

Pyrolysis of Lignins in Molten Salt Media

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Two kinds of lignins, i.e., kraft and solvolysis lignins, were pyrolyzed using mixtures of molten $ZnCl_2$ and KCl with molar ratios of 3/7 and 7/6 over the temperature range of 500–800 °C under atmospheric pressure. The yields of gaseous products and of phenolic compounds were measured. It was found that the variation of gaseous product yield with temperature was similar in pattern, irrespective of the lignin type. A higher yield of H_2 implies that the H_2O -forming reaction was partially retarded. It was also found that the mixture of molten $ZnCl_2$ and KCl with molar ratio of 7/6 had a high selectivity to cresols. The maximum yield of cresols from solvolysis lignin reached 4.6 wt %, higher than any figures reported so far. This maximum yield was attained at 600 °C.

Introduction

Lignin is a major constituent of wood and other biomass materials. Its composition differs according to their origin, but it is similar in structure; i.e., it is constructed from aromatic subunits. There is no unified lignin model accepted in general, but it has been widely agreed that lignin is primarily constructed from three distinct phenyl propane monomers (Nunn et al., 1985). Several models proposed previously (Sarkanen and Ludwig, 1971; Sakakibara, 1980) suggest that valuable chemicals such as phenolic compounds can be derived from lignin. Several methods including catalytic hydrocracking, liquid-phase hydrocracking, biochemical decomposition, and thermal decomposition have been put forward to convert lignin into useful products, and each process results in different kinds of product spectrum and distribution.

Researches on thermal pyrolysis of lignin have been carried out by some workers, and different kinds of gaseous and liquid products have been reported. Phenolic compounds resulted from those experiments, however, have never been so satisfactory due to their low yields. A "captive sample" reactor was used to pyrolyze kraft lignins over wide ranges of temperature (400–600 °C) and reaction time, and a maximum yield of phenolic compounds of about 3.22 wt % was reported (Iatridis and Gavalas, 1979). Other workers (Chan and Krieger, 1981) used microwave to pyrolyze kraft and organosolv lignins and reported that only a small fraction (0.5 wt %) of lignin was converted to phenolic compounds. The result by these workers also accounts for a low yield of aromatic products (about 2 wt % including phenolic compounds). If high yields of phenolic compounds are more preferred compared to other products, consequently, a pyrolysis method which is able to promote production of aromatic compounds should be used. Meanwhile, the use of zinc halides in hydrocracking of coal has been widely known (Scarra, 1980; Struck and Zielke, 1981). These salts have a superior selectivity to produce single-ring aromatic compounds, because they have a little hydrocracking activity on single-ring coal derivatives. Furthermore, addition of a viscosity reducer into molten zinc halide does not reduce the activity of the salt for pyrolysis, yet it will improve separation of products (Scarra, 1980).

In this paper, we report clear evidence on the superiority of molten $ZnCl_2$ and KCl mixture used in lignin pyrolysis in order to obtain a higher yield of phenolic compounds compared to other pyrolysis methods.

Table I. Summary of Pyrolysis Conditions

no.	salt ratio $ZnCl_2/KCl$	lignin species	temp range, °C	sample wt, g	N_2 flow rate, L/min
A	3/7	kraft	500–800	0.8–1.3	0.2
B	3/7	solvolysis	500–700	1.25	0.2
C	7/6	kraft	500–650	1.25	0.2
D	7/6	solvolysis	500–650	1.25	0.2
E	7/6	solvolysis	600	1.25	0.1–0.3

Experimental Section

Procedure. The pyrolysis of lignin in molten salt media was carried out in a quartz reactor having a dimension of 5-cm internal diameter and 45-cm length. This reactor was heated externally during the reaction, and the temperature was controlled at a prescribed value. The temperature of the molten salt bath ranged from 500 to 800 °C. The Pt–Rh thermocouple was installed in the space between the reactor's outer wall and the heater. The difference between temperatures of the measuring point and the molten salt medium has been confirmed in advance to be within 5 °C. The nitrogen with a flow rate of 0.1–0.3 L/min was passed through the reactor to collect the products. The melt is not very viscous at temperatures of interest and is considerably well mixed at such nitrogen flow rates. A specified amount of lignin powder (0.8–1.3 g) was blown off into the molten salt medium with nitrogen. Condensables were collected from the outlet gas in ice–water and dry ice–methylene chloride cooled U-tube condensers. The reactor arrangement is shown in Figure 1. The gas from the reactor was collected in a gas holder (volume approximately 6 L) for analysis. The pyrolysis run was continued for ca. 50 min.

