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Hydrogenolysis Of A
Sub-Bituminous Coal With
Molten Zinc Chloride Solutions

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

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ABSTRACT

Hydrogenolysis of undried Wyodak sub-bituminous coal, Illinois, No. 6 bituminous coal, and solvent-refined coal (SRC) with liquid zinc chloride containing water and certain additives has been studied at the relatively mild conditions of 250°C and hydrogen partial pressures less than 600 psia. Various inorganic and organic additives have been examined with regard to possible catalytic activity.

The extractibility of Wyodak coal in pyridine increased from 12.8 to 21.4 percent after one hour in zinc chloride without additives, at 250°C with a hydrogen partial pressure of 575 psia. Three-hour treatment increased the total solubility to 27.5 percent. A similar one-hour treatment of Illinois No. 6 coal increased its pyridine extractibility from 18.2 to 45.4 percent. The solubility of Tacoma-plant solvent refined coal in pyridine was complete, both before and after zinc chloride treatment. However, its solubility in benzene actually decreased from 36.5 to 20.5 percent, probably due either to new covalent crosslinking or to strengthened acid-base interactions.

Organic additives increased the pyridine extractibility of the treated coal, with some indication that such additives

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are consumed. The use of 1,4-diisopropylbenzene (a possible hydride donor) and hydrogen chloride increased the solubility of Wyodak coal in pyridine to 39.7 percent. When tetralin, a known hydrogen-donor solvent, was added to a zinc chloride melt for a one-hour treatment, over 70 percent of the Wyodak coal was converted to pyridine-soluble products, and the benzene-extractibility increased to 16.6 percent (compared with 1.1 percent for the raw coal). Qualitative evidence (i.e. the presence of naphthalene in the reaction product) was obtained that tetralin partly transferred hydrogen catalytically to the coal structure at 250°C, in contrast to the known inability of tetralin to donate hydrogen thermally below 250°C.

In experiments with model compounds, it was found that zinc chloride melt at 250°C has little activity for cracking carbon-carbon bonds in anthracene and 9,10-dihydroanthracene. However, it does have hydrogenation-dehydrogenation activity, as shown by the formation of tetrahydroanthracene to the extent of about 30 percent in one-hour runs with each of the two precursor model compounds.

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Contents

	<u>Page</u>
Abstract	i
I. Introduction	1
A. Alternatives for Coal Utilization	1
B. Coal Liquefaction	4
1. Processes	4
2. Liquefaction Chemistry	6
C. Molten Salt Catalysis	11
1. Rationale	11
2. Zinc Chloride Catalysis	13
3. Metal Halide/Hydrogen Halide Catalysis	23
D. Objectives of the Present Research	24
II. Experimental Apparatus and Procedure	26
A. Coal and Other Materials	26
1. Coal Procurement and Preparation	26
2. Sources and Purities of Chemicals Used	29
B. Equipment and Procedure	29
1. Molten Salt Treatment	29
a. Equipment	29
b. Properties of ZnCl_2 melts	34
c. Procedure	36
2. Product Work-Up	37
3. Soxhlet Extractions	38
4. Other Analytical Methods	40

	<u>Page</u>
C. Experiments Performed	40
III. Results and Discussion	43
A. Extractions of Feed Materials	43
B. Coal Experiments with Glass Apparatus	43
C. Coal Experiments with Parr Autoclave	46
1. Effect of Time and Feed Material	46
2. Effect of MoO_3 and CoCl_2	51
3. Effect of a Different Metal Chloride Melt	52
4. Effect of $\text{ZnCl}_2/\text{HCl}/\text{Hydride Donor}$ Systems	53
5. Effect of Carbon Monoxide	56
6. Effect of Tetralin	58
7. Other Analyses of Reaction Products	64
a. Changes in H/C Ratios	64
b. Physical Property Changes	66
c. Initial Filtrate Analyses	67
D. Model-Compound Experiments	67
IV. Conclusions and Recommendations	72
A. Conclusions	72
B. Recommendations for Future Work	73a
V. References	74
Appendixes	78
A. Corrosion Studies	78
1. Gold-Plated Materials	78
a. Samples	78
b. Parr Autoclave	81

	<u>Page</u>
2. Hastelloy C Materials	82
B. Vapor Pressures of ZnCl_2 Melts	84
C. Determination of Percentage Tetralin Retained by MTC	87

List of Figures

	<u>Page</u>
Figure 1. Representative Atomic H/C Ratios for Coal and Other Fuels	3
Figure 2. A Model for Bituminous Coal Structure	8
Figure 3. Parr Autoclave	32
Figure 4. Solubility and Boiling Curves for the Zinc Chloride/Water System	35
Figure 5. Benzene Solubles vs. Time for Run 3	45
Figure 6. Solubility vs. Time for Runs 7,8	49
Figure 7. Dependence of Yield on Hydrogen Partial Pressure	57
Figure 8. Change in H/C Ratio with ZnCl_2 Treatment	65
Figure 9. Vapor Pressure of H_2O over $\text{ZnCl}_2/\text{H}_2\text{O}$ Melts	86
Figure 10. Determination of Tetralin Retained by MTC	88

List of Tables

		<u>Page</u>
Table I	Direct Hydrocracking of a Bituminous Coal with ZnCl_2 Under Mild Conditions	18
Table II	Direct Hydrocracking of Bituminous and Sub-Bituminous Coals with ZnCl_2	19
Table III	Coal and SRC Analyses	28
Table IV	Sources and Purities of Chemicals Used	30
Table V	Experiments Performed	41
Table VI	Extraction Yields of Feed Materials	44
Table VII	Extraction Yields for Experiments with Parr Autoclave	47
Table VIII	Extraction Yields of Different Feed Materials after ZnCl_2 Treatment	50
Table IX	Extraction Yields for Tetralin Experiment	60
Table X	Composition of Solid Products from Experiments 21 and 22	70
Table XI	Corrosion of Hastelloy C Stirring Shaft	83

I. INTRODUCTION

The growing energy shortage in the United States clearly calls for increased utilization of abundant domestic coal resources. Oil and gas production in this country has peaked, resulting in an extraordinary dependence on foreign supplies. Nuclear, solar, and geothermal resources will be only partial solutions to this problem. Even when more fully developed, they will be incapable of replacing oil and natural gas used for petrochemicals, transportation liquids, and residential and industrial heating. Domestic coal resources must play the central role in fulfilling these needs.

A. Alternatives for Coal Utilization

Numerous methods of coal utilization are described by Hottel and Howard (H1) and by the Institute of Gas Technology (I1). Because of government restrictions on sulfur dioxide emissions, the high sulfur content of many American coals limits their direct use as boiler fuels. The Solvent Refined Coal process (SRC) of the Pittsburgh & Midway Coal Mining Company produces a low-sulfur, low-ash solid fuel from coal, which is suitable for boiler use, but at a price far from competitive with those of other available fuels. In addition, use of solid SRC would only indirectly alleviate the shortage of liquid and gaseous fuels.

Of the routes for converting coal to liquid and/or gaseous fuels, coal gasification has advanced furthest toward large-scale utilization. This is partly due to the fact that domestic proved reserves of natural gas, an exceptionally clean and efficient fuel, are being depleted rapidly. While coal gasification may reach commercialization first, it alone will not solve this country's energy problem. There is also a need for new sources of liquid transportation fuels for automobiles, trucks, trains, and airplanes. Coal liquefaction can help increase the supply of transportation liquids, either directly or by production of a low-sulfur fuel oil which would release a greater portion of domestic petroleum for gasoline, diesel oil, and jet-fuel production.

Beyond helping to fill the need for transportation fuels, coal liquefaction has an inherent conversion efficiency advantage over gasification which can be seen by considering the atomic H/C ratios of various fuels as shown in Figure 1. To move up the scale from coal to liquid and then gaseous fuels requires hydrogen addition, carbon rejection, or both. Since gaseous fuels are higher up the scale than liquid fuels, gasification processes require more extreme changes.

The general scheme of coal conversion processes involves separating the coal into two fractions, one which is enriched with hydrogen to become liquid or gaseous fuel, and one which is sacrificed as reject carbon to produce the

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Figure 1. Representative Atomic H/C Ratios
for Coal and Other Fuels

hydrogen needed for the first fraction. Consider the reactions needed to convert a coal with a H/C ratio of 1.0 (CH_1) to a high-quality liquid fuel with a H/C ratio of 2.0 (CH_2):

Reaction (1) represents hydrogen production and carbon rejection, while reaction (2) represents conversion to liquid fuel. Reaction (3) depicts the net conversion process, which shows a carbon yield of 83 percent for the liquid product. Calculations for a gasification process producing methane with an atomic H/C ratio of 4.0 give a carbon yield of 63 percent. The decrease in heating value is minor because of the heat of combustion of the hydrogen. However, the process fuel requirement is higher per unit of coal converted by gasification than by liquefaction and results in a lower overall conversion efficiency.

B. Coal Liquefaction

1. Processes

The conversion of coal to liquid products has been accomplished by pyrolysis, synthesis gas reduction, and catalytic hydrogenation. Pyrolysis is a non-catalytic process in which coal is heated in the absence of air to

temperatures of 500°C and higher, resulting in thermal rupture of chemical bonds. The COED process (FMC Corporation) is an example. Pyrolysis processes cannot be considered a major source of liquid fuels because of substantial yields of char and gases.

The Fischer-Tropsch process is an example of the synthesis gas reduction route. Steam and oxygen are contacted with coal, as in a gasification process, to produce a mixture of hydrogen and carbon monoxide. This "synthesis gas" is converted catalytically to liquid alcohols or a synthetic gasoline at high temperatures and pressures. As practiced in Germany during World War II, the process thermal efficiency was only 38 percent (Pl). Due to poor process economics, the Fischer-Tropsch process has not been used since World War II except in a small plant in Sasol, South Africa, which produces 5000 bbl of oil per day from 5000 tons of coal. Improvements in catalysis technology made over the last thirty years may have changed the situation, though. The Ralph M. Parsons Company, under ERDA sponsorship, is currently preparing new conceptual designs and economic evaluations for a Fischer-Tropsch plant in the United States (Ol).

Coal hydrogenation was also practiced in Germany during World War II, in the form of the Bergius process. The extreme pressures required (10,000 psi) and high hydrogen consumption resulted in an expensive process with a process thermal efficiency of only 55 percent (Pl).

Several new processes, operating in the ranges 400 to 500°C and 2000 to 4000 psi, have been developed recently in the United States based on the use of conventional cobalt molybdate catalysts. The H-Coal (Hydrocarbon Research, Inc.) and Synthoil (Bureau of Mines) processes employ direct hydrogenation, wherein the feed coal is slurried in a recycle oil and contacted directly with the catalyst and hydrogen at high pressures. The Exxon Donor Solvent process (Exxon Research and Engineering Company (Fl)), an indirect hydrogenation process, contacts the coal with a hydrogen-donor solvent at low pressures to solvate and convert the coal to products. The donor solvent is then separated from the products and unconverted feed, and contacted with hydrogen over a catalyst at high pressure to restore its capacity for hydrogen donation. The Consol Synthetic Fuel Process (CSF, Consolidation Coal Company) is a hybrid. In this process the feed coal is solvated at low pressures by a weak hydrogen-donor recycle solvent. The coal extract is then contacted with the catalyst and hydrogen at high pressure to convert it to products.

2. Liquefaction Chemistry

Models of a "typical" coal molecule have been proposed by Given (G1), Hill (H2), Wiser (W1), and others, based on extensive chemical and spectroscopic examinations. These models can only be taken as qualitatively correct, due to the great variations in coal from rank to rank, mine to mine, seam to seam, and even from particle to particle.

The models are instructive, however, in showing the types of attack that must be made on the coal structure to produce liquid fuels.

The Wiser model, Figure 2, suggests a coal structure consisting of clusters of condensed aromatic, hydroaromatic, and heterocyclic rings, bridged by various linkages to form a two-dimensional network. Wiser (W2) estimated that the average cluster contains three condensed rings. He further predicted that a product which is to be liquid at room temperature could contain very little anthracene (3-fused-ring) and virtually no naphthacene (4-fused-ring) structures. This means that a process to convert coal to liquid products must not only break the clusters apart but must also reduce the size of many of them.

