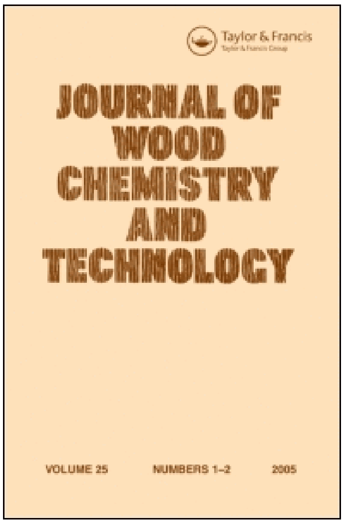

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MATHEMATICAL MODEL FOR ACID SULPHITE PULPING PROCESS

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ABSTRACT

The mathematical model for acid sulphite pulping process is represented by a linear logarithmic straight line dependence of the main characteristics of pulping, i.e. yield and lignin content in pulp versus time and temperature parameters, both determined by the H-factor. The logarithmic plot of the ratio and product of the mentioned characteristics and parameters of pulping is linear for the content of lignin in pulp lower than 15 % and the value of H-factor higher than 100. The most suitable way for the calculation of the main characteristics of pulping is using a power form of the logarithmic straight line dependence of the ratio yield/lignin vs. lignin content, yield/H-factor vs. H-factor, lignin/H-factor *vs.* H-factor and their mathematical equivalents, i.e. reciprocal ratios and/or products. Individual constants of the model for sulphite pulping of spruce wood expressed by means of a logarithmic straight line equation for dependence studied, are summarized in Tables.

INTRODUCTION

On a worldwide scale the production of pulp by the alkaline process prevails. The kraft process represents namely 80 % of the total pulp production [1]. Despite this fact, there are many mills where the acid sulphite process has been applied. Even new sulphite mills with a capacity exceeding 200 000 t of pulp per year have been commissionated recently. Most of them, however, are able to regenerate both the cationic and the anionic parts of the cooking liquor, utilize sugars contained in the spent liquor, produce required lignin preparations from a part of the lignin contained in the liquor and burn the rest of the lignin soluble in the liquor [2].

In the last years the main effort of the pulp producer has been aimed at the production of unbleached pulp with a lower content of lignin. They are forced by the necessity to improve the economy of the production and at the same time to reduce the pollution of the enviroment. Bleaching of pulp with a lower content of lignin yields a reduction of the consumption of bleaching agents and a decrease of the formation of toxic waste waters. For this reason the effort of the producers of sulphite pulp is focused towards the improvement of the conventional sulphite technology and apply a two-stage sulphite procedure, in which the value of the kappa number of the unbleached pulp can be decreased from 17 (range 16-18) to 12 (range 11-13) without negative influences on mechanical properties of the pulp [3]. The value of the kappa number for unbleached sulphite rayon grade pulp is 8 (range 7-9). For low degree of pulping, a linear dependence of the yield on the lignin content and/or kappa number cannot hold.

From the foregoing follows that the necessity to control the new technology of sulphite delignification requires the development of a new and sufficiently precise model for the pulping process. This model should characterize the relationship yield - degree of pulping and especially the plot of the lower value of the degree of pulping *vs.* used parameters of cooking.

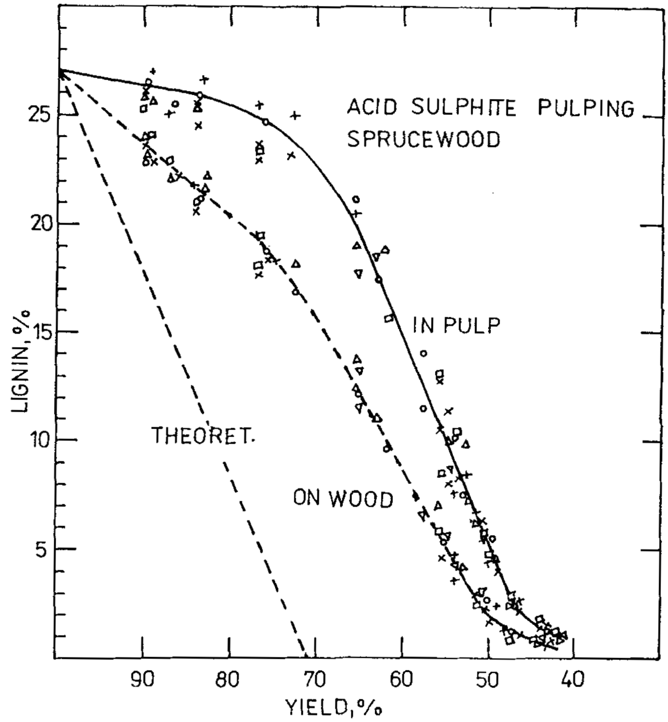

FIGURE 1. Change of the lignin content with the drop of yield in acid sulphite delignification of spruce wood. Values taken from the results published in reference [4].

In the development of the new model of the relationship dependent variables of sulphite pulping *vs.* cooking condition, we used laboratory results obtained in acid sulphite delignification of Canadian spruce chips , published by Strapp, Kerr and Vroom [4].