H_2 , CH_4 , and CO were analyzed by using a Molecular sieve 13X (particle size 60–80 mesh) column, while CO_2 , C_2H_4 , and C_2H_6 gases were analyzed using a similar column packed with Porapak QS (particle size 80–100 mesh) on a Shimadzu GC-7A gas chromatograph with a thermal conductivity detector.

The liquid products collected in the condensers were extracted with 3 mL of ethyl alcohol, and 1 μ L of the substrate was subjected to analysis for phenolic compounds. A KG02-Uniport (particle size 80–100 mesh) with a flame ionization detector was used to separate 2,5- and 2,6-xyleneol, phenol, and *o*-, *m*-, and *p*-cresol.

Lignin and Molten Salt. Kraft lignin supplied by Westvaco (US) and solvolysis lignin supplied by the Japan Paper and Pulp Research Co. were used as samples. Both lignins were used directly without pretreatment. The weight of sample used and reaction conditions in every run are shown in Table I.

$ZnCl_2$ and KCl mixtures with molar proportions as listed in Table I were used as reaction media. The salts were of

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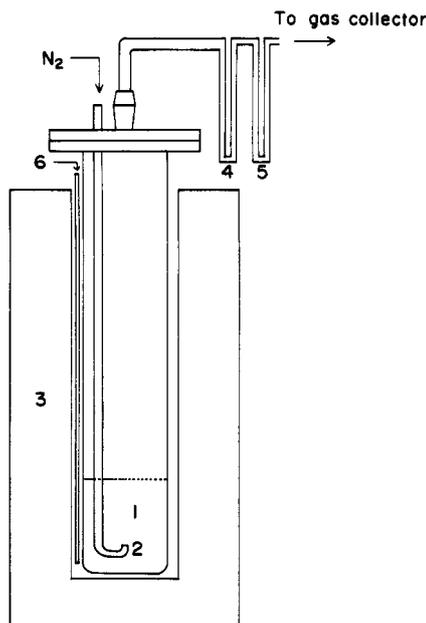


Figure 1. Schematic diagram of experimental apparatus: 1, molten salt; 2, single nozzle; 3, heater; 4, ice trap; 5, methylene chloride trap; 6, thermocouple.

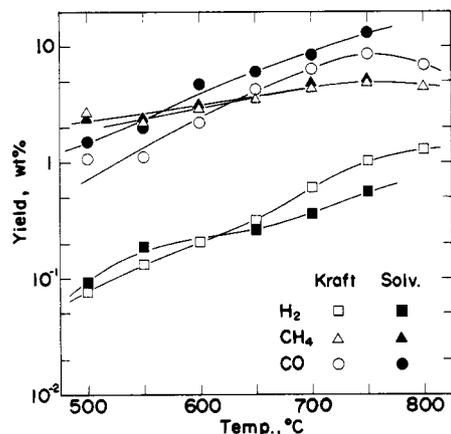


Figure 2. Dependence of yields of gaseous products from kraft and solvolysis lignins on temperature for $\text{ZnCl}_2/\text{KCl} = 3/7$.

