NEW INFORMATION ON THE REACTIONS OF LIGNIN IN KRAFT PULPING

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EARLIER WORK ON THE PART PLAYED BY SULPHUR IN KRAFT PULPING

The part played by sulphur in kraft pulping has been investigated extensively, *i.e.* by the Swedish chemists Klason, Holmberg and Hägglund. It has been found to be very complicated. My co-workers and I have investigated one of these experimentally which holds that the main effect is caused by the reducing properties of sulphide or hydrogen sulphide. In fact, the redox potential E_h, measured after the digestion at pH 11, in a kraft liquor has a value of about -0.30, whereas the corresponding soda or sodium hydroxide liquor shows a value of about -0.15. It is well known from the work of Schuerch and co-workers[1], among others, that pulping of wood can be achieved by hydrogenation in alkaline solution in the presence of catalysts. In our experiments[2] we adjusted the redox potential of an alkaline cooking to the same value as for a kraft liquor, with the aid of a reducing reagent liquor other than sodium sulphide; we used pyrocatechol and other reducing reagents. The effect of the cooking was, however, still about the same as with sodium hydroxide alone. Thus, the main part of the rôle played by sulphur in kraft pulping cannot be explained by the reduction theory.

Modern theories about the kraft process are founded on the assumption that some active group in lignin reacts chemically with a sulphide ion, *i.e.* with a sulphide or hydrogen sulphide ion. During the digestion an amount ranging from about one-fifth to one-half of the sulphide is consumed, depending on the concentration of sulphide used[3]. The sulphur consumed is mainly found organically bound in the kraft or thiolignin. The latter is dissolved during the digestion and can be precipitated if the liquor is acidified after the cooking. That kraft lignin contains, as a rule, about 2.5 per cent of organic sulphur. It is, however, not homogeneous[4] but contains fractions of very different molecular weight, varying from about 7,000 according to Gralén[5], to about 1,000 or less. The low molecular, dialysable fraction seems to contain more sulphur, about 4 per cent, the high molecular part less, about 2 per cent or less[6].

Research carried out by Hägglund, my co-workers and myself in Stockholm and Helsinki proved that lignin can be sulphurized to thiolignins which have sulphur contents varying between about 2 and 21 per cent, and very different solubilities, stabilities, reactivity and spectroscopic properties. The scheme in *Figure 1* was published 7 years ago[7] and shows the various types of thiolignins. If spruce wood is digested in neutral or almost neutral sodium hydrogen sulphide solution of pH 7 or 8.5 there
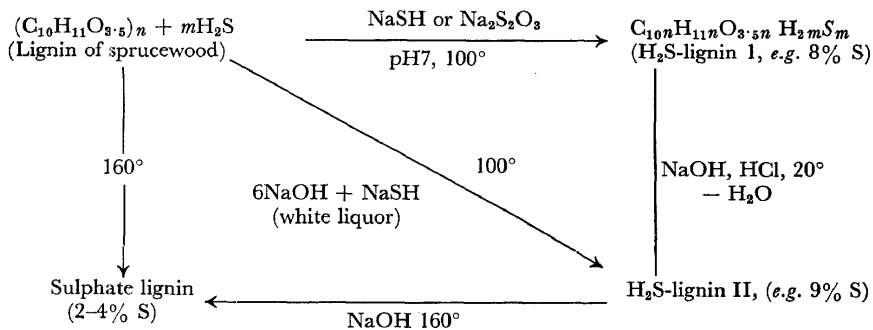
$(C_{10}H_{11}O_{3 \cdot 5})_n + mH_2S$
(Lignin of sprucewood)

$\xrightarrow[\text{pH7, }100°]{\text{NaSH or Na}_2S_2O_3}$

$C_{10n}H_{11n}O_{3 \cdot 5n} H_{2m}S_m$
(H$_2$S-lignin 1, $e.g.$ 8% S)

160°

100°
6NaOH + NaSH
(white liquor)

Naoh, HCl, 20°
— H$_2$O

Sulphate lignin
(2–4% S)

$\xleftarrow[\text{NaOH 160°}]{}$

H$_2$S-lignin II, ($e.g.$ 9% S)

Figure 1. Scheme for the formation and reactions of thiolignins (By permission *Tappi*
37, 350 (1954))

is addition of the elements of hydrogen sulphide. A hydrogen sulphide lignin I is formed, with, for instance, 8 per cent sulphur content. At first it remains in the wood, but microphotographs in ultra-violet light show that it melts and flows out in the open spaces, the lumina, of the wood fibre cells[8]. This thiolignin can be dissolved easily in alkaline solutions, and also in neutral organic solvents, such as 75 per cent alcohol, alcohol–acetone or dioxan. If carefully prepared at 80°, it shows a sharp ultra-violet spectrum of about the same type as the lignosulphonic acids. It is, however, unstable. On dissolution in an alkaline solution at room temperature and reprecipitation with hydrochloric acid, it loses the elements of water. Thus, it forms hydrogen sulphide lignin II, which has a higher sulphur content, $i.e.$ 9 per cent, and a rather flat ultra-violet absorption curve. This spectral change is probably caused by the formation of carbonyl groups, or other groups with double bonds, in conjugation with the benzene nucleus[9]. By heating with sodium hydroxide solution at 160°, hydrogen sulphide lignin II loses half or more of its sulphur in the form of sodium sulphide. Thus the lignin is changed to a product very like kraft lignin. Also at the beginning of a usual kraft digestion, at 100°, a lignin, often rich in sulphur, which closely resembles the hydrogen sulphide lignin II, is formed. Comparative studies of the dissolution of lignin from wood at different temperatures with kraft and sodium hydroxide liquors have been made[2,10] In those studies, the greatest difference has been observed at early stages of the digestion, at 130 or 140°. At this temperature, the dissolution of lignin in the kraft cooking proceeds continuously. In contrast, digestion with sodium hydroxide leads, at first, to the same rapid dissolution of the lignin as in the kraft pulping, but when about a third of the lignin has been dissolved, practically no more lignin is soluble in sodium hydroxide at 140°. This shows that the explanation of the part played by sulphur in kraft pulping is to be sought in the early stages of the digestion, and in the thiolignins which are formed as intermediates. Further, a great number of widely varied sulphurizations of spruce wood have shown that only those thiolignins which have a sulphur content of not less than 4 per cent can be dissolved from wood by neutral or alkaline solvents at low temperatures. The facts point to a kind of cyclic process comprising an addition and

subsequent elimination of hydrogen sulphide, which can then react again with new molecules of lignin.   The sulphide ions thus react as a kind of catalyst.   The final kraft lignin in the black liquor, with its sulphur content of about 2 per cent only, is a product formed by rather deleterious side reactions, a kind of catalyst poisoning, in which utilizable sulphur has been bound to stabilized, non-reactive sulphur compounds, and can no longer be removed by alkali.