RESULTS AND DISCUSSION

The results of the study of *sulphite* delignification can be most advantageously expressed by

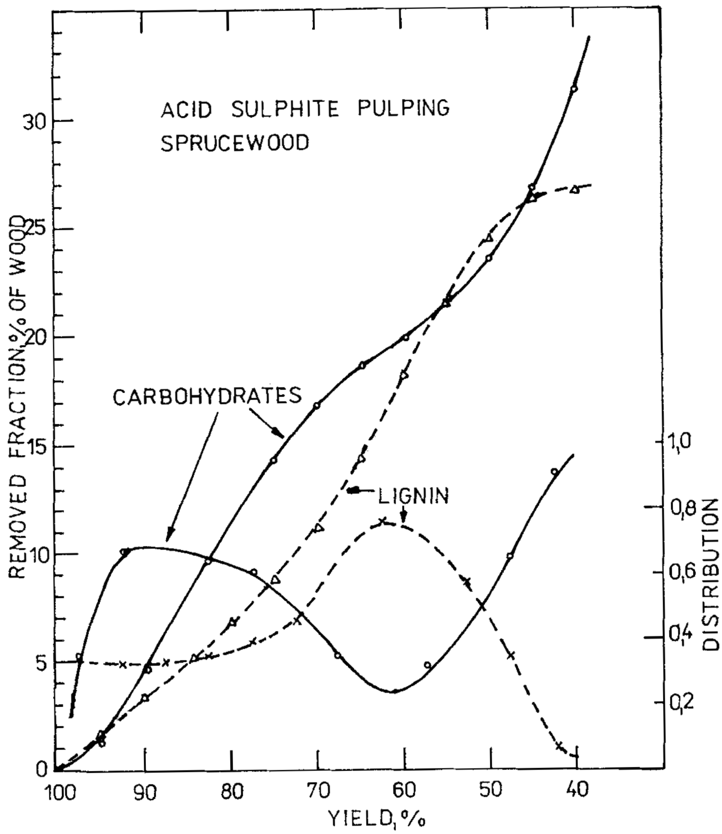

FIGURE 2. Extraction of lignin and hydrolysis of carbohydrates in the course of acid sulphite pulping of spruce wood in dependence on the drop of yield. Values calculated from the results given in Fig. 1.

the change of the lignin content with the decrease in the yield. This dependence for spruce wood is shown in Fig. 1, which summarize the results obtained by Strapp, Kerr and Vroom [4]. These authors used the following cooking liquor: total SO_2 = 6.2-6.4 %, free SO_2 = 5.0-5.2 %, bound SO_2 = 1.2 %; ratio of cooking liquor to

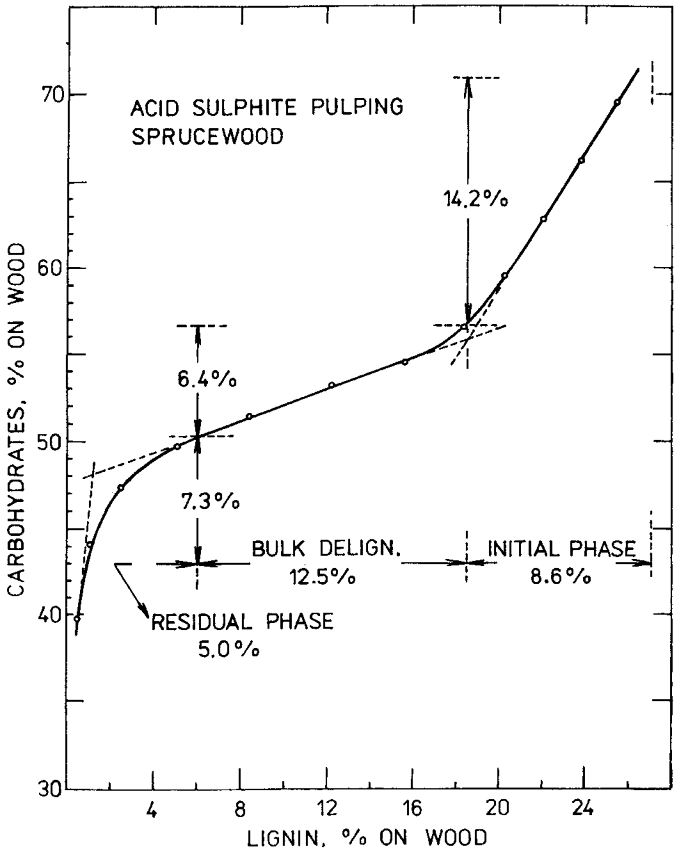

FIGURE 3. Change of the carbohydrates content in dependence on the drop of lignin content in acid sulphite pulping of spruce wood.

weight of wood = 5 : 1, maximum temperature of cooking 140^{0}C. Values of permanganate, kappa and Roe numbers obtained by these authors were recalculated on the lignin content according to reference [5-7]. Both extraction of the lignin fraction and hydrolysis of the carbohydrate fraction from chips during sulphite cooking are given in Fig. 2. The change of the latter in partially delignified chips versus decrease in the content of lignin is illustrated in Fig. 3.