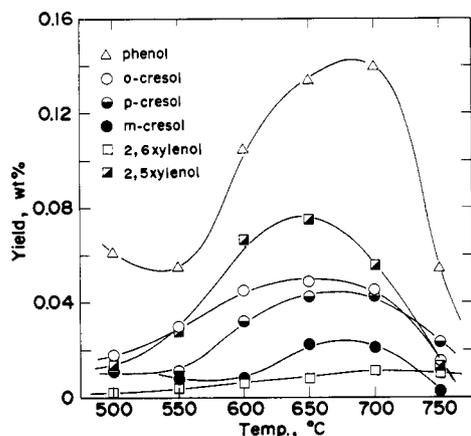


Figure 3. Dependence of yields of phenolic compounds from kraft lignin on temperature for $\text{ZnCl}_2/\text{KCl} = 3/7$.

technical grades and used without pretreatment. The melts were prepared in the same reactor used for the pyrolysis reactions. The initial moisture present in the salts and air in the reactor was flushed out substantially by purging with nitrogen at least 5 times the reactor volume before the reaction was initiated.

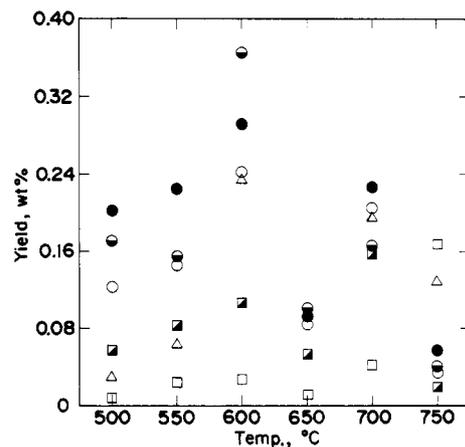


Figure 4. Dependence of yields of phenolic compounds from solvolysis lignin on temperature for $\text{ZnCl}_2/\text{KCl} = 3/7$. Symbols as in Figure 3.

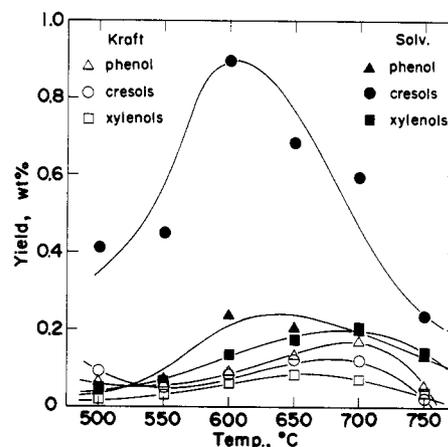


Figure 5. Dependence of lumped yields of phenolic compounds from kraft and solvolysis lignin on temperature for $\text{ZnCl}_2/\text{KCl} = 3/7$.

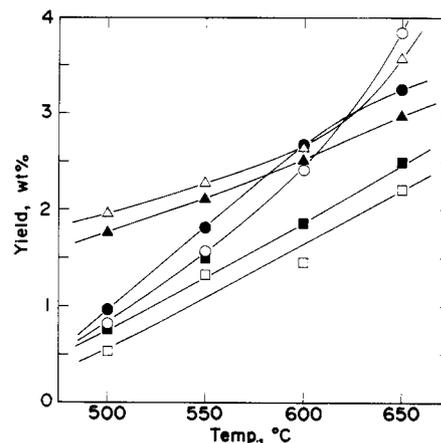


Figure 6. Dependence of yields of gaseous products from kraft and solvolysis lignins on temperature for $\text{ZnCl}_2/\text{KCl} = 7/6$. Symbols as in Figure 2.

Experimental Results and Discussion

The experimental results on the yields of pyrolysis products are presented graphically in Figures 2–10. Figures 2–5 represent the pyrolysis results with a molten salt mixture of ZnCl_2 – KCl with molar ratio 3/7, while Figures 6–9 represent similar pyrolysis results with ZnCl_2 – KCl molar ratio 7/6. Figure 10 demonstrates the effect of N_2 gas flow rate on the yields of phenols.

