Studies on the Cooking Mechanism of Wood. XVI[1]. *On the Mechanism of Kraft Cooking*

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Hydrogen Sulphide Cooking of α-Guaiacyl Propanol

Hägglund and Enkvist found that the lignin in wood combines with sulphur, when the wood is cooked by a neutral aqueous solution of hydrogen sulphide at 100°[2]. This so-called hydrogen sulphide cooking was thought by them to represent the initial reaction of the ordinary kraft cooking. It was shown by us, that the sulphur, introduced to lignin by the hydrogen sulphide cooking, combined with the so-called X group of the lignin[3], a group which was most easily sulphonatable by a neutral sulphite solution. The structure of this group is now believed to be benzyl alcohol or benzyl ether group with free phenolic hydroxyl group in its para position[3,4]. It is, therefore, very important for the elucidation of the mechanism of the kraft cooking reaction, to investigate the behavior of the model compounds for the X group toward hydrogen sulphide cooking. Among others[5], only vanillyl alcohol (I), *p*-hydroxybenzyl alcohol (II) and its ethers are investigated in some detail by Enkvist[6] and ourselves[7]. It has been shown, that they gave the corresponding monosulphide (III, IV) and disulphide (V), while recently Zentner[8] reported that α-guaiacyl propanol (VI) gave only its dehydrated product, isoeugenol, under the condition of the ordinary

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[1] Part XV, This Bulletin, **29**, 259 (1956).

[2] a) E. Hägglund, *Svensk Papperstidn.*, **44**, 183 (1941); b) T. Enkvist, M. Moilanen and B. Alfredsson, *Svensk Papperstidn.*, **52**, 517 (1949).

[3] H. Mikawa, K. Sato, C. Takasaki and H. Okada, *J. Chem. Soc. Japan* (*Ind. Sect.*), **54**, 299 (1951); H. Mikawa, ibid., 651.

[4] B. Lindgren, *Acta Chem. Scand.*, **5**, 603 (1951).

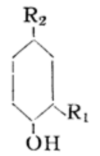
[5] T. Enkvist and M. Moilanen, *Svensk Papperstidn.*, **55**, 668 (1952).

[6] T. Enkvist and M. Moilanen, *Svensk Papperstidn.*, **52**, 183 (1949).

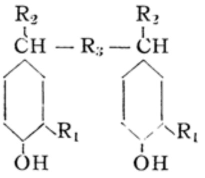
[7] H. Mikawa, This Bulletin **27**, 50. 53 (1954).

[8] T. Zentner, *Tappi.*, **36**, 517 (1953)

hydrogen sulphide cooking. It seemed, therefore, to be quite important to reinvestigate the propanol with special attention to the sulphur containing reaction products, if any.



	R_1	R_2
I	OCH_3	$-CH_2OH$
II	H	$-CH_2OH$
VI	OCH_3	$-CH(OH)C_2H_5$
IX	OCH_3	$-CHO$
X	OCH_3	$-CH_2SH$
XI	OCH_2	$-CHS$



	R_1	R_2	R_3
III	OCH_3	H	–S–
IV	H	H	–S–
V	OCH_3	H	–S–S–
VII	OCH_3	$-C_2H_5$	–S–S–
VIII	OCH_3	$-C_2H_5$	–S–

Reaction products obtained from the α-guaiacyl propanol by the hydrogen sulphide cooking at 100° during six hours, gave four spots by paper chromatography, those of unreacted propanol, bis-(1-(4-hydroxy-3-methoxyphenyl)-1-propyl) disulphide (VII), bis-(1-(4-hydroxy-3-methoxyphenyl)-1-propyl) monosulphide (VIII) and some unknown compound. The separation of these compounds in larger scale was performed by developing the product adsorbed on a Florizil column with benzene. The disulphide, thus separated, showed no melting point depression on admixture with the product synthesized according to Zentner[8]. The monosulphide was separated as dibenzoate and its structure was determined from the analytical values and the molecular weight measured according to Rast's method.

Thus confirming the formation of mono- and disulphide also from α-guaiacyl propanol, the mechanism of the formation of monosulphide and disulphide from p-hydroxybenzyl alcohols by hydrogen sulphide cooking discussed in the previous communication[7] seems to be applicable in general.

Alkaline Decomposition of Vanillyl Monosulphide (III)

The sulphur introduced to lignin by hydrogen sulphide cooking was partly split off by the treatment with alkali at 160°[2b,9], resulting in a formation of thiolignin with rather low content of sulphur, thus explaining why the sulphur content of the thiolignin isolated from the black liquor of the industrial cooking was comparatively low.

