

Compressive energy absorption in the pulping kinetics of white pine: the shrinking core model

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ABSTRACT *Cylindrical rods 2.5 cm in diameter were kraft pulped with and without anthraquinone at 143°C with 46 g/L NaOH and liquor of 25% sulfidity. Samples were analyzed for lignin content. Compressive energy absorption (CEA) was measured as a function of radial position and time. As measured by CEA, the strength could be phenomenologically explained by a shrinking core model during the initial period. The lignin content, however, did not substantially decrease during this time. The strength-reducing reactions occur before significant delignification occurs, and these reactions follow a shrinking core model.*

KEYWORDS

Compression
Delignification
Lignin
Pulping
Strength

Veeravalli and Lacksonen showed the relationship to be nonlinear for the strength and lignin content of a partially pulped wood block subjected to axial compression coincident with the grain (1, 2). They suggested that the pulping process could be modeled as a cracking core model and assumed the lignin profile across the block to be linear. We studied the actual lignin profile during kraft pulping and its relationship to the strength profile in the wood.

We used cylindrical geometry rather than rectangular blocks, as used in the previous work. Cylindrical geometry would more easily limit the liquor transport to one dimension, the radial dimension. Also, rather than consider the elastic modulus of the wood as the best "strength" indicator, the area under the stress-strain curve was used, because this gave a measure of the sample's compressive energy of absorption (CEA) per unit volume. Figure 1 shows the area under consideration.

Results

Figures 2 and 3 show how the samples were cut from the cylindrical rods that were pulped and how they were cored to give samples as a function of radius. Data for averaged core volumes were obtained from the samples. Table I gives the experimental data for the lignin content and the energy absorbed per unit area as a function of radial position and time for kraft and kraft pulped with anthraquinone (AQ) after 1 h and after 3 h of pulping.

Table II gives the CEA values calculated for kraft and kraft + AQ pulping as a function of core size and the time of pulping. Data from Table II are plotted in Fig. 4., which shows that the ability of the wood to support a load varies with the radius of the cylinder.

After 1 h of pulping, regions that represent Core Volumes B and C for both the kraft and kraft with AQ show almost the same energy absorbed per

unit area as that for wood pulped only in water. However, the outer Volume A lost most of its compressive energy strength, yet it contains about 90% of its original lignin content. These findings support the concept that pulping as measured by fiber separation should be based on the residual strength of the wood and not on its lignin content (1).

Discussion

Model for strength reduction

In Fig. 4, CEA was plotted as a function of core volume, which is also equivalent to the radius. The maximum CEA profile line was drawn based on the unreacted wood cooked only in pure water. For this case, the CEA would be linear with respect to cumulative core volume because the CEA per unit volume is constant for unpulped wood.

Figure 4 suggests that a shrinking core model for strength offers a reasonable explanation of the data.

The basic premise of the shrinking core model is that during pulping there is a well-defined core of "unreacted" wood (no measurable chemical changes). As pulping continues, the reacting front moves into the core and causes the reacting core to shrink. The CEA of the reacted core would have a low CEA, approaching zero. In these experiments, as the cooking chemicals in the liquor penetrate the wood, they are consumed and form a reaction front.

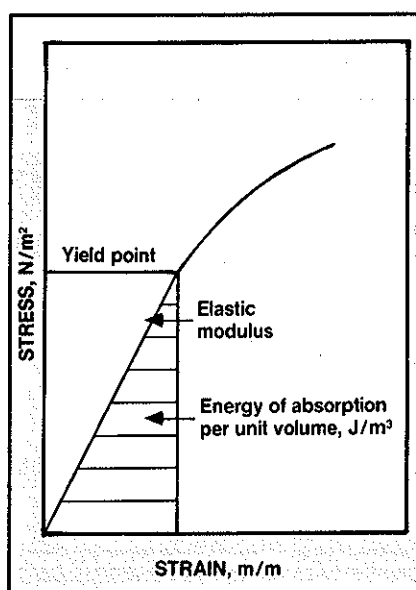
The shrinking core model for short pulping times appears to describe the phenomenon of the CEA reduction as a function of distance into the wood. Kojima (3) states that the rate of delignification in the initial period increases with decreasing chip thickness, showing that the initial period proceeds by a process influenced by liquor transport. If the pulping reactions were slow relative to liquor transport into the wood, the strength reduction of the wood should appear more uniform with respect to position. At pulping temperatures common to industrial pulping (above the range of our study), the reaction rates would be even higher, and the shrinking core model should fit even better.

