THE CHEMISTRY OF ACID-CATALYZED COAL DEPOLYMERIZATION

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Since its introduction in the early 1960's, acid-catalyzed depolymerization has become a widely used method to convert coal into soluble products for structural investigations. It was first shown by Heredy and Neuworth[1] that coal could be depolymerized by reacting it with phenol-BF_3 at temperatures as low as 100°C. The method was based on the assumption that coal contains aromatic structures linked by aliphatic bridges, such as methylene bridges, which are sufficiently reactive to participate in an acid-catalyzed transaryl-alkylation reaction. This general type of structure was proposed by Neuworth, et al.,[2] to explain the chemistry of low-temperature pyrolysis of coal. The overall reaction of this proposed structure with phenol-BF_3 is illustrated in Figure 1. One of the final products of the depolymerization is dihydroxy-diphenylmethane.

The depolymerization reaction was modified by Ouchi, Imuta, and Yamashita[3] who substituted p-toluenesulfonic acid (PTSA) for BF_3 as the catalyst and increased the reaction temperature to 180-185°C. A very high degree of depolymerization, with pyridine soluble product yields over 90%, was achieved under these conditions. Darlage and Bailey[4] investigated the effects of reaction temperature, various solvents and coal preoxidation on depolymerization product yields using a number of acid catalysts. They found that meta-substituted phenols were more effective aromatic substrates for the depolymerization reaction than phenol. The preoxidation of coal, particularly of some sulfur-rich bituminous coals, with dilute aqueous nitric acid considerably increased the yield of depolymerization products.[5]

A general review of the acid-catalyzed coal depolymerization method has been published recently by Larsen and Kuemmerle.[6] The objective of this paper is to discuss some specific aspects of the chemistry of coal depolymerization.

I. THE RELATIVE REACTIVITIES OF VARIOUS BRIDGE STRUCTURES TOWARD PHENOL-BF_3

Although no systematic studies have yet been reported regarding the relative reactivities of aliphatic bridge structures, or more generally, aliphatic-aromatic carbon-carbon bonds, which may be present in various coals, toward phenol-BF_3, some important trends have been established in model compound experiments.[1,7] The results of these experiments are summarized in Tables 1 and 2 and in Figure 2.

The data on isopropyl group transfer in Table 1 show that the secondary aliphatic-aromatic carbon-carbon bond is much more reactive when it is located on either a phenolic ring or on a phenanthrene ring than on a nonactivated benzene ring. The relative reactivities of the secondary carbon bond in the first two structures could not be evaluated because the isopropyl group transfer went to completion both in the case of ortho-isopropylphenol and of retene. The data on n-propyl group transfer in Table 2 show, as expected, that a bond between a primary aliphatic carbon and an aromatic carbon is less reactive than a secondary carbon-aromatic carbon bond under otherwise similar conditions.

Figure 2 shows the comparison of the relative reactivities of four aromatic-aliphatic carbon-carbon linkages. A comparison of the reactivities of the two linkages a' and b', which involve primary aliphatic carbon atoms, clearly show enhanced reactivity at bond a' due to the activating effect of the phenolic hydroxyl group. A comparison of the reactivity of linkage a' with that of the corresponding bond in para-n-propylphenol (Table 2) indicates that the reactivities of ($-CH_2-CH_2-$) substituted aromatics are similar whether the substitution is in a bridge or in a chain structure. The relative reactivities found with model

compound B indicate that $-CH_2-$ bridges can play a special role in coal depolymerization because in this case bonds on both sides of the bridge structure are activated (compare the reactivities of bonds b and b', respectively).

