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**Catalytic Conversion Of Solvent
Refined Coal To Liquid Products**

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February 1978

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CATALYTIC CONVERSION OF SOLVENT REFINED COAL
TO LIQUID PRODUCTS

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ABSTRACT

Catalytic reactions of solvent refined coal (SRC) were studied using mixed metal oxide and low melting Lewis acid catalysts in extracting solvent media. From characterization of the benzene and cyclohexane soluble products, ZnCl_2 and SnCl_2 were determined to be the most effective at hydrogenating and solubilizing SRC while assisting in heteroatom removal. ZnCl_2 and SnCl_2 were also found to be more effective at producing oil-like products rather than asphaltene-like products. Further enhancement of the solubilization of SRC could be achieved by the addition of isopropanol to the Lewis acid-substrate-solvent reaction mixture. Dry HCl was also investigated for its effect on the solubilization of SRC. Characterization of the solubilized products and residues was performed by elemental analysis, ^1H -NMR, and gel permeation chromatography.

Investigations were performed to determine what effect reaction temperature, hydrogen pressure, and catalyst loading had on the yield of soluble products as well as the chemical analyses of the products.

* M.S. Thesis.

The results showed that the conversion of SRC to soluble products increases monotonically with hydrogen pressure and catalyst loading. The effect of temperature is not as straightforward. The yield of soluble products was found to increase with temperature up to a plateau beginning at about 350°C. At the same time, the H/C and H_{Al}/H_{Ar} ratios were found to pass through maxima at around 350°C.

To see how well SRC modeled raw coal, the solubilization of Illinois No. 6 coal with $ZnCl_2$ and $SnCl_2$ was investigated. These catalysts proved to be more effective at enhancing the solubilization of Illinois No. 6 and produced a much more aliphatic product than SRC. Finally, a correlation of the H/C and H_{Al}/H_{Ar} ratios is given for all of the products obtained throughout this investigation.

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To the greatest man who ever lived,
my Dad;
And to the women who give life its very meaning,
my Mom and my Wife.

CHAPTER 1: INTRODUCTION

To meet future demands for clean-burning liquid fuels, economically viable processes must be developed for converting coal to a synthetic crude oil. Consideration of such processes suggests that one or more catalysts will be required to promote the hydrogenation and cracking of coal structures and the removal of heteroatoms (S, N, and O). While a number of catalysts have already been proposed for such purposes, the fashion in which they operate is not well understood. Furthermore, these catalysts (e.g. CoMoO_3) have severe limitations with regard to their activity, selectivity, stability, and capacity for regeneration.

The present studies were undertaken in an effort to further define the types of catalysts suitable for coal liquefaction and the influence of specific catalysts on the nature of the products obtained. Since it was desired to study the effects of the catalyst on the organic portion of coal and to eliminate the influence of the inorganic portion, a solvent refined coal (SRC) was used for the majority of this work. By working with SRC as a coal model it was also possible to eliminate the nonhomogeneous microstructural variations characteristic of coal while maintaining many of the complex organic structures characteristic of coal.

In the balance of this chapter, a review is presented of the process for making SRC as well as the chemical features of SRC. A brief survey is then given for the types of catalysts that might be used to liquefy coal. Finally, a brief statement is presented as to the purpose and scope of the present work.

I. Solvent Refined Coal

One of the simplest processes for upgrading coal to a cleaner fuel is solvent refining. A typical flowsheet for this process is illustrated in Fig. 1-1. Coal is first ground, then slurried in the mixer with 2-4 volumes of a process derived solvent, and sparged with hydrogen. This three phase mixture of coal, solvent, and hydrogen is preheated and then passed through the reactor. The temperature in the reactor is typically 420 - 470°C and the hydrogen pressure is 1000 - 3000 psig (1,2). After passage through the reactor, the unused hydrogen and light hydrocarbons are removed for eventual separation and re-use of the hydrogen. Next, the dissolved coal is filtered in the solids separator where about half of the coal's total sulfur (mostly the pyrites and some sulfates) is removed along with other mineral matter and char. Finally, the liquid filtrate is flashed to remove the recycle solvent required in the beginning of the process, leaving the low melting SRC product behind.

Several variations of this process are being tested in developmental pilot units ranging in size from 5 - 250 tons/day of feed coal. These units typically produce SRC yields of 60 - 80% and light hydrocarbon yields of 10 - 30% from the feed coal on a moisture and ash free basis.

In addition to acting as a vehicle for the dissolved coal, the solvent plays an active chemical role as a hydrogen donor in shuttling hydrogen from itself to active sites in the coal. The solvent serves to react with fragments resulting from the thermal cleavage of the polymeric components of coal. Hydrogen gas does not react directly with the coal, but rather reacts with the solvent which in turn hydrogenates the coal. For this reason, the presence of H₂ gas during the early

Temperature: 420-470°C

H₂ Pressure: 1000-3000 psig

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Fig. 1-1. SRC Process Flowsheet.

stages of conversion is not critical. However, the presence of a good hydrogen donor is critical for the achievement of high conversions.

Some general comments can be made regarding the overall chemical changes which accompany the conversion of raw coal to SRC. While the nitrogen content of reacted coal is substantially unaffected by SRC processing, approximately 40% of both the organic sulfur and oxygen are relatively easily removed (3,4). Furthermore, it has been shown that sulfur and oxygen are removed in a parallel fashion. Hence, as the coal is converted to SRC, equal proportions of sulfur and oxygen are removed simultaneously. Removal of the initial 40% of sulfur and oxygen requires a hydrogen consumption equivalent to that needed to produce H_2S and H_2O . To remove the remaining heteroatoms requires consumption of hydrogen in excess of that needed to form H_2S and H_2O .

It is important to note that while hydrogen is consumed in the SRC process, the hydrogen content of SRC is less than that of the coal from which it is made. Furthermore, as the processing temperature and reaction time are increased, the heteroatom content decreases but the aromaticity of the SRC increases. Evidently, the depolymerization of coal and its conversion to SRC is accompanied by the loss of hydrogen through internal chemical rearrangements and aromatization.

The precise chemical structures of coal and SRC are very complex and thus still largely unknown. However, significant insight into the nature of the organic structures present in coal and coal derived products has been obtained by characterization of the materials which can be extracted by different solvents. Solvent extraction leads to the identification of three major classes of compounds: oils--compounds which are

hexane or pentane soluble; asphaltenes--compounds which are benzene soluble but hexane insoluble; and pre-asphaltenes or asphaltols--compounds which are pyridine soluble but benzene insoluble. The physical and chemical characteristics of each of these classes of compounds have recently been characterized by groups at Mobil Research and Development (1,3,4).

The Mobil work shows that the primary characteristic of asphaltols is the presence of a large number of functional groups per molecule (primarily hydroxyl and basic and non-basic nitrogen). In fact, the particularly frequent occurrence of hydroxyl groups led to their naming these compounds asphaltols. By means of gel permeation chromatography (GPC) and vapor pressure osmometry (VPO) measurements, asphaltols were found to have molecular weights from 500 - 1000 gm/mole.

The asphaltenes obtained from SRC have fewer functional groups per molecule than the asphaltols and have molecular weights in the range of 300 - 600 gm/mole. Work at the Pittsburgh Energy Research Center has demonstrated that coal derived asphaltenes have essentially an acid-base structure (5,6). Separation of the acidic and basic components is achieved by dissolving the asphaltenes in toluene and passing dry HCl gas through the solution. The basic component precipitates as an insoluble HCl adduct while the acidic component stays in solution. The acidic component contains oxygen as phenolic hydroxyl and nitrogen as acidic nitrogen (e.g. pyrrole). The basic component contains oxygen as ether or ring oxygen and nitrogen as ring nitrogen (e.g. pyridine). The data left no doubt that the acidic component contained all of the acidic hydrogen (deuterium exchangeable) while the basic component contained none. Hence, asphaltenes will not contain both an acidic hydroxyl and a basic nitrogen on the same molecule.

A further conclusion, deduced from ^1H -NMR spectra, was that asphaltene complexes could be formed as a result of hydrogen bonding between acidic phenol and basic nitrogen groups. The fact that asphaltenes can be separated into acidic and basic components suggests that coal itself may well be less of an amphoteric substance than has been previously postulated.

Coal derived oils are characterized by their low viscosity and their low molecular weight, usually less than 350 gm/mole. Oils are more aliphatic in character than either the asphaltenes or asphaltols and are soluble in a wider variety of solvents. Significant quantities of heteroatoms are still present in oils although they contain fewer functional groups than asphaltenes or asphaltols.

The conversion of coal to asphaltols, asphaltenes, and oils has been the subject of considerable investigation (1,3,5,6,7,8). It was commonly believed that conversion of coal to oils proceeds by the sequential formation of products as shown below:

and that at each stage the heteroatom content was reduced as indicated by the figures shown in parenthesis. As shown, the asphaltols were viewed as the sole precursor to asphaltenes. This relationship led, in fact, to the asphaltols being called pre-asphaltenes in much of the earlier literature. Unfortunately, the use of the term pre-asphaltene can be misleading. The work of the Mobil group has shown that while the proposed sequence of reactions is essentially correct in the absence of a hydrogen donor solvent, the presence of a hydrogen donor solvent leads to a different reaction network.

In a hydrogen donor solvent, the coal produces asphaltols which are then converted in parallel fashion to asphaltenes and oils. The Mobil group points out that while asphaltols and asphaltenes are capable of producing all solvent fractions, asphaltols are much more prone to producing an intractable char than either asphaltenes or oils. In fact, asphaltols yield up to 80% char on pyrolysis in an inert atmosphere at temperatures up to 800°C, while asphaltenes and oils yield only 20% char. Hence, asphaltols are thought to be the primary source of the char formed during the SRC process.

II. Catalysts

In the search for progressively milder reaction conditions for the liquefaction of coal, catalysts will unquestionably play a major role. However, much work still needs to be done to overcome current catalyst limitations. Major improvements are to be sought in the areas of catalyst activity, selectivity, thermal and chemical stability, and regenerability. Because of the capital intensive nature of coal liquefaction plants, improvements in any of these characteristics could have a favorable effect on the process economics.

In a recent report by Catalytica Associates (9), catalysts were ranked according to their relative promise for use in coal liquefaction processes. The basic criteria they used for the evaluation of catalytic materials included the physico-chemical properties and the catalytic properties of the catalyst. The physico-chemical properties considered were the thermal and chemical stability of the catalyst to withstand a coal liquefaction environment while the catalytic properties considered were the ability of the catalyst to accommodate hydrogenation, cracking, desulfurization, and denitrogenation. Table 1-1 summarizes the classes of catalysts considered and associates with each class a priority rating.

Those catalysts which received a high priority ranking included the metal oxides, solid acids, and metal sulfides. Oxides and solid acids were highly rated in view of their demonstrated catalytic activity for cracking hydrocarbons and removing heteroatoms. These materials are also known to be thermally and chemically stable under coal liquefaction conditions and can be freed of coke by oxidative regeneration. The sulfides also possess catalytic activity and offer excellent thermal and H_2S stability.

Table 1-1

Summary of Coal Liquefaction Catalysts Evaluation

Research Priority	Catalyst Class	Examples
High	Oxides	Simple: Al_2O_3 , CoO , Cr_2O_3 ; Complex: MgAl_2O_4 , FeTiO_3 , CuCrO_2 , BaTiO_3
	Solid Acids	$\text{TiO}_2/\text{SiO}_2$, $\text{ZrO}_2/\text{SiO}_2$, Zeolites, Natural Clays (montmorillonite), Super Acids (SbF_5/HF), Supported halides ($\text{AlCl}_3/\text{Al}_2\text{O}_3$)
	Sulfides	Simple: VS , V_5S_8 , MoS_2 ; Complex: CoV_2S_4 , SrZrS_3 , $\text{Al}_{0.5}\text{Mo}_2\text{S}_4$
Medium	Carbides, Nitrides	WC , PtZnC ; Fe_2N , Ni_3N_2 , Ni_3AlN
	Borides, Silicides, Phosphides	Ni_3B , FeB ; TiSi , RhSi , TaSi_2 ; MnP , NiP , TaP_2
	Molten Salts	ZnCl_2 , NaCO_3
Low	Solid Bases	CaO , MgO , NaNH_2 , BaO , K_2O , Na_2O
	Metals, Multimetallics	NiCu , PtAu , NiW , RuCu , Cu_3Au , ZrPt_3
	Homogeneous Catalysts	$\text{Co}_2(\text{CO})_8$, RhCOCl_2
	Anchored Catalysts	$\text{SiO}_2\text{-OSi}(\text{C}_2\text{H}_4)(\text{Ph}_2\text{P})\text{RhCl}(\text{CO})_2$

Carbides, nitrides, borides, silicides, and phosphides were rated as medium priority catalysts. These materials possess some cracking, isomerization, and hydrogenation activity and are thermally stable. However, most of these catalysts react with H_2S and cannot be oxidatively regenerated. Catalytica also gave a medium priority rating to molten salts. Molten salts have demonstrated catalytic activity for cracking hydrocarbons and removing heteroatoms (20). These melts also have the unique ability to wet the surfaces of the coal and eventually disperse and dissolve the reactants in a liquid for better catalyst coal contacting. Molten salts have high thermal conductivities which permit rapid removal of the heat of the reaction for better reaction temperature control. The disadvantages of molten salts include the difficulty of catalyst recovery and the high catalyst to coal ratios required for adequate reaction.

