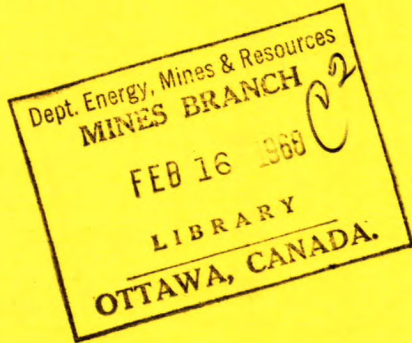


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OTTAWA



*THE HYDROGENATION OF ALBERTA
BITUMEN OVER COBALT
MOLYBDATE CATALYST*

M. A. O'GRADY AND B. I. PARSONS

FUELS RESEARCH CENTRE

SEPTEMBER 1967

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THE HYDROGENATION OF ALBERTA BITUMEN
OVER COBALT MOLYBDATE CATALYST

by

M.A. O'Grady* and B.I. Parsons**

ABSTRACT

A laboratory investigation of the hydrogenation of Alberta bitumen over oxide and sulphide forms of commercial cobalt molybdate catalyst is described. Experiments were made with four reaction bed-preheater arrangements: a) porcelain berl saddles in both the preheater and the reaction bed (a no-catalyst system); b) porcelain packing in the preheater section, followed by the oxide form of cobalt molybdate catalyst in the reaction bed; c) the oxide form of the cobalt molybdate catalyst in both the preheater and the reaction bed; and d) the sulphide form of the cobalt molybdate catalyst in both the preheater and the reaction bed. Coke was found to form quickly in the systems where porcelain packing was used in the preheater section. Much improved operating life and activity were observed when the oil feed was brought up to temperature on catalyst packing. A marked increase in activity and operating stability was also observed when the bitumen was diluted slightly with a heavy gas-oil fraction. From the standpoint of the conversion of residuum to distillable oil, the all-sulphide catalyst system was more effective than the oxide, but the all-oxide system was more stable in operation and removed more sulphur. Under conditions where a high proportion of the products was in the liquid phase, the activity of the oxide system changed little with operation, whereas the activity of the sulphide catalyst decreased rapidly.

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Direction des mines
Rapport de recherches R 194

L'HYDROGÉNATION DU BITUME D'ALBERTA EN
PRÉSENCE DU CATALYSEUR "COBALT MOLYBDATE"

par

M. A. O'Grady* et B. I. Parsons**

RÉSUMÉ

Les auteurs décrivent des expériences de laboratoire en l'hydrogénation du bitume d'Alberta en présence des formes oxydées et sulfurées du catalyseur commercial "cobalt molybdate". L'expérience portait sur quatre arrangements du lit de réaction et du préchauffeur: a) selles de Berl en porcelaine à la fois dans le préchauffeur et dans le lit de réaction (système sans catalyseur); b) garnissage en porcelaine dans la section du préchauffeur, suivi de la forme oxydée du catalyseur "cobalt molybdate" dans le lit de réaction; c) la forme oxydée du catalyseur "cobalt molybdate" à la fois dans le préchauffeur et dans le lit de réaction; et d) la forme sulfurée du catalyseur "cobalt molybdate" à la fois dans le préchauffeur et dans le lit de réaction. On a constaté que le coke se formait rapidement dans les systèmes où le garnissage de porcelaine était utilisé dans la section du préchauffeur. Une grande amélioration de la durée d'utilisation et de l'activité a été observée quand l'huile d'alimentation sur le garnissage catalytique a été amenée à la température du catalyseur. Un accroissement marqué de l'activité et de la stabilité de fonctionnement a été aussi observé quand le bitume était dilué légèrement par une fraction lourde de gas-oil. Du point de vue de la conversion du résidu en huile distillable, le système utilisant la forme sulfurée du catalyseur s'est avéré plus efficace que le système à forme oxydée, mais ce dernier a fait preuve d'une plus grande stabilité de fonctionnement et éliminait plus de soufre. Quand une forte proportion des produits était à la phase liquide, l'activité du système à catalyseur oxydé a peu varié avec le temps, tandis que l'activité du catalyseur sulfuré a diminué rapidement.

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INTRODUCTION

The object of the present investigation was to determine the effect of the chemical form of the catalyst and preheater packing on the hydrogenation and refining of Alberta bitumen. High-pressure hydrogenation, as a general refining process for petroleum, has been under study at the Mines Branch for many years. The investigations have been largely concerned with the development of suitable engineering equipment and arrangements for the processing of coker distillates (1, 2). Many of the problems involved in the treatment of such distillates have been resolved, and hydro-treating has been shown (3) to be a practical process for both the purification and the upgrading of heavy oils.

In recent years, more interest has been shown in the hydrogenation of extreme residual fuels, such as vacuum bottoms, from refinery distillation systems. This added interest has been due, mainly, to newly proposed regulations with regard to air pollution in and around the large cities where residual fuels are usually marketed. Vacuum bottoms possess all the undesirable properties and problems generally associated with coker distillates (high nitrogen and sulphur content) along with extra processing difficulties attributable to the low hydrocarbon quality* and to the presence of mechanical impurities such as mineral matter or clay. Unlike a coker distillate, vacuum bottoms will not distill under practical conditions. Any process for the treatment of such material will have to begin, at least, with the feed in the liquid phase.

In broad terms, the technical ability to hydrogenate heavy oils and tars in the liquid phase on a commercial scale has been available since the turn of the century. The limiting factor has almost always been the high cost of the hydrogen required**. During the past ten years, however, considerable technical progress has been made in the manufacture of hydrogen from natural gas. The latest reported cost figure for hydrogen, based upon production in a large plant, is 22¢/1000 cubic feet (4). At a cost of this order of magnitude, the hydrogenation of heavy residuum appears more practical.

* Residuum from vacuum stripping towers is sometimes more difficult to process than the residuum in the original crude, because thermal coking which occurs to some degree in the separation process results in the formation of high-molecular-weight species of abnormally low hydrogen content.

**Very successful coal-hydrogenation plants were operated in Germany during World War II, at a time when costs were of secondary consideration.

Two liquid-phase industrial processes are presently in operation on a small scale, a) the "H-Oil" process at Cities Service Oil Company's Lake Charles Refinery in Louisiana (5), and b) the "Combi" process operated by Scholven Chemie A.G. in Germany (6). In the "H-Oil" process, the heavy feed stocks are hydrogenated in an ebullated bed over a cobalt molybdate catalyst. The "Combi" process uses a liquid-phase reactor and a finely powdered iron-carbon black catalyst. In both processes, the feed material is heated in the final stages in the presence of catalyst, and the unreacted heavy oils and residua are recycled.

The advantages of either preheating over catalyst or diluting the feed stocks with heavy oil have not been fully reported, and one of the purposes of the present study is to establish whether the added steps are of marginal value or whether they are, in fact, operational necessities. Catalyst materials generally have poor heat-transferring properties, and a much larger preheater system would be required to bring the reactants up to temperature over catalyst. It would also seem impractical to recycle heavy hydrocarbons stocks which might otherwise be suitable for finishing as lubricating oils.

Reports of the economic advantages of dilution with heavy gas-oil fractions have appeared from Hungary (7) in connection with the high-pressure hydrocracking of residuum (the Varga process). In hydrocracking, it was found that the pressure of hydrogen needed to effect reaction could be greatly reduced if naphthenic-aromatic compounds, such as tetralin, were present in the diluent oil. Such compounds are pictured as being capable of transferring nascent hydrogen to free radicals formed in the course of cracking. In a more recent study of the hydrocracking reaction (8), it has been proposed that the addition of a diluent to the feed stock reduces the thickness of the oil layer on the catalyst surface, thereby allowing more hydrogen to diffuse to the catalyst in a given time. Such a mechanism would predict that almost any hydrocarbon diluent would be of advantage, regardless of composition, provided it reduced the viscosity and surface tension of the feed at the reaction temperature.

In the present investigation a high residuum oil feed and hydrogen were pumped, at predetermined rates and pressures, to the head of a heated reaction vessel, mixed, and passed over various preheater and catalyst arrangements. The products of reaction were removed and analysed to establish the best operating conditions. The feed stock selected for study was untreated bitumen separated from the bituminous sand deposits at Mildred Lake, Alberta. Various heavy oil fractions from a pitch distillate derived from the bitumen were used as diluents. Experiments were

made with oxide and sulphide forms of conventional, commercial cobalt molybdate catalyst.

EXPERIMENTAL

General Description of the Apparatus

The apparatus consisted of two high-pressure flow systems similar to those used previously (1, 2) in the Mines Branch. Photographs of the apparatus are shown in Figures 1 and 2, and a flow diagram is given in Figure 3. For the sake of simplicity, only one of the flow systems is shown in Figure 3. The hydrogen compressor, storage tank, and inlet pressure regulators were common to both set-ups. The liquid feed pump used in one of the tests beds was of a positive-displacement type (Ruska Instrument Co., Houston, Texas), suitable for metering highly viscous feeds such as the undiluted bitumen. The liquid feed pump in the second system was a diaphragm-type pump (Lapp Insulator Co., LeRoy, N.Y.), suitable only for pumping the diluted, less viscous feed stocks. Otherwise, the two flow systems were identical. A list of the principal components of the apparatus, e.g. pumps, regulators, etc., and of the manufacturers and the particular model numbers is given in Appendix 1.

Each flow system consisted of a reaction vessel and two receiver vessels, so connected that the products of reaction could be passed into either receiver by simply opening and closing appropriate valves. During the starting-up period of an experiment, the products of reaction were collected in one receiver (usually the smaller, 1-liter vessel) until all the required adjustments had been made to bring the flow rates, temperatures, etc., to the desired values and the system attained a dynamic equilibrium. When the system was functioning as required, the flow was changed into the other receiver for a specified sampling period. At the end of the sampling period, the flow was changed back to the original receiver and the system was shut down. When such a procedure was followed, the sample of products collected was representative of the conditions of the test and free of extraneous effects due to start-up or shut-down.

The reaction vessels and the 2-liter receiver vessels used in the flow systems were designed by the Fuels and Mining Practice Division and manufactured in the Mines Branch machine shops. The 1-liter receivers were purchased from Autoclave Engineers, Erie, Pa. Diagrams of the vessels are shown in Figures 4 and 5. All vessels, whether purchased or manufactured by the Mines Branch, were tested hydraulically at the pressure for which they were designed before being put into use. Seal-ring closures

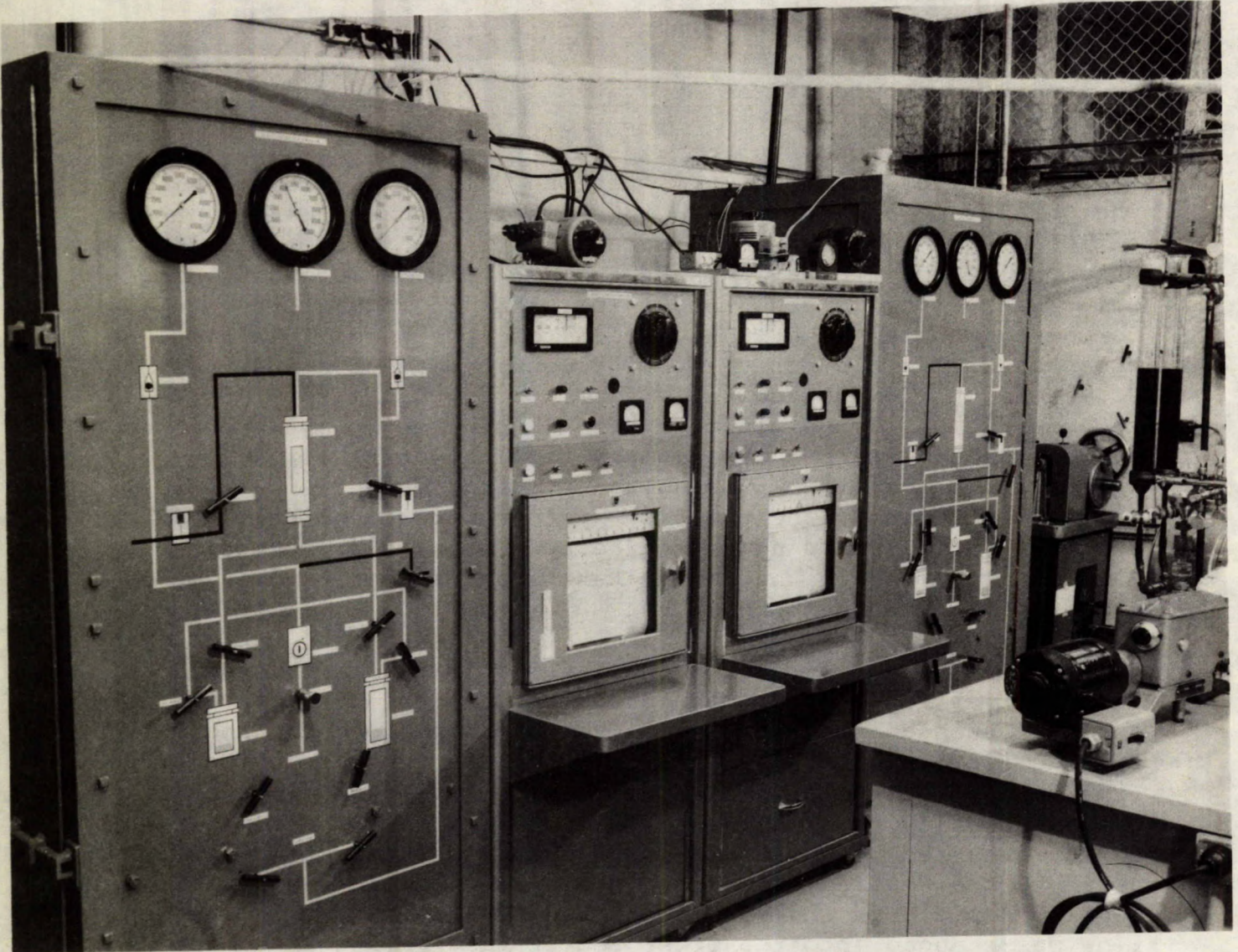


Figure 1 - A photograph of the apparatus - front view.

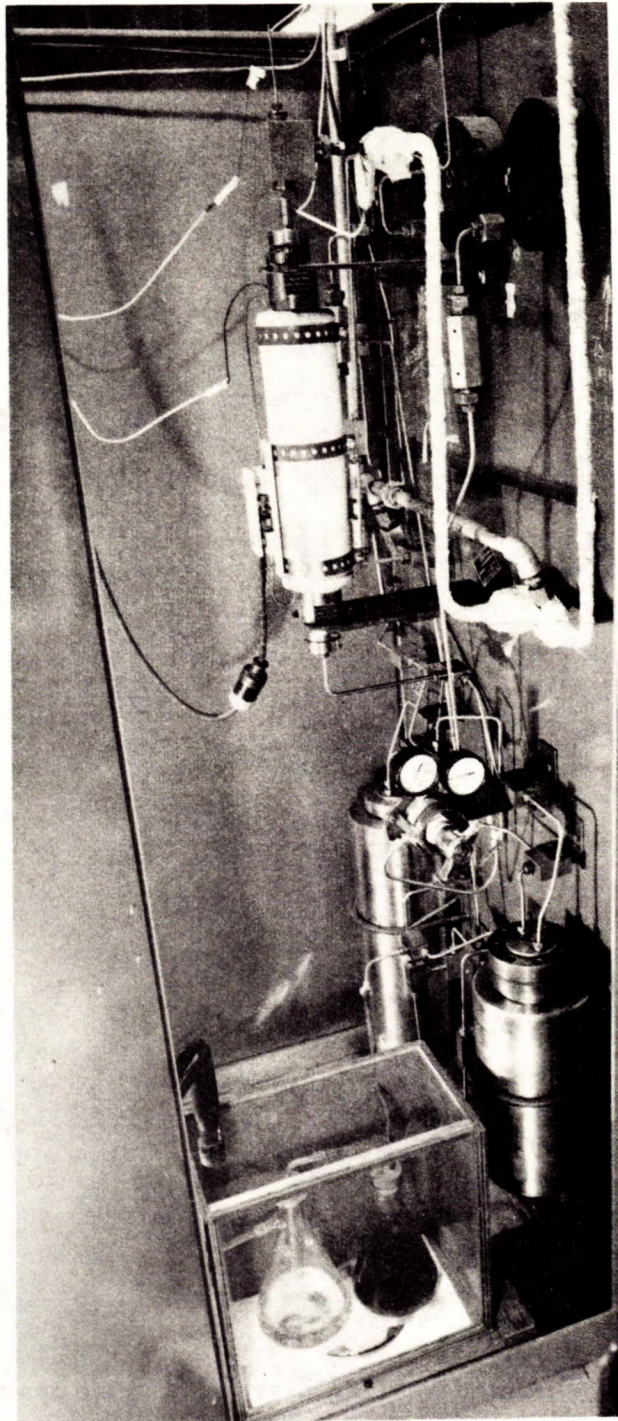


Figure 2 - A photograph of the reaction system.

