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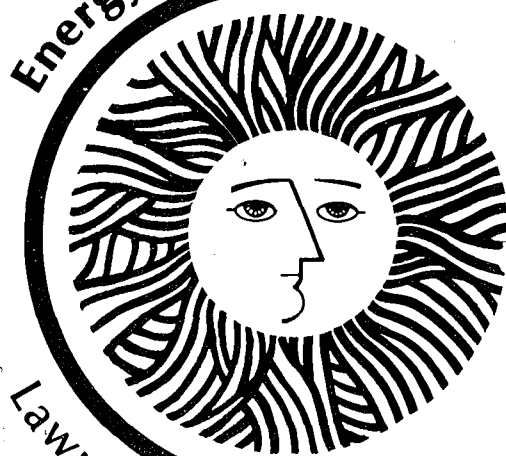
Coal Liquefaction Studies Using Phosphoric Acid At Moderate Temperatures And Pressures

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COAL LIQUEFACTION STUDIES USING PHOSPHORIC
ACID AT MODERATE TEMPERATURES AND PRESSURES

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COAL LIQUEFACTION STUDIES USING PHOSPHORIC ACID AT MODERATE TEMPERATURES AND PRESSURES

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ABSTRACT

Concentrated phosphoric acid solutions (65-100% H_3PO_4) were studied as a potential homogenous catalytic medium for coal liquefaction at temperatures of up 250°C and hydrogen pressures up to 600 psig. Possible catalytic additives, both organic and inorganic, were investigated. Sulfuric acid and molten phosphate and sulfate salt systems were also briefly studied. Illinois No. 6 bituminous coal was used in most of the experiments, while Wyodak sub-bituminous and Solvent Refined coal were also used. Asphaltene and presasphaltene contents of the treated coals (as determined by successive Soxhlet extractions with benzene and pyridine) were compared with those of the feed coal materials to determine the relative success of the treatment procedures used.

Sodium pyrophosphate was found to be a beneficial additive to phosphoric acid, in that it reduces the tendency toward foaming upon contacting coal with hot acid, and was used in all subsequent experiments.

*M.S. thesis

When no other additives were used, anhydrous phosphoric acid (100% H_3PO_4) was ineffective in that the treated coal gave lower extraction yields (8-12% DAF coal) than the untreated coal (19%) due to the occurrence of polymerization reactions. More dilute concentrations (88-96%) gave slight increases in extraction yields, 25% being obtained by using 92% H_3PO_4 at 200°C with no hydrogen present.

Sulfuric acid was ineffective as a liquefaction catalyst, promoting gasification and carbonization of the solid residue at 175°C and 600 psig. Unfavorable results were also obtained with molten sulfate and phosphate salts.

A number of organic additives were tried, the most successful being tetraphydrofuran (THF), para-toluenesulfonic acid (PTSA), and tert-butanol. The use of THF led to extremely high extraction yields (up to 88% of the total product), but with the expense of high THF incorporation. PTSA and tert-butanol both led to high extraction yields (30-40%) with no significant incorporation, and were more successful when used in combination than separately.

Approximately 30% of the sulfur in coal is removed by phosphoric acid treatment, while no effect on nitrogen content is evidenced. Some deashing occurs, with Al,Ca components most affected. Phophorus is chemically incorporated into the product coal at levels of 2% or less with most of the incorporated P ending up in the pyridine extract. B.E.T. surface area and scanning electron microscope studies indicate that increased extraction yields of product coals are due more to chemical effects than simply to exposure of more surface area to the extraction solvent used.

I. INTRODUCTION

In recent years, because of depletion of the world's reserves of petroleum and natural gas, the utilization of solid fossil fuel – coal, oil shale, and tar sands – has received considerable attention. Of these, coal is the most recoverable and available.

U.S. coal reserves, suitably utilized, could supplant natural gas and crude oil for the equivalent of 500 years under total dependency (Cl). In particular, there is a need for the development of processes to produce liquid fuels from coal as a petroleum substitute for both transportation fuels and petrochemical feedstocks.

A. COAL STRUCTURE

Coal is the anaerobic decomposition product of vegetation from previous geological ages. It is composed primarily of carbon, hydrogen, and oxygen, lesser amounts of nitrogen and sulfur, along with varying amounts of mineral matter ("ash") and moisture. As coals increase in age (or rank), they decrease in both moisture and volatile constituents, becoming more like graphite in chemical structure.

A number of models for coal structure have been developed, several of which are summarized by Lowry (Ll). A model of bituminous coal structure by Wiser (Wl) is present in Fig. 1. About 70% of the carbon is contained in condensed polynuclear aromatic clusters, but only about 23% of the hydrogen is attached to these rings. Thus, contrary to earlier theories, the aromatic rings must be highly substituted, with an average number of 3 to 5 rings per cluster. These clusters are connected by hydroaromatic or aliphatic linkages. Sulfur is also found
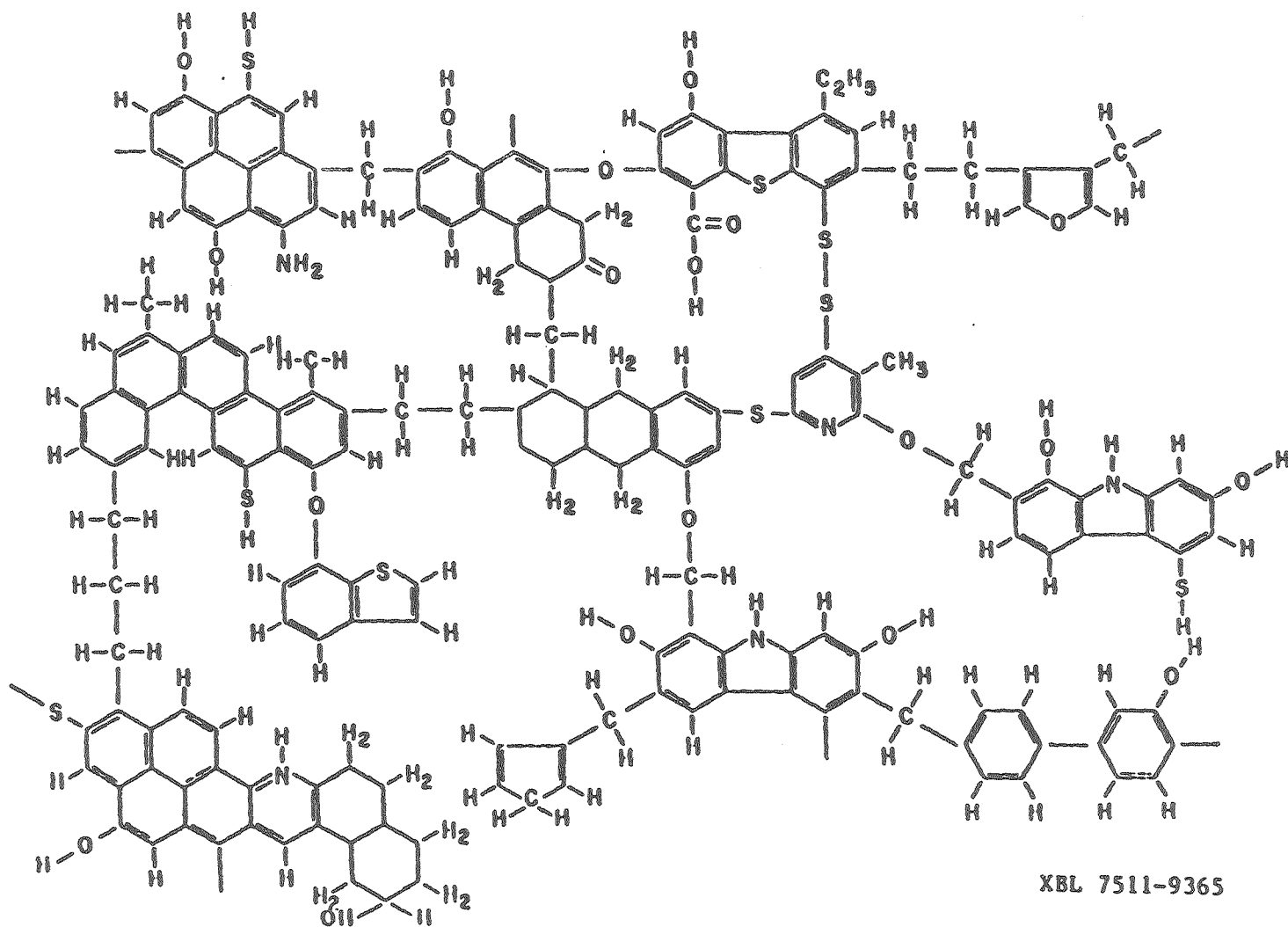
Fig. 1. Wiser Model for Bituminous Coal Structure

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-2-

in an inorganic state as part of the ash, usually as FeS_2.

Recent studies (Z1) indicate that acid-base interactions are also important, with hydrogen bonding occurring between acidic structures such as phenolic hydroxyl and pyrrole-type nitrogen groups, and basic components like ether oxygen or pyridine-type nitrogen.

B.   ALTERNATIVE PATHS OF LIQUID FUELS FROM COAL

1.   Indirect Liquefaction (Fisher-Tropsch Synthesis)

Liquid Fuels can be produced in a two-stage process as follows (G1):

(a) Gasification in a controlled oxygen stream to produce synthesis gas (CO/H_2 mixture) according to the following representative reactions:

$$C_xH_{2y} + 1/2 \; (x + y)O_2 \rightarrow xCO + yH_2O$$

$$C_xH_{2y} + x \; H_2O \rightarrow (x + y)H_2 + xCO$$

(b) Reaction of synthesis gas over a supported catalyst to form hydro-carbons, along with CO_2 and H_2O by-products:

$$(2n + 1-m)H_2 + (n+m)CO \rightarrow C_nH_{2n+2} + nH_2O + mCO_2$$

$$(wn - m)H_2 + (n+m)EO \rightarrow C_nH_{2n} + nH_2O + mCO_2$$

A commercial plant is currently operating in Sasol, South Africa (B1) using this process. Its main disadvantage is low yield (bbl. oil produced per ton of coal fed), since a significant fraction of the fuel value of the original coal is lost as H_2O and CO_2 by-products of the above reactions.

2.   Pyrolysis

Thermal decomposition results from heating coal in the absence
(or in the presence of limited quantities) of air, producing a complex
range of gaseous, liquid, and solid products. Short residence times
and high temperatures are required, necessitating a means for obtain-
ing extremely rapid heat-up of the coal particles. Several pyrolytic
conversion processes have been developed including the COED (B1,C1),
TOSCOAL (B1), and Garrett (S1) processes. Such processes involve
nonselective degradation, which is undesirable when liquid products
are desired. Also the solid char product must be viable as a solid
fuel, for an acceptable overall efficiency to be obtained.

3.   Solvent Extraction

As far back as the 1930's (F1), considerable attention has been
given to the liquefaction of coal by dissolution in organic solvents.
Van Krevelen (V1) classifies coal-solvent interactions into four basic
categories:

a)   Non-specific extraction involves removal of waxes and resins (a
small fraction of the coal) at low temperatures (below 100°C) and is
generally of little interest.

b)   Specific extraction leads to higher yields at temperatures below
200°C by the use of nucleophilic solvents. The test specific extrac-
tion solvents generally contain a nitrogen (e.g. pyridine) or oxygen
(e.g. phenol) atom which interacts with the coal in an acid-base fashion.

c)   Extractive disintegration, carried out about 200°C, leads to higher
yields through degradation of the coal structure. Draemel (D3) has

shown that more than 50% (dry ash-free basis) of a sub-bituminous coal
can be dissolved using phenol at 300°C (i.e. below pyrolysis condi-
tions), with some phenol being incorporated into the extracted material.

d)   Extractive chemical disintegration usually uses a hydrogen-donor
solvent (such as tetralin, discussed below) at temperatures above 300°C.
The chemical composition of both coal and solvent are affected during
the process.

The phenomenon of hydrogen donation by some solvents is particularly
useful for coal dissolution. An example of a hydrogen donor solvent
is tetralin. At temperatures above 325°C, tetralin can transfer hydro-
gen atoms to coal, forming naphthalene and unknown coal products:
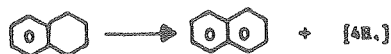
These atoms appear to hydrogenate and/or crack the organic
structure of the coal, resulting in lower-molecular-weight material
which is more soluble. While hydrogen-donor processes (such as SRC
or EDS, discussed below) are actually hydroliquefaction operations,
they are often classified under solvent extraction.

The Solvent Refined Coal or "SRC" process (B1) yields as its
major product a solid fuel which is reduced in ash and sulfur, and
thus is more suitable than the feed coal as a solid fuel. The SRC
product can also be used as a feed for further hydroprocessing to
produce liquid fuels.

The Exxon Donor Solvent (EDS) process uses a coal-derived donor
solvent. Spent solvent is separated from the liquefaction products

and is catalytically rehydrogenated for recycle back to the liquefaction step. Once liquefied, the extracts can also be hydro-treated with solid catalysts for upgrading to desired products.

4. Direct Hydrogenation

Hydroliquefaction involves the reaction of coal with hydrogen to produce liquid products, and was first successfully practiced in Germany during World War II. When carried out without the presence of a catalyst, extremely high operating temperatures and pressures are required, resulting in high capital and operating costs. Like low pressure pyrolysis, thermal (non-catalytic) hydrogenation is also non-selective, in that degradation of the coal structure results in high hydrogen consumptions.

A suitable catalyst could lead to improvements over a direct hydrogenation process in two ways. By increasing reaction rates, desired conversions could be obtained at lower temperatures and pressures, resulting in economic improvements. Also, a catalytic reaction could be done more selectively, reducing hydrogen consumption and resulting in a more efficient process.

Catalytic hydrocracking using heterogeneous catalysts in a well-developed and widely practiced process in the petroleum industry. As a result, considerable work has been done concerning the use of such catalysts with coal. In the Synthoil Process (B1, Y1), coal is slurried with a recycled oil product and reacted over a cobalt molybdate on silica-alumina catalyst to yield a low-sulfur fuel oil.

There are several drawbacks to using heterogeneous hydrocracking catalysts with coal. The two solids do not interact directly, and the liquid medium must serve as a hydrogen transfer agent. Coal and its breakdown products have a higher basic nitrogen content than petroleum, and this poisons acid catalysts more readily. Also the ash components of coal can lead to irreversible poisoning by plugging of catalyst pores, resulting in a loss of surface area.

C. CHEMISTRY OF COAL CONVERSION

1. Reactions Involved

Since coal is a very complex high molecular weight material, analytical procedures are needed for measuring the success of treating processes aiming at liquefaction. One such procedure utilizes the following classification scheme (K1). "Oil" is defined as the pentane-soluble (or sometimes hexane or cyclohexane-soluble) components of the untreated or treated coal. Oil comprises the lowest molecular weight molecules, distillable at atmospheric pressure below pyrolysis temperatures. Typical values reported for the oil fraction from SRC are 350 for number-average molecular weight (K1) and 1.3 for aliphatic-to-aromatic-hydrogen ratio (T2). Asphaltenes are the pentane-insoluble benzene-soluble fraction, higher in molecular weight (number average 565) and more aromatic in character than oils (aliphatic-to-aromatic H ratio 1.1). Preasphaltenes are defined as the benzene-insoluble, pyridine-soluble components. They are still higher in molecular weight (number average 800) and contain more heteroatoms, particularly basic nitrogen and phenolic oxygen, with an aliphatic to aromatic H

ratio less than 1.0. Chemical characterization of the different
extract fractions has been well documented in a number of sources
(K1, S2, W2, S3, S4). Thus the reaction sequence for a liquefaction
process would be:

Coal → Pre-asphaltenes → Asphaltenes → Oil

On a molecular level, reactions involved in coal liquefaction
include hydrogenolysis, hydrogenation, depolymerization, alkylation, and
dealkylation. Each of these is discussed in detail below.

a) Hydrogenolysis is a cracking reaction which involves the cleavage
of a bond (illustrated below as a C-C bond) and insertion of hydrogen:

$$R-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-R' + H_2 \rightarrow R-\overset{|}{\underset{|}{C}}H + H-\overset{|}{\underset{|}{C}}$$
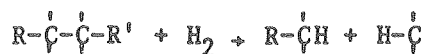
In coal liquefaction, hydrogenolysis of C-O, C-S, and C-N bonds can
also occur. When no catalyst is used, hydrogenolysis reactions are
induced by pyrolysis. Thus, at any temperature in the pyrolysis range,
the reaction products at high hydrogen pressures are very different
than those formed without hydrogen.

b) Hydrogenation involves the addition of hydrogen to an olefinic
bond or, under more severe conditions, to an aromatic ring. A reaction
typical of those occurring in liquefaction processes is the conversion
of anthracene to 9,10-dihydroanthracene:

Selective hydrogenation refers to a combination of hydrogenolysis and
hydrogenation which leads to the liquefaction of coal at the lowest
possible hydrogen consumptions. The reactions involved include removal
by hydrogenolysis of heteroatoms in both ring and connecting structures,
and partial hydrogenation of aromatic ring cluster (such as illustrated
by anthracene above) followed by hydrogenolysis of the resulting
aliphatic C-C bonds, allowing the cracked fragments to retain their
aromatic character.

c)   Depolymerization as applied to coal liquefaction usually refers
to the cleavage of a connecting bridge structure between aromatic ring
cluster and replacement with a single-ring molecule, leading to a
molecular-weight reduction. Since depolymerization does involve
consumption of this replacement ring, it is mainly used as a tool
for structural determination studies. One example of depolymerization
(01, 02, 03, 04, L2) uses phenol in conjunction with an acidic catalyst
according to the following mechanism:
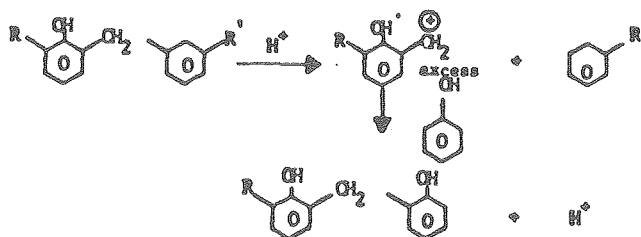
d) Alkylation involves the addition of alkyl groups to aromatic rings. It has been shown (B2, S3, S5, L3) that alkylation of coal can result in increased extraction yields. While this has been used primarily as a tool for structural studies, it is also possible that an alkylating agent (preferably coal derived) could be found which would be cheap enough to justify its use in an alkylation-based liquefaction process.

