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*A COMPARISON OF BOTTOM-FEED AND  
TOP-FEED REACTION SYSTEMS FOR  
HYDRODESULPHURIZATION*

T. TAKEMATSU AND B. I. PARSONS

FUELS RESEARCH CENTRE

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A COMPARISON OF BOTTOM-FEED AND TOP-FEED  
REACTION SYSTEMS FOR HYDRODESULPHURIZATION

by

T. Takematsu\* and B. I. Parsons\*\*

ABSTRACT

The bulletin describes a bench-scale investigation of top-feed (mixed phase) and bottom-feed (liquid phase) continuous-flow systems for the hydrodesulphurization of a heavy "coker" gas-oil derived from the Athabasca bitumen. The specific gravity of the feed stock was 0.95 and the sulphur content was 3.4 wt %. The catalyst used was a commercially prepared mixture of the oxides of cobalt and molybdenum on alumina. In almost every respect the bottom-feed system was found to be more effective than the top-feed arrangement. The greater heat transferring capability of the liquid phase and the mixing effected by the bubbling hydrogen improved temperature control within the reactor considerably. More extensive desulphurization (at higher space velocities) was possible with the bottom-feed arrangement because of the longer residence time and improved temperature control. Fuel oil containing 1 % sulphur could be produced at a space velocity of 3, 355°C and 2000 psi with only 3 to 4 % hydrocracking to low-boiling fractions. Fuel oil containing only 0.5 % sulphur could be produced at similar temperatures and pressures at a space velocity of 2.

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Bulletin technique TB 161

UNE COMPARAISON DES SYSTÈMES DE RÉACTION  
D'ALIMENTATION PAR LE BAS ET D'ALIMENTATION  
PAR LE HAUT POUR LA HYDRODESULFURATION

par

T. Takematsu\* et B.I. Parsons\*\*

RÉSUMÉ

Ce bulletin décrit une recherche faite au laboratoire sur les systèmes à écoulement continu d'alimentation par le haut (phase mixte) et d'alimentation par le bas (phase liquide) pour la hydrodesulfuration d'un gas-oil lourd dérivé du bitume d'Athabasca.

La gravité spécifique de la charge d'alimentation était de 0.95 et la teneur en soufre était de 3.4 wt %. Ils ont utilisé un catalyseur qui était un mélange préparé commercialement des oxydes de cobalt et de molybdène sur l'alumine. Ils ont trouvé presque dans tous les cas que le système d'alimentation par le bas était plus efficace que la disposition d'alimentation par le haut. Ils ont aussi remarqué que la plus grande capacité de transfert de chaleur de la phase liquide et du mélange effectuée par le bouillonnement d'hydrogène a considérablement amélioré le contrôle de la température à l'intérieur du réacteur. Une plus grande désulfuration (à de hautes vitesses spatiales) a été possible par un séjour plus long dans un réacteur et par un contrôle amélioré de température avec une disposition d'alimentation par le bas. L'huile combustible contenant 1% de soufre pourrait être produite à une vitesse spatiale de 3, 355°C et 2000 psi avec seulement 3 à 4% d'hydrocraquage aux fractions à bas point d'ébullition. L'huile combustible qui contient seulement 0.5% de soufre pourrait être produite aux températures et pressions semblables à une vitesse spatiale de 2.

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## INTRODUCTION

The following report describes an investigation of the prospects for a continuous, liquid phase system for the hydrodesulphurization of heavy gas-oils and fuel oils. Basically, the investigation consists of comparing the bottom-feed, or liquid phase, mode of operation with the conventional top-feed, or mixed-phase, system. The main objective was the production of low-sulphur fuel oils for commercial use.

Industrial catalytic hydrodesulphurization reactors are generally fixed-bed units operated as mixed phase, down-flow systems (1). The contact time of the oil feed with the catalyst is controlled partly by the gravity flow of the oil down through the reaction bed and, partly, by the flow of hydrogen and other gases through the system. Under normal conditions, with the relatively light fractions obtained from conventional crude sources, the bulk of the feed stock is in the vapour phase with only a small proportion in the liquid phase. With heavier, high-sulphur fractions derived from low-grade residual oils, however, the proportion of the feed stock in the liquid phase increases quite substantially and the reaction temperature (and pressure) must be raised to effect sufficient desulphurization to meet market specifications. An unfortunate side effect of increasing the temperature is a considerable increase in the rate of cracking. This usually results in more coke and tar formation on the catalyst (which requires more frequent regeneration), increases light-ends production and increases hydrogen consumption (2).

In the present work many of the above difficulties have been partially, or wholly overcome by changing the mode of operation of the reactor to bottom-feed. The unit was operated, in effect, as a continuous flow, liquid phase system with the oil and hydrogen percolating up through a fixed bed of catalyst. 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, on the other hand, remains in the liquid phase and progresses slowly through the catalyst bed by displacement only. Because



of the increased contact time the permissible range of operating temperatures was lower which, relative to the case of the top-feed reactor, increases further the proportion of the feed in the liquid phase.

