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**SULFITE-ANTHRAQUINONE PULPING OF SOUTHERN PINE
FOR BLEACHABLE GRADES**

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ABSTRACT

Sulfite-anthraquinone (SAQ) pulping was investigated as a process for the manufacture of bleachable pulp from southern pine. The effects of the relative proportions of Na_2SO_3 , Na_2CO_3 , and NaOH on rate, selectivity and pulp composition were systematically studied. Additional pulping experiments at constant chemical concentration demonstrated that the rates of removal of both lignin and carbohydrates increase with increasing liquor alkalinity. By contrast, pulp viscosity retention passes through a maximum at intermediate alkalinities. Compared to kraft, the SAQ pulps had 5-8% higher carbohydrate yield (o.d. wood basis), were more easily bleachable, lost slightly more yield upon bleaching and were at least as strong. In separate experiments, the SAQ process was shown to be capable of pulping to very low kappa numbers while retaining high viscosity and acceptable yield. This can be achieved by employing high liquor-to-wood ratio and correspondingly high chemical charge. Current kinetic studies are expected to identify other routes to the same end.

KEYWORDS: Sulphite pulping, alkaline pulping, anthraquinone, bleached pulps, mechanical properties, selectivity

INTRODUCTION

Since its introduction in the late 1970's, the potential benefits of sulfite-anthraquinone (SAQ) pulping have been well established (1-6). Relative to kraft and kraft-AQ pulping, SAQ pulping under mildly alkaline conditions (terminal pH about 9) possesses advantages in terms of yield, pulp beatability, pulp bleachability, elimination of causticizing, and reduced potential for odor emissions. It also has the disadvantages of a slower pulping rate, potential for increased recovery boiler corrosion, and the need for chemical conversion

and liquor regeneration systems. The strength properties of the pulp are similar to those of kraft, although it has been found, at least in some cases, to have slightly lower tear strength.

Compared to the kraft process, SAQ pulping under mildly alkaline conditions is very selective, giving both a higher yield and a higher viscosity at a given lignin content or kappa number. This would make it attractive for the production of bleachable grades of low kappa number and correspondingly low bleaching chemical requirements were it not for the fact that the process slows down and loses selectivity at a kappa number somewhat above the usual 30-35 level. This is illustrated in Fig. 1 by data from laboratory cooks of southern pine. The ordinate, yield selectivity, is defined as the mass of lignin dissolved since the beginning of the cook per unit mass of carbohydrate dissolved. It is a quantity that should obviously be maintained at as high a value as possible. When plotted against kappa number it passes through a maximum at the point of transition from bulk delignification to the relatively slower residual delignification. Beyond this maximum, selectivity suffers because carbohydrate dissolution undergoes no corresponding rate decrease and continues unabated. It is apparent that, at kappa numbers above 50, SAQ pulping displays a pronounced selectivity advantage over kraft pulping. It can also be seen that as delignification is continued this advantage diminishes, owing to the earlier onset of residual delignification in the SAQ system.

(Fig. 1 here)

Another factor which may limit the degree of delignification that can practically be achieved in the pulping step is loss of pulp strength, which is associated with the cleavage of glycosidic bonds in cellulose. If allowed to proceed far enough, the resulting reduction in cellulose chain length manifests itself as a loss in pulp strength. Pulp viscosity is a good indicator of the extent of chain breakage and can be used for an approximate calculation of the number of bonds broken. Figure 2 shows that cellulose chain shortening exhibits the same type of dependence on degree of delignification as dissolution of cellulose (a different process) and other carbohydrates. Again the pronounced

advantage of SAQ pulping diminishes as delignification is extended below a kappa number of about 50.

(Fig. 2 here)

If the reason for this behavior can be determined, it may become possible to modify or redesign the SAQ process to make it a very attractive alternative to kraft for the production of bleached grades. We are currently investigating this possibility by studying the kinetics of SAQ pulping. In the meantime, the good bleachability of the pulp and the high selectivity of the process at moderate degrees of delignification make it a candidate for the production of bleachable grades in its present form. Accordingly, we have conducted an experimental study of its applicability to southern pine. We have also done some experiments to demonstrate that, surprisingly, SAQ processes are capable of selectively pulping to very low kappa numbers.

EFFECTS OF LIQUOR COMPOSITION

The effects of varying the initial liquor composition, although they have been the subject of considerable research, are not well delineated in the literature. Data are available on the effect of varying the sulfite content at constant total chemical charge (1,5,6,9) but not on the effect of varying the ratio of Na_2CO_3 to NaOH . Table I contains the results of a series of experiments systematically designed to define both types of effects. Pulping conditions were maintained constant and were chosen to characterize the period preceding the transition to residual delignification. The wood pulped was in the form of thin (1 mm) wafers to minimize mass transfer effects. In all cases the total chemical charge was 24% Na_2O , based on o.d. wood weight. Liquor composition was varied over the ranges 60 to 100% Na_2SO_3 , 0 to 40% Na_2CO_3 , and 0 to 40% NaOH , all expressed as Na_2O . The compositions were chosen to form a simplex lattice design of the special cubic type described by Gorman and Hinman (8), and all cooks but one were duplicated to improve precision. Regression analysis of the data gave equations that were used to plot the contour diagrams shown in Fig. 3 to 5.

(Table I and Fig. 3 here)

Since pulping conditions were constant, the kappa number attained in liquor of a given composition is an indicator of the rate of pulping in that liquor. Thus, compositions giving equal rates are found on the same contour lines in Fig. 3, and regions of low kappa number define liquor compositions that give high rates. It is apparent that pulping is fastest in NaOH-rich liquors and slowest in 100% Na_2SO_3 , with Na_2CO_3 -rich liquors being intermediate. In liquors containing 0 to 10% NaOH, a maximum rate is found at about 75% Na_2SO_3 .

(Fig. 4 and 5 here)

The yields in Table I are not directly comparable with one another because of the differing degrees of delignification. Yield selectivity, the mass of lignin dissolved per unit mass of carbohydrate dissolved, is less dependent on degree of delignification and therefore is more comparable. Figure 4 shows that yield selectivity is best in pure sodium sulfite and poorest in liquors rich in NaOH, with Na_2CO_3 -rich liquors being intermediate but relatively poor. In liquors containing 75 to 80% Na_2SO_3 , yield was moderately good and insensitive to the ratio of Na_2CO_3 to NaOH. Note that all of the liquor compositions of Fig. 4 gave yield selectivities that were better than typical kraft values (about 1.0).

Viscosity retention is best in Na_2CO_3 -rich liquors, as shown in Fig. 5. Pure Na_2SO_3 gave the lowest viscosity selectivity, and the strongly alkaline liquors were intermediate. In liquors containing about 80% Na_2SO_3 , viscosity, like yield, was moderately high and was insensitive to the ratio of Na_2CO_3 to NaOH. All compositions, with the exception of pure or nearly pure Na_2SO_3 , were equal to or better in this respect than kraft (about 8).

The effects of varying the liquor composition at constant total Na_2O concentration are summarized in Fig. 6. A choice must be based on the best compromise among the 3 factors discussed above.

(Fig. 6 here)

Removal of Individual Wood Components

Further insight into the effects of liquor composition on the rates of dissolution of the various wood components is provided by Table II, which also contains analytical data for a comparable kraft pulp and the wood from which the pulps were made. Under the pulping conditions used, the liquor containing only sodium sulfite removed no cellulose, about one third of the glucomannan, about one quarter of the arabino-xylan and about two thirds of the lignin. The residual lignin was heavily sulfonated, containing 4% sulfur (about one sulfonic acid group for every 3 C₉ units).

(Table II here)

Replacing 20% of the Na₂SO₃ with Na₂CO₃ (Na₂O basis) had no effect on cellulose but nearly doubled the amount of glucomannan removed and reduced the residual lignin content by 50%. The sulfur content of the residual lignin was also decreased, indicating that the added Na₂CO₃ functioned by extracting sulfonated lignin. Replacing an additional 20% of the Na₂SO₃ with Na₂CO₃ caused a slight decrease in the amount of lignin removed and a slight increase in the amounts of carbohydrates removed, including cellulose. A simultaneous increase in residual lignin content and decrease in sulfur content suggests that the main effect of the additional replacement was to reduce the Na₂SO₃ charge below the level required for complete lignin sulfonation.

Replacing Na₂SO₃ with NaOH instead of Na₂CO₃ gave more efficient lignin removal but also resulted in the removal of larger amounts of all carbohydrate components.

Isolating the Effects of Alkalinity

To better characterize the effect of liquor alkalinity, a second series of laboratory cooks was done under conditions which resulted in all other variables being maintained approximately constant. These cooks differed from those already described by being conducted at a high liquor-to-wood ratio (and correspondingly high chemical charge). This was done so that the concentrations of chemicals in the liquor would remain nearly constant throughout the cook.

Figures 7-9 show the effect of increasing alkalinity at a fixed concentration of Na_2SO_3 and fixed total Na_2O concentration. In other words, they show the effect of varying the composition of the nonsulfite component of the cooking chemical without varying its amount. It consists of a mixture of Na_2CO_3 with either NaHCO_3 or NaOH , depending on whether the liquor pH is below or above the value marking complete conversion of bicarbonate to carbonate ions (about 12). At one end of the range studied it was a mixture of 8 g NaHCO_3/L and 4 g $\text{Na}_2\text{CO}_3/\text{L}$, while at the other end it was 12 g NaOH/L .

(Fig. 7, 8, and 9 here)

The effects on kappa number and yield were observed to be quite nonlinear in liquor pH. Both were insensitive to pH over the range 10-13, but strong pH effects were evident above and below this range. When plotted against alkalinity, both were approximately linear. The rate of pulping increases continuously with liquor alkalinity, as shown by the decreasing kappa numbers of Fig. 7. The rate of carbohydrate dissolution is similarly affected, as is evident from Fig. 8.

Unlike delignification and carbohydrate dissolution, cellulose chain cleavage is slowest at intermediate pH values, as shown by the viscosity maximum in Fig. 9. The maximum occurs when the pulping liquor contains a small amount of free sodium hydroxide; larger amounts result in a precipitous drop in viscosity. Liquors containing no free sodium hydroxide but increasing proportions of sodium bicarbonate also give progressively lower viscosity. The latter effect has also been observed by Thompson (10); its mechanism is not known.