It is probable that cleavage of aliphatic ether bonds contributes to coal depolymerization, particularly in the case of lignites and subbituminous coals. Although the reactivity of various ethers with phenol-BF_3 has not been investigated, several studies on the BF_3-catalyzed cleavage of various aliphatic ether linkages have been reported.[8,9] It was shown that the reaction of ethers with benzene gives alkylbenzenes. The relative ease of reaction varied considerably with different ethers. Diisopropyl ether and dibenzyl ether reacted vigorously with benzene upon saturation with BF_3. Isopropyl, phenyl, and benzyl ethyl ethers reacted violently. On the other hand, ethyl, isoamyl, and *n*-amyl ethers reacted only at higher temperatures and elevated pressures (150°C and 10-20 atm).

II. INVESTIGATION OF THE KINETICS OF BF_3-CATALYZED BENZYL GROUP TRANSFER

Kinetic investigations of BF_3-catalyzed benzyl group transfer in benzylphenol systems were reported by Heredy.[10] These systems were chosen for investigation because of the particular interest in the role that $-CH_2-$ bridges may play in coal depolymerization.

One of the investigations was made with para-benzylphenol. Experiments were made first with the para-benzylphenol/phenol (1-^{14}C)/BF_3 system to study the rate of benzyl group transfer from benzylphenol to phenol (1-^{14}C). It was found, however, that the rate of benzyl group transfer to para-benzylphenol was much faster than to phenol (1-^{14}C), and therefore, no meaningful kinetic measurements could be made on the latter system. In another experiment, the kinetics of benzyl group transfer was studied in the para-benzylphenol-BF_3 system. The kinetic measurements were made in sealed glass tubes at 100°C using a para-benzylphenol to BF_3 mole ratio of 6.25/1.0. The two principal reactions which take place in this system are shown in Figure 3. In agreement with the reaction scheme shown in Figure 3, the rate of disappearance of the sum of para- and ortho-cresols followed a second order rate equation. The ratio of the initial reaction rates of reaction 1a to 1b was found to be approximately 4.0. In addition to phenol and benzene, significant amounts of diphenylmethane and some para-cresol were formed during the latter part of the reaction. Also, isomerization to ortho-benzylphenol took place as a result of the reverse reactions of 1a and 1b.

A more detailed kinetic study of benzyl group transfer was made using the 4-benzyl-2,6-dimethylphenol/BF_3 system. This system was selected for investigation for the following reasons: (a) In the benzylphenol/BF_3 system two parallel major reactions have taken place giving dibenzylphenol and phenol in one reaction, and hydroxybenzylphenols and benzene in the other. It was expected that the additional activating effect of the two methyl groups on the phenolic ring will sufficiently enhance the reactivity of the methylene-aromatic carbon-carbon bond on the side of the phenolic ring to make the cleavage of that bond the predominant reaction; (b) The chemical shifts of the benzyl protons and of the 2-methyl protons of the starting material and of the main products were sufficiently different to permit the quantitative analysis of the reaction mixture by proton NMR spectrometry. The chemical shifts of the benzyl $-CH_2-$ groups and of the methyl groups in the starting material and in the products are shown in Table 3.

The reaction which was studied is shown in the following equation:

$$2\ (CH_3)_2(HO)C_6H_2\text{-}CH_2\text{-}C_6H_5 \underset{k_{-1}}{\overset{BF_3\ k_1}{\rightleftharpoons}} (CH_3)_2(HO)C_6H_3 + (CH_3)_2(HO)C_6H(CH_2\text{-}C_6H_5)_2$$

4-benzyl-2,6-dimethylphenol → 2.6-dimethylphenol + 3,4-dibenzyl-2,6 dimethylphenol