Enkvist investigated the behavior of vanillyl disulphide (V) against alkali, as the model for the "hydrogen sulphide lignin". He confirmed the fact that the disulphide sulphur was split as hydrogen sulphide, resulting in a formation of vanillin[2b]. The stability of the disulphide sulphur of this model compound was, however, much lower than the sulphur contained in the hydrogen sulphide lignin. The alkaline decomposition of 4,4′-dihydroxydibenzyl monosulphide (IV) and of vanillyl monosulphide (III), synthesized by us, was investigated previously very briefy[7]. The latter compound was investigated also by Enkvist spectroscopically[10]. These monosulphides were found to be much more stable against hot alkali than the disulphide, although they also split sulphur as hydrogen sulphide just as in the case of vanillyl disulphide and hydrogen sulphide lignin. As it seems to be very important to know the decomposition products of the vanillyl monosulphide against hot alkali, the behaviour of this compound was investigated rather precisely in the present communication.

Vanillyl monosulphide was decomposed with 5% alkali and the products were examined by paper chromatography. A spot for the starting monosulphide was too strong even after heating for six hours at 120° as yet and the decomposition condition of three hours at 130° was found to be suitable for the investigation of the products. The chromatogram was not so simple, and the materials which were isolated as crystals and identified by mixed melting point determinations, were unreacted starting monosulphide, vanillin and vanillyl alcohol. By comparing the chromatogram with that of the products of the alkaline decomposition of vanillyl alcohol alone, however, almost all of the unidentified spots were found to be due to the secondary reaction products of vanillyl alcohol. Only one spot remained

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[9] T. Enkvist, *Svensk Papperstidn.*, 51, 225 (1948); T. Enkvist and E. Hägglund, *Festskr. J. A. Hedvall*, 149 (1948).

[10] J. Lindberg and T. Envist, *Societas Scientiarum Fennica Commentationes Physico-Mathematicae* (1953), XVII, 4.

unidentified, which corresponded to the direct decomposition product of the vanillyl monosulphide. The decomposition proceeds, therefore, as follows: III→IX+I+$(I)_x$+SH^-.

As stated above, Enkvist investigated spectroscopically the decomposition of vanillyl monosulphide at 100°. Comparing the UV-absorption spectrum of vanillyl monosulphide and its decomposition products and from the vanillin odor of the product, he assumed that some amount of vanillin may be formed by the alkaline decomposition of the monosulphide. From the fact that the adsorption maximum of the monosulphide at 284 $m\mu$ shifts 4 $m\mu$ to the shorter wave-length side after the alkaline decomposition, he pointed out also the possibility that the monosulphide was degraded to smaller molecules, possibly to vanillyl alcohol or to vanyllyl mercaptan. From these considerations he assumed the mechanism of the decomposition of the monosulphide as follows: 2III→X+I+XI, XI→IX+SH^-.

In so far as the reaction products are concerned, the mechanism agrees rather well with our findings. The fact that both monosulphide and disulphide, the products of the hydrogen sulphide cooking of the model compounds for the X-group, gave vanillin when decomposed with hot alkali, suggests to us that thiolignin contains carbonyl group at the same position, where the X-group was situated before the cooking.

On the Mechanism of the Kraft Cooking and the Structure of the Thiolignin

It was pointed out at first by Kullgren[11], that the combination of sulphur and lignin was the main reason why wood was delignified much more easily by the kraft cooking process than by the soda process. At the beginning of the ninteen forties, Hanson, Brauns and Ahlm investigated the sulphur atoms contained in the ordinary thiolignin, recovered from the black liquor[12]. All of them though that it was in the form of mercaptan. Hägglund and Enkvist, however, made clear that thiolignin contained mainly only monosulphide (thioether) sulphur[2]. They also showed that the sulphur contained in the hydrogen sulphide lignin was in monosulphide and disulphide form[2] and that this sulphur was partly split off by alkali at 160° resulting in the formation of the ordinary thiolignin.

As stated previously, it was shown by us that the sulphur introduced to lignin by the hydrogen sulphide cooking combined with the X-group of lignin[3] and the hydrogen sulphide cooking of the model compounds for the X-group were investigated in the present paper and by Enkvist[5,6] and ourselves[7]. They gave monosulphide and disulphide just as in the case of the hydrogen sulphide cooking of lignin. The alkaline decomposition of these compounds was also investigated not only in this paper but also by them[6,7,10] and it was found that the monosulphide sulphur was much more stable than the disulphide sulphur, although both of them were split as hydrogen sulphide. The behaviour of the hydrogen sulphide lignin against alkali was thus confirmed with the model compound.