These relationships between liquor alkalinity and the rates of delignification, carbohydrate dissolution and cellulose chain cleavage help to explain the effects of liquor composition on the outcome of the pulping process under conditions of low liquor-to-wood ratio and chemical charge. When the proportion of nonsulfite alkali is low, the products of the delignification and carbohydrate dissolution reactions neutralize a sufficiently large fraction of it to cause a rapid pH drop into the region where the liquor is effectively buffered by dissolved lignin, the carbonate-bicarbonate system, or both. Under these conditions, the alkalinity prevailing during most of the cook is insensitive to the

initial ratio of NaOH to Na_2CO_3 . This is why neither rate nor selectivity is much affected by the nonsulfite alkali composition when the Na_2SO_3 charge is in the neighborhood of 80% of the total alkali charged (Fig. 3-6).

As the proportion of Na_2SO_3 is reduced to about 60% of the total alkali charged, there is sufficient nonsulfite alkali present for its composition to have a substantial effect. NaOH-rich liquors remain strongly alkaline throughout the cook, while Na_2CO_3 -rich liquors quickly become buffered in the 9-10 pH range. Consequently, kappa number, yield and viscosity decrease as Na_2CO_3 is replaced by NaOH. It has been stated that, unlike kraft pulping, sulfite anthraquinone pulping is accelerated by Na_2CO_3 . At first sight, the data in Fig. 7 seem to bear this out, inasmuch as they show that kappa number decreases with increasing Na_2CO_3 concentration in the absence of free NaOH. However, it should be noted that the experimental relationships shown in Fig. 7, 8 and 9 were obtained under conditions of constant total nonsulfite alkali composition and must be interpreted in this light to avoid erroneous conclusions. Thus an increase in Na_2CO_3 concentration implies a corresponding decrease in the concentration of NaHCO_3 and an increase in pH. If the pH (and therefore the ratio of Na_2CO_3 to NaHCO_3) is held approximately constant and the Na_2CO_3 concentration is increased, it is found that the pulping rate is decreased, not increased as may be expected (Fig. 10). Na_2CO_3 serves as a buffer, not as an active pulping chemical.

(Fig. 10 here)

COMPARISONS WITH THE KRAFT PROCESS

In considering sulfite-anthraquinone pulping as an alternative to the kraft process, it is of interest to compare the two with regard to pulping rate, selectivity, pulp quality and pulp bleachability.

Selectivity and Rate

Selectivity, as already discussed, is better in the case of SAQ pulping, but the advantage diminishes with decreasing kappa number (Fig. 1 and 2). If pulping is terminated at a kappa number of 40 or above, SAQ pulping possesses significant yield and viscosity advantages. This is apparent from the data of

Table III, which were obtained by laboratory pulping of southern pine chips from two different sources. The SAQ process gave carbohydrate yields that were, respectively, 6 and 8 percentage points higher. The latter figure represents a potential for obtaining 18% more pulp from the same amount of wood, although bleach plant losses would reduce this figure somewhat, as described below.

(Table III here)

SAQ pulping also gives very much higher pulp viscosity than kraft pulping, as is also apparent from Table III. On the basis of the available information on the relationship between strength and viscosity for SAQ pulps, it seems likely that it is similar to the corresponding relationship for kraft pulps. If this is true, the implication is that the SAQ pulps can be treated more severely in subsequent processing, for example, by extensive oxygen bleaching, without incurring strength loss by reducing the viscosity below a critical value.

The rate disadvantage of SAQ pulping can be diminished by raising the temperature, but the yield and viscosity advantages are somewhat reduced at the higher temperature. Another way of accelerating the cook is to use NaOH as makeup chemical. The effect shown in Table III is somewhat greater than anticipated on the basis of the results of the experiments on liquor composition effects described above. This may be due to beneficial effects of NaOH on swelling and mass transfer. The earlier experiments were designed to eliminate the influence of mass transfer limitations and were accordingly conducted with wood in the form of thin wafers; the data of Table III were obtained on chips.

Bleachability

SAQ pulp bleachability differs from that of kraft pulp in two important respects: the higher lignin content of the unbleached pulp and the greater ease of bleaching the chlorinated and extracted pulp to high brightness. Thus, previous studies of Canadian and Scandinavian softwoods have shown that although SAQ pulps require higher charges of chlorine and caustic in the first two bleaching stages, they can be fully bleached with chlorine dioxide in only one additional stage. The data of Table IV show that the same is also true of southern pine pulps.

(Table IV here)

Their high chlorine requirement and exceptionally high viscosity make SAQ pulps natural candidates for oxygen bleaching. Our studies have shown that, like pulps from other species, southern pine SAQ pulps respond normally to oxygen bleaching. For example, the kappa number of pulp from cook 167 (Table III), was reduced from 41 to 20 by oxygen bleaching with 2.5% NaOH to give pulp having a viscosity of 32 mPa.s at a yield of 49.4% based on o.d. wood.

Bleaching Yield

The literature provides little information on the relative yield losses in the bleaching of SAQ and kraft pulps. Ingruber et al. (6) determined shrinkages in the bleaching of pulps made from an eastern Canadian softwood mixture. Their results, expressed as yield reduction (based on unbleached pulp) per unit of kappa number reduction, were 0.216 and 0.167 for SAQ and kraft pulps, respectively. Finnish workers (5,9) concluded that shrinkage was no worse for SAQ than kraft pulps, but they reported high levels for both.

The results of our determinations are presented in Table V. For pulps from both wood sources SAQ pulp suffered a greater yield loss than kraft pulp. Nevertheless, the major part of the unbleached yield advantage of the former remained after bleaching.

(Table V here)

Bleached Pulp Strength

Bleached SAQ pulps from southern pine are slightly superior in strength to the corresponding kraft pulps. Data to support this statement are presented in Table VI and Fig. 11 and 12. The SAQ pulps have a higher ultimate tensile strength and a higher tensile strength at a given degree of refining. Equivalently, they require less refining energy to attain a given strength. At a given tensile strength, the tear strengths are the same as the corresponding kraft pulp values.

(Table VI and Fig. 11 and 12 here)

THE FUTURE - LOW-LIGNIN SAQ PULPS

In spite of the natural tendency for SAQ pulping to slow down and lose selectivity at rather high kappa number levels, we have found that the process is capable of pulping to very low kappa numbers with good selectivity. This can be achieved by using high liquor-to-wood ratios and correspondingly high chemical charges, as illustrated by the data of Table VII. High liquor ratio SAQ pulping may be conducted in either moderately alkaline (HLS₁₀AQ) or strongly alkaline (HLS₁₃AQ) liquors. (In these designations, the subscript refers to the terminal pH of the pulping liquor.) At the lower pH low kappa numbers can be obtained at very high viscosity levels and carbohydrate yields that are better than the corresponding kraft yields. Operating at the higher pH level accelerates the process and gives extremely low kappa numbers with acceptable viscosities but at the cost of about 2% yield. Both types of pulp are as strong as or stronger than kraft.

(Table VII here)

The marked beneficial effect of increasing liquor ratio and chemical charge is characteristic of the SAQ process. The data in the table show that there is no corresponding effect on the selectivity of the kraft or kraft-AQ processes when the liquor ratio and chemical charge is increased.

These results suggest two different possibilities. One is the development of a process based directly on the use of high liquor ratios. It would involve efficient separation of spent liquor from the chips at the end of the cook, followed by fortification and reuse. Although the total charge of pulping chemicals would be very high in such a process, the actual consumption of chemicals would be limited to that required to fortify the liquor prior to reuse. A precedent for this approach is the SCMP chemimechanical pulping process, which employs a very concentrated pulping liquor and therefore a high chemical charge (11).

A second possibility is that determining the mechanism of the selectivity improvement will provide the insight needed to achieve the same end by other means. For example, a knowledge of the relative concentration dependencies of delignification, cellulose chain cleavage, and carbohydrate dissolution will

allow optimal liquor concentration - time profiles to be specified and suggest ways of achieving them, such as staging and liquor injection. This is the objective of our current studies of the kinetics of the process.

EXPERIMENTAL

Materials

Bolts of southern yellow pine, believed to be loblolly pine, were chipped in a Carthage chipper or, in some cases, sawn into discs from which 1 mm thick wafers were subsequently cut. Wood from two different sources was used. Both were characterized by chemical analysis and determination of specific gravity. The results are summarized in Table VIII.

(Table VIII here)

Pulping liquors were prepared from reagent grade sodium sulfite, sodium hydroxide and sodium sulfide. SAQ liquors were made by absorbing carbon dioxide in sodium sulfite-sodium hydroxide solutions until the desired pH was reached. Liquor concentrations were checked by acidimetric titration. The kraft pulping liquors contained no sodium carbonate.

Pulping

The cooks done to determine liquor composition effects were carried out in 500-mL bomb microdigesters heated by rotating them in an oil bath. To eliminate mass transfer effects, these cooks were conducted with 1-mm thick wood wafers as raw material. Before cooking, the wafers were impregnated by submerging them in the pulping liquor and applying a vacuum. At the end of the cook the bombs were removed from the oil bath and cooled, first with steam and then in a shower of cold water.

The cooked wafers were fiberized in a blender and washed with deionized water. The pulp pad was dewatered, air-dried, weighed and sampled for moisture to determine yield. The remaining sample was reslashed in a TAPPI disintegrator and screened on a 0.006-inch cut flat screen. Kappa number was determined on the screened pulp by the standard TAPPI procedure.

Larger scale cooks were carried out in a stainless steel vessel of about 50-L capacity fitted for external circulation and indirect steam heating. In these cases the wood pulped was in the form of chips screened to pass a 3/4-inch opening and to be retained on a screen with 1/4-inch openings. The chips were charged to a stainless steel basket which closely matched the interior contours of the digester and which could be removed with the contents following the cooks. After charging with chips and liquor the digester was evacuated to assist chip impregnation with the SAQ liquor. Subsequently, the temperature-time profile was controlled by manually regulating the steam input to the heat exchanger. Pulping conditions are appended to the data tables.

At the end of the cook the blow valve was opened to expel the spent liquor through a cyclone separator into a muslin-covered wash box where any entrained fibers were collected. The cooked chips were washed and fiberized in a Williams disintegrator.

The pulp was screened through a 0.006-inch cut screen plate on a Valley flat screen. The rejects were oven dried, weighed, and discarded. The accepted pulp was dewatered by centrifugation, mechanically subdivided, weighed and sampled for moisture to determine yield.

Bleaching

Oxygen bleaching was done at 100 psia O_2 and 25% consistency in a reactor equipped with stainless steel mesh trays and heated by direct steam. Chlorination and chlorine dioxide stages were done either in a 30-gallon glass-lined stirred reactor or in polyester bags. Caustic extraction was accomplished by mixing caustic with the pulp at 10% consistency in a Hobart mixer and transferring the pulp to polyester bags, which were then placed in a thermostat.

