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OTTAWA

*A COMPARISON OF  
THERMAL AND CATALYTIC  
HYDROGENATION AS A PRELIMINARY  
STEP IN THE REFINING OF  
ATHABASCA BITUMEN*

J. J. CAMERON, M. A. O'GRADY AND B. I. PARSONS

FUELS RESEARCH CENTRE

DECEMBER 1969

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A Comparison of Thermal and Catalytic Hydrogenation as  
a Preliminary Step in the Refining of Athabasca Bitumen

by

J.J. Cameron\*, M.A. O'Grady\* and B.I. Parsons\*\*

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## ABSTRACT

The report describes a laboratory-scale investigation of thermal (non-catalytic) and catalytic hydrogen treatment processes for converting the residuum material (+990°F) in Athabasca bitumen to distillable hydrocarbon fractions. The experiments were made in the liquid phase, using a conventional flow apparatus with a bottom-feed pipe reactor at pressures from 500 to 3500 psi. The rate of accumulation of sludge (combined tar, coke, and mineral matter) in the reaction vessel was greatest at high conversion levels and low pressures. Continuous operation was not possible at 500 psi, but at 1000 psi the concentration of residuum (including clay) could be reduced to 18-20% without serious difficulty. Considerable gas formation occurred at all pressures in the thermal experiments and at low pressures in the catalytic system. It was only at high pressures that the catalyst suppressed gasification relative to the conversion of the residuum, resulting in a marked increase in the yield of liquid product. The maximum permissible extra cost for catalytic processing, compared to thermal hydrocracking (capital cost plus catalyst), is estimated at 25-30¢/bbl.

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Rapport de recherche R 217 de la Direction des mines  
ÉTUDE COMPARATIVE DE L'HYDROGÉNATION THERMIQUE ET DE  
L'HYDROGÉNATION CATALYTIQUE COMME ÉTAPE PRELIMINAIRE  
DU RAFFINAGE DU BITUME DE L'ATHABASCA

par

J.J. Cameron,\* M.A. O'Grady\* et B.I. Parsons\*\*

RÉSUMÉ

Le présent rapport décrit l'essai à l'échelle expérimentale des procédés d'hydrogénation thermique (non-catalytique) et catalytique servant à convertir les résidus (+990°F) de bitume de l'Athabasca en fractions d'hydrocarbures distillables. Les essais ont été effectués à l'état liquide, au moyen d'un appareil d'écoulement classique comportant un réacteur tubulaire alimenté par le fond sous des pressions de 500 à 3500 livres au pouce carré. Le taux d'accumulation des déchets de raffinage (combinaison de goudron, de coke et de matière minérale) le plus élevé a été enregistré lorsque la pression était au minimum et le niveau de conversion au maximum. Le fonctionnement continu était impossible à une pression de 500 livres au pouce carré, mais à 1000 livres il était possible de réduire la concentration de résidus (y compris l'argile) de 18 à 20 p. 100 sans difficulté. Une quantité considérable de gaz était produite à toutes les pressions lors des essais thermiques et à basse pression lors des essais catalytiques. Ce n'est qu'à hautes pressions que le catalyseur supprimait la gazéification relative à la conversion des résidus, ce qui avait pour effet d'augmenter sensiblement la production de liquide. Le coût estimatif supplémentaire admissible du traitement par catalyseur comparative-ment au coût de l'hydrocraquage (installation plus le coût du catalyseur) est de 25 à 30 cents le baril.

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## INTRODUCTION

The refining of residual oils and tars by hydrogenation processes has been the subject of considerable research (1-6) at the Mines Branch for a number of years. The experimental work has been largely concerned with catalytic hydrogenation, usually with industrial cobalt-molybdate catalysts. The present investigation represents a preliminary examination of the thermal aspects of the hydrogenation process relative to the type of effect and product we have grown to associate with a commercial catalyst. We have elected to describe the experiments done in the absence of catalyst as "thermal hydrogenation". Other names, such as destructive hydrogenation, hydro-visbreaking or hydrogenolysis, are equally applicable. When a material like Alberta bitumen is heated to a high temperature, either with or without hydrogen present, undoubtedly almost every type of reaction takes place (abstraction, hydrogenation, isomerization, etc.) and no name properly describes the chemistry of the situation.

The bitumen, as separated from the sands, retains many refining problems, e.g., 1.5 to 2.5% fine clay mineral matter, 300-500 parts/million of chemically bound nickel and vanadium, 4 to 5% sulphur, 1% oxygen, and 0.4 to 0.6% nitrogen. These properties make catalytic hydrogenation difficult, although not impossible (7). High hydrogen pressures minimize many of the problems but the catalyst does become coated with mineral matter and metals over a period of a few hundred hours and loses activity. The nature of the deposit makes regeneration of the catalyst impractical, and catalyst costs are consequently high.

From the standpoint of the catalyst, the problems appear to be concentrated in the residuum fractions. Once the asphaltene residues 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,

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\* Any fraction distilling below an atmospheric-equivalent temperature of 1000°F.

fixed-bed reactors under conditions suited to the particular boiling range of the feed stock. Satisfactory catalysts are cobalt or nickel molybdates, or some combination of the two, depending on the nitrogen content of the fractions to be treated. Both catalyst types are highly versatile and function well with straight-run feed stocks or with fractions produced thermally (coking) or by hydrogenation.

