Hydrocracking of Montana coals through the use of massive quantities of molten salt catalysts
by Warren Philip Scarrah

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY in Chemical Engineering
Montana State University

Abstract:
C The use of massive quantities of molten salt catalysts was investigated for the hydrocracking of two Montana coals: Colstrip subbituminous and Savage lignite. The catalytic component of the molten salt was ZnC12; various alkali metal halides were used as the noncatalytic component to reduce the viscosity of the molten salt and promote phase separation between the hydrocarbons and salt mixture. Experiments were run in a 500-ml rocking-bomb reactor and conversions were based on reaction products that were soluble in benzene.

Tests used to simultaneously investigate the importance on conversion of seven process parameters showed no effect of the following between the levels indicated: pressure (2000-3000 psig); salt:coal weight ratio (2:l-4:l); and KC1:ZnC12 mole ratio (1:2-l:l). Significant effects were attributed to these parameters between the levels indicated: temperature (350-450°C); time (l5- 60 min.); mixing (static-rocking); and coal size (-40+100 - -100 mesh). Good conversions (>85 wt-%) were attained using both coals and the parameters affected conversion essentially the same for both coals. Additional tests showed that the pressure should be greater than 2000 psig and the coal particle size smaller than 140 mesh. It was also observed that KCl:ZnC12 mole ratios as low as 0.2:1 might be feasible and that the noncatalytic component of the salt mixture affects conversion and product appearance.

NaCl was superior to KCl relative to conversion when used as the noncatalytic component of the salt mixture. The ZnC12 in the molten salt mixture eventually became poisoned with resultant lower conversions, poorer phase separations, and more tar-like products. The use of expendable quantities of ZnC12 in noncatalytic molten salt mixtures was not promising. Metal chlorides of metals more and less active than zinc did not act as catalyst accelerators (compounds that would react with the catalyst poisons in preference to ZnC12). Comparison of gas removal at reactor operating temperatures and at ambient temperatures showed the former retarded the onset of poor phase separation and more tar-like products. It also resulted in a higher H:C mole ratio in the products and less retention of nitrogen (the suspected catalyst poison) in the salt mixture.

HYDROCRACKING OF MONTANA COALS THROUGH THE USE OF MASSIVE QUANTITIES OF MOLTEN SALT CATALYSTS

by

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ABSTRACT

The use of massive quantities of molten salt catalysts was investigated for the hydrocracking of two Montana coals: Colstrip subbituminous and Savage lignite. The catalytic component of the molten salt was $ZnCl_2$; various alkali metal halides were used as the noncatalytic component to reduce the viscosity of the molten salt and promote phase separation between the hydrocarbons and salt mixture. Experiments were run in a 500-ml rocking-bomb reactor and conversions were based on reaction products that were soluble in benzene.

Tests used to simultaneously investigate the importance on conversion of seven process parameters showed no effect of the following between the levels indicated: pressure (2000-3000 psig); salt:coal weight ratio (2:1-4:1); and KCl:$ZnCl_2$ mole ratio (1:2-1:1). Significant effects were attributed to these parameters between the levels indicated: temperature (350-450°C); time (15-60 min.); mixing (static-rocking); and coal size (-40+100 - -100 mesh). Good conversions (> 85 wt-%) were attained using both coals and the parameters affected conversion essentially the same for both coals. Additional tests showed that the pressure should be greater than 2000 psig and the coal particle size smaller than 140 mesh. It was also observed that KCl:$ZnCl_2$ mole ratios as low as 0.2:1 might be feasible and that the noncatalytic component of the salt mixture affects conversion and product appearance.

NaCl was superior to KCl relative to conversion when used as the noncatalytic component of the salt mixture. The $ZnCl_2$ in the molten salt mixture eventually became poisoned with resultant lower conversions, poorer phase separations, and more tar-like products. The use of expendable quantities of $ZnCl_2$ in noncatalytic molten salt mixtures was not promising. Metal chlorides of metals more and less active than zinc did not act as catalyst accelerators (compounds that would react with the catalyst poisons in preference to $ZnCl_2$). Comparison of gas removal at reactor operating temperatures and at ambient temperatures showed the former retarded the onset of poor phase separation and more tar-like products. It also resulted in a higher H:C mole ratio in the products and less retention of nitrogen (the suspected catalyst poison) in the salt mixture.

I INTRODUCTION

A. Historical Background

1. Consolidation Coal Company

The Consolidation Coal Company developed the Consol Synthetic Fuel process for converting coal into liquid fuels. As one of the principal steps in the process is the catalytic hydrocracking of coal extract into liquids, Consol made an intensive study of potential catalysts (1,2,3). Consol concluded that catalytic hydrocracking involves two simultaneous and independent reactions: cracking and hydrogenation.

The types of catalysts investigated were (1) contact catalysts of the hydrofining type; (2) dual-function contact catalysts, and (3) molten metal halide catalysts. Consol's initial work was concentrated on the contact catalysts of the hydrofining type (sulfides of molybdenum, nickel, and/or cobalt on an alumina gel support). These are good hydrogenation catalysts but have very little cracking activity. To add cracking activity dual-function contact catalysts were prepared by incorporating acidic cracking agents into hydrofining-type catalysts; the basic nitrogen compounds in the coal extract quickly poisoned the acidic, cracking sites on the catalyst.

Studies were then directed toward molten metal halides that were strong Lewis acids and their use in massive quantities to overcome the nitrogen compounds in the coal extract. These are primarily cracking catalysts but it had been shown that at least

one of them, zinc chloride ($ZnCl_2$), was also "capable of activating hydrogen for the hydrogenation and hydrocracking of polynuclear aromatic hydrocarbons" (1).

Massive quantities of molten metal halide catalysts were found to be superior to the hydrofining-type contact catalysts in the following respects:

1. Higher conversion rates
2. Higher levels of conversion
3. Greater yields of gasoline range distillates
4. Milder operating conditions of temperature and pressure

Due to the high yield of gasoline range distillates, Consol felt it might be possible to produce gasoline directly from coal and eliminate the coal extraction step in the CSF Process.

Of the metal halides tested, zinc chloride was selected for intensive development because:

1. It was durable; i.e., it would not be destroyed by steam formed during the hydrocracking process.
2. It was relatively incorrosive, as it was not hydrolyzed into halogen acids by steam released during hydrocracking.
3. It was relatively inexpensive.

However, there was one important disadvantage associated with using massive amounts of molten zinc chloride catalyst for hydro-

cracking: after removal of the gaseous products the remaining materials formed an apparently homogeneous mass. This latter mass consisted of the zinc chloride catalyst, liquid hydrocarbon products, unreacted coal or coal extract, and inorganic and organic compounds formed from the ash components of the coal or coal extract. The fact that these materials would not segregate led to problems in (1) recovery of the liquid hydrocarbon products and (2) regeneration of the zinc chloride catalyst. Consol devoted a great deal of effort towards solving these problems and developed sophisticated and correspondingly expensive processes to overcome them (4).

2. Montana State University

A significant contribution was made by Malsam (5) at Montana State University relative to the separation into two different phases of the hydrocarbons and inorganic salts contained in the essentially homogeneous mass that resulted when massive quantities of molten zinc chloride were used to hydrocrack coal. A tremendous potential existed for gravity separation of the two phases, as the hydrocarbon phase had a density slightly less than 1.0 g/ml and the salt phase a density of about 2.5 g/ml. Also, it was quite unlikely that the two phases formed a true solution when mixed together. Malsam hypothesized that failure of the two phases to separate might be caused by the high viscosity of the zinc chloride

(about 75 centipoises at 450°C) (3), which could inhibit their separation by settling.

Malsam conducted a literature search and discovered that the viscosity of a mixture of potassium chloride and zinc chloride was appreciably lower than that of pure zinc chloride. He combined a potassium chloride-zinc chloride mixture with both anthracene oil and coal, heated them above the melting point of the salt phase, and cooled them; in both cases he found good separation between the hydrocarbon and salt phases.

He next determined if the hydrocracking activity of the zinc chloride had been lost due to the addition of the potassium chloride. With a potassium chloride-zinc chloride catalyst mixture and coal, he was still able to attain high conversions (up to 90 wt.%) of the hydrocarbons into benzene-soluble compounds. Some preliminary parameter studies were made of the effects of temperature, pressure, and time on conversion. Catalyst life was investigated with a short series of five consecutive runs in which the same catalyst was used with new charges of coal.

The result of Malsam's research was the issuance of U. S. Patent No. 3,736,250.

B. Research Objectives

In the previous discussion it was shown that molten zinc chloride is an attractive hydrocracking catalyst for coal and that the addition of potassium chloride results in good separation between the hydrocarbon and salt phases. The objectives of this project were:

1. To determine the suitability of this process for hydrocracking two types of Montana coals--Colstrip subbituminous and Savage lignite.
2. To investigate the effect on coal conversion of the simultaneous variation of a relatively large number of process parameters.
3. To determine if the hydrocracking cost could be reduced by:
    a. decreasing the cost of the catalytic and inactive components of the molten salt mixture, and
    b. extending the life of the catalyst.

Montana subbituminous and lignite coals account for about one-third of the Fort Union formation. As this latter deposit contains about twenty-five percent of the United States' known coal reserves, the importance of finding a satisfactory hydrocracking process for Montana coals was obvious.

The only process parameters investigated by Malsam (5) were temperature, pressure, and time; his procedure consisted of varying only one parameter at a time. There were additional process parameters that needed to be investigated to determine their importance relative to coal conversion (see Section II-A). To determine if the parameters interacted with each other, statistically designed experiments were required in which all the parameters could be changed simultaneously.

A single salt mixture was used by Malsam (5) to achieve phase separation between the hydrocarbons and salt. It was unlikely that this was the most economical salt mixture. Malsam also recognized that the catalyst had a limited life before it had to be regenerated; it was desirable to determine if process modifications could extend catalyst life.

II EXPERIMENTAL

A. Outline of Research

Figure 1 is a block flowsheet showing the areas that were investigated. Occasionally several areas were investigated simultaneously; the sequence of experimental runs dictated by some experimental designs resulted in time gaps that would have been wasted had they not been used to investigate another area. A description of the research done in each area will be given below.

1. Parameter Tests

These were the initial tests run in this project. Their purpose was to determine the significant process parameters and to allow for the development of experimental techniques. To study the interactions of process parameters, factorial and fractional factorial experimental designs were used where applicable. The advantage of a fractional factorial design over a factorial design is that partial evaluations of the parameter interactions can be made with a smaller number of experimental runs.

Parameter Screening Tests were used to study seven process parameters and determine if they affected the conversion of Colstrip subbituminous and Savage lignite coals differently. The seven parameters (factors), the values (levels) used for each, and the reasons for choosing these values are listed in Table I. Due to the large number of parameters, a fractional factorial design was used (2^7 =

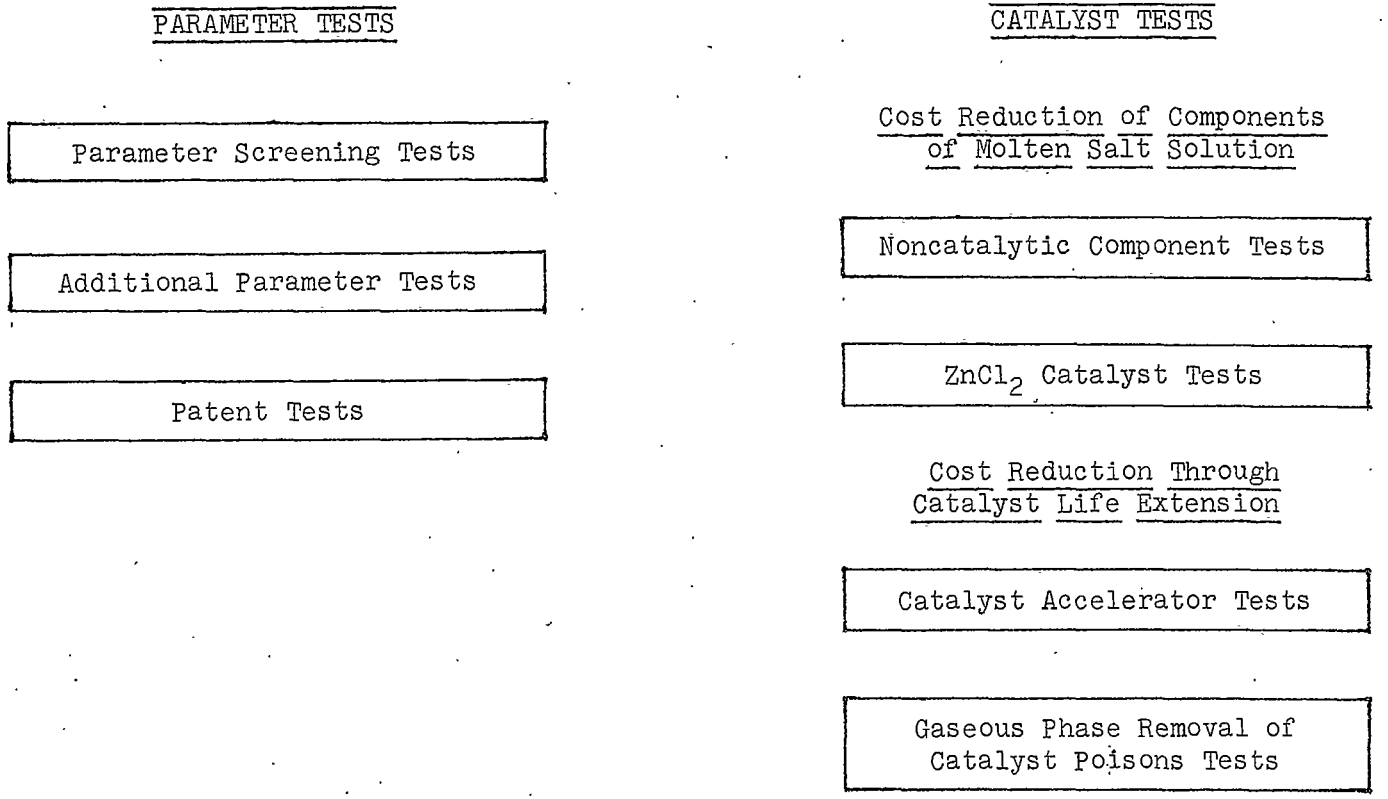


Figure 1. Block Flowsheet of Coal Hydrocracking Experiments Using Molten Salt Catalysts

Table I. Parameter Screening Tests: Selection of Parameters (Factors) and Their Values (Levels).

Temperature

350°C(-): This was the optimum reaction temperature as determined by Consolidation Coal.

450°C(+): Maximum conversions were obtained by Malsam at 450°F.

Pressure

2000 psig(-): No apparent increase in conversion was noted by Consolidation Coal at hydrogen partial pressures greater than 1500 psig.