The low priority catalysts, with the exception of the solid bases, were determined to be both thermally and chemically unstable in coal liquefaction environments. The solid bases, while quite stable, show very little catalytic activity.

The Catalytica Associates survey concludes that future generation liquefaction catalysts will likely be composites of two or more materials, each providing a different function. Catalysts might involve the use of materials which have stable and controlled acidity for cracking coupled with a hydrogenation function. Ideally, the hydrogenation function would selectively catalyze hydrogenation of only those bonds which are broken during cracking and heteroatom removal, thereby minimizing costly hydrogen consumption.

III. Purpose and Scope

The objective of this investigation was to study the chemical and structural changes accompanying coal conversion to a synthetic crude oil at relatively moderate temperatures and pressures. Toward this end, the catalytic effects of mixed metal oxides and low melting Lewis acids on SRC were studied. As stated previously, SRC was used as a coal model since it retains many of the organic chemical and structural features of coal while eliminating the nonhomogeneous physical and chemical character of coal.

Mixed metal oxides were chosen for examination in this study because they had received a high priority rating in the Catalytica Associates survey. As noted earlier, these catalysts possess both hydrogenation and cracking activity. Molten Lewis acid catalysts were also studied since they too can provide both types of catalytic activity as well as facilitate heteroatom removal. In addition, they are capable of achieving excellent contact with the SRC.

A solvent, either benzene or cyclohexane, was used in all of the experiments performed in this study to continuously disengage the reaction products from the unreacted SRC and catalyst. It was felt that this in situ type of extraction would prevent possible condensation, polymerization, or further reaction of the products with the reacting SRC and catalyst.

The initial phases of this investigation were concerned with screening a number of mixed metal oxide and low melting Lewis acid catalysts. It was of particular interest to determine what effect the catalysts had on the chemistry of the products and the extent to which they

solubilized SRC in benzene. Simple organic additives were also screened to see if they could perform some chemical role to help increase the extent to which SRC was solubilized. After investigating the relative catalyst and/or additive activities, the effects of switching solvents from benzene to cyclohexane were investigated. Besides extracting a more oil-like product rather than an asphaltene-like product, cyclohexane was expected to eliminate some solvent-catalyst interactions as well as some reactions of the solvent with the organic additive.

As a result of the initial screening efforts, ZnCl_2 and SnCl_2 were found to be particularly active with regards to solubilizing SRC. Consequently, further studies were conducted using these two catalysts. In the course of these experiments, the effects of temperature, pressure, and catalyst to SRC ratio on SRC solubilization were investigated. Dry HCl gas was also tested as a catalyst promotor for its effect on SRC solubilization. Finally, it was decided to conclude this study by taking a step back from using SRC as a coal model and substituting raw coal as a substrate. For the experiments reported here, all products were characterized by elemental analysis and ^1H -NMR while selected products were characterized by gel permeation chromatography.

CHAPTER 2: EXPERIMENTAL

I. Experimental Apparatus

The principal apparatus used for this work was a magnetically driven stirred autoclave, housed in an explosion proof bay. High pressure gases could be fed directly to the autoclave while the temperature and pressure could be continuously monitored on gauges and recorders located outside the explosion proof bay. Figure 2-1 illustrates the autoclave, stirring system, heating and cooling system, gas feed system, and instrumentation. A more detailed description of each of the components is given below.

A. The Autoclave

The autoclave (Autoclave Engineers, Inc. Model ABP-300) was constructed of 316 stainless steel and was rated for operation up to 350°C at 5000 psig. The internal volume of the autoclave was 300 cm³. However, since glass liners were used to facilitate introduction and removal of reactants and products, the working volume was reduced to 280 cm³.

The body of the autoclave contained three ports. One was used as a gas inlet while the second was connected to a three-way valve (two ports open on pressure). In normal operation the leg of the valve connected to the vent line was closed. When it was desired to vent the autoclave, this leg was opened. The second leg of this valve led to a pressure gauge and a pressure transducer. The third port in the autoclave body was connected to a safety assembly containing a teflon coated Inconel rupture disc rated at 5394 psig at 72°F and 5016 psig at 400°F. For safety, the line leading from the rupture disc holder was connected into the vent line.

1. Tachometer
2. Tachometer Pickup Coil
3. Stirring Assembly
4. Variable Speed Motor
5. Motor Controls
6. Temperature Recorder
7. Temperature Controller
8. Autoclave Cover
9. Autoclave Body
10. Jacket-type Heater/Cooling H₂O Bath
11. Thermowell
12. Agitator Shaft and Impeller
13. Cooling Coil
14. Sampling Tube
15. Solenoid Valve
16. Gate Valve
17. Sampling Valve
18. Check Valve
19. Shutoff Valve
20. Line Filter
21. Safety Head with Rupture Disc
22. Three-way Valve
23. Pressure Gauge
24. Pressure Transducer
25. Power Supply
26. Pressure (MV) Recorder
27. Pneumatically Driven Diaphragm Booster Pump
28. Voltage Control

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Fig. 2-1. Experimental Apparatus.

B. Stirring System

Stirring of the autoclave contents was accomplished by a rotating propeller attached to a shaft that was magnetically coupled to a rotatable outside housing. This housing was linked by a V belt to a DC motor (1/4 hp, 2500 rpm maximum) powered by an AC/DC converter. During operation, a stator assembly was fitted over the top cylindrical portion of the magnetic drive assembly. With this stator acting as a pick-up coil for the tachometer, a direct readout of the stirrer speed could be obtained. By controlling the power to the motor, the agitator speed could be monitored and varied up to a maximum of 2000 rpm.

C. Heating and Cooling System

The autoclave was constructed with a heating and cooling system to enable rapid heat-up, to maintain temperature within close tolerances, and to allow for rapid quenching. Heating was accomplished by a 1200 watt heating mantle supported in a manner so that it could be removed and replaced with a tap water fed cooling bath. Power to the heater was controlled by means of a Honeywell Pyrovane automatic temperature controller which acted in response to a signal from an iron-constantan thermocouple located in a thermowell on the cover of the autoclave. The thermowell also contained a copper-constantan thermocouple which provided the signal for a Leeds and Northrup Speedomax Type G temperature recorder. This set-up allowed a double check of the temperature since the controller and recorder were entirely independent of one another. For runs carried out at temperatures less than 300°C, a voltage control to the heating mantle was installed to facilitate better control of the autoclave temperature. At a voltage of 120 v, heat-up rates of 15°C/min were

typically achieved from room temperature.

Cooling of the autoclave was accomplished by two systems acting simultaneously to ensure rapid quenching. A solenoid valve connected to an on-off switch controlled the flow of tap water to both systems. Cooling coils extending to the bottom of the autoclave comprised one system, while a cooling jacket raised around the body of the autoclave comprised the other. Since the cooling coils were fed water from connections located on the sides of the autoclave cover, this system not only cooled the internal contents of the autoclave, but the autoclave cover as well. Typically with this internal and external cooling arrangement, it would take 2 minutes to cool the autoclave contents from 350°C to 60°C while it would take an additional 2 minutes to cool from 60°C to room temperature.

D. Gas Feed System

The gas inlet system was used to pressurize the autoclave with hydrogen, nitrogen, or hydrogen chloride either separately or in combination. Each gas was supplied from a cylinder equipped with a high pressure regulator (delivery pressure 100-2500 psig). A check valve was placed in the line from each cylinder, except the HCl tank, to prevent the flow of gas from one cylinder to the other if both cylinders were accidentally opened simultaneously. The H₂ and N₂ lines were then connected into one line which contained a dual disc (5/10 micrometers) line filter to trap out any particulate matter originating in the cylinders. The gas line then came to a booster pump which could be bypassed with the valves shown in Fig. 2-1 for direct filling. Another check valve was placed between the autoclave and the inlet shutoff valve to ensure that the autoclave

contents were confined when the pressure in the autoclave rose above the pressure in the gas manifold. Finally, the HCl inlet line was connected between the check valve and the autoclave to expose a minimum of parts to this corrosive gas.

The aforementioned boosting pump was a pneumatically driven diaphragm boosting pump manufactured by American Instrument Company. Its function was to allow the autoclave to be filled with gas above cylinder pressure up to 5000 psig. For runs above 2000 psig, the boosting pump allowed the pressure to be trimmed to the desired amount upon reaching run temperature. The boosting pump also proved invaluable for filling the autoclave up to maximum pressure and testing the autoclave for leaks.

The autoclave pressure was monitored as a function of time through the use of a Honeywell Model PP/I pressure transducer connected to a Leeds and Northrup Speedomax recorder. Calibration of the transducer was accomplished by comparing the recorder trace with the reading of a bourdon tube pressure gauge connected directly to the autoclave.

II. Experimental Techniques

A. Catalyst Preparation

The catalysts used together with their source, purity, and melting point are listed in Table 2-1. With the exception of the zeolites, the solid metal oxide catalysts were obtained as 1/8 - 1/16 inch extruded pellets and were ground down to pass through a 150 Tyler mesh sieve (.0041 inch openings). The zeolites were obtained as powders and were charged as received. With the exception of AlCl_3 , FeCl_3 , and SbCl_3 , each of the catalysts was weighed out and dried overnight in an N_2 purged vacuum oven maintained at 105°C .

In the case of AlCl_3 , FeCl_3 , and SbCl_3 , which are extremely hydroscopic, the catalyst was stored and weighed out in a dry box under an N_2 atmosphere before being used.

B. Substrate Preparation

Two substrates were used in this investigation: an SRC (produced from a bituminous West Kentucky coal) supplied by the Pittsburgh and Midway Coal Mining Company and a high sulfur Illinois No. 6 bituminous coal obtained through the Illinois State Geological Survey. The ultimate analyses of both substrates are presented in Table 2-2. The SRC and Illinois No. 6 were first dried in lump form overnight in an N_2 purged vacuum oven at 105°C and then ground to pass through an 80 Tyler mesh sieve (.0069 inch openings). The sieved substrate was stored in a vacuum dessicator until the day before an anticipated run. The substrate was then weighed and re-dried overnight in an N_2 purged vacuum oven before being run.

Table 2-1
Catalysts Used

Catalyst	Source	Purity (%)	m.p. (°C)
Al_2O_3	Harshaw Chem. Co.	99	-
19% Cr_2O_3 - Al_2O_3	Harshaw Chem. Co.	-	-
20% Fe_2O_3 - Al_2O_3	Harshaw Chem. Co.	-	-
10% Co_2O_3 - Al_2O_3	Harshaw Chem. Co.	-	-
5.4%NiO-19% MoO_3 - Al_2O_3	Nalco Chem. Co.	-	-
5%NiO-20% WO_3 - Al_2O_3	Nalco Chem. Co.	-	-
3%CoO-12% MoO_3 - Al_2O_3	Harshaw Chem. Co.	-	-
Residcat - 30 ^a	Davison Chem. Co.	-	-
CBZ-1 ^a	Davison Chem. Co.	-	-
AlCl_3	Mallinckrodt	99.5	190
ZnCl_2	Mallinckrodt	97	283
SnCl_2	Research Organic/ Inorganic Chem.	99	246
FeCl_3	Research Organic/ Inorganic Chem.	99	306
SbCl_3	Research Organic/ Inorganic Chem.	99	73
HgCl_2	Baker	99	276

^a Zeolite cracking catalyst.

