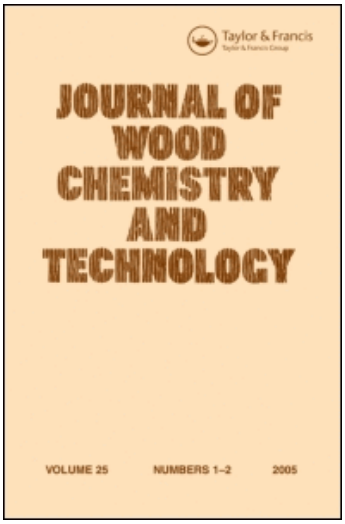

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Chemical Pulping of Steam-Exploded Mixed Hardwood Chips

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Chemical Pulping of Steam-Exploded Mixed Hardwood Chips

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Abstract: We determined the pulping yields for steam-exploded and untreated mixed hardwood chips for kraft pulping processes with and without anthraquinone and/or polysulphide. The pulp yield from steam-exploded chips was 1–3% lower than from untreated chips under similar conditions. The benefit of kraft pulping with anthraquinone and/or polysulphide was found to be more pronounced for the exploded chips than for the untreated chips.

Keywords: Chemical pulping, exploded pulps, steaming, hardwoods, chips, yield, analysis, polysulfides, anthraquinone, H factor, kappa number

INTRODUCTION

Since the patents by Delong,[1] the steam-explosion process has been proposed[2] for many ligno-cellulosic treatment applications including as an alternative to conventional chemi-mechanical pulping (CMP) and chemi-thermo-mechanical pulping (CTMP). During this process, lignin is softened

Special thanks to André Audet for the bleaching of the pulp samples. Thanks are also due to William Reed and Yves Desjardins for their technical support during the chemical impregnation of the mixed hardwood chips in preparation for steam explosion in the continuous digester. We also thank Zhi-Hua Jiang and Richard Berry for their critical review of the manuscript.

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to allow higher defibrillation without excessive damage and/or degradation to individual fibers. However, the process has not been industrially implemented[3] because pulps produced have not shown any superior properties over those from CMP or CTMP.

Preliminary studies by a member company on hybrid poplar chips had shown that pre-treating chips with the steam-explosion process prior to kraft pulping may increase the pulp yield.[4] It was speculated that the open structure of the exploded chips might lead to a higher yield and lower rejects due to efficient diffusion of cooking liquor into fibers.

The kraft pulping process accounts for more than 90% of the chemical pulp production worldwide. During the past several years a number of modifications have been proposed for improving the conventional kraft pulping process by enhancing the rate of delignification and increasing pulping yield.[5–8] Modifications in both batch[9–12] and continuous[13–16] digester systems, changes to wood furnish[17–19] and addition of pulping additives[20–24] are examples of these proposals. Of the many pulping additives evaluated over the years, only polysulphide[21–23] (PS) and anthraquinone[23,24](AQ) have been used commercially.

The objective of this work was to evaluate the potential of steam-explosion as a pretreatment prior to chemical pulping. The pulping yield of both untreated and steam-exploded mixed hardwood chips under different kraft pulping processes with and without additives (PS and/or AQ) were determined with the initial goal of obtaining a higher yield over the conventional kraft process.

EXPERIMENTAL

Wood Chip Preparation

Eight sugar maple, five white birch, and three aspen logs were obtained from a Canadian mill. The logs were debarked, chipped, screened, and classified by thickness at Paprican's pilot plant. Debarking was carried out with a Morbark PS8 cutterhead debarker and chipping was done with Morbark Eeger Beever chipper. The chips were screened separately by using an Overstorm model 1000 vibrating chip screen to remove the pin and oversized chips (chips passing through 8 cm^2 (1(1/4) $inch^2$) and retained by 2.4 cm^2 (3/8 $inch^2$) square holes were collected). The screened chips were classified by using a Domtar Chip Classifier Model No. 73-77 and chips with thicknesses between 2 and 6 mm were collected. The chips from each set of wood species were then air-dried to ~94% solids. A blend of mixed hardwood charges were made with a composition of 60% sugar maple, 30% white birch, and 10% aspen on o.d. weight basis. Three different chip charges were prepared: 50 g o.d. for the small 1-L StakeTech steam-explosion batch digester; 200 g o.d.

for chemical pulping in the 2-L bomb digester; and 185 kg o.d. for the continuous steam-explosion digester.

