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INTERACTION OF A SUB-BITUMINOUS COAL WITH MOLTEN ZINC CHLORIDE SOLUTIONS

Tibor T. Derencsenyi*
and
Theodore Vermeulen

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LBL-3265

INTERACTION OF A SUB-BITUMINOUS COAL WITH MOLTEN ZINC CHLORIDE SOLUTIONS

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ABSTRACT

The interaction of a Wyoming sub-bituminous coal with molten zinc chloride containing catalytic additives has been studied in the vicinity of 200°C, under hydrogen at atmospheric pressure. The dispersion and possible dissolution of coal into the melt was examined visually and microscopically. A "melt-treated coal", recovered from the melt by dilution with water and subsequent filtration, was found to have greatly increased benzene extractability (up to 7%).

Melt-treated coal from these treatments, analyzed by x-ray fluorescence spectroscopy, showed slight de-ashing and negligible desulfurization compared with raw coal. It has a finer particle-size distribution, and a much reduced mechanical strength.

The largest extent of extraction from melt-treated coal was obtained when KI and I_2 were used together as additives in the melt. The extract was a light brown wax melting near 70°C. Analysis by mass spectrometry, ir, uv, and nmr indicated that two major constitents of the waxy extract have the chemical formulas $C_{28}H_{56}O_2$ and $C_{26}H_{52}O_2$, and are probably esters.

The following major conclusions can be drawn from this work.

(1) The extract obtained from coal after melt-treatment may be a useful raw material.

(2) The melt-treated coal product needs more physical characterization and further chemical investigation, since the removal of wax may have opened up the coal structure to give much more rapid reaction rates in subsequent hydrogenation treatment.

(3) The zinc chloride treatment was not breaking any significant number of organic chemical bonds and not separating coal from ash, indicating a more powerful catalyst has to be found or the reaction pressure and temperature increased.

(4) Zinc chloride of similar low-temperature melts may provide an effective way of feeding solid coal to a process by reducing the grinding requirements and eliminating predrying.

Interaction of a Sub-bituminous Coal with Molten Zinc Chloride Solutions

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I. INTRODUCTION

As the petroleum and natural gas reserves in the United States and around the world diminish at an increasing rate, substitutes for these feedstocks are becoming economically attractive and essential. Whereas the domestic petroleum reserves will be exhausted in just decades, even conservative estimates indicate that the United States' coal reserves will last for several centuries. Coal is also more easily recovered and more widely available than its other non-liquid fossil-fuel source competitors, oil shale and tar sands. The energy crisis, with its growing shortages of crude oil, has revived the field of coal hydrogenation, the subject of the present study.

A. Chemical Structure of Coal

Coal is a combustible solid which originated from the accumulation and burial of partially decomposed vegetation in previous geological ages. It is composed chiefly of carbon, hydrogen, and oxygen, with minor amounts of nitrogen and sulfur, and varying amounts of moisture and mineral impurities. The mineral impurity, termed ash, is the residue left after the coal is burned. Minerals find their way into coal from (1) inorganics occurring naturally in plants, (2) occluded material absorbed through leaching processes over the aging period of the coal, and (3) soil and silt originally deposited with the plant material. The latter materials account for much of the inhomogeneity and stratification found in coal. The major elements other than carbon and hydrogen are oxygen, nitrogen, and sulfur, which are bound mainly into heterocyclic structures and as bridges between rings. (Sulfur is also found as an inorganic component present as pyrite, FeS_2.

There is no specific structure established for coal, but some typical models have been proposed. These have been summarized by Lowry(L1). The structure depends much on the age or rank of the coal, growing older from lignite, sub-bituminous, bituminous, to anthracite. The older the coal the closer it becomes to being graphite, losing volatiles and chemical impurities. It also has a decreasing hydrogen-to-carbon ratio which makes it increasingly difficult to hydrogenate. For relative ease of hydrogenation and high availability, a sub-bituminous coal has been investigated in the present study.

A representative structure for bituminous coal is given by Wiser in Figure 1(W1), related to an earlier structure for high-volatile coal, Figure 2, by Hill(H1). In a typical sub-bituminous coal, 70% of the carbon is bound in aromatic rings, but only 23% of the hydrogen is attached to these rings. This indicates that the aromatic rings are highly substituted. As a result of these recent studies the previous view, that coal is an extensive graphite-like matrix of carbon atoms with as many as twenty aromatic rings condensed into single units, has been abandoned. The number of aromatic nuclei in a cluster is now believed to have a maximum

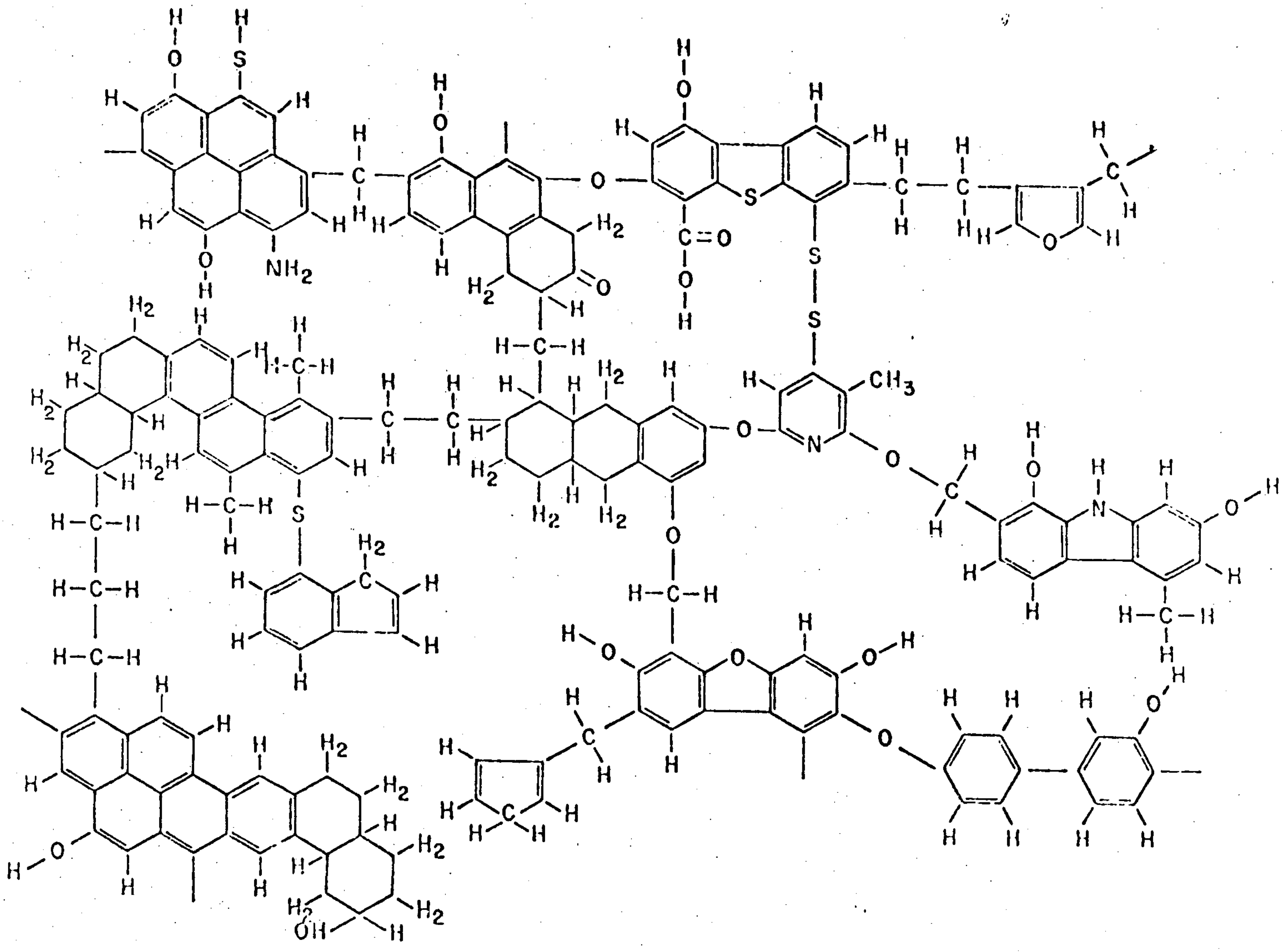
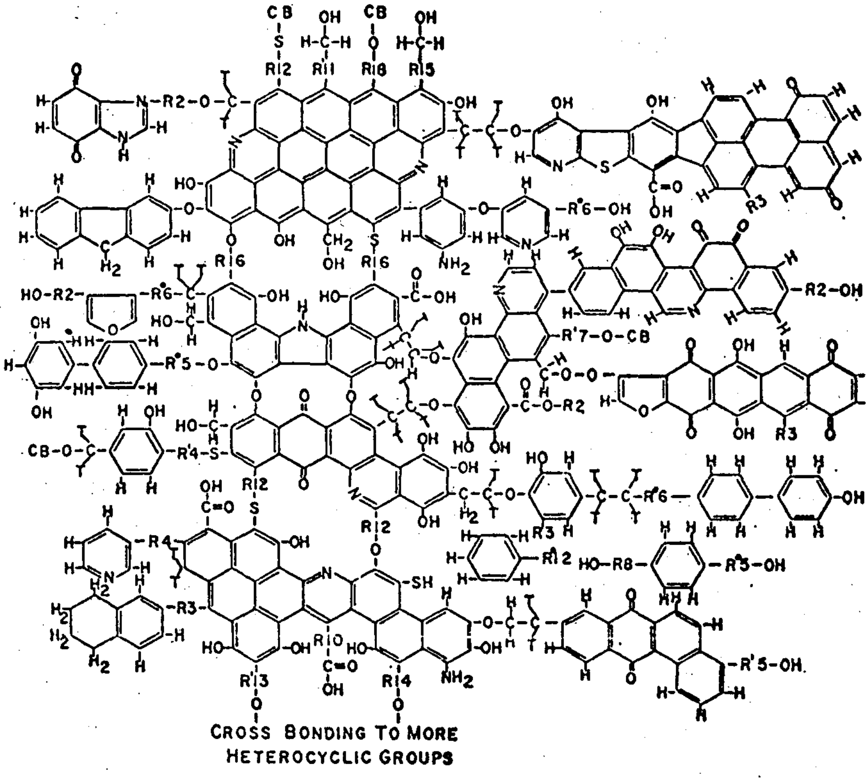


FIGURE 1. A MODEL FOR BITUMINOUS COAL STRUCTURE

Wiser, W.H. "Coal Catalysis"



R°N = Alicyclic rings of N carbons.
RN = Alkyl side chain of N carbons.
R'N = Unsaturated alkyl side chain of N carbons.
CB = Cross bonding by O or S to new heterocyclic groups with side chains.
T = Tetrahedral 3 dimensional C—C bonds, C—O bonds and C—S bonds.

FIGURE 2. MODEL FOR HIGH-VOLATILE COAL

Hill, G.R., Lyon, L.B. ISEC (June, 1962) of four or five, corresponding to about twenty carbon atoms per cluster.

The Wiser structure indicates no long aliphatic chains in coal, and no ethylenic bonds. Most of the carbon not contained in aromatic and heterocyclic structures is either hydroaromatic or in very short aliphatic bridges. The model also shows representative structure of the non-hydrocarbon elements. Sulfur, oxygen, and nitrogen are bound in the matrix both as connecting structures and as heteroatoms in rings.

The aromatic hydrogen content in sub-bituminous coal is low, amounting to approximately one atom per aromatic ring(L1). This consequence goes far to explain why many reactions of aromatics, such as sulfonation, are observed only to a limited extent with coal. It is apparent from the Wiser-Hill models that coal would have an irregular packing when compared to graphite. Consequently coal can be swollen and attacked by solvents which have no such effect on graphite. The irregular packing of molecules can also account satisfactorily for the ultrafine internal structure on the scale of 5 to 50 Angstroms, identified through surface-area measurements of 100 to 200 meters^2/gram(V1).

B. Coal Liquefaction

1. Direct Hydrogenation to Produce Liquid Fuels

Liquid hydrocarbon products from hydrogenation of coal were first produced by Berthelot in 1896. Nascent hydrogen from hydriodic acid at 270°C gave a 60% conversion to "oil"(D1). Bergius, in 1913, initiated the industrial production of liquid products from coal, using hydrogen at 200 atm. pressure and 400 to 500°C in a batch autoclave. Subsequently he devised a method of continuous operation, mixing the solid coal with a heavy oil to form a paste which could be pumped into high-pressure reactors.

In 1916 Berqius built a pilot plant using "lined" reactors to hydrogenate a coal paste, the liner being required to eliminate corrosion of the steel pressure vessel by hydrogen. Nitrogen, circulated at reaction pressure in the space between the liner and the outer pressure-vessel wall, supplied the heat for reaction. The products, gasoline, diesel fuel, and fuel oil, were inferior to their petroleum-based counterparts(D1).

The technology to make a high-quality product was provided by Badische Anilin-und Soda-Fabrik. Commercial development of the Haber process for ammonia manufacture by C. Bosch in 1910, and production of methanol from carbon monoxide introduced by M. Pier in 1924, gave experience with high-pressure equipment that the coal hydrogenation process needed. The necessity of a hydrogenating catalyst led to a screening method by which Pier developed several iron, cobalt, molybdenum, and tungsten sulfide catalysts with very good activity and sufficient life for industrial use. In 1925 brown coal was hydrogenated at 200 atm. to nearly pure gasoline in one stage over a molybdenum catalyst, without coke formation(D3).

The first commercial coal hydrogenation plant, at the Leuna works of I.G. Farbenindustrie, was brought on stream in 1927, using a mixture of Central German brown coal and coal tar as its feedstocks. Originally built for a capacity of 2,500 bbl. per day and an operating pressure of 200 atm., the plant was subsequently enlarged to 16,000 bbl. per day at 250 atm. pressure. The main products were aviation and motor gasoline. Between 1936 and World War II, Germany built eleven more plants operating at pressures between 300 and 700 atm. and temperatures up to 800°C, with a combined capacity of 100,000 bbl. per day of liquid fuels. Since 1944, eleven of the twelve plants have been adapted to other aspects of petroleum refining. At the present time, only Siberia and East Germany have coal-hydrogenation plants in operation(L2).

The retreat from coal hydrogenation resulted from a change in economic conditions. The discovery of vast new petroleum reserves after World War II, along with a drastic increase in coal prices, forced the plants to be adapted to more economic feedstocks. Under these conditions, at least two areas remained in which coal hydrogenation still had promise: production of solvents and chemical intermediates which demand a higher price than fuel, such as aromatics or tar acids; and conversion of coal to a natural gas substitute.

Looking into the near future, it appears that the economic conditions have come full circle. The availability of crude oil has dropped, whereas the reserves of coal are still large.

2. Fischer-Tropsch Synthesis Following Coal Gasification

In addition to conversion by direct hydrogenation, coal can yield liquid hydrocarbons by indirect means, using the Fischer-Tropsch synthesis process$^{(G1)}$. The following reactions are used, usually at 400 to 450 psia and 1000°C, to produce "synthesis gas", a mixture of CO and H_2:

$$C_x H_{2y} + \frac{1}{2}(x+y)\ O_2 = xCO + y\ H_2O$$

$$C_x H_{2y} + xH_2O = (x+y)\ H_2 + xCO$$

Heat for the second reaction is supplied by the first one. Purified synthesis gas is then reacted over an iron catalyst, at the same pressure and at a temperature of 150 to 250°C, to form liquid n-paraffins and n-α-olefins by the following overall reactions:

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

$$(2n-m)H_2 + (n+m)CO = C_nH_{2n} + nH_2O + mCO_2$$

Where n is near 8, and m near 2. Because the $CO:H_2$ ratio in synthesis gas usually exceeds the required proportion, the ratio must be reduced by the water-gas shift reaction:

$$CO + H_2O = CO_2 + H_2$$

The Fischer-Tropsch reaction is markedly exothermic, resulting in a large wastage of fuel value and requiring a complex reactor design to remove the heat released and thus avoid reversal of the reaction.

