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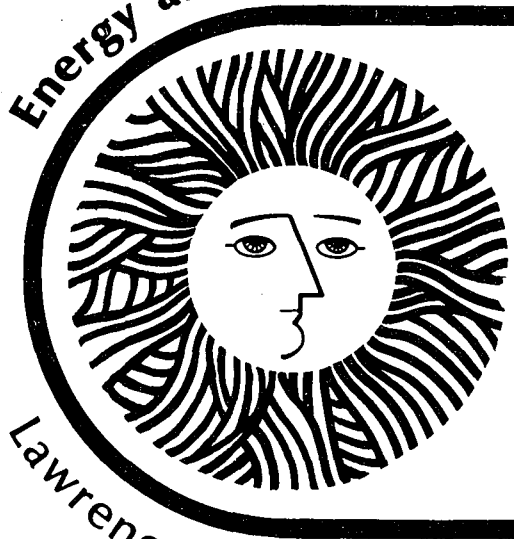
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Interaction Of A Sub-Bituminous Coal
With A Strong Acid and A Strong Base

Manu Seth and Theodore Vermeulen*

November 1977

Berkeley Laboratory University of California/Berkeley

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ACID AND A STRONG BASEContents

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ACID AND A STRONG BASE

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ABSTRACT

The interaction of a Wyoming sub-bituminous coal with molten phosphoric acid containing catalytic additives, and also with molten sodium hydroxide containing catalytic additives, has been studied at 200°C under hydrogen at atmospheric pressure. Treated coal was recovered from the melt by dilution with water and subsequent filtration.

Phosphoric acid treatment resulted in a product that had phosphorus incorporated into the organic coal matrix (up to 2.4 wt% in 4 hr). The H/C atomic ratio decreased from 1.031 to 0.923 within 1 hr of reaction, and then remained constant on further treatment. The products showed little desulfurization or deashing, and a much reduced mechanical strength, compared to raw coal. Benzene extractibility of the melt-treated coal increased to a maximum of 3.79 wt% (compared to 1.85% for untreated coal) in the first half-hour of reaction, and then declined on further treatment to reach 2.28% in 4 hr. None of the additives tested resulted in benzene extractibility greater than the maximum obtained with phosphoric acid alone. Extracts from acid-treatment experiments were characterized by mass spectrometry, ir, uv, and nmr; these extracts were found to contain no aromatics, and

thus were similar to extracts obtained in an earlier study with zinc chloride melts.⁵

Sodium hydroxide treatment of Wyodak coal resulted in a product similar to the original coal, both in appearance and mechanical strength. X-ray fluorescence analysis indicated up to 50% desulfurization of coal treated with sodium hydroxide at 200°C for 1 hr. The H/C of the product increases on treatment, the highest ratio (1.158) being obtained for an alkali melt containing sodium nitrite. A 33 to 50% increase of CCl₄ extractables is observed on alkali treatment. The presence of sodium acetate in the melt gave the largest increase in extractibility, with a total of 1.56 wt% compared to 0.96 wt% for untreated coal. Subsequent extraction with methyl isobutyl ketone was also high for this additive (9.08 wt%, compared to 5.92% for untreated coal). CCl₄ extracts of alkali treatment were wax-like, similar to those obtained with phosphoric acid or zinc chloride.

Because the amounts of material extracted are so small under these experimental conditions, the results obtained can not be used to draw general conclusions about the chemical structure of this coal or of liquefaction products from it.

Work performed under the auspices of the U. S. Department of Energy.

I. INTRODUCTION

Reserves of coal are quite abundant relative to those of petroleum, and represent a viable source to supplement or replace the hydrocarbons conventionally derived from petroleum. As reserves of crude oil continue to be depleted very rapidly, the need for economic substitutes becomes greater. The energy requirements in industrial countries have created a shortage in the supply of hydrocarbons which can be alleviated by the production of coal-derived hydrocarbons. Coal is more easily recovered and more widely available than oil shale and tar sands, its other nonliquid fossil-fuel competitors. The need for coal-conversion process development has intensified since the recent energy crisis and the consequent shifts in energy policy.

A. Coal Structure

Coal is composed primarily of carbon, hydrogen and oxygen, with lesser amounts of sulfur and nitrogen. In addition, it contains varying amounts of inorganic matter or "ash" and considerable amounts of moisture. Coals are classified by age or rank, growing older from lignite through sub-bituminous and bituminous to anthracite. Higher-rank coals exhibit an increase in carbon content and a decrease in both moisture and volatile constituents. Their structures are closer to graphite and hence are more difficult to attack chemically.

Because of its relative ease of hydrogenation and its abundant availability, a sub-bituminous coal (Wyodak mine, Roland seam) has been investigated in this study.

The structural characterization of coal has been studied extensively in recent years. Several conceptual molecular models have been visualized

to illustrate how various known molecular arrangements might be incorporated into a solid exhibiting the behavior of coal. Currently the most widely accepted model for bituminous coals is the one presented by Wiser,¹ shown in Fig. 1.

About 70% of the carbon in coal exists in highly substituted aromatic or hydroaromatic rings, while only about 23% of the total hydrogen is attached to these rings. The number of rings in such clusters is believed to be on the order of 3 to 5.² The oxygen and nitrogen occur in the rings, linkages, and functional groups, while the sulfur exists in both organic and inorganic forms. The carbon not contained in aromatic and hydroaromatic structures is present either as hetrocyclics or in very short aliphatic chains.

Results from a recent study³ indicate that coal-derived asphaltenes exhibit an acid-base structure where the acidic components are mainly phenolic hydroxyl and pyrrole-type nitrogen, while the basic constituents are ring or ether oxygen and ring nitrogen (including pyridine). Complex formation occurs by hydrogen bonding. The acidic components provide all of the donor hydrogen, precluding the possibility that any one functional group in asphaltenes is amphoteric. These results suggest that coal, too, may be held together partly by acid-base interactions.

The pore structure of coals varies widely both in pore size and porosity. Typically they have micropores on the order of 5 to 50 Å and surface areas of 150 to 360 m²/g.⁴ Such a physical structure, coupled with the obviously irregular packing, makes coal susceptible to swelling and chemical attack by reactive media.

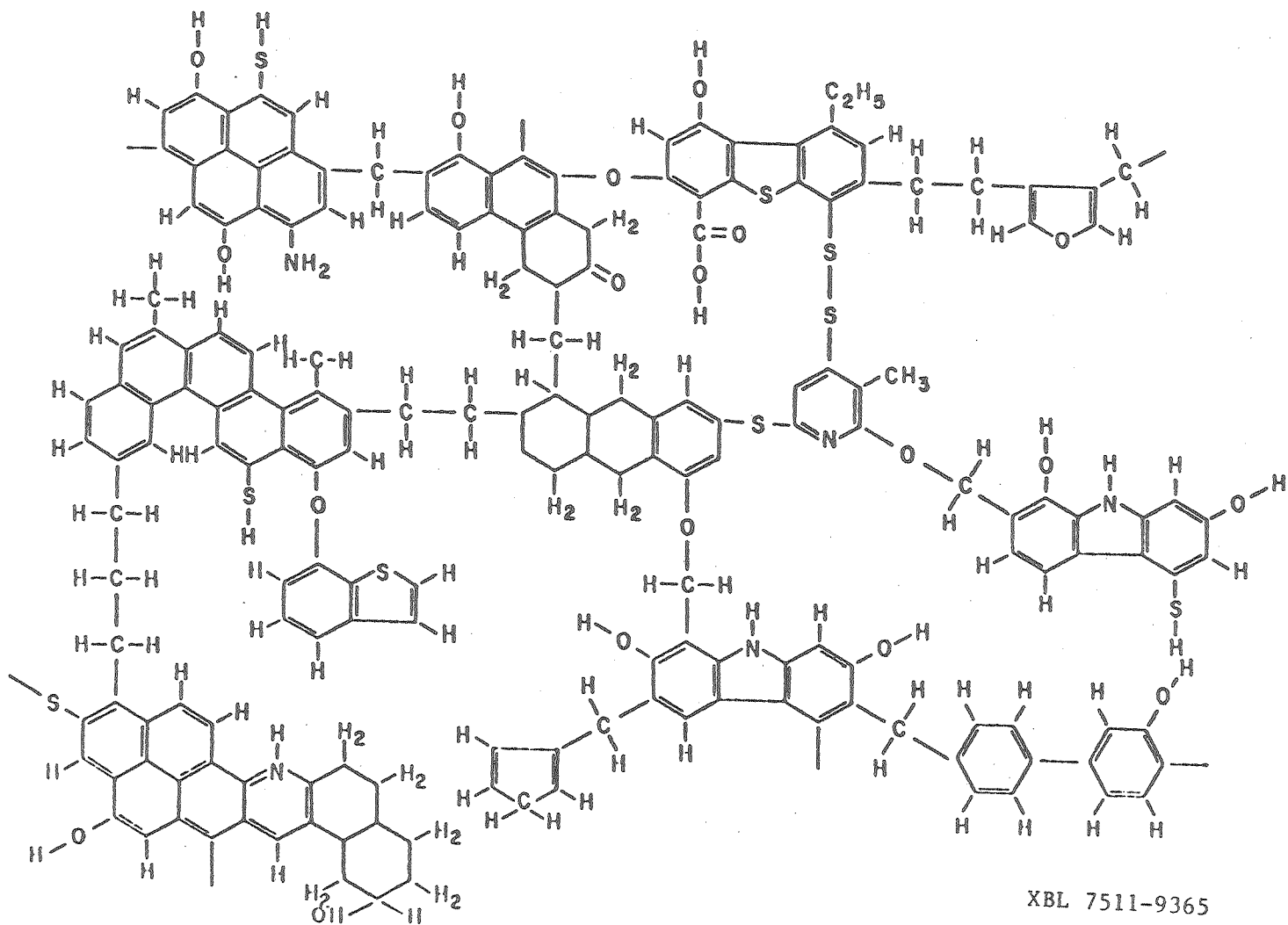


Fig. 1. A representation of the structure of bituminous coal.

B. Coal Liquefaction

Coal-liquefaction technology can be divided broadly into five approaches. Direct hydrogenation of coal at high temperatures and pressures was the first approach, the technology in this area having been developed to the point of commercial utilization in the early 1940's. At its peak, during World War II, 11 direct-hydrogenation plants supplied a substantial portion of Germany's liquid hydrocarbon demand. After the war, the availability of cheap petroleum led to the shut down of all these units.

A second approach for obtaining liquid products from coal which has been used commercially involves the formation of CO/H₂ mixtures which are converted to hydrocarbons by Fisher-Tropsch synthesis.

Pyrolysis at both low and high temperatures has also been explored as a third means of getting liquid products.

Fourth, there has been considerable recent interest in solvent extraction of coal. Typical processes and process conceptualizations involve extraction of coal with an organic solvent (or mixture of solvents), solvent recovery, and further hydrogenation of the extract to give a desirable product mix of liquid hydrocarbons. Pittsburgh and Midway Coal Company has begun operation of a pilot-plant scale facility for producing a solvent-refined coal; large-scale commercial exploitation is envisioned.

The fifth approach to obtaining liquid products from coal, which is receiving increasing attention, is catalytic hydrogenation. Currently, considerable effort is being directed into the search for catalytic systems which could be used to promote the formation

of hydrogenated molecules from coal. It is hoped that such systems will result in conversions at moderate temperatures and pressures, and hence will be more economical than conventional techniques employing pyrolytic or near-pyrolytic conditions.

1. Alkali Treatment

The utilization of alkaline solutions in the treatment of coal covers two main areas. Investigators have studied the use of concentrated alkali solutions for hydrolytic attack on the coal structure,⁹⁻¹² and, more recently, relatively dilute alkaline solutions have been found to be effective for the desulfurization of a variety of coals.^{14,15}

A prehydrogenation treatment for removing a part of the oxygen from coal by hydrolysis or mild pyrolysis may be desirable from the standpoint of hydrogen economy, because it would decrease the hydrogen requirement during hydrogenation by the amount that would have been used to form water. The success of Fry and co-workers⁶⁻⁸ in removing oxygen from various oxygenated compounds as carbon dioxide by alkali treatment suggested the possibility of removing oxygen from coal along with sufficient carbon to form carbon dioxide by subjecting the coal to the action of aqueous alkali under pressure.

The sulfur contained in coal to be used as fuel must be removed to meet environmental emission standards. This sulfur removal can be done either after burning the coal (e.g., by scrubbing stack gases) or before burning it. Sulfur contained in coal is divided broadly into pyritic, sulfate, and organic sulfur. Of these, the pyritic and sulfate forms are normally found as microscopic sized particles

amenable to attack by alkali solutions. Little is known about the action of alkali on the organic sulfur in coal.

2. Acid Treatment

Encouraging results in catalytic-hydrogenation systems for coal have almost always involved the use of acid catalysts, with or without additional hydrogenating agents. Hydrocracking (the presence of both acid and hydrogenating catalysts) is a well established petroleum-processing technique which involves dual-functional catalysis. The acid centers catalyze reactions which occur by carbonium-ion formation and proton transfer, such as cracking, polymerization, isomerization, alkalation, dealkylation, and hydration. On the other hand, hydrogenation catalysts enhance the formation of desirable products by preventing secondary cracking and char formation, and by facilitating the hydrogenation of olefins and unsaturated aromatics.

An intensive development based on the hydrocracking ability of Lewis acids was carried out by Gorin and associates of Consolidation Coal Company.³ Batch autoclave tests showed molten zinc salts, which are Lewis acids, to be superior catalysts for hydrocracking polynuclear aromatics. At severe reaction conditions of 427°C and 4250 psig with 60 min contact time and a massive 1:1 weight ratio of catalyst to hydrocarbon, they obtained 90 wt% conversion to products boiling below 450°C. These studies and others have demonstrated the activity of liquid hydrocracking catalysts. More recently⁵ the interaction of a Wyoming sub-bituminous coal with molten zinc chloride containing additives was explored in this laboratory. Reactions at 200°C under

hydrogen at atmospheric pressure yielded a "melt treated coal" having an increased benzene extractibility.

As an alternative to molten salts, inorganic acids are an obvious choice as a source of hydrogen ions for hydrocracking systems. The phosphoric acids retain their acid characteristics at high temperatures, and also exhibit other desirable properties, discussed later, which may make them effective for coal processing.

C. Phosphoric Acid Catalysis in the Petroleum and Chemical Industries

Both polymerization and isomerization are important in the manufacture of motor fuels and chemical products from petroleum. The phosphoric acids have proved to be excellent catalysts for the manufacture of high-octane gasoline¹⁶ by polymerization of refinery cracked gases. Phosphate-based acid catalysts also are very effective in acylation and alkylation of heterocyclic ring systems such as thiophene and furan, as well as in alkylation of organic amines and condensation of amides. In addition, phosphoric acid catalysts are active in other reactions exhibiting an ionic mechanism, such as the depolymerization of paraldehyde. To achieve good contact with the reacting mixture, the phosphoric acids are often supported on a relatively inert clay-type solid.¹⁸

Catalysts based on phosphoric acids have also been made which contain the phosphates of a number of different metals. In certain specified cases, phosphoric acid is used in liquid form.^{17,19} The condensed phosphoric acids which do not exhibit too high a viscosity are applicable in such cases.

Considerable literature exists also on the catalytic activity of adducts formed between boron trifluoride and phosphoric acids.²⁰ As an example, Topchiev and Paushkin²¹ have reported a catalyst, $H_3PO_4 \cdot BF_3$, prepared by saturating orthophosphoric acid with boron trifluoride, which can be used effectively in catalyzing the alkylation of isoparaffins with olefins. When used for the alkylation of isobutane with propylene at 20°C and 15 atm, it gave a yield of 68% calculated on the olefin.

D. Coal Conversion with Phosphoric Acids

Pioneering work on the use of phosphoric acid for coal hydrogenation was presented in two patents by Henry Dreyfus.^{1,2} His results indicated that substantial conversions of coal to vapor products could be obtained by slurring the coal with twice its weight of dilute solutions of phosphoric acid or ammonium phosphate, heating to drive off part of the water, and passing the impregnated coal through a rotary convertor heated to 450°C.

Neutralization of the basic constituents of coal with acids and acid salts was proposed by Pier and co-workers.²² They reported^{23,24} that pretreating the coal with phosphoric acid prior to hydrogenation above 50 atm and between 250 and 750°C resulted in improved yields of distillable products.

More recently, interest has been renewed in the use of phosphoric acids for coal processing. Schuman and associates²⁵ claimed a 45.6 wt% conversion (0.7% to gases, 13.3% to oil, and 31.6% to asphaltenes) of a bituminous coal when a 10% solution of phosphoric acid containing less than 1% $(NH_4)_2MoO_4$ was reacted under a hydrogen partial pressure

of 1500 psig at 344°C for 6 hr. Following that work, Santagelo²⁶ showed that by slurrying coal with a 5 to 10% aqueous solution of phosphoric acid, filtering to remove the excess acid, and then heating the coal to 370°C, a char of reduced sulfur content could be obtained.

Extending earlier work to demonstrate the catalytic activity of metal halides, Kiovsky²⁷ obtained a substantial improvement in gasoline-range products by combining massive quantities of molten halides with small amounts of inorganic acids. Operating conditions and results obtained in batch autoclave experiments with Illinois No. 6 coal are summarized in Table I. Antimony tribromide, when promoted with hydrogen bromide, resulted in a four-fold increase of products in the gasoline range, compared with unpromoted antimony tribromide at the same conditions. The use of phosphoric acid as a promoter results in lower conversions but with a better product distribution. Similar results were obtained when tin bromide was substituted for antimony tribromide.

E. Coal Hydrogenation with Massive Amounts of Phosphoric Acids

Recently the use of massive quantities of phosphoric acids has been investigated further by Kiovsky and Wald of Shell Oil Company, who developed pyrophosphoric acid systems containing hydrogenation catalysts for coal conversion. Batch autoclave tests showed that massive amounts of pyrophosphoric acid with small quantities of NH_4I , SbBr_3 , GaI_3 , ZnCl_2 , GaBr_3 , TiF_4 , together with halogen acids such as HI and HBr, make excellent systems for coal hydrogenation.

Kiovsky²⁸ treated a Big Horn coal (moisture-free, 150-250 mesh, 6.5% ash) with 7.5 times its weight of pyrophosphoric acid. At 350°C,

Table I. Experiments and results reported by Kiovsy (Ref. 27).

	Residence Time	1 hr				
	Coal: Illinois No. 6	20 gm				
	Pressure	1700 psig				
<u>Metal Halide</u>	<u>Antimony Tribromide</u> 175 gm			<u>Tin Bromide</u> 250 gm		
Acid	None	HBr 11 gm	H ₃ PO ₄ 20 gm	None	HBr 20 gm	H ₃ PO ₄ 20 gm
Temp. °C	280	280	280	320	350	325
	Products, MAF wt%					
C ₁ to C ₃	0.49	1.13	0.70	1.98	5.8	6.27
C ₄ to 250°C b.p.	7.12	27.0	13.81	2.29	30.4	25.3
MAF indicates "moisture- and ash-free" basis.						

for a residence time of 30 min, gasoline-range products of up to 24 wt% of MAF coal were obtained. Reactions were conducted at total pressures between 1500 and 2500 psig. The study showed that the addition of 3 to 6 wt% of hydrogenating agents to the acid increased the conversion of coal to gasoline-range products from 0.1 to 24.4 wt% MAF coal. Further, although total conversion dropped somewhat at reduced times and temperatures, the quantity of benzene-extractables produced was approximately the same. As an example, when 3 wt% of ammonium iodine was presented in the acid, a decrease of reaction temperature from 365°C to 320°C and a simultaneous decrease of reaction time from 30 to 2.5 min changed the weight of asphaltenes produced only by from 67 to 64% of total carbon in coal. At the same time, however, volatile products produced dropped from 32.3% by weight of total carbon to a mere 6.5%. A substantial reduction of sulfur in the product was also claimed as a result of the hydrocracking, due to the hydrogenation of some of the sulfur compounds to hydrogen sulfide.