Chemical Impregnation

Prior to pre-treating the chips by steam-explosion, the mixed hardwood chips (185 kg o.d.) were impregnated with 1% NaOH and 8% Na_2SO_3 solution at a liquid-to-wood ratio of 3:1. Chemical impregnation was carried out in a temperature-controlled stainless steel tank at 60°C for 24 hours. To assure complete impregnation of chips, the liquor was circulated in and out of the tank by an electrical pump and was drained completely prior to steam explosion.

Steam Explosion Pulping

The chemically impregnated mixed hardwood chips (about 185 kg o.d. basis) were steam exploded using the continuous StakeTech digester, which has a production rate of 300 kg/h (Figure 1). The digester consists of a patented Co-Ax Feeder, which compresses the impregnated chips into a dense plug thereby maintaining operating pressure in the system. The digester can operate up to a gauge pressure of 3.1 MPa (450 psig). The retention time of material through the digester is accurately controlled by adjusting the speed of the retention screw, which conveys the chips along the digester. A specialized discharge mechanism then "explodes" the chips by bringing them to atmospheric pressure (Figure 2). The operating conditions of this trial are shown in Table 1. In steam-explosion studies, it is customary to combine

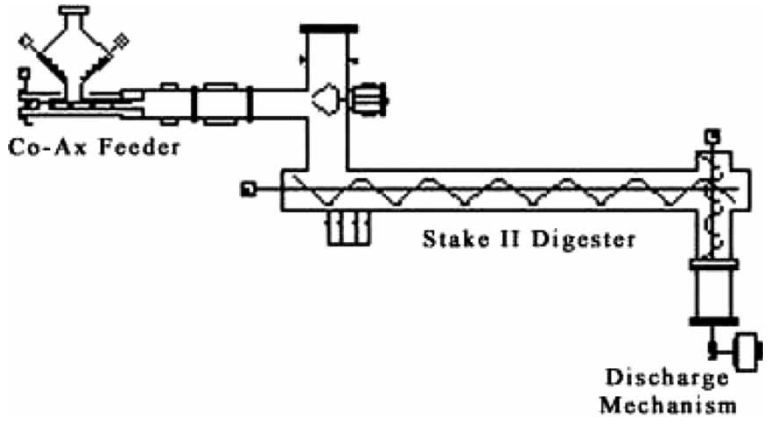

Figure 1. Schematic diagram of the StakeTech continuous digester.

Figure 2. Photograph of untreated and steam-exploded mixed hardwood chips.

the temperature (T, °C) and time (t, min) into a severity factor (R_o, min), as defined by the following equation,[25]

$$\text{Log } R_o = t \times \exp^{[(T-100/14.75)]} \quad (1)$$

The optimum operating parameters in Table 1 were selected on the basis of the highest steam-explosion pulping yields (94%), as determined from multiple steam-explosion experiments in a laboratory-scale digester (1-L StakeTech steam-explosion batch digester) under different conditions.

Chemical Pulping

Chemical pulping experiments were done in six 2-L pressure vessels at Paprican's chemical pulping pilot plant. The six vessels are rotated in an oil bath that is indirectly heated with steam. During each experiment, 200 g o.d. basis of either untreated or steam-exploded chips were placed in each vessel. The contents of the sealed vessel were de-aerated by vacuum for 5 min, which ensured good penetration of cooking liquor into the chips (a liquor-to-wood ratio of 4:1 was used with each of the 6×200 g o.d. charges). The maximum cooking temperature was 170°C and the time to temperature was 60 minutes. A RTD sensor placed directly in the oil bath

Table 1. Impregnation and steam explosion pulping conditions of mixed hardwood chips

Impregnation conditions (24 h at 60°C)		Steam-explosion parameters			
Concentration (%w/w)	L:W ratio	Log R_o	*P* (MPa)	*t* (min)	*T* (°C)
1%NaOH + 8%Na_2SO_3	3:1	3.10	1.28	2.0	195

was used to monitor and control the temperature of the cook. When the predetermined H-factor was reached, each vessel was removed from the oil bath and quenched in cold water. The spent liquor was collected for further analysis and the cooked chips were transferred to a 6-L bucket and disintegrated for 3 min using a Cowles mixer. The pulp was washed thoroughly, and soaked in water for a period of 18–40 hours prior to screening (0.25-mm wide slots). A 450-mesh screen was used in both washing and screening operations to retain fines.