Representative results on pyrolysis products from kraft and solvolysis lignins are tabulated in Table II. These

Table II. Summary of Pyrolysis Results

products	yield, g/g lignin								
	molten salt					Chan and Krieger	Iatridis and Gavalas	Jegers and Klein	Domburg
	A	B	C	D	E				
phenolics									
phenol	0.134	0.236	0.702	0.490	0.553	0.282	0.19	1.46	0.10
cresols	0.117	0.896	1.843	4.63	5.195	0.115		2.60	0.50
<i>o</i> -cresol	0.052	0.242	0.184	0.040	1.233	0.029			
<i>m</i> -cresol	0.042	0.362	1.112	1.470	1.650	0.038	0.41		
<i>p</i> -cresol	0.023	0.292	0.539	2.12	2.313	0.048			
xilenols	0.082	0.131	0.144	0.451	0.615				
2,5-xylenol	0.074	0.104	0.098	0.398	0.508				
2,6-xylenol	0.008	0.027	0.046	0.071	0.108				
gaseous products									
H ₂	0.32	0.21	1.45	0.84	1.22	0.8		tr	
CO	4.22	4.69	2.41	2.69	6.08	21.9	9.2	2.8	
CO ₂	3.28	2.74	2.84	2.73	2.30	5.1	7.2	12	
CH ₄	3.48	3.14	2.64	2.52	3.81	4.4	4.83	3.7	
C ₂ H ₄	0.13	0.087	0.04	tr	tr	1.8	0.33	0.04	
C ₂ H ₆	0.17	0.13	0.14	tr	tr	0.1	0.35	0.4	
char						33.5	34.8		

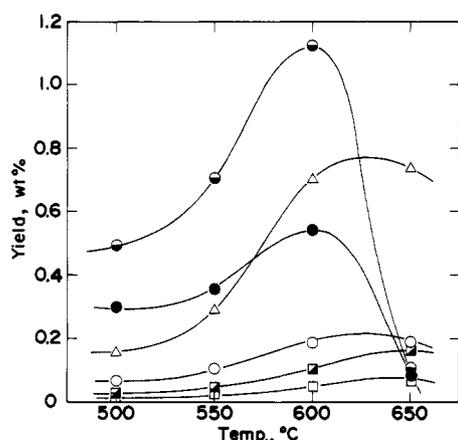


Figure 7. Dependence of yields of phenolic compounds from kraft lignin on temperature for $ZnCl_2/KCl = 7/6$. Symbols as in Figure 3.

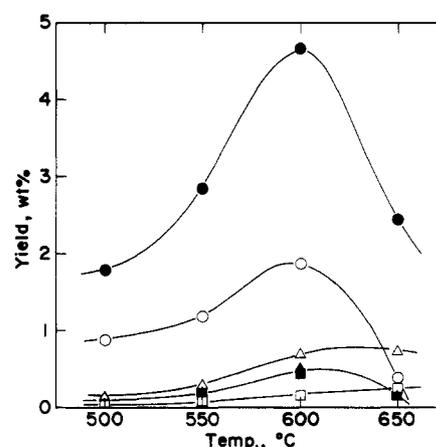


Figure 9. Dependence of lumped yields of phenolic compounds from kraft and solvolysis lignins on temperature for $ZnCl_2/KCl = 7/6$. Symbols as in Figure 5.

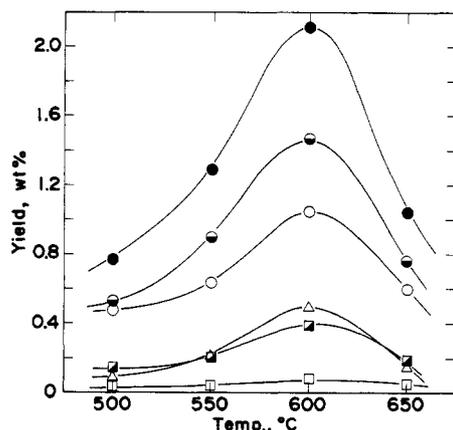


Figure 8. Dependence of yields of phenolic compounds from solvolysis lignin on temperature for $ZnCl_2/KCl = 7/6$. Symbols as in Figure 3.