Separating the clusters and reducing their size require cracking reactions carried out thermally at temperatures in excess of 350°C, or catalytically at lower temperatures. In both cases free radicals are formed where the bonds are ruptured. In the absence of hydrogen the free radicals would generally polymerize, but cracking reactions applied to coal conversion are carried out in the presence of hydrogen, and the hydrogen largely captures the free radicals before they have the opportunity to polymerize. The sequence in which bonds are ruptured and capped by hydrogen is referred to as hydrogenolysis to distinguish it from the chemical reaction of hydrogenation (involving intramolecular addition of hydrogen with no

Figure 2. A Model for Bituminous Coal Structure, from Wiser (W1)

other change). Hydrogenolysis takes place not only at carbon-carbon bonds, but also at carbon-oxygen, carbon-nitrogen, and carbon-sulfur bonds, in which cases the heteroatoms may eventually be converted to H_2O , NH_3 and H_2S respectively. Processes in which the goal is hydrogenolysis, rather than strict hydrogenation, are sometimes referred to as hydrocracking.

The liquid and solid products of coal hydrocracking contain a very large number of different organic compounds. To simplify product analysis, it is convenient to classify the compounds as oil, asphaltenes, preasphaltenes, and unconverted solid residue. These four classes may then be arbitrarily considered as analogous to separate chemical species.

Oil is the desired product. It is the material variously defined as pentane-soluble, hexane-soluble, or cyclohexane-soluble. Its solubility in light paraffins indicates that it is a low-molecular-weight product, boiling mostly below $400^{\circ}C$ at atmospheric pressure, with a higher H/C ratio (1.5 or more) than the other products. Asphaltenes are soluble in benzene but insoluble in light paraffins, with molecular weights varying from 350 to 1400 (W3). Preasphaltenes are soluble in pyridine but insoluble in benzene, with molecular weights ranging from 600 to 2500; they are less aromatic, and have a high incidence of phenolic groups leading to the alternate name asphaltols (F2). Preasphaltenes also have a high incidence of basic

nitrogen groups which may give rise to complexation by hydrogen bonding, and this would explain the overlap in molecular-weight ranges of asphaltenes and preasphaltenes. The last classification, unconverted solid residue, comprises materials insoluble even in pyridine.

Weller (W4) first proposed in 1951 that the conversion of coal to oil proceeds by two consecutive reactions:

the first reaction being more rapid than the second. Since then Liebenberg and Potgieter (L1) have proposed a more complex mechanism which adds the parallel reaction of coal being converted directly to oil without first being converted to asphaltenes.

Recently, Sternberg, Raymond, and Schweighardt (S1) have emphasized the need to consider the role of preasphaltenes in the overall mechanism as a possible intermediate between coal and asphaltenes. This suggests the mechanism:

One further complication is the possibility of coking or gas-producing reactions involving coal and/or intermediate products.

C. Molten Salt Catalysis

Catalytica Associates, Inc. (B1) has recently analyzed the potential of ten classes of catalysts for second-generation liquefaction processes. They recognize the fact that first-generation processes such as H-Coal and Synthoil will use proven cobalt molybdate catalysts. Based on a theoretical study using available physical and chemical data, the ten groups are rated as high, medium, or low priority for future consideration. The criteria used for classification are: thermal stability, chemical stability (to species such as H_2S and NH_3), catalyst activity and selectivity, ease of catalyst separation and regeneration, cost, and heat and mass transfer phenomena. Molten salts as a group are given a medium priority rating. They might have received a high priority rating, were it not for catalyst regeneration and corrosion problems. However, as will be discussed later, the regeneration problem appears largely resolved.

1. Rationale

Molten salts have been used previously in applications as (1) a reactant, (2) a solvent or reaction medium, and (3) as a catalyst. Their use as coal conversion catalysts has been practiced for at least sixty years. In the past ten years, the use of molten salts as both catalysts and reaction medium has come under consideration.

A wide range of chemical and physical properties are available with molten salt systems (B2). This allows tailoring the system to the application. Molten salts range from basic (Na_2S) to acidic (ZnCl_2) and from strongly oxidizing (FeCl_3) to reducing (Cu_2Cl_2). Molten salt systems are available with melting points from 89°C ($\text{AlCl}_3/\text{NaCl}/\text{KCl}$ eutectic) to 1003°C (Na_3AlF_6) or higher. The melting point of a molten salt system can be adapted to desired reaction temperatures by adding higher-melting or lower-melting salts, water, or other ingredients in varying quantities.

Perhaps the greatest advantage of those molten salt systems that exhibit catalytic activity, is the excellent catalyst/coal contacting possible. True homogeneous catalysis with coal itself is not involved, since the coal is not dissolved in the melt. When the coal is well dispersed the advantages of homogeneous catalysis, such as high heat and mass transfer rates, are approached.

Some of the serious problems with molten salt systems, specifically zinc chloride, are yielding to current research. A high catalyst/coal ratio, catalyst deactivation (by H_2S and NH_3 uptake and by loss of HCl), carbon residue build-up, interaction with coal minerals, and inefficiency of regeneration have caused high catalyst losses in the past. Recovery is now a less serious problem, thanks to a process developed at the University of Utah (D1,W5). The liquid products from the reactor are washed

with water to remove essentially all the ZnCl_2 . The solid char is washed with cold hydrochloric or nitric acid for further ZnCl_2 recovery, so that (at a significant cost) overall recovery approaches 99 percent. The build-up of inorganic and organic impurities could be handled by treating a slip-stream of the molten salt in a small fluidized combustion unit such as has been proposed by the Consolidation Coal Company (R1,Z1).

Two bibliographies (C1,K1), together covering the period 1917 to 1974, have been compiled for research on coal liquefaction using molten salt catalysts. In addition, Hawk and Hiteshue (H3) have reviewed extensive work by the Bureau of Mines with molten salts. Numerous metal halides have been used. Emphasis has been on the metal chlorides, presumably due to their greater availability and lower cost as compared to metal fluorides, bromides, and iodides. Much of the work has involved SnCl_2 , AlCl_3 , and ZnCl_2 . The Bureau of Mines (H3) and University of Utah (P2) have done extensive work with SnCl_2 . Kawa (K2) and Ross and Low (R2) have worked with AlCl_3 . Both of these chlorides show promise as catalysts, but they are both more corrosive, more difficult to recover, and more expensive than ZnCl_2 . In addition AlCl_3 is incompatible with water and attacks the coal structure so severely that gas yields as high as 50 percent are common.

2. Zinc Chloride Catalysis

Interest in zinc halides as hydrocracking catalysts for coal and coal extracts has intensified since 1960.

The most extensive work has been done at the University of Utah and the Consolidation Coal Company (now Conoco Coal Development Co.). The process conceived by researchers at the University of Utah involves impregnation of coal by small amounts of zinc chloride catalyst. The contrasting approach at Conoco involves the use of massive quantities of zinc chloride applied as a continuous phase.

Work at the University of Utah was first based on a continuous free-fall reactor (P2,Q1), but recently has turned to a continuous coiled-tube reactor (W5). The 3/16-inch reactor tubes are 20 to 120 feet long, giving residence times of one to six seconds. A high-volatile bituminous Utah coal (-40 + 100 mesh), fed at 100 to 200 gm/min and preimpregnated with 5.5 percent ZnCl_2 , is carried through the reactor by hydrogen in turbulent flow at 30 scfm. Reactor temperature and pressure ranges are 500 to 550°C and 1600 to 2000 psi. Total conversion to gases plus liquids for the process approaches 70 percent. The split at this conversion level is 15 percent gases and 55 percent liquids. A typical liquid analysis shows 17 percent preasphaltenes, 22 percent asphaltenes, and 43 percent oil; the balance is mostly water. The overall oil yield, based on MAF coal, is approximately 20 to 25 percent.

The Consolidation Coal Company (R3,S2,Z2,Z3,Z4) has done extensive bench-scale development work with ZnCl_2 , which was intended to be a replacement for conventional cobalt molybdate catalysts in their CSF liquefaction process.

Derencsenyi (D2) has reviewed this work. Before the ZnCl_2 catalyst could be tried on a large scale, unrelated difficulties with the CSF pilot plant in Cresap, West Virginia, resulted in a loss of funding for the whole project.

Three feed materials were used in the bench-scale studies: a fused four-ring aromatic compound, pyrene; coal extracts; and bituminous coal. Experiments with pyrene first showed the superiority of massive, unsupported quantities of molten ZnCl_2 over supported ZnCl_2 and conventional contact catalysts. Pyrene was cracked by molten ZnCl_2 at 425°C and 4200 psi. Benzene, however, was not cracked under similar conditions. This fact is the basis for the high selectivity ZnCl_2 has for gasoline production. In this sense ZnCl_2 is superior to the aluminum halides which readily crack benzene under even milder conditions.

With coal extracts, molten ZnCl_2 was found to catalyze conversion to distillates at rates higher than those for solid catalysts. The metal-halide catalyst was found to be active at milder conditions. The temperature, pressure, catalyst/extract ratio, and residence-time ranges studied were 330 to 440°C , 1000 to 4200 psi, 0.02 to 3.0, and 15 to 360 minutes respectively.

Improved selectivity (higher naphtha yield and lower gas yield) was obtained by increasing the pressure or decreasing the temperature for a given total-conversion level. Higher catalyst/extract ratios allowed the use of

milder conditions for equivalent results. Water and hydrogen chloride were found to be mild promoters in extract hydrocracking. In these studies the use of a hydrogen-donor solvent such as tetralin had little effect on yield or selectivity.

Kinetic studies of extract hydrocracking suggested the existence of three fractions in the extract. The first fraction is unconvertible to distillates, the second is converted with some difficulty, and the third is more easily converted. While they did not suggest it, it is possible that these fractions are respectively solid residue, preasphaltenes, and asphaltenes.

The coal-extract hydrocracking studies resulted in two proposed processes for producing liquid fuels. One process would be aimed at high conversion, using the relatively severe conditions of 400 to 415°C, 2500 to 3500 psi, and 1 to 3 hours contact time. This process would convert the easy fraction and some of the difficult fraction. The second process would sacrifice some yield for the opportunity to use milder conditions of 330 to 370°C, 1000 to 1500 psi, and 15 minutes to 1 hour contact time, and would convert only the easy fraction of the extract. The more refractory fraction would become part of the residue which would be used for fuel and for hydrogen production.

Experiments with direct hydrocracking of a bituminous coal showed that catalyst/coal weight ratios of at least 2.0 are desirable. For the same temperature, pressure,

and contact time, approximately equivalent MAF yields were found for coal and for coal extracts. The most significant problem found with direct coal hydrocracking is the catalyst/coal ash interaction typified by the reaction:

This and similar reactions might poison the catalyst. It was suggested that the use of an equilibrium amount of FeCl_2 in the system would inhibit this reaction.

Considering that direct hydrocracking of coal gives yields comparable with extract hydrocracking, the former process is attractive because it eliminates the extraction step. Further the Consolidation researchers concluded that the best potential for direct coal hydrocracking is at low temperatures and pressures such as 330 to 370°C and 1000 psi. One experiment was performed under such conditions. The product distribution, shown in Table I, includes good yields of minus 200°C distillate and low-sulfur fuel oil.

The original work by Consolidation, like most studies with metal halides, used bituminous coal and bituminous-coal extracts. In 1974 Consolidation researchers Zielke, Rosenhoover, and Gorin (21) reported on batch autoclave experiments with a Montana sub-bituminous coal. The results, summarized in Table II, were compared to results of experiments with a Pennsylvania bituminous coal. Relatively mild conditions (columns a, d) and relatively severe conditions (columns b, c, e) were investigated.

Table I Direct Hydrocracking of a Bituminous Coal with
 ZnCl_2 Under Mild Conditions
 Work of the Consolidation Coal Co. (R3,p.6)

$\text{ZnCl}_2/\text{MF Coal} = 2.0$

675°F

1000 psi

60 minutes in batch autoclave

<u>Product</u>	<u>Wt. % MAF Coal</u>
$\text{C}_1\text{-C}_3$	4
$\text{C}_4 \times 200^\circ\text{C}$ Distillate	42
0.3 wt % S Fuel Oil	17
Residue on Catalyst	30
Hydrogen Consumed	5.4

Table II. Direct Hydrocracking of Bituminous and Sub-Bituminous Coals with ZnCl_2
Work of the Consolidation Coal²Co. (Z1)

$\text{ZnCl}_2/\text{MF Coal} = 2.5$

Coal: SB, Colstrip
(Sub-bituminous)

Tetralin/MF Coal = 0.5 (where used)

B, Ireland
(Bituminous)

60 minutes in batch autoclave

	a	b	c	d	e
Coal	SB	SB	SB	B	B
Temp. ($^{\circ}\text{C}$)	358	385	413	358	385
PH_2 (psig)	1500	3000	3000	1500	3000
Tetralin	yes	no	no	yes	no
<u>Products</u>	<u>Wt % MAF Coal</u>				
$\text{C}_1\text{-C}_3$	1.7	5.4	9.9	5.1	8.7
$\text{C}_4 \times 400^{\circ}\text{C}$ distillate	27.5	58.7	60.2	43.8	68.6
+400 $^{\circ}\text{C}$ MEK soluble	46.9	17.1	9.2	31.3	13.9
+400 $^{\circ}\text{C}$ MEK insoluble	10.5	5.2	8.7	16.5	6.0
$\text{CO} + \text{CO}_2 + \text{H}_2\text{O}$	17.8	19.9	19.3	8.0	8.6
N,O,S + H in catalyst	1.5	2.4	2.2	2.8	3.3
Total	105.9	108.7	109.5	107.5	109.1
Hydrogen Consumed	5.9	8.7	9.5	7.5	9.1

Hydrocracking of sub-bituminous coal under mild conditions (column a) is most effective if a vehicle solvent is used. Its purpose is to increase the fluidity of the catalyst/coal mixture so that the ZnCl_2 has better access to the coal. Methylnaphthalene was tried first, but it had little effect on conversion and was severely cracked itself. Tetralin was found to be more effective and was not cracked as much. Similar experiments have shown that even with mild conditions, the fluidity of ZnCl_2 /bituminous coal mixtures is high enough for good results without the addition of a vehicle solvent.

