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*THE HYDROCRACKING OF RESIDUAL OILS  
AND TARS  
PART 2: THE CATALYTIC HYDROCRACKING  
OF ATHABASCA BITUMEN*

E. C. MCCOLGAN AND B. I. PARSONS

FUELS RESEARCH CENTRE

AUGUST 1972

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THE HYDROCRACKING OF RESIDUAL OILS AND TARS  
PART 2: THE CATALYTIC HYDROCRACKING OF ATHABASCA BITUMEN

by

E. C. McColgan\* and B. I. Parsons\*\*

ABSTRACT

The report describes a bench-scale investigation of the catalytic hydrocracking of the +975°F residuum in Athabasca bitumen with a view to a) increasing the yield of liquid hydrocarbon obtained compared with coking or purely thermal hydrocracking methods, and b) reducing the extent of on-site treatment required to produce relatively clean, stable distillates suitable for transmission to more central areas. The experiments were made in the liquid phase, using a conventional flow apparatus with a bottom-feed reactor and a commercially available cobalt molybdate catalyst. The range of pressures investigated was 1000 to 2500 psi at space velocities of 1.05 and 2.1. Comparing the yields of liquid product obtained by catalytic methods with those obtained by purely thermal hydrocracking, the permissible catalyst cost is estimated at 50 - 55¢ per barrel of feed.

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\*Technician and \*\*Research Scientist, Fuels Research Centre, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada.

Direction des mines

Rapport de recherches R 253

L'HYDROCRAQUAGE DES HUILES RÉSIDUELLES  
ET DES GOUDRONS

2<sup>e</sup> Partie: L'HYDROCRAQUAGE CATALYTIQUE DU  
BITUME D'ATHABASCA

par

E. C. McColgan\* et B. I. Parsons\*\*

RÉSUMÉ

Ce rapport décrit une recherche faite au laboratoire sur l'hydrocraquage catalytique du +975°F résidu dans le bitume d'Athabasca dans le but de a) augmenter le rendement du liquide d'hydrocarbure obtenu par la cokéfaction ou par les méthodes d'hydrocraquage purement thermique, et b) réduire le degré de traitement nécessaire pour produire des distillats relativement propres et stables convenables pour la transmission aux endroits plus centraux. Ils ont fait des expériences à la phase liquide utilisant un appareil d'écoulement ordinaire avec un réacteur d'alimentation par le bas et un catalyseur disponible commercialement au cobalt et au molybdène. La gamme des pressions étudiées a été de 1000 à 2500 psi aux vitesses spatiales de 1.05 à 2.1. En comparant les rendements du produit liquide obtenu par les méthodes catalytiques à ceux obtenus par l'hydrocraquage purement thermique, ils ont trouvé que le coût du catalyseur permissible est estimé à 50-55¢ par baril d'alimentation.

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## INTRODUCTION

### General

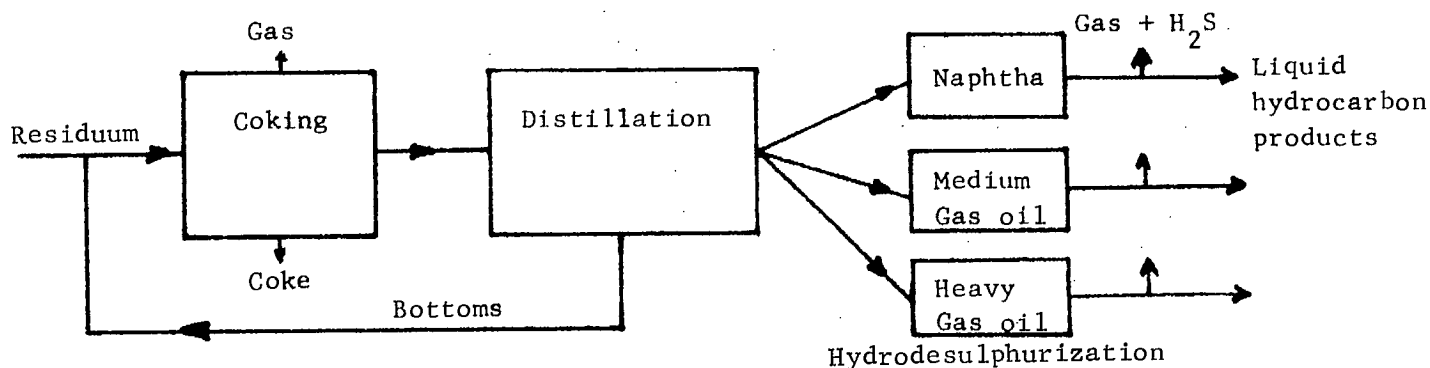
The following report is the second in a series on the investigation of techniques for hydrocracking residual oils and tars and the production of low-sulphur distillates and fuel oils. In the first report (1) the effect of feed dilution on the thermal hydrocracking of Athabasca bitumen (2) was determined. The present work is concerned mainly with the catalytic process as applied in a liquid phase system to the Athabasca bitumen. The results of catalytic and purely thermal hydrocracking are compared with a view to estimating permissible catalyst cost compatible with increased liquid yields.

The refining and upgrading of any residual petroleum is complicated (and expensive) compared with conventional crude oils. There are three main reasons for this:

1. The hydrogen content of residual oils and tars is low relative to conventional crude oil and extensive hydrogenation is required to convert the oil into usable, marketable material. The cost of the hydrogen required represents approximately half the overall refining cost (3, 4, 5, 6).
2. The average molecular weight of a residual oil is high and extensive cracking is required to reduce the boiling point. Some coke and sludge formation on the catalyst seems to be inevitable in the cracking process, regardless of how it is accomplished. The more cracking is required the more acute the catalyst fouling problem becomes.
3. Impurities are usually encountered in residual oils and tars in much higher concentrations than in conventional crude. Impurities of all types have an important bearing on the selection (and cost) of the catalysts involved and have a tremendous effect on the rate of catalyst fouling and the general effectiveness of refining. Sulphur concentrations of the order of 3 to 5 % are common in residual oils; nitrogen levels are frequently in the vicinity of 0.5 %; the oxygen content (in the case of tar sands oils) can be as great as 1 % and the concentration of combined metals (V, Ni and Fe) is often 400 ppm or greater.

A successful refining scheme for a residual oil or tar must overcome all of the above difficulties. In Canada at the present time, few residual oil stocks are being processed. Great Canadian Oil Sands Ltd. of Fort McMurray, Alberta, (refining Athabasca bitumen) is the only company currently processing a residual feed stock in significant quantities\*. Approval for the construction of a second plant in the Tar Sands area has been given to Syncrude Canada Ltd. (8) and considerable interest in Athabasca bitumen has been expressed recently by the Shell Oil Co. (9a), Texaco and Union Oil (9b). A number of plants are in operation on residual crudes from other parts of the world, notably in Japan, (10, 11) and in the Carribean (5).

The traditional procedure for upgrading residuals is a three-step process in which part of the high-molecular-weight asphaltics and resins are cracked by thermal coking, followed by distillation and the hydrodesulphurization of the vapours to form low-sulphur, marketable liquid hydrocarbons.



The only major improvement in this scheme that has taken place in recent years has occurred in the distillation step. Mechanical improvements now permit vacuum separations of undistillable and distillable hydrocarbon up to the equivalent of 1000°F at atmospheric pressure compared to 800 - 850°F previously. On a commercial scale, once the separation of the distillable and undistillable material has been accomplished the problems are minimal (3, 12). The naphtha

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\*Several refineries in eastern Canada accept a small percentage of their total requirements in the form of residual oil. Under such circumstances, substantially less upgrading is required because the lower-grade hydrocarbon is merely blended with higher-quality material.



and gas-oil fractions are desulphurized relatively easily at low pressures (700 - 1200 psi). Each stream must be handled slightly differently in conventional fixed-bed reactors to minimize gasification and carbon deposition on the catalyst.

There are, however, a number of undesirable features associated with the traditional three-step process. First and foremost, the coking step is wasteful of the resource and produces a high-sulphur coke for combustion purposes. In the coking process the best of the resin and asphaltic material in the tar is converted by cracking and hydrogen abstraction into distillate hydrocarbons by the direct application of heat, and the more refractory components in the feed degenerate to coke. Conversion of the +1000°F fractions to distillable hydrocarbons rarely exceeds 45 - 50 %, and the sulphur content of the coke usually occurs in the range 6 to 8 % by weight with the coker distillate containing approximately 4 % sulphur. A second drawback to the three-step process is the fact that it is a mechanically complicated scheme and (relatively speaking) both maintenance and labour intensive. This is perhaps of less importance in the more accessible and densely populated parts of the world but it is a very important factor in remote areas such as the Canadian North.

The purpose of the present work is to explore, in a preliminary way, the prospects for a direct (one-step) catalytic treatment of a residual oil for the production of comparatively clean, stable distillates for transmission to areas close to market. Specifically, the investigation is aimed at the treatment of the Athabasca bitumen with a view to minimizing the extent of on-site processing required before pipelining to central regions. The objective of the catalytic treatment is not to produce fractions "ready-for-market" as is the case with the existing plant (7) or, for that matter, the proposed one (8). Rather, the object is to achieve sufficient conversion and stabilization to permit transmission to areas with access to cheap hydrogen supplies from gasoline reformers operating on fractions derived from conventional crude. An inescapable aspect of the economics of the situation is that hydrogenation (and hydrogen) represent a major part of the cost, and any significant reduction in cost in this phase will be ultimately process determining.