The kinetic measurements were made in CS_2 solution at 70°C using sealed NMR sample tubes as the reactors. After the completion of the prescribed reaction period each sample tube was quickly cooled to room temperature and transferred to the NMR spectrometer for recording the spectra. When a solution of 4-benzyl-2,6-dimethylphenol and BF_3 (mole ratio 4.5 to 1.0) was used, the absorption under the methylene peak (3) and the methyl peak (2) increased from an initial value of zero as the reaction advanced, showing the formation of 3,4-dibenzyl-2,6-dimethylphenol. Independent gas chromatographic analysis showed the formation of an equivalent amount of 2,6-dimethylphenol. Reaction rate constants were determined for both the forward (k_1) and the reverse (k_{-1}) reactions for three different BF_3 concentrations. The following correlations were determined:

$$\text{Rate (forward reaction)} = k_1[BF_3][(CH_3)_2(HO)C_6H_2\text{-}CH_2\text{-}C_6H_5]^2$$

$$\text{Rate (reverse reaction)} = k_{-1}[BF_3][(CH_3)_2(HO)C_6H(CH_2\text{-}C_6H_5)_2][(CH_3)_2(HO)C_6H_3]$$

At 70°C and at a concentration of BF_3 = 1.0 moles per litre, $k_1 = 2.6 \pm 0.3 \times 10^{-4}$ min^{-1} lit. $moles^{-1}$ and $k_{-1} = 16.0 \pm 1.8 \times 10^{-4}$ min^{-1} lit. $moles^{-1}$. The benzyl group transfer in this system is clearly a bimolecular substitution reaction where the rate determining step involves a reaction between a protonated benzyl compound (benzenium ion) and a phenolic compound or its BF_3- complex. There is no indication of the formation of the benzyl cation in this particular system. It should be noted here that the data obtained on the transfer of n-propyl groups (Table 2) indicate that, similarly, the main reaction in that transfer does not involve the formation of the 1-propenium cation. If that were the case, isomerization to the 2-propenium cation would take place with the predominant formation of isopropylphenols. On the other hand, the formation of diaryl-methenium cations was indicated in model compound studies reported by Franz et al.,[11] who studied the behavior of triarylmethanes under depolymerization conditions using both PTSA and phenol-BF_3 as the catalyst.

III. COMMENTS ON THE CHEMISTRY OF COAL DEPOLYMERIZATION

After reviewing the information on the reactivities of various bridge structures which may be present in coal, it will be instructive to summarize available data on coal depolymerization yields as a function of coal rank. One can attempt then to correlate the product yields obtained by depolymerization with various structural features of coals over the coalification range which has been investigated.

Depolymerization yields determined with phenol-BF_3 at 100°C are summarized in Table 4,[12] and the yields obtained with phenol-PTSA depolymerization at 185°C are shown in Figure 4.[3] In the case of the phenol-BF_3 catalyst, the phenol-soluble product yield was the highest (75%) for the lignite. It gradually decreased to about 10% for the low-volatile bituminous coal, although the low product yield obtained with subbituminous coal does not fit this correlation. In the case of depolymerization with phenol-PTSA, the pyridine-soluble product yield was over 90% for coals of 70-84% C content; for coals with higher C content, the yield dropped sharply and it reached about 10% for a coal with 93% C. Benzene-ethanol was a more selective solvent than pyridine for fractionating the depolymerization products obtained with PTSA catalyst: a linear relationship between the yield of the soluble extract and the carbon content of the starting coal was observed.

The following comments can be made with regard to a correlation of the coal depolymerization product yields with the relative reactivites of aliphatic carbon and oxygen bridge structures in coal:

(1) In low-rank coals, particularly in lignites, the cleavage of aliphatic ether and benzyl ether oxygen bonds may contribute significantly to depolymerization. Many of the aliphatic bridges, which participate in depolymerization, may be linked to single phenolic rings. The reactivity of an aliphatic structure linked to a

phenolic ring is sufficient to permit its participation in the depolymerization reaction. On the other hand, spectrometic studies indicate[13] that these coals do not contain significant amounts of sufficiently reactive condensed aromatic structures which could participate in depolymerization.

(2) In high-volatile bituminous coals (C = 80-84%), the breaking of aliphatic bridges is seen as the major means of depolymerization. Many of these bridges may be linked to phenolic rings, others to condensed aromatic rings such as phenanthrene. Ether oxygen bonds play a less important role because most of these bonds are in aromatic ethers which do not react with BF_3.

