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An Application for a Canadian Patent for a Thermal Hydrocracking Process to Convert the Residuum in Bitumen and Heavy Oils into Low Boiling Distillates

by

B.I. Parsons, W.H. Merrill, R.B. Logie and J.M. Denis

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The following application is for a process for the conversion of the residuum hydrocarbon occurring in heavy oils and in bitumen extracted from the Alberta Oil Sands deposits into low boiling distillates by medium pressure (750-3500 psi) thermal hydrocracking.

The amount of fuel required in the processing of the Oil Sands and Heavy Oil deposits in Western Canada is large compared to that involved in the recovery and refining of conventional crude oils. Depending on the precise location and concentration of the deposits, from 10 to 30% of the separated bitumen or oil is needed as a source of energy for the in-situ recovery or mining, separation and refining steps. The economics of the industry generally dictate that the bulk of the power requirements be met by burning the residual bottoms either directly, or by gasification followed by gas clean-up and burning. While there are variations in composition, only 30 to 50% of the hydrocarbon material present in bitumen or heavy oil is in the residuum classification, i.e. distilling above an atmospheric equivalent of 1000°F. (The part of the bitumen and heavy oils distilling below an atmospheric equivalent of 1000°F can be readily processed by refining procedures known and acceptable to the industry.) Ideally then, the first step in the refining process should be able to effect conversion to low boiling distillate down to as low as 10% residuum remaining in the liquid product and be readily varied as circumstances of the deposit require.

Experimental work published earlier by the inventors (1,2) on the thermal hydrocracking process as a preliminary step for the refining of the Athabasca Bitumen indicated that sludge and coke tended to accumulate rapidly in the reaction system at high conversion levels and low pressures. With the whole bitumen as feed stock, a practical limit of operability at 1000 psi appeared to be reached under conditions effecting conversion down to only 20% +1000°F residuum in the liquid product. Such a level of conversion was only slightly improved over conventional thermal coking and scarcely justified the additional costs entailed in the construction and operation of a pressurized hydrocracking facility.

In the present work it has been found, however, that a relatively small increase in hydrogen partial pressure has a profound effect on the rate of build-up of pitch and coke in the reaction system. All things being equal, increasing the partial pressure of hydrogen to 1500-2000 psi decreases markedly the rate of accumulation of sludge and coke, and permits operation at higher temperatures such that conversion approaching 5 to 10% +1000°F residuum remaining in the liquid product can be achieved continuously. Alternatively, continuous operation of the process is possible at somewhat lower pressures with less conversion, the choice being at the discretion of the operator.

Heavy oil and bitumen feed stocks also contain high concentrations of minerals, metals, sulphur and nitrogen. For example, a typical bitumen separated from the Athabasca oil sands deposit contains 0.5 to 2.8% by weight of dispersed clay, 60-80 ppm of nickel, 180-220 ppm vanadium, 4-5% sulphur and 0.4-0.6% nitrogen. Catalytic hydrogenation of this type of feed stock is certainly possible, but costly. Even at high pressures (3000 - 5000 psi) the catalyst quickly coats with minerals, metals, and coke, and loses activity. The metals and minerals cannot be removed by conventional regeneration techniques and catalyst costs are consequently high. The problems in refining appear to be concentrated in the residuum fractions. Once the bottoms fractions have been either removed or converted to distillable hydrocarbon material, little difficulty is encountered in subsequent secondary hydrogenation steps. Distillable fractions derived from the bitumen are easily refined in conventional fix-bed reactors under conditions suited to the boiling range of the feed stock. Satisfactory catalysts are cobalt or nickel molybdates, or some combination of the two, depending upon the nitrogen content of the fractions to be treated.

In the first stage of the refining of heavy oil or separated bitumen the objective is to prepare relatively clean, distillable hydrocarbon fractions at the expense of the smallest quantity of feed required for fuel. The hydrogen content of the distillate material should be as high as possible to facilitate secondary refining and the mineral matter and problem hydrocarbon material containing nickel and vanadium must, of course, be retained in the fuel stream. All of these things can be accomplished by coking but the yield of dry coke from a coking unit is fixed and is not variable as changes in the deposit are encountered. Moreover, there is evidence to indicate that even on the average considerably more coke is formed than is required for mining or "in plant" fuel. In theory, a thermal hydrocracking process for the preliminary treatment has a number of advantages over delayed coking. First (and foremost), hydrogenation systems can be easily operated as continuous processes; second, the bottom fractions (should) contain sufficient hydrogen to be fluid at high temperatures and thereby simplify handling, storage, burning or gasification; and, third, the extent of conversion is variable over a reasonable range as fuel requirements dictate.

