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THE HYDROCRACKING OF RESIDUAL OILS AND TARS
PART 3: THE EFFECT OF MINERAL MATTER ON THE THERMAL AND CATALYTIC HYDROCRACKING OF ATHABASCA BITUMEN

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PART 3: THE EFFECT OF MINERAL MATTER ON THE THERMAL
AND CATALYTIC HYDROCRACKING OF ATHABASCA BITUMEN

by

P. S. Soutar*, E. C. McColgan*, and B. I. Parsons**

ABSTRACT

The report describes a bench-scale investigation of the effect of the concentration of residual clay and silt on the thermal and catalytic hydrocracking of bitumen separated from the Athabasca tar sands. The experiments were done in the liquid phase in a bottom-feed, continuous-flow apparatus at 1000 and 2000 psi, at liquid hourly space velocities of 1.05 and 2.1 with bitumen feed stocks containing 0.9 % and 3.8 % mineral matter. In the thermal hydrocracking process, the maximum conversion attainable and the yield of liquid distillate product were measurably higher with the bitumen containing the greater amount of mineral matter. The primary effect of the mineral matter is to suppress the coking and fouling reactions which limit the maximum operating temperature. The results indicate no significant catalytic activity attributable to the mineral matter for either the hydrocracking reaction or for desulphurization. In the catalytic process the residual clay and silt tended to foul the catalyst surfaces and the higher-mineral feed stock was found to be less reactive in every respect.

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L'Hydrocraquage des huiles résiduelles et des goudrons

3e Partie: L'Effet des matières minérales sur l'hydrocraquage
thermique et catalytique des bitume d'Athabasca

par

P. S. Soutar*, E. C. McColgan* et B. I. Parsons**

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RÉSUMÉ

Dans ce rapport, les auteurs décrivent une recherche faite au
laboratoire sur l'effet de la concentration d'argile et de limon résiduels
sur l'hydrocraquage thermique et catalytique du bitume séparé des Sables
asphaltiques d'Athabasca. Ils ont fait des expériences à la phase liquide
utilisant un appareil d'écoulement continu avec un réacteur d'alimentation
par le bas à 1000 et 2000 psi aux vitesses spatiales liquides par heure de
1.05 et 2.1 avec des stocks d'alimentation de bitume contenant de la
matière minérales de 0.9% et 3.8%. Dans le procéde d'hydrocraquage
thermique, la conversion maximum accessible et le rendement du prodiut
de distallat liquide étaient plus élevés avec le bitume contenant le plus
grand montant de matière minérales. Le premier effet de la matière
minérale est de supprimer les réactions de cokéfaction et d'encrassement
qui limitent la température maximum de fonctionnement. Les résultats
indiquent qu'il n'y a pas d'activité catalytique significative attribuable à la
matière minérale soit pour la réaction d'hydrocraquage soit pour la
désulfuration. Dans le procédé catalytique, les auteurs ont trouvé que
l'argile et le limon résiduels tendaient à encrasser les surfaces
catalytiques et que le stock d'alimentation de minéraux élevés était moins
réactif à tous les points de vue.

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INTRODUCTION

The following report is the third in a series on the investigation of techniques for hydrocracking residual oils and tars. In the first report (1), the effect of feed dilution on the _thermal_ hydrocracking of Athabasca bitumen was determined and, in the second (2), the various parameters connected with the _catalytic_ hydrocracking process were investigated. This report is concerned with the effect of the concentration of mineral matter in Athabasca bitumen on both the thermal and catalytic processes.

A tar sands operation is a complicated process compared with the recovery and refining of conventional crude oil. In very general terms, the over-all yield and cost of preparing saleable hydrocarbon fuels from tar sands depends upon three factors:

1. the mining and transportation of the tar sands to the plant site,
2. the separation of the hydrocarbon material from the sand, and
3. the refining and upgrading of the separated hydrocarbon.

From the point of view of the chemistry and engineering required, the various phases of the over-all operation are highly dependent on each other. This is particularly true when one considers the separation and refining steps.....the additives and manipulations used to facilitate the separation of the bitumen from the sand can have an important (sometimes overriding) effect on the refining processes. In recent years, considerable emphasis has been placed upon simplifying the procedure for separating the bitumen from the solid material. Though it need not necessarily be so, most of the simplifications which have been proposed result in higher concentrations of residual clay and silt in the separated bitumen, i.e., they are less effective. The purpose of the present work was to determine the degree of dependence of the first step in the refining process on the concentration of mineral matter in the bitumen.

The first step of the refining phase of the operation was the main subject matter of the initial two reports in this series. It was found that the yield of liquid fuels produced per unit of feed was greatest with catalytic hydrocracking,

somewhat less with thermal hydrocracking and considerably less with delayed coking. At the present time, because of the relatively high cost of the catalysts involved, the economic advantage appears to be with thermal hydro- cracking. It must be stressed, however, that the extent of the economic advantage is small and the situation could change radically with either an improvement in the catalyst formulation or the application of more stringent antipollution and conservation regulations (areas in which the catalytic process has a distinct advantage). Because of the uncertainties involved, the effects of higher mineral content have been determined for both the catalytic and thermal processes.

The effect of increasing amounts of residual solids on the hydrocracking process is, by no means, easy to predict. In the case of the thermal hydro- cracking process, it can be argued that the nature of the mineral matter (sand and aluminum silicates containing metals such as iron and titanium) could facilitate the hydrocracking of the bitumen by acting like a mild catalyst. It is equally possible that the potentially "catalytic" elements in the mineral matter are not in the appropriate chemical form and will, therefore, have little or no catalytic action. Conversely, the aluminum silicates which constitute a large proportion of the mineral matter could be too effective as an elementary cracking catalyst* resulting in sufficient coke and tar formation to gradually plug the reaction system and force a premature shut-down.