Then we have the question of which specific groups in lignin react with sulphur.   Moilanen and I[11] have made a series of sodium hydrogen sulphide digestions at 100° and pH 6–9 as has Gierer in Stockholm[12].   The results make it seem very probable that it is the so-called X- groups which react with sulphide ions (*Figure 2*).   The X-groups are *p*-hydroxybenzylalcohol
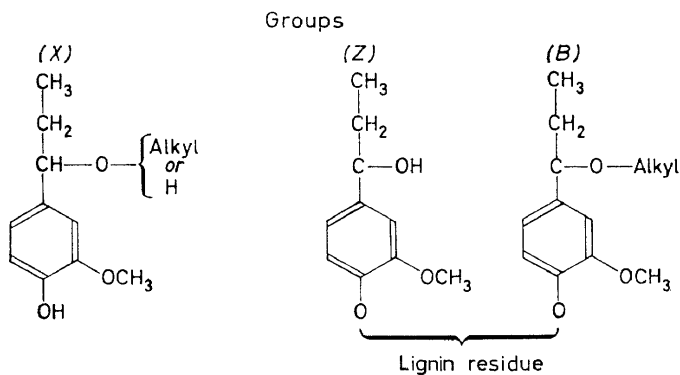
Figure 2.   X-, Z- and *B*-groups of lignin

or corresponding benzyl alkyl ether groups.   The sulphur attacks the carbinol carbon atom, and splits the benzyl alkyl ether group.   In the case of the Z- and B-groups, the phenolic hydroxyl group is etherified and no sulphur is introduced.   This contrasts with the sulphite digestion, where Z-groups also react directly with the reagent, and B-groups react after hydrolysis.

Measurements of the contents of free phenolic hydroxyl groups have been carried out by Freudenberg and Adler and their co-workers[13], and also by my co-workers and me[14].   They show that milled wood lignin, prepared according to the method of Björkman, and probably also the protolignin of wood, contains about one free phenolic group in every group of three phenylpropane units.   The hydrogen sulphide lignins contain somewhat more, *i.e.* about one free phenolic hydroxyl group for every two phenylpropane units.   Thus, in protolignin only some of the benzyl ether bonds can be cleaved by sulphidic ions.   There are also other types of bonds in lignin, for instance phenol ether bonds and carbon—carbon bonds, especially in the 5-position.   There is good reason to believe that many new carbon—carbon bonds are formed in this position during alkaline pulping[15].   Hence, it is not surprising that it is impossible to make pulp from wood by digesting with pure sodium hydrogen sulphide solutions. However, in kraft pulping we have also hydroxyl ions; they are, in fact,

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present in large amounts. I have already proposed the theory that the dissolution of lignin in kraft pulping is a result of concerted action by hydrogen sulphide ions and hydroxyl ions. The hydroxyl ions would cleave phenol ether bonds, and thus set new phenolic hydroxyl groups free. Then the hydrogen sulphide ions would split benzyl alkyl ether bonds. An interesting paper read by Gierer at the lignin symposium in Helsinki in June 1961[16] throws new light on this hypothesis. On the basis of model experiments, Gierer concludes that the hydroxyl ions are probably only able to cleave those phenol ether bonds in which the benzene nucleus has its phenolic hydroxyl group etherified, as in the Z- and B-groups. Thus, we should have a clear division of functions: the sulphidic ions splitting the H-groups and the hydroxyl ions splitting Z- and B-groups, thus creating new X-groups. Those can then in their turn be cleaved by sulphidic ions. This hypothesis could be called the *ether cleavage* hypothesis. Until now important questions in connection with this hypothesis have been left open for discussion. Firstly, it is of interest to determine the extent to which facts obtained experimentally are valid for the kraft pulping reaction, which proceeds in strongly alkaline solution. Secondly, it is highly probable that lignin contains many alkyl aryl ether bonds in the β-position. We should like to know what happens to these bonds during sulphurization.

The form in which the sulphur in the kraft liquor reacts with lignin has been the subject of some discussion. The hydrogen sulphide molecule, the hydrogen sulphide ions and the sulphide ions have all been advocated. Quantitative studies of the formation of alcohol-soluble thiolignin from spruce wood on cooking with sodium hydrogen sulphide solutions of varying pH have been made[8]. These studies have shown that the increase in the net yield of thiolignin in the range pH 5·5–8·5 follows the rise of the hydrogen sulphide ion concentration, but is inversely proportional to the concentration of undissociated hydrogen sulphide. From pH 8·5 upwards the yield remains roughly constant, in spite of the fact that at higher pH values part of the sulphur occurs as the bivalent sulphide ion. Thus, it seems that hydrogen sulphide ions and sulphide ions alike contribute to the formation of thiolignin, in contrast to the undissociated hydrogen sulphide molecule.

It is, however, probable that the thiolignin formation occurs in a somewhat different manner with hydrogen sulphide ions than with sulphide ions, *i.e.* in almost neutral as compared with strongly alkaline solutions.

SULPHATE DIGESTIONS OF THE LIGNIN MODEL VANILLYL ALCOHOL

There have been some discrepancies in the results of the sulphurization of the lignin model vanillyl alcohol at 100° and pH ∼ 7. Moilanen and I obtained vanillyl disulphide[11], whereas Mikawa and co-workers got a mixture of vanillyl disulphide and vanillyl monosulphide[17] After digestion of wood with sodium hydrogen sulphide at pH 7, some disulphidic sulphur was found by iodometric titration[7,18], in contrast to the results of analogous titrations of commercial kraft lignin. It can be assumed that the

vanillyl disulphide and the disulphidic sulphur in the sulphurized wood have been formed from the corresponding mercapto groups by aerial dehydrogenation. This has probably happened not so much during the digestion itself but during the isolation and purification of the products. This will be illustrated by the results of Hästbacka, at Helsinki[19]. He carried out kinetic studies of the reaction of vanillyl alcohol at 75–95° in strongly alkaline solutions which contained sodium hydroxide and, in most cases, sodium sulphide, corresponding to the composition of commercial soda or kraft white liquors. He rigorously excluded the air and succeeded in determining the reaction products by quantitative paper chromatography and colorimetry to an accuracy of about ±1 per cent. This is much better than the accuracy achieved in most earlier chromatographic experiments. Some of his results are presented in *Figure 3*.
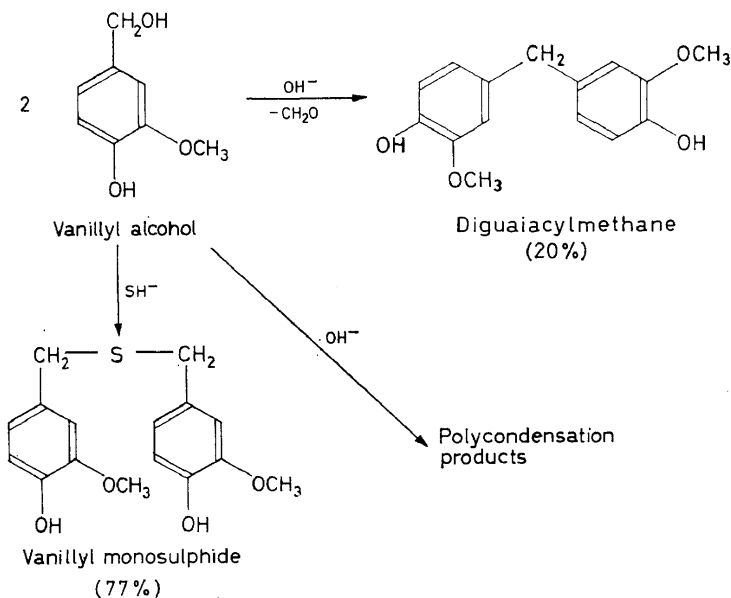

