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Improved method for evaluation of cellulose degradation

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Abstract Use of a fundamental concept, henceforth referred to as the scission fraction of cellulose unit (SFCU), was suggested to clarify the cleavage reactivity of cellulose during oxygen delignification (OD). According to the SFCU theory, the cleavage activity of pulp cellulose remains relatively undisturbed provided the experimental conditions are maintained regardless of pulp origin. SFCU is a universal variable for evaluating how processes and additives affect the degree of pulp cellulose degradation. Specifically in this study, the effects of the protector additives $MgSO_4$ and phenol on the oxygen delignification (OD) process were investigated. Both phenol and $MgSO_4$ retard the cleavage rate of the cellulose chain, but the retarding effect of $MgSO_4$ is greater than that of phenol. Phenol alone cannot significantly improve the selectivity of the OD process, whereas $MgSO_4$ can decrease the cleavage rate of cellulose and increase the selectivity of OD. Moreover, synergistic selectivity enhancement for pulp using a combination of $MgSO_4$ and phenol was observed. The protective effect of various chemical protectors was additive, whereas the retarding effect on delignification was not.

Key words Cellulose degradation · Oxygen delignification · Protective additives · Phenol · Magnesium sulfate

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Introduction

Cellulose can undergo severe depolymerization reactions during the pulping and bleaching processes currently employed in the pulp and paper industry. Because scission of cellulose not only attenuates the strength of pulps but also tends to reduce pulp yields, methods to protect and evaluate cellulose degradation are critical for improving the process. Viscosity change is typically used to measure the degree of cellulose degradation, and selectivity is a metric for the efficacy of protective additives.^{1,2} However, both viscosity change and selectivity depend not only on the degree of scission of the cellulose but also on the pulp origin. Because changes in viscosity and selectivity differ from pulp to pulp, experimental data are necessary to evaluate new processes or new protector additives. Therefore, the development of a universal method for evaluating the degradation of cellulose is important. This paper develops a unique concept to address the need for a universal method of evaluating cellulose degradation.

Materials and methods

Softwood and hardwood from commercial sources were used to manufacture the pulps for all of the experiments. The characteristics of the brown stocks are shown in Table 1. The oxygen delignification (OD) bleaching experiments were performed in a 2L horizontal PARR reactor. An oxygen atmosphere with 100 psi of pressure was used for all OD experiments; the consistency of the pulps in the reactor was maintained at 10 wt%; and $MgSO_4$ and phenol were used as protector additives. To decrease the temperature fluxes of the pulps in the reactors while increasing the oxygen diffusion rate, pulps were stirred continuously at approximately 35 rpm. At this rotation rate, oxygen diffusion is not the rate-controlling step for the OD process.³ Pulp viscosity and kappa number were determined following standard TAPPI methods, i.e., T230-om-94 and T236-cm-85, respectively.

Concept of scission fraction of cellulose unit

Viscosity of pulps is the most common property used to characterize the degradation of carbohydrates. However, the viscosity change is not linear with respect to the degree of carbohydrate damage and is sensitive to the degree of polymerization (DP) of the carbohydrates. Johansson and Ljunggren² used the number of scission equivalents per polymer chain to characterize cellulose degradation. Using the number of scission equivalents per polymer chain is a good method for characterizing cellulose degradation when the DP of the carbohydrates is the same; but it is not suitable for characterizing the “scission activity” of carbohydrates. This is because the number of scission equivalents per polymer chain of carbohydrates with a high DP is greater than that of carbohydrates with a low DP when the “scission activity” of carbohydrates is the same. A scission fraction of cellulose unit (SFCU) was suggested to characterize the scission activity of cellulose. SFCU is the ratio of cleaved glucose units to the total glucose units of a cellulose chain. DP can be calculated from the viscosity number using the Mark-Houwink equation as follows.

$$DP = \left(\frac{\eta}{2.28} \right)^{\frac{1}{0.76}} \quad (1)$$

where η is the viscosity number (ml/g) of the pulp.⁴

A decrease in DP during the OD process is evidence of cellulose cleavage. Assuming that the scission equivalents are uniformly distributed along the polymer chain, a final DP of $1/(n + 1)$ of the initial DP corresponds to n scission equivalents per polymer chain. Scission equivalents of a cellulose chain are calculated using Eq. 2.

$$n = \frac{DP_{init}}{DP_{final}} - 1 \quad (2)$$

where DP_{init} and DP_{final} are the degree of polymerization before and after the OD, respectively. The SFCU can be obtained as follows.

$$SFCU = \frac{n}{DP_{init}} = \frac{1}{DP_{final}} - \frac{1}{DP_{init}} \quad (3)$$

Results and discussion

We have offered a unique concept, referred to as the scission fraction of cellulose unit, to study the cleavage reaction of cellulose. It was found that cellulose, despite its species origin (softwood or hardwood), has the same cleavage activity for a given set of experimental conditions. It also appears that the protective effect of various chemical protectors of carbohydrates are additive, whereas their retarding effect on delignification is not. This concept is important and is elaborated further herein.

