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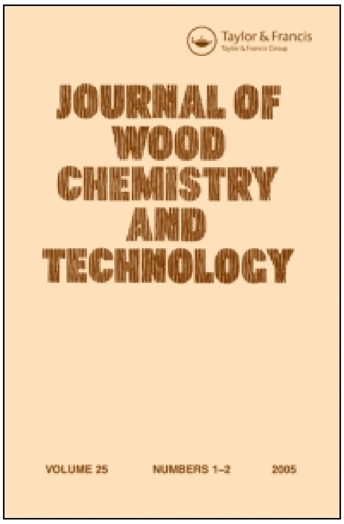

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Dietrich P. Werthemann[a]
[a] Ciba-Geigy Ltd., Basle, Switzerland

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WHY REDOX PULPING CATALYSTS FIT THE SQUARE ROOT RELATIONSHIP

Dietrich P. Werthemann
Ciba-Geigy Ltd.
Basle, Switzerland

ABSTRACT

Different mixture rates of the redox pulping additives anthraquinone with anthraquinone-2-sulfonate, and of benzindazoledione with rosindonesulfonate were investigated. The experimental results showed that additives in mixtures very strongly influence each other's efficacy. The degree of coupling indicates that the square root relationship is best explained by kinetics of the chemical reaction mechanism and not by mass transfer processes.

INTRODUCTION

It has been shown[1] that the efficacy of a redox catalyst like anthraquinone in alkaline pulping is proportional to the square root of its charge. This square root relationship has been confirmed[2-4], and found also to apply to nonquinoid pulping additives[1,5-7]. So far, no experimental evidence for the explanation of the square root relationship has been presented. This paper deals with the question of whether the square root relationship is due to mass transfer processes (diffusion, adsorption, rate of solution etc.) or to the kinetics of the chemical reactions. Investigations of the behaviour of additive mixtures (two or more) should yield an answer.

METHOD

The efficacy of an additive being proportional to the square root of its charge[1] means that the effect is proportionately greater at low additive charges than at high. Accordingly figure 1 shows the following conceptual experiment: A normalized efficacy of unity at a charge of 1% is assigned to an additive A_1. In accordance with the square root relationship this additive will show an efficacy of 0.707 $(1/\sqrt{2})$ at a charge of 0.5%. The second additive, A_2, is assumed to be as efficient as A_1.
To provide 1% of a 1:1 mixture of A_1 and A_2 to a pulping system, 0.5% of each is added. If the two additives act independently we would expect the contribution of each to be 0.707 units, yielding a total effect of $\sqrt{2}$. In other words: using 1% of the mixture would give 1.41 times the effect of a 1% addition of a pure additive, when each additive acts for itself as if alone in the system. On the other hand, if there is maximum coupling between the two additives due to complete competition, no excess effect is to be expected. Partial interaction of the additives will result in surplus efficacy between zero and 0.41 according to the degree of coupling (excluding a possible synergism).

The overall rate constant, k_L, for soda-additive pulping consists of two terms[1]: one, k_s, stands for the soda reaction, the other, proportional to the square root of the charge, for the contribution of the additive.

$$(1) \quad k_L = k_s + k_a \sqrt{A_o}$$

k_L = over all rate constant for delignification

k_s = rate constant for soda delignification

k_a = rate constant of the delignification in which the additive participates

A_o = charge of additive A

Turning now to additive mixtures, two cases have to be considered.

