



DEPARTMENT OF
ENERGY, MINES AND RESOURCES
MINES BRANCH
OTTAWA

*THE HYDROCRACKING OF RESIDUAL OILS
AND TARS*

*Part 6: Catalyst De-activation by Coke and
Metals Deposition*

E. C. McCOLGAN AND B. I. PARSONS

FUELS RESEARCH CENTRE

MAY 1974

© Crown Copyrights reserved

Available by mail from Information Canada, Ottawa, K1A 0S9
and at the following Information Canada bookshops:

HALIFAX

1683 Barrington Street

MONTREAL

640 St. Catherine Street West

OTTAWA

171 Slater Street

TORONTO

221 Yonge Street

WINNIPEG

393 Portage Avenue

VANCOUVER

800 Granville Street

or through your bookseller

Price: 50 cents Catalogue No. M38-1/273

Price subject to change without notice

Information Canada
Ottawa, 1974

Mines Branch Research Report R-273

THE HYDROCRACKING OF RESIDUAL OILS AND TARS

Part 6: Catalyst De-activation by Coke and Metals Deposition

by

E.C. McColgan* and B.I. Parsons**

ABSTRACT

The report describes the effect of metals and mineral concentration on the de-activation and regeneration characteristics of a cobalt molybdate hydrocracking catalyst. Two feed stocks were used, (a) Athabasca bitumen (high in metals and residual minerals), and (b) Leduc pitch (low in metals and residual minerals). The Conradson Carbon Residue values for both feed stocks were similar, in the range 13 to 15 wt %. The experiments were undertaken in a bench-scale flow system with bottom feed. In this mode of operation low-boiling material present in the feed, or produced in the course of reaction, vapourizes, collects as bubbles and passes quickly out of the reaction zone. High-boiling material remains in the liquid phase and progresses through the reactor by displacement. All experiments were made at a liquid-hourly-space-velocity of 1.05 and a pressure of 2000 psi.

Under the conditions of the tests, the primary cause of catalyst de-activation was found to be the fouling of the surfaces by tarry-coke deposits. There were no measurable differences in the initial rate of de-activation observed between the high-metals and low-metals feed stocks. Successful regeneration of the catalyst, however, was only possible with the low-metals and minerals feed stock (the Leduc pitch). The metals and minerals incorporated in the coke deposits obtained with the Athabasca bitumen adhered to the surfaces of the catalyst in the oxidative-regeneration process and reduced the activity considerably.

*Technician and **Research Scientist, Fuels Research Centre, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada.

Rapport de Recherche R-273 de la Direction des Mines
L'HYDROCRAQUAGE DU PÉTROLE ET DU GOUDRON RÉSIDUELS

Partie 6: La désactivation catalytique par les dépôts de coke et de métaux

par

E.C. McColgan* et B.I. Parsons**

RÉSUMÉ

Le présent rapport décrit les effets des concentrations de métaux et de minéraux sur la désactivation et la régénération d'un catalyseur en molybdate de cobalt pour l'hydrocraquage. Les auteurs ont utilisé deux sources d'alimentation: (a) du bitume de l'Athabasca (riche en métaux et en minéraux résiduels) et (b) de l'asphalte Leduc (faible en métaux et en minéraux résiduels). Les résidus de carbone Conradson avaient des valeurs similaires allant de 13 à 15% du poids. Les expériences ont été faites en laboratoire à l'aide d'un système d'alimentation par le bas. Dans ce genre d'opérations, les substances à point d'ébullition peu élevé, qui se trouvent déjà dans la source d'alimentation ou qui se forment au cours de la réaction, s'évaporent, s'agglomèrent et s'éloignent rapidement de la zone de réaction. Les substances à point d'ébullition élevée restent liquides et se déplacent ainsi dans le réacteur. Les expériences ont toutes été faites à une vitesse spatiale liquide horaire de 1.05 et à une pression de 2,000 livres au pouce carré.

Les auteurs ont découvert que, dans les conditions où ces expériences ont été faites, la cause première de la désactivation catalytique était l'accumulation de dépôt de goudron et de coke sur les surfaces. Il n'est apparu aucune différence mesurable dans le taux initial de désactivation observé entre les charges d'alimentation riches ou pauvres en métaux. Cependant, la régénération du catalyseur n'a été possible que par l'action de la charge d'alimentation faible en métaux et minéraux (l'asphalte Leduc). Les métaux et minéraux des dépôts de coke provenant du bitume de l'Athabasca se grippaient à la surface du catalyseur au cours du processus de régénération par oxydation et en réduisaient considérablement l'activité.

*Technicien et **Chercheur. Scientifique Centre de recherches sur les combustibles, Direction des Mines, Ministère de l'Energie, des Mines et des Ressources, Ottawa, Canada.

CONTENTS

	<u>Page</u>
Abstract	i
Résumé	ii
Introduction	1
Experimental	4
Feed Stocks	4
Catalyst	4
Apparatus and Procedure	6
Experimental Results and Discussion	7
Summary	9
Acknowledgements	9
References	20

TABLES

1. Properties of Feed Stocks	5
2. A Comparison of the Conversions Attained in the First and Second Runs at Low Temperature	12
3. The Yield and Sulphur Content of the Product Fractions Formed from Athabasca Bitumen	13
4. The Yield and Sulphur Content of the Product Fractions Formed from Leduc Pitch	14
5. The Yield and Sulphur Content of the Product Fractions Formed in the Life-Run with Athabasca Bitumen	17
6. The Yield and Sulphur Content of the Product Fractions Formed in the Life-Run with Leduc Pitch	18

FIGURES

1. The effect of reaction temperature on the conversion of the +975 ^o F residuum to distillable oil and on sulphur removal	10
2. The specific gravity and experimentally observed yields of liquid product	11
3. The effect of operating time and regeneration on catalyst activity with the Athabasca feed stock	15
4. The effect of operating time and regeneration on catalyst activity with the Leduc feed stock	16
5. Photographs of catalysts used in the life-runs	19

INTRODUCTION

The following report is the sixth in a series on the hydrocracking of residual oils and tars (1) and is concerned with the problem of coke formation and the deposition of metals and minerals on catalysts for the catalytic hydrocracking of Athabasca bitumen.