### EXPERIMENTAL

Experiments were undertaken to demonstrate the basic differences between conventional top-feed hydrodesulphurization and the corresponding bottom-feed system. The catalyst used was a commercial cobalt molybdate on alumina manufactured by the Harshaw Chemical Co. of Cleveland, Ohio. The catalyst, 1/8-inch-diameter pellets designated as CoMo-0603T by the manufacturer, was 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 were 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

#### Apparatus and Procedure

A schematic diagram of the flow system is shown in Figure 1 and the arrangement of the catalyst and preheater packing in the reaction vessel is shown in Figure 2. The major components of the apparatus and the general method of operation are described in Mines Branch Research Reports R 194 and R 217 in connection with earlier studies of hydrogen refining (3, 4). The reaction vessel (internal dimensions, 1-inch diameter and 12 inches long) was machined from 316 stainless steel. The oil feed and hydrogen were pumped in at the bottom of the reactor, as depicted in Figure 1, or at the top by simply changing the piping connections and inverting the reactor. The temperature profile in the reaction zone was measured by sliding a thermocouple up or down a well, located centrally in the reactor. No attempt was made to average the temperature over the reaction zone....the reaction temperatures indicated in the Tables and Figures are "peak" or "plateau" temperatures. In the case



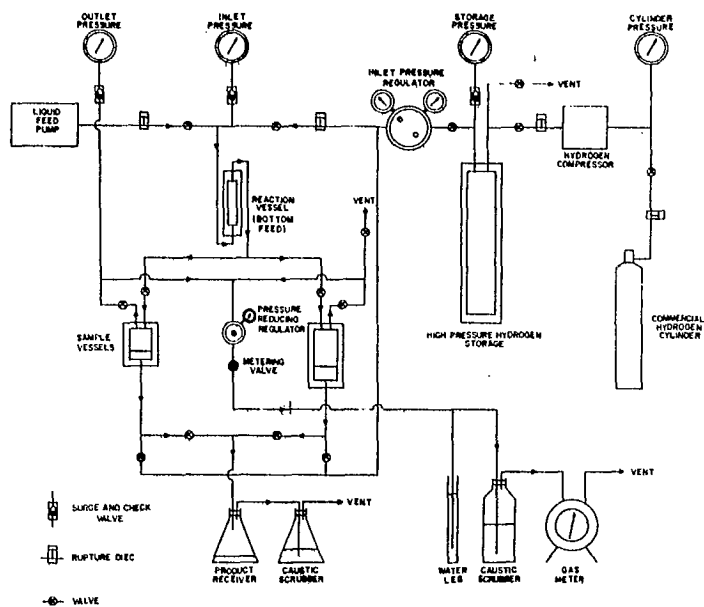


Figure 1 - A schematic diagram of the apparatus.

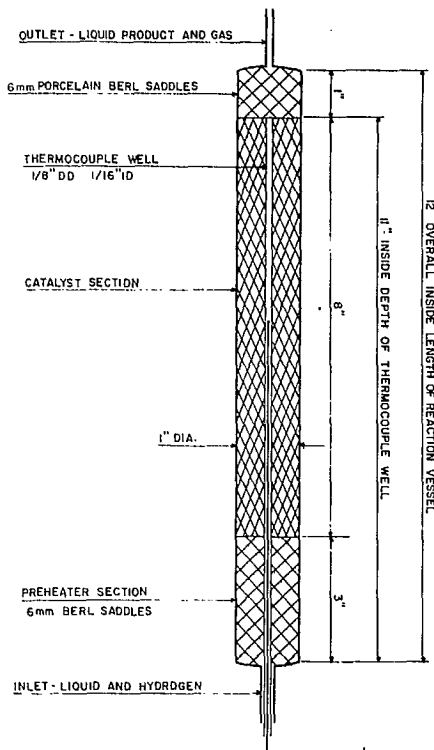


Figure 2 - The interior of the reaction vessel and the arrangement of the preheater and reaction bed systems.

of the bottom-feed experiments, the temperature profile across the reaction zone was relatively uniform. In the top-feed experiments a more distinct maximum was observed in the temperature profile.

A fresh charge of catalyst was placed in the reaction vessel for each series of experiments. The initial high activity of the catalyst (characteristic of the first few hours of operation) was dampened by pretreating each charge for five hours at 400°C, 2000 psi, liquid hourly space velocity (LHSV) = 1 and a hydrogen flow rate of 4000 standard cubic feet/barrel (scf/bbl). The activity of the catalyst after each series of tests was checked by repeating the first experiment in the series and comparing the result. The average running time for each experiment was approximately 4 hours.

#### Feed Stock

The feed stock used in all of the experimental work was a heavy gas-oil fraction derived from Athabasca bitumen by delayed coking (5). The fraction was supplied to the Mines Branch by Great Canadian Oil Sands Ltd. of Fort McMurray, Alberta. The general properties of the feed stock are listed below and the results of distillation and sulphur analyses are shown in Figure 3:

specific gravity 60°/60°F	0.950
sulphur (wt %)	3.38
nitrogen (wt %)	0.26
Conradson carbon (wt %)	0.21
ash (wt %)	0.004
vanadium (ppm)	2
viscosity, kinematic (cSt) at 100°F	18.8

#### Analytical Procedures

The extent of hydrocracking which took place, i.e., the amount of light ends formed in the course of desulphurization, was determined using a modification of the U. S. Bureau of Mines Hempel Distillation Analysis (6). A charge of 100 ml of oil was placed in a Hempel distillation flask and, using a large, fan-like flame burner, distilled rapidly in two stages at a) atmospheric pressure and b) 40 mm pressure. The temperature cuts collected are shown in Table 1. The various fractions were recorded by weight.