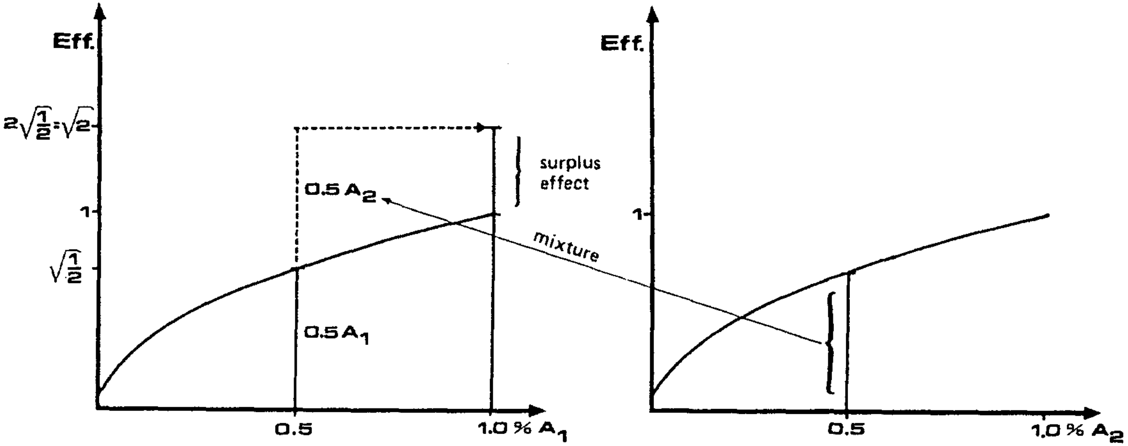


FIGURE 1: Conceptual experiment for a mixture of two additives of equal efficacy normalized to unity at a 1% charge

Case 1: Assuming that no coupling exists between the different additives, equation (1) is expanded by an additional square root term for each additional catalyst.

$$(2)\quad k_L = k_s + k_{a1}\sqrt{A_{o1}} + k_{a2}\sqrt{A_{o2}} \dots$$

$$= k_s + \sum_{i=1}^{N} k_{ai}\sqrt{A_{oi}} \qquad \text{no coupling}$$

i index of i^{th} additive
N total number of additives in the mixture

Case 2: A maximum interaction between the additives in a mixture (no surplus effect) calls for the expansion of equation (1) to

$$(3)\quad k_L = k_s + \sqrt{k_{a1}^2 A_{o1} + k_{a2}^2 A_{o2} \dots}$$

$$= k_s + \sqrt{\sum_{i=1}^{N} k_{ai}^2 . A_{oi}} \qquad \text{maximum coupling}$$

The charge of the additive mixture M_o is

$$(4)\quad M_o = A_{o1} + A_{o2} \dots = \sum_{i=1}^{N} A_{oi}$$

M_o = charge of mixture

The weight-fraction a_i of the i^{th} additive is defined by

$$(5)\quad a_i = A_{oi}/M_o$$

It follows that

$$(6)\qquad \sum_{i=1}^{N} a_i = 1$$

The efficacy of an additive in delignification relative to anthraquinone, may be expressed[1] as

$$(7)\quad r_o = \frac{k_a}{k_{a,AQ}}$$

$k_{a,AQ}$ = k_a of anthraquinone

As we anticipate that a mixture fulfills the square root relationship just as well as a single additive (for experimental evidence see below)

$$(8)\quad k_L = k_s + k_{aM}\sqrt{M_o}$$

$$k_{aM} = k_a \text{ for the mixture}$$

we can define the

$$(9) \quad \bar{r}_o = \frac{k_{aM}}{k_{a,AQ}}$$

Using equations (4)-(9) - equations (2) and (3) being rearranged to yield the two extreme cases of maximum coupling and no interaction respectively - the following $\bar{r}_o$-values for the mixture are found

no coupling:

$$(10) \quad \bar{r}_o = r_{o1}\sqrt{a_1} + r_{o2}\sqrt{a_2} \; \dots \quad = \sum_{i=1}^{N} r_{oi}.a_i$$

and maximum coupling:

$$(11) \quad \bar{r}_o = \sqrt{r^2_{o1}a_1 + r^2_{o2}a_2 \; \dots} \quad = \sqrt{\sum_{i=1}^{N} r^2_{oi}.a_i}$$

$\bar{r}_o = r_o$-value of mixture determined as described in ref. 1

Equations (10) and (11) predict the efficacy of a mixture by the fractions a_i and the r_o-values of the components. In other words, measuring the $\bar{r}_o$-values of different mixtures, where the fractions a_i of the individual additives A_i with a known r_{oi}-value are varied, enables us to determine the degree of coupling between the additives. In the following, only mixtures of two additives are considered. Figure 2 illustrates the square of the two functions (10) and (11) for a hypothetical case.

The function corresponding to a maximum coupling is a straight line. Actual $\bar{r}^2_o$-values are expected to lie somewhere between the two limits according to the degree of coupling.