The objective in the first stage of the refining of the bitumen 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. The mineral matter and the problem hydrocarbon material containing nickel and vanadium must, of course, be retained in the fuel stream. Delayed coking is a very effective way to accomplish all of these things (8-10), but it is not a process which permits any significant variation in the amount of fuel produced (and fuel requirements do change with the nature of the deposit and the season of the year).

In theory, a thermal hydrogenation 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; secondly, the bottom fractions (should) retain sufficient hydrogen to be fluid at high temperatures and thereby simplify handling and storage; and, thirdly, the extent of conversion is variable over a reasonable range as fuel requirements dictate. A marked disadvantage, of course, is the fact that thermal hydrogenation requires high-pressure facilities ( $>1000$  psi) and hence capital costs will be substantially greater.

Under normal circumstances, thermal hydrogenation of heavy crudes is never considered in refinery processing, because one cannot hydrogenate deeply enough at practical pressures. The amount of pitch formed (consisting usually of a mixture of coke, tar and unreacted residuum material) far exceeds the normal fuel requirements and the treatment is seriously out of balance. The prospects change, however, with the high fuel requirements for processing the tar sands. Depending on the location and concentration of the deposits, from



15 to 30% of the bitumen is required as a source of energy for the mining and separation steps. Approximately 50% of the hydrocarbon material initially present can be processed by refining procedures already known and acceptable to the industry. On the average, only 20 to 30% of the bitumen requires hydrogenation, hydrogenolysis or hydrocracking to bring it to the distillable specification. By normal standards this is a relatively low conversion requirement and should, in theory, be easily attainable. Our experimental work indicates that it is possible to achieve the level of conversion required, but that great care must be taken to balance pressure against temperature to prevent coke from slowly accumulating on the vessel walls and in the lines.

## EXPERIMENTAL

### Apparatus and Procedure

Two laboratory-scale, high-pressure flow systems of conventional design were used in the present work. The major components of the apparatus and the method of operation are described in Mines Branch Research Report R194 in connection with an earlier study of the hydrogen refining of bitumen over oxide and sulphide forms of cobalt and molybdenum catalysts (4). The only significant change made in the apparatus was in the manner of feeding the oil and hydrogen to the reaction vessel. In the previous experiments the oil and hydrogen were pumped to the top of the reaction vessel and allowed to flow down through the catalyst bed. For the present work the reaction vessel and the associated piping were inverted and the oil and hydrogen pumped in at the bottom. Diagrams of the flow system and reaction vessel are shown in Figures 1 and 2.

The reaction vessel was machined from 2 1/2-inch-diameter 316 stainless steel. The inside working dimensions were 1-inch diameter by 12 inches long. The main body of the vessel was heated electrically with Calrod-type cable. Additional heating cable was wound around the bottom closure and inlet pipe to act as a preheater for the oil and hydrogen. The temperature of the reaction vessel was regulated by a galvanometer-type controller operating on

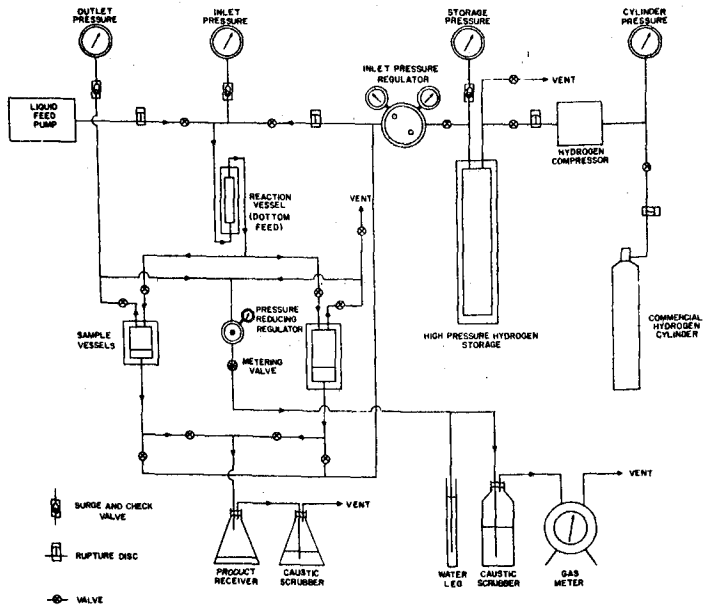


Figure 1 - A schematic diagram of the apparatus.

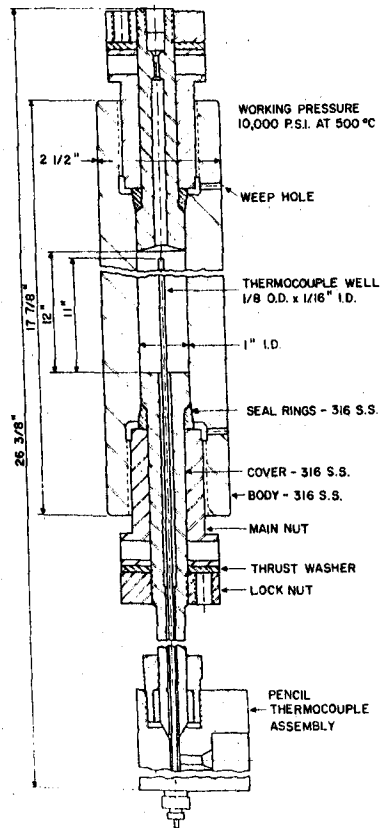


Figure 2 - A diagram of the reaction vessel.

a chromel-alumel thermocouple in contact with the outside surface. The temperature in the reaction zone was measured by means of a second thermocouple extending up a thermocouple well located centrally in the reactor. This thermocouple could be moved up and down, as desired, to determine the temperature profile from top to bottom.

