

Pyrolysis of Kraft Lignin in Molten ZnCl₂-KCl Media with Tetralin Vapor Addition

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Kraft lignin was pyrolyzed in molten salt media of ZnCl₂-KCl mixture with tetralin vapor added in 0.4 and 4 mol% diluted with N₂ in the temperature range of 400 to 700°C. The gas chromatographic analyses of pyrolysis products revealed that the yield of H₂ was not increased by tetralin vapor addition. This fact implies that the hydrogen radical produced from tetralin is consumed in the formation of phenolic compounds and light liquids but not in the formation of H₂. *p*-Cresol was the most abundant phenolic compound. The yield of total phenolic compounds with 4 mol% tetralin vapor added was increased by ca. 80% as compared to that in neat pyrolysis of Kraft lignin.

On a pyrolysé de la lignine kraft dans des mélanges de ZnCl₂-KCl sous forme de sels fondus dans lequel on a ajouté de la vapeur de tétraline à 0,4 et 4% molaire diluée avec du N₂, dans une gamme de températures de 400 à 700°C. Les analyses par chromatographie gazeuse des produits de pyrolyse montrent que le rendement de H₂ n'augmente pas avec l'addition de vapeur de tétraline. Ce fait suggère que le radical hydrogène produit par la tétraline est consommé lors de la formation des composés phénoliques et des liquides légers mais non dans la formation de H₂. Le *p*-Cresol est le composant phénolique le plus abondant. Le rendement des composés phénoliques totaux avec ajout de 4% molaire de vapeur de tétraline augmente approximativement de 80% comparativement au rendement de la pyrolyse simple de la lignine kraft.

Keywords: lignin, tetralin, molten salt, pyrolysis, cresol.

Although wood extractable lignin is approximately one half of the amount of pulp through pulping processes, the chemical value of the isolated polymeric lignin has not yet been effectively evaluated. Lignin is very rich in valuable organic chemicals such as phenolic compounds (Sada et al., 1989). Phenolic compounds can be used as a cooking liquor in the organosolv pulping process. Currently, the Kraft pulping process yields solubilized lignin in its black liquor which is not recovered but is used as an energy source for electricity and low-pressure steam through incineration. More attention should be paid to the organosolv pulping, because of its effective utilization of wood materials.

Despite intensive research for more than 150 years, a method leading to high yields of phenolic compounds has not yet been found. Several reasons may be considered for this low yield, such as the high heterogeneity of lignin structure and the occurrence of many secondary reactions which lead to decomposition of the primary products (Chan and Krieger, 1981), or repolymerization reactions which occur due to hydrogen insufficiency during reaction (Joseph, 1991).

We have reported that molten salt has high selectivity to phenolic compounds, so that it may be considered as a promising medium of lignin pyrolysis (Sada et al., 1992). However, the yield of phenolic compounds therein is only 1.8 mass% from Kraft lignin and 4.6 mass% from solvolysis lignin, and is still far from satisfactory as compared to the theoretical yield (ca. 45 mass%). In order to improve the yields of liquid products, tetralin has been used as a hydrogen donor in lignin depolymerization reactions (Coughlin and Davoudzadeh, 1986; Lalvani et al., 1991). McMillen et al. (1987) reported that diphenyl ether, one of the coal model compounds, can be converted into phenol with a very high yield in the presence of tetralin. Hydrogen transfer from tetralin is often mentioned as taking place through scission of covalent bonds, followed by capping the radicals with hydrogen abstracted from the donor (Depreys et al., 1985; Kuhlmann et al., 1985). If hydrogen is not

provided in an amount which is sufficient to stabilize the precursors of phenolic compounds, then more undesired products, such as char will be produced.

The use of tetralin vapor in coal pyrolyses has been studied extensively, but its application to lignin depolymerization has only received very scant attention. Thus, we investigated pyrolysis of Kraft lignin in molten salt media with tetralin vapor addition to study the mechanisms of product formation and the change of product distribution. Usually, tetralin has been used as a donor solvent in reactions at elevated pressures. The cost of the tetralin itself is rather substantial, and operation at elevated pressures will add additional expense to the process. By using reaction at normal pressure, the overall expenditure may be reduced greatly.

