THERMAL HYDROCRACKING OF ATHABASCA BITUMEN — REDUCTION OF REACTOR FOULING

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ABSTRACT

Experiments in a one barrel per day (1.84 cm^3/s) thermal hydro-cracking pilot plant were conducted on topped (to 260°C) Athabasca bitumen, with emphasis on continuous runs at constant conditions for up to three week's duration to study reactor fouling. The reactor was 1.5 in. (3.8 cm) ID by 13 ft (4 m) high. Experiments were carried out at pressures from 1000 to 3500 psi (6900 to 24,100 kPa), temperatures from 450 to 470°C, and space velocities of 1 and 2 reactor volumes of feed per hour. The most successful runs, from the point of view of reducing reactor fouling, were at 460°C and 470°C and 3500 psi.

Results are given and correlated on pitch conversion, distillate oil yield, hydrogen consumption, gas formation and other parameters for these runs. A comparison is made with published data on delayed coking and fluidized coking for bitumen treatment.

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HYDROCRAQUAGE THERMIQUE DE BITUME DE L'ATHABASCA
REDUCTION DE L'ENCRASSEMENT DU REACTEUR

par

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SOMMAIRE

Dans le but d'examiner la situation d'encrassement du réacteur, des expériences ont été entreprises avec du bitume décanté de l'Athabasca dans une installation pilote d'hydrocraquage thermique d'un baril par jour (1.84 cm^3/s). L'attention fut portée sur des marches continuelles à des conditions constantes et ce, jusqu'à une durée de trois semaines. Les dimensions du réacteur sont de 1.5 po. (3.8 cm) de diamètre intérieur et de 13 pieds (4 m) de haut. Les pressions utilisées pendant les essais variaient entre 1000 et 3500 lb/po^2 (6900 à 24000 kPa), les températures entre 450 et 470°C et les vitesses spatiales horaires de 1 à 2 charges d'alimentation. Les marches, qui ont eu le plus de succès quant à la réduction de l'encrassement du réacteur, étaient celles opérées à 460°C et 470°C et à 3500 lb/po^2.

La conversion du brai, le distillat pétrolifère, la consommation d'hydrogène, la formation de gaz et autres, sont tous des paramètres qui ont été calculés et comparés et dont on en donne les résultats. De plus, une comparaison est faite entre des données déjà publiées sur la cokéfaction différée et la cokéfaction fluidisée pour le traitement du bitume.

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CONTENTS

INTRODUCTION

The thermal hydrocracking process has been found, on the basis of short-term pilot-plant-scale runs (1), to give a high distillate yield and eliminate the production of waste coke in the processing of Athabasca bitumen. This work, in keeping with the Energy Research Program of the Canadian Department of Energy, Mines and Resources and its policy of ensuring the effective use of Canada's mineral and energy resources (2), was undertaken to further develop the thermal hydrocracking process. In particular, pilot-plant experiments of two to three weeks' duration (life runs) were carried out to establish suitability of the process over extended periods with regard to time-dependent processes such as coke formation and metal sulphide deposition.

The refining of residual oils and tars by hydrogenation, with emphasis on catalytic hydrogenation processes, has been the subject of considerable research by the Energy Research Laboratories (2,4,5) for many years. The present investigation is an extension of earlier work on non-catalytic hydrogenation or thermal hydrocracking, for which the names hydrovisbreaking, thermal hydrovisbreaking or hydrogenolysis are equally applicable. As a result of short (4h) pilot-plant runs it was found previously, that the thermal hydrocracking process would make a suitable first stage in the refining of Athabasca bitumen, converting a high proportion of pitch (material which boils above 524°C equivalent atmospheric boiling temperature) to distillate products. This was essential because the Athabasca bitumen contains about 50% pitch. It was also found that once the pitch had been converted to distillate hydrocarbon materials, little difficulty was encountered in subsequent secondary hydrogenation steps necessary to remove sulphur and nitrogen, and to stabilize the product. Earlier work, however, did not establish the process on a long-term basis, although there was infrequent occurrence of coke formation on reactor walls after a combined time of two to three days of short runs. The exception was at temperatures above 440°C and 7 MPa or above 465°C and 10.4 MPa pressure where even 4-hour runs yielded sufficient coke to cause operational problems.

Thermal hydrocracking is a process which could be used as the first stage in the refining of bitumen, and would compete with delayed coking, fluid

coking and flexicoking as a first-stage process. As in the other processes
it would have to be followed by catalytic hydrogenation of selected streams.
Unlike other processes, it is more flexible and operating conditions can be
established so that pitch conversions ranging from 30 to 95% are obtained.
Under normal circumstances, thermal hydrocracking of heavy crudes is not
considered in refinery processing because heavy crudes cannot be hydrocracked
deeply enough at practical pressures, and the amount of pitch remaining
(consisting usually of a mixture of coke, tar and unreacted residuum material)
would exceed the normal fuel requirements of the refinery.

The prospects change, however, with the high fuel requirements for
processing the tar sands. Depending on the locations and concentration of
the deposits, energy, equivalent to about 20 to 25% of the total bitumen is
required for the mining, separation and refining steps. This large amount of
heat can be supplied by either the residuum fraction of the bitumen or from
an external source of energy such as coal. If bitumen residuum is used, the
per cent conversion required would be low. Approximately 50% of the hydro-
carbon material initially present is distillable and can be processed by
conventional means. Of the remaining 50%, only 50 to 60% would require hydro-
genation or hydrocracking to be converted to distillable products. This is a
low conversion requirement and should be readily attainable. If some other
source of energy is used, the per cent conversion of residuum should be as
high as possible to conserve bitumen.

Literature Survey

A review of the patent literature on the hydrocracking of bitumen
and heavy oils has been made by Ranganathan (6). Only those patents directly
related to this work will be discussed in this report. The most vigorous
activity in the patent literature originated from Hydrocarbon Research
Incorporated (HRI). In 1959, HRI patented a method using solid particles as
coke carriers (7), recognizing that carbon was formed during hydrocracking of
heavy oils having high Ramsbottom (or Conradson) carbon residue, and that the
coke had to be removed or otherwise it was deposited on the reactor walls.
In 1961 the same organization patented the gas-liquid "ebullated" bed process
(8), the basis for the H-Oil process, and the basis for later patents and
ideas concerned with heavy oils. In these later patents, the process was
shown in various configurations (9,10) with and without heavy oil recycle as

part of an overall catalytic scheme to hydrocrack heavy oils.

Two patents in 1964 revealed that, for tar sands (10) and heavy oil (11) processing, the buildup of mineral matter in the reactor had a beneficial effect on processing when operating with no catalyst, and that recycle of heavy oil product was beneficial in maintaining the mineral matter in suspension. Data also showed that a liquid flux in excess of one pound of oil per second per square foot was necessary to maintain the suspension of solids in the reactor. Furthermore, hydrogen consumption was unexpectedly high, apparently due to the presence of an iron component (10).

