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*THE HYDROCRACKING OF RESIDUAL
OILS AND TARS
PART 4: CATALYST DE-ACTIVATION WITH
BITUMENS FROM ATHABASCA, COLD LAKE,
AND LLOYDMINSTER*

E.C. McCOLGAN, P.S. SOUTAR, J.M. DENIS, AND B.I. PARSONS

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THE HYDROCRACKING OF RESIDUAL OILS AND TARS
PART 4: CATALYST DE-ACTIVATION WITH BITUMENS FROM ATHABASCA,
COLD LAKE AND LLOYDMINSTER

by

E. C. McColgan*, P. S. Soutar*, J. M. Denis**
and B. I. Parsons**

ABSTRACT

The report describes an investigation of the effect of low concentrations of clay and silt (<1 %) in bitumen feed stocks on catalyst de-activation in hydrocracking and desulphurization processes. The experiments were done in the liquid phase in a bottom-feed, continuous-flow apparatus at 2000 psi and a liquid hourly space velocity of 1.05 over a commercial cobalt molybdate catalyst. Feed stocks used were bitumens from the Athabasca tar sands (0.88 % solids), Cold Lake (0.03 % solids) and Lloydminster (0.07 % solids). The extent of catalyst de-activation observed with each feed stock was essentially the same. In addition, no significant amounts of clay or silt were found in the catalyst bed at the conclusion of any series of experiments. From these observations it is concluded that finely dispersed clay and silt tend to wash out of the reaction system and, as such, are not the prime cause of catalyst de-activation.

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Direction des mines

Rapport de recherches R-261

L'HYDROCRAQUAGE DES HUILES RÉSIDUELLES
ET DES GOUDRONS

4^ePartie: LA DÉACTIVATION DU CATALYSEUR AVEC LES BITUMES
D' "ATHABASCA", DE "COLD LAKE" ET DE
"LLOYDMINSTER"

par

E. C. McColgan*, P. S. Soutar*, J. M. Denis**
et B. I. Parsons**

RÉSUMÉ

Dans ce rapport, les auteurs décrivent une recherche sur l'effet de basses concentrations d'argile et de limon dans des stocks d'alimentation de bitume sur la déactivation du catalyseur dans les procédés d'hydrocraquage et de désulfuration. Ils ont fait des expériences à la phase liquide en utilisant un appareil d'écoulement continu avec un réacteur d'alimentation par le bas à 2000 psi et aux vitesses spatiales liquides par heure de 1.05 sur un catalyseur commercial au cobalt et au molybdène. Ils ont utilisé des stocks d'alimentation qui sont des bitumes des sables asphaltiques d' "Athabasca" (solides de 0.88 %) du "Cold Lake" (solides de 0.03 %) et du "Lloydminster" (solides de 0.07 %). Le degré de la déactivation du catalyseur observé avec chaque stock d'alimentation était essentiellement le même. De plus ils n'ont pas trouvé de montants significatifs d'argile et de limon dans la couche du catalyseur à la fin de n'importe quelles séries d'expériences. D'après ces observations ils sont venus à la conclusion que l'argile et le limon finement dispersés ont tendance à s'entraîner hors du système de réaction et, de ce fait, ne sont pas la cause principale de la déactivation du catalyseur.

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CONTENTS

	<u>Page</u>
ABSTRACT	i
RÉSUMÉ	ii
INTRODUCTION	1
EXPERIMENTAL	2
Apparatus and Procedure	2
Feed Stocks	3
EXPERIMENTAL RESULTS AND DISCUSSION	4
General Comments on the Reactivity of the Three Bitumens	4
Catalyst De-activation	8
ACKNOWLEDGEMENTS	11
REFERENCES	12

Figures

1 - The effect of reaction temperature on the conversion of the +975°F residuum to distillable oil and on sulphur removal	6
2 - The specific gravity and experimentally observed yields of liquid product	7
3 - The effect of reaction temperature on the yield and sulphur content of the product fractions	10

Tables

1 - Properties of the Bitumen Feed Stocks	5
2 - Distillation and Sulphur Analyses on the Bitumen Feed Stocks	5
3 - A Comparison of the Conversions Attained in the First and Second Runs at 440°C	9