For the thermal hydrogenation study, the reaction vessel was used empty . . . . . no packing whatsoever was placed in the hot zone for those experiments. For the part of the investigation involving the catalyst, the reaction vessel was packed with 3/16 x 3/16-inch pellets of alumina-supported cobalt-molybdate catalyst manufactured by the Nalco Chemical Co. of Chicago, Illinois. The catalyst was reported to consist of 12.5% MoO<sub>3</sub> and 3.2% CoO on activated alumina. The surface area was 280 m<sup>2</sup>/g. The catalyst was purchased as a powder and formed into pellets in the Mines Branch laboratory. The interstitial volume around the pellets in the packed vessel ranged from 48 to 50 ml (the overall volume of the reaction vessel was 150 ml). The interstitial volume was determined by filling the packed reaction vessel with kerosene then draining into a graduated cylinder. Small variations were observed, attributable to changes in the degree of packing which occurred in the course of filling, but the value was never greater than 50 ml.

#### Feed Stock

The feed stock used was separated (but otherwise untreated) bitumen from the sand deposits at Mildred Lake, Alberta. It was supplied to the Mines Branch by Syncrude Canada Ltd. of Edmonton. The inspection analysis of the bitumen is given in Table 1.

#### Analysis of the Products

The extent of conversion of residual material to distillable hydrocarbon (i.e., up to 990°F atmospheric equivalent) was determined, using a modification of the U.S. Bureau of Mines Hempel distillation analysis (11). Conventional ASTM procedures were found not to be satisfactory, because of the tendency of the bitumen to crack and coke at elevated temperatures. A charge of 100 ml was placed in a Hempel distillation flask and distilled rapidly

TABLE 1

Inspection Analysis of Bitumen Feed Stock\*

Component	Weight %
Bitumen	97.35
Water	0.39
Solids	2.28
Carbon	83.12
Hydrogen	10.59
Sulphur	4.75
Nitrogen	0.40
Oxygen (by difference)	1.14
Particle size distribution:	
0-5 $\mu$	71.87% of Total Solids
5-10	13.69
10-20	9.29
20-30	1.96
30-44	0.98
44-74	0.47
74-147	1.19
>147	0.55

\* Supplied by Syncrude Canada Ltd., Edmonton.

TABLE 2

Fractions Collected in Hempel Analysis (Modified)

Fraction No.	Distillation Range		Pressure (mm)	Equivalent Distillation Range at 1 Atm**	
	(°C)	(°F)		(°C)	(°F)
1	RT-100	RT-212	760	RT-100	RT-212
2	100-200	212-392	760	100-200	212-392
3	200-250	392-482	760	200-250	392-482
4	250-275	482-527	760	250-275	482-527
5	RT-225	RT-437	40	275-332	527-630
6	225-300	437-572	40	332-421	630-790
7	RT-300	RT-572	1	421-532	790-990
8	+ 300	+ 572	1	+ 532	+ 990

\*\* Chart PD-449, UOP Method 76.

(using a large, fan-like flame burner) in three steps at a) atmospheric pressure, b) 40 mm, and c) 1 mm. The temperature cuts selected are shown in Table 2.

The sulphur content of the oil samples was determined by an oxygen-bomb microtechnique developed by Siegfriedt, Wiberley and Moore (12). The viscosity measurements were made using a Cannon-Fenske reverse-flow (opaque) viscosimeter according to ASTM procedure D445.

#### EXPERIMENTAL RESULTS AND DISCUSSION

The experimental comparisons of thermal and catalytic hydrogenation shown in the diagrams are based on conditions of equal "throughput"\* of liquid feed and hydrogen into the reactor. Under normal circumstances, with a down-flow fixed-bed arrangement, one would make any comparison on a basis of equal space velocity. The term 'space velocity', however, loses much of its meaning with a bottom-feed arrangement (in the liquid phase) when comparing the effect in packed and unpacked vessels. (In the case of the unpacked vessel used in the thermal experiments, the reaction volume available to the liquid feed and hydrogen was 150 ml, whereas in the vessel packed with catalyst the free volume available to the reactants was only 50 ml.) While not ideal, a comparison on the basis of throughput simplifies the system from the viewpoint of engineering effect.

Experiments were made at four pressures, 500, 1000, 2000 and 3500 psi, and at four temperatures, 390, 410, 430 and 440°C. Considerable operating difficulty was encountered with both systems at low pressures. At 500 psi it was not possible to operate the catalytic system at any of the selected temperatures for an appreciable period of time (24 hours). Even at 1000 psi a little operational difficulty was encountered at the higher temperatures because of the slow accumulation of coke, pitch, mineral and metal deposits on the catalyst. With the purely thermal system, it was possible to operate for extended periods at 500 psi at the low temperatures, but not at the highest temperature. At

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\* 160 ml/hr oil and 3500 cf/bbl hydrogen.