The problems associated with continuous thermal processes are largely connected with the accumulation of sludge and coke deposits and the effect of this on the duration of operation before cleaning and maintenance is required. The objective is to produce as much distillable hydrocarbon material as possible (per unit weight of feed) leaving only sufficient heavy residual fuel to meet the in-situ recovery or mining and separation requirements. To attain the maximum conversion to liquid fuel at the minimum cost, it is necessary to approach conditions favouring coke formation without actually attaining them. Obviously, to operate such a "thresh-hold" process continuously all the fractions, including the bottoms, must remain predominately fluid (to facilitate removal) and there can be virtually no accumulation of solid matter anywhere in the system. In the following examples the effect of pressure on the operability and conversion of the thermal hydrocracking process will be demonstrated.

The bitumen used in the experimental work was obtained from Great Canadian Oil Sands Limited of Fort McMurray, Alberta. In the G.C.O.S. process the bitumen from the primary separation stage is diluted with a coker naphtha fraction then centrifuged to remove the bulk of the finer sand particles. This stream is finally topped to recover the naphtha prior to charging in the coking drums. The bitumen supplied by G.C.O.S. was equivalent to the charging stock to the coking plant, i.e., centrifuged and topped. The properties of the bitumen (as received) are listed in Table 1.

The extent of conversion of the residual material to distillable hydrocarbon (up to 975°F atmospheric equivalent) was determined using a Podbielniak Equilibrium Flash Still Model 500 (3). The product distribution of the distillable oil was determined using a modified U.S. Bureau of Mines Hempel distillation procedure (4).

TABLE 1

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

Specific Gravity 60/60°F	1.009
Sulphur (wt %)	4.63
Ash (wt %)	0.68
Viscosity (cSt at 210°F)	152.2
Conradson Carbon Residue (wt %)	12.8
Pentane Insolubles (wt %)	16.0
Benzene Insolubles (wt %)	0.9
Nickel ppm	70
Vanadium ppm	190

DISTILLATION ANALYSIS

Equivalent Distillation
Range at 1 Atmosphere

Temp °C	Temp °F	Wt %	Sum %	Specific Gravity	Sulphur wt %
RT-200	RT-392	0.4	0.4		
200-250	392-482	1.9	2.3	0.858	1.43
250-334	482-634	10.6	12.9	0.902	1.92
334-419	634-787	17.5	30.4	0.951	3.10
419-524	787-975	18.7	49.1	0.989	3.77
+524	975	50.9	100.0	1.076	6.21

Example One

The following experimental work illustrates the effect of pressure on the rate and extent of coke fouling in the reactor of the thermal hydrocracking process and demonstrates the highly desirable properties imparted to the system by a moderate increase in pressure.

A bench-scale flow system of conventional design was used for the preliminary investigation of the hydrocracking process. The major components of the apparatus and the general method of operation are described in the Mines Branch Research Reports R217 and R246 (1). The reaction vessel (internal dimensions 1 inch dia. and 12 inches long) was machined from 316 ss and designed for operation up to 10,000 psi at 500°C. The bitumen feed and hydrogen were pumped in at the bottom of the reactor. The temperature in the reaction zone was measured by means of a thermocouple extending up a well located centrally in the reactor.

Thermal hydrocracking experiments were made with bitumen (topped to 510°F) at selected temperatures from 390 to 440°C and at three pressures, 1000, 1500 and 2000 psi. The liquid feed and hydrogen flow rates used in all the tests were 160 ml/hr (L.H.S.V. approximately equal to one) and 3500 std cu ft/bbl respectively. The results are summarized in Table 2. Each experiment was run for approximately 7 to 8 hours. In a normal series, the tests were run consecutively beginning at the lowest temperature. At the conclusion of a series the reactor was drained (hot), allowed to cool, then opened for inspection of coke and sludge deposits. Where pitch and coke accumulated sufficiently rapidly to plug the reactor, the system was shut down after the first positive indication of operational difficulty, i.e., pressure drop, temperature fluctuation, etc.