Deviations from the shrinking core model seem to occur at longer pulping times. These deviations are probably caused by the complex nature of the liquor transport characteristics of the wood, as the required penetration length increases with increased pulping. The liquor is likely to penetrate the wood but is not likely to reduce the strength as it did at shorter times because more of this liquor is being consumed by reactions with residual lignin and hemicelluloses. Structural changes in the wood during pulping can also affect the transport of liquor. Talton and Cornell (4) show a linear increase in the diffusion coefficient of NaOH with increases in yield. Recent studies in progress (5) also suggest that increased local concentrations of lignin in solution can affect the removal of lignin and thus influence diffusivities.

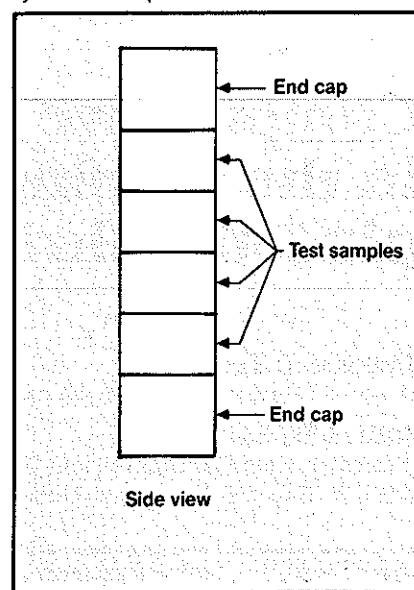
Conclusions

The results of these experiments have suggested three points. First, the lignin content of the wood is probably not the best indicator of pulping as measured by fiber separation, since

1. The stress-strain curve and CEA per unit volume for the area under consideration



2. Nomenclature for the coring of the cylindrical samples



1. Lignin content and energy absorbed per unit area as a function of radial position

Pulping time, h	Differential core volume ^a	Lignin, %	Energy absorbed/unit area, J/m ²
Kraft			
1	A	28.8	132
1	B	32.4	1302
1	C	30.7	1266
3	A	22.8	417
3	B	31.8	495
3	C	33.5	1149
Kraft + AQ			
1	A	29.6	0
1	B	32.5	1625
1	C	32.5	1143
3	A	19.8	202
3	B	32.1	823
3	C	33.6	1208

^aRadial position as shown in Fig. 3.

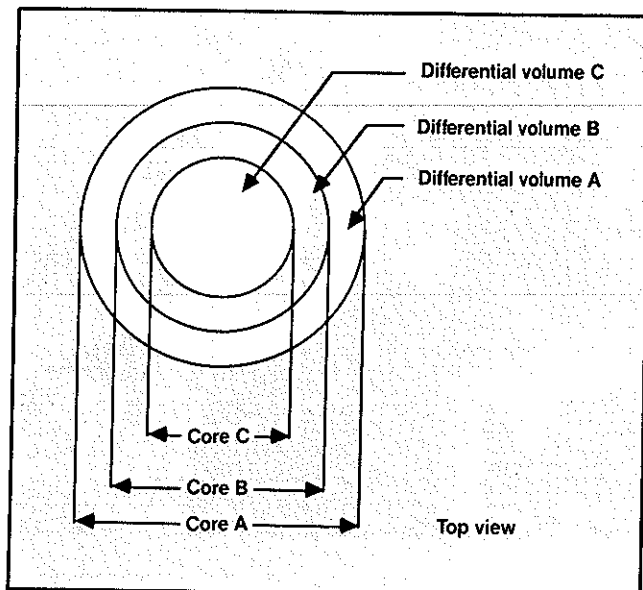
the strength (CEA) can decrease to zero without much lignin removal. Second, the CEA gives a measure of the energy necessary for satisfactory fiber separation.

Third, the strength reduction of white pine during kraft pulping under the experimental conditions of this study follows a shrinking core model for short times. The major loss of strength occurred during the initial period of pulping when the process can be strongly influenced by liquor penetration. At longer times, structural changes can cause deviations from

