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MA THERMAL HYDROCRACKING OF ATHABASCA **BITUMEN: STEADY-STATE EFFECTS ON PRODUCT** YIELDS AND QUALITIES IN THE ABSENCE OF SCRUBBING OF THE RECYCLE GAS

A.M. Shah, B.B. Pruden and J.M. Denis

AUGUST 1976

Laboratoire d' / Elliot Lake / Laboratory Mines Branch - Direction des mines

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ENERGY RESEARCH PROGRAM ENERGY RESEARCH LABORATORIES CANMET REPORT 77-44

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Available by mail from:

En vente par la poste:

Printing and Publishing

Imprimerie et Édition

Supply and Services Canada, Ottawa, Canada K1A 0S9 Approvisionnements et Services Canada,

Ottawa, Canada K1A 0S9

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Ottawa, Canada K1A 0G1

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Catalogue No. M38-13/77-44

Price: Canada: \$1.00

No de catalogue M38-13/77-44

ISBN 0-660-02141-3

Other countries: \$1.20

ISBN 0-660-01241-3

Prix: Canada: \$1.00 Autres pays: \$1.20

Price subject to change without notice.

Prix sujet à changement sans avis préalable.

THERMAL HYDROCRACKING OF ATHABASCA BITUMEN: STEADY-STATE EFFECTS ON PRODUCT YIELDS AND QUALITIES IN THE ABSENCE OF SCRUBBING OF THE RECYCLE GAS

bу

A.M. Shah*, B.B. Pruden* and J.M. Denis**

ABSTRACT

The thermal hydrocracking of Athabasca bitumen at 13.89 MPa was investigated in the absence of scrubbing of the recycle gas. The experiments were carried out in a 3.8-cm ID x 4-m long reactor at temperatures of 445 and 450° C, liquid hourly space velocities (LHSV) of 1 and 2, and recycle hydrogen gas rates of 0.0388 and 0.0425 m³/h at the system pressure and 20° C. At an LHSV of 2, three to four hours were required for the recycle gas purity to stabilize at constant values of 73.5% and 71.5% hydrogen at 445° C and 450° C respectively. However, at an LHSV of 1 and 450° C, ten to twelve hours were required to attain a constant recycle gas purity of 62.6% H₂. Once the recycle gas purity reached a constant value of 62.6% H₂, operating time had no effect on the product yields and gaseous and liquid products of consistent quality were obtained.

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^{*} Research Scientists and ** Head, Process Engineering Section, Canadian Fossil Fuel Research Laboratory, Energy Research Laboratories, Canada Centre for Mineral and Energy Technology, Department of Energy, Mines and Resources, Ottawa, Canada.

HYDROCRAQUAGE THERMIQUE DU BITUME DE L'ATHABASCA: EFFETS EN REGIME REGULIER SUR LES RENDEMENTS ET LES QUALITES DES PRODUITS EN L'ABSENCE D'EPURATION DU GAZ DE RECYCLAGE

par

A.M. Shah*, B.B. Pruden* et J.M. Denis**

RESUME

L'hydrocraquage thermique du bitume de l'Athabasca, effectué à 13,89 MPa, a été étudié en l'absence d'épuration du gaz de recyclage. Les expériences ont été faites dans un réacteur de 3,8 cm de dimension intérieure et de 4 m de longueur à des températures de 445 et 450°C, avec des vitesses spatiales horaires des liquides (V.S.H.L.) de 1 et 2, et des taux d'hydrogène recyclé de 0,0388 et de 0,0425 m³/h, à la pression du système et à 20°C. A une V.S.H.L. de 2, de trois à quatre heures ont été nécessaires pour que la pureté du gaz de recyclage se stabilise à des valeurs constantes de 73,5% et 71,5% d'hydrogène à 445°C et 450°C respectivement. Toutefois, à une V.S.H.L. de 1 et à une température de 450°C, il a fallu de dix à douze heures pour obtenir une pureté de gaz de recyclage de 62,6% d'hydrogène. Une fois que la pureté du gaz de recyclage a atteint la valeur constante de 62,6% d'H₂, le temps d'opération n'a aucun effet sur les rendements de produits, et 1°on obtient des produits gazeux et liquides de qualité constante.

Droits de la Couronne réservés

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CONTENTS

$ar{ ilde{ ilde{I}}}$	age
Abstract	i
Resumé	ii
Introduction	1
Experimental · · · · · · · · · · · · · · · · · · ·	2
Feedstock	2
Apparatus and Procedure	2
Results and Discussion	3
1. Recycle-Gas Purity and Product Yields	3
2. Gaseous Products	4
3. Liquid Products	5
Conclusions	7
Acknowledgments	7
References	8

TABLES

No.		Page
1.	Properties of Bitumen Feed Stock	10
2.	Experimental Operating Conditions	11
3.	Comparison of Product Yields and Pitch Conversion	11
4.	Comparison of Results for run 82-5-3	12