Experimental

Kraft lignin (Indulin AT, Westvaco Co., Atlanta, GA) was selected as a lignin sample and was used without any pretreatment. ZnCl₂ and KCl (Wako Pure Chemicals, Osaka, Japan) were of special reagent grade and also used without further purification. Tetralin (Nakalai Tesque, Kyoto, Japan) was of 97% purity.

The reactor arrangement used in the work has been described previously (Sada et al., 1992). A tetralin evaporator was annexed to the setup, so that a continuous and controlled flow of tetralin was achieved. Tetralin vapor was carried by N₂ and its concentration was adjusted at 0.4 and 4 mol%. The experimental temperature ranged from 400 to 700°C.

The experimental procedure is described in the following. A mixture of ZnCl₂ and KCl with a molar proportion of 7/6 and a total mass of 500 g was charged into the quartz reactor and first heated to 400°C. After keeping the salt mixture at this temperature for ca. 30 min, the temperature was raised to the prescribed one. N₂ was then introduced into the reactor to remove water vapor adsorbed on the ZnCl₂ and KCl. The reactor was closed when there was no more water formed on its surface. Before the reaction was initiated, the reactor was purged again with N₂ with about six times the reactor volume to remove the air completely. About

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1.0 - 1.2 g of lignin sample was fed into the reactor following the same procedure reported elsewhere (Sada et al., 1992). After the prescribed condition has been achieved, tetralin vapor diluted with N₂ was admitted into the reactor at a flow rate of 200 cm³(STP)/min, and the lignin sample was fed into the molten salt medium. The effluent gas then passed through two condensers cooled with ice-water and a dry ice-methylene chloride mixture to collect the liquid products, and finally to a gas holder of ca. 6 dm³ to collect gaseous products.

Products were analyzed using gas chromatography (GC7AIT Shimadzu, Kyoto, Japan) on a stainless steel column packed with Molecular Sieve 13X for H₂, CO and CH₄; on a glass column packed with FAP-S for phenolic compounds; and on a capillary column packed with Supelcowa 10M for light liquids.

Experimental results and discussion

GASEOUS PRODUCTS

The yields of the main gaseous products such as H₂, CH₄ and CO are shown in Figures 1(a) through (c). The yield here and hereafter is expressed as mass percent relative to dry lignin. Except for CH₄, hydrocarbon gases were detected only in trace amounts. In the temperature range of 500 to 650°C, the evolution of gases increased markedly as the temperature was raised. The fact that evolution of gases was well initiated at lower temperatures can be ascribed to a Lewis acid catalysis of molten ZnCl₂. Above 650°C, the temperature dependence of the yield of evolved gases was depressed due to the secondary decomposition. The molten ZnCl₂ media also seem to play a role in the shift of the secondary decomposition temperature to a lower one.

Figure 1(a) shows that the yield of H₂ is not significantly affected by tetralin addition. The yield monotonically increased from 1 mass% at 500°C to ca. 1.7 mass% at 700°C. Compared to the yield of H₂ in coal pyrolysis in the same temperature range, which is normally lower than 0.5 mass%, the yield of H₂ here is very high. As lignin has an apparent molecular formula of C₂₇₉.₁H₃₀₁.₄O₉₈ (Sada et al., 1989), thus being relatively rich in hydrogen, some hydrogen must be released during the reaction. However, it has been found (McDermott et al., 1986) that hydrogen has a tendency to be released from lignin in the form of water by association with -OH (pyrolytic hydration), so that the formation of phenolic compounds is considered to be difficult in lignin decomposition. In order to achieve a high yield of phenolic compounds, lignin must be dehydrogenated to a certain level prior to pyrolysis to prevent pyrolytic hydration. The high concentration of evolved H₂ observed here suggests the possibility that lignin pyrolysis over molten ZnCl₂ media should promote the dehydrogenation of lignin in itself.

With tetralin vapor added, the yield of H₂ should increase. However, a significant increase of H₂ was not observed. It is judged from this experimental evidence that the hydrogen produced from tetralin can be consumed in the formation of liquid products such as phenolic compounds. The subsequent figures (Figures 2(a) to (f)) indicate the trend of increased yields in phenolic compounds due to the added tetralin vapor.