The same cooking conditions were applied to both steam-exploded chips and untreated chips. The active alkali was 16% (AA as Na_2O based on o.d. chips) and the sulphidity was 25% (on a AA basis) for kraft (K) and kraft/anthraquinone (K/AQ) cooks. For the polysulphide (PS) and PS/AQ cooks, half the sulphidity of kraft cooks was converted to PS, resulting in a PS charge of 1% on o.d. wood. Synthetic polysulphide liquor was prepared by the reaction of sulphur with sodium sulphide and its concentration was determined by the gravimetric method.[26] The anthraquinone charge was 0.05% (based on o.d. wood) in K/AQ and PS/AQ cooks.

Wood and Pulp Analysis

The kappa number and viscosity of the pulp samples were determined according to TAPPI standard methods T236-cm85 and T230-om89, respectively. The brightness for all the samples was measured by the PAPTAC Standard E.1 method.

RESULTS AND DISCUSSION

Chemical Pulping of Untreated Mixed Hardwood Chips

The first series of pulping experiments was carried out on the untreated mixed hardwood chips to optimize the kraft pulping conditions by varying the AA and sulphidity. After a few exploratory experiments, 16% AA and 25% sulphidity were selected to be the most appropriate.

The rate of delignification of the untreated hardwood chips for different pulping processes is compared in Figure 3. As expected AQ accelerated both the K and PS cooks.

Because 2–6 mm thick chips were used, the amount of screening rejects was lower than 0.5%. The difference in rejects between the steam-exploded and untreated chips ranged from 0 to 0.2% only. Therefore, only the total yields are shown here. Figure 4 shows the yield-kappa number relationship for K, K/AQ, PS, and PS/AQ cooks. The yield gains of PS and K/AQ cooks relative to K cook were found to be minor at kappa number 15 (Table 2); the PS/AQ showed a yield increase of 0.8% relative to the K cook.

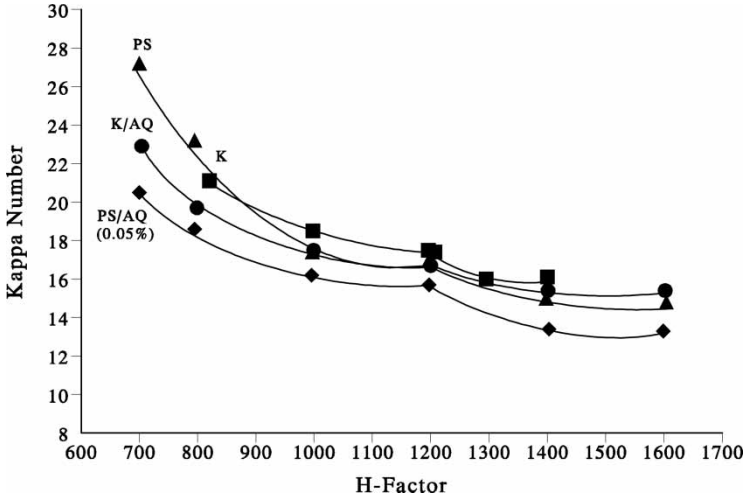

Figure 3. The effects of pulping additives on the delignification rate for untreated mixed hardwood chips showed that AQ enhanced delignification during K and PS cooks, and PS was more effective at higher than 1000 H-factor.