With mild conditions the hydrocracking of a sub-bituminous coal (column a) results in a higher yield of methyl ethyl ketone (MEK) solubles (here equated to a heavy fuel oil), a lower yield of distillates, and a lower yield of light gases as compared to the hydrocracking of a bituminous coal (column d). Total conversion to heavy fuel oil plus distillate is approximately the same, however, and hydrogen consumption is significantly lower in the case of the sub-bituminous coal.

At the more severe conditions, distillate yields improve for both bituminous and sub-bituminous coals (columns b, c, e). As can be seen from the two runs at 385°C (columns b, e), the yield and product distribution with the bituminous coal are superior to those with the sub-bituminous coal. Further, the difference in hydrogen consumption is not as significant as at the mild conditions. These results suggest that sub-bituminous coals can be best

utilized by converting them to low-sulfur fuel oils under mild conditions. The combination of mild conditions (and therefore lower equipment costs) with low hydrogen consumption would have a highly beneficial effect on process economics.

Kawa, Feldmann, and Hiteshue (K4), working at the Bureau of Mines, screened iodine and nine metal-halide catalysts and studied the effects of temperature, pressure, and time on the hydrocracking of a high-volatile A bituminous coal from their Bruceton mine, and also of asphaltenes. At 425°C, 4000 psi, and an hour of contact time, with equal weights of catalyst and coal, the four best catalysts in order are ZnBr_2 ZnI_2 ZnCl_2 I_2 . When asphaltenes are used instead of coal, NiBr_2 and $\text{NiI}_2 \cdot 6\text{H}_2\text{O}$ are also superior. The other four catalysts tried were $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, CdI_2 , $\text{FeI}_2 \cdot 4\text{H}_2\text{O}$, and SnI_2 . Of the six best catalysts, ZnCl_2 is the cheapest, and its activity is not that much lower than any of the others. For these reasons, ZnCl_2 was chosen for use in further studies with asphaltenes.

Pressures between 2000 and 8000 psi were studied, other conditions remaining as above. It was concluded that asphaltenes can be converted to oil at pressures of 2000 psi and possibly lower, at practical rates. In the narrow range of temperatures from 400 to 450°C, it appears that operation at 400°C is desirable because total conversion is only slightly lower than at 450°C and the gas/oil ratio is much lower. Reaction time was varied

from 15 to 120 minutes. The total conversion was 86 percent at 15 minutes and 92 percent at 120 minutes, indicating that contact times of an hour or less are practical at 425°C.

Still further work has been done with zinc halides. Berg and Malsam (B3) used an equimolar ZnCl_2/KCl mixture to hydrocrack coal. The KCl reduces the melt viscosity, allowing better gravity separation of organic and inorganic phases in the reactor effluent. It also reduces the melt's catalytic activity, necessitating the use of higher temperatures than with ZnCl_2 alone. Shell Oil Company (L2,L3) has patented a process for hydrocracking coal with molten ZnI_2 using catalyst/coal ratios of 7.0 to 12.0. Additional work has been done in Poland and is reviewed by Konieczynski (K3).

Derencsenyi (D2) has studied the interaction of sub-bituminous Wyodak coal with molten ZnCl_2 at very mild conditions, 200°C and 1 atm hydrogen pressure, but with the high catalyst/coal ratio of 6.0. Since 200°C is below the melting point of ZnCl_2 (315°C), small amounts of water were added to form a melt. Numerous catalytic additives were screened. The best results were obtained with the addition of small quantities of KI and I_2 . The melt-treated coal (MTC) from this run was found to have an increased benzene extractability as compared to the raw coal, the principal product being a wax of around 400 molecular weight. Pyridine was not used as an extraction solvent with the MTC, but if it had been it is likely that

it would have shown more drastic changes in extractibility than the benzene did. Physical studies of the melt/coal mixture showed that coal is well dispersed and reduced in size by the molten ZnCl_2

3. Metal Halide/Hydrogen Halide Catalysis

Wristers (W6) has been able to hydrogenate benzene to cyclohexane at 50°C , using various metal halides and the corresponding hydrogen halides, in the presence of isopentane acting presumably as a tertiary hydride source. Secondary and primary carbons were ineffective. The systems TaF_5/HF , SbF_5/HF , AlBr_3/HBr , and AlCl_3/HCl were all found to be active.

A mechanism suggested by Wristers fits the experimental observations. It begins with protonation of the benzene:

The protonated species then abstracts hydrogen from isopentane, forming an isopentyl cation:

The isopentyl cation is then reduced to isopentane by hydrogen:

Repetition of similar steps ultimately gives cyclohexane, with the acid and isopentane being regenerated. Hydrogen

partial pressures must be high enough to reduce the isopentyl cations rapidly before they become involved in alkylation of benzene. While only benzene was used as a reactant here, it appears possible that analogous reactions could be applied to coal.

D. Objectives of the Present Research

The primary objective of this work is to develop a catalyst system that will convert coal to a low-sulfur fuel oil; a low-sulfur, low-ash solid fuel; or a "synthetic crude oil" at milder conditions than those considered up to now. Many of the reactions required to convert coal to such fuels--for instance, hydrogenation--are thermodynamically favored even at room temperature, while kinetic considerations dictate the use of high temperatures to get practical reaction rates. In the trade-off between thermodynamics and kinetics, current practice is to use temperatures in the range 350 to 500°C for liquefaction processes. Below 350°C, reaction rates are too slow using present catalyst technology. Above 500°C, coking and high gas production become serious problems unless ultra high hydrogen pressures are used. Lower temperatures could be used by developing new catalyst systems that would give significant reaction rates below 350°C.

The objective of this research is to seek a catalyst system that will allow operation at mild conditions not exceeding 350°C and 750 psi. The advantages of operating under such mild conditions are immense. Process equipment and costs would be significantly reduced. Lower-temperature

operation would allow better selectivity of conversion to liquids rather than gases and coke. In addition, energy requirements and hydrogen consumption would be reduced. Overall, there would be an increased thermal efficiency..

To accomplish this objective, massive quantities of zinc chloride were used in runs aimed at direct hydrocracking of coal. A sub-bituminous coal was used in most of the studies, since a lower hydrogen consumption is possible under mild conditions with lower-rank coals.

II. EXPERIMENTAL APPARATUS AND PROCEDURE

A. Coal and Other Materials

1. Coal Procurement and Preparation

Sub-bituminous and bituminous coal and solvent-refined coal (SRC) were used as feed materials in this study. The sub-bituminous coal was supplied by the Wyodak Resources Development Corporation from the Roland top seam of its Gillette, Wyoming mine. Illinois No. 6 bituminous coal was provided by the Illinois Geological Survey. The SRC was obtained from the Pittsburgh & Midway Coal Mining Company from its Tacoma, Washington demonstration plant.

The coal was received in 55-gallon drums and had been ground by the respective suppliers to minus 3/4 inch. The Wyodak coal was immediately separated into halves. One half was passed through jaw and roller crushers to reduce the particle size to minus 1/16 inch. It was then divided into approximately 20-lb portions and stored in polyethylene bags. The coal in one of these bags, selected for this study about one year later, was milled and screened. The -28+100 Tyler mesh fraction was split into 500-gm portions using a riffler and then stored under nitrogen in 1-quart friction-lid cans. ASTM method D-346, "Sampling Coke for Analysis", was adhered to at all times during this procedure.

The Illinois No. 6 coal was retained in its 55-gallon drum for several months. Half of it was then reduced to minus 1/16 inch in the jaw and roller crushers and stored

under nitrogen in 5-gallon friction-lid cans. One of these cans was selected for this study. Milling was not necessary because a large part of the sample was already in the desired -28+100 mesh range. This size fraction was split into 500-gm samples with the riffler and stored under nitrogen in 1-quart friction-lid cans.

The SRC was received in two sealed 5-gallon cans. Approximately 500 gm was crushed with a mortar and pestle, screened, and the -28+100 mesh fraction stored under nitrogen in a 1-quart friction-lid can.

Proximate and ultimate analyses of the three materials are shown in Table III. The Illinois No.6 Coal is lower in moisture and oxygen, but higher in sulfur and ash than the Wyodak coal. The SRC is distinguished by low levels of moisture, ash, sulfur, and oxygen. The carbon and hydrogen contents of the three materials are best compared by the atomic H/C ratios, since the ratios are less affected by variations in other constituents than are the percent carbon and percent hydrogen figures. For example, consider Coal A and Coal B containing only carbon, hydrogen and ash. Coal A is 60 percent carbon, 5 percent hydrogen, and 35 percent ash. Coal B is 83 percent carbon, 7 percent hydrogen, and 10 percent ash. The two appear, at first, to be quite different but, in fact, the atomic H/C ratio is 1.0 for both of them; Coal A simply has more ash diluting the percentages of carbon and hydrogen.

Table III. Coal and SRC Analyses

<u>Proximate Analysis</u>	<u>Wyodak¹</u>	<u>Illinois No. 6^{1,3}</u>	<u>SRC²</u>
% Moisture	22.50	12.64	2.21
% Ash	10.92	14.57	-
% Volatile	37.14	32.96	-
% Fixed Carbon	29.44	39.83	-
	<u>100.00</u>	<u>100.00</u>	
<u>Ultimate Analysis</u>	<u>% MF Coal/SRC</u>		
Carbon	62.57	64.30	86.45
Hydrogen	5.00	4.47	5.55
Nitrogen	0.92	1.33	2.16
Sulfur	1.20	4.35	0.55
Ash	14.09	16.68	< 0.5
Oxygen (difference)	16.22	8.87	4.79
	<u>100.00</u>	<u>100.00</u>	<u>100.00</u>
H/C (atomic)	0.96	0.83	0.77

¹Commercial Testing & Engineering Co. (Denver, CO)

²University of California Microchemical Analysis Laboratory

³Average of two analyses

Since the three materials were not placed under nitrogen immediately upon arrival, the possibility exists that they were oxidized during the initial storage period. If so, the effect is slight. Six analyses of the Wyodak coal taken over a two-year period show oxygen contents of 17.51, 15.75, 15.63, 15.62, 16.22, and 16.54 percent (MF). If there is any trend, it is obscured by the inaccuracy involved in determining oxygen content by difference.

This problem is also minimized by the fact that once the materials were reduced to -28+100 mesh, when susceptibility to oxidation increases, they were immediately stored under nitrogen in the air-tight friction-lid cans to prevent any further oxidation. Thus each of the feed materials used in this study was consistent in composition throughout; the chemical analyses in Table III are of the materials as stored under nitrogen.

2. Sources and Purities of Chemicals Used

Reagent-grade zinc chloride (95 percent) purchased from Matheson Coleman & Bell was used in this study. All other solid reagents and all solvents used are reagent-grade products supplied by Mallinckrodt, except those listed in Table IV. The gases used and their purities are also specified in the table.

B. Equipment and Procedure

1. Molten Salt Treatment

a. Equipment

The first three experiments were carried out in a

Table IV. Sources and Purities of Chemicals Used

<u>Material</u>	<u>Source</u>	<u>Grade</u>	<u>Min. Purity (%)</u>
Anthracene	Eastman	-	98+
Cyclohexane	Aldrich	Reagent	-
9,10-Dihydroanthracene	Aldrich	Aldrich Analyzed	95.0
1,4-Diisopropylbenzene	Shell Chemical	-	-
Methyl ethyl ketone	Aldrich	Reagent	99+
1-Tetradecene	Aldrich	Aldrich Analyzed	95.0
Tetralin	Eastman	Practical	-
Molybdic Oxide	Merck	Reagent	99.5
Carbon Monoxide	Matheson	C.P.	99.5
Hydrogen	Liquid Carbonic	-	99.999
Hydrogen Chloride	Matheson	Technical	99.0

glass reactor at atmospheric pressure. This apparatus and the operating procedure used with it are described by Seth (S3). A 600-ml autoclave acquired from Barr Instrument Co., Moline, Illinois was available for the rest of the experiments. The main features of this autoclave and associated equipment are shown in Figure 3.

