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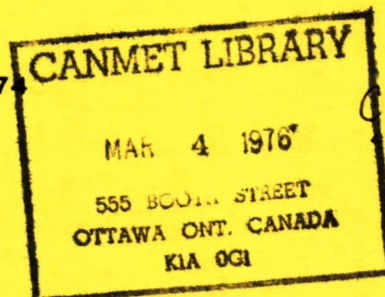
DEPARTMENT OF  
ENERGY, MINES AND RESOURCES  
MINES BRANCH  
OTTAWA

*HYDROCRACKING ATHABASCA BITUMEN  
IN THE PRESENCE OF COAL  
PART 1: A PRELIMINARY STUDY OF THE  
CHANGES OCCURRING IN THE COAL*

M. TERNAN, B. N. NANDI AND B. I. PARSONS

FUELS RESEARCH CENTRE

OCTOBER 1974



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MINES BRANCH RESEARCH REPORT R 276

HYDROCRACKING ATHABASCA BITUMEN IN THE PRESENCE OF COAL  
PART 1: A PRELIMINARY STUDY OF THE CHANGES OCCURRING IN THE COAL

by

M. Ternan\*, B.N. Nandi\* and B.I. Parsons\*

ABSTRACT

The following is the first in a series of reports on the use of pulverized coal as a processing aid, or "getter" for petroleum coke and metals in the liquid phase hydrocracking of Athabasca bitumen. This part describes a preliminary investigation of the changes which occur in two coals during the hydrocracking process. The coals selected for study were of widely dissimilar rank, i.e. Cammore semi-anthracite and Estevan lignite. The hydrocracking experiments were undertaken with Athabasca bitumen at 2000 psi pressure in a bench-scale, fixed-bed flow system with bottom feed at a liquid space velocity of  $1.05 \text{ hr}^{-1}$ . It was found that both coals are partially hydrogenated to form liquid and gaseous products at the reaction temperatures required to hydrocrack the bitumen. The solids remaining in the reactor decrease in mass and particle size as the reaction time increases. Within limits, the size of the coal particles initially placed in the reactor did not affect the hydrocracking of the bitumen. It was not possible to work with fixed beds of very small particles because of plugging problems. Positive evidence was obtained to indicate that coal particles can act as nuclei for the accumulation of petroleum coke formed in the hydrocracking process. The data also showed that nickel and vanadium metals were removed from the hydrocarbon liquid.

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*\*Research Scientists, Energy Research Laboratories, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada.*

Direction des Mines  
Rapport de recherche R 276

L'HYDROCRAQUAGE DE BITUME DE L'ATHABASCA DANS DU CHARBON

1ère partie: ETUDE PRELIMINAIRE DES  
CHANGEMENTS PRODUITS DANS LE CHARBON

par

M. Ternan\*, B.N. Nandi\* et B.I. Parsons\*

RESUME

Le présent rapport est le premier d'une série sur l'utilisation du charbon pulvérisé comme méthode additionnelle, ou getter, pour enlever le coke de pétrole et les métaux du système de réaction pendant la phase liquide de l'hydrocraquage de bitume de l'Athabasca. Cette partie décrit les changements qui se produisent dans deux types de charbon pendant le processus d'hydrocraquage. Les types du charbon sélectionnés pour l'étude étaient de classe très différente i.e. semi-anthracite de Canmore et lignite d'Estevan. Les expériences d'hydrocraquage ont été faites, en laboratoire, avec du bitume de l'Athabasca à 2,000 lbs/po<sup>2</sup> de pression avec un système d'écoulement à lit fixe avec un réacteur d'alimentation par le bas à une vitesse spatiale liquide horaire de 1.05. On a découvert qu'aux températures de réaction requises pour hydrocraquer le bitume, les deux types de charbon sont hydrogénés partiellement et forment des produits liquides et gazeux. Les particules solides qui demeurent dans le réacteur diminuent de masse et de dimension à mesure que le temps de réaction augmente. Dans une certaine limite, la dimension des particules placées dans le réacteur au début de l'opération, n'a pas influé sur l'hydrocraquage du bitume. Il a été impossible d'utiliser des petites particules dans des lits fixes à cause des problèmes de colmatage. On a obtenu des preuves indiquant que les particules du charbon peuvent agir comme noyaux pour l'accumulation de coke de pétrole formé pendant l'hydrocraquage. Les données ont démontré que les métaux de nickel et de vanadium ont été retirés de l'hydrocarbure liquide.

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## INTRODUCTION

A program of research has been initiated at the Energy Research Laboratories on the use of coal as a processing aid, "getter", and catalyst for the liquid phase hydrocracking of Athabasca bitumen. The main objectives are to increase the conversion levels attainable by hydrocracking (up to 95%) and to maximize the yield of liquid distillate fuels that can be produced from oil sands bitumen. Whereas the experimental work is directed specifically at the bitumen from the Athabasca area, it is expected that any improvement in technology that is developed will also be applicable to bitumens from the Peace River, Cold Lake and Lloydminster reserves. Very briefly, the background to the research program is as follows:

Bitumen from the oil sands is a heavy, viscous, tarry material containing high concentrations of chemically combined impurities such as sulphur, nitrogen, nickel and vanadium and as much as 1 to 2% colloidal clay. Extensive refining and upgrading is required to convert it to conventional fuels (diesel fuel, domestic furnace oil, etc.). Basically, the refining and upgrading consist of:

- (a) cracking processes to reduce molecular weight (to convert the residuum to distillate fractions), and
- (b) hydrogenation processes to stabilize the hydrocarbon fractions produced in the cracking stage and to remove sulphur and nitrogen impurities.

The only commercial operation in the Athabasca Oil Sands at the present time accomplishes the cracking phase of the upgrading process by delayed coking (1). The clay and metals impurities remain in the coke, and the coker distillate fractions are hydrogen treated in a second step. The quality of the synthetic crude generated by this technique is good but the yield is low. Delayed coking of the bitumen typically produces 22 weight percent coke and 8 weight percent gas (2). A reasonable average for the proportion of the bitumen feed required to generate the energy needed in a mining-type oil sands operation is 18-20 weight percent. This is considerably less than the 30 weight percent of gas and coke produced by delayed coking,



and as a result hundreds of tons of excess coke are being jettisoned per day.

Recently proposed processing sequences (3, 4) attempt to bring the coke and gas production more into line with that required by using fluidized coking. Pilot plant studies indicate that the fluid coking process would produce only 10 weight percent coke and approximately 13 weight percent gas. However, since the construction of the first oil sands processing plant, legislation has been enacted which precludes emissions commonly associated with the burning of high sulphur coke or residua from any source (5). Despite the obvious advantages of fluid coking over delayed coking, the technology to burn directly or to gasify the fluid coke and meet the environmental standards for sulphur emissions has not yet been commercially proven. Hence, the processing sequences based on fluid coking still entail massive "stockpiles" of jettisoned coke.

With a view to circumventing the problems connected with the gasification of high sulphur coke (as well as increasing still further the liquid yield of product), the Energy Research Laboratories have developed a thermal hydrocracking process for reducing the molecular weight of the bitumen (6, 7, 8). In this process the separated bitumen is hydrocracked in the liquid phase at pressures of the order of 1500-2000 psi in a continuous flow pipe reactor. A considerable proportion of the hydrogen required for the reduction of the molecular weight comes from the gaseous atmosphere, less hydrocarbon gas is produced and the yield of liquid distillate product is greater than that produced in fluid coking. Pilot scale experiments have demonstrated conversion levels of residuum of the order of 85-90% (the initial residuum content of the bitumen feed stock is 50 weight percent +975°F). Most important, the dregs stream from the hydrocracking process is produced as a high temperature pitch and, as such, is compatible with existing gasification technology (9, 10).

Ideally, the objective for thermal hydrocracking is to achieve conversion levels so great (say 95%) that it would then become possible to meet the sulphur emissions specifications for a direct-fired boiler system by simply blending the small dregs stream with a low-sulphur gas oil (the blend-back system currently practiced in many refineries for the production of low-

sulphur commercial fuel oils). Conversion levels of the order of 95% have been attained in the pilot plant (8) at the Energy Research Laboratories, but not without some difficulties being encountered with coke formation and metals losses. Evidence available at this time indicates the possibility of a slow but steady build-up of solids in the reaction system at conversion levels in excess of 90%.

The present program of adding coal to the hydrocracking system for Athabasca bitumen is aimed directly at resolving the problem of metals losses and sludge accumulation at high conversion levels. It is proposed to add a small quantity of pulverized coal to the feed bitumen to act as a "getter" for the metals and coke formed. The density of the coal relative to the oil is such that it will wash out of the reaction system, hopefully carrying with it the problem material. In addition to a getter-type action there is the very real possibility of a selective catalytic action by the coal (based either on the mineral content of the coal or on components deliberately added). There is also the possibility of some hydrogenation of the coal taking place, which would add to the liquid yield of the process, and of the use of the unreacted coal in the energy generation system for the plant\*. The following work is a preliminary examination of the prospects for all of these actions. It is expected that both the physical form and the rank of the coal will be important factors in the success or failure of the concept. Two western Canadian coals of widely dissimilar rank were selected for study, i.e. Canmore semi-anthracite and Estevan lignite.