INTRODUCTION

This is the fourth report in a series (1, 2, 3) on the investigation of techniques for hydrocracking residual oils and tars. In the third report the effect of gross concentrations of mineral matter (1 to 4 %) on the thermal and catalytic hydrocracking of Athabasca bitumen were described. This report is concerned with the effects of low concentrations of clay and silt (<1 %) in bitumen feed stocks, with a view to determining whether the deposition of mineral matter on the catalyst surfaces is the prime cause of the de-activation observed in the catalytic process. The experiments were done in the liquid phase in a bottom-feed, continuous-flow apparatus.

Previous work on the hydrocracking of heavy oils and tars at the Mines Branch has been done, almost exclusively, on bitumen separated from the Athabasca tar sands. The concentration of residual clay and silt retained in the separated bitumen is generally of the order of 0.8 to 1.0 % by weight (4). Hydrocracking and desulphurizing catalysts of the cobalt molybdate type are de-activated rapidly by the bitumen at moderate temperatures (430 - 460°C) and conversion levels (70 - 80 %). The practical working life of a catalyst appears to be only 50 to 200 hours in the hydrogen pressure range 1000 - 2000 psi (2). Though no experiments have been undertaken to prove the point, it has always been believed that a large part of the de-activation is due to the gradual accumulation of the residual clay and silt on the active surfaces of the catalyst (with the balance being attributed to metals deposition and carbon fouling). The purpose of the present work was to establish, semi-quantitatively, the proportion of the de-activation observed with Athabasca bitumen that is attributable to the mineral matter.

Ideally, to minimize side-effects, the proportion of the catalyst de-activation due to the mineral matter should be determined using Athabasca bitumen which has been de-mineralized to varying degrees below one per cent. Unfortunately, no practical way exists at the present time to prepare sufficient silt-free bitumen for an investigation of useful duration. Much of the clay and silt is finely dispersed in the asphaltic fractions and procedures used to

reduce the mineral content below 1 % usually result in a lowering of the asphalt concentration in the bitumen. This alters considerably the reaction characteristics of the feed stock and makes direct comparison difficult.

To circumvent the problem, two bitumen feed stocks have been selected from other areas of the deposit (south of the Athabasca region) where mineral concentrations are much less, i.e., from the Cold Lake reserve in Alberta and the Lloydminster oil field on the Alberta-Saskatchewan border. Except for the mineral concentration, these feed stocks are chemically and physically very similar to the Athabasca bitumen. Hydrocracking experiments have been made to determine the extent of catalyst de-activation with each feed stock and from these results the effect of residual clay and silt was assessed.

EXPERIMENTAL

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 an exit gas rate of 5000 standard cubic feet per barrel (scf/bbl).

A series of experiments with each feed stock consisted of four consecutive 3-hour runs at increasing temperatures, 430, 440, 450, and 460°C followed by a 3-hour repeat run at 440°C (designated as 440 (2) in the Figures). The product of the second run at 440°C was compared with that from the first to obtain a measure of the extent of catalyst de-activation. The background to this particular procedure is explained fully in the second report in this

series. The analytical procedures used on the feed stocks and products are also described in the second report.

The catalyst used was a commercial cobalt molybdate on alumina manufactured by the Harshaw Chemical Co. of Cleveland, Ohio. The catalyst, 1/8-inch-diameter 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 general physical properties were as follows:

apparent bulk density	64 lb/cu ft
crush strength	24 lb/pellet
surface area	166 m ² /g
pore volume	0.40 ml/g

Feed Stocks

Bitumen from the Athabasca tar sands was obtained from Great Canadian Oil Sands Ltd. of McMurray, Alberta. The Athabasca material is separated from the sand using the Clark Hot-Water Process and froth flotation (5) followed by dilution with naphtha and centrifuging (4). The residual concentration of 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.