It has long been known from experimental work on coal (13) that catalytic hydrocracking or hydrogenation results in substantially greater yields of liquid product, and less gasification, than the corresponding non-catalytic process. In the present work experiments have been undertaken on the bitumen both catalytically and thermally, under essentially identical conditions (equipment, feed stock, etc.) for the purpose of measuring accurately the extent of increased yield and purity attributable to the catalyst. From the increased yield of (marketable) liquid product a "break-even" permissible catalyst cost is to be estimated based on a product value of \$4.00 per barrel.

Many factors effect catalyst cost in a hydrogenation process.....the operating pressure, the degree of conversion being achieved, the ability of the catalyst to withstand regeneration and the duration of operation possible between regenerations. With crude oils of a conventional type, a hydrocracking catalyst has a comparatively long effective-life and costs are low. Some measure of difficulty is sometimes encountered because of the gradual build-up of coke deposits on the catalyst but, usually, these deposits can be burned off under controlled conditions and the catalyst activity restored to something approaching that of the original. The difficulty with residual oils, and the bitumen from the Athabasca tar sands in particular, is compounded because of the high concentration of chemically combined nickel and vanadium. As reaction proceeds in the hydrocracking process, appreciable percentages of the metals are deposited onto the active sites of the catalyst, and the effectiveness of the catalyst decreases at a much more rapid rate than can be accounted for simply by coke formation. Metal deposits cannot be removed by conventional regeneration (burning) techniques and the catalyst must be replaced.

Virtually all of the currently advertised catalytic processes being offered for license for residual oils (14) have severe limits on the permissible metals concentration. The "residuals" referred to are, generally, from middle east sources with metals concentrations of the order of 40 - 60 ppm (10). Feed stocks such as the Athabasca bitumen (with a total concentration of combined metals, V, Ni and Fe, in the range 300 - 600 ppm) are rarely mentioned. For a bitumen type of feed, catalyst life will undoubtedly be short.....of the order of 50 - 200 hours depending

upon operating pressure and the degree of conversion being achieved (15, 16). Catalysts involved must be cheap and a means must be provided in the mechanical arrangement for adding and removing catalyst because of the difficulty of operating with short on-stream times.

The simplest mechanical arrangement for adding and removing catalyst either continuously or semi-continuously occurs with a fluidized bed. A liquid phase fluidized-bed system has been assembled at the Mines Branch (17), modelled mostly on German experience (18). In Germany, liquid phase systems were operated at quite high pressures, of the order of 5000 psi, and any unreacted material passing through the reactor was recycled. There is no question that both the yield and quality of products from a hydrogenation system improves at higher pressures, but the capital cost today of the equipment involved reduces the prospects for a high pressure process. All recent experiments at the Mines Branch have been undertaken at 1000 and 2000 psi. At these lower pressures, the recycle of unreacted material is at present impractical because of the effect on catalyst life. The group effort has been concentrated on the development of a once-through liquid phase system that uses a low-cost catalyst.

The biggest problem encountered in establishing a reasonable scheme for estimating catalyst life (and cost) is really the availability of labour for long, uninterrupted, experimental runs. Without this restriction it would be a relatively simple matter to just run a catalyst "to death" with a particular feed stock under a given set of conditions, regenerate the system, and repeat ad-infinitum until one obtained an accurate measure of the practical weight of oil which can be processed by a unit amount of catalyst. However, the labour restriction does exist, and always will, therefore the challenge is to develop a scheme of bench-scale measurements which will give an indication of the desired result.

The system of experiments finally settled upon here to indicate relative catalyst activity and life was a series of four consecutive 3-hour experiments at increasing reaction temperatures, 430, 440, 450 and 460°C, followed by a 3-hour repeat run at 440°C. It was felt that the relative activity of the repeat run at 440°C reflected the activity to be expected after many hours of operation. To some degree this was confirmed by a series of runs at 440°C totalling 40 hours of

operation. The extent of deactivation encountered at 440°C indicated large differences in the effect of operating variables (pressure, space velocity, etc.) and served well to guide the experimental program to better conditions. The scheme was developed initially for the purpose of comparing catalysts but is presented here as a study on one catalyst, a typical industrial cobalt molybdate catalyst, to show the relative effect of operating variables and to establish a base easily related to experience in other laboratories.

#### EXPERIMENTAL

##### Apparatus and Procedure

The major components of the apparatus and the general method of operation have been described previously (1, 16). The reaction vessel (internal dimensions: 1-inch diameter and 12 inches long) was machined from 316 stainless steel and designed for operation up to 10,000 psi at 500°C. In almost all of the experiments, the oil feed and hydrogen were pumped in at the bottom of the reactor, i.e., the system was operated as a continuous flow, predominantly liquid phase, reactor. For the purposes of comparison, a few experiments were undertaken with the system operated in a top-feed arrangement. In this mode the feed flows down through the reactor mainly by gravity as a continuous film on the surfaces of the catalyst. The feed and products in contact with the catalyst in the top-feed arrangement are generally regarded as being mix-phased, liquid and vapour. The temperature profile through the reaction zone in all of the experiments 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 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 all Figures and Tables). A fresh charge of catalyst was placed in the reaction vessel for each series of experiments. A conventional pre-heater system was not used in the present work. The advantages of accomplishing the last stages of feed preheat in the presence of catalyst had been demonstrated previously (16). The general procedure used here was to heat the bitumen to reduce the viscosity for pumping purposes (100 - 125°C),

mix it with the hydrogen at about 150°C and deliver the mixture to the bottom of the catalyst bed (or the empty reaction tube in the case of the non-catalytic experiments) at about 300°C. The balance of the preheating was accomplished in the reaction vessel.

#### Analytical Procedures

The extent of conversion of the residual material to distillable hydrocarbon was determined using a modification of the U. S. Bureau of Mines Hempel Distillation Analysis (19). A detailed description of the modifications made to the distillation procedure (in 3 steps at atmospheric pressure, 40 mm and 1 mm) is available in the first report in this series (1). A recalibration of the procedure using standard feed stocks analysed on the Podbielniak Flash Equilibrium Distillation Apparatus indicated that the final equivalent temperature attained was 975°C (not 990°C as previously reported). The sample collection procedure was modified slightly since the first report was written so as to record the fractions by weight.

The sulphur content of the various oil fractions was determined by X-ray fluorescence using a Model 4000 Panalyzer manufactured by Panametrics, a subsidiary of the Esterline Corporation of Waltham, Massachusetts. The source of the X-rays was Fe-55. Radiation striking the oil sample caused the sulphur atoms to emit their characteristic X-ray which was measured on a detector located behind the radioactive source. The apparatus was calibrated, in an absolute sense, by the direct addition of pure sulphur compounds such as di-phenyl sulphide (17.2 % S) and di-n-butydisulphide (21.9 % S) to sulphur-free oils, and in a relative sense, by comparing results obtained independently by an oxygen-bomb technique (ASTM procedure D129).

#### Feed Stock and Catalyst

The feed stock used in all of the experimental work was bitumen separated from the Athabasca tar sands. The material was supplied to the Mines Branch by Great Canadian Oil Sands Ltd. of Fort McMurray, Alberta. The bitumen was equivalent to the charging stock to their coking plant (7), i.e., centrifuged and topped. The properties of the bitumen (as received) and the results of the distillation analysis are shown in Table 1 and Figure 1.

TABLE 1

Properties of the Bitumen Feed Stock as Received  
from Great Canadian Oil Sands Ltd.

Specific gravity 60/60°F	1.000
Ash (wt %) 700°C	0.70
Nickel (ppm)	68
Vanadium (ppm)	189
Pentane insolubles (wt %)	15.83
Benzene insolubles (wt %)	0.90
Carbon Disulphide insolubles (wt %)	0.88
Sulphur (wt %)	4.72
Nitrogen (wt %)	0.38
Oxygen (wt %)	1.0
Viscosity, Kinematic (cSt) at 210°F	85
Viscosity, Kinematic (cSt) at 130°F	1140
Viscosity, Kinematic (cSt) at 100°F	4818

The catalyst used in all of the present work was a cobalt molybdate on alumina catalyst manufactured by the Harshaw Chemical Co. of Cleveland, Ohio. The catalyst, 1/8-inch-diameter pellets designated as CoMo-0603T by the manufacturer, is recommended for the denitrogenation and desulphurization of hydrocarbons by hydrotreating. It is reported to be a non-silicated catalyst containing 3 % cobalt oxide and 12 % molybdenum trioxide supported on alumina. The general physical properties are as follows:

apparent bulk density	64 lb/cu ft
crush strength	24 lb/pellet
surface area	166 m <sup>2</sup> /g
pore volume	0.40 ml/g

#### EXPERIMENTAL RESULTS AND DISCUSSION

The experimental work presented in this report is a condensation of many experiments undertaken over a long period. The order in which the results are presented was not the order in which the experiments were made. The information has been re-arranged to show the effect of the most important variables first.