3000 psig(+): Conversions increased as the total pressure increased from 2000 to 4000 psig in Malsam's experiments.

Time

15 min(-): Short reactor retention times are desired to reduce the size and cost of commercial equipment.

60 min(+): No increase in conversion was noted by Malsam at retention times greater than 60 min.

Mixing

Static(-) and Rocking(+): These are the only two methods of varying agitation available with existing equipment.

Salt: Coal Weight Ratio

2:1(-): As the mixed KCl-$ZnCl_2$ salt has a lower viscosity than pure $ZnCl_2$, there might be adequate contact between the salt and coal at this weight ratio and thus reduce the size of commercial equipment.

4:1(+): This was the ratio used by Malsam based on Consolidation Coal's recommendation that a minimum weight ratio of 2.5:1 ($ZnCl_2$:coal) was needed for adequate contact.

KCl:$ZnCl_2$ Mole Ratio

1:2(-): This was selected because Malsam was able to recover > 85% of the hydrocarbon phase during initial tests using anthracene oil and a salt mixture with a 1:2 mole-ratio.

1:1(+): During the initial tests referred to above, Malsam recovered essentially all of the hydrocarbon phase using the lower viscosity mixture resulting from a 1:1 mole-ratio.

Table I (continued)

Coal Size

-40+100: Consolidated Coal determined that using coarser coal (-14+48) resulted in lower conversions.

-100: Malsam's experiments were run using -200 material and it was desirable to determine if the -100 would give similar conversion.

128 experimental runs would have had to have been required in order to use a factorial design). A statistical technique known as "blocking" was used to see if the parameters affected the two coals differently.

Additional Parameter Tests were used to investigate a few parameters more thoroughly after the Parameter Screening Tests had been completed. The latter tests had shown that pressure did not and coal size did have significant effects on conversion at the initial levels that had been selected. Additional Parameter Tests were run to determine if lower pressures would be feasible and to set a lower limit on the size to which the coal would have to be reduced. A factorial experimental design was used to examine these simultaneously; subsequent tests on coal size alone employed a completely randomized experimental design.

Patent Tests were run to clarify some questions raised during the examination of the patent application based on Malsam's work (see Section I-A-2). A few runs were made using different alkali metal halides as the noncatalytic component of the salt and using different ratios of noncatalytic component to the zinc chloride catalyst. These were just spot-checks of claims in a patent cited as possibly covering the work done by Malsam.

2. Catalyst Tests.

The reduction of catalyst costs was the purpose of these tests. The two approaches taken were (1) to reduce the costs of the components of the molten salt mixture and (2) to investigate methods for extending the life of the catalyst. These tests consisted of either a few experimental runs to test a concept or a comparison of two processes over a period of sequential runs. Neither method lent itself to the use of formal statistical experimental designs.

Noncatalytic Component Tests were designed to determine if a less expensive alkali chloride than potassium chloride could be used to accomplish the phase separation between the hydrocarbons and the salts. The cheapest alkali chloride is sodium chloride; it costs about 1¢/lb compared to about 1.6¢/lb for potassium chloride. Two salt mixtures were prepared. They both contained equal quantities of zinc chloride but the noncatalytic component in one was potassium chloride and in the other it was sodium chloride. Sequential runs were made with each mixture in which new coal was added to the residue from the previous run which contained the original salt mixture and the previously-reacted coal that had not been converted into benzene-soluble products. A run would be made with each salt mixture and then the pair of runs compared relative to phase separation and conversion. Then the next pair of runs in the sequence would be made.

For each pair of runs, the selection of which salt mixture would be run first was made randomly.

Zinc Chloride Catalyst Tests were made to explore the possibility of reducing the cost of the catalytic component of the salt mixture. As zinc chloride costs about 14¢/lb, it was apparent that its use in massive quantities will require catalyst regeneration to recover poisoned catalyst. Even when the salt phase is separated from the hydrocarbon phase, catalyst regeneration will add to the cost of hydrocracking. Some runs were made to explore the use of an essentially noncatalytic molten salt with zinc chloride in such small amounts that it would be economical to dispose of it without regeneration. The criteria used to select the noncatalytic molten salts were that they (1) had a low melting point ($< 400°C$), and (2) were relatively cheap. A somewhat cursory search revealed only two salt mixtures that met these standards: a lithium chloride-potassium chloride mixture and a potassium nitrate-sodium nitrate mixture. Coal conversions were determined for each of these two mixtures without any catalyst and with zinc chloride equal to one weight-percent of the coal.

Catalyst Accelerator Tests were run to determine if a compound could be added to the salt mixture to extend the life of the zinc chloride catalyst. In this case, the added compound would be a

catalyst accelerator in the sense that it would act as an acceptor of the poisons which decrease the activity of the catalyst. As sodium chloride and potassium chloride are chlorides of metals more active than zinc and failed to prevent catalyst poisoning, it was decided to use a compound of a metal less active than zinc to see if it would act as a catalyst accelerator. The only metal less active than zinc that has fairly inexpensive compounds is iron. Two iron compounds were used: ferrous chloride ($FeCl_2$), and red-mud (a compound containing a high percentage of iron oxides that is obtained as a by-product from the purification of bauxite). Sequential runs similar to those described in the Noncatalytic Component Tests were used to compare the two compounds. The salt mixture was composed of sodium chloride and zinc chloride. In this case, however, at the beginning of each pair of runs--besides adding the new coal--either ferrous chloride or red-mud was added in an amount equal to five weight-percent of the new coal. Each pair of runs was then compared relative to conversion and phase separation.

Gaseous Phase Removal of Catalyst Poisons Tests were designed to determine if catalyst poisons could be removed from the reactor before they had a chance to accumulate in the salt mixture. Earlier work done by Consolidation Coal Company (3) indicated that nitrogen compounds appeared to be the most likely source of catalyst poisoning. It was observed that the temperatures and pressures used in

this coal hydrocracking process are comparable to those used for the removal of nitrogen and sulfur impurities in petroleum refineries. Therefore, it was considered possible that the nitrogen catalyst poisons might be in the gaseous phase at reactor operating pressures and condense and accumulate in the salt mixture upon cooling. For example, diamminezinc chloride, $[Zn(NH_3)_2]Cl_2$, decomposes at 271°C and could be removed in the gaseous phase if present. In a continuous hydrocracking process it is likely that the gaseous phase would be removed at reactor temperatures. It was important to determine if the accumulation of catalyst poisons was merely the result of limitations imposed by making experimental runs on a batch basis. It was necessary to modify the reactor considerably (see Section II-C) to allow the gases to be bled off immediately after an experimental run was completed. Once again, sequential runs similar to those described in the Noncatalytic Component Tests were used to compare two modes of operation: (1) gas removal after the reactor had been cooled to ambient temperature and (2) gas removal at reactor operating temperature immediately after the run had been completed. It was obvious that for the first few runs, conversions should be higher for the ambient-temperature than the high-temperature gas removal because additional conversion could be taking place while the reactor was cooling down. Therefore, reaction temperatures and times were

kept lower for the ambient-temperature than the high-temperature gas removal runs to compensate for this difference in effective reaction time.

B. Materials

Two types of coal were used. Colstrip subbituminous coal was obtained from the Montana Power Company stockpile in Billings, Montana. The Sidney, Montana stockpile of the Montana-Dakota Utilities Company was the source of the Savage lignite. The proximate, ultimate, and ash analyses of representative samples of both types of coal are listed in York's doctoral thesis (6).

The hydrogen used was technical grade. The zinc chloride and sodium chloride were technical grade while the potassium chloride met A.C.S. Specifications. Other components of the salt mixtures (lithium chloride, potassium nitrate, sodium nitrate, ferrous chloride, potassium bromide, and potassium iodide) ranged from purified grade to those meeting A.C.S. Specifications. The red-mud was a byproduct obtained from Alcoa.

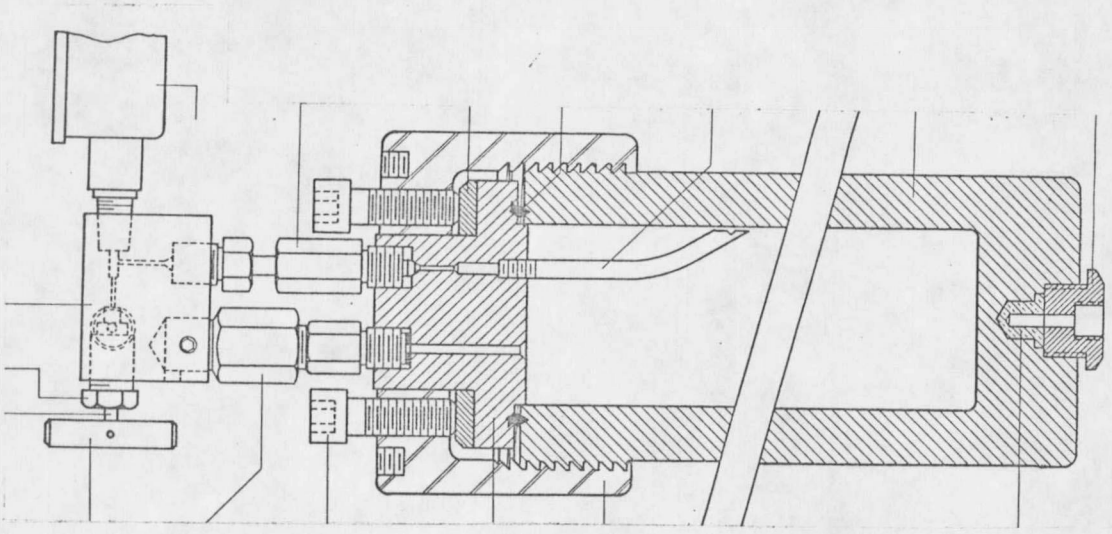
The benzene used to extract the products after hydrocracking was either purified grade or met A.C.S. Specifications.

C. Equipment

Hydrocracking reactions were carried out in a Parr Series 4000 Pressure Reaction Apparatus (7). Several sketches were copied from the Parr instruction manual to depict the reactor and how it was used (see Figure 2). The reactor was fabricated from 316 stainless steel and had a capacity of 500 ml; other significant features included:

1. A large opening for the addition of solids and liquids prior to the reaction.
2. A valve for the addition of gas either prior to or during the reaction.
3. A pressure gage to indicate the reaction pressure.
4. A copper cup in the bottom of the reactor for the insertion of a thermocouple to measure the reaction temperature.

During hydrocracking the reactor was placed in a combination rocker-heater. The bottom part of the reactor was inserted in a horizontal enclosure and during the reaction the reactor pivoted through an angle of about 45 degrees at a rate of 36 cycles/min. The enclosure contained electrical heaters which were manually ad-



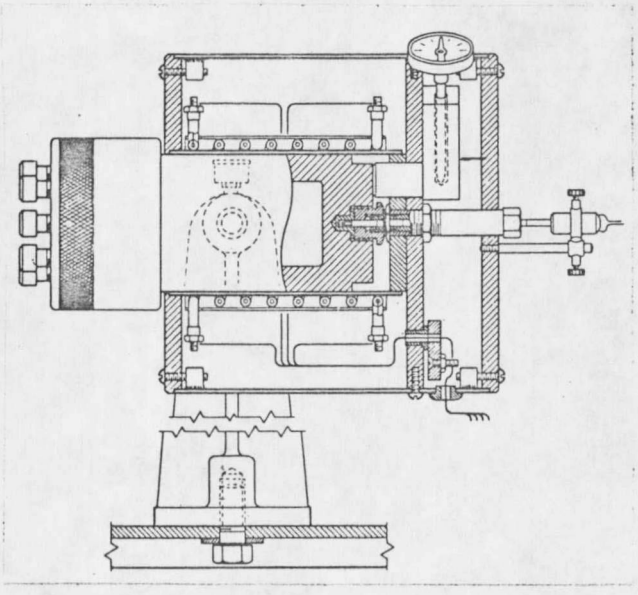


Figure 2. Sketches of Reaction Apparatus

justed to maintain the desired temperature. The temperature was continually recorded.

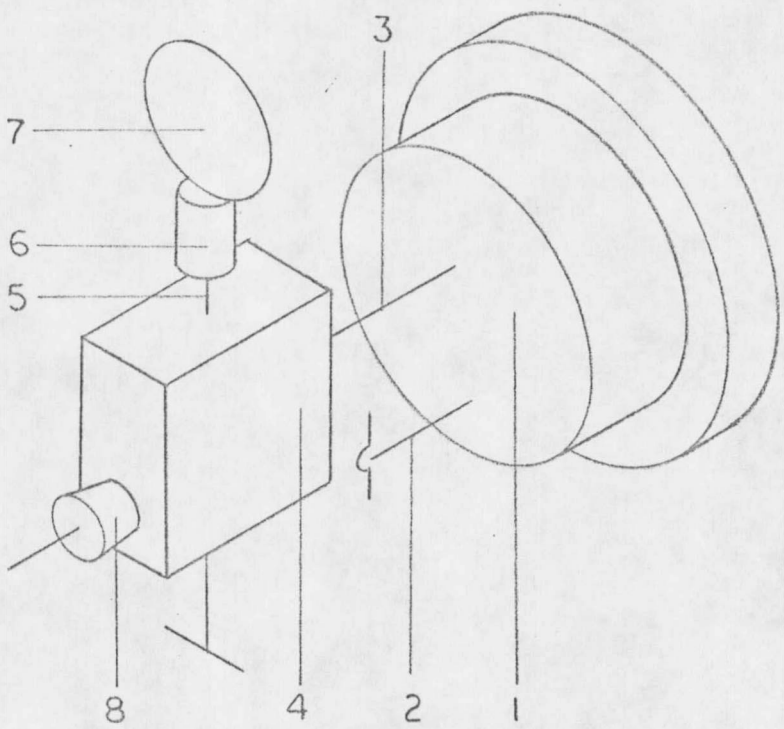
Reaction apparatus modifications were required before the Gaseous Phase Removal of Catalyst Poisons Tests could be run. The gas discharge valve was replaced with a high-temperature valve and an aluminum jacket was machined to enclose it and all the other fittings on the reactor head (see Figures 3 and 4). Electrical cartridge heaters were inserted in the aluminum jacket so that the head and all associated fittings could be maintained at the reactor operating temperature. This was necessary to prevent blockage of the discharge line by condensing compounds and to minimize the possibility of chloride stress-corrosion cracking caused by condensing hydrochloric acid that is formed in the hydrocracking process.

