Thermal Degradation Kinetics of Polysaccharides in Fibrous Materials during Hot Water Treatment: A Preliminary Study

Wei Jiang,[a] Guangting Han,[a,]* Chengfeng Zhou,[b] Yuanming Zhang,[a] and Brian K. Via [b,]*

The current Chinese Standard (GB5889-86 1986) for wet chemistry determination assumes that there is no temperature degradation of sugars during hot water extraction. There is therefore a need to quantify this level of error and propose possible solutions for future revisions. This research was performed to investigate the thermal resistance of polysaccharides in common fibrous materials. A two-factor, two-level experimental design was employed, in which pre-oven drying and water bath temperature were controlled and changes in extractive content were measured. The thermodynamic equations for polysaccharide thermal degradation in ramie and wood were calculated. High-performance liquid chromatography (HPLC) was employed to identify monosaccharide changes during the process. This study found that polysaccharides in fibrous materials have considerable thermal degradation during oven drying at 100 °C and hot water treatment. Lower temperature combinations are recommended during hot water extractive testing when sugar analysis is to be subsequently performed.

Keywords: Thermal degradation; HPLC; Water extractives; Dynamical equation

Contact information: a: Laboratory of New Fiber Materials and Modern Textiles, The Growing Base for State Key Laboratory, Qingdao University, Qingdao 266071, PR China; b: Forest Products Development Center, School of Forestry and Wildlife, Auburn University, Auburn, AL 36849, USA;
** Corresponding authors: kychgt@qdu.edu.cn; bkv0003@auburn.edu*

INTRODUCTION

Bio-based fibrous materials such as wood, rice straw, corn stover, bamboo, and ramie are important raw materials for paper-making, bioenergy research, textiles, and other related areas (Baratieri *et al.* 2008; Morris *et al.* 2000). Fibrous materials primarily contain extractives, lignin, and most significantly, polysaccharides, which provide the most value for bioproduct applications (Kaar *et al.* 1991; Pettersen 1984). Characterization of the properties and the chemical composition of these fibrous materials is essential before utilization in industrial processes or laboratory research.

In China, a national standard (GB5889-86 1986) has been established as the preferred wet chemistry analysis method for the assessment of ramie and other fibrous materials (Jiang and Shao 1986). When using this standard to determine water extractive content, the sample is placed in a water bath at 100 °C. Polysaccharide determination is often performed next. However, it is probable that some of the polysaccharides are unintentionally removed during the water bath treatment, resulting in bias (Xu *et al.* 2007). Lower temperatures (60 to 80 °C) have been shown to be more suitable for minimizing these temperature effects during water-soluble extractive content testing (Chaa *et al.* 2008; Sun *et al.* 2001). However, no work has been performed outlining the level of error present with the current standard, and there are no suggested changes for future revisions of the standard.

The objective of this study was to elucidate the thermal degradation kinetics of polysaccharides in fibrous materials for various oven drying and hot water treatments and to determine the best methodology for water extractive testing for utilization in future standards.

MATERIALS

Sample preparation

Ramie samples were collected from Hunan Province, People's Republic of China. Although loblolly pine (*Pinus taeda*) wood samples were harvested from Montgomery, AL, USA, this tree is commercially important in China (Bao *et al.* 2001). All of the samples were first placed in the lab under ambient conditions (23 to 26 °C and less than 50% humidity) for two weeks; after the samples were air-dried to a stable moisture content, 50 g of the sample was ground to 40-mesh size and utilized.

Wet chemistry and High-performance liquid chromatography (HPLC) Analysis

As shown in Fig. 1, the wet chemistry was carried out on 40-mesh raw samples, and all samples were tested in duplicate. The experimental design is shown in Table 1. Five grams of ramie or wood were oven dried under two different temperatures (60 and 100 °C), and the extractives were then removed from the sample using acetone in a Soxhlet apparatus. The samples were then oven dried, each under the same temperature as before. Then, 3 g of extractive free sample was weighed and placed in a 150-mL flask with 100 mL of distilled water. The flask was then placed in a water bath at either 60 or 100 °C. After 1 h of treatment, the samples were filtered using a quantitative paper filter, then oven dried again at the same temperature as before. The weight of the pretreated sample was measured before and after extraction to calculate water extractive content. The same pretreatment was conducted on the residue for the first process, and the water extractive content was analyzed for the second time and repeated for subsequent cycles until the extractive content was so low that it was unmeasurable by our system. To determine the monosaccharide composition (glucose, xylose, mannose, galactose, and arabinose), a Shimadzu LC-20A HPLC (Shimadzu, USA) equipped with an Aminex 87 P column (Bio-Rad, USA) and differential refractive index detector was employed. In this research, HPLC was performed on the residue after the first and second cycles for pine.