As the commercial development of the Athabasca oil sands proceeds, several problem areas in the refining of the separated bitumen are becoming more apparent. The upgrading systems in current use (2) and most of those proposed by others (3, 4) begin with either the delayed or fluid coking of the bitumen, followed by a distillation and the hydrogenation of the distillate fractions. The systems are complicated and, in the case of future plants (because of environmental considerations), it is not likely that any of the governmental agencies involved will permit the uncontrolled burning of the coke to supply the energy required for the extraction plant. The applicants currently before the Energy Resources Conservation Board of the Province of Alberta indicate that it is their intention to "stockpile" the coke residues. The technological and environmental difficulties connected with the direct firing or gasification of coke residues are such, however, that it is unlikely that any of the "stockpiled" material will ever be recovered. The search is, therefore, for ways and means:

- (a) to reduce the dregs stream (pitch or coke) of the refining process to the absolute minimum so as to simplify the environmental problems associated with the generation of the energy for the plant.
- (b) to produce the dregs stream in such a form that direct combustion or gasification is possible, i.e. in a form for which technology is presently available,
- (c) to improve the yield of saleable liquid product produced per unit of separated bitumen, and finally,
- (d) to simplify the refining scheme to minimize capital investment and reduce the labour requirement (both of which are important factors in operations located in northern Canada).

The prospects for accomplishing all these aims appear good for catalytic hydrocracking in liquid-phase, fluidized-bed systems (5, 6, 7) at

1000-2000 psi. The distillate product formed by catalytic hydrocracking is more stable than that produced by delayed or fluid-bed coking, and it should be amenable to pipeline transport to refineries in the south without further treatment, thereby eliminating the need for secondary hydrogenation systems at the point of production. Some secondary desulphurization and hydrogen treatment will undoubtedly be necessary before marketing, but the extent of additional refining needed will be much reduced and within the capability of refineries presently accepting medium-sulphur conventional crudes.

The extent of conversion of the residuum (+975^oF) that is possible over a catalyst is high ... the unreacted residuum passing through the reactor comprises only 5 to 7% of the feed. Most important, the dregs stream is produced as a high melting-point pitch and, as such, is compatible with existing gasification technology (8). Alternatively, the sulphur content of these unreacted bottoms is only 3% (compared with 7-8% for fluid coke) and could be blended with a low-sulphur gas oil to reduce the sulphur emissions in a direct fired boiler. The route followed to generate the energy required for processing will depend largely upon environmental restrictions. Gasification (to form low BTU gas) has the capability of reducing sulphur emissions from the power generation processes to virtually nil. The direct firing of the dregs blended with a heavy gas oil would reduce the sulphur emissions 75 to 80% compared with an uncontrolled coke-burning system. (In the last statement it is assumed that approximately 15-16% of the bitumen feed is required to generate the energy necessary for the mining and extraction processes.)

In spite of the many advantages, the major drawback of catalytic hydrocracking continues to be catalyst life and cost. Preliminary experiments with a fluidized cobalt molybdate catalyst system and the Athabasca bitumen in a Mines Branch pilot plant (9) at 2000 psi indicate that the practical limit of catalyst life is of the order of 200 hours (converting 85-90% of the +975^oF residuum into a distillate "synthetic crude" containing 1 to 1.5% sulphur). Catalyst consumption is in the range of 1/4 to 1/2 pounds per barrel depending upon product specification.

Reasons for the rapid catalyst deactivation are not entirely clear. In a previous report in this series (1d) it was shown that the deactivation was not due to a high concentration of mineral matter (clay) in the Athabasca bitumen. Unfortunately, with the feed stocks used at that time it was not possible to differentiate between de-activation by metals and minerals deposition and deactivation by carbon fouling*. In the present work, experiments have been undertaken with a low-metals and minerals pitch derived from Leduc crude oil as well as with Athabasca bitumen to determine the relative effects of metals deactivation and carbon fouling. (The Conradson carbon residues of the two feed stocks are similar, the only major difference is in the metals and mineral content.) The results indicate that the primary cause of catalyst de-activation is carbon fouling and that the accumulation of metals and minerals on the catalyst follows as the result of the burning off of the coke deposits in the regeneration process. Repeated successful regeneration of the catalyst was only possible with the low-metals and minerals feed stock.

*Carbon fouling is defined as the gradual accumulation and blinding of the catalyst by tarry coke deposits.

EXPERIMENTAL

Feed Stocks

The two feed stocks used for the investigation were bitumen from the Athabasca oil sands and a high-temperature pitch derived from conventional oil produced in the Leduc field of Alberta. The general properties of the feed stocks are summarized in Table 1. The Conradson Carbon Residue values for the two oils were very similar (13-15 wt %). The major difference between the two feed stocks occurred in the metals and minerals concentrations, e.g. 257 ppm combined metals and 0.7% ash in the Athabasca bitumen compared with 23 ppm metals and 0.01% ash in the Leduc pitch. It should also be noted that the concentration of +975^oF residuum in the Leduc pitch was 63% by weight compared with 51% for the bitumen.

The Athabasca material was obtained from Great Canadian Oil Sands Ltd. of McMurray, Alberta. It was separated from the sand using the Clark Hot-Water Process and froth flotation followed by dilution with naphtha and centrifuging (2). The concentration of residual clay and silt in the bitumen after recovering the solvent naphtha is about 0.9% by weight. The extent to which the clay and silt are removed in the G.C.O.S. process is the best technically attainable at the present time. The Leduc pitch was obtained from the Imperial Oil refinery at Sarnia, Ontario. Both feed stocks were used as received.

Catalyst

The catalyst used was a commercial cobalt molybdate on alumina manufactured by the Harshaw Chemical Co. of Cleveland, Ohio. The catalyst, 1/8 x 1/8-in. pellets designated as CoMo-0603T by the manufacturer, was recommended for the denitrogenation and desulphurization of hydrocarbons by hydrotreating. It is reported to be a non-silicated catalyst containing 3% cobalt oxide and 12% molybdenum trioxide supported on alumina. The surface area and total pore volume were 166 m²/g and 0.40 ml/g respectively.