Two lots of bitumen (chemically very similar to the Athabasca material) containing less than 0.1 % mineral matter were obtained from Imperial Oil Enterprises of Sarnia, Ontario. One lot was from the Cold Lake reserve in Alberta and the other from the Lloydminster oil field on the Alberta-Saskatchewan border. The Lloydminster material was supplied as the pipeline blend of the bitumen crude diluted with Rimby condensate to reduce the viscosity. Before use, this blend was topped to 500°F (removing approximately 20 % by weight light ends) in a pilot-scale, continuous distillation unit at the Fuels Research Centre. The Cold Lake bitumen was used as received.

The general properties of the three bitumens are listed in Table 1 and the results of the distillation and sulphur analyses on the various fractions are shown in Table 2. The boiling range of the fractions given in Table 2 are the same as those used in the description of the distillate properties of the products. Hydrocarbon material boiling up to the equivalent of 975°F at one atmosphere pressure is classed as distillable oil, and material boiling above 975°F equivalent temperature is residuum. The metals content, the Conradson carbon residue and the sulphur concentration in the three bitumens are all of the same order. Significant differences occur only in the ash content and in the benzene and carbon disulphide insolubles, e.g., 0.88 % CS₂ insolubles in the Athabasca material compared with 0.03 % for the Cold Lake bitumen and 0.07 % for the Lloydminster.

EXPERIMENTAL RESULTS AND DISCUSSION

General Comments on the Reactivity of the Three Bitumens

When the investigation was begun it was anticipated that, all things being equal, the extent of conversion and desulphurization observed with the Athabasca feed stock would be slightly less than with the Cold Lake or the Lloydminster bitumens. Previous work (3) had shown that gross concentrations of mineral matter (4 %) did, in fact, result in a measurable lowering of the hydrocracking activity of the catalyst, and it was expected that this effect would extend to lower concentrations as well. It was somewhat surprising then to observe that the extent of conversion of the residuum in the Athabasca feed stock was slightly greater than that measured with the Cold Lake or the Lloydminster bitumens. The differences were not large but the over-all conversion was consistently higher by about 5 % at all temperatures. A summary of the experimental results is given in Figures 1 and 2. The effect of reaction temperature on the conversion of the residuum hydrocarbon to distillable oil and on sulphur removal is shown in Figure 1 and the yields of liquid product and the specific gravities are indicated in Figure 2.

Table 1

Properties of the Bitumen Feed Stocks

Details of Analysis	Athabasca	Cold Lake	Lloydminster (reduced)
Specific Gravity 60/60°F	1.000	0.997	0.982
Ash (wt %) 700°C	0.70	0.030	0.043
Nickel (ppm)	68	65	54
Vanadium (ppm)	189	165	115
Conradson Carbon Residue (wt %)	12.6	12.3	11.5
Pentane Insolubles (wt %)	15.83	15.70	14.73
Benzene Insolubles (wt %)	0.90	0.04	0.10
Carbon Disulphide Insolubles (wt %)	0.88	0.03	0.07
Sulphur (wt %)	4.72	4.50	4.12
Nitrogen (wt %)	0.38	0.49	0.40
Viscosity, Kinematic (cSt) at 210°F	129.5	117.4	77.5
Viscosity, Kinematic (cSt) at 150°F	-	789.7	420.
Viscosity, Kinematic (cSt) at 130°F	2041	-	-
Molecular Weight (calculated)	722	725	720

Table 2

Distillation and Sulphur Analyses on the Bitumen Feed Stocks

Boiling Range of Fraction Equiv. Temp. at one atm (°C) (°F)		Athabasca		Cold Lake		Lloydminster (reduced)	
		Wt % of Fraction	Wt % Sulphur	Wt % of Fraction	Wt % Sulphur	Wt % of Fraction	Wt % Sulphur
RT-100	RT-212	-	-	-	-	-	-
100-200	212-392	2.1	-	-	-	-	-
200-250	392-482	1.5	1.15	2.6	1.09	2.2	0.67
250-275	482-527	5.2	1.65	5.3	1.64	4.3	0.97
275-332	527-630	5.5	2.49	4.9	2.43	8.2	1.53
332-361	630-682	6.9	2.78	6.2	2.68	6.8	1.91
361-391	682-736	5.1	3.10	4.1	3.03	4.7	2.25
391-421	736-790	6.7	3.38	6.1	3.27	6.8	2.53
421-524	790-975	16	3.86	16	3.55	18	2.59
+524	+975	51	6.25	55	5.89	49	5.80

