# HYDROCRACKING ATHABASCA BITUMEN IN THE PRESENCE OF COAL     PART 2: EXPERIMENTS WITH COALS OF DIFFERENT RANK

M. Ternan and B.I. Parsons

MAY 1975

This report relates essentially to the samples as received.

ENERGY RESEARCH PROGRAM

ENERGY RESEARCH LABORATORIES

SCIENTIFIC BULLETIN     CM 75-10

Hydrocracking Athabasca Bitumen in the Presence of Coal

Part 2:  Experiments with Coals of Different Rank

by

M. Ternan* and B.I. Parsons**

## ABSTRACT

This is the second in a series of reports on the hydrocracking of Athabasca bitumen in the presence of coal particles.  In the thermal hydrocracking process, the coal particles act as sites for the deposition of metals and coke and help to remove these materials from the reaction system.  The purpose of this investigation was to examine the effect of coal composition (coal rank).

Studies were performed with seven coals of varying rank.  It was found that the lower rank coals are hydrogenated to a greater extent than coals of higher rank.  As the amount of coal hydrogenation increased, the reactor volume available for thermal hydrocracking increased.  Therefore, the conversion of pitch, the removal of coke precursors, and the removal of metals were all affected by the extent of coal hydrogenation.  It was shown that as the pitch components were converted to lower boiling compounds, the coke precursors were destroyed and the concentration of metals in the liquid product was reduced.  A material balance showed that essentially all the vanadium metal removed from the feedstock was accumulated on the solids.  In contrast, it appeared that only part of the nickel removed from the liquid was deposited on the solids.

---

*Research Scientist, Catalysis Section, **Assistant Chief, Energy Research Laboratories, Canada Centre for Mineral and Energy Technology, Department of Energy, Mines and Resources, Ottawa, Canada.

L'Hydrocraquage du bitume de l'Athabasca
en présence de charbon

2$^e$ Partie:  Des expériences avec du charbon
de différentes classes

par

M. Ternan* et B.I. Parsons**

## RESUME

Le présent rapport est le deuxième d'une série sur l'hydrocraquage du bitume de l'Athabasca en présence de particules de charbon.  Dans le processus de l'hydrocraquage thermique, les particules de charbon jouent le rôle de sites pour le dépôt des métaux et du coke et aident à éliminer ces matériaux du système de réaction.  Le but de cette recherche était d'examiner l'effet causé par la composition du charbon (classe de charbon).

Des études ont été effectuées sur sept sortes de charbon de différentes classes.  On a découvert que les charbons de classe inférieure sont hydrogénés dans une plus grande proportion que ceux de classe supérieure.  A mesure que l'hydrogénation du charbon augmentait, le volume du réacteur disponible pour l'hydrocraquage thermique augmentait.  Par conséquent, la transformation du brai, l'élimination des précurseurs de coke, et l'élimination des métaux ont tous été affectés par l'étendue de l'hydrogénation du charbon.  Il a été démontré que les composants du brai ont été transformés en composants bouillants à des températures inférieures, que les précurseurs de coke ont été détruits et que la concentration des métaux dans le  produit liquide a été réduite.  Un reste du matériel indiquait que, essentiellement, tout le vanadium éliminé de la charge d'alimentation s'était accumulé sur les solides et qu'au contraire il semblerait que seulement une partie du nickel éliminé du liquide s'était déposée sur les solides.

*Chercheur scientifique, Section de la catalyse, **Chef- adjoint
Laboratoires de recherche énergétique, Centre canadien de la
technologie des minéraux et de l'énergie, Ministère de l'Energie,
des Mines et des Ressources, Ottawa, Canada.

# CONTENTS

LIST OF FIGURES

LIST OF TABLES

# INTRODUCTION

This is the second report describing results from the Energy Research Laboratories program on the use of coal as a processing aid, or "getter", and catalyst for the liquid phase hydrocracking of Athabasca bitumen. The aims and objectives of the research program, as well as the function of coal in the hydrocracking reaction system, have been documented in the first report (1) of this series. The possibility of converting heavy oils having high pitch contents into conventional fuel oils has become more widely recognized since the 1973-74 increases in the price of imported crude oil. Recently it has been predicted that the Canadian demand for fuel oil is likely to exceed the rate of domestic crude oil production (2, 3) within the next decade. One way to increase the supply of commercial fuel oil would be to convert the pitch in petroleum residua, in heavy oils, and in bitumens into higher quality products. The bitumen obtained from the Alberta Oil Sands contains approximately twice as much pitch as conventional crude oils (4). Therefore, the development of technology for high pitch conversions is essential for the rational development of the Oil Sands.

The thermal hydrocracking process for converting pitch to lower boiling distillate fractions is superior to coking processes in at least two major respects. First, the quantity of distillate obtained is significantly larger. The delayed-coking process (5) used by Great Canadian Oil Sands and the fluid-coking process (6) proposed by Syncrude, produce 70 and 70-75 weight percent yields of distillate respectively. In contrast, the thermal hydrocracking process (7c, 8) being developed at the Energy Research Laboratories produces distillate yields of 86 weight percent. The other advantage of the hydrocracking process is that it produces a higher quality of distillate than the coking processes. Reactions, resulting in sulphur removal, nitrogen removal, and the hydrogenation of unsaturated compounds, take place to a much greater extent during hydrocracking than during coking.

Thermal hydrocracking does have one potential disadvantage. Preliminary experiments indicate that at high levels of pitch conversions there is a slight build-up of solids in the reaction system. The minute amount of coke formed during the hydrocracking reaction, tends to accumulate in the reaction system. Further work is required to define the extent of this phenomena and, if it is a problem, to devise methods of circumventing it.

One potential solution to this problem involves the addition of coal particles to the hydrocracking reactor. The presence of coal particles in the system could provide sites for the deposition of coke and metals. The continuous addition and withdrawal of the coal particles would provide a mechanism for the removal of solids from the system. The fact that coke from the bitumen will deposit on the surface of the coal particles has already been established (9). It has also been shown (1) that some of the coal is hydrogenated at the conditions used to hydrocrack the bitumen.

A process for thermally hydrocracking bitumen in the presence of coal particles could have several interesting features. The concentrations of metals and coke-forming compounds (coke precursors) in the liquid product might be sufficiently low to permit subsequent catalytic processing without causing appreciable catalyst deactivation. In addition, the amount of liquid distillate formed by coal hydrogenation would defray or probably eliminate the cost of coal used in the process. Finally, the solids removed from the reactor might be burned directly to provide energy for the process or alternatively gasified to produce both hydrogen and fuel gas.

This report describes experimental results obtained using coals of widely varying rank. Several phenomena were studied: coal hydrogenation, pitch conversion, the removal of coke precursors from the hydrocarbon liquid, the removal of metals from the hydrocarbon liquid, and variations in the quality of the product. The intention of the investigation was to establish the effect of coal rank upon the above phenomena.

<div align="center">EXPERIMENTAL</div>

## Apparatus and Operating Procedure

The experimental equipment and its operation have been described in detail previously (1). Very briefly, hydrogen and bitumen at high pressure were combined and flowed continuously into the bottom of a fixed-bed reactor filled with -4+8 mesh (2.38 to 4.76 mm) coal particles. The coal was used as received and was not subjected to any pretreatment. The reaction mixture flowed up through the bed of coal particles where both bitumen hydrocracking and coal hydrogenation occurred. The reaction conditions are listed in Table 1. The products flowed out of the top of the reactor and were separated

into liquid and vapour streams. The vapour and liquid products obtained at unsteady state conditions during start-up and shut-down were discarded. Only the materials produced at the desired operating conditions were analyzed. At the conclusion of the experiments, the solids remaining in the reactor were placed in a Soxhlet apparatus and the adhering bitumen and liquid hydrocarbon products extracted with toluene. Subsequently, the solids were vacuum dried, weighed, and analyzed.

Table 1

Hydrocracking Reaction Conditions

| | |
|---|---|
| Temperature ............. | $450^\circ C$ ($723^\circ K$) |
| Pressure ............... | 2000 psig (13.9 MPa) |
| $H_2$ flowrate ............ | 5000 scf/Bbl (0.0359 l/sec) |
| Bitumen flowrate (at $60^\circ F$) | 153.6 ml/hr (42.7 ml/ks) |
| Liquid Space Velocity ... | 1.0 $hr^{-1}$ (0.28 $ks^{-1}$) |

## Analytical Procedures

Several different analytical techniques were employed. Analyses performed on the liquid product included distillation, sulphur, nitrogen, Conradson Carbon Residue, nickel, iron, vanadium, and specific gravity. Specific gravity was measured using a hand hydrometer (10). Proximate analyses, ultimate analyses (carbon, hydrogen, sulphur, nitrogen, ash, and oxygen), metal analyses (nickel, vanadium, and iron), and measurements of surface areas and particle sizes were made on the solids; screens conforming to the U.S. Standard Sieve Series (11) were used for particle size measurements.

The liquid product was distilled into ten fractions (the boiling ranges are shown in Table 7). A modified version of the U.S. Bureau of Mines Hempel distillation analysis (12) was used. A 100 ml. sample of the liquid product was measured into a Hempel distillation flask and distilled rapidly. The first four fractions were distilled at a pressure of 101 kPa (760 mm Hg), the next four at an absolute pressure of 5.33 kPa (40 mm Hg), and the ninth at 0.133 kPa (1 mm Hg). The tenth fraction remained in the distillation flask.

Results obtained using this method were compared with the results obtained from a Podbielniak Flash Equilibrium Distillation Apparatus, (13) using a number of standard feed stocks. It was shown that the final distillation conditions were equivalent to a boiling point of 975°F (524°C) at atmospheric pressure.

The sulphur content of the liquid products and distilled fractions was determined using an X-Ray fluorescence technique (14). X-Rays emitted from an Fe-55 source cause a secondary X-Ray emission characteristic of the sulphur atoms in the liquid sample, and the energy of the secondary X-Rays can be related to the quantity of sulphur in the sample. The instrument used for these measurements was a Model 4000 Panalyzer manufactured by Panametrics, a subsidiary of the Esterline Corporation of Waltham, Massachusetts.

The nitrogen content of the liquid products was determined using a hydrogenation-microcoulometric apparatus (15). The sample was diluted with toluene in a 20 to 1 ratio and placed in a heated tube through which hydrogen gas flowed. Vaporization and pyrolysis of the sample occurred in the first section of the tube which was kept at 925°C. The products of pyrolysis were hydrogenated at 700°C over a granulated nickel catalyst in the second section of the tube. A third section kept at 300°C, contained porous alumina which adsorbed the acid gases (sulphur and oxygen compounds). Therefore, the gas leaving the tube was essentially composed of hydrogen, methane and ammonia. It then entered the microcoulometer where the ammonia reacted with the hydrogen ions. The electric current required to generate sufficient hydrogen ions to maintain a constant pH in the microcoulometer was then related to the nitrogen content of the liquid sample. The equipment used for these analyses was manufactured by the Dohrmann Division of Envirotech Corp., Mountain View, California.

The Conradson carbon residue of the liquid hydrocarbon was determined in accordance with ASTM specification D-189. A weighed amount of sample was heated in a crucible for a fixed period of time. During heating the combination of pyrolysis and distillation caused a solid carbonaceous residue to be formed. The weight of the final residue was expressed as a percentage of the initial sample weight to obtain the value of the "Conradson carbon residue".

