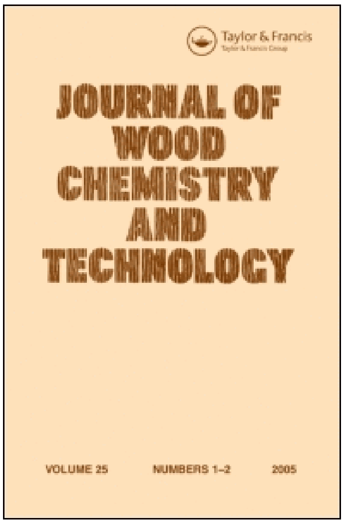

Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

Use of Difunctional Compounds During Rapid Steam Hydrolysis (Rash) Pretreatment

Jagdish Rughani; Louis Wasson; Lynn Prewitt; Gary McGinnis

To cite this Article Rughani, Jagdish , Wasson, Louis , Prewitt, Lynn and McGinnis, Gary(1992) 'Use of Difunctional Compounds During Rapid Steam Hydrolysis (Rash) Pretreatment', Journal of Wood Chemistry and Technology, 12: 1, 79 — 90

To link to this Article: DOI: 10.1080/02773819208545051

URL: http://dx.doi.org/10.1080/02773819208545051

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 12(1), 79-90 (1992)

USE OF DIFUNCTIONAL COMPOUNDS DURING RAPID STEAM HYDROLYSIS (RASH) PRETREATMENT

Jagdish Rughani, Louis Wasson, and Lynn Prewitt
Mississippi Forest Products Laboratory
P. O. Box Drawer FP
Mississippi State, MS 39762 USA
and
Gary McGinnis
Institute of Wood Research
Michigan Tech University
Houghton, MI 49931 USA

ABSTRACT

Mixed hardwood chips were treated with difunctional compounds as catalysts to study the reaction of wood with steam. The Rapid Steam Hydrolysis (RASH) pretreatment process was used for steam treatment. The difunctional compounds studied were maleic anhydride, phthalic anhydride, isophthalic acid, and terephthalic acid at 1.5% concentration based on dry wood weight. RASH pretreatment was performed for one minute at 180°C, 200°C, 220°C, 230°C, 240°C, and 260°C. These compounds strongly modified the RASH pretreated material, especially the physical structure. Overall recovery of the pretreated catalyzed and uncatalyzed solids decreased with an increase in RASH temperatures. Catalyst addition did not make a difference on the recovery of pretreated solids. Cellulose degradation increased with temperature for catalyzed systems. Hemicellulose solubilization and degradation were extremely sensitive to the type of catalyst and RASH temperatures. Almost all of the hemicellulose was lost at higher temperatures. Lignin losses did not appear to be affected by the addition of catalyst except at 260°C. Enzymatic rates were improved by addition of the catalysts, especially at the lower temperatures. The maleic anhydride gave the highest enzymatic rates at all temperatures, and phthalic anhydride gave the second highest. The water solubles generally followed the same trends as the enzymatic hydrolysis rates and increased with the addition of catalysts, especially maleic anhydride.

Keywords: Pretreatment, RASH, steam, wood, catalyst, difunctional compounds, maleic anhydride, phthalic anhydride, isophthalic acid, terephthalic acid.

INTRODUCTION

Various types of pretreatments for biomass conversion of wood have been evaluated in recent years. These pretreatments have included steam explosion, organosolv, autohydrolysis, wet-oxidation and Rapid Steam Hydrolysis (RASH)[1-10]. Processes that utilize steam or high temperature water treatment have several advantages when compared to other physical or chemical processes[1,3,11-13]. Some of these advantages are:

- Cost of chemicals (steam) is relatively cheap when compared to any other chemicals.
- Opportunity exists to fractionate the wood components.
- Pretreated solid fraction contains higher percentage of cellulose than the starting material.
- Effectively increases the enzymatic rates of hydrolysis.
- Effective with a wide variety of biomass materials.