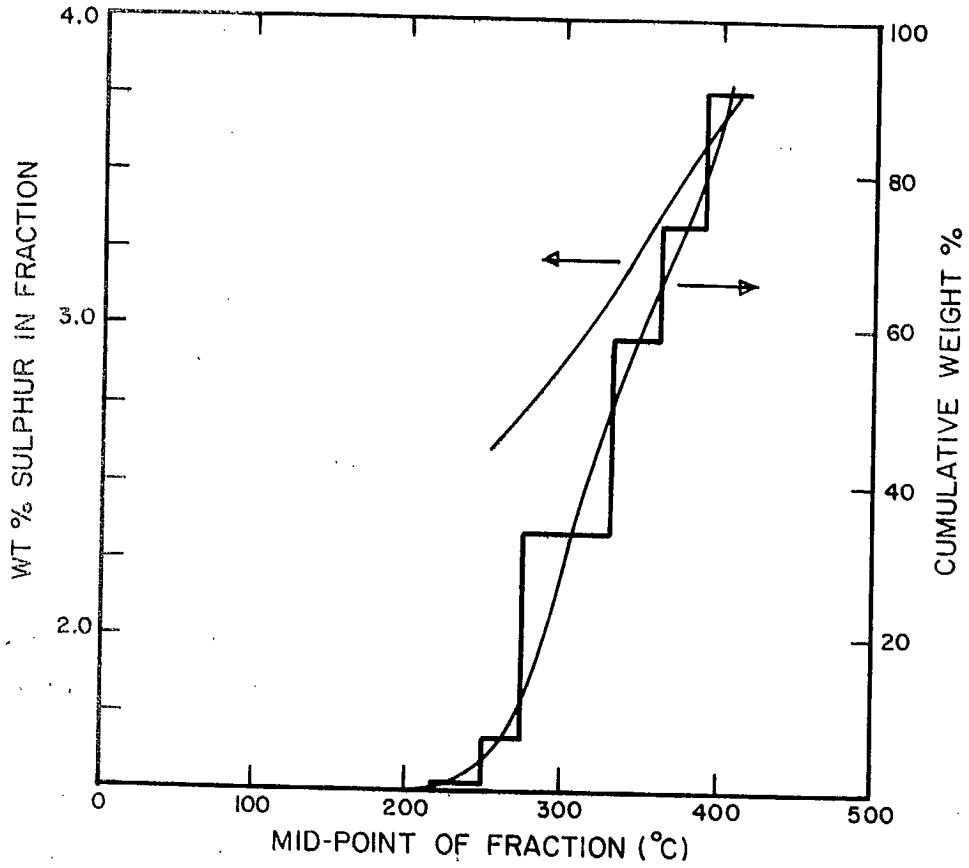


Figure 3 - The results of distillation and sulphur analyses of the gas-oil feed stock as received from Great Canadian Oil Sands Ltd.  
(Boiling range of fractions shown as segments on lower line)

TABLE 1

Fractions Collected in Hempel Analysis (Modified)

Fraction No.	(°C)	(°F)	Pressure (mm)	Equivalent Distillation Range at 1 Atm*	
				(°C)	(°F)
1	RT-100	RT-212	760	RT-100	RT-212
2	100-200	212-392	760	100-200	212-392
3	200-250	392-482	760	200-250	392-482
4	250-275	482-527	760	250-275	482-527
5	RT-225	RT-437	40	275-332	527-630
6	225-250	437-482	40	332-361	630-682
7	250-275	482-527	40	361-391	682-736
8	275-300	527-572	40	391-421	736-790
9	+300	+572	40	+421	+790

\*Chart PD-449, UOP Method 76.

The sulphur content of the 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 %) and di-n-butyldisulphide (21.9 %)) to sulphur-free oils and, in a relative sense, by comparing results with those obtained independently by an oxygen-bomb technique (ASTM Procedure D129).



## EXPERIMENTAL RESULTS AND DISCUSSION

From the standpoint of low-sulphur fuel oil production the bottom-feed (liquid phase) system was found to be vastly superior to the top-feed (mixed-phase) system. The main reasons for this are believed to be a) much improved temperature control in the reaction bed and b) a longer contact time of the liquid heavy oil fractions with the catalyst.

The first and most outstanding difference observed in the physical operation of the two systems is the great difference in the temperature profile across the reaction zone. Typical temperature profiles obtained with the bottom- and top-feed arrangements are shown in Figure 4. With the top-feed system, the region of constant temperature over the 8-inch reaction bed was scarcely one inch in length. Heat transfer from the catalyst to the vessel walls through the predominantly gaseous phase reaction medium\* (oil vapour and hydrogen) was poor and the high exothermic heat of desulphurization resulted in a sharp peak in the temperature profile. The effect was so marked that the inlet feed temperature had to be kept as low as 240 - 250°C to keep the maximum temperature from exceeding the desired temperature. By comparison, the temperature profile across the reaction zone with the bottom-feed arrangement was relatively constant.....approximately 6 inches of the 8-inch bed occurring within 15° of the peak temperature. The broad band of constant temperature is attributed to the better heat transferring properties of the liquid phase oil distributed throughout the reaction bed combined with the violent mixing effected by the bubbling hydrogen.