It was also claimed that for some runs without solids, the extent of formation of coke made the system inoperable, whereas with solids, the coke formation was suppressed, probably because of the increase in hydrogen uptake of 100-200 standard cubic feet per barrel (0.72 to 1.44 g mol/kg) feed. A later patent (12) showed an increase in uptake of 400 scf/bbl (2.88 g mol/kg) of feed or twice as much as an earlier claim. In this work (12) it was reported the pitch should contain hydrogen in excess of 6.8% to prevent coke deposition in the reactor. An example showed a four-week run operating at 449°C and 750 psig (5.27 MPa) hydrogen partial pressure, with bitumen containing over 2.7% solids. There was no coking in the final two weeks, because of the accumulation of solids in the reactor. Solids accumulation apparently caused an increase in hydrogen uptake, thereby increasing the hydrogen level in the heavy oil product to over 6.8%. Another run in which hydrogenation catalyst was used in start-up, gradually replaced by mineral matter, showed no coke formation in two weeks.

The important feature of this patent relates to a hydrogen concentration in the pitch above which no coke formation was observed, and if the feed pitch can be hydrogenated to this level before leaving the reactor, coke will not form in the reactor. Since the feed pitch contains over 11% hydrogen on an ash- and water-free basis, the requirement is to prevent the pitch from becoming depleted in hydrogen. This could be an effect, however, rather than a cause of coke formation; the claim was poorly documented.

Another fact included in the patent is the requirement that at least 20 wt % silt is necessary in the reaction zone to minimize coke formation. In a later patent (13) a claim was made that only 4-10% ash is required, contradicting claims in Reference 10 that 25 to 50% ash was required and claims in Reference 12 that over 20% "silt" was required. The only apparent

difference is that a cyclone was used to enrich ash content of the recycled oil when only 4 to 10% ash was required. This perhaps implies that a high circulation of ash material is more important than a high concentration in the reactor.

Another HRI patent (14) describes a process, which has also been disclosed by others (15), in which the H-Oil reactor replaces a simple pipe reactor. Other HRI patents relate to the prevention of coke formation in vessels downstream of the reactor, using controlled velocity (16), flash cooling or quench (17,18), or control of the vapour and liquid velocities (19).

The tubular reactor idea for hydroconversion has been developed by the Texaco group (20,21,22) who have patented the concept of high hydrogen recycle, up to 20 times that used by HRI, and controlled turbulence to prevent fouling. They patented the theory (20) involving the ratio of the average apparent viscosity to the kinematic viscosity as a parameter to aid in the control of fouling.

In the published literature the formation of coke in thermal cracking (thermal visbreaking) is well known, and runs of 120 days are normal (23) in commercial equipment for moderate severity. Evidently, as severity is increased the heavy oils and resins which act to peptize and maintain the asphaltic constituents are cracked, allowing the asphaltic constituents to separate and form deposits on the cracking coil. Concurrently the concentrations of reactive constituents, which condense to tars and coke, increase as severity is increased. Sung et al. (24) have indicated that the kinetics of coke formation are difficult to determine but, in general, high-temperature and low-residence-time operations give a low yield of coke. Consequently, the specific rate of coke formation (in thermal cracking) may have a lower temperature coefficient than the specific rate of cracking other components.

Henderson and Weber (25) have assessed the effect of thermal treatment on Athabasca bitumen and modelled the rate of cracking to a first-order rate equation. They showed, by comparing the rate of cracking with and without sand, that the thermal upgrading step was not affected by the sand. Also reported was the fact that the rate of coke formation increased markedly after 370°C, particularly at high pressures. This was based on operability of their apparatus. Of course as the severity is increased further, the

thermal cracking operation becomes a thermal coking operation with the amount of coke produced proportional to the Conradson Carbon Residue (CCR) of the original charge (26), and varying with technology employed. It has been found, as shown in Table 9, that the CCR of Athabasca bitumen is about 13. This is sufficient to produce about 23 wt % coke based on feed in a delayed coking operation (26) where all the pitch is converted to either distillate or coke.

Sawatzky et al. (27) have shown that the bitumen feed contains about 15.3 wt % asphaltic material and that this material is reduced in amount as the severity of hydrocracking is increased. However the heavy oils and resins also are reduced so that the mechanism of the separation and precipitation of asphaltic constituents to form coke (23) cannot be ruled out for thermal hydrocracking. The second mechanism proposed by Beuther et al. (23) cannot be disproved as there is no way to measure directly the concentration of reactive constituents. The indications of Sung et al. (24) are consistent with data from coking operations. The lower-coke-yielding fluid-coking operation is a short residence time, high temperature operation when compared with delayed coking.

EXPERIMENTAL APPARATUS AND PROCEDURE

A detailed description of the pilot plant including diagrams was given in a previous report (1). The schematic diagram for the apparatus is given in Fig. 1. The reactor inside dimensions were 3.81 cm diameter by 3.95 m long. The hot receiver was 3.91 cm ID by 2.73 m. Piping from the oil feed tanks to the reactor, including the preheaters (not shown), was 0.48 cm ID with all other piping 0.32 cm ID. The above dimensions will be useful in verifying calculations in this work. Not shown in Fig. 1 are the three electrically-heated preheaters, the four separate heaters on the reactor and the three heaters on the hot separator for temperature control.

In operation, the hot separator was maintained at about 350°C and the cold separator at 25°C. The off-gas flows were typically in the volumetric ratios of 29:37:31:3 for scrubber oil gas, light oil gas, heavy oil gas and sample gas respectively (run 84-1-1); with hydrogen concentrations of 26%, 23%, 63% and 85% by volume respectively, and a total off-gas flowrate of 0.91 m^3/h at 0°C and 1 atmosphere (101.34 kPa) for the four streams. Also

for this run the heavy-oil-product to light-oil-product ratio was 1.41. All the above streams can be identified in Fig. 1.

All vessels and lines were cleaned before each run. At the start of a run, the system was pressurized with pure hydrogen and tested for leaks. With gas circulating, the reactor and hot receiver were brought up to 350°C. At this temperature, the feed flow was started and set at the desired rate, the preheaters were switched on, and the reactor temperature was increased rapidly to 420°C. From 420°C it was increased at 5°C per hour until the desired temperature was reached.

The oil flow to the scrubber was started when the recycle gas purity decreased to 85% hydrogen, and was set to maintain this purity throughout the runs. For all runs except 77-1-1 the gas recycle flowrate was maintained at 1.5 ft^3/h (0.042 m^3/h) at the system pressure and 25°C. This gave the same volumetric flow of gas in the reactor for the five runs but higher molar flows for the runs at higher pressures. The overall pressure drop was measured across the recycle gas pump. All products and gas flows were measured, sampled and analyzed throughout the runs, and pressure and temperature data were taken hourly for all runs.

RESULTS AND DISCUSSION

This section is presented in four parts. In the first, Tables 1, 2 and 3 are discussed. They contain the measured and calculated data for the six long runs, as well as data for short runs. Secondly, the long runs are discussed in sequence. A general discussion follows, and finally a comparison with coking processes is made.

1. Discussion of Tables 1 to 3

Table 1 gives conditions for the runs and variations in pitch and sulphur conversion. The latter depend on the severity of cracking which is a strong function of temperature and space velocity and a weak function of pressure. Table 2 gives other important parameters. All percentages are weight per cent. Distillate yield is in weight per cent of feed. Hydrogen consumption is the chemical consumption only and not the gross consumption, which is consistent with earlier runs(1) as shown in Fig. 3 and which is a function of pitch conversion.