#### EXPERIMENTAL

##### Apparatus

All of the experiments were undertaken in an existing bench-scale flow system originally designed to evaluate catalyst performance (15).

---

\*The hydrogenation of coal has been studied many times. An extensive coal hydrogenation industry was developed in Germany during the second World War (11). Numerous pilot scale and bench-scale investigations have been undertaken by the U.S. Bureau of Mines (12, 13) and the Canadian Mines Branch (14). While all of this work cannot be related to the present study, some of the previous findings are applicable.

A schematic diagram of the flow system is shown in Figure 1, and an assembly drawing of the reaction vessel is shown in Figure 2. The major equipment items were the hydrogen storage vessel (5 litres volume), the liquid feed pump (a proportioning pump manufactured by the Ruska Instrument Co. of Houston, Texas) and two receiver vessels. The system was fabricated from type 316 stainless steel and was designed for operation at pressures up to 10,000 psi (69 MPa). The internal volume of the reaction vessel was 150 ml. The reactor was heated electrically with "Calrod" type heating cable, <sup>— wall heater</sup> and the temperature regulated by means of a galvanometer-type controller operating on a chromel-alumel thermocouple in contact with the exterior surface. The temperature profile along the length of the inside of the reactor was measured by moving a fine-wire thermocouple up and down a central well. The interior reactor temperature was monitored continuously on a strip chart recorder. Typical temperature profiles are shown in Figure 3. All liquid lines, pumping heads, and receiver vessels were traced with electric heating cable and heated to 80-100°C to reduce the viscosity (and improve the flow characteristics) of the feed bitumen and products.

Most of the experiments were made at 2000 psi. Electrolytic hydrogen was obtained from an adjacent pilot plant facility at 3000 psi and regulated to the desired operating pressure downstream of the storage vessel. The hydrogen stream, mixed with the bitumen from the liquid feed pump, passed through a preheater and entered the reactor at the bottom. The mixture flowed upwards through a fixed bed of coal particles inside the reactor. The reaction products flowed from the reactor vessel into one or the other of the two receiver vessels where the gases and liquids were separated. In the course of a usual experiment, the products from the reactor were passed into one of the receivers until steady-state conditions were attained, then the flow was switched for a three-hour sampling period to the second receiver. At the end of the test the flow was diverted back to the first receiver during the cooling down period. In this way a sample representative of specific reaction conditions was collected in the second receiver. The gases and vapours flowed from the top of the receiver vessels, through a metering valve to a caustic scrubber (to remove H<sub>2</sub>S), through a wet test meter, and finally to the atmosphere. No attempt was made to recycle the hydrogen in any of the experiments.

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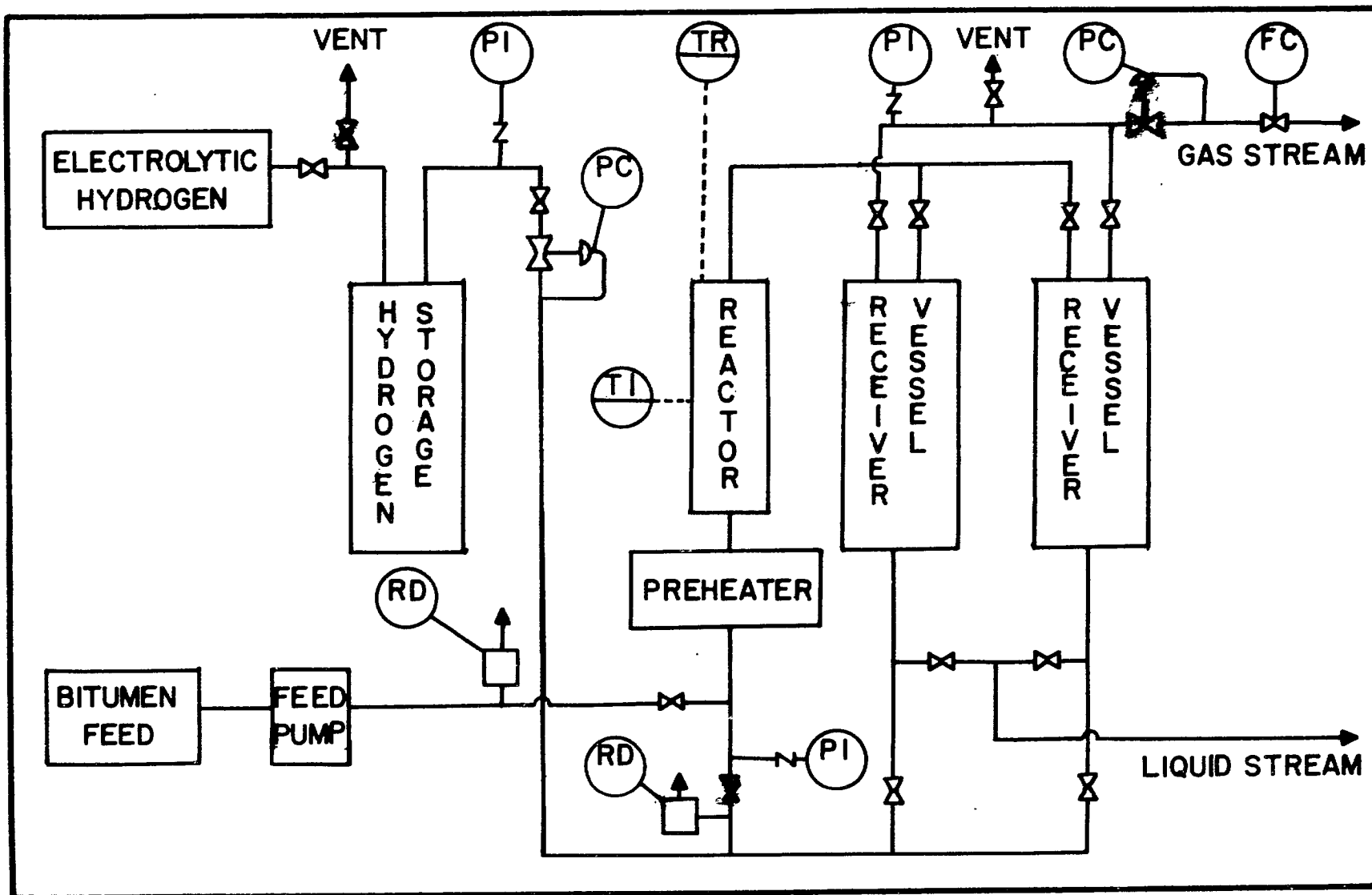


Figure 1. Process flow diagram.