440°C and 500 psi, combined coke, pitch and mineral deposits formed quickly on the vessel walls and in the lines and forced a shut-down after approximately 5 hours of operation. At 1000-psi pressure (and higher), a marked improvement in the operability of the thermal system was observed...the rate of coke and tar formation was less at the higher pressures but, more important, the coke and tar that did form did not accumulate on the vessel walls. Under such conditions it was possible to operate for periods of 40 to 50 hours with relative ease.

The most obvious difference between thermal and catalytic hydrogenation that is observed occurs in the temperature profile through the reaction zone. Typical profiles recorded under various conditions of pressure and peak temperature with the catalytic system are shown in Figure 3 and for thermal hydrogenation in Figure 4. In every case the liquid feed rate was 160 ml/hr and the hydrogen rate 3500 cu ft/bbl. The profiles observed in the presence of catalyst show a sharp peak in temperature approximately one-half to two-thirds the distance up the reaction vessel, due to the exothermic heat of desulphurization and other hydro-refining reactions. At higher pressures and temperatures the peak in the profile is more pronounced as the extent of refining achieved (and the amount of heat released) increases. It must be emphasized that we are not suggesting that a fixed-bed, bottom-feed system is a practical arrangement. The experiments were only conducted in this way to illustrate the difference between the catalytic and thermal systems.

The temperature profiles observed in the purely thermal system (Figure 4) showed a broad band of nearly constant temperature over three-quarters of the reaction vessel. At moderate temperature and pressure the exothermic heat of the refining reactions appears to be in near balance with the endothermic heat of cracking. At high temperature and pressure, where more hydrogenation occurs, there is some evidence of a shallow peak in the profile. Under almost all conditions, however, the system was generally easy to control and reliable estimates of the average reaction temperature were possible. Variations in the rate of rise of the temperature in the last stages of the inlet pipe and the first inch of two of the reactor are due to changes

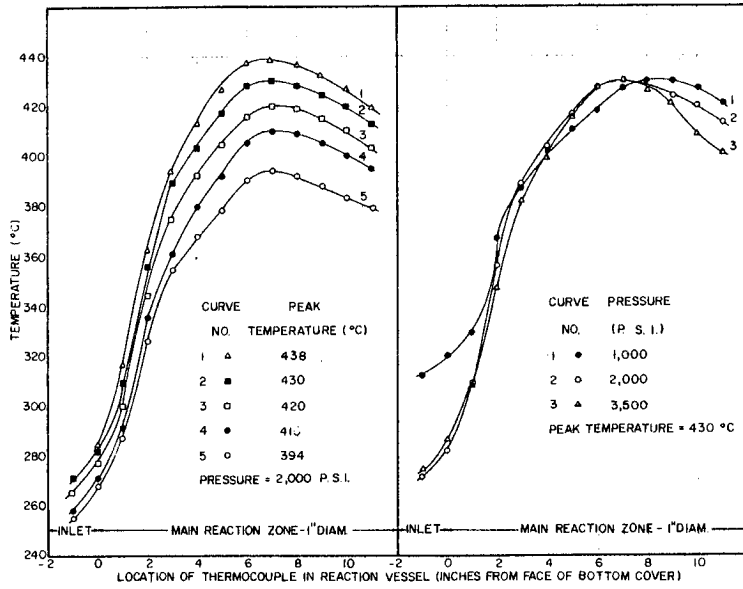


Figure 3 - Typical temperature profiles in catalytic hydrogenation.

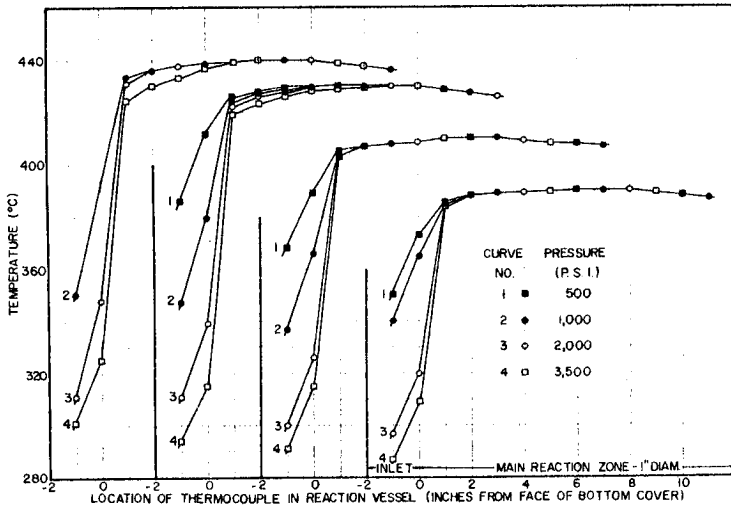


Figure 4 - Typical temperature profiles in thermal hydrogenation.

in the extent of mixing which occurs as the gas flows through the reactor.... in the experiments shown in the figures the gas flow was held constant, and the mixing caused by the gas (frequency and size of bubbles) increased at lower pressures.