At 1000 psi this topped bitumen feed could only be thermally hydrocracked continuously to a level equivalent to 26% residuum (+975°F, including clay) without serious risk of the accumulation of sludge or pitch in the reactor or receivers. It is doubtful if the process (at 1000 psi) could be extended to greater conversion levels by increasing the temperature or lowering the space velocity without providing for sludge and coke removal facilities and/or frequent shut-downs for cleaning and maintenance. Continuous operation at greater conversion levels was only possible at the higher pressures, i.e., 1500 and 2000 psi. Photographs of portions of the pitch and coke deposits obtained at 1000, 1500 and 2000 psi are shown in Figure 1 and 2. The deposits shown are the parts

TABLE 2

Summary of Experimental Results

Reaction Conditions			Overall Liquid Product				
Feed Lot No.	Hydrogen Pressure (psi)	Temp. (^{o}C)	Spec.Grav. 60/60^{o}F	Weight Yield C_4+ (%)	Sulphur Content (wt %)	Residuum +975^{o}F (vol %)	Remarks re: Accumulation of Sludge
21 (+510^{o}F)	1000	410	0.987	99.2	4.36	33.6	none
		420	0.979	97.3	3.70	30.5	"
		430	0.972	96.9	3.50	26.4	slow-in reactor
		440	0.969	–	3.61	23.3	fast-in reactor
21	1500	395	0.999	99.2	4.43	47.6	none
		410	0.986	96.6	4.06	30.2	"
		430	0.970	94.0	3.58	28.2	trace-in reactor
		440	0.959	–	3.36	23.0	slow-in reactor
21	2000	390	1.005	100.5	4.51	46.1	none
		410	0.984	100.5	4.30	41.4	"
		430	0.968	94.9	3.48	30.0	"
		440	0.958	92.2	3.33	22.0	"

attached to the thermocouple well above a locating "spider" near the top of the reactor. (Pitch gathered on almost all of the surfaces of the reaction vessel . . . . the parts shown were selected for photographing because they were the only parts which could be removed intact from the vessel.) At 1000 psi the coke and pitch accumulated rapidly, the "pod" of coke shown on the end of the thermocouple well was obtained after only 3 hours of operation at 440°C. At 1500 psi the accumulation of solid matter was still measurable, but much less than at 1000 psi and, at 2000 psi, the amount of deposited matter was negligible. The photographs at 1500 and 2000 psi were taken after approximately 20-22 hours of operation. A photograph of a massive blockage, typical of that which occurs after 6 hours operation at 1000 psi, is shown in Figure 2.

Taken as a whole, the bench-scale preliminary results indicated that a minimum hydrogen pressure of 2000 psi is required for continuous operation. Within the limits of the study, pressure had only a marginal effect on the quality of the distillable fractions formed (1). The prime function of the hydrogen was to reduce, or modify, the pitch and coke formation to a point where it did not accumulate in the reaction system. It was essential that the hydrogen pressure be sufficient to accomplish this.

Example Two

The following experimental work illustrates the effect of pressure and reaction temperature on liquid product yields. The work described in this example was undertaken in a one barrel per day, pilot-scale flow system using "as-received" bitumen from Great Canadian Oil Sands Limited at Fort McMurray, Alberta (see Table 1). The flow system equipment, and the general method of operation are described in Mines Branch Research Report R281 (2).

