



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
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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 $ZnCl_2$; 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.

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$NaCl$ 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.

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TABLE OF CONTENTS

| | Page |
|---|------|
| LIST OF TABLES | vii |
| LIST OF FIGURES | ix |
| ABSTRACT | x |
| I INTRODUCTION | 1 |
| A. Historical Background | 1 |
| 1. Consolidation Coal Company | 1 |
| 2. Montana State University | 3 |
| B. Research Objectives | 5 |
| II EXPERIMENTAL | 7 |
| A. Outline of research | 7 |
| 1. Parameter Tests | 7 |
| 2. Catalyst Tests | 12 |
| B. Materials | 16 |
| C. Equipment | 17 |
| D. Procedures | 19 |
| 1. Experimental Runs | 19 |
| 2. Conversion Calculations | 26 |
| III RESULTS AND DISCUSSION | 30 |
| A. Parameter Tests | 30 |
| 1. Parameter Screening Tests | 30 |
| 2. Additional Parameter Tests | 40 |
| 3. Patent Tests | 44 |
| B. Catalyst Tests | 48 |
| 1. Noncatalytic Component Tests | 48 |
| 2. Zinc Chloride Catalyst Tests | 52 |
| 3. Catalyst Accelerator Tests | 54 |
| 4. Gaseous Phase Removal of Catalyst Poisons Tests | 58 |

TABLE OF CONTENTS (continued)

| | Page |
|--|------|
| IV CONCLUSIONS | 66 |
| V RECOMMENDATIONS | 70 |
| A. Existing Equipment and Procedures | 70 |
| B. Improved Analytical Chemistry Procedures | 71 |
| C. Continuous Reaction Apparatus | 72 |
| VI APPENDIX | 73 |
| VII LITERATURE CITED | 99 |

LIST OF TABLES

| Table | | Page |
|-------|--|------|
| I | Parameter Screening Tests: Selection of Parameters (Factors) and Their Values (Levels) | 9 |
| II | Parameter Screening Tests: Factor Levels | 31 |
| III | Parameter Screening Tests--One sixteenth Factorial: Experimental Design and Conversions | 32 |
| IV | Parameter Screening Tests--One-sixteenth Factorial: Analysis of Variance | 34 |
| V | Parameter Screening Tests--One-eighth Factorial: Experimental Design and Conversions | 37 |
| VI | Parameter Screening Tests--One-eighth Factorial: Analysis of Variance | 38 |
| VII | Additional Parameter Tests--Factorial Investigation of Pressure and Coal Size: Factor Levels, Experimental Design, and Conversions | 41 |
| VIII | Additional Parameter Tests--Factorial Investigation of Pressure and Coal Size: Analysis of Variance | 43 |
| IX | Additional Parameter Tests--Comparison of -140+200 Mesh and -200 Mesh Coal Particles: Parameter Levels and Conversions | 45 |
| X | Patent Tests: Parameter Levels and Conversions | 47 |
| XI | Noncatalytic Component Tests: Factor Levels | 49 |
| XII | ZnCl ₂ Catalyst Tests: Factor Levels and Conversions | 53 |

LIST OF TABLES (continued)

| Table | | Page |
|-------|---|------|
| XIII | Catalyst Accelerator Tests: Factor Levels | 55 |
| XIV | Gaseous Phase Removal of Catalyst Poisons Tests: Factor Levels | 59 |
| XV | A Sequential List of Experimental Runs and the Area of Investigation Associated with Each Run | 74 |
| XVI | Parameter Screening Tests: Summary of Experimental Runs | 78 |
| XVII | Additional Parameter Tests: Summary of Experimental Runs | 81 |
| XVIII | Patent Tests: Summary of Experimental Runs | 85 |
| XIX | Noncatalytic Component Tests: Summary of Experimental Runs | 86 |
| XX | Zinc Chloride Catalyst Tests: Summary of Experimental Runs | 88 |
| XXI | Catalyst Acceleration Tests: Summary of Experimental Runs | 90 |
| XXII | Gaseous Phase Removal of Catalyst Poisons Tests: Summary of Experimental Runs | 93 |