Similarly, the effect on catalytic hydrocracking is not easily predictable. On the one hand, increasing amounts of clay and silt could coat the catalyst surfaces and reduce the catalytic activity quickly (shortening still further an already short catalyst life). On the other hand, the particle size of the clay and silt is extemely small and it could pass through the reaction system, affecting the catalyst very little.

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*as distinct from a hydrocracking catalyst which includes a strong hydrogenating component.

EXPERIMENTAL

Apparatus and Procedure

The apparatus used was the bench-scale flow system described in the first report in this series (1). In all of the experiments the oil feed and hydrogen were pumped in at the bottom of the reactor. For the thermal experiments, the reaction tube was used empty (no packing). For the catalytic experiments, the reaction tube was packed with 1/8 x 1/8-inch cylindrical pellets of a commercial cobalt molybdate catalyst manufactured by the Harshaw Chemical Co. of Cleveland, Ohio. The catalyst was the same as that used and described in the second report in this series (2). The unit was operated, in effect, as a continuous flow, liquid-phase system with the oil and hydrogen percolating up through the reactor. Any low-boiling material present in the feed (or produced in the course of reaction) vapourizes, collects as bubbles, and quickly passes out of the reaction zone. High-boiling material remains in the liquid phase and progresses slowly through the reactor by displacement only. The temperature profile through the reaction zone was determined by sliding a thermocouple up a well located centrally in the reactor. No attempt was made to average temperatures across the reaction zone.....the temperatures recorded in the Tables and Figures are "plateau" or "peak" temperatures.

A series of experiments involving the catalyst consisted of four consecutive 3-hour runs at increasing temperatures 430, 440, 450, and 460°C followed by a 3-hour repeat run at 440°C (designated as 440 (2) in the Figures). A conventional pre-heater system was not used in this work. The advantages of accomplishing the last stages of feed preheat in the presence of catalyst had been demonstrated previously (3). The procedure used here was to heat (100 - 125°C) the bitumen to reduce the viscosity for pumping purposes, mix it with the hydrogen at about 150°C, and deliver the mixture to the bottom of the catalyst bed at about 300°C. The balance of the preheating was accomplished in the reaction vessel.

The analytical procedures used to determine the extent of conversion of the residuum hydrocarbon material to distillable liquid product and the sulphur content of the various oil fractions have also been described previously (1, 2).

Some of the less common abbreviations used throughout the Figures and Tables are defined as follows:

LHSV   - liquid hourly space velocity
scf/bbl - standard cubic feet per barrel
mmf   - mineral matter free

Feed Stock

Two lots of Athabasca bitumen were used in the experimental work. One, of relatively low mineral content, was supplied to the Fuels Research Centre by Great Canadian Oil Sands Ltd. of Fort McMurray, Alberta. The procedure followed by G.C.O.S. for separating its bitumen involves two steps, a) the Clark Hot-Water Process and froth flotation (4) to separate the coarse, water-wet sand particles and b) dilution with naphtha followed by centrifuging (5) to remove the inter-mediate-sized particles. The residual concentration of clay and silt in the bitumen after recovering the solvent naphtha is about 0.9 % by weight.

The second lot of bitumen, of relatively high mineral content, was supplied by Syncrude Canada of Edmonton. The Syncrude process (still in the pilot plant stage of development) utilizes hot-water separation followed by 2 stages of froth recovery and, finally, flash dehydration (6). The concentration of residual clay and sand remaining in the bitumen supplied to the Fuels Research Centre was 3.8 % by weight.

The general properties of the two bitumens are listed in Table 1 and the results of the distillation and sulphur analyses on the various fractions are shown in Table 2. The boiling range of the fractions given in Table 2 are the same as those used in the description of the distillate properties of the products. For the purposes of this report, hydrocarbon material boiling up to the equivalent of 975°F at one atmosphere pressure is classed as distillable oil, and material boiling above 975°F equivalent temperature is residuum. The G.C.O.S. bitumen contained approximately 2 % more low-boiling (naphtha) material than the Syncrude material. This probably reflects more the inefficiency of the solvent recovery step in the dilution-centrifuging process than any important difference in the two bitumens. The only significant difference between the two, in terms of hydrocarbon quality, was a slight (but consistent) higher concentration of sulphur in the distillate fractions from the Syncrude bitumen. The sulphur content of the residuum fraction

Table 1

General Properties of the Bitumen Feed Stocks
(as received)

	Low-Mineral Matter	High-Mineral Matter
Specific gravity 60/60°F	1.000	1.035
Ash (wt %) 700°C	0.70	3.46
Nickel (ppm)	68	70
Vanadium (ppm)	189	180
Pentane insolubles (wt %)	15.83	19.13
Benzene insolubles (wt %)	0.90	3.78
Carbon Disulphide insolubles (wt %)	0.9	3.8
Sulphur (wt %)	4.72	4.77
Nitrogen (wt %)	0.38	0.52
Viscosity, Kinematic (cSt) at 210°F	85	200
Viscosity, " " at 180°F	-	523
Viscosity, " " at 150°F	-	1588
Viscosity, " " at 130°F	1140	-

Table 2

Distillation and Sulphur Analyses on the Bitumen Feed Stocks

Boiling Range of Fraction Equiv. Temp. at one atm (°C)	(°F)	0.9 % Mineral Matter		3.8 % Mineral Matter	
		Weight % of Fraction (mmf)	Weight % Sulphur	Weight % of Fraction (mmf)	Weight % Sulphur
RT - 100	RT - 212	-	-	-	-
100 - 200	212 - 392	2.1	-	0.4	-
200 - 250	392 - 482	1.5	1.15	2.5	1.82
250 - 275	482 - 527	5.2	1.65	7.2	1.87
275 - 332	527 - 630	5.5	2.49	3.0	2.85
332 - 361	630 - 682	6.9	2.78	6.5	3.03
361 - 391	682 - 736	5.1	3.10	5.1	3.30
391 - 421	736 - 790	6.7	3.38	7.3	3.59
421 - 524	790 - 975	16	3.86	17	4.06
+ 524	+ 975	51	6.25	51	5.77

(+524°C or +975°F) of the Syncrude material was measurably less than the G.C.O.S. which is in line with the observation that the over-all concentrations of sulphur in the two feed stocks were essentially equal, i.e., 4.72 % for the G.C.O.S. compared to 4.77 % for the Syncrude bitumen.