The yield of CH₄ is slightly increased with the addition of tetralin vapor, as shown in Figure 1(b). With 4 mol% tetralin vapor added, the increase in the yield of CH₄ occurred in the temperature range of 500 to 650°C, while

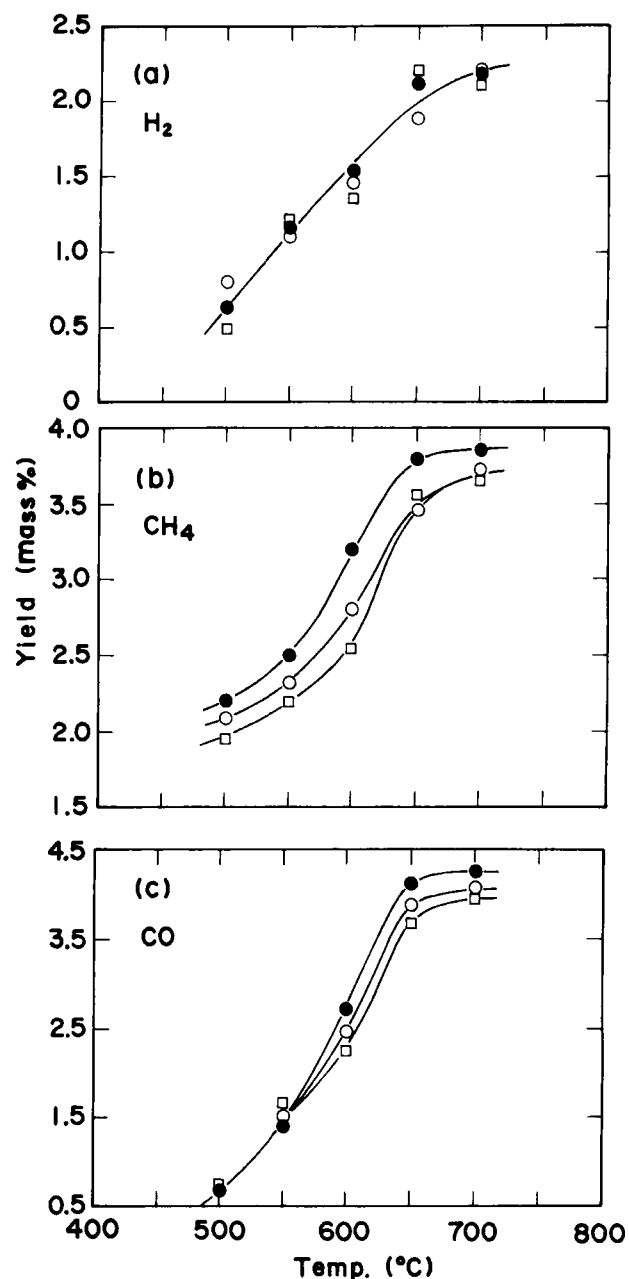


Figure 1 — Yields of gaseous products from Kraft lignin pyrolysis without (\square), or with 0.4 mol% (\circ) and 4 mol% (\bullet) tetralin vapor addition.

with 0.4 mol% tetralin vapor added, the effect of tetralin on the yield of CH₄ was suppressed at temperatures above 700°C. CH₄ is mainly produced from the methoxy group (-OCH₃) at lower temperatures and from ether bonds at higher temperatures. On the basis of previously reported data in the absence of molten salts (Avni et al., 1985; McMillen et al., 1987; Hooper et al., 1979), the rate of formation of CH₄ is greater by about two orders of magnitude than that of formation of H radicals from a common donor solvent, such as tetralin. In the molten ZnCl₂ media, on the other hand, the formation of H radicals from tetralin becomes more intense, and in the temperature range of 500 to 600°C, the rate of H radical formation seemingly matches in order of magnitude with that of the formation of additional CH₄.

Figure 1(c) reveals that the yield of CO increases considerably with rising temperature, but the yield is only slightly increased by tetralin vapor addition above 600°C.