Testing and Analysis

All pulp testing was conducted according to TAPPI standard methods as follows:

Kappa number - T236 os-76

Viscosity of pulp - T230 om-82

Brightness of pulp - T452 om-83

Physical testing - T220 om-83

Extractives - T204 os-76
Klason lignin - T222 os-74
Acid-soluble lignin - Useful Method 250

Viscosity was determined after overnight treatment with sodium chlorite in acetic acid solution at room temperature or below.

Carbohydrates were determined by acid hydrolysis followed by conversion of the resulting sugars to alditol acetates and analysis by gas chromatography (12).

CONCLUSIONS

1. In the pulping of southern pine, the sulfite-anthraquinone process possesses a marked selectivity advantage over the kraft process in terms of both yield and viscosity. Under normal conditions, the advantage diminishes rather rapidly as the kappa number at which the comparison is made is decreased below 40.

2. For a given degree of delignification, pulping in liquor containing only Na_2SO_3 results in very slow lignin removal and poor viscosity but good carbohydrate retention. Replacement of 20% of the Na_2SO_3 with Na_2CO_3 accelerates lignin removal and improves viscosity retention but gives a somewhat lower yield. Further replacement slows down the cook and reduces yield but improves viscosity. Analysis of the pulp suggests that Na_2CO_3 functions by extracting sulfonated lignin, but that too high a level of replacement of Na_2SO_3 impairs the ability of the liquor to sulfonate lignin.

3. Partial replacement of Na_2SO_3 with NaOH instead of Na_2CO_3 gives more efficient lignin removal but reduces pulp viscosity and carbohydrate retention.

4. Cooks conducted under conditions of constant chemical concentration show that the rates of removal of both lignin and carbohydrates increase with increasing alkalinity. Pulp viscosity, on the other hand, passes through a maximum as liquor alkalinity is increased. The maximum occurs at an alkalinity slightly higher than necessary to convert all bicarbonate ions to carbonate ions.

5. At constant pH, increasing the concentration of Na_2CO_3 retards delignification. The apparent activity of Na_2CO_3 as a pulping chemical in SAQ systems is related to its buffering ability.

6. The rate disadvantage of SAQ pulping relative to kraft can be diminished by raising the pulping temperature or by using NaOH as makeup chemical. In the former case, its selectivity advantage is also diminished.

7. Bleaching of SAQ pulps in conventional sequences requires more chlorine and caustic in the first two stages than kraft pulps. Subsequently, however, they can be fully bleached in only one stage, while kraft pulps require 3 additional stages.

8. The bleaching yield of SAQ pulps is lower than that of kraft pulps, but the difference is not great enough to seriously erode the overall yield advantage of the former.

9. Bleached SAQ pulps from southern pine are as strong as or stronger than the corresponding kraft pulps. They exhibit a higher ultimate tensile strength and equal tear at a given tensile level.

10. The SAQ pulping process is capable of pulping to very low kappa number levels while retaining high viscosity and acceptable yield. Currently, this can be achieved by using high liquor-to-wood ratio and correspondingly high chemical charge. Ongoing kinetic studies are expected to identify other routes to the same end.

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Chemical Charges, % o.d. wood, as Na ₂ O,			Total Yield, % o.d. wood	Kappa Number ^a	Viscosity, ^b mPa · s	pH at 25°C	
Na ₂ SO ₃	Na ₂ CO ₃	NaOH				Initial	Final
24.0	0	0	68.7 68.7	93.0 97.8	28.7 27.0	10.3 10.3	8.7 8.5
14.4	9.6	0	57.7 56.7	67.8 71.0	74.3 80.3	11.7 11.8	9.4 9.4
14.4	0	9.6	48.5 47.6	30.4 27.4	23.9 28.7	13.5 13.4	12.3 12.3
19.2	4.8	0	57.6 56.9	52.1 55.0	61.8 71.2	11.8 11.6	9.4 9.3
19.2	0	4.8	54.0 54.3	52.2 52.8	57.8 72.7	13.4 13.4	10.5 10.3
14.4	4.8	4.8	55.9 55.6	76.5 71.4	46.8 59.0	13.4 13.3	10.3 10.2
17.6	3.2	3.2	54.8 54.4	58.8 57.0	51.4 76.3	13.3 13.2	10.0 9.8
20.8	1.6	1.6	56.5 56.2	49.1 52.0	59.4 61.8	13.1 13.0	9.6 9.5
16.0	6.4	1.6	55.6	61.7	60.2	13.0	9.5
16.0	1.6	6.4	52.9 52.6	55.8 52.3	44.9 53.1	13.4 13.4	10.7 10.8

^aThe cooked wafers were fiberized in a blender (2 minutes, high speed), screened on a 0.006-inch cut flat screen, and the kappa number determined on the accepts. The percentage rejects was 1% or less in all but one case, where it was 1.6%.

^bViscosity was measured after delignification with sodium chlorite in acetic acid for 20 hours at room temperature.

^cCooking conditions: 24% total Na₂O based on o.d. wood wt.; 0.1% AQ; liquor-to-wood ratio 4.1 mL/g; vacuum preimpregnation; 90 minute linear temperature rise from 90 to 115°C; 3 hours at 175°C.

Table I. Experimental Sulfite-Anthraquinone Pulping Data: Effects of Liquor Composition^c.

24	Chemical Charges,		Total Yield, %	Cellu- lose ^a	AXC	Klason Lignin	U.V. Lignin	Total Lignin	Sulfur, % of Lignin
	o.d. wood, as Na ₂ O	Na ₂ CO ₃ NaOH							
19.2	0	0	68.7	37.5	6.6	5.4	6.7	12.1	3.9
14.4	4.8	0	57.2	37.6	5.7	3.5	2.4	5.9	2.8
14.4	9.6	0	57.2	36.0	6.0	6.0	0.7	6.7	2.0
	0	9.6	48.0	35.6	4.8	2.0	0.4	2.4	1.5
	Kraft Pulp		46.7	33.6	5.1	2.4	0.2	2.6	1.2
	Wood (Source 1)			37.6	17.0	31.0	0.8	31.8	

^aThe cellulose content of the pulp was calculated with the formula: Cellulose = glucan - Mannan/3.

^bGGM = Galactoglucomannan = galactan + (4/3) (mannan).

^cAX = Arabinoxylan = araban + xylan.

^dSee Table I for SAQ pulping conditions; the kraft pulp was from cook No. 159 - see Table III for conditions. Data shown for SAQ pulps are averages of analyses of pulps from duplicate cooks. Data for kraft pulp and wood are averages of duplicate determinations.

Table II. Effect of Liquor Composition on Yields of Pulp Components^d.

Wood Source Process Cook no.	1			2		
	Kraft	SAQ		Kraft	SAQ	
	159	190	167	2	3	4
Chemical charges, as Na ₂ O, % o.d. wood						
Na ₂ SO ₃	0	19.2	19.2	0	19.2	19.2
Na ₂ CO ₃	0	4.8	4.8	0	4.8	2.4
NaOH	15	0	0	13.7	0	2.4
Na ₂ S	5	0	0	4.6	0	0
Anthraquinone charge, % o.d. wood	0	0.1	0.1	0	0.1	0.1
Maximum temperature, °C	165	175	180	173	175	175
Time at maximum temperature, min.	121	240	210	88	240	160
Total yield, % o.d. wood	46.7	53.6	51.9	47.7	57.0	57.4
Rejects, % o.d. wood	0.4	2.8	2.2	0.4	2.9	2.7
Kappa No.	38.8	44.3	41.0	35.0	41.7	47.3
Carbohydrate yield, % o.d. wood	44.0	50.0	48.7	45.2	53.4	53.3
Viscosity, mPa · s	37.4	72.1	52.5	31.1	77.5	117
Spent liquor pH	~ 13	9.3	9.0	~ 13	9.0	9.4
Brightness	22.5	44.9	36.0	23.8	34.8	32.3

^aAll pulps were prepared in a 50-L digester equipped with external circulation and indirect heating at liquor-to-wood ratios in the range 3.8-4.1.

Table III. Kraft and SAQ Pulping of Southern Pine.

Wood Source Process Cook no.	1		2	
	Kraft 159	SAQ 167	Kraft 11 ^a	SAQ 12 ^b
Kappa no.	38.8	41.0	30.8	43.0
Viscosity, mPa · s	37.4	52.5	29.7	77.3
Chlorination ^c				
Total Cl ₂ , %	9.70	9.22	7.07	11.06
Residual Cl ₂ , %	0.53	0.20	0.04	0.19
Extraction				
NaOH, %	4.85	4.61	3.54	5.53
Kappa no.	4.7	4.8	4.5	2.3
Viscosity, mPa · s	28.8	54.3	24.2	57.5
Chlorine dioxide				
ClO ₂ , %	0.8	1.0	1.0	1.0
Residual ClO ₂ , %	0.004	0.13	0.00	0.21
Brightness	79.2	89.3	80.6	90.8
Viscosity, mPa · s		46.3		54.9
Extraction				
NaOH, %	0.5		0.5	
Chlorine dioxide				
ClO ₂ , %	0.2		0.4	
Residual ClO ₂ , %	0.02		0.05	
Brightness	89.8		89.8	
Viscosity, mPa · s	24.9		20.0	

^aSame pulping conditions as cook 2; see Table III.

^bSame pulping conditions as cook 3; see Table III.

^cIncludes 15% ClO₂ as available Cl₂ based on total available Cl₂.

^dAll chemical percentages based on o.d. unbleached pulp weight.

^eConditions (stage no.; consistency, %; time, min.; temp., °C): 1,3,45,25; 2,10,60,60; 3,6-10,80,70; 4,10,60,60; 5,6-10,180,70.

Table IV. Bleaching of SAQ and Kraft Pulps^{d,e}.

Wood Source Process Cook no.	1		2	
	Kraft 159	SAQ 167	Kraft 11	SAQ 12
Kappa no. Unbl. yield, % o.d. wood	38.8	41.0	30.8	43.0
Bleaching yield, % o.d. unbl. pulp	46.7	51.9	48.7	57.0
	93.57	91.71	93.55	89.83
	93.34	91.86	93.66	89.50
	93.22	92.19	94.21	89.83
Average	93.4 ± 0.5	91.9 ± 0.5	93.8 ± 0.5	89.7 ± 0.5
Yield loss per kappa unit, %	0.170 ± 0.013	0.198 ± 0.012	0.201 ± 0.015	0.240 ± 0.011
Bleached yield, % o.d. wood	43.6	47.7	45.6	51.1

^aSAQ pulps bleached in CED sequence, kraft in CEDED; bleaching conditions as in Table IV.