EXPERIMENTAL RESULTS AND DISCUSSION

The experimental temperatures and pressures used for the comparison of the two bitumen feed stocks were the optimum conditions established in the second report in this series (2).

Thermal Hydrocracking

The thermal hydrocracking experiments were run at various temperatures from 430 to 460°C at 1000 and 2000 psi, LHSV = 2.1 with an exit gas rate of 5000 scf/bbl. The results of the tests are summarized in Figures 1 to 3. The effect of reaction temperature on the conversion of the +975°F residuum hydrocarbon to distillable oil and on sulphur removal is shown in Figure 1, and the experimentally observed yields and specific gravity of the liquid product are shown in Figure 2. The results of the distillation analyses and sulphur determinations on the distillate fractions are given in Figure 3.

The differences between the reaction characteristics of the two bitumens were small but significant from the point of view of a commercial operation. All things being equal, the limiting factor in thermal hydrocracking is the temperature at which coke and sludge begin to accumulate in the system*. The bitumen containing the 3.8 % mineral matter is clearly much more resistant to coke formation, permitting (on the average) 10°C higher reaction temperatures. This is partially off-set by the fact that bitumen containing the 3.8 % mineral matter is also slightly more resistant to hydrocracking, requiring approximately 5°C higher reaction temperatures to achieve the same degree of conversion of residuum to distillate. The net result is a small, higher conversion-potential with the feed stock having the greater mineral content.