The same procedures were followed to determine metals content in liquids and solids. The samples were reduced to an ash, put into solution, and finally analyzed by atomic adsorption. The ashing technique described in ASTM Method D1548 was used for all the metals. Each sample was mixed with concentrated $H_2SO_4$ and heated on a hotplate until an acid sludge formed and all the sulphur oxide fumes had been emitted. After the sample had been ignited and all the hydrocarbon vapours burned, the sample was placed in a furnace at $150^{\circ}C$. The furnace temperature was raised to $525^{\circ}C$ and a small amount of air was passed through it in order to reduce the coke to inorganic ash. The ash was put into solution by adding $HNO_3$ and $H_2SO_4$ according to paragraph 8.6 of D-1548 which was as far as the ASTM procedure was followed. This solution was diluted with 5 weight percent HCl and analyzed by atomic absorption. The wavelengths and gas mixtures used for the atomic absorption measurements are listed in Table 2.

TABLE 2

Wavelengths and Gas Mixtures Used for
Metal Analysis by Atomic Absorption

| Metal | Wavelength nm | Gas Mixture | |
|-------|---------------|-------------|----------------|
| | | Fuel | Oxidizing Agent |
| Al | 309.2 | Acetylene | Nitrous Oxide |
| Co | 240.7 | Acetylene | Air |
| Fe | 248.3 | Acetylene | Air |
| Mo | 313.3 | Acetylene | Air |
| Ni | 232.0 | Acetylene | Air |
| V | 318.4 | Acetylene | Nitrous Oxide |

The procedures used to determine proximate analyses of hydrocarbon solids were in accordance with the ASTM D-3172 specification. Brief descriptions of the analyses follow:

(1) <u>Moisture</u>: ASTM Method D-3173 - the loss in weight on heating a 1 gram sample in an oven at 104 - 110°C for 1 hour.

(2) <u>Ash</u>: ASTM Method D-3174 - the residue from item (1) after all the combustible material is burned out in a muffle furnace at 700 - 750°C.

(3) <u>Volatile Matter</u>: ASTM Method D-3175 - the loss in weight of a 1 gram sample heated in a covered crucible at 950°C for 7 minutes, with item (1) deducted.

(4) <u>Fixed Carbon</u>: Items (1) to (4) are all expressed as percentages and the fixed carbon is the difference between 100 and items (1) + (2) + (3).

ASTM specification D-3176 was followed in performing the ultimate analyses on the solids. Outlines of the methods are given below:

(1) <u>Carbon and Hydrogen</u>: ASTM Method D-3178. The sample was placed in a combustion tube and was burned in a stream of oxygen. The combustion products flowed through a packing comprised of cupric oxide and lead chromate or silver gauze in order to ensure the complete oxidation of the combustion products and the removal of sulphur oxides. Water in the combustion products was subsequently absorbed on anhydrous magnesium perchlorate and the carbon dioxide was absorbed on "Ascarite", a commercial preparation of sodium and potassium hydroxide impregnated on an inert carrier. Finally, the carbon and hydrogen contents were calculated from the weight changes of the two absorbents.

(2) <u>Sulphur</u>: ASTM Method D-3177. The sample was thoroughly mixed with Eschka mixture (2 parts MgO, 1 part $Na_2CO_3$) and heated at 800°C. During this step sulphur in the sample was oxidized to form $SO_2$ which reacted to form sodium sulphate. After cooling, the solids were digested in hot water, and after 1/2 to 3/4 hour the insoluble solids removed by decantation and filtering. After adjusting the pH with NaOH and HCl and boiling the solution, a barium chloride solution was added. The barium sulphate precipitate was heated to

$925^{\circ}C$ to decompose the filter paper and then weighed. The weight percent of sulphur was obtained by comparing the weight of the $BaSO_4$ precipitate with the corresponding precipitate weight obtained in a blank run.

(3) <u>Nitrogen</u>: ASTM Method D-3179. The sample was initially digested by heating in a mixture of $K_2SO_4$, $H_2SO_4$, and cupric selenide. The purpose of this procedure was to convert the nitrogen into ammonium salts. After cooling, zinc metal and an alkali solution containing potassium hydroxide was added and the resulting mixture heated. The ammonia was distilled from the mixture and collected in an acid solution which was later titrated with NaOH to obtain the nitrogen content.

(4) <u>Ash and Moisture</u>: Ash and moisture contents were obtained by the procedures used for proximate analyses, that is ASTM methods D-3174 and D-3173 respectively. These methods are described on page 6 of this report.

(5) <u>Oxygen</u>: The percent oxygen was obtained by subtracting from 100 the percentages of hydrogen, carbon, nitrogen, sulphur, moisture and ash.

The surface areas of the solids were measured using a Perkin Elmer Shell Model 212C Sorptometer, which utilized a gas chromatographic principle (16). During the surface area determination, a particular mixture of helium and nitrogen flowed over the sample continuously. When the sample vessel was immersed in a liquid nitrogen bath, the solid adsorbed the nitrogen but not the helium in the flowing gas mixture. The resulting change in gas composition was monitored with a thermal conductivity detector, and related to the amount adsorbed. The amount adsorbed was used to calculate the solid surface area using the point-B method (17).

## Materials

The bitumen used in these studies was obtained from Great Canadian Oil Sands Ltd. (G.C.O.S.) at Fort McMurray, Alberta. The GCOS operation uses the Clark Hot Water process (18) to separate the coarse sand from the bitumen.

The bulk of the residual clay in the water-separated bitumen is removed by dilution centrifuging. The bitumen supplied to the Energy Research Laboratories was topped bitumen (diluent removed), typical of the material fed to the company's delayed coking unit. The general properties of the bitumen are shown in Table 3.

TABLE 3

Properties of Athabasca Bitumen

| | |
|---|---|
| Specific Gravity 60/60°F.......... | 1.000 |
| Ash (wt %) 700°C.................. | 0.70 |
| Nickel (ppm)...................... | 76 |
| Vanadium (ppm).................... | 191 |
| Conradson Carbon Residue (wt %).... | 12.6 |
| Pentane Insolubles (wt %).......... | 15.83 |
| Benzene Insolubles (wt %).......... | 0.90 |
| Carbon Disulphide Insolubles (wt %) | 0.88 |
| Sulphur (wt %).................... | 4.72 |
| Nitrogen (wt %)................... | 0.42 |
| Viscosity, Kinematic (cSt) at 210°F | 129.5 |
| Viscosity, Kinematic (cSt) at 130°F | 2041 |
| Molecular Weight (calculated)...... | 722 |
| Residuum (+975°F) wt %............. | 51 |

Seven different coal solids having markedly different compositions and properties were used in these studies. Except for the sample of lignite from Saskatchewan and the high volatile A bituminous coal from Nova Scotia, all of the coals were from Alberta. The predominence of Alberta coals was intentional since transportation costs to Fort McMurray will be lower for Alberta coals than for coals located in other provinces. The composition of each coal, its ASTM rank, its geographical location, its metals content and both its proximate and ultimate analyses are shown in Table 4.

TABLE 4

Analyses of Coals Used in Reaction Studies

| ASTM RANK | | Semi Anthracite | Medium Volatile Bituminous | High Volatile A Bituminous | Subbituminous A | Subbituminous B | Subbituminous C | Lignite |
|---|---|---|---|---|---|---|---|---|
| SOURCE (Geographical Location) | | Canmore Cascade Area Alberta | Cardinal River Mountain Park Area Alberta | Harbour Seam Glace Bay Nova Scotia | Henry Miller Taber Area Alberta | Whitewood Pembina Area Alberta | Star Key Edmonton Area Alberta | Estevan Saskatchewan |
| **Proximate Analyses** | | | | | | | | |
| moisture | wt % | 0.78 | 0.67 | 1.41 | 11.96 | 17.62 | 22.90 | 18.26 |
| volatile matter | wt % | 13.39 | 19.72 | 34.93 | 32.85 | 30.59 | 29.15 | 35.62 |
| ash | wt % | 7.82 | 10.25 | 2.34 | 10.08 | 10.74 | 11.41 | 10.16 |
| fixed carbon | wt % | 78.01 | 69.36 | 61.32 | 45.11 | 41.05 | 36.64 | 35.96 |
| **Ultimate Analyses** | | | | | | | | |
| carbon | wt % | 82.19 | 78.20 | 83.11 | 58.26 | 52.48 | 48.64 | 51.74 |
| hydrogen | wt % | 4.09 | 4.43 | 5.77 | 4.11 | 3.57 | 3.19 | 3.35 |
| nitrogen | wt % | 1.49 | 1.16 | 1.84 | 1.57 | 0.74 | 1.10 | 0.89 |
| sulphur | wt % | 0.72 | 0.25 | 0.79 | 1.21 | 0.22 | 0.26 | 0.30 |
| moisture | wt % | 1.18 | 0.97 | 1.40 | 13.26 | 17.58 | 22.29 | 14.88 |
| ash | wt % | 8.52 | 11.78 | 2.83 | 10.07 | 12.04 | 10.91 | 10.97 |
| oxygen | wt % | 1.81 | 3.21 | 4.26 | 11.52 | 13.37 | 13.61 | 17.87 |
| **Metals** | | | | | | | | |
| nickel | ppm | 7.6 | 3.2 | 5.3 | 14 | 6.5 | 4.7 | 2.3 |
| vanadium | ppm | <25 | <25 | <25 | 14.7 | <25 | <25 | <25 |
| iron | ppm | 2200 | 2000 | 7500 | 7900 | 3000 | 2800 | 3300 |
| Surface Area | $m^2/g$ | 2.39 | 1.36 | 0.55 | 4.07 | 6.49 | 5.35 | 1.93 |

## RESULTS AND DISCUSSION

### Coal Hydrogenation

Coal hydrogenation and bitumen hydrocracking proceed simultaneously at high temperatures and pressures. The first report in this series (1) described the relationship between coal hydrogenation and coal particle size. As the reaction time increased, the amount and the size of the solid coal particles decreased. When the solids remaining at the end of an experiment were analyzed, it was found that the carbon/ash ratio was the lowest in the smallest particles. This suggested that the smaller particles were hydrogenated to a greater extent than the larger ones. The studies described here complement the particle size studies. The purpose of the present work was to elucidate the relationship between coal hydrogenation and coal composition or coal rank. Both the amount of coal hydrogenation and the change in the composition of the remaining coal particles were monitored.