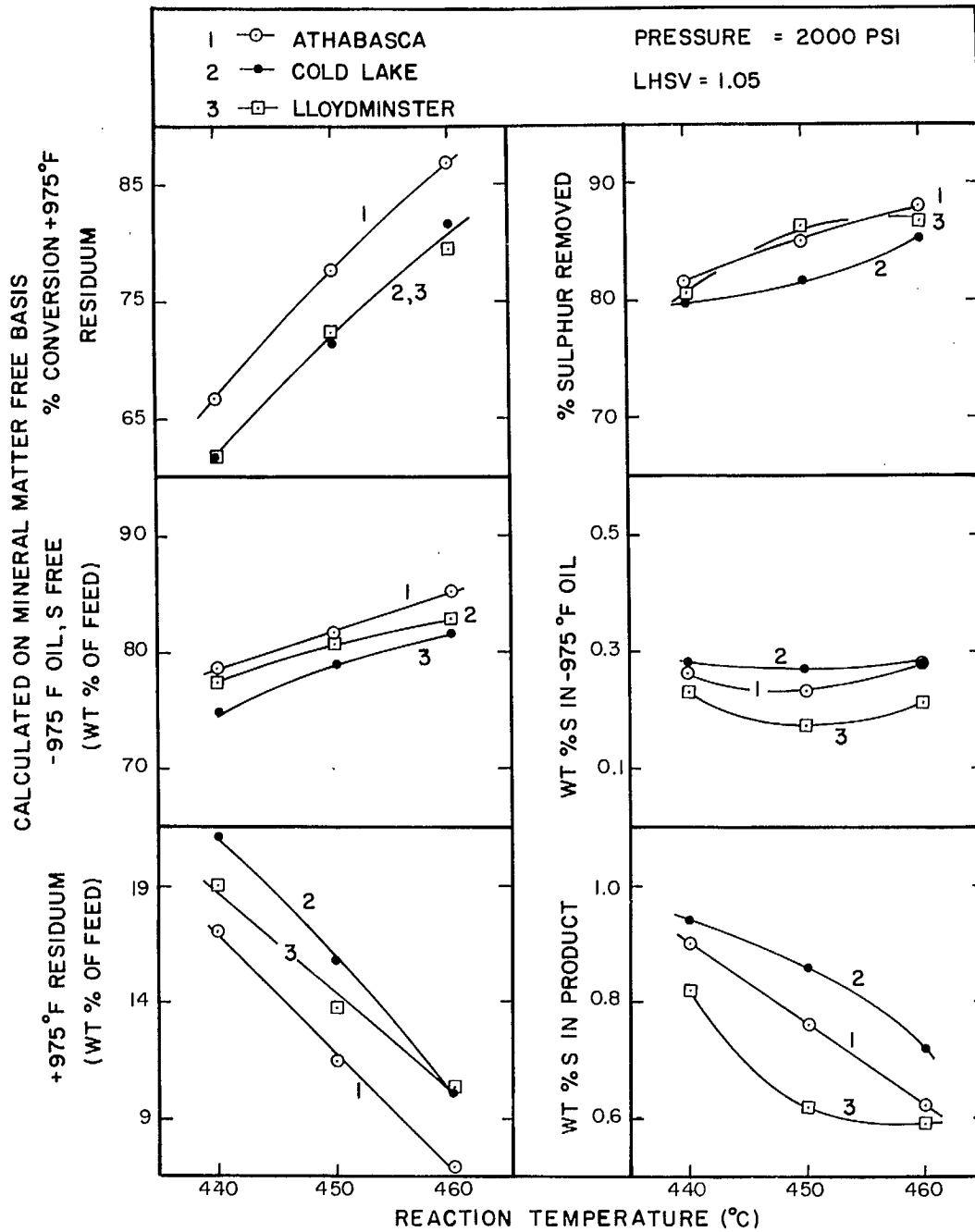


Figure 1 - The effect of reaction temperature on the conversion of the +975°F residuum to distillable oil and on sulphur removal. (Note: the residuum remaining in the product and the distillable oil produced are expressed as weight % of feed.)