Table 3 shows the overall pressure drop for all runs, and the preheater heat-transfer coefficient which was monitored throughout the test period. Preheater 3 was the final preheater in the series and the first to become fouled. Heat transfer coefficients were calculated in an attempt to predict reactor coke formation. This attempt at prediction was not successful since there was fouling for each run, probably because the gas and liquid both flowed through the same preheater and the velocity was not high enough. According to Schlinger et al.(21), the ratio of the dynamic to the kinematic viscosity should be close to 100, whereas the preheater when clean, had only 28.4. As deposits built up, the diameter probably decreased so that this ratio increased to well over 100, thereby reducing further deposits.

2. Discussion of Runs in Sequence

As discussed previously, an earlier publication(1) on thermal hydrocracking of Athabasca bitumen, established relationships between the controlled variables of temperature, pressure, recycle gas flow and LHSV, and the measured values of pitch conversion, distillate yield, hydrogen consumption, sulphur conversion and hydrocarbon gas make. These were based on four-hour runs in a reactor of fixed length-to-diameter ratio. During these runs at 2000 psi and above, there was no coke formation in the reactor, although indications from the patent literature were that it was to be expected(12), and earlier runs at lower pressure showed that it could be formed in the current experimental equipment, i.e., there was nothing unique about it to prevent coke formation. To establish that the process was feasible, it was decided that long runs of three weeks had to be made.

The first, 71-1-2, is summarized in Tables 1, 2 and 3. The run progressed smoothly with time, with small changes in the measured variables. External indications were that no deposit was forming. However, on opening the reactor after the run, it was found that the upper quarter was full of hard, black, porous material with an analysis as shown in Table 4. It was noticed that the material from the bottom of the deposit contained considerable ash or mineral matter, consistent with the coke forming at the top of the reactor and the resulting hard porous mass screening out some of the mineral matter as the products passed through. Alternatively, this ash could have come from the bottom of the reactor and deposited prior to shutdown. The benzene-insoluble material contains the ash plus coke and insoluble oils,

determined according to standard ASTM analyses(28). The benzene-soluble material contains the oil plus asphaltene fraction, and the pentane insolubles are made up of the benzene insolubles plus asphaltenes(29).

In run (71-1-2) a liquid sample was taken from the bottom of the reactor at 8-hour intervals for three days, then at 24-hour intervals for the balance of the run. While each sample was taken, the recycle gas (85% H_2) and liquid feed was discontinued. It was felt that stopping the recycle gas flow caused the coking. Workers in thermal cracking have warned of severe coking at temperatures above 370° without hydrogen(25) and the experiments were run at 460°C without hydrogen for up to 10 minutes while taking samples. Accordingly, the run was repeated with no reactor samples taken.

This repeat run was numbered 71-1-3, and was shut down after 14 days because of operator error. An inspection showed that hard coke-like material was forming in the top of the reactor. An analysis of this material is given in Table 4. For this run, the pitch conversion increased by about 2% during the run, but the hydrogen consumption decreased from 5.70 g mol/kg feed on the first day to 5.53 on day 5, and 5.42 g mol/kg feed on day 13. This is not consistent with the patent of Chervenak et al.(12), where hydrogen consumption was said to increase with time. In the earlier run (71-1-2), by contrast, both the pitch conversion and the hydrogen consumption decreased with time, the latter by 30% over the run. This was probably caused by the reduction in reactor volume due to the deposit on the reactor walls and the buildup of ash in the reactor. As shown in Fig. 2 the pitch conversion is a function of the liquid hourly space velocity (LHSV) and, since the liquid feed flow rate was held constant, the LHSV increased as the deposit was formed, reducing the pitch conversion according to Fig. 2.

The first two runs indicated formation of a reactor deposit over a two- to three-week period and that it started to form at the top of the reactor growing inward from the wall and downward.

The deposit formed in the first run (71-1-2) was sufficient to reduce the reactor volume, increasing the space velocity and thus reducing pitch conversion and sulphur removal, and increasing product gravity. However results of run 71-1-3 showed that leaving the mineral matter in the reactor to act as a catalyst (no reactor sample withdrawal) resulted in a 2% increase in pitch conversion and a 12% increase in sulphur conversion based on the initial

and final samples. The effect of leaving the mineral matter in the reactor offset the effect of reactor volume decrease due to coke formation.

Another run was designed to test the effect of continuous withdrawal of reactor material from the bottom of the reactor. This run, 77-1-1, was shut down after 380 hours because of high pressure drop. Withdrawal was achieved by piston-type Ruska pumps at 100 g/h for the first 7 days and 140 g/h thereafter. The material withdrawn contained 10% ash for the first seven days and 6.5% thereafter, showing that a balance was maintained by continuously removing reactor material. Run 77-1-1 also showed that about 75% of the ash material left the reactor with the product in both cases and that only 25% remained. In other words, 75% was fine enough to be carried out of the reactor on a once-through basis; the balance was removed by continuous withdrawal from the reactor bottom. On inspection, the reactor contained coke-like material in the top one-meter portion, similar to previous deposits, which had to be burned out. It was necessary to use controlled air and to maintain the reactor wall temperature at 500°C or less to prevent damage to the reactor interior. The pitch and sulphur conversion in this run also decreased from start to finish, again probably caused by the increase in space velocity from the decrease in reactor volume and by the lack of mineral matter to give catalytic effect.

The next run in the series, 79-1-1, was conducted at higher pressure and a temperature of 470°C to determine if an increase in severity would reduce coke formation, as the increase in temperature would result in an 85% pitch conversion. During this run make-up hydrogen was introduced at a point three-quarters of the way up the reactor. No reactor samples were taken during the run. The final product had an average of 0.58% ash, 2.3% benzene insolubles and 6.7% pentane insolubles. Pitch conversion, product gravity, weight yield and sulphur conversion were nearly constant throughout the run, as with run 71-1-3 where no reactor samples were taken. Inspection of the reactor interior revealed there was 0.45 m of hard porous material in the top of the reactor, with analysis as given in Table 5. The total liquid remaining in the reactor was also sampled, and its analysis is given in Table 5. The ash content for this liquid is consistent with previous reactor samples since the low-ash material in the top of the reactor was mixed with the high-ash material at the bottom. From the total ash value, it was estimated that the final ash content of the bottom quarter of the reactor

was 24%, consistent with what was expected based on previous reactor samples. Table 5 also shows that the top portion of the deposit in the reactor had less ash than the bottom or the bulk of the deposit, again consistent with a plug forming at the top of the reactor which slowly grows and traps or screens out ash. This deposit was not as hard as previous deposits and could be drilled and brushed out.

For run 79-1-1, it was possible that introduction of make-up hydrogen at a point three-quarters of the distance from the reactor base might have helped reduce coke formation. However this practice was discontinued in later runs, and the make-up hydrogen was again added to scrubbed recycle gas as calculations showed that this had only a small effect; furthermore, the coke deposit was at the top of the reactor near the point where pure hydrogen was admitted.

Run 79-1-1 was considered a success because of evidence that an increase in both temperature and pressure could reduce the formation of deposits in the reactor. The relative effects of temperature and pressure were determined in a series of two more runs at a higher pressure (24.23 MPa), 84-1-1 at $460^{o}C$ and 84-2-1 at $470^{o}C$. Of interest also was that sampling of the reactor contents resulted in the removal of mineral matter or ash. In two runs with no reactor sampling the product did not vary during the run (79-1-1, 71-1-3) although a deposit formed in the reactor. In the other two runs with continuous sampling (77-1-1) and intermittent reactor sampling (71-1-2) product degradation was evidenced by significant decreases in pitch conversion and sulphur removal and a slight increase in product gravity, showing the effect of sampling, or ash removal (Tables 1 and 6). It could be argued that in a commercial operation there would be ash removal to maintain a steady-state; therefore the next runs were designed with reactor sampling to maintain a steady-state, recognizing that this would be the most severe test of the system, because of loss of catalytic effect.