The second important reaction involved in the kraft cooking process is the alkaline cleavage of the arylether linkages in the lignin. The content of the phenolic hydroxyl group of alkali lignin and thiolignin has been investigated by Marshall et al.[13], Brauns[14], Enkvist[15] and ourselves[16]. According to our data, the phenolic hydroxyl group of the lignin in situ, 0.14/CH_3O as was reported in Part XIII of this series, increased to 0.4/CH_3O[16] after the kraft cooking, thus confirming the marked increase of the phenolic hydroxyl group during the digestion.

The cleavage of the ether linkage of lignin accompanies the degradation of its molecular size. The molecular weight of alkali lignin and thiolignin has been measured by a number of authors[17]. Almost all values are less than 1000 and some of them are so small as 400–500. The molecular weight determination of alkali lignin and thiolignin by the Rast method was investigated by us and it was concluded that the measurement must be made with the methylated or acetylated samples[18]. By this method, molecular weight distribution curves for alkali lignin and thiolignin were obtained and it was found that the molecular weight concentrated mainly around 1000 and 1500[19]. Enkvist reports also that the molecular weight lies

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[11] C. Kullgren, *Papierfabrikant*, **24**, 20 (1926).

[12] F. Hanson, *Paper Trade J.*, **112**, No. 2, 32 (1941); F. Brauns, ibid., **111**, No. 14, 33 (1940); C. Ahlm, ibid., **113**, No. 13, 115 (1941).

[13] H. Marshall, F. Brauns and H. Hibbert, *Can. J. Res.*, **13 B**, 103 (1935).

[14] F. Brauns and W. Grimes, *Paper Trade J.*, **108**, No. 11, 40 (1939).

[15] T. Enkvist and B. Alfredsson, *Svensk Papperstidn.*, **54**, 185 (1951).

[16] H. Mikawa, K. Sato, C. Takasaki and K. Ebisawa, This Bulletin, **29**, 254 (1956).

[17] Y. Hachihama and S. Jodai, "Chemistry of Lignin", Nihonhyronsha, Tokyo (1946), p. 270; R. Glover and J. Bain, *Can. J. Res.*, **14 B**, 65 (1936); Y. Hachihama and S. Jodai, *J. Soc. Chem. Ind. Japan*, **52**, 306 (1949); F. Lahey and J. Merewether, *Australian J. Sci. Res. Ser. A.*, **1**, 112 (1948).

[18] H. Mikawa and H. Okada, *J. Chem. Soc. Japan*, (*Ind. Sec.*,) **54**, 239 (1951).

[19] H. Mikawa, ibid., 150, 152.

mainly between 1000–1500[9].

The structure of the side chain of thiolignin has not been much investigated, especially in connection with the mechanism of the sulphidation of lignin and the subsequent splitting of the sulphur once introduced at the beginning of the kraft cooking by alkali. This problem was discussed rather precisely in the previous communication[16], and the existence of the carbonyl group and the double bond conjugated with the benzene nucleus and the carboxyl group directly attached to the nucleus was concluded, and the mechanism involved in the formation of these group was also discussed.

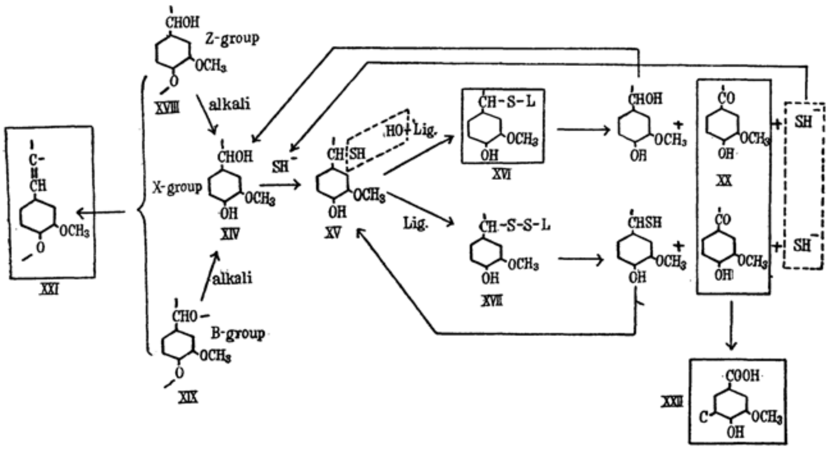
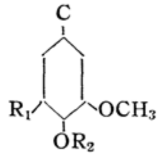


Fig. 1. Reactions of lignin during the kraft cooking.