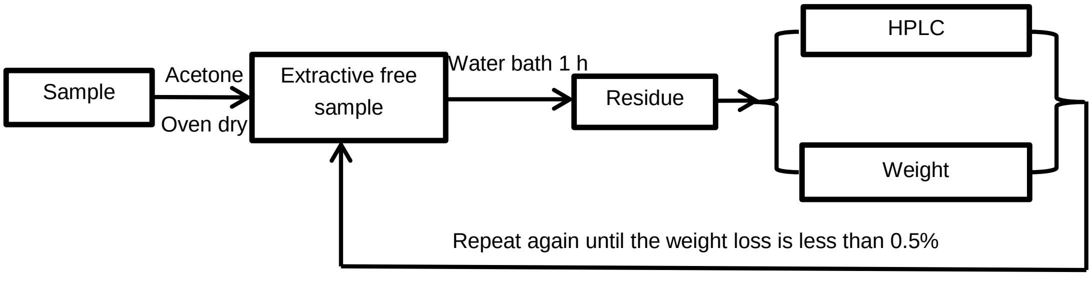


Fig. 1. Schematic diagram for testing water extractive content

RESULTS AND DISCUSSION

Effects of Temperature on the Degradation of the Polysaccharide

As shown in Table 1, four different temperature combinations were applied in this experiment. The highest water extractive content was measured under method A (Table 1), and there were demonstrable differences in extractive content between methods. Generally, the water extractives should be completely removed from the raw material by the second or third cycle. However, as shown in Table 1, there was continuous weight loss with method A until the eighth cycle. This indicated that polysaccharide degradation was responsible for the additional weight, as it is well known that lignin and cellulose have high chemical and thermal resistances below 100 °C (Brebu and Vasile 2010; Connors *et al.* 1980; Via *et al.* 2013).

Table 1. Weight Loss of Water Extractive Content of Ramie Fibers using Eight Test Cycles

Method	Factor 1: Oven dry temperature (°C)	Factor 2: Water bath temperature (°C)	Weight loss (%)							
			1st	2nd	3rd	4th	5th	6th	7th	8th
A	100	100	8.7	1.43	0.84	0.86	0.72	0.6	0.71	0.23
B		60	6.77	1.14	0.98	0.86	0.65	0.32	N/A	N/A
C	60	100	8.65	1.19	0.48	0.19	N/A	N/A	N/A	N/A
D		60	7.11	0.16	N/A	N/A	N/A	N/A	N/A	N/A

Table 2. Water Extractive Test on Wood Sample

Water extractive cycle	0	1	2	3	4	5	6
Water extractive content (%)	0	8.98	10.94	12.34	13.41	14.14	14.93
Increment rate (%)	0	8.98	1.96	1.4	1.07	0.73	0.79

Note: Both oven dry temperature and water bath temperature were 100 °C in this table.