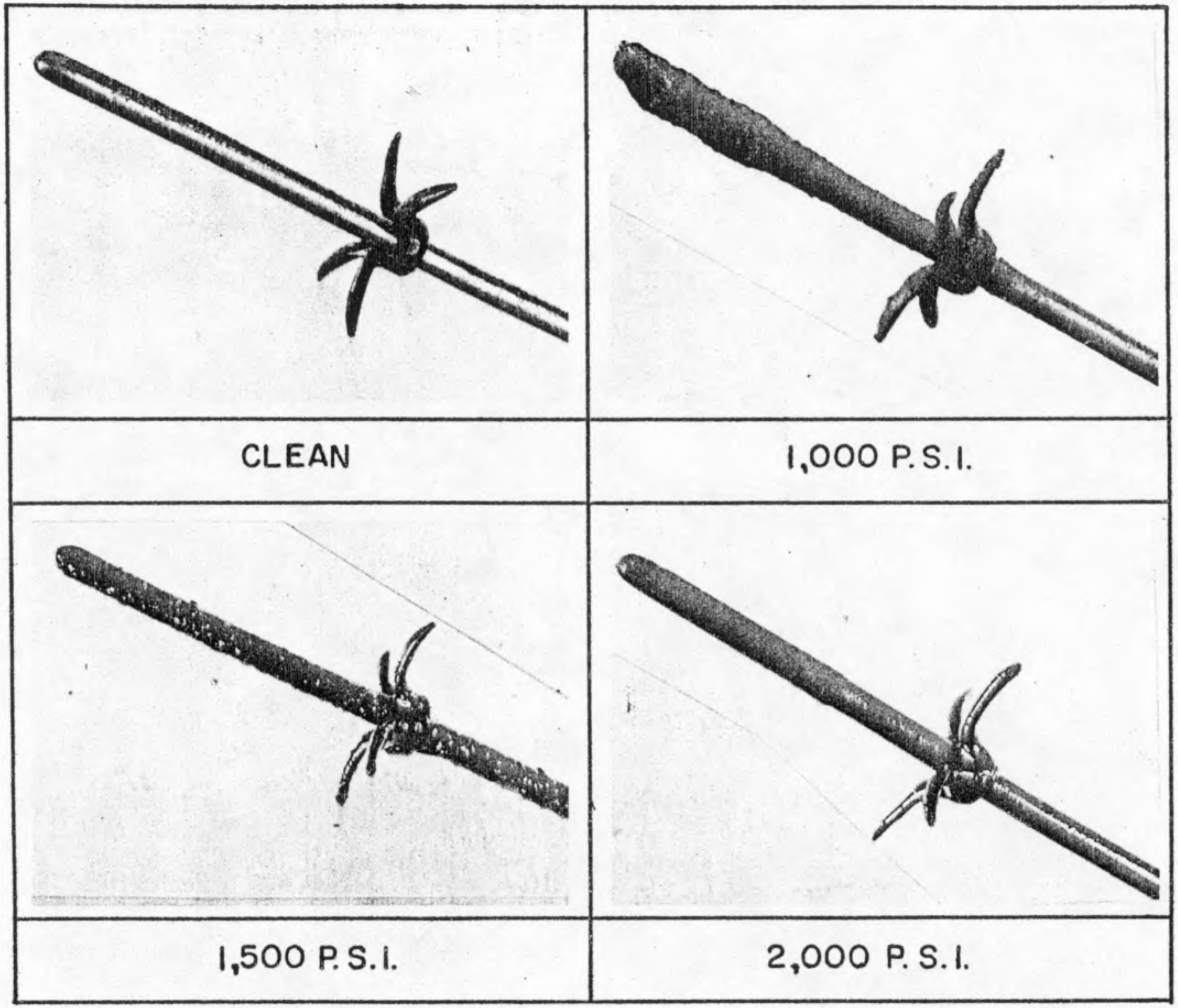
Feed oil from a weighed tank was pumped under pressure, through a preheater, to the bottom of the liquid-phase reactor. The reactor vessel was 1-1/2 inches inside diameter by 13 feet long with a length to diameter ratio of approximately 100 to 1. Hydrogen gas, also under pressure, joined the feed stream before the preheater. A constant temperature throughout the reactor was maintained by four equally spaced external heaters. The temperatures in the reaction vessel and receivers were measured by means of thermocouples placed in wells located centrally in the vessels. As the oil cracked, the vapourized portion rose with the hydrogen through the unvapourized oil, passed quickly from the reaction zone so that further cracking to gas was minimized, and moved on to a heated receiver. The heavier and less reactive fractions remained in the reactor for a longer period of time for further cracking. The liquid overflow from the liquid-phase reactor entered the hot receiver where it separated from the uncondensed vapours and hydrogen. The liquid product was withdrawn continuously through a metering valve to a heavy oil tank at atmospheric pressure. The uncondensed vapours and gases passed out the top of the hot receiver and were condensed and collected in a cold receiver. This oil was withdrawn automatically to a low-pressure light oil tank. The gas stream from the cold receiver, consisting mainly of hydrogen and containing 20 to 30% impurities such as uncondensed hydrocarbon gas, hydrogen sulphide and ammonia, was oil-scrubbed to remove about half of the impurities. The scrubbed hydrogen was blended with fresh make-up hydrogen and recycled back to the reactor at a constant controlled rate. The amounts of dissolved gas in the heavy oil product, the light oil product and the scrubbing oil were measured by wet-test-meters and samples analyzed for hydrogen and hydrocarbon gas content.

For the series of experiments undertaken to illustrate the effect of operating pressure on the hydrocracking reaction, a feed rate of 8000 grams per hour was used to give a liquid hourly space velocity (LHSV) of 2 in the 4 litre reactor. Experiments were made at 1000, 1500, 2000 and 2500 psi. The hydrogen recycle rate was adjusted to 1.9 cubic feet per hour at pressure. This was done to maintain the same volume of hydrogen passing up through the reactor at the different pressures. The volume remaining for the liquid, and therefore the residence time of the liquid, was then approximately equal. The hydrogen volume changed due to the temperature variation but this change was small. The number of standard cubic feet per barrel of hydrogen recycled was 2450, 3600, 4720 and 5770 at 1000, 1500, 2000 and 2500 psi respectively. The operating temperature was increased from 435°C by 5°C steps until operating difficulties were encountered or until 470°C was reached.