Chemical Pulping of Steam-Exploded Mixed Hardwood Chips

A similar series of pulping experiments was done on the steam-exploded chips by applying the same cooking conditions. Figure 5 shows the plot of kappa

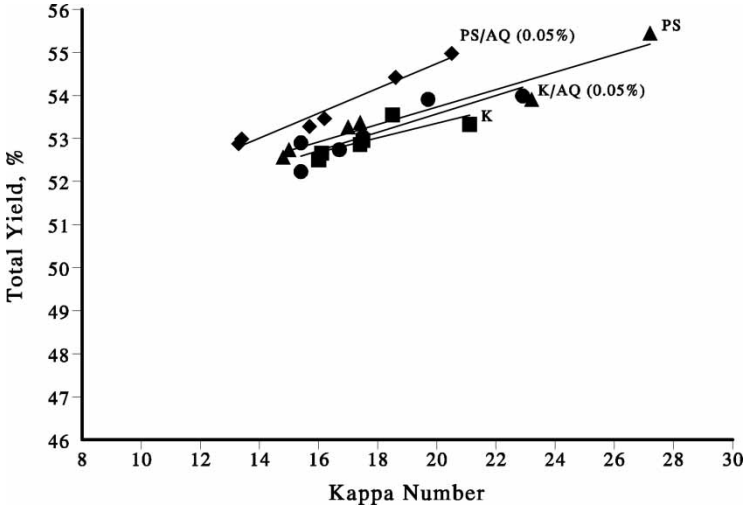

Figure 4. The yield gain from different pulping additives for untreated hardwood chips was more pronounced for PS/AQ cooking.

Table 2. Yield gains of pulping additives for untreated mixed hardwood chips at kappa number of 15

Pulping process	Total yield, % (at $\kappa = 15$)	Yield gain, % (relative to K)
Kraft (K)	52.5	—
K/AQ	52.5	0.0
PS	52.7	0.2
PS/AQ (0.05%)	53.3	0.8

number as a function of H-factor for the four types of cooks. Once again, AQ accelerated both the K and PS cooks.

The comparison of Figures 3 and 5 shows that the presence of additives has a greater impact on delignification rate for the steam-exploded chips than the untreated chips during similar chemical pulping processes. The degree of delignification at H-factors lower than 1000 are similar for both untreated and exploded chips. However, the degree of delignification of steam-exploded chips at higher H-factors is substantially greater. There appears to be a sudden release of lignin from the steam-exploded fiber, which may indicate a change in the structural integrity of the fiber

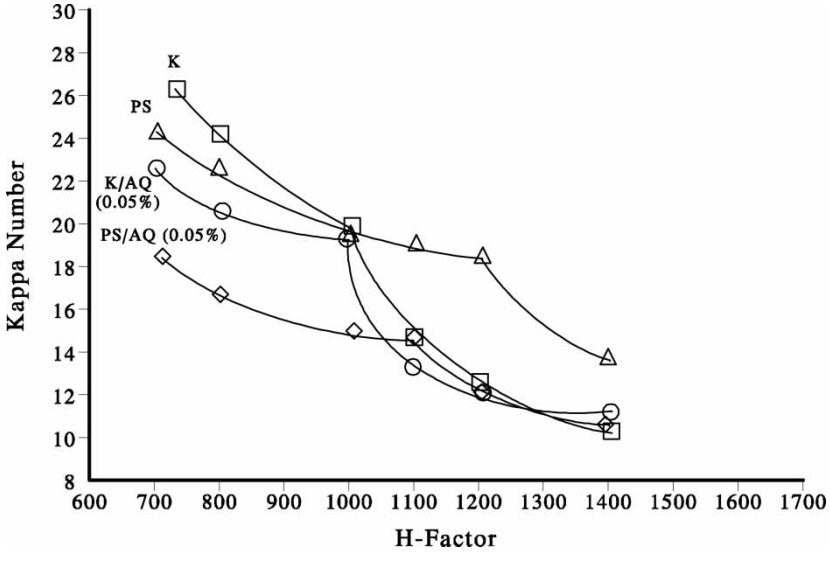

Figure 5. Pulping additives were more effective in increasing the delignification rate of the steam-exploded chips than the untreated chips (Figure 3), especially at H-factors higher than 1000.