FIGURES

No.		Page
1.	Schematic Diagram of Pilot Plant	13
2.	Recycle-Gas Purity as a Function of Operating Time	14
3.	Off-Gas Rates as a Function of Operating Time	15
4.	Effect of Operating Time on the Off-Gas Rate and the Hydrogen Rate	1.6
5.	Off-Gas Composition and Composite Composition of the Hydrocarbon Gas as a Function of Operating Time	17
6.	Product Yields and Pitch Conversion as a Function of Operating Time	18
7.	Density at 15°C of the Liquid Products and Asphaltene, Coke and Ash Contents of Total Liquid Product as a Function of Operating Time	19
8.	Liquid Product Distributions as a Function of Operating Time	20
9.	Effect of Operating Time on Saturate, Olefin and Aromatic Contents of the Distillate Fractions • • • • • • • • • • • • • • • • • • •	21
10.	Sulphur and Nitrogen Contents of the Liquid Products as a Function of Operating Time	22
11	Pitch Properties as a Function of Operating Time	23

INTRODUCTION

The refining of Canada's low grade petroleum resources to clean liquid fuels is complicated by the presence of unwanted minerals, metals and sulphur. In addition, because the heavy oils or bitumens are hydrogen poor the material must be coked to remove carbon, or hydrogenated and cracked to produce distillable liquid fuels. In keeping with the Department of Energy, Mines and Resources (EMR) policy of maximum utilization of non-renewable resources, CANMET (Canada Centre for Mineral and Energy Technology) has supported research on hydrogenation and cracking, or hydrocracking. Earlier work was focussed on catalytic hydrocracking (1-6) but more recently a thermal hydrocracking process has been developed (7).

Thermal hydrocracking of Athabasca bitumen offers an excellent alternative method to the delayed coking or flexicoking processes in the first-stage refining of bitumen or heavy oil to distillable hydrocarbons. The yield of distillate oil is 10-15% higher, the amount of pitch or fraction boiling above 525°C can be varied to suit energy requirements, and the pitch can easily be gasified. Earlier work on thermal hydrocracking of Athabasca bitumen (8,9) had established the relationships between such process variables as temperature, pressure, liquid feed rate, recycle-gas rate, and such measured quantities as pitch conversion, product yields, desulphurization, hydrocarbon-gas make, and hydrogen consumption. Recent work described in this report was carried out with a recycle-gas purity of 85 vol % H₂, obtained by oil-scrubbing the recycle-gas and adding pure hydrogen make-up.

In discussions with people from industry, the important question of whether scrubbing is necessary has often been raised because, in refinery operations, hydrogen-rich streams are available at 60-85% hydrogen and scrubbing is expensive. Accordingly, the objectives were to determine the time required to attain apparent equilibrium conditions and to study the effect of operating time on product yields and qualities during a steady-state operation.

During the transient period, the recycle-gas purity decreases in the absence of scrubbing until it reaches a minimum steady-state value. In the steady-state operation, an equilibrium is established whereby the rates of formation of hydrogen sulphide and hydrocarbon gases equal the rates of removal of these components in the off-gases. The rate of addition of fresh

make-up hydrogen to maintain the system pressure also equals the rate of chemical hydrogen consumption in the liquid product and off-gases plus the dissolved hydrogen removed in the oil products. Presumably the decrease in recycle-gas purity would affect the products over a long period such as 10 to 60 liquid residence times.

This report is mainly concerned with the effects of operating time on product yields and qualities in the absence of recycle-gas scrubbing. The effects of the recycle-gas purity on product yields and qualities have been reported elsewhere (10).

EXPERIMENTAL

Feedstock

The feedstock used was Athabasca bitumen, topped to 260°C, supplied by Great Canadian Oil Sands Limited, Fort McMurray, Alberta. Typical properties and distillation analysis of the bitumen are given in Table 1.

Apparatus and Procedure

Detailed descriptions of the pilot plant and the process were given in previous reports (8,9,11). A simplified schematic diagram of the pilot plant is shown in Fig. 1. The actual operating conditions employed for the three different experimental runs are summarized in Table 2. The temperature of the liquid-phase reactor $(3.81 \text{ cm ID } \times 3.95 \text{ m long})$ was controlled by four equally-spaced electrical heaters. Reactor temperatures were measured by six thermocouples located centrally in the vessel. In this investigation, the scrubber oil was not circulating and the recycle gas was not scrubbed.

The recycle-gas samples were analyzed every half hour for runs 40-1-1 and 40-2-1, and every two hours for run 82-5-3. Also, the heavy-oil off-gas and light-oil off-gas samples were analyzed every six hours during run 82-5-3. For runs 40-1-1 and 40-2-1, the light-oil and heavy-oil samples were collected every half hour during the four-hour test period after the runs were on-stream. For run 82-5-3, two-hour liquid samples were collected every six hours after it was on-stream. The liquid product samples were weighed accurately. The off-gas flows of the recycle-gas sample, light-oil gas and heavy-oil gas were measured by wet-test meters.

The extent of conversion of the residual material (pitch) to distillable hydrocarbons at up to $525^{\circ}C$ atmospheric equivalent was determined using a Podbielniak Equilibrium Flash Still, Model 500 (12,13), and the product distribution of the distillate oil (-525°C) was measured using a modified U.S. Bureau of Mines Hempel distillation procedure (14). The sulphur content of the liquid products was determined by X-ray fluorescence and the gas samples were analyzed by a mass spectrometer.