TABLE 1

Properties of Feed Stocks

Details of Analysis	Athabasca Bitumen	Leduc Pitch
Specific Gravity 60/60°F	1.000	0.991
Ash (wt %) 700°C	0.70	0.013
Nickel (ppm)	68	13
Vanadium (ppm)	189	10
Conradson Carbon Residue (wt %)	12.6	14.7
Pentane Insolubles (wt %)	15.83	6.12
Benzene Insolubles (wt %)	0.90	0.09
Carbon Disulphide Insolubles (wt %)	0.88	0.05
Sulphur (wt %)	4.72	0.92
Nitrogen (wt %)	0.42	0.55
Viscosity, Kinematic (cSt) at 210°F	129.5	818
Viscosity, Kinematic (cSt) at 130°F	2041	-
Molecular Weight (calculated)	722	814
Residuum (+975°F) wt %	51	63

Apparatus and Procedure

The apparatus used was the bench-scale flow system described in the first report in this series (1). In all of the experiments, the oil feed and hydrogen were pumped in at the bottom of the reactor. The unit was operated, in effect, as a continuous-flow, liquid-phase system with the oil and hydrogen percolating up through the reactor. Any low-boiling material present in the feed (or produced in the course of reaction) vapourizes, collects as bubbles, and quickly passes out of the reaction zone. High-boiling material remains in the liquid phase and progresses slowly through the reactor by displacement. All of the experiments were undertaken at a liquid-hourly-space-velocity (LHSV) of 1.05, a pressure of 2000 psi, and at a hydrogen flow rate of 5000 standard cubic feet per barrel (scf/bbl).

Experiments to obtain a measure of the extent of catalyst de-activation with each feed stock were undertaken in two ways. In the first approach, a fresh charge of catalyst was placed in the reaction vessel and five consecutive 3-hour runs made at increasing temperatures followed by a repeat run at one of the lower temperatures. The product of the second run at the lower temperature was compared with that from the first to obtain an estimate of the extent of catalyst deactivation. The particular temperatures used with the two feed stocks were:

Athabasca bitumen:	430, 440, 450, 460, 440 (2) ^o C
Leduc pitch:	440, 450, 460, 470, 450 (2) ^o C

The background to this procedure is explained fully in the second report in this series. The results of the second run at the lower temperature are listed under the heading 440(2) or 450(2) in the Tables and Figures. The reactivity of the Leduc pitch was generally lower than the Athabasca bitumen and it was necessary to operate at slightly higher reaction temperatures (10^oC) to obtain a comparable degree of conversion.

In the other approach to the problem, a fresh charge of catalyst was placed in the reaction vessel and the system was run at a fixed temperature for approximately 130 hours, with regenerations at the 50 and 90-hour points.

The reaction temperatures selected for the "life-runs" were 450°C with the Athabasca bitumen and 460°C with the Leduc pitch. Product samples were collected every four hours for analysis and evaluation. At the end of the series with each feed stock the catalyst was regenerated (for the third time); removed from the reaction vessel and photographed to record the extent of metals and mineral fouling that had occurred over the operating period.

To regenerate the catalyst, the system was first de-pressurized and the liquid oil drained from the reaction vessel. The reaction vessel was drained hot (200-250°C) to ensure that as much of the liquid oil as possible was removed from the system. The residual oil and tarry carbon deposits on the catalyst were burned off at 500-550°C with air. When the regeneration step was completed the reaction vessel was allowed to cool (overnight) then re-pressurized to 2000 psi with hydrogen.

EXPERIMENTAL RESULTS AND DISCUSSION

In the following paragraphs the two procedures for measuring catalyst de-activation are compared and the implications discussed. To be able to appreciate the differences the reader must examine the experimental data obtained in both series of tests. For ease of review and handling, the Figures and Tables are presented in sequence at the end of the text. The overall reaction characteristics of the two feed stocks at various temperatures are summarized in Figures 1 and 2. A comparison of the conversions attained in the first and second runs at low temperature is given in Table 2, and the results of the distillation and sulphur analyses on the product fractions are listed in Tables 3 and 4. The "life-run" experiments are summarized in Figures 3 and 4 and Tables 5 and 6. Photographs of the catalysts removed from the reactor at the end of the life-run experiments are shown in Figure 5.

The usual procedure for obtaining an (accelerated) estimate of catalyst deactivation by running a series of experiments at increasing temperatures is actually misleading in this particular case. On the one hand, the reactivity of the Leduc pitch was markedly lower than that of the Athabasca bitumen.

At 450°C the degree of conversion of the +975°F residuum was only 16% compared to 77-78% with the Athabasca bitumen. Above 450°C, however, the Leduc pitch was highly sensitive to reaction temperature the level of conversion of the residuum increasing from 16% at 450°C to 65% at 470°C. The combination of low reactivity and high temperature sensitivity makes the comparison of the two low temperature runs in the accelerated test (shown in Table 2) very difficult, even suspect. At low temperatures the reactivity is too small to reflect anything except large changes in catalyst activity and at higher temperatures the usual experimental tolerance of $\pm 1^\circ\text{C}$ in temperature control is equivalent to a possible error of 4 to 5% in conversion. With the conventional type of flow system such as used here, it is simply not possible to hold the reaction conditions sufficiently constant to lend the test any real meaning. The reaction characteristics detailed in Figures 1 and 2 and Tables 3 and 4 are of interest, and are essential to an understanding of the system, but do not indicate accurately the changes in the catalyst activity.

The "life-run" experiments at constant temperature, on the other hand, (Figures 3 and 4) show much more clearly the changes in catalyst activity with feed stocks and operation. Considerably more time and work are required to obtain the base measurements, however. Each experiment involved 30 individual test periods and three regeneration cycles, or approximately 150 hours of bench time. The results show that the rate of de-activation over the first 50 hours of operation as essentially the same with both the high and low metals and minerals feed stocks, i.e., that the extent of de-activation was not a function of the metals and mineral concentration. De-activation appears to be due almost entirely to the formation of coke and tarry deposits on the catalyst surfaces, which mask the activity of the catalytic ingredients and reduce considerably the degree of hydrocracking and desulphurization attainable.

The activity of the system used with the Leduc feed stock returned to very nearly the original values after the first and second regeneration cycles. When the reactor was taken apart the catalyst was found to be clean and clear of all deposits and mineral matter (see centre section of Figure 5).