The experimental results are shown in Figures 3, 4 and 5. Pressure had only a small effect on the yield of the various products. The total liquid product yield was about the same at all pressures tested. The percent of +975°F pitch decreased slightly with increasing pressure and therefore the -975°F distillate oil product yield increased. The differences are illustrated by the separation of the temperature curves at the various pressures. All weight yields were calculated on a sulphur free basis but no allowance was made for mineral matter. The percent sulphur removed and the pitch conversion increased slightly with increasing pressure. The hydrogen consumption increased with pressure while at the same time the hydrocarbon gas make decreased.

Pressure had a *great* effect on the ease of operation and the pitch conversion that could be accomplished, in that by suppressing coke formation, higher pressures allowed higher operating temperatures to be employed. At 1000 psi the highest operating temperature possible without plugging was 440°C. At 1500 psi, the plant was operated at 465°C with difficulty. At 2500 psi operation was very smooth at 470°C.

The foregoing two examples are not to be considered restrictive in any sense. Comprehensive reviews of the reaction characteristics of the thermal hydrocracking process are described by the inventors in reports listed in the Bibliography. The point to be made is that thermal hydrocracking is a viable process for the conversion of the residuum fractions in heavy oils and bitumens to low boiling distillates. When operated at low pressures the process is no better, and no worse, than conventional delayed or fluid coking. However, with a moderate increase in pressure, the process can be operated at elevated temperatures permitting conversion levels of 70 to 85% to be attained continuously. It is to be stressed, that in the process as applied for, the hydrogen and oil are introduced into the reaction vessel in a bottom-feed configuration and that no catalyst or packing is present in the reactor.



CLEAN

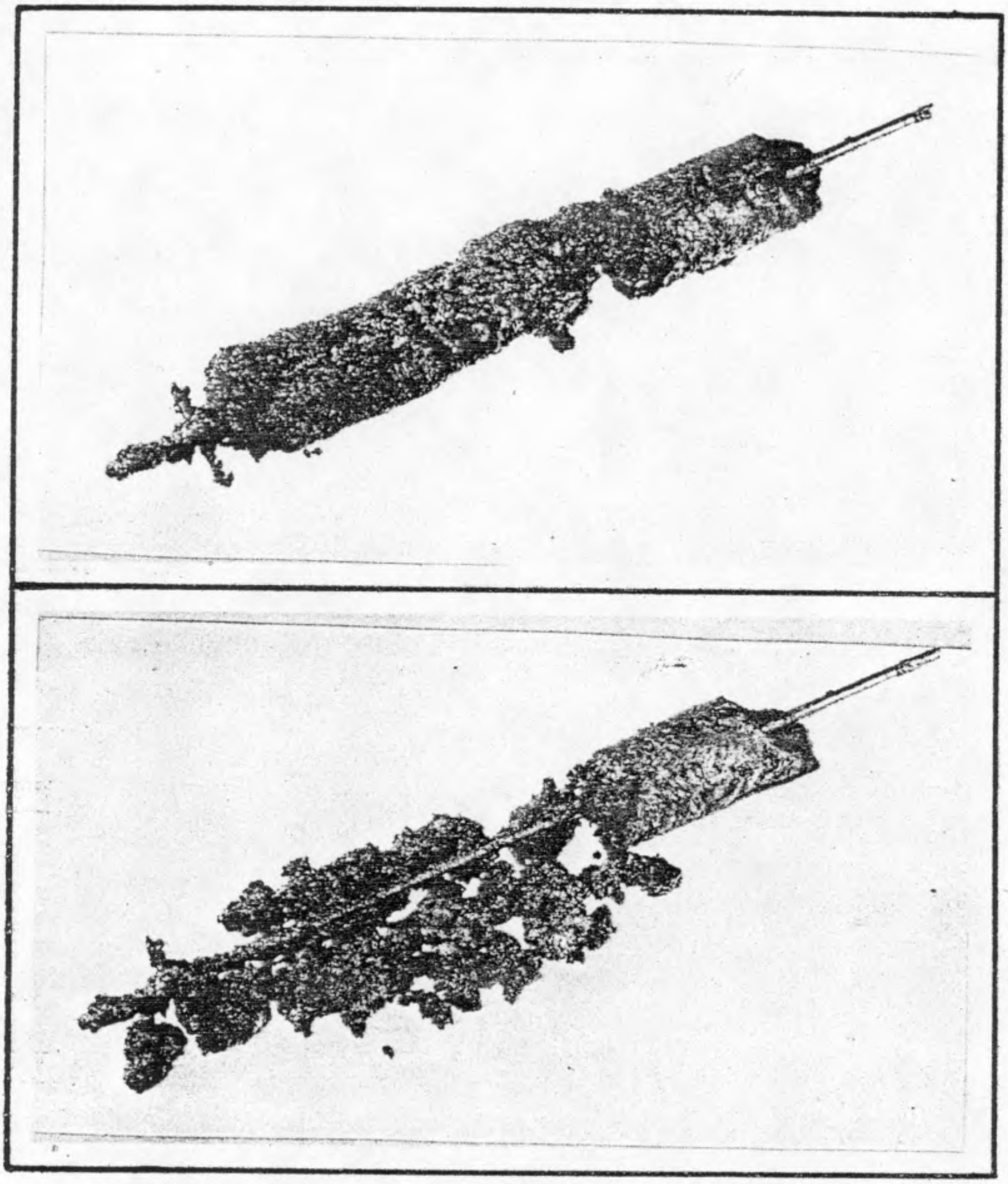
1,000 P.S.I.