During the period of 1939-1945, nine German plants using Fischer-Tropsch synthesis produced 18,000 bbl of oil per day (H2), making a significant contribution to Germany's wartime supply of gasoline, diesel oil, lubricating oil, wax, and detergents. A second generation Fischer-Tropsch plant came on stream in 1955 and is still in operation in Sasol, South Africa. This plant, over twice as large as any of its German predecessors, produces 5000 bbl of oil per day from 5000 tons of coal, a yield significantly less than the typical 3 barrels of oil per ton of coal obtained by coal hydrogenation (H3). Even 3 barrels per ton is well below theoretical.

3. Future Process Requirements

Compared to gasification with Fischer-Tropsch synthesis, direct hydrogenation is the more promising method of producing liquid fuels from coal. Even with modern techniques and newly developed heterogeneous catalysts, hydrogenation is carried out at pressures around 2500 psia and at temperatures of 400°C and above. The plant construction requirements are formidable, and are delaying any large-scale entry into this field. Therefore, the need is evident for a second-generation coal-to-liquid-fuel process, based on new principles and discoveries, that would provide an economic breakthrough. New catalytic methods may well be the key to such a breakthrough, and the purpose of this investigation is to begin the examination of such systems. The treating medium used for the present study is a Lewis-acid type of metal halide.

C. Coal Hydrogenation with Molten Metal Halides

According to G.N. Lewis' definition, a base can furnish an electron pair to form a covalent bond; that is, it is an electron donor. An acid can take up an electron pair to form a covalent bond, and is thus an electron acceptor. As an example, boron trifluoride is a Lewis acid, since it has only six electrons in its outer shell and tends to accept another two to complete the stable octet. Other Lewis acids include $AlCl_3$, $FeCl_3$, $SnCl_4$, and $ZnCl_2$.

These halides react with olefinic and aromatic hydrocarbons to bring about acylations and alkylations, grouped in the category of Friedel-Crafts reactions, and under the proper conditions also hydrogenations. Since alkylations and acylations are reversible, these Lewis acids should also produce cracking of carbon-carbon and possibly of carbon-oxygen bonds.

1. Vapor-Phase Refining

The first mention of Lewis-acid metal halides for petroleum refining was in three patents by Arthur Lachman(L3). Working at the University of California at Berkeley, Lachman patented a vapor-phase refining process in 1934 and extended it in 1935, in which petroleum fractions such as gasoline were brought into countercurrent contact with concentrated aqueous solutions of various salts. For this purpose, Lachman proposed especially $ZnCl_2$, $CuCl_2$, and $AlCl_3$, the latter known to be a very effective Friedel-Crafts catalyst when anhydrous. Lachman later reported that the zinc chloride system is also effective in removing various sulfur compounds from mineral oil vapors.

2. Coal Hydrogenation with Trace Amounts of Metal Halides

In 1938, Abe and co-workers (A1) used Lewis acids as catalysts to hydrogenate 100-gm samples of a Japanese (Fushun) Coal with 2 wt-% of catalyst in chromium-molybdenum steel autoclaves operated for 1 hour at 420°C and 1400 psi hydrogen pressure. They found $ZnCl_2$, $ZnCl_2$+$NiCl_2$(0.01%), and $SnCl_4$ to be excellent catalysts under these conditions. They concluded that the best catalytic effects were observed with metals of atomic number 26 through 30 (Fe, Co, Ni, Cu, Zn), and also 42 (Mo) and 50 (Sn). Between these elements there exist weak catalysts or promoters of catalytic activity.

Parallel studies of catalyzed and uncatalyzed hydrogenations by Abe et al. showed that water content of coal up to 20 wt-% had little effect without catalysts, and a favorable effect with catalyst present. Water appears to disseminate the catalyst through the carbonaceous material.

Following the work of Abe, other studies of catalytic coal hydrogenation with catalytic amounts of metal halides were undertaken. A notable report on the work by the Bureau of Mines between 1944 and 1956 and review of pertinent literature was compiled by Hawk and Hiteshue(H4). More recently Katzman at the Electric Power Research Institute(K1) published abstracts of articles on catalysis in coal conversion up to 1974.

3. Coal Hydrogenation with Massive Amounts of Metal Halides

After a lapse of 25 years, the use of metal halides was revived in the 1960's by C.W. Zielke, R.T. Struck, J.M. Evans, C.P. Costanza, and E. Gorin of Consolidation Coal Company in the intensive development of a catalytic process for hydrogenation of coal to liquid fuel. In a pioneer study(Z1), they investigated molten zinc chloride and zinc bromide as hydrogenating catalysts for producing gasoline-range products from coal extract containing over 50 mole percent high-molecular-weight polynuclear aromatics, plus some aliphatics, with substantial amounts of nitrogen, oxygen, sulfur, and non-filterable ash. The coal extract was easier to study, because it had already been finely dispersed and freed from ash and other solid residue of the original coal. (Hydrogenation directly of coal was also studied briefly.)

Batch autoclave tests showed the molten zinc salts, which are Lewis acids, to be superior catalysts for hydrocracking polynuclear aromatics when used in high concentrations. At severe reaction conditions, 427°C and 4200 psig pressure with 60 minutes contact time, using a massive 1:1 weight ratio of catalyst to hydrocarbon, they obtained 90 weight percent conversion to products boiling below 400°C. The molten halide catalysts were compared with conventional supported catalysts for conversion of pyrene and coal extract. The best results for such heterogeneous catalysts were obtained with sulfides of Mo, Ni, and Co on large-pore alumina gel support, but these still gave 30% less conversion at the same conditions. A graph of conversion versus residence time at constant pressures and temperatures (Figure 3) shows the superiority of the homogeneous catalyst.

Especially interesting is the short residence time, 15 minutes, for 85% conversion using molten zinc chloride. To test the catalytic activity of zinc chloride on coal, one run was conducted with a melt-to-coal weight ratio of 3.5:1, At 200 psi and 725°F (385°C), 74% of a Pittsburgh Seam coal was converted to liquid products in one hour. The higher ratio of $ZnCl_2$ appears to have been needed in order to wet or slurry the coal completely.

By using massive quantitities of catalyst, Zielke and his co-workers achieved single-stage conversion of coal extract to high-octane gasoline(Z2). As the catalyst-to-hydrocarbon weight ratio is increased to unity, the total conversion increases (see Figure 4). However, ratios greater than about 1 do not significantly improve conversion. It is noteworthy that the zinc chloride showed greater total conversion than hydrofining catalyst. The difference in the extent of conversion is even greater when gasoline-range products are desired, due to the excellent selectivity of zinc chloride. Zinc chloride also produces less gaseous by-product

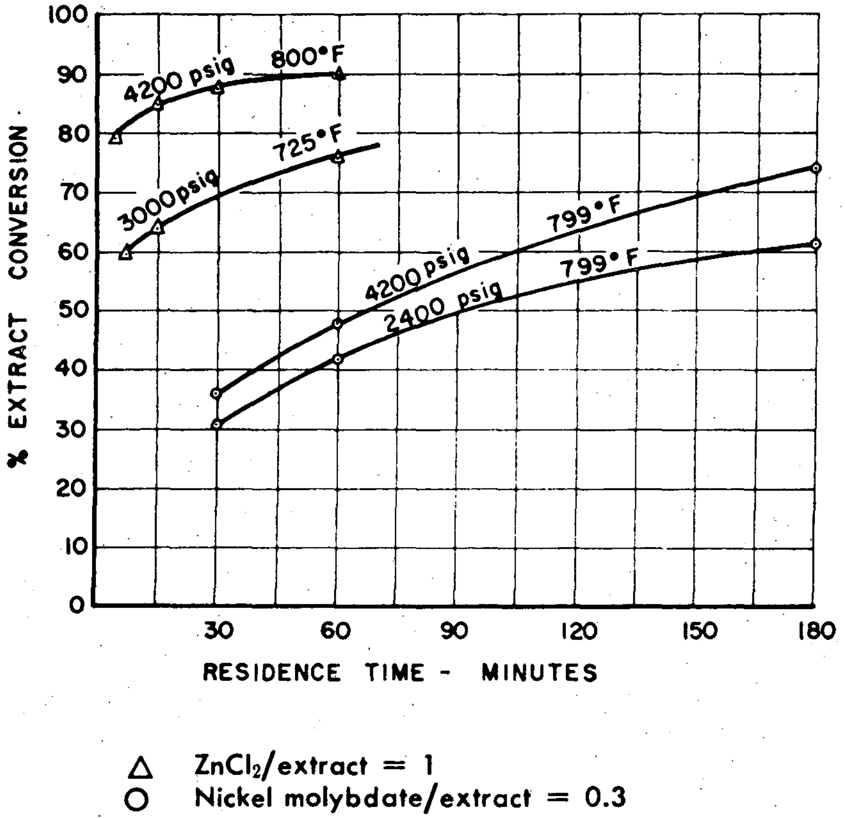


Figure 3: Effect of residence time on total conversion of coal extract with zinc chloride.

Source: Zielke, C.W. I&EC Process Design and Development (April 1966). Copied by permission.

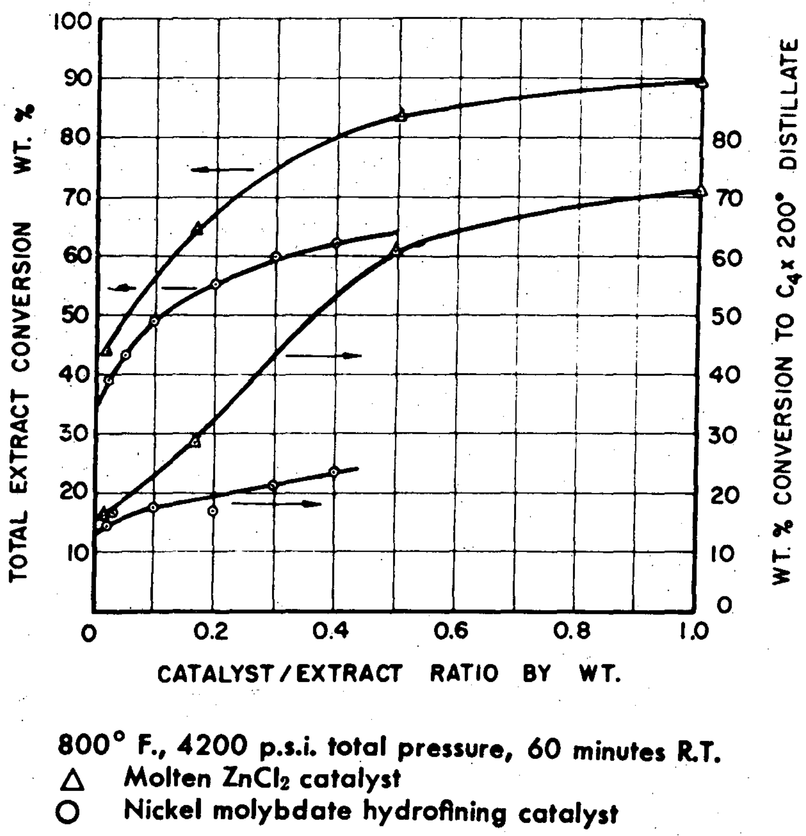


Figure 4: The effect of catalyst to extract feed ratio on total conversion of coal extract and conversion to gasoline.

Source: Zielke, C.W., I&EC Process Design and Development (April 1966) Copied by permission.

than the contact catalyst. The formation of C_3 and smaller hydrocarbons is undesirable economically, because of the drastic increase in hydrogen uptake.

D. Theoretical Aspects of Catalytic Hydrogenation in Zinc Chloride

1. Kinetics

To evaluate their process and obtain kinetic data for a proposed pilot plant, Consolidation Coal Company performed rate studies on coal-extract hydrocracking with molten zinc chloride in a batch autoclave(S2). The model fitted to their data assumed that the feed, coal extract, is composed of two different types of compounds, one of which dissociates at a fast rate and the other much more slowly. The slow reaction shows an activation energy of about 80 kcal/gram-mole; it appears to be inhibited strongly by ZnO, and is insensitive to changes in H_2 pressure. About 75 weight-percent of the extract reacts by the fast reaction, for which an Arrhenius plot gave an activation energy of 35 kcal/gram-mole. This high value indicates that the rate-determining step is probably not mass-transfer limited. The value coincides with one from Weller et al. for hydrogenation of asphaltenes derived from coal(W2).

2. Mechanisms

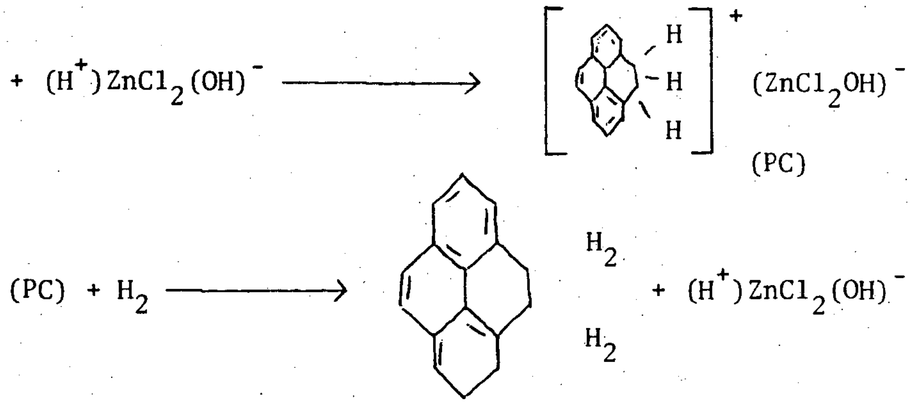
The formation of a Friedel-Crafts acid catalyst in a zinc chloride melt or solution can occur by the addition of HCl or (more weakly) of water.

$$nHCl + ZnCl_2 = (H^+)_n ZnCl_{2+n}^{n-}$$

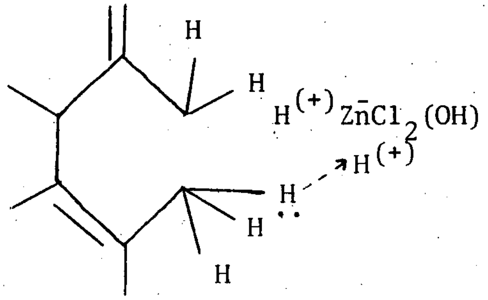
$$nH_2O + ZnCl_2 = (H^+)_n ZnCl_2(OH)_n^{n-}$$

where n = 1 or 2. The investigators at Consolidation Coal Company found that the addition of water caused an increase in acidic cracking activity, demonstrated by an increase in hydrogen uptake(Z2). Addition of HCl was undesirable because of increased coke formation, excessive hydrogen uptake, and gas formation.

The acid thus formed is believed to attack the 9- and 10-carbon atoms of fused-ring aromatics such as pyrene. The resulting aromatic-catalyst complex (PC) can react with hydrogen to regenerate the catalyst and produce 9, 10-dihydropyrene.