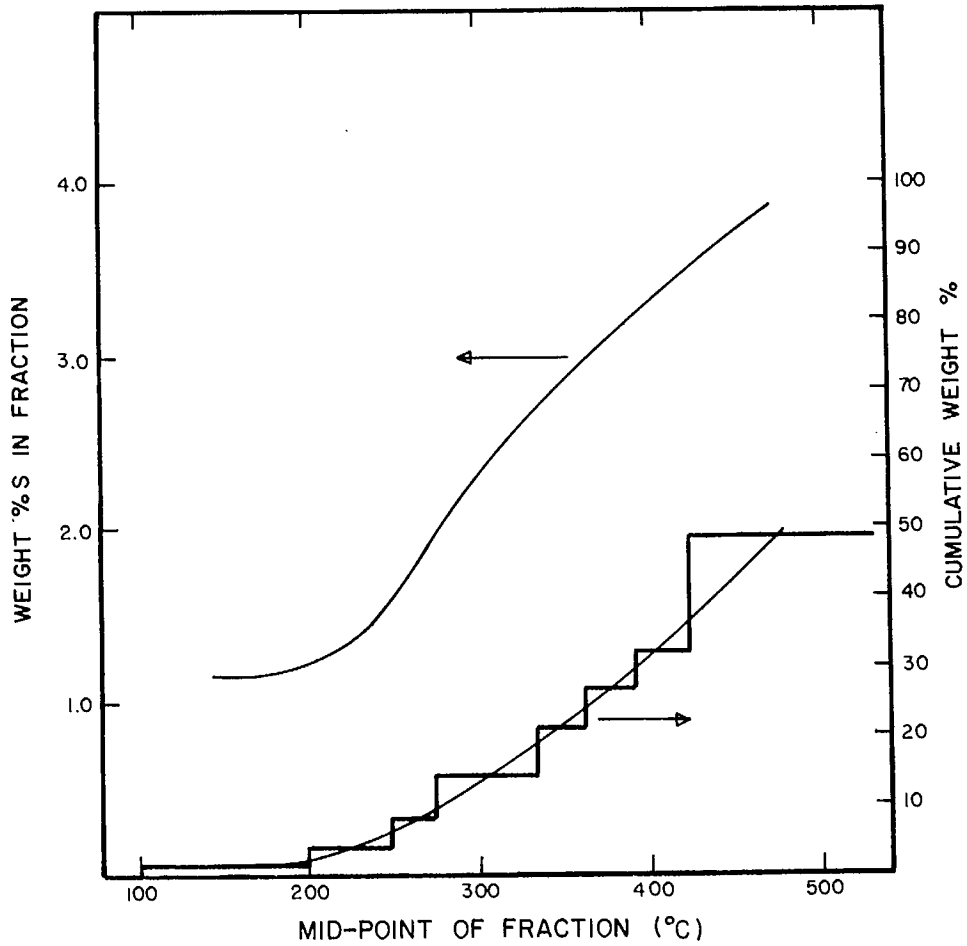


Figure 1 - Distillation and sulphur analyses on the bitumen feed stock as received from Great Canadian Oil Sands Ltd. (Boiling range of the fractions indicated as saw-tooth segments on lower curve.)

### Top-Feed versus Bottom-Feed

In general terms it was not possible to operate the top-feed system at high conversion levels for any reasonable period of time with the Athabasca bitumen. In the top-feed arrangement the part of the feed stock that is in the liquid phase flows down through the catalyst bed partly as the result of gravity and partly as the result of a "chromatographic" type of flow affected by the passage of the hydrogen. At high conversion levels the system runs sufficiently "dry" to deposit a large part of the mineral matter and chemically combined metals in the interstitial space and the system plugs rapidly. This type of behaviour was reported some years ago in this laboratory (16) and will not be commented on again in detail. The few experiments reported here now are intended only to emphasize that a conventional top-feed, or gravity-feed, system cannot bring about sufficient conversion (for a long enough time) to warrant further consideration.

The experimental conditions investigated (and some of the primary data) are shown in Table 2, and the results of the distillation and sulphur analyses are shown in Figure 2. The boiling range of the fractions used in the preparation of Figure 2 are indicated as saw-tooth segments along the 460°C curve in the lower left-hand section.

Under equal reaction conditions, both the extent of desulphurization (overall) and the degree of conversion of the residuum material to distillate oil and gas were much greater with the bottom-feed system than the top-feed. The results shown in Table 2 demonstrate this most clearly. It appears that, in the bottom-feed system because of its manner of operation, the residence time of the liquid phase material in the reaction vessel is much greater. In theory, at a liquid hourly space velocity (LHSV) of 1.05 the residence time is approximately twenty minutes\*. The actual residence time is undoubtedly greater than this because of the vapourization of the lighter fractions present either in the feed or resulting from reaction.

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\*The interstitial space around the catalyst pellets comprised one third of the reactor volume.....measured by filling the cold reaction vessel (packed with catalyst) with kerosene, then allowing the vessel to drain into a graduated cylinder.



TABLE 2

Comparison of Top-Feed and Bottom-Feed Systems

System	Reaction Temp. (°C)	Overall Product			%	%	Weight Yield Oil +S (%)	Volume Yield of Oil (%)
		Specific Gravity (60/60°F)	Sulphur (wt %)	+975°F Residuum (wt % mmf)*	Total Sulphur Removed	+975°F Residuum Converted		
Bitumen	-	1.000	4.72	51	-	-	-	-
Top Feed	440	0.965	2.67	33	45	35	100	101
	450	0.947	2.15	28	56	45	99	102
	460	0.936	1.80	22	63	57	99	103
	440(2)	0.963	2.62	32	46	37	100	101
Bottom Feed	440	0.926	1.36	15	73	71	98	102
	450	0.910	1.26	8	76	84	94	99
	460	0.899	1.25	4	77	92	90	96
	440(2)	0.937	1.94	18	61	65	98	102

Hydrogen Pressure 1000 psi

LHSV = 1.05

Exit Gas Rate = 5000 scf/bbl\*\*

\*mmf- mineral matter free

\*\*scf/bbl - standard cubic feet per barrel

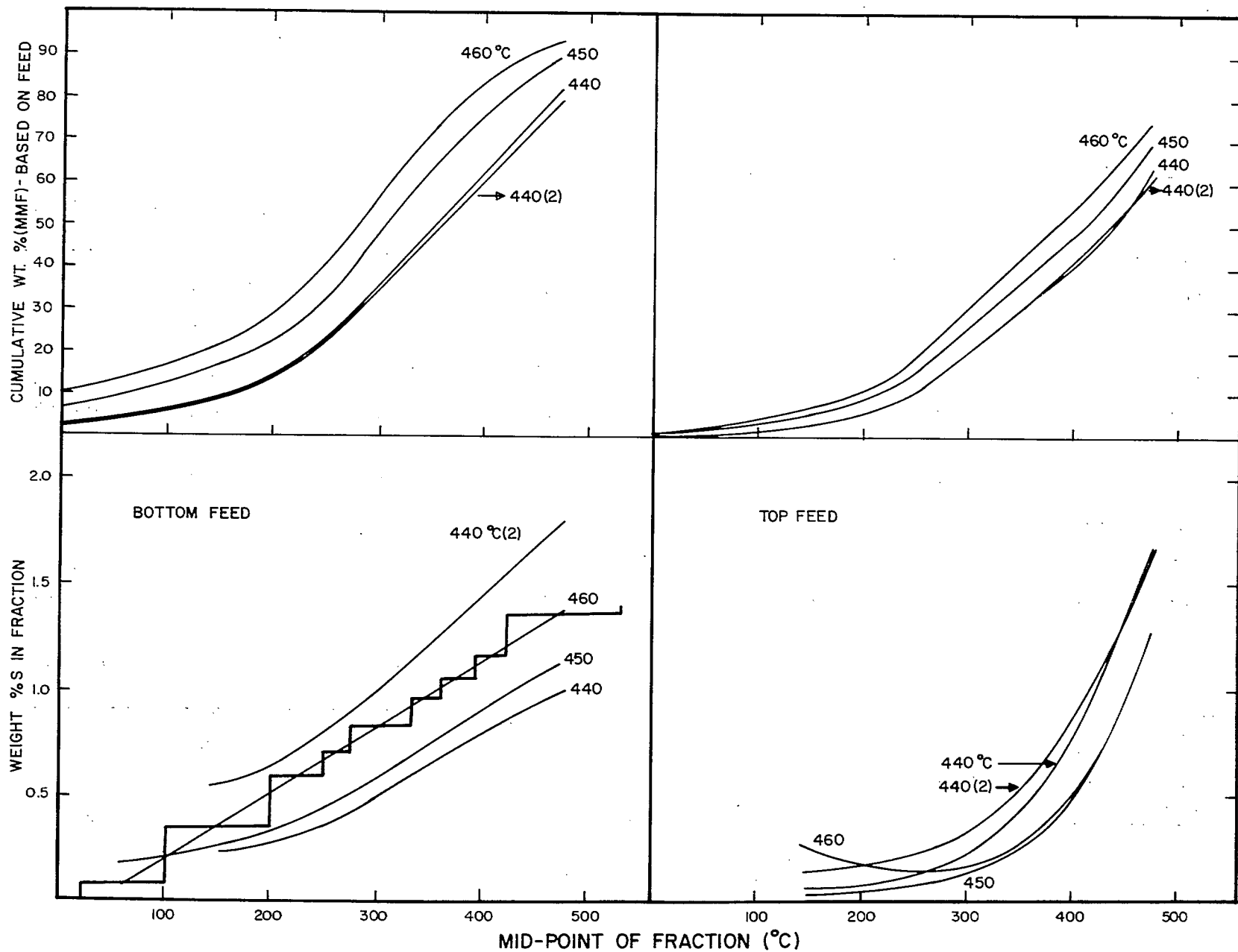


Figure 2 - The yield and sulphur content of distillate obtained with the top- and bottom-feed systems. (Boiling range of the fractions indicated as saw-tooth segments in the lower left-hand section.)