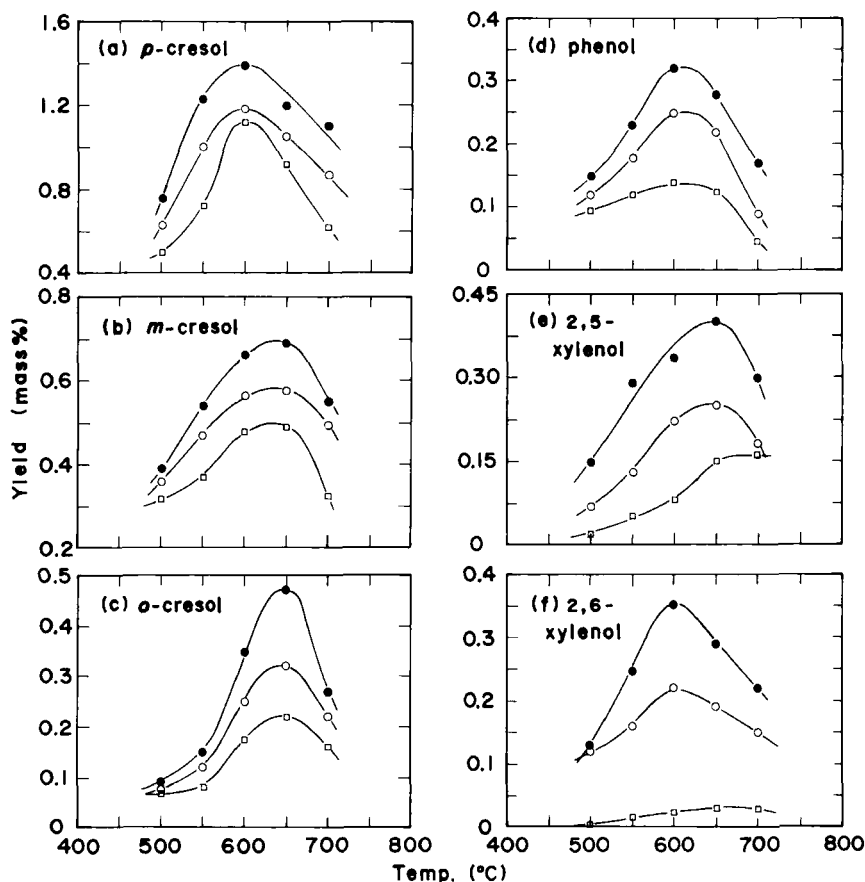


Figure 2 — Yields of phenolic compounds from Kraft lignin pyrolysis without (\square), or with 0.4 mol% (\circ) and 4 mol% (\bullet) tetralin vapor addition.

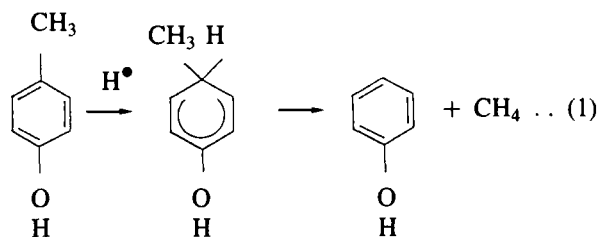
PHENOLIC COMPOUNDS

The yields of phenolic compounds such as *p*-, *m*- and *o*-cresols, phenol, 2,5- and 2,6-xylenols are shown in Figures 2(a) through (f). The yields of these phenolic compounds were increased by tetralin vapor addition. The effect of tetralin vapor was most significantly exhibited in the yield of 2,6-xylenol.

The variations of the yields of cresols and total phenolic compounds with temperature were plotted in Figure 3. The individual and total yields of phenolic compounds at 600°C are listed in Table 1. By the addition of 4 mol% tetralin vapor, the yields of cresols and total phenolic compounds at this temperature are increased by 38 and 78%, respectively, as compared to those in neat pyrolysis.

Although the amount of produced phenolic compounds has been found to be increased by the addition of tetralin vapor, the thermal decomposition of phenolic compounds cannot be suppressed completely. Therefore, the increase in the yield of phenolic compounds was limited to 78%.

Another important type of reaction of phenolic compounds with hydrogen radicals is the one resulting from their intrinsic properties. OH-substituted aromatic compounds at high temperatures are susceptible to dehydrogenation reactions and are also susceptible to hydrogen transfer to the para position to the OH group ($-\text{CH}_3$) (McMillen et al., 1987). Thus, H addition to the para position in *p*-cresol will result in a rapid elimination of the methyl group through the following reaction.