RESULTS AND DISCUSSION

The results of this investigation are presented and discussed in three sections. In the first, the results for all three runs are given for recycle-gas purity and product yields. In sections 2 and 3, the detailed results for run 82-5-3 are presented under the headings "Gaseous Products" and "Liquid Products" respectively.

1. Recycle-Gas Purity and Product Yields

The recycle-hydrogen gas purity as a function of operating time is shown in Fig. 2. As the reaction progressed, the recycle-gas purity decreased as a result of the formation of hydrocarbon gases and hydrogen sulphide and quickly reached a constant value. This represented a steady-state value in the absence of scrubbing. At an LHSV of 2, the recycle-gas purity attained a constant value of 73.5% H_2 at 445 $^{\circ}$ C for run 40-1-1 and 71.5% H_2 at 450 $^{\circ}$ C for run 40-2-1. The latter run was a continuation of the former, with a onehour delay for the temperature to increase by 5°C. Increasing the reaction temperature has the effect of increasing pitch conversion as well as increasing the formation of gases. This explains the decrease in the recycle-gas purity from 73.5% H_2 to 71.5% H_2 . While it required three to four hours at an LHSV of 2 to reach a constant recycle-gas purity, at an LHSV of 1 (run 82-5-3), ten to twelve hours were needed for the recycle-gas purity to attain a constant value of 62.6% H_2 . As the LHSV was reduced from 2 to 1, the liquid residence time in the reactor doubled and the conversion increased with higher production of gaseous and distillate oil products. The liquid product yields and pitch conversion are summarized and compared in Table 3

with previously observed results with recycle-gas purity of 85% H $_2$. The differences in value were less than 4%. The effects of LHSV and temperature were consistent with those reported previously (8). The detailed comparison of results for run 82-5-3 is made later in section 3 and Table 4.

The results for run 82-5-3 at 13.89 MPa, 450° C, LHSV of 1 and recycle-gas rate of 0.0425 m³/h at pressure and 20° C are presented in Sections 2 and 3. An experimental value at time "t" corresponds to a two-hour sampling period from (t-1) to (t+1). The variation in the liquid feed-rate was less than 2%. The gas flow-rates are expressed as m³/t of feed at 20° C and 101.34 kPa.

2. Gaseous Products

The production of off-gases (recycle-gas sample, light oil, heavy oil and total) as a function of operating time is shown in Fig. 3. The flowrates of H2, H2S and hydrocarbon off-gases, and the amounts of fresh make-up hydrogen fed and hydrogen consumed during the reaction as a function of operating time are illustrated in Fig. 4. About 93% of the hydrogen fed was consumed by the reaction, the remainder being hydrogen dissolved in oil products and sample gas. About 10.5% of the hydrogen consumed was for the formation of $\rm H_2S$, 13.5% was consumed for the production of hydrocarbon gases and 76.0% went to the oil to improve the quality of the liquid products. The quantity of $\mathrm{H}_2\mathrm{S}$ produced was calculated from the quantity of sulphur removed based on the liquid analyses. Furthermore, based on past experience, and because H2S is difficult to measure in the gas streams, it was assumed that, of the total amount of $\mathrm{H}_{2}\mathrm{S}$ formed, 0.5% would go out with the recycle-gas-sample off-gas, 3.0% with the heavy-oil off-gas and 96.5% with the light-oil off-gas. Based on this assumption and the gas analyses, the compositions of the recycle-gas, light-oil off-gas and heavy-oil off-gas were determined. The composition of the total off-gas as $\mathrm{H_2}$, $\mathrm{H_2}\mathrm{S}$ and hydrocarbon gas and of the composite hydrocarbon gas as a function of operating time are shown in Fig. 5. The total off-gas contained about 16.6% H2, 23.6% H2S and 59.8% hydrocarbon gas by The average molecular weight of the hydrocarbon gas was 31. average hydrocarbon gas analysis by volume was:

Methane	(A)	49.7%
Ethane	(B)	17.1%
Propane	(C)	13.6%
Butanes	(D)	10.9%
i-Pentane	(E)	4.4%

The balance of the gases, not shown in Fig. 5, consisted of mixed butenes (3.1%) and mixed pentenes (1.2%).

Figures 3 to 5 show that gaseous products of consistent quality were formed, unaffected by operating time.

3. Liquid Products

The effects of operating time on the liquid product yields (based on feed) and pitch conversion are shown in Fig. 6. The average total liquid product yield was 93% by weight and 102% by volume. The weight yield of -525° C distillate oil was 84% and that of $+525^{\circ}$ C pitch was 9%. The pitch conversion was 82.5%

Figure 7 illustrates the density at 15°C of the liquid products, and the asphaltene, coke and ash contents of the total liquid product as a function of operating time. While the asphaltene content was calculated as the pentane insolubles minus the benzene insolubles, coke content was determined as the difference between the benzene insolubles and the ash. The reasons for using this terminology have been discussed elsewhere (15). While the density at 15°C of the total liquid product was 0.923 kg/l, that of -525°C distillate oil and +525°C pitch were 0.898 and 1.249 kg/l respectively. The average asphaltene, coke and ash contents by weight of the total liquid product were 3.9%, 1.65% and 0.55% respectively. The distribution of the liquid products shown in Fig. 8 and the saturate, olefin and aromatic contents by volume of the distillate fractions IBP - 200°C and 200-250°C shown in Fig. 9 indicate that the operating time had no effect on the product qualities.