1,500 P.S.I.

2,000 P.S.I.

THE EFFECT OF PRESSURE ON COKE FORMATION

Figure 1



MASSIVE COKE AND SLUDGE DEPOSIT

Figure 2

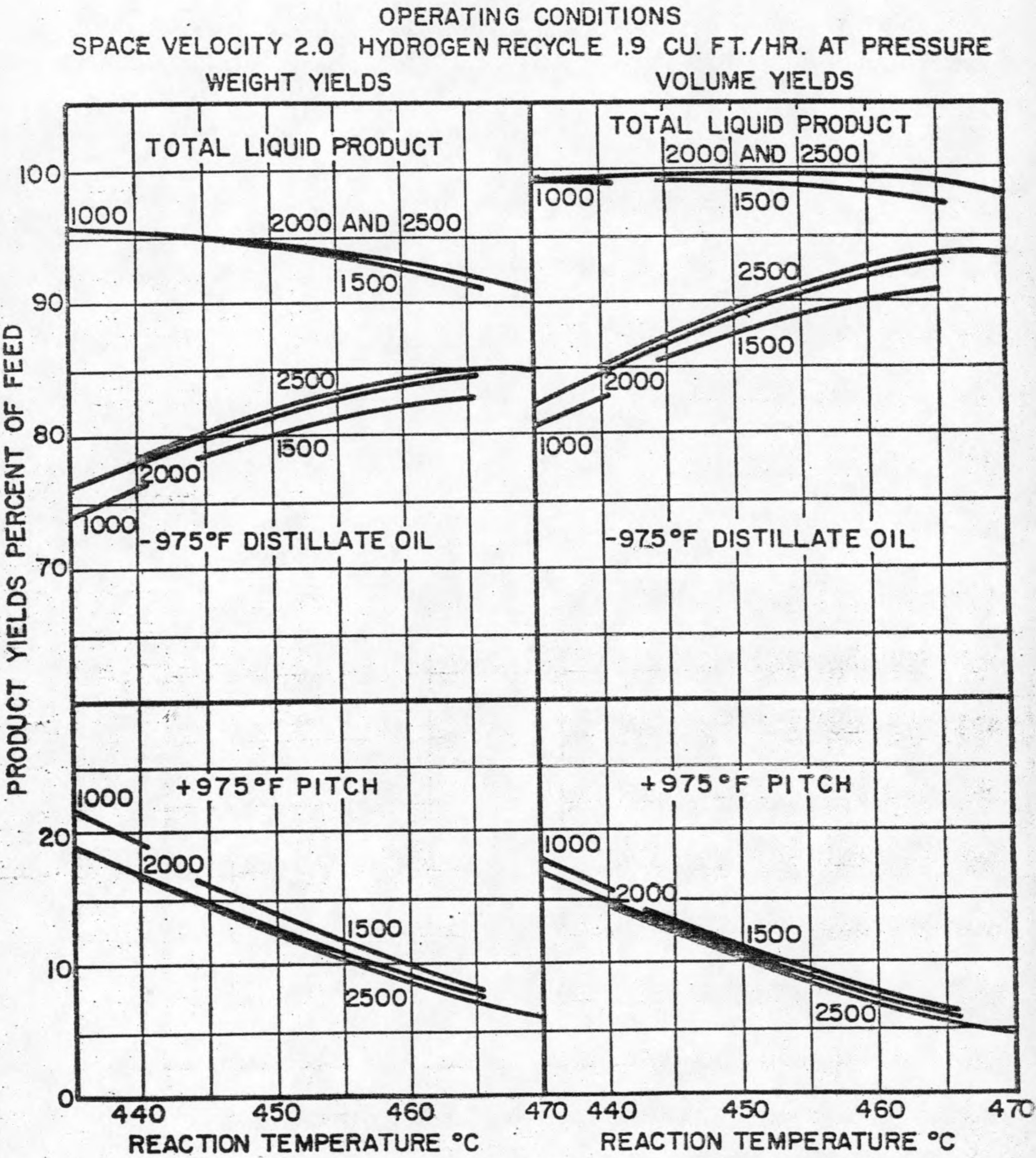


Figure 3. The effect of reaction temperature on liquid product yields at selected operating pressures.