The effects of reaction temperature and hydrogen pressure on the general nature of the product formed from the bitumen by catalytic and thermal hydrogenation are summarized in Figures 5, 6, 7 and 8. All conditions being equal, the overall specific gravity of the product formed in the catalytic system was substantially lower than that obtained thermally, but the amount of residuum (+990°F) remaining in the products was essentially the same. The difference in the specific gravity was not due to any large difference in the boiling-range nature of the product (in fact, slightly more light-ends were formed in the thermal experiments, which would tend to reverse the observed effect). Under the best of test conditions the thermal treatment removed only 25-26% of the total sulphur in the feed, as compared with 73-75% for the treatment in the presence of catalyst. A brief summary of the sulphur concentration remaining in the various fractions is given in Table 3. Higher hydrogen pressures, up to 3500 psi, had little effect on the sulphur content of the product from the thermal process but did enhance the catalytic desulphurization of the heavier fractions slightly.

The conversion of the residuum material to distillable hydrocarbon was measurably less at the higher hydrogen pressures in both the catalytic and thermal experiments. While it is essential that the hydrogen pressure be sufficient to reduce (or otherwise modify) the coke and tar formation to a point where it is possible to operate for an extended period, the use of too great a pressure appears to retard the cracking necessary for the conversion of the residuum. This effect serves again to illustrate the inadequacy of the term "hydrogenation" with reference to processing a mixture like the bitumen. Normal chemical reactions associated with hydrogenation, such as desulphurization, are enhanced by higher hydrogen pressures. Other work done at the Mines Branch with high-boiling coker distillates (3) and vacuum bottoms (6) suggests that the hydrogenation of residuum material is not greatly affected by changes in



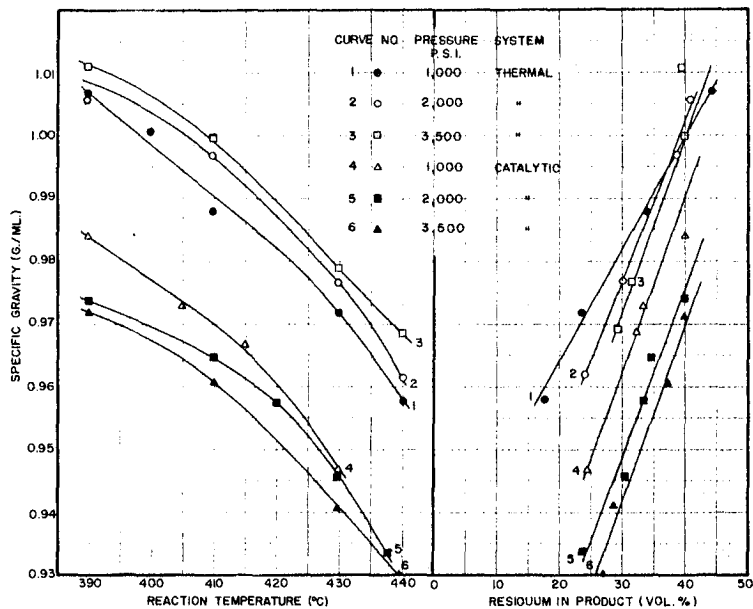


Figure 5 - The effects of reaction temperature and pressure on the specific gravity of the product and the amount of residuum material left unconverted.

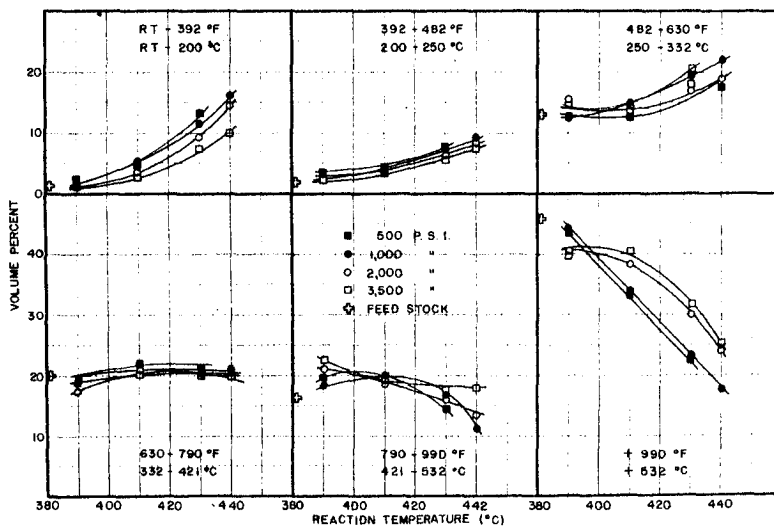


Figure 6 - The results of the distillation analyses on the products formed in the thermal hydrogenation experiments.