Conversions and product inspections for runs 84-1-1 and 84-2-1 are shown in Table 7. There was little variation in product quality in either run. At the end of run 84-2-1, the reactor was opened after a run period of 21 days and found to contain 106 g of powdery material. A number of crystals formed on the reactor wall were analysed and shown to contain sulphur and iron; the gas lines contained small amounts of ammonium sulphide. The 20 g of powdery black material from the reactor walls was examined petrographically

and was found to be organic material with some coke. The 86 g of the material at the top of the reactor forming a paper-thin, bubble-like shell with a deposit below, was analysed and found to be composed of pentane insolubles (66.2%), benzene solubles (55.7%), ash (36.5%) and sulphur (15.4%). This implies 19.2% coke and 10.5% asphaltenes. The sulphur content of the deposit was unusually high and could have contributed to the formation of the shell. Unfortunately, the material in this shell was not analysed separately because it was felt at the time that a thin shell could not form in a larger commercial reactor, i.e., this was a phenomena unique to smaller reactors. Since run 84-2-1 was conducted at the same conditions as run 79-1-1 except for the pressure, it is clear that the increase in pressure was responsible for the excellent results.

At termination of run 84-1-1 (lower temperature), the reactor was opened and found to contain a small buildup of soft, black material at the top and bottom sections of the reactor, and a paper-thin, bubble-shaped cover near the top. The total deposit, including entrained oil, was 300 g and extended 30 cm down from the top and 60 cm up from the bottom of the reactor. It was removed by brushing. Also a deposit which was difficult to remove formed on the walls. Subsequent tests showed that the deposit contained iron and sulphur. Although severity was decreased, this run represented a considerable improvement over run 79-1-1 with regard to plant operation, again indicating that hydrogen pressure was the most important variable in controlling coke formation. The residue in the reactor contained, on a weight basis, 43% ash, 13% vanadium, 5% nickel, 21.9% sulphur, 72% benzene insolubles, 48.6% carbon and 4.77% hydrogen. The sum of ash, sulphur, carbon and hydrogen should be approximately 100% for the sample. However this is not the case. Subtraction of the ash from the benzene insolubles gives a coke content of 29%. The sample was soft and probably contained considerable oil, as evidenced by the high hydrogen content.

Another consideration when comparing runs 84-1-1 and 84-2-1 is that more reactor samples were taken in the former run, as shown in Table 6, which gives ash balances for all runs. This table is based on the assumption that all samples weighed 100 g. The ash input is based on 0.57% ash in the feed; the ash removed in the samples was found by adding the ash removed in all samples for the run and dividing by the total run-time in hours. This table shows the relative amounts of material removed by reactor sampling and in

the product for each run.

Data in Table 6, along with the other evidence, gives a definite indication that the presence of mineral matter is an important factor in reducing deposits in the reactor but that it is not the most significant factor. As evidenced in earlier runs, the buildup of mineral matter seemed to offset the reduction in reactor volume due to the formation of solid deposits. This resulted in constant product quality, as opposed to runs where mineral matter was removed and the quality deteriorated. In the last two runs, the effect of ash removal was not as severe, because the hydrogen partial pressure was probably higher and less material was removed.

3. General Discussion

Speight (30) defined coke as follows:

coke = benzene insolubles - ash

Abraham (29) defined asphaltenes as pentane insolubles minus ash for a coke-free sample. He defined the benzene insolubles as "free carbon" as opposed to coke. These definitions will be considered for coke formation and other effects in the reactor. At present, no quantitative method exists for determination of coke. Therefore the definition of Speight will be used for coke, recognizing that the coke structure (31) has not been the only structure present in the benzene-insoluble material of some reactor inspection samples, and that "free carbon" may be a more appropriate term.

In considering all runs there appear to be several stages in the formation of a deposit. First a light dusting of black, carbonaceous material on the walls and a thin, bubble-shaped membrane forms near the top of the reactor, followed by deposition of a cylinder of viscous semi-liquid material as in run 84-1-1. The deposit then grows from the top down, cokes and becomes hard and porous as in run 79-1-1; eventually it occupies more and more of the reactor volume, as in run 71-1-2. The deposit formed initially appears to be coke but it grows downward with a much higher ash content (Tables 4 and 5).

Removal of ash material appears however to accelerate the process of deposit formation rather than to reduce it. The amount of ash material left in the reactor is small compared with the total fed, and it seems to act as a catalyst in maintaining the pitch and sulphur conversion in spite of a decreasing reactor volume in earlier runs (Table 5, reactor liquid analysis,

and run 79-1-1 results). However, buildup of ash material does not increase
pitch and sulphur conversion much above the values for a clean reactor.
This is contrary to the claims of Chervenak et al. (12). The ash content in
the reactor increased to 7.2% weighted average in run 84-1-1 and 10% weight-
ed average in run 84-2-1 over a three-week period, but the pitch and sulphur
conversions were nearly constant as shown in Table 7.

Furthermore, the hydrogen consumption did not increase in any run,
contrary to the claims of Chervenak et al. (12) who found a 200% increase in
hydrogen consumption when ash content was increased to 20%, and an almost
linear increase in hydrogen consumption with "sand accumulation" (ash
content). Figure 3 shows hydrogen consumption for the short runs from
Reference 1. Comparison of these values with consumption values in Table 2
is further evidence that the hydrogen consumption did not increase when
mineral matter had been accumulated.

The material forming the thin shell at the top of the reactor has
not been analysed. However, as shown in Figure 4, it has been photographed
where the shell was broken to obtain a better view. This photograph was
from the inspection after run 84-1-1.

The liquid flux in the reactor in this work was 0.45 pound of oil
per square foot per second, which was less than the flux claimed to keep the
mineral matter in suspension (1.0 lb/ft^2/s) as recommended by Layng (10).
Samples of reactor liquids at different levels confirmed that the mineral
matter could be 18.6% at the reactor bottom, 7.8% at the middle and 5.5% at
the top (Run 84-2-1, end) or 18.3% at the bottom, 6.0% at the middle and
3.0% at the top (Run 84-1-1, end). This supported Layng's claim.

This study showed that the hot separator was clean when a very
small deposit was present in the reactor as in runs 84-1-1 and 84-2-1.
Normally the hot separator was operated at a temperature of 350 to 370°C and
low liquid level. The gas and liquid from the reactor entered the separator
below the liquid level through a dip tube located about 6 cm above the
separator outlet. Presumably the agitation and contact with the gas coupled
with low residence time prevented formation of coke at the high pressure.
In earlier runs (71-1-2 and 71-1-3) with the same system, coke up to 1 cm
thick formed on the walls of the hot separator, dip tube and bottom cap.
Analyses of the material was similar to that of the reactor deposits.