A variety of catalysts have recently been used with wood to improve the rate of delignification, to lower the glass transition temperatures of the wood components, and to improve the anti-swelling properties of composite board[14-19]. The objective of this study was to evaluate various difunctional compounds as catalyst for the reaction of wood during steam treatment.

MATERIALS AND METHODS

In this study, a group of difunctional compounds were evaluated as catalysts for RASH pretreatment. The compounds included maleic anhydride, phthalic anhydride, isophthalic acid, and terephthalic acid. A single concentration for all catalysts was selected to compare their effectiveness. The wood after treatment with catalyst was pretreated for one minute at various intervals from 180°C to 260°C. The biomass material consisted of mixed hardwood composed of 42.5% cellulose, 18.5% hemicellulose (based on monosaccharide analysis after hydrolysis), and 28.5% lignin (obtained with the Klason-lignin procedure)[20,21]. The remaining material consisted of acidic carbohydrates found in the xylan and extractives. No attempt was made to monitor the changes of these constituents during RASH pretreatment.

A large amount of mixed hardwood chips (1-1.5") was ground and screened through a 6mm sieve. A spraying solution was prepared by dissolving the appropriate amount of catalyst (1.5%, based on the dry weight of wood) in 100 ml of water. To insure a uniform distribution of the catalyst, the wood chips were continuously mixed for 2 hours while being sprayed with the solution .

The wood chips were air-dried for 24 hours prior to RASH pretreatment for one minute at 180°C, 200°C, 220°C, 230°C, 240°C and 260°C. More detailed information on the RASH pretreatment can be found in previous publications[10,21]. Following the pretreatments, the solids fraction was air-dried for 24 hours. The pretreated material was then weighed to determine the percent solids and was analyzed to determine the percentage of carbohydrates, Klason lignin, water and methanol soluble materials and 72-hour enzymatic hydrolysis rates. The enzyme was "Cellulase," a commercial product produced by Meiji Seika Co., Ltd., Japan. The analytical and enzymatic procedures are described in more detail in previous publications[1,3,10,15,19]. The water solubles were determined on the pretreated solid fraction and methanol solubles were determined on the water insoluble fraction. All results are calculated on the basis of oven-dried weight of the starting material.

RESULTS AND DISCUSSION

The RASH pretreatment process was used to determine the effect of difunctional compounds on the reactions of wood with steam. Four catalytic systems--maleic anhydride, phthalic anhydride, isophthalic acid, and terephthalic acid--were evaluated at 1.5% concentration and at various temperatures. For each

TABLE 1
Percentage Solids After RASH Pretreatment
Calculated on the Basis of Starting Material.

Temp.	Control	Maleic Anhydride	Phthalic Anhydride	Isophthalic Acid	Terephthalic Acid
		(1.5%)[a]			
180°C	99.19	98.36	98.93	98.15	99.38
200°C	98.42	97.53	98.25	98.77	97.17
220°C	95.85	89.88	94.46	94.80	94.67
230°C	89.69	84.46	89.64	87.82	90.43
240°C	79.07	78.29	75.74	83.54	81.27
260°C	62.31	64.99	64.93	61.34	59.77

[a] Percentage of chemicals per 100 grams of dry wood weight.

catalytic system, the relationship between the recovered solids after RASH pretreatment and the reactor temperature are given in Table 1.

The amount of recovered solids for both the control (uncatalyzed) and the catalyzed material decreased as the temperature increased. The catalyst pretreated material gave similar results as the control sample at all temperatures.

The effects of the difunctional catalyst and the RASH temperatures on the individual chemical constituents of wood are given in Table 2. Changes in the cellulose content, based on glucose analysis, are summarized in Table 2. Since all of these values are based on starting material, a direct comparison can be made between values at various temperatures. Overall, the glucose units in the cellulose of the uncatalyzed control and in the catalyzed material were stable up to 240°C. This result agrees with earlier results[1,3,10,19,21]. With some exceptions, the catalytic systems gave slightly lower yields of glucose, especially at 260°C. This was especially true for the maleic and phthalic anhydride catalyzed systems.