Weight yields are on a sulphur free basis.

OPERATING CONDITIONS
SPACE VELOCITY 2.0 HYDROGEN RECYCLE 1.9 CU. FT./HR. AT PRESSURE

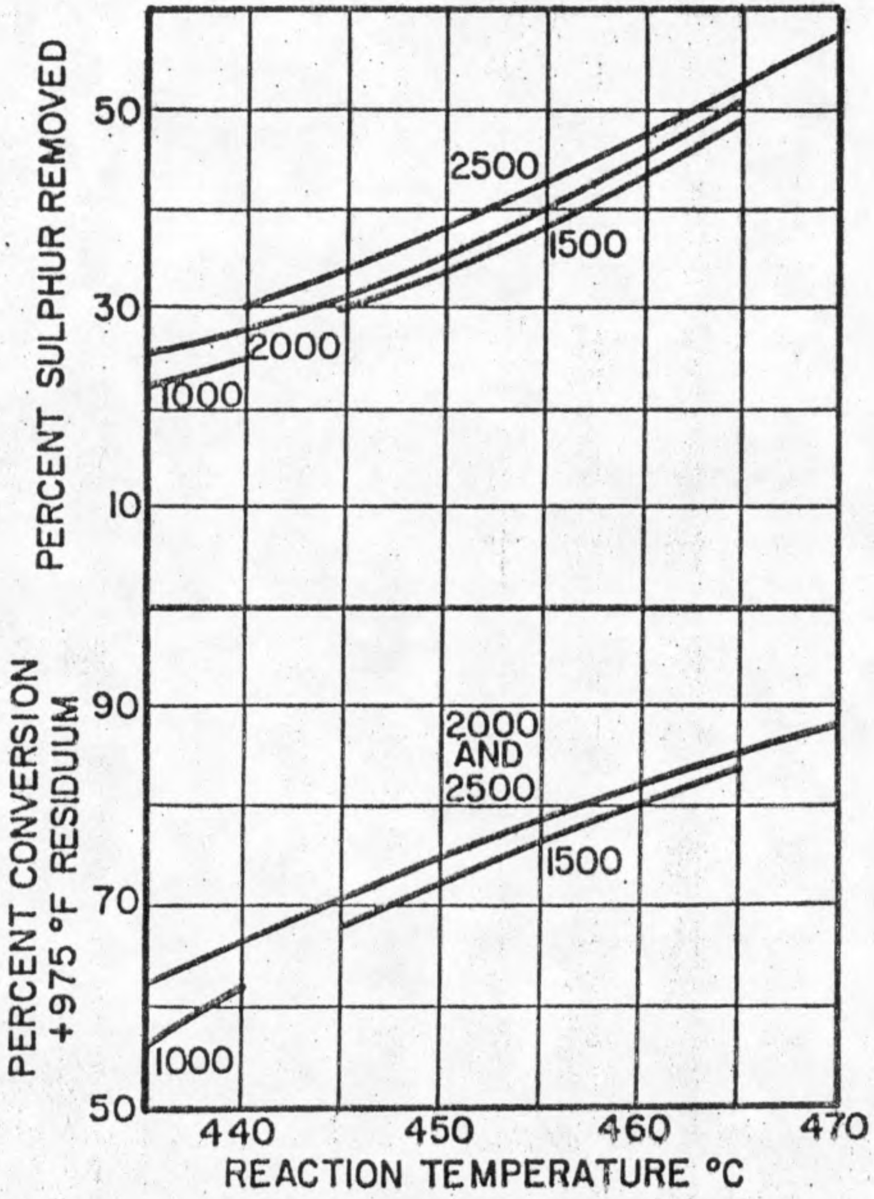


Figure 4. The effect of reaction temperature on the pitch conversion and sulphur removal at selected operating pressures.