Table 2-2

Ultimate Analysis of SRC and Illinois No. 6 Coal^a

Content	SRC	Illinois No. 6
% Carbon	87.13	56.46
% Hydrogen	5.61	4.07
% Nitrogen	2.20	1.02
% Chlorine	0.00	0.20
% Sulfur	0.53	2.90
% Ash	0.20	23.20
% Oxygen (by difference)	<u>4.33</u>	<u>12.15</u>
Total	100.00	100.00

^a Analysis on dry basis.

C. Solvents and Additives

The solvents used in this investigation were restricted to reagent grade benzene and cyclohexane, both purified by refluxing under an N_2 atmosphere over a mixture of sodium and benzophenone in a glass solvent still. Refluxing was continued overnight or until a characteristic deep blue color of the ketyl was observed, the color change signifying that the solvent was both water and oxygen free. The solvent was then distilled over into a bottle, tightly capped, and stored in a dry box under an N_2 atmosphere until used.

The organic additives used in this investigation were reagent grade isopentane, isopropanol, cumene, and tetralin. All were obtained from Aldrich Chemical Company, Inc. and all were listed as having a minimum 99% purity. Due to the relatively small amounts used, the additives were charged into the autoclave without further purification.

D. Experimental Procedure

With a few exceptions, the experimental procedure employed for all runs was quite similar. Since some of the catalysts used in this investigation were quite hygroscopic, solvent charging was carried out in an N_2 purged dry box equipped with a vacuum antichamber. A thoroughly dried glass liner was transferred into the dry box where it was filled with 70 ml of previously dried and distilled solvent. For runs with the extremely hygroscopic catalysts mentioned earlier, the catalyst was weighed out in the dry box and transferred directly into the liner. The filled liner was then transferred out of the dry box and charged with the appropriate weighed and dried catalyst, substrate, and/or additive and immediately placed into the autoclave. The cover of the autoclave was

attached to the body and the trapped air was flushed out by alternately pressurizing and venting the bomb with H_2 or N_2 three times.

After purging, the autoclave was filled with the appropriate gas to a pressure which would give the desired partial pressure at the final temperature of operation. For the HCl runs, the autoclave was purged with H_2 , pressurized with HCl, and finally pressurized with H_2 to ensure that no HCl backed up into the booster pump or gas manifold.

After pressurization, the temperature controller was turned on and the stirring speed adjusted to 1250 rpm. During heat-up the temperature versus time trace was close to linear, and it took approximately 20 minutes to reach $300^{\circ}C$ and 24 minutes to reach $350^{\circ}C$, starting from room temperature. After reaching the desired temperature and pressure, the reaction was allowed to proceed for 90 minutes. Temperature fluctuations during the latter period were almost always within $\pm 5^{\circ}C$. For the few runs where H_2 consumption was noticeable, an H_2 cylinder was opened to the autoclave to maintain constant pressure.

At the end of a run, the temperature controller was turned off and the solenoid valve to the cooling coil turned on. At the same time, the heating mantle was removed from the autoclave and replaced by the cooling bath. After quenching, the autoclave was vented and then opened to remove the glass liner and any solution trapped between the autoclave body and the liner. The liner sides were scraped to dislodge all the reaction residue from the sides for later collection.

Except for blank runs made without substrate, the mixture in the liner was filtered through a medium fritted glass Büchner funnel (pore size 10-15 microns). The filtrate was dried quickly, at a temperature below the

solvent boiling point, on a hot plate to drive off the bulk of the solvent. The resulting oily solution was then dried for 3 hours along with the insoluble residue at 105°C in an N₂ purged vacuum oven. The residue and soluble product were weighed and then characterized as described in the next section.

E. Product Analysis

1. Percent Solubility

For each experiment a determination was made of the extent to which the SRC had been solubilized. The percent of the SRC dissolved was determined by weighing the dried soluble filtrate and then determining what percentage of the original 5 grams of substrate had been solubilized in the course of the run. Since there was no segregation of products between what resided in the solvent and what was lost, any solution lost during liner transfers, filtration, reaction residue entrainment, etc. was taken into account by calculating the product yield back to a 70 ml solution basis.

2. Elemental Analysis

The elemental content of the reaction products (carbon, hydrogen, nitrogen, sulfur, chlorine, and metals) was determined by the College of Chemistry Microanalysis Laboratory at U.C. Berkeley. All samples were submitted in a tightly sealed vial placed inside a bottle containing dessicant. The carbon, hydrogen, and nitrogen tests were performed by combustion at 970°C in a Perkin Elmer Model 240 CHN Analyzer.

Samples were analyzed separately for sulfur and chlorine by combustion at 900°C to form gaseous SO₂ and Cl₂. These gases were absorbed in a 3% hydrogen peroxide solution to form SO₃(H₂SO₄) and Cl⁻(HCl). In the

case of sulfur, the sulfate was precipitated with BaCl_2 to form BaSO_4 . The BaSO_4 was then weighed to determine the amount of sulfur in the original sample. In the case of chlorine, the chloride was titrated with a standard AgNO_3 solution to determine the chlorine content of the sample. The ash content of a sample was determined in conjunction with either the chlorine or sulfur analysis from the weight of the uncombusted material left after combustion at 900°C . For all samples except raw Illinois coal, the ash content was quite low.

Oxygen could not be analyzed for by the microanalysis laboratory and so it is not routinely reported in this investigation. Since the SRC had a low oxygen content ($\sim 4\%$) to begin with, obtaining oxygen content by difference from the other components gave inaccurate and nonreproducible values.

Metal analyses for zinc, tin, mercury, antimony, iron, and aluminum were all performed by atomic absorption in a Perkin Elmer Model 360 Atomic Absorption Spectrophotometer. Samples were digested in a solution of concentrated sulfuric acid and 30% hydrogen peroxide until all organic matter was destroyed. The resulting clear solution was diluted to a known volume and run on the atomic absorption spectrophotometer. The solution's absorbance was compared with known standards and the metal content of the sample was determined.

3. ^1H -NMR

Proton nuclear magnetic resonance was used as a tool for determining the relative aliphatic to aromatic hydrogen content in the products. Sample preparation consisted of weighing exactly 0.200 gm of dried product and dissolving it into 1.00 ml of CDCl_3 (Aldrich, 99.8 atom %), or if

not totally soluble, 1.00 ml of pyridine- d_5 (Aldrich, 99 atom %).

One to two microliters of tetramethylsilane (TMS) was added to this solution which was then thoroughly mixed and filtered through a 2 ml medium fritted glass filter. Finally the sample was pipeted into a 5 mm tube and run on a 60 MHz Varian Model T60 NMR spectrometer.

4. Gel Permeation Chromatography

The molecular weight distributions of selected products were determined by gel permeation chromatography (GPC). Samples were prepared by dissolving 1 mg of product per ml of pyridine. Ten microliters of this solution was injected into a Waters Associates Model 6000A-U6K-440 gel permeation chromatograph using pyridine as the elution solvent. The chromatograph was equipped with three 25 cm columns connected in series containing 1000 Angstrom, 500 Angstrom, and 100 Angstrom microstyragel. This set of columns was calibrated with tetrahydrofuran as the elution solvent using the polystyrene standards supplied by Waters Associates. The columns were also calibrated with tetrahydrofuran and pyridine as elution solvents using some selected fused ring aromatic compounds as shown in Fig. 2-2.

The GPC used an ultraviolet absorbance detector fitted with 313 nm and 365 nm filters. The absorbance as a function of elution volume could be monitored at both wavelengths simultaneously on a dual pen strip chart recorder. Since both traces had identical forms, only the 313 nm spectra are illustrated in this presentation. Selection of 313 nm wavelength was also guided by the fact that this was the shortest wavelength where pyridine would not absorb so heavily as to mask the absorbance of condensed aromatic ring compounds. Pyridine was used as an elution solvent

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Fig. 2-2. Calibration Curve for GPC.

since it was the only solvent which could completely dissolve SRC.

Although the elution volume can be correlated in a reasonably regular fashion with molecular weight, the absorbance scale can only be correlated with the relative absorbance and not necessarily with the amount of product at a particular elution volume. At 313 nm, the major absorbing species are fused ring aromatic compounds. In interpreting GPC spectra, one assumes that the aromatic carbon content is approximately equally distributed amongst the various coal derived compounds in a particular sample. The attenuation for the absorbance response of the detector was set so that all absorbance peaks were of approximately the same height for ease of comparing one spectrum with another. This was done since some samples contained fewer aromatic compounds and would absorb less than others containing more. Again, even though one sample contains more aromatics than another, one assumes that the aromatic carbon content is approximately equally distributed in each sample.

5. Gas Chromatography

Gas chromatography was used to detect and identify volatile organic compounds present in reaction mixtures. The gas chromatograph (GC) used in this investigation was a linear temperature programmed Varian Model 1420-10 equipped with a 10 ft x 1/8" column packed with 5% OV-225 on Chromosorb P support. The column temperature could be raised up to 275°C and compounds with a boiling point as high as 325°C could be eluted. The GC was equipped with a thermal conductivity detector which for most organic compounds could detect as little as .05 micrograms.

The GC was mostly used to analyze blank runs made without substrate to determine whether or not the catalysts were causing the solvents and/or

additives to undergo any chemical changes. Also, on a limited basis, the raw reaction solution with reacted substrate and solvent was analyzed to determine whether or not any volatile compounds were present in the reaction product which might have been lost during the drying procedures. It was shown that other than solvent, additive, or solvent-additive reaction product, no more than 0.5% of the soluble SRC product boiled off under 325°C.

CHAPTER 3: RESULTS AND DISCUSSION

I. SRC Analysis

Initial efforts focused on the characterization of the SRC used throughout this investigation. To separate the SRC into oil, asphaltene, and asphaltol components, it was first Soxhlet extracted with cyclohexane. The extracted SRC, freed of oils, was then Soxhlet extracted with benzene to remove the asphaltenes, leaving a residue behind. Table 3-1 shows that the SRC consisted of 22% oils, 40% asphaltenes, and 38% residue or asphaltols. Table 3-1 also shows that the H/C ratio decreases as one proceeds from oils to asphaltenes to asphaltols. The nitrogen heteroatom content increases by 50% as one proceeds down the table while the sulfur content appears to remain essentially constant. Quite interestingly if one "reassembles" the solvent fractions to make a synthetic SRC, the stoichiometric formula becomes $\text{CH}_{.78}\text{N}_{.023}\text{S}_{.0022}$ which agrees very well with the analysis of untreated SRC.

It should be noted that the residue or asphaltols fraction was not Soxhlet extracted as were the other fractions since it was previously determined that the SRC was virtually totally soluble in pyridine. Since pyridine is well-known for heavily incorporating into coal and coal extracts, avoiding its use prevented many analytical problems. If pyridine had been used, the amount of pyridine being entrained with the product would have had to be determined in order to calculate the product elemental formulas on a pyridine-free basis.

Unlike pyridine, cyclohexane and benzene do not interact strongly with coal extracts and can be thoroughly removed by drying in a vacuum oven.

Figures 3-1 through 3-4 illustrate the ^1H -NMR spectra of SRC and its three solvent fractions. These spectra are comparable to spectra reported by other investigators who have used ^1H -NMR spectroscopy as a tool for characterizing coal derived products (3,4,5,10,11,12). These spectra can be divided into two major regions, an aliphatic region and an aromatic region. Protons on an aliphatic carbon resonate between 0 and 5ppm downscale from a TMS reference peak while protons on an aromatic carbon resonate between 6 and 10ppm. The ratio of aliphatic to aromatic hydrogen ($H_{\text{Al}}/H_{\text{Ar}}$) can be obtained by ratioing the areas under the peaks in each of these regions.

Although overall aliphatic to aromatic hydrogen ratios were deemed sufficient for the bulk of this investigation, groups at Mobil Research and Development, Stanford Research Institute, and other institutions (3,4,10,12,19) have reported methods for a more detailed analysis of ^1H -NMR spectra from coal derived products. It should be noted that investigators do not always agree on the range nor number of assignable regions for proton resonances of coal products. Using the best features of each investigator's proton resonance assignment scheme, the resonance regions, their names, and the chemical environments to which the resonance is assigned are listed below:

- a) H_{ar} ; 6.0-9.2ppm; aromatic protons, phenolic protons (Ar-H , Ar-OH).
- b) H_{α} ; 1.9-3.9ppm; protons on a saturated carbon adjacent (or α) to an aromatic ring i.e. benzylic protons, protons on a saturated carbon next to an ether linkage (Ar-CH_2^- , $-\text{CH}_2\text{-O-}$).
- c) H_{β} ; 1.1-1.9ppm; methylene, methine, or methyl protons beta from an aromatic ring, methylene or methine protons of saturated

compounds ($-\text{CH}_2-\text{C}-\text{Ar}$, $\text{R}-\text{CH}_2-\text{R}$).