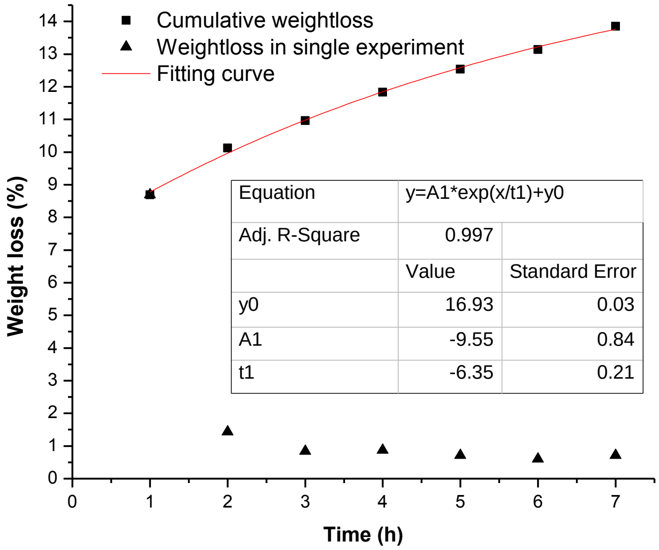
As mentioned previously, a comparison between methods A, B, C, and D showed that higher temperatures during oven drying or hot water exposure had a significant effect on polysaccharide degradation. After the first cycle (Table 1) the weight loss was more than 8% for methods A and C (100 °C treatment), while the weight loss was about 7% for methods B and D (60 °C treatment).

A higher temperature during oven drying also contributed to hemicellulose degradation when methods B and D were compared. The lowest total water extractive content was generated from method D; moreover, negligible weight loss was observed during the second cycle (0.16%) with method D. It should be noted that values less than 0.15% change were not considered measurable. In other words, prior to the experiment, efforts were made to estimate the experimental error and then a conservative threshold (0.15%) was chosen.

Analysis of the standard deviation of the residuals in Fig. 2 and 3 (next section) provides a technique for estimating the total error (experimental + unexplained) when estimating % weight loss with time for the methods herein. The standard deviation of the residuals was 0.11 and 0.08 for Fig. 2 and 3 respectively. These values support that all measurements were made within the sensitivity of the measurement system.

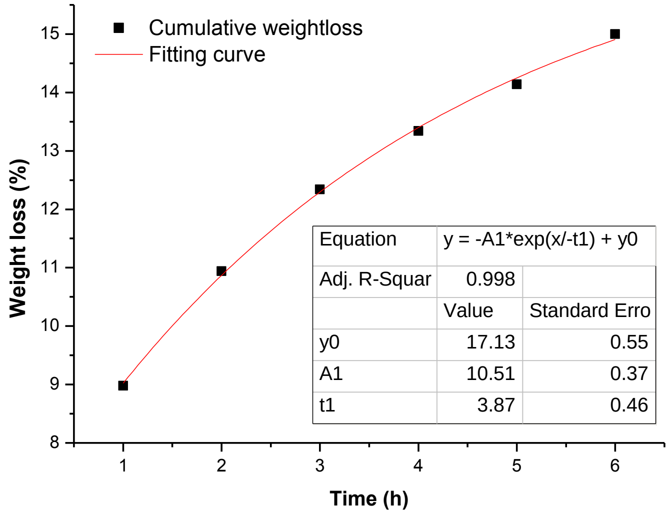
Kinetics of the Thermal Degradation of Polysaccharides

Based on the data from method A (Table 1) and the data in Table 2, the simulation curves of the total weight loss for the water extractives tested were calculated using Origin software 8.0 (OriginLab, USA), and results are shown in Figs. 2 and 3.



Equation	y=A1*exp(x/t1)+y0	
Adj. R-Square	0.997	
	Value	Standard Error
y0	16.93	0.03
A1	-9.55	0.84
t1	-6.35	0.21

Fig. 2. Fitted curve of the total weight loss during water extractive testing in ramie per one-hour intervals (cycles)



Equation	y = -A1*exp(x/-t1) + y0	
Adj. R-Squar	0.998	
	Value	Standard Erro
y0	17.13	0.55
A1	10.51	0.37
t1	3.87	0.46

Fig. 3. Simulation curve of total weight loss for water extractive testing in pine per one-hour intervals (cycles)

The simulation equation of the total weight loss for water extractive testing in ramie was,

$$y = -9.55e^{\left(\frac{x}{-6.35}\right)} + 16.93 \quad (1)$$

where the variable *"y"* represents total weight loss and the variable *"x"* represents the test time.

As shown in Fig. 2, the adjusted R-squared of the simulation equation was more than 0.99, which indicates that Eq. 1 provides the best fit for the data, resulting in a good expression of the weight loss behavior with cycle frequency.