RESULTS AND DISCUSSIONS

A series of mixtures of anthraquinone (AQ) with anthraquinone-2-sulfonate (AMS) was prepared and the accelerating efficiency of each mixture was determined in a set of soda cooks of Norway spruce (Table 1). The high correlation coefficients obtained from the

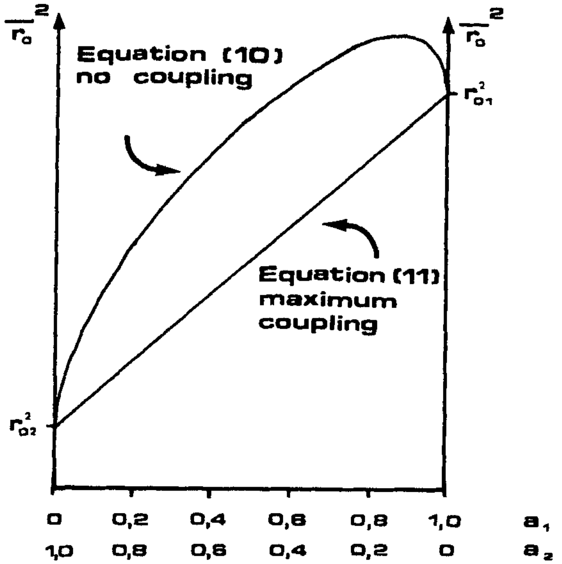


FIGURE 2: Graphical representation of equations (10) and (11) for a hypothetical case

TABLE 1

Results of Mixtures with Anthraquinone (AQ) and Anthraquinone-2-Sulfonate (AMS):

ratio AQ : AMS	$\overline{r}_o$ a)	SE b)	cor.coef. c)
0 : 1	0.37	0.03	0.999
0.1 : 0.9	0.47	0.02	0.998
0.2 : 0.8	0.54	0.05	0.989
0.3 : 0.7	0.64	0.05	0.998
0.4 : 0.6	0.68	0.05	0.997
0.5 : 0.5	0.76	0.06	0.999
0.6 : 0.4	0.86	0.06	0.985
0.7 : 0.3	0.90	0.10	0.995
0.8 : 0.2	0.95	0.12	0.968
0.9 : 0.1	0.98	0.08	0.991
1 : 0	1.0 d)		

a) determined as described in ref. 1; b) SE = Standard deviation (including scatter of AQ-control experiment[1]); c) correlation coefficient as R^2 of the square root relationship; d) by definition (see ref. 1) plots of 1/lignin (lignin content as hypochlorite number) versus square root of additive indicate that the square root relationship is fulfilled for these mixtures of additives, thus confirming the validity of equations (8) and (9).

In figure 3 the $\overline{r}_o^2$-values of the mixtures are plotted versus the fraction a_i of the components. The solid lines correspond to the $\overline{r}_o^2$-values calculated by inserting r_o-values of the pure components as well as the a_i-values into equation (10) (curved line) or equation (11) (straight line).

Figure 3 shows that the experimental $\overline{r}_o^2$-values of anthraquinone/anthraquinone-2-sulfonate mixtures neatly fit equation (11). All points differ significantly from the theoretical curve which corresponds to equation (10). This means that the two additives do not act independently. The points on the left side of the figure - where the standard deviations are lower - show maximum coupling between the two additives.

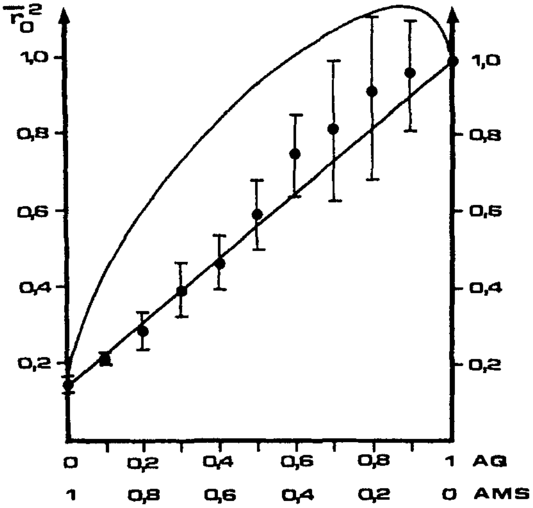


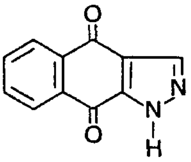
FIGURE 3: $\overline{r}_o^2$-values are plotted against weight-fractions (a_i) of anthraquinone (AQ) and anthraquinone-2-sulfonate (AMS) when mixtures of the two catalysts were used to pulp Norway spruce