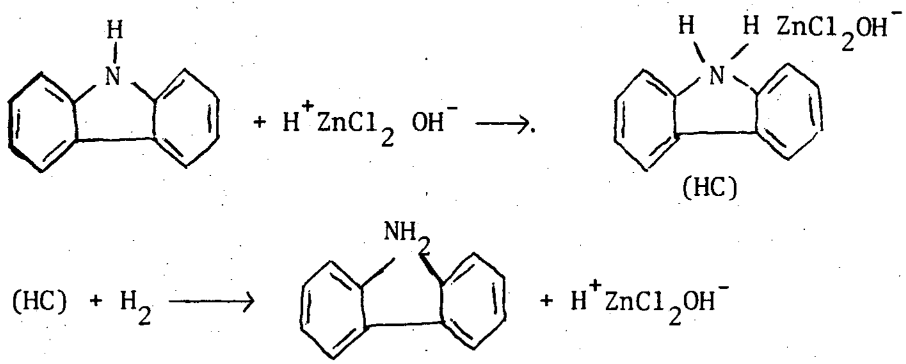


This mechanism can continue for bondings of hydrogen to other rings: or for ring opening, which might occur in the following way:

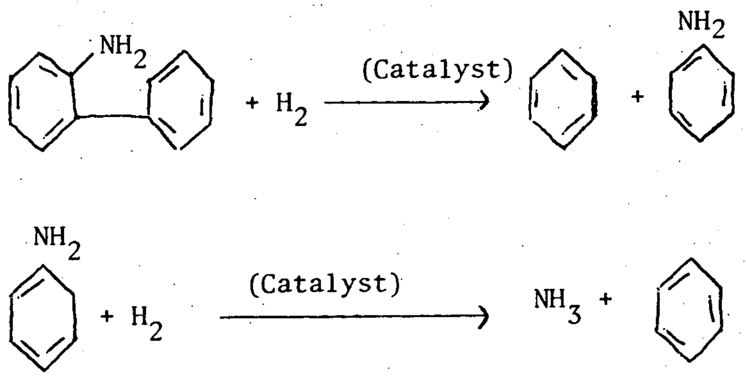


The shared carbon atoms in fused-ring structures are hydrogenated to "tertiary" aliphatic carbons. These tend to isomerize to straight chains above 200°C, but apparently such rearrangement is inhibited in zinc chloride.

The heteroatoms in coal, oxygen, nitrogen, and sulfur react with catalyst and hydrogen to form H_2O, NH_3, H_2S respectively resulting in ring opening and cross-link scission:



Single-ring compounds can be produced only by splitting inter-ring C-C bonds. Apparently C-C and C-N splitting reactions do occur in $ZnCl_2$, at least at temperatures above 400°C as used by Consolidation Coal.



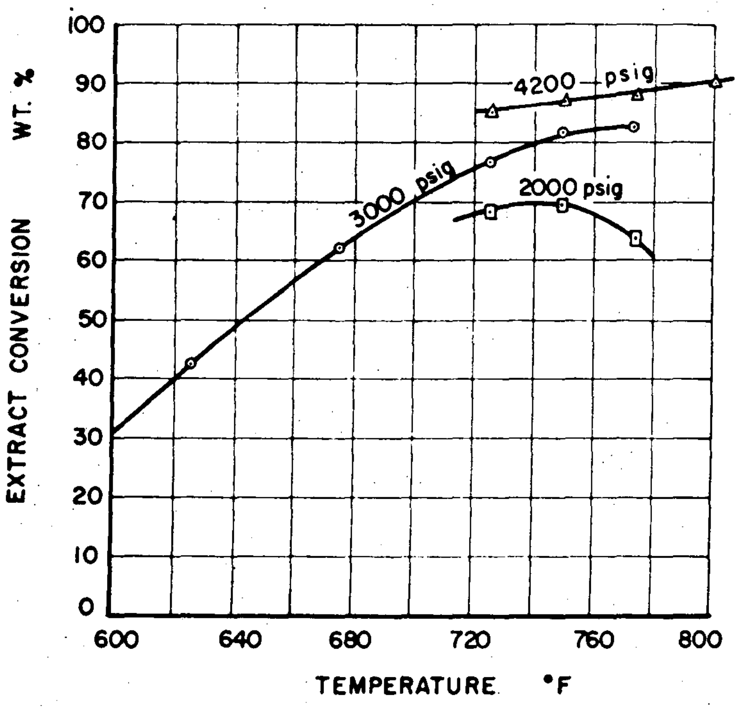
As can be seen from the Wiser structure, Figure 1, removal of the heteroatoms can give significant headway toward liquefaction.

3. Thermodynamics

Since catalysis affects only the rate of reaction, it is also important to examine the tendency for a reaction to occur. Pressure affects hydrogenation by Le Chatelier's principle; that is, higher pressure increases the equilibrium yield, because there is a volume decrease from reactants to products. Since hydrogenations are exothermic, they can be reversed at any pressure by increasing the temperature sufficiently. In general, therefore, a lower reaction temperature makes possible a lower operating pressure,provided the reaction still occurs at a satisfactory rate which is the case with coal.

a. Bond Breaking in Coal

In hydrogenating coal extract, Zielke reported the effects of temperature and pressure on the extent of conversion at a residence time of one hour in a batch autoclave. The results given in Figure 5 show that substantial conversion can be realized between 600 and 800°F. The 2000-psig contour contains one point that indicates a peak conversion of 70% at 750°F (414°C) and a downturn above this point. This may be caused by lowering of the hydrogenation equilibrium with rising temperature. Below 750°C, higher equilibrium limits are expected, but with slower rates that could explain the lower conversions in the one hour time. An alternative kinetic interpretation of the results of higher temperature and lower pressure is that unwanted polymerization reactions could occur faster than



$ZnCl_2$/extract = 21.0
Time, 1 hour

Figure 5: The effect of pressure and temperature on conversion of coal extract by zinc chloride.

Source: Zielke C.W., I&EC Process Design and Development (April 1966). Copied by permission.

the desired hydrogenation, since the rate of hydrogenation is less at lower pressures.

b. Reactions of Heteroatoms with $ZnCl_2$

Zinc chloride catalyst can be poisoned by the sulfur, oxygen, and nitrogen in coal. The melt reacts with these impurities according to the reactions:

(i) $ZnCl_2 + H_2S = 2HCl + ZnS$

$K_I = (P_{HCl})^2/(P_{H_2S})$

K_I is 0.25 at 490°K, and 400 at 700°K

(ii) $ZnCl_2 + H_2O = ZnO + 2HCl$

$K_{II} = (P_{HCl})^2/(P_{H_2O})$

K_{II} is 1.3×10^{-6} at 490°K, and 0.0134 at 700°K

(iii) $ZnCl_2 + nNH_3 = ZnCl_2 \cdot (NH_3)_n$

the equilibrium constant for reaction i was determined experimentally(B1) and the constant for reaction ii was calculated from thermodynamic data(K2).

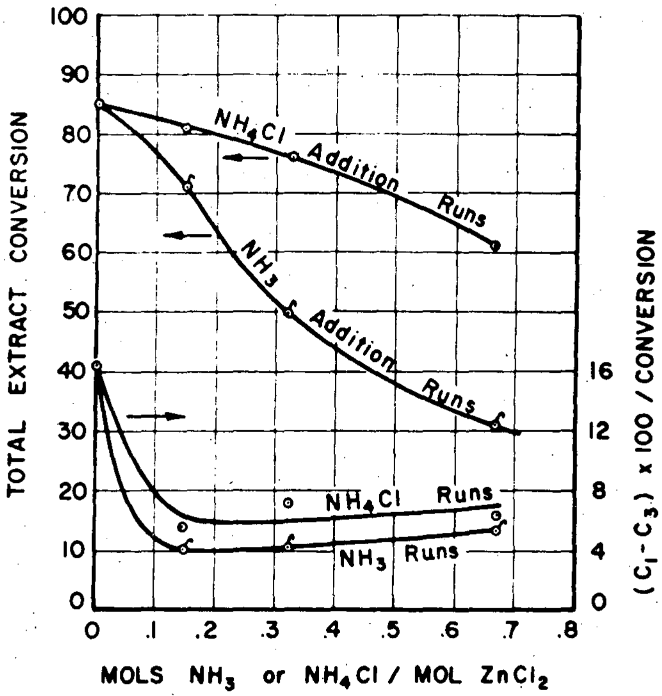
At 700°K Zielke found that practically no hydrogen sulfide was present in the gas phase; it was all absorbed into the melt to react with zinc chloride. If the reaction temperature is lowered to 500°K (227°C), hydrogen sulfide in the gas phase will be favored over hydrogen chloride by a mole ratio of 2 to 1. Around 500°K the sulfur will tend to be converted to hydrogen sulfide which can be purged, and the formation of zinc sulfide will be inhibited.

The equilibrium constant for reaction ii favors the reactants; therefore little hydrolysis of zinc chloride should occur at either 700 or 500°K. Small amounts of hydrogen chloride will be present, but addition of zinc oxide can eliminate it if necessary. At high temperatures HCl is undesirable, but at low temperatures it can be advantageous in serving to increase the cracking activity of the system.

Ammonia formed during hydrogenation is absorbed into the melt, complexing with zinc chloride by reaction iii, and strongly inhibits the conversion reactions. Any HCl in the melt combines with the NH_3 to form NH_4Cl, which is less harmful to the catalytic activity. In process use, the melt will need to be purged of the ammonia complexes in a regeneration step. However, complete removal of ammonia is not desirable because of its favorable effect on selectivity; the ammonia complexes dramatically reduce gaseous products, as shown in Figure 6.

E. Conclusion

Historically, the commercial use of coal hydrogenation has been retarded by two significant problem areas: the high pressures and temperatures required for economical reaction rates, and the difficulties in feeding the solid reactant to a continuously operating reactor. Molten-salt hydrogenation of coal has potential for alleviating both these problems. First, the zinc chloride can act as a Friedel-Crafts catalyst or as a catalyst carrier, to enhance hydrogenation rates at lower temperatures and pressures which would be favorable economically. Second, treatment of coal with zinc chloride under low pressures and temperatures may liquefy the coal



$ZnCl_2$/extract = 2.0
Temperature, 750° F.
Pressure, 3000 p.s.i.g.

Figure 6. Effect of catalyst poisons, NH_3 and NH_4Cl on selectivity and conversion of coal extract with zinc chloride.

Source: Zielke, C.W., I&EC Process Design and Development (April 1966). Copied by permission well enough to overcome the problem of solids feeding. When coal is mixed with an oil and the resulting paste is pumped into high-pressure reactors, the pumps have a short life because the paste or slurry is highly abrasive. Even if a high-pressure step is required with zinc chloride, any small amount of solids not dispersed in the melt during the low-pressure treatment can probably be separated prior to the pumping step.

II. OBJECTIVES

A. General Considerations

From an economic standpoint, it is desired to bring about coal conversion with the chemical specificity of a catalyst rather than the "brute force" of pyrolysis. A truly catalytic conversion offers the prospect of being operable at lower temperature and hence (because of the reaction thermodynamics) at lower pressure, resulting in lower equipment costs and less hydrogen consumption.

Experiments have been conducted in this study to investigate the dispersing and hydrogenating activity of molten halide salts for coal. Metal halides, especially $ZnCl_2$, have been used in massive amounts with respect to the coal feed, up to 6:1 on a mass basis. The halide serving as solvent has often been augmented by other salts (usually halides), oxides, or elemental materials, in amounts usually under 10% by weight of the melt.

As with heterogeneous catalysis, homogeneous catalysis theory lacks the ability to predict the activity of a compound for solvents and substrates not already tested. Hence, most such catalysts have been identified or developed in the past by trial and error, although both theory and prior knowledge have influenced the selection of materials to be studied. The course of this study, therefore, has been to conduct a broad-range empirical screening that would expose both the products and problems inherent in a molten-salt process.

It is desired that coal conversion should take place at low pressure and temperature. Because pyrolysis of coal, which starts at 350°C, is to be avoided, a temperature in the range of 180 to 200°C was chosen for these studies. A temperature around 200°C has the advantage that at temperatures only slightly above this range the lower-rank coals begin to soften. Softening should provide better interaction between the coal and the melt. Because of the possibility that there occurs some true solution of coal components into the melt, a few typical commercial contact catalysts have also been investigated.

The experimental program that has been developed is believed to demonstrate a workable pattern of testing and analysis that should be suitable for systematic screening of a wide range of carrier media ("solvents") and potential catalysts.

B. Experiments Performed

1. Treatment of Coal with Zinc Chloride Melt

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

2. Comparative Analyses of Coal Feed and Products

a. Analyses of Solid Products

To determine the state of subdivision of coal in the zinc chloride melt, samples of solidified coal-melt mixture were examined visually under a microscope. The zinc chloride was removed from the solid products by washing with water and filtration. The residues were also examined under a microscope, with raw coal for comparison. Representative photomicrographs were taken for more detailed examination. The raw coal and treated coal solids were further examined by X-ray fluorescence spectroscopy to determine possible desulfurization, de-ashing or both.

b. Extraction and Analyses of Extracts

Soxhlet extraction at the solvent boiling point was performed on both the raw and treated coals, using cyclohexane, benzene, and carbon tetrachloride (plus a leaching experiment with methanol), to determine the amount and nature of material that could be dissolved. Any increase in the amount of extractable material after treatment would be an indication of physical or chemical changes in the coal. The extracts were analyzed by nuclear magnetic resonance, infrared, ultraviolet, mass spectrometry, and gas chromatography. The results were also compared with a few higher-temperature extractions obtained in a companion investigation in the same laboratory.

III. EXPERIMENTAL STUDIES

A. Coal and Other Materials

1. Coal Procurement and Preparation

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

The entire sample was mixed and separated into equal 20-lb. portions by ASTM Method D-346. To avoid ageing due to oxidation, and moisture loss, each portion was stored in a sealed plastic bag until allocated for use. To obtain samples for a series of runs, an entire bagged portion was ground in a ball mill to pass a 28 Tyler-mesh screen, and stored in a stoppered glass stock bottle. To reduce the 20-lb. sample to 50-gm. aliquots representative of the original sample, a riffler was employed. The riffler, or sample splitter, is a device which separates a particulate sample into equal portions without causing segregation due to particle size or density, thus assuring a smaller sample which has the same characteristics as the original bulk sample.

2. Analyses of Coal Samples

The coal used for this study was analyzed by Commercial Testing and Engineering Company Chicago (Report 72-23683, November 24, 1974), and by the University's Microchemical Analysis Laboratory (Report of October 7, 1974). The typical seam analysis for the coal used was provided by Wyodak Corporation, the coal supplier. The proximate analysis is given in Table 1 and the ultimate analysis in Table 2.

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

An x-ray fluorescence analysis for higher-atomic-weight elements including trace components performed in LBL by Robert Giauque and his staff is given in Table 3. The ash equivalent to the elemental analysis (calculated as oxides) is seen to be 9.02% with an upper limit of about 10.9% if the analytical uncertainties are all included. Thus the total ash in Table 3 indicated as 13.6 to 14.7% on a dry basis, is not accounted for fully.

3. Purchased Chemicals

Technical grade $ZnCl_2$ powder was obtained from Matheson Coleman and Bell. The chemicals used as additives for the melt were reagent-grade chlorides--ferric, ferrous, cobaltous, nickelous, cupric, stannous, mercuric, antimony, and aluminum--and reagent-grade molybdic acid, tungsten sulfide, mercuric iodide, potassium iodide, tungstic acid, and iodine.

The heterogenous catalysts used were Raney nickel, a 5% platinum supported on alumina from Engelhard Industries, Newark, N.J.