In liquefaction processes operating at elevated temperatures (above 325°C), pyrolysis reactions (non-specific thermal degradation through free radical mechanisms) also become important. A particular type of pyrolysis reaction which has been utilized is hydrogen donation, illustrated above by tetralin.

2. The Function and Nature of Catalysts

The hydrocracking catalysts useful in coal liquefaction processes have a dual nature -- acid groups with a cracking function utilizing a carbonium-ion mechanism, and metal-atom sites with a hydrogenation function. Related acid-catalyzed reactions includ isomerization, polymerization/depolymerization, alkylation/dealkylation, and hydration/dehydration. The hydrogenation function converts either carbonium ions or free radicals to desirable products and prevents secondary cracking which leads to char (polymer) formation.

Commerical hydrocracking catalysts used in the petroleum industry have traditionally been heterogeneous, with the catalyst material dispersed on interior surfaces of a solid support. In recent years, the use of homogeneous (liquid phase) catalysts, usually metal ions and complexes, for reactions similar to those discussed above has

received considerable attention (C2). The term "homogeneous", when applied to a coal-conversion catalyst, actually refers to a catalyst present in the liquid phase. Homogeneous catalysts are particularly attractive for use in coal-hydrogenation systems, since intimate contacting can be achieved between the liquid-phase catalyst and the coal particles. In addition, irreversible poisoning by coal-ash components is much more serious with heterogeneous catalysts of high surface area than with homogeneous catalysts.

Any hydrocracking catalyst (homogeneous or heterogeneous) to be used in a coal conversion operation must be stable and retain its activity in the presence of NH_3, H_2S, and H_2O, which are formed via hydrogenolysis from the heteroatoms present in the coal structure.

The program underway at this laboratory, of which this investigation is a part, is aimed at developing a liquefaction process which combines molecular activation by an inorganic homogeneous catalyst with the capping action of an organic hydrogen-donor solvent or other suitable reagent. The proper combination of catalyst and solvent in such a system could lead to high conversions at lower temperatures and pressures than would be attainable with either catalyst or solvent alone. Also, by operating at temperatures below the pyrolytic decomposition region, hydrogenation reactions could be carried out selectively.

D.   PHOSPHORIC ACID AS A COAL CONVERSION CATALYST

1.   Physical Properties of Phosphoric Acids

Orthophosphoric acid (H_3PO_4, commonly referred to simply as phosphoric acid) is a product of the reaction of phosphorous pentoxide

with water:

$$P_2O_5 + 3H_2O \rightarrow 2 H_3PO_4$$
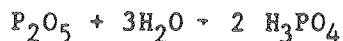
Pure orthophosphoric acid (100% H_3PO_4) has a melting point of 38.85°C, a viscosity of 151 cp at 30°C and 5 cp at 180°C, and a boiling point of 261°C (K2). However, due to equilibrium considerations of the formation of condensed polyphosphoric acids, 100% H_3PO_4 does not exist as a pure molecular compound, but as a mixture with ions (H_3O^+, $H_2PO_4^-$, $H_4PO_4^+$) and polymers ($H_4P_2O_7$, $H_3P_2O_7^-$, etc). The "dimer" $H_4P_2O_7$, known as pyrophosphoric acid (melting point 54°C, viscosity approximately 50 cp at 180°C) is formed at temperatures above 210°C by an equilibrium reaction which simplifies to:

$$2H_3PO_4 \rightleftharpoons H_4P_2O_7 + H_2O$$

Heating $H_4P_2O_7$ to redness produces metaphosphoric acid by the loss of water:

$$H_4P_2O_7 \rightarrow 2HPO_3 + H_2O$$
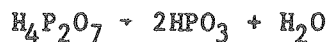
A convenient scale for measuring concentration in these acids is given by weight-percent P_2O_5. On such a scale orthophosphoric acid contains 72%, pyrophosphoric acid 80%, and metaphosporic acid 88% P_2O_5. Figure 2 (K2) shows a temperature-composition diagram from the H_2O-P_2O_5 system. At 92% P_2O_5 and 860°C an azeotrope is formed; at atmospheric boiling points up to 300°C, the vapor is essentially pure H_2O.
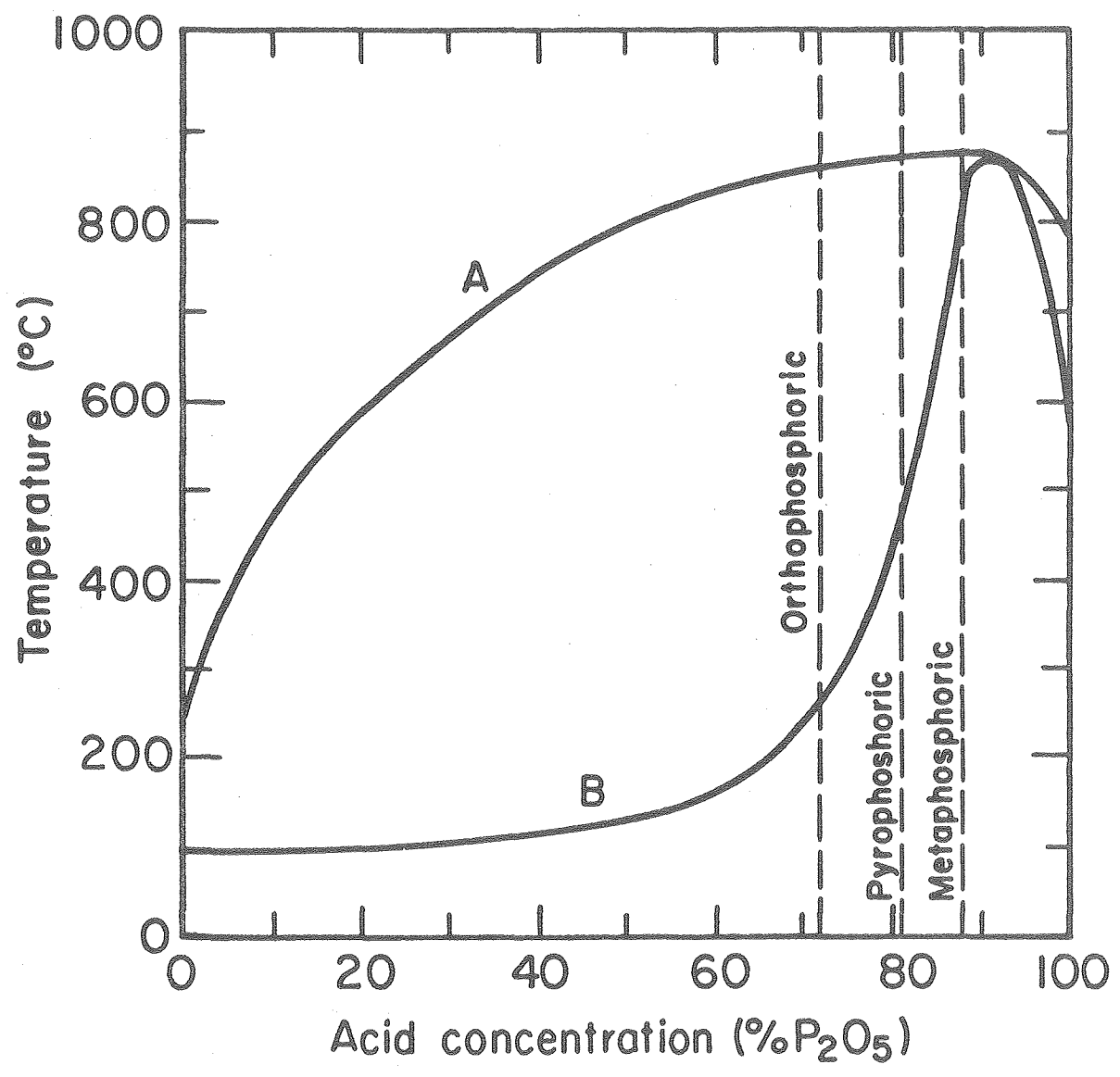
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Fig. 2.   Temperature – Composition Diagram for System

H$_2$O – P$_2$O$_5$ at 760 mm Hg Pressure

Jameson (J1) has shown by room-temperature separations, where the equilibrium is frozen, that 100% H_3PO_4 actually contains approximately 12.5% $H_4P_2O_7$, with 1.15% (the correspoinding amount) of free H_2O. Figure 3 shows a plot of species compositions vs. P_2O_5 concentration. Below about 95% H_3PO_4 (68% P_2O_5) the equilibrium content of $H_4P_2O_7$ becomes too small to detect.

2.   Potential Advantages of Phosphoric Acid as a Coal Catalyst

H_3PO_4 is a relatively strong acid, with a Hammett acidity function value well into the negative range (P2), lying below H_2SO_4 but falling into much the same range as HNO_3. Thus, it provides a source of protons which can lead to cracking reactions via carbonium ion mechanisms. Formation of the condensed acids allows the acidic character to be maintained in the liquid phase even at high temperatures. For example, $H_4P_2O_7$ and HPO_3 still contain one strongly acidic proton for each P atom. Phosphoric acid systems are compatible with a wide variety of homogeneous hydrogenating agents. For example, metal ions (from metal halides) can be used at temperatures below the melting points of the respective phosphate or halide salts in a homogeneous medium since they are soluble in the acid (W3). It may be economical to use such salts in relatively small amounts rather than in the pure state. Any water formed in the reaction will be chemically bound by the condensed acids, which will retard the hydrolysis of any sensitive catalytic additives which may be present.

Unlike other strong acids (e.g. sulfuric), phosphoric acid is essentially non-oxidizing. Phosphoric acid is compatible with the decomposition products of the heteroatoms present in untreated coal:
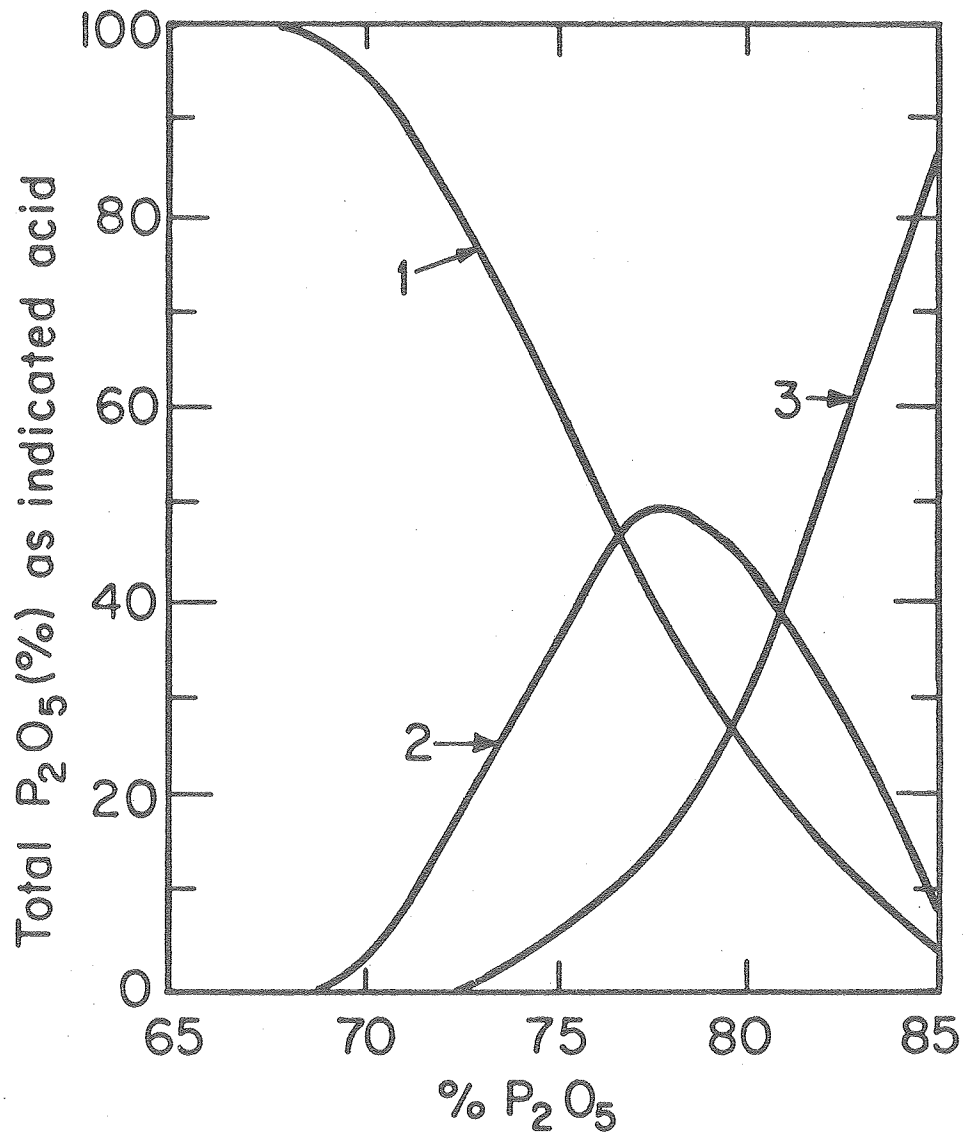
Fig. 3. The Composition of the Strong Phosphoric Acids.

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oxygen as H_2O, sulfur as H_2S, and nitrogen as NH_3 (H_3PO_4 forms ammonium dihydrogen phosphate, $NH_4H_2PO_4$). Finally, oxidative regeneration of H_3PO_4 to eliminate any carbonaceous residues is possible, an important process consideration where such a catalyst is to be recycled.

3. Industrial Use of Phosphoric Acid in Oil and Chemical Processes

Inorganic acids - phosphoric, sulfuric, and hydrofluoric - have long been used in the petroleum industry as polymerization and alkylation catalysts. Phosphoric acid, as a liquid or impregnated on clay-type solid supports (M1), has been used as a catalyst for the manufacture of high-octane gasoline (F3) by polymerization of refinery cracked gases. Other uses have been in alkylation of heterocyclic ring systems and organic amines, condensation of amides, and depolymerization of paraldehyde (S2).

Catalysts have also been made by combining phosphoric acids with metal salts. A combination Lewis and Brønsted acid can be formed by saturating orthophosphoric acid with BF_3. Topchiev and Paushkin (T1) report the use of such a catalyst for the alkylation of isobutane with propylene.

4. Use of Phosphoric Acid for Coal Conversion

Dreyfur (D2) was able to obtain substantial conversion of coal to gaseous products at $450^{\circ}C$ by first slurrying the coal in dilute solutions of phosphoric acid and ammonium phosphate, than heating to drive off water, leaving an impregnated coal. Following this, Pier et al. (P1) found that pretreating coal with phosphoric acid prior to hydrogenation above 50 atm, between 250 and $750^{\circ}C$, resulted in

higher yields of distillable products.

More recently, Schuman and associates (S6) reacted a bituminous coal with a 10% phosphoric acid solution containing small amounts of ammonium molybdate at 650°F and 1000 psig H$_2$ for six hours, and obtained 45.6 wt% conversion of coal (0.7% to gases, 13.3% to oils, and 31.6% to asphaltenes).