At 350°C the liquid linear velocity in the hot separator was always less than 0.006 feet per second, the limit, claimed by Wolk et al. (16), below which there was coke formation at 260°C. In other words, coke formation should have occurred in the hot separator in all runs according to Wolk's claim since the hot separator was operated at a higher temperature and lower velocity. Perhaps the method of introducing the gas and liquid was responsible or perhaps the analysis of Wolk et al. (16) should be modified to include either total pressure or hydrogen partial-pressure as an additional parameter.

Table 8 gives the analyses of the pitch portions of the product from four of the six runs. The carbon-to-hydrogen ratio of the pitch is a function of pitch conversion. On an ash-free basis the pitch hydrogen content is 5.14/0.8862 = 5.80% for run 84-2-1 where there was essentially no reactor coking, and 6.89/0.967 = 7.13% where there was coke formed in run 77-1-1. This is the reverse of the statements of Chervenak et al. (12) who claimed that there would be coke formed when the pitch hydrogen content of the product was below 6.8% and no coke when the pitch hydrogen was above 6.8%.

Since the pitch will ultimately contain all the ash, the ash content of the pitch increases with pitch conversion as shown in Table 8. This is also true for nickel and vanadium.

4. Comparison With Coking Processes for Bitumen Upgrading

Figure 5 shows a comparison of distillate gravity and volume yield with pitch yield for hydrocracking (1) with coke yield for delayed coking and fluid coking (32). The distillate becomes heavier with increasing coking severity or decreasing coke yield, and becomes lighter with increasing hydrocracking severity or decreasing pitch yield. The line for the coking operations as shown by Gray (32) is dotted below 16% coke yield, as this is the minimum for fluid coking with no pitch in the distillate. The minimum is about 21% for delayed coking.

The distillate yield, which excludes butanes (1), is higher for all severities of operation for thermal hydrocracking than for the coking operations where butanes have been included in distillate yield. Furthermore, the hydrocracking process is more flexible as the process could be operated

to a pitch yield as low as 5.7% of feed, resulting in a distillate yield of
94.3 vol % of feed, compared with a maximum of 84% for the best coking pro-
cess or 80.4% if butanes are excluded. Results are plotted as pitch yield
instead of pitch conversion to make a more meaningful comparison with coke
yield. Pitch conversion can be found by subtracting the pitch yield from
51.5 and dividing the result by 0.515. This gives pitch conversion in wt %.

Coke properties for delayed and fluid coking are given by Gray (32).
For fluid coking they show that on an ash-free basis the hydrogen content is
3.6% or less by weight and the sulphur and nitrogen are 10.2 and 1.7%
respectively. Comparison with Table 8 shows that the two byproducts will
have similar disposal problems although one (pitch) will flow in a pipe at
elevated temperatures and the other (fluid coke) can be made in small
particle sizes and gasified in an integrated vessel using a fluidized-bed
technique (flexicoking (33)). Other points of comparison between the pro-
cesses mentioned above were made by Gray (26,32) and Hyndman (34).

CONCLUSIONS

Pressure was found to be the most important variable in the pre-
vention of coke deposits. Higher pressures reduced reactor fouling and in-
creased pilot plant operability. Deposits always started to form at the top
of the reactor, where the hydrogen partial pressure and the ash concentration
were lowest. These deposits then grew inward and downward with time.

Removal of ash material from the bottom of the reactor by sampling
or withdrawal resulted in degradation of product quality during a run,
except at the highest pressure. Runs in which ash material was not removed
had nearly constant product quality despite build-up of deposits in the
reactor.

The hot separator was clean and free of coke deposits when the
reactor was clean. In other words, pressure had a more important effect on
coke deposition in the hot separator than velocity and separator temperature.
Also the hydrogen content of the product pitch was not interrelated with coke
formation.

An industrial upgrading plant for the processing of Alberta bitumen is not likely to operate at 24.2 MPa because of high capital costs. More experimental work is required to reduce reactor fouling at lower pressures and at pitch conversions that would maintain a tar sand plant in energy balance.

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TABLE 1

Operating Conditions and Product Quality Variation During Experimental Runs

Run No.	Pressure MPa	Temp $^{\circ}$C	Duration h	Pitch Conversion		Sulphur Conversion		Product Gravity 60/60°F	
				Near Start	Near End	Near Start	Near End	Start	End
71-1-2	13.89	460	480	77.8 (1)[*]	70.7 (20)[*]	44.8 (1)[*]	33.8 (20)[*]	.931 (1)[*]	.938 (20)[*]
71-1-3	13.89	460	308	77.7 (1)	79.4 (9)	41.5 (1)	45.5 (9)	.931 (1)	.922 (12)
77-1-1	13.89	450	380	77.5 (3)	72.2 (17)	42.3 (3)	38.2 (17)	.931 (1)	.936 (17)
79-1-1	17.34	470	498	84.9 (7)	85.0 (21)	53.1 (7)	53.1 (21)	.915 (1)	.915 (21)
84-1-1	24.23	460	493	81.9 (2)	81.9 (22)	49.6 (2)	48.0 (22)	.926 (1)	.927 (22)
84-2-1	24.23	470	477	88.7 (3)	88.3 (19)	57.2 (3)	58.7 (19)	.910 (1)	.907 (19)

[*] Number in brackets is day of run on which sample was taken.

TABLE 2

Operating Conditions and Calculated Data for Experiment Runs

Run No.	Liquid Feed g/h	Reactor Volume ℓ	Average Values for Run					
			Pitch Conversion %	Distillate Yield (1) %	H_2 Consumpt. g mol/kg	Gas Make (2) g mol/kg	Gas (2) mol wt	Sulphur Conversion %
71-1-2	7972	4	74.3	82.4	5.69	1.32	25.1	44.1
71-1-3	7936	4	79.0	82.0	5.66	1.50	24.4	45.1
77-1-1	6953	4.5	75.1	81.0	5.16	1.31	25.8	39.9
79-1-1	8962	4.5	85.7	85.0	7.15	1.79	24.8	53.1
84-1-1	9073	4.5	81.9	83.0	6.60	1.57	24.2	48.4
84-2-1	8941	4.5	88.9	86.5	8.99	1.96	24.5	58.2
Short Runs 1	8123	4	75.3	80.8	3.99	0.97	25.5	36.7
Short Runs 2	8130	4	81.7	81.8	5.68	1.48	24.3	47.5

(1) Liquid boiling below 524°C, excluding C_3 and lighter

(2) C_3 and lighter, excluding H_2S and H_2

(3) Recycle gas flow for all runs except 77-1-1 was 0.0424 m³/h at pressure and 25°C. For run 77-1-1, the recycle gas flow was 0.0354 m³/h at pressure and 25°C.

TABLE 3

Pressure Drop, Shutdown, and Preheater Heat Transfer Data

Run No.	Overall Pressure Drop kPa			Reason for Shutdown	Preheater No. 3 U* $kcal/m^2/°C/h$		
	Start	Middle	End		Start	Middle	End
71-1-2	207	310	380	end	168	73	60
71-1-3	207	170	650	(1)	412	200	112
77-1-1	138	170	690	(2)	353	176	103
79-1-1	345	1380	10,340	(3)	222	110	86
84-1-1	345	970	1100	end	225	101	105
84-2-1	414	550	550	end	281	91	81

(1) Flow of recycle gas was lost due to error for 10 minutes; decision made to shut down.

(2) High pressure drop; decision to shut down.

(3) High pressure drop, but continued to end of run.

*   Upper limit based on wall resistance is 400 $kcal/m^2/°C/h$.