(3) In higher rank bituminous coals (C > 84%), the depolymerization product yield decreases sharply with increasing rank. It is probable that this decrease is related to the nature of the aliphatic bridge structures. It is postulated that in lower rank coals a sufficient number of the bridge structures are short aliphatic chains (N_C = 1 to 4). On the other hand, in higher rank coals, nearly all of the bridge structures are condensed hydroaromatic rings; with structures of this type, several bonds must be broken between two aromatic groups to effect depolymerization.

(4) Among the aliphatic bridge structures, $-CH_2-$ bridges may play a particularly important role in coal depolymerization. Even if the number of such bridges is relatively small, the probability of their cleavage is high because, in general, both carbon-carbon bonds of the bridge are activated under the reaction conditions used in coal depolymerization. This view is supported by experimental data obtained in depolymerization studies made with phenol-BF_3 where the yield of soluble depolymerized products was proportional to the amount of $-CH_2-$ bridge structures found in the soluble products.[12]

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TABLE 1

BF_3-CATALYZED ISO-PROPYL GROUP TRANSFER TO PHENOL (1-^{14}C)

Starting Compound*	Conversion (%)	Product Distribution (wt %)		
		para-isopropyl-phenol (1-^{14}C)	ortho-isopropyl-phenol (1-^{14}C)	Residue
Cumene	8.0+	3.5	0.8	3.7
ortho-isopropylphenol	100.0	74.5	14.5	11.0
Retene (1-methyl-7-isopropylphenanthrene)	100.0++	61.5	10.2	28.3

*Starting compound to labelled phenol molar ratio: 1 to 20. Reactions performed at 100°C for four hours. Mixture saturated with BF_3

+Benzene, in an amount equivalent to the isopropylphenols, was also recovered

++A methylphenanthrene fraction, in an amount equivalent to isopropylphenols, was also recovered

TABLE 2

BF_3-CATALYZED REACTION OF PARA-N-PROPYLPHENOL WITH PHENOL (1-^{14}C)

Reaction Conditions:

Ratio of para-n-propylphenol to phenol (1-^{14}C): 1 to 20
Mixture saturated with BF_3 at reaction temperature
Temperature: 100°C
Reaction Period: 4 hours

Product Distribution (wt %):

para-n-Propylphenol (unreacted)	:	18.0
para-n-Propylphenol (1-^{14}C)	:	43.0
ortho-n-Propylphenol (1-^{14}C)	:	14.5
para-iso-Propylphenol (1-^{14}C)	:	5.3
ortho-iso-Propylphenol (1-^{14}C)	:	1.2
Residue	:	18.0
Total	:	100.0

TABLE 3

CHEMICAL SHIFT VALUES OF METHYLENE AND METHYL PROTONS OF BENZYL DERIVATIVES OF 2,6-DIMETHYLPHENOL

COMPOUND	CHEMICAL SHIFT (ppm)*			
	METHYLENE		METHYL	
	(3)	(4)	(2)	(6)
2,6-DIMETHYLPHENOL	---	---	2.08	2.08
4-BENZYL-2,6-DIMETHYLPHENOL	---	3.70	2.03	2.03
3.4-DIBENZYL-2,6-DIMETHYLPHENOL	3.80	3.70	1.95	2.10

*TETRAMETHYLSILANE = 0.00 ppm

TABLE 4

DEPOLYMERIZATION OF COALS OF DIFFERENT RANKS WITH PHENOL-BF_3 AT 100°C

Coal Type	C, % dmmf	Total Soluble[a] Yield, %	Combined Phenol Content of Soluble Fraction, %
Lignite	70.6	75.2	41.2
SubB	76.7	23.4	32.8
hvab	82.4	47.4	16.3
hvab	85.1	28.8	12.4
hvab	85.8	25.0	13.0
lvb	90.7	9.8	15.5