In a related patent²⁹ Wald reported a series of experiments using a catalytic liquid phase composed predominately of pyrophosphoric acid. The acid contained 5 to 20 wt% of polyvalent metal halides. Illinois No. 6 coal was hydrocracked at a temperature of 350°C and a pressure of 1800 to 2500 psig for 1 hr. Composition of catalyst systems, products obtained, and reaction conditions are listed in Table II. Of the phosphoric acid systems, the antimony tribromide/phosphoric acid combination gave the best results; the extent of cracking per unit weight of SbBr_3 present was two to five times as large in

Table II. Experiments and results reported by Wald (Ref. 29).

Conditions:		Temperature	350°C					
		Pressure	1800-2000 psig					
		Reaction Time	1 hr					
Coal Used:		Illinois No. 6, Moisture Free						
		Ash	15%					
		Size	100-200 mesh					
		Amount	20 gm					
Catalyst Type	None*	SbBr ₃	SbBr ₃	SbBr ₃	GaBr ₃	GaI ₃	TiF ₄	
Amount	0	150	10	40	5	8	31	
Pyrophosphoric Acid, gm	107	0	150	150	150	150	150	
Products, MAF wt%								
CH ₄ and C ₂ H ₆	tr	1.2	0.8	1.4	0.5	1.8	0.5	
C ₃ H ₈	0.1	1.7	1.9	2.1	1.5	3.1	1.7	
i-C ₄ H ₁₀	0.05	4.0	2.5	2.7	2.1	3.6	2.8	
n-C ₄ H ₁₀		1.4	0.3	0.9	0.2	0.5	0.2	
i-C ₅ H ₁₂		3.7	1.2	1.8	1.3	1.6	1.2	
n-C ₅ H ₁₂	0.04	0.6	0.1	0.4	0.1	0.1	0.1	
C ₆ H ₁₄	0.01	3.3	0.9	1.6	1.0	0.8	0.5	
Methyl cyclopentane	0.01	6.7	1.2	2.1	1.2	0.8	0.3	
C ₇ H ₁₆ and C ₈ H ₁₈	tr	15.8	3.9	7.5	6.3	1.9	0.9	
C ₉ H ₂₀ to 250°C	0	17.0	7.6	8.0	10.0	3.3	1.1	
TOTAL								
C ₄ H ₁₀ to 250°C	0.1	52.0	17.7	24.9	22.2	12.7	7.0	
Hydrogen consumed, MAF wt%	1.5	9.3	8.5	10.4	8.3	7.7	7.8	
*Reaction time, 30 min.								

the phosphoric acid/ antimony tribromide mixture as in pure antimony tribromide catalyst.

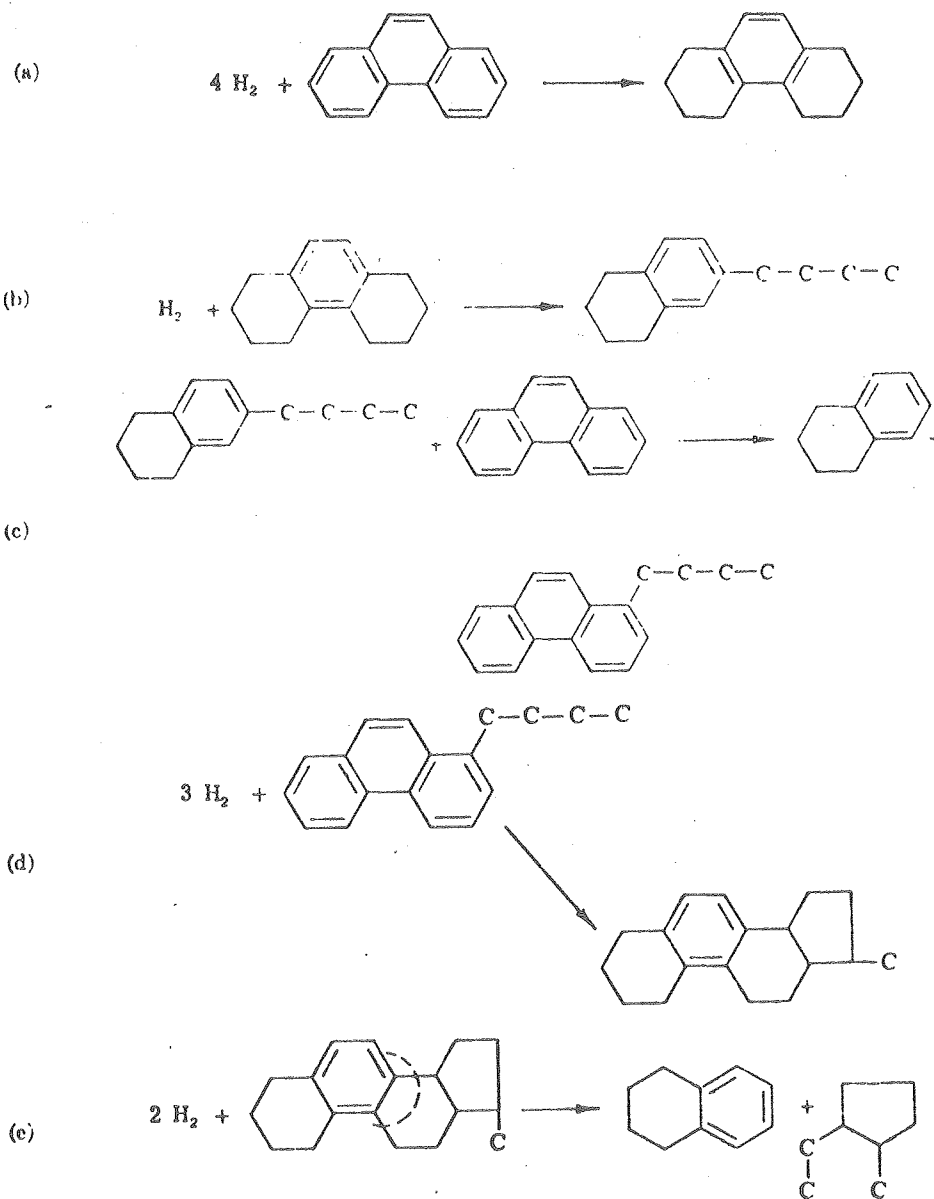
F. Aspects of Coal Catalysis in Phosphoric Acid

1. Hydrocracking Over Solid Acidic Catalysts

Extremely heavy hydrocarbons, as in coal, contain proportionately less combined hydrogen than the more valuable lower-boiling fractions. Typically the hydrogen content of sub-bituminous coals is about 5 wt%, corresponding to a H/C molecular ratio of 1.0. The hydrogen content of typical gasoline is on the order of 14%, giving a H/C molecular ratio near 2.0. Accordingly a means of converting coal to lower-boiling hydrocarbons is to provide hydrogen, and both hydrogenate and crack the large molecules. As discussed earlier, hydrocracking is an effective technique for obtaining both results simultaneously, and catalytic systems based on phosphoric acid show much promise.

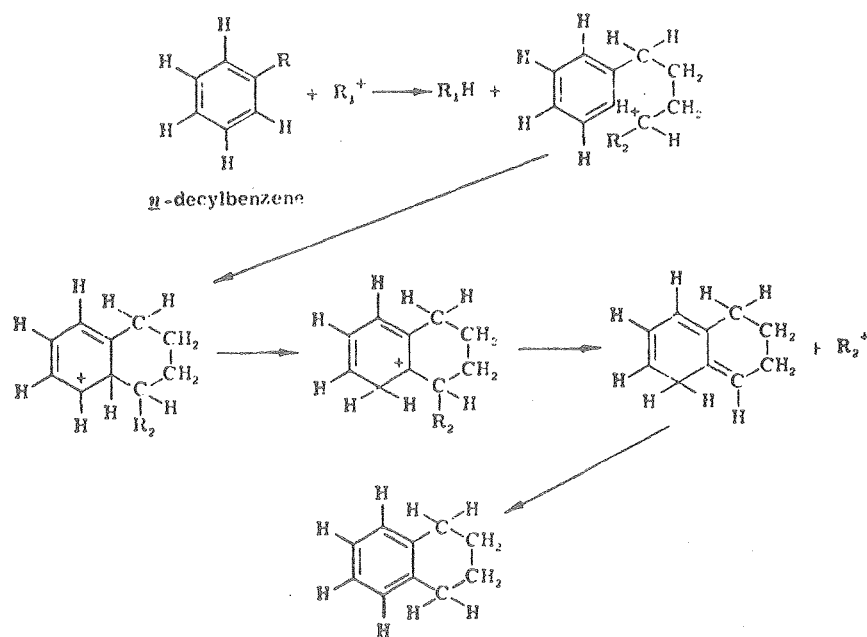
In any hydrocracking system the relative strengths of cracking and hydrogenation can be varied, as in studies of zeolite hydrocracking catalyst,³⁰ by shifting from a primarily cracking (acidic) catalyst to a primarily hydrocracking (non-acidic) catalyst. Using nonacidic catalysts, with alkylaromatics for example, there is successive removal of methyl groups from the side chains.³¹ When acidic catalysts are used, the principal reactions are isomerization, dealkylation, alkyl transfer, and cyclization.³²

Reaction mechanisms of several pure hydrocarbon compounds have been studied extensively on dual-function zeolite catalysts. The mechanisms postulated for two compounds representative of commonly occurring linkages in coal are presented in Figs. 2 and 3.



XBL 7711-11323

Fig. 2. Reaction mechanism for the hydrocracking of phenanthrene.
 (R. F. Sullivan, C. J. Egans, and G. E. Langolis, J.
 Catalysis 3, 183 (1964)).



XBL 7711-11322

Fig. 3. Reaction mechanism for the hydrocracking of alkyl benzene.
 (R. F. Sullivan, C. J. Egan, G. E. Langlois; J. Am. Chem. Soc. 83, 1156 (1961))

Products from hydrocracking of alkylbenzenes where the alkyl side chains have three to five carbon atoms are relatively simple (Fig. 2), direct alkylation being the primary reaction. Alkyl-group transfer or disproportionation to form benzene and dibutyl-benzene is also observed.³³

Reactions of polycyclic aromatics can be illustrated by the hydrocracking of phenanthrene.³⁴ The principal product is tetralin; next largest is methylcyclohexane, and partially hydrogenated C₁₄'s are important too. An unusual cracking reaction produces bicyclic hydrocarbons, principally tetralin, without producing equivalent amounts of light paraffins. A suggested mechanism (Fig. 3) involves:

- a) Partial hydrogenation of the polycyclic aromatic
- b) Opening of one of the cycloparaffin rings to form a butyl-side chain
- c) Alkyl transfer of the side chain to another reactant molecule
- d) Ring closure accompanied by hydrogenation to form tetracyclic hydrocarbons
- e) Cracking of a central cycloparaffin ring to give a tetralin and cycloparaffin

This mechanism accounts for the lack of formation of paraffins through combination of a butyl-group transfer and a cyclization reaction.

2. General Considerations

The extent to which a charge is dissolved, dispersed, or reacted with the catalyst system depends partly on the oxygen, nitrogen, and sulfur content of the charge. Petroleum oils low in these elements are relatively insoluble in phosphoric acid, which is highly polar.

Coal, which contains larger portions of these polar atoms, is considerably more soluble. Low-molecular-weight products containing polar groups would also be soluble in the acidic system, facilitating their further processing as a homogeneous phase. In addition, any water formed (by hydrogenation of bound oxygen, for example) will be chemically bound by the phosphoric acid, minimizing adverse effects it might have on added catalysts, such as through hydrolysis.

Unlike other inorganic acids (e.g., sulfuric), phosphoric acid is not reduced by hydrogen or hydrocarbons, nor adversely affected by nitrogen, sulfur, or oxygen compounds. Thus, if necessary, the acid can be freed of carbonaceous residues in a regeneration step by an oxidation (burning) without adversely affecting the acid. Because it is nonoxidizing, phosphoric acid is compatible with metal halides, even iodides. Further, the acid protects the activity of any hydrogenating catalysts that may be added by shielding them from reaction, if any ammonia is formed. Any ammonium phosphates that may be so formed could be decomposed by heating the acid/phosphate mixture in a regeneration step to liberate ammonia and hence recover the acid. Finally, numerous hydrogenating catalysts, not themselves liquids, are soluble in the acids.

As the temperature is raised, phosphoric acid tends to dehydrate and becomes more condensed. The vapor composition and boiling-point curves³⁵ for various P_2O_5 contents are given in Fig. 4. The boiling point increases slowly up to the composition corresponding to about 65% P_2O_5 (87.7% H_3PO_4). Thereafter the boiling point rises rapidly,

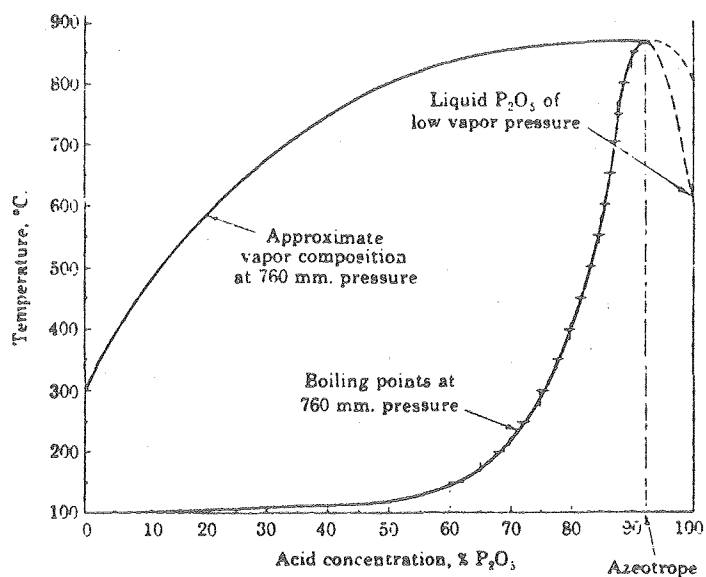
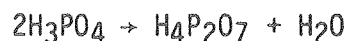


Fig. 4. Vapor-composition and boiling-point curves for phosphoric acid.

XBL 7711-11324

(Such, J. E., Phosphorous (Wiley, NY, 1967))

and the presence, in solution, of pyrophosphoric acid formed by the reaction

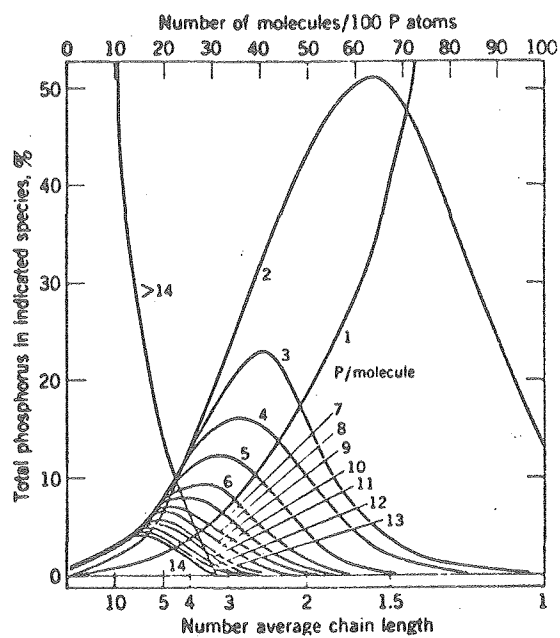


has been observed³⁴ even though the P_2O_5 content rises to only 68.8%.

Liquid orthophosphoric acid itself has been shown to contain about 12.7% of its P_2O_5 content in the form of pyrophosphoric acid and a corresponding proportion of "free" water, possibly strongly solvated by the orthophosphoric acid, in accordance with the equilibrium above.³⁸ On further heating, water continues to evaporate, and acid condensation occurs. Mixtures of polyphosphoric acids are formed in the proportions as shown in Fig. 5 (which is based on data contained in Ref. 36). Since all the unbranched acids exhibit one strong hydrogen ion for each phosphorus atom, the catalytic activity is usually not greatly affected by the degree of condensation of the acid.

Ash, the inorganic component of coal, is composed chiefly of compounds of silicon, aluminum, iron and calcium with smaller quantities of compounds of magnesium, titanium, sodium, and potassium, these occur in the ash as a mixture of silicates, oxides, and sulfates with smaller quantities of other compounds. The principal source of iron is pyrite, whereas calcium and magnesium exist primarily as carbonates. Typical limits of ash composition of bituminous coals³⁹ are shown in Table III. The ash composition of subbituminous coals may be higher in CaO , MgO , and SO_3 .

Phosphoric acid readily attacks all the metal oxides to produce the corresponding metal phosphates. Further the acid readily complexes



XBL 7711-11325

Fig. 5. Composition of phosphoric acids in terms of the constituent polyphosphoric acid.
 (Such, J. E., Phosphorous (Wiley, NY, 1967))

Table III. Typical inorganic constituents of bituminous coals.

Constituent	Ash, wt%
SiO ₂	20-60
Al ₂ O ₃	10-35
Fe ₂ O ₃	5-35
CaO	1-20
MgO	0.3-4
TiO ₂	0.5-2.5
Na ₂ O and K ₂ O	1-4
SO ₃	0.1-1.2

with metal ions. Stable complexes with aluminum, iron, and even calcium are known to exist.^{40,41} Silica, in any of its forms, when heated with orthophosphoric acid, dissolves to an extent dependent on its state of sub-division and on the temperature and concentration of the acid. Thus the acid has the potential of attacking almost all the ash constituents of coal, and hence of facilitating its breakdown.

Phosphoric acid is known to react with several classes of organic compounds. The most common and thoroughly investigated reactions are the formation of alkyl and aryl esters of phosphoric acid.⁴² Mono- and di-alkyl esters of phosphoric can be prepared by heating the acid with the corresponding alcohol. Aliphatic mono- and di-esters of the acid are syrupy liquids whereas aromatic mono- and di-phosphates are frequently solid (as a general rule most of these esters can be hydrolyzed to recover the acid and corresponding alcohol). Aldehydes and ketones yield corresponding hydroxy substituted derivatives and diazo compounds. In addition, a considerable fraction of organo phosphorus compounds are capable of polymerizing.⁴³ As one example, phosphoric acid esters which contain two or more alkyl groups usually polymerize easily to give cross-linked polymers.⁴⁴ The ability of phosphoric acid to react extensively with organic molecules indicates the possibility of complex acid-coal interactions. Thus, apart from its catalytic activity, phosphoric acid could be expected to take part in reactions producing complex organophosphorus compounds.

G. Coal Hydrolysis by Alkali Treatment

With many organic structures, hydrolysis in either acid or alkali medium is effective. For coal, there are no data indicating hydrolytic breakdown in other than alkali medium. Dilute hydrochloric or sulfuric acids are without effect, up to 120°C. Nitric acid reactions are predominately oxidative.¹²

The effect on coals by alkali at concentrations from 4% (1N) to 60% has been widely studied. (Earlier work in open vessels undoubtedly introduced some atmospheric oxidation.)

Investigations of various coals were carried out by Fischer and co-workers;⁴⁵ 5N sodium hydroxide at 250°C with a "Lohbergkohle" was found to convert at about 2.5 wt% of coal to alkali-soluble products. The whole mass of coal was altered, having developed plastic properties and caked together. At 350°C with 4N potassium hydroxide, 21% of the same coal was converted to alkali-soluble products.

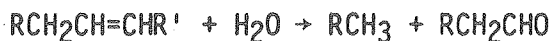
In more detailed investigations by Fischer and Schrader^{46,47} three types of reactions were recognized as taking place: hydrolysis, oxidation by water (with carbon dioxide formation and hydrogen evolution), and hydrogenation.