Table 1

Composition of Roland Seam Coal

Proximate Analysis

	C.T. & E.		Wyodak (Typical)	
	As Received	Dry Basis	As Received	Dry Basis
% Moisture	23.76		27.99	
% Ash	10.40	13.64	6.98	9.69
% Volatiles	35.52	46.59	32.65	45.34
% Fixed Carbon	30.32	39.77	32.38	44.97
	100.00	100.00	100.00	100.00
% Sulfur	0.70	0.92	0.65	0.90
Btu/lb	8259	10833		

Table 2

Composition of Roland Seam Coal

Ultimate Analysis

	C.T. & E.		U.C. Microlab
	As Received	Dry Basis	Dry Basis
% Moisture	23.76		
% Carbon	42.02	61.67	59.63
% Hydrogen	4.04	5.30	5.43
% Chlorine	0.00	0.00	0.03
% Sulfur	0.70	0.92	0.60
% Ash	10.40	13.64	14.70
% Oxygen (by difference)	13.35	17.51	18.70
	100.00	100.00	100.00

Table 3

X-Ray Fluorescence Analysis of Dried Wyodak Coal

Element	Amount in Raw Coal	±	Possible Impurity to Ash
Mg	Wt-%< 0.5	---	0.88
Al	1.41	.21	2.66
Si	1.83	.27	3.92
S	0.98	.15	
Cl	0.01		
K	0.07	.01	0.08
Ca	0.85	.06	1.02
Ti	0.12	.02	0.20
V	ppm 120		
Cr	27	7	
Mn	73	6	
Fe	0.20	.01	0.26
Ni	12	1	
Cu	51	2	
Zn	22	2	
Ga	6	1	
As	1.0	.6	
Se	2.3	.5	
Br	1.4	.5	
Rb	9	1	
Sr	208	8	
Hg	7	1	
Pb	10	2	
			9.02 %

Analysis by Robert Giauque and associates, LBL (10-9-74) and reagent-grade metallic tin, aluminum, and zinc powder. The solvents used, reagent-grade benzene, methanol, and "spectroquality" cyclohexane and carbon tetrachloride were obtained from Matheson Coleman and Bell. Gaseous nitrogen "Hi-pure" grade, and hydrogen of standard purity were obtained from Liquid Carbonic in cylinders.

B. Equipment and Procedure

1. Molten Salt Treatment

a. Apparatus

The test assembly consisted of a vessel shown in Figure 7. The reactor was a 1000-ml round-bottom flask fitted with three ground-glass-jointed necks. (Figure 8). Usually the flask was fluted to provide four internal baffles for more effective agitation. (Several runs were conducted in an unfluted flask.) The bottom of the flask was flattened to fit a 3-inch-wide crescent-shaped Teflon stirring paddle, connected to a glass shaft powered by a variable speed motor. A contact thermometer was inserted into a side neck of the flask, and connected to a relay which controlled the flask temperature to within ± 1°C by regulating the power input to a heating mantle through a variable autotransformer. The other neck of the flask was fitted with a gas sparger and a gas vent. Hydrogen (or nitrogen) was introduced into the sparger through regulator valves on the supply cylinders and needle valves in the feed lines. Water in the off gases was refluxed by an overhead water-cooled condenser.

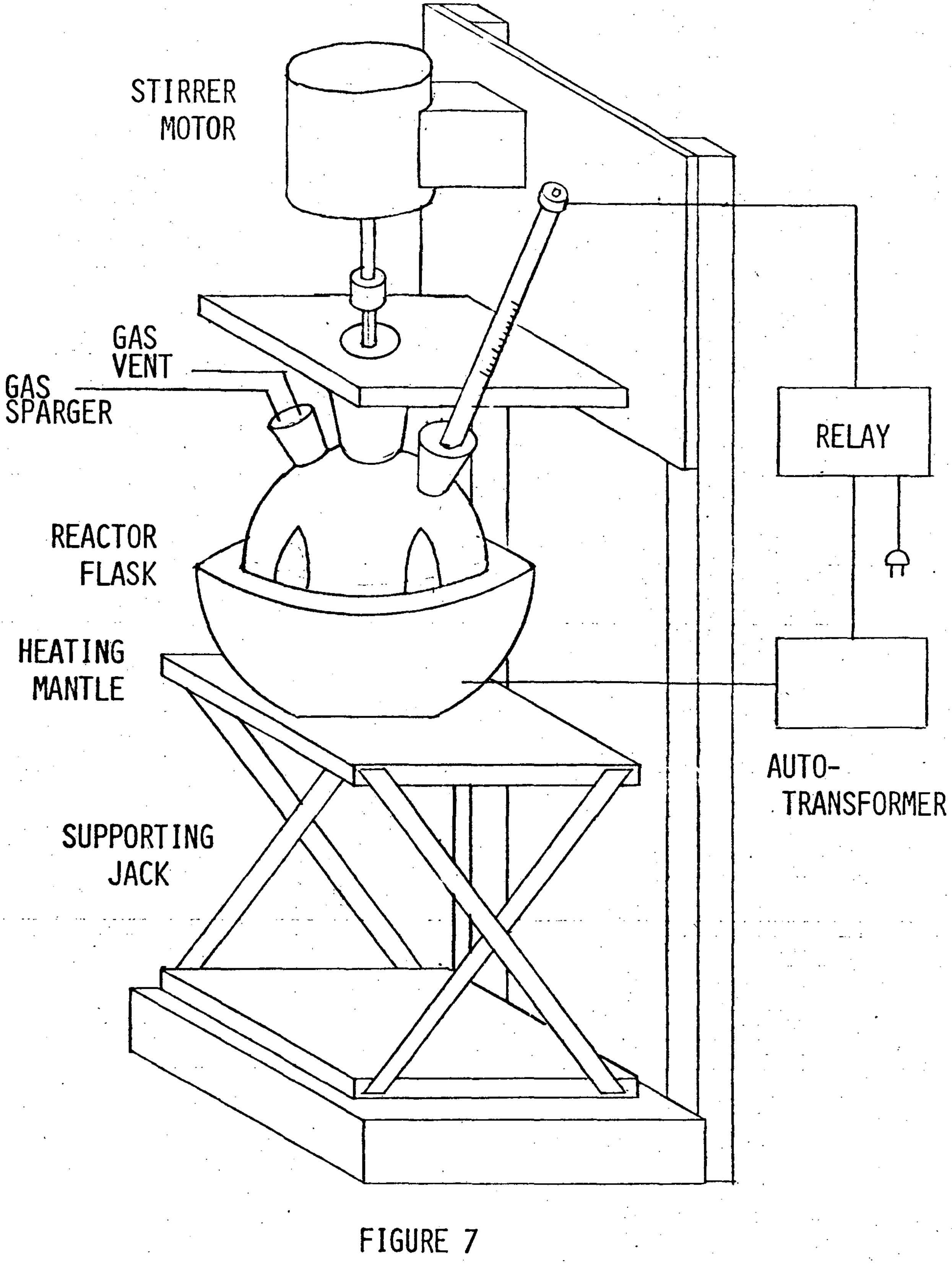


FIGURE 7

REACTOR ASSEMBLY

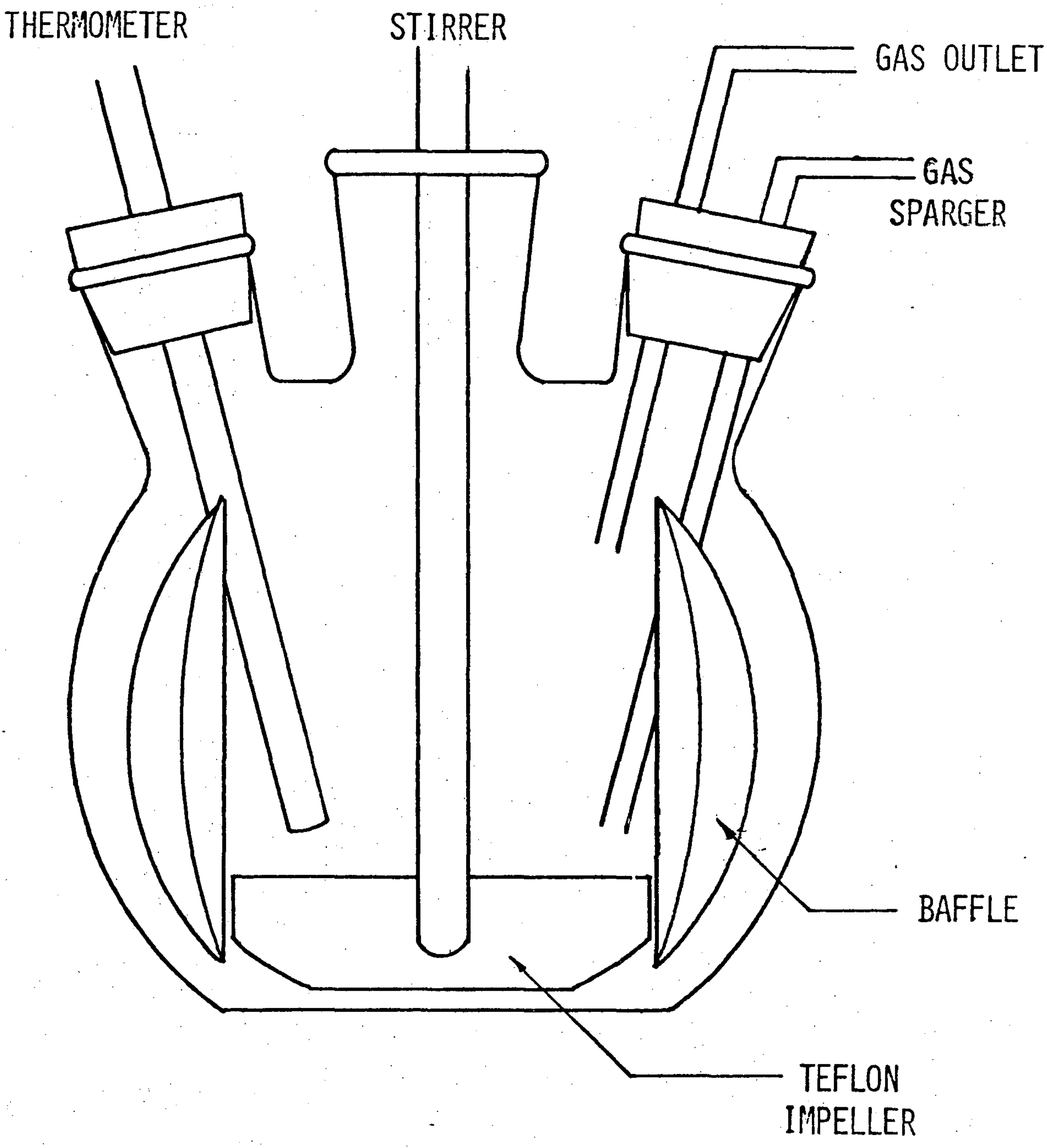


FIGURE 8

REACTION FLASK
AND STIRRER

In some runs (Nos. 9, 11, 26) the off gases were sent through a water-cooled condenser and a cold trap to collect any volatiles liberated. The cold trap consisted of a brine-ice bath at -10°C to collect water, followed by a liquid-nitrogen bath at 77°K, cold enough to liquefy all light organics except methane (which has a vapor pressure of 10 mm of Hg at 77°K, and will not condense at low partial pressures in a gas stream).

b. Properties of Zinc Chloride Melt

The solubility and boiling-point curves of the zinc chloride-water system are given in Figure 9. Anhydrous zinc chloride is highly soluble in water, reaching 81 wt-% of the solution at 25°C and 86 wt-% at 100°C.

Zinc chloride complexes with water to form $ZnCl_2 \cdot nH_2O$ where n can be 4, 3, 2½, 1½, or 1. These complexes are hydroscopic and if exposed to atmospheric moisture will pick up additional water and will melt. Once anhydrous zinc chloride has come in contact with moisture all the water cannot be removed by heating but has to be removed chemically.

The area between the boiling point and solubility curves represents the liquid melt. A constant-boiling mixture may be achieved at any determined temperature and partial pressure of water, by heating the melt from the high-water-content side until it reaches the proper equilibrium content of water and thereafter refluxing the water so that no further loss occurs.

c. Procedure

Experimental runs were conducted in the initial stages of

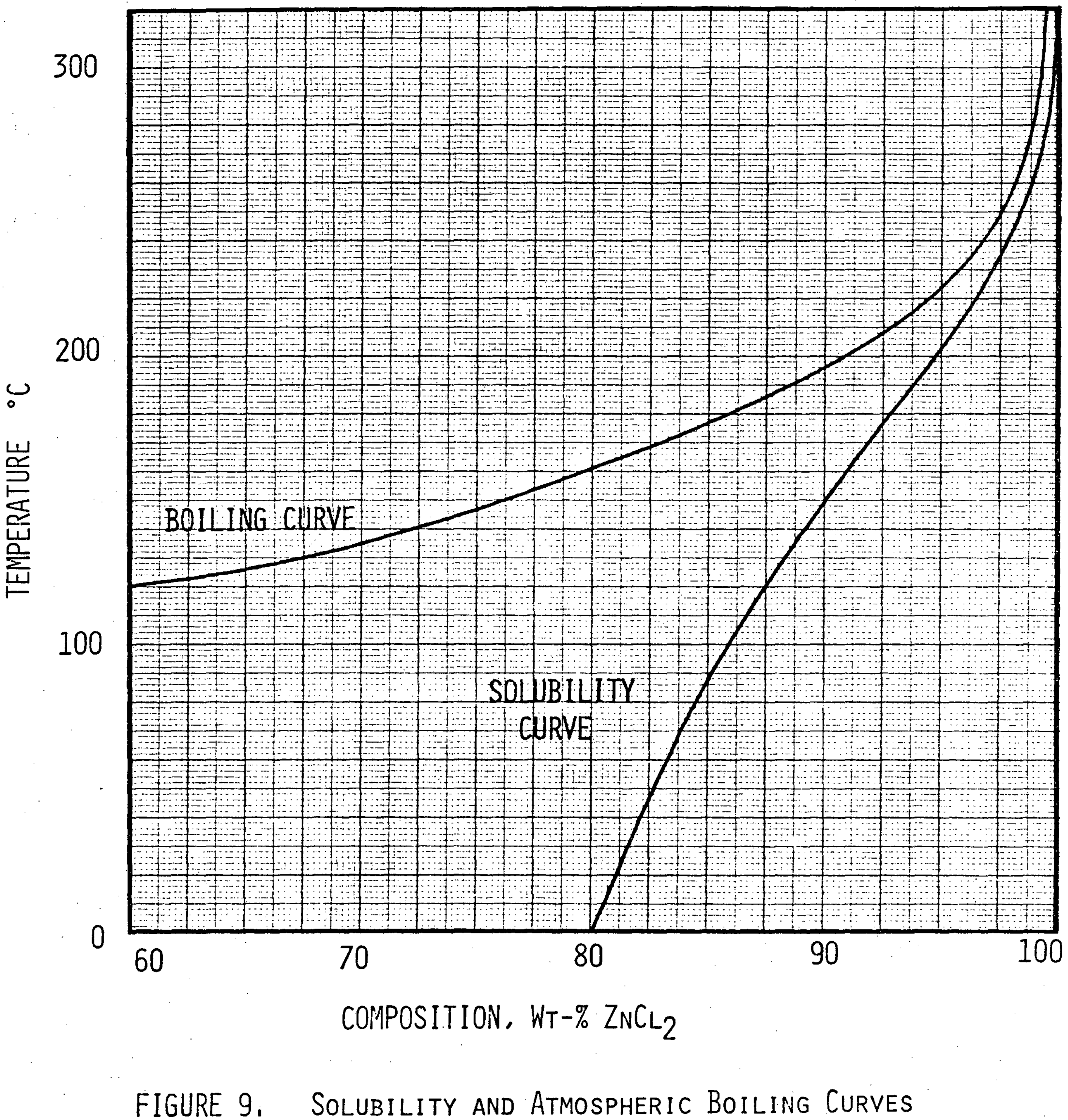


FIGURE 9. SOLUBILITY AND ATMOSPHERIC BOILING CURVES FOR ZINC CHLORIDE-WATER SYSTEM (FROM LINKE, TIMMERMANS)

the study, by mixing 50 grams of coal, 300 grams of salts, and enough water to form a slurry. The mix was introduced into the reactor, the hydrogen flow started, and the heater and stirrer turned on so that the mix could slowly come to reaction temperature. The long heating time required, with difficulty in stirring the slurry, led to early abandonment of this procedure.