PI = pressure indicator  
 PC = pressure controller  
 RD = rupture disc

TI = temperature indicator  
 TR = temperature recorder  
 FC = flow controller

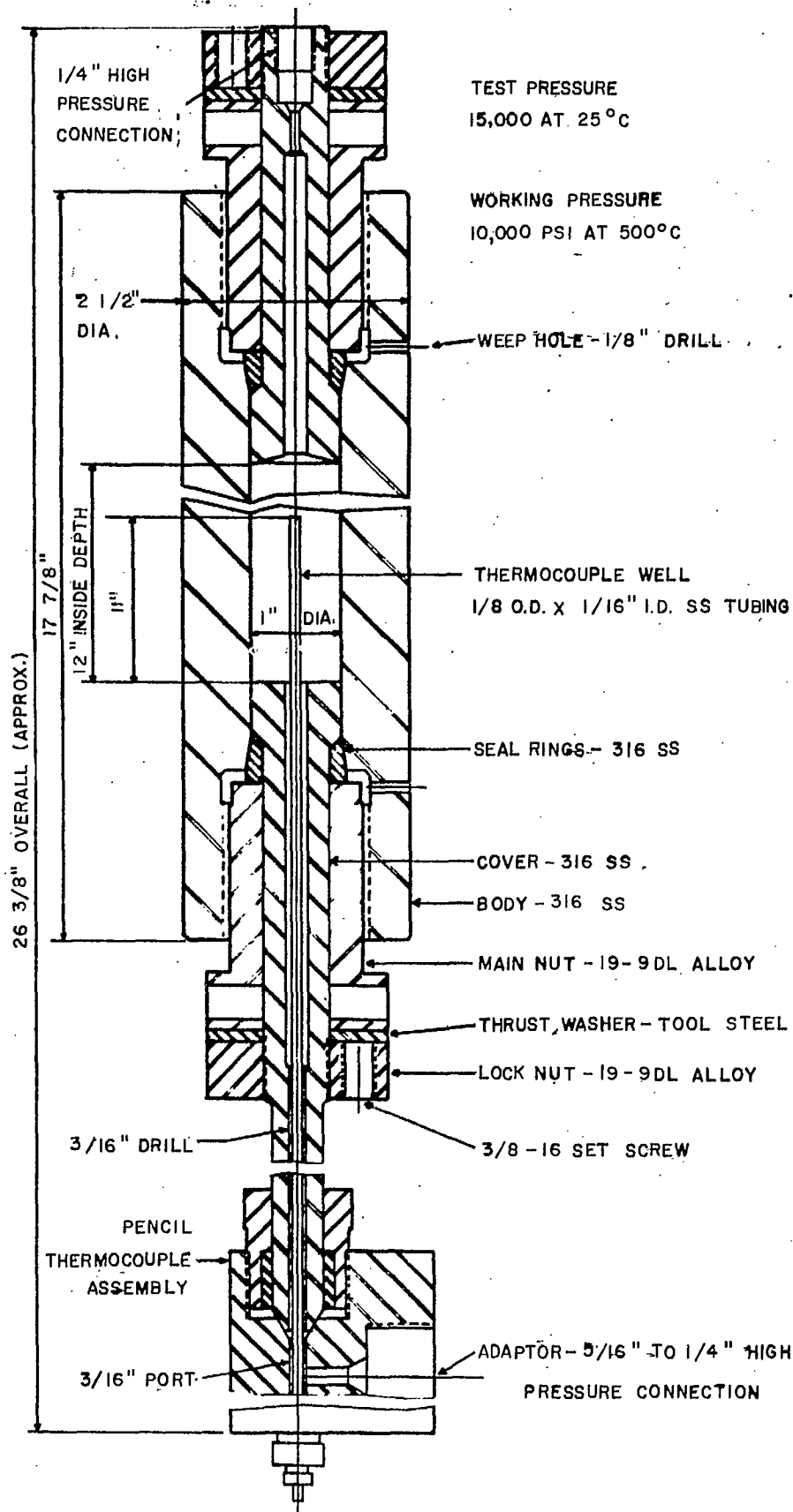


Figure 2. Reaction vessel.

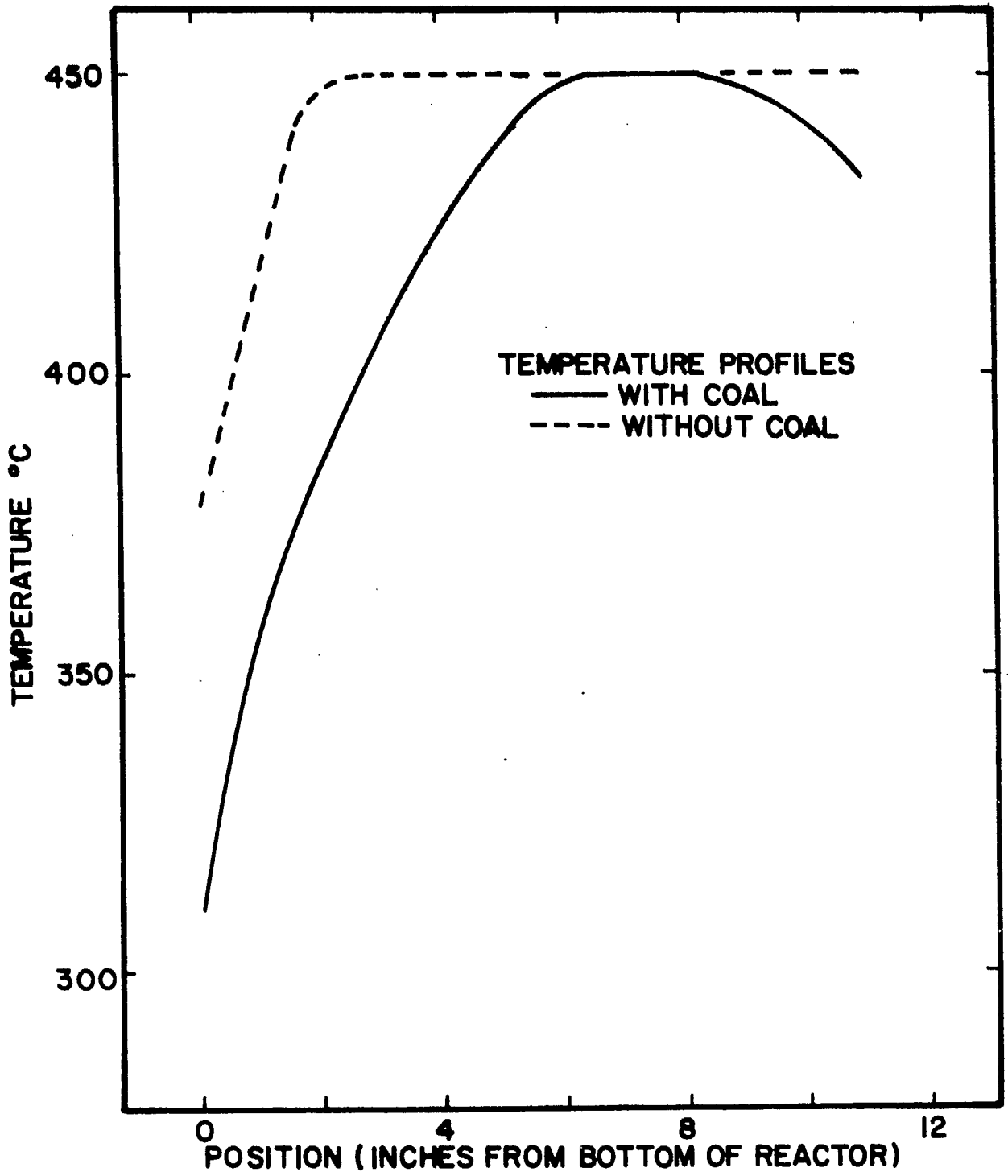


Figure 3. Reactor temperature profiles.

General Operating Procedure

The conditions and method used in the hydrocracking experiments were standardized as much as possible. The major change in each experiment was in the type (rank) and particle size of the coal loaded into the test reactor. The hydrocracking reaction conditions are listed in Table 1. To begin the experiment the reactor was filled with a particular type and size of coal, pressurized to 2000 psi, and the hydrogen flow initiated. Approximately one and a half hours were required to bring the reactor system up to standard temperature and achieve steady-state conditions. The flow of bitumen to the reactor was begun as the coal temperature approached 250°C. Product was collected at standard conditions for three hours, then the reactor system was allowed to cool. At approximately 375-350°C the flow of bitumen feed and hydrogen was stopped and the reactor depressurized and drained as quickly as possible. The solids remaining in the reactor were removed carefully and subjected to a toluene extraction in a Soxhlet apparatus to remove adhering bitumen and liquid hydrocarbon products. The solids were vacuum dried and finally weighed.

Table 1  
Hydrocracking Reaction Conditions

Temperature .....	450°C (723°K) (842°F)
Pressure .....	2000 psig (13.9 M Pa)
H <sub>2</sub> flowrate .....	5000 scf/bbl (0.0359 l/sec)
Bitumen flowrate (at 60°F) .....	153.6 ml/hr (42.7 ml/ks)
Liquid Space Velocity .....	1.0 hr <sup>-1</sup> (0.28 ks <sup>-1</sup> )

Some deviation from the above procedure was necessary in selected cases. For example, in the experiments undertaken to determine the effect of reaction time, the reactor was not depressurized until the end of a series of tests. Any other deviation from the standard procedure will be mentioned at the appropriate place in the discussion of the experimental results.

### Analytical Procedures

Several different analytical techniques were employed. Specific gravity was measured using a hand hydrometer (16). Particle size was measured using screens (17) conforming to the U.S. Standard Sieve Series. The procedure used to determine proximate analyses of solids was the ASTM D-271 method, which has been outlined by Griswold (18). A brief description of the analyses are as follows:

- (1) Moisture - the loss in weight on heating a 1 gram sample in an oven at 104 - 110°C for 1 hour.
- (2) Volatile Matter - the loss in weight of a 1 gram sample heated in a covered crucible at 905°C for 7 minutes, with item (1) deducted.
- (3) Ash - the residue from item (1) after all the combustible material is burned out in a muffle furnace at 700 - 750°C.
- (4) Fixed Carbon - Items (1) to (4) are all expressed as percentages and the fixed carbon is the difference between 100 and items (1) + (2) + (3).

The sulphur content of the liquid products was determined using an X-ray fluorescence technique. X-rays emitted from an Fe-55 source cause a secondary X-ray emission, characteristic of the sulphur atoms in the liquid sample. The intensity 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 Analyzer manufactured by Panametrics, a subsidiary of the Esterline Corporation of Waltham, Massachusetts.