The system used with the Athabasca feed stock did not return to quite the original values after the first regeneration cycle, and was measurably worse after the second regeneration cycle. When the catalyst was removed after 120 hours of operation the surfaces of the pellets were found to be coated with silt and clay (see bottom section of Figure 5). Whereas deactivation appears to be as the result of the tendency of the feed stock to form coke, the capability of the system for regeneration is limited by the mineral and metals content. The concentration of minerals and metals is high in the coke and tarry deposits (10). These are left as a residue on the catalyst surfaces in the oxidation-regeneration process. After successive regenerations the active surfaces become blinded by the metals and minerals deposit. The effect is particularly marked with the Athabasca bitumen because of the high clay concentration (0.9% benzene insolubles) relative to conventional oils and pitches.

SUMMARY

The results of the present study indicate that the primary rate and extent of catalyst de-activation observed with the Athabasca bitumen is no better and no worse than that experienced with any other feed stock characterized by a high Conradson carbon residue. The capability of the catalyst system to be regenerated, however, is much reduced by a high metals and minerals concentration. With the Athabasca bitumen, regeneration is probably limited to two cycles at most. In the design of a system to catalytically hydrocrack bitumen, the mechanical arrangement will have to include a means for adding and withdrawing catalyst while the reactor is in operation such as with a fluidized or moving bed.

ACKNOWLEDGEMENTS

The authors thank Great Canadian Oil Sands Ltd. of Fort McMurray, Alberta and Imperial Oil Enterprises Ltd. of Sarnia, Ontario for supplying the feed stocks used in the present study.

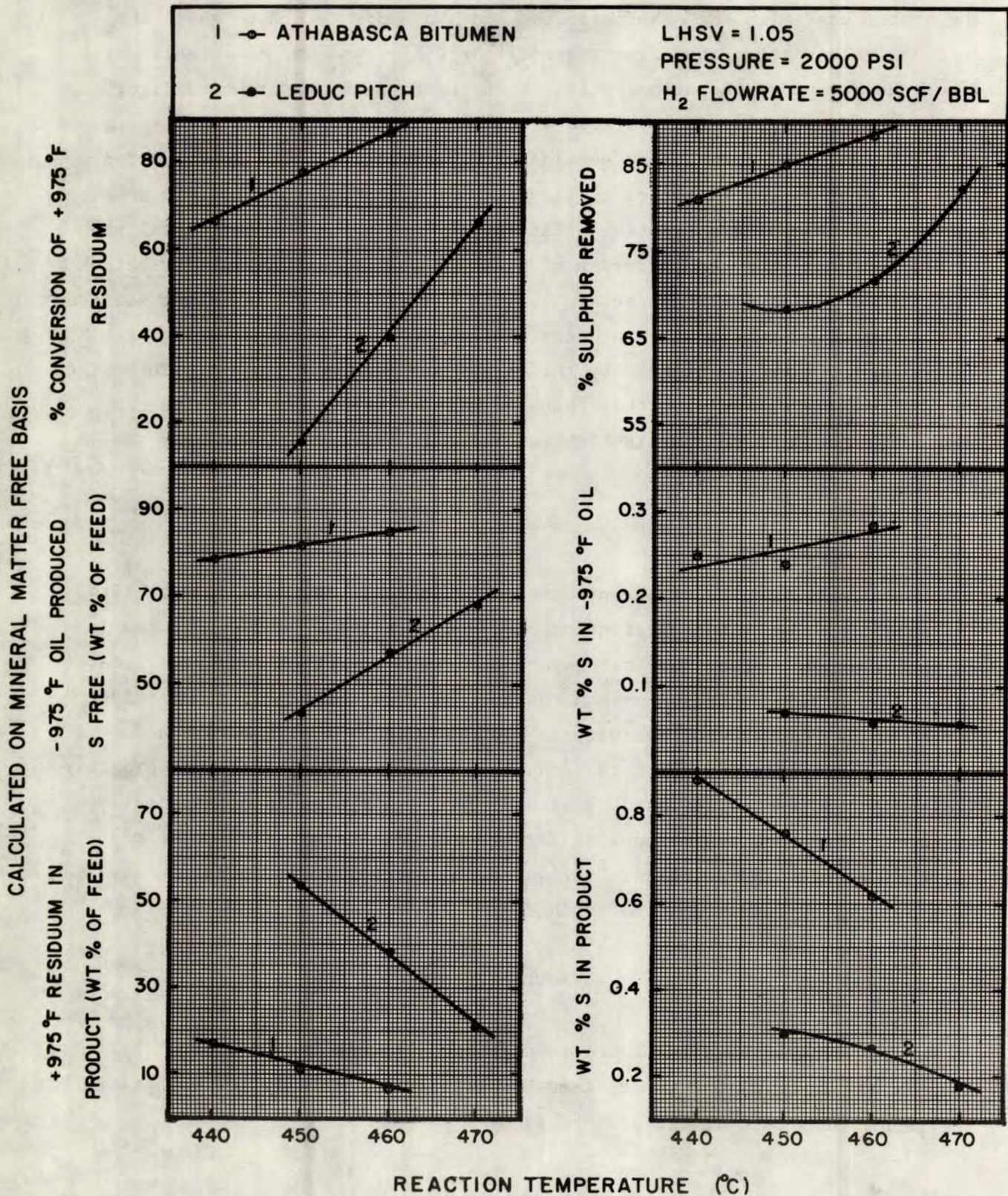


Figure 1. The effect of reaction temperature on the conversion of the +975°F residuum to distillable oil and on sulphur removal

Note: the residuum remaining in the product and the distillable oil produced are expressed as weight % of feed.