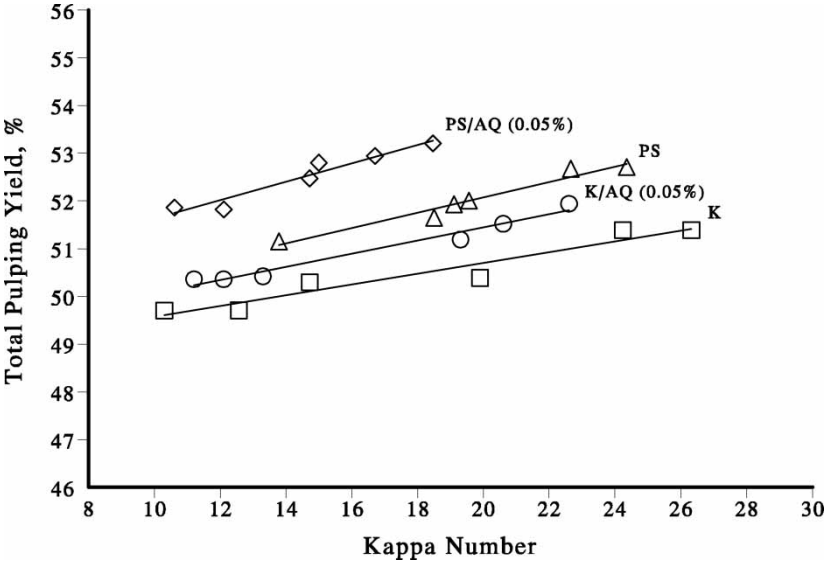

Figure 6. The pulping yield gains from different pulping additives were more pronounced for steam-exploded hardwood chips than their untreated counterparts (Figure 4).

as delignification continues. It appears to occur at 1000 H-factor for all but the PS process, which shows the same phenomenon but at 1200 H-factor.

The plot of total pulping yield as a function of kappa number for the steam-exploded chips under different kraft pulping processes is illustrated in Figure 6. A comparison of the total yield for different chemical pulping processes, at kappa number 15, shows that the yield gain relative to kraft increased significantly by using pulping additives (Table 3). The PS/AQ, for example, showed a 2.4% yield gain relative to kraft, compared to 0.8% for the untreated chips.

Table 3. Yield gains of pulping additives for steam-exploded mixed hardwood chips at kappa number of 15

Pulping process	Total yield, % (at $\kappa = 15$)	Yield gain, % (relative to K)
Kraft (K)	50.2	—
K/AQ	50.7	0.5
PS	51.2	1.0
PS/AQ (0.05%)	52.6	2.4

Pulping studies of sawdust may help to explain the better efficiency of additives in pulping of steam-exploded materials compared to untreated chips. It was found[27,28] that sawdust furnishes, although they have a lower yield with conventional pulping than do chip furnishes, the loss is much reduced when AQ, PS, or both are applied. Luthe et al.[28] offer that, "two factors contribute to the large yield advantages achieved with PS when using sawdust. The first is the increased accessibility of the furnish when sawdust is used rather than chips. The second is the consistently effective protection of the carbohydrates by polysulphide in contrast to the increasingly greater degradation and removal during kraft cooking as the furnish dimensions become smaller." These factors could also apply to steam-exploded pulp and explain the data in this work.

Comparison of the pulping data for the steam-exploded chips (Figure 6) to that of the untreated chips (Figure 4) shows that the total pulping yields for steam-exploded chips were 1–3% lower. Moreover, the difference was even larger when the overall pulp yields (Figure 7) were compared. To avoid confusion between the measured yields from the two processes, that is, (1) steam-explosion followed by kraft pulping and (2) kraft pulping only, the "overall yield" and "total yield" are used, respectively, to describe the two yields. As is customary in kraft pulping, the "total yield" considers the yield from only the kraft pulping process. The "overall yield" takes into account