### Materials

The coals used in the present work were Canmore semi-anthracite and Estevan lignite. The results of the proximate analyses of these coals are shown in Table 2. The bitumen used was obtained from Great Canadian Oil Sands Ltd. (G.C.O.S.) at Fort McMurray, Alberta. The G.C.O.S. operation uses the Clark Hot Water process (2a, 19) 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 Mines Branch was topped bitumen (diluent removed), typical of the material fed to the delayed coking



drums in the Company's processing scheme. The general properties of the bitumen are listed in Table 3.

Table 2  
Coals Used in Reaction Studies

Source of Coal	Cammore Cascade Area, Alberta	Estevan Saskatchewan
ASTM Rank .....	semi-anthracite	lignite
Proximate Analysis - wt%		
moisture .....	0.78	18.26
ash .....	7.82	10.16
volatile matter .....	13.39	35.62
fixed carbon .....	78.01	35.96

Table 3  
Properties of Athabasca Bitumen

Specific Gravity 60 <sup>o</sup> /60 <sup>o</sup> F .....	1.000
Ash (wt %) 700 <sup>o</sup> 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 <sup>o</sup> F	129.5
Viscosity, Kinematic (cSt) at 130 <sup>o</sup> F	2041
Molecular Weight (calculated) .....	722
Residuum (+975 <sup>o</sup> F) wt % .....	51

## RESULTS AND DISCUSSION

### The Effect of Reaction Time

During the initial stages of this investigation, it became apparent that the extent of coal hydrogenation had an important effect upon bitumen hydrocracking. In order to examine this phenomenon, experiments were repeated several times on the same reactor charge of coal, using the conditions shown in Table 1. This was done with both lignite and semi-anthracite coals.

The properties of the resulting hydrocracked liquid product are shown in Figure 4. Both the specific gravity and the weight percent sulphur changed as the experiment was repeated (on the same batch of coal). This was true for processing in the presence of both semi-anthracite and lignite coals. These results suggest that the properties of the reaction product changed continuously during the steady state period. Therefore, the properties shown in Figure 4, for any single experiment, are really average properties for that experiment.

The specific gravity curve for Estevan lignite, shown in Figure 4, has a maximum at experiment number 2. This is probably a real effect since a similar result was observed in an independent experiment. The much higher content of oxygen in lignite than in semi-anthracite (20) may help to explain the maximum. One possibility would be that oxygen promotes cracking reactions (21). Since most of the oxygen, originally present in both coals, is probably removed in the first experiment, then the specific gravity would be expected to be lower in the first experiment than in the second. An alternative explanation would be that the oxygen becomes incorporated in the liquid hydrocarbon to produce a product having a different structure and density than that formed in the absence of oxygen.

While the experimental points in Figure 4 are not precisely reproducible, the general trend is reproducible. The problem was made more complicated by the occasional plugging of the reaction lines with carbonaceous deposits at some point during the 3-hour steady state period. This type of difficulty was encountered more often with the lignite coal than the semi-anthracite. The plugging phenomena and the resulting irreproducibility do not negate the overall conclusion that the properties of the liquid product change markedly as the reaction proceeds.

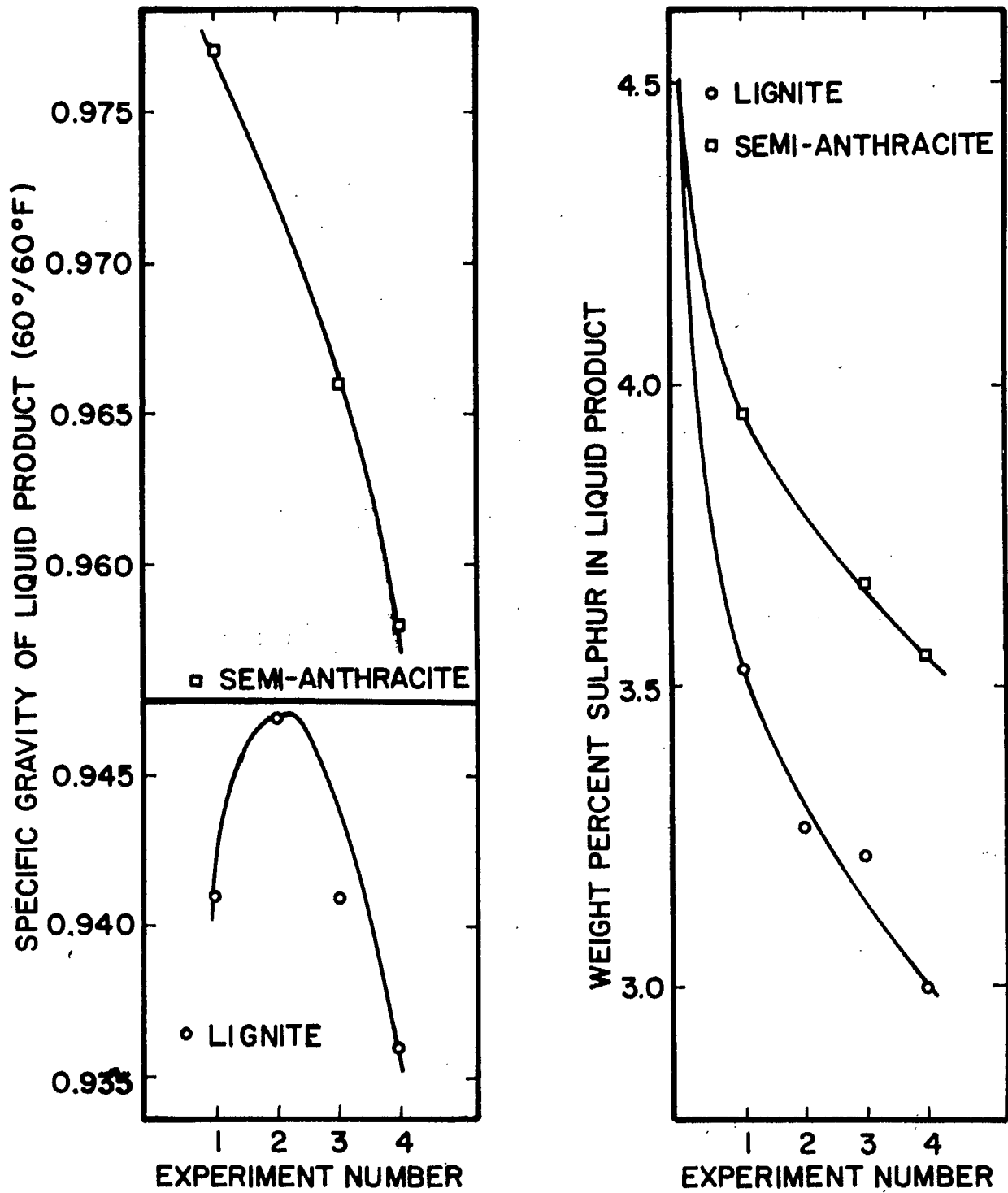
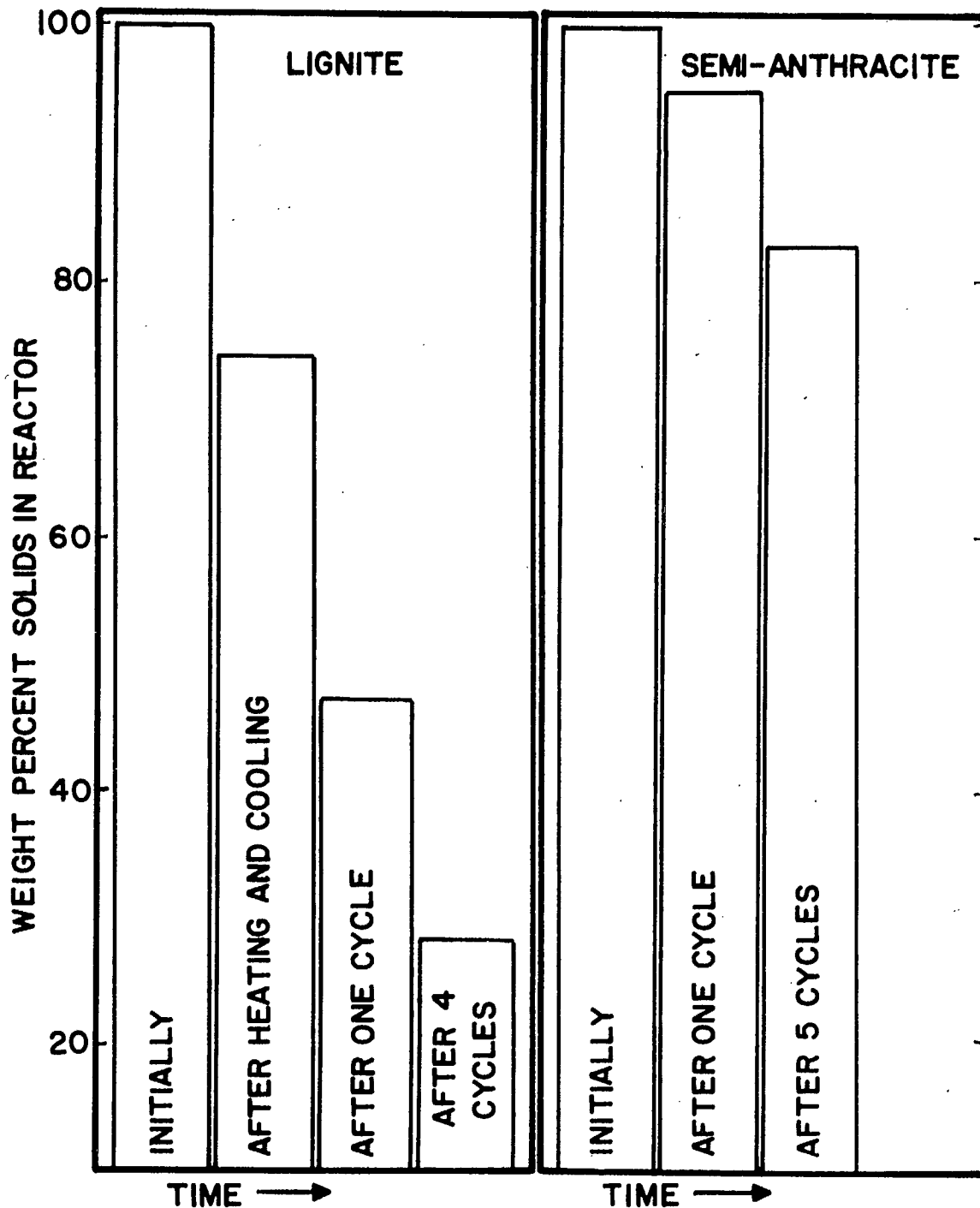


