Phenolic compounds in kraft black liquor

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SUMMARY: The prominent phenolic compounds with one aromatic ring in kraft black liquor were analysed by a combination of liquid chromatography, gas chromatography and mass spectrometry. Extracted spruce meal was cooked both under mild, conventional conditions and under extremely severe conditions. In all, the analyzed phenolic compounds amounted to 0.6 kg per 100 kg of dry wood under conventional conditions.

In addition to 2-methoxyphenol, vanillin and 4-hydroxy-3-methoxyacetophenone, several phenolic alcohols and carboxylic acids with the same aromatic substitution were isolated and identified. The yield of related 3,4-dihydroxyphenyl-substituted compounds increased under severe conditions.

☐ De fenoliska beståndsdelarna med en aromatisk kärna, som förekommer i betydande mängd i svartlut, bestämdes genom en kombination av vätskekromatografi, gaskromatografi och masspektrometri. Extraherat granpulver kokades dels under milda, konventionella betingelser dels under extremt hårda betingelser. Den totala mängden identifierade fenoliska substanser var vid det konventionella koket 0,6 kg per 100 kg torr ved.

Förutom 2-metoxifenol, vanillin och 4-hydroxi-3-metoxiacetofenon isolerades och identifierades flera fenoliska alkoholer och karboxylsyror med samma aromatiska substitution. Vid hårda kokbetingelser ökade mängden 3,4-dihydroxifenyl-substituerade föreningar.

☐ Die phenolischen Verbindungen mit einem aromatischen Ring, die in grösserer Menge in der Schwarzlauge vorkommen, wurden durch eine Kombination von Flüssigkeitschromatographie, Gaschromatographie und Massenspektrometrie analytisch erfasst. Extrahiertes Fichtenholzmehl wurde sowohl unter milden, konventionellen Bedingungen wie auch unter extremen Bedingungen gekocht. Die totale Menge identifizierter phenolischer Substanzen betrug für eine konventionelle Kochung 0,6 kg per 100 kg trockenes Holz.

Ausser 2-Methoxyphenol, Vanillin und 4-Hydroxy-3-Methoxyacetophenon wurden phenolische Alkohole und Karbonsäuren mit gleicher Substitution im Kern isoliert und identifiziert. Die Ausbeute an 3,4-dihydroxyphenylsubstituierten Verbindungen stieg bei extremen Kochbedingungen.

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As a part of a research program directed towards elimination of aromatic compounds from pulp mill effluents by adsorption on ion exchange resins and other cross-linked polymers a study was carried out on the sorption of low molecular weight aromatic compounds present in kraft black liquor. Chromatography on an anion exchange resin in aqueous ethanol by a method described in a separate paper (1) revealed that a technical black liquor contained several hundreds of compounds which gave a strong absorption in the ultraviolet. To simplify the study of phenolic compounds a liquor from a laboratory cook of spruce meal freed from extractives was investigated. The study was restricted to compounds with one aromatic ring.

Experimental

The spruce meal (0.5—1.4 mm) extracted for 24 hours with 95% ethanol and then for 24 hours with dichloromethane was subjected to sulphate cooking in a rotating autoclave for 95 min at 170°C (cook M). The ratio wood:liquor was 1:8 (w/w). The white liquor was prepared by addition of sodium hydroxide to a freshly prepared solution of sodium hydrogen sulphide. The composition corresponded to 0.092 M Na_2S+0.36 M NaOH. The yield of pulp was 48.9% and the kappa number was 47.

A second cook (S) was made under conditions which were much more severe than those used industrially. The cooking time was increased to 290 min and the white liquor concentration to 0.48 M Na_2S+2 M NaOH.

Formic acid was added to the black liquors (including washings) to decrease the pH to 10.3. After ultrafiltration (Amicon UM 05) the pH of the ultrafiltrates was decreased to 6.1 by addition of formic acid. The ultrafiltrates were evaporated to a volume of 100 ml and subjected to liquid chromatography as described below. Before rechromatography the collected fractions containing ethanol and formic or acetic acids were diluted with water and repeatedly evaporated (35°C) to a small volume to remove the volatile compounds.

Both liquors were chromatographed by the first method described below. The second method was applied as a check on the results obtained for cook M. A tentative identification of the compounds of which authentic samples were available (denoted a in the tables) was obtained from the volume distribution coefficients determined by rechromatography. Final identification was obtained by gas chromatography (GLC) and gas chromatography-mass spectrometry (GC-MS) after preparation of trimethylsilyl (Me_3Si) derivatives. The structure determination of the compounds is discussed below.