TABLE 4

Analysis of
Inspection Samples of Solid Material in Reactor After
Runs 71-1-2 and 71-1-3

	Top of Deposit wt %	Middle of Deposit wt %	Bottom of Deposit wt %
Run 71-1-2			
Ash	18.8	18.4	57.7
Benzene insolubles	86.7	96.9	60.8
Oil + asphalt	13.3	3.1	39.2
Run 71-1-3			
Ash	20.1	–	–
Benzene insolubles	57.1	–	–
Pentane insolubles	69.1	–	–
Oil + asphalt	42.9	–	–

TABLE 5

Analysis of Inspection Samples of Solid Material
in Reactor After Run 79-1-1

	Ash wt %	Nickel as Ni wt %	Vanadium as V wt %	Benzene Insolubles wt %	Pentane Insolubles wt %
Top of Deposit	26.1	0.9	2.9		
Total Deposit Composite	40	4.1	12.9	91.1	95.7
Bottom of Deposit	38.3	3.2	9.1		
Liquid from Reactor at End of Run	6.9	0.4	1.2	10.6	25.3

TABLE 6

Ash Balance*

Run No.	Ash Fed g/h	Ash Removed in Product g/h	Ash Removed in Samples g/h
71-1-2	45.4	44.2	0.7
71-1-3	45.2	44.7	-
77-1-1	39.6	26.2	10.0
79-1-1	51.1	50.6	-
84-1-1	51.7	51.5	1.0
84-2-1	51.0	52.2	0.3

* Ash determinations for feed and product may be in error by ± 3% on single determinations.

TABLE 7

Variations in Conversion and Product
with Time for Runs 84-1-1 and 84-2-1

RUN 84-1-1

Day product sample taken	2	7	13	17	22
Pitch conversion %	81.9	81.2	81.0	83.7	81.9
Sulphur conversion %	50	47	48	51	48
Liquid wt yield %	90.7	89.5	90.8	86.0	91.1
Product gravity 60/60°F	0.926	0.925	0.927	0.920	0.927

RUN 84-2-1

Day product sample taken	3	10	13	17	19
Pitch conversion %	88.7	89.1	89.5	89.1	88.3
Sulphur conversion %	57	58	58	60	59
Liquid wt yield %	88.8	90.0	89.0	88.1	88.8
Product gravity 60/60°F	0.910	0.909	0.912	0.908	0.907

TABLE   8

Analyses of Pitch Portion of Products*

Run No.		77-1-1	79-1-1	84-1-1	84-2-1
Carbon	wt %	82.3	80.2	80.4	76.9
Hydrogen	wt %	6.89	5.77	6.29	5.14
Nitrogen	wt %	-	1.88	1.74	1.80
Sulphur	wt %	5.42	4.31	4.78	4.26
Nickel	ppm	387	482	442	1189
Vanadium	ppm	1086	1481	1244	3420
Specific gravity	60/60°F	1.207	-	1.251	1.326
C.C.R.**	wt %	62.3	74.6	64.8	81.3
Ash	wt %	3.30	7.31	5.93	11.38
Benzene insol	wt %	-	26.2	19.3	37.5

* Samples taken within the last three days of the runs.

** Conradson carbon residue.

TABLE 9

Analysis of Topped Bitumen Feed

|		Topped Athabasca Bitumen Feed
Specific gravity	60/60°F	1.007
Ash	wt %	0.57
Sulphur	wt %	4.77
C.C.R.*	wt %	13.8
Pentane insol	wt %	15.6
Benzene insol	wt %	0.57
Carbon disulphide insolubles	wt %	0.88
Vanadium	ppm	196
Nickel	ppm	68
Total acid no.	mg KOH/gm	2.7
Total base no.	mg KOH/gm	1.76
Carbon	wt %	82.59
Hydrogen	wt %	10.82
Nitrogen	wt %	0.40
Oxygen	wt %	0.86
Chlorine	wt %	0.0055
C/H ratio		7.63