TABLE 2

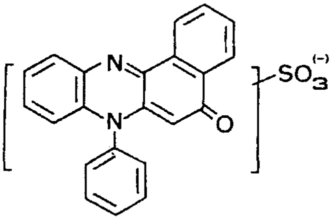
Results of Mixtures with Benzindazoledione (Bz) and Rosindonesulfonate, $[Ros]SO_3^-$

ratio $[Ros]So_3^-$: Bz	$\overline{r}_o$	SE	cor. coeff.	$\overline{v}_o$	SE	cor. coeff.
1 : 0	0.53	0.06	0.992	0.75	0.13	0.997
0.8 : 0.2	0.47	0.04	0.995	0.64	0.19	0.987
0.6 : 0.4	0.54	0.04	0.994	0.93	0.68	0.974
0.5 : 0.5	0.56	0.06	0.996	0.91	0.13	0.988
0.4 : 0.6	0.57	0.04	0.996	0.95	0.14	0.996
0.2 : 0.8	0.56	0.03	0.998	1.15	0.35	0.988
0 : 1	0.57	0.04	0.993	1.02	0.14	0.999

To rule out the possibility of the strong coupling between AQ and AMS resulting only from the fact that AQ and AMS are very similar in their chemical structure, mixtures of two additives of markedly different structures, namely benzindazoledione, Bz, and rosindonesulfonate, $[Ros]SO_3^-$, were studied.



Benzindazoledione
(Bz)



Rosindonesulfonate
$[Ros]SO_3^-$

The efficacies of benzindazoledione[8] and of rosindonesulfonate[5] have previously been described.

Since Bz and $[Ros]SO_3$ have similar r_o-values, the surplus effect achieved by mixing them should be very pronounced (curved line in figure 4). This means that the resolution between the two extreme cases described by equations (10) and (11) is larger for a $Bz/[Ros]SO_3^-$-mixture than for a AQ/AMS-mixture and therefore allows a better assignment of the experimental results to one or the other model. Again the experimental $\overline{r}_o^2$-values show maximum coupling between Bz and $[Ros]SO_3^-$ when used in a mixture (figure 4).

Figure 5 indicates that, despite the large standard deviations observed for the $\overline{v}_o$-values, the efficacies of the two additives on carbohydrate stabilization (v_o-values^1) are also strongly coupled.

If the square root relationship results from a mass transfer process, we have to think of one which allows for a maximum coupling of two additives acting simultaneously in the system.

Bz and $[Ros]SO_3^-$ are soluble in alkaline pulping liquor (25 mg in 2 ml 1N NaOH are completely dissolved at ∿80°C). Since the two additives follow the square root relationship, the rate of solution as well as other phenomena related to the solubility must be excluded as a possible reason for the square root relationship.

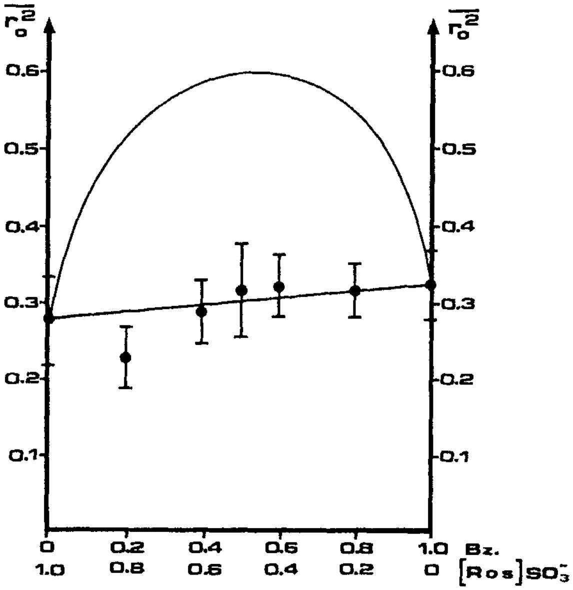


FIGURE 4: $\overline{r_o^2}$-values are plotted against weight-fractions (a_i) of benzindazoledione (Bz) and rosindone sulfonate ($[Ros]SO_3^-$) when mixtures of the two catalysts were used to pulp Norway spruce