From results given in Figs. 1-3 follow that sulphite delignification is accomplished by the similar way than kraft delignification, i.e. in three different phases: initial, bulk and residual phases. The initial phase of sulphite delignification is not so sharply separated from the bulk delignification phase as it is in kraft delignification. This phase proceeds in sulphite delignification of spruce wood via decrease of the total amount of lignin from 27.1 % to 18.5 %, expressed in % of wood (see Fig. 3). In the initial phase of delignification the total amount of lignin and carbohydrates 8.6 % and 14.2 %, respectively were removed. This amount corresponds to 31.7 % of lignin and 20.0 % of carbohydrates present in the original wood species.

The content of lignin in partially delignified chips during the bulk phase of sulphite delignification (decrease of the yield from 75 % to 53 %) drops with a decrease in yield, whereas this decrease in the content of lignin is parallel with the straight line expressing the theoretical dissolution of lignin from chips (see Fig. 1). From Fig. 3 follows that this phase of sulphite delignification is practically accomplished by a decrease in lignin content within the range from 18.5 % to 6 % and the content of carbohydrates drops within the range from 56.7 % to 50.3 %, expressed in % of wood. In this delignification phase 12.5 % of lignin and 6.4 % of carbohydrates, expressed in % of wood were dissolved. This amount corresponds to 46.1 % of lignin and 9.0 % of carbohydrates present in the original wood species.

In the residual phase of sulphite delignification, the dependence of the lignin content on the decrease of yield is not linear. From results given in Fig.1 and 3 follow, that for pulps cooked to a low content of lignin (or low kappa number of pulp), a power plot between the content of lignin and the yield exists. Just this dependence was used in the characterization of the last part of the bulk phase and the whole residual phase of sulphite delignification by a mathematical model. In the residual phase of sulphite delignification, the respective content of lignin and carbohydrates drops from 6 % to 1 % and from 50.3 % to 43 %, expressed in % of wood. It means that in the residual phase of sulphite delignification, 5.0 % of lignin and 7.3 % of carbohydrates, expressed in % of wood, were dissolved. These respective amounts corresponds to 18.4 % of lignin and 10.3 % of carbohydrates, present in the original wood species.

From results illustrated in Fig. 2 follow that in the course of sulphite pulping, the largest fraction of wood components removed during the initial and residual delignification phases is the hydrolyzed carbohydrates. In the course of the bulk phase of sulphite delignification, the largest amount of lignin is extracted from the chips, whereas the fraction of the carbohydrates hydrolyzed is the smallest.

DEVELOPMENT OF THE MODEL FOR SULPHITE PULPING

Dependence Yield on Lignin Content

In controlling the production of pulp it is very necessary to have a precise mathematical model. This model is especially important in the production of pulp with a low lignin content obtained by a two-stage sulphite procedure or for the manufacture of rayon grade

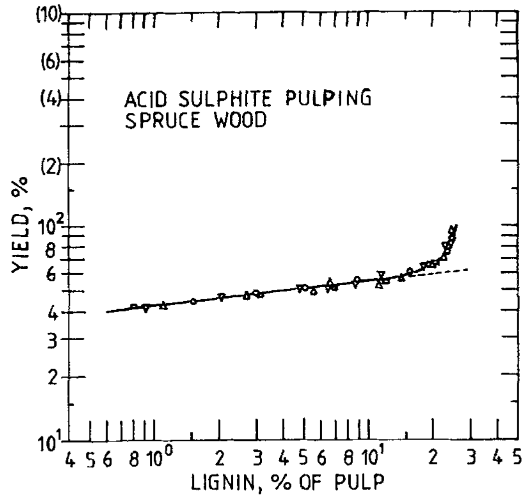

FIGURE 4. Dependence of yield vs.lignin content in pulp after acid sulphite pulping of spruce wood, expressed in logarithmic coordinates.

pulp. In addition, this model should express the real mutual relation among the degree of cooking, yield and other parameters of cooking (time and temperature parameters determined by the value of the H-factor).

The dependence yield *vs.* lignin content of pulp produced by an acid sulphite pulping of spruce wood is given in a log-log plot in Fig. 4.It is evident that the dependence yield *vs.* lignin content for the lignin content in pulp lower than 15 % is given in a log-log plot by a straight line.