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*to operate continuously, all the fractions, including the bottoms, must remain predominantly fluid (to facilitate removal) and there can be virtually no accumulation of solid matter anywhere in the system.
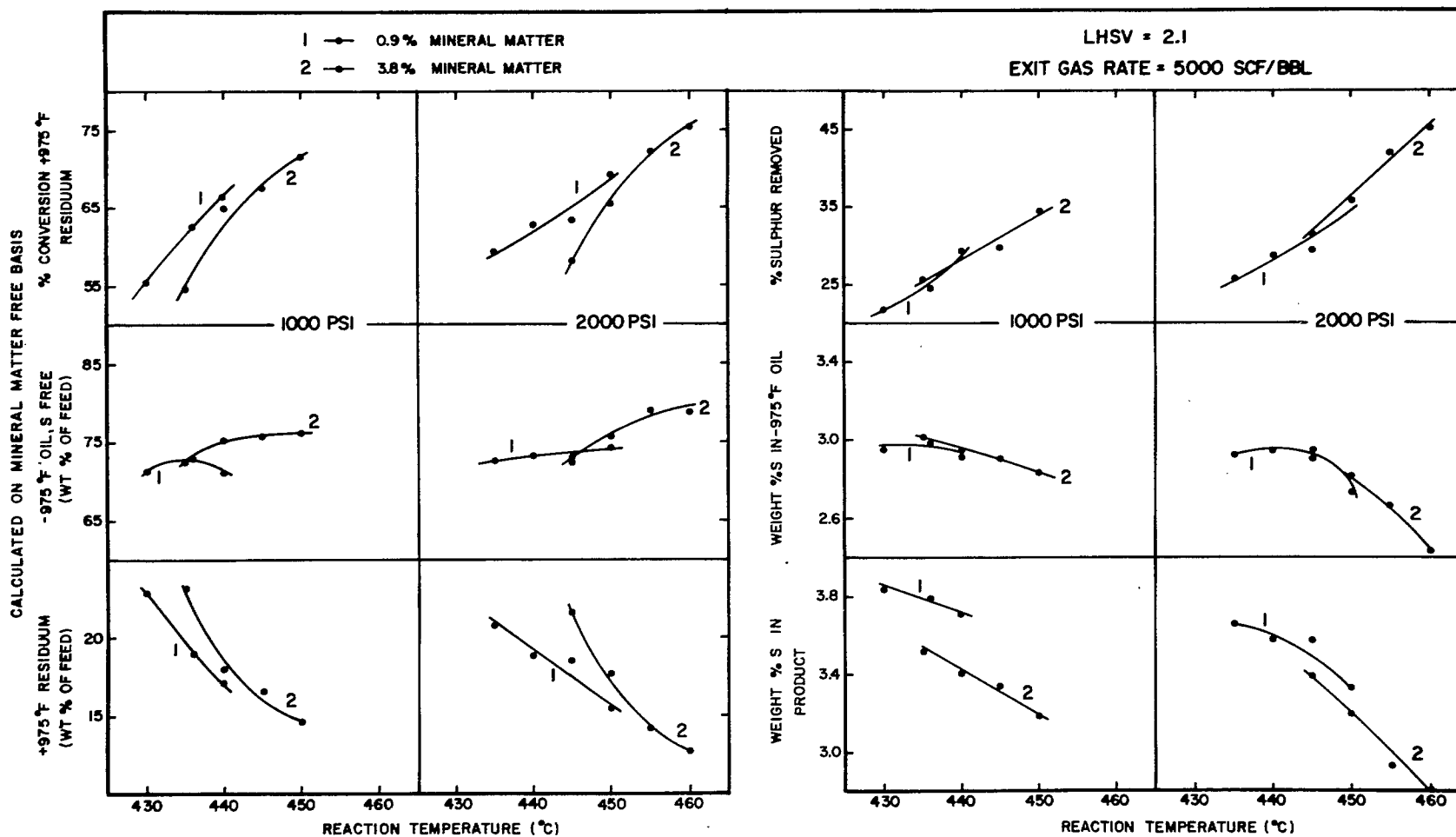
Figure 1 - The effect of reaction temperature in thermal hydrocracking on the conversion of the residuum hydrocarbon to distillable oil and on sulphur removal. (Note: the residuum remaining in the product and the distillable oil produced are expressed as weight % of feed.)
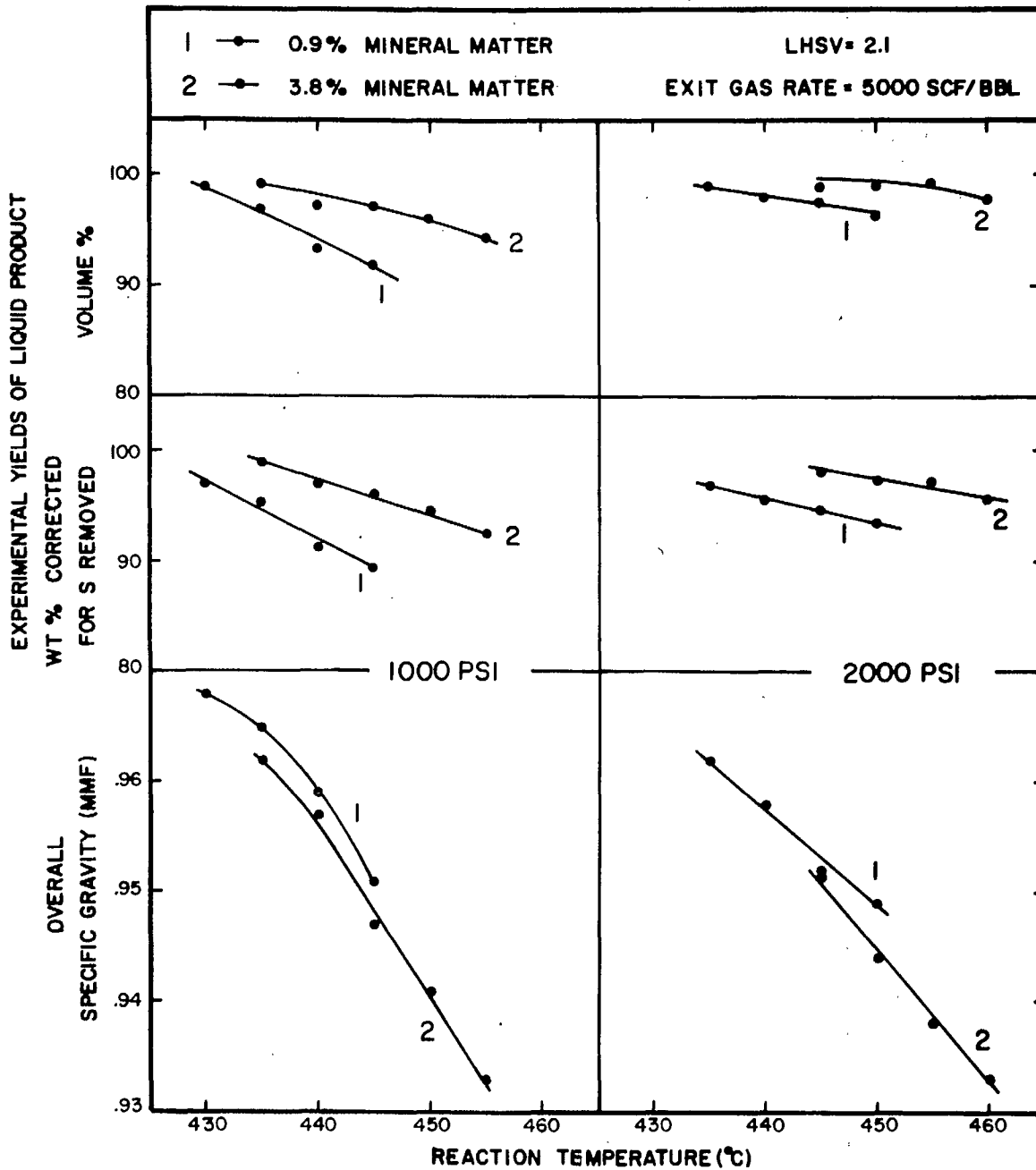
Figure 2 - The specific gravity and experimentally observed yields
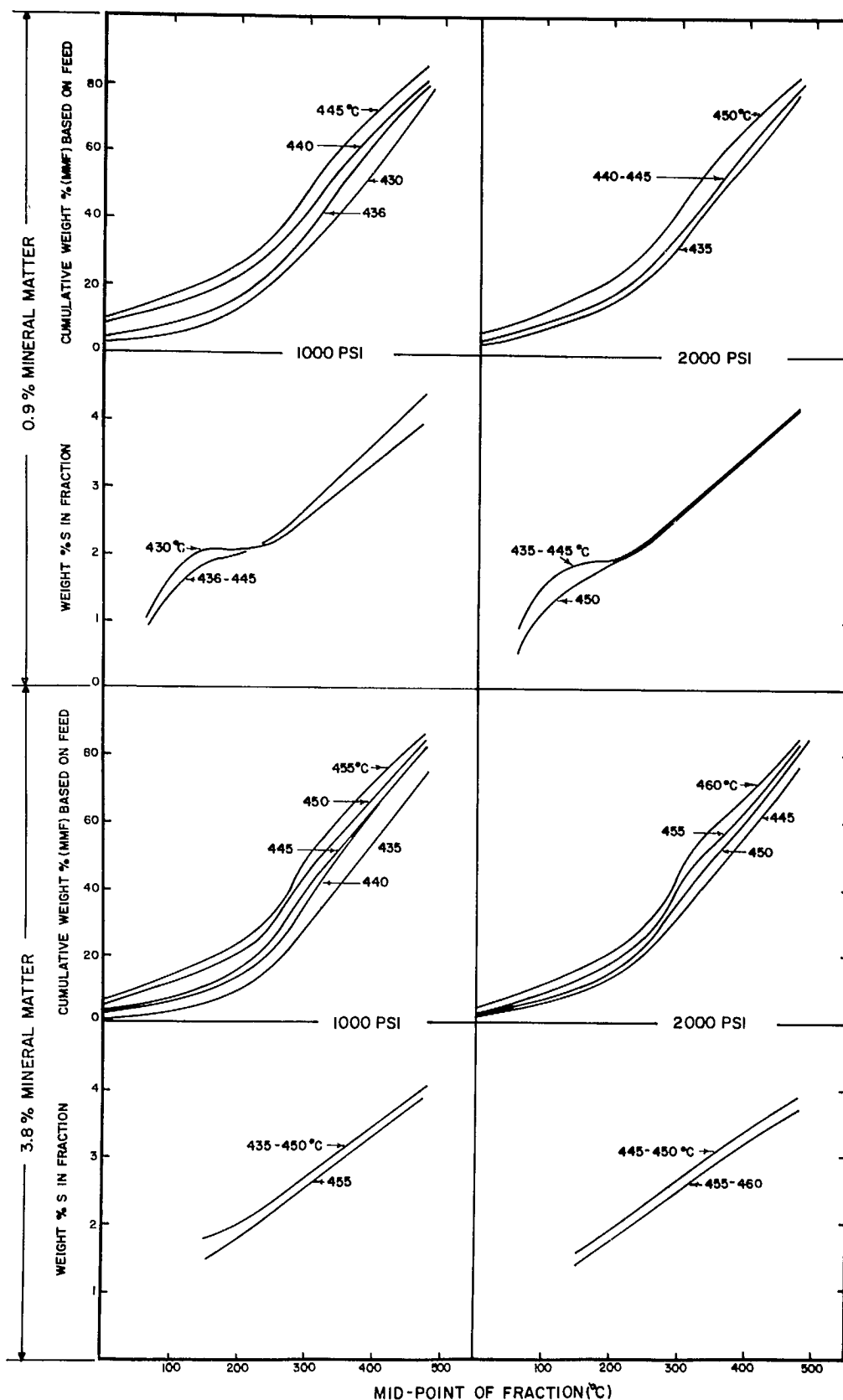of liquid product obtained in thermal hydrocracking.