The sulphur and nitrogen contents of the liquid products as a function of operating time are presented in Fig. 10. While the sulphur in the total liquid product was 2.5% (sulphur removal of about 51%) virtually no nitrogen was removed. The nitrogen content of -525° C distillate oil was consistent, whereas that of $+525^{\circ}$ C pitch showed wide variations, possibly due to errors in analysis.

Other properties related to the pitch are shown in Figure 11. The nickel and vanadium contents were 650 and 1700 ppm by weight. The Conradson carbon residue of the pitch showed slight variation of less than 5% with operating time. This variation in the Conradson carbon residue parallelled the variation in the pitch conversion indicating the interrelationship of these two quantities (Fig. 6). The average coke and ash contents of the pitch were 19 and 6.5 wt % respectively, regardless of the operating time. The metals and minerals were retained in the pitch.

The results of run 82-5-3 are compared in Table 4 with those reported by Shah, Pruden and Denis (10) at similar operating conditions in the absence of recycle-gas scrubbing. The pitch conversion, hydrogen consumption, sulphur removal and the production rates of hydrogen sulphide and of hydrocarbon gases were similar. The liquid product yields and qualities were within the limits of experimental error, indicating the reproducibility/ of the results in the absence of recycle-gas scrubbing.

As mentioned earlier, most of the thermal hydrocracking research has been carried out with recycle-gas purity of 85% H₂. In the present study with no recycle-gas scrubbing, only recycle-gas samples were analysed during the unsteady-state operation (Fig. 2). One-hour tests during the unsteady-state period and detailed analyses of gaseous and liquid products are recommended to determine the effect of the recycle-gas purity in the unsteady-state period. Of interest also would be pilot-plant experiments of two-to-three weeks duration or life runs in the absence of recycle-gas scrubbing to establish the operability of the process at industrial recycle-gas purities and to investigate how the time-dependent processes such as coke formation and metal sulphide deposition might affect the operation. If these experiments were successful, the scrubbing operation, and thus its cost, could be eliminated.

CONCLUSIONS

The thermal hydrocracking of Athabasca bitumen at 13.89 MPa has been successfully carried out in the absence of recycle-gas scrubbing. Decreasing the LHSV from two to one almost doubled the time required for the recycle-gas purity to attain a minimum steady-state value.

The experiments showed that products of consistent quality can be obtained when the recycle-gas is not scrubbed and that a steady-state is reached with most of the hydrogen sulphide and hydrocarbon gases removed in the light-oil off-gas stream.

ACKNOWLEDGEMENTS

The authors are grateful to Great Canadian Oil Sands Limited of Fort McMurray, Alberta, for supplying the bitumen feedstock used in the investigation. The contributions of M.P. Pleet and members of the Process Engineering Section in carrying out the experiments are appreciated. The authors are indebted to R.G. Draper and his staff for the analytical work, to G.J. Noel for computation of results and to R. Chagnon for preparation of drawings.

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TABLE 1
Properties of Bitumen Feed Stock

G.C.O.S. Bitumen

Density at 15°C	kg/l	1.011
Sulphur	wt %	4.77
Ash	wt %	0.56
Nitrogen	wt %	0.4
Conradson Carbon Residue	wt %	13.8
Pentane insolubles	wt %	15.6
Benzene insolubles	wt %	0.56
Nickel	ppm	68
Vanadium	ppm	196

Distillation Analysis

Temperature Range ^O C	wt %	Density at 15°C kg/1	Sulphur wt %
RT - 200	1.4	0.816	1.56
200 - 250	2.2	0.856	1.03
250 - 333	9.7	0.902	1.78
333 - 418	17.7	0.954	2.98
418 - 525	17.5	0.988	3.79
+ 525	51.5	1.072	6.39

TABLE 2 Experimental Operating Conditions

	Reac	tor	or Hot Receiver			
Run No.	Volume &	Temp °C	Temp C	Pressure MPa	LHSV *	Gas Rate ** m ³ /h
40-1-1	4.0	445	270	13.89	2.0	0.0388
40-2-1	4.0	450	270	13.89	2.0	0.0388
82-5-3	4.5	450	380	13.89	1.0	0.0425
		_				