- d) H_γ ; 0.5-1.1ppm; protons on methyl groups gamma or further from an aromatic ring, protons on methyl groups of saturated compounds ($\text{CH}_3-\text{C}-\text{C}-\text{Ar}$, CH_3-R).

The ^1H -NMR spectra shown in Figs. 3-1 through 3-4 clearly show the aliphatic and aromatic regions of proton resonances. The $\text{H}_{\text{Al}}/\text{H}_{\text{Ar}}$ ratios calculated from these spectra shown in Table 3-1 indicate that the aliphatic character of the solvent fractions increase as one proceeds from asphaltols to asphaltenes to oils. This is consistent with the description given earlier for these solvent extracts. Although the spectra illustrated terminate at 8.6ppm, all ^1H -NMR spectra obtained throughout this investigation were run and integrated down to 10.0ppm.

It is worth mentioning that some of the ^1H -NMR spectra shown contain impurity peaks due to either solvent entrainment or proton impurities in the NMR solvent. Since pyridine- d_5 has a lower isotopic purity than CDCl_3 , whenever pyridine- d_5 is used as an NMR solvent it superimposes proton resonances at 7.1, 7.5, and 8.7ppm on top of the extract spectrum. These impurity peaks are easily identified on the ^1H -NMR spectra and are subtracted out before integrating the spectra to obtain the $\text{H}_{\text{Al}}/\text{H}_{\text{Ar}}$ ratios.

Table 3-1
Analysis of SRC Fractions

Material	Fraction of SRC (%)	Formula	H_{Al}/H_{Ar}^c	Comments
SRC	100	C H .77 N .022 S .0023	1.07	Dark Brown - Black Solid
Oils	22+3 ^a	C H .87 N .018 S .0025	1.28	Dark Brown Solid
Asphaltenes	40+5 ^b	C H .81 N .023 S .0021	1.12	Dark Brown - Black Solid
Residue	38+8	C H .69 N .027 S .0022	0.74	Black Solid

^a SRC was Soxhlet extracted with Cyclohexane till the washings were clear.

^b Dried residue from the Oils extraction was Soxhlet extracted with Benzene till the washings were clear.

^c NMR solvents were $CDCl_3$ for Oils; Pyridine- d_5 for SRC, Asphaltenes, and Residue.

Fig. 3-1. ^1H -NMR spectrum of SRC.

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Fig. 3-2. ^1H -NMR spectrum of Oils Soxhlet extracted from SRC with Cyclohexane.

Fig. 3-3. ^1H -NMR spectrum of Asphaltenes Soxhlet extracted from SRC with Benzene.

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Fig. 3-4. ^1H -NMR spectrum of Residue after Soxhlet extraction with Cyclohexane and Benzene.

II. Catalyst, Additive, and Solvent Screening

A. Solid Catalysts

Table 3-2 summarizes the effectiveness of the various mixed metal oxide catalysts to promote the solubilization of SRC in benzene. All of the experiments listed were conducted at 300°C and 2000 psig H₂. Under these reaction conditions, the benzene solvent was above its critical point ($T_c = 288.9^\circ\text{C}$, $P_c = 48.6\text{atm}$) (13) and the SRC had melted into a thick liquid (m.p. $\approx 180^\circ\text{C}$) (2). The -150 mesh catalyst was finely dispersed into the liquid SRC by constant stirring.

Table 3-2 shows that about half of the SRC is solubilized in benzene regardless of whether or not one of the catalysts is present. Even the best of the metal oxide catalysts, NiO-WO₃-Al₂O₃ and NiO-MoO₃-Al₂O₃, increases the solubility of SRC by no more than 10% over that which is attainable in the absence of a catalyst. The elemental analyses of the dissolved products show a similar trend with very little variation in the stoichiometric formulas from one run to the next. The slight variations which do show up, particularly the S/C ratio, are more indicative of the experimental uncertainty than anything else. The aliphatic to aromatic hydrogen ratios are the only indications that any chemical changes took place at all with the solubilized products. This ratio is seen to increase from 1.3 to a maximum of 1.6. Later it will be shown that the H_{Al}/H_{Ar} ratio is a much more sensitive indicator of increased hydrogen content than the H/C ratio.

In order to determine whether the catalyst could alter the solvent into which the SRC was extracted, blank runs were performed in the absence of SRC. From these experiments, it was shown that only the

Co and Ni based catalysts could substantially hydrogenate benzene to cyclohexane as noted in the comment column of Table 3-2. The column labeled "mole % cyclohexane formed" represents the mole fraction of cyclohexane present in the benzene solvent at the end of the blank run. These figures represent an upper limit to the amount of cyclohexane contained in the solvent since it is expected that these catalysts might be partially deactivated in the presence of SRC.

During the course of the catalyst screening experiments, no attempt was made to operate the autoclave at temperatures below the critical temperature of the solvent. Thus, no results are presented regarding the significance of supercritical operation. It is interesting to note, however, that work at Stanford Research Institute (12) has shown that the mere fact that the solvent is subcritical or supercritical does not influence the extent to which coal is solubilized. In this work, the solubilization of Illinois No. 6 in benzene and toluene was examined at both subcritical and supercritical conditions. It was concluded that the fraction of the coal which was soluble was unaffected by whether the hot solvent was above or below its critical point.

Table 3-2

Comparison of Solid Catalysts for Reaction with SRC in Benzene

Reaction Conditions: T = 300°C
P = 2000 psig H₂
t = 90 min.
 ω = 1250 RPM

Catalyst mass = 5 gm
SRC mass = 5 gm
Solvent volume = 70 ml

Run No.	Catalyst	Sol. (%)	Filtrate Formula	H_{Al}/H_{Ar}^c	Comments on Filtrate
-	-SRC-	-	C H.77 N.022 S.0023	1.07	Dark Brown - Black Solid
6	None	46.7	C H.85 N.018 S.0026	1.33	Dark Brown Solid
26	Al ₂ O ₃	47.7	C H.85 N.018 S.0024	1.34	Dark Brown Solid
8	19%Cr ₂ O ₃ -Al ₂ O ₃	45.8	C H.82 N.018 S.0019	1.28	Dark Brown Solid, 0.1 mole % Cyclohexane formed
10	20%Fe ₂ O ₃ -Al ₂ O ₃	49.6	C H.84 N.018 S.0021	1.32	Dark Brown Solid, 0.3 mole % Cyclohexane formed
12	10%Co ₂ O ₃ -Al ₂ O ₃	50.0	C H.86 N.018 S.0025	1.40	Dark Brown Solid, 55.1 mole % Cyclohexane formed
16	5.4%NiO-19%MoO ₃ -Al ₂ O ₃	50.2	C H.86 N.017 S.0025	1.59	Dark Brown Solid, 11.0 mole % Cyclohexane formed
18	5%NiO-20%WO ₃ -Al ₂ O ₃	52.6	C H.85 N.018 S.0025	1.54	Dark Brown Solid
20	3%CoO-12%MoO ₃ -Al ₂ O ₃	46.4	C H.85 N.018 S.0029	1.30	Dark Brown Solid
22	Residcat-30 ^a	47.7	C H.85 N.017 S.0026	1.30	Dark Brown Solid
24	CBZ-1 ^a	42.3	C H.85 N.015 S.0027	1.43	Dark Brown Solid
27	CBZ-1 ^{a,b}	43.0	C H.85 N.016 S.0036	1.30	Dark Brown Solid

^a Zeolite cracking catalyst manufactured by Davison Chemical.

^b Zeolite charged as received with approx. 7% H₂O.

^c NMR Solvent: CDCl₃, except SRC done in Pyridine -d₅.

B. Lewis Acid Catalysts

Table 3-3 summarizes the effectiveness of various Lewis acid catalysts to solubilize SRC in benzene. Again, all of the experiments listed were performed at 300°C and 2000 psig H₂. Under these reaction conditions, all of the catalysts became molten and were either dissolved in the SRC or were finely dispersed as liquid droplets in a phase separate from the SRC. It is important to note that even though pure FeCl₃ has a melting point of 306°C, there were enough impurities present for it to be a liquid at the reaction temperature.

The yields of soluble products from SRC using Lewis acid catalysts show a much wider variation than the yields obtained with metal oxide catalysts. Since the two strongest Lewis acids (16), AlCl₃ and FeCl₃, appeared to extensively polymerize the SRC into an intractable tar, the yield of soluble products obtained using these catalysts was significantly lower than in run no. 6 conducted without catalyst. Of the runs conducted with catalyst, AlCl₃ and FeCl₃ also made products with the lowest H/C and H_{Al}/H_{Ar} ratios. SbCl₃ and HgCl₂ moderately reduced the solubilization of SRC relative to run no. 6 but made products with moderately higher H/C and H_{Al}/H_{Ar} ratios. ZnCl₂ and SnCl₂ gave yields of soluble products which were as good or better than yields obtained in run no. 6. Furthermore, the H/C and H_{Al}/H_{Ar} ratios of the products produced by ZnCl₂ and SnCl₂ are the highest of any of the other catalysts.

In comparing only the Lewis acid catalyst runs, one generally finds that higher SRC solubilizations accompany higher H/C and H_{Al}/H_{Ar} ratios. Furthermore, higher H/C ratios always accompany higher H_{Al}/H_{Ar} ratios.

Finally, another general trend is that the melting point of the soluble product tends to decrease as the aliphatic character of the product increases.

Although the Lewis acids may not always increase the quantity of SRC solubilized when compared to run no. 6, they are considerably more effective than the mixed metal oxides at hydrogenating SRC and increasing the H/C and H_{Al}/H_{Ar} ratios of the soluble product. Likewise, the Lewis acids are also very effective in removing nitrogen from the solubilized SRC. The removal of sulfur from the products, however, does not appear to occur. The S/C ratios listed in Table 3-3 may unfortunately be misleading since the sulfur content of the original SRC was very low. Variations in the S/C ratios of the products are probably more indicative of experimental uncertainty rather than any chemical change.

Table 3-3

Comparison of Lewis Acid Catalysts for Reaction with SRC in Benzene

Reaction Conditions: T = 300°C
P = 2000 psig H₂
t = 90 min.
ω = 1250 RPM

Catalyst mass = 5 gm
SRC mass = 5 gm
Solvent volume = 70 ml

Run No.	Catalyst	Sol. (%)	Filtrate Formula	H _{Al} /H _{Ar} ^d	Comments on Filtrates
-	SRC	-	C H .77 N .022 S .0023	1.07	Dark Brown - Black Solid
6	None	46.7	C H .85 N .018 S .0026	1.33	Dark Brown Solid
1	AlCl ₃ ^a	20.3	C H .89 N .0065 S .0024	1.32	Dark Brown Solid
29	ZnCl ₂	46.8	C H _{1.01} N .0032 S .0021	2.54	Dark Brown Caking Solid
31	SnCl ₂	57.9	C H .97 N .0105 S .0041	2.22	Dark Brown Solid
33	FeCl ₃	13.8	C H .86 N .0055 S .0037	1.04	Black Solid
55	SbCl ₃ ^b	38.2	C H .95 N .0052 S .0029	2.18	Brown Solid
58	HgCl ₂	37.8	C H .93 N .0073 S .0027	1.79	Dark Brown Solid
56	ZnCl ₂ +SnCl ₂ ^c	49.3	C H _{1.00} N .0043 S .0027	2.58	Dark Brown Solid

^a 1.0 gm AlCl₃ charged.^b SbCl₃ very soluble in Benzene. Filtrate H₂O washed before vacuum drying.^c 2.5 gm ZnCl₂ and 2.5 gm SnCl₂ charged.^d NMR Solvent: CDCl₃, except SRC done in Pyridine - d₅.