D. Procedures

1. Experimental Runs

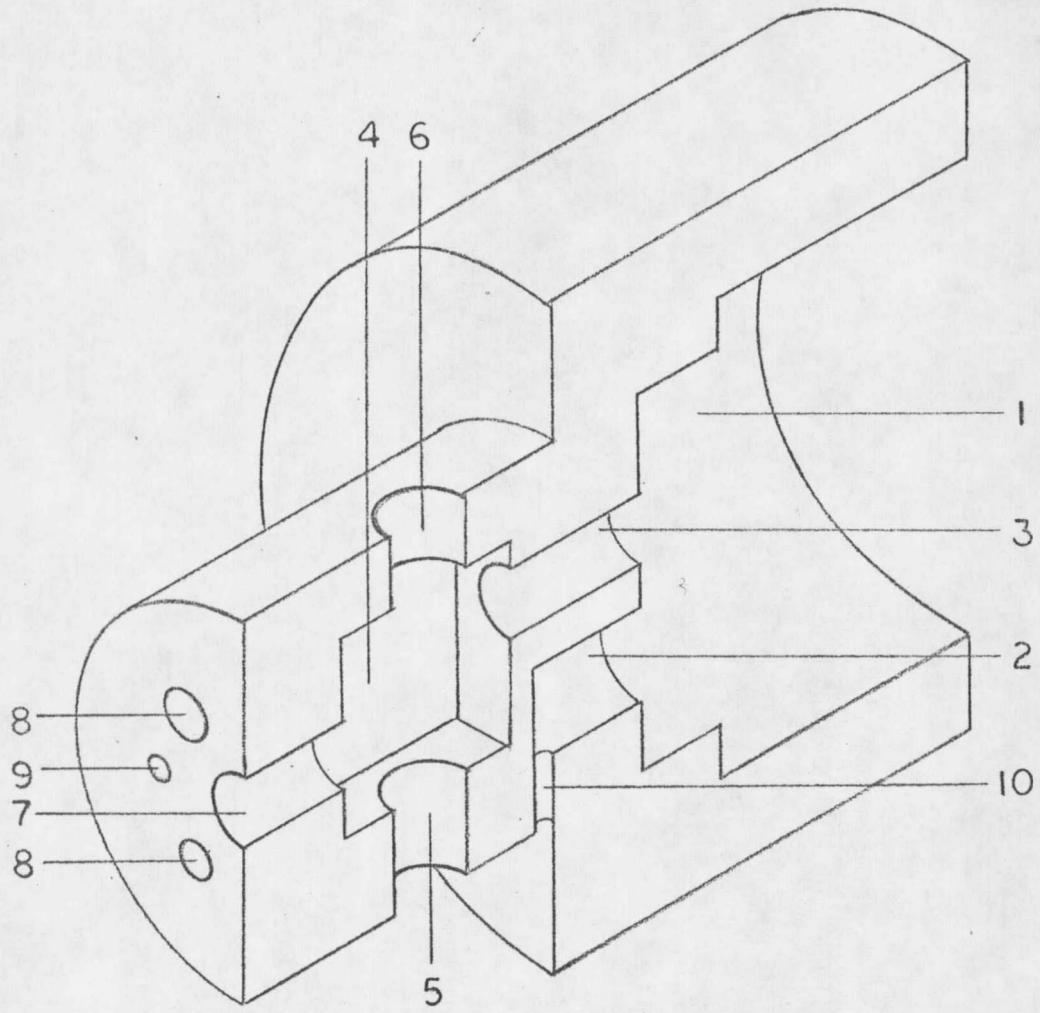
A block flowsheet of the steps followed in making a typical experimental run is presented in Figure 5. A brief description of each step will now be given.

Grind Coal. A mortar and pestle were used to grind coal for all runs except the Patent Tests and the second two sequences of runs of the Gaseous Phase Removal of Catalyst Poisons Tests; a laboratory ball mill was used to grind coal for the latter runs.



1. Reactor Head
2. Reactor Safety-head (rupture disc)
3. Nipple (1/4" x 4")
4. 3-way Valve (Autoclave Engineers No. 30VM4083HT)
5. Nipple (1/4" x 2-3/4")
6. Gage Connector (Autoclave Engineers No. 6F4483)
7. Gage (0-5000 psi)
8. Male-female Adapter (Autoclave Engineers No. 6M42B8)

Figure 3. Schematic of Reactor Head After Modification for Gaseous Phase Removal of Catalyst Poisons Tests



1. Reactor Screw-cap Cavity
2. Reactor Safety-head Cavity
3. Reactor Connection-tube Opening
4. Valve-body Cavity
5. Valve-handle Opening
6. Pressure Gage Opening
7. Gas-connection Opening
8. Heater Wells
9. Thermocouple Well
10. Vent

Figure 4. Sketch of Heating Jacket for Reactor Head for Gaseous Phase Removal of Catalyst Poisons Tests

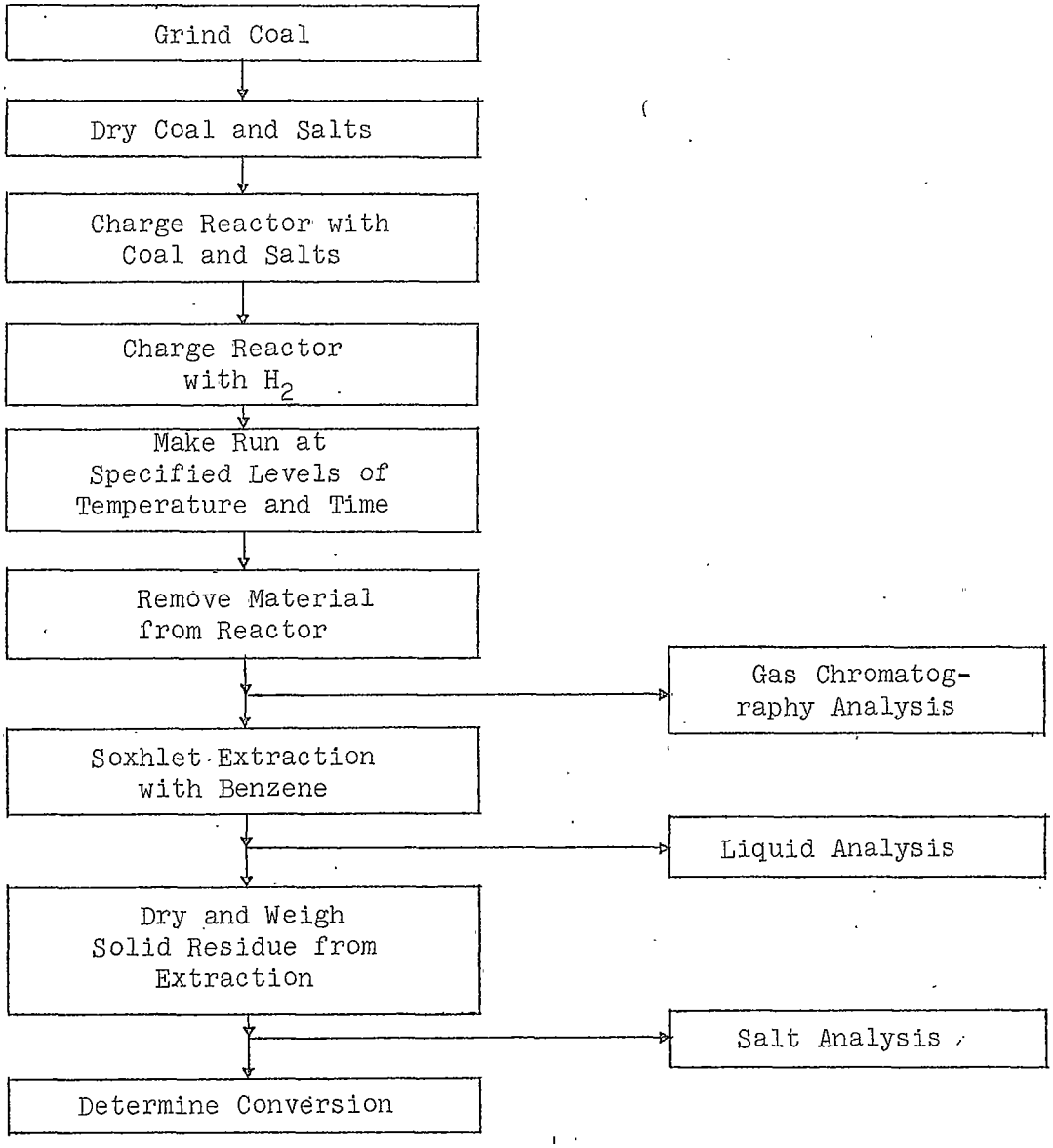


Figure 5. Block Flowsheet of a Typical Experimental Run

Coal samples that were "minus", i.e., smaller than a specified screen size, were hand screened. Coal samples that were "plus", i.e., larger than a specified screen size, were screened on a "Ro-Tap" sieve shaker for ten minutes to remove the fines. The quantity of coal ground at one time for each area of investigation is discussed in Section III.

Dry Coal and Salts. All coal and salts were dried at about 105°C for at least eighteen hours prior to being charged to the reactor.

Charge Reactor with Coal and Salts. The dried materials were weighed to the nearest hundredth of a gram using a Mettler balance and placed in the reactor; the materials in the reactor were stirred to form a fairly uniform mixture prior to reaction. The reactor head, screw cap, and valve assembly were then assembled. (The aluminum reactor-head jacket was also installed during the Gaseous Phase Removal of Catalyst Poisons Tests, the Patent Tests, and some of the Additional Parameters Tests).

Charge Reactor with H_2. Hydrogen was added through the valve; the pressure at ambient temperature was selected to give the specified pressure at the reaction temperature. The reactor was maintained at ambient temperature for at least several hours to determine if there were any hydrogen leaks.

Make Runs at Specified Levels of Temperature and Time. The reactor was placed in the rocker-heater and the rocking mechanism and electrical heaters were turned on. Powerstats were used to control the temperature; the Powerstat settings were determined by trial-and-error (significant changes in the settings were made when using the aluminum reactor-head jacket). After a heat-up period the reaction temperature was reached, maintained for the desired time, and the electrical heaters and rocking mechanism turned off during cooldown. The temperature was measured with a thermocouple in the outside, bottom of the reactor; although the measured temperature provided consistent temperatures from run-to-run, it did not accurately measure the temperature of the reaction mixture.

Remove Material from Reactor. At ambient temperatures the gas was bled from the reactor through a wet test meter to measure its volume and then through a sample bottle to collect samples for gas chromatography analysis. At reactor operating temperatures (Gas Phase Removal of Catalyst Poisons Tests) the gas was either vented to the surroundings or bled through a trap in a dry ice-acetone bath to condense any product that would be liquid at ambient temperature. The reactor was then opened and observations made of the degree of phase separation and the appearance of the product.

Solids were removed with a spatula and liquids and small solid particles flushed out of the reactor with benzene.

Gas Chromatography Analysis. Attempts were made to analyze the gas sample on a gas chromatograph using a Poropak Q column. This gas chromatograph was used by several experimenters employing different columns and temperatures. Analyses were so erratic that this step was eliminated after several runs.

Soxhlet Extraction with Benzene. The liquids and solids from the reactor were extracted with benzene for at least eighteen hours using a standard Soxhlet extraction apparatus.

Liquid Analysis. When the H:C mole ratio was to be determined, the extract from the Soxhlet extraction was distilled to remove the solvent (benzene). The solute was then combined with the liquid which had been condensed using the dry ice-acetone bath (if the bath had been used), and sent to a commercial laboratory for analysis of the H:C mole ratio.

Dry and Weigh Solid Residue from Extraction. The material retained in the Soxhlet thimble was dried for at least eighteen hours at about 105°C and weighed to the nearest hundredth gram on the Mettler balance.

Salt Analysis. The dry material remaining in the Soxhlet thimble was then extracted with distilled water using a standard Soxhlet apparatus. The extract was evaporated at temperatures up to 250°C to remove any water; the dry salt was analyzed for carbon, hydrogen, nitrogen, chlorine, sodium, zinc, aluminum, and iron. This procedure was only used for two salt samples from the Gaseous Phase Removal of Catalyst Poisons Tests.

Determine Conversion. This calculation procedure will be discussed in the next section.

2. Conversion Calculations

In this project conversion pertains only to that coal that was converted into benzene-soluble products. Before conversions could be calculated it was necessary to determine (1) the solubilities in benzene of the dried, unreacted coal and pure salt mixtures and (2) the ash and water content of the dried, unreacted coal.

Soxhlet extractions were used to determine the solubility in benzene of Colstrip subbituminous coal and a salt mixture with a $KCl:ZnCl_2$ mole ratio of 1:2. Extraction of the coal resulted in weight gains of 0.20 wt-% for a -100 mesh sample and 0.65 wt-% for a -40+100 mesh sample. The extraction of the two salt samples resulted in a gain of 0.06 wt-% and a loss of 0.10 wt-%. Therefore,

it was assumed that the coal and salt mixture charged to the reactor were insoluble in benzene.

The water content of the dried coal was determined by toluene distillation; dried coal ash content was measured by placing a sample in a porcelain crucible over a bunsen burner, driving off the volatile matter with mild heat, and burning off the fixed carbon (the remaining material was ash). Results of these analyses on two samples of each coal were:

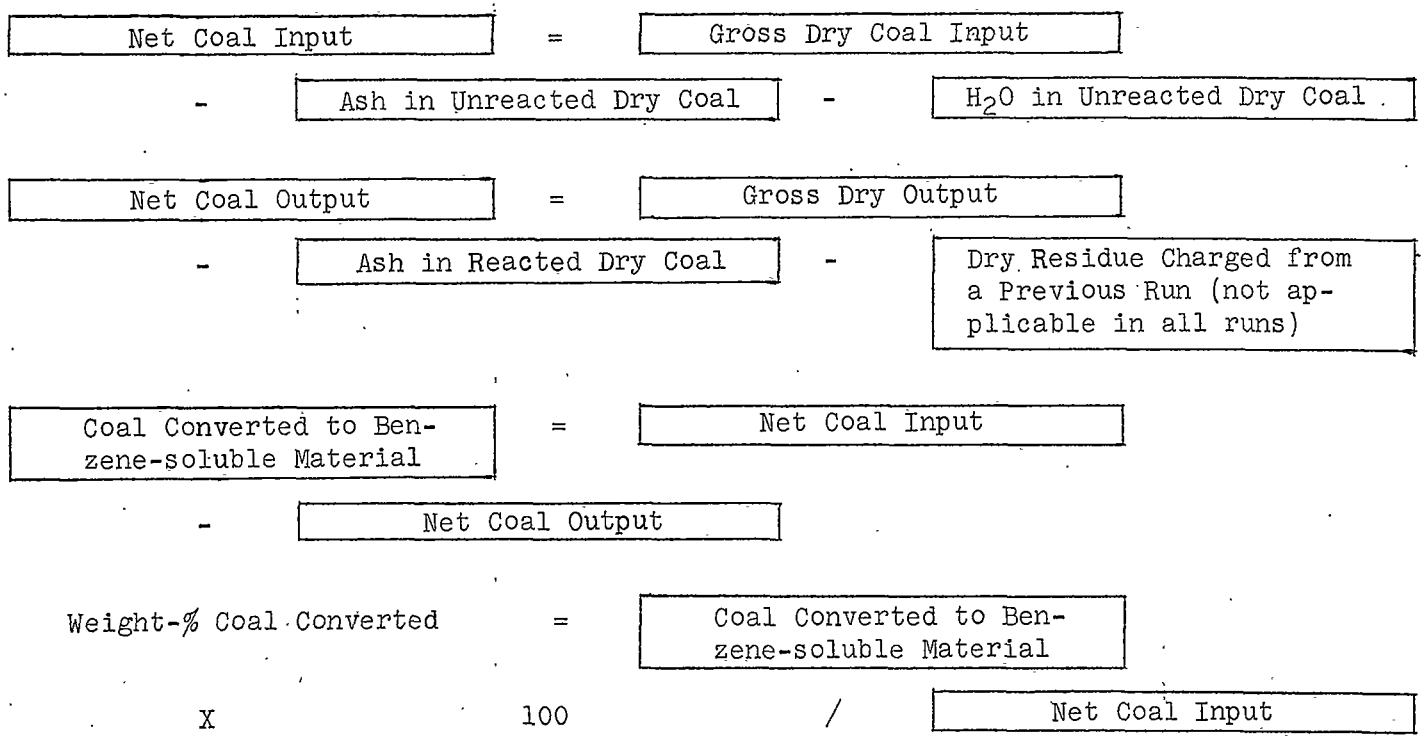
Coal	H_2O (wt-%)	Ash (wt-%)
Savage lignite(1)	2.3	12.2
Colstrip subbituminous(2)	1.0	7.5
Colstrip subbituminous(3)	0.3	11.0

(1) Used in Parameter Screening Tests.