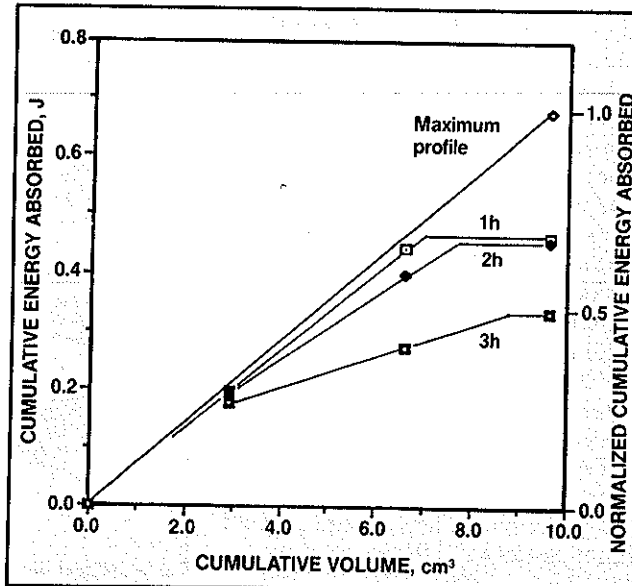
the shrinking core model.

Other pulping kinetic models usually account for only the rate of delignification and do not contend with the problem of the accompanying strength changes, which are important to satisfactory fiber liberation. Our study has shown (at least for white pine) that liquor penetration has two different roles to fulfill. First, it induces an apparent depolymerization reaction which controls the nature of the fiber separation. Second, it induces the delignification reactions.

3. An illustration of the sectioning procedure for the cylindrical samples



4. CEA and normalized CEA as a function of cumulative volume for the cylindrical samples



II. Compressive energy absorbed by the samples as a function of radial position

Pulping time, h	Core sample ^a	Cumulative energy absorbed, J	Normalized cumulative energy absorbed ^b
Kraft pulping liquor			
1	A	0.464	0.665
1	B	0.445	0.637
1	C	0.195	0.279
2	A	0.457	0.655
2	B	0.397	0.568
2	C	0.195	0.279
3	A	0.332	0.476
3	B	0.272	0.390
3	C	0.117	0.254
Kraft + AQ pulping liquor			
1	A	0.441	0.632
1	B	0.488	0.699
1	C	0.176	0.252
2	A	0.347	0.497
2	B	0.389	0.557
2	C	0.187	0.267
3	A	0.373	0.534
3	B	0.344	0.492
3	C	0.186	0.267
Pure water as pulping liquor			
3	A	0.697	

^aA = 9.62 cm³, B = 6.60 cm³, C = 2.93 cm³. Sample length = 1.905 cm.

^bBased on pure water pulping.

To make a more uniform pulp, these two factors must be considered together. The problem is complicated by the observation that there is no simple linear relationship between the strength change kinetics and the delignification kinetics for kraft pulping. Resolution of these two phenomena should help to produce a more uniform pulp, particularly for mixed wood systems.

Experimental

Clear white pine from a lumber yard was cut into 2.5-cm-diameter cylindrical rods 12.7 cm long. The grain direction was parallel to the longitudinal axis. Pulp runs were made for 1, 2, and 3 h each. Details of the experimental procedures can be found elsewhere (1).

A sample was also cooked in plain water for comparison. Four rods were pulped for each run with kraft liquor of 46 g of Na₂O/L, 25% sulfidity, and a liquor-to-wood ratio of 22:1. Identical runs were made, with anthraquinone added at 0.629 g/L. The reactor and liquor were preheated to 93.3°C with steam in the reactor jacket before adding the wood, resulting in a heat-up time of only 5 min to 143°C. There was a cool-down time of 2 min at the end of the run, providing a reasonably constant pulping temperature throughout the run.

After the wood was pulped, it was cut into 1.905-cm lengths, as illustrated

in Fig. 2, to limit liquor transport to only the radial direction during pulping and to eliminate end effects. Each run provided 15 samples that were randomly separated into three groups of five each. Five blocks were shaved to a diameter of 21 mm, and five more were shaved to a diameter of 14 mm. The shavings were analyzed for lignin content by the Klason lignin method. The shaved samples were denoted as Cores A, B and C, and their respective differential volumes were denoted as Volumes A, B, and C as shown in Fig. 3. The individual cores were then subjected to compression testing in the grain direction.

The average yield point and CEA were measured for each of the five block samples. The average percent lignin content and the average energy absorbed per unit area for each 5-sample data point are listed in Table I. The relationship between the energy absorbed per unit area and the cumulative energy absorbed (Table II) is defined by a mathematical equation. The cumulative energy from Core B is subtracted from the cumulative energy from Core A, and the difference is divided by the cross-sectional area of differential Volume A. This quotient is equal to the energy absorbed per unit area in differential Volume A.

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This paper was taken in part from the M.S. thesis by Tendam at the Univ. of Toledo, 1987.

Received for review Jan. 15, 1988.

Accepted Feb. 25, 1988.



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