For non-electrolytes of which authentic samples were available quantitative determinations based on the areas of the chromatographic peaks recorded in the UV by liquid chromatography were in good agreement with determinations by GLC as separately described (2).

Anion exchange chromatography followed by chromatography on polyvinylpyrrolidone

The ultrafiltrate (corresponding to 50 g wood) was passed through an anion exchange resin in the acetate form (Dowex 1-X8, 25—32 μm, 9×850 mm). The amount of aliphatic monocarboxylic acids was much larger than the exchange capacity of the resin which means that the major part of these acids passed into the effluent. Since $R^1CH(OH)CH(OH)CH_2OH$ (see *table 1*), which is held very loosely by the resin compared to other phenols (3), was retained under the applied conditions it is reasonable to assume that no appreciable amounts of phenols were lost.

Elution was then carried out with 0.02 M acetic acid in 9% (w/w) ethanol to obtain a crude separation of the retained phenolic compounds. The solutes (mainly aliphatic acids and their sodium salts) which appeared in the first part of the eluate (within one bed volume) were not investigated. Five fractions were cut as indicated in

Table 1. Phenolic compounds in black liquors from mild (M) and severe (S) kraft cookes

Ethanol in eluent %w/w	Fraction (bed volumes)	Compound	Yields g per 100 kg wood		Liquid chromatography D_v on Dowex 1-X8 (0.02 M HOAc)			Gas chromatography of Me_3Si derivatives	
			Cook M	Cook S	9% EtOH	30% EtOH	50% EtOH	MU^{Me}	ΔMU
9	1—3	$R'CH(OH)CH(OH)CH_2OH$[1](a)	0.4	2.9	1.6			20.55	0.11
9	3—6	$R'CH_2CH(OH)CH_2OH$ (a)	2.2	2.6	4.5			19.87	0.62
		$R'CH(OH)CH_3$	2.8		4.5			15.96	0.99
9	6—9	$R'CH_2CH_2OH$ (a)	7.3	45	7.2	2.0		17.01	1.12
9	9—15	$R'CH_2CH_2CH_2OH$ (a)	68	148	13.2	2.4		18.10	1.17
		$R'H$ (a)	158	n.d.	14.0	4.1		12.08	1.27
9	15—18	$R'COCH_3$ (a)	85	181	25.8	3.9		16.97	2.00
14	18—29	$R'CHO$ (a)	150	116	37.6	6.3		16.20	1.97
30	29—37	Unknown[2]	14	3.2		12.0		15.73	1.56
		$RCHO$ (a)	10	1.7		12.8	3.1	14.70	1.48
50	37—39	$R''CH_2CH_2OH$[1]		2.2				17.74	0.58
		$R''CH_2CH_2CH_2OH$	0.8	13			4.3	18.74	0.57
50	39—43	$R''COCH_3$	0.6	26			6.2	17.70	1.40
		$R''H$ (a)	23	17			7.4	13.04	0.77
50	43—52	$R''CHO$ (a)	1.4	14			14.1	17.02	1.32

Key: R' = 4-hydroxy-3-methoxyphenyl; R = 4-hydroxyphenyl; R'' = 3,4-dihydroxyphenyl; (a) denotes same retention data as authentic samples; n.d. = not determined.

[1] No mass spectrum

[2] Data from GC-MS suggest RCH_2COCH_3 or an isomer

table 1. After 18 bed volumes the ethanol concentration was increased and the elution continued as shown in the table. No aromatic compounds with one aromatic ring were found in a final fraction, eluted with 95% ethanol. The chromatogram indicated that compounds with two or more aromatic nuclei were present. When 60 bed volumes of the weakly acidic eluent had been passed through the column, the UV-detector indicated that the elution of phenols was complete. The phenolic carboxylic acids were then eluted as a group with 5 M acetic acid in 92% (w/w) ethanol.

The fractions eluted with 0.02 M acetic acid in aqueous ethanol were rechromatographed on an anion exchange resin in the acetate form (Dowex 1-X8, 20—27 μm, 4×280 mm). Aqueous ethanol (at least two concentrations) 0.02 M with respect to acetic acid was used as eluent and the recorded volume distribution coefficients (D_V) given in table 1 were compared with those of authentic substances. For additional identification and to obtain a resolution of compounds which gave overlapping peaks some fractions were also chromatographed on a column packed with crosslinked polyvinylpyrrolidone (PVP). In these experiments aqueous 0.02 M acetic acid was used as eluent (3).