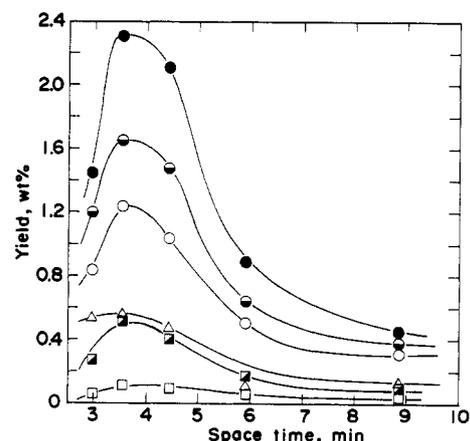


Figure 10. Yields of phenolic compounds from solvolysis lignin as a function of space time at 600 °C. Symbols as in Figure 3.

results are discussed along the following subjects.

Yields of Gaseous Products. As can be seen from Figures 2 and 6, the yields of gaseous products exhibit very similar in trends, irrespective of the type of lignin. In Figure 2, the H₂ yields increase from 0.1 wt % at 500 °C to approximately 1 wt % at 800 °C, though previous workers mostly detected only a trace amount of H₂ or did not report the presence of H₂ at all. Since pyrolysis involves a lot of radical reactions, and since the protium

radical (H) is active enough to react with other radicals such as methyl, the presence of H₂ in high concentration in the products seems to imply the inhibited action of protium radical from attacking other radicals. The high H₂ yield also seems to indicate that formation of pyrolysis water from hydrogen is partially suppressed. Formation of pyrolysis water should be avoided in order to obtain high yields of valuable liquid products such as phenolic compounds (McDermott et al., 1986). Considering this, we can expect that the formation of phenolic compound in the

present experiment is more favorable compared to the conventional pyrolysis process.

CH₄ and CO yields also increase with rising temperature, and both gases are produced from different kinds of sources with different bond energies (Avni et al., 1985). CH₄ is produced readily from a weakly bonded methoxy group -OCH₃ (bond energy 60 kcal/mol) at lower temperatures, and additional CH₄ will be produced from methylene groups -CH₂- (bond energy 72 kcal/mol) in the bridges connecting the lignin subunits at higher temperatures. CO is produced from two types of ether group. The first is the ether bridges joining the lignin subunits. Since this group has a low dissociation energy (60–75 kcal/mol), this is the main source of CO at low temperatures. Additionally, at high temperatures, dissociation of diaryl ether will also occur and act as the CO source.

Figure 6 shows yields of gaseous products from both lignins with molten ZnCl₂/KCl of molar ratio 7/6, and exhibits similar yields of gaseous products to those in Figure 2. At a lower temperature of 500 °C, H₂ yield has started from a higher value compared to that in Figure 2. The yield of H₂ at 500 °C (0.5 wt %) is higher compared to 0.1 wt % at ZnCl₂/KCl ratio equal to 3/7. By the same reasoning as above, we can expect that the yields of phenolic compounds at this condition will significantly increase compared to those resulted from using ZnCl₂/KCl = 3/7, and this will be shown later in this paper. Similar patterns of the yields in these two figures lead us to a conclusion that the formation of gaseous products in the present pyrolysis follows similar kinetics, irrespective of the type of lignin used. This similarity was also reported previously (Avni et al., 1985). As can be seen from the figures, the present experiment also obtains similar yields of gaseous products from both types of lignins, although the heating rate is rather low compared to what have been referred to in grid heating (Iatridis and Gavalas, 1979) and an enclosed microtubing reactor (Jegers and Klein, 1985). The difference that could arise from different heating rates affects the absolute yields of the product components including char and liquid or condensables.

Yields of Phenolic Products. Yields of six phenolic compounds from kraft and solvolysis lignins at ZnCl₂ to KCl molar ratio 3/7 are shown in Figures 3 and 4, while at ZnCl₂ to KCl molar ratio 7/6 they are shown in Figures 7 and 8. In Figure 3, we can predict that evolution of phenolic compounds is very similar in nature; e.g., yields of all the phenolic compounds increase with rising temperature, and after they reach maximals, they decrease due to the increased secondary decomposition reactions. In the same figure, the maximum apparently occurs at ca. 650 °C. The increase in the yields of gaseous products at temperatures above 650 °C as discussed above may be partly attributable to the decomposition of the phenolic compounds.