It is fully appreciated that on an industrial scale there are quenching techniques available to effect a more even temperature control with either arrangement. The purpose of the present work is, however, simply to demonstrate basic differences (in identical equipment) with the view to establishing the principal advantages and disadvantages.

The general properties of the oil products formed with the bottom- and top-feed systems are summarized in Table 2 and the results of the distillation analyses are shown in Figure 5. Substantially more desulphurization (at lower temperatures) was obtained with the bottom-feed arrangement than with the top-feed

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\*The alumina-based catalyst is essentially a thermal insulator.



TABLE 2  
 General Properties of the Product from the Bottom-  
 and Top-Feed Systems

Feed System	Reaction Temp. (°C)	Exit Gas Rate (scf/bbl)	Overall Product		Sulphur Removed (%)	Weight Yield of Oil (%)	Volume Yield of Oil (%)
			Specific Gravity 60/60°F	Sulphur (wt %)			
Bottom	400	4000	0.886	0.12	96.5	97.6	104
	380	4000	0.896	0.18	94.7	97.7	103
	360	4000	0.903	0.34	90.2	97.7	103
Top	390	7500	0.900	0.53	84.6	97.8	103
	370	7500	0.909	0.91	73.7	98.1	103
Catalyst - Commercial Cobalt Molybdate				Pressure = 2000 psi		LHSV = 1	

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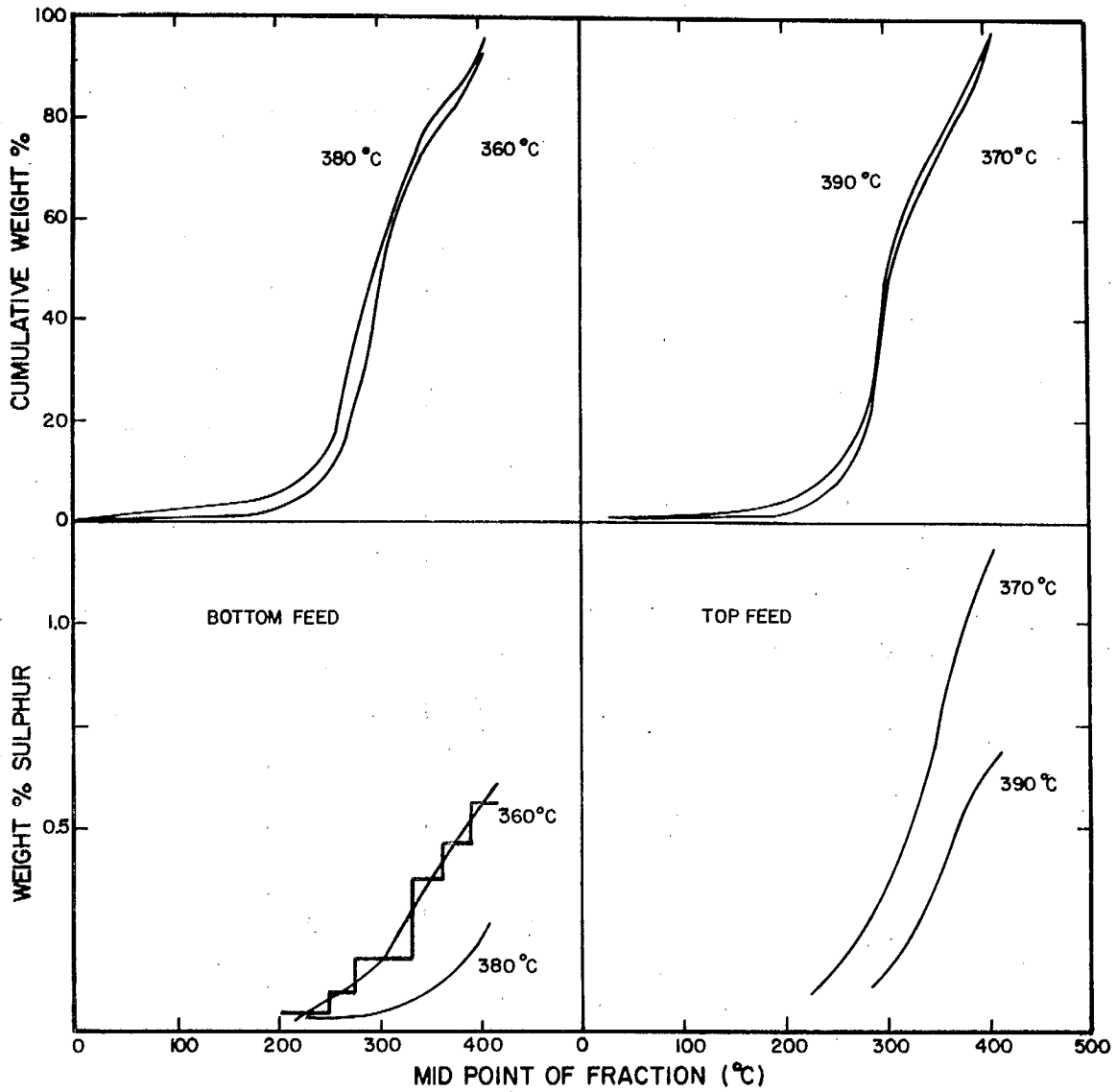


Figure 5 - The results of distillation and sulphur analyses of typical products from the bottom- and top-feed arrangements. (Boiling range of fractions shown as segments in lower left-hand section).



system. Over 90 % desulphurization was obtained at 360°C with the bottom-feed arrangement compared to only 74 % at 370°C with the top-feed system.