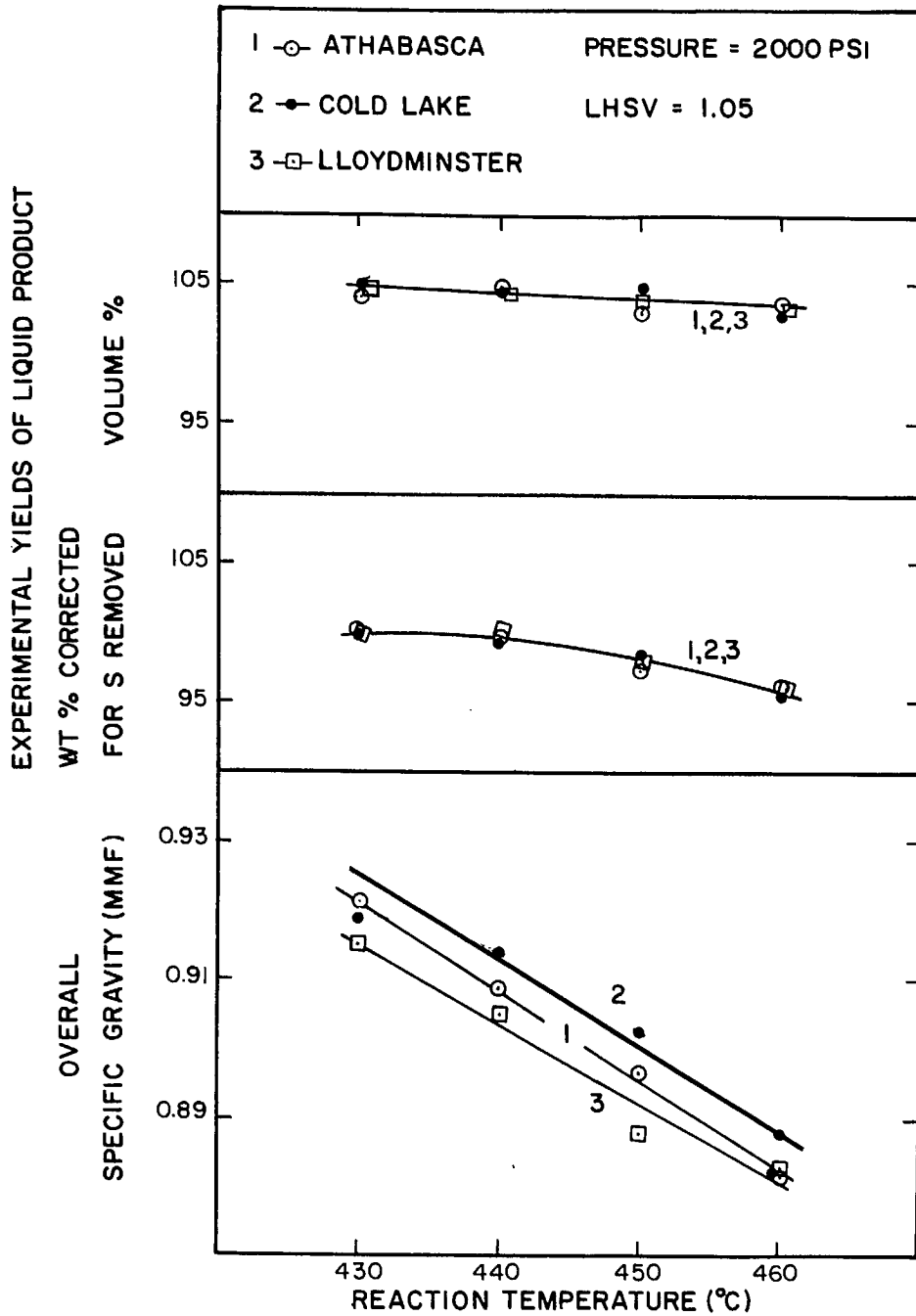


Figure 2 - The specific gravity and experimentally observed yields of liquid product.