The following method was then devised. 300 grams of $ZnCl_2$ was introduced into the flask along with appropriate additions selected as test catalysts. Then 20 to 30 ml. of water was added and the melt was heated to 200°C while stirring. Some water boiled off, until the melt reached its equilibrium concentration of about 6% water. Hydrogen was sparged into the flask to saturate the melt. The sparger was then disconnected, and 50 gm of ground coal was slowly added. Since the coal contained large amounts of water, about 24%, as can be seen from Table 1, much steam was evolved. (If the coal was added too rapidly, the steam did not have sufficient time to escape, and the melt would froth and boil out of the flask.) After the coal was added, the sparger was reinserted and gas sparging resumed.

During each experiment, the stirrer was driven at the speed that gave most vigorous observable splashing of the melt through the gas atmosphere. This treatment was continued until the mixture had been allowed to react for one hour (or less, as noted in Table 4, if the melt became too viscous in the individual experiment). The flask was disconnected and removed from the stirrer assembly, and the product mixture was quenched by pouring it into one liter of cold water. If instead the product was left to stand, the melt would freeze inside the flask and would have to be leached with water, a process requiring several days.

The water-insoluble product, identified here as "melt-treated coal" or MTC, was washed at least three times with 1-liter amounts of water, and vacuum-filtered in a Buchner funnel. The treated coal formed a cake that was dried overnight at 105°C under a vacuum of 20 inches of mercury.

2. Extraction

Ten grams of the dried melt-treated coal was extracted with 200 ml of solvent, at its atmospheric boiling point, for one hour, in a Pyrex Soxhlet extraction apparatus. Dried raw coal was also extracted for reference. Benzene extractions were performed to determine the amount of material extractable, indicating chemical or physical changes. Fifty-ml portions of extract were evaporated in pre-weighed Petri dishes to determine the amounts of extractable material. The remainder of the extract was stored in cork-stoppered bottles for later analysis. Acetone, cyclohexane, and carbon tetrachloride extractions were performed for spectroscopic examinations of the extract, since benzene would tend to interfere with the detection and measurement of extracted compounds.

3. Analytical Methods

Chemical characterization of the feed and products of a reaction for a proposed process is required to deduce the chemical

TABLE 4

Experiments Made Using Wet $ZnCl_2$ and Additives with H_2, Atmospheric Pressure

(Residence Time 60 minutes except where noted)

Run No.	Additives	Weight %	Run No.	Additives	Weight %
1	none	-	17	Zn dust Al shavings	10, 5
2	$SnCl_2 \cdot 2H_2O$	15	18	I_2, KI	1, 0.6
3	$CoCl_2 \cdot 6H_2O$	15	19[a]	Al dust	5
4	$CuCl_2 \cdot 2H_2O$	5	20[d]	HgI	2
5[a]	$CrCl_2 \cdot 6H_2O$	10	21[c]	TiO, Al, Zn, Sn dusts	3, 1, 1, 1
6[b]	$AlCl_3$	10	22	$FeCl_2 \cdot 4H_2O$, MoO_3 (85%)	3, 3
7	$MgCl_3 \cdot 6H_2O$	10	23	WS_4	2
8	$FeCl_3 \cdot 6H_2O$	15	24	$SbCl_3$	10
9	Raney Nickel	1.5	25[b]	$CuCl \cdot 2H_2O$, $CrCl \cdot 6H_2O$	7.5, 7.5
10	Raney Nickel	1.0	26	KI	5
11	Raney Nickel, $SnCl_2 \cdot 2H_2O$	1.6, 15	27	HWO_4, MoO_3 (85%)	1, 1
12	$SnCl_2 \cdot 2H_2O$	15	28	$MnCl_2 \cdot 4H_2O$	10
13	5% Pt on Al_2O_3, $SnCl_2 \cdot 2H_2O$	5, 15	29	$SnCl_2 \cdot 2H_2O$, $CoCl_2 \cdot 6H_2O$	15, 5
14	MoO_3 (85%)	1.5	30	$NiCl_2 \cdot 6H_2O$	10
15	$CoCl_2 \cdot 6H_2O$, MoO_3 (100%)	8.3, 8.3	31[e]	none	
16	$HgCl_2$	10	32[f]	$FeCl_2$	15

a=10 min. b=25 min. c=30 min. d=45 min. e= under N_2 atmosphere. f=$FeCl_3$ used as solvent.

and physical changes that may have occurred as the result of a test treatment. The analytical methods used are mass spectrometry, nuclear magnetic resonance spectrometry, infrared and ultraviolet spectroscopy, and gas chromatography.

C. Experiments Performed

To characterize the interactions of coal with zinc chloride, in relation to its possible use in converting coal to liquid or treated solid fuel, the study proceeded in three phases. First, the coal was contacted with $ZnCl_2$ melt in a glass reaction vessel to examine the properties of the slurry. It was observed that subdivision of coal particles was effected by the molten zinc chloride.

The next phase of the results was concerned with characterization of the treated coal, after recovery from the melt.

The third phase of the study yielded information about extracts from the MTC. An increase in extractables indicate a physical or chemical change in the coal. The chemical nature of the extract is also of interest, since it reflects the chemical structure of at least part of the coal.

The experiments performed are listed in Table 4. Most of the additives used have been tested in hydrogenation of coal or oil in small quantities (usually less than 5%) and have been found to have varying degrees of catalytic activity. The heterogeneous catalysts were tested for their compatibility with the melt. One experiment, Run 32, was conducted using massive amounts of $FeCl_3$ containing 15% $FeCl_2$.

IV. RESULTS AND DISCUSSION

A. Dispersion Behavior During Treatment with Zinc Chloride

1. Observations of Coal in Zinc Chloride Melt

As coal was stirred into hot agitated zinc chloride melt, the original particles started to disperse, and to color the clear melt. In one instance, only a few grains of coal were added which could be observed individually. The grains at first were visible as distinct black particles in the clear melt; but with time they dispersed, and the melt became uniformly brown.

To find out if the presence of hydrogen encourages the dispersion of coal in the $ZnCl_2$, one experiment (run 31) was made in a nitrogen atmosphere rather than in hydrogen. The same behavior was observed, indicating that this step does not require hydrogen.

The coal was not completely dispersed after two hours, as observed by the graininess of the melt. This fraction may disperse into the melt at higher temperatures, or perhaps it may be insoluble ash. The melt may have already been saturated with coal compounds and in this case no more uptake would be observed.

Photomicrographs were taken of individual particles treated by the melt and separated from it. Figure 10a is a photograph of raw coal screened to 28 to 42 mesh. The field width of the picture is 1.6mm. The coal particles are of uniform size with relatively smooth surfaces.

After treatments with zinc chloride at 200°C for one hour, 50% of the coal passed through a 60 mesh screen. The photograph of

Figure 10b is of particles left on the screen. The surfaces are very irregular owing to the etching effect of the melt. Pitting and cracking have led to appreciable size degradation.

After a total contact time of two hours, dispersion is more complete. In this case, 89% of the solid passed through the 60 mesh screen. The residual particles are still more pitted and irregular as shown in Figure 10c. Also the particles left on the screen had much less mechanical strength than the raw-coal particles of the same size. Raw coal could not be broken by crushing between the cover slip and the glass slide under manual pressure (without breaking the cover slip), while the treated coals broke up easily in the same test. Figure 11 is a photomicrograph of residual particles removed from the melt by filtration and washing, and is representative of the particulate material that passed through the 60 mesh screen. Many observable individual particles are in the size range of 10 to 50 microns.

2. Hot Filtration of Coal-Zinc Chloride Suspension

To determine if mechanical agitation was responsible for the degradation of the coal particles, and to observe the dissolution process on a large scale, a single 3/4 inch lump of coal was contracted with the melt. Only minimal agitation was provided manually with a glass stirring rod. Over the course of 40 minutes, the melt turned brown, and fragments broke off the parent coal particle. The melt was diluted with 400 ml of cold

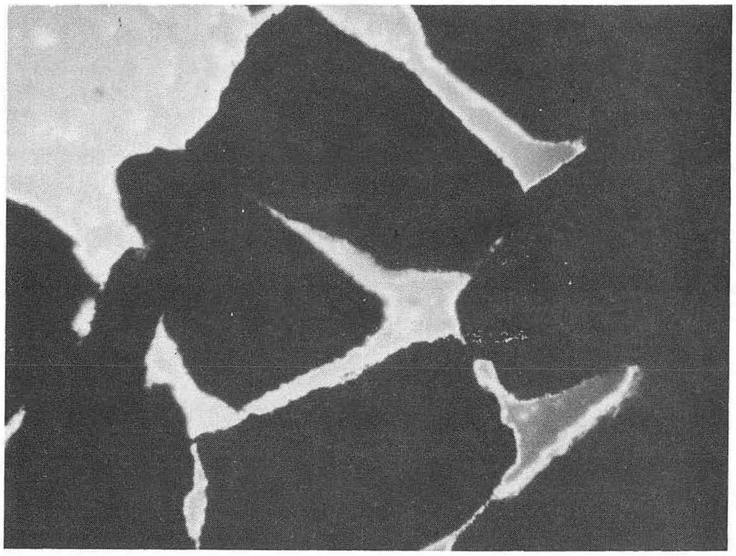


Figure 10a

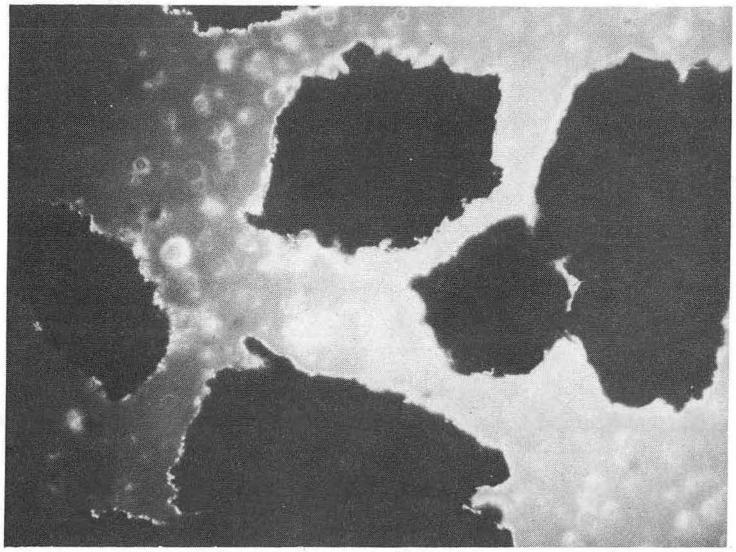


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Figure 10b

Figures 10a,b. Photomicrographs of raw and melt-treated coal. (Field width 1.6 mm. 60X).

a. Raw coal 28-42 mesh

b. Coal After one hour of melt-treatment with zinc chloride at 200°C.

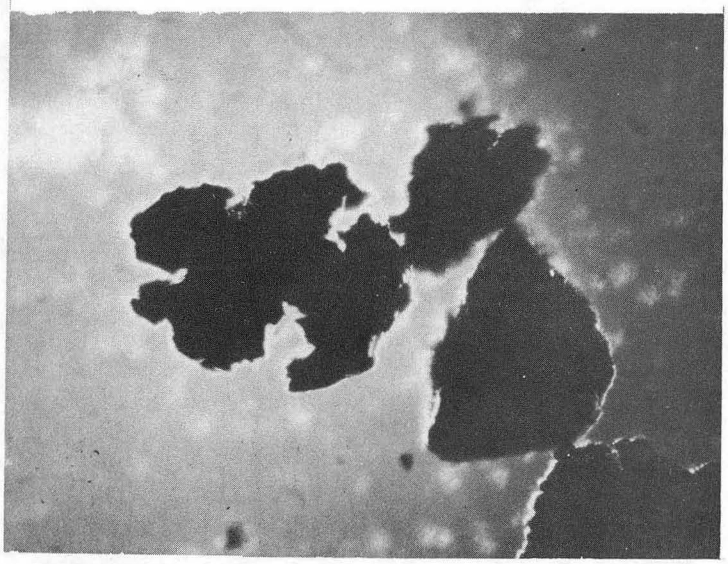

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Figure 10c. Photomicrograph of coal treated for 2 hours with zinc chloride at 200°C. (Field width 1.6 mm. 60X).

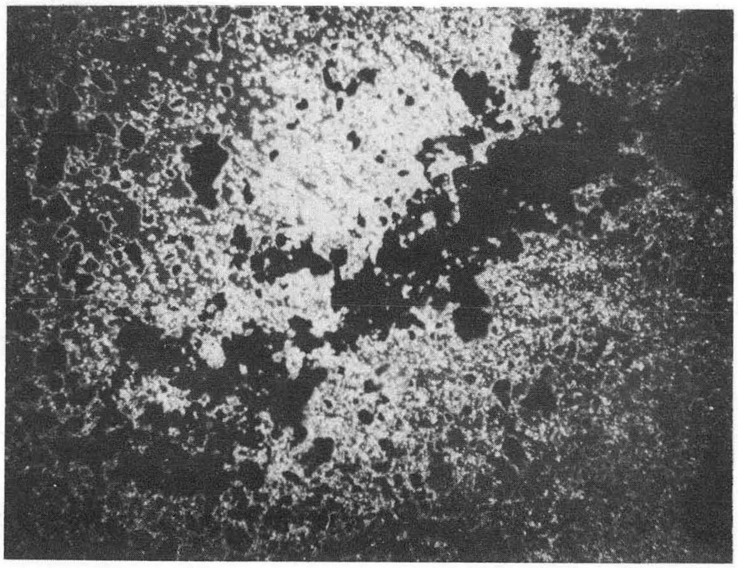

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Figure 11. Photomicrograph of original 28 -42 mesh size (595 to 354 μm) coal treated for 1 hour in $ZnCl_2$ melt at 200° C. (Field width 1.6 mm or 1600 μm. 60X).

water to 100°C, and hot-filtered twice through fine filter paper (Whatman 541, which retains particles greater than 2μm) without losing color, giving evidence of a sub-micron dispersion of coal in molten zinc chloride(S1). The dispersion could be precipitated by diluting the melt 5 to 1 with cold water.

A potentially useful phenomenon for coal processing was observed when the 3/4-inch lump of undried coal was dropped into the hot melt. The sudden temperature rise expanded the moisture in the internal capillary structure of the coal before it could diffuse out. The resulting high internal pressure caused spalling, which greatly enhances the dispersion process (and also the reactability of the coal) by exposing more surface area to the melt.

The 3/4 inch lump of coal did not undergo significant overall size reduction, since spalling is a surface effect. However, a 0.01-inch-thick outer layer was removed within the first minute or two of treatment.

Under more severe conditions of rapid heating, it is possible that bulk fracturing of the coal lumps could occur and give significant size reduction, as a substitute for grinding. One patent(S3) reports that application of heat to flash the volatiles in a coal having an initial size range of 3/32 to 200 mesh gives size reduction to essentially all under 200 mesh (70μm).

For an aged coal, melt treatment may further reduce the initial resistance to mass transfer and chemical attack by quickly removing the less reactive, oxidized outer layer.

Although spalling serves a useful part in accelerating the dispersion process, it appears that liberation of sub-micron size material from solid coal is the result of more specific chemical attack.