Hydrolysis of a "bright" Wyoming coal with 5N sodium hydroxide at 350°C for 24 hr has been reported.¹¹ The solid residue contained much less oxygen than the original coal. The product obtained (fractionated by distillation and solvent extraction and expressed in wt% of ash-free coal) are given in Table IV. Compounds identified were phenol, and acetic, propionic, butyric, and succinic acids. Also probably present were caproic and lauric acids, cresols, xylenols,

Table IV. Sodium hydroxide treatment of a Wyoming coal.¹¹

Residence Time	24 hr
Temperature	350°C
Sodium Hydroxide Concentration	5N
Products	Yield, MAF wt%
Gases: hydrogen, methane and ethane	2.8
Liquid phenols (molecular weight 90 to 180)	3.0
Solid phenols (molecular weight 300)	5.0
Fatty acids (equivalent weight 100)	13.0
Nitrogen bases	0.7
Ammonia	0.5
Hydrocarbon (molecular weight 100 to 400)	15.6
Carbonates (as carbon dioxide)	22.0
Insoluble Residue	28.3

and alkylated of partly hydrogenated cyclic hydrocarbons containing condensed rings. Elemental balances showed that the overall reaction corresponded to addition of water to coal. The products appeared to have been formed by hydrolysis, oxidation, and hydrogenation. The following additional reactions were postulated.



Kasenhagen¹⁰ has studied the action of sodium hydroxide on a Pittsburgh Seam coal over the temperature range 350°C to 400°C; the alkali concentration ranged from 4% to 150%. The maximum yield of alkali-soluble product, phenolic in nature, was obtained with rather dilute alkali (1N to 5N) at temperatures of 350° and 325°C. Above this temperature range, alkali-soluble material decreased coincident with an increase in neutral acids; this was reported to suggest a destructive reaction of alkali with the phenols and acids. The relatively small yield of alkali-soluble degradation products indicated the absence of hydrolysis.

Later experiments carried out with a similar technique on Illinois No. 6 bituminous coal¹³ showed over 30% of the carbon of this coal to be convertible to phenolic and acidic products, compared with about 12% for the Pittsburgh Seam coal.

Another important conclusion from Kasenhager's experiments¹⁰ was the lack of alkali interaction with nitrogen linkages, the nitrogen

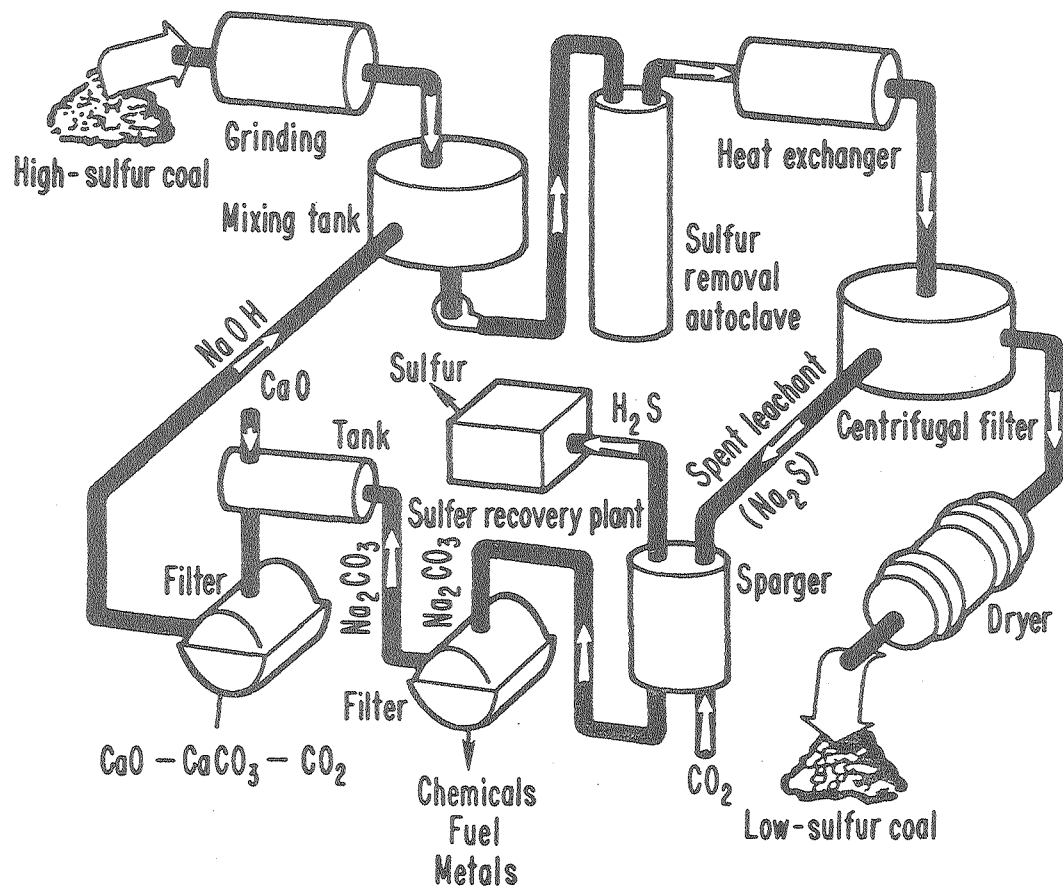
being concentrated in the insoluble residue. The results indicated that only insignificant amounts of the nitrogen in coal are bound as amide linkages.

Treatment of brown coal and sub-bituminous coal with aqueous or alcoholic alkali at about 190°C for 12 hr yielded alcohol-soluble products that contained more hydrogen and less oxygen than the original coal.⁴⁸

In a recent study, Wilson and Sharma⁹ treated two coals (a Dinnington and a Haig coal) with 2N sodium hydroxide solution at temperatures from 250°C to 350°C and pressures up to 250 atmospheres. Results of this and of previous work (by Parker et al.¹¹ and Kasehagen¹⁰) were compared with the aid of graphical statistical methods. The authors concluded that there is little increase in hydroxyl groups; that some hydrolysis occurs in the 250° to 375°C range; and that high-temperature treatment gives residues containing a lower O/C and a higher H/C ratio than the original coal.

H. Coal Desulfurization by Alkali Treatment

Recently there has been considerable interest in utilizing dilute alkali solutions for the desulfurization of coal. Battelle Memorial Institute's Columbus Laboratories is testing a desulfurization process currently in the pilot-plant stage.¹⁴ The process involves heating a slurry of coal and sodium hydroxide solution (10% by weight) to convert sulfur and a small portion of the ash to soluble forms. The process flow sheet is shown in Fig. 6. Coal is crushed, generally to 70% minus 20 mesh, and sent to a slurry tank for mixing with sodium hydroxide solution. The slurry is then pumped to an autoclave where



SOURCE: BATTELLE COLUMBUS LABORATORIES

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Fig. 6. Flow sheet of Battelle hydrothermal coal process.¹⁴

reaction occurs at pressures between 350 and 2500 psig and temperatures on the order of 225°C to 345°C. The treated slurry is cooled and centrifuged to remove the solid product. The spent leachant is regenerated by sparging the solution with carbon dioxide to convert sodium sulfide to hydrogen sulfide. The carbon dioxide also precipitates dissolved ash which is then filtered out. Regeneration is completed by reacting the sodium carbonate solution with lime, yielding sodium hydroxide solution and a precipitate of calcium carbonate.

Battelle Laboratories reports¹⁵ extraction of essentially all of the pyritic sulfur and up to 70% of the organic sulfur. Extraction efficiencies from a wide variety of high-sulfur bituminous and sub-bituminous coals have been reported. Pyritic sulfur removed ranges from 78% to 99% to produce solid fuels containing from 0.1 to 0.2% pyritic sulfur. The product from the alkaline desulfurization step can be chemically deashed with dilute acid to extract the majority of the ash. As an illustration, the coals from Ohio, Kentucky and Pennsylvania (ranged from 4.6 to 13.2% ash content) were chemically deashed hydrothermally to give products ranging from 0.7 to 5.3% ash.

Work in progress at this Laboratory¹⁹ indicates that up to 90% of the pyritic and 40% of the organic sulfur in an Illinois No. 6 coal can be removed by treating the coal for 2 hr with a 70 wt% solution of sodium hydroxide. The reactions were conducted between 150°C and 300°C with coal-to-alkali solution ratios of 1/10 at a pressure of 1,000 psig.

II. OBJECTIVES

A. General Considerations

Common coal-conversion processes are undertaken at high pressures and temperatures, generally without catalysts. Where catalysts are used they are normally variations of conventional petroleum refining catalysts. Conventional coal conversion processes require large expensive reactors and special equipment to handle abrasive slurries at high pressures. From an economic standpoint, a liquid phase catalytic process offers the prospect of better contact and operation at lower temperature and hence (because of the reaction thermodynamics) at lower pressure, resulting in lower equipment cost.

Experiments have been conducted in this study to investigate the dispersing and hydrogenating activity of a strong acid. The acid of choice has been phosphoric acid. Massive amounts of acid have been used with respect to the coal feed, up to 10:1 on a mass basis. The acid serving as a solvent has often been augmented by salts (usually halides) in amounts under 40% by weight of the coal. A combination of phosphoric acid and a donor solvent (tetralin) has also been investigated.

Alkaline media are effective in hydrolytic breakdowns of organic structures. Strong alkali medium are also known readily to attack sulfur compounds. Experiments have been conducted in this study to investigate the dispersing, depolymerizing and desulfurization activity of a strong base. The base of choice has been sodium hydroxide. As with acid treatment, massive excesses of base over coal have been used (generally a 10:1 ratio on a mass basis). Experiments were also done with small quantities of sodium salts added to the alkali melt.

It is desired that coal conversion take place at low temperature and pressure. Because pyrolysis of coal which starts at 350°C is to be avoided, a temperature in the range of 190 to 200°C was chosen for these studies. A temperature around 200°C has the advantage that at temperatures only slightly above this range the lower-rank coals begin to soften. Softening should provide better interaction between the coal and the melt.

B. Experiments Performed

1. Treatment of Coal With Phosphoric Acid Melt

To observe the interaction of coal with molten phosphoric acid, samples of a low-sulfur sub-bituminous coal were reacted with acid, alone or with small amounts of additives at 200°C, under an atmosphere of hydrogen (or nitrogen) in a mechanically stirred flask.

Products were washed and filtered to remove the phosphoric acid. Elemental analysis and x-ray fluorescence of the treated coal was undertaken to determine possible desulfurization, deashing, or both. Treated coals were extracted with benzene, to determine the amount and nature of material that could be dissolved. Any change in the amount of extractable material after treatment would be an indication of physical or chemical changes in the coal. The extracts were analyzed by nuclear magnetic resonance, ultraviolet and mass spectrometry. Results were also compared with those in a companion investigation with zinc chloride.

2. Treatment of Coal With Sodium Hydroxide Melts

The interaction of Wyodak coal with sodium hydroxide was studied at 200°C under an atmosphere of hydrogen (or nitrogen). The effects of the addition of various sodium salts was also observed.

Products were washed and filtered and the treated products were subject to x-ray fluorescence and ultimate analysis as with the products of phosphoric acid treatment. Treated coals were extracted first with carbon tetrachloride and then with methylisobutyl ketone. Both extracts were analyzed by nuclear magnetic resonances, ultraviolet and mass spectrometry. Results were compared with those of phosphoric acid treatment.

III. EXPERIMENTS AND PROCEDURES

A. Coal and Other Materials

1. Coal Procurement and Preparation

The coal selected for study was a Wyoming sub-bituminous coal from the Roland top seam of the Wyodak Resources Development Corporation's Wyodak Mine at Gillette, Wyoming. The coal was received in 55 gal drums and had been ground to $-3/4$ in. by the supplier.

The entire sample was mixed and separated into equal 10 lb portions by ASTM Method D-346. Each portion was bagged in thick PVC plastic bags, flushed with nitrogen before the bags were closed, and stored separately in 5 gal cans. Contents of one such can were mixed by pouring it to form a cone and quartering into four equal parts. One of these quarters (about 6 lb) was ground in a ball mill to a size of -28 mesh and divided into four equal parts with a riffler (each part was about 1.5 lb). Each of these portions of ground coal was separately bagged and stored until needed in a 1 qt can flushed with nitrogen. The portion being used was transferred to a stoppered glass stock bottle and flushed periodically with nitrogen.

2. Analysis of Coal Samples

The coal used for this study was analyzed by Commercial Testing and Engineering Company, Chicago (Report 72-31082, June 16, 1975) and by University's Microchemical Analysis Laboratory (Report of September 8, 1975). The typical seam analysis for the coal used was provided by Wyodak Corporation, the coal supplier. The proximate analysis is given in Table V and the ultimate analysis in Table VI.

Table V. Composition of Roland seam coal--Proximate analysis, wt%.

	As Received	Dry Basis	As Received	Dry Basis
Moisture	23.43		27.99	
Ash	11.36	14.84	6.98	9.69
Volatiles	29.04	37.93	32.65	45.34
Fixed Carbon	<u>36.17</u>	<u>47.23</u>	<u>32.38</u>	<u>44.97</u>
	100.00	100.00	100.00	100.00
Sulfur	0.87	1.14	0.65	0.90
Heating Value, btu/lb	83.72	109.34		

Table VI. Composition of Roland seam coal--ultimate analysis, wt%.

	As Received	Dry Basis	U.C. Micro Lab. Dry Basis
Moisture	23.76		
Carbon	47.02	62.67	59.63
Hydrogen	4.04	5.30	5.43
Nitrogen	0.73	0.96	0.85
Chlorine	0.00	0.00	0.03
Sulfur	0.70	0.92	0.85
Ash	10.40	13.64	14.70
Oxygen (by difference)	<u>13.35</u>	<u>17.51</u>	<u>18.51</u>
	100.00	100.00	100.00

The data of Commercial Testing and Engineering agree with typical values of the seam with respect to volatiles, fixed carbon, and sulfur, but vary somewhat for ash. The University's laboratory agrees with the ultimate analysis of Commercial Testing and Engineering in all respects except sulfur content. An x-ray fluorescence analysis confirmed the value of 0.9% for sulfur content.

An x-ray fluorescence analysis for higher-atomic-weight elements including trace components, performed at LBL by Robert Giaouque and his staff, is given in Table VII.

The ash equivalent to the elemental analysis (calculated as oxides) is seen to be 9.02% with an upper limit of about 10.9% if the analytic uncertainties are all included. Thus, the total ash in Table VII, indicated as 13.6 to 14.7% on a dry basis, is not accounted for fully.

3. Purchased Chemicals

Technical-grade sodium hydroxide pellets were obtained from Matheson Colemand and Bell. The chemicals used as catalytic additives were reagent-grade anhydrous aluminum chloride, ammonium molybdate, ammonium iodide, antimony tribromide, zinc chloride, sodium acetate, sodium phosphate, sodium nitrite, ethylene diamine, ethylene glycol, 55% hydroiodic acid, and tetralin. Phosphoric acid was obtained as the 85% H_3PO_4 solution, also from Matheson Colemand and Bell. The organic solvents used for extraction were reagent-grade benzene, carbon tetrachloride, and methyl isobutyl ketone from Matheson Coleman and Bell. Gaseous nitrogen of "Hi-Pure" grade, and hydrogen of standard purity, were obtained from Liquid Carbonic in cylinders.

Table VII. X-ray fluorescence analysis of dry Wyodak coal.

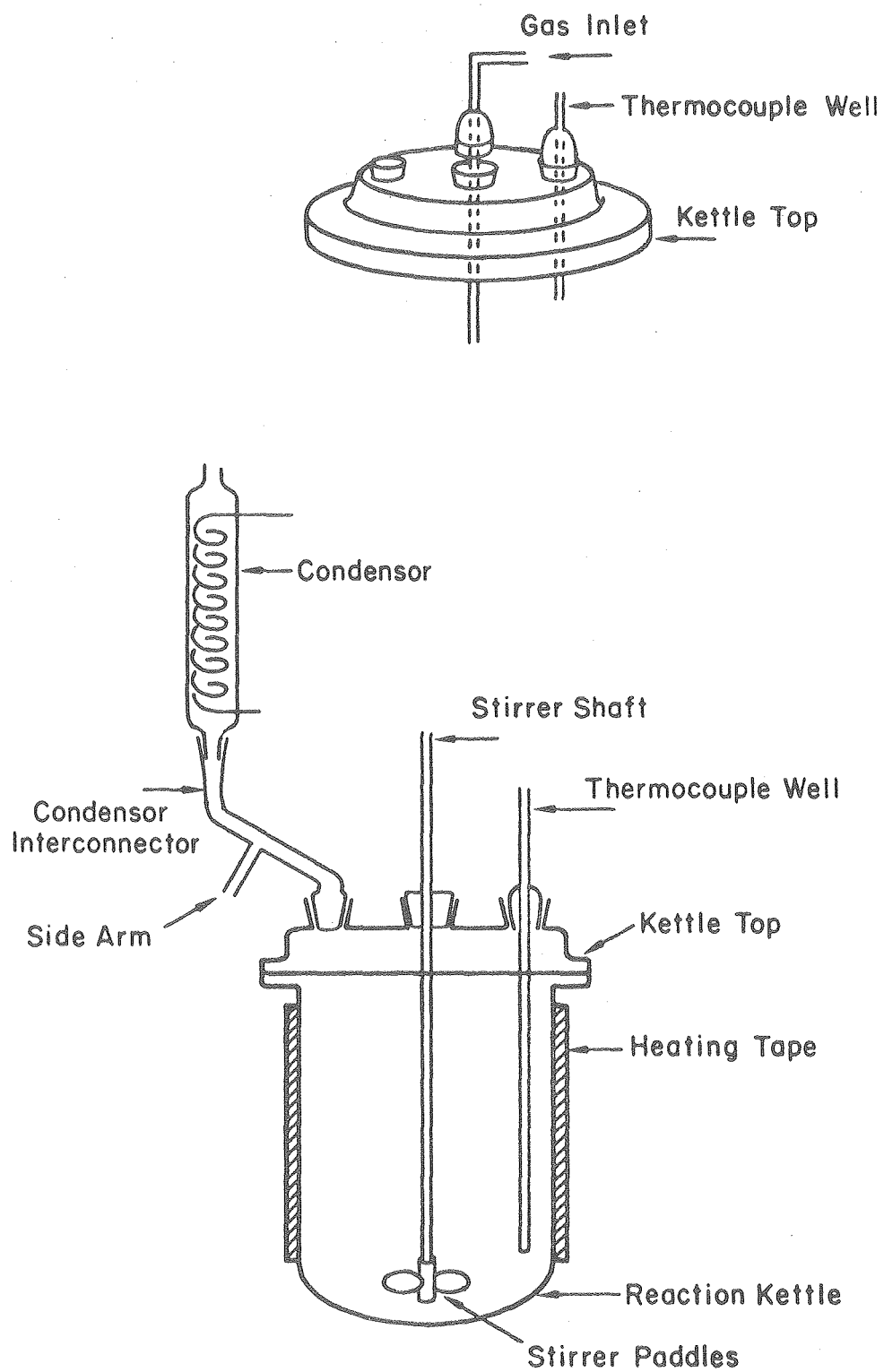
Element	Amount in Raw Coal		Possible Impurity to Ash
Mg	wt%	0.50 \pm	0.88
Al		1.41 \pm 0.21	2.66
Si		1.83 \pm 0.27	3.92
S		0.98 \pm 0.15	
Cl		0.01 \pm 0.002	
K		0.07 \pm 0.01	0.08
Ca		0.85 \pm 0.06	1.02
Ti		0.12 \pm 0.02	0.20
Fe		0.20 \pm 0.01	0.26
As	ppm	1.0 \pm 0.6	
Se		2.3 \pm 0.5	
Br		1.4 \pm 0.5	
V		120.	
Cr		27. \pm 7.	
Mn		73. \pm 6.	
Ni		12. \pm 1.	
Cu		51. \pm 2.	
Zn		22. \pm 2.	
Ga		6. \pm 1.	
Rb		9. \pm 1.	
Sr		208. \pm 8.	
Hg		7. \pm 1.	
Pb		10. \pm 2.	
			9.02%

B. Equipment and Procedure

1. Alkali and Acid Treatments

a. Apparatus. The test assembly consisted of a vessel shown in Fig. 7. The reactor was a 1-liter Pyrex resin-reaction flask, a long cylindrical vessel (6 in. in diameter and 9 in. long) tapered near the lower end. The mouth of the vessel had a ground glass rim. It was covered by a glass top with a corresponding rim, held firmly to the vessel by three spring-loaded metal clips. In the top were four openings consisting of tapered ground-glass joints. A glass stirrer (2-1/2 in. diameter with three paddles) connected to a glass shaft and powered by a variable speed motor was inserted through the center opening in the top. The second opening was fitted with a thermowell containing an iron-constantine thermocouple. The third opening housed a gas inlet, and to the fourth was connected a double-walled reflux condenser through an intervening curved glass tube. To allow the condenser to be disconnected quickly, a side arm was attached to the curved glass tube; by allowing this side arm to remain open, condensable vapors could be released to the surrounding instead of being refluxed back into the vessel.