Figure 4. Change in product quality as a function of reaction time.

At the conclusion of each experiment or each series of experiments, the solids were removed from the reactor and examined. The amounts of solids remaining in the reactor after successive reaction periods are shown in the bar chart in Figure 5. More than 70 percent of the Estevan lignite coal and approximately 20 per cent of the Canmore semi-anthracite coal are removed in the course of the reaction. Studies on coal hydrogenation have shown that low rank coals tend to hydrogenate at a greater rate than do high rank coals (13). Therefore, the hydrogenation rates for the relatively high rank semi-anthracite and the low rank lignite coals are probably close to the maximum and minimum.

When the solids are removed from the reactor they are coated with liquid hydrocarbons and tarry reaction products. These compounds are subsequently dissolved during the toluene extraction. Undoubtedly, the toluene extraction process also dissolves a fraction of the solids. The extent to which this occurred was evaluated by performing toluene extractions on the original coals. Less than 0.1 weight percent of the semi-anthracite was extracted while 8.5 weight percent of the Estevan lignite was extracted. It must be emphasized that these figures are only valid for the original coals. They are not expected to be directly applicable to the hydrogenated coal solids removed from the reactor, since hydrogenation conditions alter the chemical compounds in coal. The results shown in Figure 5 have not been corrected for toluene extraction and are therefore probably somewhat inaccurate. Regardless of this inaccuracy, the results show that a large percentage of lignite coal is converted to fluid hydrocarbons under hydrocracking conditions.

The size of the particles comprising the solids removed from the reactor were also measured. The distribution of particle sizes is shown in Figure 6 as the cumulative percent undersize. An assumed size distribution for the -4+8 mesh coal particles, initially placed in the reactor, is shown as the solid line. It is compared with the size distributions of the particles taken from the reactor at the end of one experiment and at the end of a series of four experiments. The three curves show that the particles become progressively smaller as the total reaction time increases. By combining the information in Figure 6 with that in Figure 5, it is apparent that as the total reaction time increases, more of the coal is converted to fluid hydrocarbons and that the unconverted solids become progressively smaller in size.



Note: one cycle consisted of heating to the reactor temperature, holding all variables constant for a three-hour period, and cooling the reactor to ambient temperature.

Figure 5. Quantity of solids (coal + coke) inside the reactor as a function of reaction time.

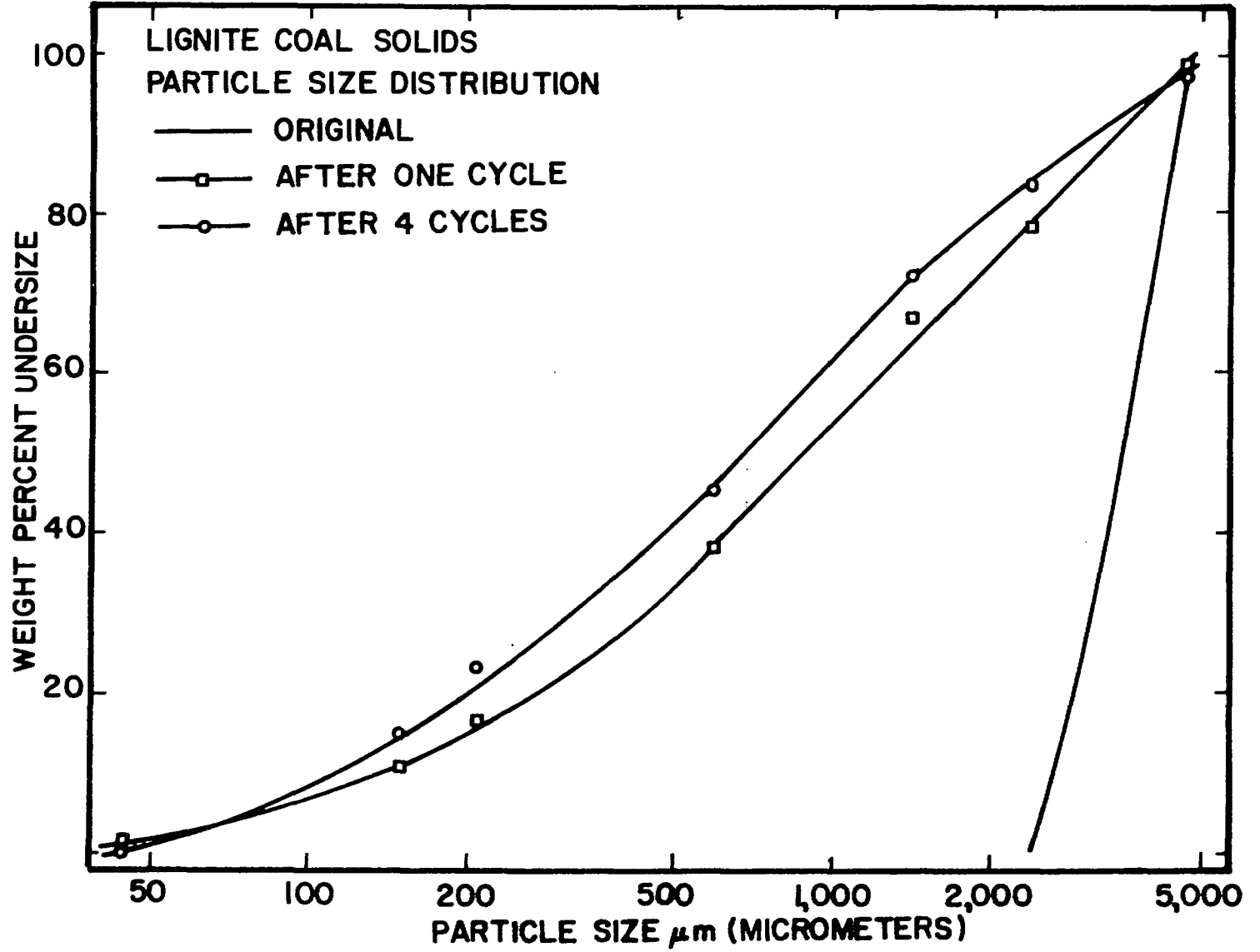


Figure 6. Particle size distribution of coal residues after various reaction periods (original particle size -4+8 mesh).

In summary, changes in the properties of the hydrocracked product, the amount of coal converted to fluid hydrocarbons, and the sizes of the unconverted solid particles have been observed. In the light of these observations, a standardized experimental procedure was adopted to compare the results of one experiment with those of another. Each experiment started with a fresh charge of coal. This ensured that all experiments were performed using samples of coal which had been exposed to hydrogenation conditions for the same time period. In this way differences in experimental results could be ascribed to differences in either the materials used or the processing conditions, rather than differences in the length of time a coal charge had been in the reactor.

#### The Origin of the Coke Deposits

The purpose of introducing coal into the hydrocracking system was to provide sites upon which coke and metals could deposit. In principle, any coke appearing at the coal surface could have originated either from the bitumen or from the coal itself. Three types of experiments were undertaken to see if coke was being formed from either or both of these sources. All the experiments described here were performed with Canmore semi-anthracite coal using the reaction conditions shown in Table 1.