The increased reactivity of the Athabasca material cannot reasonably be attributed to hydrogen donor activity or the effect of dilution (1) because the concentrations of low-boiling hydrocarbons in all of the feed stocks are very similar*. It appears that the increased conversion is due mainly to the presence of the finely dispersed mineral matter in the bitumen. The process used by Great Canadian Oil Sands Ltd. to separate the sand and clay from the Athabasca bitumen involves froth flotation followed by dilution and centrifuging. The nature of the separation process suggests that the residual mineral matter is oil-wet material intimately associated with (perhaps enveloped in) the asphaltic fractions. If this picture is correct, a small increase in conversion due to thermal hydrocracking alone would be expected, on the basis of the increased amount of surface presented to the reaction system. The results of our work indicate that any catalytic activity possessed by the residual clay and silt must be small because the differences in conversion observed are only of the order of 5 per cent.

Catalyst De-activation

Essentially the same degree of catalyst de-activation was observed with all three bitumen feed stocks. A comparison of the conversions attained in the first and second runs at 440°C is given in Table 3, and the effect of reaction temperature on the yield and sulphur content of the product fractions is shown in Figure 3. Viewed as a whole, the differences between the two runs at 440°C (and their products) are very similar for each feed stock. There is nothing in any of the experimental results to indicate that a significant part of the catalyst de-activation recorded with the Athabasca bitumen is due to the higher concentration of mineral matter.

There was also no physical indication that measurable amounts of mineral matter were being deposited on the catalyst surfaces from the Athabasca bitumen. Approximately 12,000 grams of feed oil were pumped through the catalyst

*The concentrations of hydrocarbons distilling up to 630°F were 14.3 %, 12.8 % and 14.7 % by weight, respectively, for the Athabasca, Cold Lake, and Lloydminster feed stocks.

Table 3

A Comparison of the Conversions Attained in the First
and Second Runs at 440°C

Feed Stock	% Sulphur Removed			% Conversion +975°F Residuum		
	First Run	Second Run	Change	First Run	Second Run	Change
Athabasca	82	76	6	67	61	6
Cold Lake	80	73	7	62	57	5
Lloydminster	81	75	6	61	58	3
Operating Pressure: 2000 psi				LHSV = 1.05		
Exit Gas Rate: 5000 scf/bbl						

bed (volume = 150 ml) in each series of experiments. In the case of the Athabasca bitumen the amount of mineral matter associated with this weight of feed was approximately 110 grams. If a significant proportion of the mineral matter was being deposited on the catalyst it would seem reasonable that it could be detected. However, when the covers of the reactor were removed the catalyst pellets used in the runs with the Athabasca feed stock rolled freely from the vessel, and appeared no different from the catalyst used in the experiments with the Cold Lake or the Lloydminster bitumens. From these observations it is concluded that in the bottom-feed (liquid phase) mode of operation, the mineral matter is being washed out of the reaction system with the liquid oils. Similar results have been reported in the application of ebullated bed systems to the hydrogenation of high-ash coals (6).

The apparent insensitivity of the catalyst system to finely dispersed clay and mineral matter in the feed stock focuses attention on other causes for the de-activation observed. As mentioned previously, there are at least two alternative causes of catalyst deactivation (operating separately or in some combination):