In drawing the dependence yield *vs.* lignin content in a modified form as the ratio yield/lignin *vs.* lignin content one obtains a power relationship for these parameters of sulfphite delignification of spruce wood (see Fig. 5). By linearization of this power dependence, i.e. drawing the values of the ratio yield/lignin *vs.*

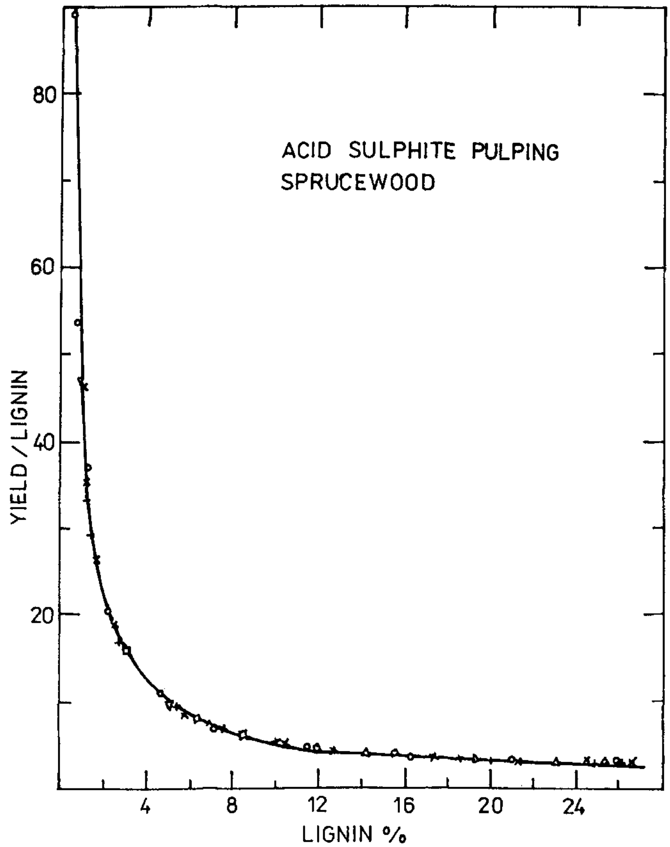

FIGURE 5. Dependence of the ratio yield/lignin on the lignin content in pulp produced by acid sulphite pulping of spruce wood.

lignin content in logarithmic coordinates (see Fig. 6), one obtains a linear straight line. In Fig. 6 is also shown the dependence of the ratio 1/yield.lignin on lignin content. Results given in Fig. 6 confirmed, that the linear dependence is valid only for pulps with a lignin content lower than 15 %.

The ratio lignin/yield and the product lignin.yield *vs.* lignin content give also a logarithmic

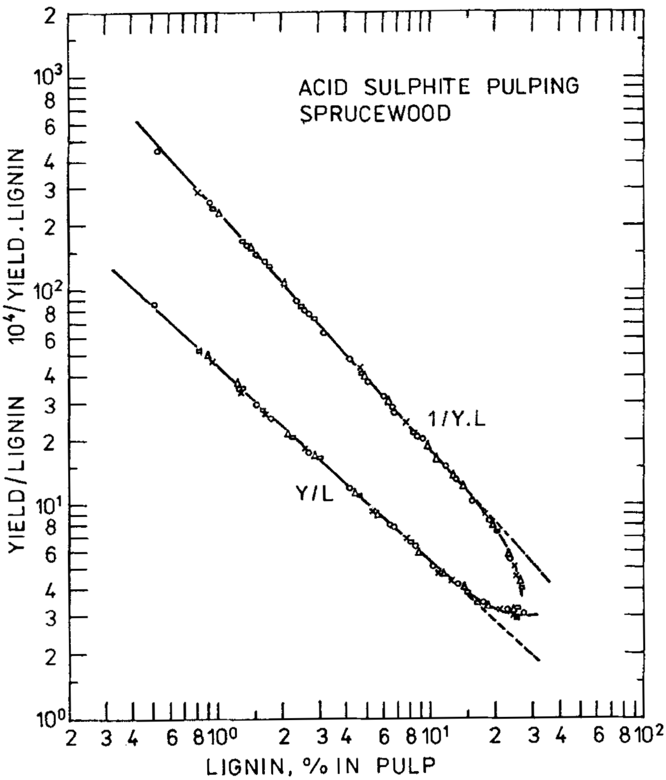

FIGURE 6. Dependence of the ratio yield/lignin and ratio 1/yield.lignin on the content of lignin in pulp produced by acid sulphite pulping of spruce wood, expressed in logarithmic coordinates.

straight line dependence (see Fig. 7). Also for this expression of the relationship yield - lignin holds that the dependence is linear only for pulps, whose lignin content is smaller than 15 %. When the lignin content in pulp is higher than 15 %, the plot shown in Figs. 4, 6 and 7 deviates from linearity. This deviation is caused by the fact that for the lignin content higher than 15 %, the relationship yield - lignin is linear in decadic, i.e. nonlogarithmic coordinates (see Fig. 1).