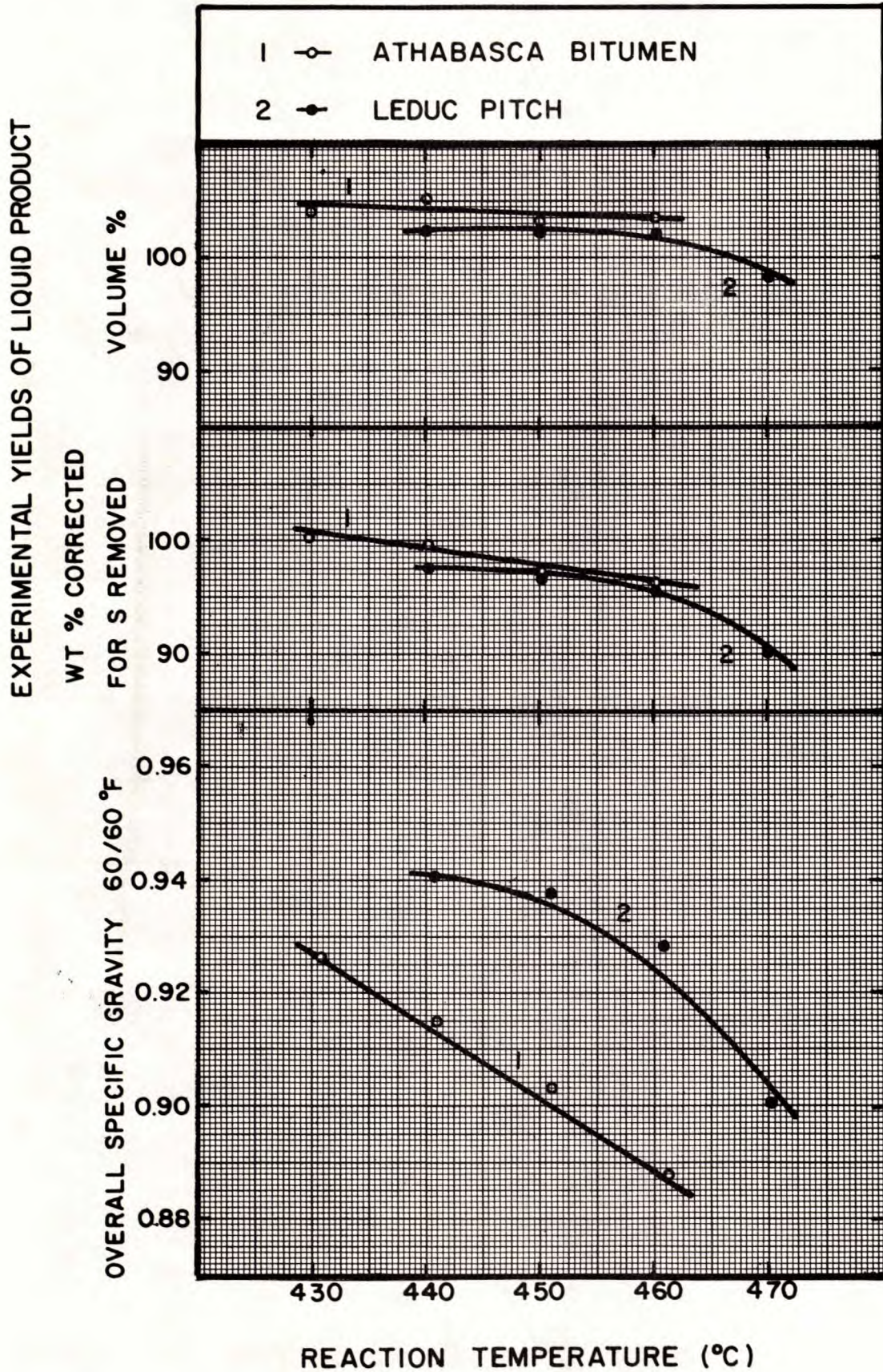


Figure 2. The specific gravity and experimentally observed yields of liquid product.

TABLE 2

A Comparison of the Conversions Attained in the
First and Second Runs at Low Temperature

Feed Stock	Reaction Temperature (°C)	% Sulphur Removed		% Conv. +975°F Residuum	
		First Run	Second Run	First Run	Second Run
Athabasca	440	82	76	67	61
Leduc	450	69	65	16	16

Operating Pressure: 2000 psi

Hydrogen Flow Rate: 5000 scf/bbl

LHSV = 1.05

TABLE 3

The Yield and Sulphur Content of the Product Fractions Formed from Athabasca Bitumen

(Note: the fractions are expressed as weight % of mineral-matter-free feed)

Reaction Temperature (°C)		440		450		460		440(2)		Bitumen Feed Stock	
		Fraction Wt %	Wt % Sulphur	Fraction Wt %	Wt % Sulphur	Fraction Wt %	Wt % Sulphur	Fraction Wt %	Wt % Sulphur	Fraction Wt %	Wt % Sulphur
Boiling Range of Fraction Equiv. Temp. at one atm. (°C) (°F)											
Gas Produced		0.3	-	2.8	-	3.8	-	0.9	-	-	-
IBP-100	IBP-212	2.4	-	1.8	-	3.9	-	1.9	-	-	-
100-200	212-392	5.5	0.17	9.8	0.19	12.0	0.32	5.2	0.24	2.1	-
200-250	392-482	7.7	0.27	9.4	0.14	12.1	0.25	6.9	0.18	1.5	1.15
250-275	482-527	6.9	0.10	7.3	0.11	8.4	0.17	6.9	0.18	5.2	1.65
275-332	527-630	13.2	0.13	14.0	0.12	15.6	0.16	13.6	0.26	5.5	2.49
332-361	630-682	10.3	0.19	10.8	0.20	11.6	0.24	10.4	0.35	6.9	2.78
361-391	682-736	5.8	0.25	4.9	0.25	4.5	0.30	4.3	0.41	5.1	3.10
391-421	736-790	8.0	0.30	7.2	0.30	5.9	0.35	7.3	0.51	6.7	3.38
421-524	790-975	19	0.52	17	0.48	11	0.55	19	0.70	16	3.86
+524	+975	17	3.2	11	3.0	7	3.2	20	3.6	51	6.2
Sulphur Removed		3.9		4.0		4.2		3.6		-	-
Totals		100		100		100		100		100	

PRESSURE = 2000 psi

LHSV = 1.05

HYDROGEN FLOW RATE = 5000 scf/bbl

TABLE 4.