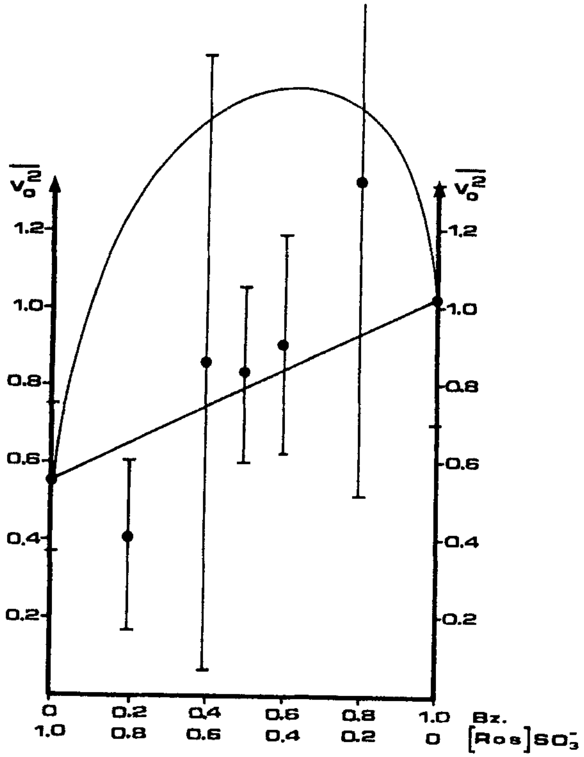


FIGURE 5: $\overline{v_o^2}$-values are plotted against weight-fractions (a_i) of benzindazoledione (Bz) and rosindone sulfonate ($[Ros]SO_3^-$) when mixtures of the two catalysts were used to pulp Norway spruce

The driving force for diffusion is the concentration gradient (1st Fick's law). In the course of work also covering competitive sorption processes, Ott and Rys[9] formulated a sorption-diffusion model for heterogeneous systems. The influence of one adsorbed species on the other is not due to diffusion but to sorption, as described by the Langmuir isotherm:

$$(12)\quad K_j = \frac{A_{jw}}{A_{j\lambda}(S-\Sigma_i A_{iw})}$$

K_j equilibrium constant for j^{th} additive

A_{jw} concentration in the wood of j^{th} additive
$A_{j\lambda}$ concentration in the liquor of j^{th} additive
S saturation (maximum possible additive concentration in the wood dependent on the number of available sites)

Rearranging equation (12) yields

$$(13) \quad A_{jw} = \frac{K_j S A_{j\lambda}}{1 + \sum_i K_i A_{i\lambda}}$$

If the sum in the denominator of equation (13) is very small compared to 1 (low additive concentrations) then

$$(14) \quad 1 + \sum_i K_i A_{i\lambda} \approx 1$$

which means that A_{jw} is not influenced by the other additive(s) in the system. Maximum coupling between additives would only be reached at saturation of the fibre. In other words, the degree of coupling would depend on the concentration, and must lead to a breakdown of the square root relationship for additive mixtures. Furthermore, the influence of the liquor-to-wood ratio on the efficacy of an additive shows that the sorption equilibrium is of a Nernst-type, rather than of a Langmuir-type[10]. The strong coupling observed here cannot therefore originate from sorption processes. Other investigations[11,12] have shown, especially for swelling fibres, that the apparent diffusion coefficient may increase by competition due to increased porosity. This, however, would result in a higher surplus efficacy. Therefore it can be concluded that the strong coupling of the additives cannot be attributed to mass transfer processes.

If mass transfer processes were responsible for the square root relationship then the concentration of an additive in the wood A_w would be

$$(15) \quad A_w = m\sqrt{A_o}$$

where m represents a proportionality factor. A succeeding bimolecular degradation reaction of lignin with A_w (e.g. nucleophilic attack) would yield a square root relationship. However, when two different additives are present in the system of which each independently (no coupling of mass transfer) fulfills equation (15), then the total additive concentration in the wood $A_{w,tot}$ would be