The reaction-vessel temperature was controlled by the on-off recorder-controller activated by an thermocouple, maintaining the vessel temperature to within $\pm 3^{\circ}\text{C}$ by regulating the power input to a heating tape wrapped around the vessel. The reaction vessel (together with the heating tape) was inserted into an insulated steel beaker. This provided physical support and ease in setting up and dismantling,



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Fig. 7. Reaction apparatus.

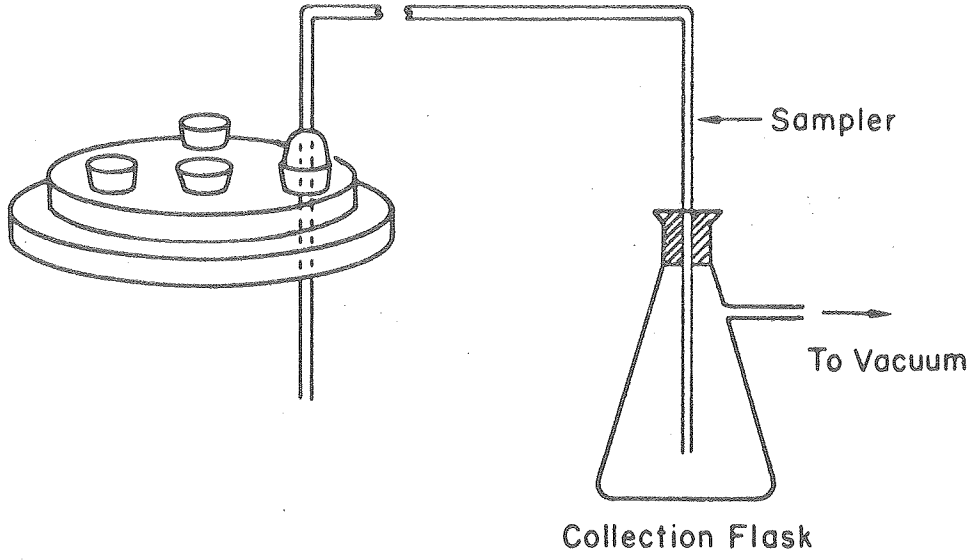
and also served as a catch vessel for holding the corrosive vessel contents in case of a thermal or pressure rupture of the glass vessel.

To take samples during the course of the experiment, an additional tube was attached to the thermowell so that a gas inlet could be housed in the same opening, thus freeing another of the openings for a sampler. The sampler, shown in Fig. 8, consisted of a U-shaped glass tube, one leg of which was dipped into the vessel and the other leg attached to a flat-bottom collecting flask with a side arm through which vacuum could be applied. This equipment, designed by the authors, was fabricated in the University's College of Chemistry shops.

b. Procedure. The following method was used for all phosphoric acid experiments. 300 gm of 85% H_3PO_4 was poured into the reaction vessel along with appropriate additions of selected test catalysts. The mixture was heated to 200°C while stirring. During this heating period, the water boiled off bypassed the reflux condenser, the side arm of the curved connector being open. The condenser was connected when the acid reached equilibrium at 200°C, which corresponds to about 95 wt% H_3PO_4 .

The sodium hydroxide experiments differed only in that 300 gm of anhydrous sodium hydroxide pellets were first introduced into the flask together with the test catalysts. Then 30 to 40 ml of water was added, and the melt was heated to boil off excess water and bring the mixture to an equilibrium concentration of about 94 wt% at 200°C.

Once the acid or alkali reached 200°C, the reflux condenser was connected, and hydrogen (or nitrogen) was sparged for about 25 min to saturate the melt and allow the system to equilibrate. The gas



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Fig. 8. Sampler.

flow was then stopped, and 30 gm of ground coal slowly added. Since the coal contained large amounts of water, about 24% as seen from Table VI, much steam was evolved, so that the vapor bypass was kept open during the coal addition and for about 2 min afterwards. When the vapor evolution had abated, the bypass was closed and the gas flow restarted.

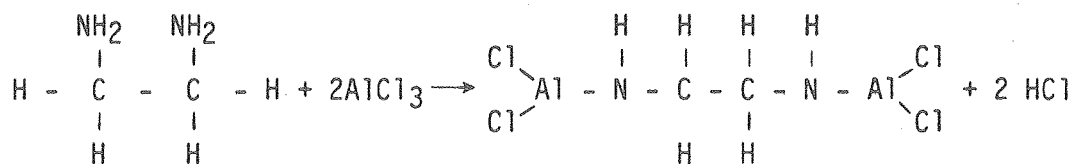
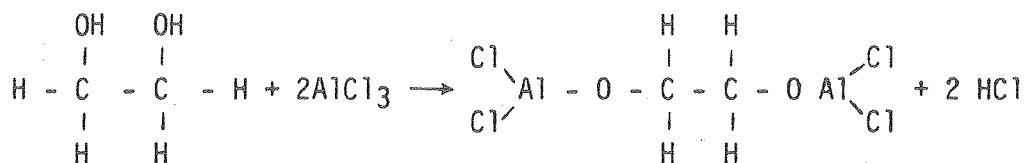
During each experiment, the stirrer was rotated at a speed that gave the most vigorous observable splashing of the reaction mass. This treatment was continued until the mixture had been allowed to react for 1 hr (except for Experiments 1, 2 and 3, as discussed below). The vessel was disconnected and removed from the stirrer assembly, and the product mixture was quickly transferred to a 500 ml Erlenmeyer flask. For the sodium hydroxide experiments, this flask contained 200 ml water, for it was found that if the product was left to stand, the melt would freeze in the flask and would have to be leached with water. Since the formation of sodium hydroxide solution is exothermic, the dissolving of the melt would be accompanied by a large temperature increase.

Three phosphoric acid experiments were exceptional. In experiments 1 and 2, the effect of time on acid treatment of coal was studied. Samples were taken at 15 min, 30 min, 1 hr, 2 hr, and 4 hr. Coal to acid proportions of 1/10 and 1/5 were used in Experiments 1 and 2 respectively. In Experiment 3 the effect of adding an organic hydrogen-donor solvent, tetralin, was explored. Since the tetralin and phosphoric acid are practically immiscible, a two-phase mixture was

formed. Twenty-five weight percent of tetralin was added to the initial acid, and the treatment was continued for 4 hr.

2. Preparation of Aluminum Chloride Additives

Two aluminum-chloride-containing catalysts were prepared by reducing the anhydrous salt with ethylene glycol and ethylene diamine respectively. The following reactions were expected to occur.



It was hoped that the resultant organometallic compounds would exhibit dual catalytic action, due to the presence of the two metal atoms, and would be more resistant to hydrolysis.

The procedure for preparing the catalysts was as follows:

A preweighed empty Erlenmeyer flask was flushed with nitrogen and sealed. Anhydrous aluminum chloride was quickly introduced, and the flask and its contents weighed to determine the quantity of aluminum chloride present. Next, the cork stopper was replaced by one having three openings. Two of these openings were used to maintain a constant flow of nitrogen gas, and through the third a weighed stoichiometric quantity of organic liquid was added. The flask was gently rocked to allow for adequate solid-liquid contact. Vigorous evolution of

hydrogen chloride was observed, and the flow of nitrogen was stopped only when the hydrogen chloride evolution had ceased. Additives produced this way were transferred to stoppered glass bottles and were stored under nitrogen. Both additives were lumpy cream-colored solids which dissolved quickly and completely in phosphoric acid.

3. Product Separation and Characterization

a. Phosphoric Acid: Catalyst Screening and Kinetic Experiments.

A weighed amount of the reaction product was diluted with an equal weight of distilled water, and the mixture was vacuum-filtered through a Buchner funnel. Next the filter residue was slurried with 500 ml of water, and filtered once more. One wash was found to suffice for removing any acid adhering to the treated coal. The washed product was then dried under vacuum in a nitrogen atmosphere at 105°C for 12 hr. An ultimate analysis of the treated coal was made by the University's Microanalytical Laboratory (results below).

A portion of the dried treated coal was extracted with benzene by the procedure described in Section 4. The dried extract was analyzed by mass spectrometry. For each of the five samples in the kinetic experiments, and for the product of Experiment 4, using aluminum chloride-ethylenediamine additive (selected because it gave the maximum yield of benzene extractables), the extracts were analyzed by ultra-violet spectroscopy and nuclear magnetic resonance spectroscopy. The phosphorus content of the extracted residues of one kinetic experiment (Experiment 2) was also determined.

b. Acid--Donor Solvent Experiment. Separation of a weighed quantity of product was effected as shown in Fig. 9, which provides the basis of the following discussion.

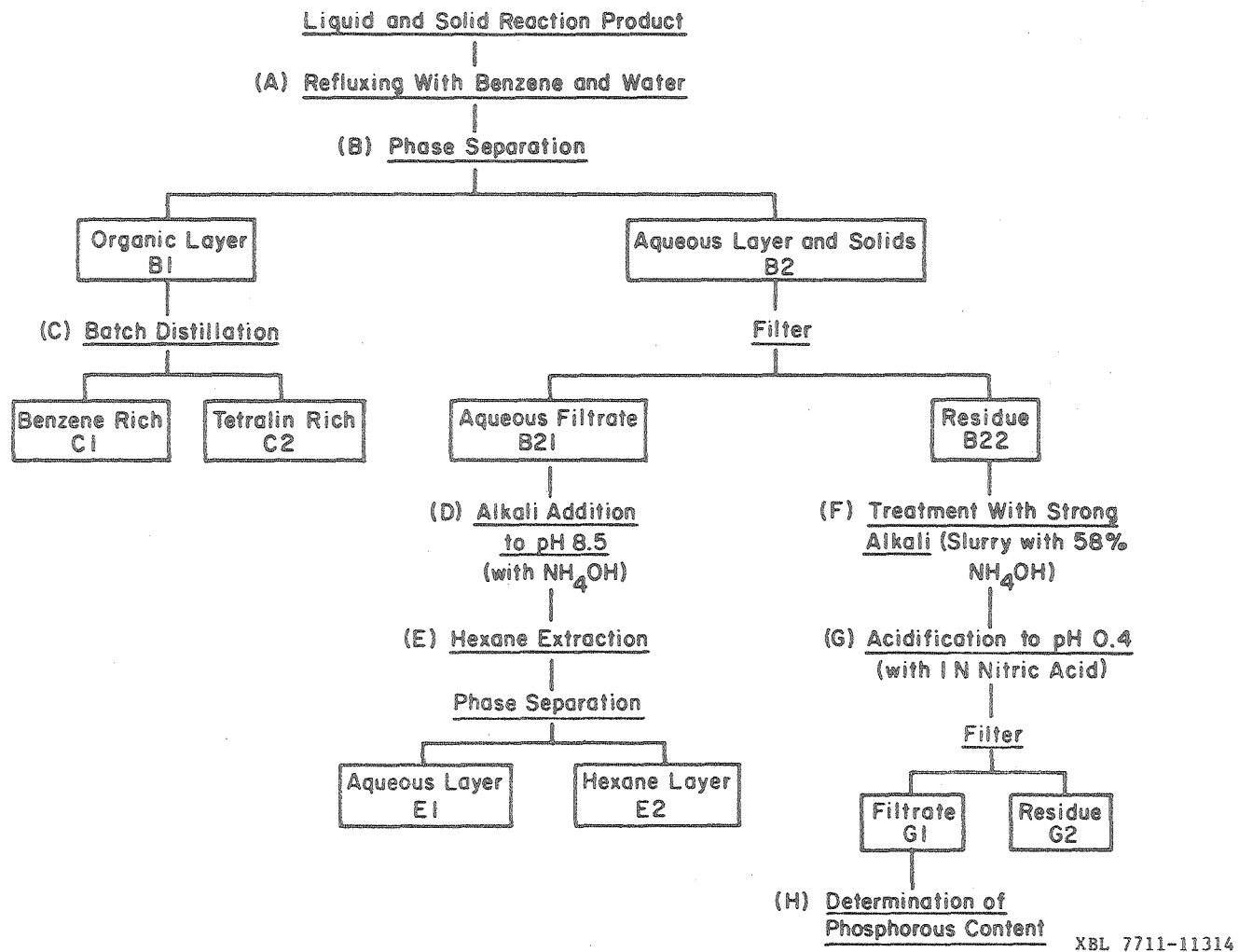
Process A: To a 125 gm sample of product was added 100 gm of benzene and 200 gm of water. The weight ratio of benzene to water used was the same (1:2) as the ratio of tetralin to phosphoric acid in the experiment. This mixture was subjected to total-reflux distillation at its boiling point (60°C) for 1 hr. Presumably the product contained phosphate esters, which would be hydrolyzed by refluxing the water. The benzene was added to allow any asphaltenes formed to transfer to the organic phase and also to avoid handling losses of products soluble in tetralin and benzene.

Process B: Two phases, one predominantly organic and the other predominately aqueous, were obtained by use of a separatory funnel. The aqueous phase B2, being heavier, contained the solid product, and was filtered in a Buchner funnel.

Process C: The entire organic layer B1 was subjected to batch distillation. The distillation temperature was allowed to rise to 94°C and the benzene-rich overhead was condensed and collected as C2.

Process D: An aliquot of the aqueous filtrate B21 was brought to a pH of 8.5 by the addition of 58% ammonium hydroxide. This process presumably would precipitate any basic organic compounds present in the product.

Process E: The alkaline mixture of process D was subjected to extraction with 250 ml of hexane at room temperature. The mixture



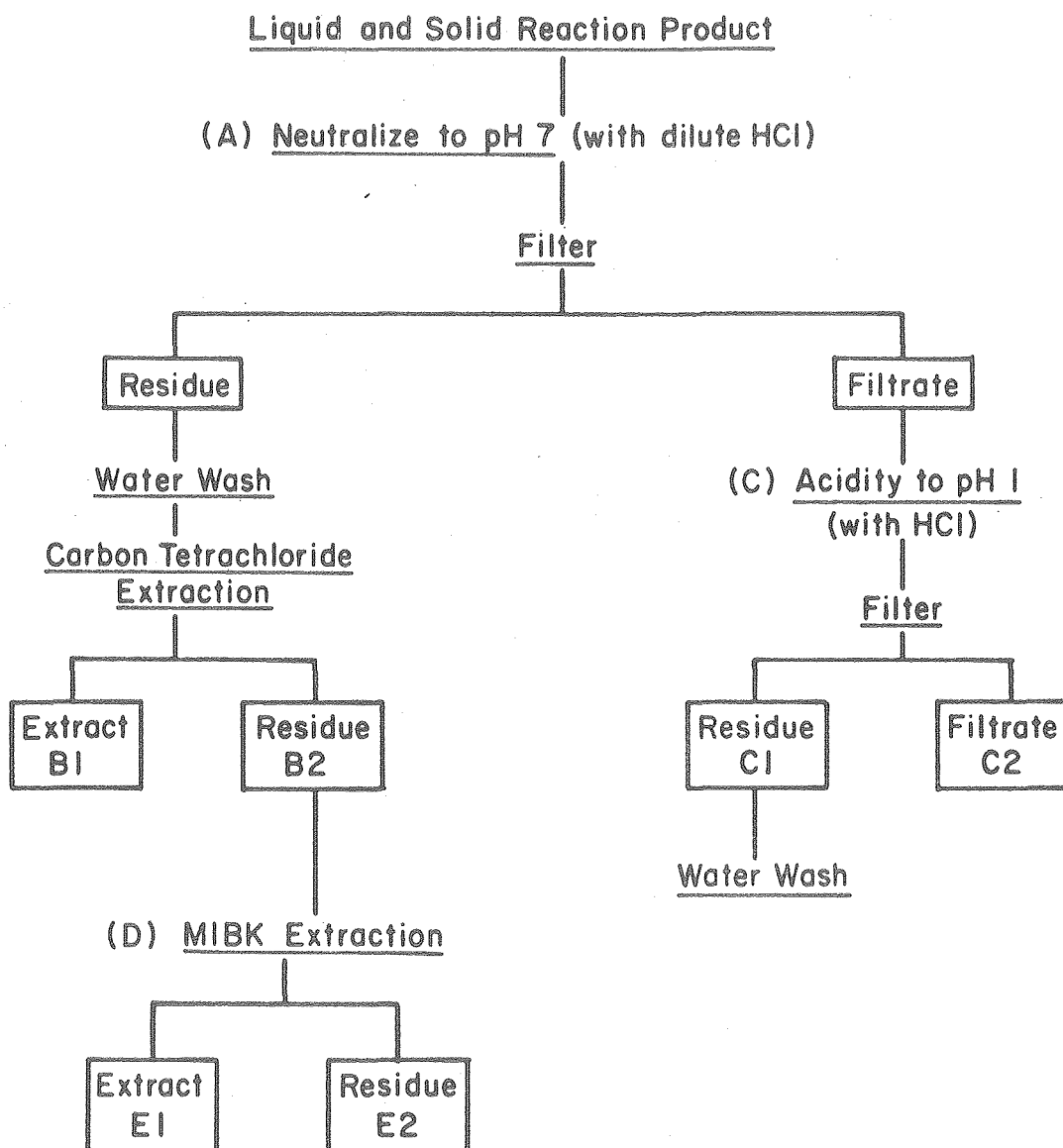
was agitated vigorously for 15 min and settled for 30 min, after which the extract and raffinate were then separated.

Process F: Residue B22 was vacuum dried for 12 hr at 110°C and 5 gm were then treated with 100 ml of 58% ammonium hydroxide solution. Any phosphorus present in the solid product was expected to be recovered as ammonium phosphate by the action of the concentrated ammonium hydroxide solution.

Process G: To precipitate any acidic organic matter, the slurry of process F was acidified to a pH of 0.4 with 1N nitric acid which would leave the phosphate ions in solution. The acidified mixture was then filtered through a Buchner funnel to obtain filtrate G1 and residue G2.

Process H: The phosphorus content of filtrate G1 was determined by precipitation as quinolinium phosphomolybdate. A 25 ml aliquot of G1 was transferred to a 400 ml beaker and diluted to approximately 50 ml with water. Fifty ml of quinoline molybdate reagent (prepared as prescribed in ASTM method E357-68) was slowly added to the solution with constant stirring. The beaker was then covered with a water glass, placed on a hot plate in a well ventilated hood, and boiled for 1 min. The solution was filtered through a Gooch crucible, and the precipitate was then washed and dried in an oven at 250°C for 2 hr. The phosphorus content was determined from the weight of the precipitated quinolinium phosphomolybdate precipitate.

c. Sodium Hydroxide Experiments. After cooling, separation was effected as shown in Fig. 10 on a weighed sample of the product:



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Fig. 10. Method of separation of alkali-treated products.