Figure 3. Reactions of vanillyl alcohol

This shows that in the presence of sulphide ions the main product was vanillyl monosulphide, with 77 per cent of the theoretical yield. No vanillyl disulphide or vanillyl mercaptan could be detected. The sulphurization reaction was found to be first order; the reaction rate of the consumption of vanillyl alcohol in sodium sulphide solution, as well as in sodium hydroxide solution, is decreased on increasing the concentration of the inorganic reagent. Hästbacka explains this behaviour by assuming that the rate-determining step in both cases is the formation of a quinone methide as an intermediate, and that this quinone methide then adds to vanillyl mercaptan or vanillyl alcohol. The formation of disulphide in the experiments by Moilanen and me might then perhaps be explained
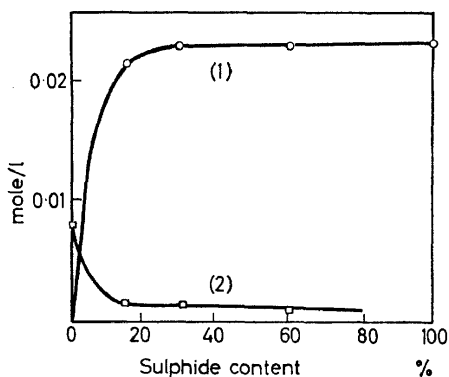
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Figure 4. The yield of vanillyl monosulphide (1) and diguaiacyl methane (2) as a function of the sulphide content after a reaction time of 8 h at 95·6° C; initial concentration of vanillyl alcohol: 0·0648 mole/l; active alkali content: 13·4 g Na_2O/l

as a kind of " catching reaction ", what the Germans call " Abfangreaktion ", for the intermediate vanillyl mercaptan by the oxygen of the air.

From the first line of *Figure 3* we see that on digestion of vanillyl alcohol with sodium hydroxide solution, diguaiacyl methane was obtained in 20 per cent yield in addition to polycondensation products. This is a polycondensation reaction very similar to that which proceeds in the reaction of phenols with formaldehyde during the formation of plastics of the bakelite type.

These results of Hästbacka have a bearing on an important aspect of the part played by sulphur in the kraft process, namely the hypothesis—or as we might now call it—the theory of the blocking effect. This theory was originally proposed by Hägglund in 1941[20]. It holds that the main effect of the sulphide ions would be a blocking by sulphurization of reactive groups in lignin, especially phenol alcohol groups. Thus, condensation
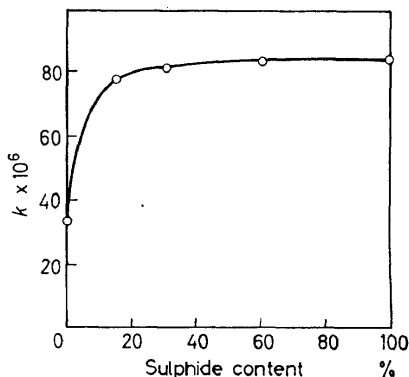

Figure 5. The effect of sulphide content on the rate of consumption of vanillyl alcohol at 95·6° C; concentrations, see *Figure 4*
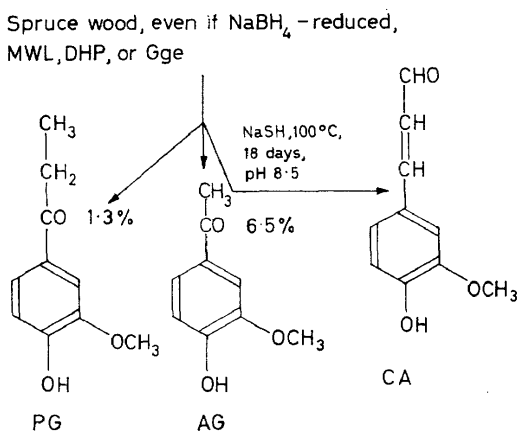
reactions of the type involved in the formation of phenol–formaldehyde plastics are prevented. The results of Hästbacka make it seem most probable that this theory of the blocking effect holds true, at least in the case of vanillyl alcohol. Furthermore, his experiments with various sulphide concentrations show that the formation of vanillyl monosulphide predominates over the formation of diguaiacyl methane and polycondensation products at sulphide contents as low as 20 or 15 per cent (*Figure 4*). The rate of consumption of vanillyl alcohol was roughly twice as fast in the presence of sulphide ions as with pure sodium hydroxide. It is quite clear that this effect also holds for sulphide concentrations down to about 15–20 per cent (*Figure 5*). Thus, the influence of the sulphide content is very much the same as in kraft digestions where sulphide concentrations of 15–20 per cent in the white liquor suffice to bring about the favourable effects of kraft pulping. It is an interesting fact that the simple lignin model vanillyl alcohol can imitate so closely the effects of sulphidity concentration at the kraft digestions, although all kinds of carbohydrate compounds are absent in the digestions.

THE DEGRADATION OF SPRUCE LIGNIN BY SULPHIDE IONS TO ACETOGUAIACOL, PROPIOGUAIACOL AND CONIFERYLALDEHYDE

The results obtained by Hästbacka also, in a way, provide an argument against the ether cleavage theory. They prove that sulphide ions, do not instigate degradation as assumed by the ether cleavage theory, but can also condense a monomeric lignin model, vanillyl alcohol, to a dimeric product, vanillyl monosulphide, of higher molecular weight. However, in May 1961 another of my co-workers, Ashorn, produced results[21] which can be said to develop the ether cleavage theory.

Ashorn detected that spruce wood, on digestion with a sodium hydrogen sulphide solution of pH 8·5 for a period of 18 days at 100° in a rotating autoclave of stainless steel, formed an ether-soluble phenolic fraction in an

Spruce wood, even if NabH$_4$ – reduced, MWL, DHP, or Gge

CH$_3$
CH$_2$
CO 1·3%

NaSH,100°C, 18 days, pH 8·5

CH$_3$
CO 6·5%

CHO
CH
CH

OCH$_3$
OH

OCH$_3$
OH
PG

OCH$_3$
OH
AG

CA

Figure 6. Formation of acetoguaiacol, propioguaiacol and coniferylaldehyde from spruce wood and other materials

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amount of about 10 per cent calculated with reference to the lignin of the wood. The main substances in this fraction were (*Figure 6*) acetoguaiacol (AG) 6·5 per cent, its homologue propioguaiacol (PG) 1·3 per cent, and, further, coniferyladehyde (CA). Neither of the ketones could be obtained by a corresponding digestion of spruce wood with a sulphur-free phosphate buffer solution of pH 8·5, and the yield of coniferylaldehyde was much less in the sulphur-free digestion. Similar results were obtained on comparing digestions of milled wood lignin (MWL) prepared according to the method of Björkman, and also from the Freudenberg enzymatic dehydrogenation polymer (DHP) of coniferyl alcohol. In this respect this dehydrogenation polymer also resembles the protolignin of spruce wood. Curiously enough, the lignin model of Adler, the guaiacylglycerol-β-guaiacyl ether (Gge), also gave the same products. This must be the result of complicated rearrangement reactions. Even spruce wood which had been treated with sodium borohydride in order to reduce any carbonyl groups in the lignin, gave the same reaction products. Thus, their formation is not dependent on any pre-formed carbonyl groups in the wood.