3. Photomicroscopy of the Zinc Chloride Melt

To investigate further the dissolution process, microscopic studies of the melt were undertaken. Coal ground to 20-50 mesh (841 to 297μm size) was treated for 1 hour with zinc chloride. Samples from the melt were placed on hot microscope slides and spread with a cover glass. The cooled slides were viewed with a microscope under polarized light at 1600 magnification. Photomicrographs of representative portions of the melt were taken, reproduced here as Figures 12a and 12b.

As the slides cooled, the melt solidified and cracked (figures 12a, b) forming dark "islands" and clear brown fissures. The melt has a uniformly dispersed brown color with a certain graininess caused by larger particles of coal. At the extremes of the "islands" of the melt, especially in the lower right corner of Figure 12b, the melt becomes thin and transluscent; this indicates that the coal is dispersed so finely that its size range (well below 1μm) is not yet known. Even the grainy portions have sizes less than one micron in diameter, a size range absent in the untreated coal.

This effect is even more pronounced when one visually

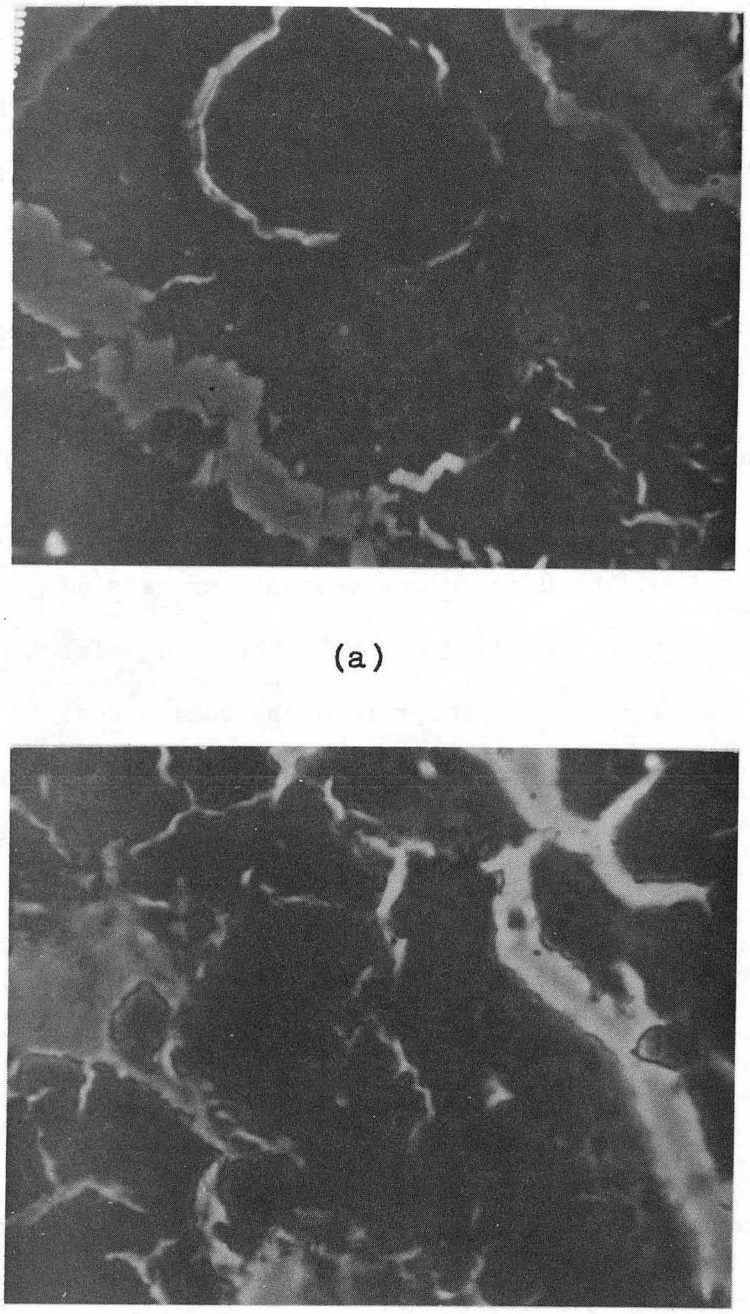

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Figure 12a, b Photomicrographs of a coal-zinc chloride melt (Field width 55 μm, 1600X).

examines large sections of thinly spread melt without polarized light. (Polarization creates the sharp dark line at the edges of the melt.) All these results indicate that considerable size reduction of the coal has taken place.

B. Chemical and Physical Characterization of Melt-Treated Coal

To determine more fully the changes caused by melt treatment, the treated coal was separated from the zinc chloride by washing, filtration, and drying. (It is recognized that nonaqueous separation would be used in any economic process.)

In characterizing the MTC, the first effect noted was that MTC has a different color than raw coal. Coal in coarse form, greater than 100 mesh, is black; however, when it is ground increasingly fine, its color turns reddish-brown. Exposure to the melt had the same effect on the color of the coal, the recovered and dried MTC being a brown cake.

The second effect noted was that the MTC cake had lost most of the mechnical strength displayed by the original coal. A few turns in a mortar with a pestle reduced the cake to a very fine powder (under 200 mesh), while the same treatment did not crush the raw coal appreciably. From the cake it was not possible to determine how finely the coal had been dispersed into the melt, before agglomerating during cooling and filtration.

1. X-Ray Fluorescence

The melt-treated coal (MTC) from three runs was analyzed by x-ray fluorescnece to determine the ash and sulfur content. Run 1 was selected because it contained no additives; Run 18, because it gave the highest amount of extractables; and Run 22 to examine the removal of metal ions by an acid wash. The results are given in Table 5.

The ash in coal is composed mainly of compounds of aluminum, silicon, and calcium. Treatment by zinc chloride substantially eliminates the calcium, and reduces the iron; but it leaves the aluminum and silicon unaltered, indicating that very little de-ashing is taking place.

The concentration of sulfur in the coal was not reduced by the zinc chloride melt. However, the odor of H_2S was detected when the MTC was washed with dilute HCl to remove $ZnCl_2$. Two analyses were made on Run 18 to see if the H_2S liberated during the acid wash may have readsorbed onto the coal surface. A dilute caustic wash and reacidification was unsuccessful in reducing sulfur content, indicating that H_2S did not adsorb. Because of the near-identity of the two analyses, only the one without caustic wash is shown.

2. Extraction Behavior

To compare further the properties of MTC and or raw coal, different samples were extracted according to a standard

Table 5

X-Ray Fluoresence Analysis of Melt-Treated Coal

Element		Raw Coal	±	Run 1		Run 18		Run 22	
Mg	Wt-%	< 0.5		< 0.5		< .4		-	
Al		1.41	±.21	1.32	±.20	1.29	± .21	-	
Si		1.83	.27	1.95	.30	1.91	.29	1.5-2.5	
S		0.98	.15	0.94	.14	1.06	.16	-	
Cl		< 0.01		1.07	.16	0.73	.11	0.5-1.0	
K		0.07	.01	0.08	.01	0.08	.02	-	
Ca		0.85	.06	0.031	.003	0.026	.005	-	
Ti		0.12	.02	0.13	.01	0.12	.01	0.11	.02
V	ppm	<120		<65		<67		-	
Cr		27	7	96	5	22	3	-	
Mn		73	6	62	3	7	2	-	
Fe		0.20	.01	0.093	.004	0.16	.01	0.12	.02
Ni		12	1	9	1	11	2	-	
Cu		51	2	62	3	18	2	-	
Zn		22	2	0.14	.01	.052	.004	0.067	.006
Ga		6	1	6	1	5	1	-	
As		1.0	.6	1.5	.6	<1		-	
Se		2.3	.5	3.2	.5	2	1	-	
Br		1.4	.5	2.1	.5	7	3	-	
Rb		9	1	9	1	9	2	-	
Sr		208	8	106	4	22	5	19	3
Mo		-		-		-		2.3	.5
Hg		7	1	31	2	.028	.005	.011	.002
Pb		10	2	4	1	5	2	-	

Due to the high concentration of Mo in Run 22, the concentrations of the trace elements were not determined.

procedure. Fifty ml samples of the benzene extracts from MTC and raw coal (see Secion III. B. 2.) were dried in a hood, in preweighed Petri dishes for two hours, to evaporate the benzene. The residue was weighted to determine the amount of material extracted from the coal. Table 6 compares the effects of the additives on the extractability. The most extractable MTC's were obtained by using zinc chloride melts with potassium iodide and iodine, Raney nickel and stannous chloride, and magnesium chloride. The percent extractables are 7.0, 3.8, and 3.5 wt-%, respectively. For the raw coal, by contrast, the benzene-extractable content is 0.5 wt-%; zinc chloride with no additive gave 2.3 wt-%.

The increased production of benzene-extractables seems to require the presence of a catalyst and hydrogen. The catalytic effects of iodine have been observed in coal hydrogenation (F1). Raney nickel is a well-known hydrogenation catalyst, which indicates that conventional commercial catalysts may enhance the dissolution of coal, even though they cannot penetrate into it. The magnesium chloride activity is promising because it is the least expensive additive on the list; it may perhaps replace zinc chloride as the carrier melt in future studies.

The high benzene-extractability caused by Raney nickel gives further evidence that the coal is dispersing, and therefore zinc chloride is a vehicle in which the catalyst and the hydrocarbons may react. Stannous chloride may have promoted the chemical

TABLE 6

Percent of Benzene-Extractables in Melt-Treated Coal

(Residence Time 60 minutes in $ZnCl_2$ except where noted*)
(Percent of Extract on moisture-and-ash-free basis**)

Run No.	Additives	Weight %
1	none	2.3
2	$SnCl_2 \cdot 2H_2O$	0.9
3	$CoCl_2 \cdot 6H_2O$	1.3
4	$CuCl_2 \cdot 2H_2O$	0.6
5[a]	$CrCl_2 \cdot 6H_2O$	1.9
6[b]	$AlCl_3$	$AlCl_3$ decomposed
7	$MgCl_3 \cdot 6H_2O$	3.5
8	$FeCl_3 \cdot 6H_2O$	0.1
9	Raney Nickel	1.4
10	Raney Nickel	1.0
11	Raney Nickel, $SnCl_2 \cdot 2H_2O$	3.8
12	$SnCl_2 \cdot 2H_2O$	0.7
13	5% Pt on Al_2O_3, $SnCl_2 \cdot 2H_2O$	2.1
14	MoO_3 (85%)	1.1
15	$CoCl_2 \cdot 6H_2O$, MoO_3 (100%)	2.6
16	$HgCl_2$	2.6
17	Zn dust Al shavings	0.6
18	I_2, KI	7.0
19[a]	Al dust	1.0
20[d]	HgI	1.1
21[c]	TiO, Al, Zn, Sn dusts	1.1
22	$FeCl_2 \cdot 4H_2O$, MoO_3 (85%)	2.8
23	WS_4	1.1
24	$SbCl_3$	1.6
25[b]	$CuCl \cdot 2H_2O$, $CrCl \cdot 6H_2O$	2.1
26	KI	3.4
32	$FeCl_2$	0.1

a=10 min. b=25 min. c=30 min. d=45 min.
e=under N_2 atmosphere.
*Runs correspond to Table 4.
**Assumed 15% ash in treated coal and 175 ml of original 200 ml benzene recovered with extract.

activity of the melt, or may have only lowered the viscosity to facilitate coal dispersion.

C. Characterization of Extracts of Melt-Treated Coal

The extracts of raw coal and MTC from Runs 18 and 22 which had I_2 + KI and $FeCl_3$ + MoO_3 respectively as additives were studied, because of the larger amounts of benzene-extractable material obtained in these particular MTC experiments. In all cases the extracts recovered from both benzene and CCl_4 were wax-like solids with a melting range of 65 to 70°C, as measured in a Thiele melting-point apparatus. For studies of the extract properties, CCl_4 was chosen because it does not interfere with nmr and UV spectra. The dried benzene-extractables were soluble in CCl_4. The CCl_4 extractions were expected to be similar to the benzene extractions, as was verified later by nuclear magnetic resonance measurements, because of the generally similar solubility behavior of the two solvents. (The solubility parameter for C_6H_6 is 9.2 $(cal/cm^3)^{\frac{1}{2}}$, and for CCl_4 is 8.6, while coal extracts range from 9.3 to 10 (A2).)

1. Mass Spectrometry

The wax residue, after evaporating the carbon tetrachloride, was analyzed by both low- and high-resolution spectrometry. The low-resolution spectra for runs 18 and 22 contain similar compounds as shown in Appendix I.

The low-resolution spectra showed abundant high mass ions at mass numbers of 424, 396, and 368. From high-resolution measurements, the exact masses were found to be 424.4274 and 396.3965 corresponding to molecular formulas of $C_{28}H_{56}O_2$ and $C_{26}H_{52}O_2$, having masses of 424.4288 and 396.3980 respectively, and suggesting $C_{24}H_{48}O_2$ for the next lower peak.

Another peak at mass 361 (for Run 22) is indicated to have a lower H/C ratio, corresponding to a formula such as $C_{26}H_{33}O$ or $C_{25}H_{29}O_2$. (Other significant masses are 382 and 397.) These results suggest the presence of aromatic and alicyclic groups in the extract. Such materials seem to be present in smaller amount than the group having masses 396 ± 28, but no estimate can be made of their contributions to the total composition.

The mass spectra of wax residue showed a large proportion of ions with mass numbers under 120, as expected from fragmentation in the electron beam. Such compounds in the original extract in large proportions, would make it liquid and also relatively volatile. It appears, therefore that more of this low-molecular-weight material comes from the fragmentation of larger molecules inside the spectrometer. To verify this conclusion, carnauba was (mol. wt. 750, m.p. 70°C) was also used to obtain a spectrum. Qualitatively, its spectrum was very similar to that of the extract, involving again a large intensity of species below 120.

Two mass spectra were also run on extracts from raw coal, prepared with different solvents: tetralin (by D. Draemel), and methanol (room-temperature leaching by L. Jossens). The principal ions observed for each type of extract are shown in Table 7. The results suggest that the melt treatment alters the CCl_4 extract

TABLE 7

Characteristic Mass Numbers in Mass Spectrographs

On Extracts From Roland Seam Coal

Common to All Extracts	CCl_4 Extract			Tetralin (Raw Coal)	Methanol (Raw Coal)
	Raw & MTC	Raw Coal	MTC		
(1)		(Add 1)	(Add 1)		
39	73	60*	44*	45	67*
41*	83*	87	109	77	81*
43*	85	112*	125	91*	153
55*	97*		135**	115*	165
57*	111		235**	116*	195
69*	185		368	127	235
71*	210		382	128*	239
93	241		397	129*	252
95*	255			149*	
121	269			165	
141	396			199	
145	424				
163					
177					
191					

*Major Peaks **Run 18 Only

spectrum significantly, and that the spectra from tetralin and methanol are even more different. Thus it may be possible to obtain a larger extent of extraction with different solvents in succession than with any one pure solvent or solvent mixture.

2. Nuclear Magnetic Resonance Spectroscopy

a. CCl_4 Extract

Since the extract was probably a set of related compounds, an attempt was made to elucidate its characteristic structures. Nuclear magnetic resonance of the CCl_4 extract with tetramethyl silane as reference (Figure 13) showed four peaks which were compared to standards in the literature (D4).