(2) Used in everything but Patent Tests and the second two sequences of runs in the Gaseous Phase Removal of Catalyst Poisons Tests.

(3) Used in the Patent Tests and second two sequences of runs in the Gaseous Phase Removal of Catalyst Poisons Tests.

The equations used to calculate coal conversions are presented in Figure 6. As these calculations are straightforward, they will not be discussed further. Modifications to this pro-



Note: All items in boxes refer to weights of the materials

Figure 6. Coal Conversion Equations for a Typical Run

cedure were made when the same salt mixture was used for a number of sequential runs; the conversion of unreacted coal from previous runs that was charged with the salt mixture had to be taken into account (see Sections III-B-1, III-B-3, and III-B-4).

It is also evident from Figure 6 that all conversions are on a moisture- and ash-free basis.

III RESULTS AND DISCUSSION

As previously discussed (Section II-A), experimental runs were made to investigate seven different areas: (1) parameter screening tests; (2) additional parameter tests; (3) patent tests; (4) non-catalytic component tests; (5) zinc chloride catalyst tests; (6) catalyst accelerator tests; and (7) gaseous phase removal of catalyst poisons tests. A sequential list of all experimental runs and the particular area of investigation for which each was used are listed in Table XV (Appendix). In the Appendix are also summarized the parameter levels, conversion, and pertinent comments for each individual experimental run. This information is consolidated relative to the area of investigation in Tables XVI-XXII.

A. Parameter Tests

1. Parameter Screening Tests.

A 1/16 fractional factorial design was initially used to screen the seven process parameters listed in Table I; therefore, the experimental design consisted of eight runs (1/16 of the possible 128 experiments). Since there is only one more experimental run than the number of parameters being investigated, this is also known as a saturated fractional factorial design. The same fractional factorial design was used for both the Colstrip subbituminous coal and the Savage lignite. Table II lists the parameter (factor) levels; the experimental design and resulting conversions are listed in Table III.

Table II. Parameter Screening Tests: Factor Levels

Factor	Factor Levels	
	-	+
Temperature (°C)	350	450
Pressure (psig)	2000	3000
Time (min)	15	60
Mixing (reactor agitation) (1)	Static	Rocking
Salt:Coal (weight ratio) (1)	2:1	4:1
$KCl:ZnCl_2$ (mole ratio)	1:2	1:1
Coal Size (U.S. Sieve series)	-40+100	-100

(1) 20 grams of coal were charged to the reactor for each run.

Table III. Parameter Screening Tests--One-sixteenth Factorial: Experimental Design and Conversions

EXPERIMENTAL DESIGN

FACTOR	FACTOR LEVEL[1]							
Temperature	-	+	-	+	-	+	-	+
Pressure	-	-	+	+	-	-	+	+
Time	-	-	-	-	+	+	+	+
Mixing	+	-	-	+	+	-	-	+
Salt:Coal	+	-	+	-	-	+	-	+
KCl:$ZnCl_2$	+	+	-	-	-	-	+	+
Coal Size	-	+	+	-	+	-	-	+

[1]See Table II for values corresponding to the factor level.

CONVERSION[2] (Wt-%)

Savage Lignite	10	36	21	38	16	36	23	85
Colstrip Subbituminous	8	41	16	33	29	33	13	90

[2]Based on MAF coal.

These tests were the first ones run and provided the opportunity to learn necessary experimental procedures. At this time the coal was ground separately for each experimental run; it was observed that some coal samples were much more difficult to grind than others and this fact was recorded in the laboratory notebook. It became apparent that pieces of coal with unusually high ash contents were those that were difficult to grind. When conversions were calculated, those experimental runs using the latter coal gave unrealistically low conversions and it was necessary to repeat several runs (Table XVI). Although the observations on ash content were very qualitative, it was felt that after the pieces that were noticeably difficult to grind were removed, the remaining pieces of coal were fairly uniform.

To interpret the data from the one-sixteenth factorial design, use was made of the analysis of variance (Table IV). The analysis of variance is a calculation technique used to determine those parameters having a significant effect on conversion. The important column is the last (F) column. Any F-value greater than 5.59 designates a factor that is significant at a significance level of 5%. "Significance level" is a statistical term that in this case states that if a parameter is determined to be significant, there is only one chance in twenty of being mistaken. The row in Table IV entitled "Blocks" refers to the two different types of coal and has an F-value of 0.01. This indicates that relative to the screening of these

Table IV. Parameter Screening Tests--One-Sixteenth Factorial: Analysis of Variance

ANALYSIS OF VARIANCE

Source	Degrees of Freedom	Sum of Squares	Mean Square	F-Value[1]
Total	16	25,876.00		
Mean	1	17,424.00		
Corrected Total	15	8,452.00		
Blocks	1	0.25	0.25	0.01
Treatments	7	8,261.00		
Temperature	1	4,096.00	4,096.00	150.0
Pressure	1	756.25	756.25	27.8
Time	1	930.25	930.25	34.1
Mixing	1	506.25	506.25	18.6
Salt:Coal	1	306.25	306.25	11.2
KCl:$ZnCl_2$	1	441.00	441.00	16.2
Coal Size	1	1,225.00	1,225.00	45.0
Error	7	190.75	27.25	

[1] Any F-Value larger than 5.59 indicates the factor is significant at a significance level of 5%; i.e., if a factor is determined to be significant there is only one chance in twenty of being mistaken.

parameters there is essentially no difference between the two coals. As the F-values are greater than 5.59 for all seven parameters, it indicates each parameter has a significant effect. However, as this is a fractional factorial design, the effect of each parameter is mixed up with the interaction effects of pairs of the other parameters. It appears that too small a fractional factorial was run--only 8 different experimental runs were made out of a possible 128. One of the advantages of a fractional factorial design is that different experimental runs can be added to clarify the effect of each parameter.

Another useful quantity obtained from Table IV is the mean square for error (27.25). This is the variance due to experimental error. As it has been evaluated in this initial series of experimental runs, there will be no need for duplicating any future run to estimate the variance due to experimental error.

The information gained from the one-sixteenth factorial design can be summarized as follows:

1. The process parameters were found to have essentially the same effects on conversion for both Colstrip subbituminous coal and Savage lignite.
2. It was apparent that a one-sixteenth factorial design was too small to separate the effects of the process parameters due to their interactions.

3. An estimate of the variance caused by experimental error was obtained.

Only Colstrip subbituminous coal was used for all subsequent tests in all areas of investigation since the one-sixteenth factorial had shown the process parameters had the same effect on conversion for both coals.

An advantage of fractional factorial designs is that it is easy to increase the size of the initial fraction to obtain more information concerning parameter interaction effects. The experimental runs of which the initial fractional factorial design is composed can be used as part of the expanded fractional factorial. In this case, eight different experimental runs were added to obtain a one-eighth factorial design. The experimental design and conversions for the one-eighth factorial are listed in Table V; the parameter levels were still the same as those listed in Table II.

Table VI is the analysis of variance for the one-eighth factorial design. The F-values allow the following interpretation of the experimental data:

1. At the particular levels of the factors investigated in this area, the following factors have no significant effect on conversion:
   (a) Pressure
   (b) Salt:Coal Weight Ratio

Table V. Parameter Screening Tests--One-eighth Factorial: Experimental Design and Conversions

EXPERIMENTAL DESIGN

FACTOR	FACTOR LEVEL[1]																
Temperature	-	+	-	+	-	+	-	+	+	-	+	-	+	-	+	-	
Pressure	-	-	+	+	-	-	+	+	+	+	-	-	+	+	-	-	
Time	-	-	-	-	+	+	+	+	+	+	+	+	-	-	-	-	
Mixing	+	-	-	+	+	-	-	+	-	+	+	-	-	+	+	-	
Salt:Coal	+	-	+	-	-	+	-	+	-	+	-	+	+	-	+	-	
$KCl:ZnCl_2$	+	+	-	-	-	-	+	+	-	-	+	+	+	+	-	-	
Coal Size	-	+	+	-	+	-	-	+	+	-	-	+	-	+	+	-	
	Conversion (Wt-%)[2]																
Colstrip Sub-bituminous	8	41	16	33	29	33	13	90	52	24	61	17	30	20	34	8	

[1] See Table II for values corresponding to the factor level.

[2] Based on MAF coal.

Table VI. Parameter Screening Tests--One-eighth Factorial: Analysis of Variance

ANALYSIS OF VARIANCE

Source	Degrees of Freedom	Sum of Squares	Mean Square	F-Value[1]
Total	16	23,099.00		
Mean	1	16,192.56		
Treatments	15	6,906.44		
Temperature	1	3,570.07	3,570.07	131.0
Pressure	1	138.06	138.06	5.06
Time	1	1,040.06	1,040.06	38.2
Mixing	1	495.07	495.07	18.2
Salt:Coal	1	1.56	1.56	0.0572
$KCl:ZnCl_2$	1	162.56	162.56	5.97
Coal Size	1	495.07	495.07	18.2
Temperature x Pressure Time x Coal Size Salt:Coal x $KCl:ZnCl_2$	1	39.06	39.06	1.43
Temperature x Time Pressure x Coal Size Mixing x $KCl:ZnCl_2$	1	280.56	280.56	10.3
Temperature x Mixing Salt:Coal x Coal Size Time x $KCl:ZnCl_2$	1	76.56	76.56	2.81
Temperature x Salt:Coal Pressure x $KCl:ZnCl_2$ Mixing x Coal Size	1	1.56	1.56	0.0572

(continued)

Table VI (continued)

Source	Degrees of Freedom	Sum of Squares	Mean Square	F-Value[1]
Temperature x $KCl:ZnCl_2$ Pressure x Salt:Coal Time x Mixing	1	495.07	495.07	18.2
Temperature x Coal Size Pressure x Time Mixing x Salt:Coal	1	60.06	60.06	2.20
Pressure x Mixing Time x Salt:Coal $KCl:ZnCl_2$ x Coal Size	1	33.06	33.06	1.21
3rd Order Interactions[2]	1	18.06	18.06	0.663

[1] F-Values are calculated by dividing the treatment mean square by the error mean square from Table IV. Any F-Value larger than 5.59 indicates the factor is significant at a significance level of 5%.

[2] 3rd order interactions refer to the interdependence of the effects of three factors at a time.

(c) $KCl:ZnCl_2$ Mole Ratio

2. Two groups of interactions show a significant interaction between two factors (this fractional factorial design does not allow the complete separation of interaction effects, but the most likely interactions in each group are marked with an asterisk):

(a) Temperature - Time*
Pressure - Particle Size*
Mixing - $KCl:ZnCl_2$ Mole Ratio

(b) Temperature - $KCl:ZnCl_2$ Mole Ratio
Pressure - Salt:Coal Weight Ratio
Time - Mixing*

2. Additional Parameter Tests.

A factorial experimental design was used to further investigate the effect of pressure at three levels (500, 1500, and 2500 psig) and coal particle size at two levels (-100 + 140 and -140 mesh). In Table VII are listed the parameter levels, experimental design, and conversions.

Several parameters and a procedure were changed relative to the Parameter Screening Tests. Smaller coal samples were charged (10 g versus 20 g) to insure there would be adequate hydrogen present for hydrogenation at the lower pressures. Based on the experimental results from earlier tests (see Section III-B-1), sodium chloride (NaCl) was used rather than potassium chloride (KCl) to reduce the

Table VII. Additional Parameter Tests--Factorial Investigation of Pressure and Coal Size: Factor Levels, Experimental Design, and Conversions

FACTOR	FACTOR LEVELS
Temperature (°C)	450
Pressure (psig)	500, 1500, 2500
Time (min)	15
Mixing (reactor agitation)	Rocking
Salt:Coal (weight ratio)(1)	4:1
NaCl:$ZnCl_2$ (mole ratio)(2)	1:1
Coal Size (U.S. sieve series)	-100 + 140, -140

(1) 10 grams of coal were charged to the reactor for each run.

(2) See discussion in Section III-B-1 for the reason NaCl was used rather than KCl.

Experimental Design and Conversion (Wt-%)(3)

Pressure (psig)	500		1500		2500	
Mesh (U.S. Series)	-100 +140	-140	-100 +140	-140	-100 +140	-140
1st Replicate	26	24	31	36	44	58
2nd Replicate	19	27	32	33	43	67

(3) Based on MAF Coal.

viscosity of the molten salt mixture; this latter change was made in all the remaining areas of investigation to be discussed except the Patent Tests and the Zinc Chloride Catalyst Tests. As noted in Table XVII, some introductory runs were made using a $NaCl:ZnCl_2$ mole ratio of 0.667:1, but the resultant poor phase separation led to the use of a 1:1 mole ratio. All the coal for the entire factorial design was ground at one time to insure that it was uniform for all the experimental runs.

The analysis of variance is presented in Table VIII. The following interpretation can be made based on the F-values and observation of the conversion data:

1. The conversions at 500 and 1500 psig were significantly lower than at 2500 psig.
2. The conversions of -140 mesh material were significantly higher than those of -100+140 mesh material.
3. At the high pressure (2500 psig) there was an interaction between pressure and particle size; i.e., the conversions of the small particle size were much higher than would be anticipated from observations made at the lower pressures.