Most important also was the fact that no catalyst deactivation was observed with the bottom-feed system over any given series of experiments (approximately 25 - 30 operating hours). This was in sharp contrast with the top-feed arrangement where consecutive experiments indicated that the catalyst was being slowly deactivated. When the catalyst was removed from the reaction vessel on the completion of the top-feed experiments, trace quantities of a hard, tarry solid were found on the catalyst near the inlet of the bed. No visible evidence of such tarry deposits was observed on any of the charges of catalyst used in the bottom-feed experiments. It would appear that the tarry deposits encountered with top-feed remained dissolved in the mass of liquid phase material flooding the system in the bottom-feed arrangement. The longer catalyst life obtainable with bottom-feed would be of considerable advantage on a commercial scale. The regeneration of the catalyst by controlled combustion, though simple in principle, is a mechanically difficult and time-consuming operation.

The yields of oil product with both systems were excellent. Within the experimental limitations of the present study the weight yields of oil product plus recoverable sulphur were all slightly greater than 100 %. The overall volume yield of oil product alone was in the range 103 - 104 % for all experiments. At the present time the emphasis throughout the world is on the development of means and techniques for the production of fuel oils containing not more than 1 % sulphur. Under reaction conditions suitable for the production of 1 % sulphur fuel oil the amount of light ends produced (boiling below 200°C) did not exceed 3 to 4 % by weight.

Ideally, a reaction system designed for fuel oil production should be sufficiently versatile to permit a reasonable range of space velocities and reaction temperatures to be used to take into account seasonal demands. This is particularly true in Canada where the demand for fuel oil fluctuates widely from winter to summer. Generally speaking, high space velocities (greater than

one) are not recommended with top-feed systems partly because of the difficulties associated with temperature control. The much improved temperature characteristics of the bottom-feed system suggested a potential advantage in this area and experiments were undertaken at space velocities of 1, 2 and 3 at 2000 psi. The results are summarized in Figure 6.

Fuel oil containing only 1 % sulphur can be produced at 355°C at a liquid hourly space velocity of 3, at 337°C at LHSV = 2 and at 320°C at LHSV = 1. Similarly, 0.5 % sulphur fuel oil (should it be required in the future) can be produced at approximately 380°, 360° and 350°C at liquid hourly space velocities of 3, 2 and 1 respectively. All of the temperatures mentioned are well below the level where hydrocracking and coke formation are serious problems. Such versatility would allow the construction of substantially smaller sized reactors which, in turn, would effect considerable saving in capital cost.

Typical results of distillation analyses and the sulphur distribution in the products formed at various temperatures and space velocities are shown in Figure 7. It was only at the highest temperature (400°C) investigated that a significant amount of hydrocracking occurred, producing 7 to 8 % of hydrocarbon boiling up to 200°C. At all of the other conditions studied the amount of light ends formed occurred in the range 3 to 4 wt %. The sulphur content of the fractions increased systematically with boiling point, more or less as one would expect on the basis of the sulphur distribution in the feed stock. While the sulphur content of the last fraction distilled, the 391 - 421°C cut, appears high in certain instances it should be pointed out that it usually represents less than 15 % of the total product and that, initially, the corresponding fraction in the feed stock contained 3.7 % sulphur. To produce a fuel oil containing not more than 1 % sulphur from the feed stock used in the present work the extent of desulphurization (overall) must be 70 % or better.

The general effects of reaction pressure and hydrogen flow rate with the bottom-feed arrangement are shown in Figures 8 and 9. The extent of change observed with either of these variables was small. The only fractions effected to a measurable degree were the heavier cuts, 332 - 421°C, where the sulphur