The nuclear structure of thiolignin was investigated rather precisely by Richtzenhain[20] and also by us in the previous communication[1]. Richtzenhain proved the existence of the nuclei of type XII and XIII and showed the increase of the proportion of the latter nucleus during the kraft cooking. We showed that the proportion of XII(R_2=H) and XIII(R_2=H) was about 25–40% and 75–60%, indicating that the nuclei belonging to the latter type increase a little during the cooking. This problem has been thoroughly discussed in the previous communication[1].



XII R_1=H
XIII R_1=–C

Summarizing these findings mentioned above, one may be allowed to formulate the mechanism of the kraft cooking as follows (cf. Fig. 1): (1) At the beginning of the cooking, the X-group of the lignin in wood (XIV) reacts with sodium sulphide to give mercaptan (XV). The mercaptan reacts rapidly with the other hydroxyl group of the lignin to give monosulphide (XVI), while it is partly oxidized with some group of the lignin to the disulphide group (XVII). The lignin isolated at this stage is the hydrogen sulphide lignin obtained by the hydrogen sulphide cooking of wood. Until this stage, only the X-group enters into reaction and the sulphur contained in the hydrogen sulphide lignin is in both monosulphide and disulphide form.

(2) Next, the temperature rises in the presence of alkali and the cleavage of the ether linkage occurs. This cleavage of the ether linkage occurs also at the Z-group (XVIII) and B-group (XIX), resulting in a formation of the X-group, which reacts further to give monosulphide and disulphide just as in the case of (1). This cleavage of the ether linkage causes the splitting of the lignin molecule and the increase of the content of the phenolic hydroxyl group.

(3) At the same time, the disulphide group (XVII) is decomposed very easily with hot alkali to give the mercaptan, regenerating SH^- ion. A certain amount of carbonyl group conjugated with the nucleus (XX) is also formed. Monosulphide group (XVI) is much more stable than the disulphide group, but it is also partly decomposed with hot alkali to give carbonyl group (XX) at its position, while partly regenerating the X-

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[20] H. Richtzenhain, *Svensk Papperstidn.*, 53, 644 (1950).

group and the SH^- ion.

(4) X, Z (XVIII) and B-groups (XIX), which are taking part in such complex reactions mentioned above, are on the other hand partly dehydrated by hot alkali to give double bond conjugated with the nucleus (XXI). The carbonyl group (XX) thus formed is converted partly to the carboxyl group (XXII) directly connected to the nucleus. Condensation reaction occurs to some extent at the same time resulting in an increase of the amount of the nuclei having C–C bond at the fifth position adjacent to the phenolic hydroxyl group.

(5) During these complicated reactions most of the very reactive X, Z and B-groups are kept in combination with sulphur, especially in the most stable monosulphide form. These groups are thus protected from the undesired condensation reason tion during the cooking. This is the main reason why the delignification is easier in kraft cooking than in the soda cooking. Thus, ultimately, thiolignin with a small amount of sulphur mainly in the form of the stable monosulphide having the molecular weight of about 1000–1500 dissolves out in alkali due to its carboxyl group and phenolic hydroxyl group.

Experimental

Hydrogen Sulphide Cooking of α-Guaiacyl Propanol (VI).—Hydrogen sulphide was bubbled through a Clark-Lubs buffer solution (100 ml.) (50 g. of KH_2PO_4 and NaOH in one liter of water, pH 7) until the concentration of hydrogen sulphide reaches 0.36 N, α-guaiacyl propanol (3 g.) added and the mixture was rotated in a stainless autoklave (150 ml.) for six hours at 100° in an oil bath.

The solution was extracted exhaustively with ether, ether was expelled, and the residue (3 g.) was tested chromatographically on a strip of the Toyo filter paper No. 50 buffered with Clark-Lubs buffer solution at pH 7 using benzene-petroleum ether 1:1 as a mobile phase. Four spots were observed by diazotized sulphanilic acid at Rf 1.0, 0.90, 0.79 and 0.52, of which the weak spot at Rf 0.52 was of the unreacted α-guaiacyl propanol.

The residue was kept in a refrigerator for two weeks and the separated crystal was filtered, washed with a mixture of benzene and petroleum ether and recrystallized from the same solvent mixture, m.p. 112–114.5°, 100 mg., Rf=0.79. This crystal did not show any melting point depression on admixture with the bis(1-(4-hydroxy-3-methoxyphenyl)-1-propyl) disulphide (VII), m.p. 115–116°, synthesized according to the method of Zentner[8].