TABLE 3 Comparison of Product Yields and Pitch Conversion

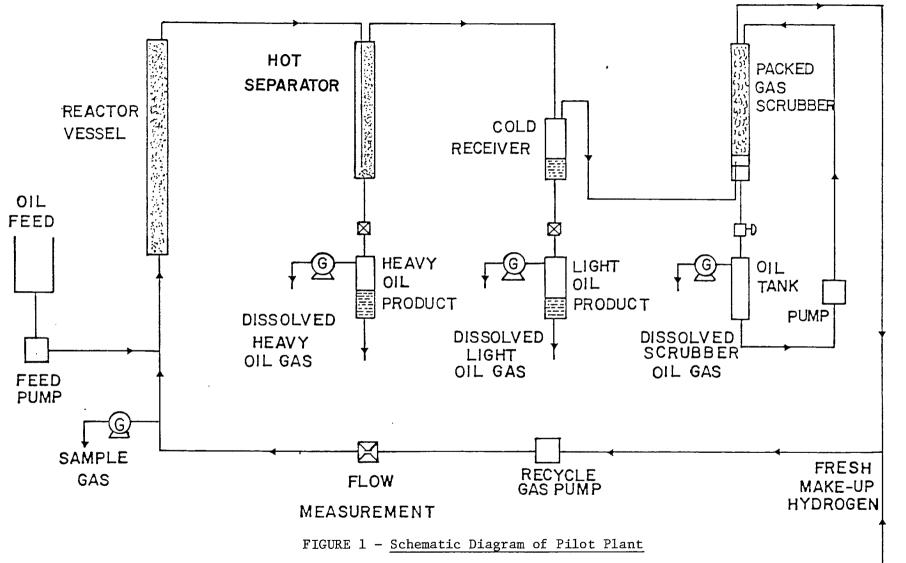
	Yields	(based on	feed)		
Run No.	Distilla Vol %		Pitch wt %	Pitch Conversion wt %	Remarks
40-1-1	N/A	77.9	14.4	72.0	No Scrubbing
Ref (8)	87.6	78.9	15.8	68.8	85% of H ₂
40-2-1	N/A	79.8	12.0	76.7	No scrubbing
Ref (8)	90.2	81.2	12.9	74.5	85% of H ₂
82-5-3	94.3	84.0	9.0	82.5	No scrubbing
Ref (10)	92.2	82.0		80.5	85% of H ₂

^{*} LHSV - Liquid hourly space velocity ** Recycle gas rate at the system pressure and 20°C

TABLE 4

Comparison of Results for run 82-5-3

	Run 82-5-3	Ref (10)
Recycle-gas purity, vol $^{\%}$ $^{\text{H}}_2$ $^{\text{H}}_2$ S formed, $^{\text{m}}_3$ /t $^{\text{H}}_2$ C gas make, $^{\text{m}}_3$ /t $^{\text{H}}_2$ consumed, $^{\text{m}}_3$ /t	62.6 18 47 173	59.9 17 52 167
Liquid Products		
Weight yields, %		
Total liquid product Distillate oil Pitch Pitch conversion, wt %	93.0 84.0 9.0 82.5	92.9 83.3 9.6 81.4
Density at 15°C, kg/1		
Total liquid product Distillate oil Pitch	0.9230 0.8980 1.2490	0.9195 0.8957 1.2355
Sulphur, wt %		
Total liquid product Distillate oil Pitch Sulphur removed, wt %	2.49 2.30 4.15 51.0	2.44 2.27 4.55 49.5