Santagelo and Dorchak (S7) showed that low-sulfur chars could be formed from coals which had been pretreated by slurrying with 5-10% solutions of phosphoric acids and then filtering. Along similar lines, Meyers (M2) has shown that phosphoric acid is an effective agent for the extraction of organic sulfur from coal.

As an extension of earlier work (W4), Kiovsky (K3) found that substantial improvements in yield are obtained by adding small amounts of mineral acids to molten halide catalyst systems. The addition of 20 gms. H$_4$P$_2$O$_7$ to 175 gms. SbBr$_3$, reacted with 20 gms. Illinois No. 6 coal at 280°C and 1700 psig increased the yield of 250°C boiling point and lighter components from 7.6% to 14.5%. Even more strikingly, the addition of 20 gms. H$_4$P$_2$O$_7$ to 150 gms. SbBr$_3$, when reacted with 20 gms of coal at 325°C and 1700 psig, increased the yield from 5.3% to 31.5% of MAF coal.

Extending these results, Kiovsky (K4) and Wald (W3) developed catalyst systems based on massive amounts of pyrophosphoric acid containing small quantities (20 wt-% or less) or HI, NaI, NH$_4$I, SbBr$_3$, GaBr$_3$, T$_i$F$_4$, GaI$_3$, ZnI$_2$, and ZnCl$_2$.

Kiovsky (K4) found that by treating a Big Horn Coal with 7.5 times its weight of pyrophosphoric acid containing 3 to wt-% of various hydrogenating agents at 350°C and 1500-2500 psig, up to 25% by weight of MAF coal was converted to gasoline range components (250°C boiling point and lower). At reduced reaction times and temperatures, conversion to gasoline-range components dropped. However, even at lower conversions, the quantity of asphaltenes produced remained high. For example, when 3% NH_4I in $H_4P_2O_7$ was used, a decrease in reaction time from 30 to 2.5 minutes accompanied by a temperature decrease from 365°C to 320°C resulted in a drop in the yield of volatile products from 32.3% to 6.5% MAF coal. At the same time the yield of non-extractable residue increased from 1.0% to 29.0%. Thus the asphaltene yield (calculated by difference) dropped only from 67% to 64%. The sulfur content of the extractable material in these experiments was significantly reduced, indicating the occurrence of hydrodesulfurization reactions.

Wald (W3) reported hydrocracking of Illinois No. 6 coal at 350°C and 1800 to 2000 psig for one hour in pyrophosphoric acid alone, in molten $SbBr_3$ alone, and in pyrophosphoric acid containing from 5-20% metal halides. The results are given in Table 1. $SbBr_3$ was the most successful additive to the pyrophosphoric acid system, with a gasoline range product yield of up to 25% of MAF coal. While the total conversion was less than for $SbBr_3$ alone, the conversion per unit of $SbBr_3$ was up to 5 times higher when the $H_4P_2O_7/SbBr_3$ combination was used. This is possibly another instance of a combination Lewis and Brønsted acid activity.

Recent studies at this Laboratory (S2) investigated the treatment
of a sub-bituminous coal by phosphoric acid (85% H_3PO_4) at 200°C and
1 atm alone and with additives. Conversion as measured by benzene
extraction yield was found to reach a maximum of 3.79% MAF coal at
30 minutes reaction time, and decreased from 30 minuts on up to 4 hours.
This most successful additives were aluminum chloride and ethylene diamine
used together, giving an extraction increase from 2.85% to 3.75% for
kone hour of reaction time. This study was incomplete, in that the
possible formation of preasphaltenes was not measured.

E. ADDITIVES IN PHOSPHORIC ACID FOR COAL HYDROGENATION

A limited amount of background information has been obtained about
additives which were investigated in parts of this research. These
fall into three main categories - other acids, inorganic additives,
and organic additives.

1. Other Acids

Ouchi and co-workers (01, 02, 03, 04) have studied para-toluene
sulfonic acid extensively as a coal depolymerization catalyst, obtain-
ing pyridic extractabilities approaching 100% of MAF coal by reacting
coal with the acid and phenol at 185°C for 24 hours. The same study
(04) which gave a 92% pyridine extraction using anhydrous para-toluene
sulfonic acid as catalyst on a Yubari coal (compared with 34% for no
catalyst) showed 96% H_2SO_4 to be only slightly less effective, yielding
83% pyridine extraction. Phosphoric acid (85%) was completely inactive
under the same conditions indicating that acid strength (Hammett acidity)
in the probable controlling factor.

Table 1. Coal Conversion by Pyrophosphoric Acid and Halide Additives
         (Wald, U.S. Patent No. 3,824,178)

Reaction Conditions:	Temperature	$350^{\circ}C$
	Pressure	1800-2000 psig.
	Reaction Time	1 hr.
		(except Experiment 1, 30 min.)
Coal Used:	Illinois No. 6	
	Moisture Free	
	Ash:	15%
	Size:	100-200 mesh
	Amount	20 gms.

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, gms./100 gm. MAF coal							
CH_4 and C_2H_6	Tr.	1.2	0.8	1.4	0.5	1.8	0.5
C_3H_8	0.1	1.7	1.9	2.1	1.5	3.1	1.7
$i-C_4H_{10}$	0.05	0.4	2.5	2.7	2.1	3.6	2.8
$n-C_4H_{10}$		1.4	0.3	0.9	0.2	0.5	0.2
$i-C_5H_{12}$	0.04	0.6	0.1	0.4	0.1	0.1	0.1
C_6H_{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_7H_{16} and C_8H_{18}	Tr	15.8	3.9	7.5	6.3	1.9	0.9
C_9H_{20} to 250°C	0	17.0	7.6	8.0	10.0	3.3	1.1
Total C_4H_{10} to 250°C	0.1	52.0	17.7	24.9	22.2	12.7	7.0
Hydrogen consumed, gms./100 gms. MAF coal	1.5	9.3	8.5	10.4	8.3	7.7	7.8

Para-toluene sulfonic acid alone would be prohibitively expensive to use as a coal-conversion catalyst on a large scale, while sulfuric acid suffers the disadvantages of being too strong an oxidizing agent, and too corrosive in both liquid and vapor phases. However, by using small amounts of either as additives to a phosphoric acid system, it would be possible in principle to utilize their catalytic activity while maintaining the bulk properties of the phosphoric acid.

2. Inorganic Additives

Along the lines of the work by Kiovsky (K4) and Wald (W3), a dual-function catalyst can be formed by adding a hydrogenating agent to phosphoric acid. In particular, Lewis acids such as metal halides, which are active catalysts when in molten form, are likely candidates. As shown earlier, several combinations of a Lewis acid and a Brønsted acid (W5) have been documented as being good hydrogenating catalyts. Massive amounts of phosphate or sulfate salts are also possibilities, since in their molten salt form they may show activities as Lewis acids similar to the corresponding Bronsted acids.

3. Organic Additives

As discussed earlier, it is possible that the combination of a donor solvent with a homogeneous catalyst could lead to higher lique-faction yields than either component alone at comparable conditions. Thus, hydrogen donors such as tetralin are possible additives. Studies in progress at this Laboratory (H2) indicate that tetrlin is an active additive to a Lewis acid (molten $ZnCl_2$) system. Treatment at $250^{\circ}C$ and 500 psig for one hour gave a product which yielded a 68% MAF pyridine extraction, compared with 16% for $ZnCl_2$ alone.

Another possible hydrogen donor is tetrahydrofuran, which has the
potential to lose 4 hydrogen atoms as follows:
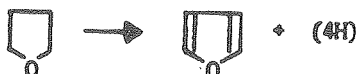
THF has been used some as a coal solvent (G2), but no evidence has
been presented that indicates hydrogen-donation processes.

Ross (R1) has presented evidence that isopropyl alcohol can act
as a hydrogen donor when promoted by basic catalysts such as potassium
isopropoxide, and suggests the formation of acetone as a product from
the isopropanol. For use in an acid medium at lower pressures, sec-
butanol is preferable since its lower vapor pressure will allow more
to remain in the liquid phase. Moreover, the proposed mechanism can
be checked by the use of tert-butanol, which cannot form the ketone
simply by losing hydrogen. Studies in progress at this Laboratory
(H2) indicate that isopropanol is also an active agent when used in
a Lewis acid system (molten $ZnCl_2$). Treatment at $250^{\circ}C$ and 600 psig
for one hour gave a product with a pyridine extraction yield of
70% MAF, as compared with 16% for $ZnCl_2$ alone.

Burkhouse (B2) showed that THF-extractabilities of a Pittsburgh
seam coal increased from 12% MAF to 54-68% by alkylation using THF
and C_2-C_4 alcohols (while only 11% was methanol was used), at $200^{\circ}C$
and 1500 psig. Thus, the use of C_4 alcohols as additives to phosphoric
acid (which is less acidic than HF) could lead to liquefaction by
alkylation, hydrogen donation, or possibly both.

Wristers (W5) has reported that benzene can be hydrogenated to cyclohexane and methylcyclopentane in the presence of a "superacid" catalyst such as $HBr-AlBr_3$ and a tertiary hydride source such as isopentane. His postulated mechanism involves the formation of a tertiary carbonium ion from the isopentane:

1) benzene $+$ H^+ $\longrightarrow$ protonated benzene

2) protonated benzene $+$ isopentane $\longrightarrow$ cyclohexadiene $+$ tertiary carbonium ion

3) cyclohexadiene $+$ H^+ $\longrightarrow$ carbonium ion

4) carbonium ion $+$ isopentane $\longrightarrow$ cyclohexene $+$ tertiary carbonium ion

5) cyclohexene $+$ H^+ $\longrightarrow$ cyclohexyl cation $+$ methylcyclopentane cation

6) R^+ $+$ H_2 $\longrightarrow$ RH $+$ H^+ where $R =$ cyclohexyl, methylcyclopentyl, isopentyl
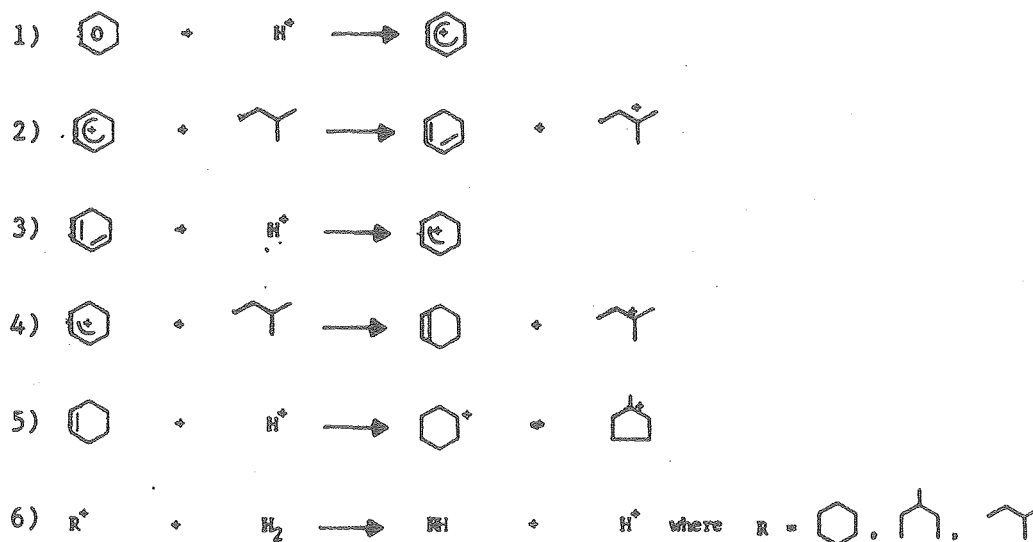
Thus it is possible that a similar effect could occur by introducing a tertiary carbonium ion source to a phosphoric acid system. Moreover, since such tertiary carbons are likely to be present in the coal structure itself, it is possible that such a mechanism could occur autocatalytically in a coal/phosphoric acid system.

II. OBJECTIVES

A. GENERAL CONSIDERATIONS

The program of which this study is a part has the aim of developing an understanding of the reactions occurring in coal-conversion processes which could ultimately lead to a liquefaction process operable at lower temperatures and pressures than those developed to date. By achieving selective hydrogenation, such a process could lead to high liquid yields at lower hydrogen consumptions per unit of liquid product than existing processes. Due to the moderate operating conditions, such a process could also result in lower costs for both plant construction and operation.

B. INVESTIGATION OF PHOSPHORIC ACID SYSTEMS

Phosphoric acid was chosen as the primary medium for this study, since it exhibits a number of potential benefits as a coal conversion catalyst. By operating in the liquid phase, intimate contacting between acid and coal can be achieved. As a strong but non-oxidizing acid, H_3PO_4 provides a source of protons to initiate carbonium ion cracking reactions. It is inexpensive compared with many other potential homogeneous catalysts, and is known to possess catalytic activity for a wide range of organic reactions, including alkylation/ dealkylation and polymerization/depolymerization. Encouraging results have been obtained in other investigations (discussed above) involving its use in coal conversion. Finally, it is compatible with a wide range or inorganic and organic additives which could be investigated for possible enhancement of its catalytic activity.

The experimental objective of this study was to optimize a system using phosphoric acid as a coal conversion catalyst operating at moderate temperatures (up to 250°C) and hydrogen pressure (up to 600 psig) at various acid concentrations (water content), and with various additives. Inorganic additives studied included sodium pyrophosphate (which reduces the tendency of the coal to release gases which create foaming conditions), sulfuric acid and sulfate salts (which could lead to higher catalytic activity due to higher acid strength), and metal ions (as halides) which are known to possess catalytic activity. Organic additives studied were hydrogen donors (tetralin and tetrahydrofuran), para-toluenesulfonic acid (a known depolymerization catalyst for coal), and alcohols (which could function as hydrogen donors, alkylation agents, or both).

C.   ANALYTICAL METHODS

Since in most cases no significant liquid products were obtained at the mild conditions of this study, analytical methods comparing the solid treated coal with the feed coal were used to measure the relative success of the treatment. The elemental analysis of the coal samples, which gave values for C, H, N, S, P, Ash, and O (by difference), was a useful guide. An observed increase in H/C ratio shows that hydrogenation of some sort has occurred, while a decreased H/C ratio may indicate undesirable gasification and/or polymerization. Sulfur and nitrogen values were compared to determine the extent of removal (or incorporation, when sulfur-containing additives were used) of these heteroatoms. Ash values provided information on the dissolution of

mineral matter by the acid, in addition to allowing the calculation of extraction yields on a DAF (dry, ash-free) basis. Phosphorus content provided an indication of incorporation of the phosphoric acid into the product coal.

Successive extractions using benzene and pyridine as solvents were performed to determine the extent of asphaltene (plus oil) and pre-asphaltene formation due to treatment, which was the major criterion used for evaluating the success of the treatment procedures used.

Several other analytical methods were utilized on a non-routine basis. Samples were observed and photographed under a scanning electron microscope to allow a visual examination of the structural changes which occurred. B.E.T surface area determinations of selected samples were also used to provide information about structural changes. X-ray fluorescence was used to determine changes in the composition of the ash constituents resulting from the treatment.

III.   EXPERIMENTAL STUDIES

A.   COAL AND OTHER MATERIALS

1.   Coal Procurement and Preparation

Three different coals were available as feed materials for this investigation. Most of the experiments were performed with a high-sulfur Illinois No. 6 bituminous coal provided by the Illinois Geological Survey. Also used were a Wyoming sub-bituminous coal supplied by Wyodak Resources Development Corporation from the Roland top seam of the Wyodak Mine at Gillette, Wyoming, and solvent-refined coal (SRC) from the Tacoma, Washington demonstration plant of Pittsburg & Midway Coal Mining Company.

Each coal was received in 55-gallon drums, and had been crushed to minus 3/4 inch by the respective suppliers. Half of each of the Wyodak and Illinois No. 6 samples were then ground to minum 1/16 inch by passing through jaw and roller crushers.

After grinding, the Illinois No. 6 was stored under nitrogen in 5-gallon friction-lid cans. One of these cans, selected for this study, was ground in a ball mill and screened into -48, -28+48, and +28 Tyler mesh portions. The -28+48 mesh fraction was separated into 500 gm portions with a riffler according to ASTM Method D-346, and stored under nitrogen in one quart cans. After crushing, the Wyodak coal was then ground in the ball mill and separated into 500 gm portions of -28+100 Tyler mesh size using the same procedure.

The SRC was ground in a mortar and pestle immediately before using. Since SRC melts below the temperatures used in this study (200-250°C),

no quantitative size distributions were obtained for it.

2. Analyses of Coal Samples

Both the Wyodak and the Illinois No. 6 coals were analyzed by Commercial Testing and Engineering Company in Denver, Colordo. Typical seam values were also given by the supplier for the Wyodak coal. In addition, all three samples were analyzed by the Microchemical Analysis Laboratory of the University of California. Proximate and Ultimate Analyses are given in Tables 2, 3 and 4.