Anal. Found: C, 61.58; H, 6.77; S, 16.32. Calc. for $C_{20}H_{26}O_4S_2$ (VII): C, 61.0; H, 6.59; S, 16.21%.

The filtrate from the crystal was concentrated, dissolved in benzene, adsorbed on a Florizil column (diameter 17 mm., length 270 mm.), developed at first with benzene, and the eluate was tested by paper chromatography. After the first fraction with Rf=1.0, 0.61 g., the second fraction, a mixture of two substances with Rf=0.90 and 0.79, 2.1 g., was obtained by eluting the column with a mixture of benzene and alcohol 9:1. The column was then washed with alcohol and a small amount of the third fraction consisting of only unreacted α-guaiacyl propanol was obtained.

The first fraction was crystallized as a benzoate having m.p. 154–155° from alcohol, 0.25 g. The analyses and the molecular weight obtained by the Rast method agree with the corresponding valueus of the dibenzoate of bis(1-(4-hydroxy-3-methoxyphenyl)-1-propyl) monosulphide (VIII).

Anal. Found: C, 71.4; H, 6.13; S, 5.7; OCH_3, 11.2; molecular weight (Rast), 630. Calc. for $C_{34}H_{34}O_6S$ (dibenzoate of VIII): C, 71.2; H, 5.93; S, 5.6; OCH_3, 10.8%; molecular weight, 574.6.

The second fraction containing the disulphide and an unknown compound with Rf=0.90 was not investigated further. The sulphur content of the fraction, 10.37%, was rather high.

Decomposition of Vanillyl Monosulphide (III) with Hot Sodium Hydroxide Solution.—Vanillyl monosulphide (1.5 g.) was dissolved in 5% sodium hydroxide (75 ml.), kept at 130° for three hours in an autoklave with nitrogen atmosphere, acidified with sulphur dioxide and extracted with ether. From the aqeous solution 2,4-dinitrophenyl hydrazone having m.p. 255–257° was obtained, 0.24 g. After recrystallization from dioxane the hydrazone did not show any melting point depression on admixture with the authentic vanillin 2,4-dinitrophenyl hydrazone.

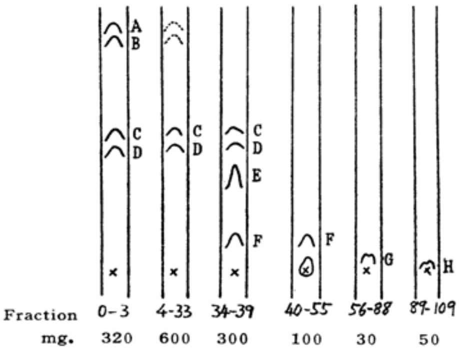

Fig. 2. Paper chromatograms of the products of alkaline decomposition of vanillyl monosulphide separated into 109 fractions by Al_2O_3 adsorption chromatograph, B: Vanillyl monosulphide, H; Vanillyl alcohol, D: ?, A, C, E, F, G: Secondary products of vanillyl alcohol.

The ether extract was concentrated, dissolved in benzene, adsorbed on a column of alumina (a mixture of 330 g. of active alumina and 33 g. of cellite, diameter 30 mm., length 580 mm.), developed with benzene and separated into 109 fractions. Paper chromatograms of these fractions are shown in Fig. 2. From the fractions O-3 vanillyl monosulphide was separated and identified by mixed melting point determination, 100 mg. Fractions 89–109 contain only vanillyl alcohol, 50 mg. These chromatograms were compared with that of the product obtained by treating the vanillyl alcohol with sodium hydroxide just in the same condition as in the case of the vanillyl monosulphide and it was found that the spots A, C, E, F and G were those of the secondary products produced from the vanillyl alcohol by alkali. Although the substance corresponding to the spot D seemed to be the direct fission product of the vanillyl monosulphide, it was impossible to isolate it, as the intensity of C was very strong. Yield; recovered monosulphide 7%, vanillin 8%, vanillyl alcohol 4%. Almost all of the remaining part consisted of secondary products from vanillyl alcohol.

Summary

1. Hydrogen sulphide cooking of α-guaiacyl propanol (VI) gave bis(1-(4-hydroxy-3-methoxyphenyl)-1-propyl) monosulphide (VIII) and disulphide (VII).

2. Vanillyl monosulphide was decomposed with alkali at 130°. Vanillin, vanillyl alcohol and the secondary products from vanillyl alcohol were identified.

3. The mechanism of the kraft cooking process was discussed and a new mechanism was proposed.

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