The amount of coal hydrogenation was determined by measuring the weight of solids remaining in the reactor at the end of an experiment. It is shown in Figure 1, as a function of coal composition. Coal composition is represented as the weight percent fixed carbon (daf) in the coal, measured by the "proximate analysis" procedure. This particular variable was chosen to represent coal composition since it is one of the characteristics used to define coal rank, according to the ASTM classification D-388. Figure 1B shows that there is a good correlation between coal composition and extent of coal hydrogenation. The percent fixed carbon in the coal is given in Table 4, and the weight percent solids remaining in the reactor is given in Table 5. The high rank coals were found to be relatively unreactive. In comparison, the low rank coals were hydrogenated to a much greater extent. These findings are consistent with results obtained during coal hydrogenation in the absence of bitumen. For example, the results summarized by Wu and Storch (19), for the coal hydrogenation process employed in Germany during the Second World War, show the same trend with coal rank.
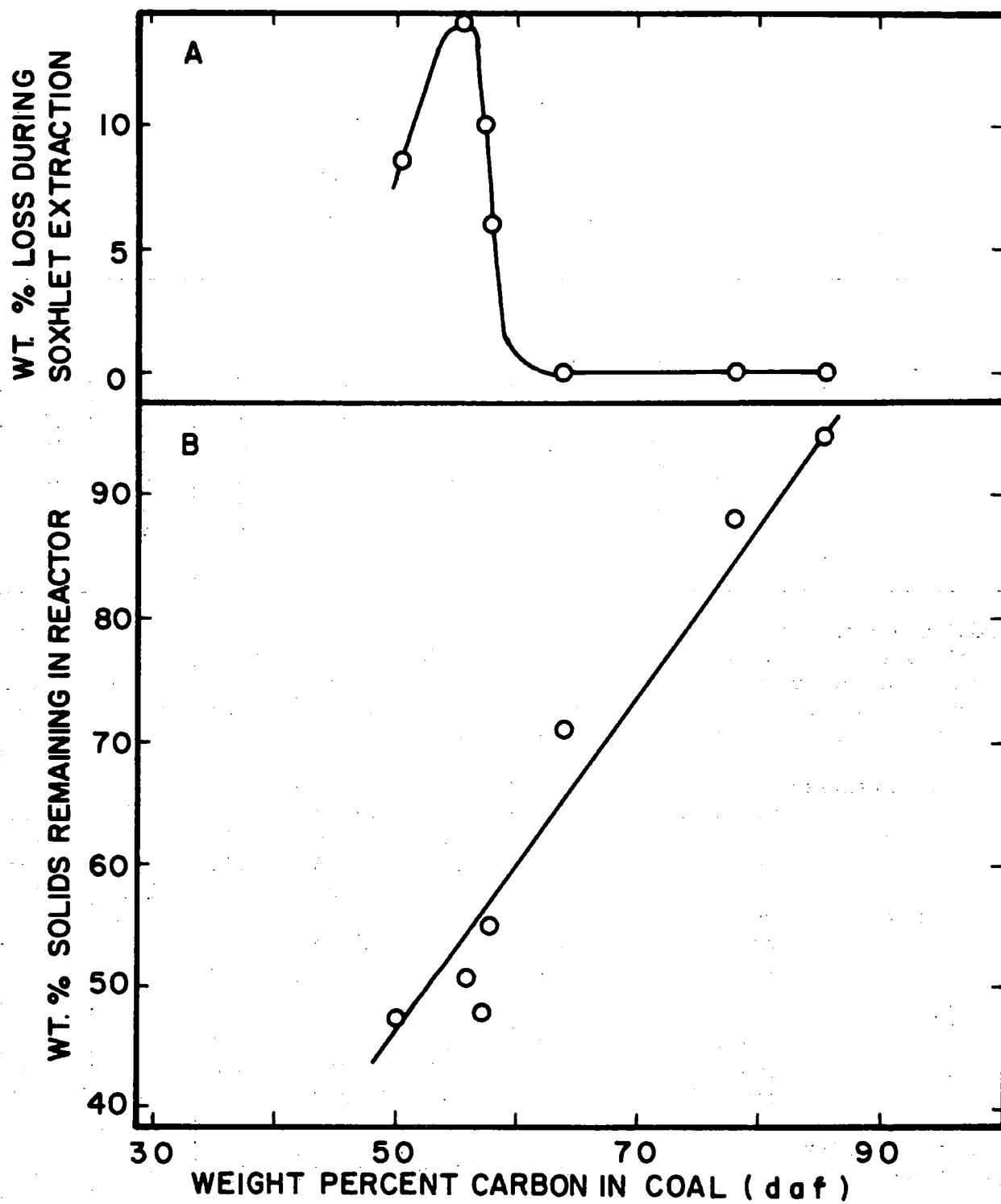
Figure 1.   Coal Hydrogenation as a Function of Coal Rank

TABLE 5

Analyses of the Solids Remaining
at the Conclusion of the Experiment

| ASTM Rank | | Semi Anthracite | Medium Volatile Bituminous | High Volatile A Bituminous | Subbituminous A | Subbituminous B | Subbituminous C | Lignite |
|---|---|---|---|---|---|---|---|---|
| **Proximate Analyses** | | | | | | | | |
| moisture | wt % | 0.70 | 2.60 | 2.00 | 4.43 | 5.43 | 3.16 | 4.99 |
| volatile matter | wt % | 13.44 | 17.51 | 15.46 | 21.69 | 23.27 | 20.67 | 24.02 |
| ash | wt % | 7.08 | 14.20 | 4.75 | 19.01 | 22.26 | 29.45 | 24.59 |
| fixed carbon | wt % | 78.78 | 65.69 | 77.79 | 54.87 | 49.04 | 46.72 | 46.40 |
| **Ultimate Analyses** | | | | | | | | |
| carbon | wt % | 83.34 | 77.39 | 85.49 | 67.24 | 63.93 | 64.50 | 62.57 |
| hydrogen | wt % | 3.93 | 3.91 | 3.83 | 3.29 | 3.52 | 3.73 | 4.00 |
| nitrogen | wt % | 1.26 | 1.41 | 1.80 | 1.75 | 0.95 | 1.58 | 1.35 |
| sulphur | wt % | 0.97 | 0.76 | 1.52 | 2.20 | 1.96 | 1.89 | 1.65 |
| moisture | wt % | 1.14 | 2.59 | 1.97 | 5.08 | 5.81 | 4.44 | 5.20 |
| ash | wt % | 7.53 | 13.65 | 4.57 | 19.45 | 24.26 | 22.60 | 22.76 |
| oxygen | wt % | 1.83 | 0.29 | 0.82 | 0.99 | 0.00 | 1.26 | 2.47 |
| **Metals** | | | | | | | | |
| nickel | ppm | 38 | 56 | 105 | 195 | 147 | 123 | 127 |
| vanadium | ppm | 154 | 340 | 373 | 1312 | 900 | 778 | 734 |
| iron | ppm | 3,500 | 4,600 | 20,000 | 15,500 | 5,600 | 4,900 | 5,400 |
| **Solids Remaining in Reactor** | wt % | 94.8 | 88.2 | 71.2 | 55.2 | 47.7 | 50.7 | 47.3 |
| Mode Particle Size | μm | 1980 | 520 | 370 | 1980 | 1670 | 1820 | 840 |
| Surface Area | m²/g | 0.71 | 2.63 | 2.04 | 8.80 | 11.53 | 4.40 | 17.85 |

Experimental error was at least partially responsible for the data point scatter in Figure 1B. Some spillage occurred when the solids were removed from the reactor. Even though this step was performed with great care, the loss of solids could not be completely avoided. After being removed from the reactor, liquid hydrocarbons on the solids were extracted with toluene using a Soxhlet apparatus. Some components of the solids may have been extracted at the same time. Evidence to support this suspicion is shown in Figure 1A. The weight loss of the original unhydrogenated coals caused by toluene extraction is shown as a function of coal composition. There was virtually no change in weight of the high rank coals. However, significant portions of the low rank coals were extracted by the toluene. The extent of toluene extraction will undoubtedly be different for the hydrogenated solids than for the original coals. Therefore, the amounts of un-hydrogenated coal extracted by toluene, shown in Figure 1A, can not be applied as a correction to the data for the hydrogenated solids presented in Figure 1B.

The extent of coal hydrogenation has a profound effect upon bitumen hydrocracking. Figure 1 indicates that when high rank coals are used, the reactor remains almost full of solids, whereas with low rank coals it is only half full at the end of an experiment. As the amount of solids in the reactor decreases, the liquid holdup and the liquid residence time will increase. As a result, a higher pitch conversion and a greater sulphur removal would be expected with fewer solids in the reactor. This indicates that there is a functional relationship between coal rank and bitumen hydrocracking (pitch conversion and desulphurization). The coal rank governs the amount of solids in the reactor and the amount of solids determines the liquid residence time which, in turn, controls the extent of bitumen hydrocracking. Therefore, the composition of the coal does not directly affect bitumen hydrocracking.

The elemental composition of the original coal is compared with the elemental composition of the solid residue removed from the reactor in Figure 2. The weight of ash in the reactor should remain relatively constant, since in general the ash does not participate in the reactions occurring in the solids. Therefore, the (weight of an element)/(weight of ash) ratios before and after the solids were in the reaction system can be compared to assess the chemical changes which occur in the solids. This has been done in Figure 2 using the elemental compositions obtained from the "ultimate analysis"
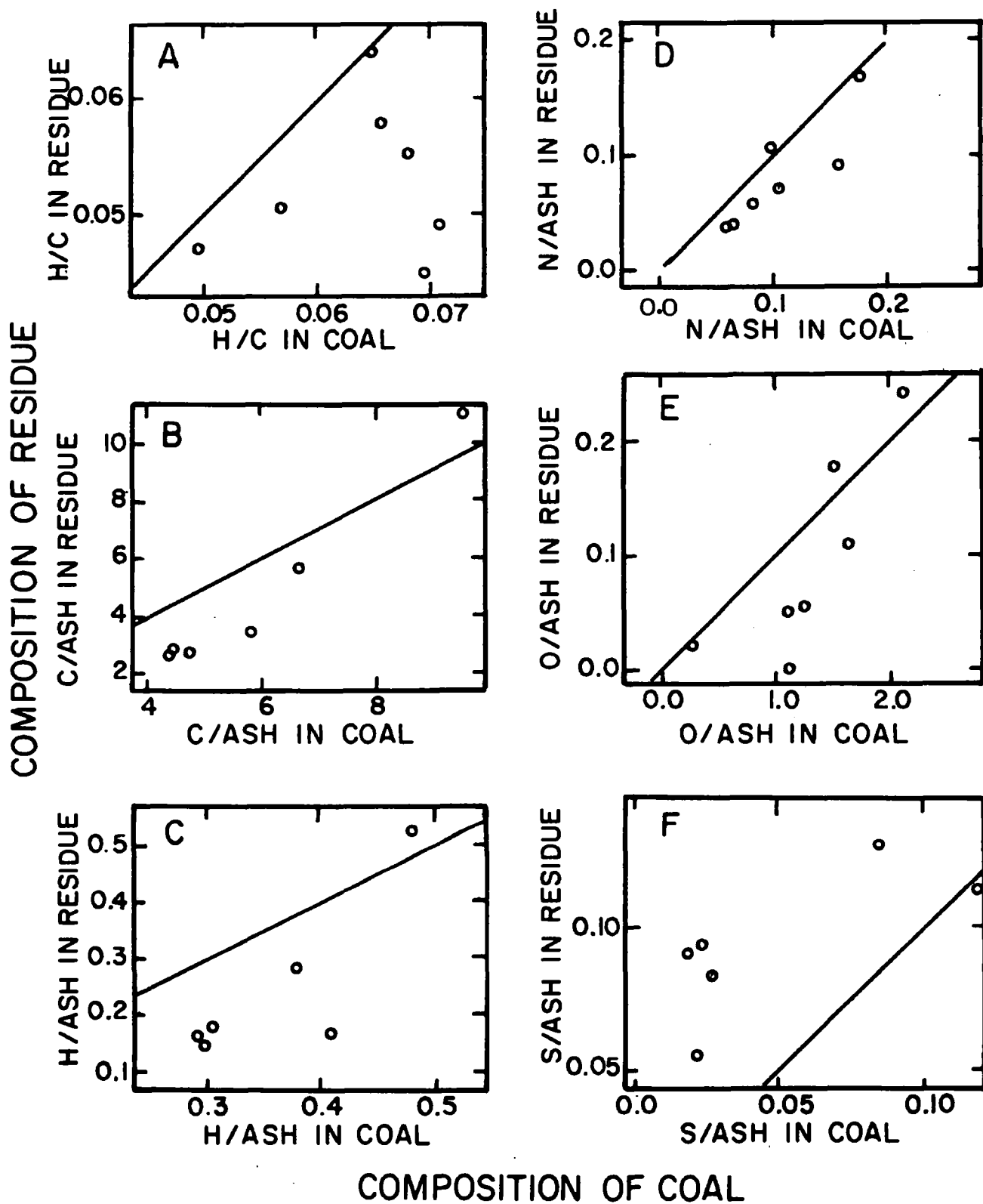
Figure 2. Comparison of the Elemental Composition of the Original Coal with the Solid Reaction Product.

procedure.  With the exception of the oxygen graph, Figure 2E, the solid lines represent ratios which are the same in the reactor residue and in the original coal.