Experimental results from the OD of softwoods and hardwoods are shown in Table 2. It was found that the OD selectivity obtained from the hardwood pulp is almost one order of magnitude less than that of softwood. Such a difference is easily accounted for by both the low degree of delignification and marked decrease in viscosity found in the hardwood. A natural corollary of the preceding statement is that any aggressive chemical attempt to remove the hardwood lignin would tend to have a high likelihood of cellulose damage. Interestingly, although the lignins among various wood species (hardwood and softwoods) have somewhat different chemical structures, the cellulose from these divergent wood sources should have the same chemical structure. However, it appears that hardwood cellulose suffers a greater degree of damage than softwood cellulose under the same OD conditions.

To investigate this issue, the general concept of a SFCU was suggested to clarify the chemical changes that occur during OD processes that involve cellulose degradation.

Table 1. Physical and chemical characteristics of brown stocks

Brown stock	Kappa no.	Viscosity (cp)	DP
Softwood	21.33	31.2	2325
Hardwood	11.26	52.7	4732

DP, degree of polymerization

Table 2. Oxygen delignification results for softwood and hardwood pulps

Sample	Base (wt%)	Kappa no.	Viscosity (cp)	Selectivity ^a	DP	SFCU ($\times 10^5$)
SW BS	–	21.33	31.24	–	2325	0
HW BS	–	11.26	52.70	–	4732	0
HW-1	1.00	9.010	37.50	0.148	2984	1.24
HW-2	2.50	7.710	27.80	0.143	1981	2.94
HW-3	3.50	7.46	22.53	0.126	1480	4.64
HW-4	5.00	7.33	18.64	0.115	1135	6.70
SW-1	1.0	14.90	24.80	0.998	1691	1.61
SW-2	2.50	10.60	20.27	0.978	1277	3.53
SW-4	3.50	9.68	18.05	0.883	1084	4.92
SW-5	5.00	8.91	15.75	0.802	893	6.90

Reactions: 90°C, 80min; protectors: 1Wt% MgSO₄ and phenol (1:1) based on oven-dried pulps HW, hardwood experiments; SW, softwood experiments; BS, brown stock; SFCU, scission fraction of cellulose unit; DP, degree of polymerization

^aSelectivity is defined as the change in kappa number divided by the change in pulp viscosity

The SFCU is calculated according to Eq. 3, and the results of its application are depicted in Fig. 1, which shows that the SFCUs of hardwood and softwood are virtually the same. This indicates that the degradation rates of the cellulose chains of both softwood and hardwood are the same. It is evident that the larger attenuation in the viscosity of hardwood kraft pulps after OD is related to its greater cellulose chain length (from the higher intrinsic viscosity) and that is much more susceptible to degradation if the SFCU is the same. Remarkably, the SFCU is almost directly proportional to the base content; and when the base concentration approaches zero, the SFCU becomes zero. This relation is reasonable, as the cellulose chain should not undergo any degradation in the absence of base.

Protector additives are typically used during industrial OD to mitigate viscosity losses. To determine if the SFCU concept can be used to explore protector additives research, MgSO_4 and phenol were used as protectors in the experiments. These particular additives have demonstrated considerable promise for improving selectivity when used in combination.⁵ The results are shown in Table 3. Both MgSO_4 and phenol can retard the cleavage rate of the cellulose chain, although the effect of MgSO_4 is much greater than that of phenol. Phenol alone does not appear to increase the selectivity, so it alone cannot be used as a protector. MgSO_4 alone, however, can decrease the degradation

rate of the cellulose chain and increase the selectivity of OD, but the selectivity was even higher when a mixture of MgSO_4 and phenol was used because of a synergy that has yet to be explained.

By comparing the kappa number and SFCU, it was noted that the protective effect of substances used in combination was synergistic, but their retarding effect on delignification was not. This characteristic of the protectors is useful when preparing protectors for OD, as a mixture of protectors may be more useful than any one alone.