In the first type of experiment bitumen was hydrocracked in the presence of hydrogen, but in the absence of coal. This is the thermal hydrocracking process outlined earlier. The large amount of petroleum-type coke produced is shown in the photograph in Figure 7a. The centimeter scale shown in the same photograph gives an indication of the dimensions of the coke deposit. The coke plug actually filled the cross-section of the reactor and had to be broken in order to be removed. Figure 7b is a macrophotograph (magnification = 10x) showing the texture of the coke surface. Since coke was formed from bitumen in the absence of coal, it was also expected to form when coal particles were present.

In the second type of experiment, -4+8 mesh coal particles were placed in the reactor and hydrogen flowed up through them in the absence of bitumen. A solid mass of porous coke filling the entire cross-section of the reactor was formed in the upper part of the vessel. No coke was formed in the lower part of the reactor, probably because it was at a considerably lower temperature than the upper part (as may be seen in Figure 3). Macrophotographs



(a)



(b)



(c)

Figure 7

- (a) Solids removed from the reaction vessel after a thermal hydrocracking experiment.
- (b) Surface of a solid particle produced during a thermal hydrocracking experiment. Magnification 10X.
- (c) Particle of semi-anthracite coal before being placed in the reaction vessel. Magnification 10X.



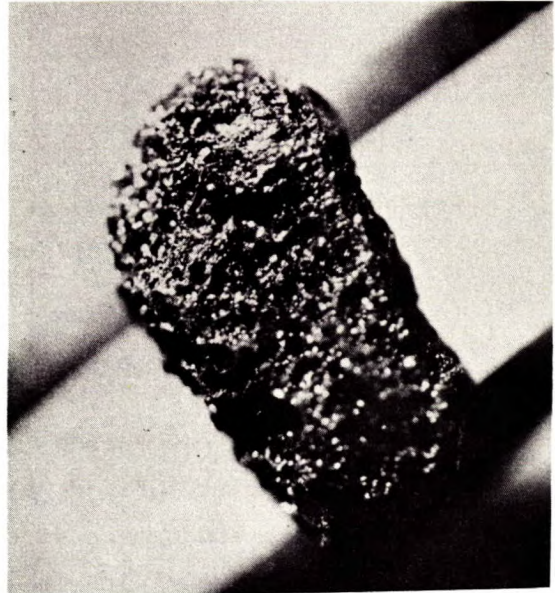
of typical particles removed from the reactor are shown in Figures 8a and 8b. Figure 8a shows a non-porous particle, formed in the bottom of the reactor, and Figure 8b shows a porous particle formed in the upper part of the reactor. The non-porous particle can be compared with the typical original coal particle shown in Figure 7c. The original coal particle has much more luster than does the particle which has been in the reactor. Perhaps this change in luster is indicative of coke deposition or of a chemical change on the particle surface. A microscopic examination of the particles indicated that coke was formed and that it was similar to coke normally made from a low volatile bituminous coal. This is in agreement with previous reports (22, 23) on the formation of coherent coke from non-coking coals (e.g. semi-anthracite) in the presence of high pressure hydrogen.

Semi-anthracite does not form coke at conditions normally used to manufacture metallurgical coke. This was verified by performing a variation of the second type of experiment. This time semi-anthracite coal was heated to 450°C (723°K) at atmospheric pressure in a closed container, initially filled with air. A microscopic examination of these solids showed no evidence of coke formation.

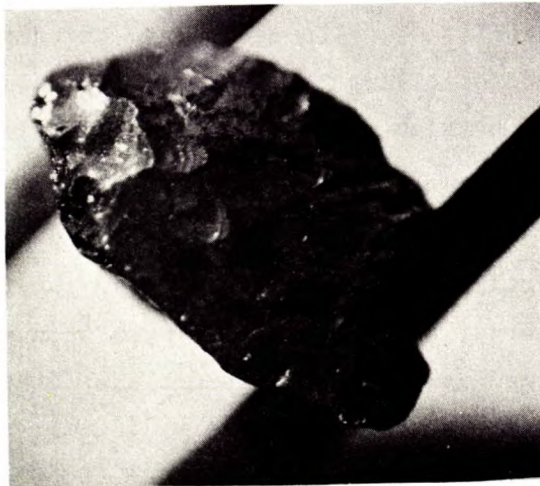
In the third type of experiment, the reactor was filled with coal particles and both bitumen and hydrogen flowed up through it. With the bitumen present, no solid plug was formed and there was no evidence of particles fusing together. The solid particles in the upper portion of the reactor, which was at the highest temperature, did acquire a porous coke-like texture, but none of them fused together. The solids from the lower part of the reactor were non-porous. Typical non-porous and porous particles are shown in the macrophotographs (magnification = 10X) of Figures 8c and 8d respectively. They appear to be essentially the same as the ones formed in the absence of bitumen, shown as Figures 8a and 8b. Separate lumps of petroleum-type coke did not form during this experiment, whereas they did form during the thermal hydrocracking experiment. A microscopic examination showed that the major part of the particle surface appeared to have a petroleum coke-like structure. However, there were a few parts of the surface structure that looked like coke from a low volatile coal. By combining the evidence from both the macroscopic and microscopic examinations several conclusions were drawn.



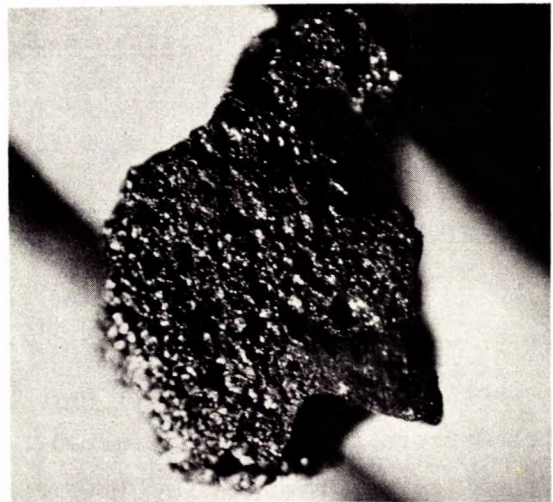
(a)



(b)



(c)



(d)

Figure 8

- (a) Surface of a relatively non-porous particle produced from semi-anthracite coal in the presence of hydrogen. Magnification 10X.
- (b) Surface of a relatively porous particle produced from semi-anthracite coal in the presence of hydrogen. Magnification 10X.
- (c) Surface of a relatively non-porous particle produced from semi-anthracite coal in the presence of hydrogen and bitumen. Magnification 10X.
- (d) Surface of a relatively porous particle produced from semi-anthracite coal in the presence of hydrogen and bitumen. Magnification 10X.

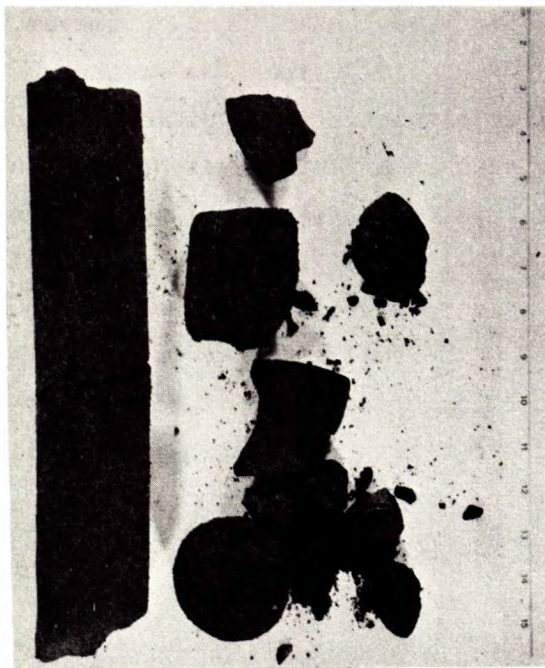
- (a) The semi-anthracite coal particles were transformed into porous coke particles.
- (b) Petroleum-like coke, originating from the bitumen, was deposited on the surface of these porous coke particles.
- (c) The presence of bitumen in the reaction system prevented adhesion of the porous coke particles.

It must be emphasized that the above conclusions are important from a practical standpoint. First, the object of this series of investigations is to deposit coke and metals on the coal surface so that they can be removed from the reaction system with the coal. The deposition of petroleum-like coke on the coal surface, discussed above, is positive evidence that the desired phenomena are occurring. Second, the presence of coal particles prevents the formation of separate lumps of petroleum-like coke. Third, coke will deposit on the coal without particle fusion taking place. The second and third points mean that there will be little likelihood of a large solid mass forming in the reactor, blocking the flow of fluid, and halting the reactor operation.