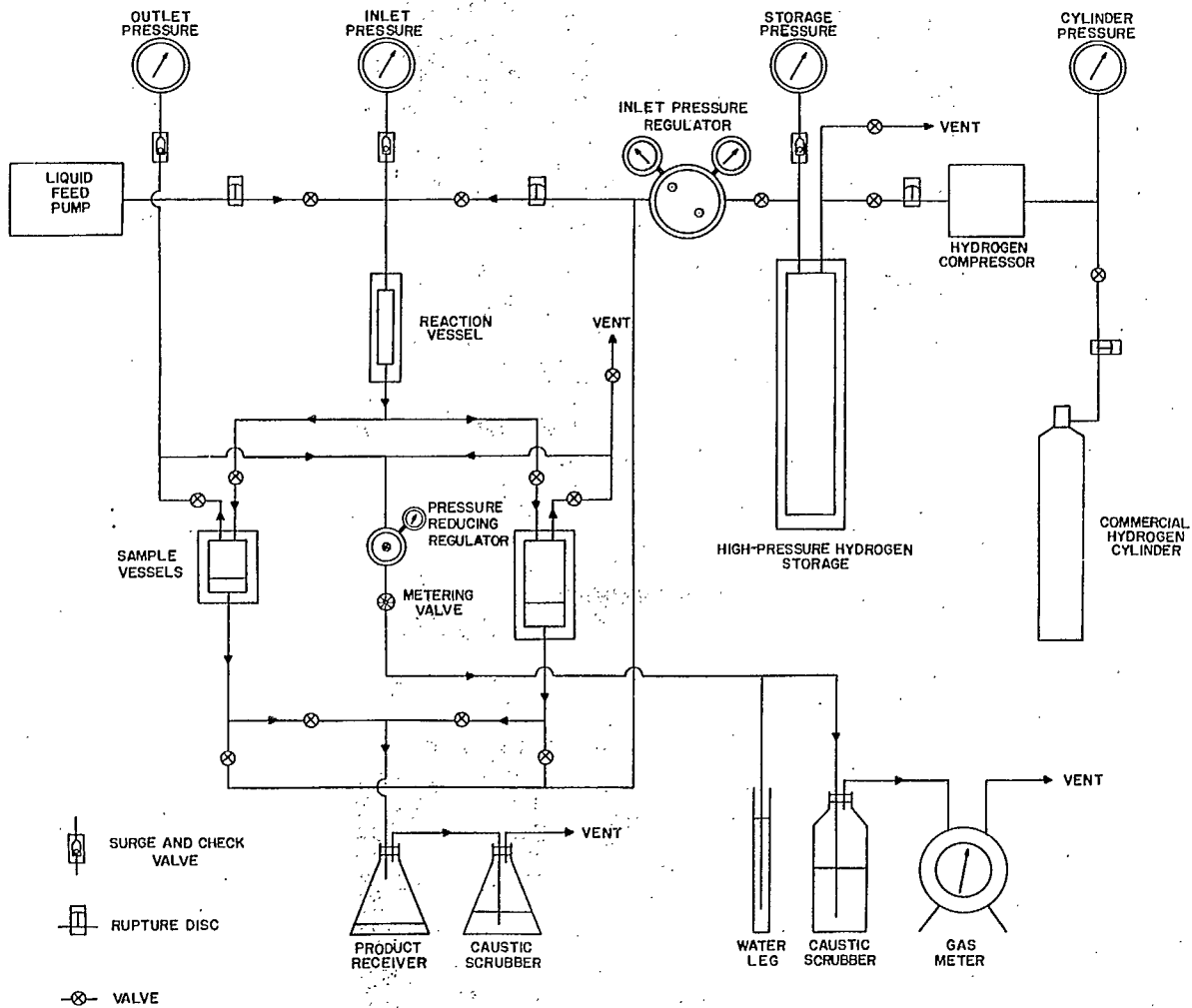


Figure 3 - A schematic diagram of the apparatus.

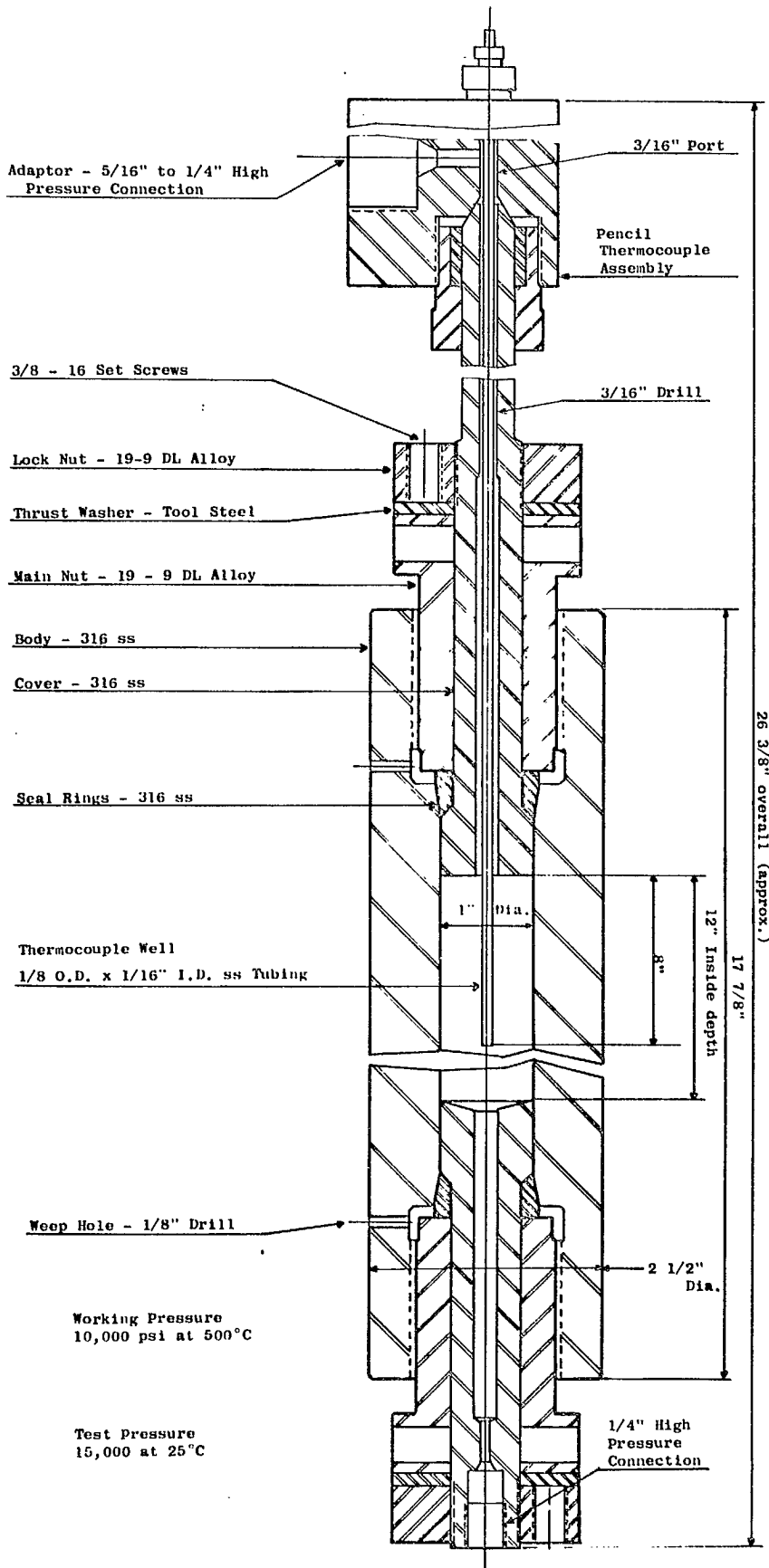


Figure 4 - The reaction vessel.

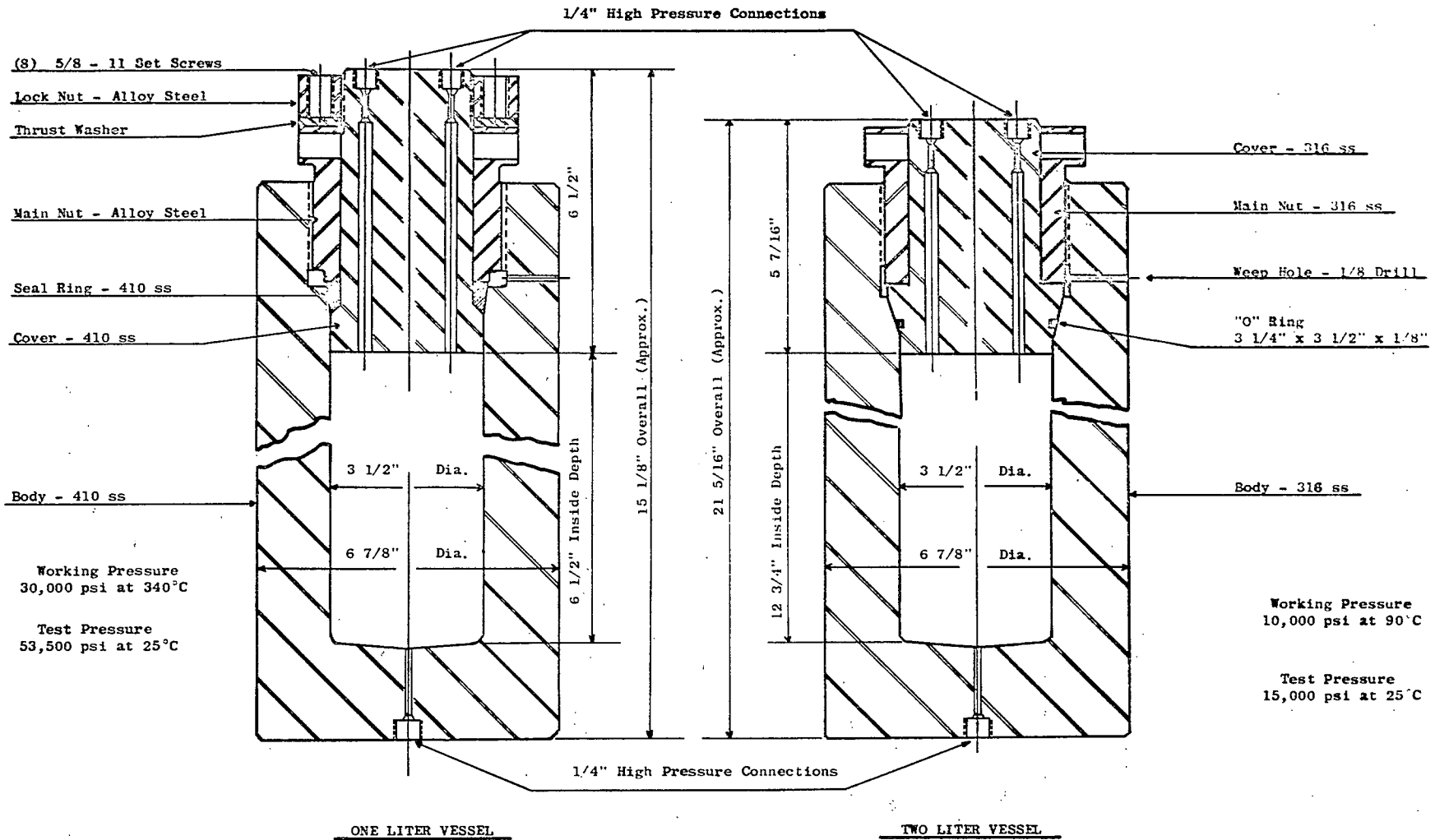


Figure 5 - The receiver vessels.

were used in the reaction vessels (because of the high temperatures involved) and neoprene "O"-ring-type closures were used on the 2-liter receiver vessels. The "O"-ring closures have been in service for approximately 20 months and, to date, there is no evidence of any serious deterioration of the neoprene as the result of exposure to the raw oil products. One closure was opened for inspection after 15 months and the "O" ring renewed; the other is still in service. The neoprene loses much of its resiliency after 15 months, but will hold pressure if left undisturbed.

Four reaction vessels, identical with the drawing shown in Figure 4, were used in the investigation*. Each vessel was heated electrically by means of 15 feet of heating cable (stainless steel sheath, magnesium oxide insulation, nominal 1/8-in. diameter, 1 ohm per foot). Nineteen turns of the cable were spaced about the center over 13 in. of the vessel body and then covered with a 1/4-in. layer of "Thermon" heat-transferring cement. The heat-transferring cement ensured a more uniform heating over the surface and reduced the possibility of overheating the steel adjacent to the cable. For handling ease, and also partly as thermal insulation, the area of the vessel walls covered with the "Thermon" cement was wound with four layers of 1/8-in.-thick asbestos sheet. The thermal insulation of the reaction vessel was completed when the reaction vessel was connected into the test bed. Once in place, with the lines connected, the entire body and heads were wrapped with 4 in. of fiberglas insulation.

The temperature of the reaction vessel was controlled by a galvanometer-type controller, operating on a chromel-alumel thermocouple in firm contact with the outside surface of the vessel. The thermocouple was inserted through the insulation at the center of the vessel and secured to the main body by a metal strap. The temperature controller (with time-proportioning action) regulated the outside surface of the reaction vessel to $\pm 1^{\circ}\text{C}$, or better, at any predesignated temperature.

The temperature in the preheater and the catalyst bed was measured by means of a second chromel-alumel thermocouple placed down the well extending into the reaction vessel (see Figure 4). This thermocouple could be moved up and down the well, as desired, to determine the temperature profile from the top of the preheater section to the bottom of the main reaction zone. The temperature measured by this central thermocouple was recorded

* While two vessels were "on-stream" in the flow systems, the other two were being cleaned and loaded with catalyst for the next series of experiments.

continuously on a single-pen chart recorder. The recorder was equipped with a multi-range and zero-suppression unit which permitted the scale to be expanded to 1 millivolt per inch of chart. Blank runs with the equipment indicated that the temperature in the center of the reaction vessel could be easily held constant to $\pm 0.2^{\circ}\text{C}$. In the course of an experiment, variations greater than 0.4°C could usually be traced to fluctuations in the flow rate of either the gas or the liquid. The chart recorder was calibrated at least once during every test, using a standard laboratory potentiometer. It should be mentioned that the stability of the chart recorder was quite good and the calibration step was carried out only as part of the operating technique involved in making an experiment.

Hydrogen gas was taken from commercial cylinders and compressed into the storage tank to approximately 3500-4000 psi. The inlet pressure to each system was controlled at 2000 psi by a high-pressure regulator. Hydrogen flowed from the regulator to the head of the reaction vessel, where it mixed with the liquid feed and passed through the preheater and catalyst bed to the sample receivers. The liquid products of reaction collected in the receivers, and the gaseous products and excess hydrogen passed on to the exit system. The amount of hydrogen flowing through the reaction vessel was controlled by regulating a metering valve on the downstream side of the receivers. The rate and amount of gas flowing from the metering valve were measured using a conventional wet-test meter. Before passing into the wet-test meter, the gas stream was scrubbed with caustic solution to remove any hydrogen sulphide present.

During the first few runs it was attempted to operate the metering valve at the full pressure of the system, i.e., to meter the gas from 2000 psi to atmospheric pressure directly across the orifice of the valve. To obtain low gas flows under such conditions, the metering valve was opened only very slightly and control was neither easy nor accurate. Moreover, it was found that under these conditions any small droplet of liquid entrained in the exit gas tended to block the valve and completely stop the gas flow. These problems were overcome by installing a corrosion-resistant, pressure-reducing regulator in the line ahead of the metering valve. The regulator was set to reduce the pressure to 10 psig, thereby allowing the metering valve to be opened considerably, improving the degree of control, and reducing the effect of trace amounts of liquid on the gas rate.

Catalyst and Preheater - Loading and Pre-treatment

The catalyst used throughout the present study was an alumina-supported cobalt and molybdenum catalyst* manufactured by the Union Oil Co. of California (research center located at Brea, California). It was described by the manufacturer as a Type N-5 catalyst, Sample No. H 2260, and was in the form of 1/8-in.-diameter pellets.

Two types of packing material were used in the preheater section of the reaction vessel: a) porcelain berl saddles, nominal 6-mm size; and b) an alumina-supported cobalt molybdenum catalyst manufactured by the Union Oil Co., similar to the main catalyst but in the form of extremely hard 1/4-in.-diameter pellets with convex ends. This material was described as a Type N catalyst, Sample No. H-812. The berl saddles were used as an example of the various classes of material which are regarded as inert, or non-reactive, packings for preheater systems. The 1/4-in. pellets of cobalt molybdate catalyst were used, on the other hand, as an example of a packing material outside the usual concept of an "inert" preheater. The hard pellets withstood rough handling quite effectively and were regenerated easily by calcination. Any mineral matter adhering to the pellets after regeneration could usually be blown away with compressed air. Occasionally it was necessary to roll the pellets between two soft bristle brushes in order to remove the more adherent mineral deposits.

A diagram showing the interior of the reaction vessel, the thermocouple well, and the preheater and catalyst sections is given in Figure 6. The reaction vessel was mounted vertically in the flow system, and the oil passed from top to bottom. To load the preheater and catalyst, the top cap and thermocouple well were tightened into the body of the vessel and the reactor was clamped upside down in a vice. Measured amounts of preheater and catalyst, corresponding to 4 1/2 in. of preheater and 3 1/4 in. of catalyst, were then poured into the reaction chamber..... occasionally rapping the body with a machine hammer to settle the pellets to minimum volume. The space remaining after the preheater and catalyst were located was filled with porcelain berl saddles and the bottom cap and seal ring were tightened into place. At this point the reaction vessel was ready to be connected to the high-pressure lines in the flow system.