Also presented in tables 2, 3 and 4 are figures of oil, asphaltene, and preasphaltene contents, determined by Soxhlet extractions according to procedures described below. Since one of the major analytical measures used in this study was the pyridine extractability (or preasphaltene content) of the treated coals, the figures for the untreated coals are important as a basis for comparison.

The Illinois No. 6 coal was chosen as the main feed material for this study; since it has a higher preasphaltene content than the Wyodak in its untreated state, it was assumed that similar treatment procedures would produce higher preasphaltene product levels, thus giving more accurate quantitative yield information. The Illinois No. 6 coal is also higher in sulfur, nitrogen, and ash, thus allowing a better indication of the effectiveness of different treatments for removal of these components. SRC, being totally pyridine-soluble, provides a medium for the study of the conversion of preasphaltenes to asphaltenes and oils, as well as of any repolymerization reactions to insoluble material.

Table 2. Analysis of Wyodak Roland Seam Coal

Proximate Analysis

	C.T. & E.		Typical Wyodak	
	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	36.17	47.23	32.38	44.97
	100.0	100.0	100.0	100.0

Ultimate Analysis

	C.T. & E.		U.C. Microlab
wt %	As Received	Dry Basis	(Dry Basis)
Moisture	23.76		
Carbon	47.02	61.67	59.63
Hydrogen	4.04	5.30	5.43
Nitrogen	0.73	0.96	0.85
Sulfur	0.70	0.92	0.85
Ash	10.40	13.64	14.70
Oxygen(by difference)	13.35	17.51	18.51
	100.0	100.0	100.0
H/C (atomic)		1.03	1.09

wt % DAF: Oils   <0.1
            Asphaltenes   1.6
            Preasphaltenes   8.5

Table 3. Analysis of Illinois No. 6 Coal

Proximate Analysis (C.T.&E.)

Wt %:	As Received	Dry Basis
Moisture	12.64	
Ash	14.57	16.68
Volatiles	32.96	37.73
Fixed Carbon	39.83	45.59
	————	————
	100.0	100.0

Ultimate Analysis

	C.T.&E.	U.C. Microlab
wt % dry basis:	(Drum Sample)	(28-48 mesh)
Carbon	64.16	57.4
Hydrogen	4.49	4.1
Nitrogen	1.34	1.1
Sulfur	4.17	3.9
Ash	16.73	21.8
Oxygen (by Difference)	8.98	11.7
	————	————
	100.0	100.0
H/C (atomic)	0.84	0.86

wt % DAF:	Oils	<0.1
	Asphaltenes	0.39
	Preasphaltenes	18.89

Table 4. Analysis of Solvent Refined Coal

Ultimate Analysis (Dry basis) for U.C. Microlab

Wt %:

Carbon	86.45
Hydrogen	5.55
Nitrogen	2.16
Sulfur	0.55
Ash	<0.5
Oxygen (by difference)	4.79

H/C (atomic)		0.77
wt% DAF:	Oils	19.0-24.5
	Asphaltenes	34.2-45.6
	Preasphaltens	29.9-46.8

3. Purchased Chemicals

Table 5 is a list of suppliers and purities of all chemicals used in this study.

B. APPARATUS

A few runs (Runs 2, 3, 8, 17 and 29 described below) were made at atmospheric pressure in glass apparatus. This consisted of a three-neck Pyrex flask fitted with an electrical heating mantle, and a teflon-and-glass impeller powered by a low-wattage motor. Hydrogen (when used) was provided from a cylinder through a sparge tube to the flask and temperature was measured by a glass thermometer, both entering the flask through the same neck. The third neck was fitted with a reflux condenser, so as to condense and return any water in the vent gases, and thus maintain constant acid concentration and constant temperature in the reaction flask.

The remaining experiments were performed using a 600 ml autoclave from Parr Instrument Company (moline, Illinois). Figure 4 is a diagram of this equipment. Maximum ratings for the autoclave were 2000 psig and 350°C. Since relatively low pressures were used in this study, a 1000 psig pressure gauge and rupture disc were substituted for 2000 psig parts. The stirrer was attached through a self-sealing packing gland to the adjustable-speed motor (0 to 800 rpm). Temperature was measured by an iron-constantan sheathed thermocouple connected to a dial on the heater-control panel, and was controlled by a solid-state potentiometric system connected to the 780-watt heating mantle.

Table 5. Purchased Chemicals

Material	Supplier	Grade	Min. Purity(%)
Hydrogen	Liquid Carbonic	--	99.999
Phosphoric Acid	Mallinckrodt	Analytical Reagent	85% H_3PO_4
Sulfuric Acid	J. T. Baker	Reagent	96
Para-toluene Sulfonic Acid	Eastman	--	98
Sodium Phosphat ($Na_3PO_4 \cdot 12H_2O$)	Mallinckrodt	Analytical Reagent	98
Zinc Chloride	Mallinckrodt	Analytical Reagent	97
Cuprous Chloride	Mallinckrodt	Analystical Reagent	90
Lithium Sulfate	Matheson, Coleman & Bell	Reagent	--
Potassium Bisulfate	Baker & Adamson	Reagent	--
Sodium Hydroxide	Mallinckrodt	Analytical Reagent	85
Benzene	Mallinckrodt	Analytical Reagent	--
Pyridine	Mallinckrodt	Analytical Reagent	--
Tetralin	Eastman	Practical	--
Methanol	Mallinckrodt	Analytical Reagent	--
Tetrahydrofuran	Mallinckrodt	Analytical Reagent	--
Tert-butanol	Aldrich	Reagent	--
Sec-butanol	Matheson, Coleman & Bell	--	--
Isobutanol	Mallinckrodt	Analytical Reagent	--

110V(ac)

Speed control

Motor and Drive

Gas supply

Rupture disc assembly

Seal & Bearing

Pressure gauge

Check valve

Closure

Glass liner

Temperature indicator

Temperature controller

110V (ac)

Stirrer

Thermowell

Heating mantle
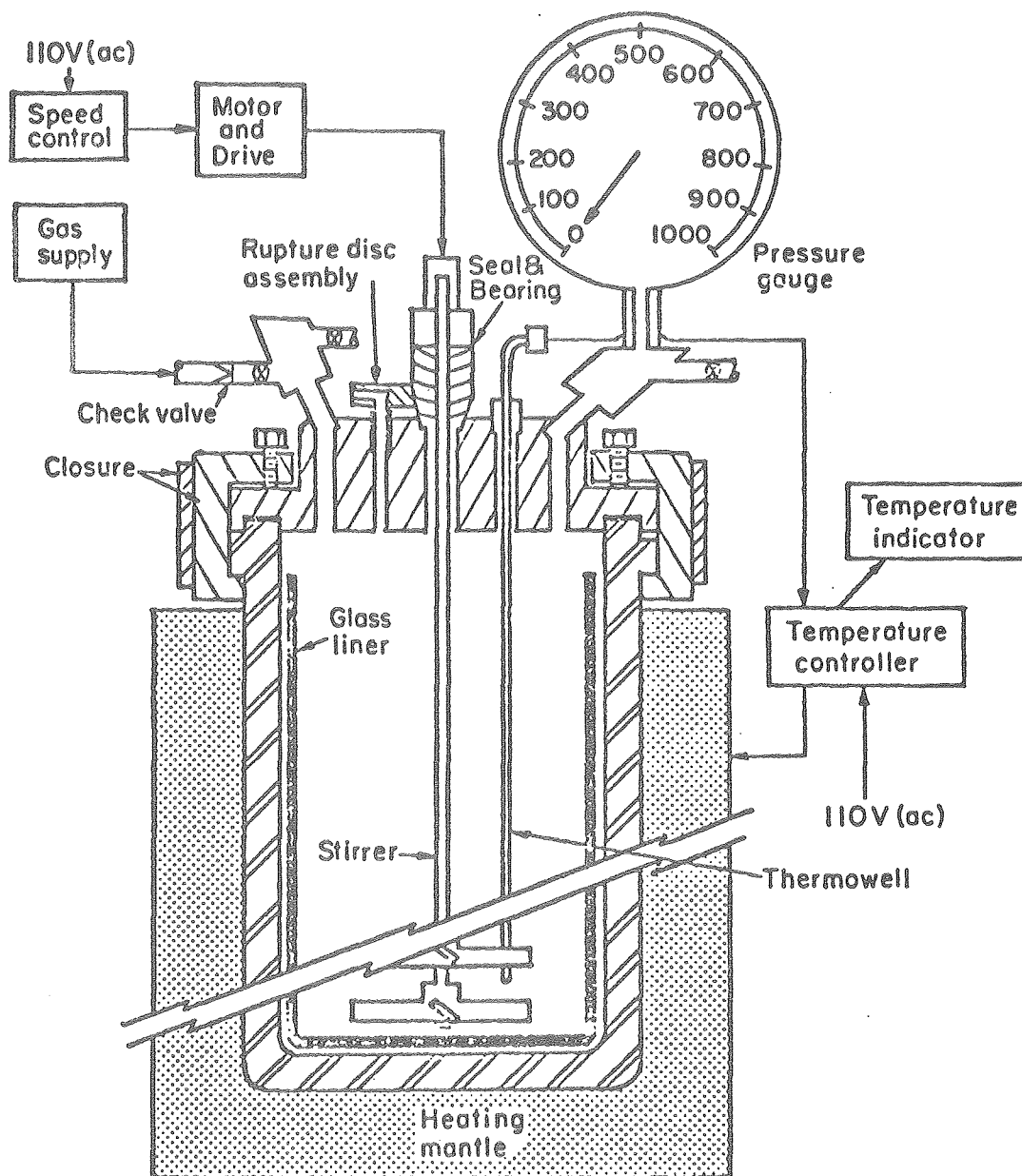
XBL7711-4006

Fig. 4 Parr Autoclave

Provisions also existed for using an internal cooling loop and a sample dip-tube. Since intermediate sampling of the complicated multi-phase system was not feasible with this apparatus, the sample tube was removed. Also, due to the corrosive acid media used, the cooling loop was removed to avoid the possibility of a blowout of the hot reaction mixture.

The reactor cylinder and head were made of Monel 400 (67% Ni, 30% Cu) which has been plated with successive layers of copper, nickel, and gold to give corrosion resistance. A Pyrex liner was used to protect the cylinder itself from contact with the corrosive reaction mixture. The reactor internals (thermowell and stirrers) were Hastelloy C; the connections for the cooling loop were fitted with plugs of Hastelloy B. The rupture disc was made of Inconel 600 with gold facing on the exposed side, and all external valves fittings were of 316 stainless steel.

Corrosion tests were performed (H2) on several different metals using boiling phosphoric acid at $190^{\circ}C$ (92% P_3PO_4). The results, given in Table 6, indicate that the preferable materials in a system specifically designed for phosphoric acid would be Hastelloy B or Tantalum. The equipment used was already available from a previous study, and the corrosion resistance of the materials which would actually contact the reaction mixture was deemed acceptable from this study.

C. PROCEDURES

The actual procedures used were continuously revised and up-dated over the course of the study, based on experience from previous runs.

Table 6.   Corrosion Test Results

92% H_3PO_4 at 190^OC under N_2 for 8 hours

(tests performed by F. Hershkowitz)

Material	Corrosion Rate (mils/yr)
Hastelloy C	214
Welded 316 SS	3434
304 SS	∞
Inconel	729
Monel 400	433
316 SS	2321
Nickel	3302
Tantalum	negl.
Hastelloy B	31
Hastelloy G	1240

The procedures outlined below in each category are the ones used in a majority of the runs, especially in the latter part of the study. Important run-to-run differences will be noted where they apply.

Three basic categories of experiments were made: (1) reactions in glassware at atmospheric pressure; (2) reactions in the Parr autoclave using phosphoric acid concentrations greater than the 85% H_3PO_4 level supplied (on an additive-free basis), with or without additives; and (3) reactions in the Parr unit at or below the 85% H_3PO_4 level, with or without additives. Product work-up, the same for all categories, is discussed below in a separate section.

1. Runs in Glassware (2, 3, 8, 17, 29)

All reactants except the coal were charged to the flask and heated to the desired reaction temperature, with any water released allowed to boil out. Once the desired run temperature was reached, the coal was slowly added. More water boiled out as the moisture in the coal was released, causing a drop in temperature. As soon as all the coal had been added the reaction temperature was again reached, cooling water was circulated through the reflux condenser in order to prevent further concentration change. In runs 2 and 3, coal was added under a nitrogen purge. A hydrogen purge, used in run 3, was begun upon attaining reaction temperature after coal addition. (In other runs, the system was open to the atmosphere). After the desired run time had elapsed, heating was discontinued, and the reaction mixture was cooled by diluting with distilled water. The products were then recovered as discussed below.

2.   Reactions at High H_3PO_4 Concentrations (4-7, 9-16, 19-21, 33)

The phosphoric acid and any inorganic salt additives were mixed in the Parr glass liner vessel, and heated by using a hot plate and electrical heating tape. Sodium pyrophosphate, a known deflocculating agent (K2), was added (as $Na_3PO_4 \cdot 12H_2O$) in all runs after run 9, since it was found to eliminate frothing during addition of the coal. By heating the feed mixture to drive off excess water, acid of the desired concentration was obtained. For most of these runs this concentration was 100% H_3PO_4 (neglecting other additives), corresponding to a heat-up temperature of 261°C; somewhat lower concentrations were occasionally used.

Next, the coal and other reactants were added. In early runs, this was done at heat-up temperature (usually 260°C). Later it was found that coal addition accurred more smoothly at around 175°C. When low-boiling organic additives were used, they were added immediately prior to sealing the reactor, at still lower temperatures.

At this point the liner was transferred to the (preheated) bomb cyclinder, and the reactor assembly put together and closed. The reactor was purged several times with hydrogen to remove air, and (where hydrogen pressure was to be used) pressurized to 100 psig with H_2 to prevent splashing during heat-up. The heating and stirring (450 rpm) were begun. When reaction temperature was reached, more hydrogen was added to bring the total pressure to the desired value (usually 600 psig). This was designated as the start of the run, with run time defined as time at both reaction temperature and pressure. An initial temperature overshoot of 5-10°C was usually observed,

which normally lasted 10 minutes or less. After this the temperature remained constant at the desired level.

At the end of the run the heater and stirrer were turned off and the entire reactor assembly immersed in an ice bath or provide rapid cooling. the Reactor was depressurized and opened, and the products handled according to the procedure below.

3.   Reactions at Lower H_3PO_4 Concentrations (18, 22-28, 30-32, 34-38)

For reactions with the H_3PO_4 level below 85%, the phosphoric acid, coal, and any additives were mixed in the glass liner, and sealed in the reactor while cold. The reactor was purged with hydrogen to remove air, pressurized to 100 psig, and heated to the desired temperature. Then the total pressure was adjusted to the desired value, and the run started. End-of-run procedures were the same as in the concentrated acid runs.

4.   Product Work-Up

The reaction mixture was diluted with distilled water and transferred to a 1000 ml beaker. The reactor internals were rinsed with water to recover as much of the product as possible (in runs 20 and 32 a benzene rinse was also necessary due to the oily nature of the product formed). The acid was then diluted by partial neutralization with sodium hydroxide to reduce viscosity and aid in filtering. Since sodium phosphate was already present as an additive in most cases, this had no effect on the product coal.

The mixture was then separated by vacuum filtration in a Buchner funnel with Whatman No. 1 filter paper, and washed with distilled water

(usually 3 to 5 liters) until the effluent filtrate was neutral to a pH test. A sample of the initial filtrate was retained for later analysis.

In runs where tetralin was used as an additive, a noticeable organic liquid-phase product was obtained, and the entire aqueous filtrate was extracted with benzene in a separatory funnel to recover the organics. When THF was used as an additive, the oily nature of the product made it necessary to wash with benzene as well as with water (until the effluent benzene became clear). Then the entire filtrate (aqueous and organic) was separated, and the benzene phase was concentrated by evaporation. The extracts in both cases were then heated at 105°C under vacuum to remove residual water and benzene.

D.   ANALYTICAL METHODS

The treated coal from each run was dried overnight in a vacuum oven (at 130°C, around 20 in. Hg gauge, under a nitrogen sweep). A sample was analyzed by the University Microchemical Analysis Laboratory for C, H, N, S, P, and ash. The dried product was weighed to obtain an estimated recovery. Material was lost by adhering to reaction surfaces, valves, filter paper, and glassware, so that accurate mass balances were not possible. Semi-quantitative information was obtained by comparing recoveries from one run to the next. A feed of 20 gm undried coal was used for all runs, with recoveries of 15-18 gm (dry) being typical. Only in run 20, with a total recovery of 27.1 gm (treated coal plus liquid extract), was there evidence of measurable additive incorporation into the product coal.