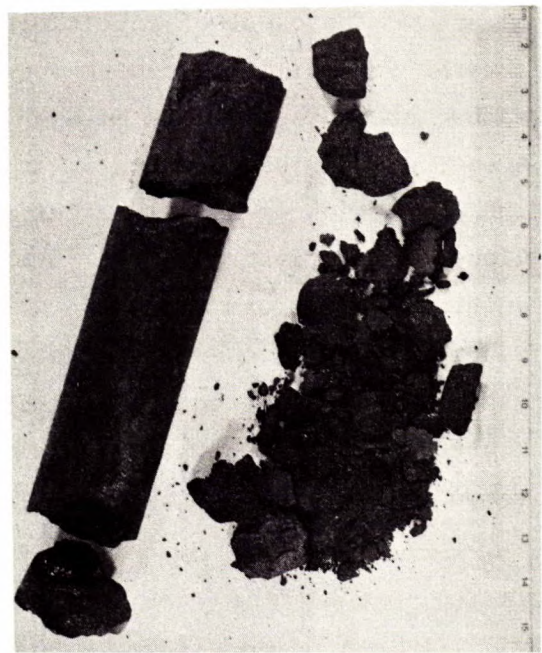
#### The Effect of Initial Particle Size

The size fractions of coal particles, initially placed in the reactor, were varied to evaluate the role of external particle surface area upon the reaction rate. Experiments were performed using five different size fractions of Canmore semi-anthracite coal, -4+8 mesh (av particle size = 3640 $\mu$ m), -14+30 mesh (av particle size = 1000 $\mu$ m), -30+70 mesh (av particle size = 400 $\mu$ m), -70+100 mesh (av particle size = 180 $\mu$ m), and -100+200 mesh (av particle size = 112 $\mu$ m).

During experiments using the two smallest size fractions the coal particles fused into a solid mass having the dimensions of the reactor. Photographs of the fused material are shown in Figures 9a and 9b. During the experiment with the -30+70 mesh size particles, a loosely fused disc was formed. It was approximately 1 cm thick and had the diameter of the reactor. It is shown in Figure 9c. Figure 9d is a macrophotograph (magnification 10x) of the fused surface. No fusion of particles was observed with the two largest particle sizes.



(a)



(b)



(c)



(d)

Figure 9

- (a) Fused particles made from -100+200 mesh semi-anthracite.
- (b) Fused particles made from -70+100 mesh semi-anthracite.
- (c) Fused particle made from -30+70 mesh semi-anthracite.
- (d) External surface of coke made from -100+200 mesh semi-anthracite.  
Magnification 10X.

The cause of particle fusion has not been established. However, several possibilities can be suggested. One would be that the greater number of contact points between the smaller particles would promote fusion. A second would be that fusion is caused by the same factors responsible for the production of metallurgical-type coke from coal. (For example, the previous section described the formation of metallurgical-type coke when semi-anthracite coal was contacted with high pressure hydrogen, in the absence of bitumen.) A third explanation would be that the smaller sized particles might have a different composition than the larger ones. This can be discounted since the proximate analyses of the different particle size fractions, shown in Table 4, indicate that all particles have similar compositions.

Table 4

Variation in Proximate Analysis of Canmore  
Semi-Anthracite Coal with Particle Size

Mesh Size	Moisture	Ash	wt % Volatile	Fixed Carbon
-4+8	0.78	7.82	13.39	78.01
-14+30	0.63	5.46	13.70	80.21
-30+70	0.52	5.81	13.82	79.85
-70+100	0.55	6.85	12.98	79.62
-100+200	0.42	6.43	13.82	79.33

Liquid product was obtained for the experiments with the three larger particle sizes. Since the sulphur content of all the liquid products was approximately the same, no particular trend with particle size could be identified. In contrast, there was a slight decrease in specific gravity as the particle size was decreased. The specific gravity results are shown in Figure 10. The correlation displayed in this figure may be fortuitous since there is only a small variation in the magnitude of the three specific gravity results. In any case, it shows that the initial coal particle size has very little effect upon specific gravity.

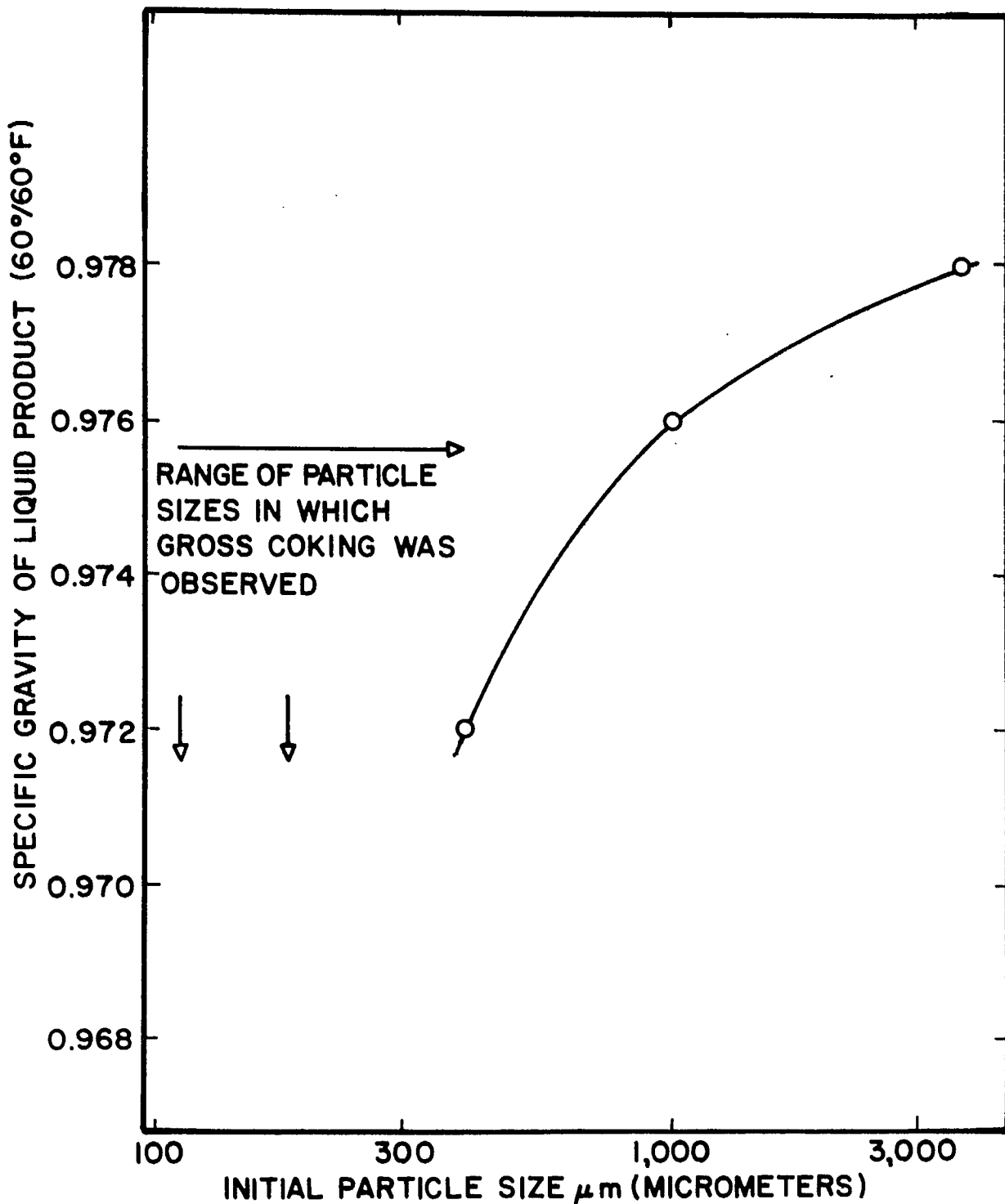


Figure 10. Effect of the initial particle size of semi-anthracite coal on specific gravity of the liquid product.

Phenomena occurring in the presence of coal particles will not be identical to those occurring in the presence of conventional catalysts, since the two have different internal particle geometries. In Co-Mo-Al hydrocracking catalysts, diffusion through pores is considered to be the rate limiting step (24). As the particle size of these catalysts decreases, the reaction rates improve considerably, presumably because more internal surface area becomes accessible. In contrast, the pores in coal are at least one order of magnitude smaller than those in conventional catalysts, so that the coal internal surface area will probably be inaccessible to the bitumen under all circumstances. As a result only the external surface area would be expected to influence the reaction rate. A simple calculation of particle external surface area can be made by assuming that all particles are spheres having the mode diameter of their fraction and that particle shape and surface roughness can be ignored. On this basis the -4+8 mesh fraction and the -30+70 mesh fraction would have surface areas of 1.9 and 17.2 m<sup>2</sup>/kg respectively. This relatively large variation produced no identifiable improvement in sulphur removal and only a miniscule improvement in specific gravity. Therefore, it may be concluded that the amount of catalytic hydrocracking occurring at the particle surface is negligible with respect to the amount of thermal hydrocracking occurring in the bulk liquid.