The above reaction should be favourable to the formation of phenol, but in the present experiments, the flow system with respect to the gas phase employed N_2 as the carrier gas, and the residence time of the gas was limited. Accordingly, the reaction described by Equation (1) cannot proceed to attain a high yield of phenol. In fact, a slight increase in the yield of CH_4 resulted from the tetralin vapor addition, as depicted in Figure 1(b).

As shown in Figures 2(e) and (f), a considerable increase in the yields of 2,5- and 2,6-xylenols was observed. The formation of these compounds is more difficult than that of other phenolic compounds, since these compounds are sterically hindered. Their yields, however, were increased by the added tetralin vapor.

LOW-MOLAR-MASS LIQUID PRODUCTS

Liquid products whose presence seemed to be unimportant without tetralin vapor addition in our previous work (Sada et al., 1992), appeared to be significant products in

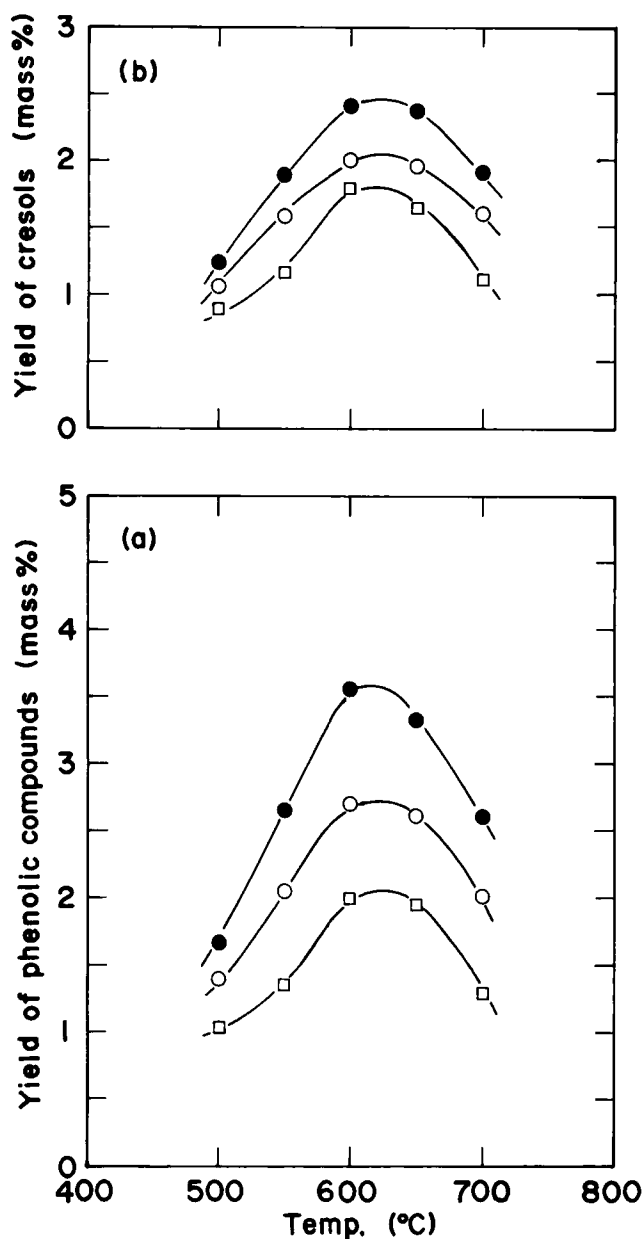


Figure 3 — Variation of yields of phenolic compounds (a) and cresols (b) with temperature during pyrolysis of Kraft lignin with 0.4 mol% (○) and 4 mol% (●) added tetralin vapor, or without (□) tetralin vapor addition.

TABLE 1
Yields [mass% (lignin-base)] of Phenolic Compounds from Pyrolysis of Kraft Lignin at 600°C

Compound	Tetralin Added		
	0	0.4 mol%	4 mol%
<i>p</i> -Cresol	1.10	1.20	1.40
<i>m</i> -Cresol	0.47	0.55	0.66
<i>o</i> -Cresol	0.17	0.25	0.34
Phenol	0.13	0.25	0.32
2,5-Xylenol	0.08	0.20	0.33
2,6-Xylenol	0.02	0.22	0.35
Total	1.97	2.67	3.50

the present experiment. The relative yields of light liquids are presented in Table 2, which also shows their yields in the absence of tetralin vapor. It should be noted that in a