The Yield and Sulphur Content of the Product Fractions Formed from Leduc Pitch

(Note: the fractions are expressed as weight % of feed)

Reaction Temperature (°C)		450		460		470		450(2)		Leduc Pitch Feed Stock	
Boiling Range of Fraction		Fraction	Wt %	Fraction	Wt %	Fraction	Wt %	Fraction	Wt %	Fraction	Wt %
Equiv. Temp. at one atm.		Wt %	Sulphur	Wt %	Sulphur	Wt %	Sulphur	Wt %	Sulphur	Wt %	Sulphur
(°C)	(°F)										
Gas Produced		2.6	-	3.7	-	10.0	-	3.0	-	-	-
IBP-100	IBP-212	0.5	-	0.9	-	2.2	-	1.0	-	1.9	-
100-200	212-392	4.4	-	6.4	-	11.3	0.01	4.1	0.01	3.1	0.29
200-250	392-482	3.5	-	5.3	0.02	8.0	0.01	4.6	0.03	6.9	0.33
250-275	482-527	4.2	0.02	3.6	0.01	5.3	0.02	4.2	0.07	} 3.3	0.42
275-332	527-630	4.7	0.06	7.3	0.05	9.0	0.06	4.1	0.08		
332-361	630-682	4.7	0.06	5.4	0.04	7.3	0.07	4.7	0.10	3.6	0.48
361-391	682-736	3.2	0.05	3.8	0.08	3.7	0.07	3.3	0.10	} 18.2	0.59
391-421	736-790	4.6	0.08	4.9	0.07	5.4	0.09	4.4	0.14		
421-524	790-975	14	0.12	20	0.14	16	0.14	13	0.19		
+524	+975	53	0.49	38	0.56	21	0.55	53	0.61	63	0.89
Sulphur Removed		0.6		0.7		0.8		0.6		-	
Totals		100		100		100		100		100	

PRESSURE = 2000 psi

LHSV = 1.05

HYDROGEN FLOW RATE = 5000 scf/bbl

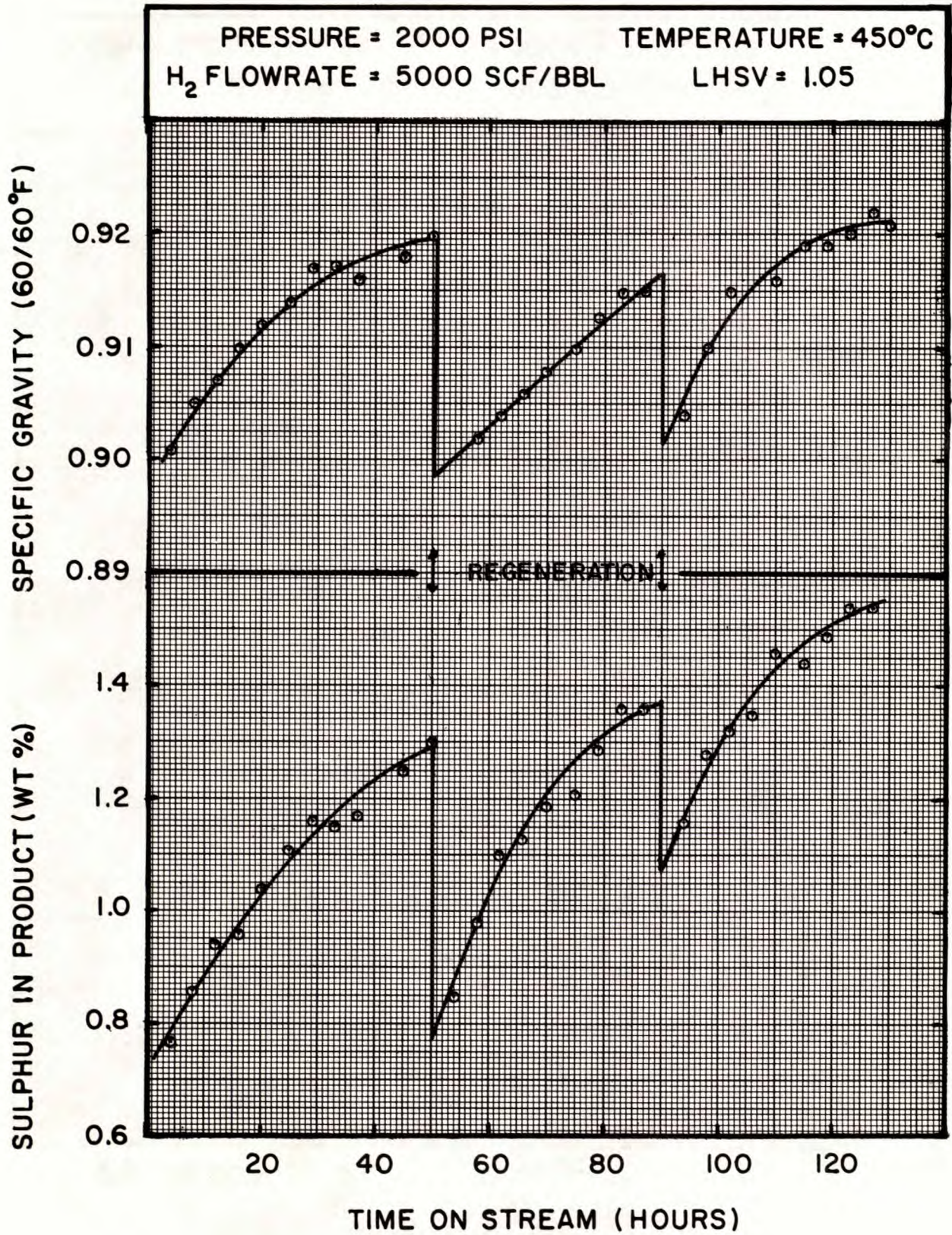


Figure 3. The effect of operating time and regeneration on catalyst activity with the Athabasca feed stock.