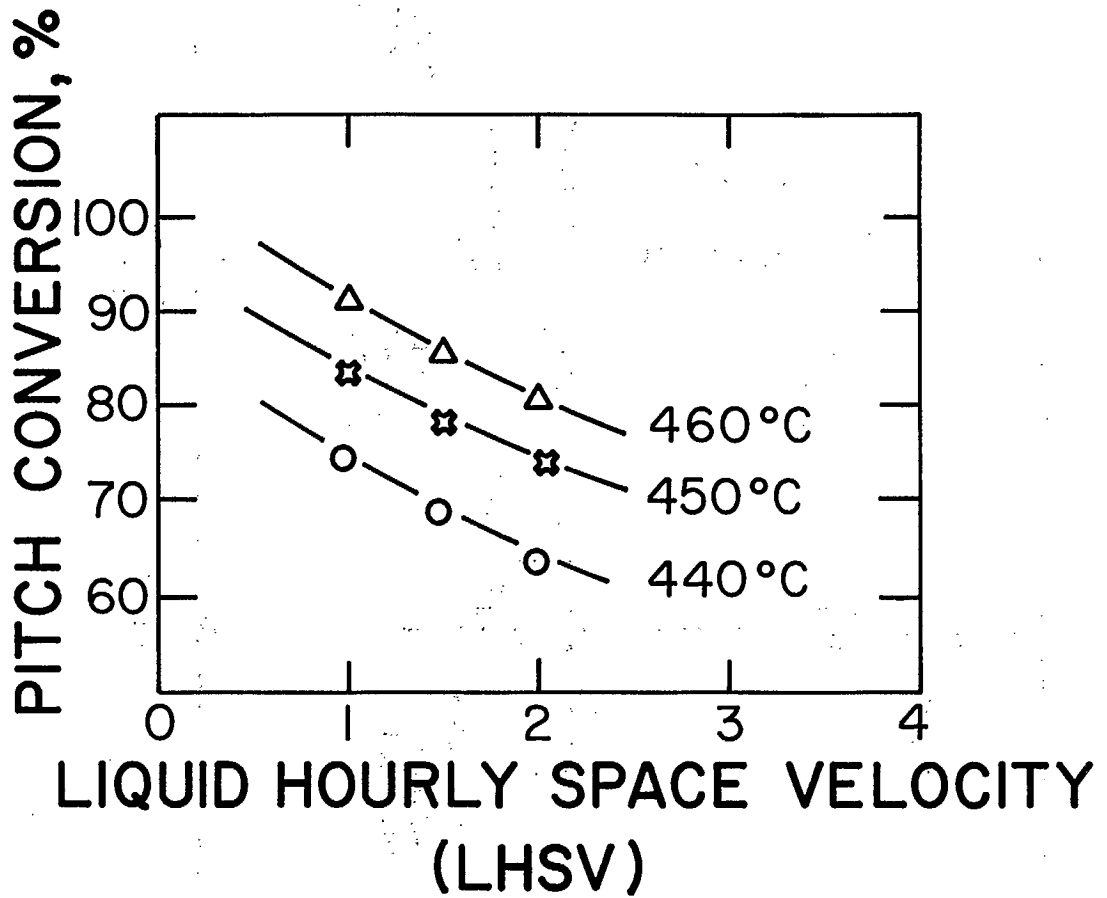* Conradson carbon residue.
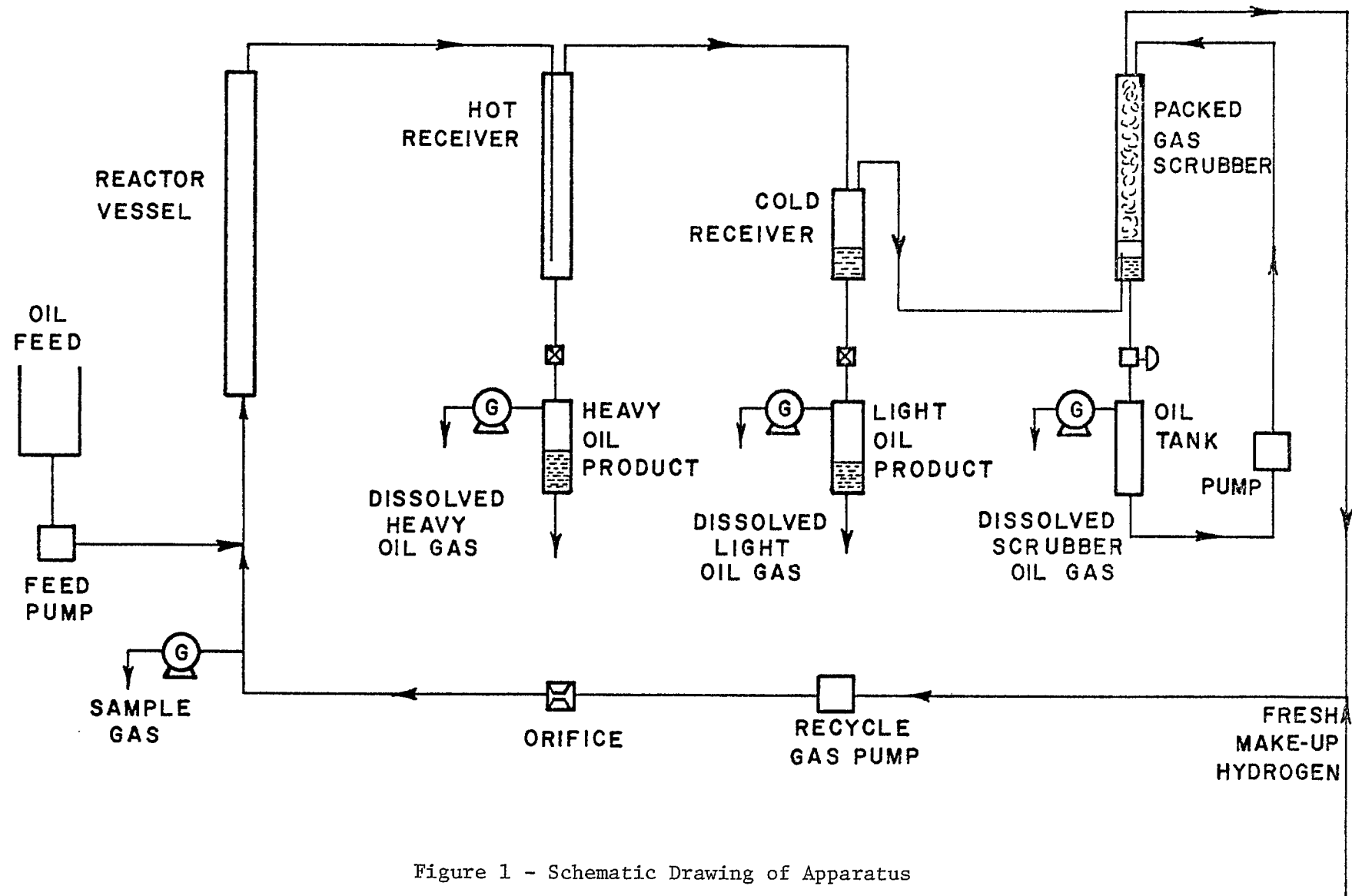
Figure 1 - Schematic Drawing of Apparatus
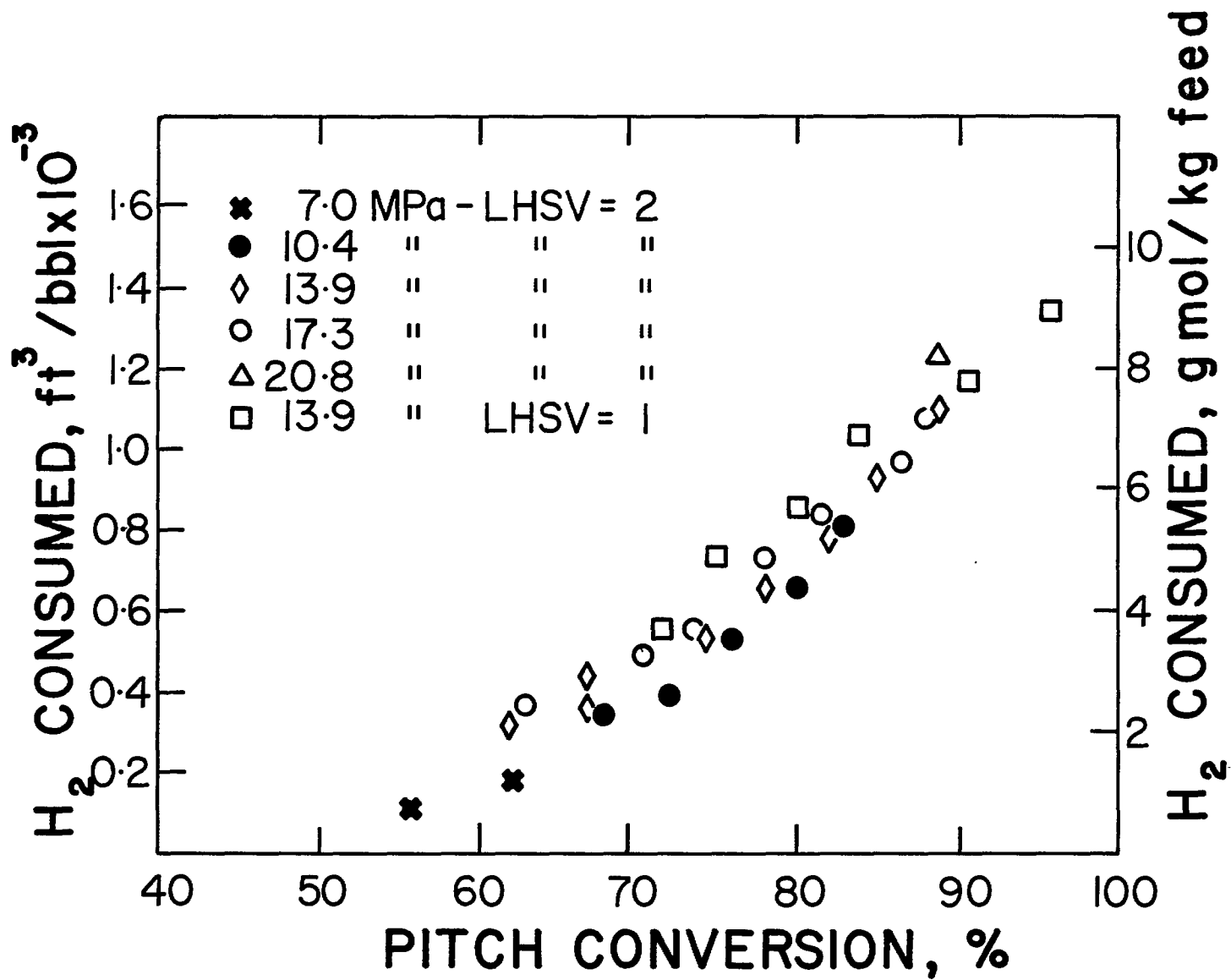
Figure 2 – The Effect of LHSV on Pitch Conversion