Since the lower pressure limit relative to effect on conversion had been determined, the subsequent tests in this area were

Table VIII. Additional Parameter Tests--Factorial Investigation of Pressure and Coal Size: Analysis of Variance

Source	Degrees of Freedom	Sum of Squares	Mean Square	F-Value
Total	12	18,327.27		
Mean	1	16,096.69		
Corrected Total	11	2,230.58		
Treatments	5			
Pressure	2	1,756.56	878.28	66.6(1)
Coal Size	1	215.90	215.90	16.4(2)
Pressure x Coal Size	2	178.98	89.49	6.78(1)
Error	6	79.14	13.19	

(1) A F-Value larger than 5.14 indicates the factor is significant at a significance level of 5%.

(2) A F-Value larger than 5.99 indicates the factor is significant at a significance level of 5%.

concerned with coal particle size only. Sizes of -140+200 mesh and -200 mesh were compared; the parameter levels and conversions are listed in Table IX.

Prior to these latter tests, the reactor had been modified to run the Gaseous Phase Removal of Catalyst Poisons Tests. It can be seen that the initial runs in these coal size comparison tests had to be discarded (Table XVII) because the proper heat-up procedure had to be developed. This modified heat-up procedure was also used in the Patent Tests and the Gaseous Phase Removal of Catalyst Poisons Tests.

A statistical technique known as a "Student's" t-test was used to interpret the conversion data. The t-test statistic for comparing the means of the conversions of the two particle sizes was calculated to be -0.443. At a 5% significance level, the test statistic would have to be smaller than -4.30 for the means to be significantly different. Therefore, it was obvious that there was no increase in conversion to be gained by using coal particles smaller than -140 mesh.

3. Patent Tests.

In the course of obtaining the patent referred to in Section I-A-2, a previously issued patent was cited as possibly already covering the process developed at Montana State University. The pertinent claim was: "A process for conversion of heavy petroleum

Table IX. Additional Parameter Tests -- Comparison of -140+200 Mesh and -200 Mesh Coal Particles: Parameter Levels and Conversions

Factor	Factor Level
Temperature (°C)	450
Pressure (psig)	3000
Time (min.)	15
Mixing (reactor agitation)	Rocking
Salt:Coal (weight ratio)(1)	4:1
$NaCl:ZnCl_2$ (mole ratio)	1:1
Coal Size (U.S. sieve series)	-140+200 and -200

(1) 20 grams of coal were charged to the reactor for each run

	Conversion (wt-%)(2)	
Coal Size (U.S. sieve series)	1st Trial	2nd Trial
-140+200	67	75
-200	77	71

(2) Based on MAF coal.

fractions having at least 50% boiling above about 450°F and containing heteroatomic contaminants which comprises contacting the fraction with hydrogen at elevated temperature and pressure with a molten salt mixture comprising zinc halide wherein the halide is selected from the group consisting of bromide, chloride, and iodide and from about 5% to about 60% w. of an alkali metal chloride, bromide or iodide (8)". Table X lists the parameter levels and conversions for the experiments used for a cursory check of the relevant claim of the cited patent; due to time limitations only the alkali metal halides on hand could be used for this investigation.

Relative to conversion and phase separation, all four runs were successful. Several other observations were:

1. At a low KCl:$ZnCl_2$ mole ratio of 0.2:1, good phase separation was attained.
2. When LiCl was used as the noncatalytic component the salt was very difficult to remove after reaction and there appeared to have been conversion to a product that was tar-like but not soluble in benzene.
3. The use of both KBr and KI as the noncatalytic component of the salt resulted in unexpectedly high conversions.

Table X. Patent Tests: Parameter Levels and Conversions

Factor	Factor Level
Temperature (°C)	450
Pressure (psig)	3000
Time (min.)	15
Mixing (reactor agitation)	Rocking
Salt:Coal (weight ratio)(1)	4:1
Coal Size (U.S. sieve series)	-140

(1) 20 grams of coal were charged to the reactor for each run

Noncatalytic Component	Percentage of Noncatalytic Component in Salt (wt-%)	Conversion(2) (wt-%)
KCl	10.0	46
LiCl	23.8	39
KBr	46.6	90
KI	54.9	83

(2) Based on MAF coal.

B. Catalyst Tests.

1. Noncatalytic Component Tests.

The parameter levels for this area of investigation are listed in Table XI. An initial run using NaCl as the noncatalytic component of the salt mixture showed it was similar to KCl in that good conversion and phase separation could be attained. To compare NaCl and KCl as noncatalytic components of the salt mixture, a statistical technique was used. Two sequences of runs were made; a NaCl-$ZnCl_2$ salt mixture was used in one sequence and a KCl-$ZnCl_2$ mixture in the other. The same initial salt charge was used for every run in each of the two sequences and the effects of the two salt mixtures compared after equivalent runs.

Several items should be clarified concerning this area of investigation. The mole ratio of NaCl:$ZnCl_2$ was 1.25:1 and of KCl:$ZnCl_2$ was 1:1. This difference occurred because both the quantity of $ZnCl_2$ and the total quantity of mixed salts were the same in both salt mixtures. Large enough samples of coal were ground at each time to be used for equivalent runs with both salt mixtures; this insured that uniform samples of coal were charged in equivalent runs and enabled the two salt mixtures to be compared. At the time this area was investigated, the optimum coal size of -140 mesh had not yet been determined--the coal size used was -100 mesh. Conversions were calculated on the basis that the coal would remain reactive for three

Table XI. Noncatalytic Component Tests: Factor Levels

FACTOR	FACTOR LEVELS
Temperature (°C)	450
Pressure (psig)	3000
Time (min)	15
Mixing (reactor agitation)	Rocking
Salt:Coal (weight ratio)[1]	4:1
Noncatalytic Component:$ZnCl_2$ (mole ratio)	
$KCl:ZnCl_2$	1:1
$NaCl:ZnCl_2$	1.25:1
Coal Size (U.S. sieve series)	-100

[1] 20 grams of coal were charged to the reactor for each run. As the sequential runs contained the original molten salt components plus non-benzene-soluble coal products, this ratio decreased as the number of runs increased.

consecutive runs. This procedure was introduced to assist in overcoming the problem of trying to simulate a continuous process with a sequence of batch runs. Undoubtedly, some of the unconverted coal residue was converted when it was charged again with the salt mixtures. Therefore, the conversion should be based on the amount of new coal charged plus part of the coal residue that was charged. Some previous experimental work indicated that at 450°C the coal would remain reactive for a time about equal to three runs.

The conversions using the two salt mixtures are compared as a function of the number of runs for which they were used in Figure 7. It appears from Figure 7 that higher conversions were obtained using the $NaCl-ZnCl_2$ mixture than the $KCl-ZnCl_2$ mixture. The "Student's" t-test was used to determine if there was a significant difference between the conversions attained with the two salt mixtures. The t-test statistic for comparing the two salt mixtures was calculated to be 2.45. This was also the value that the test statistic would have to be equal to or greater than for the conversions to be significantly different at a significance level of 5%. Therefore, it has been found that the $NaCl-ZnCl_2$ mixture results in higher coal conversions than the $KCl-ZnCl_2$ mixture.

It was also desirable to compare the conversions obtained using the two salt mixtures with that obtained using pure zinc chloride:

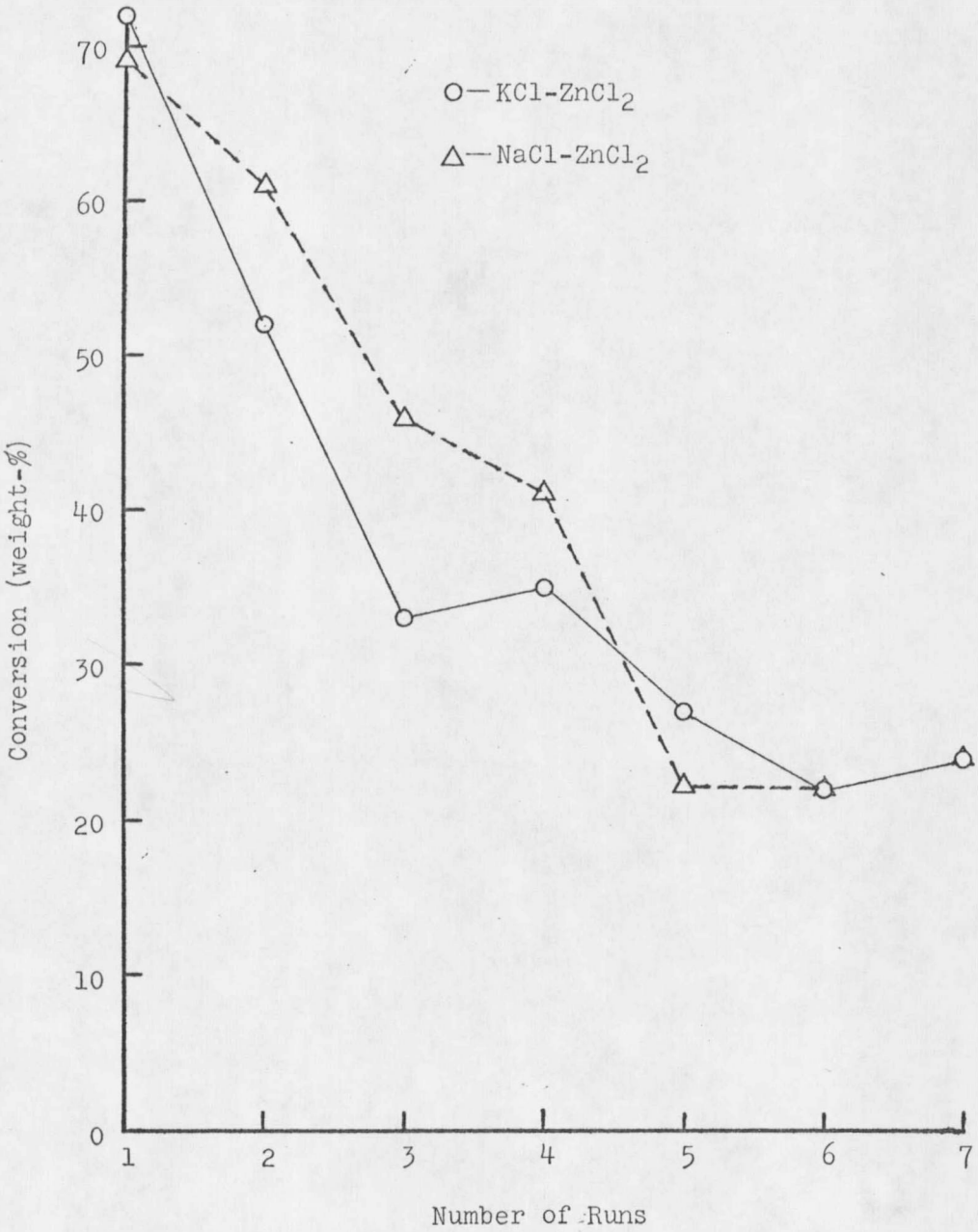


Figure 7. Noncatalytic Component Tests: Conversion vs. Number of Runs for $KCl-ZnCl_2$ and $NaCl-ZnCl_2$ Salt Mixtures

Run No.	Salt	Conversion (wt-%)
34	$ZnCl_2$	29
33	$KCl-ZnCl_2$	72
32	$NaCl-ZnCl_2$	69

Probably the low conversion attained using pure zinc chloride was due to less efficient mixing caused by the high viscosity of the molten salt.

Another observation was that the catalyst activity decreased as the number of runs increased. The catalyst poisoning was apparent by the following changes associated with increased catalyst use:

1. A decrease in coal conversion
2. A reduction in the quality of phase separation
3. A change in product appearance from a light distillate material to a heavy tar-like material.

2. Zinc Chloride Catalyst Tests.

The effectiveness of using a noncatalytic molten salt with expendable quantities of zinc chloride catalyst was tested by determining coal conversions with the noncatalytic salts alone and comparing them with conversions obtained after one wt-% of zinc chloride (based on coal charged) had been added. The noncatalytic salt mixtures investigated were LiCl-KCl (58.5 mole-% LiCl) and KNO_3-NaNO_3 (50 mole-% KNO_3). The parameter levels and conversions are listed in Table XII.

Table XII. $ZnCl_2$ Catalyst Tests: Factor Levels and Conversions

FACTOR	FACTOR LEVELS	
	LiCl-KCl Soln	KNO_3-$NaNO_3$ Soln
Temperature (°C)	450	350
Pressure (psig)	3000	3000
Time (min)	15	15
Mixing (reactor agitation)	Rocking	Rocking
Salt:Coal (weight ratio)(1)	4:1	4:1
Noncatalytic Salt Composition (mole %)		
LiCl/KCl	58.5/41.5	
$KNO_3/NaNO_3$		50/50
Coal Size (U.S. sieve series)	-100	-100

(1) 20 grams of coal were charged to the reactor for each run. 0.2 grams of $ZnCl_2$ (1 wt-% of the coal) were charged for those tests using a catalyst.

Conversions (weight-%)(2)	
LiCl-KCl Salt Solution	
No Catalyst	19.9
$ZnCl_2$ (1 wt-% of coal)	13.4
KNO_3-$NaNO_3$ Salt Solution	
No Catalyst	7.0
$ZnCl_2$ (1 wt-% of coal)	4.2

(2) Based on MAF Coal.

The compositions of the noncatalytic salt mixtures were set by those binary mixtures melting in the desired temperature range (<400 °C). Enough coal was initially ground to be used for all these tests.

From Table XII, it is obvious that coal conversions were extremely poor whether or not the one wt-% $ZnCl_2$ catalyst had been added. It was felt that these conversions were too low (4-13 wt-%) to justify more experimental work in this area.

3. Catalyst Accelerator Tests.

To investigate catalyst accelerators paired observations were used. This technique was also used in the Noncatalytic Component Tests and is described in Section III-B-1. In this case, however, two sequences were run in which different catalyst accelerators ($FeCl_2$ and red-mud) were used. The catalyst accelerators were added at the beginning of each run in an amount equal to 5 wt-% of the new coal. Table XIII lists the parameter levels for these tests.

As in the Noncatalytic Component Tests, enough coal was ground at each time for a run in each of the sequences being compared; also, -100 mesh coal was used because the optimum size of -140 mesh had not yet been determined. The initial run in this series had a somewhat lower conversion than anticipated--it was felt that possibly some of the noncatalytic salts from the $ZnCl_2$ catalyst tests that immediately preceded it were reducing the catalytic activity. Several attempts

Table XIII. Catalyst Accelerator Tests: Factor Levels

FACTOR	FACTOR LEVELS
Temperature (°C)	450
Pressure (psig)	3000
Time (min)	15
Mixing (reactor agitation)	Rocking
Salt:Coal (weight ratio)[1]	4:1
$NaCl:ZnCl_2$ (mole ratio)	1:1
Coal Size (U.S. sieve series)	-100

[1] 20 grams of coal and 1 gram of catalyst accelerator were charged to the reactor for each run. As the sequential runs contained the original salt components plus non-benzene-soluble coal products, this ratio decreased as the number of runs increased.

were made (Table XXI) to use a glass liner inside the reactor, but it was not feasible with molten salt mixtures for the reason that upon cooling, the salt would freeze around the ground joint in the glass liner and make it impossible to open. Conversions were based on the coal remaining reactive for three consecutive runs.