It is widely postulated that the protective mechanism of MgSO_4 lies in its ability to sequester metal ions. Metal ions are known to produce extremely reactive radicals (e.g., Fenton reaction), which can attack the cellulose chains and degrade them. Phenol may engage in a reaction to scavenge reactive free radicals that are harmful to cellulose, producing the free radicals shown in Fig. 2.

Conclusions

The SFCU has been shown to be a valid concept for characterizing the cleavage activity of cellulose. This activity in pulps is the same, regardless of its source, if the reaction conditions are the same. *SCFU* is a universal variable for

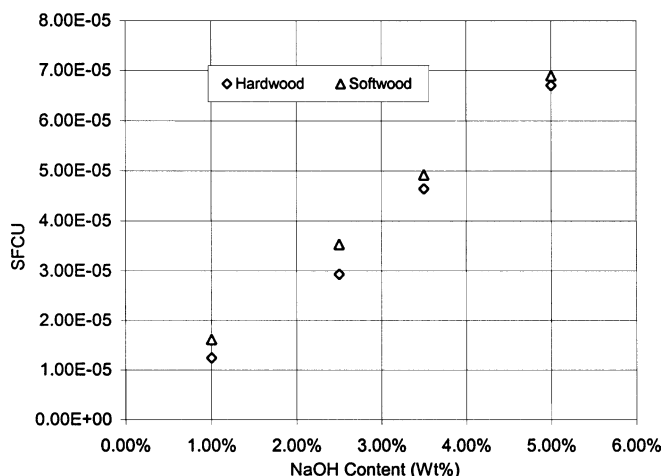


Fig. 1. Scission fraction of cellulose unit (*SFCU*) of softwood and hardwood at various base contents (90°C, 80 min, 100psi oxygen)

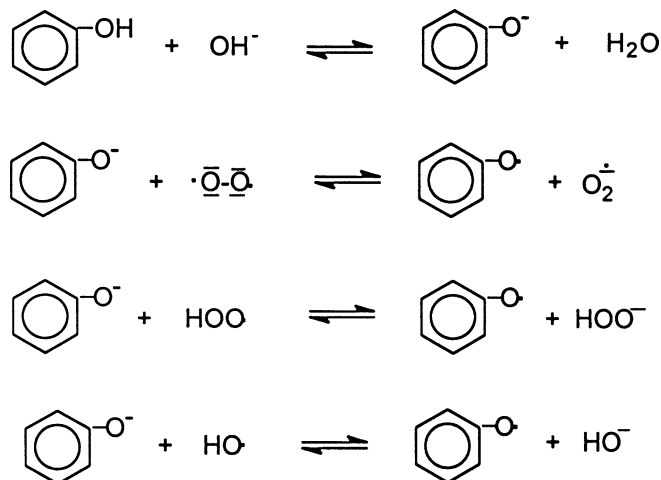


Fig. 2. Potential mechanism for scavenging reactive free radicals by phenol under alkaline conditions

Table 3. Effect of MgSO_4 and phenol additives on the OD process

Sample	Additive	Kappa no.	Viscosity	Selectivity ^a	SFCU ($\times 10^5$)
SW BS		20.90	30.77		0
		4.00			
SW-8	NA	8.01	14.44	0.79	8.29
SW-10	MgSO_4 0.5 wt%	9.14	19.12	1.01	4.11
SW-11	MgSO_4 0.5 wt%	9.28	20.70	1.16	3.21
	phenol 0.5 wt%				
SW-12	Phenol 0.5 wt%	8.68	15.30	0.79	7.28

Reactions: 90°C, 80 min, NaOH 5.0 wt%. Additive content was based on oven-dried pulps OD, oxygen delignification; NA, not available

^a Selectivity is defined as the change in kappa number divided by the change in pulp viscosity

evaluating the effect of the process and additives on the viscosity of cellulose in wood pulps. Both MgSO_4 and phenol can retard the cleavage rate of the cellulose chain, but the effect of MgSO_4 is much greater than that of phenol. Phenol alone cannot significantly improve the selectivity of the OD process, whereas MgSO_4 alone can decrease the cleavage rate of the cellulose chain and increase selectivity. Selectivity was even high when a mixture of MgSO_4 and phenol was used. The protective effect of various additives was synergistic, but their retarding effect on delignification was not. A mixture of additives appears to be better than any one individual agent.

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