The autoclave has maximum pressure and temperature ratings of 2000 psig and 350°C. Since pressures used in this study were to be less than 750 psig, it was equipped with a 1000 psig pressure gauge and rupture disc. Agitation is accomplished with a direct-drive stirrer using a self-sealing packing gland; the speed can be varied from 0 to 800 rpm. Heat is supplied by a 780-watt quartz-fabric-covered mantle. Automatic temperature control is provided by a solid state potentiometric system operating from an iron-constantan thermocouple; temperature can be read from a deviation meter mounted on the control panel. An internal cooling loop and a sample dip tube, also provided with the autoclave, were removed in this study because of freezing and plugging problems with the reaction mixture.

The corrosion resistance of the autoclave and internals was an important consideration. Pure ZnCl_2 is somewhat corrosive by itself, but in the presence of water hydrolysis occurs to give ZnO and HCl . More important, several experiments called for direct addition of anhydrous HCl which, in combination with water from the melt, presents a significant corrosion problem.

XBL7711-4006

Figure 3. Parr Autoclave

The autoclave available for this study is made of Monel 400, so chosen to withstand reagents used in a previous study. This alloy (67 percent nickel and 30 percent copper) is not well suited for use with wet HCl at 200 to 300°C, so a method of protecting the autoclave cylinder and head was needed. Gold has good resistance to HCl solutions provided strong oxidizing agents are not present (VI). Several other alternatives were considered, for example vapor deposition of Hastelloy C, but gold plating was selected for the following reasons: (1) it is not as drastic a measure as the other alternatives, (2) it provides a pin-hole free surface necessary to prevent chloride pitting, (3) it is not an expensive procedure, since the gold layer is only 0.5 ml thick, and (4) it could be done in several days, whereas shop turn-around time for the alternatives was much longer.

Prior to plating the autoclave, corrosion tests were undertaken with gold-plated samples in ZnCl_2 melts, with and without the direct addition of HCl. The results of these tests, given in Appendix A with other pertinent corrosion data, were encouraging enough to proceed. The autoclave was plated by the Lawrence Berkeley Laboratory Plating Shop. Since gold does not plate well directly onto Monel, the autoclave was first plated with copper and then nickel.

Other precautions were taken in addition to plating the autoclave itself. A Pyrex glass liner was used to

protect the autoclave walls from its liquid contents. The Monel 400 internals (stirring shaft, impellers, and thermowell) were replaced with ones made of Hastelloy C. The rupture discs used are made of Inconel 600 with gold facing on the exposed side, while all external valves and fittings are stainless steel.

Relatively drastic measures were taken here to adapt existing equipment for use in a wide range of corrosive environments. It is important to recognize that these measures could likely be avoided on an industrial scale with proper design. Liquid ZnCl_2 melts can probably be contained by stainless steel. The gas phase can also be contained by stainless steel if the temperature is kept above the dew point of HCl where it is present. In areas where this is not possible, plastic-lined materials or corrosion-resistant alloys such as the Inconels or Hastelloys can be used.

b. Properties of ZnCl_2 Melts

Solubility and boiling-point curves for the $\text{ZnCl}_2/\text{H}_2\text{O}$ system are given in Figure 4. The solubility and atmospheric boiling-point curves, shown as solid lines, have been drawn using data from Timmermans (T1). The other boiling-point curves, shown as dashed lines, were drawn using vapor-pressure data measured with the Parr autoclave. The vapor-pressure curves and the technique used in determining them are discussed in Appendix B. The superatmospheric boiling-point curves are useful in

XBL7711-4005

Figure 4. Solubility and Boiling Curves for the Zinc Chloride/Water System

determining the partial pressure of water over the ZnCl_2 melts during each experiment.

c. Procedure

Four basic steps were involved in each of the different experiments using the Parr autoclave: (1) introduction of melt and feed into autoclave; (2) heat-up and pressurization; (3) timed run; and (4) cool-down and depressurization. Product work-up is discussed in the next section.

The metal halide melts were prepared outside the autoclave to assure complete solubilization before feed addition and to reduce heat-up time. The melt components were weighed into a glass liner, which was then placed on a 750-watt hot plate. The melt (300 gm) was heated to 170°C under a blanket of nitrogen. At this time, the glass liner was placed in the preheated autoclave, the feed (usually 50 gm) and any organic-liquid additives carefully mixed in, and the autoclave closed. Heating and stirring (450 rpm) were begun immediately.

The autoclave was purged with hydrogen to remove air, and at 200°C enough hydrogen was charged so that when the run temperature was reached the total pressure would be close to 600 psig. In one experiment a 50/50 mixture (by volume) of hydrogen and carbon monoxide was used; the mixture was available from a cylinder which had been evacuated and filled with equal volumes of the two gases.

The gas-phase composition could be determined by using the boiling-point curves of Figure 4 to determine

the water partial pressure, given the composition of the ZnCl_2 melt and the temperature. The partial pressures of organic-liquid additives were determined from their vapor-pressure data. Since the organic liquids and the ZnCl_2 melts are for the most part immiscible, they each exert their full vapor pressure. When used, the partial pressure of HCl was determined from the psi charged at a known temperature. This number was then corrected for temperature. The balance of the total pressure is equal to the hydrogen partial pressure.

The final temperature was usually attained within 25 minutes after the autoclave was closed. At this time, the total pressure was adjusted to the desired level by adding hydrogen or by venting some of the autoclave gases, and in this same manner the pressure was held approximately constant during the run.

At the end of the run, the heating mantle was immediately dropped and depressurization begun. A water-soaked sponge was cautiously applied to the autoclave to reduce the temperature, typically to 175°C within 10 minutes and to 125°C within 20 minutes. The feed material was exposed to temperatures in excess of 125°C for about 105 minutes in a 60-minute run and for 225 minutes in a 180-minute run.

2. Product Work-Up

When coal or SRC was the feed material, the reaction mixture in the glass liner, diluted with a small amount of

water used to rinse the internals, was vacuum filtered with a 6-inch Buchner funnel using a fast or medium-fast filter paper. The initial filtrate was saved for later analysis. The product, referred to as melt-treated coal (MTC), was washed successively with 3 to 5 liters of distilled water, 0.5 liter of 20 percent hydrochloric acid, 1 liter of distilled water warmed to 50°C, and 3 to 5 liters more of distilled water. This is a very slow process, often taking more than a full day to complete. The MTC was then placed in a vacuum oven to dry.

When 9,10-dihydroanthracene was the feed material, a different work-up procedure was used. The reaction mixture in the glass liner, again diluted with rinse water from cleaning the internals, was poured into a 500-ml separatory funnel and extracted with 250 ml of CCl_4 . The CCl_4 phase was removed and washed with 100-ml portions of water until an AgNO_3 test indicated that no ZnCl_2 remained (AgCl forms a white precipitate). The CCl_4 with its extract was stored for later analysis by gas chromatography.

3. Soxhlet Extractions

A standard Soxhlet apparatus was used to extract approximately 10 gm of dried MTC successively with 200 ml of cyclohexane, benzene and pyridine at their normal boiling points. According to Kiebler (K5), successive extractions with different solvents at their normal boiling points give, within experimental error, the same total yield as could be obtained with the best solvent alone.

In other words, prior extraction with cyclohexane should not affect the total benzene yield (computed as cyclohexane yield plus benzene yield). Likewise, prior extraction with cyclohexane and benzene should not affect the total pyridine yield (computed as cyclohexane yield plus benzene yield plus pyridine yield). This extraction sequence is well suited to separation of the oil, asphaltenes, pre-asphaltenes, and residue from the MTC.

The extractions were run to completion (solvent in syphon arm colorless) or until a practical time limit had been reached. The time limits used are 4 hr. for cyclohexane and benzene and 48 hr. for pyridine. The only exception is that 24 hr. was allowed for benzene extractions with SRC and melt-treated SRC (MTSRC) and 20 hr. was allowed for the benzene extraction of the MTC from experiment 20.

The liquid extracts were dried in weighed Petri dishes, sometimes with the aid of a slightly warmed hot plate. Once most of the solvent was removed, the Petri dishes were placed in a vacuum oven at 40 mm Hg, purged with a steady stream of nitrogen, to be further dried overnight. (Although this treatment would also vaporize any low-boiling products formed from coal, the low solubility of MTC in cyclohexane indicated that no significant amount of material boiling below 300°C could have been present.) Cyclohexane and benzene extracts were dried at 105°C while pyridine extracts were dried at 115°C. Extraction yields are reported on a MAF basis.

4. Other Analytical Methods

Several other analytical methods were used to characterize the solid, liquid, and gaseous products of this study. Except for the raw-coal analyses supplied by Commercial Testing & Engineering Co., all elemental analyses were performed by the University of California Microchemical Analysis Laboratory. Mass spectra of various samples were prepared by the University of California Mass Spectrometer Laboratory. Booras and Petersen (B4) determined surface areas of raw-coal and MTC samples. Gas chromatography analyses were also made, using a Varian Aerograph instrument equipped with a 1/8-inch by 10-foot column packed with 4 percent Dexsil 300 GC on Chromsorb-W H.P. Column temperatures of 140 and 215°C were used.

C. Experiments Performed

The experiments performed are listed in Table V. Several experiments (1,2,3) were run in glass apparatus until the Parr autoclave became available. The largest group of experiments (4-8,13,18,19) were aimed at determining the effect of additives and different feed materials with ZnCl_2 melts. In one experiment (10), a $\text{KCl/MgCl}_2/\text{FeCl}_2$ melt was used. The application of metal halide/hydrogen halide/hydride source catalyst systems to coal (9,11,12,14,15) was also studied. One experiment combining tetralin and ZnCl_2 was undertaken. Finally, several experiments were performed with model compounds as the feed material (16,17,21,22).

Table V. Experiments Performed

Run No.	Feed Material (gm melt/ gm feed)	Residence Time (minutes)	Temp. (°C)	Total Pressure (psia)	Gas Partial Pressures (psia)	Melt Composition ^a (% by wt.)	Additives (gm melt/ gm additive)
1.	Wyodak (16)	10	200	14.7	H ₂ (11.8) Melt H ₂ O (2.9)	ZnCl ₂ (73) MgCl ₂ (14) KI (4)	I ₂ (100)
2.	Wyodak (6.6)	120	200	14.7	H ₂ (11.8) Melt H ₂ O (2.9)	ZnCl ₂ (73) MgCl ₂ (14) KI (4)	I ₂ (100)
3.	Wyodak (6.6)	120	200	14.7	H ₂ (11.8) Melt H ₂ O (2.9)	ZnCl ₂ (73) MgCl ₂ (14) KI (4)	I ₂ (100)
4 ^b .	Wyodak (6)	10	250	615	H ₂ (575) Melt H ₂ O (40)	ZnCl ₂ (91)	-
5 ^b .	Wyodak (6)	60	250	615	H ₂ (575) Melt H ₂ O (40)	ZnCl ₂ (91)	-
6.	Wyodak (6)	60	250	615	H ₂ (575) Melt H ₂ O (40)	ZnCl ₂ (91)	-
7.	Wyodak (6)	60	250	615	H ₂ (575) Melt H ₂ O (40)	ZnCl ₂ (91)	-
8.	Wyodak (6)	180	250	615	H ₂ (575) Melt H ₂ O (40)	ZnCl ₂ (91)	-
9.	Wyodak (6)	60	250	615	H ₂ O (560) Melt H ₂ O (40) 1-tetra- decene (15)	ZnCl ₂ (91)	1-tetradecene (30)
10.	Wyodak (6)	60	250	615	H ₂ (430) Melt H ₂ O (170)	KCl (36) MgCl ₂ (27) FeCl ₂ (27)	
11.	Wyodak (6)	60	250	615	H ₂ (470) Melt H ₂ O (40) HCl (60) Dipb (45)	ZnCl ₂ (91)	Dipb (30)
12.	Wyodak (6)	60	250	615	H ₂ (235) CO (235) Melt H ₂ O (40) HCl (60) Dipb (45)	ZnCl ₂ (91)	Dipb (30)
13.	Wyodak (6)	60	250	615	H ₂ O (515) Melt H ₂ O (40) HCl (60)	ZnCl ₂ (91)	MoO ₃ (20) CoCl ₂ (20)
14.	Wyodak (6)	180	250	675	H ₂ (470) Melt H ₂ O (40) HCl (60) Dipb (45)	ZnCl ₂ (91)	Dipb (30)