The carbon/ash ratios and the hydrogen/ash ratios are generally lower in the reactor solid residues than in the original coals.  The only exception to this was with semi-anthracite coal, in which the least amount of hydrogenation occurred.  The carbon/ash and hydrogen/ash ratios would tend to be lower after hydrogenation, since liquid and/or gaseous hydrocarbon compounds (ash free) are formed from compounds in the coal.

Figure 2A shows that the hydrogen/carbon ratio was also lower in the solid residue than in the original coal.  This suggests that the removal of high H/C ratio material (hydrocarbon liquid and/or gas) predominated over the incorporation of gaseous hydrogen into the solid phase.  The lower H/C ratio in the reactor residue would be significant in a commercial-scale operation.  The solids removed from the reactor would either be burned directly or gasified to produce fuel.  Since hydrogen is an expensive material, its use in combustion should be minimized.  The lower H/C ratio in the reactor residue indicates that gaseous hydrogen is not being incorporated into the solids when they are present in the reactor, only to be burned subsequently when the solid residue is used for fuel.

The nitrogen, oxygen and sulphur contents of the coal solids are all affected differently by hydrogenation.  Figure 2D shows that very little change in nitrogen/ash ratio occurs.  The oxygen content decreases approximately by a factor of 10 as depicted in Figure 2E.  In contrast, Figure 2F indicates that the solids act as a getter for sulphur.  The 0.25 - 1.4 weight percent sulphur in the original coals increased to 0.8 - 2.3 weight percent in the reactor solids residues.  A higher sulphur content in the solids will augment the $SO_2$ pollution when the solids are burned.  While the sulphur content of the solids is substantial, it is still considerably below the 5-6 weight percent sulphur contained in the +975°F (797 K) pitch stream.  Any pollution system designed to process the pitch stream should also be capable of treating the reactor solids residue.

## Pitch Conversion

The extent of pitch conversion (+975°F residuum) to lower molecular weight compounds, in the presence of coal particles, is shown in Figure 3. The molecular weight reduction has been expressed in three different ways: (a) the yield of +975°F residuum on a sulphur-free basis, (b) the total yield of +975°F residuum, and (c) the conversion of +975°F residuum into other products. The data used to calculate these quantities are given in Tables 6 and 7. A linear correlation of each of these quantities with the amount of solids in the reactor was observed. This suggests that thermal hydrocracking is the predominent process and that any catalytic influence of the coal is minor. The data points corresponding to zero solids in the reactor are the ones obtained during thermal hydrocracking experiments in which no coal particles were in the reactor. The points shown as open circles were obtained in the present bench-scale study using different coals. The data points shown as solid circles were taken from the pilot plant-scale studies reported by Merrill, Logie, and Denis (8). The straight line correlation shows that conversion decreased with increasing solids in the reactor. The larger quantities of solids in the reactor correspond to smaller reactor void spaces, shorter gas and liquid residence time, and therefore lower conversions. Since the amount of solids in the reactor is related to the reaction volume available for thermal hydrocracking, it is a useful variable for comparing pitch conversion results.

The comparison in Figure 3 indicates that the thermal hydrocracking bench-scale and pilot plant-scale results for pitch conversion agree quite closely. However, some significant differences between bench-scale and pilot plant-scale results were observed. The yields of -975°F distillate tended to be somewhat lower in the bench-scale experiments. Also, substantial amounts of coke were formed during the bench-scale work whereas no coke formation was reported in the pilot plant studies. These differences in the bench-scale and pilot plant results are undoubtedly caused by different experimental conditions. For example, the hydrogen circulation rate was higher in the pilot plant experiments, 7440 sft$^3$/bbl as opposed to 5000 sft$^3$/bbl. This causes a smaller liquid holdup and therefore a shorter hydrocarbon residence time in the pilot plant reactor. In addition, the pilot plant reactor length to diameter ratio was 104
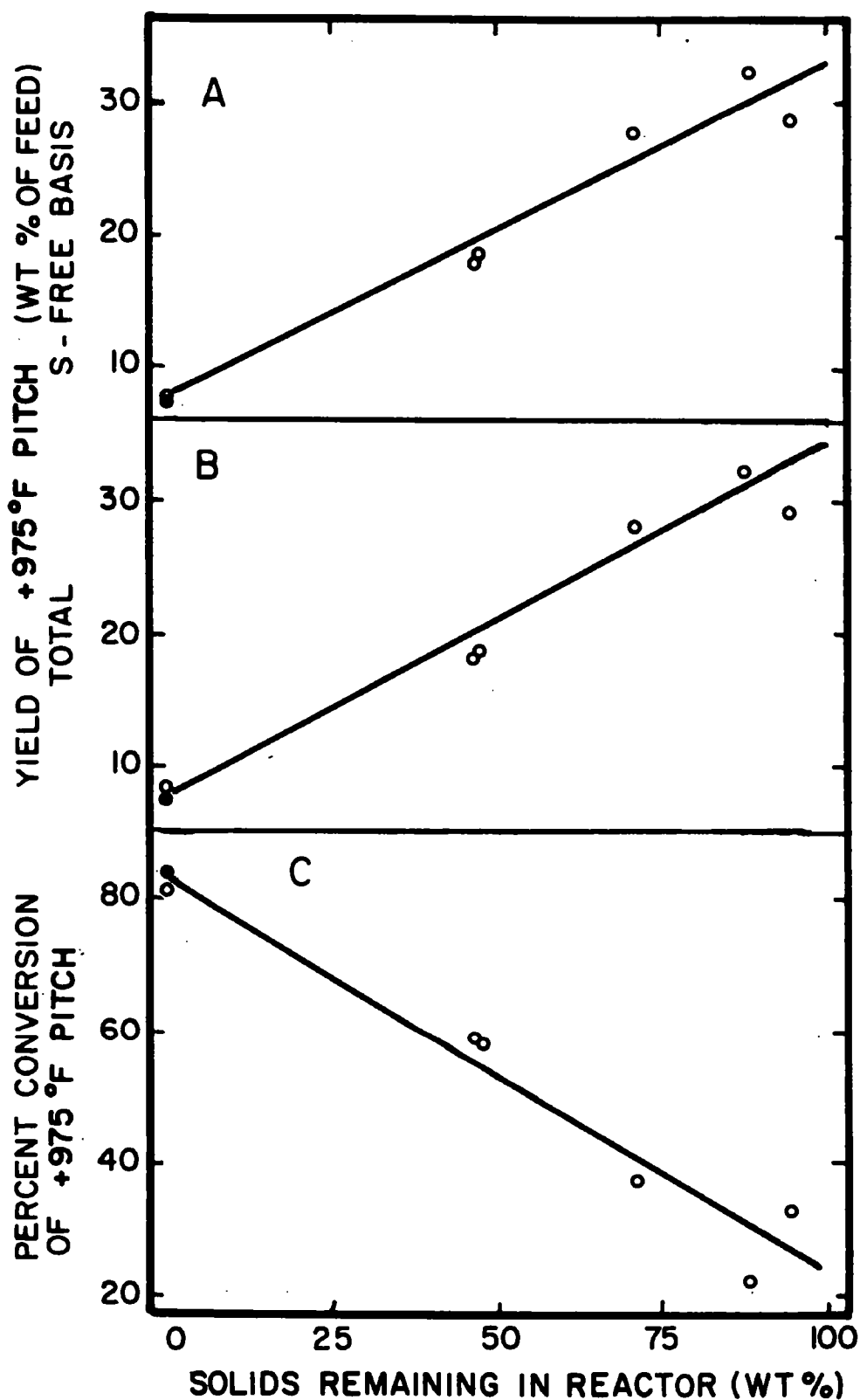
Figure 3. Pitch Hydrocracking as a Function of the Amount of Solids in the Reactor.

open circles - data from this study
solid circles - data from reference 8

TABLE 6

Analyses of Liquid Products Produced with Different Coals

| Coal Rank | Product Yield wt % of feed | Specific Gravity 60°/60°F | Sulphur wt % | Nitrogen wt % | Conradson Carbon wt % | Nickel ppm | Vanadium ppm | Iron ppm |
|---|---|---|---|---|---|---|---|---|
| Semi-anthracite | 99 | 0.978 | 3.93 | 0.30 | 12.2 | 63 | 161 | 54 |
| Medium Volatile Bituminous | 100 | 0.988 | 4.11 | 0.38 | 11.9 | 61 | 142 | 176 |
| High Volatile A Bituminous | 94 | 0.973 | 3.98 | 0.40 | 12.0 | 66 | 160 | 148 |
| Subbituminous A | — | 0.956 | 3.22 | 0.33 | 11.4 | 52 | 90 | 153 |
| Subbituminous B | 92 | 0.951 | 3.25 | 0.31 | 11.4 | 49 | 98 | 204 |
| Subbituminous C | — | 0.944 | 3.24 | 0.29 | 9.3 | 34 | 82 | 39 |
| Lignite | 88 | 0.947 | 3.23 | 0.27 | 10.9 | 37 | 82 | 142 |
| Bitumen Feedstock | — | 1.009 | 4.72 | 0.42 | 12.6 | 76 | 191 | 358 |