As illustrated above, the value of *"y"* includes the true-value of the water extractive content and the content of the thermal degradation of polysaccharides in ramie, which was

$$y = z + f(x) \tag{2}$$

where *"z"* represents the true-value of the water extractive content and the function *"f(x)"* is the polysaccharide thermal degradation kinetics equation.

Combining Eqs. 1 and 2 results in Eq. 3:

$$z + f(x) = -9.55e^{\left(\frac{x}{-6.35}\right)} + 16.93 \tag{3}$$

When $x = 0$, $f(0) = 0$; therefore, *"z"* can be calculated from Eq. 3 and was found to be $z = 7.38$. Finally, the equation *"$f(x)$"* was as follows:

$$f(x) = -9.55e^{\left(\frac{x}{-6.35}\right)} + 16.93 - \mathrm{z} = -9.55e^{\left(\frac{x}{-6.35}\right)} + 9.55 \tag{4}$$

It was interesting to find that the total weight loss in method D from Table 1 was 7.27% (7.11% + 0.16%), which was significantly close to the true-value of the total water extractive content in ramie (7.38%), as calculated from Eq. 3 above. This indicates that the water extractive content could be determined more accurately using a temperature system at 60 °C (both oven dry and water treatment were 60 °C).

The polysaccharide thermal degradation kinetics equation of pine (Eq. 5) was analyzed in the same way from Table 2 and Fig. 3:

$$f(x) = -10.51e^{\left(\frac{x}{-3.87}\right)} + 10.51. \tag{5}$$

The true value of the water extractive content for pine can be calculated from Eq. 5, which results in $z = 6.63$ for pine.

HPLC Verification of the Degradation of Polysaccharides

The degradation of polysaccharides can be further verified by calculating the differences in total sugar content before and after water treatment. In this study, the sugar content of raw pine was determined after 100 °C water treatment, and after 2 cycles of water treatment at 100 °C (in which the oven dry temperature was 100 °C during the whole treatment) using HPLC. As discussed before, the weight loss in the first cycle contains the true value of water extractives and the degradation of polysaccharides; the weight loss in the second cycle was mostly caused by the degradation of polysaccharides. Therefore, the weight loss for the second cycle of hot water treatment should be similar to the total sugar decrease. As can be seen from the results in Table 3, the contents of glucan, xylan, and other sugars (araban, galactan, and mannan) were tested. The decrease in total sugar content was 3.42% and 2.07% after water treatment for the first and second cycles, respectively. The weight losses were 8.98% and 1.96% for the first and second cycles of water treatment on pine, respectively. The decrease in total sugar for the second cycle was 2.07%, which was fairly close to the weight loss for the second cycle (1.96 %) and helps to validate the need for reduced temperatures during drying or water extraction.

Table 3. HPLC Testing on Wood Sample (%)

Water extractive cycle	Glucan	Rate of Glucan decrease	Xylan	Rate of Xylan decrease	Other sugars	Rate of decrease of other sugars	Rate of decrease of total sugars
0	39.96	0.00	17.67	0.00	6.07	0.00	0.00
1	37.69	2.27	17.27	0.40	5.33	0.74	3.42
2	36.40	1.29	16.93	0.34	4.89	0.44	2.07

CONCLUSIONS

1. The dynamic equations for polysaccharide thermal degradation in ramie and pine were simulated as below:

   $f(x) = -9.55e^{\left(\frac{x}{-6.35}\right)} + 9.55$ (Ramie) and $f(x) = -10.51e^{\left(\frac{x}{-3.87}\right)} + 10.51$ (Pine)
2. A lower temperature system (oven drying and water treatment both at 60 °C) to test water extractives is more accurate.
3. Testing sugar contents using HPLC can verify the polysaccharide thermal degradation.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (50973048), the National Natural Science Foundation of Shandong Province (ZR2012EM002), the Special Foundation of "Taishan Scholar" Construction, the National Science & Technology Pillar Program (2012BAD32B06), and the Forest Products Development Center at Auburn University.

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Article submitted: March 17, 2014; Peer review completed: May 1, 2014; Revised version received: May 12, 2014; Accepted: May 14, 2014; Published: May 27, 2014.