* The same catalyst as used previously in a pilot-plant investigation of the hydrodesulphurization of a coker distillate (3) derived from Alberta bitumen.

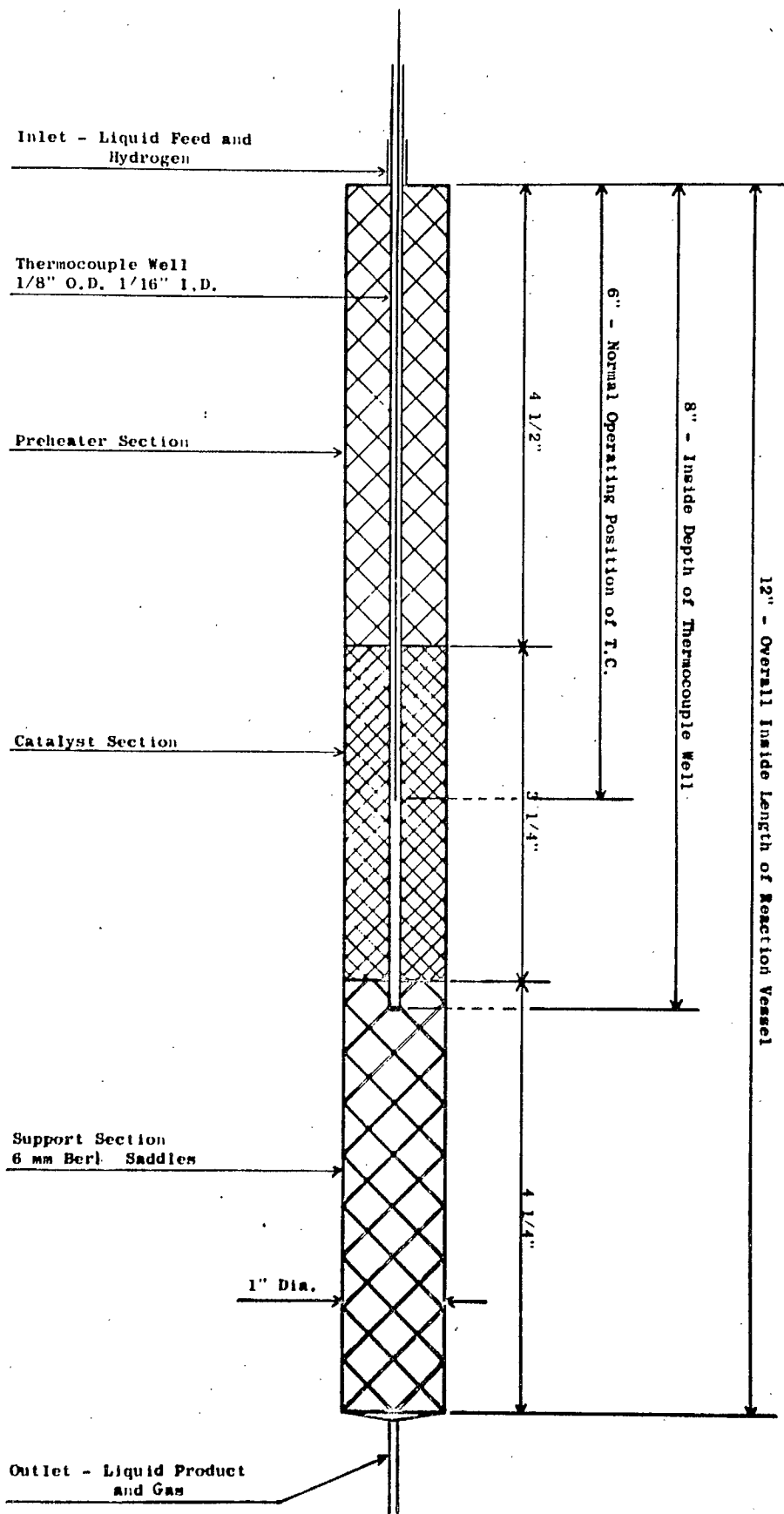


Figure 6 - The interior of the reaction vessel and the arrangement of the preheater and reaction bed sections.

For many of the experiments, the catalyst and preheater were used in an "as is" condition, i.e., the pellets, as supplied by the manufacturer, were loaded into the reaction chamber and the vessel was connected into the system, pressurized with hydrogen, and set in operation. In some series of tests, however, the catalyst and the preheater were treated with hydrogen sulphide gas at 450-475°C before being used. Very briefly, the sulphide treatment was done as follows: A cylinder of hydrogen sulphide gas (reagent quality - supplied by the Matheson Co. of East Rutherford, N.J.) was connected to the inlet tube of the reaction vessel, and the outlet opening was connected to a small laboratory gas bubbler*. The flow of hydrogen sulphide gas through the reaction vessel was started at room temperature. The controller was then turned on and the reaction vessel brought up to 450-475°C over a period of one hour. This temperature was maintained for at least 45 minutes; then the H₂S gas flow was stopped, the lines quickly removed, and the reaction vessel connected to the flow system and pressurized to 2000 psi with hydrogen. Depending entirely on the schedule of the experiments, the treated catalyst was either used immediately or allowed to cool slowly overnight in anticipation of a run the following day.

Experimental Procedure

A detailed description of the operation of the flow systems and the steps involved in the collection of the samples is given below. As mentioned previously, a schematic diagram of one of the flow systems is shown in Figure 3.

Prior to a series of experiments, hydrogen was taken from commercial cylinders and compressed to 3500-4000 psi in the storage vessel. The liquid feed pumps were primed and the reservoirs filled with the oil feed to be tested. The catalyst and preheater were loaded into the reaction chamber, sulphided where required (described on page 11), and the vessel connected into the flow system. The reaction vessel and sample receivers were pressurized by opening the inlet valve, allowing hydrogen to flow from the storage system into the apparatus. The vessels and connections were always pressure-tested before proceeding with an experiment. The system was considered tight if no measurable pressure change (± 10 psig) occurred in a one-hour period.

* The bubbler simply provided visual evidence that gas was flowing. It was found that the rate of flow was not critical as long as an excess of H₂S was present at all times.

Any operating pressure up to 3000 psi could be selected, by the adjustment of control settings on the inlet pressure regulator. The 3000-psi maximum was the highest allowable working pressure of the outlet pressure-reducing regulators. For all of the experiments discussed here, the operating pressure was 2000 psig.

To begin an experiment, all valves except the liquid feed valve were opened and the pressure was equalized throughout the system. The flow of hydrogen was started by adjusting the outlet pressure regulator to deliver 10 psig and cautiously opening the metering valve. The hydrogen flow rate was controlled relative to the amount of liquid feed pumped to the reaction vessel.....the usual rate was 7500 cubic feet per barrel* of liquid feed. Allowance was made, in the calculation of the gas rate, for the displacement of hydrogen in the sample receivers due to the accumulation of liquid product, i.e., the overall gas rate was equal to

- a) an amount equivalent to 7500 cf/barrel of oil, plus
- b)
$$\frac{(\text{volume of feed in cf}) \times (\text{operating pressure in psia})}{(\text{atmospheric pressure, psia})}$$

It was our experience that, at a high flow rate of 7500 cf/barrel, small changes in the hydrogen flow (± 10 percent) had no significant effect on the result of the experiment. For this reason, no attempt was made to correct the gas rate for hydrogen consumption; or for the formation of light hydrocarbon gases in the course of reaction, or for slight variations in operating temperature and the non-ideality of the gas. To a degree, the errors as the result of hydrogen consumption and gas formation were self-compensating.

As soon as hydrogen was flowing through the system and the major adjustments to the gas rate were completed, the valves connecting the large sample vessel (right-hand vessel, Figure 3) to the reactor were closed and the flow directed through the small sample vessel. The temperature recorder and controller were then turned on and the reaction vessel brought up to temperature. As the reactor approached the operating temperature, the liquid feed pump was started and adjusted to deliver the required flow of feed to the catalyst bed.

* The "barrel" is the traditional unit of measure for liquid feeds in refinery practice. It is defined as 42 gallons (U.S.), which is the estimated average content of the nominal 45-gallon (U.S.) drum.

By convention, the liquid feed rate in heterogeneous systems is defined in terms of the volume occupied by the catalyst in the reaction vessel:

$$\text{Liquid Hourly Space Velocity (LHSV)} = \frac{\text{Volume feed over catalyst per hour}}{\text{Volume (apparent) of catalyst bed}}$$

In the present study, the volume of catalyst was 41 ml and the liquid pumping rate was 20.5 ml/hr for most of the experiments. The Liquid Hourly Space Velocity (LHSV) was, therefore, 0.5.

The volume occupied by the catalyst depends on the diameter of the tube, the size of pellets, and the way the pellets pack into the space available. In large-diameter tubes the packing is virtually unaffected by the walls, but in a small tube with a central thermocouple well (such as used here), the apparent volume occupied by the catalyst is greater than that which would be measured in a wide-diameter pipe, because the pellets tend to "hang up" on the walls. For this reason the values reported here for the feed rate are probably low by 5 to 8 percent, as compared with the packing arrangement encountered in a large reactor.

In the first 30-60 minutes of an experiment, all final adjustments in the liquid and gas flow rates were made and the temperature of the catalyst bed was stabilized at the desired value. It usually required about 30 minutes for the system to come to a steady state. Primary control of the temperature in the catalyst bed was obtained by the regulation of the power to the heaters via the temperature controller. However, the exothermic nature of various refining reactions (combined with the poor heat-transferring properties of the catalyst) usually caused the catalyst temperature to rise 5 to 10° above the set-point of the controller. The more effective the refining action, the greater the amount of heat generated and the higher the apparent temperature would become. To obtain a particular temperature for a test, it was necessary to "balance" the setting on the temperature controller against the exothermic heat generated. When equilibrium was attained the sampling period was begun.

At the start of the sampling period, the valves connecting the 1-liter sample vessel to the reaction vessel were closed and the valves to the 2-liter vessel were opened. Simultaneously, readings were made on the wet-test meter (gas flow) and on the liquid feed systems and the time of day was noted. At the end of the sampling period, usually 6 to 7 hours, similar readings were made and the valves to the sample vessels were

reversed to direct the flow back again to the 1-liter vessel*. During the sampling period, the flow rates, reaction temperature, etc., were held constant. The sample collected in the 2-liter vessel was regarded as representative of the operating conditions, independent of effects due to the start-up or shut-down of the system.

At the end of the experiment, the sample was withdrawn by cautiously opening the valve in the line connected to the bottom of the sample vessel. The gas pressure in the vessel above the liquid sample forced the oil product out into a weighed Erlenmeyer flask (the product receiver, Figure 3). The amount of sample was determined by direct weighing and compared with the amount of feed pumped into the system, to establish the weight yield for the conditions of the test. The sample vessel was then repressurized, either by flowing hydrogen through the reaction vessel or by opening the valve in a by-pass line directly connected to the inlet pressure regulator. When only short daily experiments were being made, the extra hydrogen flow due to the draining of the sample was usually passed through the reaction vessel to help flush off any oil or tars retained on the catalyst prior to shutting the system down.

Analysis of the Products

The primary purpose of the investigation was to establish whether there was any advantage to be gained by either diluting the oil feed or carrying out the final stages of the preheating over catalyst. To a very large extent these factors could be evaluated simply by noting the extent of change in the specific gravity of the product obtained under various reaction conditions, or by determining the change in the specific gravity as a function of time under constant reaction conditions. There was, however, the danger that the specific gravity of the overall oil product could be misleading, i.e., a mixture of high- and low-molecular-weight hydrocarbons could show the same apparent specific gravity as did a mixture of hydrocarbons of intermediate molecular weight. For this reason, and also because chemically different catalyst species were tested, each sample of oil products was distilled to determine the percentage gasoline, gas-oils, etc., that were present.

* When sufficient operators were available, the systems were run on shifts--allowing one hour between sample periods for changing to new operating conditions and the establishment of a new equilibrium. To shut the systems down, the liquid feed was stopped and the hydrogen allowed to flow for 30-40 minutes to clear the catalyst bed before closing all valves and turning off the heaters, etc.

The oil products were distilled according to the U.S. Bureau of Mines' Hempel distillation analysis procedure (9), using conventional laboratory apparatus. Because the volume of sample available was small, only 100 ml of oil was used in the distillation (the normal procedure calls for a 300-ml charge). The temperature cuts selected and the fractions collected are shown in Table 1.

TABLE 1

Fractions Collected in Hempel Analysis (Modified)

Fraction No.	Temperature Range (°C)	General Designation*
<u>Atmospheric distillation</u>		
1	RT-100	Light gasoline
2	100-200	Heavy gasoline
3	200-250	Kerosene distillate
4	250-275	Light gas-oil
<u>Vacuum distillation - 40 mm</u>		
5	RT-225	Heavy gas-oil
6	225-300	Lubricating distillate
7	Resid. (over 300)	Residuum

* For the present purpose, the names used indicate the general boiling range only.

The sulphur content of the various oil samples was determined by a micro-oxygen-bomb technique developed by Siegfriedt, Wiberley and Moore (10). In this procedure the sulphur content of a solution containing the combustion products of the sample are estimated by titration with a standardized barium chloride solution, using tetrahydroxyquinone as indicator.

Description of the Feed Stocks

The principal feed stock used in the investigation was untreated bitumen from the bituminous sand deposits at Mildred Lake, Alberta. It was supplied to the Mines Branch by Cities Service Ltd. The diluent used was a fraction distilled from bituminous sands at the Alberta Government's demonstration plant at Bitumount, Alberta. Inspection analyses of the untreated bitumen and the Bitumount diluent (as received) are given

in Appendix 2 at the end of this report.

A series of preliminary tests with the diluent indicated that the light ends present were cracking at the reaction temperatures required to process the heavier fractions in the bitumen. For the main part of the investigation, a portion of the diluent was topped to 250°C in a conventional laboratory distillation apparatus to remove the light hydrocarbons. The heavier fractions of the diluent (specific gravity 0.913 at 60/60°F) were used to make up feed mixtures with the untreated bitumen. Portions of all the feed mixtures were distilled and the fractions analyzed for sulphur, using the same methods and apparatus as used for the products of the experiments. A summary of the specifications of the feed stock mixtures as determined by these tests is given in Table 2.

To demonstrate the difference between the reaction characteristics of the untreated bitumen and those of the more conventional feed stocks, a few experiments were also made with a pitch distillate derived from the bitumen. The inspection analysis of this feed stock is shown in Appendix 2, and a summary of the distillation analysis (as carried out in the present investigation) is also given in Table 2. Approximately 100 gallons of pitch distillate were made by subjecting three barrels of bitumen to a pyrolytic distillation in a sloping-plate tower. The preparation of this feed material was undertaken by the Petroleum Process Engineering Group of the Branch. The distillate yields were 55 wt percent and 60 vol percent, based upon the separated bitumen.

DESCRIPTION OF EXPERIMENTS AND DISCUSSION OF RESULTS

In the description and discussion of the experiments which follow, the text has been divided into sections pertaining to the chemical nature of the preheater and catalyst, the effect of feed dilution, the recycle experiments, and the life tests. As much as possible of the factual, operating information has been incorporated into the captions and figures, with a view to simplifying the description.

The Chemical Nature of the Catalyst-and-Preheater System

The results of preliminary experiments with the separated bitumen indicated that the life of the conventional preheater-and-catalyst system was very short, of the order of a few hours. A marked improvement in both the degree of hydrogenation achieved and the operating life of the catalyst was

TABLE 2

Specifications of Oil Feed Stocks

Feed	Cities Service Bitumen	Bitumount Diluent	Mixtures of Bitumen and Diluent			Pitch Distillate
Diluent (wt %)	0	-	13.4	26.8	40.0	-
Specific Gravity, 60/60°F	1.044	0.913	1.01	0.999	0.988	0.957
Ash (wt %)	3.08	nil				0.03
Sulphur (wt %)	4.69	2.29	4.38	4.02	3.51	3.28
<u>Distillation Analyses, Concentration of Sulphur and Specific Gravity of Fractions</u>						
Atmospheric Distillation						
(1) Vol %, RT to 100°C	nil	nil	nil	nil	nil	nil
(2) Vol %, 100 to 200°C	nil	nil	nil	nil	nil	2.2
(3) Vol %, 200 to 250°C	1.7	5.6	1.7	2.7	3.3	3.3
Specific Gravity		0.859				
Sulphur (wt %)	1.59	1.17		1.38		1.92
(4) Vol %, 250 to 275°C	10.5	21.5	8.6	11.7	9.5	5.4
Specific Gravity	0.897	0.872		0.886		
Sulphur (wt %)	1.86	1.34	1.34	1.42	1.32	1.71
Vacuum Distillation at 40 mm Hg Pressure						
(5) Vol %, RT to 225°C	2.7	39.6	9.7	13.5	17.0	15.0
Specific Gravity		0.907		0.917		
Sulphur (wt %)	2.80	2.14	2.20	2.17	1.95	1.68
(6) Vol %, 225 to 300°C	14.3	26.3	16.7	20.0	22.0	25.4
Specific Gravity	0.951	0.942		0.947		
Sulphur (wt %)	3.14	2.98	2.95	2.82	2.61	3.11
(7) Vol %, Residuum	70.6	7.0	63.2	53.5	48.0	47.5
Specific Gravity	1.083	0.988		1.075		
Sulphur (wt %)	5.25	3.60	5.07	5.12	5.26	3.77

observed when the bitumen was diluted with a hydrocarbon fraction, such as a heavy gas-oil or light lubricating oil distillate. To begin the investigation proper, a study was made of the chemical nature of the catalyst and preheater, using a diluted feed stock. The feed mixture selected (on the basis of the preliminary tests) consisted of 73.2 percent by weight of bitumen and 26.8 percent by weight of the topped diluent.