Process A: The reaction products were first neutralized with 37% hydrochloric acid, and the neutralized mixture was filtered through a Buchner funnel.

Process B: The residue was slurried with 500 ml of distilled water and filtered once more. This water-washed residue was vacuum-dried for 12 hr at 110°C under flowing nitrogen. Next, a 5 gm sample of the residue was extracted with carbon tetrachloride. Solids B2 were dried for 4 hr in an open dish.

Process C: Neutralized filtrate was acidified to pH 1, and the precipitate was collected by refiltration.

Process D: Four grams of B2 were extracted with methyisobutyl ketone for 1 hr to obtain residue D2 and extract D1.

All solid residues were carefully weighed and characterized by proximate analysis. Residues B from experiments 1 and 3 were subjected to X-ray Fluorescence to determine the ash and sulfur content. Extracts were characterized by mass spectrometry, ultraviolet spectrometry, and nuclear magnetic resonance spectrometry.

4. Extraction

Five grams of the dried treated coal were extracted for 1 hr at the atmospheric boiling point of the solvent, in a Pyrex Soxhlet extraction apparatus. Dried raw coal was also extracted for reference. Extractions with organic solvents (benzene, methyisobutyl ketone, and carbon tetrachloride) were performed to determine the amount of material extractable, indicating chemical or physical changes. Fifty milliliters of extract was evaporated in a pre-weighed Petri dish to determine the amount of extracted material. The remainder of the

extract was stored in cork-stopped flasks for later analysis. Results were reported as weight percent of extractables on a moisture- and ash-free basis.

C. Experiments Performed

1. Phosphoric Acid

To characterize the interaction of coal with phosphoric acid in relation to its possible use in converting coal to liquid or purified solid fuel, the study proceeded in three phases. To begin, the effect of contacting time on the properties of the product was investigated. Two experiments were performed, the first using coal with ten times its weight of acid and the second using coal with five times its weight of acid. Both experiments were performed at 200°C, with samples being taken after 15 min, 30 min, 1 hr, 2 hr, and 4 hr.

The next phase of the study yielded information about the effect of the presence of additives. Most of the additives used have been tested in the hydrogenation of coal or oil at higher temperature (350°C-400°C) and pressures (1000-1500 psig). Experiments performed with additives are listed in Table VIII.

The products for both kinetic and catalyst-screening experiments were characterized. Information about extracts from the treated coal was also obtained. An increase in extractables indicates a physical or chemical change in the coal. The chemical nature of the extract is also of interest, since it reflects the chemical structure of at least a part of the coal.

The third phase of the study was concerned with the coal-acid interaction in the presence of a hydrogen-donor solvent, tetralin.

Table VIII. Experiments made using phosphoric acid and additives with hydrogen.

Conditions: Atmospheric Pressure
 Temperature: 200°C
 Coal:Acid = 1:10 (wt)
 Residence Time: 1 hr

Experiment No.	Additive	wt% (rel. to raw coal)
4	Aluminum chloride/ethylene diamine	20
5	Aluminum chloride/ethylene glycol	20
6	Ammonium molybdate	40
7	Ammonium iodide	20
8	Antimony tribromide	20
9	Aluminum chloride	20
10	Hydroiodic acid (55%)	40
11	Zinc chloride	20
12	None*	--

*Under nitrogen atmosphere.

Product obtained by contacting the coal-solvent-acid mixture for 4 hr at 200°C was extensively characterized in an effort to obtain an indication of the magnitude and types of physical and chemical changes that could have occurred.

2. Sodium Hydroxide

The interaction of coal with concentrated sodium hydroxide proceeded in two phases. The first phase was concerned with the characterization of the treated coal, recovered after neutralization of the reaction product.

The second phase of the study aimed to gain information about the extracts from the alkali-treated coal. Extractions with carbon tetrachloride and methylisobutyl ketone, and the chemical nature of these extracts, yield information about the nature of the coal-alkali interaction. The experiments performed are listed in Table IX.

Table IX. Experiments with sodium hydroxide and additives under hydrogen (1 atm) at 200°C.

Conditions: Coal:Alkali = 1:10 (wt)
Residence time: 1 hr

Experiment No.	Additive	Wt% (Rel. to Raw Coal)
1	None	--
2	Sodium acetate	20
3	Sodium nitrite	20
4	Sodium phosphate	20
5	None*	--

*Under nitrogen atmosphere.

IV. RESULTS AND DISCUSSION

A. Phosphoric Acid Treatment

1. Chemical and Physical Characterization of Acid-Treated Coal

In characterizing the phosphoric acid reaction product, it was noted that the coal appeared to have dispersed in the acid and that the product was uniformly brown in color. The kinetic experiments indicated that when a coal:acid ratio of 1:5 was used, the coal required up to 2 hr for complete dispersion. At the lower coal:acid ratio of 1:10, dispersion was substantially complete at the end of 0.5 hr. The product appeared to become grainy on cooling to room temperature. When diluted with water, a dark brown suspension was obtained.

The same behavior was observed with each of the additives, and also when nitrogen sparging replaced hydrogen.

From these results it may be concluded that coal disperses slowly in the highly acidic medium, that the dispersion process is complete within 2 hr, and that reduction in melt acidity either by cooling or by dilution results in a substantial precipitation of the dispersed coal. The presence of additives or a hydrogen atmosphere seems not to affect this dispersion phenomenon.

The acid-treated product was separated from the reaction mixture by diluting with water, filtration, washing, and drying. The product, a little lighter in color than the original coal, crumbled easily and thus appeared to have lost most of the mechanical strength displayed by coal.

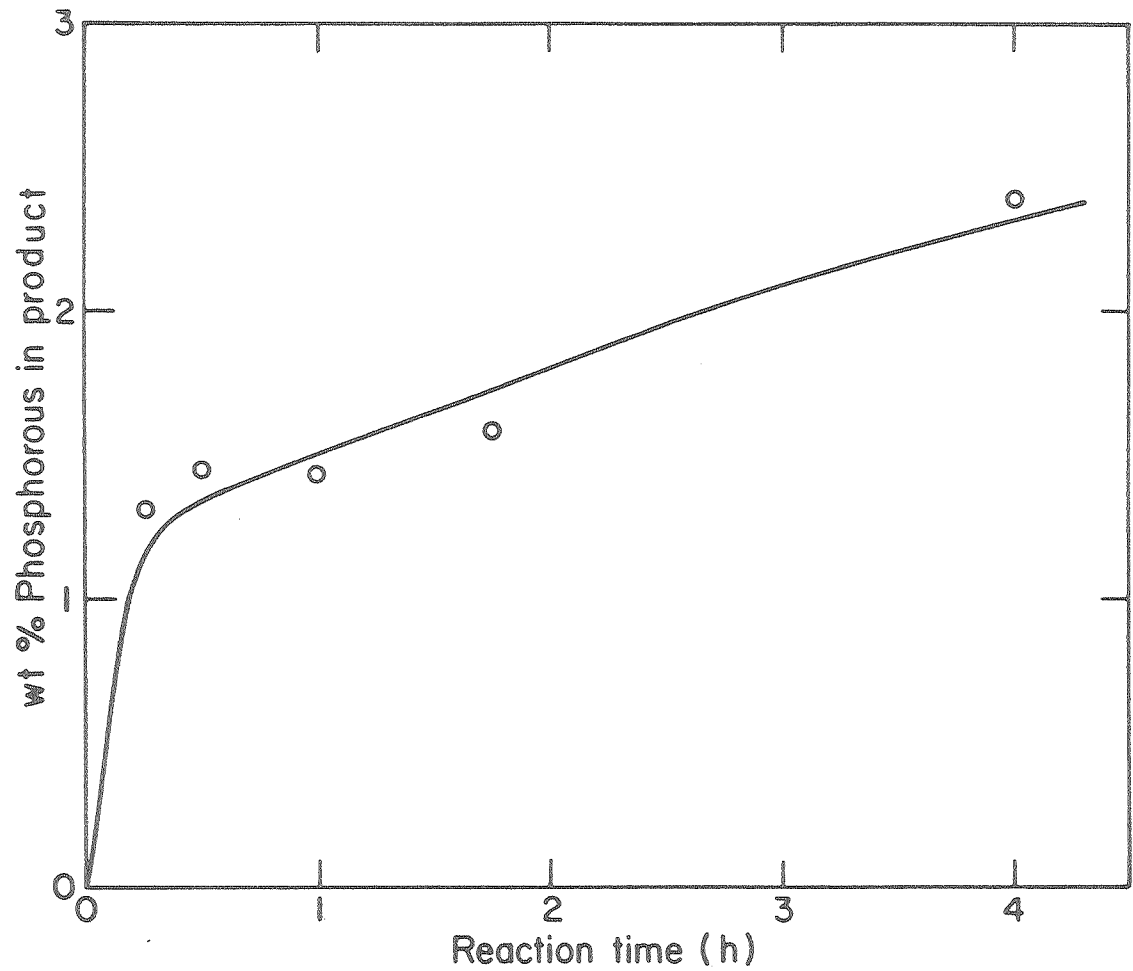
a. X-Ray Fluorescence. One acid-treated coal sample was analyzed by x-ray fluorescence to determine the ash and sulfur content. The reaction conditions of the experiment and the results of the product analysis are given in Table X.

Due to the presence of approximately 1% by weight of phosphorus, accurate x-ray fluorescence analysis could not be undertaken. The approximate values, reported in Table X, seem to indicate little change in the concentrations of silicon, sulfur, and chlorine.

b. Phosphorus Content. Samples of acid-treated coal from one of the kinetic experiments (coal:acid ratio of 1:5) were analyzed for their phosphorus content by the University's Microanalytical Laboratory. Results of the analysis are given in Table XI, and plotted against reaction time in Fig. 11.

The reaction product in every case was water-washed until the washings were neutral, and then was dried at 110°C under vacuum in an atmosphere of nitrogen. The neutrality of the washings together with the monotonic increase in phosphorus content with time preclude the possibility of the observed phosphorus resulting merely from phosphoric acid adhering to the reaction product. The phosphorus in the acid-treated coal, then, appears to be chemically bound.

The results indicate that the rate of incorporation of phosphorus into the organic coal matrix is initially rapid, and after the first hour increases linearly with time. It appears that within the first hour the coal breaks down rapidly possibly into ionic species. A salt-like structure may be envisioned with ionic coal-derived intermediates attached to phosphate ions.



XBL7711-11318

Fig. 11. Phosphorus content of product vs time in phosphoric acid treated coal. Coal/acid = 1/5, temp. 200°C, atmosphere, H₂.

Table X. X-ray fluorescence analysis of phosphoric-acid-treated coal.

Reaction Conditions: COAL:ACID = 1:10
Temperature: 200°C
Residence Time: 15 min
Atmosphere: Hydrogen
Additives: None

Element	wt% (Rel. to Dry Coal)
Si	3.
P	1.
S	1.
Cl	0.1

Table XI. Phosphorus content of phosphoric-acid-treated coal:
Effect of residence time.

Reaction Conditions: Coal:Acid = 1:5 (wt)	
Temperature: 200°C	
Atmosphere: Hydrogen	
Additives: None	

Reaction Time	Phosphorus, wt% (Rel. to MAF Coal)
15 min	1.32
30 min	1.45
1 hr	1.43
2 hr	1.58
4 hr	2.40

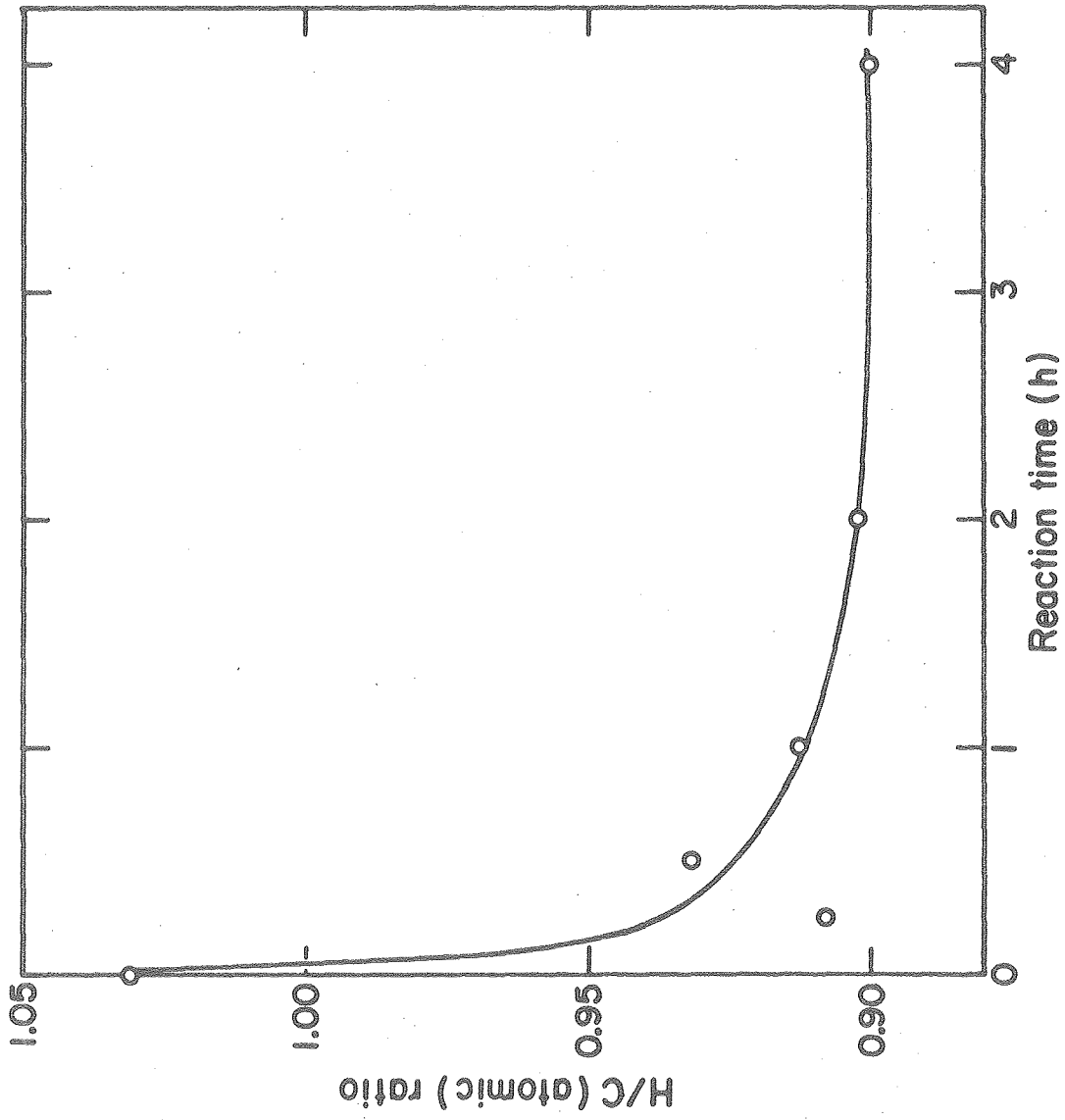
Untreated Coal	0.05
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c. Ultimate Analysis. Ultimate analyses of dried acid-treated coal samples were determined for one kinetic experiment (coal:acid ratio of 1:5), and for all experiments with additives in the melt. All these analysis were done at the University's Microanalytical Laboratory.

The ultimate analyses (weight percent on a moisture- and ash-free basis) for the kinetic experiment are given in Table XII. Hydrogen/carbon atomic ratios are plotted against reaction time in Fig. 12. The hydrogen/carbon ratio of the acid-treated coal decreases rapidly within the first hour of reaction, and then remains constant on further treatment. Rapid decrease in the H/C atomic ratio initially (from 1.03 to about 0.92) is probably caused by the evolution of lower-molecular-weight gases of high H/C ratio such as methane. Such gases would not recondense in the reflux condensor, and would be lost during the reaction.

There appears to be no definitive pattern in the ultimate analysis and the H/C ratios of products obtained with additives present in the phosphoric acid. Results of the analysis are given in Table XIII. The addition of ammonium molybdate resulted in the product of lower H/C atomic ratio (0.837), whereas the presence of aluminum chloride/ethylene diamine in the phosphoric acid yielded a product with the highest H/C ratio (0.962).

d. Extraction Behavior. To compare the properties of the phosphoric-acid-treated coal, samples were extracted with benzene by a standard procedure as described in Section III-B-4. Fifty milliliter samples of benzene extract were dried in a hood for 8 hr



XBL7711-11319

Fig. 12. H/C ratio of phosphoric-acid-treated coal vs reaction time. The coal/acid ratio is 1/5. Reaction temperature is 200°C.

Table XII. Ultimate analysis of phosphoric acid treated coal: effect of residence time.

Reaction Conditions: Coal:Acid = 1:5 (wt)							
Temperature: 200°C							
Atmosphere: Hydrogen							
Additives: None							
Reaction Time, Hr.	Analysis, wt% (Rel. to Dry Coal)						H/C (Atomic)
	C	H	N	S	O	Ash	
0.25	64.21	4.82	1.00	0.91	15.76	13.22	0.908
0.5	63.89	4.96	0.90	1.28	19.83	9.14	0.932
1	62.40	4.75	0.96	1.44	20.82	9.63	0.913
2	64.12	4.82	0.94	1.28	18.04	10.28	0.902
4	63.04	4.73	0.89	1.02	18.02	12.30	0.900
Untreated Coal	61.67	5.30	0.96	0.92	13.64	17.51	1.031

to evaporate the benzene. The residue was weighed, and the total benzene extractables determined. Results are reported as percentage extractables on a moisture and ash-free basis.

Benzene extractibility of the dried acid-treated product from the two kinetic experiments is shown in Table XIV, and is plotted against reaction time in Fig. 13. The benzene-extractable material increased in the first 0.5 hr of reaction, declined rapidly in the next 0.5 hr, and then declined more slowly. The same general behavior was found for coal/acid ratios of 1/5 and 1/10. A greater proportion of phosphoric acid led to reduced extractability in the first hour, and enhanced extractability at longer reaction times. The highest benzene extractability was obtained for the mixture containing 10% by weight of coal, reacted for 0.5 hr. Untreated coal produced only 1.85% by weight of benzene extractables.

Initial increase in benzene-extractability may be caused by the depolymerization of coal in the highly acidic media. The concomitant decrease in H/C ratio and increase in phosphorus content seem to suggest that such depolymerization occurs by the loss of low-molecular-weight high H/C gases, and results in the formation of high-molecular-weight organophosphorus compounds.

Some insight into possible products can be gained by determining the atomic ratio of carbon to phosphorus. For example, coal reacted with phosphoric acid for 0.5 hr results in product containing 1.45 wt% phosphorus (Table XI) and 63.80 wt% carbon (Table XII). This results in a P/C atomic ratio of 0.0088. If, as a simplification, it is assumed that an average representative molecule of the product contains only

Table XIII. Ultimate analysis of phosphoric acid treated coal: effect of additives.

Reaction Conditions: Coal:Acid = 1:10

Temperature: 200°C

Atmosphere: Hydrogen

Residence Time: 1 Hr

Amounts of additive used as weight percent of raw coal are listed in Table VIII.

Experiment No.	Additive	wt% (Rel. to Dry Coal)					Ash	C/H
		C	H	N	S	O		
4	Aluminum chloride/ethylene diamine	64.09	5.04	0.95	0.88	18.83	10.21	0.943
5	Aluminum chloride/ethylene glycol	62.64	5.02	1.01	0.75	21.54	9.04	0.962
6	Ammonium molybdate	61.6	4.30	0.75	0.90	19.72	12.72	0.837
7	Ammonium iodide	60.80	4.65	0.86	1.02	10.11	9.48	0.917
8	Antimony tribromide	63.12	4.60	0.90	0.86	19.30	11.22	0.876
9	Aluminum chloride	63.02	4.88	0.84	1.41	20.40	9.45	0.930
10	Hydriodic Acid (55%)	63.16	4.83	0.87	0.97	21.75	8.42	0.917
11	Zinc Chloride	63.87	4.96	0.94	1.22	16.13	12.88	0.932
12	None*	64.74	4.98	0.92	.16	19.11	9.09	0.920
Untreated Coal		61.67	5.30	0.96	0.92	13.64	17.51	1.031

*Under nitrogen atmosphere.