As expected, the carboxylic acid fraction contained large amounts of aliphatic acids. One half of the fraction was rechromatographed on PVP (60—75 μm, 6× 650 mm). The aliphatic acids were eluted with 0.02 M aqueous acetic acid (1.6 bed volumes). To permit a separation of these from aromatic acids held loosely by this resin, the elution was made at a very low nominal linear flow (0.3 cm min^{-1}). In addition to aliphatic acids which, as expected, were eluted first (3) three distinct peaks containing four identified aromatic acids (*table 2*)

Table 2. Aromatic carboxylic acids in black liquors from mild (M) and severe (S) kraft cooks

Compounds	g per 100 kg wood		Liquid chromatography D_V on PVP 0.02 M HOAc	D_V on Dowex 1-X8 3 M HOAc	Gas chromatography Retention of Me_3Si derivatives	
	Cook M	Cook S			MU^{Me}	ΔMU
$R'CH_2CH(OH)COOH$(a)	11	85	2.2	13.9	20.26	1.15
$R'CH_2C(CH_3)(OH)COOH$	14	100	2.6	10.8	20.27	0.86
$R'CH_2CH_2CH(OH)COOH$	23	147	5.0	26.2	21.46	1.18
$R'CH_2COOH$(a)	1.1	18	5.3	6.8	17.60	1.70
$R'COOH$(a)	38	59	25	12.7	17.57	1.58

were obtained. To elute vanillic acid and other compounds retained more strongly the eluent was changed to 0.02 M acetic acid in 50% ethanol.

Group separation on XAD-2 followed by anion exchange chromatography

Another separation scheme was used for the analysis of a second ultrafiltrate from liquor M (corresponding to 25 g wood). The solution was passed through a column packed with Amberlite XAD-2 (20×270 mm) which at pH 6 effectively retains phenolic compounds such as vanillin (4) while both aliphatic and aromatic acids should be easily displaced with water. After washing with 10 bed volumes of water the aromatic compounds were eluted with 92.5% (w/w) ethanol.

The eluate was chromatographed on the acetate form of Dowex 1-X8. Fourteen fractions were taken by stepwise elution with water, followed by ethanol of increasing concentration (acidified with acetic acid) and analyzed by GLC and GC-MS. All phenolic compounds found by the first method were present in the eluate except for $R'CH(OH)CH(OH)CH_2OH$. The amount of $R'CH_2CH(OH)CH_2OH$ was only about half of that observed in the previous experiment. Evidently, these strongly polar compounds passed into the effluent from the treatment with the XAD-2 resin. The determinations of the other compounds differed from the mean by less than ±5%.

The effluent from the XAD-2 column, including washings (water), was passed through a cation exchange column (Dowex 50-X8, H^+; 20×300 mm) to liberate H_2S. After washing with 10 bed volumes of water and evaporation, the solution (10 ml) was neutralized with sodium hydroxide (pH 10) and applied to a column (9×850 mm) packed with Dowex 1-X8, 25—32 μm in the acetate form. Only trace amounts of UV-absorbing compounds were eluted with water followed by 50% ethanol. After rinsing with water the aliphatic acids were eluted with 15 bed volumes of 0.16 M sodium acetate solution. No absorption in the UV was recorded. The column was again rinsed with water. The aromatic acids were then eluted with 3 M aqueous acetic acid. Twelve fractions were collected. They were rechromatographed on PVP to remove aliphatic acids. These were washed out with water. The aromatic acids were then eluted with 50% ethanol and analyzed by GLC and GC-MS. The same acids as obtained in the previous run were identified. In addition to the acids listed in table 2, minor amounts of several unidentified acids were present.

Analysis by gas chromatography

Water was removed from the fractions by repeated evaporations with ethanol to a small volume. After evaporation to dryness the samples were dissolved in pyridine. The fractions suspected to contain aldehydes or ketones were reacted with CH_3ONH_2, HCl to convert these compounds to *O*-methyl oximes. All samples were silylated in pyridine to convert hydroxyl and carboxyl groups to the corresponding Me_3Si ethers and esters.