Four combinations of catalyst and preheater were examined. In the first series of experiments, the entire reaction vessel was packed with porcelain berl saddles..... a "no catalyst" system. These tests were run to establish a base line for comparison purposes. Thermal cracking occurs to a small extent in any system, and to evaluate the changes brought about by the catalyst, it was necessary to determine directly the nature of the products produced in the absence of a reactive surface.

In the second series of experiments, the preheater section of the reaction vessel was packed with porcelain berl saddles and the reaction section was filled with cobalt molybdate catalyst. The catalyst was used in the oxide form, as received from the manufacturer. This second arrangement was typical of the conventional method of loading the reaction vessel, i.e., an inert preheater section followed by the catalyst bed. In the third series, the preheater section was filled with 1/4-in.-diameter pellets of the cobalt molybdate catalyst and the reaction bed with 1/8-in.-diameter pellets -- both in the oxide form, as received from the manufacturer. In the fourth series of experiments, the preheater and the reaction bed were filled with catalyst as in the third series, and then converted to the sulphide form as described on pages 11-13. In summary, the four systems were as follows:

<u>Series</u>	<u>Preheater</u>	<u>Reaction Bed</u>
1	Berl saddles	Berl saddles
2	Berl saddles	Oxide catalyst
3	Oxide catalyst	Oxide catalyst
4	Sulphide catalyst	Sulphide catalyst

In each experiment, the LHSV was 0.5 and the hydrogen flow rate was 7500 cf/bbl.

The effect of temperature on the performance of the four systems is shown in Figure 7. In each series the experiments were run in order, beginning at the highest temperature. The relative merits of the various systems are shown best in the

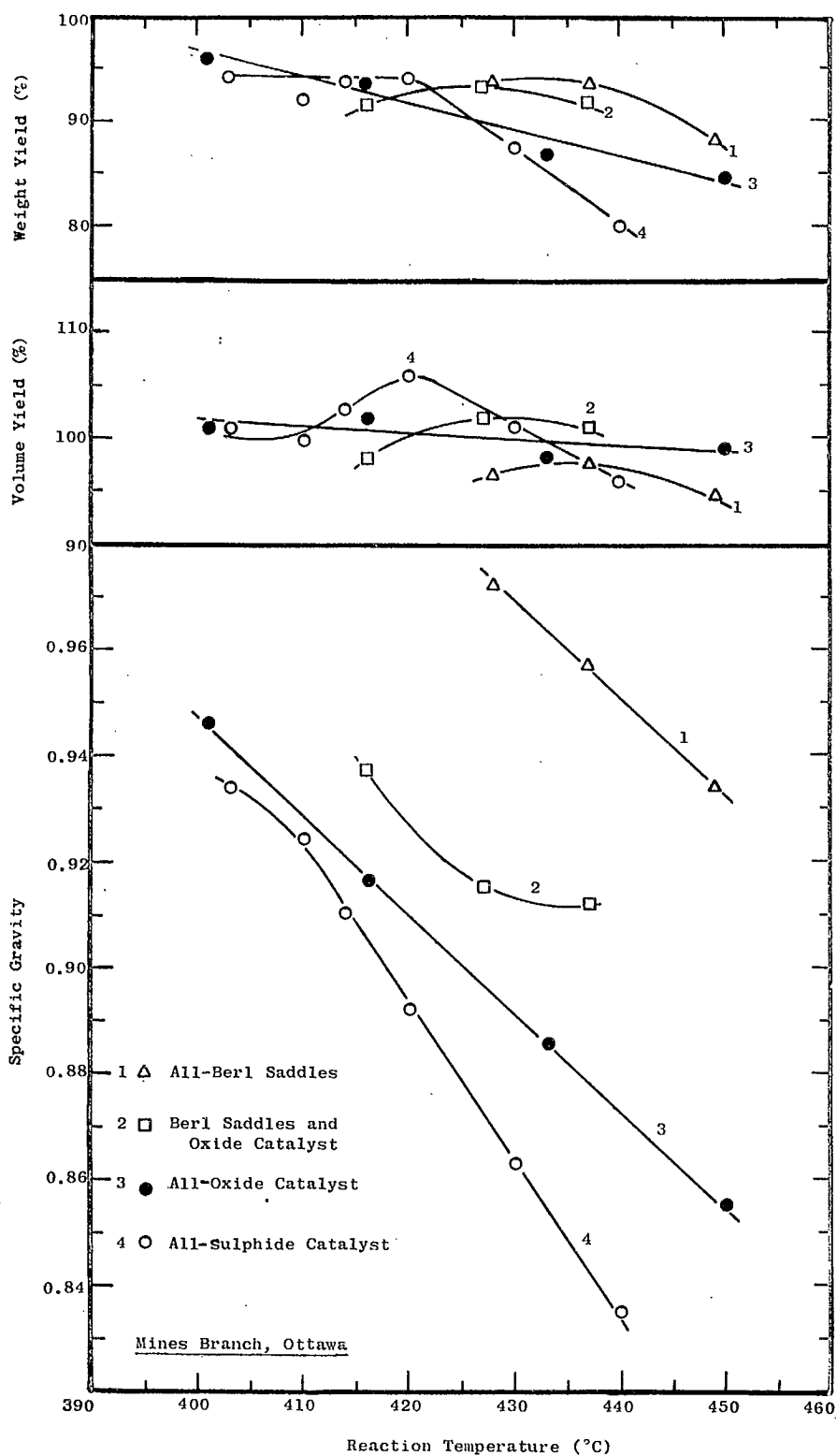


Figure 7 - The effect of the chemical form of the catalyst and preheater on the specific gravity of the product and on volume and weight yields.

graph of the specific gravity of the product versus the reaction temperature, i.e., in the lower part of Figure 7. Comparatively little refining action occurred over the porcelain berl saddles, a small amount occurred over the combined berl saddles (pre-heater) and oxide catalyst, progressively more took place with the all-oxide catalyst system, and most of all occurred with the all-sulphide reaction system.

In addition to the improved refining action, there was also a marked improvement in the life characteristics with the systems made up with catalyst preheater sections. At the end of each series of tests, the reactor was unloaded carefully to determine if (and where) mineral or coke deposits occurred. Large amounts of coke were found in the porcelain-berl-saddle preheater systems. Relatively little matter was found in the main reaction bed of these systems (probably because the systems could not operate long enough with the porcelain preheater), but what coke and foreign matter did accumulate was found at the top of the catalyst bed. In the systems made up entirely of catalyst, small amounts of mineral matter and coke were found, spread uniformly throughout the preheater and the main reaction bed section. By comparison with the "all-catalyst" systems, the porcelain preheater appeared to produce material that tended to form coke more readily on the catalyst. Definitive experiments were difficult to make on this particular point.....where berl saddles were used in the preheater, viscous tars and cokes formed quickly to plug the flow in approximately 25-30 hours. With catalyst in the preheater section (either oxide or sulphide), the life and activity characteristics of the system improved considerably, allowing experiments to be run for 100 hours or more.

The effect of reaction temperature on the weight and volume yields obtained with the four arrangements is shown in the upper part of Figure 7. Higher weight yields were obtained with the systems made up with berl saddles, but it must be pointed out that relatively little reaction occurred under these circumstances and the weight yields would be expected to be higher. In the systems made up entirely with catalyst, the highest volume and weight yields occurred in the region of 420°C with the sulphide catalyst. The yields with the "all-oxide" catalyst arrangement decreased linearly as the temperature was increased, whereas the yields obtained with the sulphide system increased up to 420°C and decreased thereafter with increasing temperature. Molybdenum disulphide has been used commercially as a mild cracking catalyst as well as a hydrogenation catalyst. The change in the slope of the plot of the yield versus reaction temperature at 420°C

indicates that more cracking is occurring at elevated temperatures.

Further evidence of the cracking ability of the sulphide form of the cobalt molybdate catalyst was obtained from the distillation analyses of the products. The results of these analyses, plotted as a function of the reaction temperature, are shown in Figure 8. Approximately equal amounts of the gas-oil fractions were produced over the oxide and sulphide catalysts, but considerably more light hydrocarbon (gasoline and kerosene distillate) and less residuum and less lubricating oil were detected in the products from the "all-sulphide" catalyst system. The larger amount of light hydrocarbon produced could only result over a catalyst possessing a higher cracking activity.

Whereas more light hydrocarbon was formed over the sulphide catalyst than over the oxide, the amount of sulphur remaining in the products from the sulphide system was considerably higher. This can be seen from the results of the sulphur analyses made on the products (prior to their distillation) summarized in Figures 9 and 10. In Figure 9 the sulphur content is plotted as a function of temperature in the same way as the specific gravity and yield measurements were presented in the previous figures. A better picture of the relative desulphurizing ability of the various catalyst arrangements, however, is obtained by plotting the results of the sulphur analyses versus the specific gravity of the product--as shown in Figure 10*. This method takes into account (at least partially) the other forms of refining which have also occurred. The results of almost every sulphur analysis indicate that the desulphurizing capacity of the oxide form of the catalyst was much greater than that of the sulphide form.

Typical results of the sulphur analyses on the fractions collected in the distillation analyses are presented in Table 3. As was expected, relatively high concentrations of sulphur were detected in all the fractions produced by thermal cracking over the porcelain berl saddles. In the thermal system, the sulphur is distributed evenly (more or less) throughout the entire boiling range. The distribution of sulphur in the fractions produced over catalyst was quite different. In the catalytic systems, the amount of sulphur in the lighter fractions (gasoline, kerosene, and gas-oil) was very low. Virtually all of the sulphur which remained in the products occurred in the residuum and lubricating oil fractions.

* The results of the analyses on the products from the system made up with a berl-saddle preheater and an oxide catalyst fell between those of the systems made up entirely of porcelain and catalyst, and have been omitted from this graph for reasons of clarity.

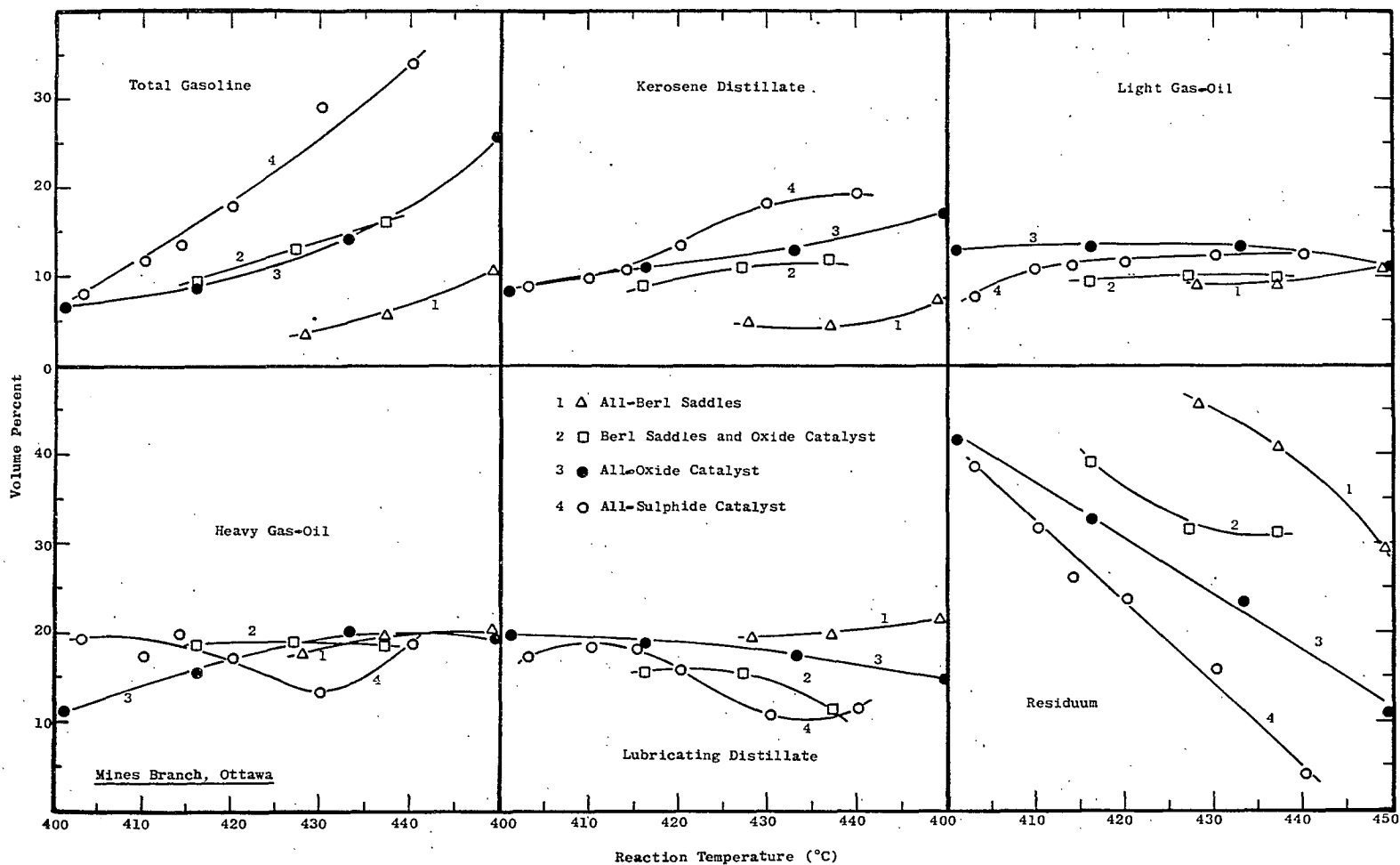


Figure 8 - The results of the distillation analyses on the products formed over the various catalysts.

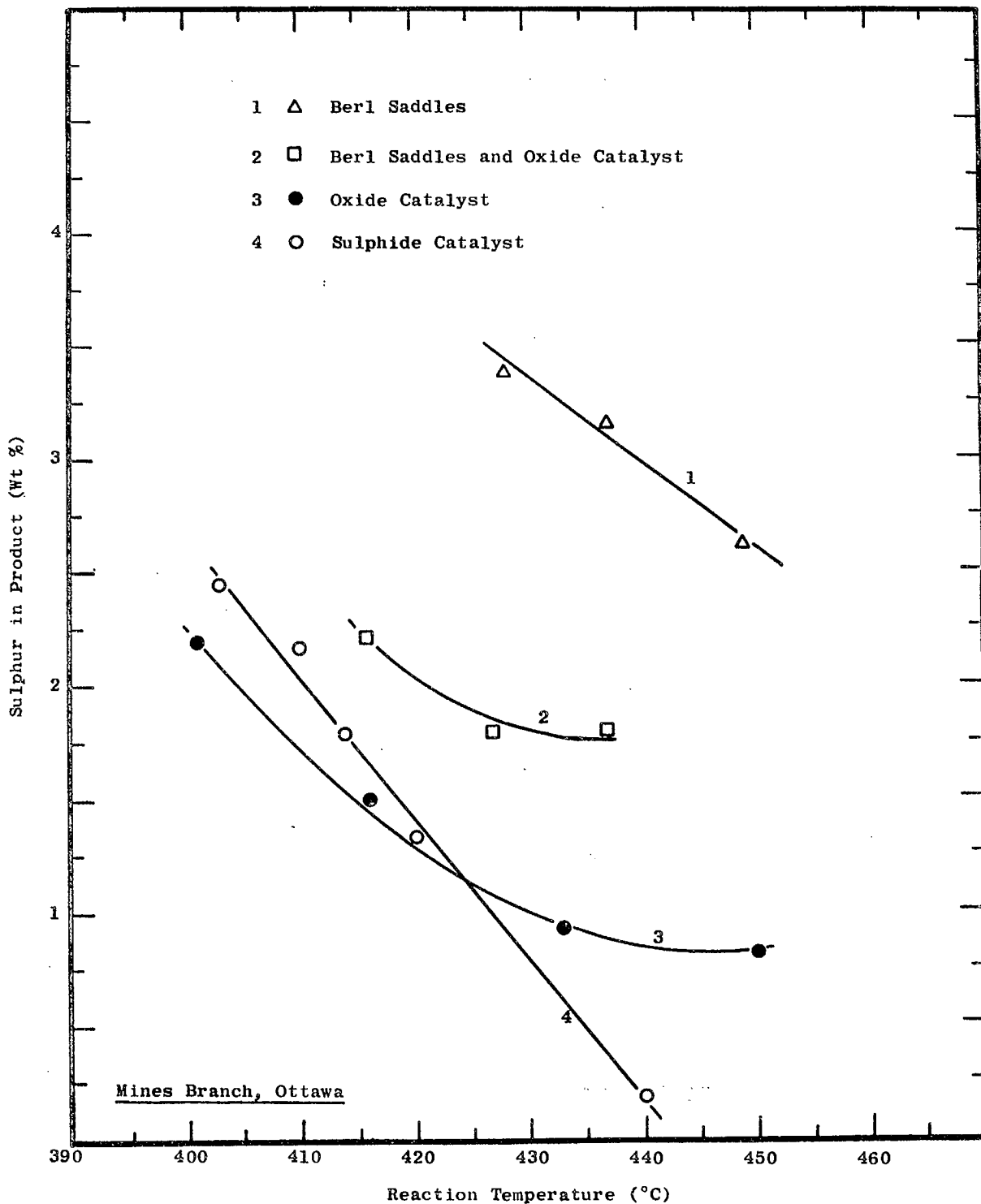


Figure 9 - The amount of sulphur remaining in the products formed over the various catalysts.