Table V. Bleaching Yield Data^a.

Wood Source	Process	Cook No.	PFI Revs.	CSF, mL	Density, g/cm ³	Burst. Index, kPa · m ² /g	Tear Index, mN · m ² /g	Tensile Index, Nm/g	Zero-span Breaking Length, km	log ₁₀ (MIT Fold)	Bendtsen Porosity, mL/min	Scattering Coefficient, cm ² /g	
1	Kraft	159	500	725	0.587	4.69	21.7	59.3	17.2	2.88	>3000	200	
			1500	665	0.631	6.44	15.5	75.4	17.9	3.10	2849	165	
			3000	560	0.653	7.21	13.5	83.8	18.2	3.27	1245	151	
			4500	455	0.677	7.36	13.2	90.0	18.2	3.31	421	141	
			5250	380	0.680	7.88	12.1	90.6	21.4	3.42	190	140	
1	SAQ	167	500	735	0.600	4.86	21.2	60.1	17.5	2.94	3188	186	
			1500	660	0.648	6.43	15.6	75.9	19.2	3.13	2008	156	
			3000	585	0.673	7.46	12.7	92.0	19.8	3.30	896	130	
			5000	480	0.688	8.00	11.6	95.7	20.4	3.45	304	124	
			7000	370	0.702	8.36	10.9	100.1	19.4	3.46	130	118	
2	Kraft	11	500	700	0.575	3.29	32.1	46.1	17.7				
			2000	630	0.628	5.92	19.9	76.9	19.3				
			3000	490	0.649	6.56	15.6	81.0	20.5				
			4000	365	0.655	6.83	15.1	85.5	19.0				
			5000	280	0.685	7.14	15.0	88.4	19.9				
2	SAQ	12	500	730	0.583	3.60	28.0	50.3	17.7				
			2000	600	0.648	6.63	16.1	86.7	19.4				
			3000	500	0.654	7.72	15.0	88.9	19.0				
			4000	350	0.677	8.00	13.8	95.9	19.1				
			5000	315	0.693	7.90	13.6	100.4	19.6				

Table VI. Physical Properties of Bleached Pulps.

Process	HLS10AQ	HLS13AQ	K	HLK	HLKAQ
Cook no.	161	160	159	189	192
Initial concentrations, g Na ₂ O/L					
Na ₂ SO ₃	48	48	0	0	0
Na ₂ CO ₃ + NaOH	12	12	37.5	37.5	37.5
Na ₂ S	0	0	12.5	12.5	12.5
Initial AQ concentration, g/L	0.25	0.25	0.00	0.00	0.25
Maximum temperature, °C	180	180	165	165	165
Time at max. temp., min	210	120	121	118	120
Liquor-to-wood ratio, mL/g	20	20	3.8	20	20
Initial pH	11.0	13.4	n.d. ^a	n.d.	13.5
Final pH	10.0	13.1	n.d.	13.5	n.d.
Total yield, % o.d. wood	46.8	43.5	46.7	40.2	40.2
Rejects, % o.d. wood	1.1	0.1	0.4	0.1	0.0
Kappa no.	22.8	12.9	38.8	16.8	13.5
Carbohydrate yield, % o.d. wood	45.2	42.6	44.0	39.2	39.4
Viscosity, mPa · s	51.9	25.0	37.4	14.1	13.6
Unbleached brightness	42.2	42.7	22.5	40.9	43.0
No. of bleaching stages	3	3	5	n.d.	n.d.
Bleaching chemical cost index	51	44	100	n.d.	n.d.
Bleached yield, % o.d. wood	44.0	41.8	43.6	n.d.	n.d.
Tensile index at 4000 PFI rev., N · m/g ^b	90	93	86	75	n.d.
Tear index at 80 tensile index, mN · m ² /g ^b	16.2	14.6	14.5	14.8	n.d.

^an.d. = not determined.

^bPhysical properties given were determined after bleaching except in the case of the HLK pulp.

^cProcess designations: HLS10AQ, HLS13AQ - high liquor-to-wood ratio sulfite-anthraquinone (subscript density terminal liquor pH); K - kraft; HLK - high liquor-to-wood ratio kraft; HLKAQ - high liquor-to-wood ratio kraft-AQ.

^dAll pulps prepared from chips in a 50-L digester equipped with external circulation and indirect heating.

Table VII. Comparison of high liquor ratio SAQ pulping with kraft variants^{c,d}.

Source	Cellulose	Galactogluco- mannan, %	Arabino- xylan, %	Lignin, %	Extractives, %	Specific Gravity
1	37.6	17.0	8.4	31.8	4.5	0.411
2	38.8	17.9	8.4	30.8	2.6	0.505

Table VIII. Wood furnish characteristics.

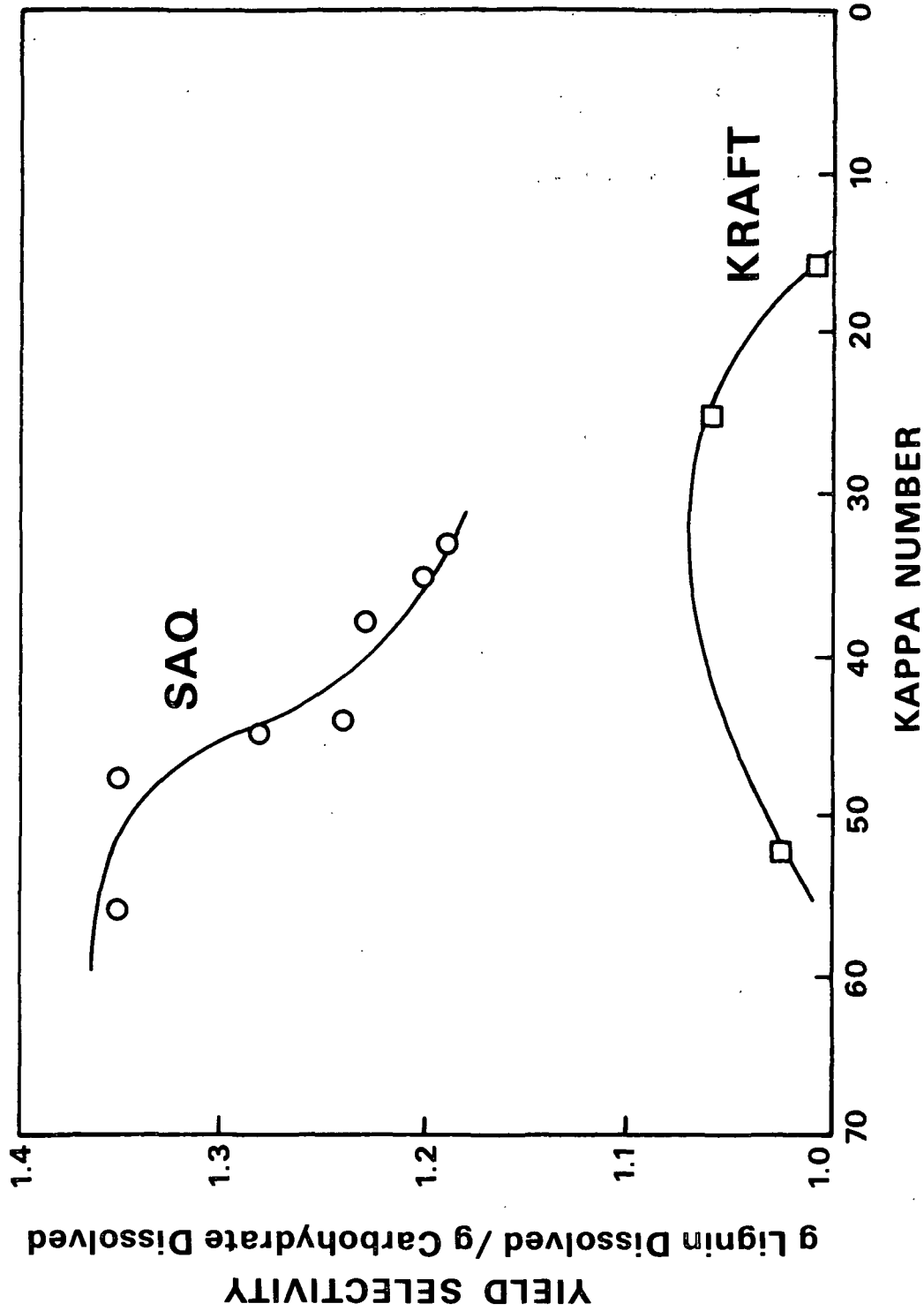


Figure 1. Yield selectivity of SAQ and kraft pulping as a function of degree of delignification. SAQ conditions: 24% Na₂O on wood, 80% as Na₂SO₃, 20% as Na₂CO₃, 0.1% AQ, L/W 4 mL/g, 1 1/2 to 4 1/2 h at 180°C; kraft conditions: 18% eff. alk. 25% sulfidity, L/W 4 mL/g, max. temp. 173°C, H-factor 1074-3724.