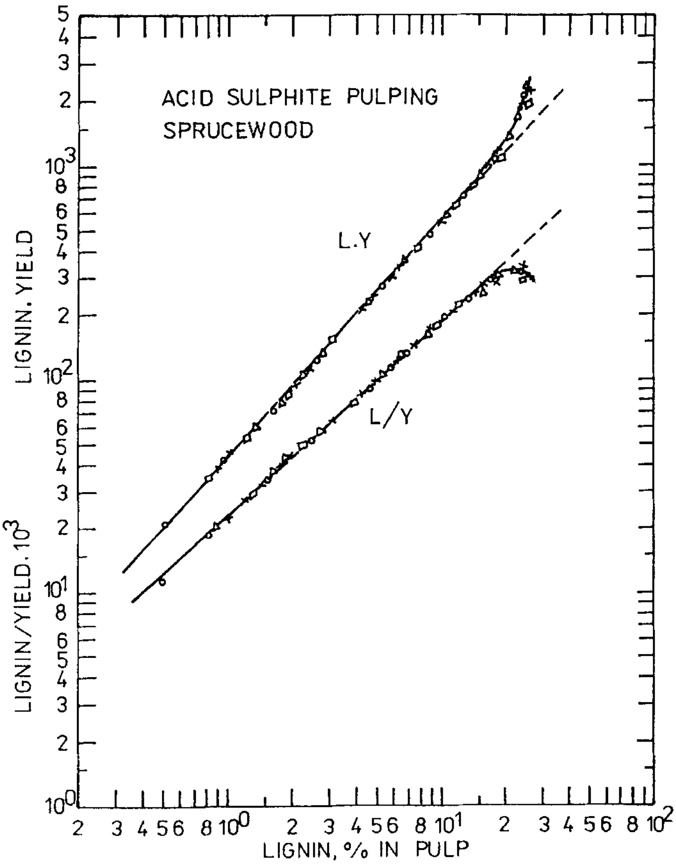

FIGURE 7. Dependence of the ratio lignin/yield and the product lignin.yield on the content of lignin in pulp prepared by acid sulphite pulping of spruce wood, expressed in logarithmic coordinates.

By mathematical and graphical linearization of the relationship yield - lignin the development of a precise mathematical model of sulphite delignification was substantially simplified. Results given in Figs. 4-7 confirmed that the relation of the values of yield and ratios yield/lignin, lignin/yield, 1/lignin.yield and the product yield.lignin on the lignin content can be expressed by the following logarithmic straight line equation:

$$\ln y = k \ln x + \ln b \qquad [1]$$

in which:

y = yield, ratio yield/lignin, lignin/yield, 1/lignin.yield and product lignin.yield

x = lignin content, % of pulp

k = a slope of the straight line

ln b = an intercept constant

Values of the appropriate constants and correlation coefficients were calculated by means of Eq. [1] using the least squares method and a computer. The values of constants and coefficients listed in Tab. 1 were obtained.

The data listed in Tab. 1 reveal that the correlation coefficient of the logarithmic equation [1] of the dependence yield vs. lignin content of pulp is low and corresponding to the value of R^2 = 0.961. For the modified form of the dependence, expressed as the ratio or product, values of correlation coefficients are, however, determined by the value of R^2 = 1.000. The values of constants and correlation coefficients correspond only to the linear part of the dependences studied, i.e. that part, related to the lignin content lower than 15 %. High values of the correlation coefficients reveal that the derived Eq. [1] characterizes the relationship yield - lignin, valid for the sulphite delignification of spruce wood, with a high precision.

TABLE 1

Values of Constants and Correlation Coefficients in Eq.[1] and [2] of the Dependence Yield vs. Lignin Content in Pulp Producet by Acid Sulphite Pulping of Spruce Wood. For the Calculation the Experimental Results Given in 4 Were Used.

Relationship	Slope constant k in Eq.[1]	Intercept constant ln b in Eq.[1]	Correlation coefficient R^2 in Eq. [1]	Constant A in Eq.[2]	Exponent a in Eq.[2]	Degree of freedom
Yield vs. lignin content	0.09929	3.765	0.961	43.16370	0.09929	20
Yield/lignin vs. lignin content	-0.89658	3.754	1.000	42.69151	0.10342	59
1/yield.lignin vs. lignin content	-1.1045	-3.752	1.000	42.62071	0.1045	59
Lignin.yield vs. lignin content	1.1074	3.750	1.000	42.52108	0.1074	59