TABLE 2
Percentage Composition of RASH Pretreatment
Calculated on the Basis of Starting Material.

Temp.	Control	Maleic Anhydride	Phthalic Anhydride	Isophthalic Acid	Terephthalic Acid
		(1.5%)[a]			
Cellulose[b]					
180°C	42.92	41.79	41.56	44.00	41.31
200°C	41.89	42.29	42.87	39.88	43.39
220°C	44.16	41.36	39.81	40.31	43.67
230°C	42.29	41.81	41.29	39.80	40.60
240°C	41.65	39.54	39.04	40.75	42.33
260°C	38.51	32.06	33.48	37.31	37.11
Hemicellulose[c]					
180°C	17.41	15.54	13.25	16.42	16.99
200°C	17.34	16.24	16.12	14.85	17.19
220°C	16.57	13.56	12.49	13.30	14.85
230°C	13.12	6.77	10.22	11.43	11.75
240°C	6.10	2.71	3.78	7.15	6.13
260°C	0.74	0.38	0.00	0.56	0.58
Lignin[d]					
180°C	29.61	34.55	30.05	32.09	32.21
200°C	31.40	29.93	30.96	30.47	30.78
220°C	31.32	29.81	33.87	30.28	32.55
230°C	30.92	32.37	32.42	34.45	29.90
240°C	28.05	30.10	27.15	28.89	28.98
260°C	23.44	30.23	28.49	21.14	20.32

[a] Percentage of chemicals per 100 grams of dry wood weight.
[b] Based on glucose analysis after hydrolysis.
[c] Based on carbohydrate analysis after hydrolysis.
[d] Based on Klason-lignin values.

The changes in the hemicellulose component after pretreatment are given in Table 2. The original starting material contained approximately 18.5 % hemicellulose based on the total content of arabinose, xylose, and mannose units. The control material pretreated at 180°C lost approximately 6% of the hemicellulose and decreased gradually with the increase in temperature. The presence of catalyst resulted in the increased loss of hemicellulose above 180°C, particularly with the maleic and phthalic anhydride systems as compared to the control or to the isophthalic and terephthalic acids catalyzed systems. The major loss of hemicellulose occurred at 230-240°C, with the exception of the maleic anhydride system where the major loss occurred at 220-230°C. At 260°C, most of the hemicellulose had been destroyed or lost with both the catalyzed and the control systems.

The Klason-lignin content of the various pretreated samples is reported in Table 2. Between 180° and 240°C, the lignin content of the control and catalyzed pretreated material varied from 29.6% to 34.6% with no apparent pattern. At 260°C, 18% lignin loss was observed for the control, whereas 28-30% lignin losses were observed for isophthalic and terephthalic acids. However, no Klason lignin losses were observed for maleic and phthalic anhydride treated samples. Apparently, these systems stabilized or protected lignin in a degraded form.

Changes in the constituents are determined by chemical analysis of the starting material. However, this analysis does not provide information on chemical changes which lead to lower molecular weight or physical changes, which could cause changes in accessibility. In order to determine if the catalysts had any effect on these properties, rate studies were performed using enzymatic hydrolysis. Enzymatic hydrolysis using cellulase enzymes provides a sensitive indicator of physical and chemical changes of the lignin, hemicellulose, and cellulose during pretreatment. The results after 72 hours are shown in Figure 1 and Table 3. The enzymatic hydrolysis rate for the control material increased gradually up to 220°C and then increased rapidly at 240°C. The highest rate was observed at 260°C. Early studies showed that the further increase in temperature decreased the rate[10,19,21].