The yield of coniferylaldehyde after 24 hours was only 0·08 per cent of the lignin obtained from unreduced spruce wood, and 0·25 per cent from sodium borohydride reduced wood. On prolonged digestion it was still lower. *Figure 7* shows that coniferylaldehyde is not stable on digestion with sodium hydrogen sulphide solutions. It is thus possible that fairly large amounts of the lignin are degraded to coniferylaldehyde which then reacts further, probably forming resinous products.
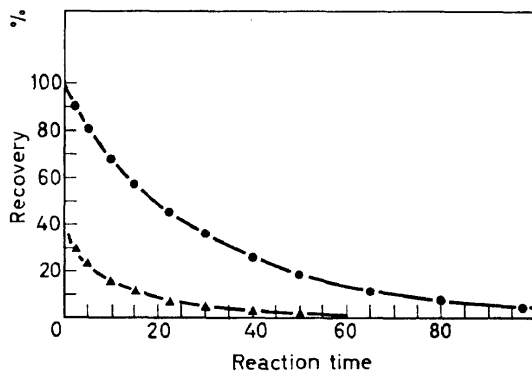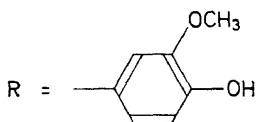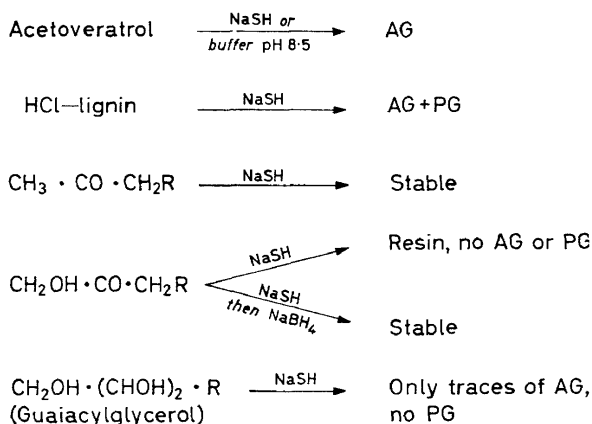

Figure 7. The stability of coniferylaldehyde to digestion with sodium hydrogen sulphide (—▲—) and sulphur free (—●—) buffer solutions at 110° and pH 8·5

Figure 8 shows some further results by Ashorn obtained in similar digestions with sodium hydrogen sulphide or phosphate buffer solutions. We see that acetoveratrol is easily demethylated to acetoguaiacol even by the buffer solution. This probably has something to do with the fact that acetoveratrol is a vinylogue of methyl acetate and is thus easy to hydrolyze. Hydrochloric acid lignin gives acetoguaiacol and propioguaiacol, but several model substances for lignin, including guaiacylglycerol, do not.

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Acetoveratrol $\xrightarrow[\text{buffer pH 8·5}]{\text{NaSH or}}$ AG

HCl—lignin $\xrightarrow{\text{NaSH}}$ AG + PG

$CH_3 \cdot CO \cdot CH_2R$ $\xrightarrow{\text{NaSH}}$ Stable

$CH_2OH \cdot CO \cdot CH_2R$

    $\xrightarrow{\text{NaSH}}$ Resin, no AG or PG

    $\xrightarrow{\text{NaSH then NaBH}_4}$ Stable

$CH_2OH \cdot (CHOH)_2 \cdot R$ $\xrightarrow{\text{NaSH}}$ Only traces of AG,
(Guaiacylglycerol)   no PG

R = (structure with OCH₃ and OH on benzene ring)

AG = acetoguaiacol

PG = propioguaiacol

Figure 8. Sodium hydrogen sulphide digestions of lignin models and hydrochloric acid lignin

Thus, the formation of acetoguaiacol, propioguaiacol and coniferylaldehyde under these conditions would appear to be very specific.

Figure 9 shows the behaviour of the lignin model ω-hydroxypropioguaiacol. With sodium hydrogen sulphide this substance gives an organic mono-

$$R \cdot CO \cdot CH_2 \cdot CH_2OH \xrightarrow{\text{NaSH}} (R \cdot CO \cdot CH_2 \cdot CH_2)_2S + AG + PG$$
ω-hydroxypropioguaiacol

Buffer pH 8·5 → AG (13% by wt.)

NaBH₄ → $R \cdot CHOH \cdot CH_2 \cdot CH_2OH$ → NaSH → AG   PG   CA

Buffer pH 8·5 → AG + PG traces

NaSH → AG (2 parts) PG (1 part)

$(R \cdot CO \cdot CH_2 \cdot CH_2)_2O$
or
$R \cdot CO \cdot CH_2 \cdot CH_2 \cdot OC_2H_5$

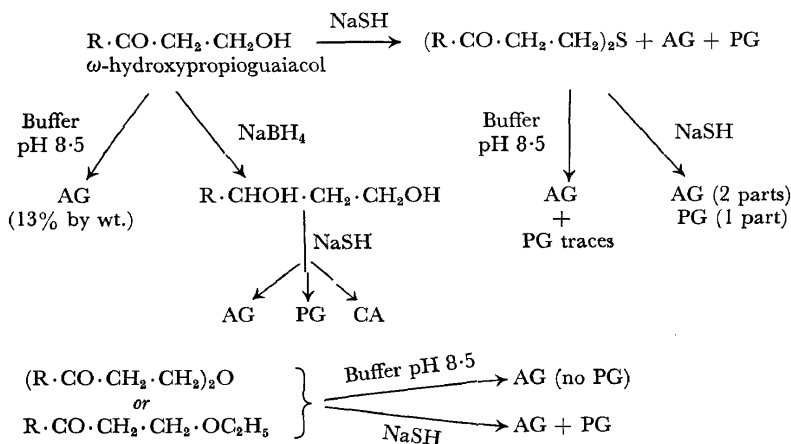$\xrightarrow{\text{Buffer pH 8·5}}$ AG (no PG)

$\xrightarrow{\text{NaSH}}$ AG + PG

Figure 9. Reactions of ω-hydroxypropioguaiacol and some of its ethers

sulphide, which on further digestion is split into acetoguaiacol and propioguaiacol. ω-Hydroxypropioguaiacol was reduced with sodium borohydride to the corresponding diol. On sodium hydrogen sulphide digestion the latter gives acetoguaiacol and propioguaiacol, as well as coniferyl aldehyde. Also alkyl ethers of ω-hydroxypropioguaiacol give acetoguaiacol and propioguaiacol on sulphurization.