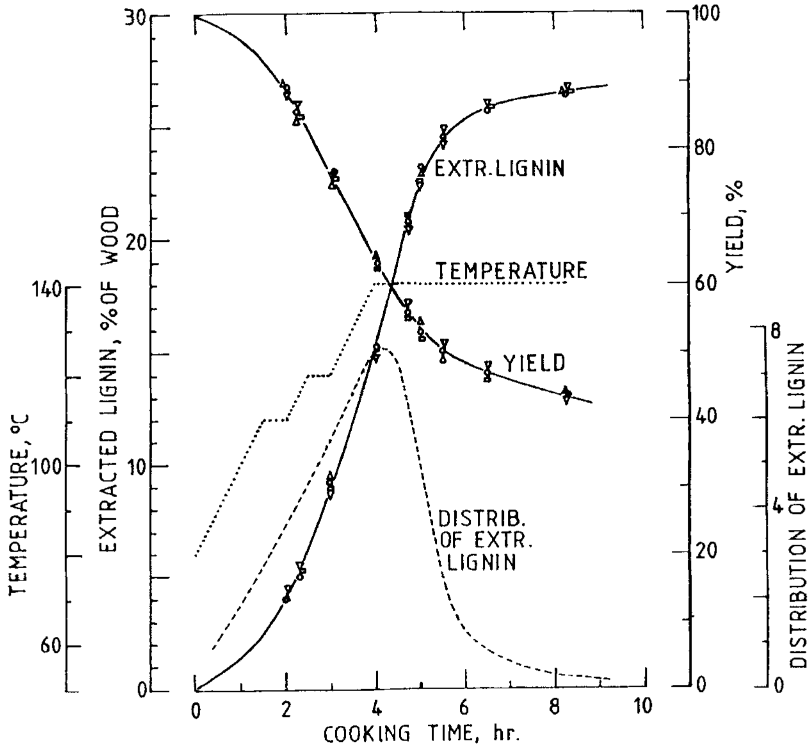

FIGURE 8. Extraction of lignin from chips and drop of yield in dependence on cooking time at acid sulphite pulping of spruce wood.

Dependence Yield and Lignin Content on H-factor

For monitoring and controlling the process of sulphite cooking by means of a computer, a dependence of such cooking variables is important, which determine the results of pulping.

Fig. 8 shows the kinetics of lignin extraction from chips along with the change of yield depending on the time of pulping. From this figure it is evident that the rate of lignin extraction from chips, i.e. the delignification rate reaches a maximum by increasing the temperature to a maximum value of 140^{0}C. Maintaining a maximum temperature of pulping at 140^{0}C, the delignification rate abruptly decreases. This decrease is caused by degasing the digestor and by consuming a part of SO_2 for sulphonation of lignin. The result is a decrease in partial pressure of SO_2 (pSO_2) in the digestor. A decrease in the delignification rate after reaching a maximum temperature of pulping is also caused by diminishing the lignin content in chips. By an increase of the delignification temperature to a maximum value of 140^{0}C, 55 % of lignin present in the spruce wood was removed (see Fig. 8).

In addition, Fig. 8 reveals that the delignification reaction expressed by the extraction of lignin from chips is carried out, in contrast to kraft pulping, immediately from the beginning of sulphite pulping. From the mentioned follows that the rate of the sulphite delignification reaction is expressed by Arrhenius equation $K = Ae^{-Ea/RT}$. From experimental results reported in reference [4], H-factor corresponding to acid sulphite pulping was calculated by a similar way as that employed by Vroom for kraft pulping [8]. The relative rate of delignification expressed by the value of K at different temperatures was calculated by the Arrhenius equation taking the value 90 KJ (21.5 Kcal.) as the energy of activation [9,10,11] and setting K = 1.0 by assuming Ea = 0, due to immediate reaction at 80^{0}C.

An abrupt decrease of the delignification rate after reaching a maximum temperature (4 hours) shows that drop of the partial pressure of SO_2 (pSO_2) occurs. It means that the delignification rate is not exactly proportional to the product $K(pSO_2)^{0.75}$ (see reference [9]), but the rate of the acid sulphite delignification must be calculated from the time and temperature parameters by a similar way as that used by Vroom [8].

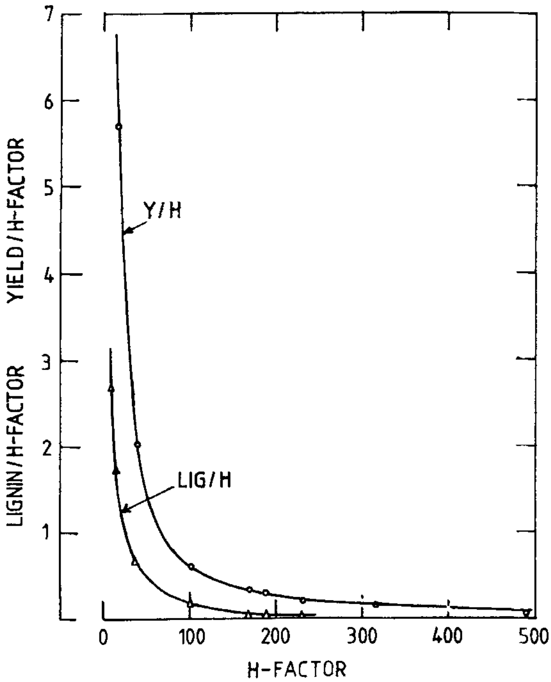

FIGURE 9 . Dependence of the ratio lignin/H-factor and the ratio yield/H-factor on the value of H-factor used in the production of pulp by acid sulphite pulping of spruce wood.

Results summarized in Fig. 9 confirmed that the values of ratio yield/H-factor and values of the ratio lignin/H-factor drawn *vs.* the values of H-factor are expressed by power form curves. By linearization of these curves in logarithmic coordinates one obtains straight line shown in Fig. 10. The values of the relation yield/H-factor *vs.* H-factor are characterized in Fig. 10 by a straight line over the entire range of values of the H-factor used, i.e. from 9 to 500.