Figure 8 shows the conversions versus the number of runs for the $FeCl_2$, red-mud, and no accelerator. There appears to be little difference between conversions obtained with the two accelerators and this is supported by a "Student's" t-test. The calculated t-test statistic is 0.476; it should be greater than 2.78 for the two accelerators to have significantly different conversions at a significance level of 5%.

The conversion data from the $NaCl-ZnCl_2$ salt mixture in the Noncatalytic Component Tests was plotted in Figure 8 to show how conversions compared when accelerators were used and when they were not used. This does not provide a direct comparison because different coal samples were used for the catalyst accelerator runs. It is obvious that the conversions without the catalyst accelerator were higher.

A single run was also made using $FeCl_3$ as an accelerator. Although the same coal sample was used only for the $FeCl_2$ and red-mud runs, a comparison of initial conversions is:

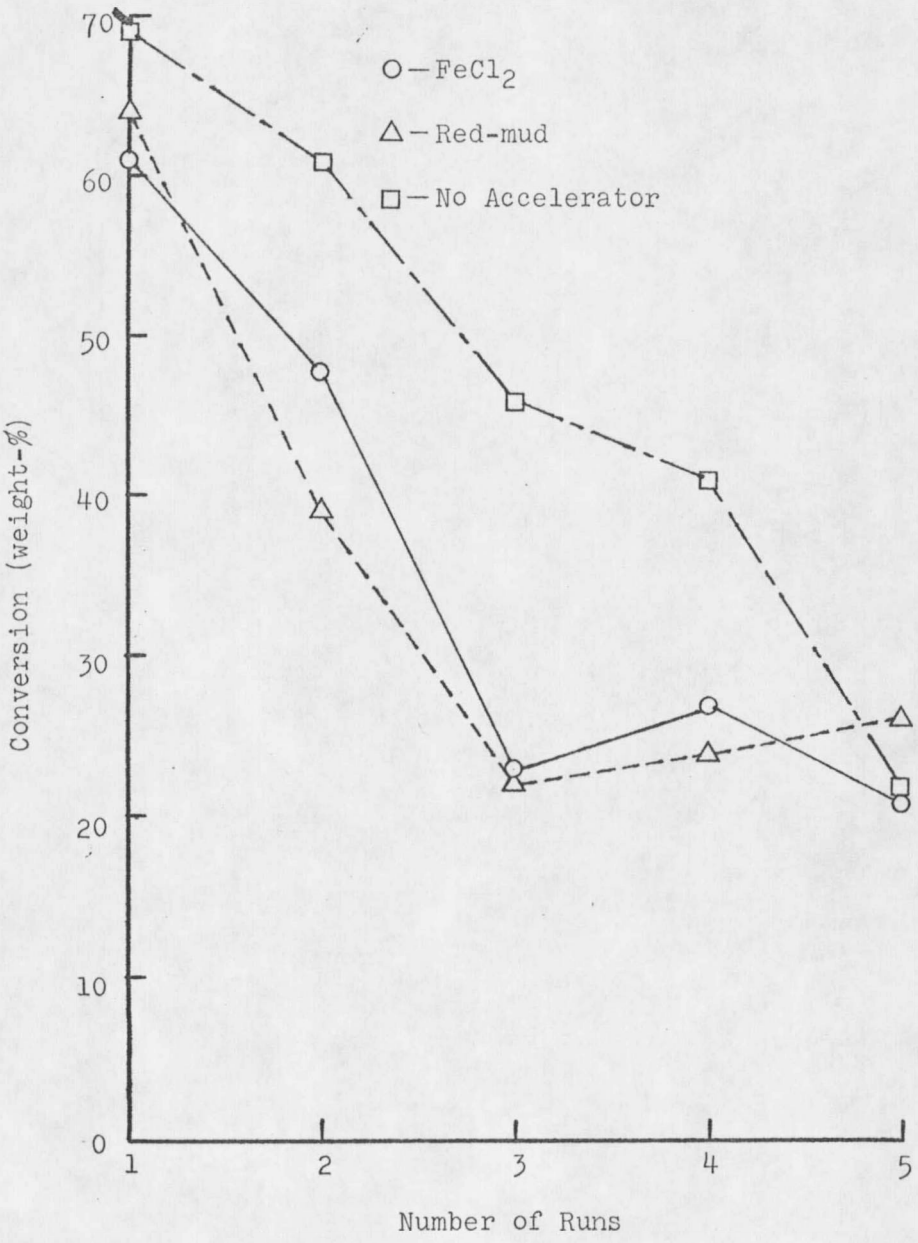


Figure 8. Catalyst Accelerator Tests: Conversion vs. Number of Runs for $FeCl_2$, Red-mud, and No Accelerator

Run No.	Catalyst Accelerator	Conversion (wt-%)
54	Red-mud	64
55	$FeCl_2$	61
64	$FeCl_3$	70
32	None	69

As the number of runs increased, it was observed that conversion decreased, phase separation became poorer, and the product changed from a light distillate type of material to a heavy tar-like type of material. Since catalyst poisoning occurred even with the use of catalyst accelerators and there was no apparent advantage of accelerators relative to not using them, no further experimental work was done in this area.

4. Gaseous Phase Removal of Catalyst Poisons Tests.

The effects of removing the gaseous phase from the reactor at operating temperature versus removal at ambient temperature were investigated through the use of paired observations (see Section III-B-1 for a discussion of this technique). The parameter levels for this investigation are listed in Table XIV.

Several weeks were spent before starting experimental runs in which a batch of -140 mesh coal and a batch of -200 mesh coal were ground; these two batches provided enough coal for all these runs.

The initial two sequences of runs comparing the high-temperature and ambient-temperature gas removal methods were discontinued

Table XIV. Gaseous Phase Removal of Catalyst Poisons Tests: Factor Levels.

Factor	Factor Levels
Temperature (°C)	425, 450[1]
Pressure (psig)	3000
Time (min.)	0, 15[1]
Mixing (reactor agitation)[2]	Rocking
Salt:Coal (weight ratio)	4:1
NaCl:$ZnCl_2$ (mole ratio)	1:1
Coal Size (U.S. sieve series)	-140, -200[3]

(1) The 425°C temperature and 0 minute reaction time were used for the ambient-temperature gas removal runs in the second two sequences of runs; these changes were made to compensate for conversion occurring during reactor cooldown.

(2) 20 grams of new coal were charged to the reactor for each run; this ratio decreased as the sequential runs increased due to the unreacted coal carried over from previous runs.

(3) -200 mesh coal was used for the initial two sequences of runs and -140 mesh for the second two sequences of runs.

due to the development of gas leaks during the reaction. In effect, this made both sequences the same since the catalyst poisons could leak out of the ambient-temperature gas removal runs while the gas was at the operating temperature. Subsequent gas leakage was prevented by removing all reactor fittings at the end of each run and coating them with new lubricant. The high-temperature gas removal sequence was continued for fourteen runs (Table XXII) to determine if the conversions would eventually become negligible. They did not.

It was previously mentioned (Section II-A-2) that reaction times and temperatures were not the same for the two sequences to compensate for conversion occurring during cooling of the ambient-temperature gas removal runs. During the initial two sequences of runs the reaction time and temperature were the same. However, additional experiments led to changing both the reaction time and temperature for all ambient-temperature gas removal runs during the second two sequences of runs. Unfortunately, the conversion data for the two sequences were still not directly comparable; the adjustments of reaction times and temperatures did not exactly compensate for the differences between the two gas removal methods.

The problem of simulating a continuous process with a series of batch runs still remained. For the high-temperature gas removal sequences it was felt that considering the coal to be reactive for

three consecutive runs was still a good assumption. However, the ambient-temperature gas removal sequence was run at a lower temperature and no previous data was available for estimating coal reactivity. Therefore, two conversions were calculated for the ambient-temperature gas removal runs: one conversion was based on the coal remaining reactive for three consecutive runs and the other was based on it remaining reactive for four consecutive runs.

In Figure 9 , the two methods of gas removal are compared relative to conversion. The shaded area represents the uncertainty caused by considering the coal to be reactive for three or four consecutive runs when calculating conversions for the ambient-temperature gas removal runs. As conversions leveled off or increased slightly as the number of runs increased for both methods of gas removal, it cannot be concluded that the high-temperature gas removal was significantly better. However, the high-temperature was better than the ambient-temperature gas removal in two aspects other than conversion: (1) it took longer for the phase separation to become poor, and (2) the product was lighter and less tar-like. The observation comparing phase separation is quite qualitative but quantitative data is available to support the belief the products were different.

The hydrogen:carbon mole ratio of the product from the final high-temperature gas removal run was 1.15:1 and for the ambient-

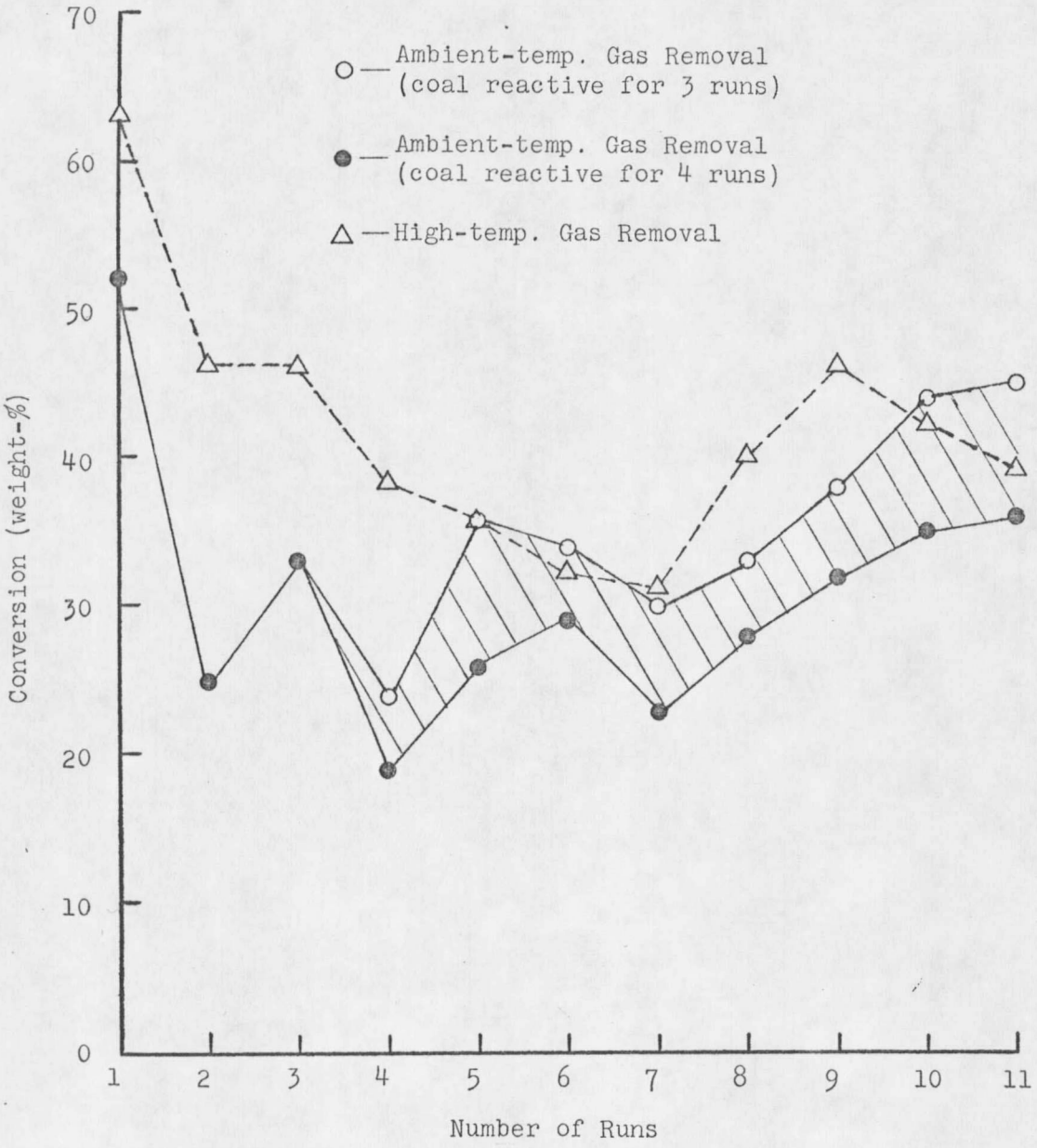


Figure 9. Gaseous Phase Removal of Catalyst Poisons Tests: Conversion vs. Number of Runs for High-temperature and Ambient-temperature Gas Removal

temperature gas removal was 1.03:1; therefore, more hydrogenation occurred using the former method (an analysis made earlier (6) on a different sample of coal indicated the hydrogen:carbon ratio of the starting coal was 0.81:1). It must be emphasized, however, that hydrogen:carbon mole ratio gives only a rough estimate of the type of product. This is obvious from the following data:

Run No.	Gas Removal Method	Age of Salt Mixture (runs)	H:C (mole ratio)
143	Ambient-Temp.	12	1.03:1
144	High-Temp.	12	1.15:1
145	High-Temp.	1	1.11:1

The product from the run in which the salt mixture was used only once was much more like a light distillate than the product from either of the other two runs, but its hydrogen:carbon ratio was in between those ratios for the other runs.

Another indication that the high-temperature gas removal might be the better method of the two is related to the nitrogen accumulation in the salt mixture. Following the final benzene extractions of the second two sequences, the residues were extracted with water to recover the salt mixtures. Analysis of the recovered salt mixtures showed a nitrogen content of 1.20 wt-% in the ambient-temperature gas removal salt mixture and a content of 0.59 wt-% in

the high-temperature gas removal mixture. Obviously, more nitrogen (catalyst-poisoning) compounds had been removed using the high-temperature gas removal method.

It had been postulated that possibly the aluminum and iron from the coal ash would accumulate in the salt mixture when using the ambient-temperature gas removal scheme. The reaction of these compounds with the salt mixture to form $AlCl_3$ and $FeCl_3$ could be beneficial as these are hydrocracking catalysts. It was felt these latter compounds might be compensating for the decrease in catalytic activity of the $ZnCl_2$. However, analysis of the same two water-extracted salts mentioned above showed only negligible quantities of aluminum and iron in both salt mixtures. In the process of drying the water-extracted salts, they were heated above 200°C, however, and this could possibly have driven off these compounds before analysis.