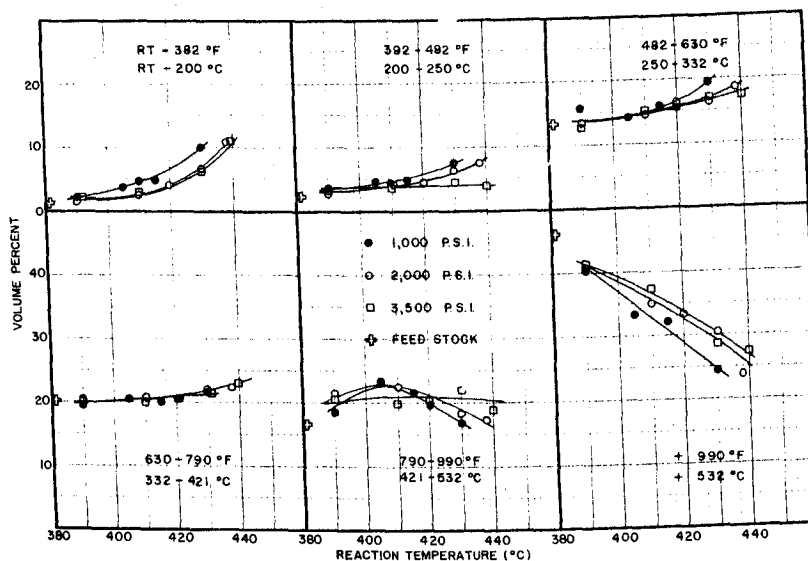


Figure 7 - The results of the distillation analyses on the products formed in the catalytic hydrogenation experiments.

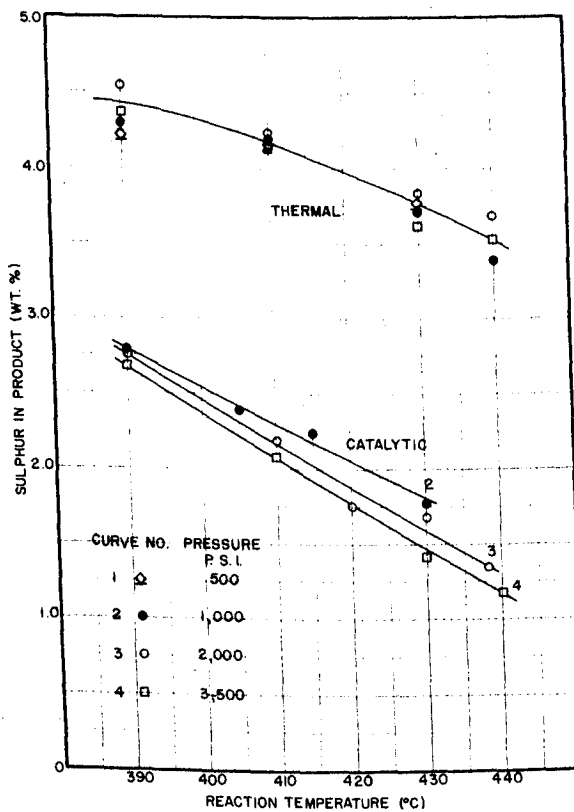


Figure 8 - The effects of reaction temperature and pressure on the sulphur concentration in the product.

TABLE 3

A Summary of the Specific Gravity and Sulphur Concentration in the Various Fractions

BOILING RANGE (Atmos Equiv Temp)		FEED STOCK		CATALYTIC HYDROGENATION					
				430°C 1000 psi		430°C 2000 psi		430°C 3500 psi	
°C	°F	sp gr	% S	sp gr	% S	sp gr	% S	sp gr	% S
RT-100	RT-212	-	-	0.722	0.17	0.737	0.16	-	0.19
100-200	212-392	-	-	0.796	0.19	0.802	0.19	0.808	0.25
200-250	392-482	-	1.75	0.850	0.28	0.848	0.20	0.849	0.27
250-275	482-527	0.876	2.26	0.873	0.35	0.870	0.24	0.868	0.27
275-332	527-630	0.912	2.59	0.901	0.60	0.893	0.44	0.891	0.25
332-421	630-790	0.953	3.20	0.931	0.81	0.920	0.50	0.916	0.52
421-532	790-990	0.987	3.90	0.966	1.28	0.949	0.94	0.940	0.85
+532	+990	1.106	6.10	1.106	3.97	1.069	3.73	1.059	3.70
THERMAL HYDROGENATION									
		430°C 500 psi		440°C 1000 psi		440°C 2000 psi		440°C 3500 psi	
		sp gr	% S	sp gr	% S	sp gr	% S	sp gr	% S
RT-100	RT-212	0.715	0.59	-	0.45	-	0.69	0.722	0.67
100-200	212-392	0.804	2.06	0.786	1.38	0.785	1.24	0.792	1.65
200-250	392-482	0.858	2.18	0.852	1.82	0.852	2.00	0.852	1.89
250-275	482-527	0.883	2.23	0.881	2.62	0.886	2.44	0.886	2.47
275-332	527-630	0.916	2.71	0.920	2.76	0.916	2.63	0.907	2.57
332-421	630-790	0.962	3.36	0.973	3.46	0.955	3.18	0.953	2.80
421-532	790-990	1.022	3.91	1.043	4.58	1.012	4.18	1.000	3.84
+532	+990	1.192	5.90	1.194	6.20	1.176	5.35	1.161	5.42

pressure in the range 1000-3000 psi. Deep hydrogenation of high-molecular-weight hydrocarbons occurs only at elevated pressure (5000-10,000 psi). The effects and changes observed at relatively low hydrogen pressures are largely the result of the hydrogenation of the products of the primary cracking reaction.