TABLE 7

### Analyses of Distillate Fractions
### Produced with Different Coals

| Boiling Range of °C<br>Distillate Fraction °F | | RT-100<br>RT-212 | 100-200<br>212-392 | 200-250<br>392-482 | 250-275<br>482-527 | 275-332<br>527-630 | 332-361<br>630-682 | 361-391<br>682-736 | 391-421<br>736-790 | 421-524<br>790-975 | +524<br>+975 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Coal Rank | Anaylsis | | | | | | | | | | |
| Semi-<br>Anthracite | wt% of product<br>sp gr 60°/60°F<br>wt% sulphur | 1.46<br>0.627<br>— | 5.30<br>0.761<br>1.99 | 4.93<br>0.778<br>1.99 | 5.03<br>0.793<br>2.18 | 10.91<br>0.891<br>2.56 | 8.52<br>0.917<br>2.92 | 4.30<br>0.925<br>3.16 | 7.41<br>0.936<br>3.42 | 22.98<br>0.971<br>3.80 | 29.16<br>—<br>5.57 |
| Medium<br>Volatile<br>Bituminous | wt% of product<br>sp gr 60°/60°F<br>wt% sulphur | 0.30<br>—<br>— | 3.89<br>0.765<br>1.67 | 3.96<br>0.796<br>1.83 | 4.63<br>0.826<br>2.07 | 8.82<br>0.904<br>2.34 | 9.77<br>0.932<br>2.76 | 4.11<br>0.943<br>3.02 | 7.92<br>0.954<br>3.34 | 21.82<br>0.983<br>3.77 | 34.78<br>—<br>5.62 |
| High<br>Volatile A<br>Bituminous | wt% of product<br>sp gr 60°/60°F<br>wt% sulphur | 1.47<br>0.700<br>— | 5.55<br>0.778<br>1.85 | 5.30<br>0.802<br>2.01 | 5.27<br>0.838<br>2.15 | 11.01<br>0.905<br>2.59 | 10.25<br>0.923<br>2.94 | 3.41<br>0.929<br>3.05 | 7.76<br>0.961<br>3.41 | 20.40<br>0.991<br>3.79 | 29.58<br>—<br>5.79 |
| Sub-<br>Bituminous<br>A | wt% of product<br>sp gr 60°/60°F<br>wt% sulphur | 2.25<br>0.650<br>— | 8.75<br>0.763<br>1.81 | 7.63<br>0.820<br>1.97 | 6.46<br>0.853<br>2.20 | 14.84<br>0.897<br>2.57 | 12.18<br>0.923<br>2.90 | 2.23<br>0.936<br>— | 9.00<br>0.945<br>3.12 | 15.74<br>0.989<br>3.64 | 20.91<br>—<br>5.07 |
| Sub-<br>Bituminous<br>B | wt% of product<br>sp gr 60°/60°F<br>wt% sulphur | 2.40<br>0.691<br>— | 10.10<br>0.775<br>1.66 | 8.39<br>0.830<br>1.82 | 6.49<br>0.853<br>2.26 | 13.29<br>0.899<br>2.55 | 10.97<br>0.919<br>2.79 | 5.51<br>0.922<br>3.10 | 7.87<br>0.965<br>3.25 | 14.95<br>0.981<br>3.68 | 20.06<br>—<br>5.09 |
| Sub-<br>Bituminous<br>C | wt% of product<br>sp gr 60°/60°F<br>wt% sulphur | 3.16<br>0.666<br>0.24 | 10.90<br>0.778<br>1.71 | 8.94<br>0.829<br>1.88 | 7.46<br>0.854<br>2.29 | 14.76<br>0.895<br>2.59 | 10.99<br>0.919<br>2.93 | 3.03<br>0.878<br>— | 8.45<br>0.956<br>3.13 | 14.25<br>0.979<br>3.39 | 18.06<br>—<br>5.27 |
| Lignite | wt% of product<br>sp gr 60°/60°F<br>wt% sulphur | 2.80<br>0.668<br>0.30 | 12.89<br>0.774<br>1.64 | 9.38<br>0.842<br>2.03 | 7.03<br>0.861<br>2.23 | 11.37<br>0.866<br>2.52 | 10.87<br>0.929<br>2.78 | 2.86<br>0.959<br>3.02 | 7.19<br>0.972<br>3.31 | 13.94<br>0.994<br>3.77 | 20.58<br>—<br>5.6 |
| Thermal<br>Hydro-<br>Cracking | wt% of product<br>sp gr 60°/60°F<br>wt% sulphur | 3.42<br>0.693<br>0.34 | 17.22<br>0.766<br>1.52 | 12.09<br>0.843<br>1.93 | 9.01<br>0.874<br>2.34 | 14.81<br>0.905<br>2.74 | 11.66<br>0.929<br>3.03 | 3.46<br>0.936<br>3.27 | 7.63<br>0.973<br>3.64 | 9.20<br>0.995<br>4.13 | 11.50<br>—<br>5.66 |

compared to 12 for the bench-scale reactor. As a result, the linear velocity of the hydrocarbon components is almost one order of magnitude higher in the pilot plant reactor.

Yields were calculated on a total content basis and on a sulphur-free basis. The yields of +975°F pitch are shown in Figure 3 and those for -975°F distillate and total liquid product are shown in Figure 4. The liquid yield is normally calculated by dividing the weight of sulphur-containing product by the weight of sulphur-containing feed. Since the product contained less sulphur than the feed, the desulphurization process caused some yield lowering. This was avoided by expressing yields on a sulphur-free basis. The yields could be further refined by correcting for hydrogen addition to the product, denitrogenation, and metals removed. Corrections for the latter two phenomena are insignificant, whereas the correction for hydrogen addition is appreciable. Since hydrogen consumption measurements were not made in these studies, the hydrogen addition correction could not be calculated. However, previous thermal hydrocracking studies (8) have indicated that it would be of the order of 1-2 weight percent.

The optimum hydrocracking conditions will maximize the yield of -975°F distillate. With the hydrocracking conditions used in this study, shown in Table 1, the yield increased with decreasing amount of solids in the reactor and approached 75 wt %, as shown in Figure 4B. In comparison, Merrill, Logie, and Denis (8) reported yields of 86% in their purely thermal hydrocracking studies. Higher yields might be obtained with less solids in the reactor or with lower liquid space velocities.

From a practical standpoint, the only use for the pitch and gas produced is as a process fuel. Fuel requirements have been estimated as being in the order of 18-20 weight percent of the feed. The pitch yields obtained in these experiments are shown in Figure 3B. A rough estimate of the gas yield may be obtained by subtracting the total liquid yield, shown in Figure 4A, from 100 and adding 2-3 wt % to account for hydrogen addition and other minor corrections. It is immediately apparent that the yields of gas and pitch obtained in the present experiments with coal exceed the amount required for fuel. Figure 3B indicates that the yield of pitch could be reduced by operating the reactor with a lower solids content. The yield of gas could probably be reduced by adding a catalytic material having a high hydrogenation component to the reaction system.
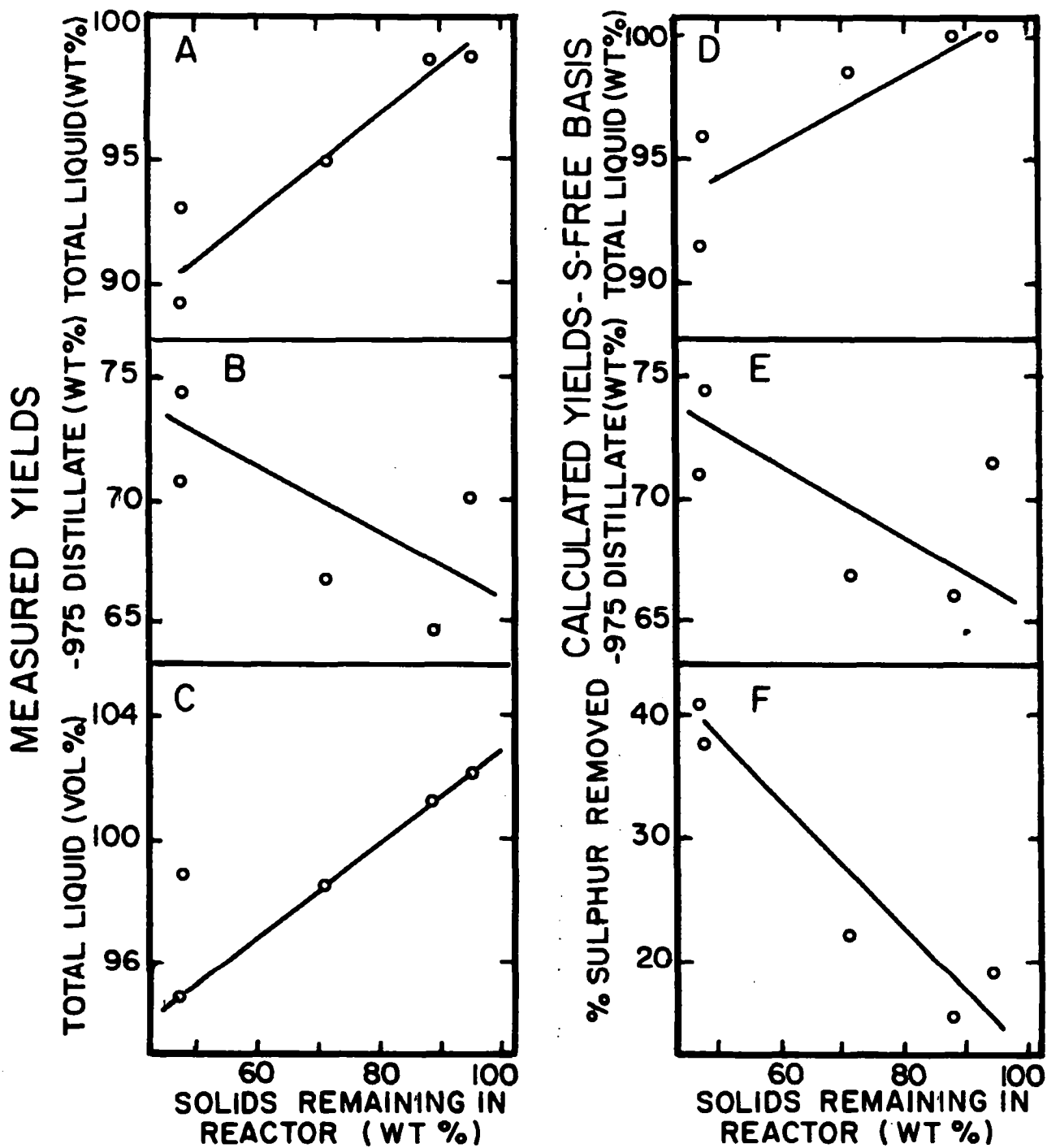
Figure 4.  Product Yields as a Function of the Amount of Solids
Remaining in the Reactor.

## Conversion of Coke Precursors

Coke formed from compounds in the bitumen (coke precursors) deactivates hydrocracking catalysts more rapidly than do metal or clay impurities. Recent experimental results (7f) indicate that the sulphur concentration, in catalytically hydrocracked bitumen, increases by 50 percent after the catalyst has been used for 30 hours. Most of this loss in hydrodesulphurization activity has been attributed to coke formation on the catalyst. In principle, the rate of catalyst decay could be decreased by converting or destroying coke precursors in the bitumen before it contacts the catalyst. The Conradson Carbon Residue (CCR) is an empirical measurement of the tendency of a hydrocarbon material to form coke. It is expected that hydrocarbon materials with lower CCR values would decrease conventional hydrocracking catalyst activity less rapidly. The results in Figure 5 suggest that the thermal hydrocracking process does destroy coke precursors. Furthermore, like pitch conversion, the reduction in CCR depends upon the extent of thermal hydrocracking (solids in the reactor).

## Metals Removal

The thermal hydrocracking process is known to produce a liquid product having a lower metals concentration than the bitumen feed stock. This phenomenon was noted in the preceding report (1) of this series, which described hydrocracking in the presence of coal particles. The purpose of adding the coal particles to the reaction system is to accumulate the metals from the liquid phase. It is hoped that the presence of coal particles will minimize the deposition of metals inside the reaction vessels and process piping. One of the objectives of the present study was to evaluate the efficiency of the coal particles as a getter for the metals. To do this the mass of metals accumulated by the solids was compared with the mass of metals removed from the liquid.