C. Organic Additives with Lewis Acids

Organic additives were charged into the autoclave in an effort to further increase the extent to which SRC could be solubilized in benzene. Based upon previous work reported in the literature, isopentane, isopropanol, cumene, and tetralin were investigated. Again, these screening experiments were performed at a temperature of 300°C and a pressure of 2000 psig H₂. At this temperature, isopentane and isopropanol are both above their critical point.

Work at Exxon Research and Engineering (14) has indicated that hydrogen on a tertiary carbon atom in the presence of a strong acid can act as a hydride donor to facilitate hydrogenation of benzene to cyclohexane. Isopentane has such a hydrogen and so its effect on the solubilization of SRC both with and without a catalyst was studied. Table 3-4 shows that no significant changes were observed with either the extent of SRC solubilization or the chemical analysis of the product by using isopentane.

Work at Stanford Research Institute (12) has indicated that isopropanol significantly increases the pyridine Soxhlet extractability of Illinois No. 6 coal over and above what would normally be expected for a polar solvent. Specifically, their work showed that pyridine extractions of coal which had been reacted in isopropanol were far above a linear curve obtained when plotting pyridine extractions versus Hildebrand solubility parameters for other solvents. This meant that isopropanol was performing some chemical role over and above that of a mere solvent.

For the above reason, isopropanol was investigated for its enhancement

effect on the solubilization of SRC in benzene. Table 3-4 shows that even without catalyst, isopropanol enhances the yield of soluble products from SRC by almost 40% over run no. 6 conducted without isopropanol. ZnCl_2 and SnCl_2 with isopropanol increase the amount of SRC solubilized by about 30% and 70% over their respective reactions without isopropanol. Indeed, SnCl_2 almost solubilizes the entire SRC substrate. The chemical analyses of the soluble products are equally favorable, showing an increase in the H/C and $\text{H}_{\text{Al}}/\text{H}_{\text{Ar}}$ ratios accompanied by only a modest increase in the N/C ratios.

While the presence of isopropanol with ZnCl_2 and SnCl_2 increases the yield of soluble products, large quantities are catalytically alkylated onto the benzene solvent to form cumene and water. This is a typical Friedel-Crafts type of alkylation which proceeds via the following mechanism (15, 16):

Unfortunately, the cumene formed is not as volatile as isopropanol and tends to incorporate somewhat into the product. The specific effects of isopropanol on the chemical nature of the solubilized SRC will be discussed later.

To determine whether the cumene formed via the reaction of isopropanol with benzene was responsible for the enhanced solubilization of SRC, cumene was tested as an additive itself. In addition, cumene would be expected to be an even better hydride donor than isopentane due to the resonance stabilization of the benzyl carbonium ion. Table 3-4 shows that cumene had no significant effect on either the extent of SRC solubilization or the chemical analysis of the product.

Tetralin was investigated as an organic additive due to its well-known hydrogen donation capability. Work at Stanford Research Institute (12) has shown that for Illinois No. 6, tetralin does not perform well as a hydrogen donor until a temperature of 325-350°C is reached. The results tabulated in Table 3-4 indicate that tetralin moderately enhances the yield of soluble products, however this may be misleading since the ^1H -NMR spectrum showed a large incorporation of tetralin in the sample. Since tetralin has a high boiling point, it could not be entirely removed from the product. The $\text{H}_{\text{Al}}/\text{H}_{\text{Ar}}$ ratio confirms that the H/C ratio of the products is perhaps larger than it would have been if no tetralin were incorporated. Due to the entrainment problems with tetralin, no further experiments with it were performed.

Table 3-4

Effects of Additives on Reactions of SRC in Benzene

Reaction Conditions: T = 300°C
P = 2000 psig H₂
t = 90 min.
ω = 1250 RPM

Catalyst mass = 5 gm
SRC mass = 5 gm
Additive mass = 5 gm
Solvent volume = 70 ml

Run No.	Catalyst	Additive	Sol. (%)	Filtrate Formula	H _{Al} /H _{Ar} ^a	Comments on Filtrate
-	-SRC-	-	-	C H .77 N.022 S.0023	1.07	Dark Brown - Black Solid
6	None	None	46.7	C H .85 N.018 S.0026	1.33	Dark Brown Solid
29	ZnCl ₂	None	46.8	C H _{1.01} N.0032 S.0021	2.54	Dark Brown Caking Solid
31	SnCl ₂	None	57.9	C H .97 N.0105 S.0021	2.22	Dark Brown Solid
39	None	Isopentane	44.0	C H .86 N.017 S.0043	1.28	Dark Brown Solid
47	ZnCl ₂	Isopentane	44.6	C H _{1.00} N.0031 S.0020	2.42	Dark Brown Caking Solid
49	SnCl ₂	Isopentane	56.8	C H .97 N.0099 S.0026	2.11	Dark Brown Solid
37	None	Isopropanol	65.0	C H .90 N.018 S.0025	1.56	Black Solid
43	ZnCl ₂	Isopropanol	60.4	C H 1.04 N.0048 S.0017	2.71	Black Caking Solid, some Cumene incorporation, 10 mole % Cumene formed
45	SnCl ₂	Isopropanol	99.4	C H _{1.06} N.012 S.0025	3.07	Black Solid, some Cumene incorporation, 5 mole % Cumene formed, Propane formed
51	ZnCl ₂	Cumene	47.7	C H .97 N.0043 S.0022	2.33	Dark Brown Caking Solid some Cumene incorporation
53	SnCl ₂	Cumene	64.0	C H .98 N.0102 S.0021	2.03	Dark Brown Caking Solid some Cumene incorporation
35	None	Tetralin	64.8	C H .89 N.016 S.0030	1.38	Black Solid, some Tetralin incorporation

^a NMR Solvent: CDCl₃, except SRC and Run 37 done in Pyridine - d₅. Incorporated Solvents, Additives, and Solvent-Additive reaction products are not included in measurement of H_{Al}/H_{Ar} ratios.

D. Solvent Effects

The use of benzene as a reaction solvent leads to the extraction of products which have both oil and asphaltene-like character. To better assess the ability of the catalysts to promote the conversion of asphaltenes and asphaltols to oils, experiments were conducted in cyclohexane. At the temperature used in these experiments, the cyclohexane was above its critical point ($T_C = 280.4^\circ\text{C}$, $P_C = 40 \text{ atm.}$) (13).

The first part of Table 3-5 compares the products of reactions run in benzene and cyclohexane without catalyst. The table shows that the extent of SRC solubilization is much lower in cyclohexane than in benzene, but that the H/C and H_{Al}/H_{Ar} ratios are higher. The N/C ratio decreases 20% when switching from benzene to cyclohexane while the S/C ratio remains quite low and relatively unchanged. The changes in the composition of the products extracted from SRC reflect the fact that cyclohexane solubilizes a more aliphatic product than benzene. Similar results are obtained when the best of the metal oxide catalysts, $\text{NiO-MoO}_3\text{-Al}_2\text{O}_3$, is used. This suggests that the metal oxide was rather inert and did not participate in any reactions with the SRC.

By contrast, ZnCl_2 and SnCl_2 cause dramatic increases in the extent to which SRC can be solubilized in cyclohexane. Indeed, these catalysts can more than double the yield of soluble products. The fact that ZnCl_2 and SnCl_2 only moderately help to solubilize SRC in benzene, but do so dramatically in cyclohexane indicates that these catalysts are much more effective at producing an oil-like product than an asphaltene-like product.

The H/C ratios of the products from ZnCl_2 and SnCl_2 reactions

conducted in cyclohexane are significantly higher while the N/C ratios are significantly lower than the corresponding ratios in run no. 59, carried out without catalyst. Even the S/C ratios appear to be lower for the ZnCl_2 and SnCl_2 products than the S/C ratios in previous runs. It is noteworthy that the H/C ratios are higher and the N/C ratios are lower for the cyclohexane extracted products than for the benzene extracted products. Based upon the $\text{H}_{\text{Al}}/\text{H}_{\text{Ar}}$ ratios, the products derived using ZnCl_2 and SnCl_2 are significantly more aliphatic than the product produced in run no. 59 without catalyst.

One result which is not reported in Table 3-5 is the amount of metal from the catalyst which is incorporated into the soluble product. Elemental analyses show that for the ZnCl_2 reaction products, the Zn contents are 0.9% and 0.07% for extractions with benzene and cyclohexane solvents respectively, while for the SnCl_2 reaction products, the Sn contents are 5% and 0.6%. This means then that the metal from the Lewis acid is incorporated about a factor of 10 less upon switching the solvent from benzene to cyclohexane. The $\text{NiO-MoO}_3\text{-Al}_2\text{O}_3$, quite naturally, did not incorporate into the soluble product in either solvent.

The last column of Table 3-5 also shows that in addition to chemical changes, physical changes are taking place with these extracted products. The ZnCl_2 product in particular has finally reached a point where its melting point is low enough for it to be a liquid at room temperature.

Figures 3-5 through 3-12 show the $^1\text{H-NMR}$ spectra from which the $\text{H}_{\text{Al}}/\text{H}_{\text{Ar}}$ ratios were determined for the ZnCl_2 , SnCl_2 , and $\text{NiO-MoO}_3\text{-Al}_2\text{O}_3$ reactions carried out in both benzene and cyclohexane. These spectra clearly indicate the increased aliphatic (0-5ppm) to aromatic (6-10ppm)

hydrogen content resulting from the use of these catalysts. ZnCl_2 and SnCl_2 seem particularly capable of increasing the content of aliphatic hydrogen which resonates in the lower H_α region as well as hydrogen which resonates between the centers of the H_α and H_β regions.

Figures 3-13 through 3-14 show the molecular weight distributions of SRC and the various products from the catalyst-substrate-solvent reactions. Figure 3-13 shows the soluble reaction products obtained in benzene, while Fig. 3-14 shows the soluble reaction products obtained in cyclohexane. Both figures show that ZnCl_2 and SnCl_2 produce a lower molecular weight product than the reactions performed without catalyst in either solvent. The cyclohexane extracted products also appear to have a lower molecular weight distribution than the benzene extracted products. This should be expected since oils are known to have lower average molecular weights than asphaltenes.

Table 3-5

Effects of Solvent on Reactions with SRC

Reaction Conditions: T = 300°C
P = 2000 psig H₂
t = 90 min.
ω = 1250 RPM

Catalyst mass = 5 gm
SRC mass = 5 gm
Solvent volume = 70 ml

Run No.	Catalyst	Solvent	Sol. (%)	Filtrate Formula	H _{Al} /H _{Ar} ^a	Comments on Filtrate
-	-SRC-	-	-	C H .77 N .022 S .0023	1.07	Dark Brown -Black Solid
6	None	Benzene	46.7	C H .85 N .018 S .0026	1.33	Dark Brown Solid
59	None	Cyclo-hexane	15.1	C H .91 N .014 S .0020	1.50	Brown Solid
16	5.4%NiO-19%MoO ₃ -Al ₂ O ₃	Benzene	50.2	C H .86 N .017 S .0025	1.59	Dark Brown Solid, 11 mole %, Cyclo-hexane formed
70	5.4%NiO-19%MoO ₃ -Al ₂ O ₃	Cyclo-hexane	15.4	C H .92 N .014 S .0028	1.72	Brown Solid
29	ZnCl ₂	Benzene	46.8	C H _{1.01} N .0032 S .0021	2.54	Dark Brown Caking Solid
61	ZnCl ₂	Cyclo-hexane	35.4	C H _{1.06} N .0013 S .0016	3.38	Dark Brown Viscous Oil, 0.5 mole % Methyl-cyclopentane formed
31	SnCl ₂	Benzene	57.9	C H .97 N .0105 S .0041	2.22	Dark Brown Solid
63	SnCl ₂	Cyclo-hexane	29.8	C H _{1.00} N .0051 S .0017	2.68	Dark Brown Solid

^a NMR Solvent: CDCl₃, except SRC done in Pyridine - d₅.

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Fig. 3-5. ^1H -NMR spectrum of filtrate from SRC reacted without catalyst in Benzene: 300°C, 2000 psig H_2 .

XBL 7712-11258A

Fig. 3-6. ^1H -NMR spectrum of filtrate from SRC reacted with ZnCl_2 in Benzene: 300°C, 2000 psig H_2 .

Fig. 3-7. ^1H -NMR spectrum of filtrate from SRC reacted with SnCl_2 in Benzene: 300°C , 2000 psig H_2 .