#### Changes in Chemical Composition

Exposure to hydrogenation conditions will change the moisture, hydrogen, and carbon contents of the coal, but the major components of the ash will be unreactive. Therefore, the amount of ash in the coal, initially charged to the reactor, should be approximately the same as the amount of ash in the solid residue removed from the reactor, at the end of the experiment. The quantities in Table 5 and compositions in Tables 2 and 6 have been used to compare ash contents. For semi-anthracite coal the solids removed from the reactor contained only 85% of the ash in the solids charged to it. For lignite coal, the solids removed from the reactor appeared to contain 15% more ash than the solids charged to it.

Table 5

Quantities of Solids Charged to and Removed from the Reactor

Source of Original Coal	Canmore Cascade Area, Alta.	Estevan Saskatchewan
ASTM Rank .....	semi-anthracite	lignite
Weight of coal charged to the reactor - grams .....	91.3	100.0
Weight of residue removed from the reactor - grams ...	86.5	47.3

Table 6

Residues Removed from the Reactor at the Conclusion of the Experiments

Source of Original Coal	Canmore Cascade Area, Alta.	Estevan Saskatchewan
ASTM Rank .....	semi-anthracite	lignite
Residue proximate analysis, wt %		
moisture .....	0.70	4.99
ash .....	7.08	24.59
volatile matter .....	13.44	24.02
fixed carbon .....	78.78	46.40

Slight changes in the ash content are to be expected. A slight decrease in the weight percent of ash could be due to metal reduction and sulphur removal. Also, a slight increase in ash content might be due to deposition of metals contained in the bitumen. However, there are no readily apparent explanations for the 15 percent changes in ash content which have been observed.



It is difficult to evaluate the concurrent reactions of coke deposition and coal hydrogenation. Nevertheless, the net effect may be identified by considering the carbon/ash ratio. The quantity of ash in the solids was constant within limits, as discussed above. Therefore, an increase in the carbon/ash ratio would indicate coke deposition and a decrease would indicate coal hydrogenation. For semi-anthracite the ratio decreased from 10.0 in the initial coal charge to 9.8 in the reactor residue. For lignite it decreased from 3.6 to 1.9. The net loss in weight of total solids charged to the reactor was another indication of coal hydrogenation. It amounted to 5 percent for semi-anthracite and 53 percent for lignite. Both sets of numbers indicate that coal hydrogenation predominates, but to a much greater extent with lignite than with semi-anthracite.

Further insight into the reaction may be gained by examining the carbon/ash ratio as a function of particle size. The reactor residue was screened into the following mesh size fractions, +4, -4+8, -8+14, -14+30, -30+70, -70+100, -100+200, -200+325, and -325. The carbon/ash ratio for each size fraction of the residue has been plotted as a function of its mode size, in Figure 11. The results for lignite appear to be quite reasonable, decreasing from 3.6 in the initial coal, to approximately 3.0 in the large residue particles, to approximately 1.4 in the smallest residue particles. This is likely caused by the increase in surface/volume ratio as the particle size decreases. The greater surface area permits a greater extent of reaction (in this case, hydrogenation of the coal). The results obtained with the semi-anthracite coal are more complex. They suggest that coal hydrogenation predominates for the largest and smallest particles and that coke deposition predominates for the particles of intermediate size.

It was also anticipated that nickel and vanadium metals would be removed from the liquid hydrocarbon and deposited on the surfaces on the coal particles. The amount of metals removed is shown in Table 7. The concentration of both vanadium and nickel metals is lower in the liquid products than in the bitumen feedstocks. It is also apparent that a considerably larger quantity of metals was removed in the presence of lignite coal than in the presence of semi-anthracite coal.

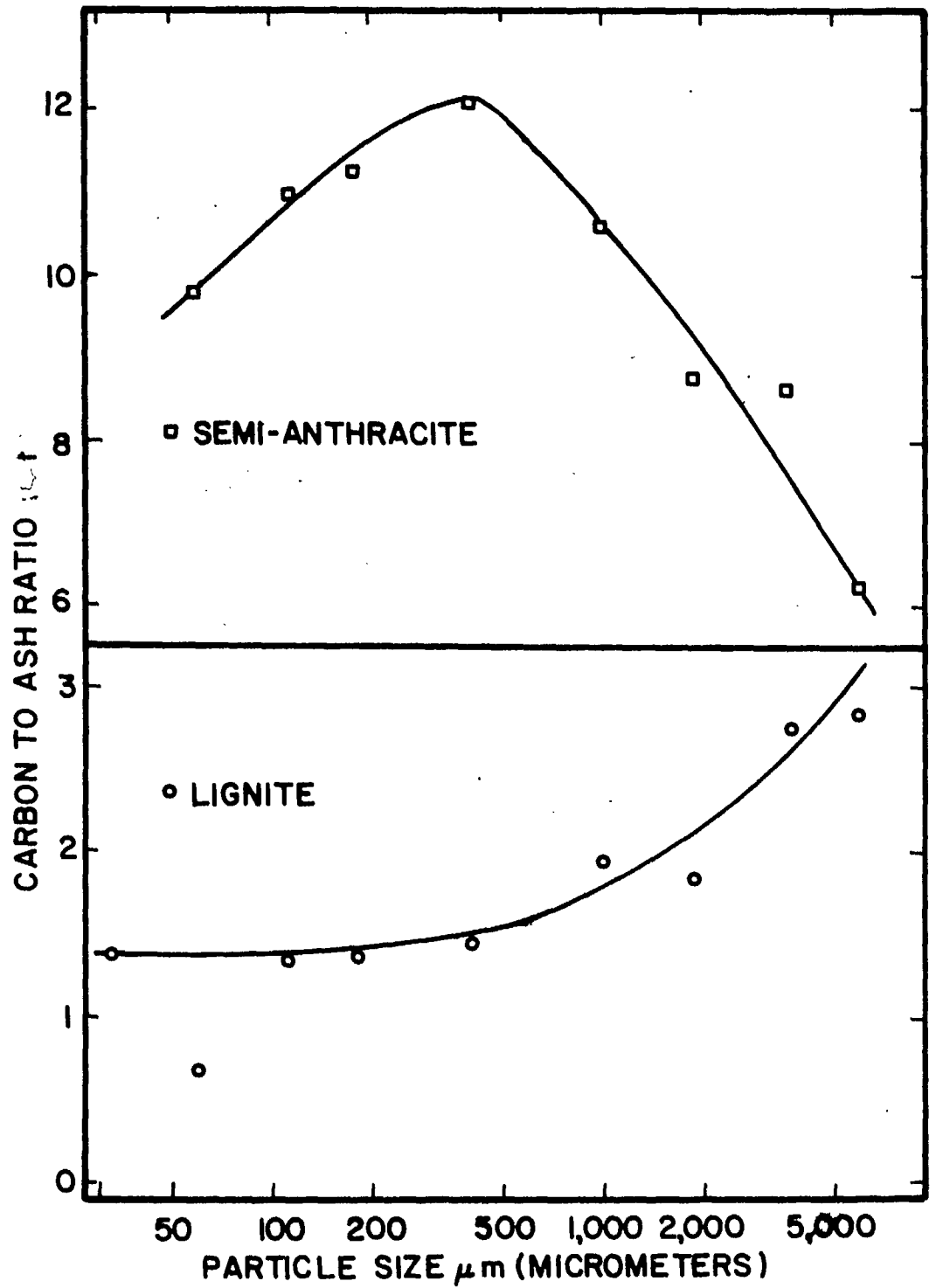


Figure 11. Variation of carbon to ash ratio, with particle size in coal residues.

Table 7  
Metals Removed from the Liquid Hydrocarbon

	Metals Content of Liquid ppm	
	<u>V</u>	<u>Ni</u>
Bitumen Feedstock .....	191	76
Product from Semi-Anthracite Experiments	161	63
Product from Lignite Experiments .....	82	37

#### CONCLUSIONS

The experimental findings discussed in this report may be itemized as follows:

- Coal hydrogenation occurs at the same conditions as bitumen hydrocracking.
- Both the mass of coal solids and the size of solid particles decrease with increasing reaction time.
- Particles of semi-anthracite coal are converted to a metallurgical type coke-like material, and petroleum-type coke is deposited on their surfaces.
- Metals are removed from the liquid hydrocarbon.
- The size of coal particles initially placed in the reactor does not have a significant effect on the properties of the hydrocracked liquid product. However, when small particles (those having size ranges of -30+70 mesh and smaller) were used, the particles fused together and, in some cases, formed a single solid plug occupying the dimensions of the reactor.

#### ACKNOWLEDGEMENTS

The authors would like to thank Mr. R.G. Draper, Mr. W.J. Montgomery, and their staffs for analyzing some of the samples. Also, the instruction provided by Mr. E.C. McColgan and Mr. P.S. Soutar on the operation of the reaction equipment was greatly appreciated.

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