The metals concentrations in both the liquid and solid products are shown in Figure 6. For the liquid product, the metals concentrations are plotted as a function of the amount of solids which remained in the reactor.
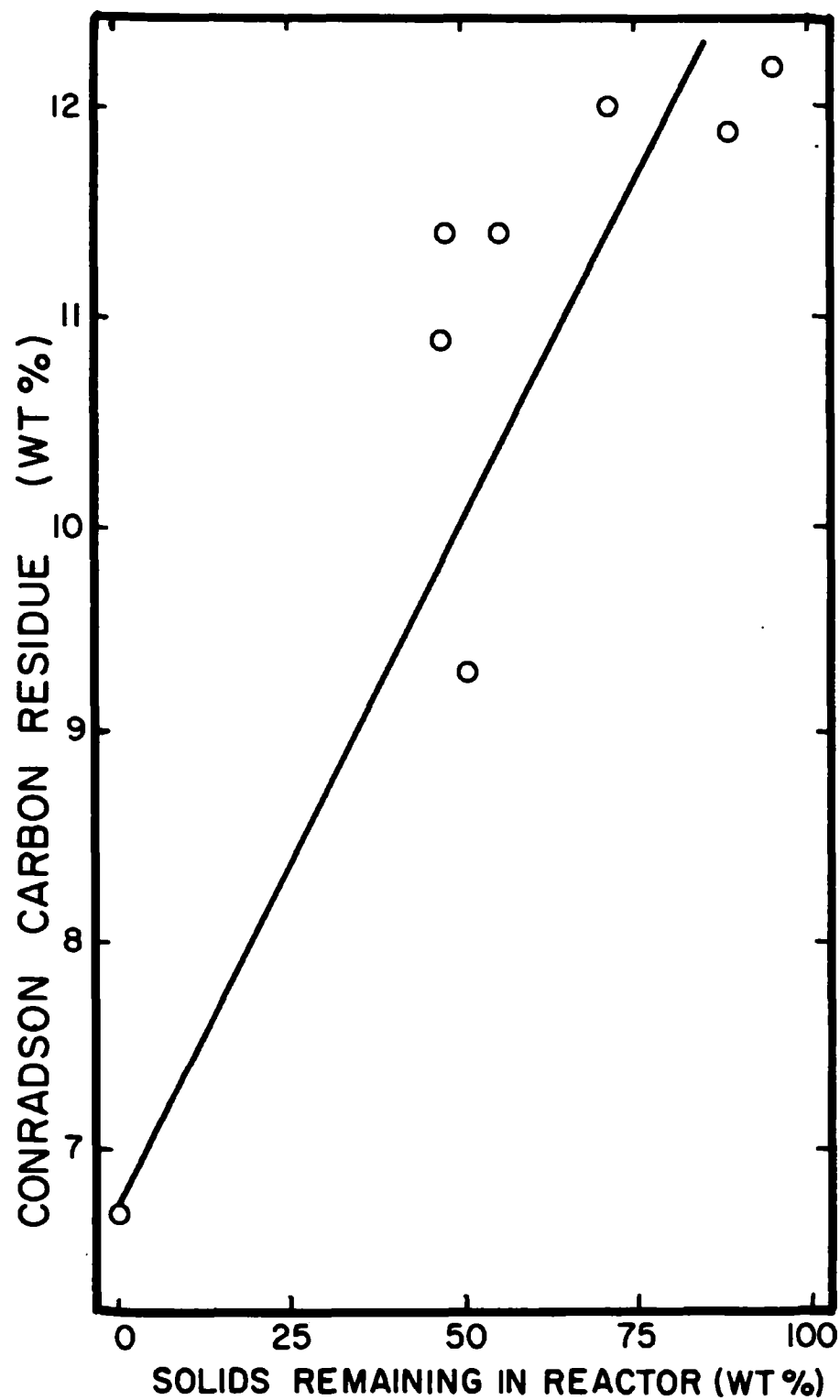
Figure 5.   Conradson Carbon Residue as a Function of the
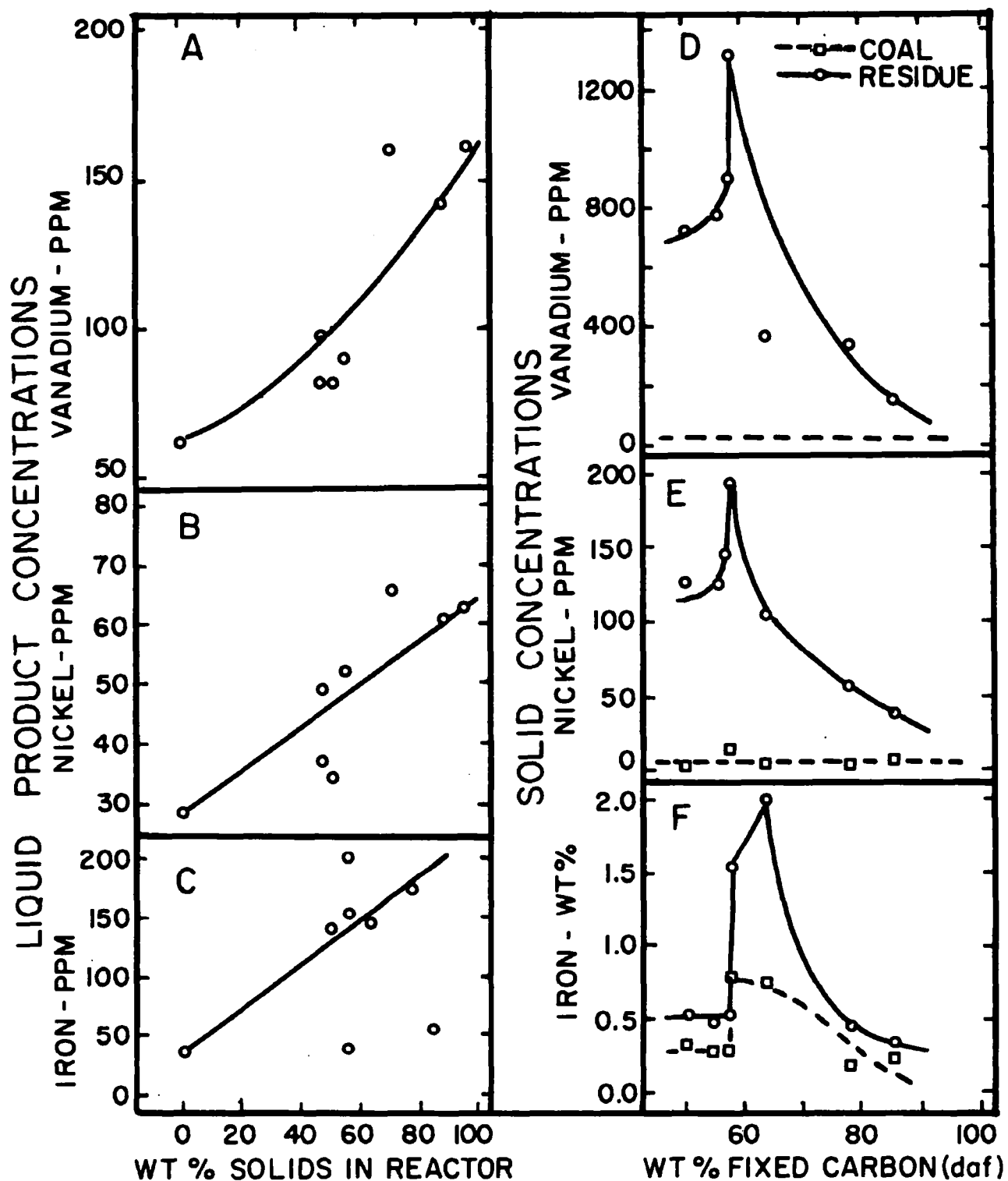Amount of Solids Remaining in the Reactor.

Figure 6.  Metal Concentrations in the Liquid Product and in the
Carbonaceous Solids Removed from the Reactor.

As discussed earlier this variable controls the extent of thermal hydrocracking. The concentrations of nickel and vanadium suggest that there is a correlation between the extent of thermal hydrocracking and metals removal. It appears that conditions which cause more thermal hydrocracking also cause a greater removal of nickel and vanadium metals. Considerably more scatter exists in the iron results. Therefore, the possibility of a relationship between thermal hydrocracking and iron removal can not be established on the basis of this data.

The scatter of the iron concentration data shown in Figure 6C may be caused by iron being present in the hydrocarbon in a different form than nickel or vanadium. Large portions of nickel and vanadium metals are thought to be present as porphyrin molecules. Orgel (22) has shown that the ligand field stabilization energy is three times higher for nickel and vanadium porphyrin structures than for iron. On this basis the number of iron porphyrin molecules should be substantially less than the nickel and vanadium ones. In fact, the concentration of iron in most conventional crude oils is an order of magnitude lower than the concentration of vanadium (21, 23). Athabasca bitumen does not follow this pattern. As may be seen in Table 3 or in the work of Scott et al (24), Athabasca bitumen contains much higher concentrations of iron. The form of iron in the bitumen has not been identified. It could exist as organometallic compounds, perhaps in structures resembling chlorophyll. Hodgson (23) has suggested that the high iron content might be due to either (a) small amounts of oil field water being retained in the sample, or (b) contamination from the steel equipment used in producing the bitumen. Another possible source would be the traces of suspended mineral matter, sand and clay, which are not removed from the bitumen in the separation process. In any event, if the iron is present in the oil in a non-hydrocarbon form, its removal from the oil would not be affected by hydrocracking porphyrin or other hydrocarbon molecules. Since the abscissa in Figure 6C is directly related to the amount of thermal hydrocracking, no correlation between it and the removal of non-hydrocarbon iron would be expected.

No correlation between thermal hydrocracking and metals concentration on the solids was found. Therefore, the metal concentration on the solids has been plotted as a function of the weight percent fixed carbon in the different coals used. Figures 6D and 6E show that both the nickel and vanadium

contents of the original coals were extremely low in comparison with the concentration of these metals in the solids removed from the reactor. In contrast, the iron content of the original coal was appreciable as shown in Figure 6F. When the metal concentrations in the solids removed from the reactor are compared with those in the original coals, the percent increase in iron is not nearly as great as the percent increases in vanadium and nickel.

A comparison of the amounts of metals removed from the liquid with the amounts accumulated by the solids is shown in Table 8. The amounts of metal removed from the liquid were calculated as follows:

$$
\begin{matrix} \text{Metal} \\ \text{Removed} \end{matrix} = \begin{pmatrix} \text{weight of} \\ \text{bitumen} \end{pmatrix} \begin{pmatrix} \text{conc. of metal} \\ \text{in solids} \end{pmatrix} - \begin{pmatrix} \text{weight of} \\ \text{liquid prod.} \end{pmatrix} \begin{pmatrix} \text{conc. of metal} \\ \text{in liquid prod.} \end{pmatrix}
$$

$$\text{Equ. (1)}$$

$$
\begin{matrix} \text{Metal} \\ \text{Accumulated} \end{matrix} = \begin{pmatrix} \text{weight of} \\ \text{solids} \\ \text{removed} \\ \text{from reac-} \\ \text{tor} \end{pmatrix} \begin{pmatrix} \text{conc. of} \\ \text{metal in} \\ \text{solids} \end{pmatrix} - \begin{pmatrix} \text{weight of} \\ \text{original} \\ \text{coal} \end{pmatrix} \begin{pmatrix} \text{conc. of} \\ \text{metal in} \\ \text{coal} \end{pmatrix}
$$

$$\text{Equ. (2)}$$

Table 8 shows that the amount of vanadium removed from the liquid is in excellent agreement with the amount accumulated by the solids. For nickel, the agreement is only fair. In general, less nickel was accumulated on the solids than was removed from the liquid. This suggests that some of the nickel may have been deposited within the reaction system. The results for iron are quite poor in all cases. One reason for this is that the weight of iron in the solids removed from the reactor is similar to the weight of iron in the original coals. When the subtraction shown in Equation (2) is performed, the possible error in the result is much higher than was the case for the vanadium and nickel metals where the two quantities were of different orders of magnitude.