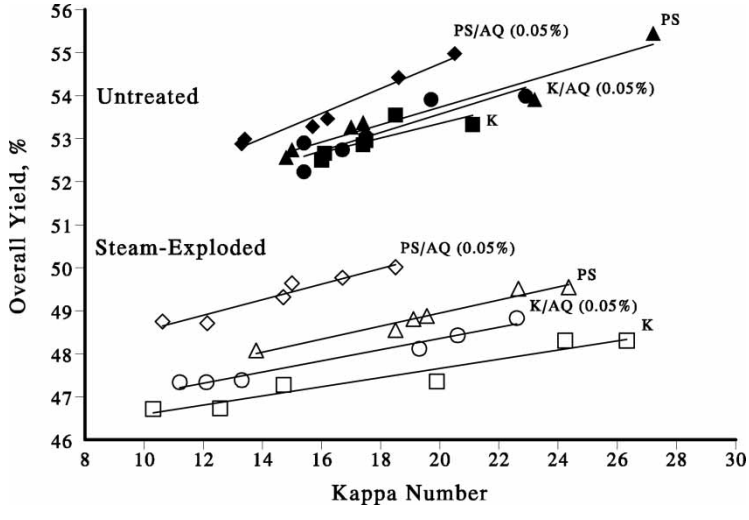

Figure 7. The overall pulping yields for steam-exploded chips, cooked under different chemical processes, were significantly lower than their corresponding untreated chips.

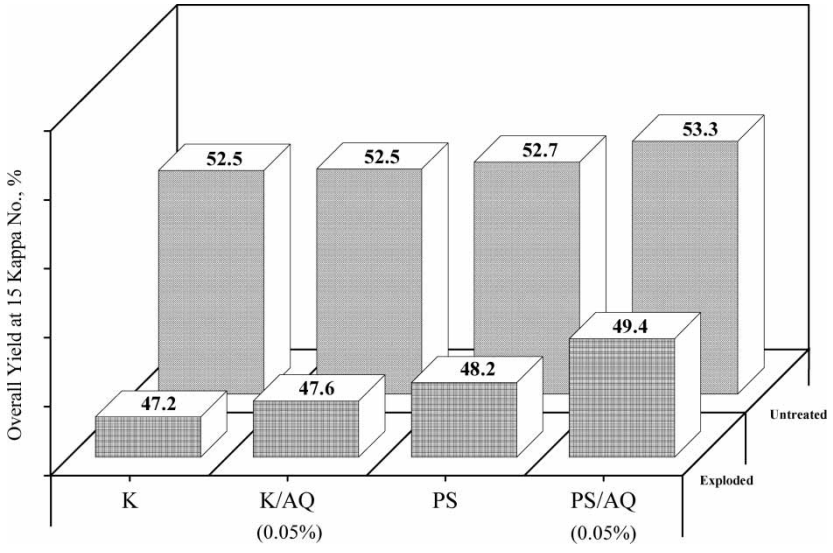

Figure 8. Although the additives responded better to the exploded chips than the untreated ones, the overall pulping yields are much lower (3.9 to 5.3%) for the steam-exploded chips within a given pulping process.

the yield loss during steam explosion and the yield from the kraft pulping process. It is important to note that for the kraft pulping only process the "overall yield" is equivalent to the "total yield." The overall yield for exploded chips was determined by multiplying the total pulping yield with that of the steam-explosion pretreatment yield (94%). Figure 8 summarizes the overall yields at kappa number 15 for both unexploded and exploded chips during different chemical pulping processes. [Note the overall yield for untreated chips is the same as the total pulping yield.] Clearly, the exploded chips have 3.9 to 5.3% lower yield than the untreated chips. The best performer, PS/AQ, in the steam-exploded group still has a 3.9% lower yield than its untreated counterpart.

Soda Pulping and Bleachability (D_0EoD) Studies

Additional pulping experiments were performed on the steam-exploded mixed hardwood chips to examine if the rate limitations of soda cooking might be overcome by the greater accessibility achieved through steam explosion.