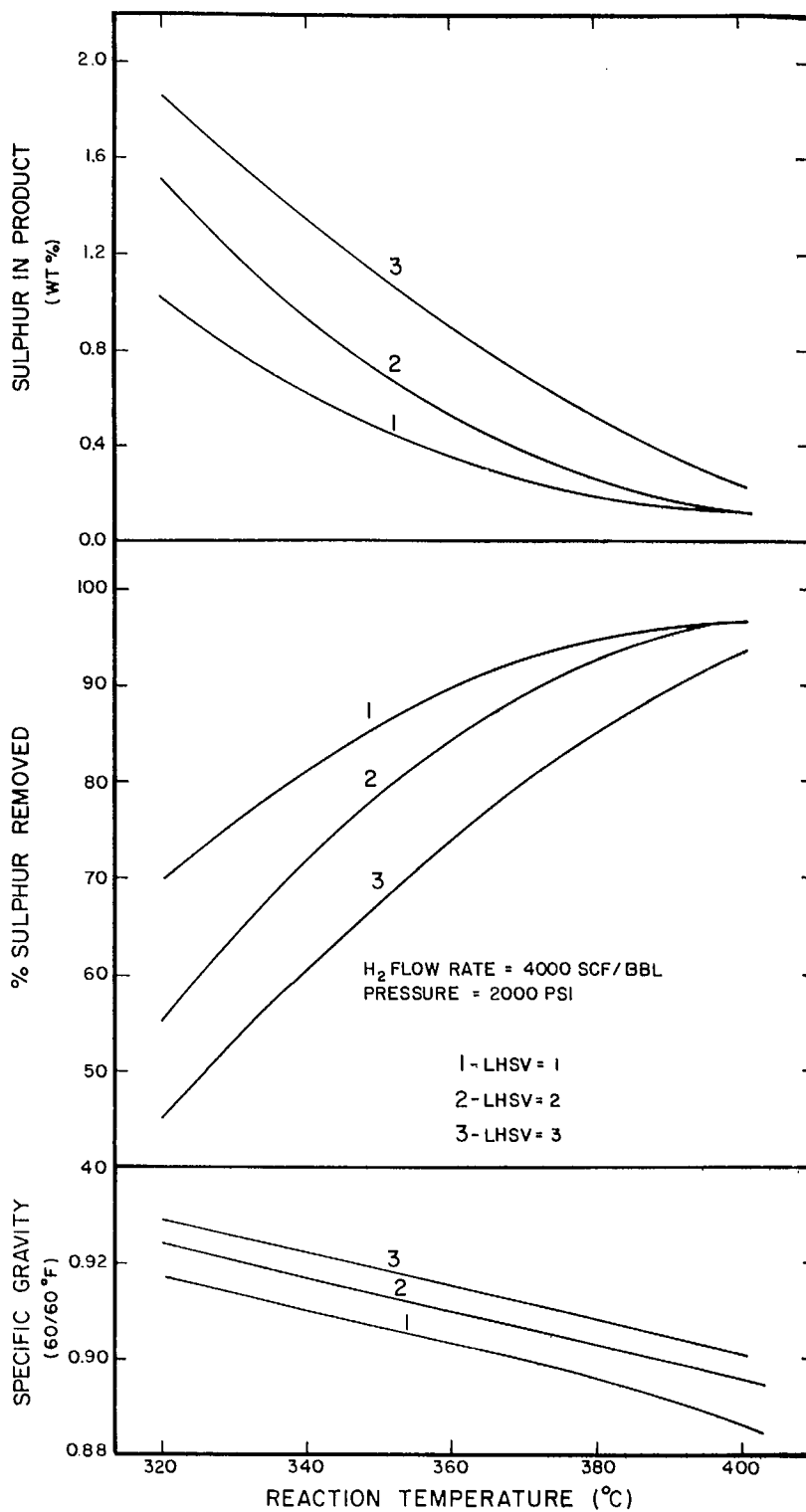


Figure 6 - The effect of space velocity on the extent of desulphurization and specific gravity of the product. (Bottom-feed arrangement).