- a) metals poisoning, and
- b) coke (or high-polymer tar) fouling

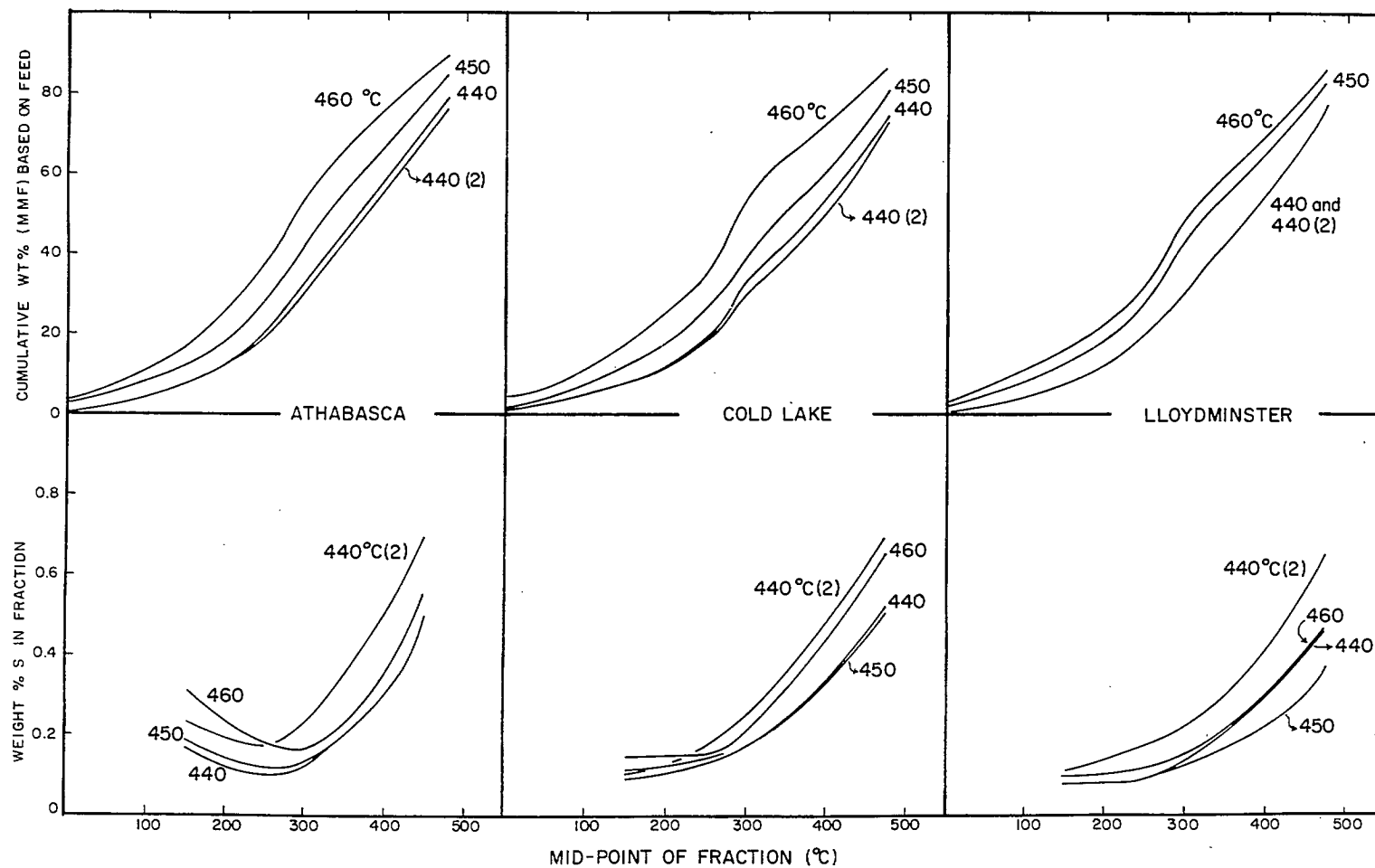


Figure 3 - The effect of reaction temperature on the yield and sulphur content of the product fractions. (Note: the product fractions are expressed as weight % of feed with the extent of gas formation indicated at 0°C. The boiling range of the fractions used are the same as those shown in Table 2.)

In the case of the three feed stocks used here, the metal contents and Conradson carbon residues are all comparable (and high). Therefore, the degree of catalyst de-activation observed with each would be expected to be similar whichever mechanism applied.

One way to differentiate between metals poisoning and carbon fouling is to experiment with feed stocks of similar character but widely differing metals concentration. In a precise way, it is probably not possible to obtain such feed stocks, i.e., widely differing metals concentration and similar chemical character, but a qualitative assessment should be possible using residuum feed stocks derived from low-metal, sweet crude oil. This will be the subject matter of another report in the series.

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