Figure 3 - The effect of reaction temperature in thermal hydrocracking on the
yield and sulphur content of the product fractions. (Note: the
product fractions are expressed as weight % of feed with the extent
of gas formation indicated at 0°C. The boiling range of the fractions
used are the same as those shown in Table 2.)

Considering the net result, the higher mineral concentration would appear to be a beneficial catalyst for the over-all thermal hydrocracking process. It must be emphasized, however, that the effect is not straight-forward. The present work indicates that the mineral matter is not acting as a hydrocracking catalyst, i.e., measurably higher reaction temperatures were required to achieve the same degree of conversion with the 3.8 % mineral matter bitumen than with the 0.9 % bitumen. The primary effect of the mineral matter is to suppress the coking and fouling reactions that limit operating temperatures. The mineral matter is acting as a negative catalyst which, over-all, is beneficial to the effectiveness of the process.

The increase in the extent of conversion possible (at higher temperatures) is more apparent at high pressure than at low pressure. At 2000 psi, 75 - 76 % of the +975°F residuum hydrocarbon present in the high-mineral-content bitumen can be hydrocracked to distillate fractions compared to only 68 - 69 % with the low-mineral bitumen. The corresponding conversion figures at 1000 psi are 71 - 72 % and 66 - 67 % respectively. The increased conversion observed (at both pressures) with the 3.8 % mineral matter bitumen shows up almost entirely as an increase in liquid distillate hydrocarbon produced. This is in sharp contrast to the lower-mineral feed stock where the higher reaction temperatures are associated with extensive gas formation.

Some gas formation can be tolerated in a commercial operation for use as fuel in the pre-heaters of the secondary refining stages, but the over-all requirement is limited and excessive gas formation is wasteful* of the resource. The extent of gas formation encountered with the two bitumens is summarized in Table 3. It is drawn to the attention of the reader that the data shown in Table 3 were calculated by difference from the material balance of the experiment. In the bench-scale apparatus used for this work, there was no provision for measuring directly the amount of hydrocarbon gases formed. At all the temperatures

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*Experience has shown that crack-gas from high-sulphur feed stocks cannot be recycled for hydrogen generation because of the difficulty of removing trace quantities of certain sulphur-containing contaminants and the detrimental effect these have on the reforming catalysts. To date, long-term (successful) hydrogen production is only possible on a large scale with natural gas.

studied, the extent of gas formation was significantly less with the high-mineral bitumen than with the low. This is undoubtedly due, in part, to the smaller amount of light-ends present in the high-mineral feed stock. Low-boiling fractions are notoriously prone to gas formation in high-temperature processes. High pressures tend to suppress this (as indicated in Table 3) but cannot eliminate it entirely.