TABLE 2
Relative Yields of Low-molar-mass Compounds from Kraft Lignin Pyrolysis with Tetralin Vapor Addition*

Compound	Relative Yield (arbitrary unit)			
	550°C	600°C	650°C	700°C
Ethanol	70 (30)	130 (80)	175 (110)	280 (130)
1-Propanol	105 (45)	220 (150)	260 (230)	710 (580)
2-Propanol	45 (35)	70 (60)	230 (200)	460 (380)
Benzene	0 (0)	35 (0)	120 (0)	530 (25)
Toluene	0 (0)	20 (10)	40 (40)	120 (70)
Xylene	0 (0)	40 (0)	100 (40)	160 (70)

*Figures in parentheses show the yields of the compounds without tetralin addition.

blank test, none of the compounds listed in Table 2 were detected when only tetralin diluted with N₂ (4 mol% tetralin) was passed through the molten salt media. This table shows that the yields of 1- and 2-propanols increase considerably with rising temperature. 1-Propanol can be formed through the cleavage of the propane chains from the phenylpropane subunits.

Ibrahim and Seehra (1991) reported that the population of active radicals generated from coal is increased markedly even at low temperatures in the presence of molten ZnCl₂. The increase in active radicals and the sufficient supply of hydrogen radicals may obviously result in an increase of liquid products and a decrease of undesired products of high molar mass.

Another important fact obtained from the present experiments is that the formation of benzene, toluene and xylene (BTX) is enhanced by the tetralin vapor addition. These compounds may be produced from the reactions of lignin tar with hydrogen radicals. The amount of liquids produced at 700°C, shown in Table 2, was about 2 mass% of the original liquid sample.

The total yield of phenolic compounds detected in Kraft lignin pyrolysis with 4 mol% tetralin vapor added reached 3.5 mass%, as shown in Table 1. The yield of char could not be determined accurately, due to the impregnation of molten salt in the interstices of the char. However, in our recent experiments using small batch-type reactors, the yield of char ranged from 48 to 58 mass%, and that of water ranged from 15 to 20 mass% (Kudsy et al., 1993). The yield of char in the previous reports ranged from ca. 35 mass% in fast pyrolysis to 55 mass% in slow pyrolysis (Chan and Krieger, 1981). The yield of tar typically ranged from 10 to 20 mass% (Chan and Krieger, 1981). Table 3 summarizes the yields of char, water, gases, phenolic compounds and low-molar-mass liquids. If the yield of tar, except for phenolic compounds, is estimated to be 10~20 mass%, as measured by Chan and Krieger (1981), the mass balance is approximately satisfied.

Conclusion

From the present experiment on pyrolysis of Kraft lignin in molten salt media with added tetralin vapor, the following findings were obtained. The yield of H₂ was not influenced

TABLE 3
Mass Balance During Pyrolysis of Kraft Lignin

Species	Yield	[mass% (lignin-base)]
Char	48 ~ 58	35 ~ 55 (Chan and Krieger, 1981)
Water	10 ~ 20	
Tar	α^{**}	10 ~ 20 (Chan and Krieger, 1981)
Gases	~ 10	
L. M. M. compds*	2.0	
Phenolics	3.5	
Total	(73.5 ~ 93.5) + α	

*Low-molar-mass compounds

** α means the yield of tar. It cannot be estimated exactly, but typically ranges from 10 to 20% (Chan and Krieger, 1981).

by tetralin vapor addition. It is judged that hydrogen radicals produced from tetralin vapor are consumed by the formation of phenolic compounds and light liquids. The yield of CH₄ was slightly increased by the addition of tetralin vapor. The formation of hydrogen radicals from tetralin matched in order of magnitude with the formation of CH₄. *p*-Cresol was the most abundant phenolic compound, since the bond strength between α and β atoms in lignin subunits was the lowest in the phenylpropane subunits. With 4 mol% tetralin vapor added, the yields of cresols and total phenolic compounds were increased by ca. 40 and 80%, respectively, as compared to those in neat pyrolysis. The yield of benzene, toluene and xylene (BTX) were increased by tetralin vapor addition. The increases of BTX and other light liquids may result from reactions between lignin tar and hydrogen radicals. The total yield of light liquids was about 2 mass%, in Kraft lignin pyrolysis with 4 mol% tetralin vapor added.

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