The viscosity of the product formed under various conditions of reaction temperature and pressure is shown in Figure 9. In the purely thermal experiments the viscosity was generally lower the greater the reaction temperature and the lower the pressure...in accordance with the relative amounts of residuum matter left in the product. In the presence of catalyst the effect was not so straightforward. The viscosity of the catalytic product was low at high reaction temperatures, but increased hydrogenation and refining of the distillable fractions at higher pressures appear to offset the adverse effect of pressure on the conversion of the residuum. The net effect is that the viscosity is independent of operating pressure (1000 to 3500 psi).

The volume and weight yields of liquid product obtained under the various test conditions are summarized in Table 4 and Figure 10. By "liquid product" is meant the oil and residuum (including clay) drained from the receivers, with a minor correction for the  $C_4$  hydrocarbons contained in the off-gases. For the purpose of the present laboratory-scale investigation, the yields have not been corrected for sulphur removal.

The yields obtained in both the thermal experiments and at low pressures in the catalytic system indicate a marked increase in gas formation at the higher reaction temperatures. At 1000 psi and  $440^\circ C$  (corresponding to a conversion level equivalent to approximately 20% residuum in the product), the weight yields were only 93%. At lower temperatures, where comparatively less conversion of the residuum material occurred, the weight yields were greater, approaching 100% at  $390^\circ C$ . The changes in the specific gravity were such that, at 1000 psi, the volume yield was nearly 100% at all temperatures with the purely thermal system and between 101 and 102% for the catalytic experiments. Much improved yields were generally observed at the higher pressures. The best yields obtained were in the region 105 to 106% (volume yield) with the catalytic system at 3500 psi. It is only at the higher pressures that the

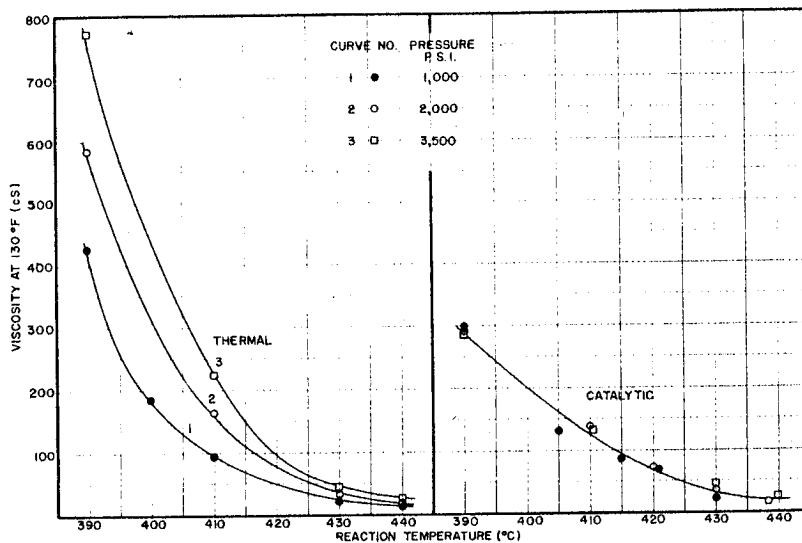


Figure 9 - The effects of reaction temperature and pressure on the viscosity of the product.

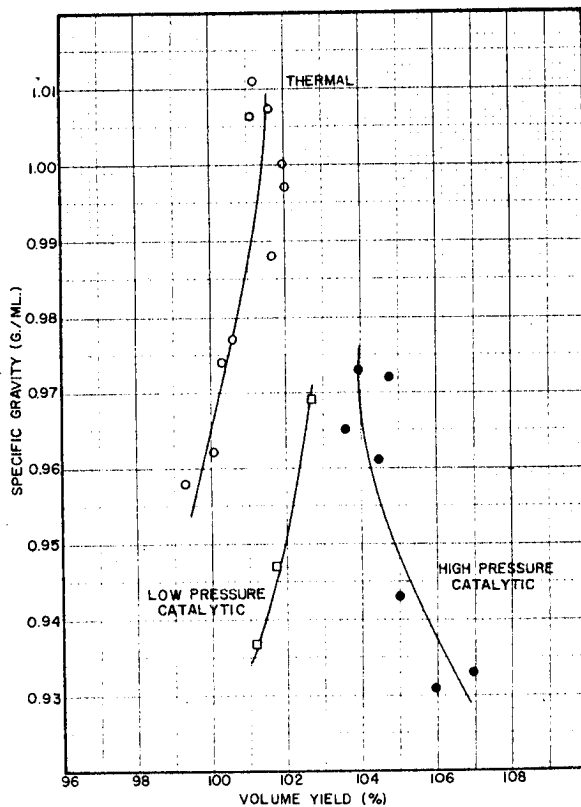


Figure 10 - The effect of the level of conversion (as reflected in the overall specific gravity of the product) on the volume yield of liquid product.