Hydrogen Pressure = 1000 psi; LHSV = 1.05; Exit Gas Rate = 5000 scf/bbl

In only one respect was the top-feed system superior to the bottom-feed. There was much less sulphur in the low-boiling fractions produced with the top-feed system than with the bottom-feed (Figure 2). The explanation of the difference is, once again, undoubtedly due to the difference in residence time affected by the manner of operation. In the bottom-feed system the material vapourizing rises due to buoyancy and leaves the reaction system quickly. With the top-feed system, on the other hand, the vapours are only flushed out of the system by the slowly flowing hydrogen and tend to remain in contact with the catalyst for a much longer period of time and, hence, are desulphurized more extensively.

#### The Effect of Hydrogen Pressure

The subject matter of the following section is principally the effect of hydrogen pressure on the deactivation of the catalyst. The effect of pressure and space velocity relative to catalyst cost will be discussed in the last section. From this point onwards in the report all experiments were undertaken in the bottom-feed, or liquid phase, mode of operation. The range of pressures investigated was 1000 to 2500 psi at a space velocity of 1.05. The general effects of hydrogen pressure on hydrocarbon yield, sulphur removal and specific gravity are shown in Figure 3, and the results of the distillation analyses and the sulphur content of the distillate fractions formed at the various pressures are shown in Figure 4.

Hydrogen pressure had a very profound effect on catalyst activity and the rate of catalyst deactivation. At 1000 psi pressure, the sulphur content of the heavy fuel oil fractions produced at 440°C (the fraction boiling 350 - 530°C equivalent temperature at one atmosphere) was initially less than 1 % by weight. The sulphur content of the same fraction produced in the second run at 1000 psi and 440°C (designated as 440°C (2) on the Figures) was over 1.5 %. In the corresponding series of runs at 2000 psi, the sulphur contents of these fractions were approximately 0.35 and 0.55 % respectively.

The emphasis throughout the world, at the present time, is on the development of means for producing heavy fuel oils containing not more than 1 % by

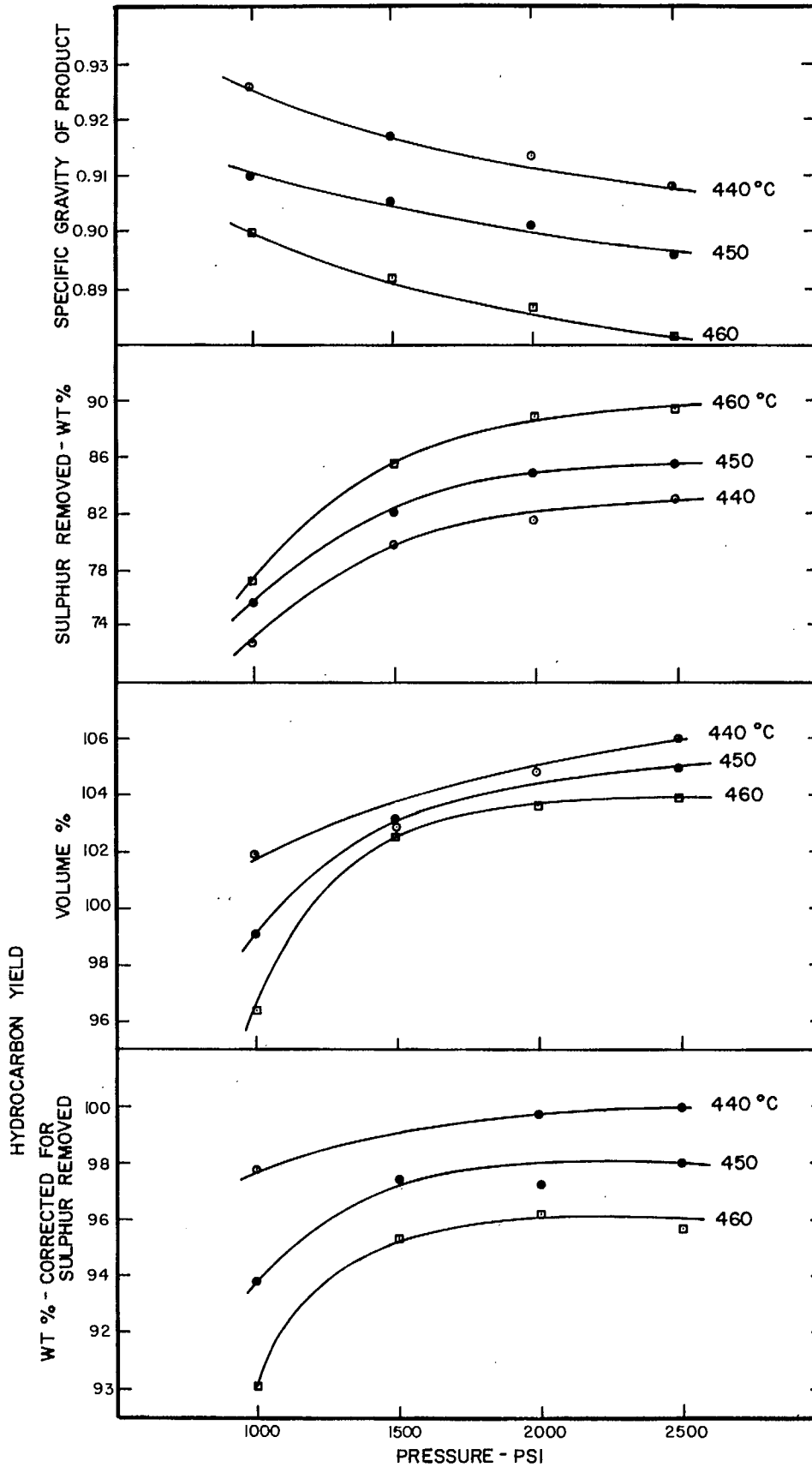


Figure 3 - Effect of hydrogen pressure on hydrocarbon yield, specific gravity and sulphur removal.

LHSV = 1.05; Exit Gas Rate = 5000 scf/bbl.