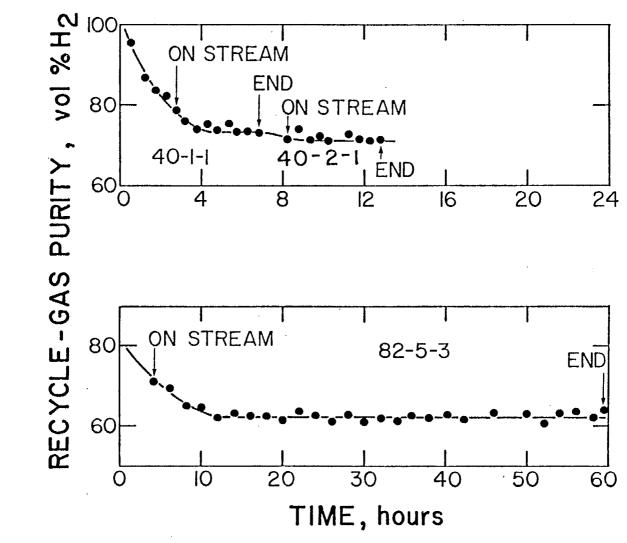


FIGURE 2 - Recycle-Gas Purity as a Function of Operating Time

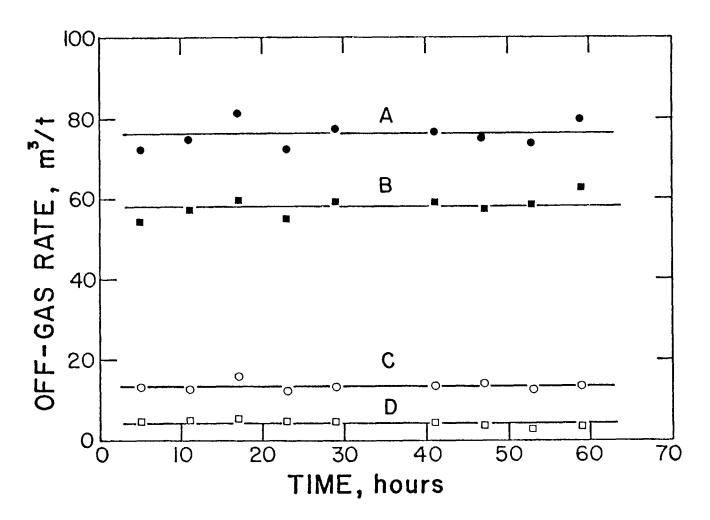


FIGURE 3 - $\underline{\text{Off-Gas}}$ Rates as a Function of Operating Time

Λ - Total off-gas, B - Light-oil off-gas, C - Heavy-oil off-gas,

D - Recycle-gas sample off-gas

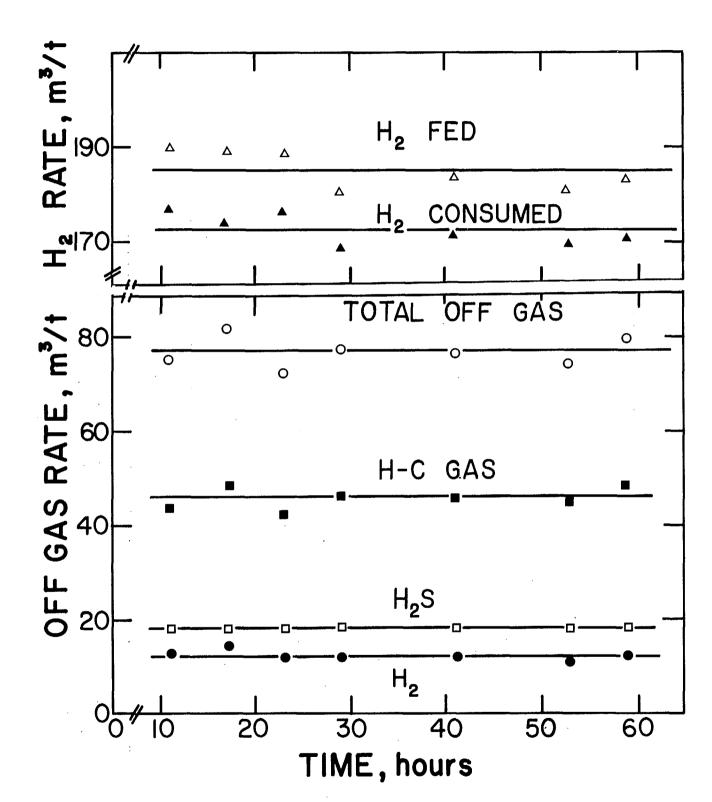


FIGURE 4 - Effect of Operating Time on the Off-gas Rate and on the Hydrogen Rate

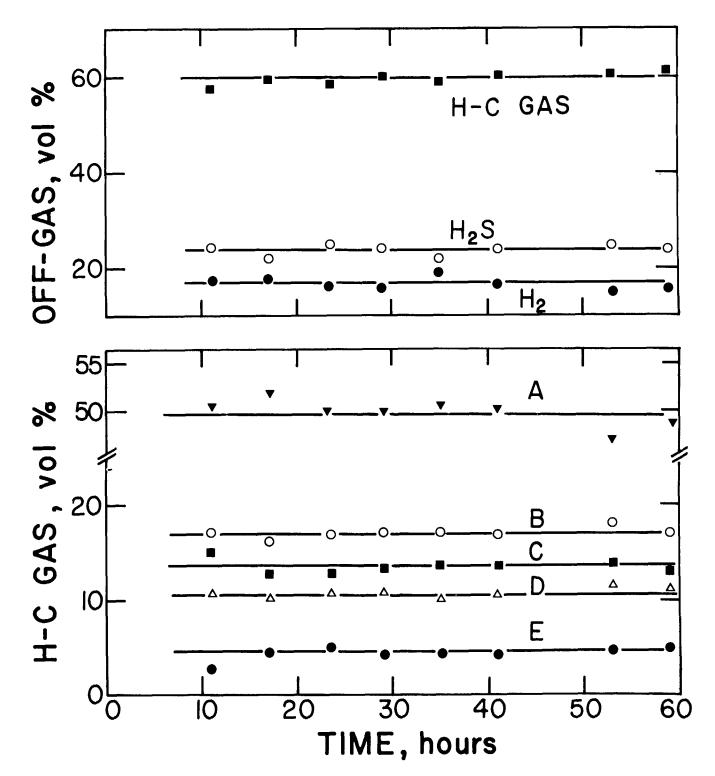


FIGURE 5 - Composition of Off-gas and of the Composite
Hydrocarbon Gas as a Function of Operating Time

A - Methane, B - Ethane, C - Propane, D - Butanes, E - i-Pentane

Balance - mixed butenes and mixed pentenes (not shown)