The yield of phenol depicted in Figure 3 is the highest compared to the other phenolics. It reaches a value of 0.13 wt % at 650 °C, further increases slightly to a value of 0.14 wt % at 700 °C, and then decreases. The final yield of phenol, however, is still high compared to other phenolic compounds.

The higher proportion of phenol compared to other phenolic compounds in Figure 3 seems to be reasonable since during the kraft pulping lignin has been subjected to severe degradation, so that on pyrolysis a lower molecular weight compound such as phenol would be produced.

The yield of 2,5-xylenol, however, is rather peculiar in nature, for despite its complexity in molecular structure,

it yet reached a higher yield compared to *p*- and *m*-cresol. Among the three cresol isomers, only *o*-cresol has a yield comparable to 2,5-xylenol. In contrast to its isomer, 2,6-xylenol yield is very low and appears to be an unimportant pyrolysis product.

The result presented in Figure 3, although appearing trivial due to such a small yield of phenol, is not surprising, since a very similar result not only on the phenolic compounds, but also on gaseous components, has been reported previously (Chan and Krieger, 1981).

Higher yields of phenolic compounds are shown from pyrolysis of solvolysis lignin in Figure 4. In this figure, it appears that the maximum yields of the phenolic compounds are achieved at a temperature of 600 °C. This figure shows that higher proportions of cresols are produced and at 600 °C the total yield of cresols reaches approximately 0.9 wt %. At temperatures higher than 600 °C the yields decreased due to further decomposition reactions.

The solvolysis lignin used in the present experiment was specified to have a high molecular weight (>1000), so the formation of the simple phenol would be more facile at higher temperatures as can be seen in Figure 4. At 500 °C only a small amount of phenol (0.03 wt %) was detected, but its yield increased significantly to 0.24 wt % at 600 °C. The complexity of solvolysis lignin structure will complicate the reaction path; however, from the product spectrum shown in Figure 4, it can be predicted that the major products in solvolysis lignin pyrolysis are cresols at lower temperatures and cresols and phenols at higher temperatures. Solvolysis lignin can be obtained from the liquor produced in the organosolv pulping process using cresols as the cooking chemical. Therefore the recovery of cresols directly from the spent liquor seems to be desirable.

The yield of phenolic compounds at ZnCl₂ to KCl molar ratio 7/6 differs considerably from that for the previous molten salt composition. In Figure 7, a maximum yield of cresols occurs at 600 °C. Phenol still slightly increases its yield at temperatures higher than 600 °C. The slower decrease of phenol yield, as above, mainly results from contribution of decomposition of cresols.

Figure 8 shows the yields of phenolic compounds from solvolysis lignin. It is important to note that the maximum yields of all phenolic compounds occur at the same temperature, 600 °C. Low yield of phenol at higher temperature seems to be strange, since the concentration of phenol in the product should be more or less constant due to contribution from decomposition of other phenolic compounds. Figure 9 shows that the yield of total cresols at 600 °C reaches a value of as high as 1.8 and 4.6 wt % for kraft and solvolysis lignins, respectively. The yields of xylenols are very minor compared to other identified phenols.

Effect of N₂ Flow Rate. As the N₂ flow rate increases, the residence time of the pyrolysis products in the reactor decreases and the possibility of the decomposition of primary reaction products is reduced, since those products are taken out from the reaction zone into the low-temperature zone.