It may be mentioned that Oksanen, at Helsinki has obtained strong chromatographic evidence in four different systems[22] indicating that free ω-hydroxypropioguaiacol occurs in the bark of pine. Free guaiacylglycerol also seems to be present. After spruce wood had been digested with sodium hydrogen sulphide Ashorn found a chromatographic spot which could be due to ω-hydroxypropioguaiacol.

$$
\begin{array}{c}
CH_2OH \\
| \\
CH_2 \\
| \\
CO \\
| \\
R
\end{array}
\quad
\xrightarrow[\substack{\text{Retro-aldol} \\ \text{condensation}}]{OH^-}
\quad
\begin{array}{c}
CH_3 \\
| \\
CO \\
| \\
R
\end{array}
+ CH_2O \;\text{found}
$$

(AG)

$$\downarrow +H_2S$$

$$
\begin{array}{c}
CH_2-S-CH_2 \\
| \qquad\quad | \\
CH_2 \quad\; CH_2 \\
| \qquad\quad | \\
CO \quad\;\; CO \\
| \qquad\quad | \\
R \qquad\;\; R
\end{array}
\;\xrightarrow{H_2O}\;
\begin{array}{c}
H_2C\cdot SOH \\
| \\
CH_2 \\
| \\
CO \\
| \\
R
\end{array}
\;\xrightarrow{-H_2S}\;
\begin{array}{c}
CHO \\
| \\
CH_2 \\
| \\
CO \\
| \\
R
\end{array}
\;\xrightarrow[-HCO\cdot OH]{H_2O}\;
\begin{array}{c}
CH_3 \\
| \\
CO \\
| \\
R
\end{array}
$$

$$CH_3\cdot CH_2\cdot CO\cdot R$$

(PG)
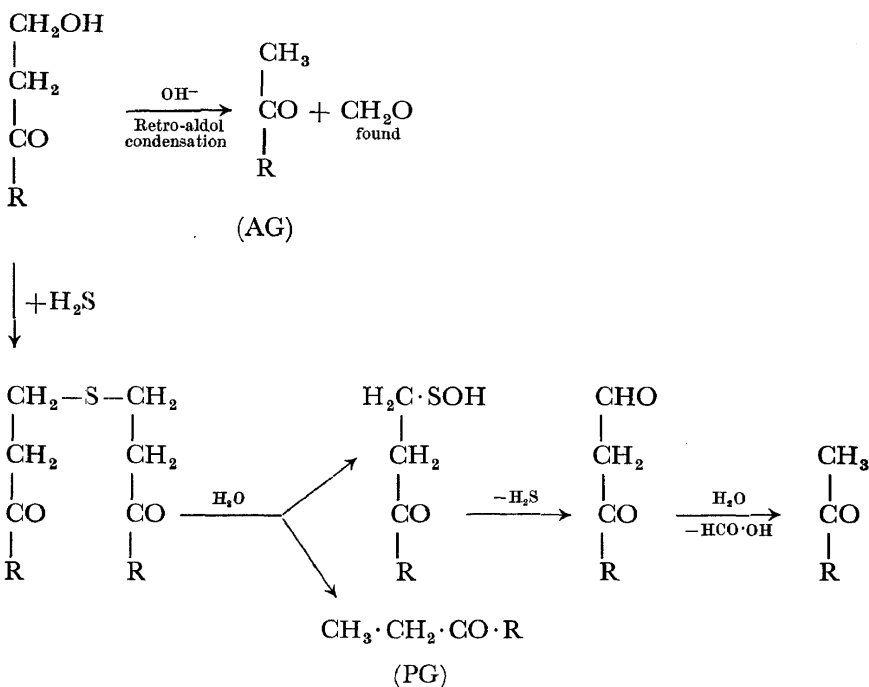
Figure 10. Formation of acetoguaiacol and propioguaiacol from ω-hydroxypropioguaiacol

Figure 10 gives a possible reaction mechanism for the formation of acetoguaiacol with an alkaline buffer solution in the absence of sulphur; the retro-aldol reaction would lead to the formation of formaldehyde, which was, in fact, found in the solutions. The figure also indicates mechanisms for the sulphurization, for the conversion of the sulphide to propioguaiacol, and, *via* a sulphenic acid, to acetoguaiacol.

At this stage I might mention that acetoguaiacol[23] in particular, but also propioguaiacol, have been found in considerable amounts in kraft black liquor, and also that acetoguaiacol is formed on further heating of
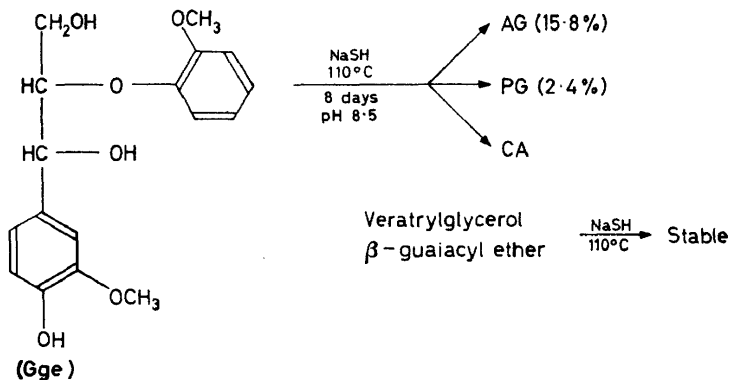
Figure 11. Yields of acetoguaiacol and propioguaiacol from guaiacylglycerol-β-guaiacyl ether

isolated kraft or even soda lignin with sodium hydroxide solution at 170°[23,24]. Acetoguaiacol can thus be formed, even without any sulphur containing reagent, but its formation is very much stimulated by the presence of sulphide ions.

It would be tempting to assume that the formation of acetoguaiacol, propioguaicol and coniferylaldehyde from lignin on digestion with sodium hydrogen sulphide proceeds *via* ω-hydroxypropioguaiacol. In Ashorn's opinion it is not impossible that ω-hydroxypropioguaiacol could be formed from guaiacylglycerol β-guaiacyl ether (Gge) and analogous groups in lignin (*Figure 11*). With sodium hydrogen sulphide this substance gives a considerable yield of acetoguaiacol, and also some propioguaiacol and coniferylaldehyde. If the phenolic hydroxyl group in Gge is etherified we arrive at veratrylglycerol β-guaiacyl ether, which, however, is stable under the sulphurization conditions. This coincides well with the
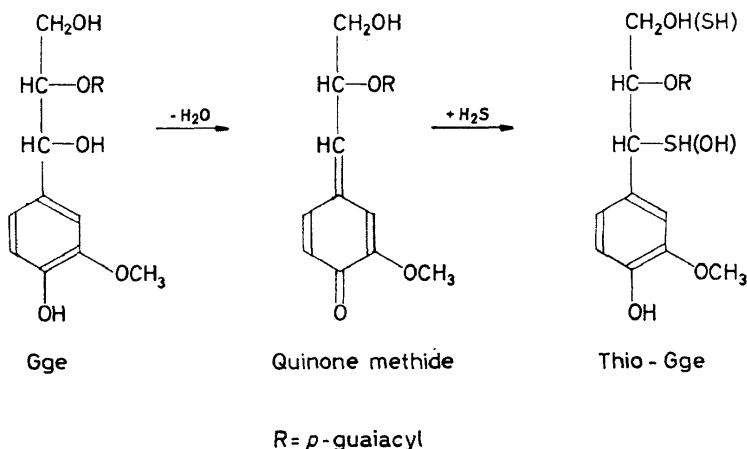
R = *p*-guaiacyl