Table XIV. Benzene-extractables in phosphoric-acid-treated coal--
effect of residence time and coal:acid ratio.

Reaction Conditions: Temperature: 200°C		
Atmosphere: Hydrogen		
Additives: None		
Experiment No.	1	2
Coal:Acid Ratio (wt)	1:10	1:5
Reaction Time	Benzene-Extractables, wt% (MAF)	
15 min	3.23	3.59
30 min	3.79	3.65
1 hr	2.56	3.02
2 hr	2.43	2.89
4 hr	1.94	2.28

one phosphorus atom, then the minimum molecular weight (considering it to be graphite) would be 1,387 $((113 \times 12) + 31)$. Asphaltenes are known to have molecular weights in the 1,200 to 2,500 range.⁵² Such an "average" molecule may then be considered to be an organophosphorus compound similar to asphaltene but insoluble in benzene.

The rapid decline in benzene solubility upon further treatment of the coal could be explained by either of two plausible phenomena. First, the initially formed benzene-soluble material may be cracked by the strongly acidic melt into lower-molecular-weight gaseous products. Such a loss of hydrocarbons would be expected to show as a change in the H/C ratio of the acid-treated product. Since there is no significant change in the H/C ratio after 1 hr of reaction, such cracking may be precluded.

Second, the benzene-soluble material forming within the first hour of reaction may repolymerize upon longer contact with the acidic media. Such a repolymerization could account for both unchanged H/C ratio and for the increased phosphorus content at longer reaction times. The higher-molecular-weight products so formed could be expected to be insoluble in benzene. Strongly acidic media are known to be effective polymerization catalysts.⁵⁴

Table XV compares the effect of additives on the extractability of treated coal. All reactions were carried out for 1 hr at 200°C. Six of the additives gave benzene extractables greater than or equal to those obtained when coal and phosphoric acid alone were reacted for 1 hr. These additives were aluminum chloride/ethylene diamine; aluminum chloride/ethylene glycol; ammonium iodide; zinc chloride;

Table XV. Benzene-extractables in phosphoric acid treated coal:
effect of additives.

Conditions: Temperature: 200°C

Residence Time: 1 Hr

Atmosphere: Hydrogen

Coal:Acid = 1:10 (wt)

Amounts of additives used are listed in Table VIII.

Experiment No.	Additive	Wt% (Rel. to MAF Coal)
4	Aluminum chloride/ ethylene diamine	3.75
5	Aluminum chloride/ ethylene glycol	3.37
6	Ammonium molybdate	1.36
7	Ammonium iodide	3.17
8	Antimony tribromide	2.38
9	Aluminum chloride	3.05
10	Hydroiodic acid (55%)	3.09
11	Zinc chloride	3.33
12	None*	2.85

*Under nitrogen atmosphere.

hydroiodic acid; and aluminum chloride alone. However, in no case did the presence of an additive result in benzene-extractability greater than 3.79% which was the maximum obtained when coal and acid were reacted for 0.5 hr at the same conditions.

The presence of ammonium molybdate in the phosphoric acid mixture resulted in a substantial lowering of benzene extractables in the product. Percentage extractables in this case were found to be 1.36 by weight, lower even than the 1.85% obtained from raw coal. There was no appreciable lowering in the amount of benzene extractable material when the reaction atmosphere was changed from hydrogen to nitrogen.

2. Characterization of Extracts of Acid-Treated Coal

The extracts of raw coal and acid-treated coal from selected reaction products were studied. In all cases extracts recovered from benzene were wax-like solids. For studies of the extract properties, CCl_4 was chosen because it does not interfere with nmr and uv spectra. The dried benzene-extractables were soluble in CCl_4 . This is not surprising, since the solubility parameter for C_6H_6 is $9.2 \text{ (cal/cm}^3)^{1/2}$ and for CCl_4 is 8.6, while coal extracts range from 9.3 to 10.50 (When a solute is solid, its melting point also influences its solubility.)

a. Mass Spectrometry. Extracts of these samples from a kinetic experiment were analyzed by low-resolution mass spectroscopy. Spectra obtained for extracts of product after 15 min and 4 hr of reaction are shown in Appendix I (Figure A1 and A2). The 4 hr product extract was analyzed at two temperature levels in the mass spectrometer.

A greater portion of high-molecular-weight high-boiling components

would volatilize at the higher temperature, hence higher mass ions could be expected to appear in this mass spectrum. The principal ions for all extracts are shown in Table XVI.

The mass spectra of the two samples contained different compounds. Extract from coal treated for only 15 min showed mass numbers up to 480 in contrast to masses of 324 after 4 hr of reaction. These results suggest a depolymerization of benzene-extractable material at longer reaction times.

When the sample reacted for 4 hr was run at two different temperature levels in the mass spectrometer, some masses disappeared from the spectra at the higher temperature, possibly due to fragmentation into smaller ions. Additional higher-mass peaks were also found under the same conditions. The entire extract is probably not volatilized under normal mass-spectrometer conditions, so that the observed masses possibly represent only a portion of the total extract.

The mass spectra of all extracts showed a large portion of ions with mass numbers under 150, as expected from fragmentation in the electron beam. Such compounds in the original extract in large proportions would make it a relatively volatile liquid. It appears, therefore, that most of this low-molecular-weight material comes from the fragmentation of larger molecules inside the spectrometer.

b. Nuclear Magnetic Resonance Spectroscopy. Since the extract was probably a set of related compounds, an attempt was made to elucidate its characteristic structure. Nuclear magnetic resonance data for CCl_4 solutions of benzene extracts were obtained for all five samples from

Table XVI. Characteristic mass numbers in mass spectrographs on extracts from phosphoric-acid-treated coal.

Common to All Extracts	15-min Treatment Low Temp.	4-Hrs Treatment		
		Low and High Temp.	Low Temp. Only	High Temp. Only
55*	60*	45	53	96
56	73*	91*	68	99
57	84	110	77	145
58	96	119	79	177
67*	98*	131	84	195
69*	99	163	93	204*
70	112	165	105	220*
71*	125*	169*	106	239
81	129*	183	107	248*
82	145*	233	108	252
83	227	276	113	262
85*	231		121	324
95*	239		124	
97*	257		125	
109*	325		128	
111*	354		132	
123	368*		135	
149	382		137	
191*	396*		141	
	397*		143	
	410		154*	
	424*		171	
	425*		178*	
	438		184	
	452*		206	
	453		241	
	480			

*Major peaks.

one kinetic experiment. Tetramethyl silane was used as reference. Peaks obtained for products obtained after 0.25 hr, 0.5 hr, 1 hr, 2 hr, and 4 hr are given in Table XVII. These peaks were compared to standards given in the literature.⁵¹

The resonance at 0.85 to 1.00 ppm is characteristic of a methyl group attached to a saturated carbon ($\text{CH}_3\text{-C-}$). The peak at 1.24 may indicate the same group; or it may also show R_2NH or $\text{CH}_3\text{-C-(C)}_n\text{-X}$ where $n > 1$ and X can be Cl, Br, I, OH, OR, C = O, or N. The peak at 1.78 to 2.12 shows either $\text{CH}_3\text{-C=C-}$ or $\text{CH}_3\text{-C=O}$. The lack of aromatics, which resonate around 7, is very surprising, and had to be confirmed.

Extract of product obtained after 0.5 hr of treatment showed an additional peak at 3.00 ppm. This peak may be due to $\text{CH}_3\text{-N-}$ or nonconjugated H-C=C- .

c. Ultraviolet Spectroscopy. The ultraviolet spectrum was obtained for benzene extract dissolved in CCl_4 . The sample absorbed so strongly that the solution had to be diluted 25 to 1 from the original concentration. The spectrum showed a broad peak at 2600 wavelength, which can be caused by the double bond in carbonyl groups, or by aromatics. Since aromatics are largely absent in the nmr spectrometry, the adsorption provides evidence for large concentrations of carbonyls.

3. Conclusion

When Wyodak coal is reacted with phosphoric acid, the coal appears to disperse in the melt within 2 hr. The acid treated coal has a much reduced mechanical strength. There is no significant desulfurization or de-ashing of the coal. The product contains organically bound

Table XVII. Proton nmr of benzene extracts of phosphoric-acid-treated coal: effect of residence time.

Conditions: Temperature: 200°C
 Coal:Acid = 1:5 (wt)
 Atmosphere: Hydrogen
 Additives: None

Residence Time, Hr	Resonance Shifts () ppm (measured in CCl ₄)				
0.25	1.00	1.23	1.252	2.12	
0.50	0.91 - 1.00		1.25	2.12	3.00
1	0.85 - 1.00		1.24	2.10	
2	0.85 - 1.00		1.24	2.12	
4	0.88		1.24	1.78	

phosphorus, the content increasing with reaction time to a maximum of 2.4% in 4 hr. the H/C ratio of the product decreases rapidly within the first hour and then remains constant up to 4 hr time. Benzene-extractable material in the product increases to a maximum of 3.79 wt% (for a coal-to-acid ratio of 1/10) in 0.5 hr of reaction, and drops more gradually to 1.94 wt% in 4 hr. A lesser proportion of phosphoric acid leads to enhanced extractability at shorter constant times (15 min and less) and reduced extractability thereafter. Presence of additives does not increase the benzene solubility above the maximum obtained with phosphoric acid alone.

Phosphoric acid treatment results in the release of wax-like benzene extracts. Extracts from longer reaction time contain less high-molecular-weight material. The extracts contained no detectable aromatic structures.

Our results show that no liquid products are formed with phosphoric acid at 200°C. The acid does appear to depolymerize the coal and evolve gases. The acid system is thus less effective for Wyodak coal at 200°C than reported by Kiovsky²⁸ who found that at 320°C a Big Horn coal gave 64% benzene soluble material in 2.5 min. The difference in the two results can be attributed to the difference in temperature and the coal used.

B. Phosphoric Acid-Donor Solvent Treatment

Coal was treated for 4 hr at 200°C in a mixture of phosphoric acid (75% by weight) and tetralin (25% by weight) to study the effect of the presence of the hydrogen-donor solvent. The procedure for product separation and characterization is discussed in Section III-B,

Chapter III, and represented in Fig. 9. This figure provides the basis of the following discussion.

The reaction products were refluxed with benzene and water, and then separated into an organic phase, an aqueous phase, and solids (Process A and B in Fig. 9). The organic phase was subjected to batch distillation (Process C) to obtain a benzene-rich condensate and a tetralin-rich residue. The benzene condensate was analyzed by gas chromatography, a 5- μ l sample of the condensate being injected into a 6-ft long 0.25-in. diameter column filled with Carbowax on Chromosorb W, and operated at 200°C. Only a single peak corresponding to benzene was obtained, indicating that the condensate was pure benzene.

The tetralin-rich residue was a light brown solution, and contained a small amount of suspended tar-like material. The entire residue was transferred to a weighed petri dish, and tetralin was removed by first evaporating under a hood and then drying the dish in a vacuum oven at 130°C. The dried residue (C₂) was less than 2% by weight of the original coal. This residue represents both the benzene-extractable material from coal and any compounds which might have been formed by cracking and polymerization of tetralin.

The aqueous filtrate obtained in process B (B21 in Fig. 9) was brought to pH 8.5 with NH₄OH (Process D), and this weakly basic solution was extracted with hexane (Process E). The hexane phase was separated and dried in a weighed petri dish; the residue represented less than 0.5% by weight of the original coal. Addition of alkali would presumably precipitate any basic organic compounds in the product.

The hexane extracts thus should represent the hexane-soluble fraction of the basic compounds.

The solid residue (B22) was slurried with 57% ammonium hydroxide solution. The slurry was then acidified to pH 0.4 with 1N nitric acid, and filtered to obtain filtrate G1 and residue G2 (Fig. 9). Both solid samples were analyzed for phosphorus by the University's Microanalytical Laboratory. The solid reaction products (B22) had a content of 2.11 wt% whereas the residue after treatment with NH_4OH , acidification, and filtration (G2) had a content of only 0.46%. The phosphorus present in filtrate G2 was determined quantitatively by precipitation as quinelinium phosphomolybdate (ASTM Method E 359-68); the result was used to complete a phosphorus mass balance, which matched within 0.5% the total in a 5 gm sample of B22 (i.e., 0.105 gm).

The high degree of phosphorus removal by treatment with a strong alkali seems to indicate that the phosphorus may be present as organo--phosphorus molecules held together by hydrogen-bonding forces. A strongly alkaline medium such as NH_4OH may then be expected to disintegrate such a structure. Furthermore, if the phosphorus were present as phosphate ions, these would exchange with the hydroxyl ions in solution to form ammonium phosphate and organic hydroxyl molecules. On neutralization of the mixture, the phosphate ions would remain in solution and the large coal-derived molecules could be expected to reform a hydrogen-bonded matrix.

C. Sodium Hydroxide Treatment

1. Chemical and Physical Characterization of Alkali-Treated Coal

To determine the changes caused by alkali treatment, the treated coal was separated from the sodium hydroxide by neutralization with hydrochloric acid, followed by filtration, washing, and drying. The dried product in all experiments was similar to the original coal both in appearance and mechanical strength.

On filtering the neutralized mixture, a light brown filtrate was obtained. This filtrate was acidified to pH 1. In all cases the acidification of the filtrate resulted in a clear supernatant liquid and a small amount of light brown precipitate (usually less than 0.1 g) which was discarded.

a. X-Ray Fluorescence. Sodium hydroxide-treated coal, obtained by filtering the neutralized reaction product, was analyzed by x-ray fluorescence to determine the ash and sulfur content. Experiment 1 was selected because it contained no additives; Experiment 2 and 4 because they gave the highest amounts of ketone-extractables. The results are given in Table XVIII.

Accurate analysis could not be obtained, due to the high concentration of chlorine in all the samples. The chlorine was incorporated in the residue during neutralization of the reaction product with hydrochloric acid. Despite water-washing the filter residue until the washings were neutral, some acid appears to have been retained in the product. The approximate values, reported in Table XVIII,

Table XVIII. X-ray fluorescence analysis of sodium-hydroxide-treated coal, wt% relative to coal.

Reaction Conditions: Temperature: 200°C

Atmosphere: Hydrogen

Residence Time: 1 Hr

Coal:Alkali = 1:10 (wt)

Amounts of additive used are listed in Table IX.

Experiment No.	1	2	4	Untreated Coal
Additive Element	None	Sodium Acetate	Sodium Phosphate	
Al	1.5			1.41
Si	6.	5	5.	1.83
S	0.5	0.5	0.5	0.98
Cl	0.1	1.	1.	0.01
Ca	1			0.85
Ti	0.1			0.12
Cr	0.01-0.1			0.003
Fe	0.05			0.20
P	0.5		0.1-0.5	0.00

show that alkali treatment reduces the sulfur concentration from about 0.98% by weight to about 0.5%. These results confirm that sodium hydroxide treatment is an effective method for desulfurization. A comparison of sulfur concentrations of products from Experiments 1, 2, and 4 further suggests that the addition of either sodium acetate or sodium phosphate to the melt does not affect the degree of desulfurization.

Some pitting and corrosion of the glass reaction vessel was observed for each of the sodium hydroxide experiments. The observed increase in silicon content is probably due to the formation of insoluble silicates possibly as a result of reaction between molten sodium hydroxide, coal ash, and glass.

b. Ultimate Analysis. Ultimate analyses of dried neutralized alkali-treated coal samples were determined for all experiments, in the University's Microanalytical Laboratory. The ultimate analysis (wt% on a moisture and ash-free basis) are given in Table XIX. H/C ratios are reported on a wt% basis.

Treatment with sodium hydroxide (with or without additives) results in an increase in H/C ratio, with or without hydrogen present. When sodium acetate is added to sodium hydroxide, the H/C ratio of the product shows the smallest rise compared to the untreated coal, changing from 1.031 to 1.036. The presence of sodium nitrite results in a product of H/C ratio 1.158, the highest obtained.

Results from Experiments 1 and 4 seem to indicate an increase in H/C ratio when nitrogen (instead of hydrogen) is present over the sodium hydroxide melt. This is contrary to the expected increase in H/C ratio

Table XIX. Ultimate analysis of sodium-hydroxide-treated coal.

Reaction Conditions: Temperature: 200°C
 Coal:Alkali = 1:10 (wt)
 Atmosphere: Hydrogen
 Residence Time: 1 Hr

Amounts of additives used are listed in Table IX.

Experiment No.	Additive	wt% (Rel. to MAF Coal)					H/C (Atomic)
		C	H	N	S	O	
1	None	73.36	6.39	1.14	0.03	19.08	1.045
2	Sodium acetate	65.77	5.68	0.95	0.10	27.50	1.036
3	Sodium nitrite	65.37	6.31	1.29	0.06	26.96	1.158
4	Sodium phosphate	70.46	6.16	1.00	0.28	22.10	1.049
5	None*	69.88	6.38	1.00	0.23	22.51	1.096
Untreated							
Coal		61.67	5.30	0.96	0.92	13.64	1.031

*Under nitrogen atmosphere.

by possible uptake of hydrogen. The results, however, clearly indicate that the presence of hydrogen does not improve the H/C ratio of the product.

c. Extraction Behavior. To compare the properties of the sodium hydroxide-treated coal with those of raw coal, samples were extracted successively with carbon tetrachloride and methyl isobutyl ketone. The reaction product was neutralized, filtered, dried, and extracted first with carbon tetrachloride in a Soxhlet apparatus. Residue from this first extraction was dried and extracted with methyl isobutyl ketone. Both extractions were done by the standard procedure described in Section III-B-4. Fifty milliliter samples of the extracts were dried in a hood for 8 hr to evaporate the solvent. The residues were weighed, giving the total carbon tetrachloride and methyl isobutyl ketone extractables which are reported as percentages of the original coal on a moisture and ash-free basis.

Carbon tetrachloride extractability of the alkali-treated products are shown in Table XX. Results from Experiments 1 and 5 indicate that sodium hydroxide treatment decreases the yield in carbon tetrachloride extractions to between 33 and 50% of the corresponding extraction of untreated coal. Further, the presence of hydrogen during the reaction results in a lowering of extractable material.

The addition of sodium acetate or sodium phosphate to sodium hydroxide substantially improves the yield of carbon tetrachloride extractable material. Additions of sodium acetate to the melt results in a product containing 1.56% by weight of carbon tetrachloride extractables; and addition of sodium phosphate yields a product 1.44%

Table XX. Carbon tetrachloride extractables in sodium-hydroxide-treated coal.

Reaction Conditions: Temperature: 200°C
 Residence Time: 1 Hr
 Atmosphere: Hydrogen
 Coal:Alkali = 1:10 (wt)

Amounts of additives used are listed in Table IX.

Experiment No.		wt% (Rel. to MAF Coal)
1	None	0.47
2	Sodium acetate	1.56
3	Sodium nitrite	0.67
4	Sodium phosphate	1.44
5	None*	0.66
Untreated Coal		0.96

*Under nitrogen atmosphere.

soluble in the solvent. Both yields are significantly better than the 0.96 wt% extractability of untreated coal.

Extractability of the alkali-treated coal with methyl isobutyl ketone follows the same general trends observed with carbon tetrachloride. Treatment with sodium hydroxide results in a lower yield of methyl isobutyl ketone soluble material. Untreated coal contains 5.42 wt% of ketone-extractables. On treatment with sodium hydroxide under a hydrogen atmosphere, the product extractability drops to 3.57%. Again, when the hydrogen atmosphere is replaced by a nitrogen atmosphere, the yield of ketone-extractables increases (to 4.48 wt%).