LIST OF FIGURES

| Figure | Page |
|--|------|
| 1. Block Flowsheet of Coal Hydrocracking Experiments Using Molten Salt Catalysts | 8 |
| 2. Sketches of Reaction Apparatus | 18 |
| 3. Schematic of Reactor Head After Modification for Gaseous Phase Removal of Catalyst Poisons Tests | 20 |
| 4. Sketch of Heating Jacket for Reactor Head for Gaseous Phase Removal of Catalyst Poisons Tests | 21 |
| 5. Block Flowsheet of a Typical Experimental Run | 22 |
| 6. Coal Conversion Equations for a Typical Run | 28 |
| 7. Noncatalytic Component Tests: Conversion vs. Number of Runs for $KCl-ZnCl_2$ and $NaCl-ZnCl_2$ Salt Mixtures | 51 |
| 8. Catalyst Accelerator Tests: Conversion vs. Number of Runs for $FeCl_2$, Red-mud, and No Accelerator. | 57 |
| 9. Gaseous Phase Removal of Catalyst Poisons Tests: Conversion vs. Number of Runs for High-temperature and Ambient-temperature Gas Removal | 62 |

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 ($2^7 =$

PARAMETER TESTS

Parameter Screening Tests

Additional Parameter Tests

Patent Tests

CATALYST TESTS

Cost Reduction of Components
of Molten Salt Solution

Noncatalytic Component Tests

ZnCl₂ Catalyst Tests

Cost Reduction Through
Catalyst Life Extension

Catalyst Accelerator Tests

Gaseous Phase Removal of
Catalyst Poisons Tests

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-ZnCl₂ salt has a lower viscosity than pure ZnCl₂, 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 (ZnCl₂:coal) was needed for adequate contact.

KCl:ZnCl₂ 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 ($<400^{\circ}\text{C}$), 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, $[\text{Zn}(\text{NH}_3)_2]\text{Cl}_2$, 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-

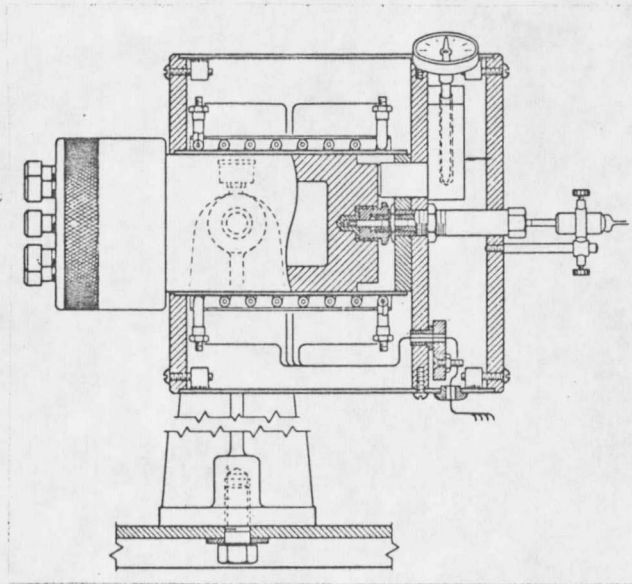
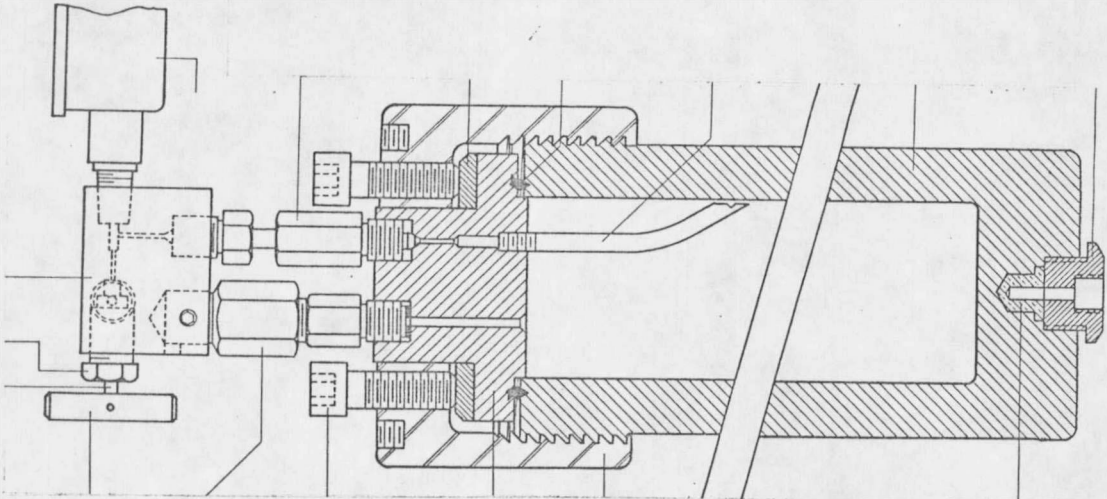


Figure 2. Sketches of Reaction Apparatus

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.