Figure 3 - Hydrogen Consumption as a Function of Pitch Conversion

THREADED
PORTION

SEAL
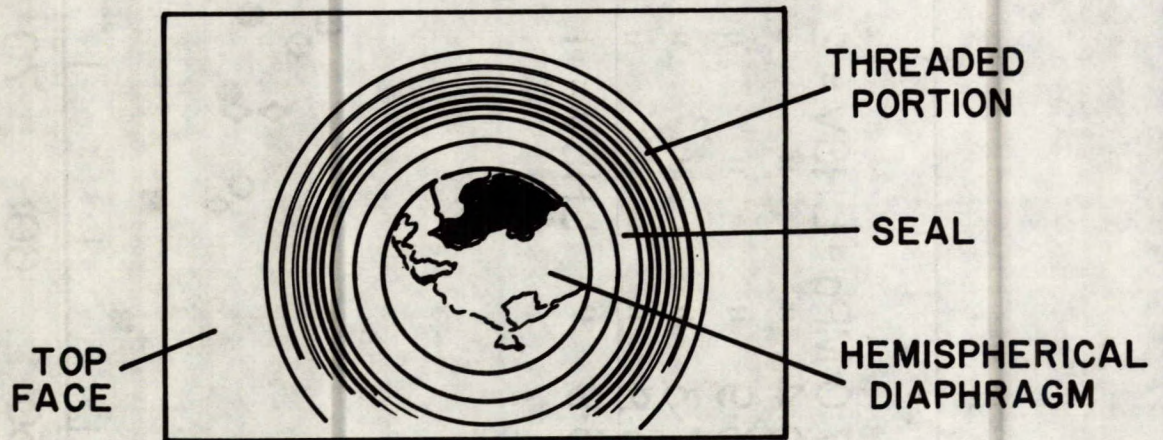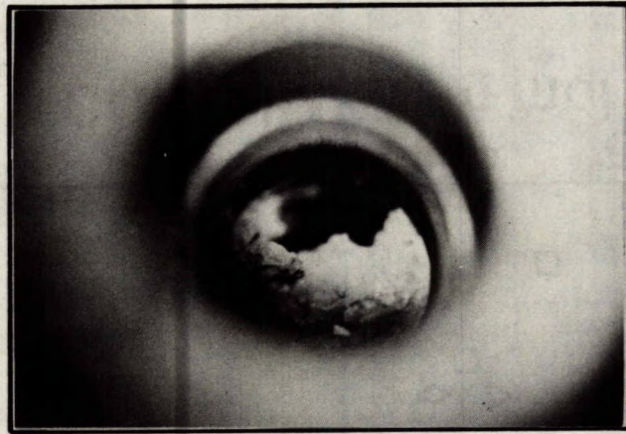
TOP
FACE

HEMISPHERICAL
DIAPHRAGM

Figure 4 - Picture of Hemispherical, Paper-Thin Diaphragm
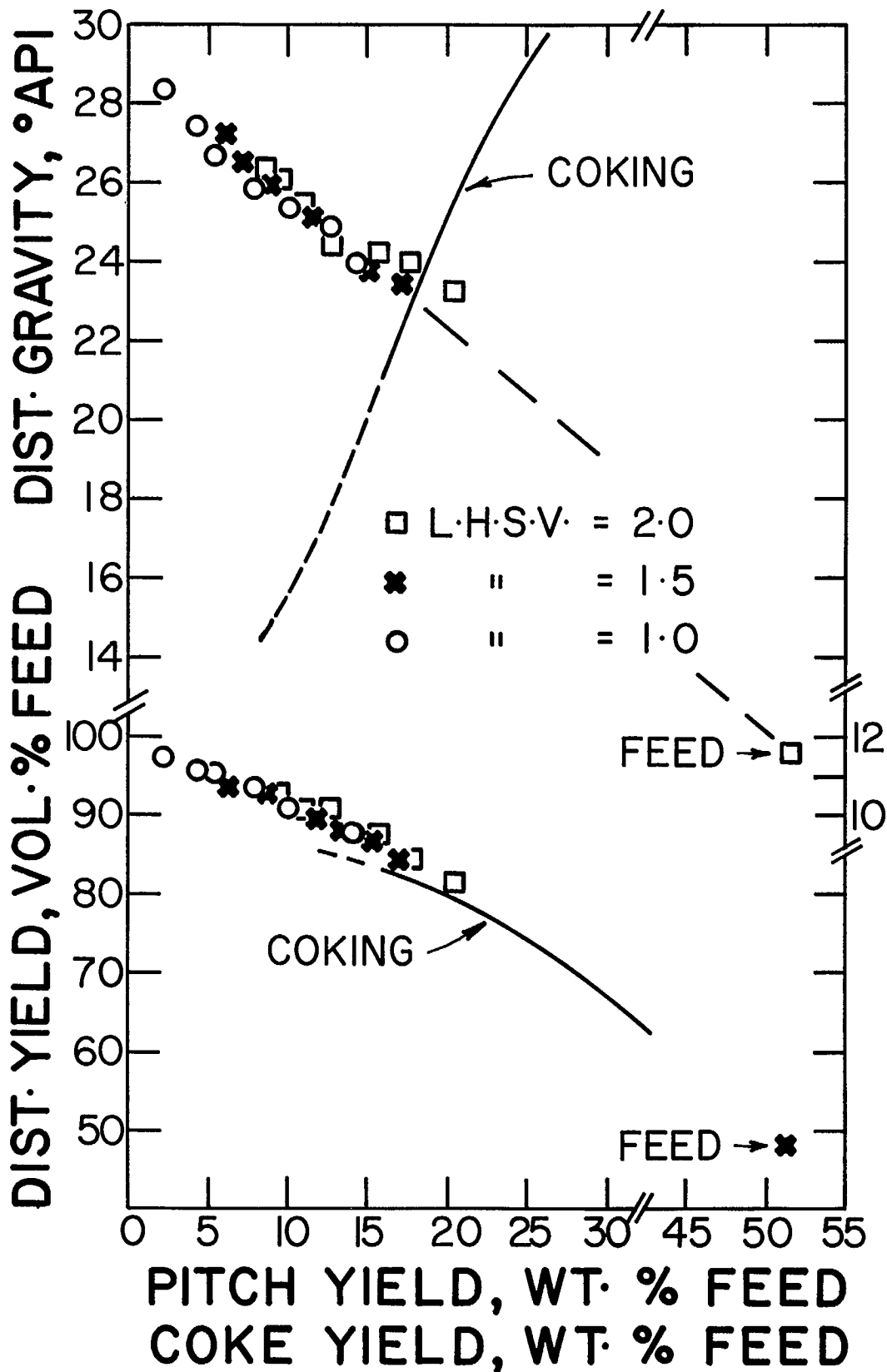Formed at Top of Reactor.
Broken to Improve Perspective.

Figure 5 – Comparison of Distillate Yield and Gravity for
Coking and Thermal Hydrocracking Processes

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