Temperature-programmed GLC was performed on an instrument with two parallel packed columns coupled to one injector but with separate flame ionization detectors and recording devices. A methyl silicone and a phenyl silicone were used as stationary phases. Methylene unit (MU) values which relate the retention of a compound to the *n*-alkane series were used as the measure of retention (tables 1 and 2). The value on the non-polar methyl silicone (MU^{Me}) is determined by the molecular size of the solute while the difference ΔMU defined as (MU^{Ph}—MU^{Me}) reflects polar properties of the solute. Relations between the structures of Me_3Si derivatives and their retentions (MU^{Me} and ΔMU) have been demonstrated in a GLC study of different structural categories of phenolic compounds (2). Lignin-related compounds with one aromatic nucleus tend to have $MU^{Me} < 22$ and $\Delta MU < 2.5$ permitting a distinction from compounds with two or more nuclei which normally have higher values. The ΔMU values are higher with the phenolic acids and oximes (aldehydes and ketones) than with the phenolic alcohols (2). They tend to decrease with increasing molecular size and increase with increasing number of methoxyl groups.

Mass spectrometry and structural analysis

The characteristic features of and the conclusions drawn from the mass spectra of the compounds from the mild cook are summarized in *table 3.*

Four alcohols were identified by their mass spectra and their chromatographic behaviour. The masses (M) of the molecular ions were obtained directly from prominent peaks in the spectra. The molecular weight was confirmed by the presence of M-15 peaks which are characteristic of Me_3Si derivatives. Benzylic cleavage gives rise to prominent and very characteristic ions containing the aromatic ring. Thus, the abundant *m/e* 209 ions indicate one MeO and one Me_3SiO substituent on an aromatic ring linked to a methylene group. A loss of 30 atomic mass units (amu) from several ions retaining the aromatic ring is ascribed to an *ortho* effect and indicates that the OMe and $OSiMe_3$ groups are *ortho* to each other. The 1,3-elimination of Me_3SiOH (90 amu), which occurs more easily than 1,2-elimination, is promoted by benzylic activation for the prominent 3-aryl-1-propanol and the resulting abundant ions confirm the structure. Analogous M-90 ions can be formed with the corresponding 3-aryl-1,2-propanediol, and the abundant and characteristic *m/e* 205 ions formed by a favoured benzylic α-cleavage confirm this structure. The interpretations of the spectra were supported by comparisons with the spectra of the derivatives of several related phenolic alcohols. Comparison of the MU and ΔMU values with those of related reference samples (2) provided additional support for the structures deduced. The 4-hydroxy-3-methoxyphenyl structure, characteristic of lignin, would be expected to be retained and the substitution pattern of the aromatic ring was not further studied.

The molecular weight of the aldehyde and ketone

Table 3. Mass spectrometric[1] characteristics of prominent phenolic compounds as O-methyl oxime and trimethylsilyl (T) derivatives

Deduced structure	$M^{+\cdot}$		$[M-15]^+$		$Ar-\overset{\vert}{\underset{\vert}{C}}+$		Other specific ions					
	m/e	%	m/e	%	m/e	%	m/e	%	ion	m/e	%	ion
Alcohols												
(MeO, TO)$C_6H_3CH(OT)CH_3$	312	10	297[2]	100	223[2]	20	267	10	$[M-30]^{+\cdot}$	192	80	$[M-90-30]^{+\cdot}$
(MeO, TO)$C_6H_3CH_2CH_2OT$	312	20	297	10	209	100	282	5	$[M-30]^{+\cdot}$	223	20	$[M-89]^+$
(MeO, TO)$C_6H_3CH_2CH_2CH_2OT$	326	20	311	10	209	20	236	40	$[M-90]^{+\cdot}$	206	100	$[M-90-30]^{+\cdot}$
(MeO, TO)$C_6H_3CH_2CH(OT)CH_2OT$	414	2	399	2	209	20	205	40	$TOCH_2CH=\overset{+}{O}T$	324	20	$[M-90]^{+\cdot}$
Aldehydes and ketones												
(TO)$C_6H_4C=NOMe$	223	40	208	40	—		176	100	$[M-15-32]^+$	191	20	$[M-32]^{+\cdot}$
(MeO, TO)$C_6H_3CH=NOMe$	253	40	238	20	—		223	100	$[M-30]^{+\cdot}$	191	100	$[M-32-30]^{+\cdot}$
(MeO, TO)$C_6H_3C(CH_3)=NOMe$	267	40	252	20	—		237	60	$[M-30]^{+\cdot}$	236	20	$[M-31]^+$
Acids												
(MeO, TO)C_6H_3COOT	312	60	297	100	223	60	253	40	$[M-15-44]^+$	282	40	$[M-30]^{+\cdot}$
(MeO, TO)$C_6H_3CH_2COOT$	326	10	311	10	209	20	267	10	$[M-15-44]^+$	296	5	$[M-30]^{+\cdot}$
(MeO, TO)$C_6H_3CH_2CH(OT)COOT$	428	2	413	2	209	100	338	10	$[M-90]^{+\cdot}$	385	1	$[M-15-28]^+$
(MeO, TO)$C_6H_3CH_2CH_2CH(OT)COOT$	442	2	427	2	209	40	220	20	$TOCH^{+\cdot}-C(OH)OT$	235	10	$[M-117-90]^+$
(MeO, TO)$C_6H_3CH_2C(CH_3)(OT)COOT$	442	1	427	1	209	80	325	5	$[M-117]^+$	399	2	$[M-15-28]^+$