Figure 12. Sulphurization of guaiacylglycerol β-guaiacylether

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assumption that the reaction (*Figure 12*) involves a quinone methide inter-mediate. The latter cannot be formed if the hydrogen atom of the free phenolic hydroxyl group has been substituted with a methyl group, or a group larger than methyl. By addition of hydrogen sulphide the quinone methide can give thioguaiacylglycerol β-guaiacyl ether. Later, I will give experimental evidence which makes it probable that the thiocompound and the corresponding group in hydrogen sulphide lignin have their sulphur partly in the γ-position. This is indicated by the parentheses in the for-mula. Then (*Figure 13*) the phenol ether group OR is split off under the influence of the sulphur atom, for instance by formation of an episulphide intermediate. This would be similar to epoxides known in analogous fissions of phenolglycosides and saccharides. Epoxides are also supposed by Gierer to be intermediates in the digestion of lignin with sodium hydrox-ide. Such an episulphide would then by hydrolysis and rearrangement eventually give ω-hydroxypropioguaiacol. If treated with more hydrogen sulphide ion or mercaptan the episulphide would give a dithiol or a thiol ether. This would then be rearranged into a model for a hydrogen sul-phide lignin, with a high sulphur content. *Figure 14* again shows the way from ω-hydroxypropioguaiacol to acetoguaiacol and propioguaiacol, and, further, how coniferylaldehyde can be formed from the thioguaiacylglycerol

$CH_2OH(SH)$

$HC—OR$

$HC—SH(OH)$

R

Thio-Gge
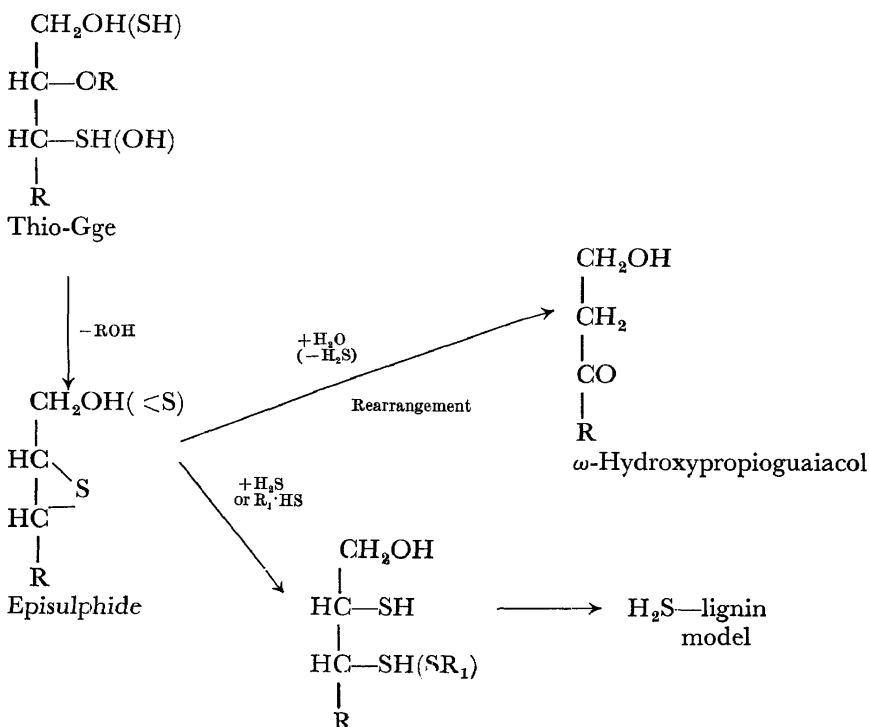
Figure 13. Formation of ω-hydroxypropioguaiacol and a hydrogen sulphide lignin model *via* a hypothetical episulphide; $R_1 \equiv$ alkyl group

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β-guaiacyl ether and analogous groups in lignin. The ratio of acetoguaiacol to propioguaiacol obtained, and also the rate of the formation of acetoguaiacol are considerably greater in the sulphurization of guaiacylglycerol β-guaiacyl ether than in the corresponding treatment of ω-hydroxypropioguaiacol. Therefore, Ashorn assumes that at least one other reaction mechanism, involving an unknown intermediate, is at work at the same time, forming about two thirds of the acetoguaiacol. The remaining third of the acetoguaiacol, and the whole of the propioguaiacol, could be formed *via* ω-hydroxypropioguaiacol.

These reaction mechanisms and possible intermediates are, of course, to a great extent hypothetical. But, independently of the nature of the intermediates, there remains the experimental fact that, on treatment with sodium hydrogen sulphide solutions, lignin and dimericlign in models, such as guaiacylglycerol-β-guaiacyl ether give considerable yields of the monomeric products acetoguaiacol, propioguaiacol and coniferylaldehyde. This proves that the hydrogen sulphide ion can split not only dialkyl ethers but also alkyl aryl ethers as well, provided that the phenolic hydroxyl group is free. This gives strong support to the ether cleavage theory.
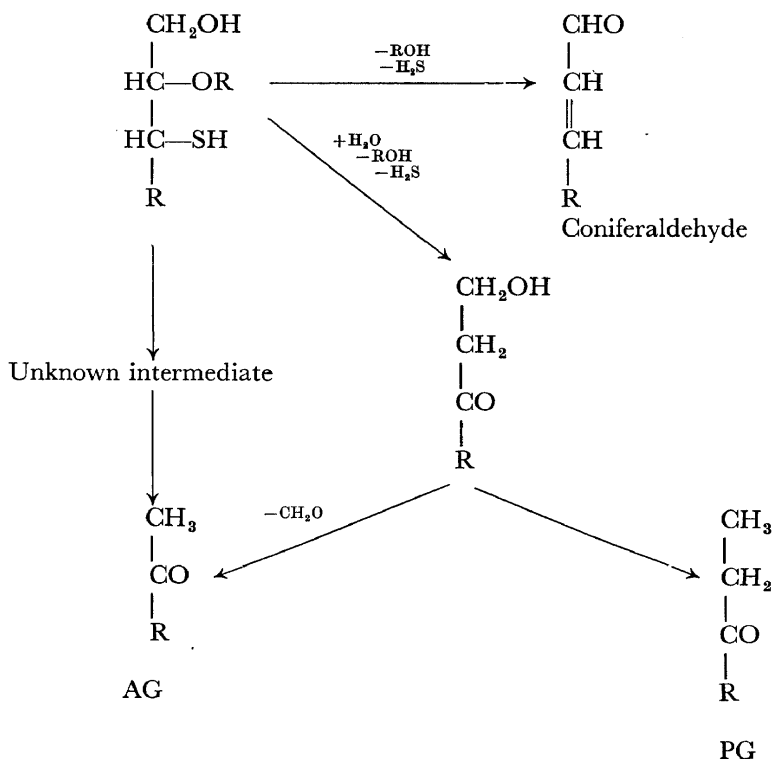