In the first two soda cooks, the exploded chips were pulped at 16% AA corresponding to 31.0 g/L of NaOH. The first experiment was conducted at

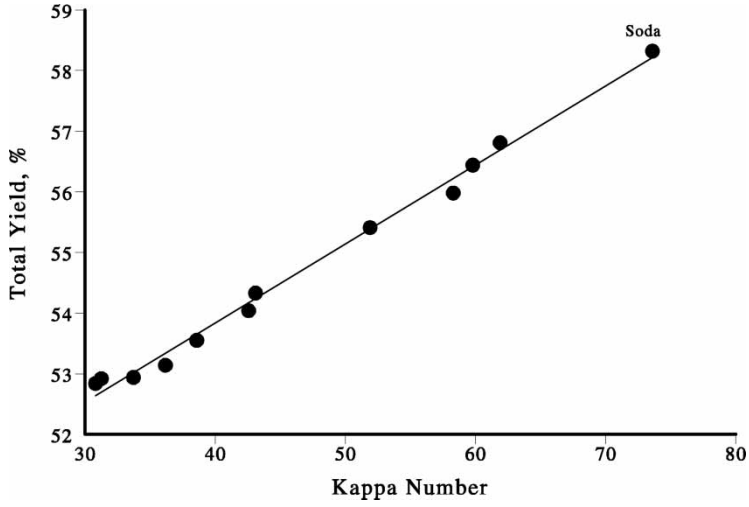

Figure 9. Total yield determination of two separate soda cooks for steam-exploded chips at the same chemical charge as the kraft pulping process (16% AA).

H-factors ranging from 800 to 1600, a similar range to that used in the kraft pulping studies. These cooks gave a low screened yield and a high level of rejects.

In the second series of soda cooks, the exploded chips were pulped for a longer time (1600 to 2500 H-factor) at 16% AA charge. Although this increased the screened yield, the kappa numbers were still higher (28 to 43) than those of their kraft counterparts.

Figure 9 shows that there is a good correlation ($r^2 = 0.997$) between yield and kappa number for the two sets of soda cooks of steam-exploded chips. Figure 10 shows that the rate of lignin degradation is very slow during soda pulping but then again there is a change in rate that occurs between 1100 and 1200 H-factor.

The next series of soda cooks was conducted with 18% AA (34.9 g/L NaOH) with H-factors ranging from 1800 to 2800. We found that, under these conditions, the kappa numbers were in the same range as those of the kraft cooks (Figure 11). The yield curve from soda pulping is slightly higher ($\sim$0.4% at kappa number 15) than the kraft process. This improvement was achieved, however, by pulping the exploded chips under harsher conditions (1800 to 2800 H-factor and higher AA).

Further work was done to compare the bleachability of kraft pulps from untreated chips with soda pulps from steam-exploded chips. The furnishes were pulped to a similar kappa number ($\sim$14). Both pulps were then bleached with the D_0EoD sequence. The experimental data for both sets of chips are reported in Table 4.

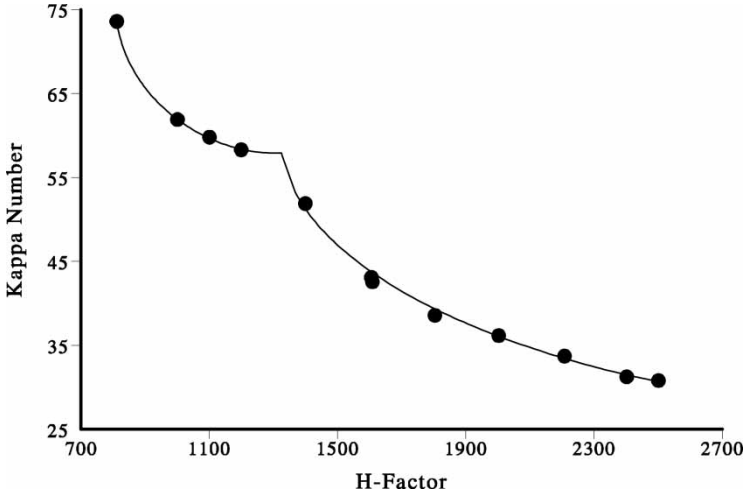

Figure 10. Rate of delignification of steam-exploded chips, under two sets of H-factors for soda pulping at 16% AA, shows the rate of delignification changes at H-factors higher than 1200.