XBL 7712-11259A

Fig. 3-8. ^1H -NMR spectrum of filtrate from SRC reacted with $\text{Ni/Mo-Al}_2\text{O}_3$ in Benzene: 300°C , 2000 psig H_2 .

Fig. 3-9. ^1H -NMR spectrum of filtrate from SRC reacted without catalyst in Cyclohexane: 300°C, 2000 psig H_2 .

XBL 7712-11260A

Fig. 3-10. ^1H -NMR spectrum of filtrate from SRC reacted with ZnCl_2 in Cyclohexane: 300°C, 2000 psig H_2 .

Fig. 3-11. ¹H-NMR spectrum of filtrate from SRC reacted with SnCl₂ in Cyclohexane: 300°C, 2000 psig H₂.

XBL 7712-11261A

Fig. 3-12. ¹H-NMR spectrum of filtrate from SRC reacted with Ni/Mo-Al₂O₃ in Cyclohexane: 300°C, 2000 psig H₂.

XBL 7712-11247A

Fig. 3-13. Molecular Weight Distributions by Gel Permeation Chromatography of SRC reacted in Benzene.
Reaction Conditions: T = 300°C, P = 2000 psig H₂

XBL 7712-11248A

Fig. 3-14. Molecular Weight Distributions by Gel Permeation Chromatography of SRC reacted in Cyclohexane.
Reaction Conditions: T = 300°C, P = 2000 psig H₂

E. Residue and Filtrate Comparison

In all of the results reported thus far, no mention has been made of the effects of these reaction conditions on the part of the SRC which is not solubilized. Table 3-6 shows the chemical analyses of both the cyclohexane solubilized SRC (filtrate) and the insoluble SRC residue after it was washed free of catalyst. It is clear from the residue analyses that the filtrate is not the only component of the SRC which is hydrogenated. The H/C ratios are clearly higher for the residues which have been reacted with ZnCl_2 or SnCl_2 than the residue which has not been reacted with catalyst. Although the H/C ratios change significantly, the N/C and S/C ratios of the residues remain as high or higher than the original SRC from which the residues were derived.

It should be noted that while the ZnCl_2 -SRC residue mixture came out of the autoclave as a homogeneous mixture, the SnCl_2 -SRC residue did not. For SnCl_2 , the catalyst formed separate white globules which dispersed themselves into the black residue matrix.

Table 3-6

Comparison of Filtrate and Residue Analyses for
Reactions of SRC in Cyclohexane

Reaction Conditions: T = 300°C Catalyst mass = 5 gm
 P = 2000 psig H₂ SRC mass = 5 gm
 t = 90 min. Solvent volume = 70 ml
 ω = 1250 RPM

Run No.	Catalyst	Sol. (%)	Filtrate Formula	Filtrate ^a H _{Al} /H _{Ar}	Residue Formula	Residue ^{b,c,d} H _{Al} /H _{Ar}	Mass ^e Balance (%)	Comments on Residue
-	-SRC-	-	C H .77 N .022 S .0023	1.07	-	-	-	-
59	None	15.1	C H .91 N .014 S .0020	1.50	C H .80 N .022 S .0023	1.08	100	Black Solid, some Cyclohexane incorporation
61	ZnCl ₂	35.4	C H _{1.06} N .0013 S .0016	3.38	C H .95 N .027 S .0031	2.98	94	Black Solid, Homogeneous Solid
63	SnCl ₂	29.8	C H _{1.00} N .0051 S .0017	2.68	C H .93 N .021 S .0032	2.19	91	Black Solid, some SnCl ₂ -SRC Segregation, some Cyclohexane incorporation

^a NMR Solvent: CDCl₃, except SRC done in Pyridine - d₅.

^b NMR Solvent: Pyridine - d₅.

^c Incorporated Solvent is not included in measurements of H_{Al}/H_{Ar} ratios.

^d All residues washed with hot H₂O and dried 5 hr in vacuum oven at 105°C.

^e % Recovery of Catalyst and SRC Products.

F. Solvent and Isopropanol Effects

In the discussion of Table 3-4 it was noted that cumene was formed as a result of Friedel-Crafts catalytic alkylation of benzene by isopropanol. Elimination of this side reaction could be facilitated by switching the reaction solvent from benzene to cyclohexane. Table 3-7 summarizes the effectiveness of isopropanol to promote the solubilization of SRC in both benzene and cyclohexane. As with benzene, the quantities of SRC solubilized in cyclohexane are definitely increased when isopropanol is used. Although the total amount of cyclohexane extracted product is less than the benzene extracted product, the H/C ratios and the H_{Al}/H_{Ar} ratios for the isopropanol runs are both much higher for the cyclohexane extracted product. This again reflects the more oil-like character of the cyclohexane extracted product versus the benzene extracted product.

Figures 3-15 through 3-18 show some of the 1H -NMR spectra from which the H_{Al}/H_{Ar} ratios were calculated for isopropanol runs conducted in benzene and cyclohexane. Normally, an isopropyl group would be expected to show a sharp doublet centered about 1.2-1.3ppm for the protons on the terminal methyls and a septet centered about 2.8-2.9ppm for the lone proton. Furthermore, the areas of these two resonances would be in the ratio of 6:1. This is what is shown in Fig. 3-16 where the doublet and the septet of the isopropyl group on cumene are superimposed on the spectrum of the soluble SRC products. However, if the isopropyl group were to be alkylated onto a host of different aromatic clusters, the sharp methyl resonance would be expected to broaden out, possibly to the extent that a doublet would not longer be observed.

This is exactly what happens, as shown in Figs. 3-16 and 3-18 in the region between 1.1 and 1.6ppm.

In an effort to get a rough idea of how much of the isopropanol charged was alkylating the SRC, a ^1H -NMR spectrum for a run made without isopropanol was superimposed on a spectrum of the same run with isopropanol. Under the assumption that the only function the isopropanol served was to alkylate the SRC, the difference in peak area from 1.1 to 1.6ppm was compared to the peak area for the doublet of pure isopropanol. Since the sample concentration and the ^1H -NMR spectrum attenuation were known exactly, the percentage of the isopropanol which was charged that alkylated the SRC could be calculated. These values are shown in the next to last column of Table 3-7.

Table 3-7 shows that higher percentages of isopropanol are alkylated onto the soluble product in cyclohexane than in benzene. As mentioned earlier, this results from the elimination of the side reaction of isopropanol with benzene. If one takes 12% as the highest percentage of isopropanol which alkylates the soluble products in cyclohexane and assumes an average molecular weight of 300 from the molecular weight distributions shown in Fig. 3-14, one finds that the soluble product contains 1 isopropyl groups per molecule.

Before leaving this section, it is interesting to note the very different spectrum obtained in Fig. 3-15 for the product of the isopropanol run made without catalyst in benzene. Note that the H_γ peak to the right of the H_β peak is quite pronounced. This indicates that isopropanol is somehow able to increase the number of terminal methyl groups γ or further from an aromatic ring.

Table 3-7

Effects of Solvent and Isopropanol on Reactions of SRC

Reactions Conditions: T = 300°C
P = 2000 psig H₂
t = 90 min.
ω = 1250 RPM

Catalyst mass = 5 gm
SRC mass = 5 gm
Additive mass = 5 gm Isopropanol
Solvent volume = 70 ml

Run No.	Catalyst	Additive	Solvent	Sol. (%)	Filtrate Formula	H _{Al} /H _{Ar} ^a	Isopropanol Alkylated (%)	Comments on Filtrate ^b
-	-SRC-	-	-	-	C H .77 N.022 S.0023	1.07	-	Dark Brown - Black Solid
6	None	No	Benzene	46.7	C H .85 N.018 S.0026	1.33	-	Dark Brown Solid
37	None	Yes	Benzene	65.0	C H .90 N.018 S.0025	1.56	0	Black Solid
29	ZnCl ₂	No	Benzene	46.8	C H _{1.01} N.0032 S.0021	2.54	-	Dark Brown Caking Solid
43	ZnCl ₂	Yes	Benzene	60.4	C H _{1.04} N.0048 S.0017	2.71	6	Black Caking Solid, 10 mole % Cumene formed, some Cumene incorporation
31	SnCl ₂	No	Benzene	57.9	C H .97 N.0105 S.0020	2.22	-	Dark Brown Solid
45	SnCl ₂	Yes	Benzene	99.4	C H _{1.06} N.012 S.0025	3.07	8	Black Solid, 5 mole % Cumene formed, Propane formed, some Cumene incorporation
59	None	No	Cyclohexane	15.1	C H .91 N.014 S.0020	1.50	-	Brown Solid
68	None	Yes	Cyclohexane	25.3	C H .89 N.017 S.0022	1.34	0	Brown Solid
61	ZnCl ₂	No	Cyclohexane	35.4	C H _{1.06} N.0013 S.0016	3.38	-	Dark Brown Viscous Oil, 0.6 mole % Methylcyclopentane formed
65	ZnCl ₂	Yes	Cyclohexane	57.5	C H _{1.14} N.0053 S.0021	5.27	10	Black Solid, 1.2 mole % Methylcyclopentane formed, Propane formed
63	SnCl ₂	No	Cyclohexane	29.8	C H _{1.00} N.0051 S.0017	2.68	-	Dark Brown Solid
67	SnCl ₂	Yes	Cyclohexane	54.5	C H _{1.11} N.0069 S.0025	4.82	12	Brown Solid, Propane formed

^a NMR Solvent: CDCl₃, except SRC and Run 37 done in Pyridine - d₅.

^b Approx. 10 mole % Isopropanol charged in reaction.

Fig. 3-15. ^1H -NMR spectrum of filtrate from SRC reacted with Isopropanol in Benzene: 300°C, 2000 psig H_2 .

XBL 7712-11262A

Fig. 3-16. ^1H -NMR spectrum of filtrate from SRC reacted with ZnCl_2 and Isopropanol in Benzene: 300°C, 2000 psig H_2 .

Fig. 3-17. ^1H -NMR spectrum of filtrate from SRC reacted with Isopropanol in Cyclohexane: 300°C, 2000 psig H_2 .

XBL 7712-11263A

Fig. 3-18. ^1H -NMR spectrum of filtrate from SRC reacted with SnCl_2 and Isopropanol in Cyclohexane: 300°C, 2000 psig H_2 .

III. Temperature Effects

Based upon the previous screening studies, ZnCl_2 and SnCl_2 were selected as the two most active SRC liquefaction catalysts and were used for investigating the effects of temperature on the solubilization of SRC. Table 3-8 summarizes the amounts of SRC solubilized and the analyses of the products for runs made between 250 and 400°C at 2000 psig H_2 . Figure 3-19 plots the H/C and N/C ratios versus reaction temperature for runs made with and without catalyst while Fig. 3-20 plots the $\text{H}_{\text{Al}}/\text{H}_{\text{Ar}}$ ratios and the extents of SRC solubilization versus temperature for the same runs.

These results show that as the reaction temperature is increased from 250°C, both ZnCl_2 and SnCl_2 markedly increase the solubilization of SRC for temperatures up to 350°C, where the amount of SRC extracted levels off at about 50%. By contrast, in the absence of catalyst, no increase is observed in the amount of SRC solubilized until the pyrolysis temperature of coal is surpassed (~350°C). The fact that ZnCl_2 and SnCl_2 produce yields of soluble products below 350°C which are far above those obtained without catalyst, implies that these catalysts are actively contributing to the catalytic cleavage of SRC.

The N/C and S/C ratios for the ZnCl_2 and SnCl_2 runs show a marked decrease with increasing temperature while the same ratios remain relatively unchanged regardless of temperature for the runs made without catalyst. One possible explanation for the removal of basic nitrogen is the formation of Lewis acid-Lewis base pairs of the type shown below.

However, since such reactions are normally exothermic, one would expect the "free" nitrogen in the product to increase with higher temperatures. The fact that the nitrogen content decreases monotonically as the temperature increases suggests that the removal of nitrogen is controlled by kinetics and/or mass transfer.