TABLE 8

Material Balances on V, Ni, and Fe Metals

| ASTM RANK OF COAL | Vanadium-mg | | Nickel-mg | | Iron-mg | |
|---|---|---|---|---|---|---|
| | Removed from Liquid | Accumulated on Solids | Removed from Liquid | Accumulated on Solids | Removed from Liquid | Accumulated on Solids |
| Semi-Anthracite | 15 | 11-13 | 6.0 | 2.6 | 141 | 101 |
| Medium Volatile Bituminous | 24 | 27-30 | 6.9 | 4.6 | 84 | 205 |
| High Volatile A Bituminous | 19 | 22-24 | 6.2 | 6.2 | 101 | 605 |
| Subbituminous A | - | 71 | - | 9.4 | - | 66 |
| Subbituminous B | 47 | 40-43 | 14 | 6.4 | 78 | -33 |
| Subbituminous C | - | 35-38 | - | 5.5 | - | -30 |
| Lignite | 56 | 32-35 | 20 | 5.8 | 107 | -74 |

## The Effect of Pitch Conversion on the Removal of Coke Precursors and Metals

The fraction of pitch (+975°F residuum) in the liquid product has a significant effect on concentrations of both the metals and the coke precursors in the liquid product. Evidence for this is presented in Figure 7. As the pitch content of the liquid decreased from 45 weight percent (pitch content of the bitumen) to 20 weight percent, very little change in the Conradson Carbon values of the liquids occurred. Below 20 weight percent pitch, the Conradson Carbon Residue decreased markedly with pitch content. This would suggest that the compounds in pitch which are responsible for coke formation, as measured by Conradson Carbon Residue, are the ones which are most difficult to hydrocrack.

Linear relationships between pitch content and metals concentration in the liquid product are shown in Figure 7. The correlations for nickel and vanadium metals are quite good. The data points for iron are scattered quite markedly. All the graphical relationships in Figure 7 show that as the pitch is converted to lower boiling compounds, both metals and coke precursors are eliminated from the liquid product.

The liquid product was distilled into several fractions, and the metals contents of the two heaviest fractions, +975°F pitch and 790-975°F heavy gas oil, were measured. The results listed in Table 9 show that virtually all the metals are contained in the pitch. The concentrations of metals in the gas oil are approximately two orders of magnitude below those in the pitch. However, the pitch does not contain all of the undesirable components. For example, significant quantities of sulphur are present in most fractions distilled from the liquid product. The data in Figure 7 and in Table 9 show conclusively that the pitch fraction does contain the major portion of at least two undesirable components of the liquid product, the coke precursors and the metals. This suggests that as the proportion of pitch in the hydrocracked product decreases, the problems caused by coking and metals deposition during subsequent catalytic processing would diminish.
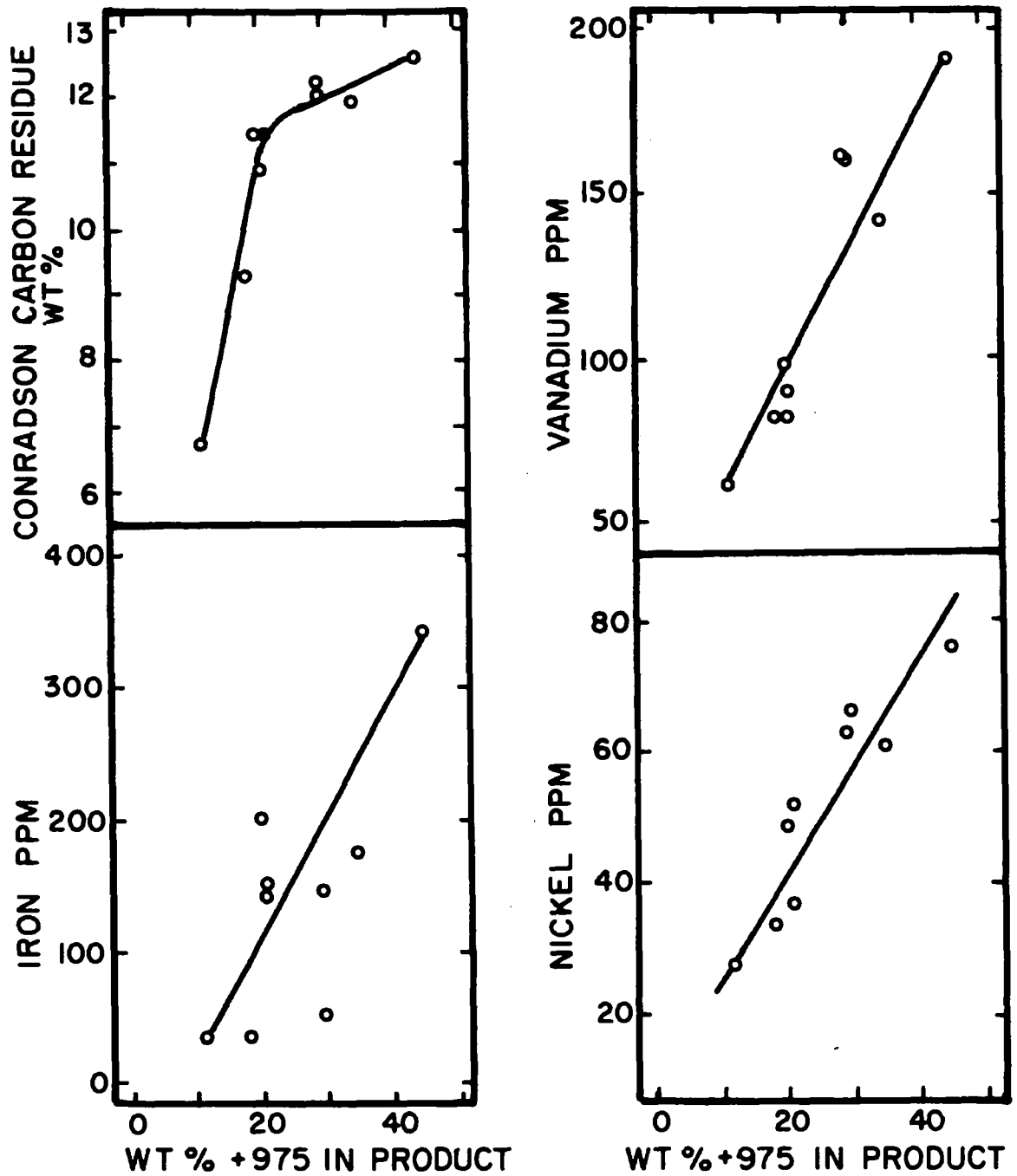
Figure 7.    Concentrations of Metals and Coke Precursors in the
             Liquid Product as a Function of the +975°F Pitch
             Content of the Liquid Product.

## TABLE 9

### Comparison of Metals and Sulphur
### in 790-975°F Gas Oil and +975°F Pitch
### Produced in the Presence of Different Coals

| | Heavy Gas Oil 790-975°F (694-797°K) | | | | Pitch +975°F (+797°K) | | | |
|---|---|---|---|---|---|---|---|---|
| | Nickel ppm | Vanadium ppm | Iron ppm | Sulphur wt % | Nickel ppm | Vanadium ppm | Iron ppm | Sulphur wt % |
| Semi-Anthracite | 1.3 | <10 | <5 | 3.80 | 193 | 977 | 870 | 5.67 |
| Medium Volatile Bituminous | 1.6 | <10 | <5 | 3.77 | 149 | 578 | 461 | 5.62 |
| High Volatile A Bituminous | 1.3 | <10 | <5 | 3.79 | 180 | 829 | 567 | 5.79 |
| Subbituminous A | 2.7 | <10 | <5 | 3.64 | 215 | 817 | 691 | 5.07 |
| Subbituminous B | 3.2 | <10 | <5 | 3.68 | 227 | 958 | 1004 | 5.09 |
| Subbituminous C | 4.6 | <10 | <5 | 3.39 | 246 | 1084 | 370 | 5.27 |
| Lignite | 2.6 | <10 | 9.7 | 3.77 | 149 | 300 | 23 | 5.38 |
| No coal (thermal hydrocracking) | 5.7 | <10 | <5 | 4.13 | 220 | 627 | 371 | 5.66 |

## Product Quality Correlations

Several possible relationships between the quality of the liquid product, i.e. specific gravity, weight percent sulphur, and weight percent nitrogen, and various characteristics of the reaction system have been examined. These variables included weight percent carbon in the coal, weight percent moisture in the coal, surface areas of both coal and residue solids, mean particle size of residue solids, and the weight percent solids in the reactor. The correlation between weight percent solids in the reactor and product quality was mentioned earlier (Figures 4B and 4F). The only other meaningful correlation involved the weight percent moisture in the coal.

The correlations of product quality with weight percent moisture are shown in Figure 8. There are at least two possible explanations for these relationships. The first relates moisture content to the amount of coal hydrogenation. The moisture content of coals used in this study, (listed in Table 4), generally increased as the coal rank decreased. The greater extent of hydrogenation occurring to low rank coals, shown in Table 5, produces a larger void space in the reactor so that a greater extent of thermal hydrocracking can occur. Thus moisture content is related to coal rank which is related to amount of coal hydrogenation, which in turn is related to the extent of the thermal hydrocracking reaction. This would suggest that there is only a functional relationship between moisture content and product quality.