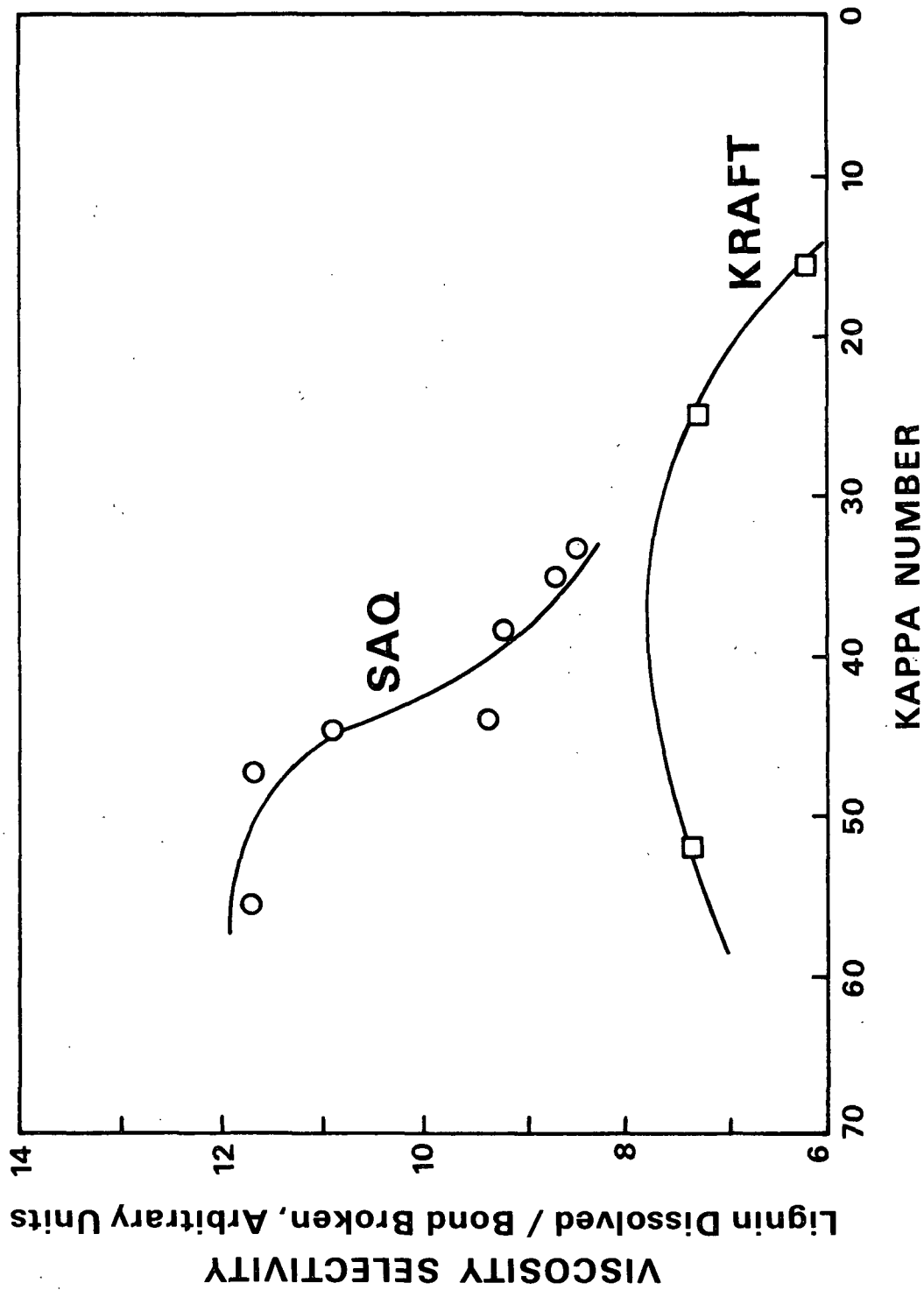


Figure 2. Viscosity selectivity of SAQ and kraft pulping as a function of degree of delignification. For conditions, see Figure 1.

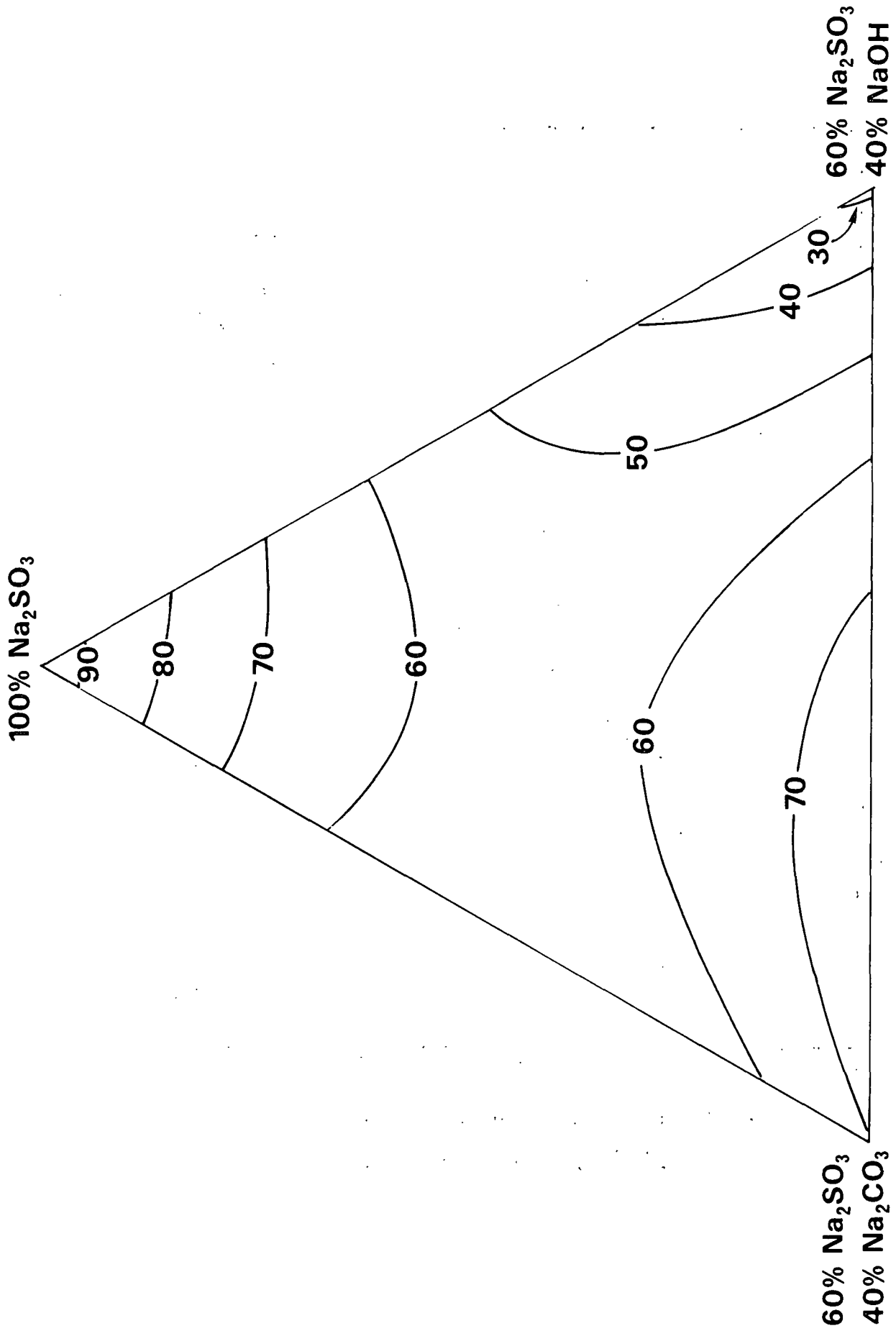


Figure 3. Contours of constant kappa number.

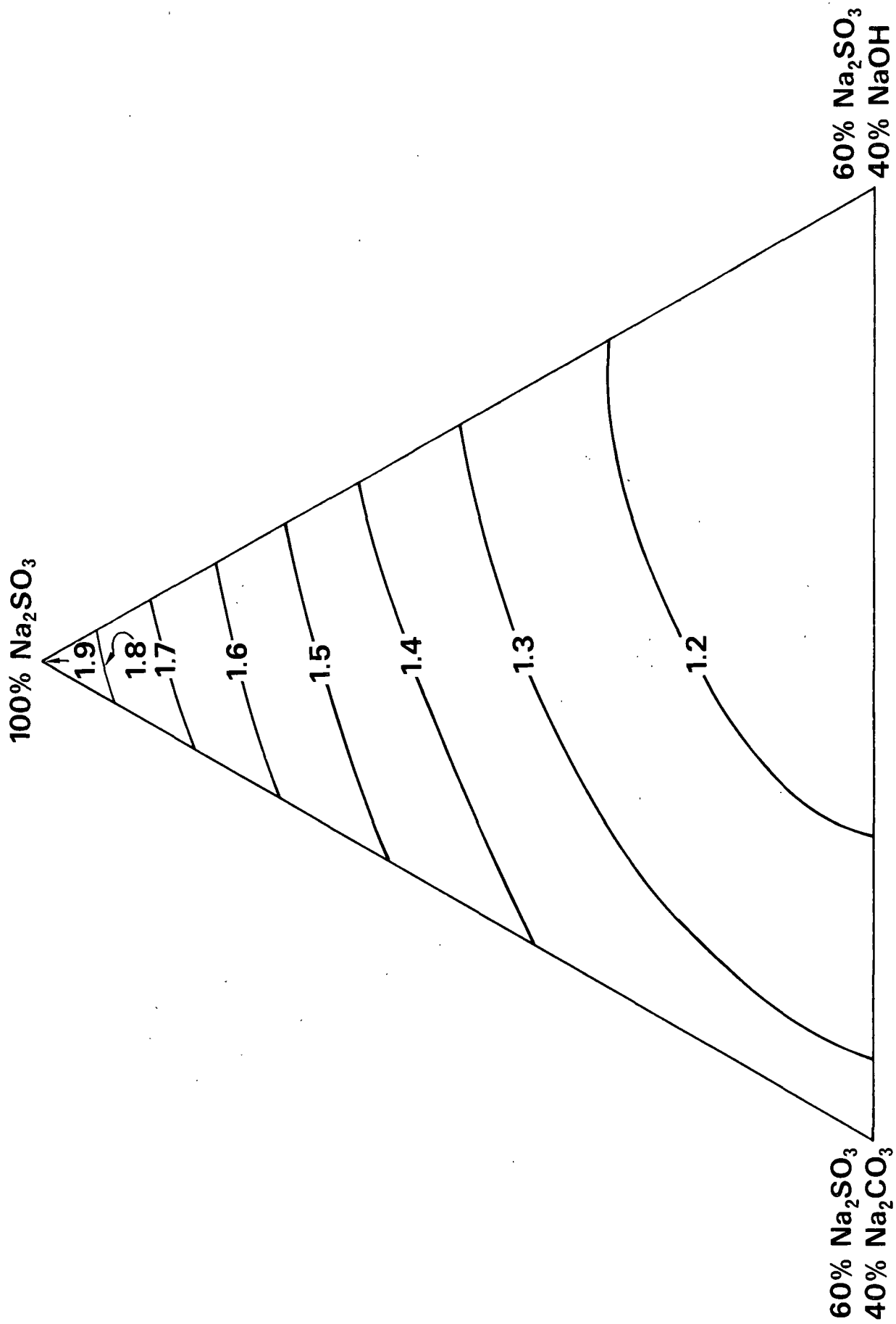


Figure 4. Contours of constant yield selectivity (g lignin dissolved/g carbohydrate dissolved).