From results given in Fig. 10 follow that the dependence lignin/H-factor *vs.* H-factor is expressed by

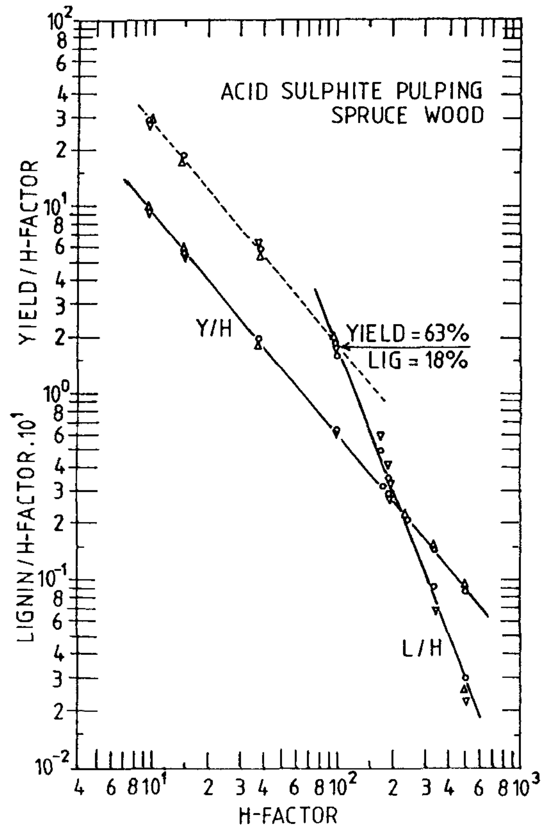

FIGURE 10. Dependence of the ratio yield/H-factor and the ratio lignin/H-factor on the value of the used H-factor during the production of pulp by acid sulphite pulping of spruce wood, expressed in logarithmic coordinates.

two different phases. At the beginning of pulping, i.e. at the value of H-factor below 100, the dependence of the ratio lignin/H-factor *vs*. H-factor is expressed by a straight line (drawn by a dotted line) parallel with a straight line manifesting the dependence of the ratio yield/H-factor on H-factor. The value of the slope constant of this straight line given in Tab. 2 is ($k = -1.14$) near to the slope constant of the dependence of the ratio yield/H-factor *vs*. H-factor ($k = -1.18$). In the further phase of cooking the dependence of the ratio lignin/H-factor *vs*. H-factor changes the slope constant of the straight line to $k = -2.90$.

By the evaluation of experimental results given in reference [4] and by mathematical and graphical linearization one can express the dependence of the ratio yield/H-factor and the ratio lignin/H-factor on the H-factor used (see Fig. 10) rather simply by the logarithmic equation of a straight line [1], in which:

y = ratio yield/H-factor, H-factor/yield, 1/yield.H-factor, lignin/H-factor, H-factor/lignin and product yield.H-factor

x = H-factor calculated for acid sulphite cook

k = a slope constant of the straight line

ln b = an intercept constant

Constants and correlation coefficients for individual dependences were calculated from Eq. [1] by the least squares method using the appropriate computer program. These values are given in Tab. 2. In the evaluation of the dependence of the lignin content on the H-factor for acid sulphite delignification it is necessary to use the values of the ratio lignin/H-factor, which correspond to the value of H-factor above 100.

The results obtained allow to claim that by means of the derived model expressed by Eq. [1] one can calculate from the values of H-factor the yield and the lignin content of pulp relatively precisely. In addition to it, the pulping model facilitates the calculation of

TABLE 2

Values of Constants and Correlation Coefficients of the Dependence Yield and Lignin Content in Pulp vs. H-factor Used at Sulphite Pulping of Spruce Wood. For Calculation the Experimental results Given in [4] Were Used.

Relationship	Slope constant k in Eq.[1]	Intercept constant ln b in Eq. [1]	Correlation coefficient R^2 in Eq. [1]	Constant A in Eq.[2]	Exponent a in Eq.[2]	Degree of freedom
Yield/H-factor vs. H-factor	-1.1847	4.945	1.000	140.5052	-0.1847	36
Lignin/H-factor vs. (+) H-factor	-2.8735	11.876	0.991	143809.5	-1.8735	67
Lignin/H-factor vs. (++) H-factor	-1.1394	3.657	0.997	38.75442	-0.1394	32

(+) Valid for the values of H-factor higher than 100
(++) Valid for the values of H-factor lower than 100

the H-factor required for the production of pulp with the given lignin content.

Power Form of the Linear Logarithmic Dependence

By solution of Eq. [1] one obtains a power equation, which enables a simple calculation of the sought parameters by means of a pocket calculator.

The simplest way for the calculation of the yield and lignin content is the employment of the power form of the linear logarithmic dependence expressed by Eq. [1]. This form is given by relation:

$$Y = A \; X^{a} \qquad [2]$$

in which:

Y = yield, lignin content or H-factor
X = lignin content % in pulp or H-factor
A = a constant = $e^{\ln b}$
e = Eulerian number
ln b = an intercept constant in Eq. [1]
a = exponent, whose value depend on the relation being expressed

Constants corresponding to Eq. [2] for individual dependences of sulphite delignification of spruce wood were calculated from Eq. [1] by the least squares method using the appropriate computer program. These values are listed in Tabs. 1-2.