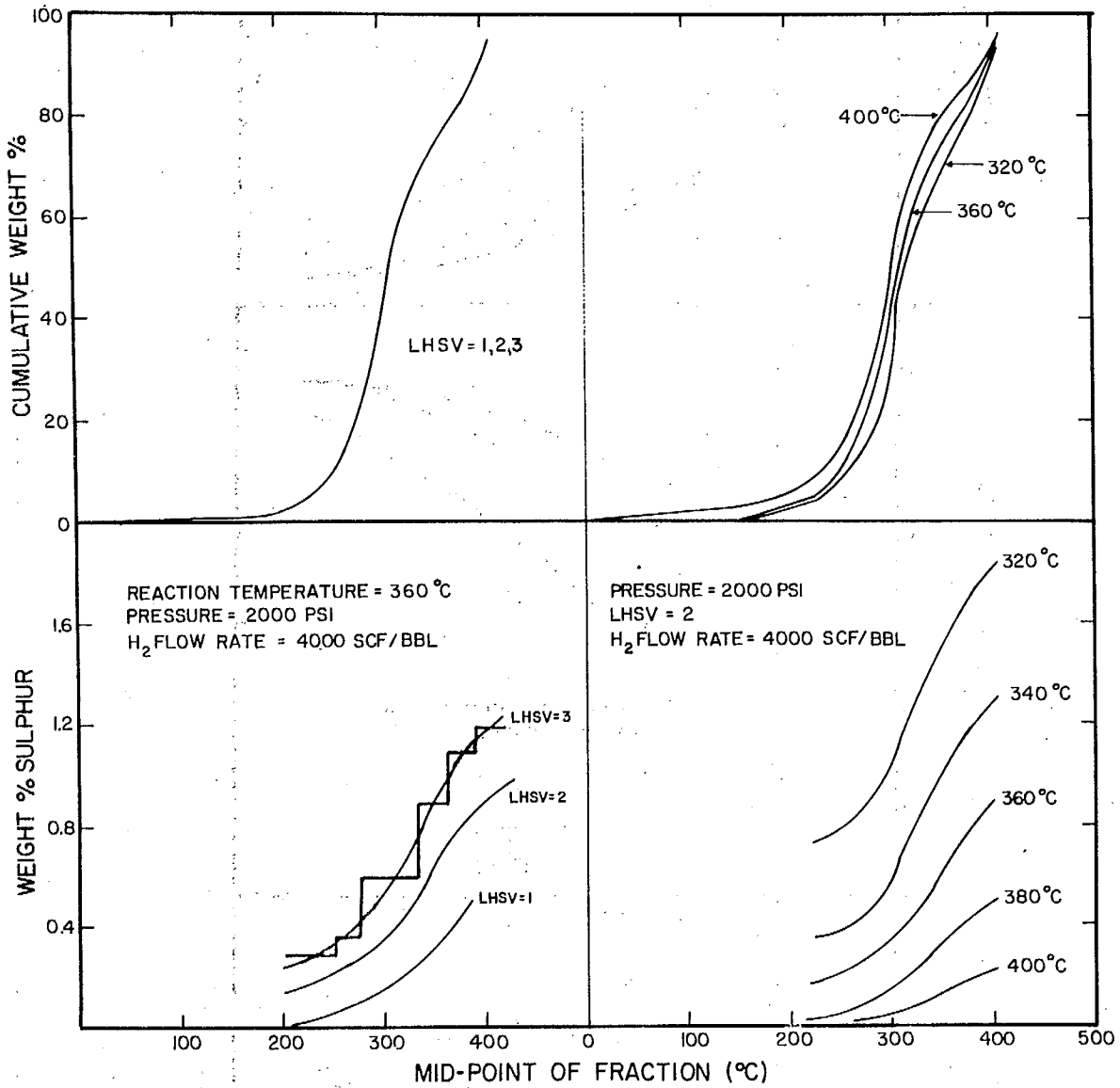


Figure 7 - The results of distillation and sulphur analyses of products formed at various temperatures and space velocities. (Bottom-feed arrangement; boiling range of fractions shown as segments in lower left-hand section).



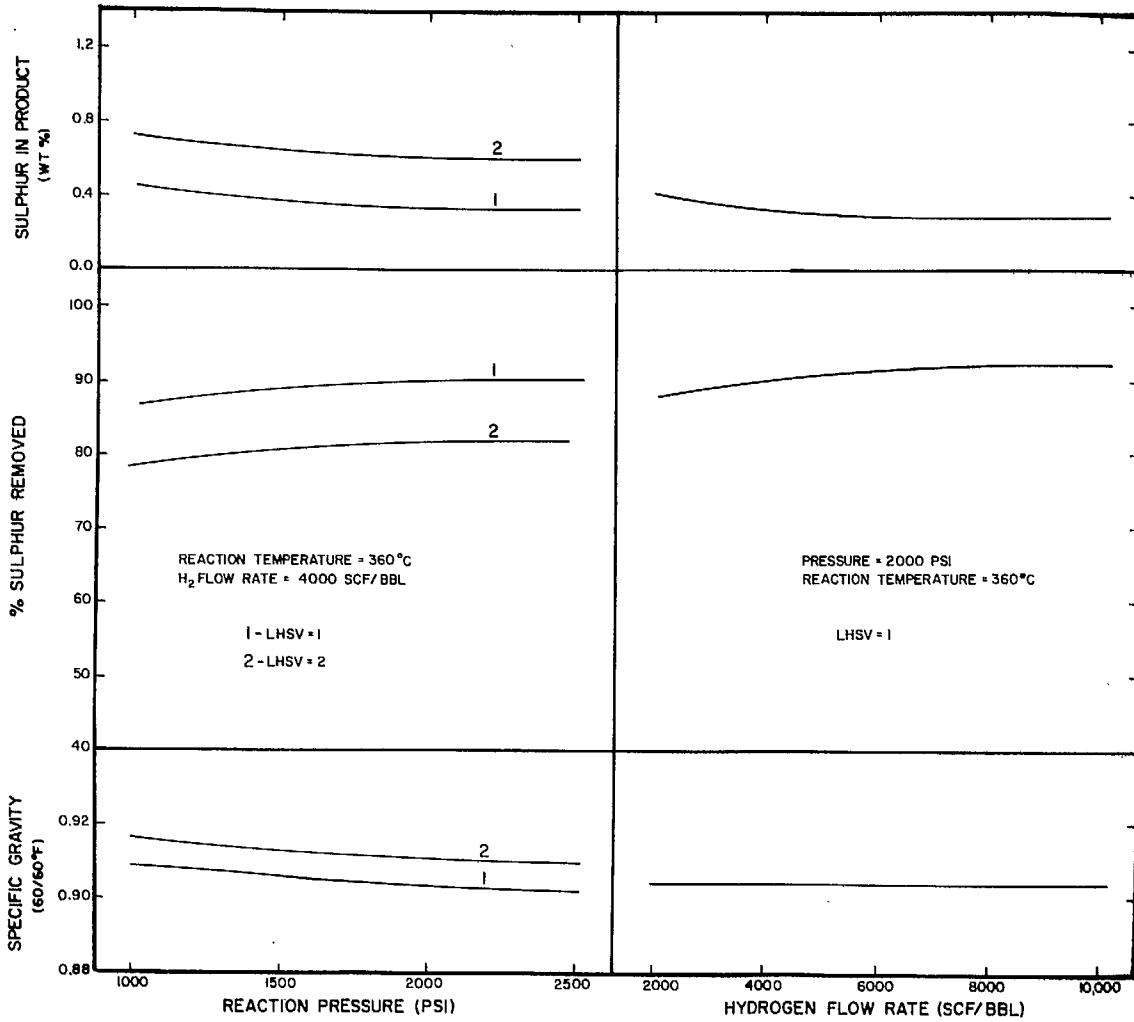


Figure 8 - The effect of reaction pressure and hydrogen flow rate on the extent of desulphurization and specific gravity of the product. (Bottom-feed arrangement).