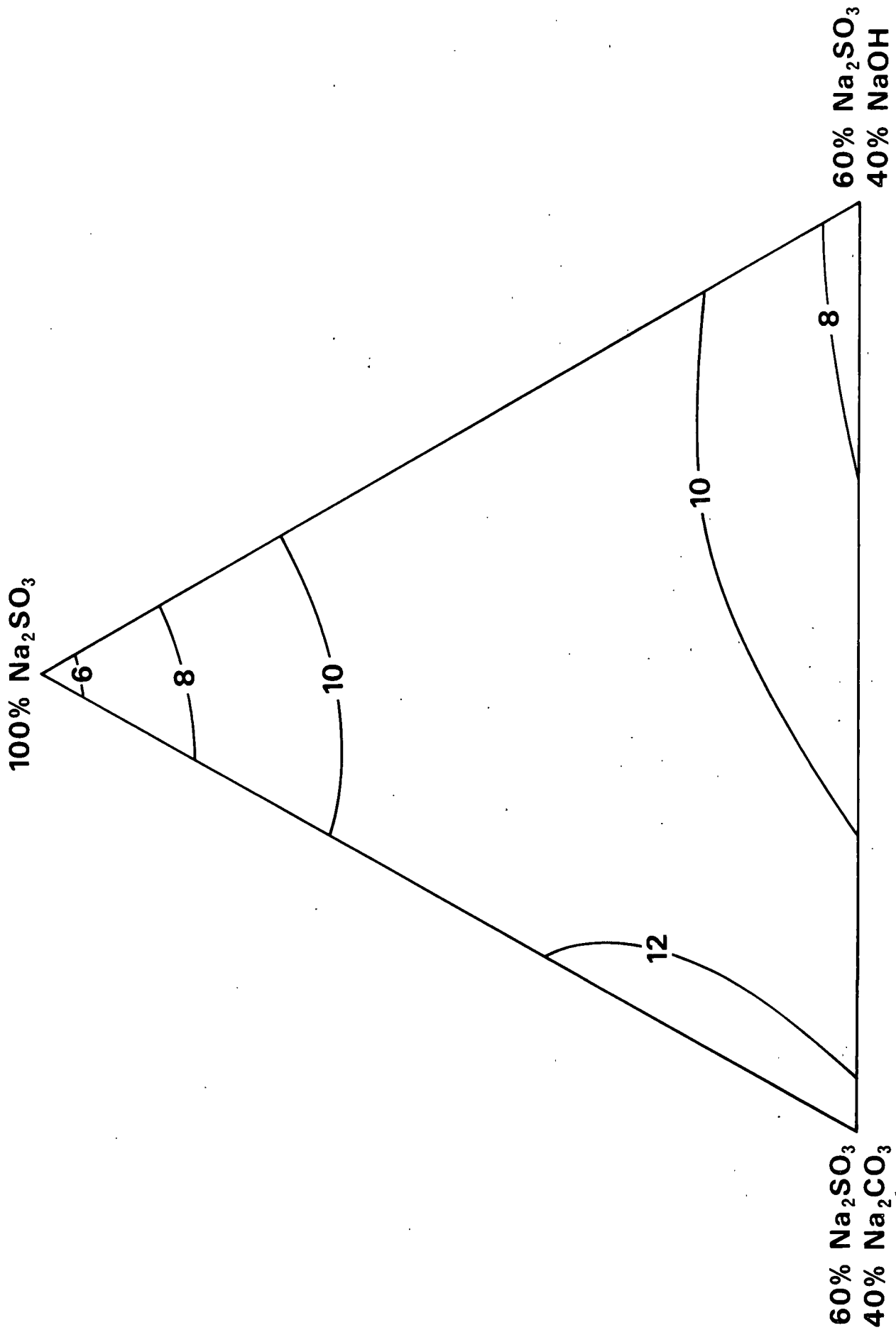


Figure 5. Contours of constant viscosity selectivity (10^{-4} x g lignin dissolved/mole glycosidic bonds broken in cellulose).

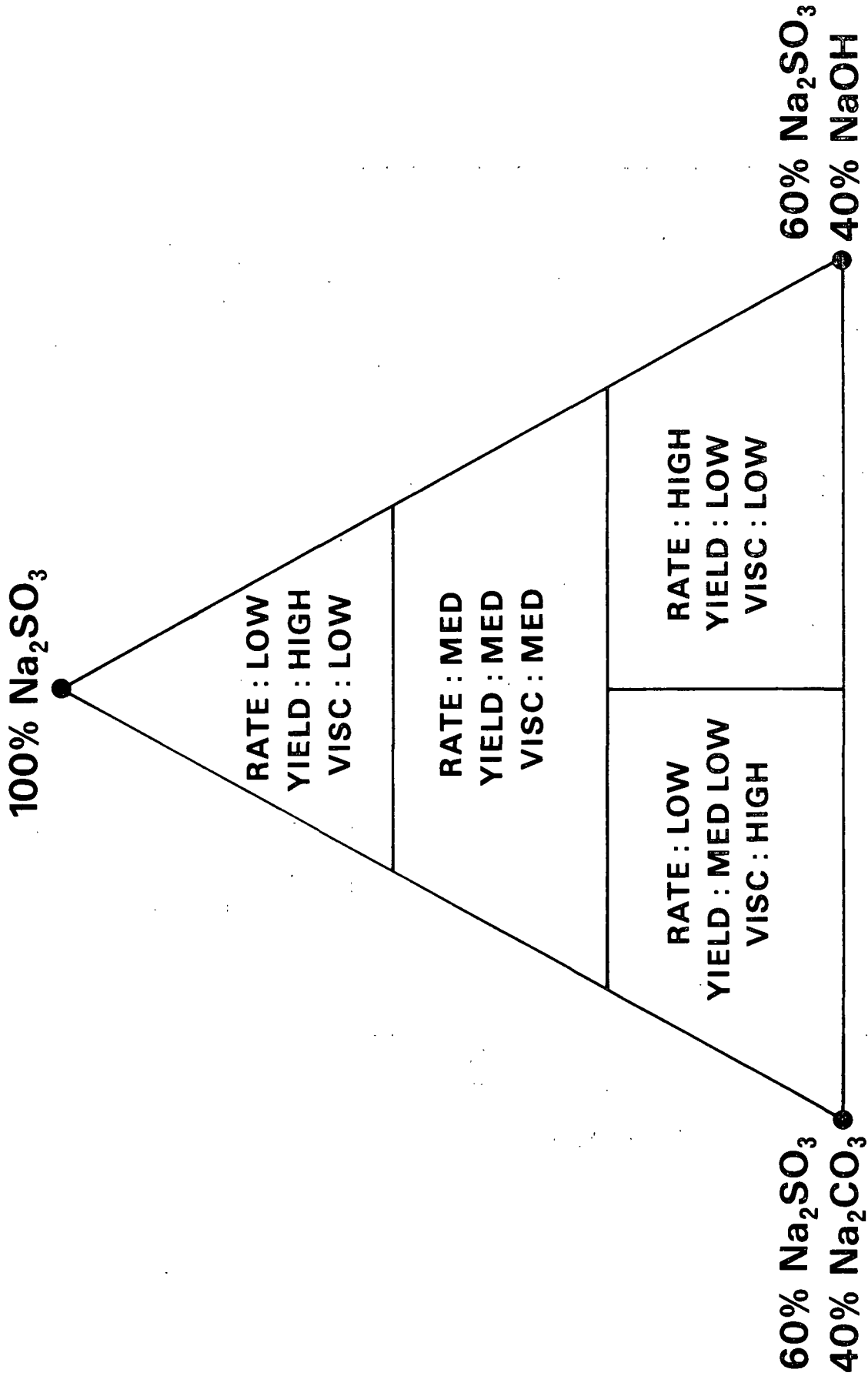


Figure 6. Characteristics of various alkaline sulfite-anthraquinone pulping systems.

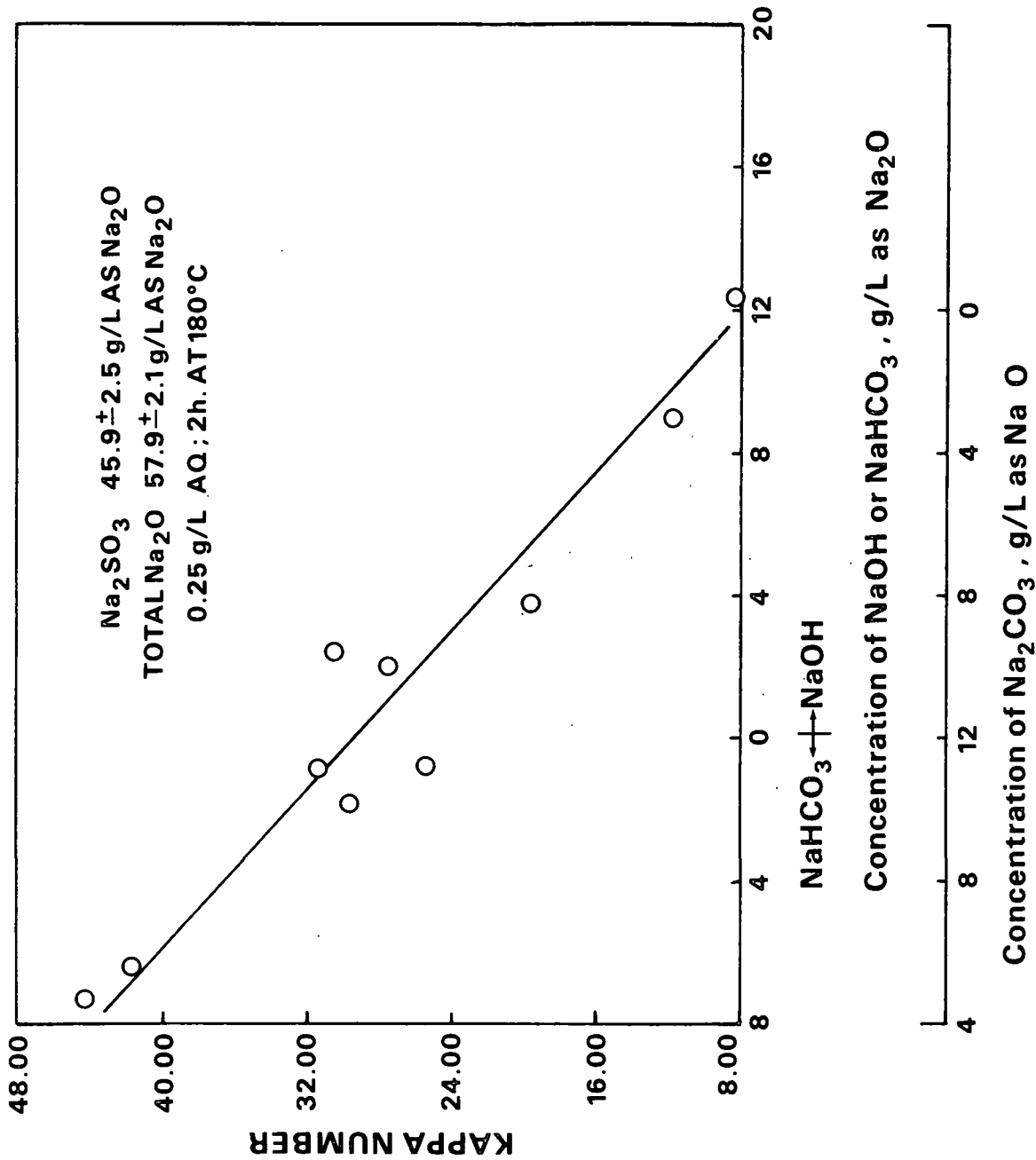


Figure 7. Effect of liquor alkalinity on kappa number at constant sulfite concentration and constant total Na_2O concentration. Cooking conditions: liquor-to-wood ratio 20 mL/g; 1 mm thick loblolly pine wafers; vacuum impregnation; 90 minute linear temperature rise from 90 to 180°C.