Table V. (continued)

Run No.	Feed Material (gm melt/ gm feed)	Residence time (minutes)	Temp. (°C)	Total Pressure (psia)	Gas Partial Pressures (psia)	Melt Composition ^a (% by wt.)	Additives (gm melt/ gm additive)
15.	Wyodak (6)	60	250	615	H ₂ (515) Melt H ₂ O (40) HCl (60)	ZnCl ₂ (91)	-
16.	9,10-dihydro- anthracene (10)	60	250	615	H ₂ (470) Melt H ₂ O (40) HCl (60) Dipb (45)	ZnCl ₂ (91)	Dipb (30)
17.	-	60	250	615	H ₂ (470) Melt H ₂ O (40) HCl (60) Dipb (45)	ZnCl ₂ (91)	Dipb (30)
18.	Illinois No. 6 (6)	180	250	615	H ₂ (575) Melt H ₂ O (40)	ZnCl ₂ (91)	-
19.	SRC (6)	180	250	615	H ₂ (575) Melt H ₂ O (40)	ZnCl ₂ (91)	-
20.	Wyodak (6)	60	250	615	H ₂ (430) Melt H ₂ O (40) Tetralin (45)	ZnCl ₂ (91)	Tetralin (15)
21.	9,10-dihydro- anthracene (10)	60	250	615	H ₂ (575) Melt H ₂ O (40)	ZnCl ₂ (91)	-
22.	Anthracene (10)	60	250	615	H ₂ (575) Melt H ₂ O (40)	ZnCl ₂ (91)	-

^a balance is H₂O^b temperature overshoot^c 1,4-dihydropropylbenzene

III. RESULTS AND DISCUSSION

A. Extractions of Feed Materials

Soxhlet-extraction yields of reaction products are the primary measure used to determine the degree of success or failure of each experiment. By successively extracting with cyclohexane, benzene, and pyridine, the products are fractionated into oil, asphaltenes, preasphaltenes, and unconverted solid residue. Extractions of untreated Wyodak and Illinois No. 6 coal and SRC were performed for comparison with extractions of reaction products. The yields from these blank extractions are given in Table VI.

B. Coal Experiments with Glass Apparatus

The purpose of the three experiments performed in the glass apparatus was to explore the feasibility of using zinc chloride melts diluted with cheaper metal halides. Iodine was used as an additive because Derencsenyi (D2) found it to be effective in increasing the benzene solubility of Wyodak coal at 200°C and atmospheric pressure. Because of the simplicity of the apparatus, samples could be removed during the run. The benzene extraction yields of samples taken at 15, 30, 60, and 120 minutes exhibit unusual behavior as shown in Figure 5 for Run 3. The point at zero hours represents untreated coal. There is a sharp rise in solubility in the first 15 minutes followed by a sharp decline. It is tempting to dismiss the 15-minute result as experimental error, but nearly identical behavior was observed in Run 2. Concurrent hydrogenolysis and

Table VI. Extraction Yields of Feed Materials

<u>Fraction</u>	<u>Solvent</u>	<u>Wyodak</u>	<u>% Yield (MAF)</u> <u>Illinois No. 6</u>	<u>SRC</u>
Oil	cyclohexane	0.7	0	3.1
asphaltenes	benzene	1.1	0.5	36.5
preasphaltenes	pyridine	11.0	17.7	60.4
Total		12.8	18.2	100.0

XBL7711-3972

Figure 5. Benzene Solubles vs. Time for Run 3

polymerization reactions are the likely cause for this behavior. In the early stages, hydrogenolysis produces a small amount of additional benzene-soluble material. After about 30 minutes, though, polymerization reactions have crosslinked the coal structure enough to give a net decrease in benzene solubility.

C. Coal Experiments with Parr Autoclave

Runs 4 through 22 were performed at elevated pressure in the Parr autoclave. Extraction yields of the products (except for experiments 16, 17, 21 and 22 in which model compounds were used) are given in Table VII. Related groups of experiments will be discussed together.

1. Effect of Time and Feed Material

The results of one-hour and three-hour experiments, Runs 7 and 8, with Wyodak coal are given in Figure 6. The points at zero hours are untreated coal extraction yields. The benzene yield does not increase significantly after the first hour, but the total yield is still increasing after three hours. This implies that, after one hour, coal is still being converted to pre-asphaltenes, but these are not in turn being converted to asphaltenes.

The results of three-hour runs with Wyodak coal, Illinois No. 6 coal, and SRC, Runs 8, 18, and 19 are compared in Table VIII. Raw Illinois No. 6 is more soluble in pyridine than raw Wyodak coal, and it appears to be more susceptible to increase after the ZnCl_2 treat-

Table VII. Extraction Yields for Experiments with Parr Autoclave
250°C, 615 psia total pressure, 6 gm melt/gm feed

Run No.	Feed Material	Residence Time (hr)	Gas Partial Pressure (psia)	Melt Composition ^a (% by wt.)	Additives (gm melt/gm additive)	Successive Extraction Yields (% MAF)			
						Cyclohexane	Benzene	Pyridine	Total
7	Wyodak	1	H ₂ (575) H ₂ O (40)	ZnCl ₂ (91)	-	0	4.6	16.8	21.4
8	Wyodak	3	H ₂ (575) H ₂ O (40)	ZnCl ₂ (91)	-	2.1	3.2	22.2	27.5
9	Wyodak	1	H ₂ (560) H ₂ O (40) 1-tetradecene (15)	ZnCl ₂ (91)	1-tetradecene (30)	0.9	3.1	12.4	16.4
10	Wyodak	1	H ₂ (495) H ₂ O (170)	KCl (36) MgCl ₂ (27) FeCl ₂ (27)	-	0.6	1.0	10.2	11.8
11	Wyodak	1	H ₂ (470) H ₂ O (40) HCl (60) Dipb (45)	ZnCl ₂ (91)	Dipb (30)	3.8	4.0	31.9	39.7
12	Wyodak	1	H ₂ (235) CO (235) H ₂ O (40) HCl (60) Dipb (45)	ZnCl ₂ (91)	Dipb (30)	3.3	2.9	22.4	28.6
13	Wyodak	1	H ₂ (515) H ₂ O (40) HCl (60)	ZnCl ₂ (91)	MoO ₃ (20) CoCl ₂ (20)	1.2	1.0	8.4	10.6

Table VII. (Continued)

Run No.	Feed Material	Residence Time (hr)	Gas Partial Pressure (psia)	Melt Composition ^a (% by wt.)	Additives (gm melt/gm additive)	Successive Extraction Yields (% MAF)			
						Cyclohexane	Benzene	Pyridine	Total
14	Wyodak	3	H ₂ (470) H ₂ O (40) HCl (60) Dipb (45)	ZnCl ₂ (91)	Dipb (30)	4.6	3.9	27.6	36.1
15	Wyodak	1	H ₂ (515) H ₂ O (40) HCl (60)	ZnCl ₂ (91)	-	2.1	2.5	16.0	20.6
18	Illinois No. 6	3	H ₂ (575) H ₂ O (40)	ZnCl ₂ (91)	-	0.3	3.7	41.4	45.4
19	SRC	3	H ₂ (575) H ₂ O (40)	ZnCl ₂ (91)	-	3.6	16.9	79.5	100.0
20	Wyodak	1	H ₂ (530) H ₂ O (40) Tetralin (45)	ZnCl ₂ (91)	Tetralin (15)	-	16.6	60.4	77.0

^a Balance is H₂O

^b 1,4-diisopropylbenzene

XBL7711-3971

Figure 6. Solubility vs. Time for Runs 7,8

Table VIII. Extraction Yields of Different Feed Materials
After ZnCl_2 Treatment

<u>Fraction</u>	<u>Solvent</u>	<u>Wyodak</u>	<u>Illinois No. 6</u>	<u>SRC</u>
oil	cyclohexane	2.1	0.3	3.6
asphaltenes	benzene	3.2	3.7	16.9
preasphaltenes	pyridine	22.2	41.4	79.5
Total		27.5	45.4	100.0

% Improvement over total yield for raw feed	115	149	0
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ment. In this sense, Illinois No. 6 might be a more sensitive feed material to use for future exploratory bench-scale work. As discussed previously, though, sub-bituminous coals such as the Wyodak offer the potential of lower hydrogen consumption with only slight reduction in yields.

There can be no improvement in the total yield for melt-treated SRC because SRC is totally soluble in pyridine to begin with. It was hoped that there would be increases in the yields of oil and asphaltenes, however. Actually, the yield of oil increased only slightly and there was a significant reduction in the yield of asphaltenes relative to raw SRC, indicating that asphaltenes were converted to preasphaltenes. An increase in molecular weight, possibly due to polymerization, is the likely cause of the decreased asphaltene yield.

2. Effect of MoO_3 and CoCl_2

Molybdenum trioxide has been used as an additive to zinc chloride in pyrene hydrocracking studies (R3, Book 1, p. 38) to improve hydrogenation activity, resulting in lower gas yields and slightly better distillate yields. In view of this, one experiment was performed with MoO_3 as an additive to a zinc chloride melt. An equal weight of CoCl_2 was also added to the melt. It was felt that this compound, by itself or in combination with the MoO_3 (a simulated cobalt molybdate catalyst), might be a promoter also. Anhydrous hydrogen chloride (60 psia) was added to the gas phase. (This experiment was used to screen several possible promoters simultaneously.)

The total extraction yield for the product of this experiment is lower than even that of the untreated Wyodak coal. One of the additives, or possibly the combination used, has a detrimental effect on the ZnCl_2 melt. In addition, the MoO_3 could not be easily recovered from the reaction products because its solubility in water is extremely low.

3. Effect of a Different Metal Chloride Melt

It has been mentioned that the use of equilibrium amounts of certain metal chlorides, such as FeCl_2 , in ZnCl_2 melts would reduce zinc losses to the ash. Therefore, the hydrocracking activity of chlorides of metals found in coal ash is of interest, and this prompted Run 10 using a melt of $\text{KCl/MgCl}_2/\text{FeCl}_2$. Of the three melt constituents, only FeCl_2 is thought to have hydrocracking activity.

The total extraction yield is again slightly lower than for untreated Wyodak. While this melt appears to have no activity at 250°C , one or more of the three constituents might still be used as additives to ZnCl_2 melts to reduce zinc losses.

This experiment may be looked upon as a temperature blank for Run 7 with a pure ZnCl_2 melt. If the $\text{KCl/MgCl}_2/\text{FeCl}_2$ melt is assumed to be inert, then it can be said that simply subjecting Wyodak coal for 1 hour to 250°C and 600 psig total pressure (approximately 430 psia hydrogen partial pressure) in an inert dispersing medium will not increase its solubility in benzene or pyridine.

The increase in solubility must truly be due to catalytic activity of the ZnCl_2 melt.

4. Effect of ZnCl_2/HCl /Hydride Donor Systems

The application of strong acid/hydride donor systems directly to coal is a relatively new concept. The intention here was to supplement the hydrocracking activity of ZnCl_2 as such with the hydrogenation activity of a ZnCl_2/HCl /hydride donor combination. Two different hydride donors were used, 1-tetradecene and 1,4-diisopropylbenzene. It is not anticipated that either of these compounds would be used in a large-scale process. They were chosen to represent two classes of compounds that are believed capable of hydride donation.

Alpha olefins such as 1-tetradecene form stable allylic carbonium ions, and in the process of doing so, transfer a hydride ion as shown in equation (13).

Compounds with tertiary carbons, such as 1,4-diisopropylbenzene with two, can also supply a hydride ion in the process of forming a stable carbonium ion, as shown in equation (14).

A representative of each class with boiling points above 200°C was needed so that the vapor pressure of the hydride donor would be less than about 50 psi at 250°C. The two compounds selected meet the requirement; 1-tetradecene boils at 251°C and 1,4-diisopropylbenzene boils at 210°C.

In Run 9, using 1-tetradecene, the hydrolysis of ZnCl_2 was relied upon as a source of HCl. The reaction product had a reduced solubility in pyridine compared to the product of Run 7, in which a pure ZnCl_2 melt was used. It is possible that alkylation of the coal structure with the 1-tetradecene occurred, but this usually increases solubility by increasing the H/C ratio. It is more likely that the 1-tetradecene actually cross-linked the coal structure. This explanation has also been proposed by Larsen and Kuemmerle (L4) in relation to their work with sulfuric acid-catalyzed alkylation of coal with isobutylene, done concurrently with this research. Whether or not hydride transfer to the coal structure occurred is difficult to say. Nevertheless, the reduced solubility led to the abandonment of the use of alpha olefins in this study.