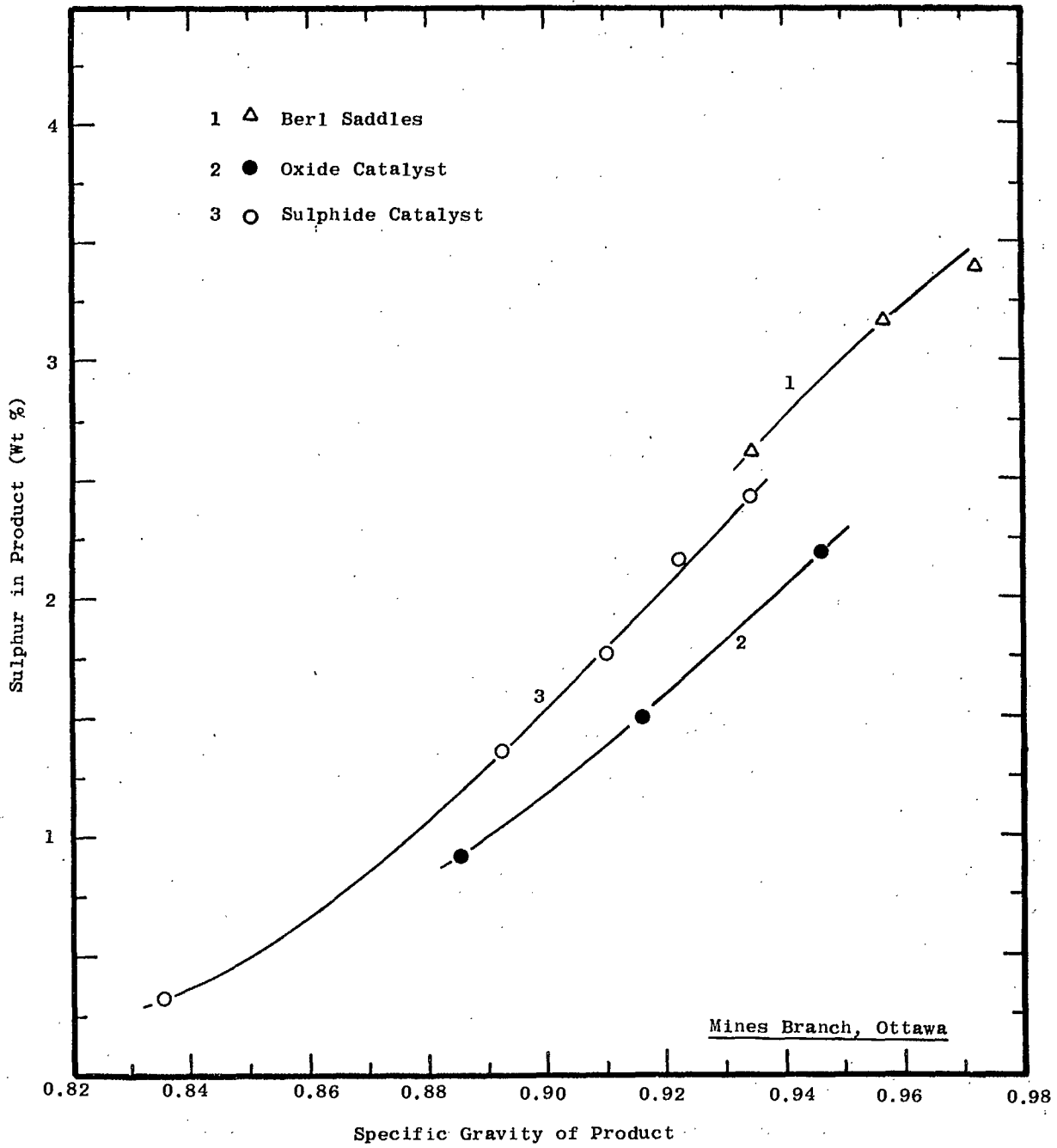


Figure 10 - The sulphur content of the products plotted as the function of the specific gravity.

TABLE 3

Typical Results of Sulphur Analyses on Fractions from Hempel Distillation

Catalyst	All-Berl Saddles		Berl Saddles and Catalyst		All-Oxide Catalyst		All-Sulphide Catalyst	
Temperature (°C)	437	428	426	416	433	416	430	414
Gravity of Product 60/60°F	0.957	0.972	0.915	0.937	0.885	0.916	0.863	0.910
Sulphur in Product (wt %)	3.17	3.39	1.79	2.22	0.93	1.50	1.97	1.78
Distillation Analyses and Concentration of Sulphur in Fractions								
Atmospheric Distillation								
(1) Vol %, RT to 100°C	1.8	1.8	5.6	3.5	4.6	3.9	7.3	5.8
Sulphur (wt %)	0.75	1.30	0.10	0.30	-*	-*	t	0.25
(2) Vol %, 100 to 200°C	3.9	1.5	7.4	5.3	9.4	4.5	21.5	7.5
Sulphur (wt %)	1.50	1.26	0.07	0.09	t	t	t	t
(3) Vol %, 200 to 250°C	4.8	5.1	11.1	9.0	13.0	11.3	18.4	10.9
Sulphur (wt %)	1.49	1.44	t	t	t	t	t	t
(4) Vol %, 250 to 275°C	9.1	9.0	10.3	9.5	13.6	13.4	12.8	11.7
Sulphur (wt %)	1.59	1.40	t	t	t	t	0.04	0.04
Vacuum Distillation at 40 mm Hg Pressure								
(5) Vol %, RT to 225°C	19.8	17.8	18.9	18.2	20.0	15.4	13.3	20.0
Sulphur	1.98	1.94	t	0.19	t	t	0.12	0.34
(6) Vol %, 225 to 300°C	19.8	19.3	15.3	15.6	17.2	18.9	10.9	18.1
Sulphur (wt %)	2.76	2.70	0.39	0.64	0.18	0.26	0.27	0.45
(7) Vol %, Residuum	40.8	45.5	31.4	39.0	23.2	32.6	15.8	26.0
Sulphur (wt %)	4.14	4.48	3.92	4.31	2.85	3.36	4.08	4.69
Feed: 26.8% by weight diluent LHSV = 0.5 Gas Rate = 7500 cw ft/bbl Pressure = 2000 psi (For comparison analysis, see Table 2.)								

* No analysis made - samples invalidated by evaporation.

The desulphurizing abilities of the oxide and sulphide catalysts are best compared by considering the sulphur remaining in the residuum. On the average, the sulphur in the residuum from the system made up entirely with the oxide form of the catalyst was a full percentage point below that of the sulphide system. The higher concentration of sulphur in the product from the sulphide system (shown in Figure 10) is attributable almost completely to the amount of sulphur left in the residuum. The sulphur content of the heavy ends from the sulphide system is similar to that produced over the berl saddles. This fact reinforces still further the idea that the cobalt and molybdenum sulphides function more as cracking catalysts than by a desulphurizing mechanism.

The effect of reaction temperature on the sulphur content of the residuum from the catalytic systems was not clear-cut. The results of these analyses are shown in Figure 11. The sulphur left in the residuum from the oxide catalyst passed through a minimum with reaction temperature in the region of 430°C, while that from the sulphide system passed through a maximum at 415°C.* At first glance the results suggest that the bitumen contains "hard-core sulphur" which cannot be removed easily by either catalyst. However, the experiments made, in which the heavy ends were re-cycled over fresh catalyst, do not indicate that the residuum material separated from the products of a preliminary treatment is, in fact, significantly less reactive than the original (see Figure 15). The conversion rates were higher at elevated temperatures, and the effects shown in Figure 11 may be due partly to the sharp decrease in the amount of oil (residuum and diluent) in the liquid phase. At this stage in our investigations, we do not have a satisfactory explanation for the shape of the curves shown in Figure 11.

The Effect of Feed Dilution

The catalyst-and-preheater system used to determine the effect of feed dilution was the "all-sulphide" arrangement described in the previous section. Mixtures of the separated

* In the assessment of these results, one must also keep in mind that, at equivalent temperatures, much more residuum was converted to distillable oil by the sulphide system (refer to Figure 8).

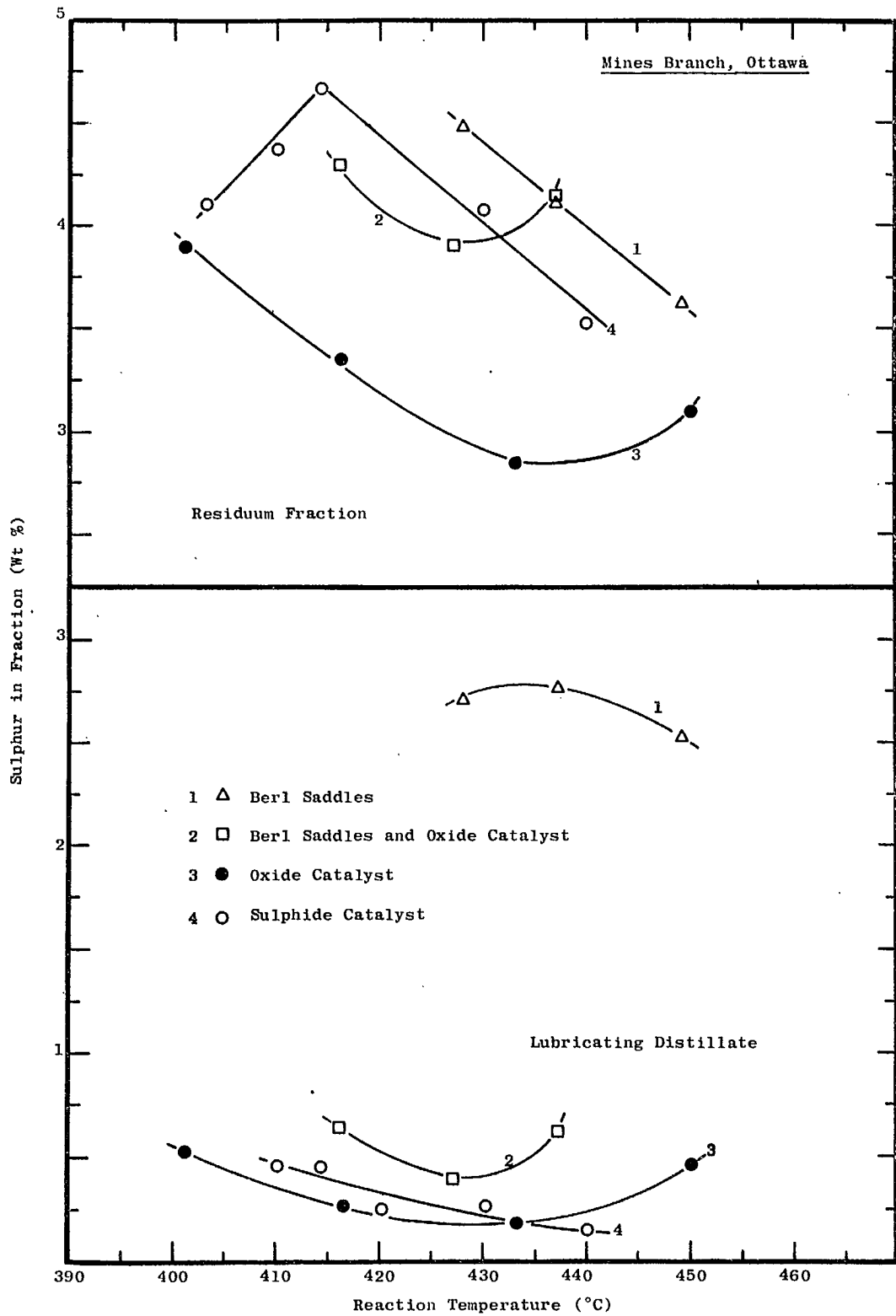


Figure 11 - The effect of reaction temperature on the sulphur remaining in the lubricating distillate and residuum fractions.

bitumen and topped diluent were prepared, corresponding to 0, 13.4, 26.8 and 40.0 percent by weight of diluent (see Table 2). Each series of experiments was made on a fresh lot of catalyst, beginning with the experiment at the highest temperature and proceeding systematically to the lowest temperature. The results of the study are summarized in Figure 12. The effect of reaction temperature on the specific gravity of the product obtained from the feed mixtures is shown in the bottom part of the figure, and the corresponding weight and volume yields are given in the upper sections.

There was a marked improvement with dilution, both in the quality of the product and in the operating life. With the undiluted bitumen feed, general operation of the system was difficult; the coking rate was high and the experimental reproducibility not good. (The graphs shown in Figure 12 for undiluted bitumen should not be regarded as accurate but, rather, as typical of the results that could be obtained.) On the other hand, at even the lowest dilution studied, 13.4 percent, the experimental reproducibility and the operating life of the system were an order of magnitude better.

There are many factors involved in the evaluation of the effect of dilution. Among them the most important are:

- a) the space velocity with respect to the residuum fraction;
- b) the thickness of the layer of liquid on the catalyst; and
- c) the ability of the chemical species present in the diluent to transfer hydrogen to a heavier (and less reactive) molecule.

Consider first the matter of space velocity - by diluting the feed, one lowers the volume of residuum being delivered to the catalyst per hour. The space velocity with respect to the residuum fraction in the case of the pure bitumen was approximately 0.35 vol/vol of cat/hr, whereas with the 13.4, 26.8 and 40.0 percent mixtures the residuum velocities were 0.32, 0.28 and 0.24 respectively. This lowering of the space velocity of the residuum fraction is partially offset by the increase in the volume of heavy (but distillable) oil fed to the catalyst from the diluent.

The improved refining action as the result of dilution, however, would appear to be substantially more than can be accounted for by a mere change in the space velocity of the

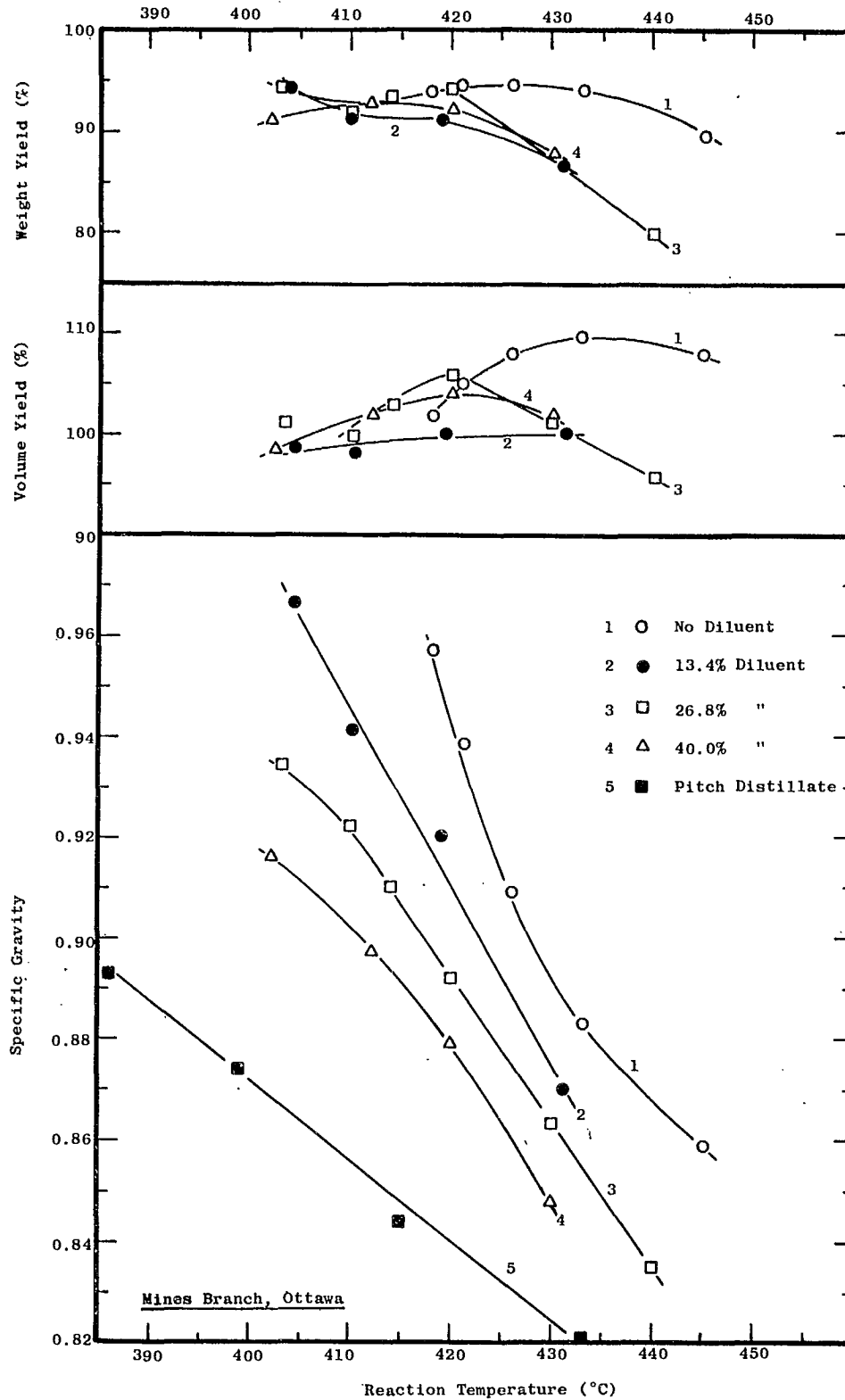


Figure 12 - The effect of feed dilution on the specific gravity of the products and on the volume and weight yields.

residuum fraction. The results of a previous investigation with a coker distillate derived from bitumen (3) indicate a decrease of 0.050 to 0.060 unit in the specific gravity of the product, with a four-fold change in space velocity. In the present study, a decrease of 0.035 unit was observed at 26.8 percent dilution (corresponding to a 1.25 change in the residuum space velocity) and a decrease of 0.050 unit at 40.0 percent dilution (a 1.5 change in space velocity).