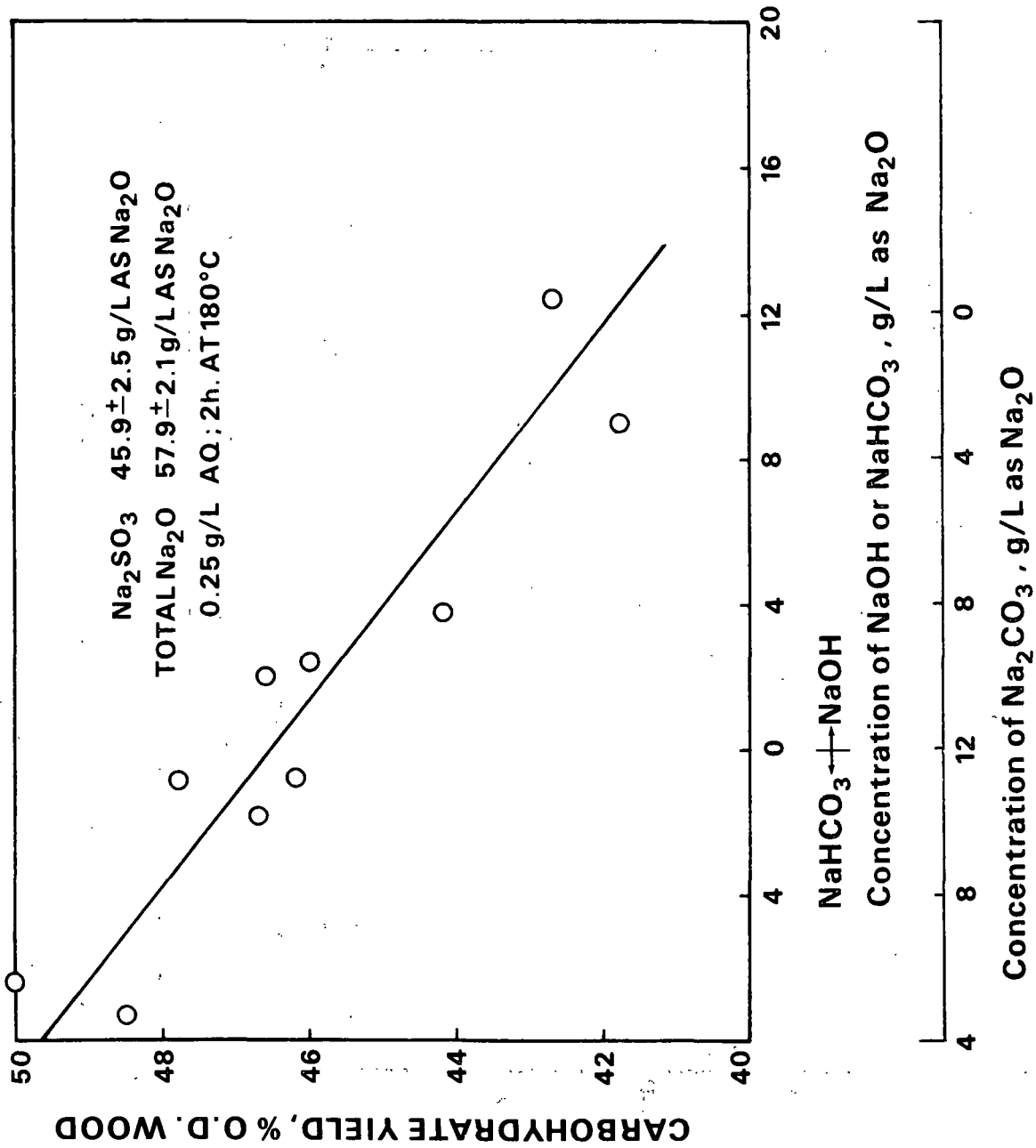


Figure 8. Effect of liquor alkalinity on carbohydrate yield at constant sulfite concentration and constant total Na_2O concentration.

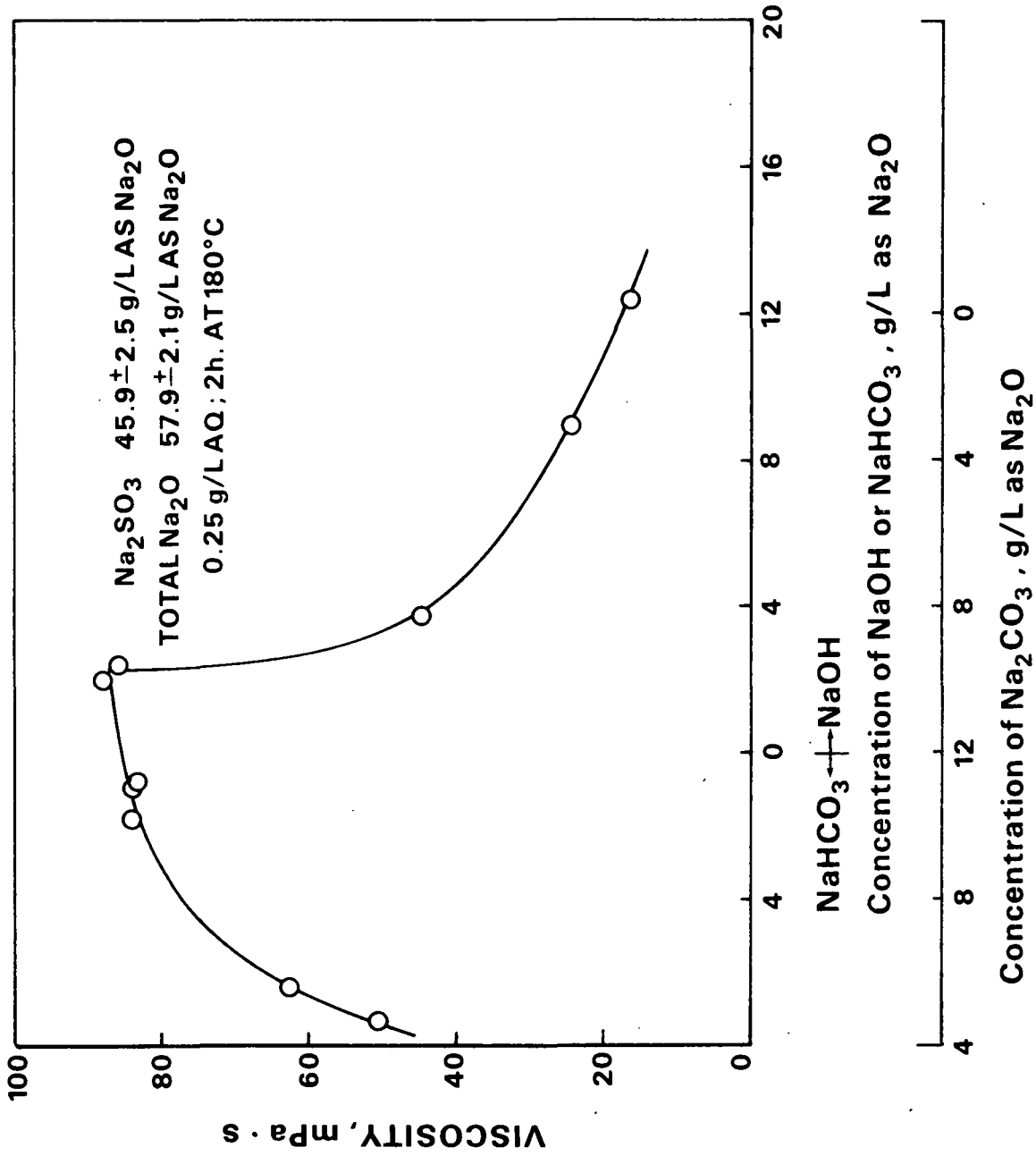


Figure 9. Effect of liquor alkalinity on pulp viscosity at constant sulfite concentration and constant total Na_2O concentration.