[a] Coal-derived part of phenol soluble material

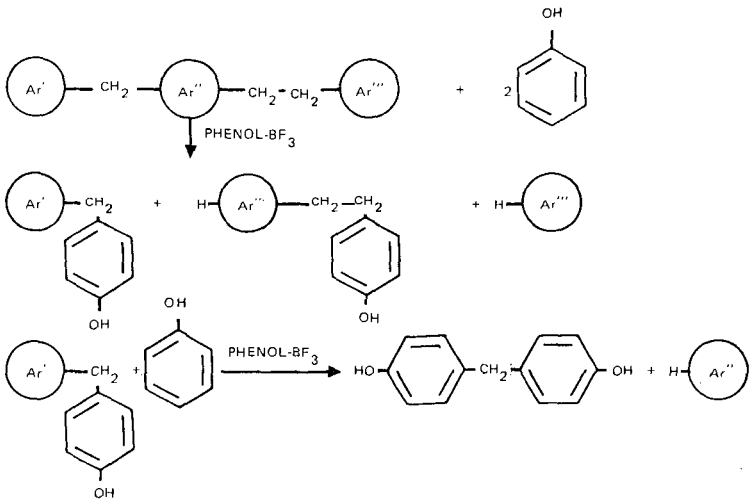


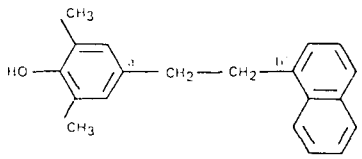
Figure 1. Coal Depolymerization via Transaralkylation with Phenol-BF_3

FIGURE 2

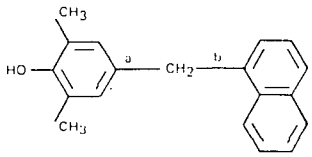
RELATIVE REACTIVITIES OF MODEL COMPOUNDS WITH PHENOL-BF_3

Model Compound	Reacting Bond	Relative Reactivity
A	a'	77
A	b'	2
B	a	70
B	b	41

Model Compound A:



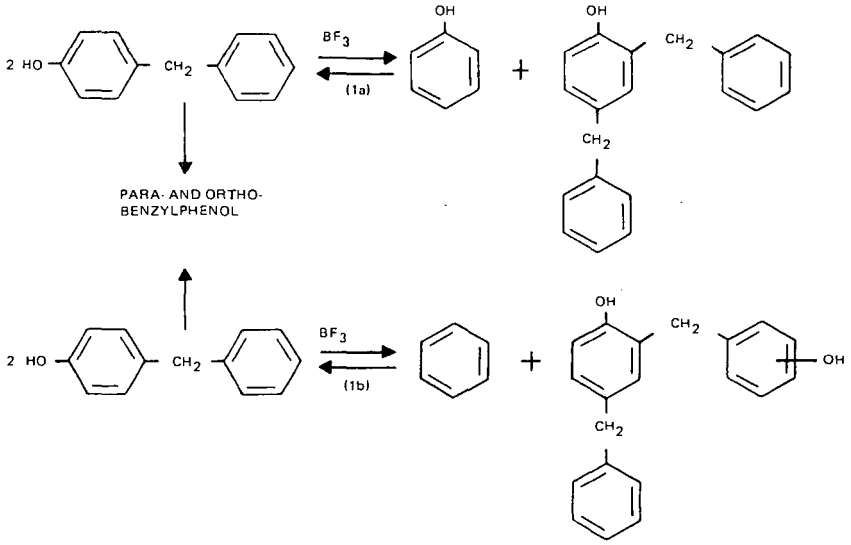
Model Compound B:

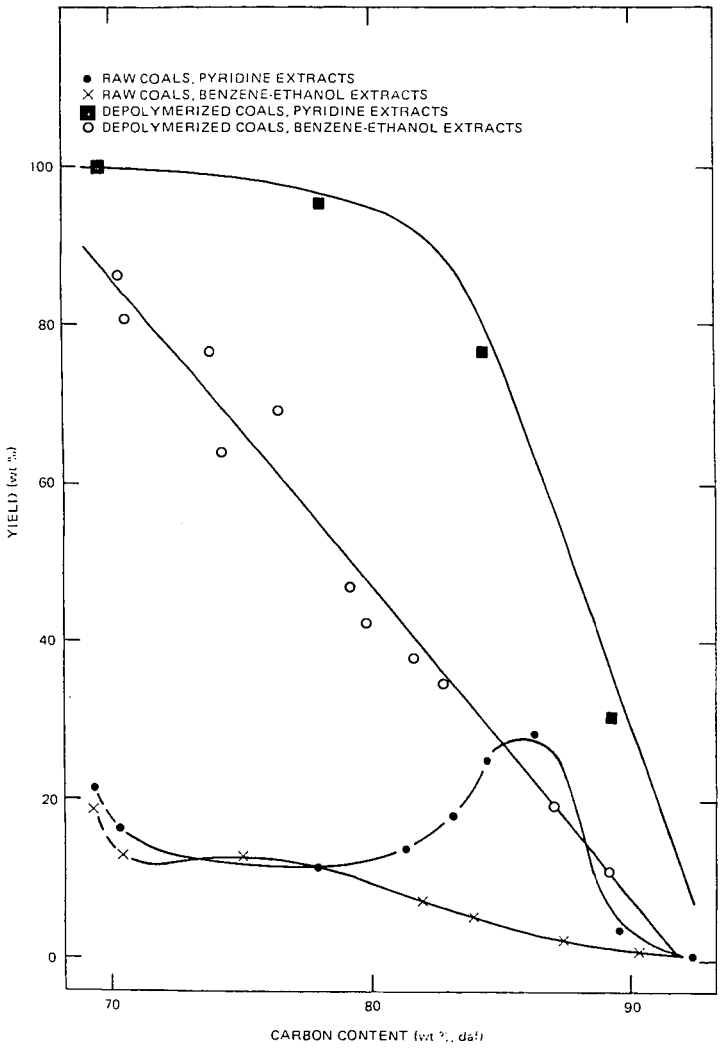


Reaction Conditions: Ratio of Model Compounds to Phenol: 1 to 10
Mixture Saturated with BF_3 at Reaction Temperature
Temperature: $100^{o}C$
Reaction Period: 4 hours

FIGURE 3.

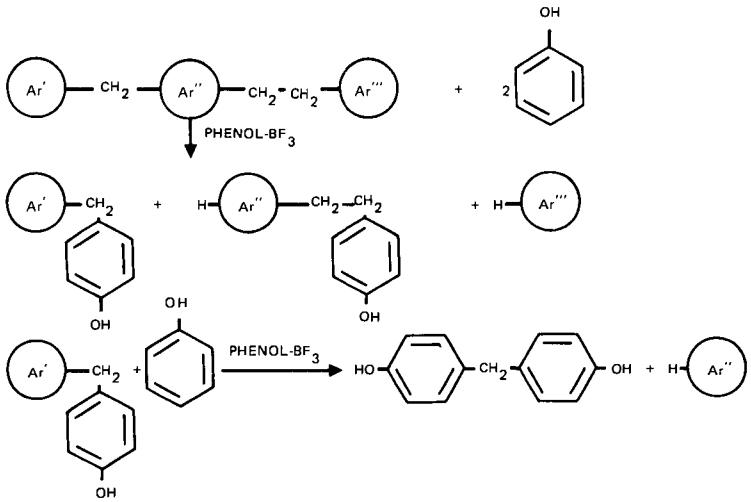
BF_3-CATALYZED BENZYL GROUP TRANSFER IN BENZYLPHENOLS





YIELDS OF PYRIDINE AND BENZENE-ETHANOL EXTRACTS FROM COALS AND DEPOLYMERIZED COALS[3]

FIGURE 4.