The data show that soda pulp from steam-exploded chips has significantly lower viscosity and zero-span strength than kraft pulp from untreated chips. Although steam-explosion may contribute to some extent, this is largely caused by the severe conditions of the soda cook (18% AA and 2800

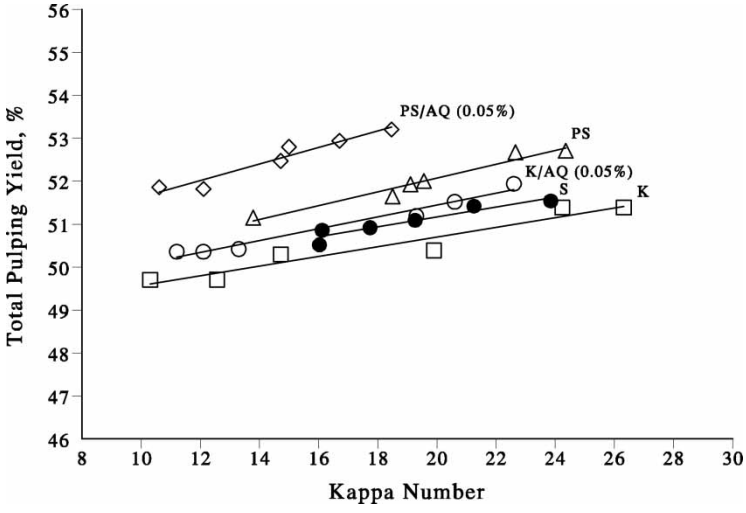

Figure 11. Comparison of the total pulping yield for steam-exploded mixed hardwood chips under kraft and soda pulping processes shows that soda has a higher yield.

Table 4. D_0EoD bleaching sequence of kraft pulp from untreated hardwood chips and soda pulp from steam-exploded hardwood chips

	Kraft (untreated chips)			Soda (S.E. chips)		
Pulping						
Active alkali, %		16			18	
Kappa number		14.5			13.9	
Viscosity, mPa · s		40.4			16.2	
D_0Eo stage						
Kappa number		5.0			3.5	
Viscosity, mPa · s		31.0			13.5	
D_0EoD						
D_1:ClO_2, % on Pulp	0.5	0.75	1.0	0.5	0.75	1.0
Brightness, % ISO	84.3	85.1	86.3	83.8	85.8	87.1
Z-span, km	16.5	16.2	16.7	12.7	12.5	12.2
Viscosity, mPa · s	28.9	29.6	26.1	13.2	12.8	12.0

D_0: 30 min; 50°C; 3.5% Cs; 0.22 ACM; Final pH 3.0–3.2.
Eo: 10 min @ 20 psi; 50 min @ 0 psi; 70°C; 10% Cs.
D_1: 180 min; 70°C; 10% Cs; 0.5, 0.75, and 1.0% ClO_2; Final pH 4.0–4.5.

H-factor) needed to reach a kappa number of 14; kraft pulping of untreated chips required only a 16% AA charge at 1600 H-factor. Both pulps, however, responded similarly to bleaching.

CONCLUSIONS

The potential of the steam explosion pre-treatment of mixed hardwood chips to produce chemical pulp with 85% ISO brightness and significantly higher yield than the conventional kraft pulp from untreated chips was assessed. Conclusions from this work are:

- The yield gains of PS, AQ, and PS/AQ relative to its kraft counterpart were higher for steam-exploded chips than for untreated chips.
- In all four types of cooks, the steam-exploded chips gave lower overall yield (3.9 to 5.3%) than the untreated chips.
- At the same temperature and active alkali (AA) charge on wood, the steam-exploded chips cooked faster than the untreated chips, hence the steam-exploded chips can be pulped at a lower temperature and/or lower AA to maintain the same production rate.
- Soda pulping of steam-exploded chips under similar conditions to those of kraft delignified slower and had higher amounts of rejects. Increasing the H-factor and AA charge in soda pulping with steam-exploded chips

increased the ratio and gave a pulp with a higher yield than that of kraft pulping at a similar kappa number, but with a significantly lower viscosity and zero-span strength.

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