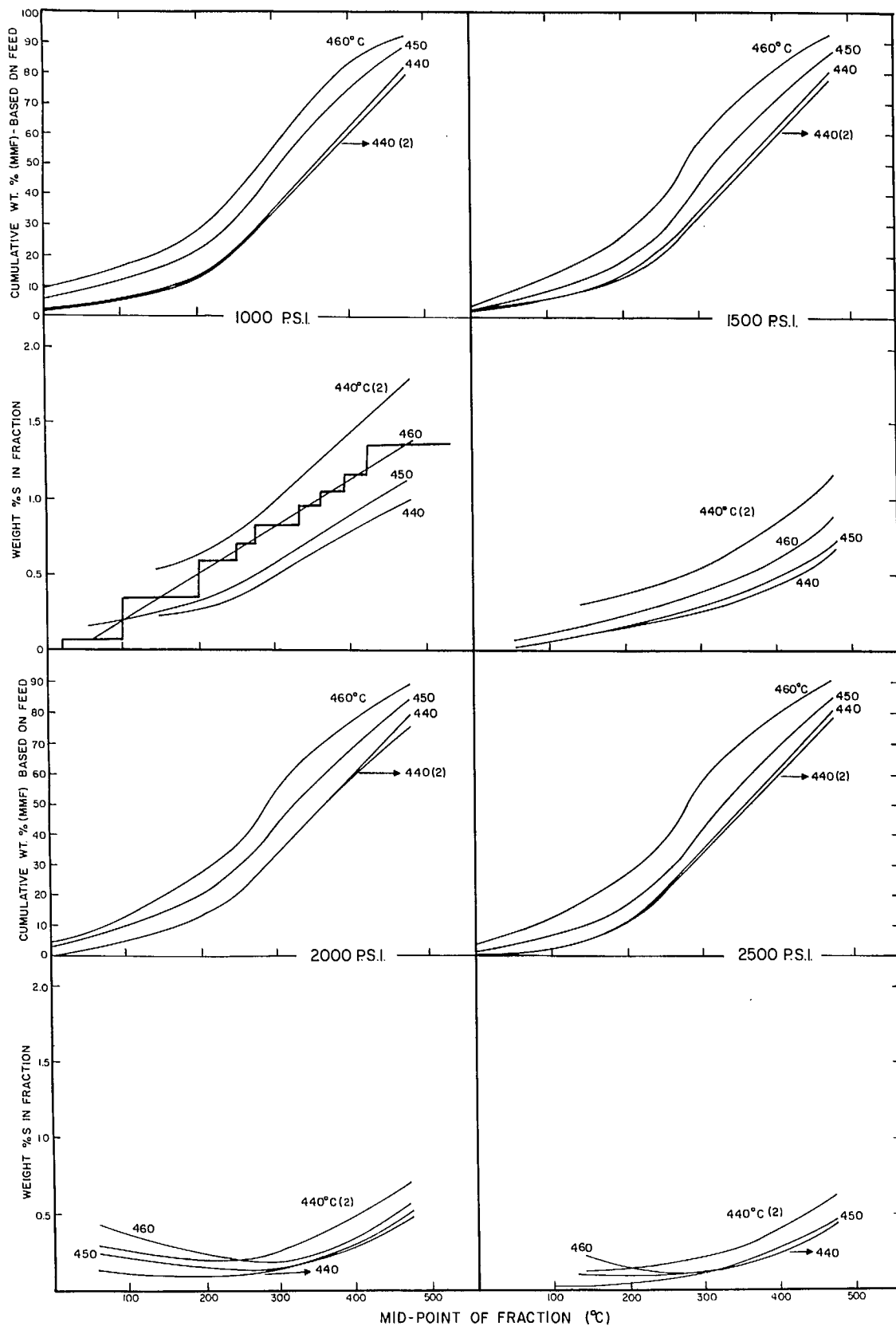


Figure 4 - Effect of hydrogen pressure on the yield and sulphur content of the distillate fractions. (Boiling range of the fractions indicated as saw-tooth segments in the upper left-hand section.)

LHSV = 1.05; Exit Gas Rate = 5000 scf/bbl.

weight of sulphur\*. In normal refinery practice, the operating temperature of a reactor is raised gradually to compensate for catalyst deactivation (to form a product of uniform quality). There appears to be substantially more scope for this type of manipulation at 2000 psi than at 1000 psi. It is difficult to estimate precisely how much longer a cobalt molybdate catalyst could produce a 1 % sulphur fuel oil at 2000 psi than at 1000 psi, but it seems reasonable to predict at least, 10 times longer.

There was also a marked increase in the overall yield of liquid product with increasing hydrogen pressure (Figure 3). A 6 % increase in the overall yield of liquid product was observed at the highest conversion level, 460°C, as the pressure was increased from 1000 to 2000 psi. This difference decreased, of course, at lower temperatures to 4 % at 450°C and to only 2 % at 440°C. The changes in the weight yield of liquid product are due almost entirely to the lessening of gas production at the higher pressures. On the matter of sulphur removal, the extent of desulphurization increased from approximately 77 % to nearly 90 % as the pressure was increased from 1000 to 2000 psi. There was little to indicate that there would be any economic advantage to be gained by increasing the pressure from 2000 to 2500 psi. In all of the quantities measured, any changes observed between 2000 and 2500 psi were marginal.

An additional point of interest is that, at the elevated pressures, 2000 and 2500 psi, the sulphur content of the distillate fractions passes through a minimum with increasing boiling point. This is most noticeable at the higher temperatures and conversion levels. For example, at 460°C the sulphur content of the lightest fractions was virtually equal to that of the heaviest fractions. The higher sulphur content in the light ends probably comes about as the result of interplay between two factors, a) increased light-ends production at elevated pressures and b) critical temperature. At 2000 and 2500 psi more light distillate is formed than at 1000 psi where gas-make is more prevalent. The

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\*In the foreseeable future, mainly for economic reasons, it is not expected that the sulphur specification will be set lower than 1 %, except perhaps in isolated problem areas of high industrial development in the U. S. and Eastern Canada.

temperature range of interest, 440 - 460°C, on the other hand, is above the critical temperature of the fractions distilling up to 250°C (20). As formed (and as the solubility of these fractions in the remaining liquid is exceeded) this material would tend to collect as bubbles and rise quickly out of the reaction zone. At elevated temperatures and pressures more such material is produced which would tend to further shorten the contact time. The shorter contact time combined with the fact that more material is being formed (requiring desulphurization) would result in higher sulphur contents.

It would seem that some additional (secondary) refining and sulphur removal would be required to bring the lighter fractions to acceptable market specifications. However, the sulphur levels are not sufficiently great to interfere with the transmission of the distillate to areas possessing existing refinery capacity and surplus hydrogen.

#### Coke Formation and Hydrogen Pressure

An important factor in catalyst life (in addition to metals poisoning) is the rate of build-up of tar and coke deposits on the catalyst. In the present work, the relative amounts of distillable oil and non-distillable "char" remaining on the separate charges of catalysts used in the various series of pressure tests were determined using a Carle Thermal Analyser System (21) developed by the Shell Oil Co.

The percentage by weight of distillable hydrocarbon material remaining on and within the pore structure of the catalyst was measured by heating a small, weighed, specimen of ground catalyst (as removed from the reactor) at 16°C/min in flowing hydrogen to a maximum of 530°C. The percentage by weight of combustible (but not distillable) char remaining on the same specimen was then determined by combustion in air at 600°C for 15 minutes. The results of the tests were as follows:

<u>Pressure at Which Catalyst was Operated</u>	<u>Ratio of Non-Distillable Char to Distillable Hydrocarbon Retained on Catalyst</u>
1000 psi	1.08
1500	0.91
2000	0.69
2500	0.63

As viewed by eye, the amount of coke and muck on the external surfaces of the pellets was not great. The physical amounts of distillable oil and char, however, represented 5 to 15 % by weight of the charge to the analyser. Undoubtedly, most of the char and distillable oil was located within the pore structure of the catalyst.

The ratio of char to distillable hydrocarbon decreased markedly as the pressure increased. The extent of change was greatest in the range 1000 to 2000 psi, with relatively little change occurring between 2000 and 2500 psi. Balancing the various factors involved: a) conversion, b) coke formation and c) operating life, the minimum practical working pressure appears to be 2000 psi.

#### The Effect of Operating Time

The effect of operating time was determined at a space velocity of 1.05 at 440°C and 1000 psi. The results of 10 consecutive experiments under these conditions, totalling 40.5 hours of operation are shown in Figure 5 and 6. Only three of the products were subjected to full-scale distillation and sulphur analyses, i.e. at 4.5, 16.5, and 40.5 hours (Figure 6).

A gradual increase in both the specific gravity and the sulphur content of the overall product occurred over the operating period, indicating a gradual deterioration in the catalytic activity. With regard to the extent of conversion of the residuum material to distillate fractions, there was very little change in the amounts of the individual fractions produced after the first 16 hours, but the sulphur content of each fraction continued to increase over the whole 40-hour period. The results of the distillation and sulphur analyses obtained on the products from the 4.5- and 40.5-hour runs correspond very closely to those obtained at 1000 psi in the temperature series 440, 450, 460 and 440°C (repeated) shown in Figure 4. The results of the second run at 440°C in the temperature sequence agree almost exactly with those obtained after 40 hours of operation.

The yields of hydrocarbon product (corrected for sulphur removal) shown in Figure 5 were almost constant with operating time. The scatter of points indicates more the difficulties associated with obtaining precise results