Table 3

Gas Formation in the Thermal Hydrocracking Process
(by difference)

Reaction Temp (°C)	Operating Pressure (psi)	Wt % Feed Converted to Gas	
		0.9 % min mat	3.8 % min mat
435	2000	3.1	-
440		4.2	-
445		5.1	1.9
450		6.3	2.5
455		Coking	2.2
460		Coking	4.3
430	1000	2.8	-
435		4.6	0.9
440		8.7	3.0
445		10.4	3.6
450		Coking	5.3
455		Coking	7.5

LHSV = 2.1   Exit gas rate = 5000 scf/bbl

On the matter of sulphur removal the results indicate that the mineral matter possesses little, or no, catalytic activity for desulphurization. The graphs (Figure 1) obtained with the 3.8 % mineral matter bitumen are virtually all extensions (at higher temperatures) of the corresponding lines obtained with the bitumen containing only 0.9 % mineral matter. The only exception to this statement is a minor change in slope in the graph of the "% Sulphur Removed" observed at 2000 psi.....however, this change is small and the over-all sulphur removal is still low, of the order of 30 - 40 % compared to the 80 - 90 %

normally observed in the catalytic reaction. The small improvements in desulphurization obtained with the higher-mineral feed stock appears to reflect only those which would be expected at the higher operating temperatures.

Note: At first glance there appears to be a discrepancy between the "% Sulphur in the Product" and the over-all "% Sulphur Removed". (On the one hand, the sulphur content of the liquid products formed from the 0.9 % mineral content bitumen is measurably greater than that produced from the 3.8 % mineral bitumen, yet the over-all conversion levels are essentially equal). There is actually no conflict of results here. The equivalent conversion levels observed come about as the result of the greater gas-make with the low-mineral bitumen (and the lower yield of liquid product) compared to the 3.8 % mineral feed stock. The calculations involving liquid yields, gas production, and sulphur removal are entirely consistent with one another.

Catalytic Hydrocracking

The series of experiments with each bitumen feed in catalytic hydro-cracking consisted of four consecutive 3-hour runs at increasing temperatures 430, 440, 450, and 460°C followed by a 3-hour repeat run at 440°C. The product of the second run at 440°C was compared with that from the first to obtain a measure of the extent of catalyst deactivation. (The background to this particular procedure is explained fully in the second report of this series). All of the experiments involving the catalyst were undertaken at 2000 psi pressure at a LHSV = 1.05. In the case of the bitumen feed stock containing 3.8 % mineral matter an additional run was made at 470°C at the conclusion of the series to determine the activity of the catalyst at elevated temperatures. The results are summarized in Figures 4 to 6. The effect of reaction tempera-ture on the conversion of the residuum hydrocarbon to distillable oil (and on sulphur removal) is shown in Figure 4, and the specific gravity and the experimentally observed yields of liquid product formed are indicated in Figure 5. The yields and sulphur contents of the various distillate fractions are given in Figure 6.