As the number of runs in a sequence increases, the unreacted coal residue builds up until it is present in a larger amount than the salt mixture. The hypothesis was made that the effects attributed to catalyst poisoning as the number of runs increased might really be due to poorer contact of the reactants caused by the accumulation of coal residue. To test this concept the salt mixture from the initial sequence of high-temperature gas removal runs was extracted with water after it had been used for fourteen con-

secutive runs. The weight of the recovered salt mixture was 68.6 grams; 80.0 grams of salt mixture had been charged originally. Although this was good recovery, the composition of the salt mixture had undoubtedly changed. This recovered salt mixture was charged to the reactor with new coal and a run made. A comparison with the first run in the sequence is:

Run No.	Salt Mixture	Conversion (wt-%)	Phase Separation	Product Appearance
85	New	57	Good	Lots of liquid
116	Recovered after 14 runs	64	Good	A little liquid and tar, but mostly solid

The difference in appearance of the two products was conspicuous. As the mixing was essentially the same in both cases, the difference must have been due to a change in catalyst activity.

IV CONCLUSIONS

Based on the experimental data obtained from these experiments, the following conclusions have been reached:

1. The use of massive amounts of molten salt catalyst in the hydrocracking of Savage lignite and Colstrip subbituminous appears to be feasible as high conversions (>85wt-%) have been obtained for both coals.
2. At the parameter levels listed in Table I:
   a. The parameters have essentially the same effect on conversion of both Colstrip subbituminous and Savage lignite coals.
   b. Pressure, salt:coal weight ratio, and KCl:$ZnCl_2$ mole ratio have no significant effect on conversion.
   c. Some interaction effects which appear likely are temperature-time, pressure-particle size, and time-mixing.
3. Pressures below 2000 psig significantly reduce conversion.
4. Particle sizes smaller than 140 mesh (U.S. sieve series) are required to eliminate the effect of particle size on conversion.

5. Conversion and type of product appear to be significantly altered by the use of alkali metal halides other than sodium chloride and potassium chloride as the noncatalytic component of the salt mixture.
6. Good separation between the hydrocarbon and salt phases is attainable at KCl:$ZnCl_2$ mole ratios as low as 0.2:1.
7. When using the same salt mixture for a number of consecutive runs, a NaCl-$ZnCl_2$ mixture gives better conversions than a KCl-$ZnCl_2$ mixture.
8. Molten salt mixtures using zinc chloride as a coal hydrocracking catalyst eventually become poisoned with resultant lower conversions, poorer phase separations, and more tar-like products.
9. Small amounts (1 wt-% of the coal) of $ZnCl_2$ in LiCl-KCl and KNO_3-$NaNO_3$ salt mixtures give poor conversions; the use of noncatalytic salt mixtures with economically expendable quantities of $ZnCl_2$ catalyst does not appear to be promising.

10. Chlorides of more active metals (sodium and potassium) and a less active metal (iron) than zinc as well as red-mud (iron oxide) do not act as catalyst accelerators to prevent a decrease in $ZnCl_2$ catalytic activity.
11. Gas removal after reaction at reactor operating temperatures rather than ambient temperatures retards the trend towards poorer phase separation and more tar-like products.
12. High-temperature relative to ambient-temperature gas removal after reaction appears to be superior as indicated by these measurable effects after the same salt mixture had been used for eleven consecutive runs:
    a. The product had been hydrogenated to a higher degree; the H:C mole ratio was 1.15:1 versus 1.03:1 (the original coal had a H:C mole ratio of 0.81:1).
    b. The nitrogen content in the salt mixture was lower--0.59 wt-% versus 1.20 wt-%.
13. The change in product from a liquid to a tar-like material as the same salt mixture is used

for a number of runs is not due to poor contact of the reactants and catalyst caused by a buildup of unreacted coal.

V. RECOMMENDATIONS

Recommendations for future studies will be made relative to three possible stages in the development of this project:

1. Use of existing equipment and procedures
2. Use of improved analytical chemistry procedures
3. Use of continuous reaction apparatus

A. Existing Equipment and Procedures

Prior to starting these studies the head of the rocking-bomb reactor should be modified so that a thermocouple can be inserted to accurately measure the temperature of the molten salt suspension. Areas needing clarification are:

1. A comparison of the effect on conversion of high-temperature and ambient-temperature removal of gas should be determined. This will involve studies of conversion versus time at different temperatures for both new and unreacted coal from previous runs.
2. The effect on conversion of lower ($<1:1$) non-catalytic salt:$ZnCl_2$ mole ratios should be investigated, particularly with the use of NaCl.
3. Means for eliminating the effect on conversion of mixing should be investigated; e.g., the use

of baffles inside the reactor or an increase in the rocking frequency.

B. Improved Analytical Chemistry Procedures

Identification of different product fractions and their relative amounts would be required; possibly a gas chromatograph could be used to simulate an ASTM distillation. The following areas should then be studied:

1. Rate expressions should be developed for the various product fractions.
2. Knowing the rate expressions it would be possible to:
   a. Determine the levels of process parameters to optimize the value of the reaction products.
   b. Select the type of reactor to give the desired product distribution.
3. The effects on conversion and yields of product fractions of alkali metal halides other than NaCl as noncatalytic components of the salt mixture should be investigated.

C. Continuous Reaction Apparatus

Before catalyst poisoning can be adequately studied, continuous reaction equipment will be required. These studies should then be made:

1. The effects of different percentages of catalyst make-up should be determined.
2. Methods for regenerating spent catalyst should be investigated.
3. The levels of the process parameters should be selected to optimize economic return relative to conversion, yields of the various product fractions, and catalyst regeneration costs.
4. The effects of hydrogen partial pressure rather than total gas pressure should be determined.

VI APPENDIX

Table XV. A Sequential List of Experimental Runs and the Area of Investigation Associated with Each Run.

Run No.	Area of Investigation
1	Patent Screening Tests
2	" " "
3	" " "
4	" " "
5	" " "
6	" " "
7	" " "
8	" " "
9	" " "
10	" " "
11	" " "
12	" " "
13	" " "
14	" " "
15	" " "
16	" " "
17	" " "
18	" " "
19	" " "
20	" " "
21	" " "
22	" " "
23	" " "
24	" " "
25	" " "
26	" " "
27	" " "
28	" " "
29	" " "
30	" " "
31	Noncatalytic Component Tests
32	" " "
33	" " "
34	" " "
35	" " "
36	" " "
37	" " "
38	" " "
39	" " "
40	" " "

Table XV (continued)

Run No.	Area of Investigation
41	Zinc Chloride Catalyst Tests
42	Noncatalytic Component Tests
43	" " "
44	Zinc Chloride Catalyst Tests
45	Noncatalytic Component Tests
46	" " "
47	" " "
48	" " "
49	Zinc Chloride Catalyst Tests
50	" " " "
51	Catalyst Accelerator Tests
52	" " "
53	" " "
54	" " "
55	" " "
56	" " "
57	" " "
58	" " "
59	" " "
60	" " "
61	" " "
62	" " "
63	" " "
64	" " "
65	Additional Parameter Tests
66	" " "
67	" " "
68	" " "
69	" " "
70	" " "
71	" " "
72	" " "
73	" " "
74	" " "
75	" " "
76	" " "
77	" " "
78	" " "
79	" " "
80	" " "

Table XV (continued)

Run No.	Area of Investigation
81	Gaseous Phase Removal of Catalyst Poisons Tests
82	" " " " " " "
83	" " " " " " "
84	Additional Parameter Tests
85	Gaseous Phase Removal of Catalyst Poisons Tests
86	" " " " " " "
87	Additional Parameter Tests
88	Gaseous Phase Removal of Catalyst Poisons Tests
89	" " " " " " "
90	Additional Parameter Tests
91	Gaseous Phase Removal of Catalyst Poisons Tests
92	" " " " " " "
93	" " " " " " "
94	" " " " " " "
95	" " " " " " "
96	" " " " " " "
97	" " " " " " "
98	" " " " " " "
99	Additional Parameter Tests
100	Gaseous Phase Removal of Catalyst Poisons Tests
101	" " " " " " "
102	Additional Parameter Tests
103	" " "
104	" " "
105	" " "
106	Gaseous Phase Removal of Catalyst Poisons Tests
107	" " " " " " "
108	" " " " " " "
109	" " " " " " "
110	" " " " " " "
111	" " " " " " "
112	" " " " " " "
113	" " " " " " "
114	" " " " " " "
115	" " " " " " "
116	" " " " " " "
117	" " " " " " "
118	" " " " " " "
119	" " " " " " "
120	" " " " " " "

Table XV (continued)

Run No.	Area of Investigation
121	Patent Tests
122	" "
123	" "
124	" "
125	Gaseous Phase Removal of Catalyst Poisons Tests
126	" " " " " " "
127	" " " " " " "
128	" " " " " " "
129	" " " " " " "
130	" " " " " " "
131	" " " " " " "
132	" " " " " " "
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136	" " " " " " "
137	" " " " " " "
138	" " " " " " "
139	" " " " " " "
140	" " " " " " "
141	" " " " " " "
142	" " " " " " "
143	" " " " " " "
144	" " " " " " "
145	" " " " " " "

Table XVI. Parameter Screening Tests: Summary of Experimental Runs

Factor	Factor Levels −	+
Temperature (°C)	350	450
Pressure (psig)	2000	3000
Time (min.)	15	60
Mixing (reactor agitation) (1)	Static	Rocking
Salt:Coal (weight ratio)	2:1	4:1
$KCl:ZnCl_2$ (mole ratio)	1:2	1:1
Coal Size (U.S. sieve series) (2)	-40+100	-100

(1) 20 grams of coal were charged to the reactor for each run.

(2) Separate coal samples were ground for each run.

Run No.	Temp	Pres	Time	Mixing	Wt R	Mole R	Size	Conv wt-%	Phase Sep'n	Prod App.	Comments
				One-Sixteenth Factorial Design							
1	-	+	-	-	+	-	+	16			Colstrip subbitum.
2	-	-	+	+	-	-	+	36			Colstrip " . Rep. due to low reaction temp.
3	+	+	+	+	+	+	+	85			Savage lignite.
4	-	-	+	+	-	-	+	16			Savage lignite.
5	+	-	+	-	+	-	-	47			Savage lignite. Rep. due to heater problem.
6	+	-	-	-	-	+	+	36			Savage lignite.

Table XVI (continued)

Run No.	Temp	Pres	Time	Mixing	Wt R	Mole R	Size	Conv wt-%	Phase Sep'n	Prod App.	Comments
7	-	-	-	+	+	+	-	8			Colstrip subbitum.
8	+	-	+	-	+	-	-	33			Colstrip " .
9	-	-	-	+	+	+	-	10			Savage lignite.
10	+	+	+	+	+	+	+	67			Colstrip subbitum. Rep. due to high ash.
11	+	+	-	+	-	-	-	23			Colstrip subbitum. Rep. due to high ash.
12	-	+	-	-	+	-	+	12			Savage lignite. Rep. due to high ash.
13	-	+	+	-	-	+	-	23			Savage lignite.
14	+	-	-	-	-	+	+	41			Colstrip subbitum.
15	-	+	+	-	-	+	-	13			Colstrip " .
16	+	+	-	+	-	-	-	38			Savage lignite.
17	-	+	-	-	+	-	+	21			Savage lignite. Repeat of Run #12.
18	+	-	+	-	+	-	-	36			Savage lignite. Repeat of Run #5.
19	-	-	+	+	-	-	+	29			Colstrip subbitum. Rep. of Run #2.
20	+	+	+	+	+	+	+	90			Colstrip subbitum. Rep. of Run #10.

Table XVI (continued)

Run No.	Temp	Pres	Time	Mixing	Wt R	Mole R	Size	Conv wt-%	Phase Sep'n	Prod App.	Comments
21	+	+	-	+	-	-	-	33			Colstrip subbitum. Rep. of Run #11.
22	-	-	+	+	-	-	+	21			Savage lignite. Check on Run #4.
											Added Runs for One-Eighth Factorial Design (all Colstrip subbituminous)
23	-	+	-	+	-	+	+	20	Poor	Dry coal-Tar-like	
24	+	+	+	-	-	-	+	52	Fair-Good	Tar-like	
25	-	+	+	+	+	-	-	24	Good	Tar-like	
26	+	-	-	+	+	-	+	34	Good	Liquid	
27	+	+	-	-	+	+	-	30	Fair-Good	Dry coal	
28	+	-	+	+	-	+	-	61	Good	Liquid	
29	-	-	-	-	-	-	-	8	Poor	Dry coal	
30	-	-	+	-	+	+	+	17	Fair-Good	Dry coal	

Table XVII. Additional Parameter Tests: Summary of Experimental Runs
Factorial Investigation of Pressure and Coal Size

Factor	Factor Levels
Temperature (°C)	450
Pressure (psig)	500, 1500, 2500
Time (min.)	15
Mixing (reactor agitation)	Rocking
Salt:Coal (weight ratio) (1)	4:1
$NaCl:ZnCl_2$ (mole ratio)	0.667:1 (-), 1:1 (+)
Coal Size (U.S. sieve series) (2)	-100+140 (-), -140 (+)

(1) 10 grams of Colstrip subbituminous coal were charged to the reactor for each run

(2) the coal for all runs was ground at the same time

Run No.	Pres	Mole R	Size	Conv wt-%	Phase Sep'n	Prod App.	Comments
65	500	-	+	29	Poor	Liquid	Repeated at a higher NaCl: $ZnCl_2$ mole R due to poor phase separation.
66	1500	-	-	33	Fair Good	Liquid	Same.

Table XVII (continued)

Run No.	Pres	Mole R	Size	Conv wt-%	Phase Sep'n	Prod App.	Comments
67	500	+	+	24	Fair-Good	Tar-like	Repeat of Run #65 at a higher $NaCl:ZnCl_2$ mole ratio
68	1500	+	-	31	Good	Liquid	Repeat of Run #66 at a higher $NaCl:ZnCl_2$ mole ratio
69	1500	+	+	36	Good	Liquid	
70	2500	+	+	58	Fair-Good	Liquid	
71	500	+	-	26	Poor	Tar-like	
72	2500	+	-	44	Good	Liquid	
73	1500	+	-	32	Good	Liquid	
74	1500	+	+	33	Good	Liquid	
75	500	+	-	19	Poor	Dry coal	
76	500	+	+	27	Poor	Liquid	
77	2500	+	-	43	Good	Liquid	
78	2500	+	+	67	Good	Liquid	

Table XVII (continued)

Comparison of -140+200 Mesh and -200 Mesh Coal Particles

Factor	Factor Levels
Temperature (°C)	450
Pressure (psig)	3000
Time (min.)	15
Mixing (reactor agitation)	Rocking
Salt:Coal (weight ratio) (1)	4:1
$NaCl:ZnCl_2$ (mole ratio)	1:1
Coal Size (U.S. sieve series) (2)	-140+200 (-), -200 (+)

(1) 20 grams of Colstrip subbituminous coal were charged to the reactor for each run

(2) The coal for all runs was ground at the same time.