Approximately 10 gm of the dried product was extracted in a standard Soxhlet apparatus successively with approximately 20 ml each of benzene, then pyridine. The extractions were run to completion, as indicated by a colorless solvent in the Soxhlet sidearm. Typical extraction times were 2 hours for benzene and 24 hours for pyridine, with longer times necessary when higher extraction yields were obtained. The extracts were concentrated by evaporation and dried overnight in a vacuum oven in pre-weighed Petri dishes ($105^{\circ}C$ for benzene, $130^{\circ}C$ for pryidine; 15-25 in. Hg vacuum, nitrogen sweep). The dishes were then weighed to determine extract yields, and extraction yields conculated on a DAF basis. For runs where a liquid benzene extract was obtained, this was added to the Soxhlet product asphaltene content.

B.E.T. surface area measurements using CO_2 at $196^{\circ}K$ were obtained on selected coal samples (treated and untreated, both before and after extraction) according to the method discussed by Medeiros (M3). Some of these same coal samples were also observed under a scanning electron microscope in order to obtain a visual representation of reaction and extraction effects on the coal surface.

E. EXPERIMENTS PERFORMED

The experiments carried out, with their relevant parameters, are listed in Table 7. The acid composition is given as weight per cent of each of H_3PO_4, H_2SO_4, and H_2O present in the liquid phase, and was calculated from the boiling points of the heated acid before coal addition where applicable, otherwise from the known acid and water

compositions charged to the reactor and corrected for water vapor pressure effects. The total pressure includes vapor pressures of all components present plus hydrogen. Run 29 was a study of a bisulfate molten salt system, thus the acid composition is listed as zer. Due to similarities in procedures used in other runs, H_2SO_4 is listed as part of the acid while PTSA is listed as an additive. Illinois No. 6 was used as the feed coal for all except runs 35-37. Ground SRC was used in run 35, pyridine pre-extracted Illinois No. 6 coal in run 36, and Wyodak coal (28+100 mesh) in run 37. All runs were at an acid/coal weight ratio of 10/1, except run 29, which used a melt/coal ratio of 6/1. In addition to run 11 (40% Na_3PO_4), sodium phosphate was also present (5% of the acid on a water-free basis) in all runs ecept 2-7, 24, and 29.

Table 7. Experiments Performed

Run No.	Relative Acide Composition $H_3PO_4/H_2SO_4/H_2O$	Additive(s) (wt % of acid)	Run Time min	Temperature ^{o}C	Pressure psig
H_3PO_4/Na_3PO_4 treatment:					
*4	100/0/0	---	60	250	0(flowing H_2)
*5	100/0/0	---	60	250	600
*6	100/0/0	---	60	250	50
8	100/0/0	---	0(Blank)	250	0
9	100/0/0	---	30	250	600
10	100/0/0	---	60	250	600
*11	100/0/0	Na_3PO_4(40)	(run failed)		
17	92/0/8	---	60	200	0
18	88/0/12	---	60	250	600
22	65/0/35	---	60	250	600
23	65/0/35	---	60	200	600
H_2SO_4/HSO_4^- salt additives:					
*2	90/10/0	---	0(Blank)	250	0
*3	90/10/0	---	60	250	0(flowing H_2)
*24	0/80/20	---	30	175	600
*29	0/0/0	$LiHSO_4$(50)	30	200	0
(also see Run 16 below)		$kHSO_4$(50)			
Other inorganic additives:					
21	100/0/0	$ZnCl_2$(5)	60	250	600
		$CuCl$(5)			

Table 7. Experiments Performed (continued)

Run No.	Relative Acid Composition $H_3PO_4/H_2SO_4/H_2O$	Additive(s) (wt % of acid)	Run Time min	Temperature $^\circ C$	Pressure psig
Hydrogen-Donor Additives:					
12	96/0/4	Tetralin (10)	60	200	600
13	100/0/0	Tetralin (10)	60	200	100 (N_2)
14	100/0/0	Tetralin (10)	60	200	600
15	100/0/0	Tetralin (10)	60	250	600
16	95/5/0	Tetralin (10)	60	250	600
20	100/0/0	THF (20)	60	250	600
32	83/0/17	THF (10)	30	200	600
Other Organic Additives:					
19	100/0/0	Methanol (20)	60	250	600
25	83/0/17	tert-butanol (10)	60	200	600
26	83/0/17	isobutanol (10)	60	200	600
27	83/0/17	sec-butanol (10)	30	200	600
28	83/0/17	sec-butanol (10)	60	200	600
30	83/0/17	tert-butanol (10)	30	200	600
31	83/0/17	isobutanol (10)	30	200	600
33	100/0/0	tert-butanol (10)	20	250	600
36	83/0/17	tert-butanol (10)	30	200	600
37	83/0/17	tert-butanol (10)	30	200	600
34	84/0/17	PTSA (10)	30	200	600
38	83/0/17	tert-butanol (10) PTSA (10)	30	200	600

*5% Na_3PO_4 also added to acid in all runs except those marked *

IV. RESULTS AND DISCUSSION

A list of H/C atomic ratio, weight percentage of S, N, P, and ash, and benzene and pyridine extractabilities of all treated and untreated coal samples is presented in Table 8. Elemental analyses are from the University Microchemical Analysis Laboratory. The extraction yields are on a DAF basis for Soxhlet extractions carried to completion in atmospheric boiling solvent. Since benzene was the initial solvent used in successive extractions, the benzene extraction yield given represents the sum of oils and asphaltenes while the pyridine yield represents only preasphaltenes. Thus the total extraction yield given is the sum of the benzene and pyridine yields, and represents the total soluble material present.

Because direct analysis for oxygen was not available, the oxygen content of the samples was determined by difference. Such a procedure combines the inaccuracies on each of the other constituents, and leads to widely varying and unreliable results. As calculated, the oxygen values ranged from below 1% to as high as 24%, and showed no correlation with either the type of treatment or the extraction yields. As a result they are considered inaccurate, and are omitted from Table 8.

1. Untreated Coals

Untreated coal data from Table 2-4 presented again in Table 8, for comparison with the treated coals. Also listed is pre-extracted Illinois No. 6 coal, used as feed for run 36, which had all asphaltenes and preasphaltenes removed by extraction with pyridine. The high nitrogen content of the residue (2.3%, approximately double that of the raw coal) is probably due to strongly held pyridine. A nitrogen

Table 8. Elemental Analysis and Extraction Results.
Run Conditions are given in Table 6.

Sample or Run No.	Atomic Ratio H/C	N	S	P	Ash	Benzene (incl. oils)	Pyridine	Total
H_2PO_4/Na_3PO_4 treatment:								
4	0.79	1.2	2.7	1.5	15.9	0.29	11.77	12.06
5	0.75	1.3	3.0	1.8	9.4	0.34	9.20	9.54
6	0.79	1.2	3.5	1.5	11.6	0.14	12.34	12.48
8	0.78	1.4	3.8	1.0	7.9	0.18	10.14	10.32
9	0.82	1.6	3.6	1.3	8.0	0.28	12.21	12.49
10	0.79	1.3	3.3	1.4	10.0	0.20	11.21	11.41
11				(no product analyzed)				
17	0.84	1.4	3.5	0.7	8.8	0.05	25.06	25.11
18	0.82	1.5	3.6	1.1	12.5	0.22	21.07	21.29
22	0.81	1.5	2.7	1.9	8.4	0.18	18.15	18.33
23	0.85	1.5	3.9	1.6	12.5	0.04	18.38	18.42
H_2SO_4/HSO_4^- salt additives:								
2	0.59	1.1	3.8	–	12.1	0.28	7.30	7.58
3	0.67	0.9	3.7	–	20.2	0.34	6.41	6.75
24	0.53	1.1	7.0	<0.05	11.3	0.49	2.11	2.60
29	0.82	1.4	5.7	–	6.0	0.09	13.75	13.84
(also see Run 16 below)								
Other inorganic additives:								
21	0.76	1.3	2.9	5.0	29.4	0.13	8.40	8.53

Table 8. Elemental Analysis and Extraction Results (continued).

Sample or Run No.	Atomic Ratio H/C	N	S	wt. % P	Ash	Extraction Yields (wt% DAF) Benzene	Pyridine	Total
Hydrogen donor additives:								
Tetralin								
12	0.79	1.3	3.4	1.1	7.4	1.52	11.94	13.27
13	0.76	1.3	3.4	1.6	7.9	0.92	15.11	16.03
14	0.77	1.4	3.3	1.4	7.0	1.38	14.34	15.72
15	0.76	1.3	3.1	1.8	8.1	0.51	15.98	16.49
16	0.66	1.0	7.6	3.8	12.6	6.61	18.96	25.57
THF 20	0.93	1.1	2.5	2.6	10.0	(after benezene wash)		
					(total recovery)	59.81	28.18	87.99
					(coal only)	29.33	28.18	57.51
32	0.91	1.4	3.1	1.5	6.6	(after benezene wash)		
					(total recovery)	11.48	21.11	32.59
Other organic additives:								
Menthanol								
19	0.82	1.4	2.9	1.4	14.5	0.27	7.54	7.81
Cy alcohols								
25	0.90	1.1	3.0	1.5	11.4	0.29	19.91	20.20
26	0.84	1.3	3.7	1.1	12.1	0.25	19.26	19.51
27	0.87	1.3	3.3	1.5	14.8	0.61	25.40	26.01
28	0.83	1.4	3.2	1.7	11.9	0.08	17.44	17.52
30	0.86	1.2	2.8	1.8	13.2	0.29	29.80	30.09
31	0.88	1.2	3.2	1.4	9.9	0.80	23.14	23.94
33	0.92	1.4	3.7	1.4	11.1	0.64	19.87	20.51
*35			(no product analyzed)					
*36	0.79	1.3	3.2	1.5	14.5	0.19	10.10	10.29
*37	0.96	0.9	1.1	0.7	7.2	5.08	23.04	28.12

Table 8. Elemental Analysis and Extraction Results (continued).

Sample or Run No.	Atomic Ratio H/C	N	S	wt. % P	Ash	Extraction Yields (wt% DAF) Benzene	Pyridine	Total
PTSA								
34	0.88	1.1	6.0	1.4	12.5	0.42	34.39	34.81
PTSA/t-butanol								
38	0.91	1.0	3.8	1.7	12.9	0.88	39.12	40.00
Untreated Coals:								
Illinois No. 6 (-28	0.86	1.1	3.9	–	21.8	0.29	18.78	19.07
+48 mesh)	0.88	0.9	4.0	0.11	16.8	0.39	18.89	19.28
(duplicate analyses)	0.86	1.1	4.2	–	22.2			
-20 + 28 mesh	0.85	1.2	3.3	–	24.4			
-48 mesh								
Wyodak (-28+100 mesh	0.98	1.1	0.5	–	13.1	1.6	8.5	10.1
SRC	0.77	2.2	0.6	–	0.5	53-70	30-47	100
Pre-extracted Illinois No. 6	0.81	2.3	3.5	–	20.2	0	–	0

*Feed Coals used: Run 35 – Ground SRC
Run 36 – Pre-extracted Illinois No. 6
Run 37 – Wyodak (-28 + 100 mesh)
All other runs – Illinois No. 6 (-28 + 48 mesh)

mass balance indicated that essentially all the incorporated pyridine remained in the residue and not in the extracts. Therefore the extraction yields were calculated directly by comparing the dried extract weights to the weight of the original coal sample, rather than indirectly (by difference) using the weight of the residue.

2. H_3PO_4 / Na_3PO_4 Treatment

Runs 4, 5, and 6 tested the effects of hydrogen pressure on reaction of coal in phosphoric acid alone. Anhydrous (100%) H_3PO_4 was used at a 10/1 acid/coal ratio at 250°C for one hour, with varying hydrogen pressures (atmospheric, 50 psig, and 600 psig) used. In each case the treated coal actually had a lower extraction yield than the untreated coal, indicating that some sort of polymerization or carbonization occurred. The accompanying decrease in H/C ratio indicates that dehydration followed by repolymerization could be responsible. Increasing the hydrogen pressure from atomospheric to 600 psig was beneficial, but the yield at 50 psig was lower than at atmospheric pressure. This effect has no simple explanation and could result from experimental errors in one or both of the lower-pressure runs.

For each of these three runs the coal was added slowly at a temperature of 250-260°C. During this period, considerable foaming occurred due to release of water or fixed gases (CO_2 or CH_4) from the added coal, thus making it necessary to add the coal slowly over a period of up to one hour. In order to reduce foaming and thus shorten the start-up time, studies were made of the use of sodium pyrophosphate ($Na_4P_2O_7$), a known industrial deflocculating agent (K2) which can be formed

by dehydration of Na_3PO_4 and H_3PO_4. A relatively small amount (5%
relative to the acid, calculated as anhydrous Na_3PO_4) made it possible
to avoid foam formation during coal addition; the actual additive used
was $Na_3PO_4 \cdot 12\ H_2O$. Thus 5% Na_3PO_4 was used in all subsequent experiments.

Run 8 was then conducted as a blank to test the effects of the
heat-up procedure alone using the H_3PO_4/Na_3PO_4 system. Runs 9 and 10
then tested the effects of residence time (30 and 60 min.) at 250°C and
600 psig after following the heat-up procedure of run 8. The low
extraction yield for run 8 (10.32% total) compared with raw coal indicates
that the undesirable reactions noted in the earlier runs occur during
the initial period of contact with coal with the hot acid. During the
first 30 minutes following heat-up, an increase in extraction yield is noted
(from 10.32 to 12.49%), but from 30 to 60 minutes the yield again decreases
(to 11.41%). This generally downward trend with time is consistent with the
results observed by Seth (S2) at lower tempreatures and pressures, as well
as with the results of later runs in the present study.

The extraction yields for all runs made up to this point were con-
siderably lower than for the untreated coal. This was an indication
that the phosphoric acid system was active enough to have an effect on
the coal structure, but that the reaction environment (moderate hydrogen
pressure only) was not severe enough to take advantage of this activity.

Two approaches were taken to try to compensate for the undesirable
action of the H_3PO_4. One was to try to tame the activity of the acid
by altering its concentration. The other, discussed later, was to change
the environment with inorganic or organic additives, in an attempt to
exploit the activity of the acid toward achieving more desirable reactions.

The first attempt at changing the acid system was to add a massive quantity of sodium phosphate, creating a type of molten phosphate salt. Although true melting-point data of phosphate salts are lacking in the literature, it was hoped that the solubility of any pyrophosphate-type salts would be high enough to preserve the liquid phase character of the melt. Run 11 involved trial use of a melt composed of 40% Na_3PO_4 and 60% H_3PO_4, containing an equilibrium water concentration at $250^{\circ}C$. However, upon heating above $150^{\circ}C$, so much water was lost that precipitation began to occur, and at about $170^{\circ}C$ so much solid was present that the run could not be continued. Because of this unfavorable solubility behavior, no further trials were made with phosphate salt melts.

While the results of Kiovsky (K2, K4) and Wald (W3, W4) indicated that pyrophosphoric acid is an active catalytic agent for coal, the results obtained in this study for the high (100% H_3PO_4) acid concentration seemed to indicate the opposite trend with concentration, especially in light of the positive results obtained by Seth (S2) at 85-92% H_3PO_4 levels. Thus a series of runs was made using lower acid concentrations.

Run 17 was made using boiling phosphoric acid at $200^{\circ}C$ and atmospheric pressure (92% H_3PO_4 concentration). The extraction yield (25.11%), in addition to being considerably higher than in the experiments using more concentrated acid, is also substantially higher than for untreated coal. This indicates the occurrence of desirable cracking reactions, despite the fact that no hydrogen at all was present. One possibility is hydrolysis (of ether linkages, for example) which could not occur in a system where no free water was present. Another possibility is phosphoric acid

addition to ether linkages, yielding one alcohol group and one phosphate ether.

Run 18 was made at a higher temperature (250°C) with a lower acid concentration (88%) than run 17, and was made at 600 psig total (H_2 plus H_2O) pressure. The resulting extraction yield (21.29%), while higher than for the untreated coal, is lower than for run 17. This indicates that more than simple hydrolysis is occurring, since the yield is lower despite a partial pressure of water approximately 15 times as high (200 psig vs. atmospheric).

Runs 22 and 23, made using a 65% acid concentration at 250 and 200°C respectively, showed little difference from the untreated coal. Apparently, the acid concentration is too low to have any appreciable activity. It should be noted here that unfortunately the trend of extraction yield with acid concentration parallels that of corrosive behavior, which could be an important process consideration. The corrosiveness of phosphoric acid on metallic materials increases steadily with concentration up to about 95% H_3PO_4, then falls off markedly as the formation of condensed acid forms begins to predominate. This effect was substantiated by color comparison of the acid reaction product from the runs described above. In all cases the acid was green due to dissolved nickel (and possibly chromium) from the reactor internals. When 100% acid was used, the green color was rather pale; a considerably deeper color was obtained in the 65% acid runs. When 88-92% acid was used, the green was so dark that the transparency of the solution could only be detected by holding the container up to a light source, indicating that massive corrosion had occurred.