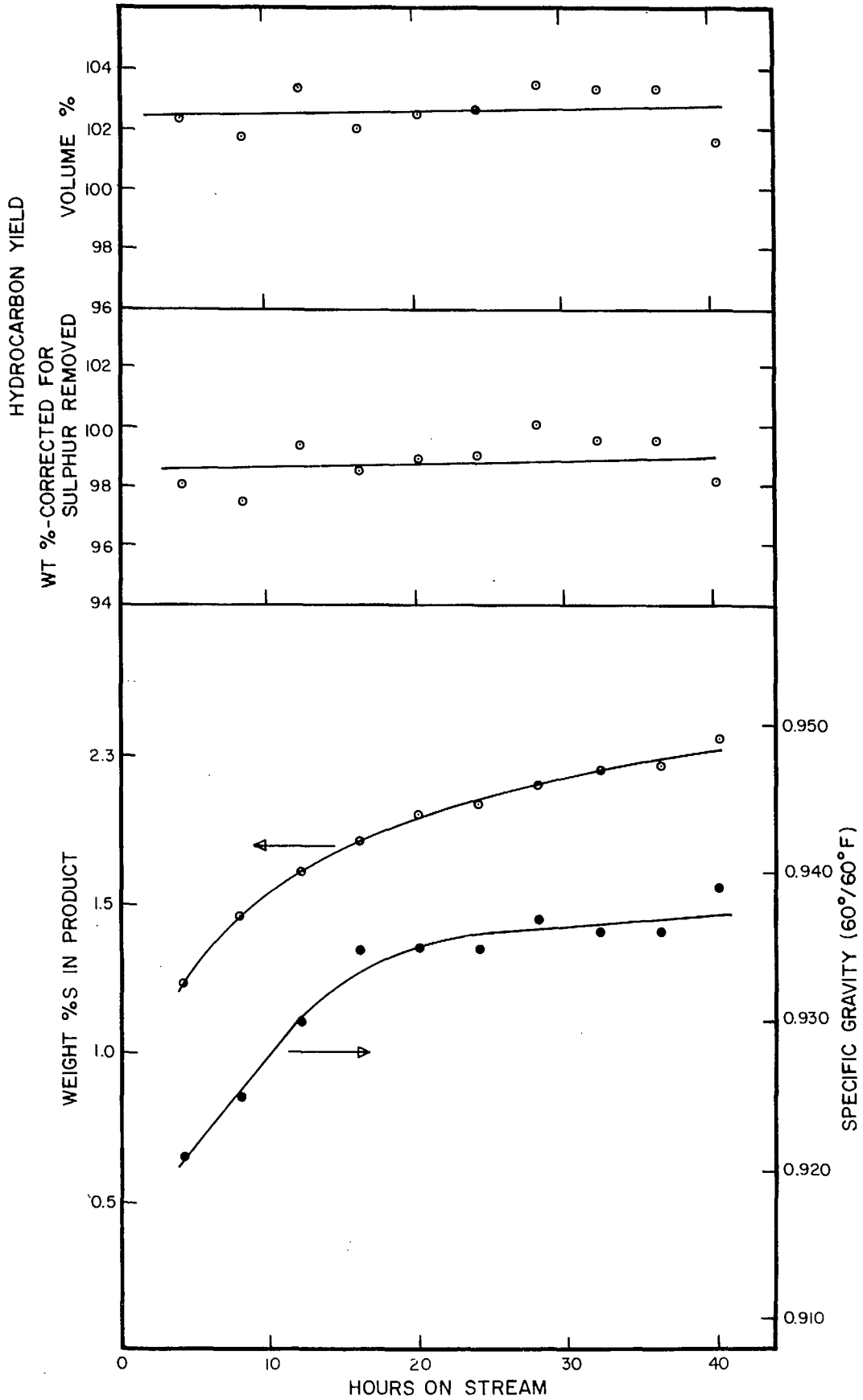


Figure 5 - Effect of operating time on hydrocarbon yield and sulphur content

Temperature = 440°C; Pressure = 1000 psi; LHSV = 1.05;

Exit Gas Rate = 5000 scf/bbl.

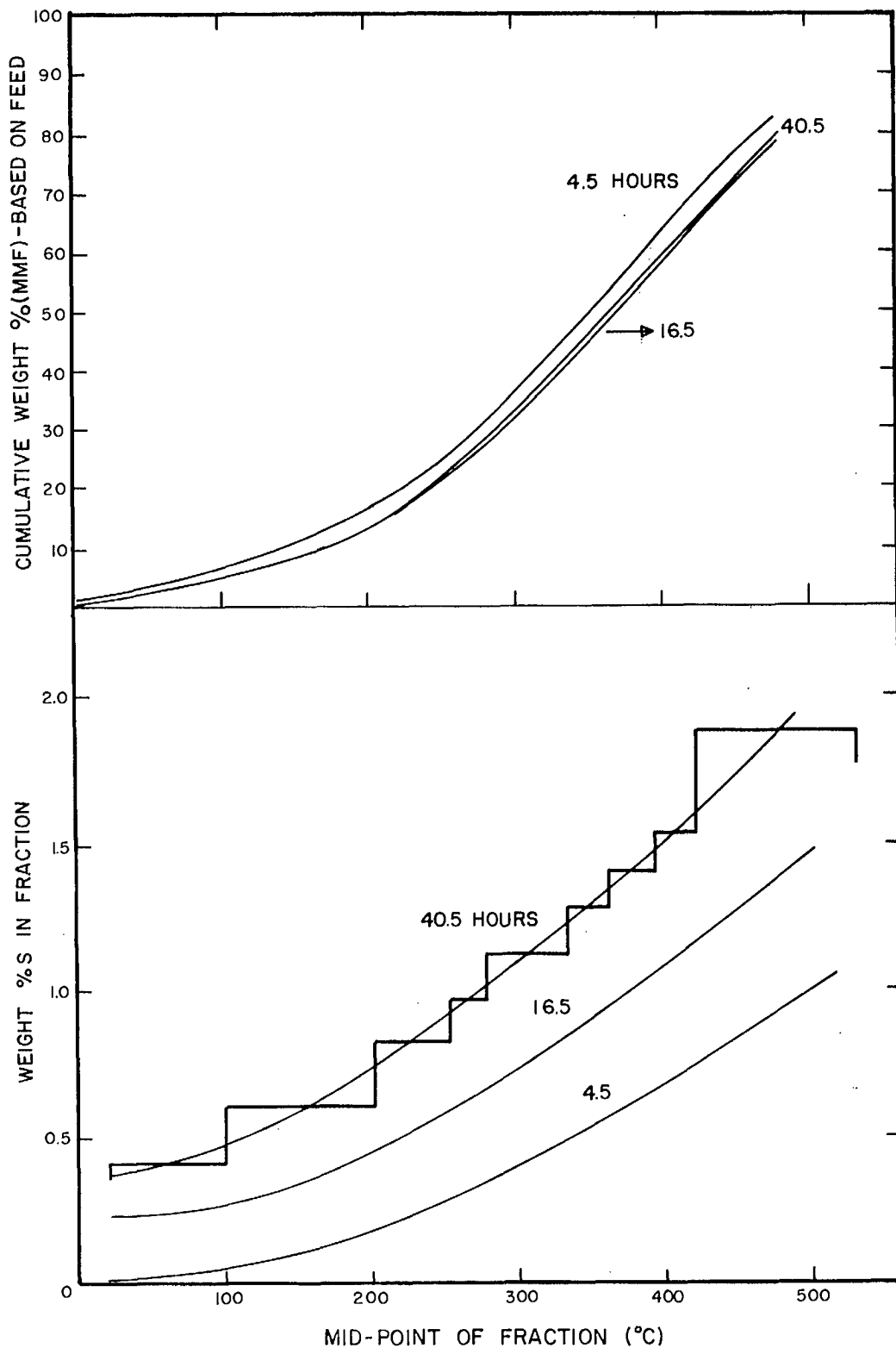


Figure 6 - Effect of operating time on the yield and sulphur content of the distillate fractions. (Boiling range of the fractions indicated as saw-tooth segments in the lower section.)

Temperature = 440°C; LHSV = 1.05; Pressure = 1000 psi;  
Exit Gas Rate = 5000 scf/bbl.

in small-scale\* experiments than significant differences in operating conditions. It should be pointed out that the experiment was terminated arbitrarily after 40.5 hours. When the reaction vessel was opened there was no visible evidence of large accumulations of coke or sludge. The catalyst pellets rolled out of the reaction tube the moment the covers were removed.

#### The Effect of Hydrogen Flow Rate

Previous work (22) with top-feed, mixed-phase systems has shown that the general effect of hydrogen flow rate is small compared to other variables. It was not expected that the effect would be much different with a bottom-feed (liquid phase) system; but it was felt that the point should be explored to establish the effect with certainty.

The experiments to determine the effect of hydrogen flow rate were conducted at a space velocity of 1.05 and at a low pressure, 1000 psi, where improvements in product quality, and quantity, could be most easily seen. Three series of tests were made at exit gas rates of 3000, 5000 and 7000 standard cubic feet per barrel (scf/bbl) of oil feed. In each series the experiments were run in the order 430, 440, 450, 460°C followed by a repeat run at 440°C as previously described. The results are shown in Figures 7 and 8.

The amounts of the fractions produced at each gas rate, the sulphur contents and the observed yields of hydrocarbon product were all very similar. Essentially the same degree of catalyst deactivation was observed at all three exit gas rates. Also, as indicated previously, the sulphur content of the fractions obtained at each gas rate increased systematically (and equally) as the reaction temperature was increased.

In theory, a higher gas flow should distill\*\* more of the lighter fractions out of the reaction vessel, and one might have expected the sulphur content of the lighter and middle fractions to be greater.....because of a shorter contact time

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\*where one or two grams, retained on the walls of the receiver vessel, represents a significant portion of the product.

\*\*in the sense of a steam distillation.