Run No.	Size	Conv wt-%	Phase Sep'n	Prod App.	Comments
79	+	34	Poor	Liquid	Repeated due to modified heat-up procedure with reactor-head heater.
80	+	41	Good	Liquid	Repeat of Run #79; also repeated due to modified heat-up procedure with reactor-head heater.

Table XVII (continued)

Run No.	Size	Conv wt-%	Phase Sep'n	Prod App.	Comments
84	-	32	Good	Liquid	Repeated due to modified heat-up procedure with reactor-head heater.
87	+	24	Poor	Tar-like	Repeat of Run #80; also repeated due to modified heat-up procedure with reactor-head heater.
90	+	26	Poor	Tar-like	Duplicate of Run #87; repeated due to modified heat-up procedure with reactor-head heater
99	-	74	Good	Liquid	Repeat of Run #84; also repeated due to excessive reaction time.
102	+	77	Good	Liquid	Repeat of Run #87.
103	-	67	Good	Liquid	Repeat of Run #99.
104	+	71	Good	Liquid	Repeat of Run #90.
105	-	75	Good	Liquid	Duplicate of Run #103.

Table XVIII. Patent Tests: Summary of Experimental Runs

Factor	Factor Level
Temperature (°C)	450
Pressure (psig)	3000
Time (min.)	15
Mixing (reactor agitation)(1)	Rocking
Salt:Coal (weight ratio)	4:1
Coal Size (U.S. sieve series)(2)	-140 mesh

(1) 20 grams of coal were charged to the reactor for each run.

(2) The coal for all runs was ground at the same time.

Run No.	Noncat-altyic Comp.	Frac. of Non-cat. Comp. in Salt-- wt-%	Conv wt-%	Phase Sep'n	Prod App.	Comments
121	KCl	10.0	46	Good	Liquid	
122	LiCl	23.8	39	Good	Liquid	Salt mixture glassy-like after reaction; some liquid and tar-like product not soluble in benzene.
123	KBr	46.6	90	Good	Liquid	Unexpectedly high conversion.
124	KI	54.9	83	Good	Liquid	Unexpectedly high conversion.

Table XIX. Noncatalytic Component Tests: Summary of Experimental Runs

Factor	Factor Levels
Temperature (°C)	450
Pressure (psig)	3000
Time (min.)	15
Mixing (reactor agitation)(1)	Rocking
Salt:Coal (weight ratio)	4:1
Noncatalytic Component:$ZnCl_2$ (mole ratio)	
KCl	1:1
NaCl	1.25:1
Coal Size (U.S. sieve series)(2)	-100

(1) 20 grams of new coal were charged to the reactor for each run; this ratio decreased as the sequential runs increased due to the unreacted coal carried over from previous runs.

(2) Enough coal was ground each time for a pair of equivalent runs; one for the KCl-$ZnCl_2$ system and one for the NaCl-$ZnCl_2$ system.

Run No.	Source of Salt Mixture	Conv wt-%	Phase Sep'n	Prod App.	Comments
31	New		Good	Liquid	No conversion was determined; this was an exploratory run to determine if a NaCl-$ZnCl_2$ system would result in good phase separation.
32	New	69	Good	Liquid	#1 NaCl-$ZnCl_2$ run.
33	New	72	Good	Liquid	#1 KCl-$ZnCl_2$ run.

Table XIX (continued)

Run No.	Source of Salt Mixture	Conv wt-%	Phase Sep'n	Prod App.	Comments
34	New	29	Poor	Liquid	Salt consisted of 80 grams of $ZnCl_2$; run was made to determine conversion using $ZnCl_2$ only.
35	Run #32	61	Good	Liquid	#2 NaCl-$ZnCl_2$ run.
36	Run #33	52	Good	Liquid	#2 KCl-Zn-Cl_2 run.
37	Run #36	33	Good	Liquid-tar-like	#3 KCl-Zn-Cl_2 run.
38	Run #35	46	Good	Liquid	#3 NaCl-$ZnCl_2$ run.
39	Run #38	41	Good	Liquid-tar-like	#4 NaCl-$ZnCl_2$ run.
40	Run #37	35	Good	Liquid-dry coal	#4 KCl-$ZnCl_2$ run.
42	Run #40	27	Good	Liquid	#5 KCl-$ZnCl_2$ run.
43	Run #39	22	Good	Tar-like	#5 NaCl-$ZnCl_2$ run.
45	Run #43	22	Fair	Liquid-tar-like	#6 NaCl-$ZnCl_2$ run.
46	Run #42	22	Fair	Tar-like	#6 KCl-$ZnCl_2$ run.
47	Run #45	24	Poor	Dry coal	#7 NaCl-$ZnCl_2$ run.
48	Run #46	24	Poor	Tar-like-dry coal	#7 KCl-$ZnCl_2$ run.

Table XX. Zinc Chloride Catalyst Tests: Summary of Experimental Runs

Factor	Factor Level
Temperature (°C)	450 (LiCl-KCl), 350 (KNO_3-$NaNO_3$)[1]
Pressure (psig)	3000
Time (min.)	15
Mixing (reactor agitation)	Rocking
Salt:Coal (weight ratio)[2]	4:1
Noncatalytic Salt Composition (mole %)	
LiCl/KCl	58.5/41.5
$KNO_3/NaNO_3$	50/50
Coal Size (U.S. sieve series[3]	-100

(1) A lower temperature for the KNO_3-$NaNO_3$ salt mixture was used because pure $NaNO_3$ decomposes at 380°C,

(2) 20 grams of coal were charged to the reactor for each run; 0.2 grams of $ZnCl_2$ (1 wt-% of the coal) were charged for those tests using a catalyst.

(3) The coal for all runs was ground at the same time.

Table XX (continued)

Run No.	Salt Component	Catalyst	Conversion	Phase Separation	Comments
41	LiCl-KCl	No	20	Good	Tar-like; salt mixture glassy-like after reaction.
44	LiCl-KCl	Yes	13	Good	Tar-like.
49	KNO_3-$NaNO_3$	No	7	Fair	No distinguishable product.
50	KNO_3-$NaNO_3$	Yes	4	Good	No distinguishable product.

Table XXI. Catalyst Acceleration Tests: Summary of Experimental Runs

Factor	Factor Level
Temperature (°C)	450
Pressure (psig)	3000
Time (min.)	15
Mixing (reactor agitation)	Rocking
Salt:Coal (weight ratio) (1)	4:1
$NaCl:ZnCl_2$ (mole ratio)	1:1
Coal Size (U.S. sieve series) (2)	-100

(1) 20 grams of new coal were charged to the reactor for each run; this ratio decreased as the sequential runs increased due to the unreacted coal carried over from previous runs. 1 gram of catalyst accelerator ($FeCl_2$ or red-mud) was charged to the reactor for each run.

(2) Enough coal was ground each time for a pair of sequential runs: one for the $FeCl_2$ catalyst accelerator and one for the red-mud catalyst accelerator.

Table XXI (continued)

Run No.	Source of Salt Mixture	Conv wt-%	Phase Sep'n	Prod App.	Comments
51	New	60	Good	Liquid	Red-mud run; repeated because it appeared KNO_3-$NaNO_3$ from previous run might have affected conversion.
52	New				Repeat of Run #51 with glass liner. Glass liner broken attempting to remove product.
53	New				Repeat of Run #52 with glass liner. Glass liner broken attempting to remove product.
54	New	64	Good	Liquid	Repeat of Run #53; #1 red-mud run.
55	New	61	Good	Liquid	#1 $FeCl_2$ run.
56	Run #54	39	Good	Liquid	#2 red-mud run.
57	Run #55	48	Good	Liquid	#2 $FeCl_2$ run.
58	Run #56	22	Good	Liquid-tar-like	#3 red-mud run.
59	Run #57	23	Good	Tar-like-dry coal	#3 $FeCl_2$ run.
60	Run #58	24	Fair	Tar-like-dry coal	#4 red-mud run.
61	Run #59	27	Fair	Tar-like-dry coal	#4 $FeCl_2$ run.

Table XXI (continued)

Run No.	Source of Salt Mixture	Conv wt-%	Phase Sep'n	Prod App.	Comments
62	Run #60	26	Fair	Tar-like-dry coal	#5 red-mud run.
63	Run #61	21	Fair	Tar-like-dry coal	#5 $FeCl_2$ run.
64	New	70	Fair	Liquid	$FeCl_3$ was used as a catalyst accelerator.

Table XXII. Gaseous Phase Removal of Catalyst Poisons Tests: Summary of Experimental Runs

Factor	Factor Levels
Temperature (°C)	425, 450 (1)
Pressure (psig)	3000 (1)
Time (min.)	0, 15 (1)
Mixing (reactor agitation)	Rocking
Salt:Coal (weight ratio) (2)	4:1
NaCl:$ZnCl_2$ (mole ratio)	1:1
Coal Size (U.S. sieve series)	-140, -200 (3)

(1) The 425°C temperature and 0 minute reaction time were used for the ambient-temperature gas removal runs in the second two sequences of runs; these changes were made to compensate for conversion occurring during reactor cooldown.

(2) 20 grams of new coal were charged to the reactor for each run; this ratio decreased as the sequential runs increased due to the unreacted coal carried over from previous runs.

(3) -200 mesh coal was used for the initial two sequences of runs and -140 mesh for the second two sequences of runs; two batches of coal were ground --one contained enough coal for all the initial two sequences of runs and the other enough coal for all the second two sequences of runs.

Table XXII (continued)

Initial Two Sequences of Runs

Run No.	Source of Salt Mixture	Conv wt-%	Phase Sep'n	Prod App.	Comments
81	New	--	Poor	Tar-like	Trial run; first time aluminum heating jacket was used.
82	New	60	Fair-Good	Tar-like	#1 high-temp; repeated due to uncertainty about heat-up procedure.
83	New	32	Fair-Good	Liquid	#1 ambient-temp; repeated due to unexpectedly low conversion.
85	New	57	Good	Liquid	Repeat of Run #82; #1 high-temp.
86	New	29	Poor	Liquid-dry coal	Repeat of Run #83; #1 ambient-temp; repeated after heat-up procedure change.
88	Run #86	23	Poor	Tar-like	#2 ambient-temp; repeated after heat-up procedure change.
89	Run #85	38	Poor	Tar-like	#2 high-temp.
91	Run #89	27	Fair	Liquid	#3 high-temp.
92	New	57	Fair-Good	Liquid	Repeat of Run #86; #1 ambient-temp; new heat-up procedure.
93	Run #91	28	Good	Tar-like	#4 high-temp.
94	Run #92	51	Good	Liquid	Repeat of Run #88; #2 ambient-temp; new heat-up procedure.
95	Run #93	28	Poor	Tar-like-dry coal	#5 high-temp.

Table XXII (continued)

Run No.	Source of Salt Mixture	Conv wt-%	Phase Sep'n	Prod App.	Comments
96	Run #94	45	Fair-Good	Liquid	#3 ambient-temp.
97	Run #95	26	Fair-Good	Tar-like	#6 high-temp.
98	Run #96	47	Good	Tar-like	#4 ambient-temp.
100	Run #98	53	Good	Tar-like	#5 ambient-temp; a gas leak developed after reaction.
101	Run #100	--	--	--	#6 ambient-temp; discontinued ambient-temp sequence due to gas leaks.
106	Run #97	28	Fair	Dry coal	#7 high-temp.
107	Run #106	34	Fair	Dry coal	#8 high-temp.
108	Run #107	60	Fair	Tar-like-Dry Coal	#9 high-temp.
109	Run #108	43	Poor	Tar-like-Dry coal	#10 high-temp.
110	Run #109	58	Poor	Tar-like-Dry coal	#11 high-temp.
111	Run #110	35	Poor	Tar-like-Dry coal	#12 high-temp.
112	Run #111	35	Poor	Tar-like-Dry coal	#13 high-temp.

Table XXII (continued)

Run No.	Source of Salt Mixture	Conv wt-%	Phase Sep'n	Prod App.	Comments
113	New	65	Good	Liquid	Ambient-temp; run to determine conversion at zero time.
114	Run #112	34	Poor	Dry coal	#14 high-temp.
115	New	54	Good	Liquid	Ambient-temp; run to determine conversion at zero time and 425°C.
116	Run 114	64	Good	Tar-like-Dry coal	High-temp; the salts had been water-extracted from residue from Run #114.
		Second Two Sequences of Runs			
117	New	52	Good	Liquid	#1 ambient-temp.
118	New	63	Good	Liquid	#1 high-temp.
119	Run #117	25	Fair	Tar-like	#2 ambient-temp.
120	Run #118	46	Good	Tar-like	#2 high-temp.
125	Run #120	46	Fair-Good	Tar-like	#3 high-temp.
126	Run #119	33	Good	Liquid	#3 ambient-temp.
127	Run #126	19-24[4]	Fair	Tar-like-Dry coal	#4 ambient-temp.

[4] The first conversion is based on the coal being reactive for four runs and the second that it is reactive for three runs.

Table XXII (continued)

Run No.	Source of Salt Mixture	Conv wt-%	Phase Sep'n	Prod App.	Comments
128	Run #125	38	Good	Tar-like	#4 high-temp.
129	Run #127	26-36	Fair	Tar-like-Dry coal	#5 ambient-temp.
130	Run #128	36	Good	Tar-like	#5 high-temp.
131	Run #129	29-34	Poor	Tar-like-Dry-coal	#6 ambient-temp.
132	Run #130	32	Fair	Tar-like	#6 high-temp.
133	Run #132	31	Fair	Tar-like-Dry coal	#7 high-temp.
134	Run #131	23-30	Poor	Dry coal	#7 ambient-temp.
135	Run #133	40	Poor	Tar-like-Dry coal	#8 high temp.
136	Run #134	28-33	Poor	Tar-like	#8 ambient-temp.
137	Run #135	46	Fair	Tar-like-Dry coal	#9 high-temp.
138	Run #136	32-38	Poor	Tar-like	#9 ambient-temp.
139	Run #137	42	Poor	Tar-like-Dry coal	#10 high-temp.
140	Run #138	35-44	Poor	Dry coal	#10 ambient-temp.
141	Run #139	39	Poor	Tar-like-Dry coal	#11 high-temp.
142	Run #140	36-45	Poor	Tar-like	#11 ambient-temp.

Table XXII (continued)

Run No.	Source of Salt Mixture	Conv wt-%	Phase Sep'n	Prod App.	Comments
143	Run #142	--	Poor	Tar-like	#12 ambient-temp; run made to collect product for H:C analysis.
144	Run #141	--	Poor	Tar-like	#12 high temp; run made to collect product for H:C analysis.
145	New	62	Good	Liquid	High-temp; run made to collect product for H:C analysis.

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