[1] AEI Organic MS 20 coupled via a Biemann separator (210°C) to a Varian Model 1200 gas chromatograph; 70 eV electron energy; 250 V accelerating voltage; 250°C ion source temperature.

[2] The M-15 ions also include ions of the $Ar\overset{\vert}{\underset{\vert}{C}}+$structure.

derivatives was obtained from abundant M and M-15 ions. The nitrogen-containing oxime derivatives are characterized by an odd mass number of the molecular ion. The carbon-nitrogen double bond prevents benzylic cleavage and stabilizes the molecule towards fragmentation. The *O*-methyl oximes of aldehydes typically eliminate methanol (32 amu). The loss of 30 amu, characteristic of OMe and $OSiMe_3$ groups in the *ortho* position, was not observed with the first aldehyde listed in the table.

The mass spectra of the five compounds identified as acids, permitted determination of the molecular weight from M and M-15 peaks in the same way as with the other aromatic compounds. The abundant *m/e* 209 ions and observed losses of 30 amu from several ions indicated the structure of the aromatic part of the molecules. The loss of carbon monoxide (28 amu) is often observed with Me_3Si esters, particularly from M-15 ions of derivatives of α-hydroxy acids. Other Me_3Si esters may lose carbon dioxide (44 amu). By analogy with the spectra of the phenolic alcohols, M-90 ions may be formed from a 3-arylpropanoic acid. The spectra of the last two compounds indicate isomeric structures. The abundant *m/e* 220 ion is likely to be the product of a McLafferty rearrangement (specific migration of a γ-hydrogen atom to the carbonyl group) and demonstrates an unbranched structure. The M-117 and M-117-90 ions, originating from loss of $COOSiMe_3$ (117 amu) by α-cleavage of the molecular ions, indicate that both compounds have hydroxyl groups adjacent to the carboxyl groups.

The relations between the MU and ΔMU values of the last three compounds were found to parallel those between the derivatives of 2,3-dihydroxypropanoic (glyceric), 2,4-dihydroxybutanoic and 2,3-dihydroxy-2-methylpropanoic acids in support of the structures given. The introduction of a methylene group into the carbon chain increases MU by approximately one unit whereas the effect of an added methyl group is to decrease ΔMU.

The mass spectra of the compounds encountered in the severe cook only (table 1) can be interpreted by comparison with those discussed above. A loss of 88 amu from ions containing the aromatic moiety indicates the presence of two $OSiMe_3$ groups in *ortho* positions. This fragmentation replaces the loss of 30 amu from ions with one OCH_3 and one $OSiMe_3$ group in *ortho* positions. Other fragmentations and structural deductions were analogous to those described above.

Determination of 2-methoxyphenol and 1,2-benzenediol

2-Methoxyphenol is essentially completely lost during evaporation of aqueous non-alkaline solutions and can therefore not be determined by the methods described above. The black liquors were instead acidified with hydrochloric acid to pH 6. The solution and the precipitated lignin were extracted with diethyl ether. The ether was removed by evacuation at room temperature. The residue was treated with 10% aqueous ethanol, and this solution was chromatographed directly on the acetate form of an anion exchange resin in 20% ethanol. The fraction with the position corresponding to that of 2-methoxyphenol was divided in two parts. One aliquot was rechromatographed under the same conditions to check the purity and determine the quantity (UV detector). Sodium hydroxide was added to the rest of the fraction to obtain pH 11.7. The solution was evaporated to dryness and analyzed by GC (2). The deviations obtained by the two methods were within ±2%.