Each of the experiments in this category yielded a product coal with a considerably reduced ash content (8-12%) due to the dissolution of mineral constituents by the acid. The sulfur content was also reduced by treatment, but never exceeded 35% removal of the original sulfur; probably only organic sulfur reacts. No apparent change in nitrogen content was observed. The amount of chemically incorporated phosphorus varied from 0.7.9%. It shows a steady increase with both reaction time and temperature, but no apparent correlation with acid concentration. Unlike sulfur incorporation, phosphorus incorporation does not pose a serious obstacle to combustion since it remains in the ash upon burning. Nevertheless, it could be an obstacle to subsequent catalytic reforming, and would also increase the H_3PO_4 requirement (and expense) for the process. Except in cases where specifically noted below, the same general trends were observed when additives were used.

In summary, treatment with anhydrous H_3PO_7 reduces the pyridine-extractability of the test coal used. Dilution with water has a beneficial effect, with a maximum extractibility one-third more than for untreated coal being reached near 92% H_3PO_4 (at which extreme corrosion of the reactor intervals occurs.)

3. H_2SO_4 / HSO_4^- Additives

Runs 2 and 3 were done in glassware at atmospheric pressure as a preliminary attempt to combine the strong acidity of H_2SO_4 with the bulk characteristics of H_3PO_4. Run 2 was a blank, where the coal was added to the 90% H_3PO_4 / 10% H_2SO_4 at 250°C. The low yield (7.58%) indicates the occurrence of the same kinds of adverse reactions discussed above in

the early runs made with H_3PO_4 alone. The results of run 3 indicate
that atmospheric hydrogen treatment has very little effect. The extremely
low H/C ratios of the products of these runs (0.59, 0.67) could be due to
the occurrence of gasification, which (by releasing CH_4) would lead to
a carbonization of the residual solid. Because this study was exploratory
in nature, no provisions were made for analyses of possible gaseous by-
products.

Run 24 was a test of the effect of H_2SO_4 alone. The coal was reacted
at 175°C in 80% H_2SO_4 for 30 minutes. An initial hydrogen pressure of 600
psig was used, but after 30 minutes the pressure had risen to 800 psig,
indicating large amounts of gasification without hydrogen consumption.
The low H/C ratio in product (0.53) and correspondingly low extraction
yield (2.60%) are a further indication that the potentially soluble
matter in the coal had been gasified and/or carbonized. In addition, a
significant amount of sulfur incorporation (3% increase) occurred.

In run 29 a molten sulfate salt system was studied. A melt composed
of equal weights of potassium bisulfate ($KHSO_4$) and lithium bisulfate
($LiHSO_4$) was used. The coal was reacted for 30 minutes at 200°C and atmo-
spheric pressure. The product exhibited a low extraction yield (13.84%),
again with significant sulfur incorporation (1.7% increase). Thus no
further runs were made with sulfate salts.

In summary, concentrated sulfuric acid destroys the normal pyridine-
extractability of untreated coal, perhaps by increasing the amount of
crosslinking in the coal structure. It can be said that this acid is
highly effective in "activating" the coal structure, but that it provides
no opportunity at all for bond scission at the activated sites.

4. Other Inorganic Additives

In run 21, small amounts (5%) of $ZnCl_2$ and CuCl were added to the phosphoric acid in an attempt to create a combination Lewis and Brønsted acid system. A metallic precipitate was formed in the product, probably Zn metal formed by reduction of Zn^{++} accompanied by oxidation of Cu^+ to Cu^{++}. Since the product showed a low extraction yield (8.53%) combined with an extremely high phosphorus incorporation (5.0%), no further runs were made with these similar additives.

5. Hydrogen-Donor Additives

Two additives were studied which exhibit the possible capacity for hydrogen donation, tetralin and tetrahydrofuran (THF). Runs 12-16 were made with tetralin present. In these runs an organic liquid phase (tetralin solution) was obtained in the product. The extract in this phase was added to the benzene Soxhlet extraction yield to obtain the total benzene extract, according to the method outlined in the previous section.

The results of runs 12-15, while somewhat better than runs made at corresponding conditions with no tetralin present (4-6 and 8-10), still show lower extraction yields than for the untreated coal. Also, the almost identical results of run 13 (100 psig N_2) and 15 (600 psig H_2, all other conditions the same) indicate that no regenerable hydrogen donation from the tetralin is occurring.

In run 16, sulfuric acid was added to the phosphoric acid / tetralin system. The high extraction yields obtained (6.61% benzene, 25.57% total) indicate that the more strongly acid medium is more catalytic. However, it

is quite possible that the apparent yield increase is at least partially
due to incorporated tetralin. Although accurate mass balances were not made
here, similar work using tetralin with a $ZnCl_2$ melt (H2) has shown that
significant incorporation of tetralin into the treated coal can in fact
occur.

Run 20 was made under conditions identical to runs 10 and 15 except
that THF was used as an additive (2/1 based on coal, although some flashed
off in the addition process). In this experiment a significant amount of
liquid product was formed, making it impossible to recover the reaction
product by the usual water-washing technique. As a result the product was
washed with both water and benzene, resulting in the further extraction
of benzene soluble material from the treated coal. The elemental analysis
given in Table 8 is of the solid which remained after the benzene wash,
and thus does not represent the entire reaction product.

The liquid-product yield was determined by evaporating the
benzene-product solution. A total recovery of 27.1 gms. (liquid plus
treated solid) was obtained from only 20 gms. of feed coal, indicating
massive incorporation of THF. Due to the mass-balance problems just
discussed, it was not possible to determine precisely how much of the
extremely high extraction yield (59.81% benzene and 87.99% total) was
actually coal extract and how much was incorporation. However, this
was estimated by assuming that the coal recovery would have been 17.0 gms
(a typical value for other runs) and that the rest was incorporated THF.
The extraction yields based on this assumption are reduced to 29.33%
benzene and 57.51% total. These are still extremely high, much better
than any others obtained in this study, but they are of limited utility

since they involve the expense of a large consumption of THF.

Run 32 also used THF as an additive at lower acid concentration (83%), temperature (200°C), and reaction time (30 minutes) than run 20. Again a liquid product was obtained, and the benzene-wash procedure was followed. However in this case the total recovery of 19.7 gms was not inordinately high, so no attempt was made to back out the THF incorporation. The extraction yields from this run (11.48% benzene and 32.59% total) are good but not nearly as high as for run 20 despite the fact that the dilute phosphoric acid used alone would have given better results than the concentrated acid used alone. This points out the important fact that conditions optimized for the acid alone are not necessarily optimum when an additive is used.

In summary, phosphoric acid with a suitable coreactant (specifically, tetrahydrofuran) can give a net pyridine-extractability approaching 60%. Conversion of coal to preasphaltene in this manner is substantially greater with 100% than with 83% acid.

6. Other Organic Additives

The successful results obtained in run 17 (with free water present) suggest the possibility that similarly good results could be obtained with other oxygen containing additives. The least expensive such organic compound is methanol. Therefore run 19 was made at conditions identical to run 10 (phosphoric acid alone) with methanol used as an additive. The resulting extraction yield (8.53%) was very low, lower even than for run 10 (11.41%). Thus no further experiments were made with methanol.

A series of experiments (25-28, 30, 31) using butyl alcohols as additives was performed. All were made at 200°C, 600 psig total pressure, and 83% acid concentration. Reaction times of 30 and 60 minutes were used with each of sec-, iso-, and tert-butanol as additives. From Table 8, it is clear that the 30 minute reaction time was preferable to the 60 minute run for each of the three alcohols. In addition, the order of effectiveness for both 30 and 60 minute reaction times was tert- iso- sec-. with the most favorable result (tert-butanol at 30 minutes) giving an extraction yield of 30.09%.

The hydrogen donation theory presented by Ross (R4) for isopropanol in basic catalysts obviously does not apply here. The formation of a ketone by-product would be possible from sec-butanol (MEK) but not from tert-butanol. The fact that tert-butanol gives better results than sec-butanol indicates that a different mechanism occurs in the acidic system.

It is possible that the increased extraction yields could be at least in part due to alkylation. The products show consistently higher H/C ratios (0.83-0.92) than products of runs made at similar conditions with no additives present (e.g. run 18, H/C 0.82), supporting the possibility that aliphatic side chains are being added to the coal structure. Since accurate mass balances were not made, neither the possible weight increase due to alkylation nor the possible losses of alcohol could be assessed. However, any alcohol consumed via alkylation was small compared to the total amount present (20 gms in each run) since the amount of coal recovered in these runs (16.9-17.8 gms) showed no variation from typical recoveries obtained at similar conditions with no additives.

All the butanol runs discussed above used an acid concentration of 83%. While the runs made with phosphoric acid alone indicated that the more dilute acid at 200°C was preferable to the more concentrated acid at 250°C, the results of the experiments using THF showed that this is not necessarily true when an additive is present. Thus run 33 was made using tert-butanol in 100% acid at 250°C. Since all previous results indicated that short reaction times were preferable, a reaction time of 20 min. was used in this experiment. While the benzene extraction yield was significantly higher than for run 30 (0.64% to 0.29%), the total yield decreased from 30.09% to 20.51%, indicating that the undesirable reactions evidenced in runs 8-10 were still occurring even in the presence of the additive.

Runs 35-37 duplicated the conditions of run 30 using different feed coals. Run 35 used ground SRC. Apparently at the reaction conditions employed the SRC was completely liquefied. Upon cooling, re-solidification occurred, causing the SRC product to form a solid mass which stuck to the reactor internals, glass liner, etc. As a result it was impossible to collect and analyze the product; the only way to clean the reactor assembly was by washing with pyridine. From this it was apparent that future work with SRC should be done in a suitable organic solvent, or else a method devised for handling the product while it is still hot.

Illinois No. 6 coal which had been pre-extracted with pyridine was used in run 36. The extraction yield of 10.29%, when added to the 19.28% removed by extraction before reaction, gives a total yield nearly identical to the 30.09% obtained in run 30. Thus it appears that, under these conditions, only the forward reaction of coal to preasphaltene is

occurring, with no significant effects of repolymerization reactions. A significant nitrogen removal was evidenced in this run (from 2.3% to 1.3%). However this was probably due entirely to the strongly bound nitrogen which was apparently incorporated into the coal during the preliminary extraction, since the final value of 1.3% N is well in line with values for both untreated coal and treated coals from runs at similar conditions. No detectable odor of either ammonia or pyridine was noticed on depressurization.

Run 37 used Wyodak Roland seam sub-bituminous coal. Consistent with the comparison of the untreated coals, the product of this run had a much higher benzene extractability (5.08% to 0.29%) but a lower total yield (28.12% to 30.09%) than the product of run 30, made with Illinois No. 6, while the phosphorus incorporation (0.7%) was somewhat less.

The use of para-toluene-sulfonic-acid (PTSA) in phosphoric acid was investigated in runs 34 and 38. Both runs were made at $200^{o}C$ and 600 _ psig total pressure for 30 minutes. In run 34 PTSA alone was used as an additive, while in run 38 it was used in conjunction with tert-butanol, a combination which could result in possible alkylation or depolymerization mechanisms.

The extraction yield for run 34 (34.81% total) shows PTSA to be an effective additive. When used in conjunction with tertbutanol, the resulting extraction yields (0.88% benzene and 40.00% total) are significantly higher than for either additive used separately at the same conditions, indicating a synergistic effect. The coal recoveries for the two runs (17.8 and 18.0 gms) are well within the typical range, indicating that any alkylation or incorporation occurring is minor.

Since both additives are soluble in the acid and water wash, no attempt was made to recover either to determine the consumption and/or chemical changes. Thus, while it is impossible that some alkylation or depolymerization according to a mechanism similar to that proposed by Ouchi (01, 02, 03, 04) for PTSA with phenol may be occurring, it appears unlikely that the large increases in extraction yields observed could be entirely due to these factors. The actual reactions which are occurring are not known at this time and would require further investigation, perhaps by model compound studies.

It is interesting to compare the sulfur contents of the treated coals from the two runs. In run 34, with PTSA only as an additive, a net incorporation of sulfur is observed (to 6.0%), while the value for run 38 (3.8%) shows a slight decrease from the untreated coal. No apparent reason can be determined for this discrepancy, which was later reinforced (although to a somewhat lesser extent) by X-ray fluorescence analyses.

B. X-RAY FLUORESCENCE ANALYSIS OF UNTREATED AND TREATED COAL SAMPLES

Samples of untreated Illinois No. 6 and treated coals from runs 17, 34, and 38 were analyzed in order to determine the breakdown of ash components present by X-ray fluorescence. The results are presented in Table 9, along with the values for sulfur, phosphorus, and total ash from elemental analysis. In each case the concentration units (wt % of ppm) are the same for the treated coals as those listed for the untreated coal sample.

It is immediately apparent that the observed reductions in ash

Table 9
X-Ray Fluorescence Analyses of Untreated
and Treated Coal Samples

Run No.	Untreated Ill. No. 6	17	34	38
Ash(wt% from Combustion)	16.8 – 21.8	8.8	12.5	12.9
P(wt% from Microlab)	---	0.7	1.4	1.7
*A	1.6%	0.4	0.6	0.7
*Si	3.2%	3.4	4.4	4.2
**S	4.2%(4.2%)	3.6(3.6)	5.6(6.0)	4.9(3.8)
C	0.2%	0.1	<0.1	0.4
Ca	1.0%	<0.1	<0.1	<0.1
Ti	0.1%	∿0.02	∿0.05	∿0.05
V	---	<20 ppm	<50	<50
Cr	---	70 ppm+3	16+3	16+3
Mn	49ppm+4	<7	<8	6+3
Fe	1.6%+.08	2.94+.15	4.74+.24	4.56+.23
Ni	12ppm+1	322+16	112+6	163+8
Cu	13ppm+1	190+10	54+3	180+9
Zn	63ppm+1	29+2	7+2	25+2
Ga	4ppm+1	2+1	2+1	2+1
As	2ppm+1	3+1	3+1	4+1
Sc	2ppm+1	9+1	7+1	3+1
Br	4ppm+1	---	---	---
Rb	42ppm+1	<3	<3	<3
Sr	52ppm+1	3+1	32+2	14+1
Hg	9ppm+2	---	---	---
Pb	6ppm+2	<6	<7	<6

*Results are most likely low due to particle size effects for X-ray fluorescence analysis.

**wt % S by combustion analysis in parentheses.

content cannot be accounted for by the X-ray fluorescence analyses, especially in light of the fact that the treated coal ash contains a significant amount of phosphorus which is not present in the untreated sample. The only elements which show drastic reductions are aluminum and calcium, on the order of 1% each. Ti, Mn, Zn, Ga, Br, Rb, Sr, and Hg are all also significantly reduced in the products when compared with the feed coal, but are present at such low levels that the total ash value would not be significantly affected. The observed increases in Fe, Ni, and Cu are almost certainly due to dissolved traces of these elements caused by the corrosive action of phosphoric acid on the reactor internals, which then become incorporated in the coal ash structure, possibly via an ion-exchange mechanism. The sulfur values show good agreement with those obtained by combustion analysis, except for the sample from run 38. This higher value of 4.9% indicates that some sulfur incorporation may have taken place in both runs using PTSA as an additive, although not to nearly as great an extent when tert-butanol was also used as when PTSA alone was used.

C. SURFACE AREAS OF UNTREATED AND TREATED COAL SAMPLES

Samples of untreated Illinois No. 6 and treated coals from runs 17, 20, 24, and 38 were used for B.E.T. surface area determination. In each case the surface area was determined both before and after successive extraction with benzene and pyridine. The results are presented in Table 10, along with the total extraction yield obtained from each sample. The multiple values presented are results of duplicate determinations, and provide an indication of the reproducibility of the results.

Table 10
B.E.T. Surface Areas of Untreated and
Treated Coal Samples

| Run No. | Coal Surface Area(m^2/gm dry basis) | | Extraction Yield (wt % DAF) |
	Before Extraction	After Extraction	
Untreated Illinois No. 6	166.1 164.4	86.8 88.5	19.28
17	170.4 168.6	116.4 112.2	25.11
20	129.9 121.0	168.1 173.1	57.51
24	355,8 360.7	167.6 172.5	2.60
38	39.97 38.40 41.23	140.3 144.9	40.00

A significant reduction in surface area of the untreated coal occurs as a result of pyridine extraction. Solvent retention is one factor which may contribute to this result, with the solvent molecules blocking the micropores present in the coal structure.

The treated coal from run 17 shows very little surface area change from the untreated coal. Apparently the increased extraction yield is due to chemical effects of the treatment rather than mere physical degradation which would expose more area for extraction. The surface area of this sample also decreased as a result of extraction, although not as much as the untreated coal.