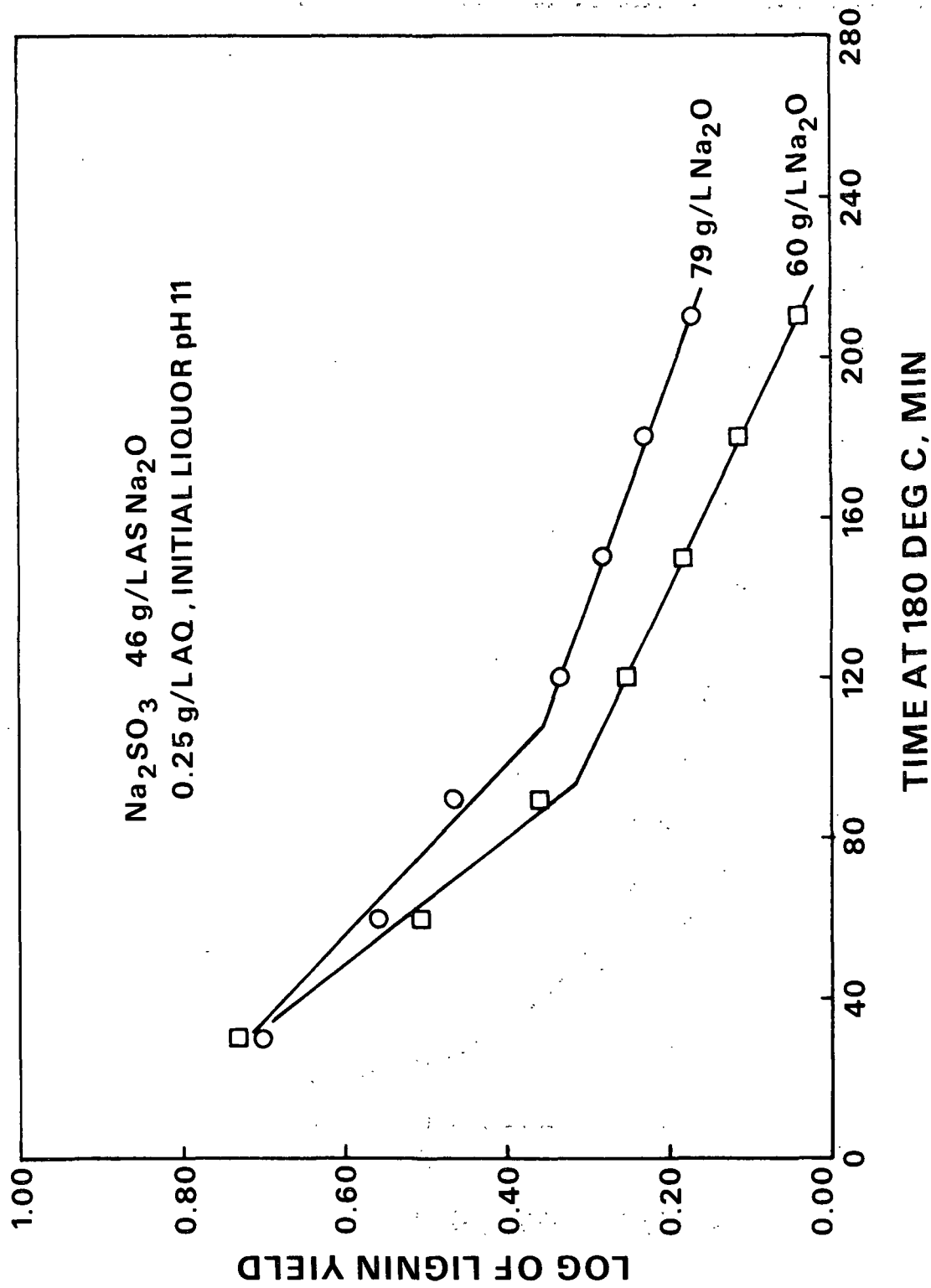


Figure 10. Effect of total Na_2O concentration on delignification rates at constant concentrations of Na_2SO_3 and anthraquinone and constant total pH.

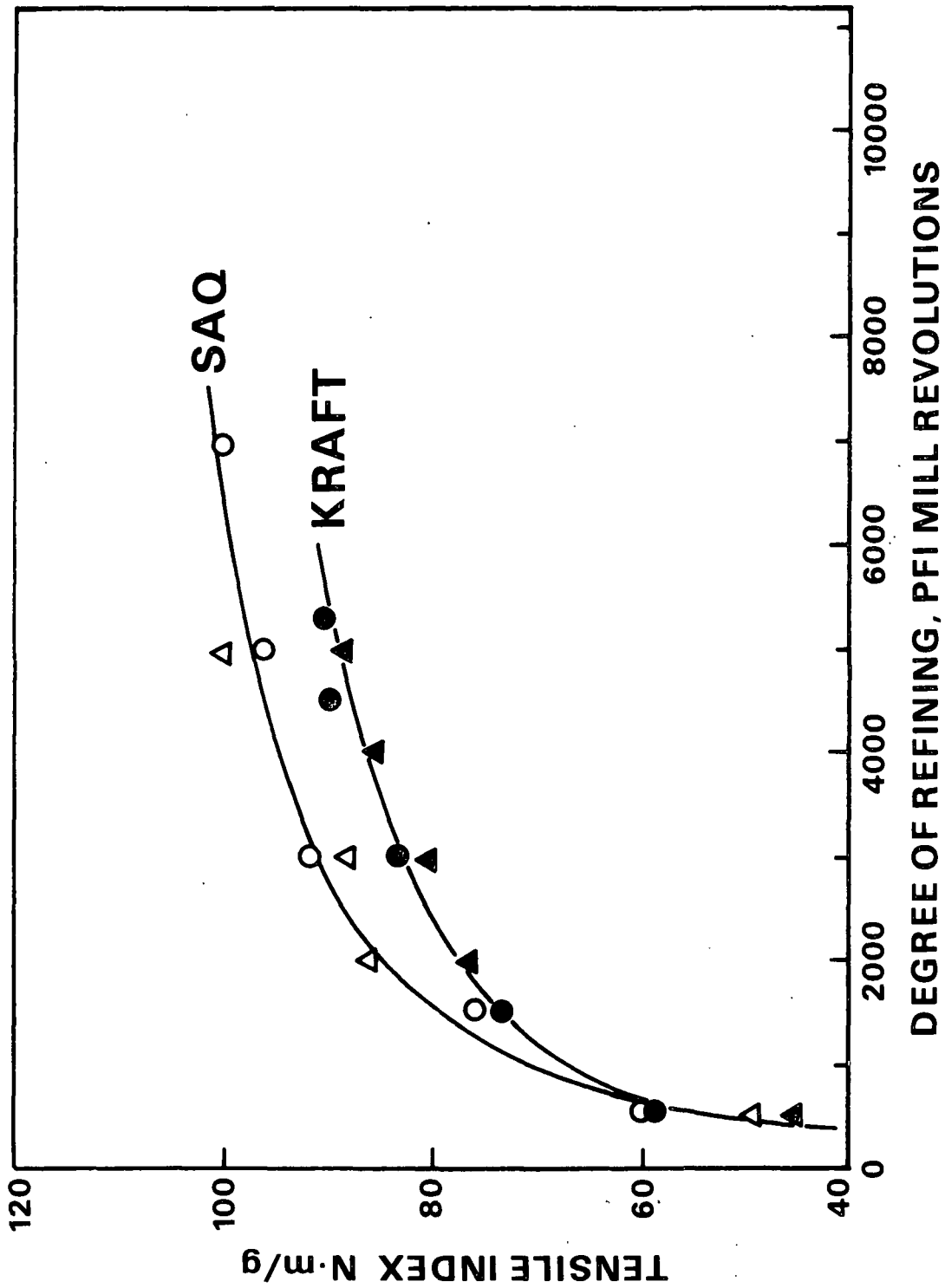


Figure 11. Tensile strength development for SAQ and kraft pulps from two wood sources. Circles and triangles represent data from wood sources 1 and 2, respectively. Open symbols represent SAQ pulp data; filled symbols are for kraft pulps.

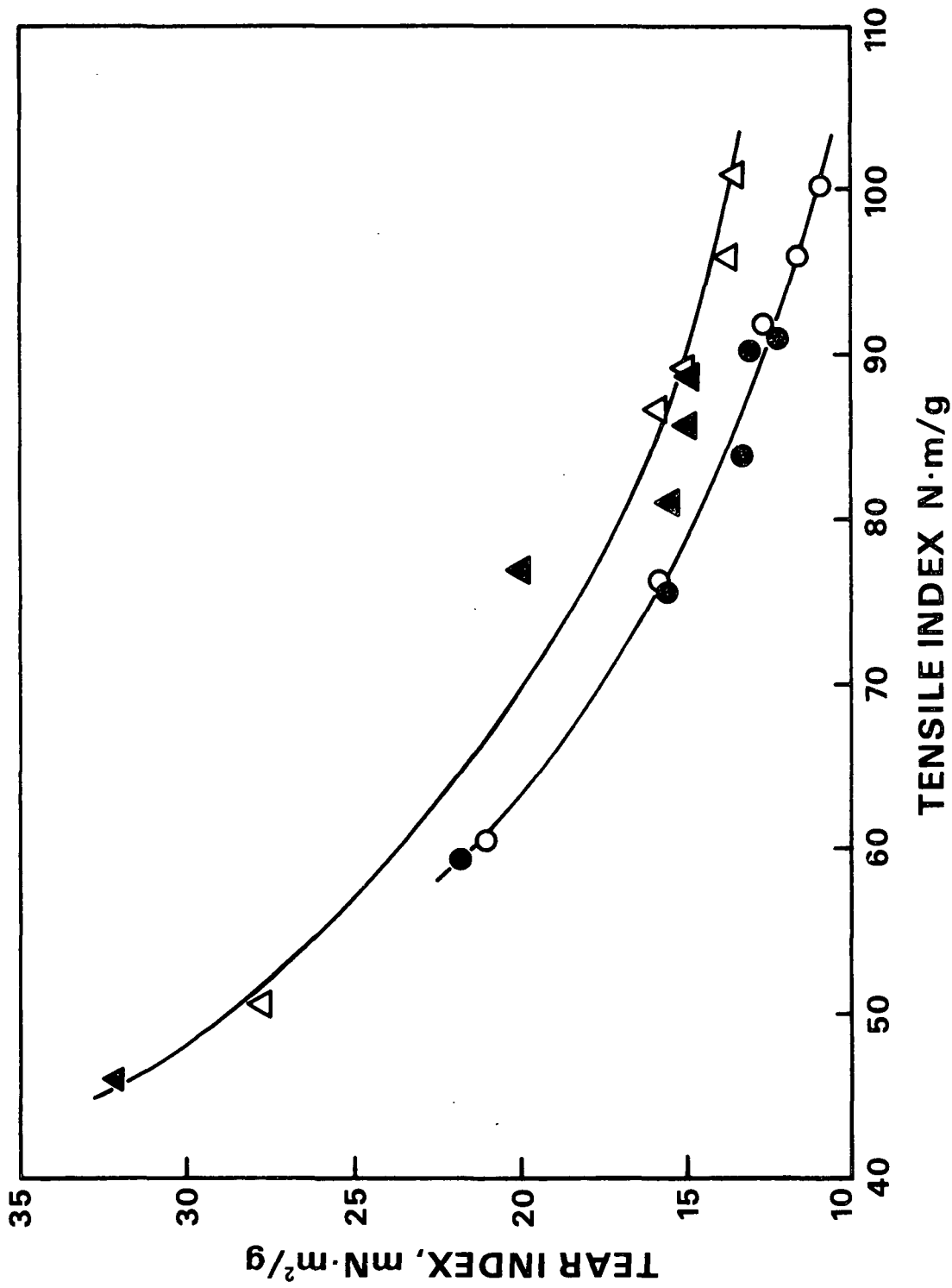


Figure 12. Tear-tensile relationships for SAQ and kraft pulps from two wood sources. Circles and triangles represent data from wood sources 1 and 2, respectively. Open symbols represent SAQ pulp data; filled symbols are for kraft pulps.