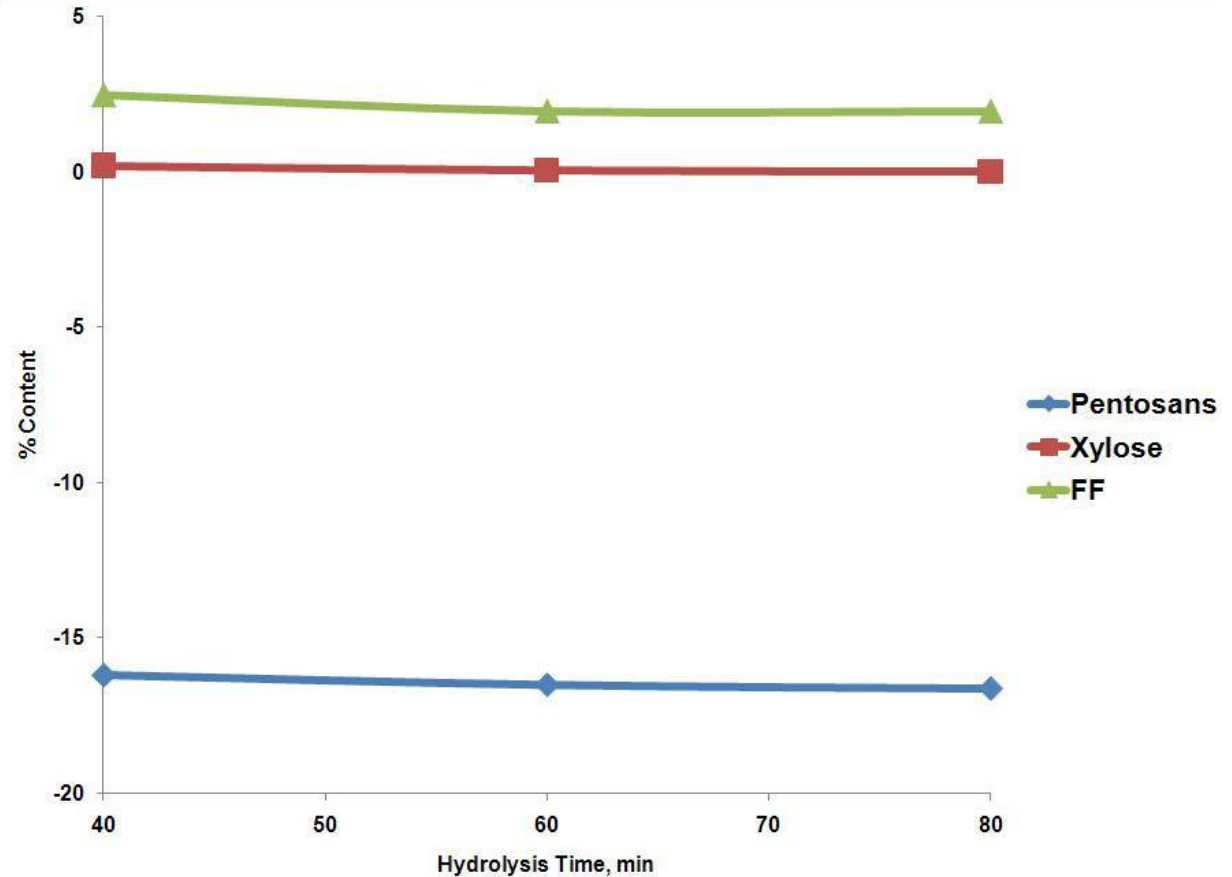
FF content increased with time as pentosan and xylose content decreased

However the FF and xylose mass recovery accounted for only a small fraction of the pentosan mass loss



Sugar and pentosan content of secondary hydrolysates from primary autohydrolysates produced at 200 C

The xylose and FF mass recovery in the catalyzed hydrolysates accounted for even a smaller fraction of the pentosan mass loss compared to the non-catalyzed autohydrolysates



Sugar and pentosan content of secondary hydrolysates from primary autohydrolysates produced at 200 °C in the presence of a Lewis acid catalyst

Conclusions



- Approx 3.5% and 1.4% of FF and HMF respectively could be produced under conditions described in this study
- Longer reaction times or inclusion of the Lewis acid catalyst, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ promoted degradation of FF
- HMF production, unlike that of FF did not decrease under any of the reaction conditions studied

Future research



- Determination of the rate of hemicellulose degradation
- Determination of the contribution of other hemicellulose sugars to FF and HMF formation in the early stages of degradation
- Determination of the contribution of cellulose to HMF formation
- Determination of role of lignin and pectins in self-bonding of wood fiber

Thank you for your attention



USDA Forest Products Laboratory