The resonance at δ 0.6 is characteristic of the methyl group attached to a saturated hydrocarbon ($CH_3-\overset{|}{\underset{|}{C}}-$). The peak at δ 0.97 may indicate the same group; or it may also show R_2NH or $CH_3-\overset{|}{\underset{|}{C}}-(\overset{|}{\underset{|}{C}})_n-X$ $(n \geq 1)$ where X can be Cl, Br, I, OH, OR, C=O, or N. If the compounds identified by high-resolution mas spectra were actually predominant, X could only be OH, OR, or C=O. The peak at δ 1.3 shows either RSH or most likely $-CH_2-$. Finally, the peak at δ 1.93 could be given by $CH_3-\overset{|}{C}=\overset{|}{\underset{|}{C}}$, $CH_3-\overset{|}{C}=O$. The lack of aromatics, which resonate around δ 7, is very surprising, and had to be confirmed. The spectra do not preclude saturated cyclics such as cyclohexane, which resonate near δ 1.45.

b. Volatiles from $ZnCl_2$ Treatment

The cold trap used in Runs 9, 11, and 22 collected volatiles given off from the melt. This material accumulated on the

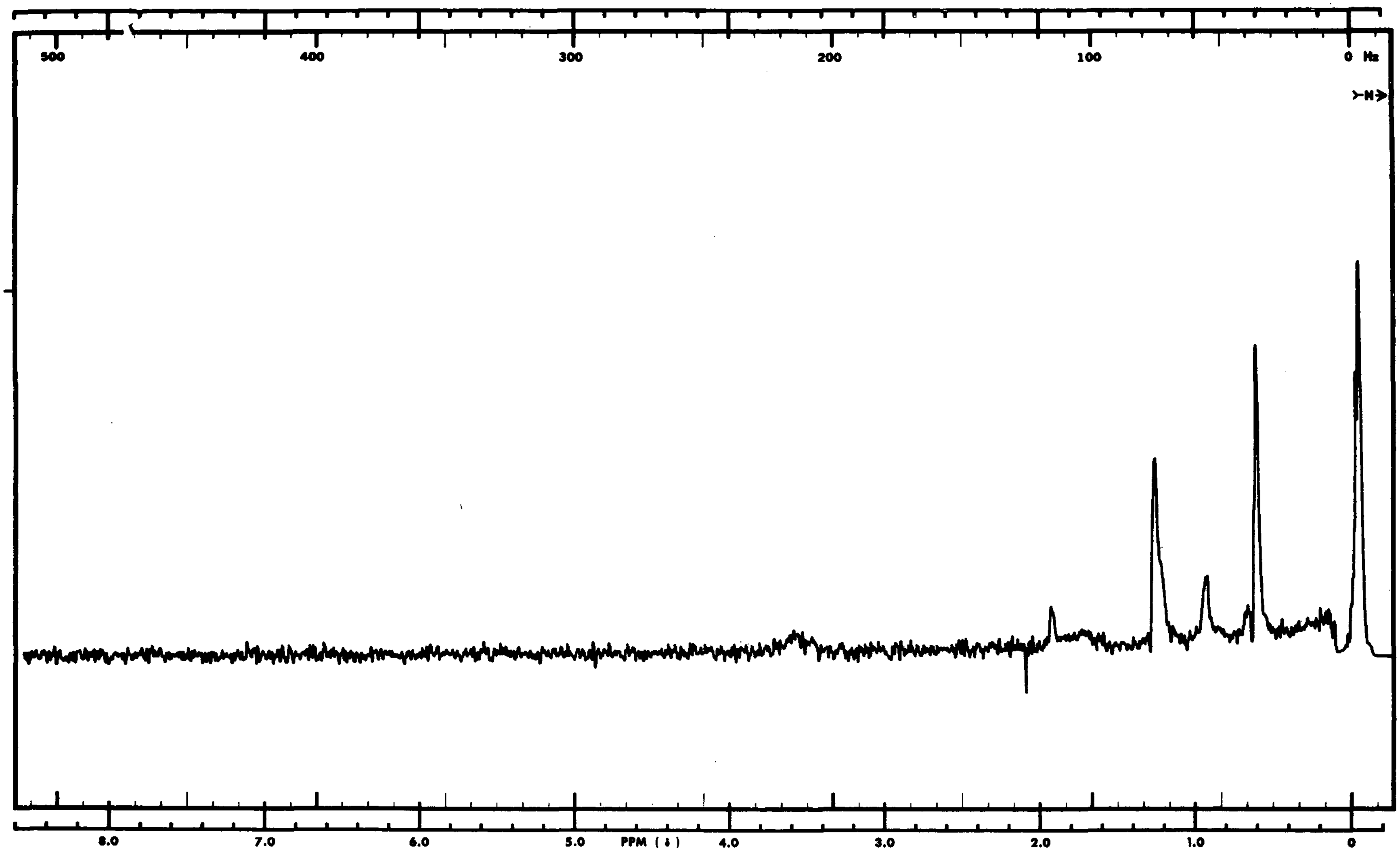

Figure 13. Nuclear Magnetic Resonance Spectrum of CCl_4 Extract of Melt-Treated Coal

condenser as a grease or wax. Only a small amount was removed by dissolving it in benzene. The benzene was evaporated, and the residue was redissolved in CCl_4. An nmr spectrum is given in Figure 14. It differs from the nmr of the extracts by having one less peak at δ 2.0. The peaks are also shifted upfield slightly.

The peak at δ 0.5 may be a very dilute ROH or R_2NH functional group. The peak at δ 0.98 represents a saturated $CH_3\text{-}\overset{|}{\underset{|}{C}}\text{-}$ resonance or $CH_3\text{-}\overset{|}{\underset{|}{C}}\text{-}\overset{|}{\underset{|}{C}}\text{-}X$ where X is the same as above. The final peak at δ 1.55 can be caused by both the hydrogen on a saturated carbon $(\text{-}\overset{|}{\underset{|}{C}}\text{-}H)$ and $CH_3\text{-}\overset{|}{\underset{|}{C}}\text{-}X$.

Again the lack of aromatics is evident. The nmr of the volatiles closely resembles the spectra of the extracts, suggesting that some of the lighter portions of the extract may boil off or evaporate during melt treatment of the coal.

3. Infrared Spectroscopy

The solid extract was melted onto a NaCl window, and the infrared spectra was measured as shown in Figure 15. The spectrum is calibrated by a .05 mm polystyrene film absorbing at 1028 cm^{-1}. The spectra confirmed the nmr results; there are no aromatics, ethers, alcohol, or carboxylic acid. The major absorbance peaks can be attributed to C-C and C=O structures.

There are five major absorbance peaks on the spectrum at 3.3, 5.8, 6.8, 13.7, and 13.9 which give useful information for discerning the characteristic structures of the extract. The peak at 3.3 μm wavelength is caused by C-H streching in alkene, alkane,

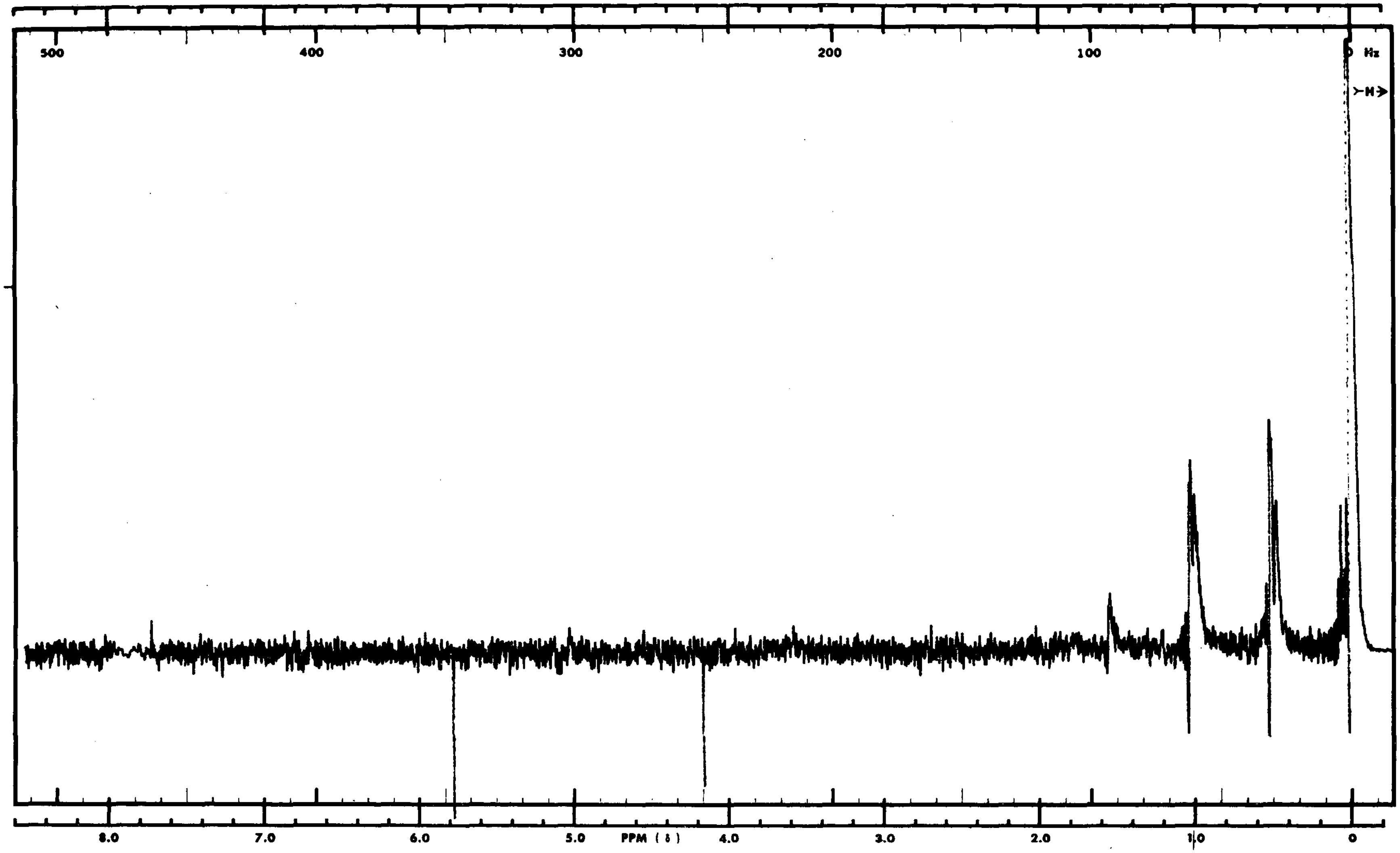

Figure 14. Nuclear Magnetic Resonance Spectrum of Volatiles from Zinc Chloride Treatment

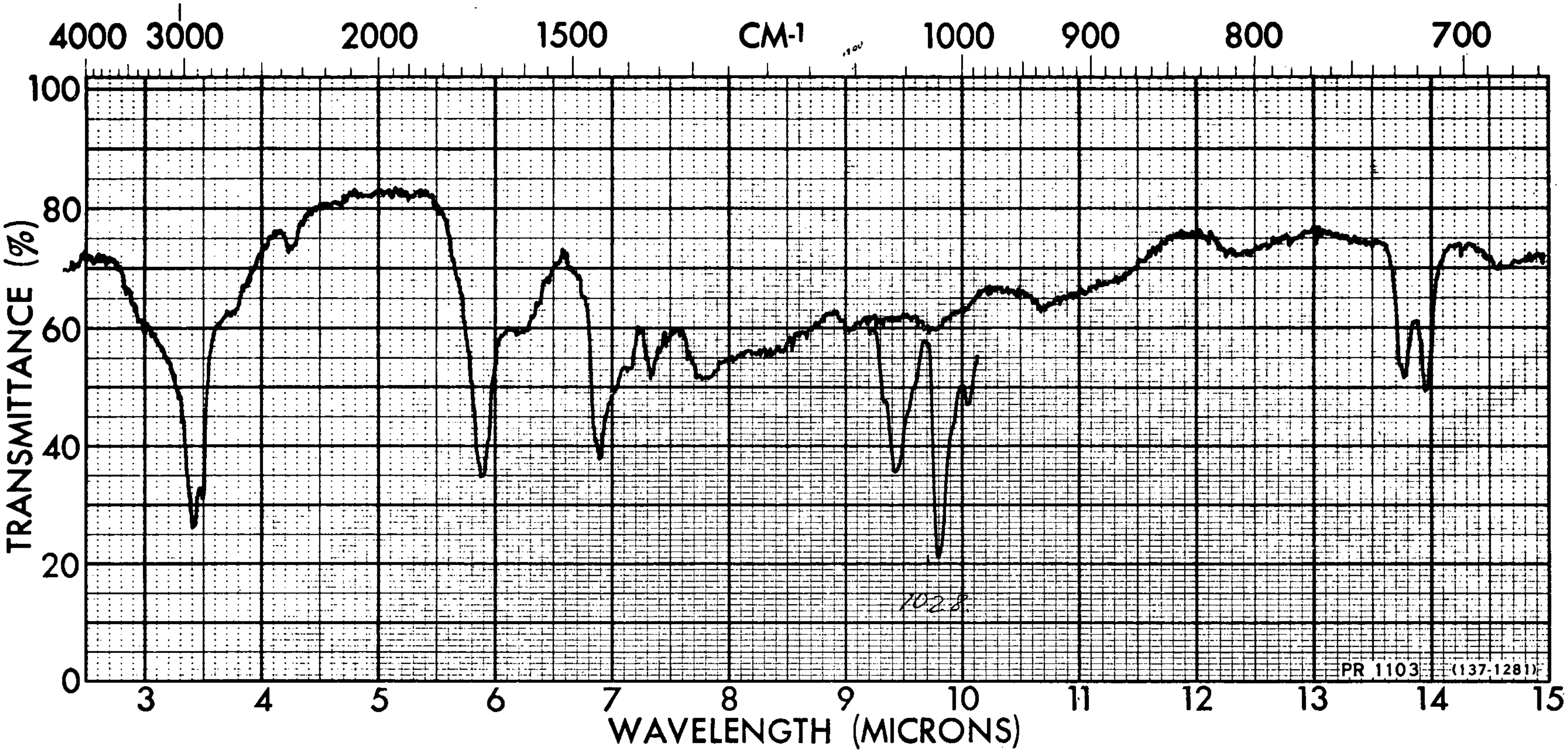

Figure 15. Infrared Spectrum of CCl_4 Extract of Melt-Treated Coal

carboxylic acid, and aromatic structures. The absorbance at 5.8 μm may be attributed to C=O stretching in carbonyl groups. Alkanes absorb strongly at 6.8 μm due to C-H bending modes of vibration. The final two peaks at 13.7 and 13.9 are produced by C-H rocking in longer alkanes, $H(CH_2)_nH$ where n is greater than 3, or in aromatics. Due to the multiplicity of the compounds in the extract, the small peaks in the "fingerprint" region of the spectrum, 7 to 11 microns, cannot be identified with certainty.

The value of spectra lies in their negative evidence. If the spectrum does not contain an absorbtion peak typical of a certain functional group, the molecules do not contain that group. On this basis several structures are precluded: aromatic (14 to 15), alcohols (2.9), ethers (9.5),and carboxylic acids (8.5-9.5). The weak absorbance at these wavelengths indicates that only minor amounts of such structures could be present. Under these constraints, with the nmr evidence, and using the empirical formula derived from mass spectral data, the extract compound with an empirical formula of $C_{28}H_{56}0_2$ appears to be an aliphatic ester.

4. Ultraviolet Spectroscopy

An ultraviolet spectrum of the CCl_4 extract was obtained. The sample absorbed so strongly that the solution had to be diluted 20 to 1 from the original extraction concentration. The spectrum showed a broad peak at 2600Å wavelength which can be caused by the double bond in a carbonyl groups, or by aromatics. Since aromatics are largely absent in the infrared, nmr, and mass spectrometry, this absorption provides evidence for large concentration of carbonyl.

5. Gas Chromatography

Because indications were found from mass spectrometry that the CCl_4 extract of MTC was not a single compound, a sample of the extract of Run 18 was analyzed by gas chromatography, by Amos S. Newton in L.B.L.