Anhydrous HCl was added to the gas phase in the experiments using 1,4-diisopropylbenzene. In Run 11, with one hour's contact, 39.7 percent of the coal had become pyridine-soluble; this is a significant increase over untreated coal and over coal treated with ZnCl_2 alone. The extracts in this run, and in other runs with 1,4-diisopropylbenzene, were dried at 180°C in the vacuum

oven to be certain that the additive was removed by vaporization and was not being counted as extract.

Treatment with the partial pressure of HCl doubled and the time increased to three hours (Run 14) resulted in the slightly reduced pyridine solubility of 36.1 percent. This implies that HCl partial pressures greater than 60 psia and contact times greater than one hour are not justified. Run 15, using HCl but no 1,4-diisopropylbenzene, indicates that HCl by itself is not a promoter; the extraction yield is even lower than for Run 7 with ZnCl_2 alone. Again, it is difficult to say whether or not hydride transfer occurred, and if so, what effect it had on the solubility of the product. It is possible that the increased extraction yields are due to alkylation of the coal structure by the 1,4-diisopropylbenzene. Alkyl groups could increase the coal solubility by increasing the H/C ratio. In addition, the weight of the coal is increased by the weight of the alkyl groups added, and some of this weight ultimately ends up in the extracts. Concurrent work by Ross and Low (R2) using the system $\text{AlCl}_3/\text{HCl}/\text{dimethylbutane}$ with Illinois No. 6 coal led them to the same conclusion that alkylation could be occurring.

It was hoped that alkylation would be minimized by the 470 psia partial pressure of hydrogen. The carbonium ions formed in equations 13 and 14 would be re-hydrogenated before alkylation could occur. Even if alkylation did occur, this may not be so serious. While 1,4-diisopropylbenzene is too expensive to use if it is

consumed, cheaper hydride donors such as isobutane might be used. Indeed, the group added by alkylation is not entirely lost by being incorporated into the product.

5. Effect of Carbon Monoxide

Metal carbonyls are attractive as liquefaction catalysts because they are highly selective for specific reactions. It is conceivable that these compounds could be formed in situ by reaction between carbon monoxide and metals in the ash. This was the motivation for Run 12, in which a 50/50 mixture (by volume) of hydrogen and carbon monoxide was used in the gas phase. All other conditions were identical to those in Run 11. The total extraction yield of the product is intermediate between Run 11 with 1,4-diisopropylbenzene and Run 7 with a pure ZnCl_2 melt. Thus it appears that carbon monoxide does not interact favorably with the ash.

There are two possible explanations for the reduced yield in Run 12: (1) the carbon monoxide has a negative effect or (2) the carbon monoxide is essentially inert, but its use has resulted in a reduced hydrogen partial pressure, upon which the total yield is dependent. There is no obvious reason why the carbon monoxide would have a negative effect. If the second explanation were correct, this experiment could be considered a study of the dependence of yield on hydrogen partial pressure, and a plot of yield versus hydrogen partial pressure would be called for. Such a plot is shown in Figure 7. The point at zero time is

XBL7711-3969

Figure 7. Dependence of Yield on Hydrogen Partial Pressure

for untreated coal, which is tentatively considered equivalent to an experiment with zero hydrogen partial pressure. The surprisingly simple result is that, at least below 500 psi, the yield is directly proportional to hydrogen partial pressure.

The correct explanation could also be a combination of a negative effect of carbon monoxide and the reduction in hydrogen partial pressure. An experiment in which inert nitrogen is used in place of carbon monoxide as a diluent is needed to clarify this question; in this study, a higher priority was given to other experiments.

6. Effect of Tetralin

Tetralin is frequently used in coal liquefaction studies because of its hydrogen-donating capability. The idea of using tetralin with ZnCl_2 was originally dismissed for several reasons. Tetralin had been used with ZnCl_2 by Consol (R3, Book 1, p. 7) in studies with coal extracts at 400°C. Only a slight improvement over the use of pure ZnCl_2 was observed. Seth (S3) had used tetralin with phosphoric acid in treating Wyodak coal at 200°C. He found no improvement over the use of phosphoric acid alone. Finally, Draemel and Grens (D3) had found no hydrogen transfer with tetralin below 350°C in extraction studies with Wyodak coal. The more recent work at Consol (Z1), however, in which tetralin was found to increase the conversion of a sub-bituminous coal in ZnCl_2 at 358°C whereas it had less effect at higher temperatures, suggested that at 250°C it might have a more substantial effect. In Run 20, tetralin

was added to a ZnCl_2 melt to test its effect on Wyodak sub-bituminous coal.

The conversion to soluble materials in this experiment far surpasses the results of any previous experiment in this study. The distribution of soluble products is given in Table IX, along with the extraction yields for untreated Wyodak coal and Wyodak coal treated with ZnCl_2 alone. The solubility in pyridine is 77.0 percent. In addition, the 16.6 percent yield of benzene solubles is much higher than for any previous experiment.

It was not possible to determine the distribution of tetralin among the products. This is due to lack of provision for gas analysis. Much of the tetralin undoubtedly flashed from the liquid mixture during depressurization. The rest would be distributed between the solid reaction product and the aqueous filtrate collected after filtration.

The amount of tetralin in the solid reaction product was estimated to be 5.7 percent. The procedure used to determine this percentage is presented in Appendix C. The extraction yields were corrected for this inclusion, so that they are on a moisture-free, ash-free, and tetralin-free basis. While it is important to make this approximation to be able to correct the extraction yields, the retention of tetralin by the MTC should not be a serious problem in a large-scale process. The logical steps to follow the ZnCl_2 /tetralin treatment are a recovery step for the ZnCl_2 , and then solvent extraction of the MTC.

Table IX. Extraction Yields for Tetralin Experiment

<u>Fraction</u>	<u>Solvent</u>	Untreated <u>Wyodak</u>	% Yield (MAF) ZnCl_2 treated <u>Wyodak (Exp.7)</u>	% Yield (MAF) ZnCl_2 , tetralin treated <u>Wyodak (Exp.20)</u>
oil	cyclohexane	0.7	0	-
asphaltenes	benzene	1.1	4.6	16.6
pre- asphaltenes	pyridine	11.0	16.8	60.4
<hr/>				
Total		12.8	21.4	77.0

The tetralin could be recovered by distillation from the solvent.

The filtrate from the product work-up was extracted with CCl_4 to remove tetralin. The CCl_4 phase was yellow, possibly due to the presence of coal extract removed by the tetralin during the reaction. Tetralin and naphthalene were identified in the CCl_4 phase by gas chromatography at 140°C in a ratio of 60 moles tetralin/40 moles naphthalene. The total amount of tetralin plus naphthalene in the filtrate was small, though, probably on the order of one gram out of the twenty grams charged.

Tetralin is converted to naphthalene in the process of hydrogen donation in the following manner:

The presence of naphthalene along with tetralin is a reliable indication that hydrogen transfer occurred during the reaction. However, hydrogen transfer may not have occurred to exactly the observed extent of 40 percent. First, the mole ratio of tetralin to naphthalene was determined on the basis of about five percent of the tetralin used in the experiment. The mole ratios of tetralin and naphthalene in the solid product or in the gas phase may have been different than in the initial filtrate. Also, it is possible that some of the naphthalene produced by hydrogen transfer was converted back to tetralin

by the reverse reaction in equation (15). If this is the case, it is possible that hydrogen transfer occurred to an extent even greater than 40 percent of the charged tetralin.

The occurrence of hydrogen transfer is further supported by the elemental analysis of the MTC from Run 20. In Run 7, with pure ZnCl_2 , the atomic H/C ratio of the MTC (0.85) is lower than untreated Wyodak coal (0.96). The reasons for this are discussed in Section 7a. The H/C ratio of the MTC from Run 20 (0.96), on the other hand, is unchanged from the untreated coal. Either the tetralin retards the processes by which hydrogen is lost, or it adds enough hydrogen to make up for these losses. In either case, its effect is beneficial.

The role of ZnCl_2 in increasing the solubility of the coal so significantly is not known for sure. The comparison in Table IX of the results of the experiment with ZnCl_2 alone and the experiment with ZnCl_2 and tetralin combined indicate that tetralin has a critical role.

To be certain that ZnCl_2 itself is even necessary, an experiment in which Wyodak coal is treated with tetralin alone at 250°C was needed. Such an experiment had essentially been done by Draemel and Grens (D3) in their extraction studies. In these studies a pressurized Soxhlet extraction apparatus was constructed so that solvents could be used at temperatures greater than their normal boiling points. In one experiment, Wyodak coal was extracted for four hours at 250°C with tetralin. No

hydrogen was used, but this should not invalidate the comparison since the role of gaseous hydrogen is only to replenish the tetralin by hydrogenating naphthalene as shown in equation 15. It is not likely that the tetralin was depleted during the extraction.

The tetralin extraction yield in this experiment was 9.6 percent (MAF). Some of the residue from this extraction, which had been stored in a nitrogen atmosphere, was extracted with pyridine for comparison with the MTC from Run 20. The pyridine extraction yield was 6.1 percent (MAF); so that the total tetralin-plus-pyridine yield was 15.7 percent (MAF). This is far less than the 77 percent yield (MAF) for the MTC of Run 20. This is a strong indication that ZnCl_2 has a critical role in activating either the tetralin or the coal.

The MTC from Run 20 was also extracted with methyl ethyl ketone so that a comparison could be made with the Consol experiment cited earlier (see Table II), in which a Montana sub-bituminous coal was treated with ZnCl_2 and tetralin at 358°C and a hydrogen partial pressure of 1500 psia. The combined C_4 - 400°C distillate, 400°C^+ MEK soluble, and 400°C^+ MEK insoluble products in Table II are comparable to MTC. Considering only these products, and assuming that the C_4 - 400°C distillate is soluble in MEK, the total solubility in MEK is 87.5 percent. The solubility in MEK of the MTC from Run 20 is 46.6 percent.

7. Other Analyses of Reaction Products

a. Changes in H/C Ratio

The atomic H/C ratios of the MTC products are generally lower than those of the untreated feed materials. An unequivocal explanation for this is not possible since many processes affecting the H/C ratio occur simultaneously. Mass spectrometric analyses of the gases produced in Runs 6 and 7 indicate that NH_3 , CO , CO_2 , and CH_4 and other light hydrocarbons are evolved. Inasmuch as the atomic H/C ratios of these gases are different from that of the raw coal, their evolution will result in a product with a H/C ratio not necessarily equal to that of the raw coal. In addition, experiments with model compounds have shown that both hydrogenation and dehydrogenation take place at 250°C . The net effect of the various processes occurring is to remove more hydrogen than carbon.

The change in H/C ratio levels off after the first hour of treatment with pure ZnCl_2 melts, as shown in Figure 8 for Runs 7 and 8. This suggests that the various reactive groups which lead to the evolution of the gases (for example, carboxylic acid groups decomposing to produce CO_2) are nearly depleted in one hour.

In two experiments, the H/C ratios of the products were not lower than the untreated feed material. Such was the case in the tetralin experiment, Run 20; as discussed earlier, this supports the possibility that hydrogen transfer occurred in this experiment. In Run 19 with SRC,

XBL7711-3973

Figure 8. Change in H/C Ratio with ZnCl₂ Treatment

the atomic H/C ratio of the MTSRC (0.78) was found to be substantially the same as untreated SRC (0.77). Gases which could evolve to alter the H/C ratio were probably already removed in the SRC process itself.

b. Physical Property Changes

The MTC and the Soxhlet extraction residue of the MTC exhibit changes in physical properties as compared to the raw coal. The BET surface area of raw Wyodak coal is approximately $100 \text{ m}^2/\text{gm}$. The MTC from Run 4 (10 minutes at 250°C) has a surface area of $140 \text{ m}^2/\text{gm}$, and the residue of a benzene extraction of this MTC has a surface area of $176 \text{ m}^2/\text{gm}$. It is likely that the surface area of the residue of a pyridine extraction would be higher yet, were it to be measured. This trend toward increased surface areas is favorable for liquefaction since reaction rates are proportional to surface area. It suggests that a two-liquid-phase reaction system involving a zinc chloride melt and an organic extraction solvent should be considered. The purpose of the organic solvent would be to continuously extract reaction products as they are formed thereby removing them from the inorganic reaction phase and increasing the surface area of the remaining coal.