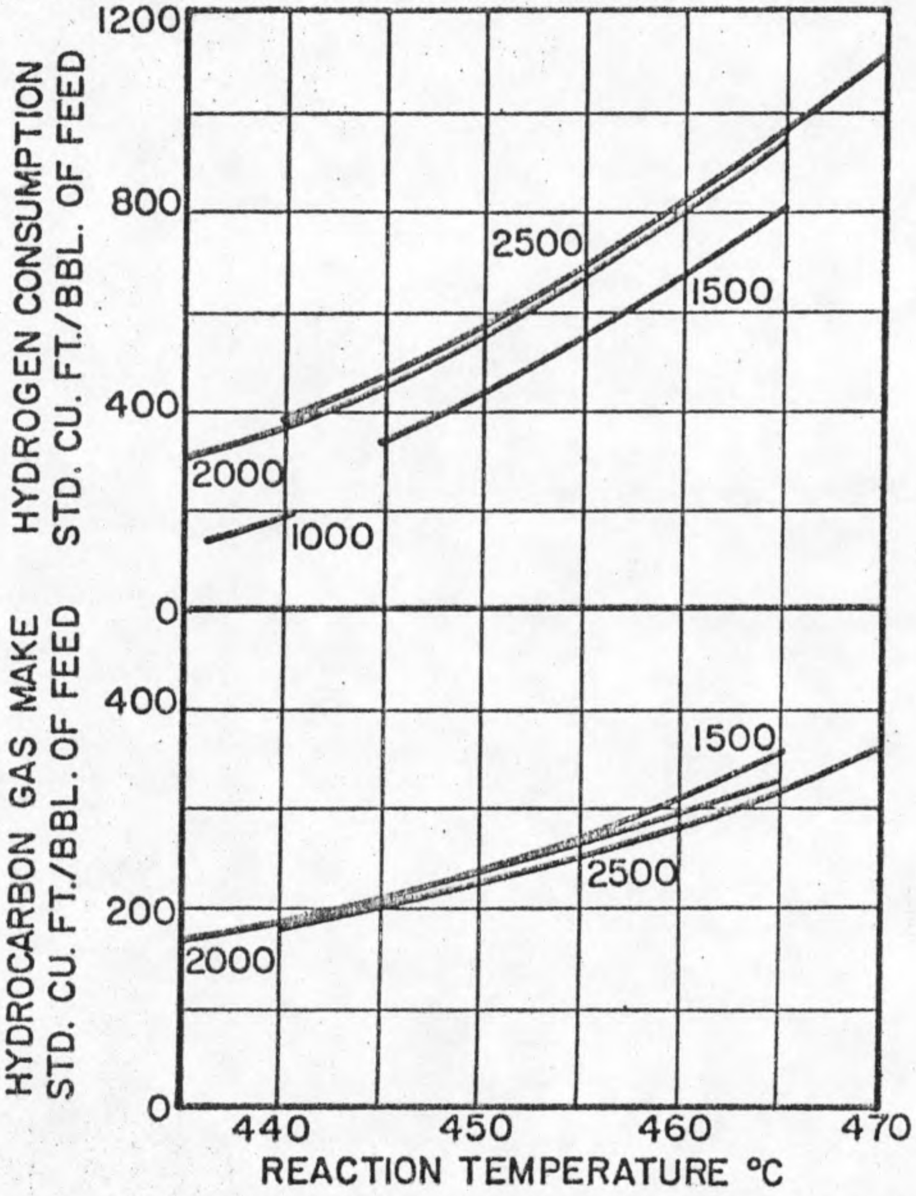


Figure 5. The effect of reaction temperature on the hydrogen consumption and hydrocarbon gas make at selected operating pressures.

Claim 1

A process for the conversion of most of the residuum hydrocarbon (60-90%) present in heavy oil and bitumen into low-boiling distillate fractions by heating the feed oil with medium-pressure hydrogen (750-3500 psi) and passing the mixture up-glow through a continuous pipe reactor at liquid hourly space velocities of 0.5 to 4.

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