Delcos et al. (8) propose that dilution enhances the reaction rate by reducing the thickness of the layer of liquid oil and residuum spread over the catalyst, and thereby increasing the rate at which hydrogen can permeate the layer to the catalyst surface. In considering the physical nature of the liquid-phase material present on the catalyst, the point should be made that at a low space velocity, i.e. 0.5, the catalyst cannot be regarded as operating within a thick film of oil. The viscosity of many types of heavy hydrocarbon oil decreases rapidly with an increase in temperature and, in general, tends to approach a common value of 0.2 to 0.3 centipoise (11) in the region of 400-500°C. The feed material proceeds down the reaction vessel under the combined forces of gravity and the gentle blowing action of the gas passing through the reaction bed. The liquid feed thins out as it enters the preheater section, partly because of a decrease in the viscosity as the temperature rises and partly because of the conversion of residuum to lighter hydrocarbon fractions. (This thinning-out process tends to be partially offset by volatilization of the light ends.) Products of equal quality, as judged by the specific gravity measurements shown in Figure 12, are obtained at progressively lower temperatures as the extent of dilution is increased. At lower temperatures, the degree of volatilization would be less and the viscosity slightly greater - both factors tending in the direction to make the liquid layer thicker rather than thinner.

The specific gravity of the product, however, is not a complete measure of product quality. Mixtures of low- and high-boiling hydrocarbons have the same apparent specific gravity as is shown by those in the medium-boiling range. The results of the distillation analyses on the products* (shown in Figure 13)

* As reported in the previous section, there was very little variation in the amount of the gas-oil fractions and lubricating distillate in the products formed with any one feed mixture at different reaction temperatures. The proportion of lighter hydrocarbons (gasoline and kerosene) increased systematically with reaction temperature, and the amount of residuum decreased systematically.

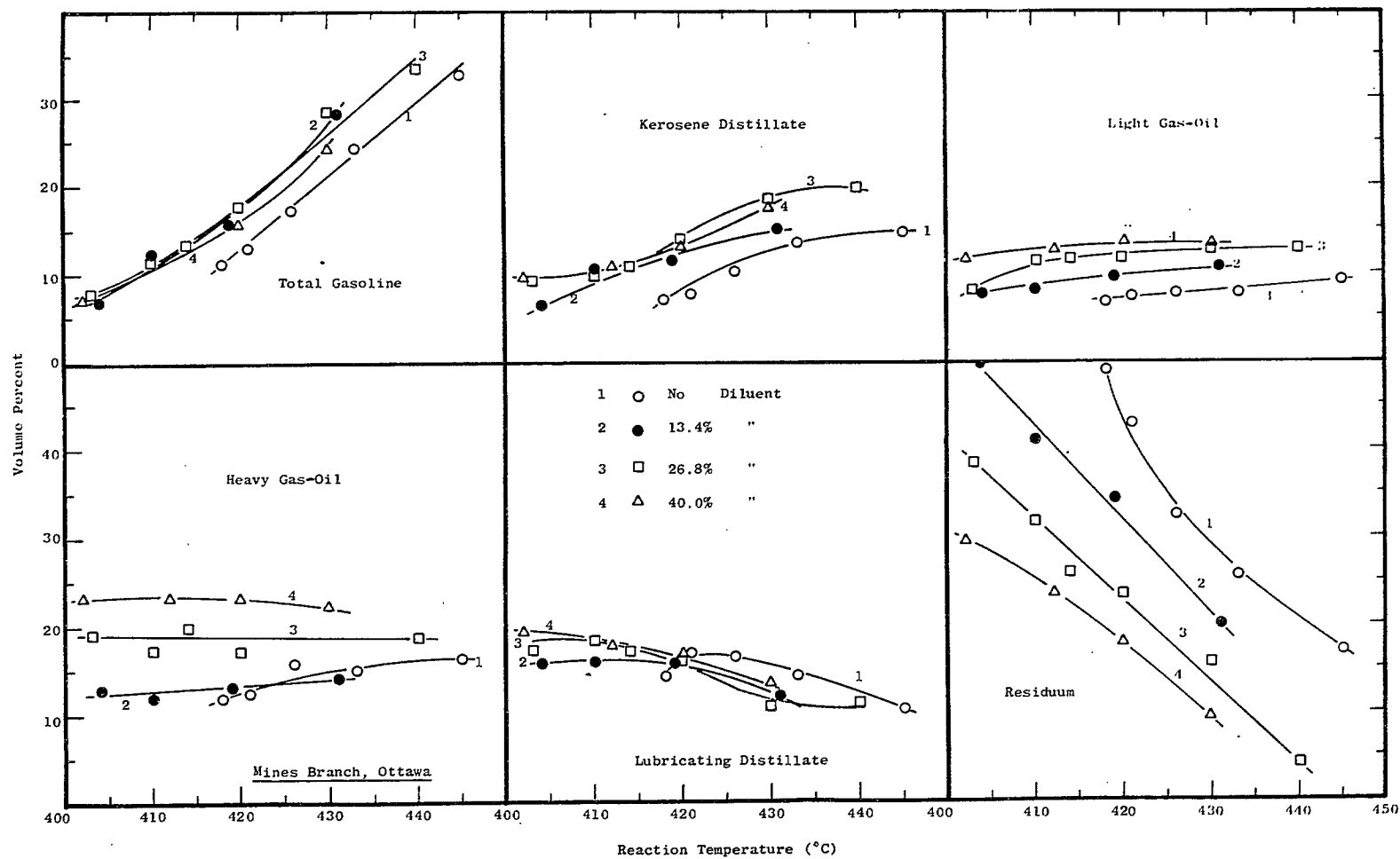


Figure 13 - The results of the distillation analyses on the products from the dilution experiments.

give a slightly better picture. The only major change in the results of the analyses with dilution occurred in the gas-oil fractions and in the residuum. The proportion of hydrocarbon in the gas-oil boiling range, particularly in the heavy gas-oil fraction, increased with dilution and the proportion of residuum decreased. The effect of pressure on the volatilization of hydrocarbons in the heavy gas-oil range, or on the solution of these hydrocarbons in still heavier fractions or in the residuum itself, is not known. It is therefore difficult to assess whether the amount of hydrocarbon in the liquid phase would be significantly less, especially at low dilutions. Certainly, at high dilution rates, 40 percent or greater, there would be less in the liquid phase, mainly because there is less residuum present. The fact remains that the effects are greatest at low dilution.

The dramatic effect of relatively small amounts of diluent on the operating life suggests that the added hydrocarbon is acting as a hydrogenation catalyst, or at least as a hydrogen transfer agent, either in conjunction with the main catalyst or in addition to it. In an investigation of the hydrocracking process, Hesp (7) reported that the pressure of hydrogen needed for satisfactory operation can be reduced considerably if naphthenic-aromatic compounds, such as tetralin, are present in the feed. Naphthenic-aromatic hydrocarbons are capable of transferring hydrogen to free radicals formed in the course of cracking. The type of mechanism proposed by Hesp would, in particular, account for the great reduction in the coking rate, as high-molecular-weight free radicals are generally regarded as precursors to the formation of polymer tars or coke. Large free radicals can form polymer tars in several ways: a) by combining directly, b) by adding on to other heavy hydrocarbon molecules, or c) by splitting-off olefin or paraffin gases, thereby reducing the hydrogen content of the radical until coke is ultimately formed. The transfer of hydrogen to the free radical would effectively terminate any of the above processes.

One would expect to find naphthenic-aromatic hydrocarbons, of the type described by Hesp, in the gas-oil fractions present in the diluent. It is not likely that the lubricating distillate fractions would contain hydrocarbons of the tetralin form, but in the course of reaction they may well be created.

The results of the sulphur analyses on the products from the dilution experiments are shown in Figure 14. The amount of sulphur remaining in the product decreased as the extent of dilution was increased. The general trends were very similar to the effects of reaction temperature and dilution on the specific

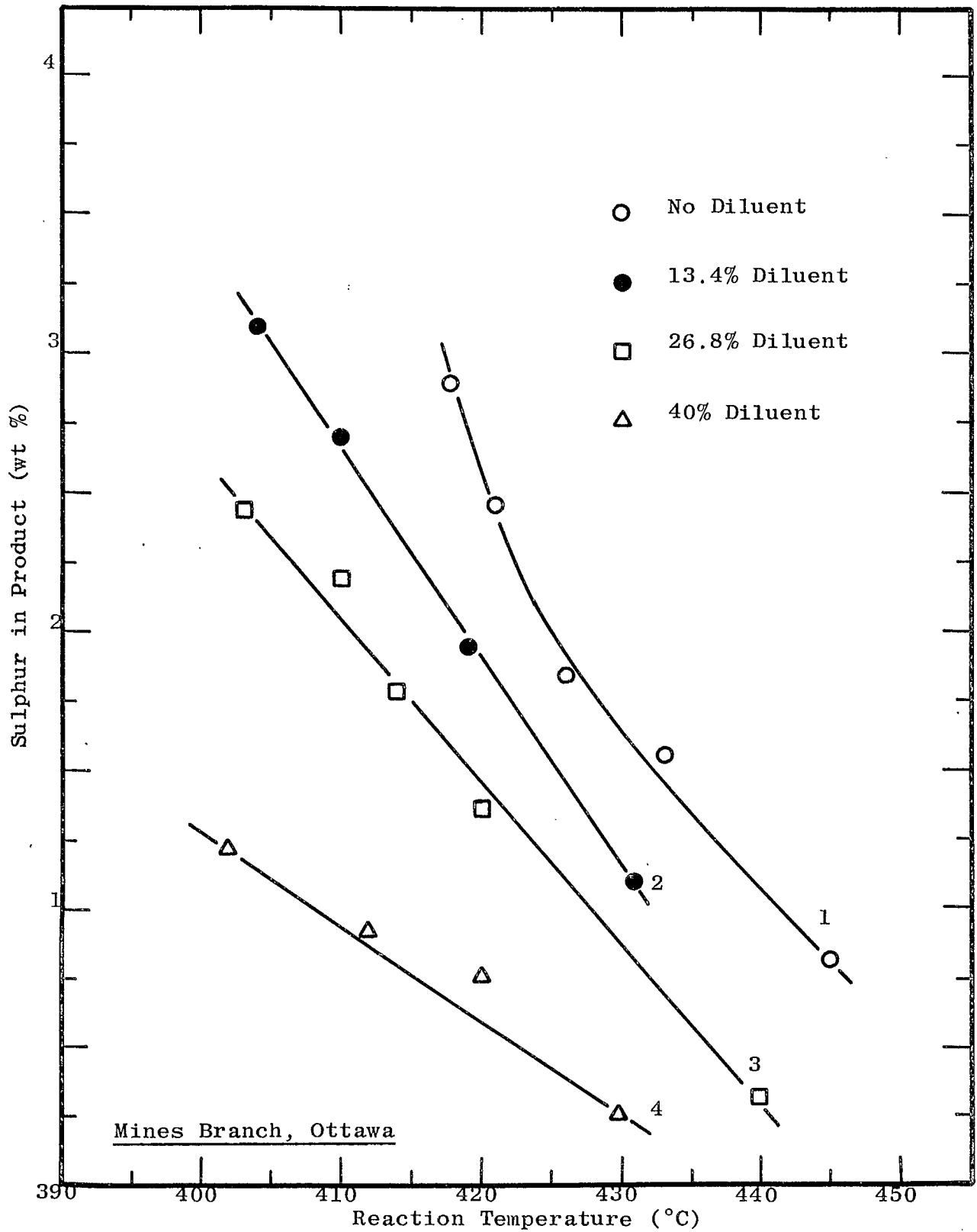


Figure 14 - The results of the sulphur analyses on the products from the dilution experiments.

gravity of the products. Sulphur determinations were also made on the fractions obtained in the distillation analyses. The results of these tests indicated that virtually all of the sulphur remaining in the product occurred in the residuum. No measurable amounts of sulphur were detected in any of the distillable fractions.

The sulphur remaining in the residua did not follow any definite trend with reaction temperature. The numerical values are given in Table 4, arranged in order according to reaction temperature (approximate). At high reaction temperatures there was definitely less sulphur in the residuum fractions than at low temperatures. The changes, though, were not systematic. There appears to be a point in the region of 420-425°C at which the sulphur content changes from 4.5 (at temperatures below 420°C) to 3.5 percent (above 425°C). No large change in the sulphur content of the residua occurred at low dilutions, i.e. at 13.4 and 26.8 percent dilution, but the residua of the products formed from the feed mixture containing 40.0 percent diluent were significantly lower at all reaction temperatures, i.e., 3 percent compared to 4.5 percent sulphur.

There has been considerable interest, during the past year, in "hydrogen treating" residual furnace oils, e.g., Bunker "C" or U.S. No. 6 fuel oil, as a means of reducing the sulphur content to meet air pollution regulations around large centers, such as New York or Chicago. In general terms, the processes have not been too successful. While the overall product from hydrogen treatment contains less sulphur, the portion of the product still in the residual-fuel-oil class contains almost the same amount of sulphur as the original feed stock. The apparent lower sulphur content is the result of the formation of lighter fuel oils by either refining or hydrocracking reactions. At the present time, the demand is for residua that are sulphur-free. The lowering of the sulphur content of the residuum fractions at high dilution rates, observed in the present study, indicates that some refining action without excessive decomposition might be possible at high dilution rates. It would only be practical, of course, where diluent and residua are available and both require treatment to meet market specifications.

The Recycle Experiments

It was readily apparent, from the short runs made to determine the effect of temperature and the chemical nature of catalyst, that complete refinement of the feed in one pass

TABLE 4

Sulphur Content of the Residuum Fractions from
the Dilution Experiments

NO DILUENT		13.4% DILUENT		26.8% DILUENT		40% DILUENT	
Reaction Temp. (°C)	Sulphur (Wt %)	Reaction Temp. (°C)	Sulphur (Wt %)	Reaction Temp. (°C)	Sulphur (Wt %)	Reaction Temp. (°C)	Sulphur (Wt %)
445	3.5			440	3.5		
433	3.7	431	3.3	430	4.1	430	2.1
426	3.5						
421	4.1			420	3.8	420	3.1
418	4.5	419	3.9	414	4.7		
		410	4.3	410	4.4	412	3.0
		404	4.7	403	4.1	402	2.8

through the reaction vessel was not practical. At high temperatures, where approximately 80 to 85 percent conversion of the residuum to distillable oil occurred, any one of the catalyst systems could be seen to be losing activity hour by hour*. Much more stable operation resulted under reaction conditions where only one-half of the residuum was being converted to distillable oil. In the course of evaluating the various arrangements, the question immediately arose as to whether the heavy oil and residuum fractions from oils produced by mild treatment would be more or less reactive than those present in the original feed.

Three long runs (75-100 hours) were made under conditions of feed, catalyst and temperature which formed products containing approximately 30 to 32 percent residuum (approximately 50 percent conversion). The products from these three experiments were then distilled to remove all hydrocarbons up to the end of the heavy gas-oil fraction, i.e., up to 225°C at 40 mm Hg. The remaining heavy ends (the lubricating oil and residuum fractions) were recycled over fresh catalyst similar to that which had been used to produce them, and the reactivity of the recycled material was compared with that of the original feed. The systems and conditions selected for the three long runs were as follows:

	A	B	C
Catalyst and preheater	Sulphide	Sulphide	Oxide
Feed	26.8% diluent	No diluent	26.8% diluent
Temperature (°C)	415-17	425-427	426-430
LHSV	0.5	0.5	0.5
Pressure (psi)	2000	2000	2000
Gas rate (cu ft/bbl)	7500	7500	7500

The effect of reaction temperature on the overall specific gravity of the products formed in the tests is shown in Figure 15, and the amount of residuum in the products at various temperatures is shown in Figure 16. As in previous experiments, the order and temperature at which the short runs were made were approximately constant for comparison purposes. Because of the limited amounts of recycle material available, however, the duration of the tests

* As mentioned on page 15, to arrive at a specific reaction temperature it was necessary to balance the temperature controller against the heat generated in the refining reactions. At high reaction temperatures the amount of heat created in the catalyst bed decreased significantly over the course of an eight-hour experiment, requiring several adjustments in the setting on the controller.