Addition of sodium acetate or sodium phosphate to the sodium hydroxide enhances the ketone-extractability of the product. When sodium acetate is added to the melt, the product yields 9.08% ketone-extractable material. When sodium phosphate is added, the product contains 9.14 wt% of ketone-extractables.

2. Characterization of Extracts of Alkali-Treated Coal

The extracts of raw coal and of selected alkali-treated reaction products were studied. In all cases extracts recovered from carbon tetrachloride were light brown wax-like solids. Methyl isobutyl ketone extracts were also wax-like solids but they were dark reddish brown. The dried ketone extracts were soluble in carbon tetrachloride, which was chosen for studies of extract properties because of its non interference with nmr and uv spectra.

a. Mass Spectrometry. Methyl isobutyl ketone extracts of raw coal and products from Experiments 1, 3, and 4 (see Table IX for reaction conditions and additives) were analyzed by mass spectrometry.

Low-resolution spectra are shown in the Appendix (Figs. A3 to A6). Principal ions for all extracts are shown in Table XXI. The low-mass ions are, again, probably due to fragmentation in the electron beam. Spectra varied widely for each treatment.

Extracts from raw coal showed three high-molecular-weight ions at 368, 396, and 424 respectively. No prominent masses appeared in the 200 to 380 mass range. Coal treated with sodium hydroxide alone (Experiment 1) showed no major ions greater than 250 mass number. When sodium nitrite was also present in the melt (Experiment 3), two high-molecular-weight species were detected, one of mass 424 and the other of 452. Almost no masses were found in the 150 to 400 range. With sodium phosphate in the melt, the MIBK extract contained few masses greater than 250.

These results seem to suggest that mass spectrometry only detects fragments of the parent molecules, and that most constituents of the MIBK extracts are high-molecular-weight low-volatility species that do not vaporize.

b. Nuclear Magnetic Resonance Spectroscopy. To elucidate characteristic structures of the extracts, nuclear magnetic resonance of CCl_4 solutions was obtained for selected reaction products, using tetramethylsilane as reference. Peaks obtained for carbon tetrachloride extracts of Experiments 1, 2, and 4 are given in Table XXII. All methyl isobutyl ketone extracts were dissolved in CCl_4 and analyzed by nmr. Peaks obtained for the ketone extracts are given in Table XXIII. All peaks were compared to standards in the literature.⁵¹

Table XXI. Characteristic mass numbers in mass spectrographs on ketone extracts from sodium hydroxide treated coal.

Raw Coal		Experiment 1			Experiment 3		Experiment 4	
45	111	45*	100	165	45	191	45	101
55*	112	53	105	177	53	424*	51	103
56	113	55*	107	179	54	425	53*	105
57*	121	56*	109*	183	55*	452*	55*	107
58	123*	57*	110	197	56*	480	56	109*
59	125	58*	111*	198	57*		57*	111*
60*	129	59	112	211	58		58*	113
61	135	60	113*	219	60*		59	121
67	137	67*	119	221	61		65	123*
69*	139	68	121*	237	67*		67*	124
70	145	69*	122	252	68		68	125
71*	149	70	123		69*		69*	136
73*	163*	71*	124		70		70	137*
81*	165	73	125		71*		71*	138
82	167	77	127		73		77	140
83*	171	79	128		79		79	141
84	183	81*	129		81*		81*	143
85*	191	82*	135		82		82	165
87	205	83*	137*		83*		83	178
91	340	84	138		84		85*	179
95*	368*	85*	139		85*		91	180
96	396*	86	140		91		93	191
97*	424	91	141*		95*		94	198
98*		93	149		96		95*	199
99		95*	151		97*		96*	237
101		96*	153		98		97*	
107		97*	155		109		98*	
109*		98*	156		111		99	
110		99*	163		129		100	

*Major peaks.

Each of the carbon tetrachloride extracts (Table XXII) showed resonance at 0.85 to 1.0 ppm; 1.24 to 1.3 may indicate the same group, or it may also show R_2NH or $CH_3-C-(C)_n-X$ where $n \neq 1$ and X can be Cl, OH, OR, C=O, or N. The CCl_4 extract of product obtained with sodium phosphate present in the melt contained an additional peak at 2.03 ppm which may indicate the presence of R_2NH or $CH_3-C=O$. When raw coal was extracted with carbon tetrachloride, an additional peak at 1.12 ppm was obtained which may indicate the presence of RSH or RNH_2 in addition to the compound types for 1.0 and 1.3 ppm.

All methyl isobutyl ketone extracts of treated coal (Table XXIII) had two peaks in common at 0.8 to 1.0 and 1.27 to 1.30 ppm. These resonance shifts were also found to be common among the CCl_4 extracts, as discussed above. Since ketone extraction followed CCl_4 extraction, the common resonance shifts indicate that methyl isobutyl ketone further extracts compounds containing similar functional groups. However, extraction yields with the ketone were in the 3 to 9 wt% range, as compared to carbon tetrachloride extraction yields which were under 2%.

When sodium phosphate was present in the melt, the ketone extract of the product showed an additional shift at 1.79 ppm which may indicate the presence of CH_3-C-X or $CH_3-C=C$ (where X may be Cl, OH, OAr, or N). Raw-coal extract gave an additional peak at 2.12 ppm which may be due to the presence of $CH_3-C=O$, CH_3-S- , or $CH_3-N=$. Two new resonance shifts were observed for the ketone extract of coal treated with sodium hydroxide under a nitrogen atmosphere (Experiment 5). Both resonance shifts may represent CH_3-C-X . The resonance at 1.48 ppm may also

Table XXII. Proton nmr of carbon tetrachloride extracts of sodium-hydroxide-treated coal.

Reaction Conditions: Temperature: 200°C
 Coal:Alkali = 1:10 (wt)
 Atmosphere: Hydrogen
 Residence Time: 1 Hr

Amounts of additives used are listed in Table IX.

Experiment No.	Additives	Resonance Shifts (δ) ppm		
1	None	1.00	1.3-1.24	
2	Sodium acetate	0.85-1.00	1.27	
4	Sodium phosphate	1.00	1.30	2.03
Untreated Coal		0.93	1.12	1.33

Table XXIII. Proton nmr of methyl isobutyl ketone extracts of sodium-hydroxide-treated coal.

Reaction Conditions: Temperature: 200°C
 Coal:Alkali = 1:10
 Atmosphere: Hydrogen
 Residence Time: 1 Hr

Amounts of additives used are listed in Table IX.

Methyl isobutyl extracts were dissolved in carbon tetrachloride.

Experiment No.	Additive	Resonance Shifts (δ) ppm			
1	None	1.0-0.8	1.28		
2	Sodium acetate	1.0-0.8	1.28		
3	Sodium nitrite	1.0-0.8	1.27		
4	Sodium phosphate	2.0-0.9	1.30		1.79
5	None*	1.09	1.28	1.48	1.69
Untreated Coal		1.09	1.28		2.12

*Under nitrogen atmosphere.

be due to the presence of RSH or RNH₂ groups and the resonance at 1.69 may also represent CH₃-C=C .

The new peaks in the spectra of ketone extract for the experiment under nitrogen atmosphere may represent the additional extractable material formed when nitrogen instead of hydrogen is used (Table XXI).

c. Ultraviolet Spectroscopy. Ultraviolet spectra were obtained of dilute CCl₄ solutions of carbon tetrachloride and methyl isobutyl ketone extracts of Experiment 1. Both spectra showed a broad peak at 2600 , which could be caused by the double bond in carbonyl groups, or by aromatics which the nmr indicates are largely absent.

3. Conclusion

Sodium hydroxide treatment of Wyodak coal results in a product similar to the original coal both in appearance and mechanical strength. Alkali treatment results in up to 50% desulfurization at 200°C for 1 hr. The H/C ratio decreases upon treatment with sodium hydroxide melts, the maximum H/C ratio product being obtained from an alkali melt containing sodium nitrite. A 33 to 50% increase in CCl₄ extractability is observed after alkali treatment of coal. The presence of sodium acetate results in the largest increase in CCl₄ extractables and also enhanced MIBK extractability.

Carbon tetrachloride extracts of alkali-treated coal are wax-like substances. Methyl isobutyl ketone extracts were darker in color but again appeared wax-like. Resonance shifts were found to be common between the two extracts, indicating that MIBK is a stronger solvent than CCl₄ for compounds containing the same functional groups.

D. Comparison of Various Melt Media

The interaction of Wyodak coal with molten zinc chloride has been the subject of two studies in this laboratory.^{5,52} Results of these studies and those of this work will be compared in this section.

1. Treated Coals

The interaction of Wyodak coal with molten zinc chloride containing catalytic additives was studied in the vicinity of 200°C.⁵ The coal did not completely disperse in the melt after 2 hr. Zinc-chloride-treated product had much reduced mechanical strength, and showed little deashing or desulfurization. Melt-treated coal was extracted with benzene, the largest extent of extraction being obtained when KI and I₂ were used together as additives in the melt. Raney nickel, stannous chloride, and magnesium chloride also improved the extractability, giving extractables in the range 3.5 to 3.8 wt%.

In another study in this laboratory,⁵² the effect of residence time on the interaction between Wyodak coal and molten zinc chloride at 200°C was studied. Reactions were run at atmospheric pressure under hydrogen. Iodine was added to the zinc chloride melt, and samples taken at 15, 30, 60, and 120 min. A sharp rise in benzene extractability in the first 15 min (to about 2.7% from 1.8%) was followed by an equally sharp decline. The product after 30 min of treatment was found to be less soluble in benzene than untreated coal.

When Wyodak coal (28-50 mesh) is reacted with phosphoric acid, the coal appears to disperse completely in the melt (to below 200 mesh) within 2 hr. The acid-treated product appears to lose most of its mechanical strength. Phosphoric acid with or without additives does

not appear to de-ash or desulfurize the coal. The product contains organically bound phosphorus, the content increasing with reaction time (reaching 2.4% in 4 hr). The H/C ratio of the product decreases rapidly within the first hour of reaction, and then remains constant up to 4 hr time. Benzene extractability of phosphoric-acid-treated coal shows the same general behavior as was found with zinc chloride. Extractable material increases to a maximum of 3.79 wt% (for a coal-to-acid ratio of 1/10) in 0.5 hr of reaction, and drops more gradually to 1.94 wt% in 4 hr. A lesser proportion of phosphoric acid leads to enhanced extractability at shorter contact times (15 min and less) and reduced extractability thereafter. Presence of additives does not increase the benzene solubility above the maximum obtained with phosphoric acid alone.

Sodium hydroxide treatment of Wyodak coal results in a product similar to the original coal both in appearance and mechanical strength. X-ray fluorescence analysis indicates up to 50% desulfurization of the coal when it is treated with sodium hydroxide at 200°C for 1 hr. the H:C ratio also decreases upon treatment with sodium hydroxide melts, the maximum H:C ratio being obtained from an alkali melt containing sodium nitrite. A 33% to 50% increase in carbon tetrachloride extractables is observed for coals treated with sodium hydroxide melts. The presence of sodium acetate gives the largest increase in extractability from 0.96 wt% (for untreated coal) to 1.56 wt%. Successive extraction with methyl isobutyl ketone also shows enhanced extractability. With sodium acetate and sodium phosphate present in the melt, the MIBK extractability increases

to 9.08 wt% and 9.14 wt% respectively. Untreated coal subjected to similar extraction yields only 5.42 wt% MIBK extractables. The presence of additives results in a definitive improvement in extract yields. When coal is subject to treatment with sodium hydroxide alone, only 0.47 wt% carbon tetrachloride-soluble materials are obtained. Successive extraction with MIBK removes only an additional 3.57 wt% as extract (both extraction yields are less than untreated coal).

2. Extracts

Benzene extracts of zinc-chloride-treated coal were analyzed by mass spectrometry, ir, uv, and nmr.⁵ Large proportions of ions with mass numbers under 120 were found in mass spectrographs of the waxy extracts. Exact masses of two abundant high mass ions indicated the presence of $C_{28}H_{56}O_2$ and $C_{26}H_{52}O_2$ in the extract. Nuclear magnetic resonance of carbon tetrachloride extracts from the same treatment showed a lack of aromatics. Resonance characteristic of methyl groups attached to saturated hydrocarbons were present. $CH_3-C=C$, $CH_3-C=O$ and $CH_3-C-(C)_n-X$ (where X could be OH, OR or C=O) were also suggested as being present. Major ir absorbances were attributed to C-C and C=O structures. Ultraviolet spectra showed a broad peak at 2600 which could be caused by carbonyl double bonds. The extracts contained a multiplicity of compounds identified by ir to be mostly aliphatic esters (with much smaller amounts of aromatics and alicyclics).

Phosphoric acid treatment also led to the formation of wax-like benzene extracts. Here again mass spectroscopy showed an abundance of ions with low mass numbers. Extracts from longer contact times appeared to contain less high-molecular-weight material. There was

a concomitant decline in some low-mass ions. Nuclear magnetic resonance of the extracts gave resonance shifts very similar to those obtained with zinc chloride melts. At shorter contact times (0.5 hr) an additional peak at 3.00 ppm was obtained, which may be due to $\text{CH}_3\text{-N-}$ or nonconjugated H-C=C- . The lack of aromatics in the extracts was again observed. The spectra of phosphoric-acid-treated coal extracts were similar to those obtained with zinc chloride treatment.

Carbon tetrachloride extracts of sodium-hydroxide-treated coal appeared to be waxy substances much like those obtained with ZnCl_2 and phosphoric acid. Nuclear magnetic resonance showed one additional shift relative to the benzene extracts discussed above; this shift at 2.03 may indicate the presence of R_2NH or $\text{CH}_3\text{-C=O}$. Methyl isobutyl ketone extracts were darker in color, but again appeared wax like. Resonance shifts were found to be common with the CCl_4 extracts; indicating that MIBK is a stronger solvent than CCl_4 for compounds containing the same kinds of functional groups. Ultraviolet spectra of both CCl_4 and MIBK extracts had a broad absorbance at 2600, as found in the extracts from both phosphoric acid and zinc chloride treatments. Mass spectrographs of alkali-treated extracts in general showed a greater abundance of lower mass ions. A few high mass ions (e.g., 424, 480) were also found which do not appear in the other extracts.

V. SUGGESTIONS FOR FUTURE WORK

A. General Considerations

The results of this study indicate three broad areas for future work: (i) Deeper extraction of melt-treated coal and further characterization of the extracts. (ii) Increased activity of the molten systems, by using more severe conditions and more active hydrogenation catalysts. (iii) Investigation of molten-salt/organic-solvent combinations.

B. Deeper Extraction of Melt-Treated Coals

Benzene, carbon tetrachloride, and methyl isobutyl ketone, although known to be valid extraction solvents, do not extract adequate quantities of the treated coals. Use of polar "reactive" solvents such as pyridine, cresol, and phenol may be more useful, because they should result in greater solubility which could have two important advantages. First, use of more effective solvents would show greater differences between various treatments, and hence would allow better differentiation between competitive conversion conditions. Second, extraction of a larger portion of the treated product would give information about a larger portion of the original coal.

C. Increasing the Activity of Inorganic Molten Systems

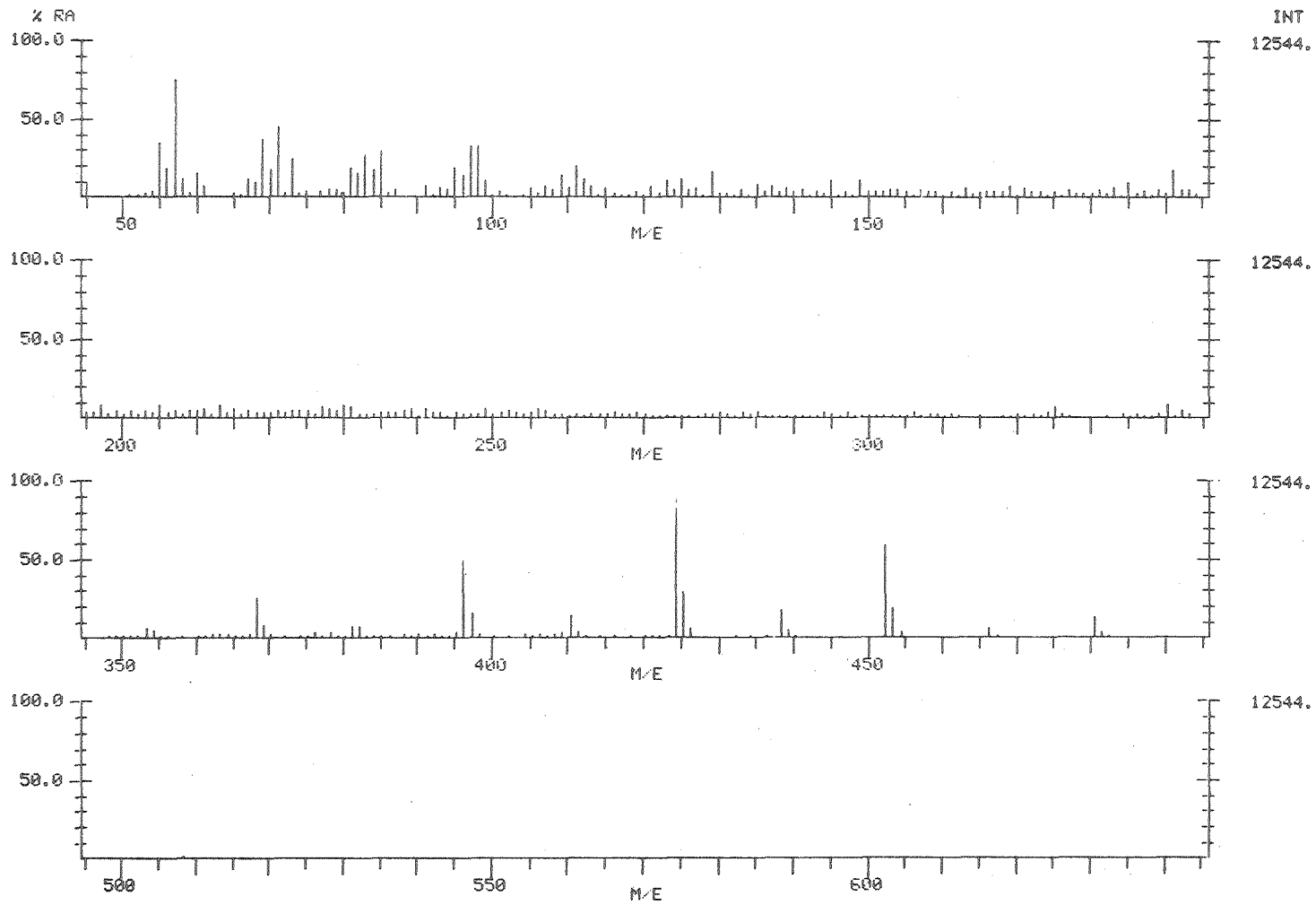
Improvement in the amount of soluble products may be obtained by using more severe reaction conditions, as has already been noted. Wald²⁹ has shown that phosphoric acid/SbBr₃ melts give up to 25 wt% of liquid hydrocarbons at 350°C and 1800 psig of hydrogen. These results, together with the rapid dispersion observed at 200°C in the present study, indicate that reactions at higher temperatures and/or

longer reaction times could lead to substantial amounts of liquid products.

Another area of future study should be a two-step treatment of coal. The product from the first treatment could be further upgraded by catalytic hydrogenation in a separate step.