All the catalyzed pretreated material had a higher rate of enzymatic hydrolysis than the controls with two exceptions at

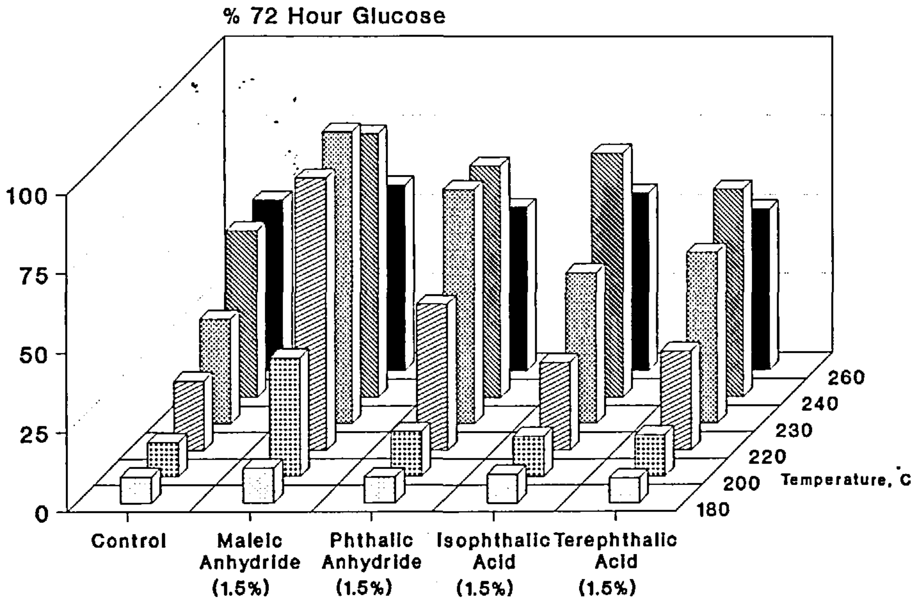

Figure 1. Rate of cellulose hydrolysis after RASH pretreatment calculated on the basis of starting wood weight.

TABLE 3
Percentage Glucose After Enzymatic Hydrolysis (72 Hours) on the Basis of Starting Wood Weight.

Temp.	Control	Maleic Anhydride	Phthalic Anhydride	Isophthalic Acid	Terephthalic Acid
		(1.5%)[a]			
180°C	8.27	11.03	8.21	9.07	7.79
200°C	10.76	37.38	14.15	12.70	13.06
220°C	21.79	85.83	45.97	27.58	31.10
230°C	33.00	92.00	73.93	47.56	53.94
240°C	52.61	83.05	73.08	76.96	65.62
260°C	53.91	58.59	51.55	56.15	50.94

[a] Percentage of chemicals per 100 grams of dry wood weight.