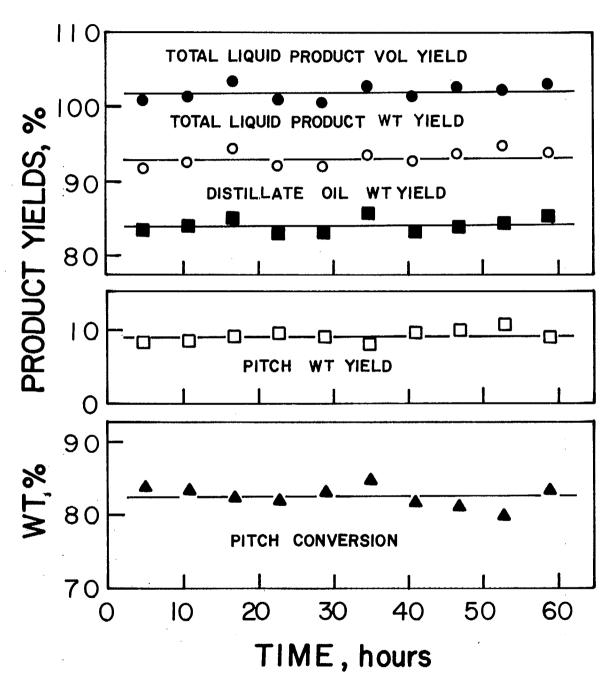


FIGURE 6 - Product Yields and Pitch Conversion as a Function of Operating Time

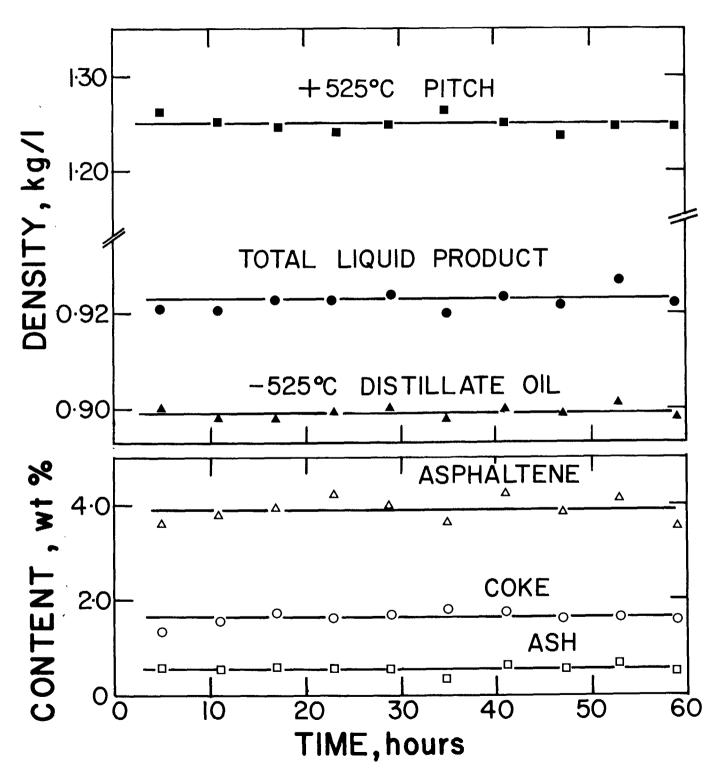


FIGURE 7 - Density at 15°C of the Liquid Products and Asphaltene, Coke and Ash Contents of Total Liquid Product as a Function of Operating Time