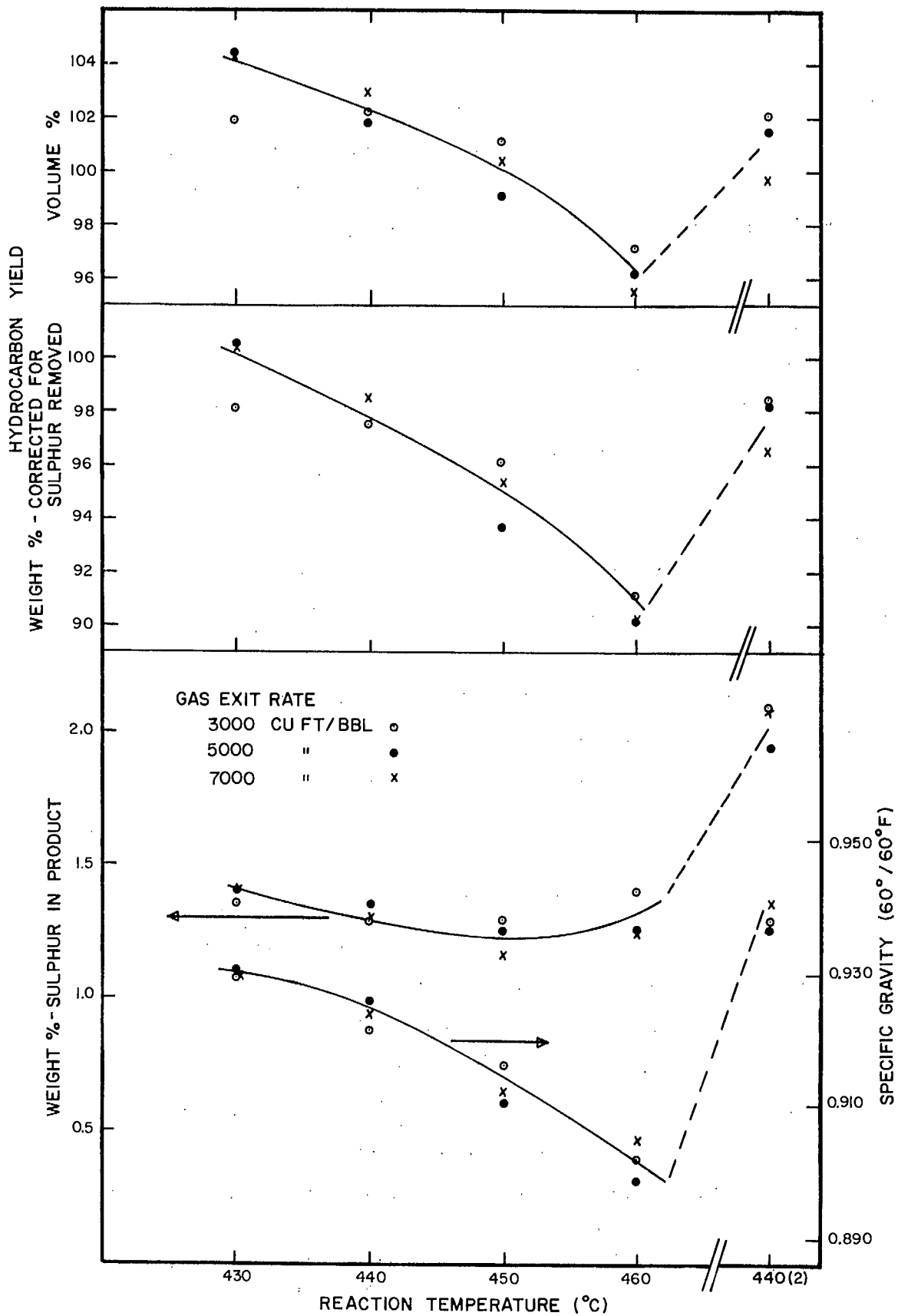


Figure 7 - Effect of exit gas rate on hydrocarbon yield and sulphur content.  
Pressure = 1000 psi; LHSV = 1.05.

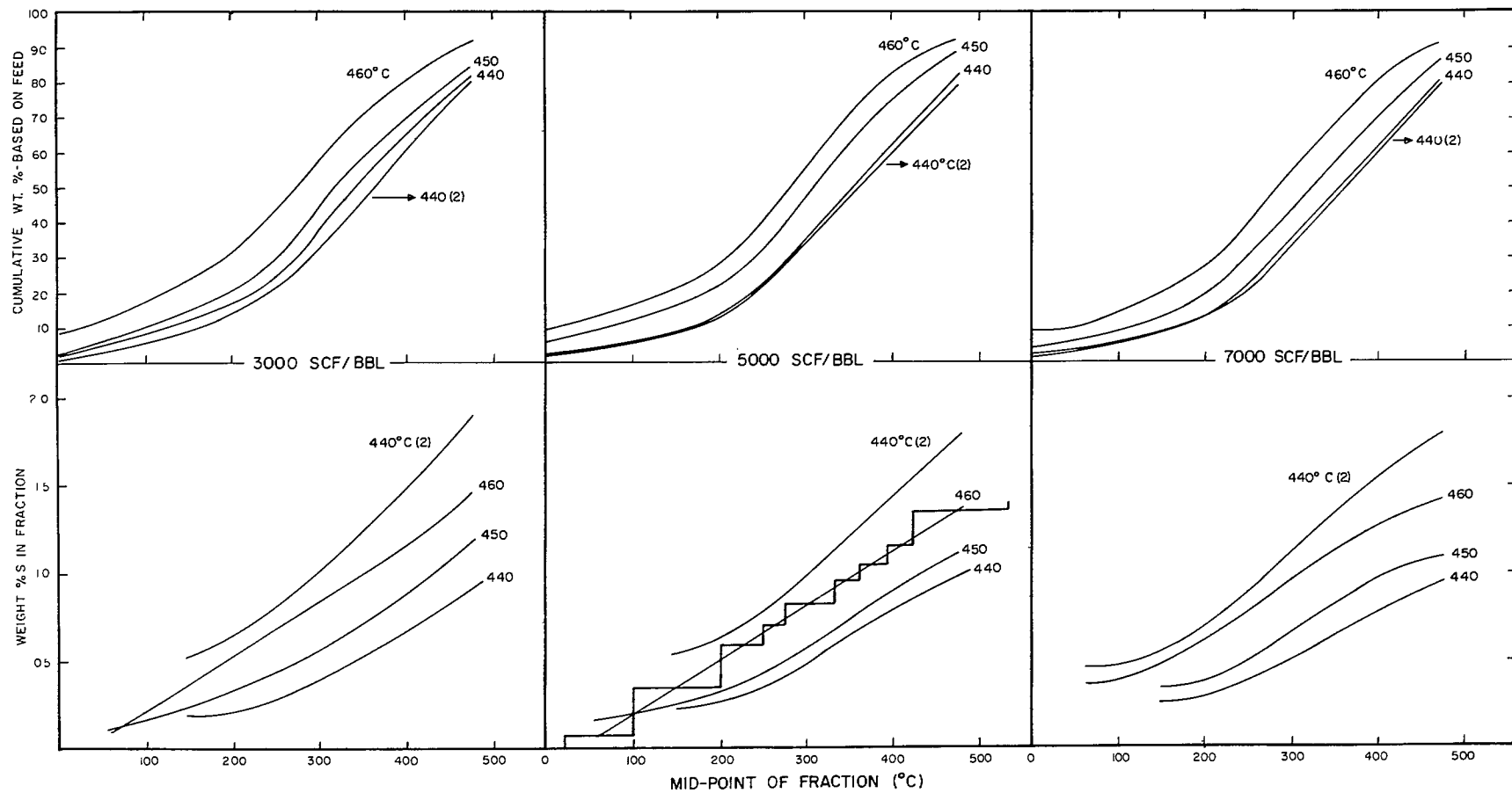


Figure 8 - Effect of exit gas rate on the yield and sulphur content of the distillate fractions. (Boiling range of the fractions indicated as saw-tooth segments in the centre section.)

Pressure = 1000 psi; LHSV = 1.05.

with the catalyst. However, this does not appear to be a significant factor within the relatively narrow limits of commercial flow rates, i.e. 3000 - 7000 scf/bbl.

#### The Effect of Liquid Feed Rate

The effect of liquid feed rate was determined at 2000 psi hydrogen pressure and a gas exit rate of 5000 scf/bbl. The results of the experiments are shown in Figures 9 and 10. The curves to be compared are marked as lines 2 and 5 in all sections. (In the interest of brevity, other data are included in Figures 9 and 10 for discussion in the next section).

Both the degree of conversion of the residuum and the extent of desulphurization of the distillate increased dramatically as the space velocity was reduced. At a space velocity of 2.1 the conversion of residuum at 460°C was only 70 % compared to 90 % at a space velocity of 1.05. It was possible to run at slightly higher temperatures (without apparent difficulty) at a space velocity of 2.1..... the maximum recorded conversion of residuum being approximately 80 % at 472°C. Some operating difficulties were encountered at the lower space velocity at 470°C and these runs were scrapped. At a space velocity of 2.1 the maximum degree of desulphurization obtained was only 70 % (at 472°C) compared to 85 - 87 % at a space velocity of 1.05 and 460°C. The trend of the results is more or less as one would predict, except to note that there does appear to be an upper temperature limit in the region of 470 - 475°C, beyond which it was not possible to operate the present system. To obtain a high degree of conversion of residuum, or desulphurization without extensive coking, it would appear that the reactor must be operated at a relatively low space velocity. Within the limits of the pressure range (1000 - 2500 psi) investigated, a space velocity of approximately one seemed to be the practical limit.