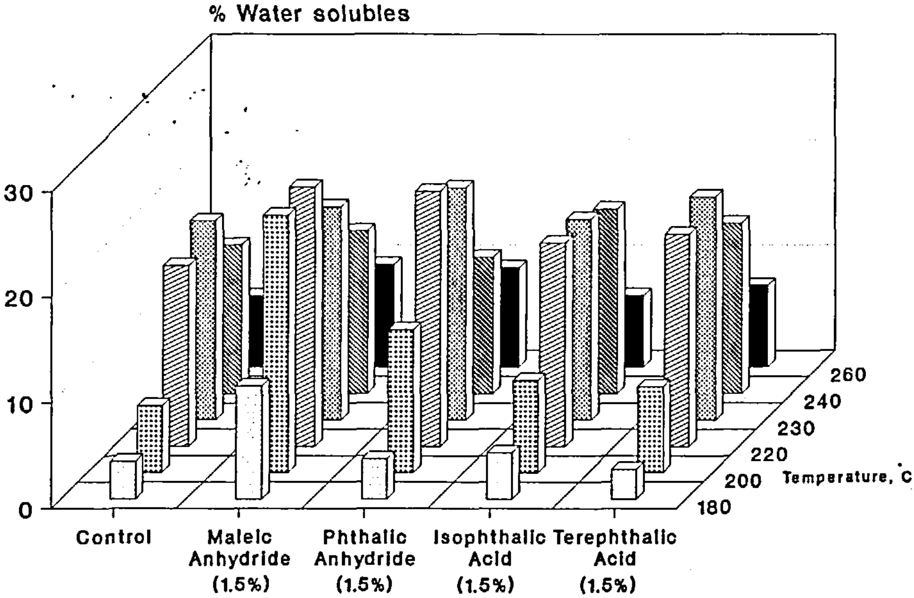

Figure 2. Percent water solubles of RASH pretreated material calculated on the basis of starting wood weight.

260°C. The maleic anhydride catalyzed system gave the highest enzymatic rates at all temperatures. At a 230°C treatment temperature, 92% cellulose was hydrolyzed to glucose. The other catalyst system also reached optimum yields at 220-240°C. A comparison of these results with the data in Table 2 indicates that the amount of Klason lignin present had a minor effect on the enzymatic rates. The highest enzymatic rates were observed at the RASH temperatures where drastic losses of hemicellulose were observed and where the Klason-lignin content was unchanged. One explanation for the observed effects is that the catalyst disrupts the lignin structure and solubilizes hemicellulose which increases the amount of cellulose accessible to the enzyme, thereby increasing the enzymatic hydrolysis rate.

TABLE 4
Percentage Solubles of RASH Pretreatment
Calculated on the Basis of Starting Material.

Temp.	Control	Maleic Anhydride	Phthalic Anhydride	Isophthalic Acid	Terephthalic Acid
		(1.5%)[a]			
Water Solubles					
180°C	3.57	10.69	3.81	4.39	2.79
200°C	6.30	24.37	13.51	8.73	8.12
220°C	17.08	24.55	24.51	19.25	20.11
230°C	18.86	20.19	22.02	19.03	21.15
240°C	14.07	15.42	12.94	17.43	16.18
260°C	6.70	9.72	9.43	6.80	7.75
MeOH Solubles					
180°C	1.94	1.96	3.68	2.68	3.10
200°C	2.03	4.57	3.26	4.59	2.36
220°C	4.74	5.18	5.10	4.69	6.25
230°C	4.94	8.55	8.10	6.01	6.74
240°C	5.86	10.42	9.21	8.83	10.82
260°C	8.46	12.91	13.08	13.08	8.25

[a] Percentage of chemicals per 100 grams of dry wood weight.

At 260°C, considerable losses of lignin occurred, and the enzymatic rates decreased. One possible explanation for this observed rate decrease is that the recombination and crosslinking of the lignin leads to a decrease in accessibility by the enzyme. This conclusion is supported by recent accessibility studies of the RASH pretreatment[22].

The relationship between the amount of water soluble products and the RASH temperature is shown in Figure 2 and Table 4. At the lower temperature, the most likely source of the water soluble products is the hemicellulose fraction. At the higher temperatures, most of the water soluble products probably come from the cellulose and the Klason-lignin fraction. The relationship between the water soluble products and the extent of enzymatic hydrolysis is very similar. Catalyst systems (maleic anhydride and phthalic anhydride) which give the greatest amount of water soluble products also give the highest enzymatic yields. In contrast, the yield of methanol (MeOH) solubles reaches a maximum of 260°C where the greatest change occurs with the lignin fraction. Therefore, one would expect that the MeOH soluble fractions at 260°C probably come mainly from the lignin fraction or from the highly degraded carbohydrate. Again, the maleic anhydride system appears to be the most effective in catalyzing the reactions leading to the production of methanol soluble products.