Figure 14. Scheme for the formation of acetoguaiacol, propioguaiacol and coniferylaldehyde from sulphurized guaiacylglycerol β-guaiacyl ether

OTHER REACTIONS

Figure 15 contains a scheme for the results obtained by Hästbacka on hydrogenation of hydrogen sulphide lignin with Raney nickel and boiling ethanol. He got a high yield, about 40 per cent, of ether-soluble products, which he then investigated by chromatography. It had previously been discovered, *e.g.* by model experiments by Juslén in Helsinki[25], that Raney nickel in such a procedure replaces sulphur by hydrogen. *p*-Propyl-guaiacol, 3-guaiacyl- and 1-guaiacylpropanol were detected chromato-graphically. In an analogous hydrogenation of the monosulphide of ω-hydroxypropioguaiacol, *p*-propylguaiacol and 1-guaiacylpropanol were obtained. The fact that thiolignin in addition gave also 3-guaiacylpro-panol makes it probable that it contains sulphur bound in the 3-(or γ-) as well as in the 1- (or α-) position, as indicated earlier by the parentheses in *Figure 13*.
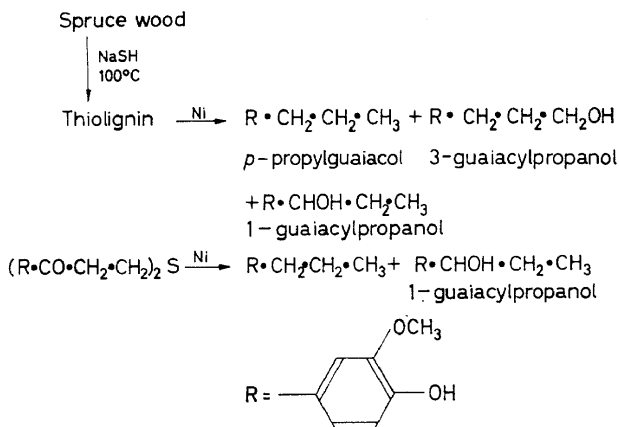
Figure 15. Desulphurization of thiolignin with Raney nickel

In addition to the ether cleavage and blocking reactions described, other reactions also occur with lignin in kraft pulping. This can be proved, *e.g.* by chromatography of the ether-soluble phenolic and acidic fractions of kraft black liquor. The amount of ether-soluble phenolic fraction alone is about 4 per cent of the organic matter, or 8 per cent of the original lignin. The ether-soluble acidic fraction is still greater, but it contains much material of carbohydrate origin. My co-workers and I have studied these fractions, and also the interesting products which are formed on heating kraft black liquors under pressure with sodium sulphide–sodium hydroxide solutions at 250–290°/65 atm. This reaction, in a way, is a continuation of the kraft pulping reaction after the cellulose has been removed. At this elevated temperature the sulphide ion has a still stronger ether splitting effect, cleaving also the simple methoxyl groups of lignin and forming methyl sulphide. This is now a commercially important reaction of which I will give a more detailed description at the *Tappi* Lignin Symposium in Chicago.

Here I will first describe some of the chromatographic methods used for the investigation of the ether soluble fractions.

CHROMATOGRAPHIC INVESTIGATIONS

The ether-soluble phenols and acids of the original and alkali-heated spent liquors have been investigated, mainly by the use of column and paper chromatography, but partly with the aid of new systems specially developed by Halmekoski. He uses, among other things, papers impregnated with sodium molybdate or sodium tungstate[26]. In paper chromatography we have worked extensively with the Freudenberg-Lehmann system II[27], *i.e.* using papers impregnated with formamide, with xylene and methylethyl-ketone as developing solvents. Interesting variations of this system which have been tried out in collaboration with Räisänen are the use of formamide-impregnated paper and chloroform, or a mixture of light petroleum with 2 per cent xylene. Other systems which we have used are simply 2 per cent acetic acid, ethanol–ammonia, butanol on phosphate buffer impregnated paper of various pH, *etc.* For column chromatography we use columns filled with polycaprolactam or Perlon powder, and water with rising contents
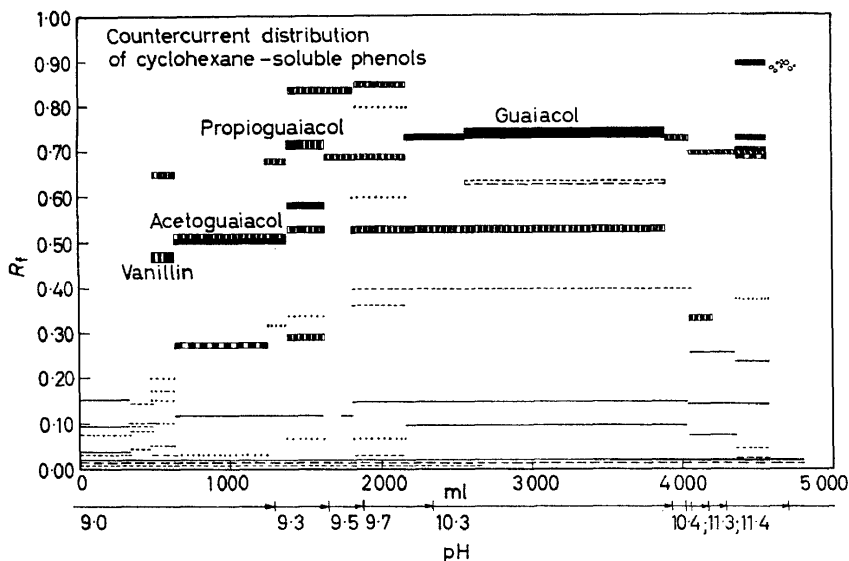

Figure 16. Countercurrent distribution of cyclohexane-soluble phenols of kraft black liquor in butanol-phosphate buffer and paper chromatography of the fractions in the Freudenberg-Lehmann system

Spots coloured with diazotized *p*-nitroaniline ————————————————

Spots fluorescing in ultra-violet light — — — — — — — — — —

Spots fluorescing in ultra-violet light after treatment with ammonia only ·

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of methanol as solvent according to Grassmann *et al.*[28]. Better results are obtained with polycaprolactam powder impregnated with formamide, followed by elution with chloroform or other solvents insoluble in formamide. Electrophoresis, thin layer chromatography according to Stahl[29], and countercurrent distribution by means of apparatus developed in the Biochemical Research Institute in Helsinki by Hietala[30] have also been used.

The spots containing phenolic substances can be coloured by diazotized sulphanilic acid or diazotized *p*-nitroaniline which give characteristic colours for various types of compounds.

Figure 16 summarizes the results of countercurrent distribution of the original spent kraft liquor phenols soluble in cyclohexane, with butanol–phosphate buffer systems with pH values rising from 9 to 11·5, and paper chromatography of the fractions. Throughput in ml are put on the abscissa and the R_f values in the Freudenberg-Lehmann system on the ordinates. Various colourations in ultra-violet light, or after spraying with soda-alkaline diazotized *p*-nitroaniline, are marked by a dotted line. In this way every line represents one substance and the thickness of the lines represents, very roughly, the amounts. We see that this rather simple phenolic fraction contains at least 50 substances, most of which, however, are present only in small amounts. However, the system has proved to be very effective as the homologues vanillin, acetoguaiacol and propio-guaiacol have been completely separated from each other, without any overlapping.