As in the case of the thermal process, the bitumen containing the higher mineral content was observed to be (generally) more resistant to hydrocracking than the bitumen containing the smaller amount of mineral matter. The situation,
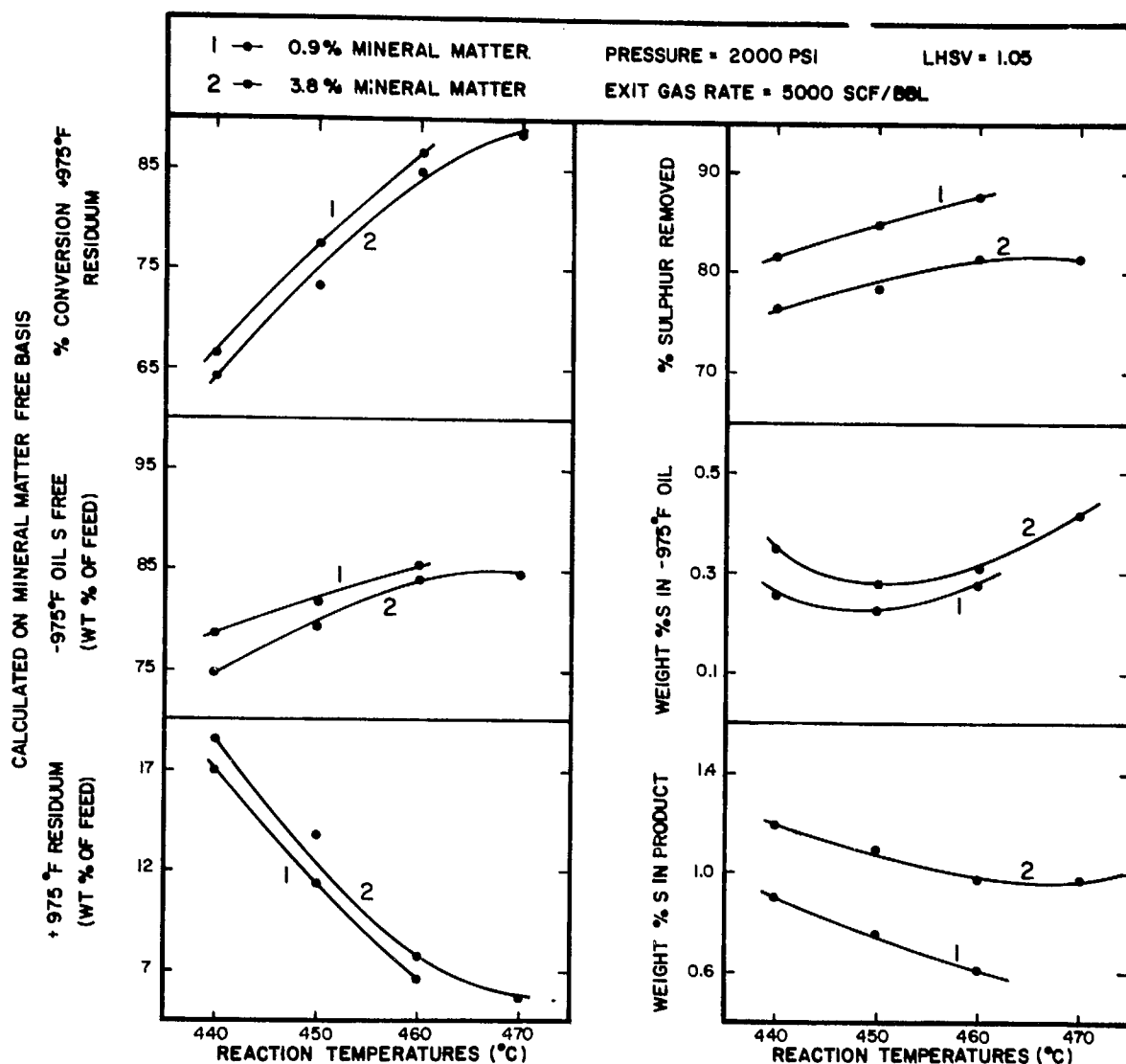
Figure 4 - The effect of reaction temperature in catalytic hydrocracking on the conversion of the residuum hydrocarbon to distillable oil and on sulphur removal. (Note: the residuum remaining in the product and the distillable oil produced are expressed as weight % of feed.)
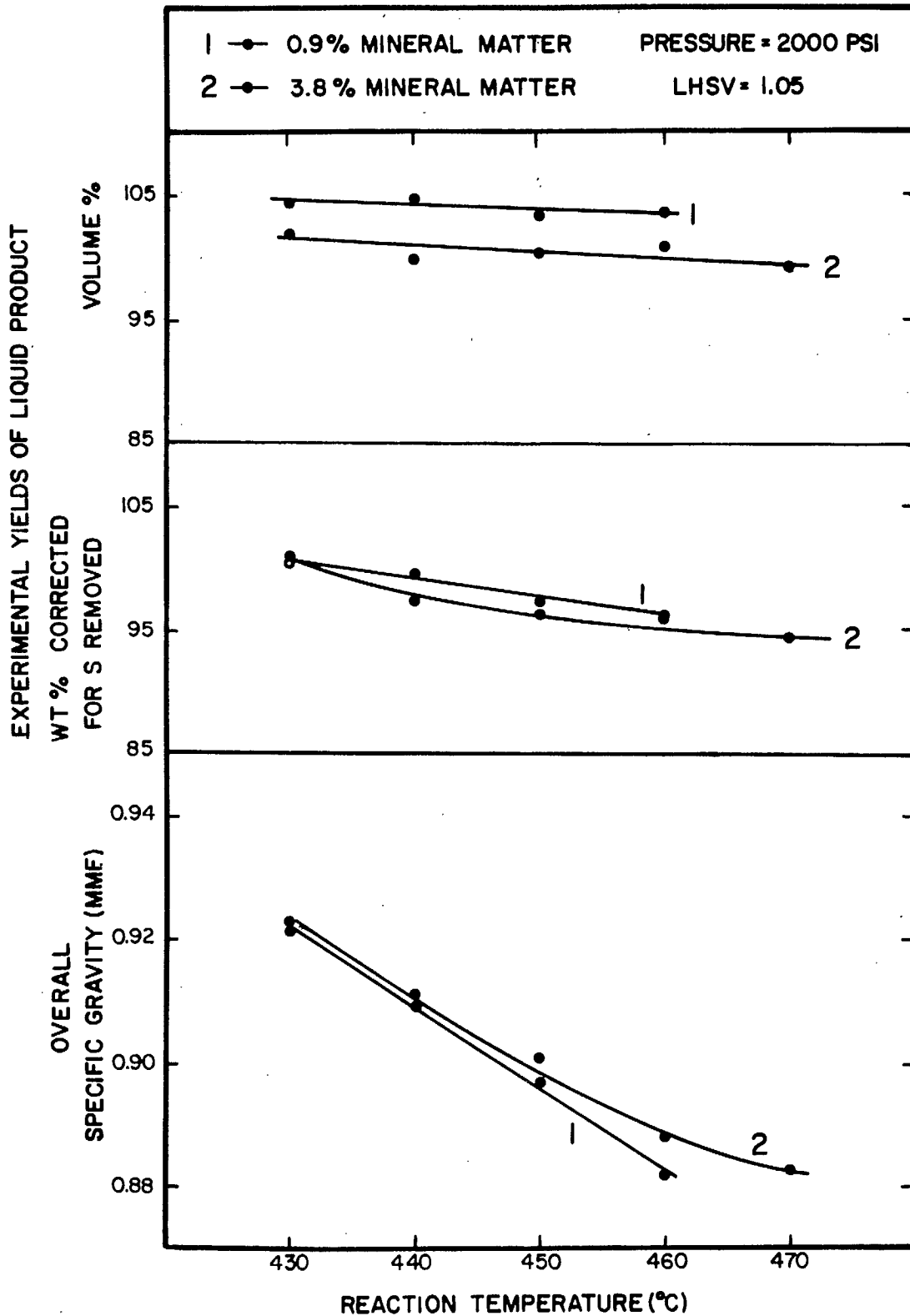
Figure 5 - The specific gravity and experimentally observed yields
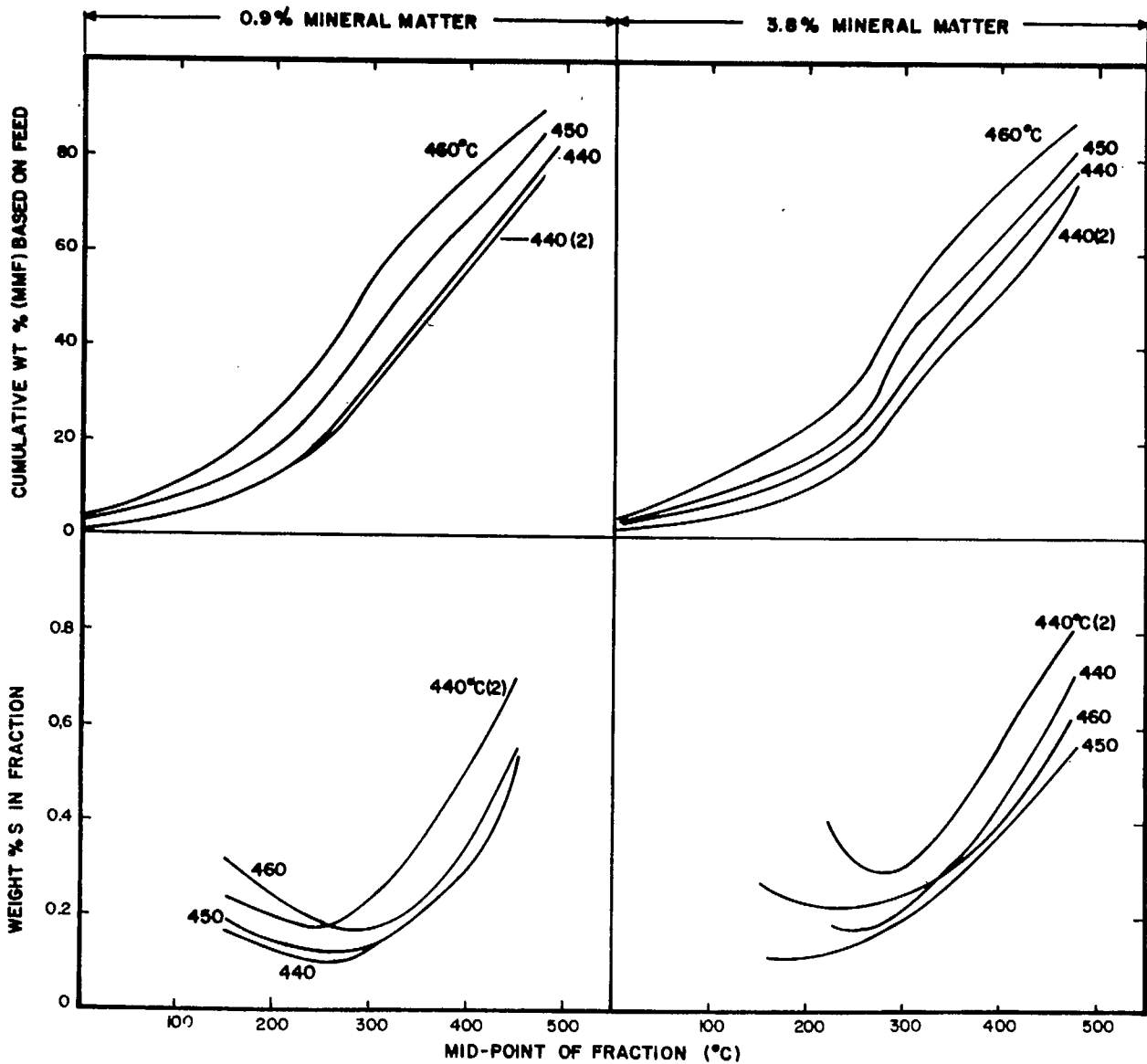of liquid product obtained in catalytic hydrocracking.