While the heteroatom to carbon ratios appear to decrease with increasing temperature, the H/C and H_{Al}/H_{Ar} ratios do not. Once again, little change is observed in the H/C ratios for the runs made without catalyst until the pyrolysis temperature is reached ($\sim 350^{\circ}\text{C}$). On the other hand, both ZnCl_2 and SnCl_2 produce an increase in the H/C and H_{Al}/H_{Ar} ratios from 250°C up to about 350°C where both ratios suddenly decrease from 350 to 400°C . This maximum in the H/C ratio versus temperature plot shown in Fig. 3-19 has been observed at slightly higher temperatures by other investigators using coal as a substrate (3,17,18). The appearance of such a maximum might be indicative of the approach to equilibrium conversion of the exothermic hydrogenation of aromatic to aliphatic compounds. At low temperatures, conversion increases with temperature since the hydrogenation is kinetically limited. However, at higher temperatures, equilibrium is attained making the conversion of aromatics to aliphatics decline with further increases in temperature.

Table 3-8

Effects of Temperature on Reactions of SRC in Cyclohexane

Reaction Conditions: P = 2000 psig H₂
 t = 90 min.
 ω = 1250 RPM

Catalyst mass = 5 gm
 SRC mass = 5 gm
 Solvent volume = 70 ml

Run No.	Catalyst	Temp. (°C)	Sol. (%)	Filtrate Formula	H _{Al} /H _{Ar} ^a	Comments on Filtrate
-	-SRC-	-	-	C H .77 N.022 S.0023	1.07	Dark Brown - Black Solid
79	None	250	15.3	C H .92 N.013 S.0024	1.53	Dark Brown Solid
59	None	300	15.1	C H .91 N.014 S.0020	1.50	Brown Solid
75	None	350	17.1	C H .92 N.014 S.0033	1.63	Brown Solid
84	None	375	22.6	C H .94 N.015 S.0030	1.85	Brown Solid
73	None	400	26.2	C H .96 N.016 S.0017	1.80	Black Solid
72	ZnCl ₂	250	23.2	C H .96 N.0039S.0041	2.16	Brown Solid
61	ZnCl ₂	300	35.4	C H _{1.06} N.0013S.0016	3.38	Dark Brown Viscous Oil
71	ZnCl ₂	350	45.9	C H _{1.08} N.0008S.0019	3.52	Brown Oil
82	ZnCl ₂	375	47.9	C H _{1.06} N.0006S.0009	3.03	Brown Oil
74	ZnCl ₂	400	48.0	C H .99 N.0004S.0009	2.19	Dark Brown Light Oil
76	ZnCl ₂	400	46.6	C H _{1.00} N.0005S.0012	2.13	Dark Brown Light Oil
80	SnCl ₂	250	20.6	C H .95 N.0072S.0026	1.92	Brown Solid
63	SnCl ₂	300	29.8	C H _{1.00} N.0051S.0017	2.68	Dark Brown Solid
81	SnCl ₂	350	43.3	C H _{1.05} N.0045S.0030	2.89	Dark Brown Viscous Oil
83	SnCl ₂	375	48.2	C H _{1.06} N.0043S.0009	2.78	Brown Oil
77	SnCl ₂	400	48.4	C H .99 N.0032S.0010	2.20	Dark Brown Oil

^a NMR Solvent: CDCl₃, except SRC done in Pyridine - d₅.

XBL 7712-11251A

Fig. 3-19. Effects of Temperature on H/C and N/C Ratios for Reactions of SRC in Cyclohexane.

Reaction Conditions: P = 2000 psig H₂

XBL 7712-11250A

Fig. 3-20. Effects of Temperature on Solubility and H_{Al}/H_{Ar} Ratio for Reactions of SRC in Cyclohexane.

Reaction Conditions: P = 2000 psig H_2

IV. Pressure Effects

Since a reaction temperature of 350°C at 2000 psig H₂ gave the most aliphatic product, this was the temperature selected for investigating the effect of hydrogen pressure on solubilizing SRC. Table 3-9 summarizes the amounts of SRC extracted into cyclohexane as well as the analyses of the products for runs made between 0 and 4000 psig H₂. Figure 3-21 shows plots of the H/C and N/C ratios versus hydrogen pressure for runs made with and without ZnCl₂ while Fig. 3-22 shows plots of the H_{Al}/H_{Ar} ratios and the extents of SRC solubilization versus pressure for the same runs.

In comparing Table 3-8 with 3-9, it is interesting to note that over the ranges studied, the effect of hydrogen pressure with ZnCl₂ and SnCl₂ on the extent of SRC solubilization is even more pronounced than the effect of temperature. On the other hand, increasing the hydrogen pressure for reactions performed without catalyst has almost no effect on the solubilization of SRC. From Fig. 3-21, the N/C ratios appear to decrease with increasing hydrogen pressure while the H/C ratios increase dramatically with increasing pressure. Figure 3-22 shows the same dramatic increase in the H_{Al}/H_{Ar} ratios as well as in the amount of SRC solubilized with increasing hydrogen pressure.

Figure 3-23 and 3-24 show two ¹H-NMR spectra of products obtained from ZnCl₂-SRC-cyclohexane runs made at 0 psig H₂ and 4000 psig H₂. The proton resonance increase in the aliphatic portion of the 4000 psig H₂ spectrum and decrease in the aromatic portion is quite apparent. It is interesting to note that for the aliphatic portion, the regions most affected are the resonances between the centers of the H_α and

H_β regions as well as the resonances in the H_γ region.

Table 3-9

Effects of Hydrogen Pressure on Reactions of SRC in Cyclohexane

Reaction Conditions: T = 350°C Catalyst mass = 5 gm
 t = 90 min. SRC mass = 5 gm
 ω = 1250 RPM Solvent volume = 70 ml

Run No.	Catalyst	H ₂ Partial Pressure ^a (psig)	Sol. (%)	Filtrate Formula	H _{Al} /H _{Ar} ^b	Comments on Filtrate
-	-SRC-	-	-	C H .77 N .022 S .0023	1.07	Dark Brown - Black Solid
89	None	0	9.9	C H .92 N .014 S .0022	1.45	Brown Solid
90	None	1000	15.9	C H .93 N .014 S .0023	1.70	Brown Solid
75	None	2000	17.1	C H .92 N .014 S .0033	1.63	Brown Solid
92	None	4000	15.1	C H .94 N .015 S .0025	1.76	Brown Solid
85	ZnCl ₂	0	17.1	C H .91 N .0040 S .0031	1.30	Dark Brown Viscous Oil
91	ZnCl ₂	1000	38.4	C H _{1.01} N .0029 S .0012	2.32	Brown Oil
71	ZnCl ₂	2000	45.9	C H _{1.08} N .0008 S .0019	3.52	Brown Oil
93	ZnCl ₂	4000	58.5	C H _{1.17} N .0008 S .0011	5.08	Fluorescent Green - Brown Oil
86	SnCl ₂	0	14.4	C H .94 N .0045 S .0030	1.40	Black Viscous Oil
81	SnCl ₂	2000	43.3	C H _{1.05} N .0045 S .0030	2.89	Dark Brown Viscous Oil

^a 0 psig H₂ runs done at 2000 psig N₂.

^b NMR Solvent: CDCl₃, except SRC done in Pyridine - d₅.

XBL 7712-11254A

Fig. 3-21. Effects of Pressure on H/C and N/C Ratios for Reactions of SRC in Cyclohexane.

Reaction Conditions: $T = 350^\circ\text{C}$

XBL 7712-11252 A

Fig. 3-22. Effects of Pressure on Solubility and H_{Al}/H_{Ar} Ratio for Reactions of SRC in Cyclohexane.

Reaction Conditions: $T = 350^{\circ}\text{C}$

Fig. 3-23. ^1H -NMR spectrum of filtrate from SRC reacted with ZnCl_2 in Cyclohexane: 350°C , 0 psig H_2 .

XBL 7712-11264A

Fig. 3-24. ^1H -NMR spectrum of filtrate from SRC reacted with ZnCl_2 in Cyclohexane: 350°C , 4000 psig H_2 .

V. Catalyst Loading Effects

Table 3-10 summarizes the analyses of products obtained from reactions of SRC at 300°C and 2000 psig H₂ where the amount of catalyst charged to the autoclave was varied. Figures 3-25 and 3-26 show plots of the yields of soluble products as well as the H/C, N/C, and H_{A1}/H_{Ar} ratios as a function of catalyst to SRC loading ratio. It appears that the solubilization of SRC is rather dependent on the amount of catalyst charged to the autoclave. As with the reaction temperature and pressure results, higher H/C and H_{A1}/H_{Ar} ratios with lower N/C ratios seem to accompany the increase in yield of soluble products.

Table 3-10

Effects of ZnCl_2 Loading on Reactions of SRC in Cyclohexane

Reaction Conditions: $T = 300^\circ\text{C}$ SRC mass = 5 gm
 $P = 2000$ psig H_2 Solvent volume = 70 ml
 $t = 90$ min.
 $\omega = 1250$ RPM

Run No.	Catalyst Mass (gm)	Sol. (%)	Filtrate Formula	$\text{H}_{\text{Al}}/\text{H}_{\text{Ar}}$ ^a	Comments on Filtrate
-	-SRC-	-	C H .77 N.022 S.0023	1.07	Dark Brown - Black Solid
59	0.0	15.1	C H .91 N.0140 S.0020	1.50	Brown Solid
96	1.25	20.8	C H .96 N.0086 S.0021	2.27	Brown Solid
94	2.5	26.3	C H _{1.01} N.0047 S.0017	2.43	Brown Caking Solid
61	5.0	35.4	C H _{1.06} N.0013 S.0016	3.38	Dark Brown Viscous Oil
95	10.0	39.7	C H _{1.09} N.0008 S.0017	4.00	Brown Viscous Oil

^a NMR Solvent: CDCl_3 , except SRC done in Pyridine - d_5 .

XBL 7712-11255A

Fig. 3-25. Effects of ZnCl₂ Loading on Solubility, H/C, and N/C Ratios for Reactions of SRC in Cyclohexane.

Reaction Conditions: T = 300°C, P = 2000 psig H₂

XBL 7712-11253A

Fig. 3-26. Effects of ZnCl₂ Loading on Solubility and H_{Al}/H_{Ar} Ratio for Reactions of SRC in Cyclohexane.

Reaction Conditions: T = 300°C, P = 2000 psig H₂

VI. HCl Effects

Work at Stanford Research Institute (12) has shown that the presence of HCl gas with reactions of Illinois No. 6 and AlCl_3 can moderately increase the pyridine and THF Soxhlet extraction yields of the product. While cracking of hydrocarbons by simple pyrolysis is generally agreed to begin by free radical formation, cracking of hydrocarbons by acid catalysis is generally agreed to begin by protonation of the reactant molecule. As a Bronsted acid, HCl could conceivably aid in the protonation step of the reaction by either protonating the reactant directly or perhaps forming an intermediate with the catalyst (e.g. $\text{H}^+\text{AlCl}_4^-$) which would then protonate the reactant.

Table 3-11 summarizes the results obtained with and without the presence of HCl in the reaction mixture. The results show that HCl gas alone without catalyst more than doubles the yield of soluble products over run no. 59 conducted without HCl or catalyst. The chemical analyses are equally favorable showing an increase in the H/C and $\text{H}_{\text{Al}}/\text{H}_{\text{Ar}}$ ratios and a decrease in the N/C ratio upon using HCl. By contrast, the presence of HCl with ZnCl_2 -SRC reactions reduces the yield of soluble products by a factor of $3\frac{1}{2}$ from run no. 61 conducted with ZnCl_2 but without HCl. The H/C and $\text{H}_{\text{Al}}/\text{H}_{\text{Ar}}$ ratios are equally unfavorable undergoing a significant decrease upon using HCl. The N/C ratio for the HCl- ZnCl_2 -SRC run, however, is the lowest of any reported value in this entire study. This low N/C ratio reflects the fact that the addition of more Lewis acid results in the complexation of more Lewis base nitrogen containing compounds. Finally, it should be noted from Table 3-11 that very little of the chlorine from the HCl was entrained in the soluble product.

Table 3-11

Effects of HCl on Reactions of SRC in Cyclohexane

Reaction Conditions: T = 300°C
 P = 2000 psig H₂
 = 1000 psia HCl
 t = 90 min.
 ω = 1250 RPM

Catalyst mass = 5gm
 SRC mass = 5 gm
 Solvent Volume = 70 ml

Run No.	Catalyst	HCl	Sol. (%)	Filtrate Formula	H _{Al} /H _{Ar}	Comments on Filtrate
-	-SRC-	-	-	C H .77 N .022 S .0023 Cl .0000	1.07	Dark Brown - Black Solid
59	None	No	15.1	C H .91 N .014 S .0020 Cl .0000	1.50	Brown Solid
87	None	Yes	30.4	C H _{1.08} N .0009 S .0018 Cl .0010	3.57	Fluorescent Green - Dark Brown Oil
61	ZnCl ₂	No	35.4	C H _{1.06} N .0013 S .0016 Cl .0004	3.38	Dark Brown Viscous Oil
88	ZnCl ₂	Yes	10.0	C H _{1.00} N .0003 S .0038 Cl .0004	1.97	Green - Light Brown Oil

^a NMR Solvent: CDCl₃, except SRC done in Pyridine - d₅.