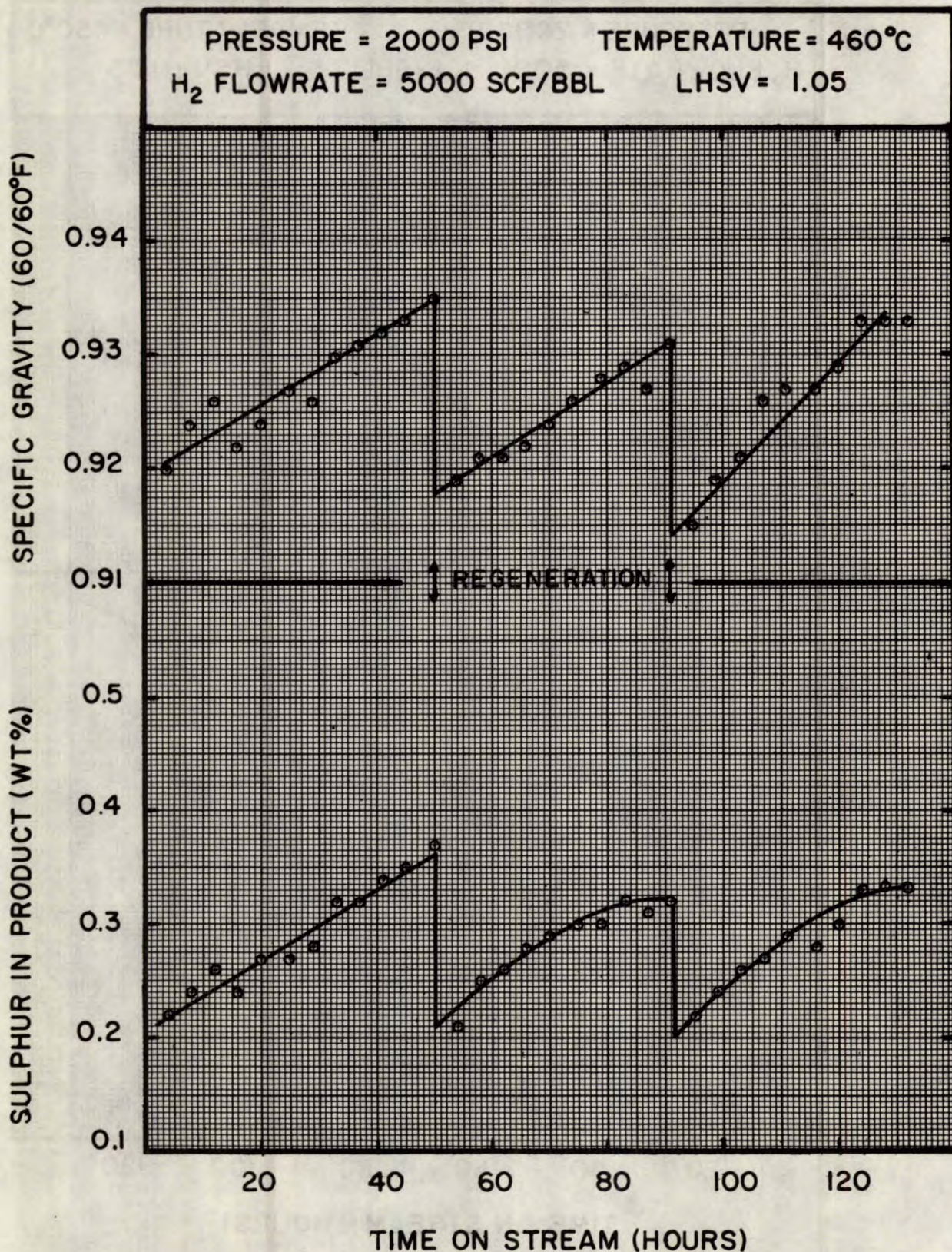


Figure 4. The effect of operating time and regeneration on catalyst activity with the Leduc feed stock.

TABLE 5

The Yield and Sulphur Content of the Product Fractions Formed in the Life-Run with Athabasca Bitumen

(Note: the fractions are expressed as weight % of mineral-matter-free feed)

		Fresh Catalyst				Regenerated Once				Regenerated Twice			
Total Hours on Stream		8		45		58		87		99		128	
Hours After Regeneration		-		-		8		37		8		37	
Boiling Range of Fraction		Fraction	Wt %	Fraction	Wt %	Fraction	Wt %	Fraction	Wt %	Fraction	Wt %	Fraction	Wt %
Equiv. Temp. at one atm.		Wt %	Sulphur	Wt %	Sulphur	Wt %	Sulphur	Wt %	Sulphur	Wt %	Sulphur	Wt %	Sulphur
(°C)		(°F)											
Gas Produced		0.8	-	1.1	-	0.5	-	1.0	-	1.1	-	1.2	-
IBP-100	IBP-212	2.6	nil	1.7	nil	2.0	nil	1.8	nil	2.0	trace	2.6	0.09
100-200	212-392	7.2	0.05	7.4	0.21	10.3	0.21	8.9	0.36	9.4	0.25	7.7	0.52
200-250	392-482	8.4	0.03	7.4	0.25	9.4	0.33	7.9	0.34	9.7	0.25	9.2	0.39
250-275	482-527	6.5	0.04	7.0	0.27	7.6	0.16	7.7	0.32	6.2	0.31	4.5	0.46 [†]
275-332	527-630	15.6	0.08	13.5	0.36	16.8	0.19	13.5	0.43	14.5	0.43	14.5	0.62 [†]
332-361	630-682	10.7	0.15	9.9	0.47	8.2	0.26	12.1	0.55	10.2	0.49	11.6	0.76
361-391	682-736	6.7	0.23	6.6	0.54	6.4	0.31	4.7	0.64	7.3	0.61	3.8	0.85
391-421	736-790	7.6	0.31	7.9	0.69	7.0	0.42	7.0	0.79	7.1	0.76	4.7	0.96
421-524	790-975	16	0.48	17	0.91	15	0.65	16	1.08	15	1.09	20	1.31
+524	+975	14	3.0	17	4.1	13	3.9	16	4.4	14	4.4	17	4.7
Sulphur Removed		3.9		3.5		3.8		3.4		3.5		3.2	
Totals		100		100		100		100		100		100	

PRESSURE = 2000 psi

REACTION TEMPERATURE = 450°C

LHSV = 1.05

HYDROGEN FLOW RATE = 5000 scf/bbl

TABLE 6

The Yield and Sulphur Content of the Product Fractions Formed in the Life-Run with Leduc Pitch

(Note: the fractions are expressed as weight % of feed)