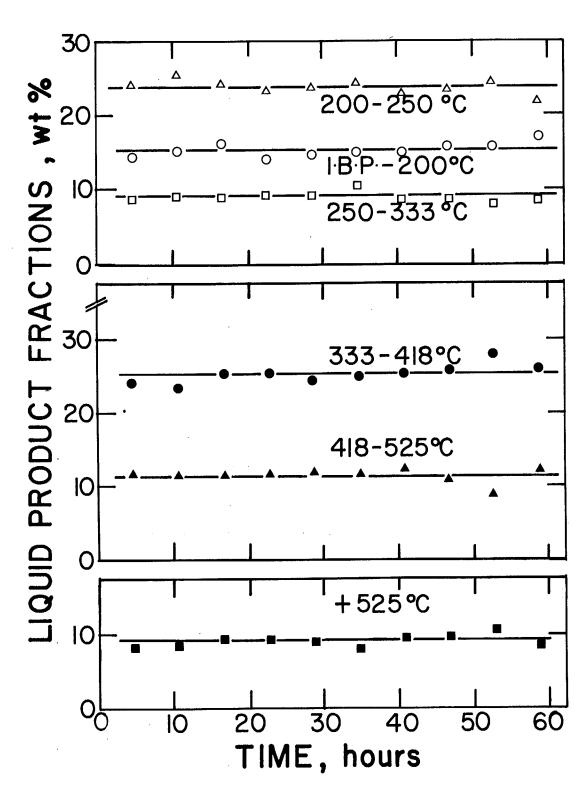


FIGURE 8 - Liquid Product Distributions as a Function of Operating Time

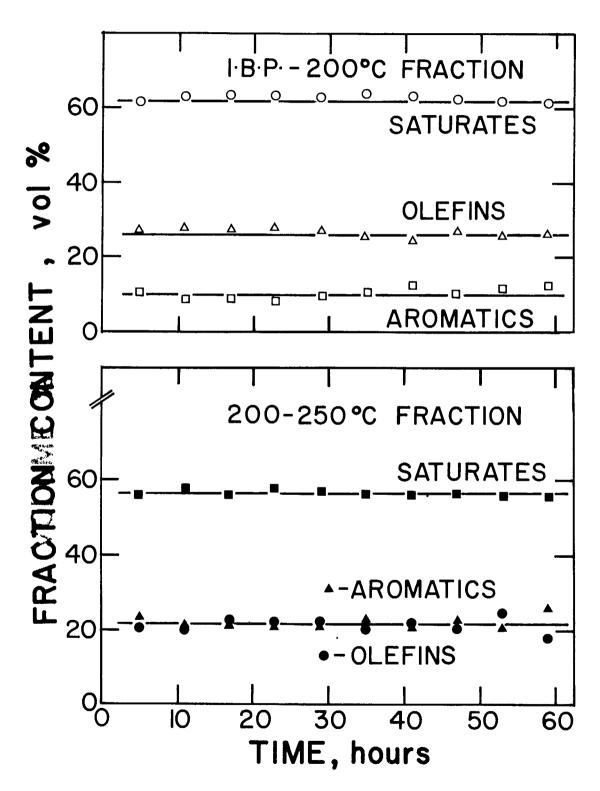


FIGURE 9 - Effect of Operating Time on Saturate, Olefin, and Aromatic Contents of the Distillate Fractions

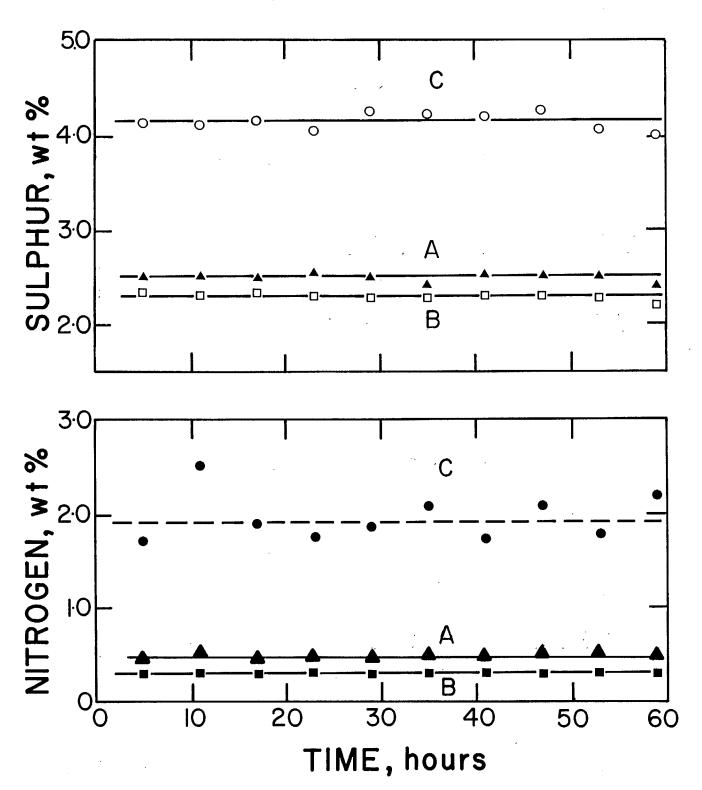


FIGURE 10 - $\frac{\text{Sulphur and Nitrogen Contents of the Liquid}}{\text{Products as a Function of Operating Time}}$

A - Total liquid product

B - Distillate oil

C - Pitch

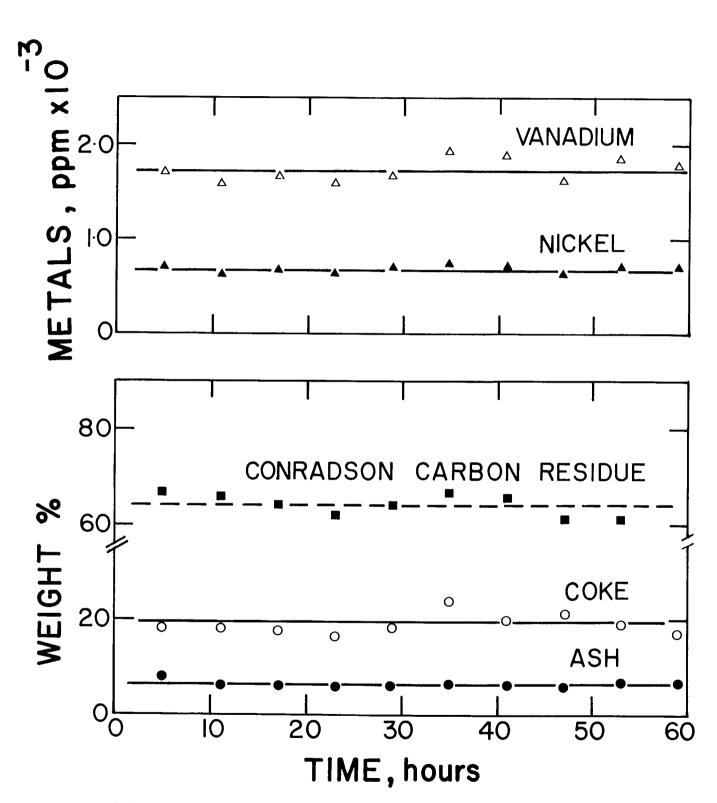


FIGURE 11 - Pitch Properties as a Function of Operating Time

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