VII. Reactions of an Illinois No. 6 Coal

To conclude the experimental phase of this study, it was decided to investigate what effect switching substrates from SRC to Illinois No. 6 coal might have. Table 3-12 compares the analyses of the soluble products from SRC and Illinois No. 6 obtained under reaction conditions of 350°C and 2000 psig H₂.

Although Illinois No. 6 and SRC are similar in some respects, they differ in many others. Table 3-12 shows that the H/C ratio of the coal is higher than SRC, implying that Illinois No. 6 is more aliphatic than SRC. While the N/C ratios of the two substrates are comparable, the S/C ratio of Illinois No. 6 is much higher than the S/C ratio of SRC since the raw coal contains both the organic and inorganic sulfur.

Both ZnCl₂ and SnCl₂ increase the solubilization of Illinois No. 6 over a run conducted without catalyst (run no. 98), and it is seen that SnCl₂ is even more effective than ZnCl₂. By contrast, upon using SRC as a substrate, both ZnCl₂ and SnCl₂ produce approximately equal yields of soluble products.

In the absence of catalyst, the soluble product obtained from Illinois No. 6 is considerably more aliphatic than the product obtained from SRC. When ZnCl₂ is used as the catalyst, both the H/C and H_{Al}/H_{Ar} ratios decrease. By contrast, the use of SnCl₂ leads to an H/C ratio of the product which is unchanged relative to that found in run no. 98 and an H_{Al}/H_{Ar} ratio which is slightly higher. Finally, both the N/C and S/C ratios of the Illinois No. 6 products show a marked decrease with the use of either ZnCl₂ or SnCl₂ relative to the product made without catalyst.

Figure 3-27 illustrates the ^1H -NMR spectrum of the cyclohexane soluble product from Illinois No. 6 reacted without catalyst, while Fig. 3-28 illustrates the ^1H -NMR spectrum when SnCl_2 is used. It can be observed that the only really distinguishable difference between the ^1H -NMR spectra obtained from Illinois No. 6 and SRC is the pronounced H_γ peak found in Fig. 3-27 for the Illinois No. 6 product.

The molecular weight distributions from the soluble products obtained using Illinois No. 6 as a substrate are shown in Fig. 3-29. The SnCl_2 -Illinois No. 6 and no catalyst-Illinois No. 6 runs produced quite similar molecular weight distributions and both spanned molecular weights in the same range as those obtained using SRC as a substrate. By contrast, the ZnCl_2 -Illinois No. 6 molecular weight distribution spans a much lower range of molecular weights than any distribution obtained throughout this investigation.

Table 3-12

Comparison of SRC and Illinois #6 Coal Reactions in Cyclohexane

Reaction Conditions: T = 350°C
P = 2000 psig H₂
t = 90 min.
ω = 1250 RPM

Catalyst mass = 5 gm
Substrate mass = 5 gm
Solvent volume = 70 ml

Run No.	Catalyst	Substrate	Sol. ^a (%)	Filtrate Formula	H _{Al} /H _{Ar} ^b	Comments on Filtrate
-	-SRC-	-	-	C H .77 N.022 S.0023	1.07	Dark Brown - Black Solid
-	-Ill. #6-	-	-	C H .87 N.016 S.0193	- ^c	Black Solid
59	None	SRC	17.1	C H .92 N.014 S.0033	1.63	Brown Solid
98	None	Ill. #6	6.7	C H _{1.12} N.0066 S.0101	3.93	Black Caking Solid
71	ZnCl ₂	SRC	45.9	C H _{1.08} N.0008 S.0019	3.52	Brown Oil
99	ZnCl ₂	Ill. #6	20.5	C H _{1.06} N.0001 S.0023	3.38	Brown Viscous Oil
81	SnCl ₂	SRC	43.3	C H _{1.05} N.0045 S.0030	2.89	Dark Brown Viscous Oil
100	SnCl ₂	Ill. #6	36.9	C H _{1.12} N.0023 S.0055	4.13	Brown Viscous Oil

^a Moisture and ash free basis.

^b NMR Solvent: CDCl₃, except SRC done in Pyridine - d₅.

^c Illinois #6 Coal not soluble enough in Pyridine - d₅.

Fig. 3-27. ^1H -NMR spectrum of filtrate from Illinois #6 coal reacted without catalyst in Cyclohexane: 350°C, 2000 psig H_2 .

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Fig. 3-28. ^1H -NMR spectrum of filtrate from Illinois #6 coal reacted with SnCl_2 in Cyclohexane: 350°C, 2000 psig H_2 .

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Fig. 3-29. Molecular Weight Distributions by Gel Permeation Chromatography of Reactions of Illinois #6 Coal in Cyclohexane.

Reaction Conditions: $T = 350^\circ\text{C}$, $P = 2000$ psig H_2

VIII. Correlation of H/C and H_{Al}/H_{Ar} Ratios.

It may be recalled that throughout this investigation, increases in the H/C ratios were almost always accompanied by even larger increases in the H_{Al}/H_{Ar} ratios. This observation led to the investigation whether or not a correlation existed between the H/C and H_{Al}/H_{Ar} ratios. Although one might normally expect that the H_{Al}/H_{Ar} ratio would necessarily increase if the H/C ratio increased, there are many possible organic reactions which could occur (e.g. linking together of aromatic clusters) which would increase the overall aliphatic to aromatic hydrogen content of the sample while decreasing the H/C ratio.

Figure 3-30 shows the plot of the H/C ratio versus the H_{Al}/H_{Ar} ratio for the soluble products obtained under many different reaction conditions and with many different catalysts. The products which are represented in Fig. 3-30 include all the soluble products obtained throughout this investigation with the exception of those formed in runs made with organic additives which would entrain or react with the product. Despite the wide variations in reaction conditions and substrates, the correlation between the H/C and H_{Al}/H_{Ar} ratio is remarkably good. While the H/C ratio spans from 0.69 to 1.17, the H_{Al}/H_{Ar} ratio spans from 0.75 to 5.08. Thus this correlation curve clearly shows how much more sensitive the H_{Al}/H_{Ar} ratio is to increased hydrogen content than the H/C ratio.

A fairly good empirical formula which fits this correlation is shown below:

$$\frac{H_{Al}}{H_{Ar}} = \frac{H_{Al \text{ old}} + H_{\text{added}}}{H_{Ar \text{ old}} - \frac{1}{2} H_{\text{added}}}$$

$$\frac{H_{Al}}{H_{Ar}} = \frac{(H_{Al}/C)_o + [H/C - (H/C)_o]}{(H/C)_o - (H_{Al}/C)_o - \frac{1}{2} [H/C - (H/C)_o]}$$

where $(H/C)_o$ and $(H_{Al}/C)_o$ are the total hydrogen to carbon aliphatic hydrogen to carbon ratios of a particular product. If one substitutes the appropriate values for asphaltols ($(H/C)_o = .69$, $H_{Al}/H_{Ar} = .74$, $H_{Al}/C = 0.293$), one obtains:

$$\frac{H_{Al}}{H_{Ar}} = \frac{-0.397 + H/C}{0.742 - \frac{1}{2}(H/C)}$$

Physically, this formula indicates that the aliphatic hydrogen is increased by the same amount as the hydrogen which is consumed in increasing the H/C ratio, while the aromatic hydrogen is decreased by half of the consumed hydrogen.

Fig. 3-30. Correlation of H/C Ratio with H_{Al}/H_{Ar} Ratio.

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CHAPTER 4: CONCLUSIONS

The work performed in this investigation has shown that the metal oxides of Al_2O_3 , $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$, $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$, $\text{Co}_2\text{O}_3\text{-Al}_2\text{O}_3$, $\text{NiO-MoO}_3\text{-Al}_2\text{O}_3$, $\text{NiO-WO}_3\text{-Al}_2\text{O}_3$, $\text{CoO-MoO}_3\text{-Al}_2\text{O}_3$, Residcat -30, and CBZ-1 are all relatively inactive for promoting the hydrogenation and solubilization of SRC in benzene at 300°C and 2000 psig H_2 . Under these same reaction conditions, AlCl_3 , ZnCl_2 , SnCl_2 , SbCl_3 , and HgCl_2 were found to give benzene soluble products from SRC with much higher H/C ratios and much lower N/C ratios than runs conducted in the absence of catalyst. Only ZnCl_2 and SnCl_2 gave yields of soluble products which were as good or better than runs performed without catalyst. The other Lewis acids reduced the yields of soluble products.

Using cyclohexane rather than benzene, ZnCl_2 and SnCl_2 were shown to give much greater improvements over runs conducted without catalyst for the solubilization of SRC. In addition, the cyclohexane soluble products were shown to have very high H/C and $\text{H}_{\text{Al}}/\text{H}_{\text{Ar}}$ ratios with very low N/C ratios. It was also determined that increasing the ZnCl_2 loading would increase the amount of SRC solubilized in cyclohexane, increase the H/C and $\text{H}_{\text{Al}}/\text{H}_{\text{Ar}}$ ratios of the soluble product, and decrease the N/C ratio of the product. Besides giving a more aliphatic product with lower heteroatom content, ZnCl_2 and SnCl_2 were shown to be very effective at catalyzing hydrogenation of the cyclohexane insoluble residue. However, both these catalysts were ineffective at accomplishing any heteroatom removal from this residue.

Isopentane and cumene, both hydride donors in the presence of a strong acid, were shown to be ineffective with or without ZnCl_2 and

SnCl_2 at either increasing the solubilization of SRC or changing the chemical analysis of the product. Isopropanol, however, proved to be a very effective additive which increased the yield of benzene and cyclohexane soluble products from SRC both with and without ZnCl_2 and SnCl_2 over runs performed in the absence of isopropanol. Proton NMR data proved that in the presence of these catalysts, isopropanol could increase the solubilization of SRC by alkylating up to 1.5 isopropyl groups per molecule of soluble product. Dry HCl also proved to be effective at promoting the solubilization of SRC as well as increasing the H/C ratio and decreasing the N/C ratio of the cyclohexane soluble product relative to a run made with SRC alone. However, when used in conjunction with ZnCl_2 , HCl dramatically reduced both the solubilization of the SRC and the H/C ratio of the soluble product relative to a run made with ZnCl_2 but without HCl.

Studies on the effects of reaction temperature at 2000 psig H_2 revealed that ZnCl_2 and SnCl_2 increase the solubilization of SRC with increasing temperature up to about 350°C , where the percentage of SRC extracted by cyclohexane remains constant at about 50%. The H/C and $\text{H}_{\text{Al}}/\text{H}_{\text{Ar}}$ ratios of the cyclohexane soluble products from reactions of ZnCl_2 and SnCl_2 with SRC reached maxima at around 350°C with lower ratios above and below this temperature. Hence, the products became more aliphatic up to 350°C but then became more aromatic as the temperature rose above 350°C . By contrast, the N/C ratios of the ZnCl_2 and SnCl_2 products were shown to decrease monotonically with increasing temperature.

Studies on the effects of pressure with ZnCl_2 and SnCl_2 at 350°C

revealed that both the amount of SRC solubilized and the extent of hydrogenation of the soluble product increased sharply with increasing hydrogen pressure. By contrast, products obtained without catalyst showed virtually no dependence on hydrogen pressure for either the yield or H/C and H_{Al}/H_{Ar} ratios of the cyclohexane soluble product.

Using Illinois No. 6 as an alternate substrate proved that $ZnCl_2$ and $SnCl_2$ were even more effective at increasing the extent to which raw coal could be solubilized in cyclohexane. Although the H/C and H_{Al}/H_{Ar} ratios were not increased, the use of these catalysts did markedly reduce the N/C ratios of the Illinois No. 6 soluble product.

Finally, using the analyses of all the products obtained under widely varying reaction conditions, a correlation between the H/C and H_{Al}/H_{Ar} ratios was determined.

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