#### Catalyst Benefits and Permissible Cost

The benefit derived from the catalyst is measured primarily in terms of the quantity and quality of the liquid distillate produced compared to the case where no catalyst is present, i.e. catalytic versus thermal hydrocracking. In some respects this comparison is difficult to make.....because of differences in the

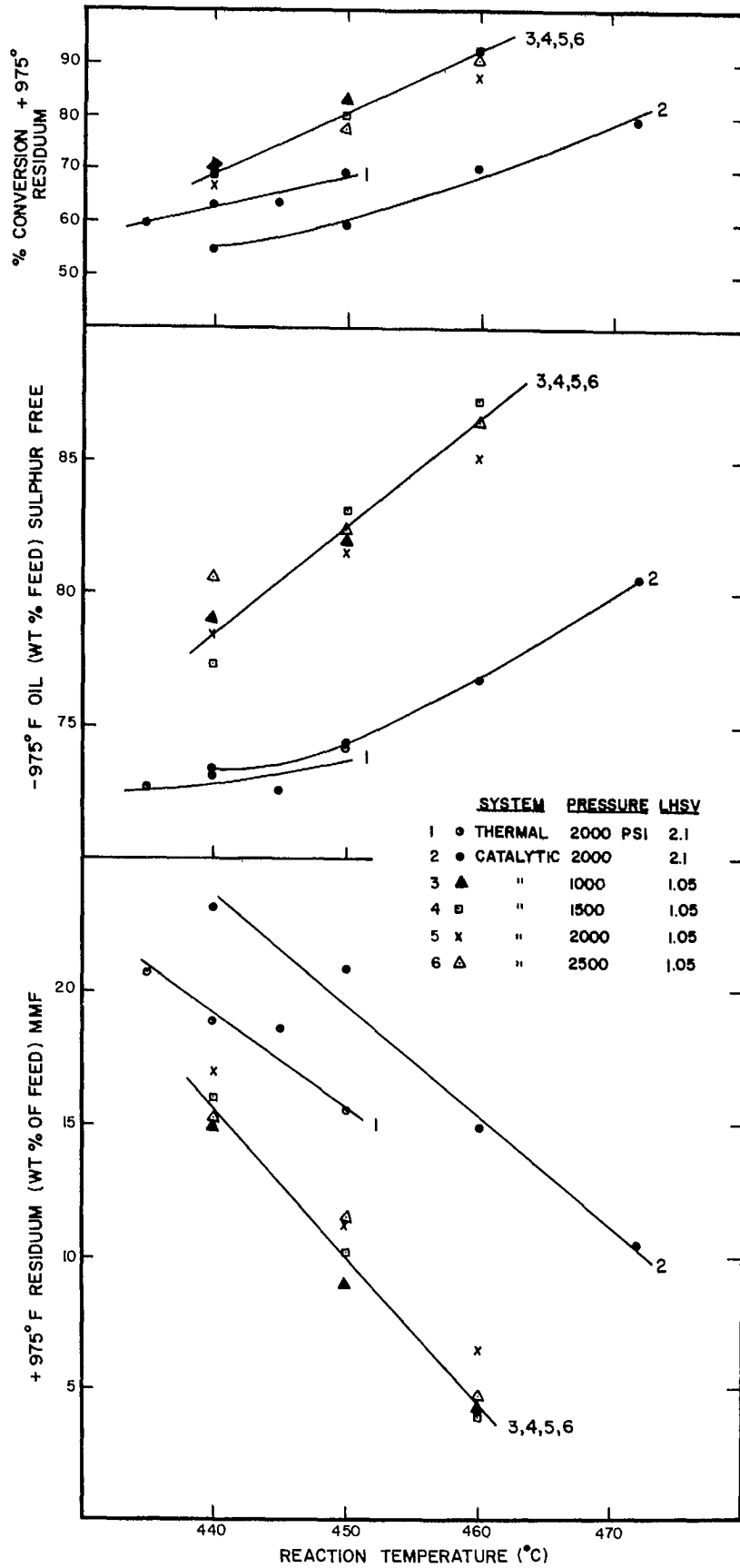


Figure 9 - Effect of catalytic and thermal hydrocracking on the conversion of the +975°F residuum fraction.

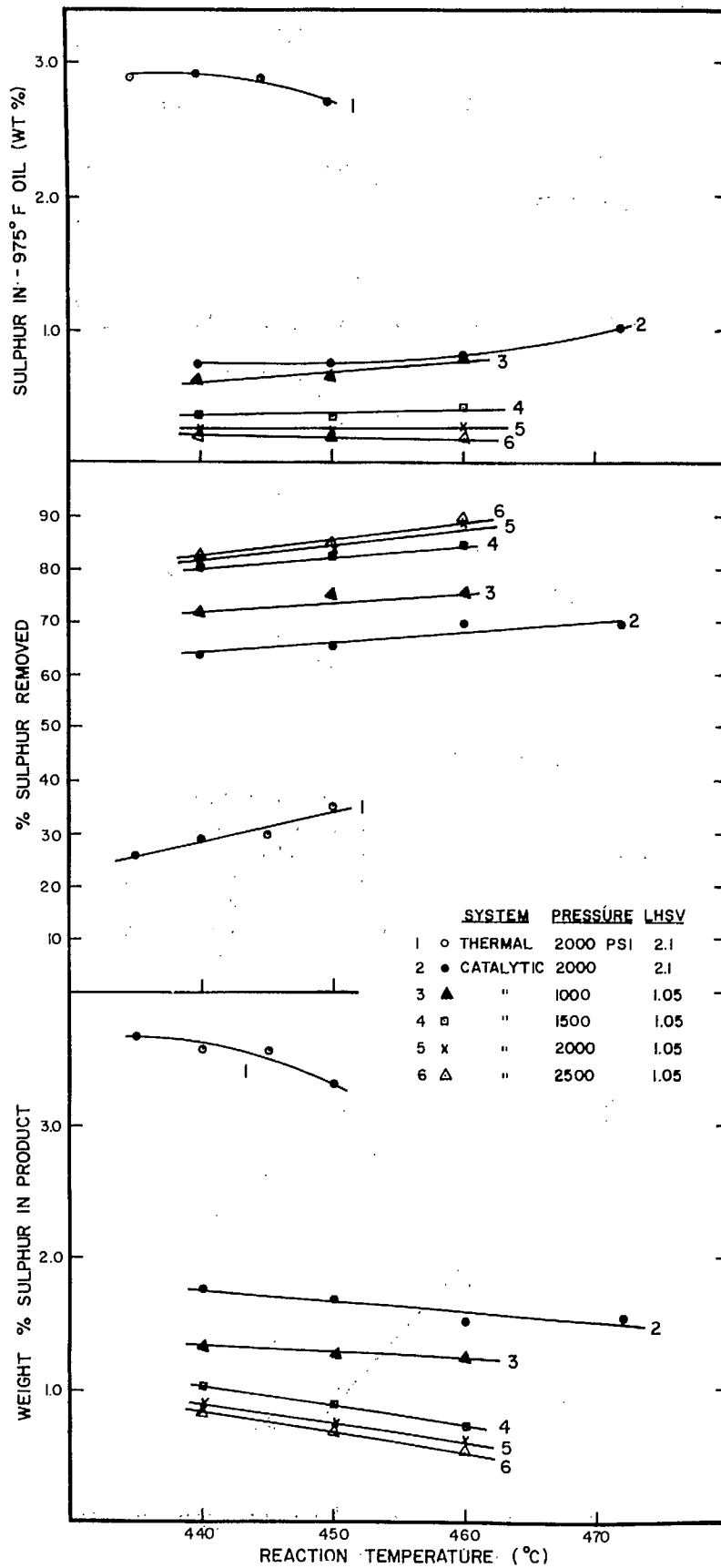


Figure 10 - Sulphur content of the products formed by catalytic and thermal hydrocracking.



residence time in packed and unpacked vessels, apparently identical reaction conditions are not necessarily "equal" conditions. From the commercial standpoint, however, the logical place to make the comparison is under optimum conditions for each process and this is, essentially, what has been done here.

Previous experience (1) has shown that the thermal process can be operated easily only at the higher liquid throughputs, whereas the catalytic process functions most efficiently at low space velocities. A series of direct comparison experiments were undertaken at the optimum for the thermal process, 2000 psi, LHSV = 2.1 and an exit gas rate of 5000 scf/bbl. (In one case the reactor was packed with catalyst pellets and, in the other, the system was operated as an open tube without packing.) In other comparison series the catalytic system was operated at a lower space velocity, 1.05, at various pressures. The results of all the experiments are summarized in Figures 9 and 10.

Under all the conditions examined, the catalytic system produced as much, or more, distillate hydrocarbon (the principal, marketable product) as the purely thermal system. Even at 440°C with the catalytic system at LHSV = 1.05 (where catalyst life would be expected to be greatest, but the extent of conversion the least) approximately 70 % conversion of the residuum was achieved and the yield of liquid distillate was 5 % greater than that observed under the optimum conditions for the purely thermal system. Placing a value of \$4.00/bbl on the additional product formed, this difference would represent approximately 6 million dollars of additional revenue per year for a 100,000-bbl/day plant. Comparing the two systems under the optimum conditions for each, i.e., 460°C and LHSV = 1.05 for the catalytic system and 450°C and LHSV = 2.1 for the thermal, the difference in yield of distillate hydrocarbon increases to 12 % by weight with a 90 % conversion of the residuum catalytically compared to only 70 % conversion thermally. The value of the additional product under these conditions would be over 14 million dollars per year for a 100,000-bbl/day plant.

The differences in sulphur removal were even more pronounced. At the optimum, the thermal system removes only 35 % of the sulphur present in the feed compared to 80 - 90 % under any of the conditions examined with a catalyst.

Neglecting the enormous benefit of the added sulphur removal, and the obvious benefit associated with the elimination of the need for secondary refining of the distillate (before transmission to sites of cheaper hydrogen) the value of the additional liquid product formed catalytically would appear to place the permissible catalyst cost in the range 50 - 55¢ per barrel. It is, of course, not feasible to conjecture on the savings in capital cost.....the above figures are based solely on the additional amount of liquid distillate produced per barrel of feed to the reactor.

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