In addition to increased surface area, a general reduction occurs in the particle size distribution of the MTC compared to the 28-100 mesh Wyodak coal charged to the system. The MTC from Run 8, for example, is 40 percent minus 100 mesh, 10 percent minus 170 mesh, and 3 percent

minus 200 mesh. This size reduction is possibly due to a "popcorn effect" in which undried coal at ambient temperature is abruptly subjected to a 250°C medium. The moisture within the coal structure vaporizes rapidly and, in the process of escaping, fractures the coal particle into smaller particles. The general size reduction undoubtedly aids further processing of the coal.

c. Initial Filtrate Analyses

The initial filtrate is the liquid collected upon filtering the reaction product to remove the MTC. It is composed of the zinc chloride melt and any liquid organic materials that might have been formed during the experiment. The initial filtrate was extracted with CCl_4 . The CCl_4 phase was then washed with water to remove traces of ZnCl_2 . It was then analyzed by gas chromatography to detect the presence of organic reaction products. Only in Run 20 was anything detected, and in this case the only compounds found were tetralin, charged to the reactor, and naphthalene formed by tetralin dehydrogenation.

D. Model-Compound Experiments

The activity of zinc chloride for hydrocracking 9,10-dihydroanthracene and anthracene was studied in Runs 16, 17, 21 and 22. In Run 16 the catalyst system $\text{ZnCl}_2/\text{HCl}/1,4$ -diisopropylbenzene was used with 9,10-dihydroanthracene to determine whether the latter could be cracked or hydrogenated at 250°C. Run 17 was performed without the 9,10-dihydroanthracene. From gas

chromatographic analysis of the products of these experiments, it can be concluded that the 1,4-diisopropylbenzene cracks to a small degree to mono-isopropylbenzene (cumene), and that the 1,4-diisopropylbenzene polymerizes with itself to a small degree. It is possible that the 1,4-diisopropylbenzene also alkylates the 9,10-dihydroanthracene. These are unwelcome results, and they confirm the fact that the 1,4-diisopropylbenzene is not a good choice for a hydride donor. As mentioned earlier, although not yet tried, isobutane might be a better choice.

The presence of 1,4-diisopropylbenzene and its reaction products made it difficult to determine whether or not the 9,10-dihydroanthracene had been cracked or hydrogenated. To clarify this, 9,10-dihydroanthracene (Run 21) and anthracene (Run 22) were treated with only the ZnCl_2 melt. Anthracene was not cracked and 9,10-dihydroanthracene was cracked only to the extent of about one percent. This is disappointing, but the cracking activity might be increased by the addition of proton acids such as H_2SO_4 or H_3PO_4 . The ZnCl_2 melt did show hydrogenation activity, however. In both experiments there were four products: anthracene, 9,10-dihydroanthracene, tetrahydroanthracene, and unidentifiable polymerization products. Tetrahydroanthracene was identified by mass-spectrometric analysis. A sample for this analysis was collected in a capillary tube after separation by gas chromatography at 215°C .

The compositions of the solid products of Runs 21 and 22, determined by gas chromatography peak areas, is given in Table X. Since the polymerization products produced no peaks, the compositions are on a polymerization-product-free basis. The compositions determined by peak areas are mole-percent, but since the molecular weight of the three products vary by only about two percent, the compositions may also be taken as weight percents. Two solid products were collected in Run 22, about 28 gm of a black solid in the glass liner and about 2 gm of a white solid from the autoclave head. A similar white solid was present in Run 21 but it was not saved since it was thought to be ZnCl_2 .

Due to the hydrogenation-dehydrogenation equilibrium between anthracene and 9,10-dihydroanthracene, whichever is used as the feed, the other is present in the products. The presence of the tetrahydroanthracene could be explained by various reactions depending on its specific structure. The most likely structures are 2,3,9,10-tetrahydroanthracene and 1,2,3,4-tetrahydroanthracene (possibly both are present). If it is the former, then the reactions taking place should be:

If it is the latter, then the following reactions should be involved:

Table X. Composition of Solid Products from Experiments 21 and 22
mole% on polymerization-product-free basis

	Experiment 21 <u>9,10-dihydroanthracene Feed</u>	Experiment 22 Anthracene Feed	
		<u>White Solid</u>	<u>Black Solid</u>
anthracene	35	36	45
9,10-dihydroanthracene	22	25	9
tetrahydroanthracene	43	39	46

In either event, these experiments have illustrated that

ZnCl_2 melts are active for hydrogenation at 250°C .

IV. CONCLUSIONS AND RECOMMENDATIONS

A. Conclusions

The following conclusions can be drawn on the basis of the results obtained in the present study:

1. Experiments with ZnCl_2 melts at 200°C show that hydrogen partial pressures on the order of one atmosphere are not sufficient to produce the hydrogenolysis reactions necessary to increase significantly the extractibility of coal in benzene.

2. Treating Wyodak coal with a ZnCl_2 melt for one hour at 250°C and a hydrogen partial pressure of approximately 575 psia increases total extractibility in pyridine from 12.8 percent to 21.4 percent. Similar treatment in what appears to be an inert medium ($\text{KCl}/\text{MgCl}_2/\text{FeCl}_2$) produces neither an increase nor a significant decrease in the extractibility. This indicates that ZnCl_2 melts are definitely catalytic at 250°C .

3. Similar experiments with Wyodak coal, Illinois No.6 coal, and SRC show that Illinois No. 6 is most susceptible to solubility increase using ZnCl_2 melts. The solubility of SRC in benzene actually decreased after the treatment, due to polymerization or to enhanced acid-base complexing.

4. Addition of 1,4-diisopropylbenzene, a possible hydride donor, along with HCl to a ZnCl_2 melt used to treat Wyodak coal was found roughly to triple the extractibility of the coal in pyridine. It cannot be definitely concluded

whether the increased solubility is due to hydride transfer to the coal structure, or to alkylation of coal by the 1,4-diisopropylbenzene.

5. Because partial replacement of hydrogen by carbon dioxide leads to proportionate reduction in the amount of coal converted, it appears that carbon monoxide does not combine with coal-ash constituents at 250°C to form catalytically active metal carbonyls which might aid the conversion.

6. By far the best results in the study occurred when Wyodak coal was treated with a ZnCl_2 melt in the presence of tetralin. The total solubility of the coal in pyridine increased from 12.8 to about 77.0 percent with one hour's treatment at 250°C and a hydrogen partial pressure of approximately 530 psia. There is direct evidence that some hydrogen transfer from tetralin to coal occurred in this experiment, although tetralin incorporation also may have occurred.

7. The MTC product resulting from treatment with ZnCl_2 melt generally exhibits increased surface area, particle-size reduction, and reduced atomic H/C ratios.

8. Experiments with anthracene and 9,10-dihydroanthracene as model compounds show that ZnCl_2 melt at 250°C has significant hydrogenation/dehydrogenation activity, but negligible activity for breaking carbon-carbon bonds of the types present in the model compounds or in their 1,2,3,4-tetrahydroanthracene product.

B. Recommendations for Future Work

In view of the results of this study, the following recommendations for future work are put forward:

1. The effects of ZnCl_2 melt with tetralin and similar compounds with hydrogen-donating capability, should be explored further. The effect of varying contact time, temperature, hydrogen pressure, and the relative quantities of coal, ZnCl_2 melt, and hydrogen-donor solvent should be determined.

2. The use of temperatures in the range of 275 to 325°C should be considered to increase reaction rates and improve contacting by reducing viscosity.

3. Melts combining ZnCl_2 with other metal halides should be sought to reduce the cost of the melt, reduce the loss of Zn to the coal ash (which appears to involve ion exchange), and reduce its viscosity.

4. Provision should be made with the experimental apparatus for the collection and analysis of gaseous products. This is necessary to allow the calculation of an accurate mass balance for the reacting system. Analytical techniques for determining the information now missing should be selected or developed.

REFERENCES

- B1 Boudart, M., J. A. Cusumano, and R. B. Levy, New Catalytic Materials for the Liquefaction of Coal, Catalytica Associates, Inc., Palo Alto, California, prepared for Electric Power Research Institute, October 1975.
- B2 Bloom, Harry, The Chemistry of Molten Salts, W. A. Benjamin, Inc., New York, p.p. 154-169, 1967.
- B3 Berg, Lloyd and John S. Malsam, U.S. Patent 3,736,250 assigned to U.S. Dept. of Interior, May 29, 1973.
- B4 Booras, G. S. and E. E. Petersen, Lawrence Berkeley Laboratory Report LBL-5272 (1976).
- C1 Coal Processing - Gasification, Liquefaction, Desulfurization: A Bibliography 1930-1974, Atomic Energy Commission, October 1974.
- D1 Davis, John C., Chem. Engr., 83, 77, July 19, 1976.
- D2 Derencsenyi, Tibor T. and Theodore Vermeulen, Lawrence Berkeley Laboratory Report LBL-3265 (1975).
- D3 Draemel, Dean C. and E. A. Grens II, Lawrence Berkeley Laboratory Report LBL-4434 (1975).
- F1 Furlong, L. E., E. Effron, L. W. Vernon, and E. L. E. L. Wilson, Chem. Engr. Progr., 72(8), 69 (1976).
- F2 Farcasiu, M., T. O. Mitchell, and O. D. Whitehurst, Preprints, ACS Div. of Fuel Chem., Am. Chem. Soc., 21(7), 11 (1976).
- G1 Given, P. H., Fuel, 39, 147 (1960).
- H1 Hottel, H. C., and J. B. Howard, New Energy Technology - Some Facts and Assessments, MIT Press, Cambridge, Ch. 3 and 5, 1971.
- H2 Hill, G. R., and L. B. Lyon, Ind. Eng. Chem., 54, No. 6 37 (1962).
- H3 Hawk, C. O. and R. W. Hiteshue, U. S. Bureau of Mines Bulletin No. 622(3), 1965.
- I1 Institute of Gas Technology, Symposium Papers - Clean Fuels from Coal, Chicago, September 10-14, 1973.
- K1 Katzman, H., A Research and Development Program for Catalysis in Coal Conversion Processes, Electric Power Research Institute Report No. 207-0-0, Palo Alto, Calif., 1974.

- K2 Kawa, W., S. Friedman, L. V. Frank, and R. W. Hiteshue, Preprints, ACS Fuel Chem., Am. Chem. Soc., 12(3) 4347 (1968).
- K3 Konieczynski, Jan, Koks, Smola, Gaz, 18(7), 202-7 (1973), as cited in Chem. Abstr. 82(12), 75204W (1973).
- K4 Kawa, W., H. F. Feldmann, and R. W. Hiteshue, Preprints, ACS Fuel Chem., Am. Chem. Soc., 14(4), Part 1, 19 (1970).
- K5 Kiebler, M. W., Chemistry of Coal Utilization, John Wiley and Sons, New York, Vol. 1, 715-60, 1945.
- L1 Liebenberg, Barend J. and Hendrik G. J. Potgieter, Fuel, 52, 130 (1973).
- L2 Loth, Rene A., U. S. Patent 3,790,468, assigned to Shell Oil Co., Feb. 5, 1974.
- L3 Loth, Rene A. and Milton M. Wald, U. S. Patent 3,790,469, assigned to Shell Oil Co., Feb. 5, 1974.
- L4 Larsen, John W. and Edgar W. Kuemmerle, Fuel, 55, 162 (1976).
- O1 O'Hara, J. B., A. Bela, N. E. Jentz, and S. K. Khaderi, Chem. Engr. Progr., 72(8), 65 (1976).
- P1 Perry, Harry, Chem. Engr., 81, 88, July 22, 1974.
- P2 Project Western Coal: Conversion of Coal Into Liquids - Final Report, Research and Development Report No. 18, prepared by the University of Utah for the Office of Coal Research, May 1970.
- Q1 Qader, S. A., K. Duraiswamy, R. E. Wood, and G. R. Hill AIChE Symposium Series, 69(127), 102 (1973).
- R1 Regeneration of Zinc Chloride Catalyst, Research and Development Report No. 39, Vol. III, Book 2, prepared by the Consolidation Coal Company for the Office of Coal Research, 1968.
- R2 Ross, David S. and James Y. Low, "Homogeneous Catalysis - Acid Catalysis," in Homogeneous Catalytic Hydrocracking Processes for Conversion of Coal to Liquid Fuels, Stanford Research Institute, Menlo Park, Calif., Quarterly Report Nos. 2, 3, 1976.
- R3 Research on Zinc Chloride Catalyst for Converting Coal to Gasoline, Research and Development Report No. 39, Vol. III, Books 1,2, prepared by the Consolidation Coal Company for the Office of Coal Research, 1968.