TABLE 4

A Summary of the Effect of Temperature and Pressure on the Weight and Volume Yield of Product

Liquid feed rate: 160 ml/hr Gas flow rate: 3500 cu ft/bbl		HYDROGEN PRESSURE (psi)											
		500			1000			2000			3500		
		sp gr (g/ml)	wt yield %	vol yield %	sp gr (g/ml)	wt yield %	vol yield %	sp gr (g/ml)	wt yield %	vol yield %	sp gr (g/ml)	wt yield %	vol yield %
SYSTEM	Reaction Temperature (°C)												
THERMAL	390	1.014	100.0	100.9	1.007	100.0	101.6	1.006	99.4	101.1	1.011	100.0	101.2
	410	0.996	96.2	98.8	0.988	98.2	101.7	0.997	99.5	102.1	1.000	99.7	102.0
	430	0.971	91.8	96.8	0.974	95.5	100.3	0.977	93.6	98.0	0.977	96.1	100.6
	440	-	-	-	0.958	93.0	99.3	0.962	94.1	100.1	0.969	96.6	102.0
						0.984	100.1	104.0	0.973	99.0	104.0	0.972	99.7
CATALYTIC	390		-		0.969	97.3	102.7	0.965	97.7	103.6	0.961	98.1	104.5
	410		-		0.947	94.2	101.7	0.943	96.9	105.1	0.942	98.9	107.4
	430		-		0.937	92.7	101.2	0.931	96.7	106.3	0.933	97.5	106.9
	440		-										

catalyst is able to suppress gasification relative to the conversion of residuum, with the obvious benefits of increased volume yield of liquid product.

The ultimate objective, of course, is to minimize costs. In this direction, a qualitative estimate of the maximum permissible "extra" cost for catalytic processing (catalyst cost plus extra capitalization for the higher pressure requirement) can be obtained from the differences in a) the yield of liquid product and b) the amount of hydrogen to be generated (the additional gas formed thermally would have to be recycled through the hydrogen generator in order to sustain the process). In round numbers, the best volume yield of liquid product observed with catalyst was 106% and the lowest in the thermal experiments was 99%. Placing a value of \$2.00/bbl on the product, the value of the lost liquid is approximately 14-15 cents. The extra cost involved in regenerating the additional 700-800 cu ft of hydrogen/bbl required in the thermal system is probably of the order of 10-15 cents. The resultant maximum permissible additional cost for a catalytic pretreatment of the bitumen is therefore in the range of 25-30 cents per barrel. Obviously there are a great many other factors involved than the two mentioned, but the figure does represent an interesting (and difficult) target.

In conclusion, it should be pointed out that not everyone is in agreement on the use of the bottoms as the primary energy source. Proponents of stricter air-pollution regulations would like to see almost any other fraction used as fuel. In principle, it should be possible to catalytically hydrogenate the residual fractions (or, at least, a large part of them) to distillable hydrocarbon and use the off-gases as the main fuel. The gases, of course, would be much easier to clean up than the coke. However, this is an awkward position from which to argue, because it seems unreasonable to use that part of the feed upon which the most work has been done, i.e. hydrogenation, as fuel... particularly when the amount of hydrogen required would be very large! Exhaustive catalytic hydrogenation will only become practical with the development of a catalyst which will permit extensive cost recovery: either a long-lived species, amenable to hydrogenation at low-medium pressures and unaffected by nickel or vanadium, sulphur, nitrogen or mineral matter, or an inexpensive

catalyst which could be used once, then jettisoned. Another possibility is the development of a catalyst that would act as a "getter" or concentrator for a valuable impurity such as vanadium. Overall catalyst and processing costs must be kept low to be competitive.

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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, 1951, pp 289-305.
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, Dept. of Mines and Technical Surveys, Ottawa (1958).
3. A.R. Aitken, W.H. Merrill and M.P. Pleet - Canadian Journal of Chemical Engineering, Industrial Section, 1964, pp 234-238.
4. M.A. O'Grady and B.I. Parsons - "The Hydrogenation of Alberta Bitumen over Cobalt-Molybdate Catalyst", Mines Branch Research Report R-194, Dept. of Energy, Mines and Resources, Ottawa (1967).
5. B.I. Parsons - "A Method of Estimating the Amount of Hydrogen Required to Upgrade Residual Oils and Tars", Mines Branch Technical Bulletin TB 100, Dept. of Energy, Mines and Resources, Ottawa (1968).
6. D.H. Quinsey, W.H. Merrill, W.A.O. Herrmann and M.P. Pleet - "Combined Liquid- and Vapour-Phase Hydrocracking of Heavy Oils", Can. J. Chem. Eng., 47, 418-421 (1969).
7. D.H. Quinsey, M.P. Pleet and W.H. Merrill - "Hydrocracking of Athabasca Bitumen by a High Pressure Catalyst-Slurry Process", 19th Canadian Chemical Engineering Conference, Edmonton, Alberta, October 19-22, 1969, Preprint Number 5.
8. L.E. Djingheuzian and T.E. Warren - Canadian Journal of Technology, 29, 170-189 (1951).
9. T.E. Warren, E.J. Burrough and L.E. Djingheuzian - Canadian Oil and Gas Journal, 3, 32-34 (1950).
10. E.D. Innes and J.V.D. Fear - "Canada's First Commercial Tar Sand Development", Seventh World Petroleum Congress, Mexico, 1967, Vol.3, pp 633-650.
11. 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).
12. R.K. Siegfriedt, J.S. Wiberley and R.W. Moore - Analytical Chemistry, 23, 1008-1011 (1951).

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