The surface area of the treated coal from run 20 is significantly less than that of the untreated coal, undoubtedly due to retention in the solid of reacted THF, since massive incorporation was in fact observed in this experiment. Unlike the unreacted coal, this sample actually shows an increase in surface area as a result of extraction. This is probably due to the fact that the high extraction yield has resulted in the exposure of large amounts of new surface area previously blocked by the molecules which have been extracted. Similar increases after high-yield extractions have been observed by Medeiros (M3) for Wyodak coal using tetralin and phenol as solvents.

The treated coal from run 24 (sulfuric acid treatment) shows a temendous surface area increase (to 360 m^2/gm). As noted earlier, significant amounts of gasification occurred during this run, apparently resulting in a pitting of the surface which exposed large amounts of new surface area. Even though the extraction yield for this sample was extremely low (2.60%), the surface area decreased markedly to a value

nearly the same as for the untreated coal, indicating that the newly

exposed micropores are particularly susceptible to solvent retention.

A large decrease in surface area is observed for the treated coal

from run 38, probably due to physical or chemical incorporation of one

or both of the additives used (PTSA and tert-butanol), even though no

evidence of large amounts of incorporation was indicated by the mass

balance. The high extraction yield (40%) results in an increased area

(similar to the results from run 20), although the final value of

approximately 140 m^2/gm is still less than the original untreated coal.

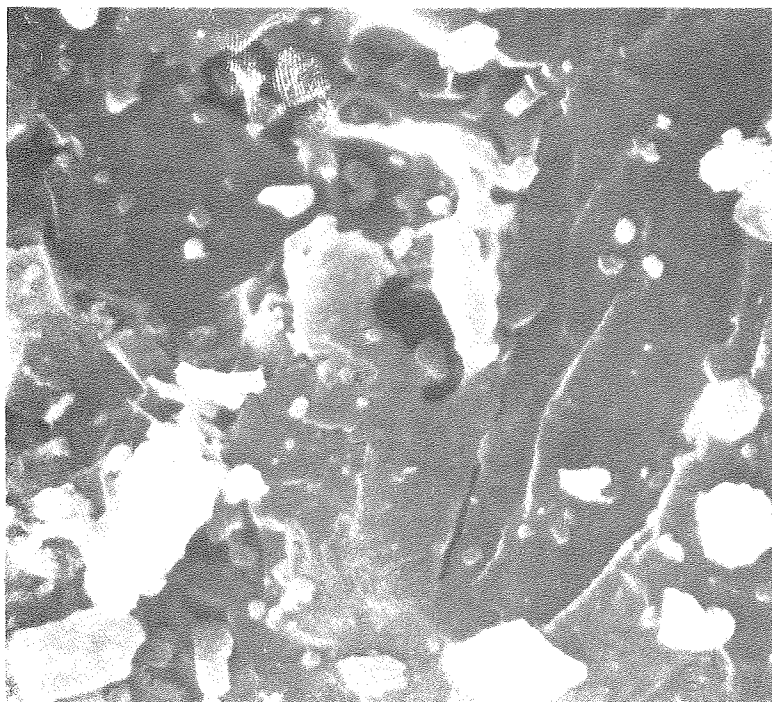D. SCANNING ELECTRON MICROGRAPHS OF UNTREATED AND TREATED COAL SAMPLES

Selected coal samples for which surface areas were obtained were

observed using a scanning electron microscope (SEM) in order to obtain

a visual representation of the changes in physical structure which

occur during reaction and extraction. Samples for which SEM photos

were obtained were untreated Illinois No. 6 (Fig. 5), phosphoric acid

treated coal from run 17, both before (Fig. 6) and after (Fig. 7)

extraction, and sulfuric acid treated coal from run 24 (Fig. 8).

The SEM photos of the untreated coal show the surface to be

relatively smooth, with most of the visible cracks being long and

narrow. (The lighter colored areas are dust particles on the coal

surface). A few crater-like holes are visible in Fig. 5a, indicating

the presence of a macropore structure. Even at the higher magnifica-

tion of 3000X (Fig. 5b), there is little evidence of surface roughness

or pitting.

Figure 6 shows SEM photos of treated coal from run 17 (treatment
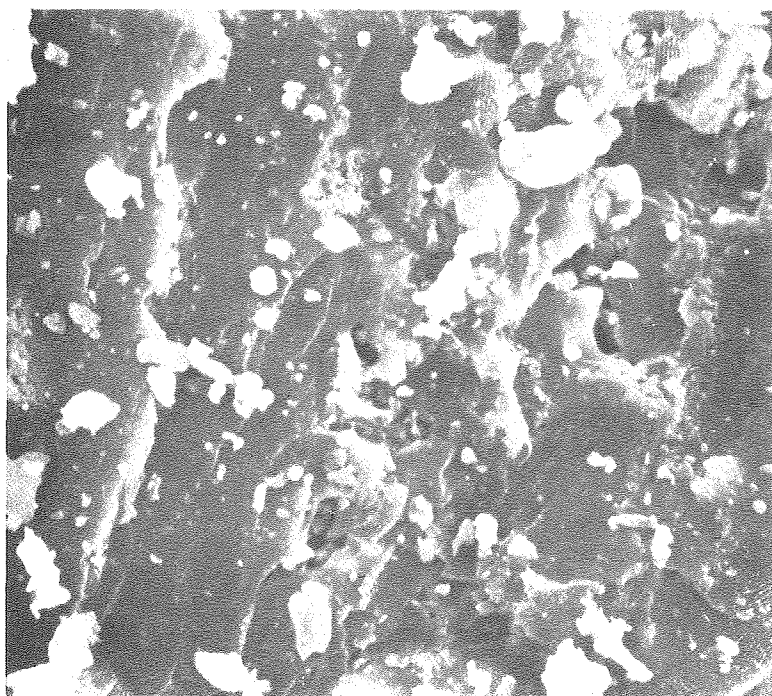
(a)

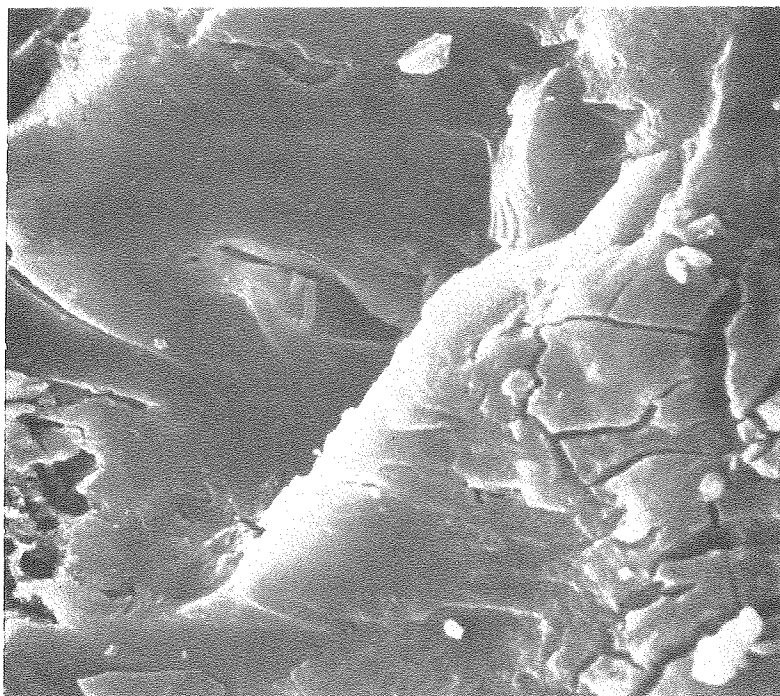(b)   XBB781-8

Fig. 5.   Scanning Electron Micrographs of

Untreated Illinois No. 6 Coal

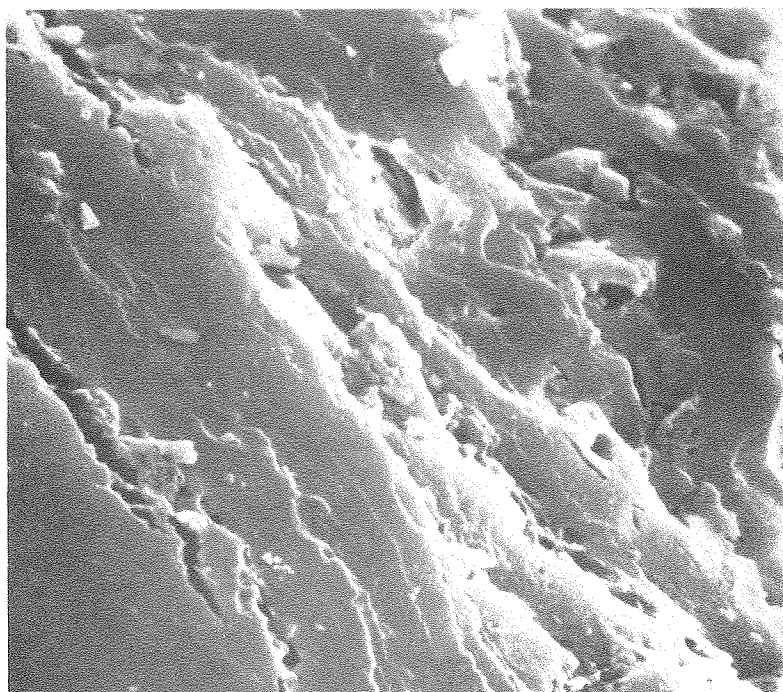a)   1000 x   b)   3000 x

(a)

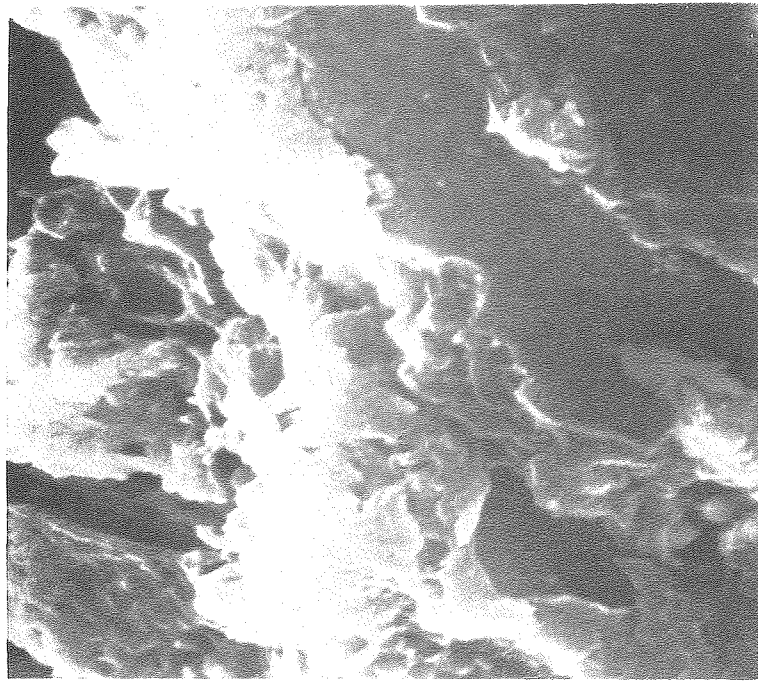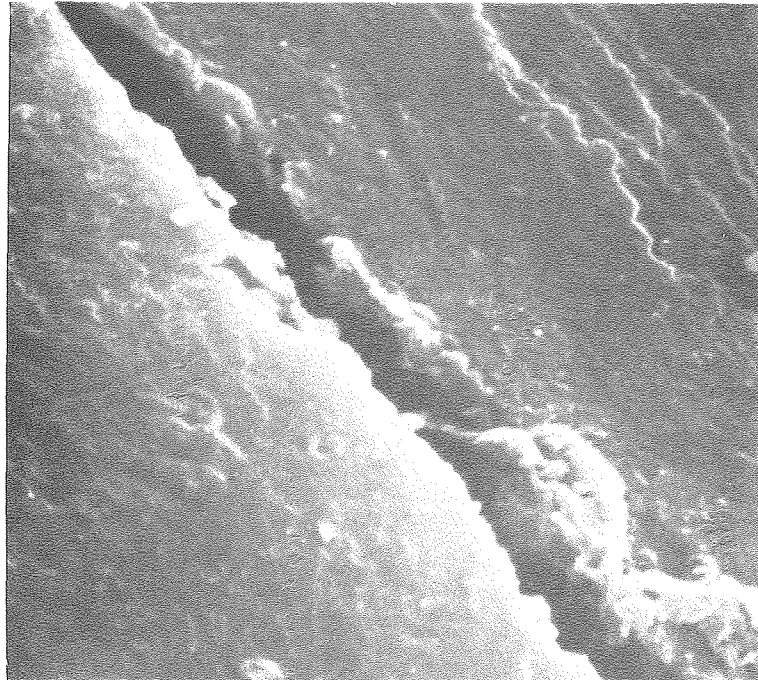(b)   XBB781-9

Fig. 6.   Scanning Electron Micrographs of

Treated Coak from Run 17

a)   1000 x   b)   1000x

(c)

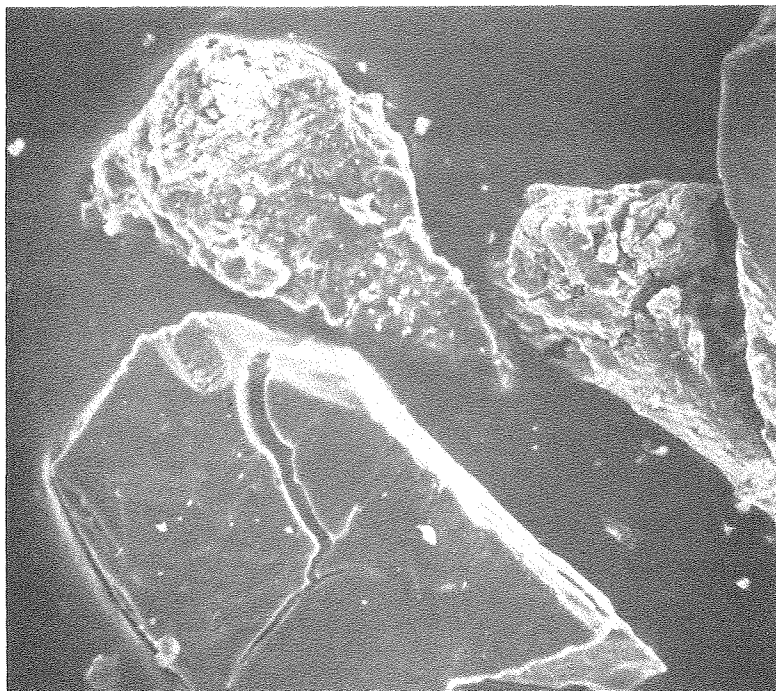(d)   XBB781-11

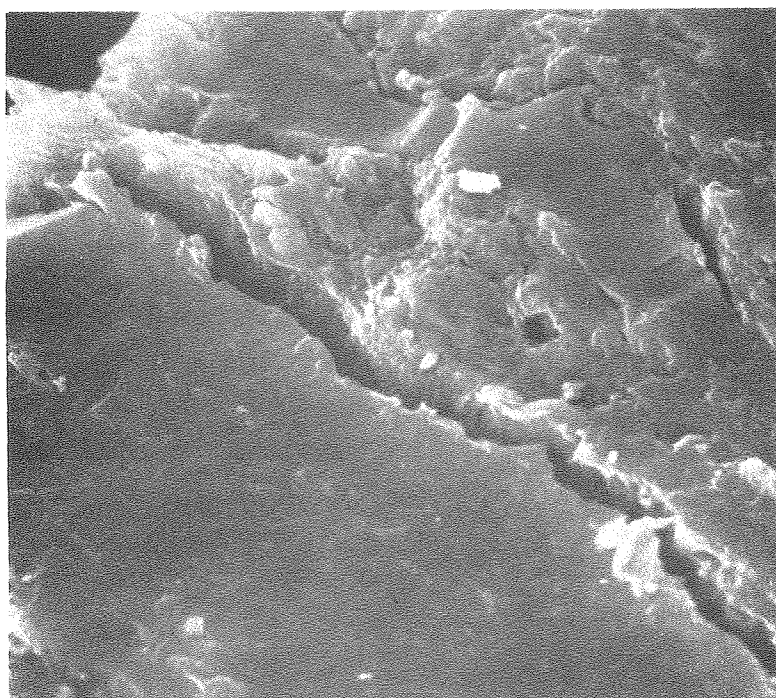Fig. 6.   Scanning Electron Micrographs of