In original kraft black liquor $(R = guaiacyl, p)$:

C_6H_5OH, $C_6H_4(OH)_2$ (o), $\underline{RH}$, $(HO)_2C_6H_3 \cdot CHO$ (p), $\underline{R \cdot CHO}$,

$\underline{R \cdot COOH}$, $\underline{R \cdot CO \cdot CH_3}$, $R \cdot CO \cdot C_2H_5$, $R \cdot CH_2CH_2OH$, $R \cdot CH_2 \cdot COOH$

$R \cdot CH_2 \cdot CH_2 \cdot CH_2OH$, $R \cdot CH_2 \cdot CH_2 \cdot COOH$, $R \cdot CH=CH \cdot R$,

$HOC_6H_4 \cdot COOH$

(all p), methylcyclopentenolone.

*In* Na_2S-*pressure heated kraft black liquor*, 255 *or* 285°C:

$\underline{C_6H_4(OH)_2}$, $\underline{CH_3 \cdot C_6H_3(OH)_2}$, $\underline{C_2H_5 \cdot C_6H_3(OH)_2}$,

RH, $(HO)_2C_6H_3 \cdot CHO$, $R \cdot CHO$, $(HO)_2C_6H_3 \cdot CO \cdot CH_3$,

$\underline{(HO)_2C_6H_3 \cdot CH_2 \cdot COOH}$ (all p)

Homoprotocatechuic acid

Figure 17. Formulae of ether-soluble substances found in original and pressure heated kraft black liquor; underlined formulae belong to substances found in considerable amounts
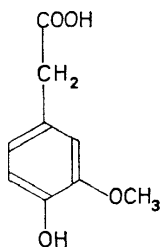
Figure 17 shows some of the ether-soluble substances which my co-workers and I found in the original kraft black liquor, and in the same liquor after pressure heating with sodium sulphide at about 280° and 65 atm pressure.
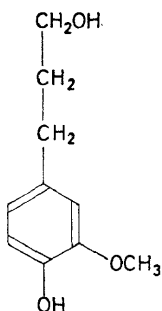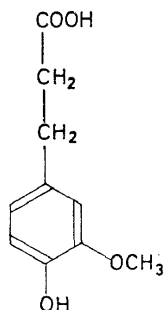
CH₂OH

CH₂
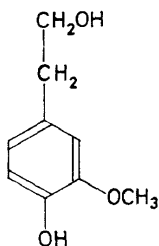
2-guaiacylethanol

COOH

CH₂

Homovanillic or 2-guaiacylacetic acid

CH₂OH

CH₂

CH₂

3-guaiacylpropanol

COOH

CH₂

CH₂

3-guaiacylpropionic acid

Figure 18. Formulae of pairs of phenol alcohols and phenol carboxylic acids found in original kraft black liquor

Most of the substances have been identified chromatographically, usually in four different systems. The formulae underlined belong to substances which have been found in considerable amounts. We see that, in the original black liquors, phenol alcohols occur together with the corresponding phenolcarboxylic acids, for instance guaiacylethanol and homovanillic acid, guaiacylpropanol and guaiacylpropionic acid (*Figure 18*). This

CH₃

H₂C—C=C—OH

H₂C——CO

Methylcyclopentenolone

CH₃

CH₂

CO

Propioguaiacol

CHO
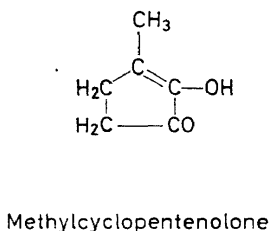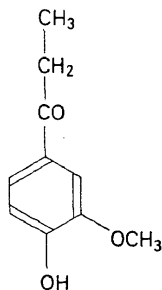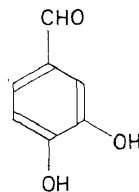
Protocatechualdehyde

Figure 19. Formulae for 3-methvl-cyclopent-2-en-2-ol-1-one, propioguaiacol and proto-catechualdehyde

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indicates, perhaps, disproportionation reactions of the Cannizzaro type. Guaiacol, vanillin, vanillic acid and acetoguaiacol are all found to be present in considerable amounts, from 2 to 5 pounds per ton of pulp.

The occurrence of phenolcarboxylic acids in black liquor is of interest in view of the fact that commercial kraft and soda lignin also contain carboxylic groups to the extent of about one carboxylic group for every five phenylpropane units. This has been shown by Ekman in Helsinki[9]. Since the carboxyl groups occur also in soda lignin, it is possible that the Cannizzaro-type reactions are mainly due to the hydroxyl ions, and not to the sulphide ions.

The methylcyclopentenolone (*Figure 19*) is an alicyclic compound that we have shown to be formed from galactose, and probably other simple sugars, and also from spruce wood with a 4 per cent sodium hydroxide solution at 100° [31].

Most of the substances found in the pressure-heated black liquors are products of strong demethylation. We have found that pyrocatechol, to the extent of about 2 pounds per ton of pulp, and also some protocatechualdehyde (*Figure 19*) occur in the original kraft black liquor. This seems to show that the demethylation reactions start to some extent in the kraft digestion (*cf*. 32, 33).

The question open to discussion is whether some of the ether-soluble substances found in commercial kraft black liquor originate from lignans or other simple compounds occurring in the wood, or even in the bark. Oksanen, in Helsinki, provided chromatographic evidence for the occurrence of the following substances, among others, in the bark of pine: *p*-hydroxybenzoic, vanillic, ferulic, protocatechuic, caffeic, 3-guaiacylpropionic acid, 1-guaiacylpropanol, ω-hydroxypropioguaiacol and guaiacylglycerol. A series of pressure heatings of lignin models with sodium sulphide solution at 250–290° may help to answer this question. Among other things, pyrocatechol was derived from methylcatechol and guaiacol, and pyrocatechol and methylcatechol were obtained from pinoresinol, dehydrodi-isoeugenol and dihydrodehydrodi-isoeugenol. The two latter compounds gave propylguaiacol and propylcatechol as well[34]. Thus, there can be no doubt that heating with sodium sulphide at elevated temperatures can break carbon–carbon bonds. For instance, the pyrocatechol in the kraft black liquor might have been formed by a reaction which involves cleavage of carbon–carbon bonds. To what extent this is an effect of hydroxyl ions or of sulphidic ions is still an open question.

CONCLUSION

To summarize, it seems that the favourable effect of sulphur in kraft pulping depends partly on sulphurization of reactive groups in lignin, probably phenolic alcohol groups. These are thus prevented from reacting by condensation. Another important effect is the fission of dialkyl- and arylalkyl ether bonds in phenylpropane units carrying a free phenolic hydroxyl group. Fissions of carbon—carbon bonds, and oxidation–reduction reactions of the Cannizzaro type, also occur during kraft pulping, but it is quite possible that these reactions are mainly due to the hydroxyl

ions of the liquor. Many questions are still open, but the development of new qualitative and quantitative chromatographic and other methods offer improved facilities for further research.

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