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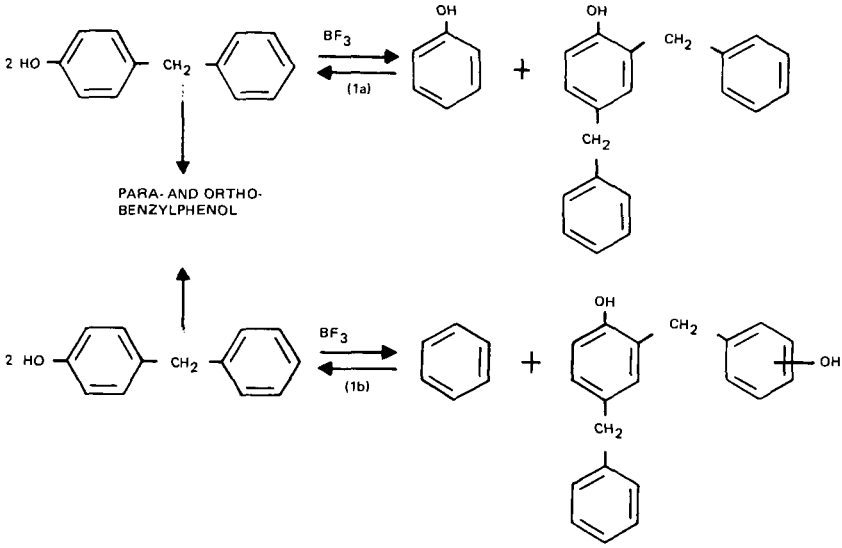

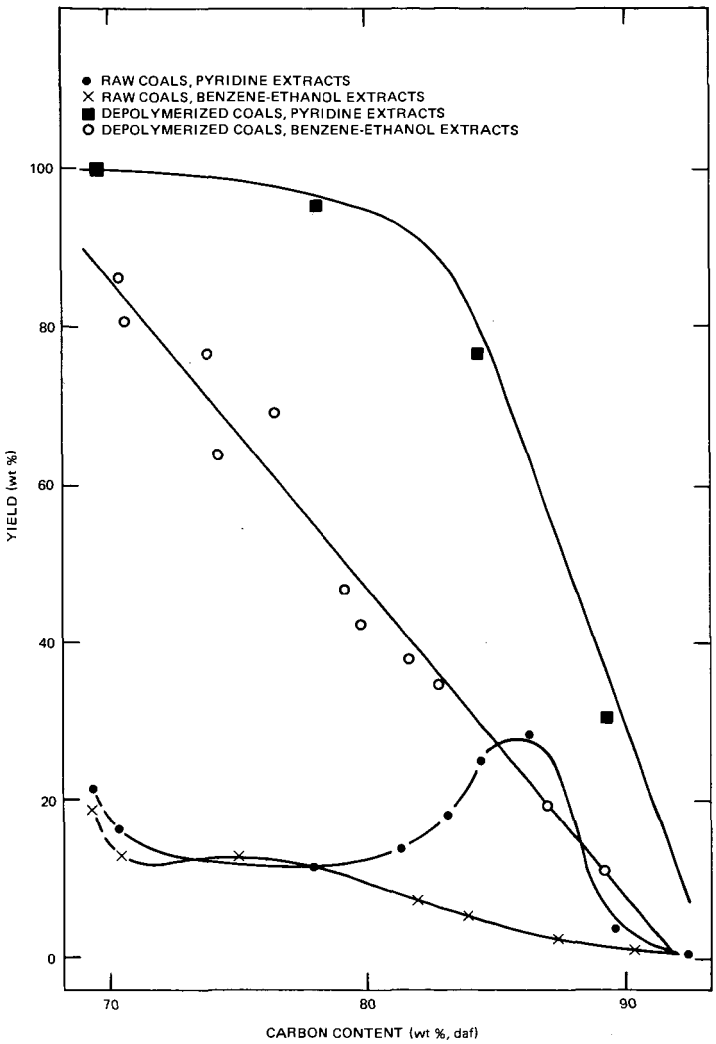

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