A 5 μl sample of 2 wt-% solution of MTC extract in benzene and chloroform was injected into a 6 foot long 1/4 inch diameter column filled with 5% Dexsil-300 on 60-to-80- mesh Chromosorb-W. The column was operated at 300°C, with the flame-ionization detector at 350°C and the collector at 300°C. Both isothermal and temperature-programmed runs were made, the latter from 100 to 250°C at 6 deg/min. Sixteen peaks were observed, indicating that at least 16 compounds comprise the MTC extract. Calculations showed that only 10% of the injected sample was eluted, indicating that more compounds may have been retained by the column.

6. Conclusions Regarding the Nature of Extract

The extracts of MTC, recovered in amounts up to 7.0% is a yellowish waxy substance with a melting range of 65 to 70°C. It contains a multiplicity of compounds that were identified by infrared spectroscopy as mostly aliphatic esters with smaller amounts of aromatics and alicyclic groups as determined by low-resolution mass spectroscopy. The mass spectra of the extracts of MTC from Runs 18 and 22 are similar to the spectrum of the extract from untreated coal, indicating the same types of materials are being extracted but the untreated coal is much less extractable.

In contrast, methanol leaches material from raw coal, part of which is insoluble in CCl_4 and has a lower maximum molecular weight of 276. (See Appendix II for mass spectrum.) This effect can probably be accounted for by the differences in polarity and thus in solubility parameters. The polarity of the methanol enables it to extract compounds not found in the benzene and CCl_4 extracts.

V. SUGGESTIONS FOR FUTURE WORK

A. General Considerations

This study, the beginning step of an extensive program of coal liquefaction research, was initiated to secure data on molten salt-coal systems that would give direction to subsequent studies. Three areas of research are suggested by the results. Future work should include (1) further identification of the MTC extract, (2) methods to increase the reactivity of the zinc chloride melt with coal, and (3) investigation of other melt systems.

B. Identification of the Chemicals Comprising the Extract

Characterization of the extract of melt-treated coal has been advanced to the extent that some of the properties, including dominant chemical structures, have been identified. This work should be extended because of possible industrial utilization of such an extract. One appropriate procedure for continued study is separation of the compounds by gas chromatography, and analysis by mass spectrometry, nmr, and IR.

Deeper extractions are needed to indicate the upper-limit amounts of the present kind of extract, and also to yield information about a larger portion of the coal. Such extractions can be achieved by longer reactions times and more severe conditions, both for melt treatment and subsequent extraction.

Kinetic studies of the dissolution of coal were not included in the exploratory stage work, but should give valuable information. Two areas should be studied, the rate of extract formation during the melt treatment, and the rate of coal-particle break-up. Historically the rate of extraction has been thought to depend on new surface area exposed by grinding, but the dissolution process seems also to involve chemical interaction with the melt. Comparison of rates at different temperatures may show whether the extraction rate depends mainly upon diffusional transport or upon chemical reaction.

The potential economic value of the extract, together with size reduction and some removal of ash and sulfur, could even justify the use of molten-salt treatment as the first step in coal gasification.

C. Increasing the Activity of the Zinc Chloride Melt

The increase of benzene-extractibles from coal by melt treatment indicates that the coal is being altered physically, chemically, or both; but the low yield suggests that more could be accomplished. The activity of the melt can be increased in several ways: suitable catalysts or promoters may be added, the treatment may be run at more severe conditions, or an organic solvent (possibly a hydrogen donor) may be added to effect extraction simultaneously with melt treatment. The most effective process might involve all these conditions in a three-phase reactor of solid coal, liquid organics, and melt. Combination experiments of these variables performed in parallel and series runs would be an efficient way to screen the effect.

More complete physical characterization of MTC, in comparison with raw coal, is also important field for measurement.

D. Investigation of Other Melt Media

In this study the medium chosen to treat coal was zinc chloride, since it was a Lewis acid which had been shown to be effective for hydrogenating coal and coal extract under more severe conditions. Several other compounds could be used, some of which might be found to have distinct advantages by being more reactive, less expensive, or both. Two compounds worth investigating are ferrous chloride and magnesium iodide, both of which have adequate water solubility. The magnesium iodide has the potential of being reactive due to the hydrogenation capacity of iodine, while ferrous chloride may be more compatible with catalysts than zinc chloride previously used. Both the ferrous chloride and magnesium iodide would be easier to recover from the coal after treatment, because their melts would contain higher percentages of water.

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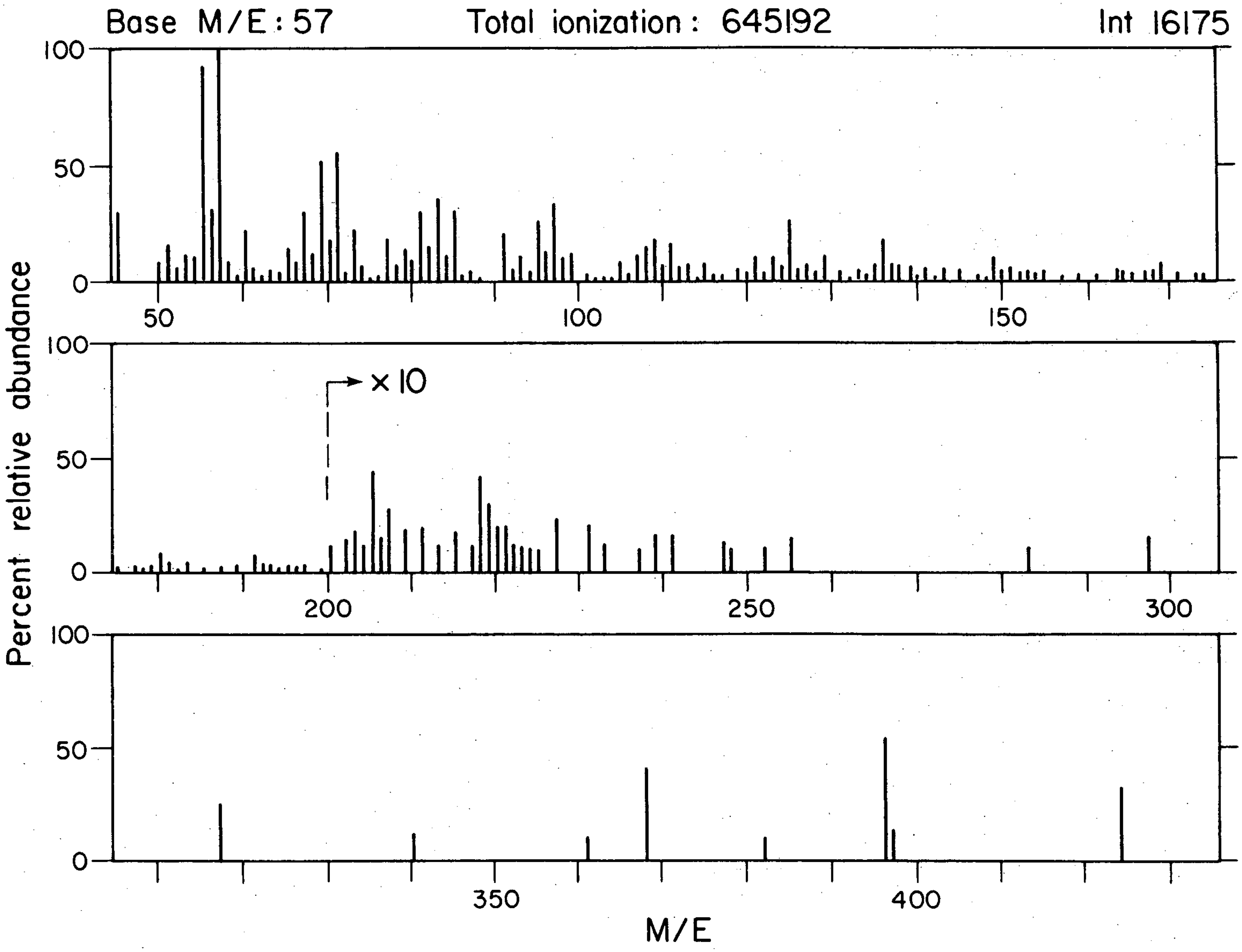
APPENDIX

Mass Spectrometry Data



XBL 756-3304

Fig. 16. Low resolution mass spectrum of run 22.

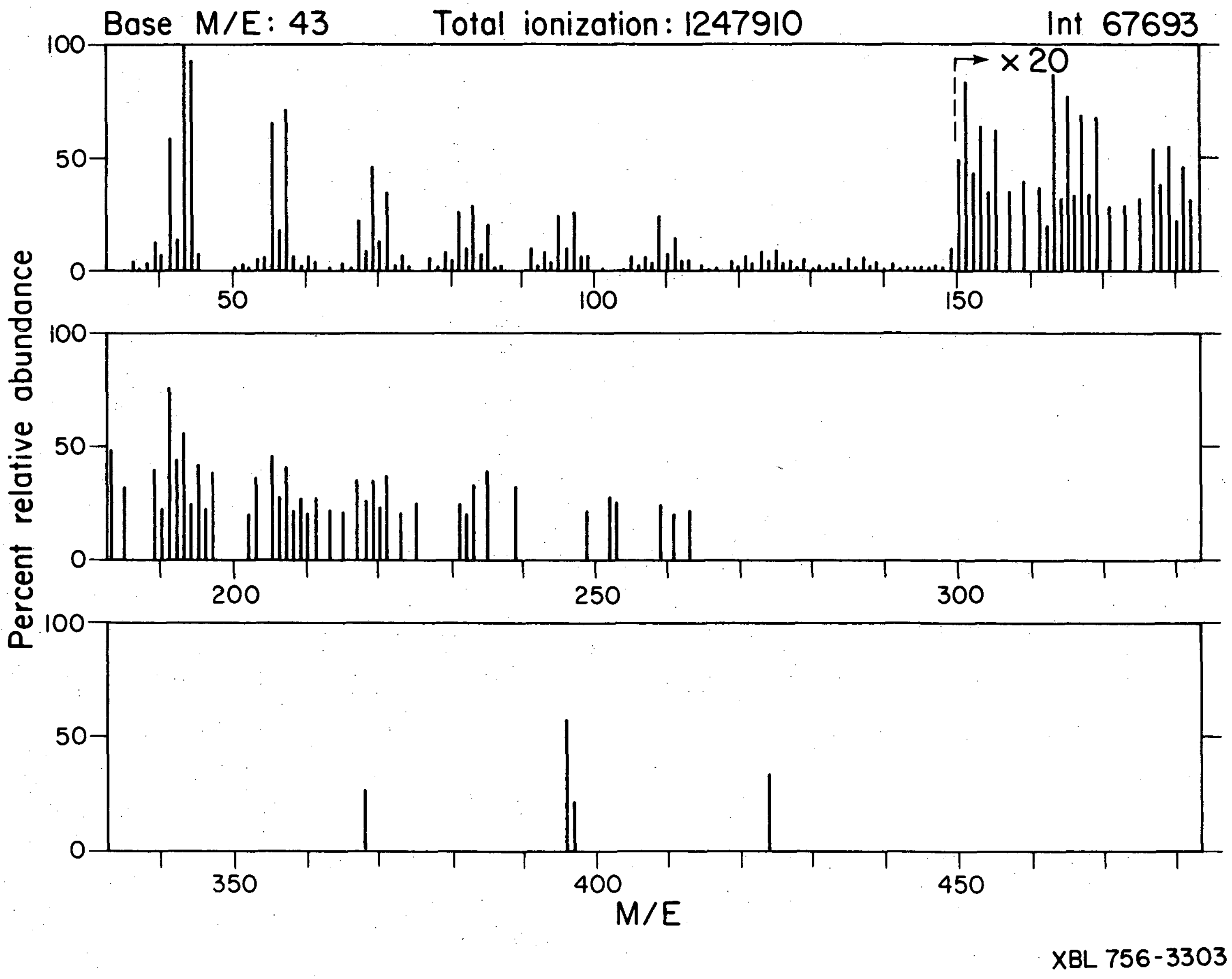


Fig. 17. Low resolution mass spectrum of run 26.

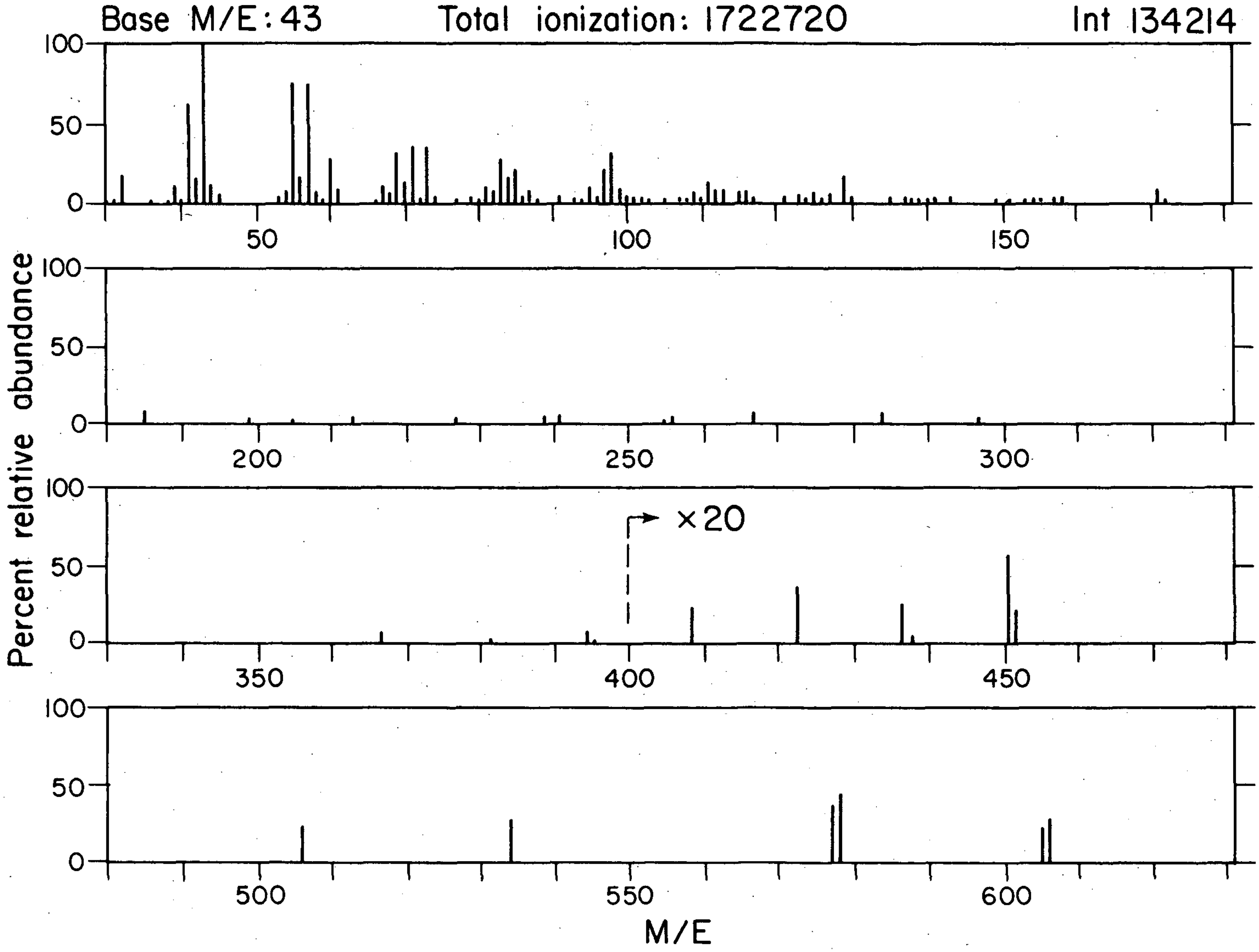


Fig. 18. Low resolution mass spectrum of carnauba wax. XBL 756-3305

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