The second possible explanation relates moisture to solid surface area. Under reaction conditions the coal is dehydrated. Therefore, high moisture coals might have the greatest internal pore volume. If all coals had pores of the same diameter, then the ones with the greatest pore volume would also have the greatest surface area and presumably more reaction would occur on the high surface area solids. Solid surface areas were measured using the point B variation of the BET method in an attempt to establish a correlation. The data indicated that there was no simple relationship between moisture and surface area. Undoubtedly, different coals have pores of different diameters. This means that a coal having large pore diameters can have a high void volume and still have a relatively low surface area. Thus the first explanation relating moisture content to reactor void space seems more plausible.
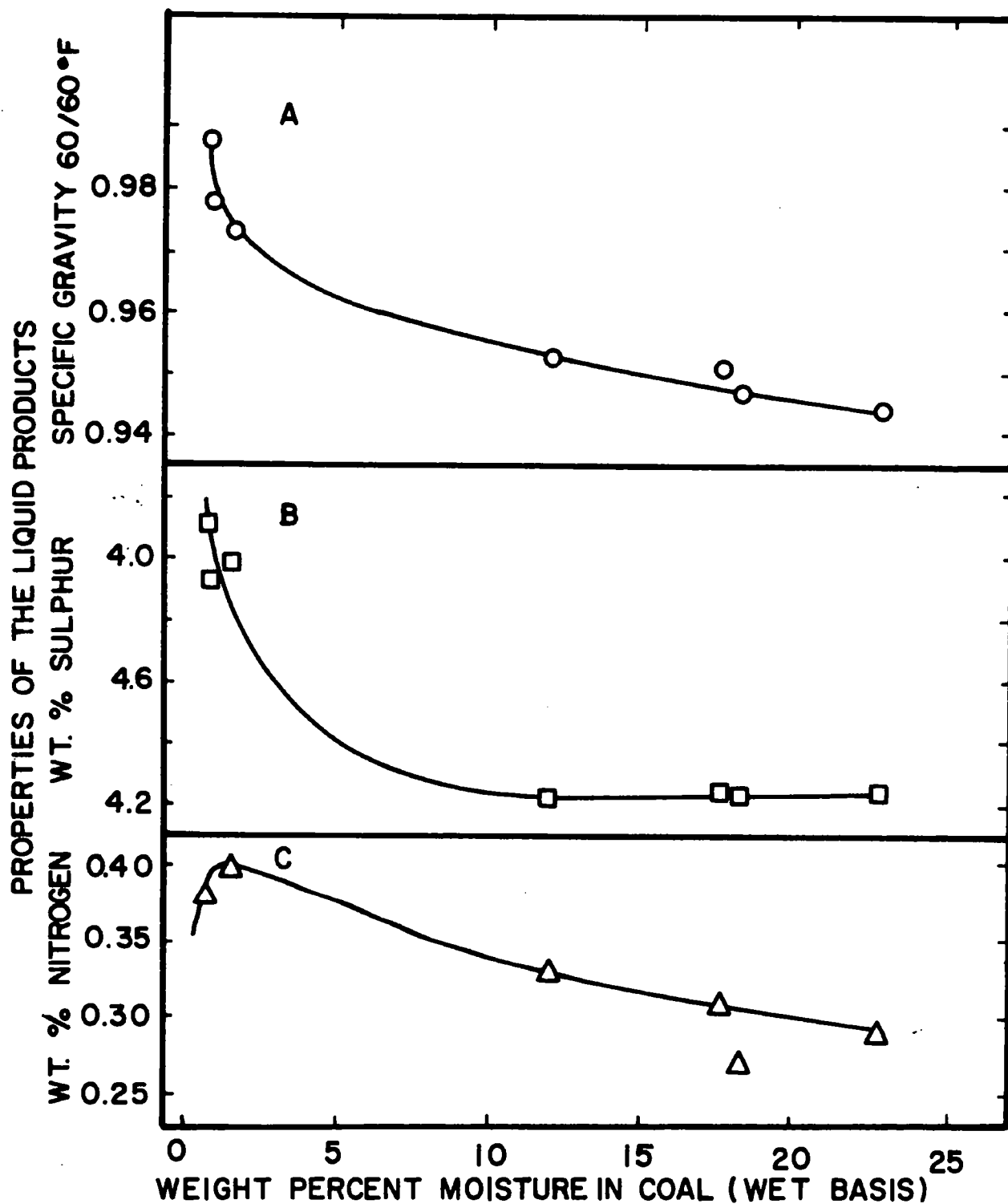
Figure 8.  Properties of the Liquid Product as a Function of Coal Moisture Content.

## CONCLUSIONS

The experimental findings reported here are summarized below:

1. Low rank coals are hydrogenated to a greater extent than high rank coals.

2. As more coal was hydrogenated, a greater reactor void volume was created, thus pitch hydrocracking, desulphurization and other reactions occurred to a greater extent with low rank coals than with high rank coals.

3. Changes in the composition of the solids caused by chemical reaction were as follows: The oxygen content was lowered by a factor of ten. The hydrogen and carbon contents were lowered, the hydrogen to a greater extent than the carbon. The nitrogen content remained about the same and the sulphur content increased.

4. The coking tendency of the liquid product, as measured by Conradson Carbon Residue, produced in the presence of low rank coals was considerably less than that produced using high rank coals.

5. Essentially all the vanadium metal removed from the liquid was accumulated on the solids. In contrast only a portion of the nickel metal removed from the liquid was deposited on the solids.

6. The concentrations of coke precursors and metals in the liquid were found to be directly related to the $+975^\circ$F pitch content of the liquid. The very low metals concentrations in the heavy gas oil fractions (790-975$^\circ$F) suggest that almost all of the metals could be removed by hydrocracking all of the $+975^\circ$F pitch. Of course this would require some means to prevent the undesirable deposition of metals in the reaction system.

## ACKNOWLEDGEMENTS

## REFERENCES

1.	M. Ternan, B.N. Nandi and B.I. Parsons, "Hydrocracking Bitumen in the Presence of Coal, Part 1:  A Preliminary Study of Changes Occurring in the Coal", Mines Branch Research Report R-276, Department of Energy, Mines and Resources, Ottawa (1974).

2.	F.K. North, Chemistry in Canada, 26 (10), Nov. 1974, p  5.

3.	D.N. Clay, "The Contribution of Alberta's Tar and Heavy Oil Sands to Canada's Intermediate-Term Oil Supply", Research Branch Background Paper MR-3, Library of Parliament, Ottawa (1974).

4.(a) W.L. Nelson, "Petroleum Refinery Engineering", 4th ed., McGraw Hill, New York, 1958, p  14.

  (b) G.A. Purdy, "Petroleum, Prehistoric to Petrochemicals", Copp Clark, Toronto, 1958, p  76.

5.	G.F. Andrews, H.M. Lewis and E.W. Dobson, Am. Chem. Soc., Div. Petrol. Chem., Preprints 13(2), F5(1968).

6.	G.R. Gray, AIChE Symposium Series, 69 (127), 99 (1973).

7.  E.C. McColgan, P.S. Soutar and B.I. Parsons, "The Hydrocracking of Residual Oils and Tars", Department of Energy, Mines and Resources, Ottawa
    (a) Part 1: Mines Branch Research Report R-246 (1971)
    (b) Part 2: Mines Branch Research Report R-253 (1972)
    (c) Part 3: Mines Branch Research Report R-256 (1973)
    (d) Part 4: Mines Branch Research Report R-261 (1973)
    (e) Part 5: Mines Branch Research Report R-263 (1973)
    (f) Part 6: Mines Branch Research Report R-273 (1974)

8.  W.H. Merrill, R.B. Logie and J.M. Denis, "A Pilot Scale Investigation of Thermal Hydrocracking of Athabasca Bitumen", Mines Branch Research Report R-281, Department of Energy, Mines and Resources, Ottawa (1974).

9.  B.N. Nandi, M. Ternan, B.I. Parsons and D.S. Montgomery, Fuel, 54, 197 (1975).

10. R.H. Perry and C.H. Chilton, "Chemical Engineers' Handbook", 5th ed., McGraw Hill, New York, 1973, pp 22-48.

11. ibid, pp 21-40.

12. N.A.C. Smith, H.M. Smith, O.C. Blade and E.L. Garton, "The Bureau of Mines Routine Method for the Analysis of Crude Petroleum", U.S. Bureau of Mines, Bulletin 490 (1951).

13. R.B. Smith, T. Dresser, H.F. Hopp and T.H. Paulsen, Ind. Eng. Chem., 43, 776 (1951).

14. G. Frechette, J.C. Herbert, T.P. Thinh and Y.A. Miron, Hydrocarbon Processing, 54 (2), 109 (1975).

15. L.A. Fabbro, L.A. Filachek, R.L. Iannacone, R.T. Moore, R.J. Joyce, Y. Takahashi and M.E. Riddle, Anal. Chem.; 43, 1671 (1971).

16.   S.J. Gregg and K.S.W. Sing, "Adsorption, Surface Area, and
      Porosity", Academic Press, London and New York, 1967, p 339.

17.   ibid, p 54.

18.   K.A. Clark, Trans. Can. Inst. Mining Met., 47, 257(1944).

19.   W.R.K. Wu and H.H. Storch, "Hydrogenation of Coal and Tar",
      U.S. Department of the Interior, Bulletin 633  (1968).

20.   G.W. Hodgson, B.L. Baker and E. Peake, "Geochemistry of
      Porphyrins", in Fundamental Aspects of Petroleum Geochemistry
      (eds. B. Nagy and V. Colombo), Elsevier, Amsterdam, 1967, p 250.

21.   ibid, p 212.

22.   L.E. Orgel, "An Introduction to Transition Metal Chemistry -
      Ligard Field Theory", Wiley, New York, 1960, p 180.

23.   G.W. Hodgson, Bull. Am. Assoc. Petrol. Geologists, 38,
      2537 (1954).

24.   J. Scott, G.A. Collins and G.W. Hodgson, Trans. Canadian
      Inst. Min. Met., 57, 34(1954).

## HELP PLEASE!

Please assess this report, Number_____

| | | |
|---|---|---|
| Report useful - | Yes____ | No____ |
| Report pertinent to an industry problem - | Yes____ | No____ |
| Subject is of high priority - | Yes____ | No____ |

Comments:_____

_____

_____


Mail to:    CANMET Editor, E. M. & R.
            Room 340
            555 Booth Street
            Ottawa, Ontario
            K1A 0G1

Recent CANMET publications available through Information Canada (addresses on inside front cover) or from CANMET Publications Office, 555 Booth Street, Ottawa, K1A 0G1

## CANMET Scientific Bulletin Series

CM 75-2    Relationship between dynamic and static low-temperature disintergration test; by J. T. Price & D. A. Reeve; Cat. No. M38-9/75-2; Price $0.50 Canada, $0.60 other countries.

CM 75-3    The determination of lead in ore slurries by gamma-ray attenuation; by T. R. Churchill, J. L. Dalton & H. P. Dobbs; Cat. No. M38-9/75-3; Price $0.50 Canada, $0.60 other countries.

CM 75-4    The determination of low concentrations of uranium in ores and solid mill products by X-Ray fluorescence spectrometry; by J. B. Zimmerman & V. Reynolds; Cat. No. M38-9/75-4; Price $0.50 Canada, $0.60 other countries.

CM 75-7    Reverse Osmosis for the treatment of metal waste solutions; by V. S. Sastri; Cat. No. M38-9/75-7; Price $0.50 Canada, $0.60 other countries.

## CANMET Miscellaneous Reports

DS 75-2    (INFO) Catalogue of scientific and technical papers published by the staff of the Canada Centre for Mineral and Energy Technology (formerly Mines Branch) during 1974; Cat. No. M2-1/1975; Price $1.00 Canada, $1.20 other countries.

## CANMET Laboratories' reports

MRP/MSL 75-21 (IR)  Mineralogical investigation of ores from the Kidd Creek deposit of Texas Gulf Sulphur; by W. Petruk & D. D. Owens; Cat. No. M38-10/75-21; Price $0.75 Canada, $0.90 other countries.

MRP/MSL 75-25 (LS)  Certified and provisional reference materials available from the Canada Centre for Mineral and Energy Technology as of 1975; compiled by G. H. Faye; Cat. No. M38-10/75-25; Price $0.75 Canada, $0.90 other countries.

MRP/MSL 75-29 (TR)  Gold ore, MA-1:  Its characterization and preparation for use as a certified reference material; compiled by G. H. Faye, W. S. Bowman & R. Sutarno; Cat. No. M38-10/75-29; Price $0.50 Canada, $0.60 other countries.

MRP/MSL 75-36 (IR)  Mineralogical and textural study of ores from the Copper Mountain area, south-central British Columbia; by A. E. Johnson; Cat. No. M38-10/75-36; Price $0.50 Canada, $0.60 other countries.