Yield, lignin content in pulp and H-factor necessary for the production of pulp with required lignin content can be calculated using the constants summarized in Tabs. 1-2 from following equations:

$$\text{Yield} = 42.5210 \text{ lignin}^{0.1074} \qquad (R^2 = 1.000)$$
$$\text{Yield} = 140.5052 \text{ H-factor}^{-0.1847} \qquad (R^2 = 1.000)$$

$$\text{Lignin} = 143\,809.5\ \text{H-factor}^{-1.8735} \qquad (R^2 = 0.991)$$
$$\text{H-factor} = 566.2662\ \text{lignin}^{-0.53376} \qquad (R^2 = 0.991)$$

The obtained facts reveal, that the relation between the lignin content and H-factor is more sensitive to the change of experimental conditions, i.e. in the given case to the change of the base used in the cooking liquor, than the relation between the yield and the H-factor.

<u>Verification of the Accuracy of the Derived Model</u>

The dependence of the yield on the lignin content shown in Fig. 1 is obviously expressed for the range of lower yields after a 90^0 turning (see Fig. 11). Results given in work [4] and shown in Fig. 11 confirm, that experimental results are scattered and one can hardly drawn from their values a real curve, which expresses the dependence of the yield on the lignin content in pulp. The dependence transferred from Fig. 1 to Fig. 11 is expressed by a curve drawn by a dashed line. The curve shown by a full line expresses the dependence of the yield on the lignin content in pulp, obtained by sulphite delignification of spruce wood, calculated using the derived Eq. [2] and values of constants given in Tab. 1.

Results shown in Fig. 11 confirm that the value of yield, for the given values of lignin, calculated by means of the derived model using Eq. [2], agree with experimental results in the region of low lignin content up to 10 %. A method of mathematical and graphical linearization used for deriving the dependence yield *vs.* lignin content and also yield and lignin content *vs.* H-factor, used at acid sulphite pulping, is suitable for the evaluation of a set of significantly scattered data.

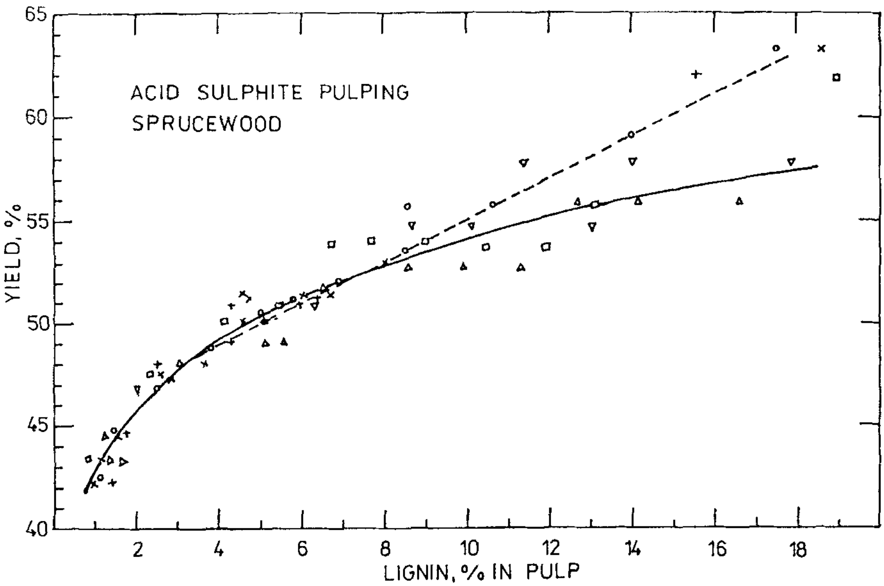

FIGURE 11. Dependence of the yield on the lignin content in pulp prepared by acid sulphite pulping of spruce wood. Dashed line expresses the plot taken from Fig. 1. The full line was obtained by calculation by means of the derived model for the pulping process.

CONCLUSION

From results given in Figs. 4-7 and 11 it is obvious, that the dependence of yield on the lignin content in pulp prepared by acid sulphite pulping is over the range of low lignin content and low yield a power or logarithmic function. A precise mathematical model is especially necessary for the characterization of the last part of the bulk phase and the whole residual phase of acid sulphite delignification. The importance of a precise model is stressed especially in pulping to a lower lignin content or kappa number, e.g.

by a two-stage sulphite process yielding kappa number 12 or in the production of rayon grade pulp with kappa number 8, which corresponds to the lignin content 2.3 % or 1.5 %, respectively.

From the obtained high values of correlation coefficients expressing the dependence of both the yield and lignin content on H-factor obtained by application of Eq. [1] one can deduce that the derived model of sulphite pulping characterizes this dependences very precisely. The developed model represented by Eq. [1] expresses various dependences of the cooking process, i.e. the dependence of the yield on lignin content in pulp, the dependence of both yield and lignin content on time and temperature parameters (expressed by the H-factor), which confirms its general validity.

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