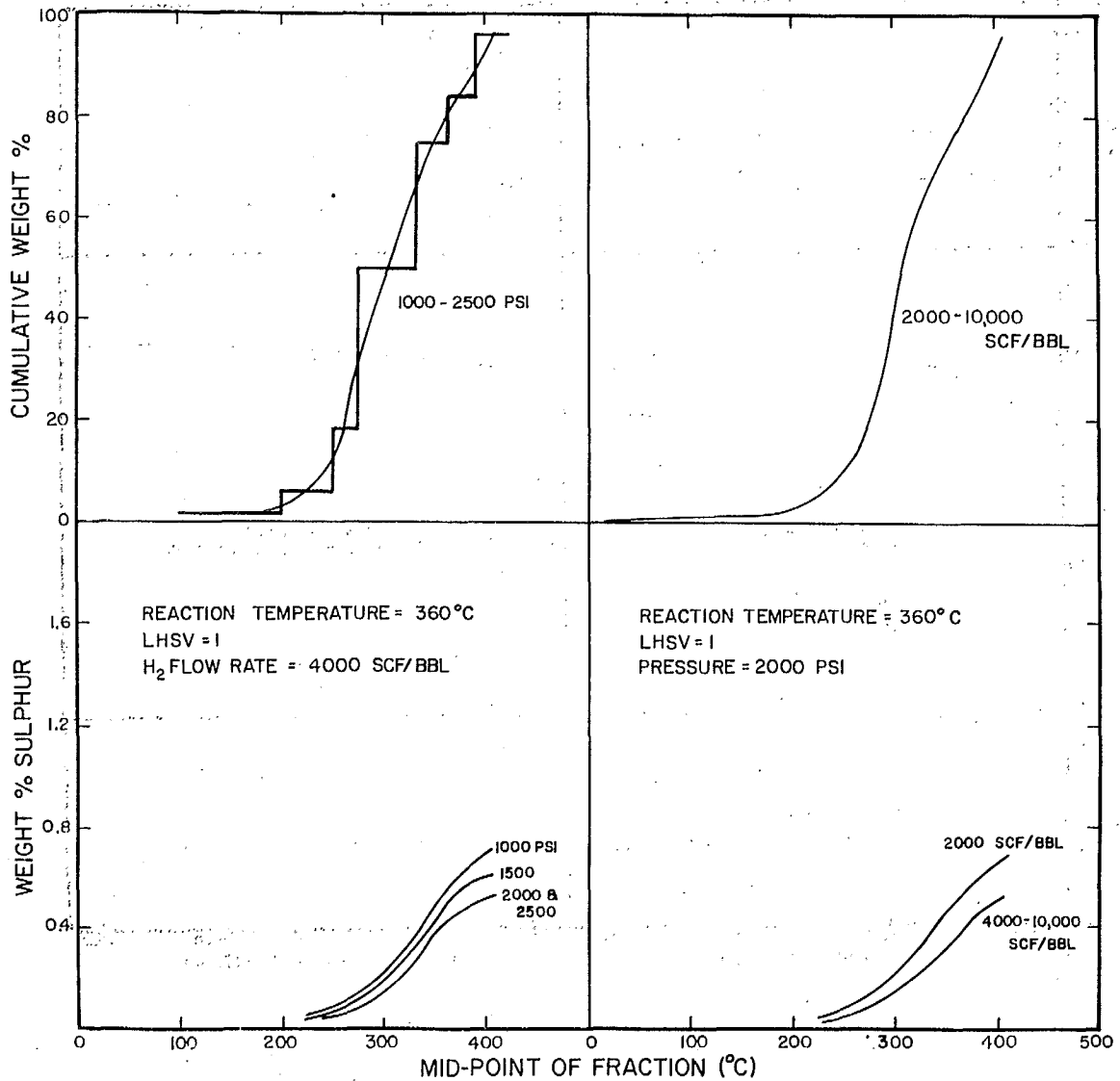


Figure 9 - The results of distillation and sulphur analyses of the products formed at various pressures and hydrogen flow rates. (Bottom-feed arrangement; boiling range of fractions shown as segments in upper left-hand section).

content on the average was definitely lower at the higher pressures and hydrogen flow rates. When considering the relatively small changes, however, it must be remembered that the present experiments were short runs, of approximately 4 hours duration, that would not reflect long-term effects. This is particularly true of the effect of pressure. Previous investigations in our own laboratories (7) and in others (8, 9) indicate that a pressure of the order of 2000 psi is required to prevent the rapid build-up of coke on the catalyst with thermally produced gas-oils such as used here. In theory also, with a bottom-feed system, a higher gas flow rate should result in more (and faster) distillation of the vapourizable material out of the reactor. Within the range of flow rates investigated in the present study, 2000 - 10,000 scf/bbl, this did not appear to be a significant factor.

In summary, the investigation has demonstrated four basic advantages of bottom-feed over top-feed for a continuous flow, hydrodesulphurization system:

1. improved conversion
2. improved temperature control
3. higher practical space velocities and
4. longer effective catalyst life.

#### ACKNOWLEDGEMENTS

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