$$(16) \quad A_{w,tot} = m_1 \sqrt{A_{o1}} + m_2 \sqrt{A_{o2}}$$

Equation (16) together with the assumption that the succeeding chemical reaction is a bimolecular type leads to an overall rate constant as described by equation (2) which is the basis of equation (10). This, however, is not compatible with the experimental results of this paper. In addition, the validity of equation (15) would be contrary to the conclusion of a previous paper[10], namely that the partition of an additive between the liquor and the wood is of a Nernst type. Therefore we conclude that the square root relationship is best explained by the kinetics of a chemical reaction and not by mass transfer processes. A recent paper by Obst and Sanyer[13] who investigated the guaiacol yield, Y, of a model lignin reaction as a function of AQ dose (see figure 4 in ref. 13) supports this statement. Replotting their data and taking into account that they worked under pseudo first order conditions (excess alkali) shows that even for experiments on model lignins performed in a homogeneous system (no mass transfer process) the square root relationship holds surprisingly well (figure 6). Yaguchi's results (see figure 1 in ref. 14) give a similar plot. An explanation for the square root relationship by the kinetics of a chemical reaction was given in a previous paper[1]. The oxidation of hydroquinone to anthraquinone sets free two electrons. If the delignification step in which the reduced catalyst is involved requires only one electron then, on the basis of stoichiometry, one mole of reduced catalyst degrades two moles of lignin linkages. Such a reaction may be formulated with the help of the semiquinone $AQH^{\cdot}$ as follows:

$$L + AQH_2 \xrightarrow{k_1} AQH^{\cdot} + \text{product}$$

$$L + AQH^{\cdot} \xrightarrow{k_2} \text{product} + AQ$$

$$(17)\quad 2L + AQH_2 \longrightarrow 2\ \text{products} + AQ$$

If $k_2 \gg k_1$ (assuming that the semiquinone is highly reactive) then the factor of two in equation (17) leads consequently to a square root relationship. ESR experiments by Canadian workers[15,16] show that under pulping conditions semiquinones are present at a low concentration. A kinetic expansion of equation (17) for an additive mixture leads to an equation of the type as given by equation (11) and would agree with the experimental results of this paper.

We shall not give a more detailed chemical reaction mechanism here, but only an electron balance for the reaction. None of the detailed anthraquinone mechanisms proposed so far is consistent

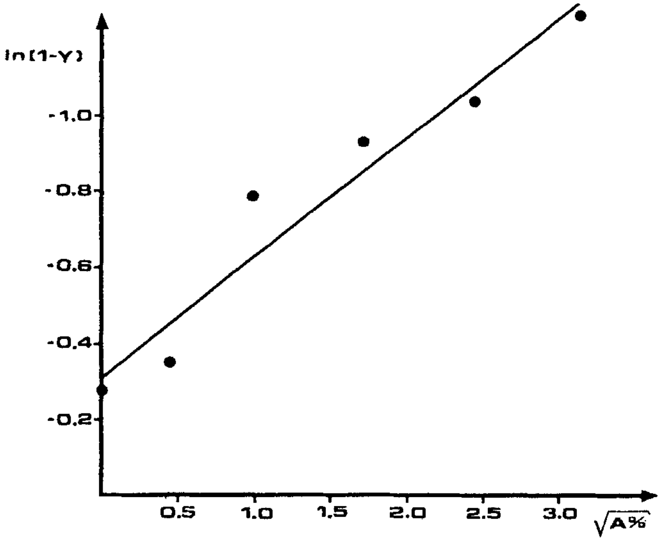


FIGURE 6: 1st order dependence of guaiacol yield, Y, versus square root of additive dose. Replotted data taken from ref. 13, figure 4

with this electron balance requirement and so none is able to offer the necessary explanation of the square root relationship by chemical kinetics. Further investigations are needed to clarify this discrepancy.

CONCLUSIONS

It has been shown that, when a mixture of redox pulping catalysts is used, the interaction of the catalysts is very strong. The degree of coupling indicates that the square root relationship is best explained in terms of the chemical reaction kinetics. Mass transfer processes can be ruled out as responsible for the square root relationship.

EXPERIMENTAL

Carefully homogenized handmade chips of Scandinavian spruce (Picea abies) were used. The pulping conditions were: Liquor to wood ratio 4:1, alkalinity, 1.11 mol/L NaOH; time to 173°C, 93 min., time at 173°C, 120 min. Procedure and determination of r- and v-values were the same as described earlier[1].

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