- S1 Sternberg, H. W., R. Raymond, and F. K. Schweighardt, "The Nature of Coal Liquefaction Products," Symposium on Progress in Processing Synthetic Crudes and Residues, Division of Petroleum Chemistry, Amer. Chem. Soc., Chicago (1975).
- S2 Struck, R. T., W. F. Clark, P. J. Dudt, W. A. Rosenhoover, C. W. Zielke, and E. Gorin, Ind. Eng. Chem. Process Des. Dev., 8(4), 546 (1969).
- S3 Seth, Manu and Theodore Vermeulen, Lawrence Berkeley Laboratory Report LBL-5997 (1976).
- T1 Timmermans, J., The Physical-Chemical Constants of Binary Systems in Concentrated Solution, Vol. 3, Interscience, New York, p. 838, 1960.
- V1 Vines, R. F., "Noble Metals", in Corrosion Resistance of Metals and Alloys, F. L. LaQue, and H. R. Copson, ed., Reinhold Publishing Corp., New York, p. 609, 1963.
- W1 Wiser, W. H., Proceedings of Electric Power Research Institute Conference on Coal Catalysis, Palo Alto, California, pp. 3-53 to 3-96, 1973.
- W2 Wiser, W. H., "Conversion of Coal to Liquids--Research Opportunities", in Research in Coal Technology - The University's Role, State University of New York at Buffalo, October 21-22, 1974.
- W3 Wiser, W. H., "Applied Research and Evaluation of Process Concepts for Liquefaction and Gasification of Western Coals", in proceedings of ERDA/NSF/EPRI University Principal Investigators' Conference - Coal Research, Colorado School of Mines, Golden, CO., Sept. 3,4, 1976.
- W4 Weller, Sol, M. G. Pelipetz, and S. Friedman, Ind. Eng. Chem., 43, 1575 (1951).
- W5 Wood, R. E. and W. H. Wiser, Ind. Eng. Chem. Process Des. Dev., 15(1), 144 (1976).
- W6 Wrister, J., J. Am. Chem. Soc., 97(15), 4312 (1975).
- Z1 Zielke, C. W., W. A. Rosenhoover, and Everett Gorin, Preprints, Div. of Fuel Chem., Am. Chem. Soc., 19(2), 306 (1974).
- Z2 Zielke, C. W., R. T. Struck, J. M. Evans, C. P. Costanza, and E. Gorin, Ind. Eng. Chem. Process Des. Dev., 5(2), 151 (1966).

- Z3 Zielke, C. W., R. T. Struck, J. M. Evans,
C. P. Costanza, and E. Gorin, Ind. Eng. Chem. Process
Des. Dev., 5(2), 158 (1966).
- Z4 Zielke, C. W., R. T. Struck, and E. Gorin, Ind. Eng.
Chem. Process Des. Dev., 8(4), 552 (1969).

APPENDIX A

Corrosion Studies

1. Gold-Plated Materials

a. Samples

Before gold plating the autoclave, corrosion tests with several gold-plated samples were undertaken. A magnetically stirred 1000-ml three-checked glask was used. A thermometer was inserted in one neck. The temperature was maintained at 200°C by regulating power input to a heating mantle with a variable autotransformer. A steady flow of nitrogen was introduced through the second neck to purge the flask of oxygen which might otherwise affect the corrosion rate. Samples were suspended from the third neck so that they were approximately half submerged in the melt.

The melts were prepared by adding an 80 percent solution of zinc chloride in water to the flask and heating to 200°C. At this temperature enough water had vaporized to give a 91 percent melt. During the run, additional water was added to replace further vaporization losses, so that the melt composition remained constant. In some cases 37 percent hydrochloric acid was added at a rate of about 150 gm per hour from a buret protruding through one of the flask necks. Litmus paper tests indicated that the melt was maintained acidic; the HCl did not all flash off.

The results of these corrosion tests are mostly qualitative since the gold layer is only 0.5 ml thick and

there is very little material to work with. Also, ZnCl_2 and HCl are more likely to pit the samples rather than cause uniform erosion, so that the concept of corrosion rates in mls per year (mpy) would be misleading.

Four separate tests were made. First, a piece of 316SS, not plated, was subjected to a ZnCl_2 melt with no added HCl . After one hour, the submerged half of the sample had become black, but there was no other evidence of attack. A second piece of 316SS was gold plated (all gold plated samples were first plated with copper and nickel to give a surface amenable to gold plating) and bent slightly to introduce stress. It was subjected to the ZnCl_2 melt, again with no added HCl . After one hour there was no change except that a copper color developed where a steel clamp had held the sample. Copper apparently diffused through the nickel and gold to the surface. After three hours more, five pin-point-size pits developed on the submerged part of the sample, near the stressed area.

The third test was made with a heavily scratched piece of Monel 400 which was gold plated. The sample was subjected to a ZnCl_2 melt with HCl added for two hours. Six pin-point-size pits developed, all of them on or near surface scratches. Much of the gold plate along the sharp edges of the sample was gone. A copper color appeared where the clamp contacted the sample. This sample was weighed before and after the test. The corrosion rate was determined to be about 100 mpy. However, as mentioned earlier, this type of analysis is misleading due to the

localized nature of chloride pitting. The corrosion rate would have been much lower if it were not for the heavy losses of gold around the edges.

The final test was made with two gold-plated samples of 316SS. The two sides of each piece had been differently finished before plating. The four finishes are:

- I. Vapor Honed; similar to sand blasting--puts tiny pits in the sample
- II. Sandpapered; No. 320 paper--puts fine scratches in the sample
- III. Polished
- IV. No Special Finish; left as is.

Both pieces were bent to compare corrosion effects in stressed and non-stressed areas.

After one hour (no HCl added) there was no change in any of the samples, except that a small amount of gold was etched away from the sanded sample for about 1/16 inch along one of the scratches in the stressed area. After a second hour (still no HCl added) there was still no change except the etched area on side II had enlarged slightly. During the next two hours HCl was added. The vapor-honed side developed several small pits along the stressed area to the extent of about 15 percent of the total area. The polished side also peeled along the stressed area but only to the extent of about 5 percent of the total area. The side, with no special finish, was etched slightly along the stressed area but completely intact in non-stressed areas.

b. Parr Autoclave

In view of the sample tests, the Parr autoclave was gold plated with no special finishing. The original finish of the bomb was quite smooth and there are no stressed areas. Sharp edges are restricted to the fitting holes through the head. All the fittings attached to the head were removed prior to plating so that all surfaces of the head and cylinder were well covered by gold.

The gold plate served its purpose in protecting the autoclave during the coal experiments, but did not survive completely itself. After the first experiment (Run 4), the bomb cylinder surface had several copper-colored blotches. This again is apparently due to copper diffusing through the nickel and gold layers. The reaction mixture in the experiment was 250°C , but the autoclave walls were much hotter than this because of the heat transfer resistance of the glass liner and the air space between the liner and the walls. This factor affected the rate of copper diffusion since diffusion increases with temperature. After three experiments with direct HCl addition (Runs 11, 12 and 13) most of the autoclave cylinder had a copper appearance and a yellow solid, identified as AuCl , was found at the bottom of the autoclave outside the glass liner.

The head is not heated so its temperature during use is 250°C or less. At this temperature, copper did not diffuse to the surface. Some of the gold plate did flake off, though, beginning slowly with Run 10 and continuing

until about 25 percent of the exposed face of the head was gone after Run 20. None of the gold on the internal surfaces of the head was lost.

Overall, gold-plating the autoclave was successful in preventing serious attack on the Model 400. The only serious effect is a small groove about 1/32 inch deep (the total wall thickness is 1/4 inch) and about an inch long in the cylinder wall that developed during Run 17. It did not become worse after this experiment.

2. Hastelloy C. Materials

The stirrer shaft, impellers, and thermocouple sheath used are made of Hastelloy C. No pitting occurred on these components, but there was a slight uniform erosion. The results of micrometer readings of the stirrer shaft diameter, taken after most of the experiments are given in Table VI. Measurements were taken at three locations: in the liquid phase, protected by an impeller body; in the liquid phase, unprotected; and in the gas phase. The shaft diameter is 0.1875 (3/16) inch, nominally. Corrosion in the gas phase and in protected areas in the liquid phase is negligible. The exposed area was corroded significantly only in Run 10 when an $\text{FeCl}_2/\text{MgCl}_2/\text{KCl}$ melt was used. ZnCl_2 melts did very little in comparison. The overall corrosion rate in the section of the shaft exposed to the liquid phase is only about 9×10^{-3} mpy based on 24 hr of reaction time (heat-up and cool-down times not included) for Runs 4 through 20.

Table XI. Corrosion of Hostelloy C Stirring Shaft

	Shaft Diameter (inches)		
	<u>Liquid Phase</u>		<u>Gas Phase</u>
<u>Before Run</u>	<u>Unexposed</u>	<u>Exposed</u>	
4	-	0.1883	0.1880
5	-	0.1878	0.1878
6	-	0.1877	0.1880
7	-	0.1875	0.1874
8	-	0.1876	0.1875
11	0.1874	0.1834	0.1874
12	0.1875	0.1839	0.1872
13	0.1874	0.1830	0.1872
14	0.1873	0.1879	0.1873
15	0.1876	0.1820	0.1869
20	0.1875	0.1830	0.1870

APPENDIX B

Vapor Pressures of ZnCl_2 Melts

Vapor pressures of melts with compositions of 80, 90 and 95 weight percent ZnCl_2 were measured in the Parr autoclave up to 325°C . Since the 1000 psig gauge cannot be read accurately at low pressures, a 100 psig gauge was added. At pressures above 80 psig a valve between the autoclave and this gauge could be closed to protect the extra gauge.

Each melt was made up at room temperature and placed in the autoclave, which was immediately closed. The autoclave and contents were heated at a slow rate and stirred to maintain equilibrium while temperature and pressure readings were taken. The reactor contained one atmosphere of air at room temperature, and since the air's partial pressure increased with increasing temperature, a variable correction was made to the actual gauge pressure readings to get the absolute vapor pressures of the melts.

Two factors affect the vapor-pressure curves. First, the 95 percent claimed by the manufacturer. Thus, any comparison of these vapor-pressure curves with data reported in the literature for pure ZnCl_2 must not be taken too seriously. Purification would not be desirable because it is the reagent-grade ZnCl_2 that is used in the experimental studies with coal, not pure ZnCl_2 . Second, as water selectively vaporizes from the melt, the weight percent of ZnCl_2 increases. Conservative estimates of the magnitude

of this effect show that the 80, 90, and 95 percent solutions would only increase to 81.0, 90.6, and 95.3 percent respectively, so no corrections were made.

The three vapor-pressure curves are given in Figure 9. The large geometric symbols represent atmospheric boiling points of the three melts taken from Timmermans (T1). These points do not fall directly on the experimental curves due to the impurities in the ZnCl_2 reagents. The atmospheric boiling point of a 97.5 percent melt is also shown, and an estimated vapor-pressure curve (dashed line) is drawn through it. These curves are used to determine the super-atmospheric boiling curves in Figure 4 of the Experimental Apparatus and Procedure section.

XBL7711-3968

Figure 9. Vapor Pressure of H₂O over ZnCl₂/H₂O Melts

APPENDIX C

Determination of Percentage Tetralin

Retained by MTC

In Run 20, tetralin was added to the ZnCl_2 melt, and some of it was retained by the MTC after product work-up. Since the retained tetralin would be included in weight of the MTC extracted and since it would be soluble in benzene, it is important to determine its percentage in the MTC so that the extraction could be calculated on a moisture-free, ash-free, and tetralin-free basis. The procedure used to determine the percentage tetralin in the MTC is illustrated in Figure 10.

The MTC with retained tetralin (A) was first extracted with benzene; it is assumed that all the tetralin was removed in this step. The benzene extract and tetralin were dried in a preweighed Petri dish at 130°C and 40 mmHg of pressure. All the benzene (not shown in mass balance) and most of the tetralin are driven off at this temperature. The weight of the tetralin driven off (B) is not known. The Petri dish and its contents were weighed, dried at 210°C and then weighed again to determine the weight loss (C) and the weight of benzene extract (D). The residue from the benzene extraction was extracted with pyridine. The pyridine extract (E) and final residue (F) were dried to remove pyridine (also not shown in mass balance) and weighed.

Figure 10. Determination of Tetralin Retained by MTC.
(Total Mass Balance: $A = B + C + D + E + F$.)

The only unknown is the weight of the tetralin removed by drying at 130°C (B). This was determined from the total mass balance. The weight of retained tetralin could still not be determined because the relative amounts of benzene extract and tetralin removed by drying at 210°C is not known. Since the total weight involved (C) is only about seven percent of the total weight of products, it was assumed that one half of the weight loss is tetralin and the other half is benzene extract. This gives the total weight of tetralin of B plus one half of C. This is a conservative estimate (tends to reduce benzene extraction yield) because the vapor pressure of tetralin at 130°C is about 90 mm Hg, and so it should have been almost completely removed in the vacuum oven at 40 mm Hg during the initial drying.

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