As can be seen from Figure 10, the yields of phenolic compounds increase to maximum values at V/F (space time) = 3.5 min, where V refers to the total reactor volume (in the present runs 885 mL) and F to the total gas flow rate. Unfortunately, the capability of the condenser seems to have a physical limitation, so that a further increase in N₂ flow rate does not bring about any advantage. In contrast, the yields of collected phenolic compounds be-

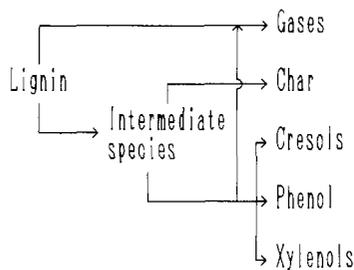


Figure 11. Plausible sketch for reaction path of lignin pyrolysis in mixed molten ZnCl_2 and KCl .

come lower due to an excessive N_2 flow rate. In the region of space time > 3.5 min, the decomposition of phenolic compounds is evidenced by decreasing phenolic compound products. All phenolic compounds including phenol itself decompose with the same trend, and this demonstrates that the increase in space time is more crucial in causing decomposition compared to the effect of temperature increase, since by increasing space time, all phenolic compounds evidently decompose completely into low-value gaseous products or char.

Catalytic Activity of Molten Salt. The catalytic activity of zinc halides in coal depolymerization reaction has been reported (Scarrah, 1980; Struck and Zielke, 1981). Recently, it has also been found that zinc halides have a catalytic activity in coal depolymerization even at temperatures near 100°C (Ibrahim and Seehra, 1991). The advantage of molten salt usage in coal depolymerization is that zinc halides have no catalytic activity on a single-ring aromatic compound. For this reason, this salt is very suitable for synthesis of single-ring aromatic compounds, such as single-ring phenols.

However, molten zinc halides are rather viscous, hence causing difficulty in process reactions and making it difficult to separate the products. Addition of a viscosity reducer such as potassium chloride can improve separation of pyrolysis products. On the other hand, addition of such a viscosity reducer is also able to reduce the melting point of the salts and hence enable us to alter the process condition according to the desirable product distribution.

As can be seen from Figures 3–5 and Figures 6–8, each molten salt composition has a different selectivity, especially to phenolic compound products. The similar patterns of gaseous product yields depicted in Figures 2 and 6 are primarily effected by pure thermal decomposition rather than by the catalytic activity of molten ZnCl_2 .

Reaction Pathways. There is no unified lignin model which is generally acceptable up to now. It is very difficult therefore to propose what type of pyrolysis reaction model is appropriate to the present lignin samples. Almost all the models, however, were developed on the basis of the phenylpropane ($\text{C}_6\text{--C}_3$) subunits.

The actual reaction pathway in pyrolysis involves many, if not hundreds of, radical reactions. Many researchers make an approximation of pyrolysis reaction as a combi-

nation of many parallel reactions of first order with distributed activation energies.

From the present result, a plausible reaction scheme can be proposed, as in Figure 11.

Conclusion

From the present experiments on pyrolysis of kraft and solvolysis lignins in a molten salt mixture of ZnCl_2 and KCl , the following conclusion can be drawn.

Gaseous products are produced mainly through thermal pyrolysis, and their yields increase with rising temperature. There is no distinction of gaseous product yields from both kraft and solvolysis lignins.

The yields of phenolic compounds are influenced by the molten salt composition. By use of a mixture of ZnCl_2 and KCl with the molar ratio of 7/6, the maximum yield of cresols attained as high as 1.8 and 4.6 wt % from kraft and solvolysis lignins, respectively, at 600°C . The phenolic compounds, however, are very prone to decompose into gases and char, but these decomposition reactions can be minimized by using molten ZnCl_2 and by removing the primary products by a N_2 stream.

Registry No. ZnCl_2 , 7646-85-7; KCl , 7447-40-7; H_2 , 1333-74-0; CO , 630-08-0; CO_2 , 124-38-9; CH_4 , 74-82-8; C_2H_4 , 74-85-1; C_2H_6 , 74-84-0; kraft lignin, 8068-05-1; solvolysis lignin, 108778-53-6; phenol, 108-95-2; *o*-cresol, 95-48-7; *m*-cresol, 108-39-4; *p*-cresol, 106-44-5; 2,5-xyleneol, 95-87-4; 2,6-xyleneol, 576-26-1.

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