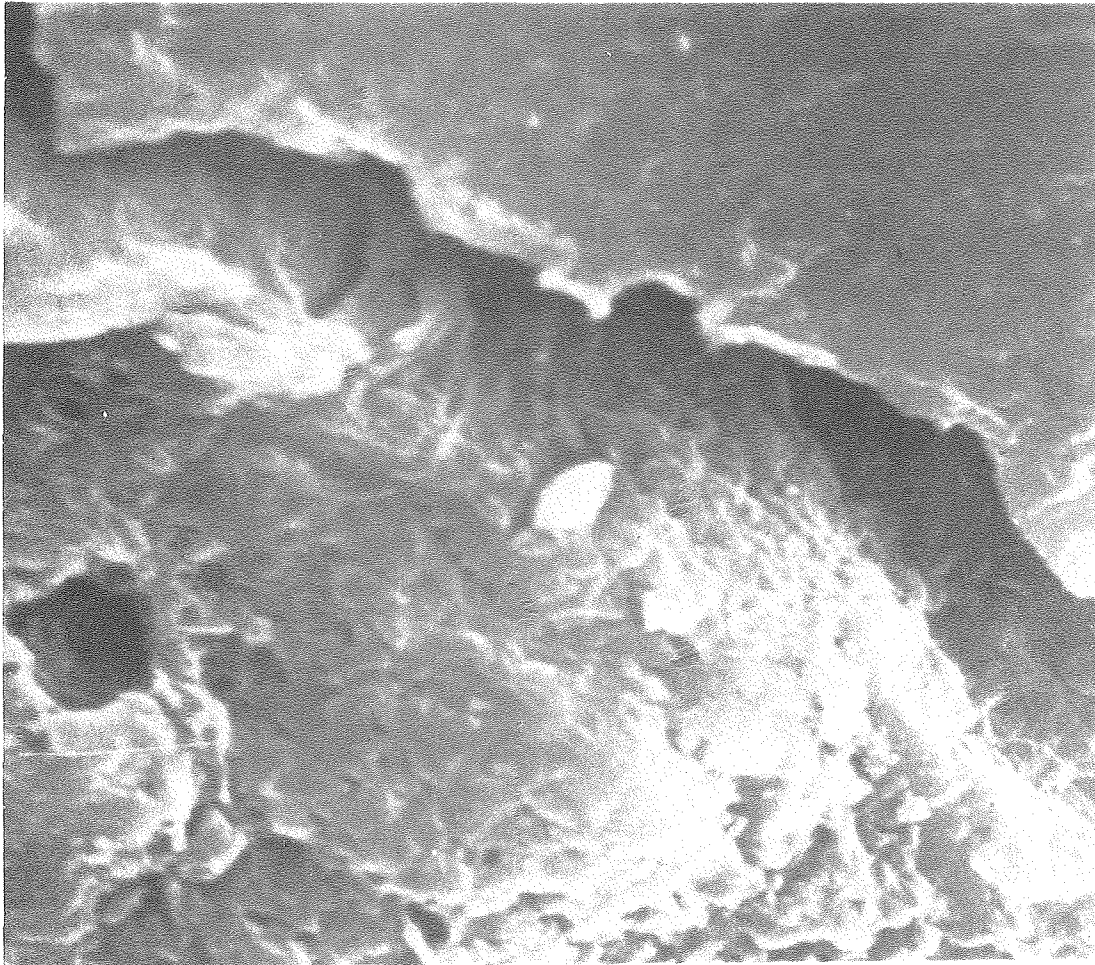   Treated Coal from Run 17

          c)   5000 x   d)   3000 x

(a)

(b)   XBB781-10

Fig. 7. Scanning Electron Micrographs of

        Extracted Treated Coal from Run 17

        a) 100 x   b) 1000 x

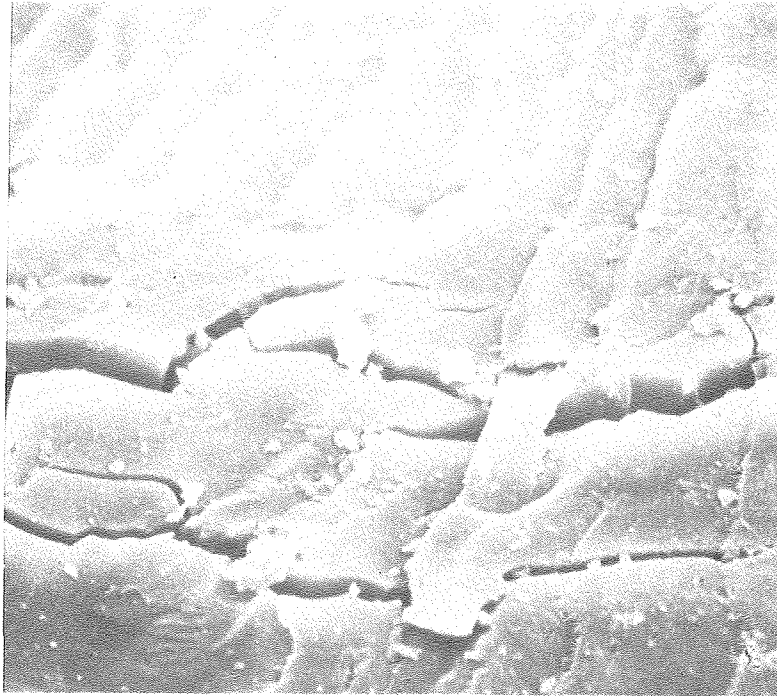(c)   XBB781-12

Fig. 7.   Scanning Electron Micrograph of Extracted Treated Coal

        from Run 17.

        c)   3000 x

(a)

(b)   XBB781-7

Fig. 8.   Scanning Electron Micrograph of Treated

Coal from Run 24.

a)   1000 x   b)   3000 x

with 92% H_3PO_4 at atmospheric pressure) at 1000X (a,b) and 3000X (c,d).
Comparison of Fig. 6a,b with Fig. 5a shows that the effect of treat-
ment has been to increase the general roughness of the surface (illus-
trated in greater detail in Fig. 6c) and to widen some of the previously
mentioned long and narrow cracks (Fig. 6d). While both of these effects
would tend to lead to an increase in surface area, the fact that no
significant increase was found indicates the effects to be minor in
comparison with the area which is contained in pore structures too
small to be visible in the SEM.

SEM pictures of the extracted coal from run 17 are shown in
Fig. 7. The 1000X magnification shown (Fig. 7a) is an indication
of the tremendous variation of surface characteristics seen in this
sample, with one particle showing a very smooth surface with several
major large cracks, while the adjacent particle shows a very rough
surface which is highly pitted. This type of variation was typical
of the extracted sample, but was observed only to a minor extent in
the unextracted samples. This trend is illustrated even further in
Fig. 7a,b,c where the same types of variation are seen even within the
same particle. The conclusion to be drawn from this is that different
areas of the coal are more reactive with respect to interaction with
the solvent due to differences in chemical structure. The rough and
pitted regions (possibly vitrinite) have undergone significant extrac-
tion, while the smooth areas (ash or more carbonized organic) show no
change from the unextracted coal.

Figure 8 shows SEM pictures of treated coal from run 24 (80% H_2SO_4

treatment). The surface appears extremely smooth, with only large, deep cracks and ridges. This is somewhat surprising in light of the fact that significant gasification occurred during this experiment, resulting in a product with a greatly lowered H/C ratio surface area. Apparently this increased area was due entirely to the creation of micropores too small to be observed in the SEM. This explains the large reduction in surface area observed after extraction despite the very low extraction yield, since the retention of relatively few solvent molecules would be enough to close off such small pores.

E. CHEMICAL COMPOSITION OF COAL EXTRACTS

Elemental analyses were obtained for benzene and pyridine extracts from runs 16, 20, 37, and 38, as well as pyridine extracts from run 17 and untreated Illinois No. 6 (benzene extraction yields from these coals were too low to warrant analysis). The results are presented in Table 11, along with the extraction yield (wt % DAF) obtained in each case.

The benzene extracts in general show a higher H/C ratio than the coal itself. The low H/C ratio for the extract from run 16 is probably related to the high sulfur content of the sample, since sulfuric acid was used in this experiment. Each of the benzene extracts has a low nitrogen content (less than 1%) and very little phosphorus or ash. The sulfur contents of extracts from runs 20 and 37 are less than for the coal itself, while for runs 16 and 38, where sulfur containing additives were used (H_2SO_4 and PTSA), a much higher sulfur level is obtained. The lower sulfur level and higher H/C ratio

Table 11
Elemental Analyses of Coal Extracts

Benzene Extracts

Run No.	16	20	37	38
Feed Coal	Ill. No. 6	Ill. No. 6	Wyodak	Ill. No. 6
% Extracted(DAF)	6.61	59.81	5.08	0.88
C	78.87	86.49	80.32	76.42
H	4.59	9.82	10.78	7.65
N	0.04	0	0.40	0.92
S	14.70	1.84	0.76	5.86
P	0	0.39	0.16	0
Ash	0.1	0.9	0.5	0.6
O(by difference)	1.80	0.56	7.08	9.99
H/C(atomic)	0.70	1.36	1.6.	1.20

Pyridine Extracts

Run No.	(untreated)	16	17	20	37	38
Feed Coal	Ill.No.6	Ill.No.6	Ill.No.6	Ill.No.6	Wyodak	Ill.No.6
% Extracted (DAF)	18.78	18.96	25.06	28.18	23.04	39.12
C	73.33	57.88	69.97	60.46	67.35	64.12
H	5.31	4.36	5.32	5.46	5.26	5.22
N	3.27	2.17	2.48	2.51	2.11	2.87
S	3.44	10.17	4.80	2.17	1.35	2.09
P	0.09	11.80	3.08	8.07	2.50	3.68
Ash	0	0.9	1.6	1.6	0.8	0.9
O(by difference)	14.56	12.72	12.75	19.73	20.63	21.12
H/C(atomic)	0.87	0.90	0.91	1.08	0.94	0.98

for the extract from run 37, where Wyodak coal was used, is consistent
with the differences in the original coal. Very little oxygen is present
in the benzene extracts from runs 16 and 20. This is especially
interesting in the case of run 20, since a large part of the benzene
extract from this experiment was formed by THF incorporation, suggesting
that the THF reacts in such a fashion that the oxygen levels in the
extracts from runs 37 and 38 could be due to the reaction mechanism
when tert-butanol is present as an additive, although it is possible
that they are merely a function of the errors inherent in the oxygen-
by-difference analysis.

As expected, the pyridine extracts show generally lower H/C ratios
and higher sulfur, nitrogen, and oxygen levels than the corresponding
benzene extracts. Significant amounts of phosphorus are also present,
as high as 11.8% in the case of run 16. In each case the phosphorus
content represents essentially all of the phosphorus incorporation
present in the treated coal, indicating that the incorporation occurred
in such a fashion that the resultant product is pyridine-soluble. For
run 16, as with the benzene extract, the pyridine extract shows a much
higher sulfur content than the others due to the sulfuric acid used.
Except for a lower sulfur level, the Wyodak-derived preasphaltenes from
run 37 do not appear to be significantly different from the Illinois
No. 6-derived preasphaltenes. Higher oxygen levels were obtained for
the runs which used oxygen containing additives (20, 37, and 38) than
for the other samples, including the extract from the untreated coal.
All the extracts show a higher H/C ratio than the extract of the
untreated coal, indicating that hydrogenation of some sort may be
responsible for the observed increase in extraction yields.

V. CONCLUSIONS AND RECOMMENDATIONS

A. CONCLUSIONS

The following conclusions can be drawn as a result of this study:

1. Phosphoric acid, without additives, does not appear to be an effective coal conversion catalyst. Under the range of conditions studied, anhydrous acid (100% H_3PO_4) showed activity but did not exhibit the characteristics necessary to produce the desired reaction products. Lower acid concentrations, in the 85-95% range, gave products showing higher extraction yields than the untreated coal, probably due to hydrolysis, but not high enough to be economically significant. A much lower acid concentration (65%) showed no catalytic activity at all.

2. Sodium pyrophosphate (formed in situ from addition of Na_3PO_4) shows a highly beneficial ability to reduce foaming problems which occur when coal is contacted with phosphoric acid at temperatures above $175^{\circ}C$. Thus this additive should be present in any use of phosphoric acid as a coal catalyst.

3. No noticeable effect of hydrogen pressure (up to 600 psig) on yields was observed in this study when additives were absent. Reaction yields at $200^{\circ}C$ were generally better than at $250^{\circ}C$, although concentration effects must also be considered in the comparison.

4. Sulfuric acid, used alone or as an additive to phosphoric acid, shows only negative effects as a liquefaction catalyst. In addition to being highly corrosive, H_2SO_4 leads to significant gasification of the coal, resulting in a product showing a lower H/C ratio and lower extraction yields. Molten bisulfate salts ($LiHSO_4/KHSO_4$) also were effective.

Significant incorporation of sulfur into the reaction product also occurred whenever sulfates were used.

5. Tetralin does not appear to be an effective hydrogen donor when used as an additive to phosphoric acid under the conditions of this study.

6. Tetrahydrofuran is extremely effective as an additive which leads to high product extraction yields, but it is consumed in the process and incorporated into the coal liquefaction products. THF is more effective at 250°C in 100% H_3PO_4 than at 200°C in 83% H_3PO_4, indicating that the optimum conditions for H_3PO_4 alone are not necessarily optimum when additives are used.

7. $ZnCl_2$ does not appear to be an effective additive to phosphoric acid. Although it was studied here only in combination with CuCl, the drastically reduced extraction yield indicated an absence of any favorable activity.

8. Methanol is not an effective additive to phosphoric acid.

9. The butanols are effective as additives in increasing the extraction yields, without appreciable incorporation into the product coal. At 200°C, higher yields were obtained at reaction times of 30 minutes than at 60 minutes, indicating that the desired reactions occur quickly, with polymerization effects predominating at longer times. The order of effectiveness is tert-butanol isobutanol sec-butanol, thus eliminating the possibility that hydrogen donation through ketone formation is occurring. Tertiary butanol is a more effective additive at 200°C in 83% H_3PO_4 than at 250°C in 100% H_3PO_4, similar to the results obtained with H_3PO_4 alone.

10. Para-toluenesulfonic acid is also an effective additive in increasing product extraction yields. In addition, PTSA and t-butanol used in combination lead to a higher yield than either used alone, indicating the possibility of desirable interactions between the additives.

11. Some deashing of the coal is obtained by treatment with H_3PO_4, with Ca and Al being the components most effected.

12. Incorporation of phosphorus into the treated coal samples occurred to some extent. Most of the incorporated phosphorus is removed by pyridine extraction, indicating that organophophorus compounts are formed.

13. The nitrogen content of the coal changes very little with H_3PO_4 treatment. Sulfur content is reduced by approximately 30%, indicating that possibly only the inorganic sulfur is effected, except in cases where sulfur-containing additives were used.

14. Consistent with the properties of the untreated coals, Wyodak sub-bituminous coal gives a product with a higher asphaltene yield but a lower preasphaltene yield than Illinois No. 6 bituminous coal when identical treatment procedures are used. No increase in overall yield is obtained by pre-extracting the feed coal with pyridine before reaction.

15. B.E.T. surface areas and scanning electron microscope studies indicate that increased extraction yields of product coals are due more to chemical effects than simply to exposure of more surface area to the extraction solvent used.

B. RECOMMENDATIONS FOR FUTURE WORK

On the whole, the results obtained in this study were not as encouraging as was expected. Concurrent work involving another catalyst system, molten $ZnCl_2$, has led to results which are, on the whole, more positive, indicating that further efforts may be better directed towards it. Nevertheless, the results of this study lead to the following suggestions which might be pursued should it be deemed desirable to conduct further investigations of phosphoric acid systems.

The number and types of additives tried here are only a small fraction of those which could be tried. One possibility is phosphorous acid (H_3PO_3 and its related forms) and phosphate salts, which might reduce the corrosive behavior of H_3PO_4 and at the same time inhibit the repolymerization reactions which appear to be occurring. Among organic additives, nitrogen compounds (such as ethylene diamine or piperidine) might be tried, as well as other oxygen compounds based on the favorable results obtained with THF and the butanols.

The THF results indicate that different optimum conditions may exist for any different additive used. Thus it is likely that higher yields could be obtained by studying different conditions for additives which have been shown to be successful. However, at this point it seems preferable to emphasize further exploratory research as opposed to process development studies.

The combination of high yield and massive incorporation obtained using THF as an additive indicates that reactions other than hydrogen donation are occurring. While THF consumption is too high to warrant

its use in this fashion to achieve liquefaction, a more detailed study of the reaction mechanisms occuring could lead to a better understanding of the reactions which occur in liquefaction systems. More accurate mass balances and more detailed analytical methods would need to be developed, with studies involving model compounds used to provide additional information.

A similar investigation seems warranted of the H_3PO_4/PTSA t-butanol system. Although a relatively high extraction yield was obtained with no measurable incorporation, more detailed procedures are required to investigate possible consumption and recovery of the additives. Should recovery prove to be feasible, further study of different process conditions might lead to even higher yields.

Finally, any process involving phosphoric acid as a catalyst would require an analysis of acid recovery and regeneration before proceeding past the development stage. Problems in this area would differ greatly depending on the additives and conditions used.

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