Total Hours on Stream Hours After Regeneration	Fresh Catalyst				Regenerated Once				Regenerated Twice			
	8		50		58		91		99		132	
	-		-		8		41		8		41	
Boiling Range of Fraction Equiv. Temp. at one atm. (°C) (°F)	Fraction Wt %	Wt % Sulphur	Fraction Wt %	Wt % Sulphur	Fraction Wt %	Wt % Sulphur	Fraction Wt %	Wt % Sulphur	Fraction Wt %	Wt % Sulphur	Fraction Wt %	Wt % Sulphur
Gas Produced	2.8	-	4.4	-	4.5	-	3.8	-	6.0	-	5.0	-
IBP-100 IBP-212	2.2	0.01	1.9	0.04	2.7	-	1.1	-	4.3	0.01	1.9	-
100-200 212-392	5.7	0.03	5.7	0.06	6.8	0.01	6.7	0.01	4.3	0.02	8.2	0.02
200-250 392-482	5.5	0.04	4.9	0.07	5.3	0.03	5.1	0.04	6.0	0.02	1.6	0.03
250-275 482-527	4.2	0.05	4.2	0.09	4.0	0.03	4.1	0.06	3.8	0.01	3.7	0.06
275-332 527-630	8.4	0.07	5.6	0.13	7.0	0.06	6.0	0.05	8.0	0.02	6.6	0.10
332-361 630-682	5.1	0.07	4.9	0.17	5.5	0.06	5.4	0.09	9.6	0.05	3.9	0.08
361-391 682-736	2.8	0.09	4.0	0.19	4.3	0.06	3.0	0.08	0.7	-	2.5	0.08
391-421 736-790	6.6	0.15	4.8	0.20	4.2	0.07	5.2	0.13	3.6	0.05	6.0	0.13
421-524 790-975	20	0.22	22	0.27	19	0.15	21	0.17	19	0.09	20	0.18
+524 +975	36	0.52	37	0.62	36	0.40	38	0.43	34	0.41	40	0.63
Sulphur Removed	0.7		0.6		0.7		0.6		0.7		0.6	
Totals	100		100		100		100		100		100	

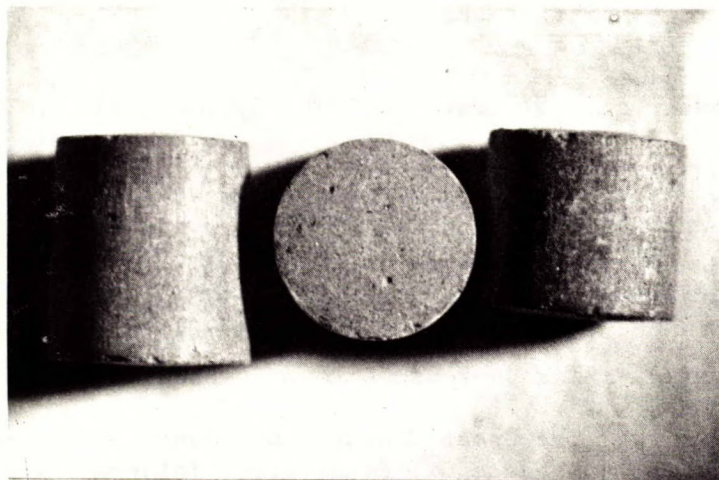
18

PRESSURE = 2000 psi

REACTION TEMPERATURE = 460°C

LHSV = 1.05

HYDROGEN FLOW RATE - 5000 scf/bbl



New catalyst.



Catalyst used with
Leduc pitch.
(regenerated 3 times)



Catalyst used with
Athabasca bitumen.
(regenerated 3 times)

Figure 5. Photographs of catalysts used in the life-runs.

REFERENCES

1. E.C. McColgan, P.S. Soutar and B.I. Parsons, "The Hydrocracking of Residual Oils and Tars"
 - Part 1 - Mines Branch Research Report R-246 (1971)
 - Part 2 - Mines Branch Research Report R-253 (1972)
 - Part 3 - Mines Branch Research Report R-256 (1972)
 - Part 4 - Mines Branch Research Report R-261 (1973)
 - Part 5 - Mines Branch Research Report R-263 (1973)Department of Energy, Mines and Resources, Ottawa, Canada.
2. A.R. Allan and E.R. Sanford, "The Great Canadian Oil Sands Operation", published in a Guide to the Athabasca Oil Sands Area, Information Report Series 65, Alberta Research, Edmonton, Alberta (1973).
3. An application to the Energy Resources Conservation Board of the Province of Alberta to amend Approval No. 1725 under Part 8 of the Oil and Gas Conservation Act by Atlantic Richfield Canada, Ltd., Canada-Cities Service, Ltd., Gulf Oil Canada Ltd., and Imperial Oil Ltd., March 5, 1973, and
A.W. Hyndman, "Athabasca Bitumen High Conversion to Synthetic Crude", 22nd Canadian Chemical Engineering Conference, Toronto, Ontario, September 19th, 1972.
4. Proposed Petrofina Tar Sands Plant, Oilweek Magazine published by Maclean Hunter Ltd., Calgary, Alberta, pages 12-13, January 28th issue, 1974.
5. 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, and
D.H. Quinsey, W.H. Merrill, W.A.O. Herrmann and M.P. Pleet, Can. J. Chem. Eng., 47, 418-421 (1969).
6. S.B. Alpert, M.C. Chervenak, S.C. Schuman and R.H. Wolk, "The H-oil Process - Recent Advances", Preprint 21D presented at the 64th National Meeting of the American Institute of Chemical Engineers, New Orleans, March 16-19, 1969.
7. C.A. Johnson, M.C. Chervenak, E.S. Johanson and R.H. Wolk, "Scale-up Factors in the H-Coal Process", presented at the 65th Annual Meeting of the American Institute of Chemical Engineers, New York, November 26-30, 1972.

8. Plants to produce synthesis gas (H_2 and CO) by the reaction of liquid fuels with oxygen and steam using the Koppers-Totzek process.
 - (a) Heinrich Koppers GmbH, 43 Essen 1, Postfach 8, Moltkestrasse 29, Germany.
 - (b) Koppers Co. Inc., Pittsburgh, Pennsylvania 15219, U.S.A.
9. W.H. Merrill, R.B. Logie and J.M. Denis, "A Pilot-Scale Investigation of Thermal Hydrocracking of Athabasca Bitumen", Mines Branch Research Report R-281, Department of Energy, Mines and Resources, Ottawa, Canada (1974).
10. C.M. Frost and P.L. Cottingham, "Hydrodesulphurization of Venezuelan Residual Fuel Oils", Report of Investigations 7557, U.S. Department of the Interior, Bureau of Mines (1971).