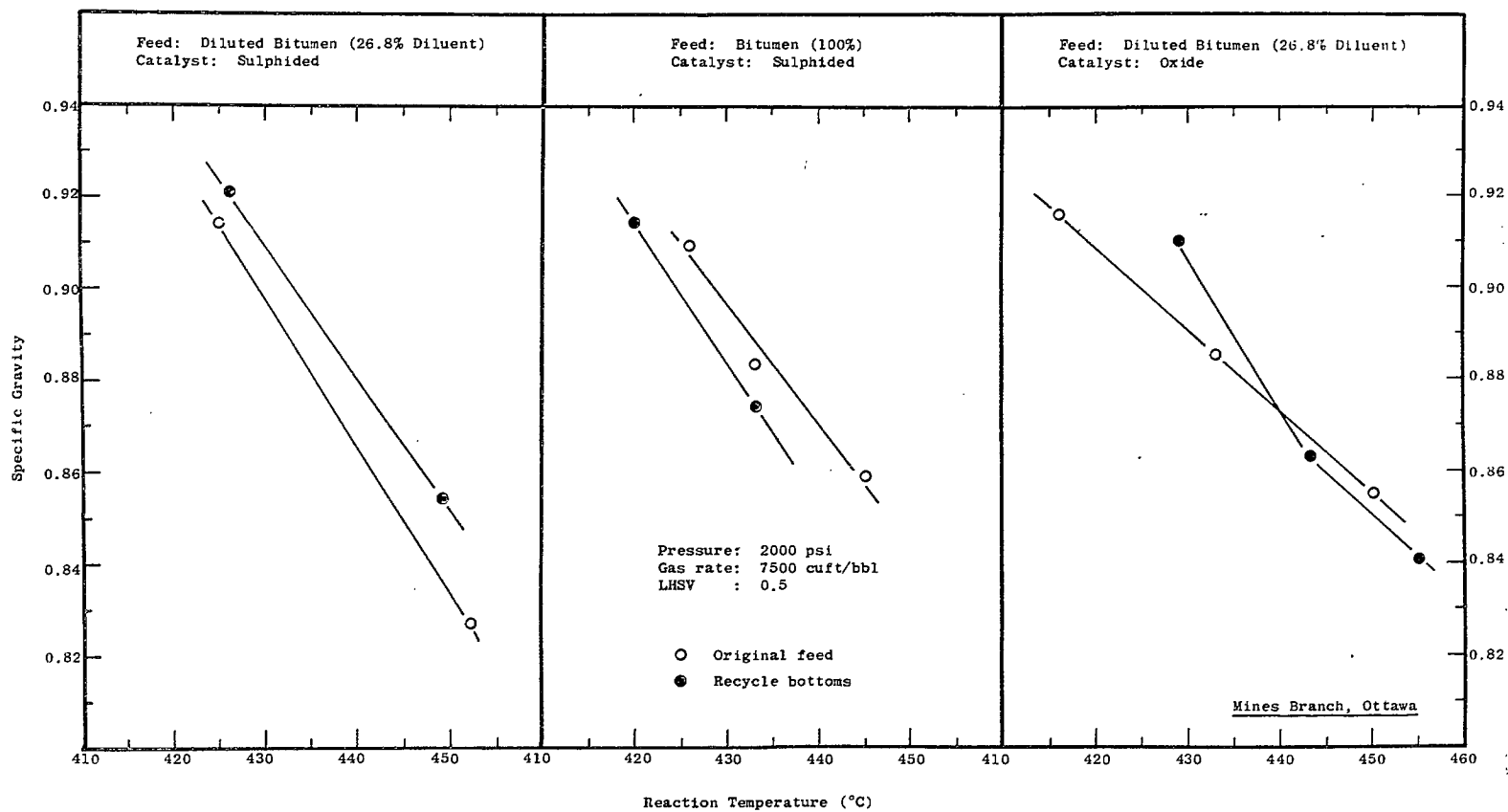


Figure 15 - The effect of reaction temperature on the specific gravity of the products formed from the original bitumen and recycled heavy ends.

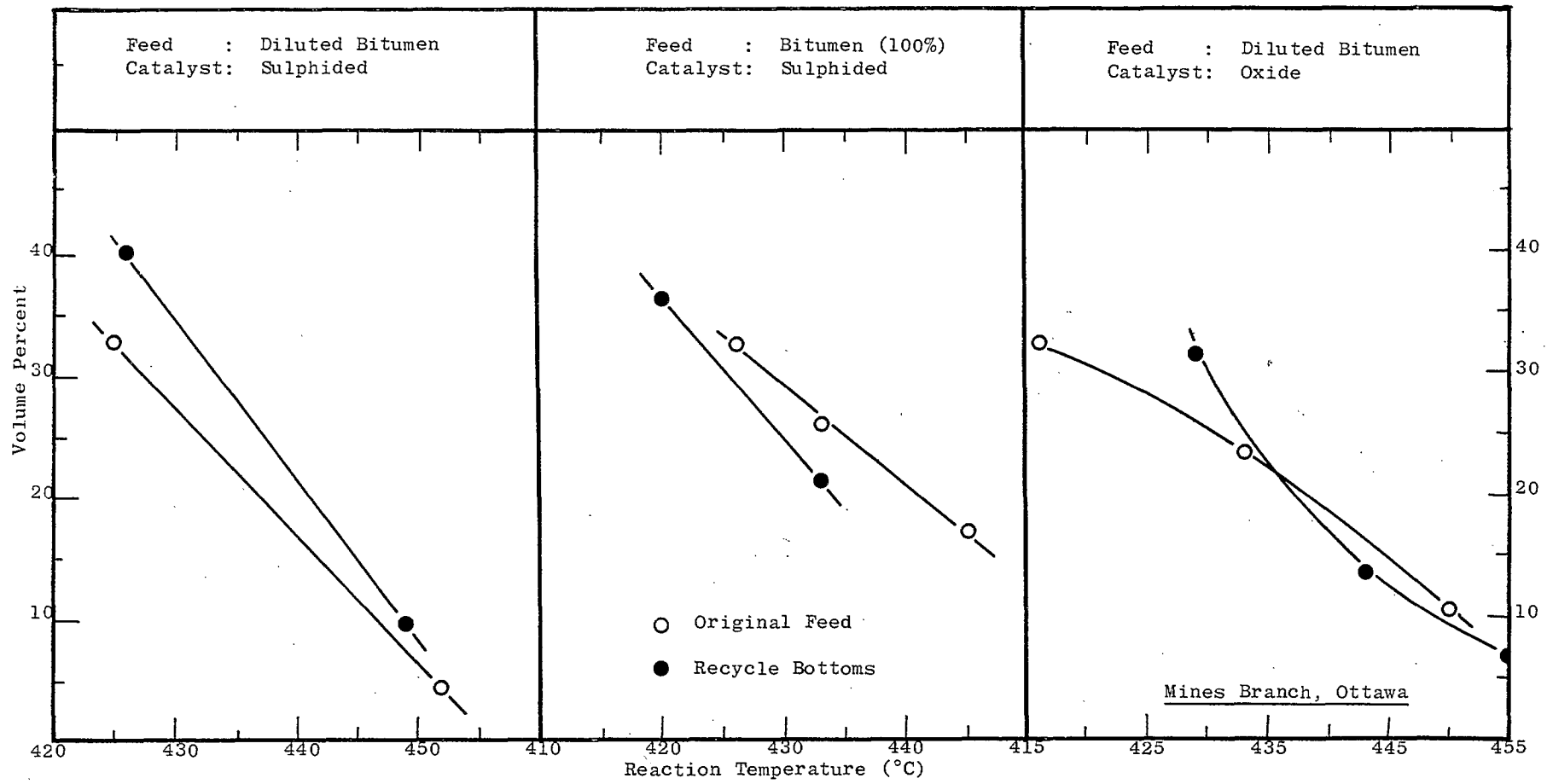


Figure 16 - The effect of reaction temperature on the amount of residuum remaining in the recycle experiments.

was short; and the numerical data should not be compared directly with the results shown in Figure 7.

The differences between the products formed from the original feed and the recycle material were marginal in all three series of experiments. While there were small variations, these were well within those which might be expected with small changes in dilution. As described in the previous section, dilution is an important factor, and the ratio and type of distillable oil to residuum were different in the original and recycle materials.

At the time that the experiments were made, it was suspected* that there might be some accumulation of hard core material in products formed over the oxide and sulphide catalysts. The recycle material from the diluted feed over the sulphide catalyst was, in fact, slightly less reactive than the original (see the left-hand sections in Figures 15 and 16). However, when the experiment was made using the undiluted bitumen feed, the recycle material was found to be slightly more reactive than the original (center sections of Figures 15 and 16). The difference between the recycle feed and the original diluted feed is probably attributable more to the enhancement of the reactivity by the diluent than to an accumulation of hard-core residuum in the recycle material. Within the limits of reproducibility with the sulphide system, there is virtually no difference between the reactivity of the recycle feed from the experiment made with the diluted feed and the reactivity of undiluted bitumen under similar conditions of temperature, etc.

The Life Tests

The only systems examined in the program of life experiments were those in which the preheater section was packed with catalyst, i.e., the "all-oxide" and the "all-sulphide" systems. In the course of the short experiments reported in the previous sections, there was considerable evidence to indicate that the maximum life expectancy of the systems in which porcelain packing was used in the preheater was only about 35-40

* From the occurrence of a maximum and minimum in the sulphur content of the residuum fraction with reaction temperature, shown in Figure 11.

hours. This was deemed too short to be of practical interest, and all the experimental effort was concentrated on the catalytic systems.

The catalyst for the life tests was loaded into the reaction vessel and brought up to pressure and temperature in the normal way. Once started, the system was operated continuously for approximately 100 hours. Throughout the test period, all reaction conditions (temperature, pressure, flow rates, etc.) were held constant. The products were collected periodically and recorded as a function of the number of hours the catalyst had been in operation (hours on stream). The feed material used in the life tests was the same as that used for the short activity experiments, i.e., 26.8 percent diluent, 73.2 percent bitumen. Two life runs were made on the sulphide catalyst system. The first experiment was made at 425-426°C and LHSV = 0.5, and the second run at LHSV = 1 and 440-441°C. Two similar tests were made with the oxide catalyst at 425-426°C and 440-441°C, both at LHSV = 0.5. The hydrogen flow rate used in all the life tests was 7500 cu ft/bbl and the operating pressure was 2000 psig. The low-temperature experiments were considered representative of the conditions of mild treatment (requiring recycling of the unreacted heavy ends) and the high-temperature runs were considered to be representative of the usual refinery conditions, where a much greater proportion of the feed is converted to marketable oils in a single pass. The results of the experiments with the sulphide catalyst are shown in Figure 17, and those with the oxide form in Figure 18.

There were marked differences between the results obtained with the sulphide and oxide catalysts. The specific gravity of the product formed in both experiments with the sulphide catalyst increased almost linearly with operating, or stream, time. The specific gravity at space velocity 0.5 increased 0.00055 unit per hour, and that in the test made at a space velocity of 1 increased twice as fast at 0.00110 unit per hour.....a two-fold change in the rate of deterioration with a two-fold increase in space velocity. The usual explanation for the deterioration of a catalyst used for the processing of residual oils is that coke is forming on the surface, masking the active sites. However, the regularity of the changes in the specific gravity suggests that the catalyst is being poisoned by some element in the liquid feed (possibly by nitrogen in the hydrocarbon) or by one of the components of the mineral matter.

At the time that the experiments with the sulphide catalyst were being run, it was thought that possibly the

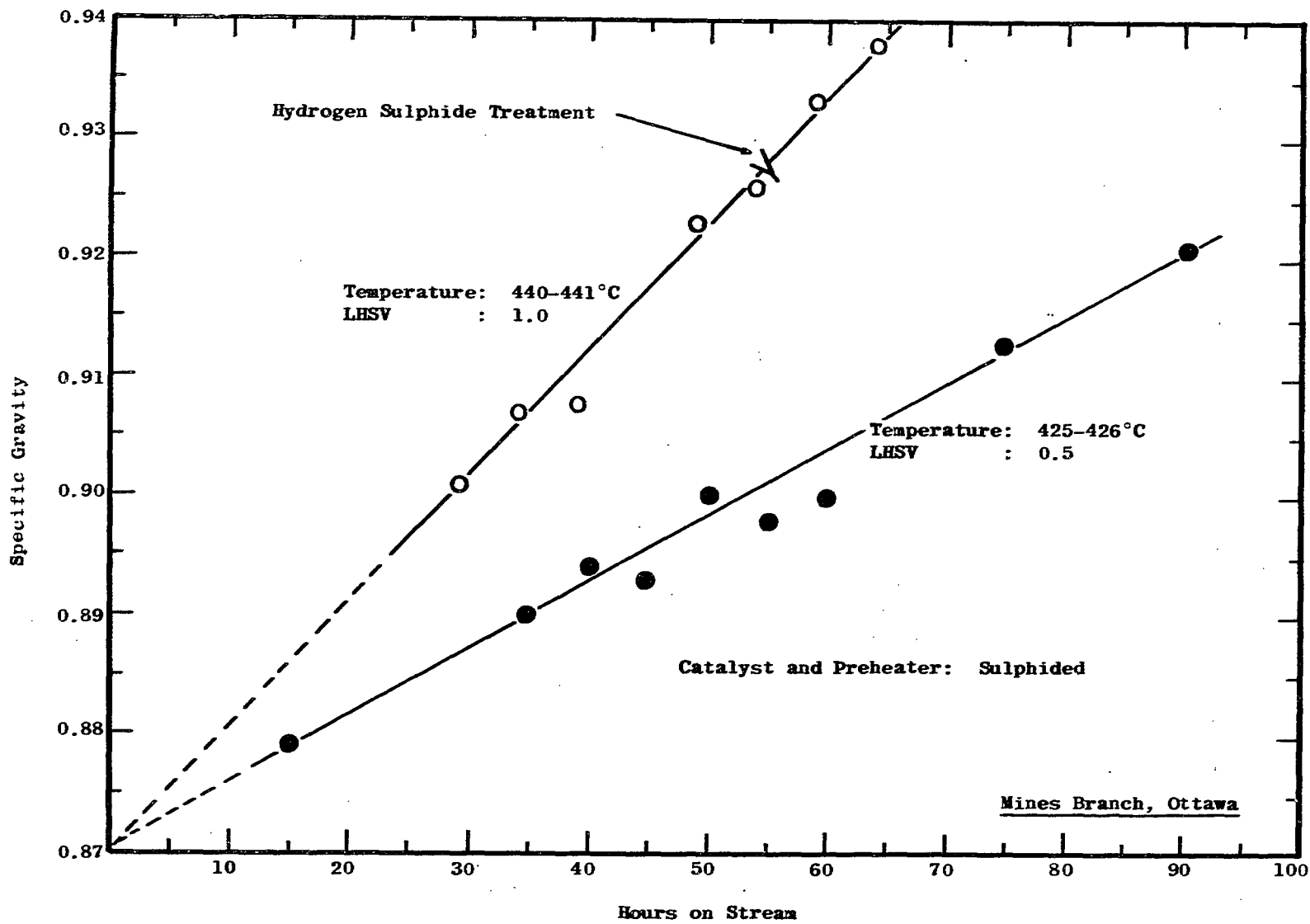


Figure 17 - Life tests made with the sulphide catalyst system.