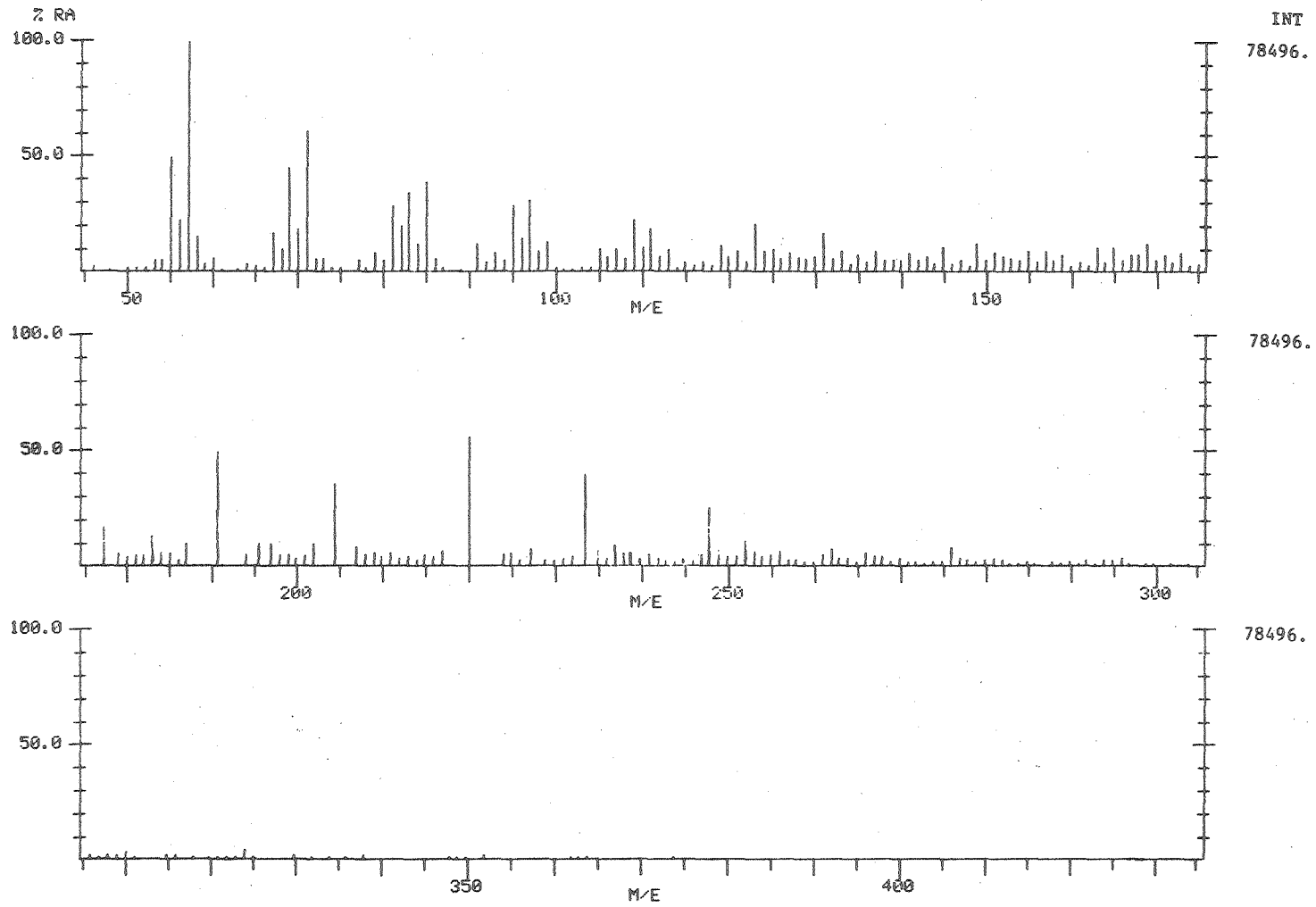
D. Investigation of Molten-Salt/Organic-Solvent Combinations

Combinations of molten salt and organic solvents could be used to effect extraction simultaneously with melt treatment. Two classes of organic solvents could be studied. First, solvents such as pyridine, which would be expected to accelerate removal from the coal particles of molecules produced in the coal by action of the melts, increasing the recovery of such breakdown species, and also increasing the surface area of the treated coal to enhance its further treatment by the melt. Second, donor solvents such as tetralin, which would be expected to donate hydrogen to coal fragments and hence enhance product quality and yields. The most effective process might involve all these conditions in a three-phase reactor containing solid coal, liquid organics, and melt.



XBL 7711-11384

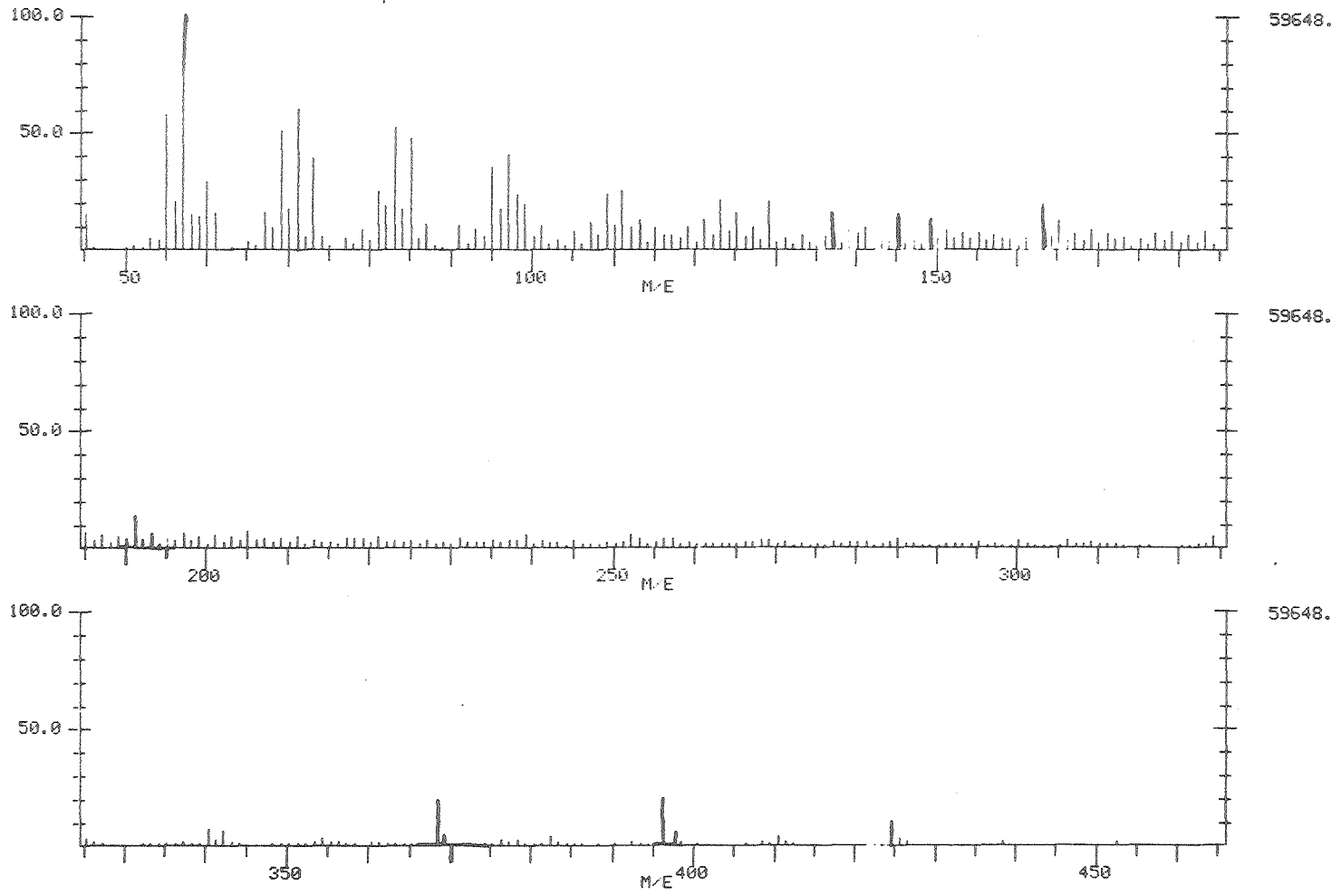
Fig. A1. Mass spectrograph of extract from coal treated with phosphoric acid for 15 min.



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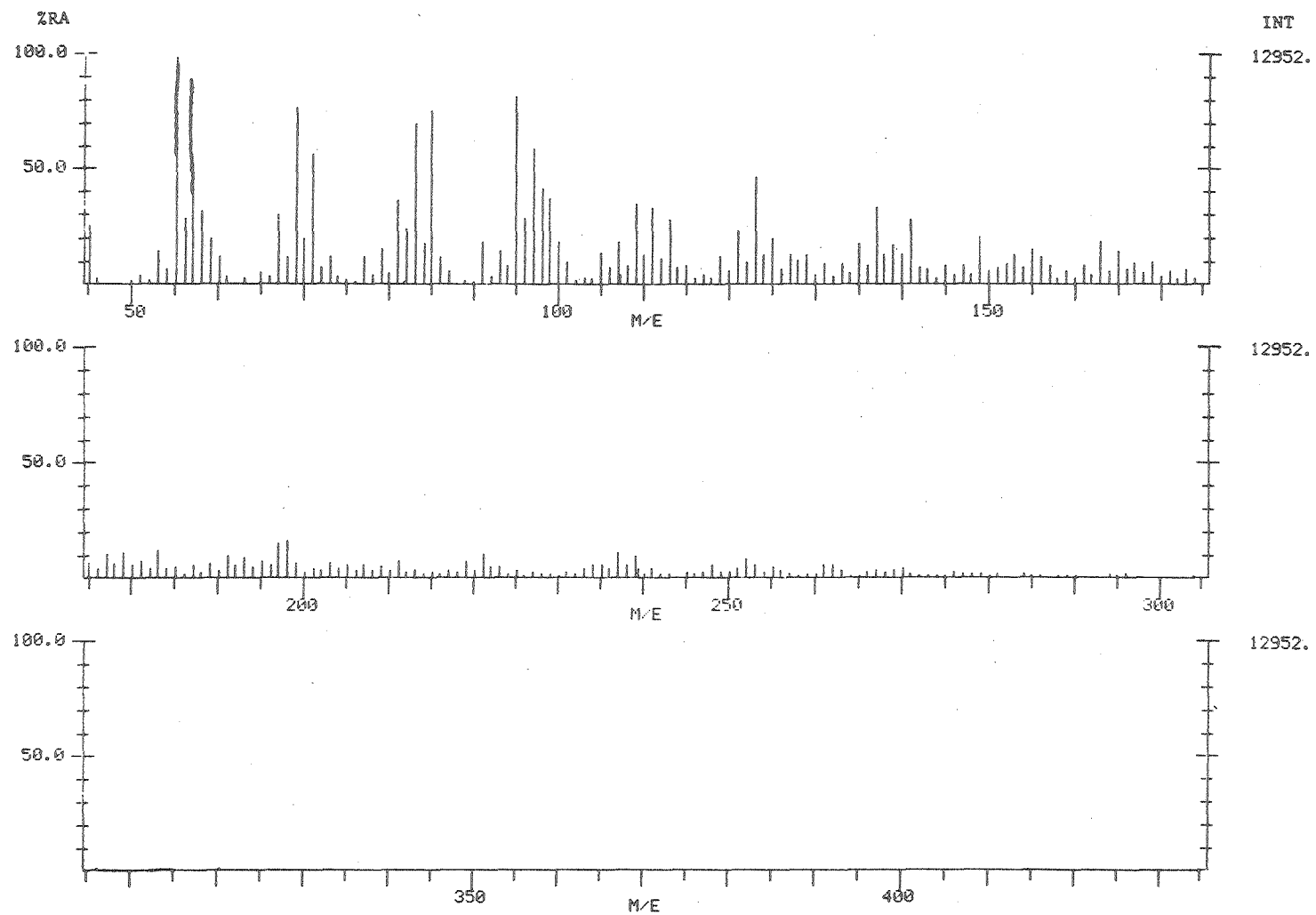
XBL 7711-11385

Fig. A2. Mass spectrograph of extract from coal treated with phosphoric acid for 4 hr.



XBL 7711-11386

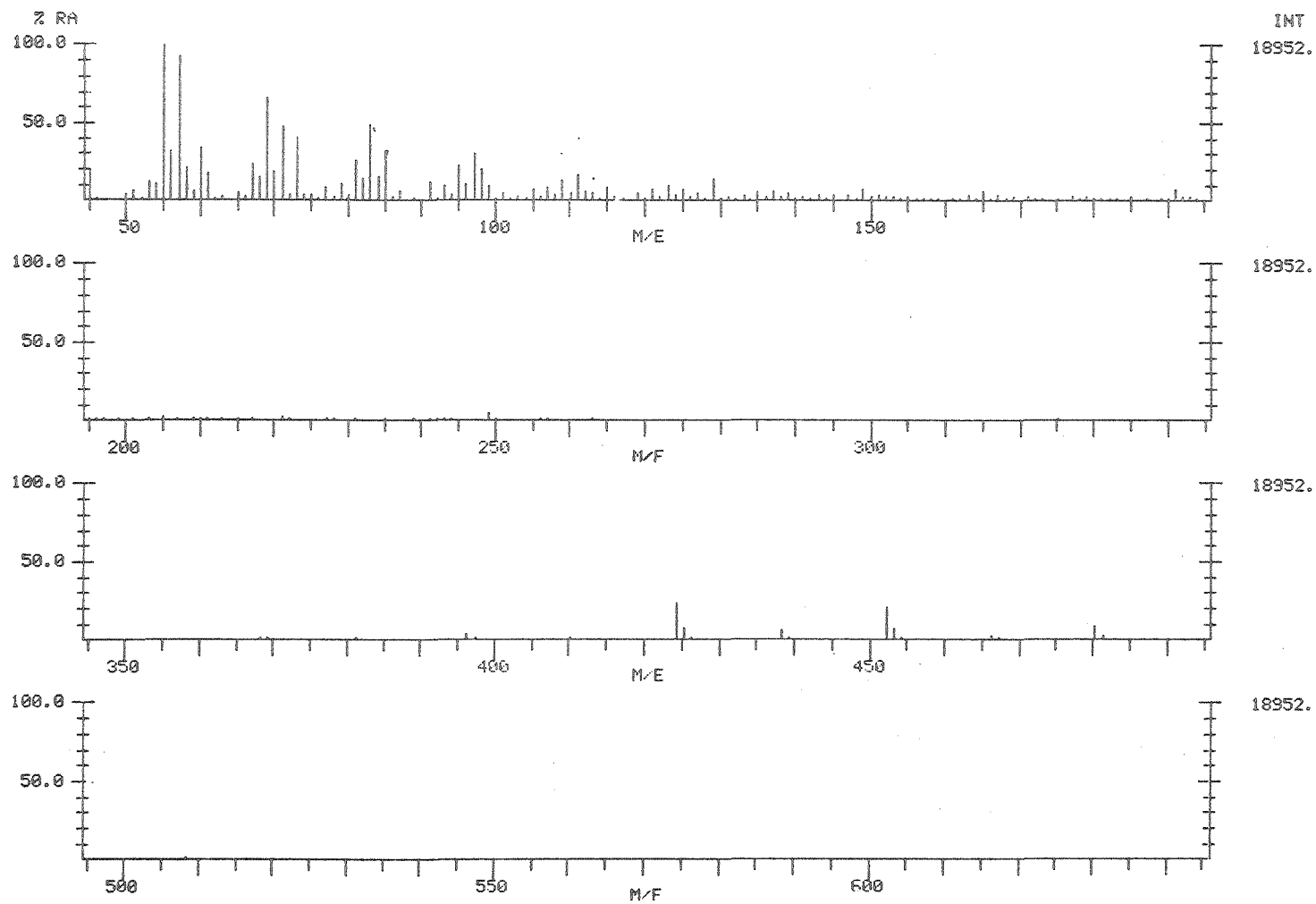
Fig. A3. Mass spectrograph of MIBK extract from raw coal.



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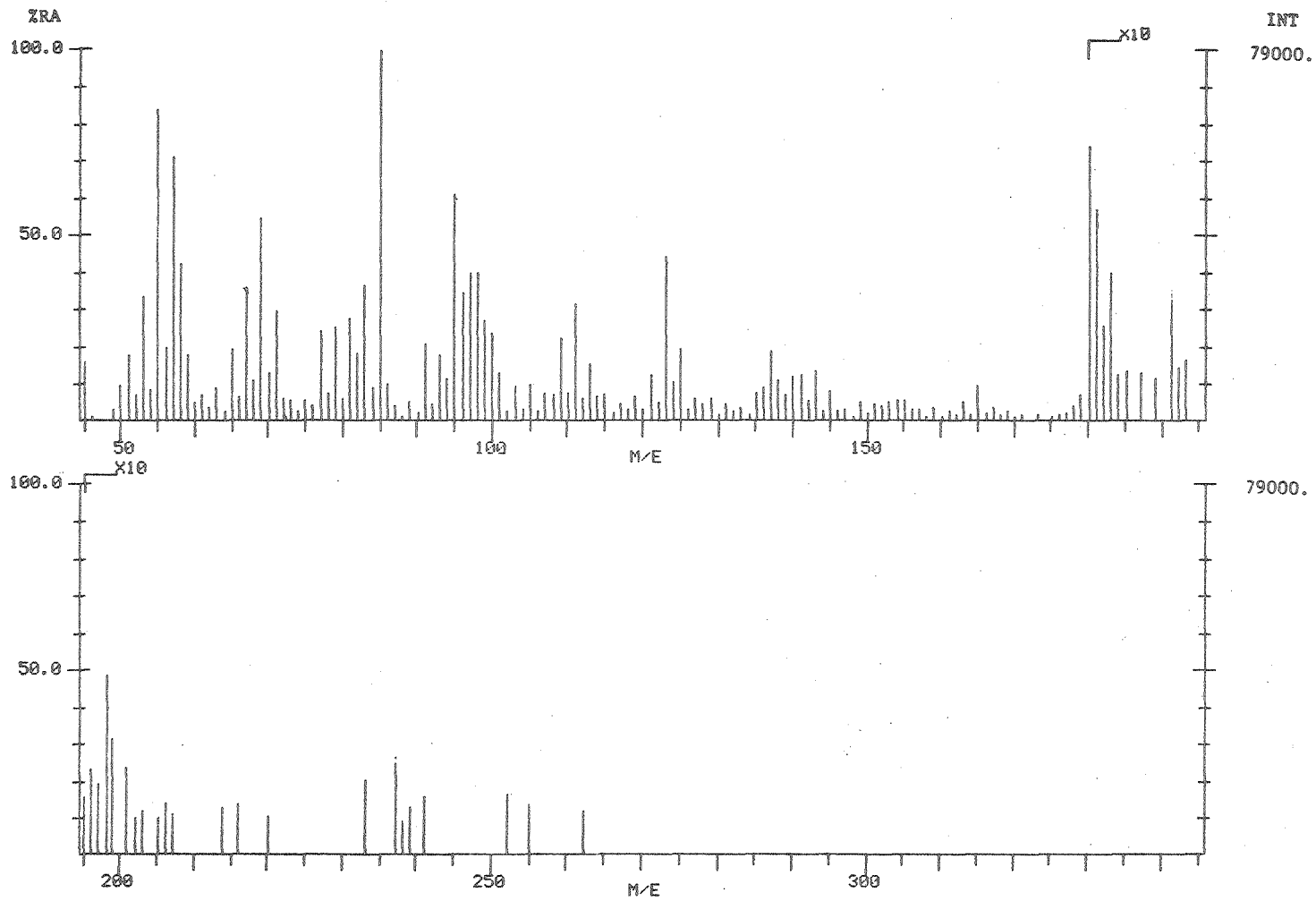
XBL 7711-11387

Fig. A4. Mass spectrograph of MIBK extract of coal treated with sodium hydroxide.



XBL 7711-11388

Fig. A5. Mass spectrograph of MIBK extract of coal treated with sodium hydroxide and sodium nitrite.



XBL 7711-11389

Fig. A6. Mass spectrograph of MIBK extract of coal treated with sodium hydroxide and sodium phosphate.

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