1,2-Benzenediol was also determined by chromatography of the ether extract since it is likely that losses occurred by oxidation during ultrafiltration.

Results and discussion

The results given in table 1 and 2 show that 19 phenolic compounds with one aromatic ring were identified and determined in the investigated liquors. Five of these were carboxylic acids. All prominent compounds were present both in liquor M from a cook under mild (conventional) conditions and liquor S obtained under extremely severe conditions which led to a very low yield of over-cooked pulp. The total yield of identified compounds with one aromatic ring was 0.6 kg per 100 kg wood in liquor M.

In agreement with the results given by Enkvist, Turunen and Ashorn (6) 2-methoxyphenol (guaiacol, denoted $R'H$ in table 1) was found to be among the most prominent compounds in liquor M. No quantitative determination was made in liquor S. Other prominent components present in both liquors contain a 4-hydroxy-3-methoxyphenyl (guaiacyl) group and are typical degradation products of lignin or lignin-related compounds. 2-Methoxyphenol, the aldehyde $R'CHO$ (vanillin), the ketone $R'COCH_3$ and the phenolic alcohol $R'CH_2CH_2CH_2OH$ which in both liquors were present in much larger amounts than the other compounds, have been found in investigations by Enkvist et al. of black liquor (6) and in Lundquist's model experiments with Björkman lignin (7). In agreement with the results reported by these authors, $R'CH_2CH_2OH$ was also present in both liquors. A minor amount of $R'CH(OH)CH_3$ was found in liquor M. The more polar species $R'CH_2CH(OH)CH_2OH$ and $R'CH(OH)CH(OH)CH_2OH$ previously found after NaOH cooking of lignin under severe conditions belonged to the minor products in liquor M. Somewhat larger amounts were present in liquor S. Small amounts of 4-hydroxybenzaldehyde were detected in both liquors.

An appreciable amount of pyrocatechol ($R''H$) previously found by Enkvist et al. was also found in the liquors. Compounds containing 3,4-dihydroxyphenyl groups have previously been obtained in Lundquist's model experiments carried out under severe conditions. The formation of such compounds by pressure heating of black liquors has also been demonstrated (6). Four compounds of this type were present in liquor S. Among these demethylated products 3,4-dihydroxyacetophenone was more abundant than 3,4-dihydroxybenzaldehyde found by the previous investigators (6, 7). These compounds as well as 3-(3,4-dihydroxyphenyl)-1-propanol were also present in small amounts in liquor M.

Five carboxylic acids with one aromatic ring were isolated and identified (table 2). All of them contained a guaiacyl group. Only vanillic acid ($R'COOH$) which was obtained in the largest amount in liquor M and $R'CH_2COOH$, present in a small amount, have been reported by the earlier investigators. The total yield of identified acids was 87 g per 100 kg wood in liquor M compared to 409 g in liquor S. The acids were the same in liquor S but their relative amounts differed markedly. Hence, the acids present in largest amounts were $R'CH_2CH_2CH(OH)COOH$ and $R'CH_2C(CH_3)(OH)COOH$ with four carbon atoms in the aliphatic side chain. The third largest acid was $R'CH_2CH(OH)COOH$. No demethylated carboxylic acids were detected.

A common feature of the identified compounds with one aromatic ring (except for guaiacol) is that they contain a phenolic hydroxyl group and at least one additional hydrophilic (carboxyl, carbonyl or hydroxyl) group. On a laboratory scale non-polar adsorption resins such as porous styrene-divinylbenzene resins can be used for concentrating compounds of this type from aqueous solutions. However, their capacity for the removal of the more hydrophilic compounds from effluents containing black liquor is low. The structure of the identified compounds with one aromatic ring suggests that adsorption resins containing proton-accepting groups (e.g. carbonyl groups) and anion exchange resins will remove these compounds more effectively. On the other hand, black liquors contain appreciable amounts of less hydrophilic compounds e.g. solutes with more than one aromatic ring. These are held very strongly by non-polar resins. It is likely that the optimum procedure for purification of pulp mill effluents by adsorption on crosslinked polymers requires that more than one type of polymer be used.

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