CONCLUSIONS

This study indicated that the addition of difunctional catalyst can modify the RASH reaction of wood. Addition of all catalysts increased the breakdown of hemicellulose at lower temperatures and the cellulose at higher temperatures, but only maleic and phthalic anhydride altered the yield of Klason lignin. Enzymatic rates were improved by the addition of all the catalysts, especially at the lower temperatures. Maleic anhydride gave the highest enzymatic yield at all temperatures, and the phthalic anhydride gave the second-highest yield. The catalysts not only increased the rate of enzymatic hydrolysis, but also lowered the optimal RASH pretreatment temperature. Apparently, the maximum enzymatic yields can be co-related to the loss of hemicellulose and water soluble products but not to the Klason-lignin content. The maleic anhydride system was the most effective in catalyzing the reactions leading to the production of methanol soluble products.

REFERENCES

1. T. P. Schultz, G. D. McGinnis, and C. J. Biermann, In: Energy Recovery from Lignin, Peat and Lower Rank Coals, Chapter 8, D. J. Trantolo and D. D. Wise (ed.), Elsevier Science Publisher, Amsterdam, 1989.

2. T. P. Schultz, J. Rughani and G. D. McGinnis. App. Biochem. and Biotech., Vol. 20/21 (9), 1989.

3. T. P. Schultz, G. D. McGinnis, and C. J. Biermann, Symp. Pap. Ener. Biomass Wastes, 8th USA, 8, 1171 (1984).

4. A. R. Humprey, Adv. Chem. Series, 181, 25 (1979).

5. C. G. April, R. Bharoocha, J. Cheng, and S. Hensen, TAPPI, 65(2), 41 (1982).

6. C. G. April, R. Bharoocha, J. Burton, and S. Hensen, NSF Contract No. AER78 02651, 1980.

7. P. Foody, Final Report to DOE, contract AC02-79ETZ3050, 1980.

8. J. H. Lora and J. Wayman, Can. J. Chem. 58, 669 (1980).

9. J. H. Lora and J. Wayman, TAPPI, 61(6), 47 (1978).

10. C. J. Biermann, Ph.D. Thesis, "The Development of a New Pretreatment Method (RASH) and the Comparison of Rapid Steam Explosion, Autohydrolysis, Wet-Oxidation as Pretreatment Process for Biomass Conversion of Southern Hardwood," Mississippi State University, 1983.

11. M. M. Hartree, C. Hogan, R. D. Hayes, and J. N. Saddler, Biotech and Bioeng., 25, 101 (1983).

12. R. E. H. Dekkar and A. F. A. Wallis, Biotech and Bioeng., 25, 3027 (1983).

13. J. Karchesy and P. Koch. USDA Forest Services, Tech. Report SO-24 (1979).

14. T. K. Ghose, P. V. Pannir Selvan and P. Ghosh, Biotech. and Bioeng., 25, 2577 (1983).

15. P. V. Pannir Selvam, T. K. Ghose and P. Ghosh, Process Biochemistry, 18(3), 13 (1983).

16. K. V. Sarkanen and D. A. Tillman, Prog. Biomass Conversion, 2, 128 (1980).

17. I. Sakata and R. Senju, J. Appl. Polymer Sci., 19, 2799 (1975).

18. H. Fujimoto, T. Anazawa and K. Yamagishi, Mokusai Gakkaishi, 33(7), 610 (1987).

19. J. Rughani, L. Wasson, and G. McGinnis. J. of Wood Chem. and Tech., 10(4), 515 (1990).

20. I. S. Goldstein, Biomass Availability and Utility for Chemical in Organic Chemicals from Biomass, CRC Press, Baco Raton, Florida, 1981.

21. J. R. Rughani and G. D. McGinnis. Biotech and Bioeng. 35, 681 (1989).

22. I.-L. Shiau and G. D. McGinnis, Evaluation of Accessibility of Cellulosic Materials by Solute Exclusion Method. J. of Wood Chem. and Tech. (Submitted)