Figure 6 - The effect of reaction temperature in catalytic hydrocracking on the yield and sulphur content of the product fractions. (Note: the product fractions are expressed as weight % of feed with the extent of gas formation indicated at 0°C. The boiling range of the fractions used are the same as those shown in Table 2.)

however, differs markedly from the thermal process in that it does not appear to be possible to compensate for this higher resistance by increasing the reaction temperature. Comparing the runs at 440°C in Figure 6, the degree of catalyst deactivation observed with the high-mineral bitumen feed stock is substantially greater than that observed with the low-mineral feed stock..... increasing the reaction temperature under these circumstances only compounds the deactivation problem further resulting in no real (or only marginal) improvement in conversion. With the bitumen containing 3.8 % mineral matter, the extent of conversion of the residuum hydrocarbon was 2 to 3 % less and the sulphur removal was 5 to 7 % less than those obtained in the corresponding experiments with the low-mineral bitumen. Consistent with these observations, the over-all yields of liquid product at all temperatures were also measurably less than those obtained with the bitumen containing 0.9 % mineral matter.

The present work leaves no doubt whatsoever that the higher-mineral content reduces the effectiveness of the catalytic hydrocracking process. None of the experiments undertaken here indicate precisely the mechanism of the deactivation but a reasonable hypothesis would be that a part of the clay and silt present in the feed is gradually accumulating on the catalyst surface, and further, that the physical amounts involved increase in proportion to the concentration of the residual solids in the feed. The amounts of solids deposited on the catalyst surface were not (visibly) large, or significantly different with the two bitumens, but if the clay particles are laid down directly on the active sites in the course of the reaction of the oil attached to the particle* the effect on catalyst activity would be (and apparently is) extensive.

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*most of the residual solids particles must be at least partially oil wet or they would have been removed in the froth flotation steps of the separation process.

To summarize, the investigation has demonstrated:

1. Thermal Hydrocracking - higher reaction temperatures are
   possible with the bitumen containing the greater concentration
   of mineral matter (resulting in potentially greater conversion
   and higher yields of distillate product),

   a) the action of the mineral matter is to suppress coke and
      gas formation (and general reactor fouling),

   b) the experimental evidence indicates no direct hydrocracking
      or desulphurizing activity attributable to the mineral matter;

2. Catalytic Hydrocracking - the higher mineral content of the
   bitumen is detrimental to the effectiveness of the reaction
   in every respect.

ACKNOWLEDGEMENTS

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