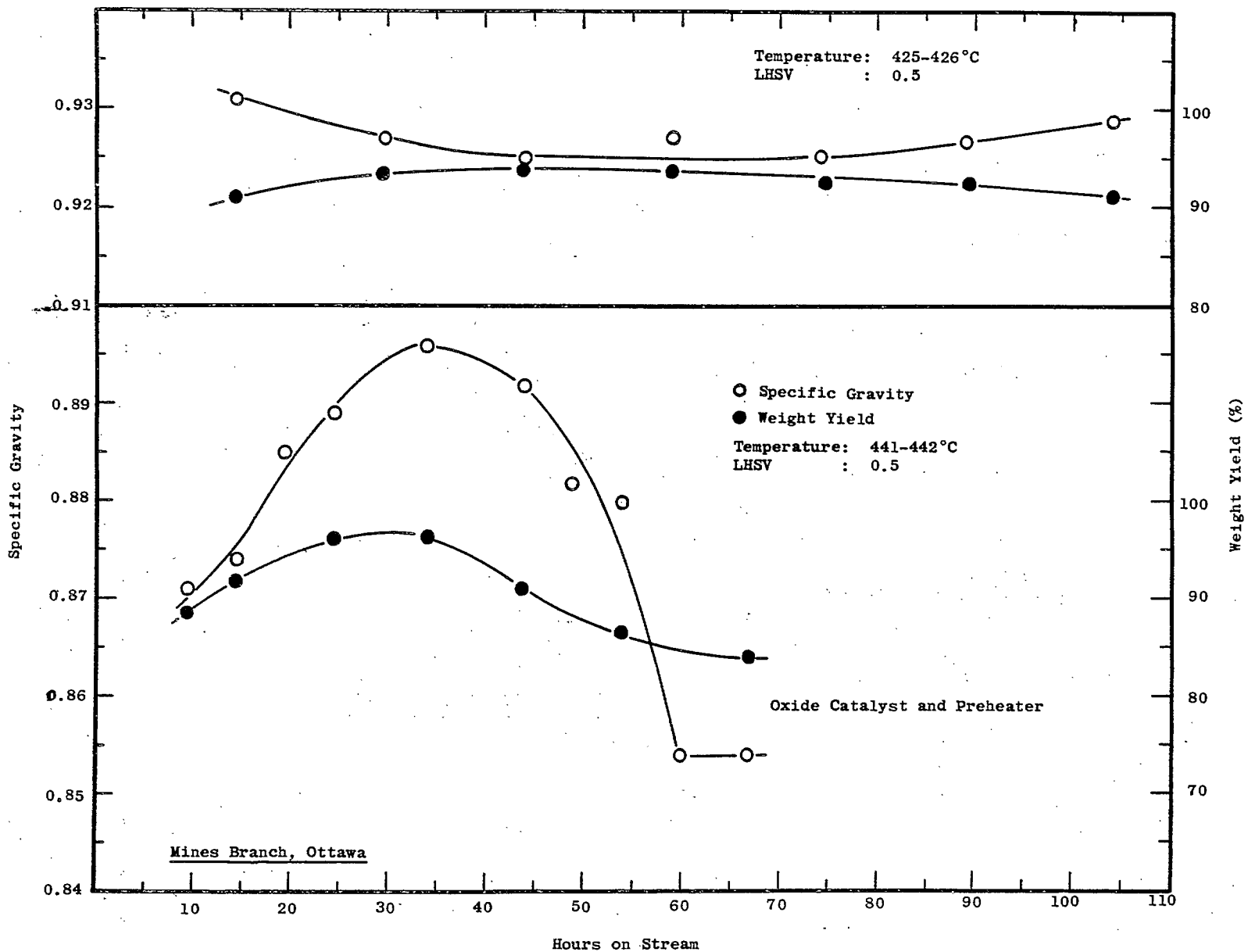


Figure 18 - Life tests made with the oxide catalyst system.

catalyst was being stripped of its sulphide character by reaction with some component in the hydrocarbon feed. In the test at 440-441°C, the run was stopped after 55 hours of operation, the system re-sulphided with H₂S at atmospheric pressure according to the normal procedure, and the run re-started. There was no improvement in the quality of the product as the result of re-sulphiding. In fact, the specific gravity of the products collected over the course of the next 20 hours fell exactly on the line predicted from the first 55 hours of operation. Whatever was happening to the catalyst was obviously not the result of the loss of sulphide character.

By comparison with the sulphide catalyst, the activity of the oxide form was very stable. The results of the life experiments with the oxide catalyst are shown in Figure 18. In the low-temperature test there was virtually no change in either the specific gravity or the yield of the product over the 100-hour test period. There was no evidence of plugging at any time during the experiment*, although considerable mineral matter was found throughout the system when the reaction vessel was unloaded. As mentioned previously, at 425-426°C approximately 1/3 to 1/2 of the feed material and products would be in the liquid phase.

The specific gravity of the product formed over the oxide catalyst at 440-441°C increased at first (indicating a gradual de-activation of the catalyst), then began to decrease after approximately 40 hours of operation. In this particular experiment the reaction system began to plug after about 70 hours' running, and the test was stopped. A large accumulation of coke and mineral matter was found in the reaction vessel when it was unloaded. The improvement in the quality of the product during the last half of the test period was apparently caused by the retention of the residuum fractions in the catalyst bed. The results of the yield calculations plotted with the specific gravity measurements in Figure 18 show a definite decrease in the amount of product recovered after 40 hours of operation, in keeping with this explanation.

It would appear that, with the oxide catalyst system, sufficient feed and products must remain in the liquid phase to wash the high-molecular-weight species and the mineral deposits through the reaction bed. The experiments carried out in the present investigation suggest that the optimum operating

* As indicated by an abnormally high pressure drop across the reaction bed.

temperature is 425°C. It is doubtful that the temperature could be raised above this value significantly to sustain a comparable conversion rate at a higher space velocity. The results of the short activity tests indicate that the rate of coke formation increases sharply with temperature above 430°C, and that the catalyst bed would plug under such circumstances even in the presence of a large amount of liquid-phase material. The liquid-feed rates are quite small relative to the flow capacity of the pipes and tubes used in the apparatus, and no scouring action can be attributed to the liquid-phase material present. The amount of tarry material and mineral matter which can be carried from the surface of the catalyst is probably limited by the solubility and dispersability of the substances involved.

SUMMARY

1. Higher conversion rates and longer operating life were observed when the bitumen was:
 - a) brought up to reaction temperature in a preheater section packed with catalyst, and
 - b) diluted approximately 15 to 20 percent with a heavy gas-oil fraction.
2. The sulphide form of the cobalt molybdate catalyst was more effective in the conversion of residuum fractions to distillable oil than was the conventional oxide form, but possessed a lower desulphurization activity.
3. Maximum operating life was observed with the oxide form of the catalyst at low temperatures (below 430°C), where approximately 1/3 to 1/2 of the oil present in the system was in the liquid phase. The sulphide form of the catalyst was found to be poisoned rapidly by some species present in the bitumen.
4. Heavy oil and residuum fractions separated from products of a mild hydrogenation treatment were not found to be either less or more reactive than those present in the original bitumen.

ACKNOWLEDGEMENTS

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REFERENCES

1. T.E. Warren, F.L. Booth, R.E. Carson and K.W. Bowles, "Hydrodesulphurization of Coker Distillate from Athabasca Bitumen", Proc. Athabasca Oil Sands Conf., Edmonton, Alberta, 289-305 (1951).
2. F.L. Booth, R.E. Carson, K.W. Bowles and D.S. Montgomery, "Low Pressure Hydrogenation of Coker Distillate from Athabasca Bitumen". Mines Branch Research Report R-30, Department of Mines and Technical Surveys, Ottawa (1958).
3. A.R. Aitken, W.H. Merrill and M.P. Pleet, "Hydrogenation of a Coker Distillate Derived from Athabasca Bitumen", Can. J. Chem. Eng., Industrial Section, 234-238 (1964).
4. H. Beuther, R.F. Mansfield and H.C. Stauffer, "Costs of Lubricating Oil Hydrogenation Processes". Paper presented at the 31st Midyear Meeting of the American Petroleum Institute's Division of Refining (preprint 30-66), Houston, Texas (1966).
5. C.R. Griswold and R.P. Van Driesen, "Commercial Experience with H-Oil". Paper presented at the 31st Midyear Meeting of the American Petroleum Institute's Division of Refining (preprint 53-66), Houston, Texas (1966).

6. W. Urban, "Petroleum Processing in a 300 Atmosphere Combi Hydrogenation Stall", *Erdöl und Kohle*, 8, 780-782 (1955). Translation by H. Frisch and W. Herrmann, Fuels and Mining Practice Division Internal Report 60/103-HPC, Department of Mines and Technical Surveys (1960).
7. W.R. Hesp, "Hydrocracking of Heavy Mineral Oils", *Mining and Chemical Engineering Review*, 53, No. 4 (1961). Reprinted by Tait Publishing Co. Pty, Ltd., Melbourne and Sydney, Australia.
8. J. Delcos, R.D. Presson, W.G. Shaw and H.A. Strecker, "Fluid Bed Hydrocracking of Residual Stocks". Paper presented at the 152nd National Meeting of the American Chemical Society, Division of Petroleum, New York (1966).
9. N.A.C. Smith et al., "The Bureau of Mines Routine Method for the Analysis of Crude Petroleum, I. The Analytical Method", U.S. Bureau of Mines Bulletin 490 (1951).
10. R.K. Siegfriedt, J.S. Wiberley and R.W. Moore, "Determination of Sulphur after Combustion in a Small Oxygen Bomb", *Analytical Chemistry*, 23, 1008-1011 (1951).
11. W.L. Nelson, "Petroleum Refinery Engineering" (published by McGraw-Hill Book Co. Inc., New York), 4th ed. (1958), p. 144.

MAO'G:BIP: (PES) gf

APPENDIX 1. - List of Main Components and Their
Manufacturers and Model Numbers

<u>Component</u>	<u>Manufacturer and Model No.</u>
Gas Compressor	American Instrument Co., Washington, D.C. Model 46-14035.
Hydrogen Storage Vessel (s.s. sleeve construction)	Autoclave Engineers Inc., Erie, Pa. 0-178 cu ft capacity, 30,000 psi rating.
Inlet Pressure Regulator	Victor Equipment Co., Los Angeles, Calif. Model GD 81 A.
Outlet Pressure Regulators	(i) The Matheson Co., East Rutherford, N.J. Model 11-330. (ii) Hoke Equipment Co., Cresskill, N.J. Model 640.
Liquid Feed Pump	(i) Ruska Instrument Co., Houston, Texas. Model 2296 WII. (ii) Lapp Insulator Co., Le Roy, N.Y. Model LS-30.
Temperature Controllers (Galvanometer type with time-proportioning action)	Philips Electronic Equipment Ltd., Toronto, Ontario. Model PT 4003.
Temperature Recorders (chart recorders)	Philips Electronic Equipment Ltd., Toronto, Ontario. Model PR 2210- A/21.

APPENDIX 1 (cont'd)

Pressure Gauges
(s.s. tube, solid front)

U.S. Gauge Co.,
Sellersville, Pa.
Model 1936T.

Wet Test Meters

American Meter Co.,
Erie, Pa.
Model AL-18.

Metering Valves

Hoke Equipment Co.,
Cresskill, N.J.
Model 2 PY 281.

High Pressure Tubing,
Fittings and Valves, and
the one-liter Receiver
Vessels. (30,000 psi series)

Autoclave Engineers Inc.,
Erie, Pa.

Reaction Vessels and the
two-liter Receiver Vessels

Manufactured in the Mines
Branch shops.

Heating Cable (Reaction
Vessels)

Pyrotenax of Canada,
Trenton, Ontario.

Heat Transfer Cement
(Reaction Vessels)

Thermon Manufacturing Co.,
Houston, Texas.

APPENDIX 2. - Inspection Analyses Results

1. INSPECTION ANALYSIS - CITIES SERVICE BITUMEN

Details of Analysis:

Specific gravity at 60°F	1.041	A.P.I. gravity at 600°F	4.4
Sulphur, percent by weight	4.69	Pour point, °F	+80
Saybolt Universal Viscosity		Calculated Molecular Weight	880
at 250°F, sec.	725.5(155cS)	Carbon residue, percent by	
at 300°F, sec.	260.8(55.6cS)	weight (Conradson)	- 17.8

DISTILLATION, U.S. Bureau of Mines Routine Method

Stage 1 - Distillation at atmospheric pressure, 754 mm Hg
 First drop, 248°C (478°F)

Fraction No.	Cut at °C	at °F	Per cent	Sum per cent	Specific gravity, 60°F	Degrees A.P.I., 60°F	Corre- lation index	Aniline point, °C	Viscosity, S.U. 100°F	Cloud test °F
1.	50	122								
2.	75	167								
3.	100	212								
4.	125	257								
5.	150	302								
6.	175	347								
7.	200	392								
8.	225	437								
9.	250	482								
10.	275	527	5.9	5.9	0.891	27.3	-	40.0		

Stage 2 - Distillation continued at 40 mm Hg

11.	200	392	0.2	6.1	0.905	24.8	60	-	39	-
12.	225	437	2.6	8.7	0.916	23.0	61	41.0	44	-30
13.	250	482	4.5	13.2	0.929	20.8	64	42.1	60	-10
14.	275	527	5.7	18.9	0.945	18.2	68	45.3	122	10
15.	300	572	8.4	27.3	0.958	16.2	72	47.2	302	30
Residuum			69.2	96.5	1.084					
Carbon residue of residuum					24.7%					
Carbon residue of crude										17.8%

APPROXIMATE SUMMARY

	Percent by vol.	Specific gravity	Degrees A.P.I.	Viscosity, S.U. 100°F
Light gasoline	-	-	-	
Total gasoline and naphtha	-	-	-	
Kerosene distillate	-	-	-	
Gas-oil	8.7	0.889	25.9	
Nonviscous lubricating distillate	5.6	0.921-0.939	22.1-19.2	50-100
Medium lubricating distillate	4.8	0.939-0.951	19.2-17.3	100-200
Viscous lubricating distillate	8.2	0.951-0.966	17.3-15.0	Above 200
Residuum	69.2	1.084	-	
Distillation loss	3.5			

(Appendix 2, cont'd) -

2. INSPECTION ANALYSIS - BITUMOUNT DILUENT

Details of Analysis:

Specific gravity at 60°F	0.883	Degrees A.P.I. at 60°F	28.8
Sulphur, percent by weight	1.90	A.S.T.M. Colour No. Lighter than No. 7	
Water, percent by volume (A.S.T.M.)	0.2	Flash point, °F (Tag closed tester)	116
Test for Hydrogen Sulphide	Negative	Pour point, °F: Below	-60
Viscosity, Saybolt Universal, at 70°F	47.9 sec.	; at 100°F	40.2 sec.

DISTILLATION, U.S. Bureau of Mines Routine Method

Distillation at atmospheric pressure, 765 mm Hg: First drop: 64°C (147°F)

Fraction No.	Cut at °C	°F	Per cent cut	Sum per cent	Specific Gravity, 60°F	Degrees A.P.I., 60°F	Corre- lation index	Viscosity, Say.Univ. at 100°F	Cloud test, °F
1.	50	122							
2.	75	167							
3.	100	212	1.0	1.0)					
4.	125	257	0.3	1.3)					
5.	150	302	0.7	2.0)	0.767	53.0	-		
6.	175	347	3.2	5.2	0.806	44.1	39		
7.	200	392	5.9	11.1	0.822	40.6	40		
8.	225	437	13.9	25.0	0.836	37.8	41		
9.	250	482	19.5	44.5	0.855	34.0	45		
10.	275	527	13.7	58.2	0.879	29.5	51		
Distillation continued at 40 mm Hg									
11.	200	392	9.0	67.2	0.897	26.3	56	42	
12.	225	437	11.4	78.6	0.914	23.3	60	52	
13.	250	482	8.4	87.0	0.932	20.3	65	80	
14.	275	527	6.3	93.3	0.947	17.9	69	169	
15.	300	572	4.0	97.3	0.957	16.4	71	496	
Residuum			2.7	100.0	-	-	-	-	

APPROXIMATE SUMMARY

	Percent by Volume	Specific Gravity	Degrees A.P.I.	Viscosity, Say.Univ. at 100°F
Total gasoline and naphtha	11.1	0.807	43.8	
Kerosene distillate	-	-	-	
Gas-oil	59.9	0.866	31.9	Below 50
Nonviscous distillate	13.4	0.911-0.935	23.8-19.8	50-100
Medium distillate	6.2	0.935-0.948	19.8-17.8	100-200
Viscous distillate	6.7	0.948-0.961	17.8-15.7	Above 200
Residuum	2.7			
Distillation loss	0.0			

(Appendix 2, concluded) -

3. INSPECTION ANALYSIS - PITCH DISTILLATE

Details of Analysis:

Specific gravity at 60°F	0.957	A.P.I. gravity at 60°F	16.4
Sulphur, percent by weight	3.28	Pour point, °F.	-15
Saybolt Universal Viscosity		Calculated molecular weight	374
at 100°F, sec.	270(58.2cS)	Carbon residue, percent by	1.5
at 130°F, sec.	124(26.1cS)	weight (Conradson)	

DISTILLATION, U.S. Bureau of Mines Routine Method

Stage 1 - Distillation at atmospheric pressure, 754 mm Hg.
First drop, 132°C (270°F)

Fraction No.	Cut at °C	Per cent °F	Sum per cent	Specific gravity, 60°F	Degrees A.P.I., 60°F	Correlation index	Aniline point, °C	Viscosity, S.U. 100°F	Cloud test, °F
1.	50	122							
2.	75	167							
3.	100	212							
4.	125	257							
5.	150	302	0.4)						
6.	175	347	0.9)						
7.	200	392	0.8)	2.1	0.845	36.0	-	-	
8.	225	437	1.2	3.3	0.850	35.0	48	35.1	
9.	250	482	2.1	5.4	0.860	33.0	47	35.9	
10.	275	527	7.1	12.5	0.890	27.5	57	37.9	

Stage 2 - Distillation continued at 40 mm Hg

11.	200	392	3.9	16.4	0.904	25.0	59	38.9	38	-
12.	225	437	7.6	24.0	0.918	22.6	62	41.3	46	-25
13.	250	482	7.3	31.3	0.932	20.3	65	42.5	66	-10
14.	275	527	9.6	40.9	0.948	17.8	70	44.0	130	5
15.	300	572	12.9	53.8	0.963	15.4	74	46.1	377	25
Residuum			46.4	100.2	0.996	10.6				
Carbon residue of residuum					3.2%					
Carbon residue of crude										1.5%

APPROXIMATE SUMMARY

	Percent by vol.	Specific gravity	Degrees A.P.I.	Viscosity S.U. 100°F
Light gasoline	-			
Total gasoline and naphtha	-			
Kerosene distillate	-			
Gas-oil	21.7	0.889	27.7	
Nonviscous lubricating distillate	10.5	0.921-0.940	22.1-19.0	50-100
Medium lubricating distillate	7.1	0.940-0.952	19.0-17.1	100-200
Viscous lubricating distillate	14.5	0.952-0.972	17.1-14.1	Above 200
Residuum	46.4	0.996	10.6	
Distillation gain	0.2			

