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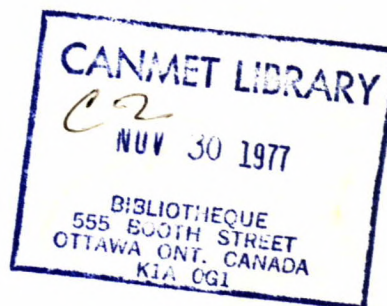
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CATALYTIC HYDROCRACKING OF ATHABASCA BITUMEN IN A FLUIDIZED BED REACTOR - EFFECT OF PRESSURE ON CATALYST DECAY

R. Ranganathan, R.B. Logie and J.M. Denis

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CATALYTIC HYDROCRACKING OF ATHABASCA BITUMEN
IN A FLUIDIZED BED REACTOR
EFFECT OF PRESSURE ON CATALYST DECAY

by

R. Ranganathan*, R.B. Logie* and J.M. Denis**

ABSTRACT

This report describes a study of the effect of pressure on catalyst decay during the hydrocracking of Athabasca bitumen in a fluidized-bed reactor. A cobalt-molybdenum catalyst (Nalcomo 471, 60-140 mesh, 3.2 wt % CoO-12.5 wt % MoO₃/alumina) was evaluated. Two stages of deactivation occurred; initially a rapid deactivation followed by slow deactivation. The deposition of mineral matter and strong chemisorption of heavy aromatic hydrocarbons might have been responsible for the initial rapid deactivation. These stages can be fitted to a linear equation (slow deactivation) and an exponential equation (rapid deactivation). The results of the experiment are shown to be reproducible. A qualitative discussion on the comparison of catalyst deactivation in fixed fluidized bed reactors is given.

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HYDROCRAQUAGE CATALYTIQUE DE BITUME D'ATHABASCA SUR LIT
FLUIDISE EFFETS DE LA PRESSION SUR LA
DESACTIVATION DU CATALYSEUR

par

R. Ranganathan*, R.B. Logie* et J.M. Denis**

RESUME

Les auteurs rendent compte des résultats d'une étude sur les effets de la pression sur la désactivation du catalyseur, pendant l'opération d'hydrocraquage sur lit fluidisé de bitume d'Athabasca. Ils évaluent un catalyseur cobalt molybdène (Nalco 471, maille 60-140, 3,2% de CoO-12,5% de MoO₃/alumine en poids). La désactivation se produit en deux étapes: l'activité du catalyseur décroît rapidement au début, et lentement par la suite. Le dépôt de matière minérale et la forte chimisorption d'hydrocarbures aromatiques lourds pourraient être la cause de la désactivation rapide du début. Ces étapes peuvent être représentées par une équation linéaire (désactivation lente) et par une équation exponentielle (désactivation rapide). Les résultats de l'expérience s'avèrent reproductibles. Les auteurs établissent également une comparaison qualitative entre la désactivation du catalyseur dans un réacteur à lit fixe et celle qui s'opère sur lit fluidisé.

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CONTENTS

	<u>Page</u>
ABSTRACT	i
RESUME	ii
INTRODUCTION	1
EXPERIMENTAL	2
Feedstock and Catalyst	2
Catalyst Decay Studies	2
RESULTS AND DISCUSSION	3
Reproducibility of Catalyst Decay Studies	3
Effect of Pressure on Catalyst Decay	3
Comparison of Fixed- and Fluidized-Bed Reactors	5
Models for Catalyst Deactivation	6
SUMMARY	8
REFERENCES	9
TABLES 1-4	11-14
FIGURES 1-8	15-22

INTRODUCTION

Catalytic hydrocracking has been extensively evaluated for upgrading residual feedstocks (1,2). Several studies have been conducted at the Energy Research Laboratories to evaluate catalytic hydrocracking as an alternative process for upgrading Athabasca bitumen (3,4). This study is a part of the Energy Research Program at CANMET (Canada Centre for Mineral and Energy Technology, formerly Mines Branch) to develop an economically feasible process for obtaining synthetic crude from Athabasca bitumen. The main problem with catalytic hydrocracking is the rapid activity decline of the catalyst. This necessitates frequent replacement of the poisoned catalyst resulting in excessive catalyst costs. McColgan and Parsons (3) estimated 50-55¢/bbl as the permissible cost of catalyst in upgrading Athabasca bitumen. Additional catalyst costs can be held to a minimum if either a stable catalyst with long active life or a cheap throw-away catalyst is used. In both cases, catalyst activity-decay studies are essential to establish catalyst requirements and process parameters.

Catalyst decay in Athabasca bitumen processing is extremely rapid because of the deposition of mineral matter, metals and coke. The active life of some catalysts is as low as 100 hours. The coke deposited on the catalyst can be removed by burning in air, hence the activity lost because of coke deposition is only a temporary deactivation. However, the mineral matter and metals deposited on the catalyst lead to a permanent deactivation as the catalyst can not be restored to its original activity by conventional regenerating procedures (5). It has also been shown that non-distillable char (containing coke, mineral matter and metals) on a cobalt-molybdenum catalyst decreased as reaction pressure increased from 7.0 MPa to 17.3 MPa (3).

So far, the catalyst decay studies in Athabasca bitumen processing have been carried out mainly in a fixed-bed reactor (3,4,5). Catalyst decay studies in fluidized-bed reactors have not been reported. However, many patents on the upgrading of residual feedstocks use either fluidized or ebullated-bed systems. The ability of fluid-bed reactors to maintain constant catalyst activity by continuous catalyst addition and removal is an important advantage over a fixed-bed reactor. Development of a cheap throw-away catalyst for bitumen upgrading would lead to a slurry-type reactor and hence catalyst decay studies in a fluid-bed reactor are essential to

provide helpful information for both fluidized and slurry-type bitumen upgrading systems.

EXPERIMENTAL

Feedstock and Catalyst

Athabasca bitumen feedstock was supplied by Great Canadian Oil Sands Ltd. of Alberta. The properties of the bitumen are given in Table 1. It is seen that this bitumen contains a high weight percentage of mineral matter, metals, sulphur, nitrogen and oxygen. A cobalt-molybdenum/alumina catalyst (Nalcomo 471) was used for the catalyst decay studies. This catalyst is widely used in residual feedstock desulphurization (1) and is a powder (60-140 mesh) containing 3.2 wt % CoO and 12.5 wt % MoO₃. The catalyst surface area, pore volume and average pore diameter were 2.8×10^5 m²/kg, 1.2×10^{-4} m³/kg and 17.1 nm respectively.

Catalyst Decay Studies

The catalyst decay studies were carried out in the pilot plant shown in Figure 1. The details of the pilot plant are described elsewhere (6). The reactor was operated as a batch fluidized-bed for the catalyst decay studies. Initially, 1500 cc of catalyst was charged to the reactor; bitumen and hydrogen were then pumped into the reactor from the bottom. The hydrogen flow rate was maintained at 0.042 m³/h at reactor pressure. This high flow rate of hydrogen maintained the catalyst in a fluidized state. These flow rates were selected after preliminary studies at atmospheric conditions in a plastic model of the reactor. The bed expansion was low enough so that no catalyst was carried over from the reactor. The product from the top of the reactor (gas-liquid mixture) flowed into a hot receiver. The hot receiver was maintained at 350°C for all experiments. The condensed liquid is known as heavy oil. The gases from the hot receiver were then sent to a cold receiver and light oil was withdrawn. The uncondensed gases then went through a scrubber and were recycled with make-up hydrogen. The total liquid product was obtained by combining heavy- and light-oil products. The sulphur content and specific gravity were determined for all products. The conversion temperature of pitch (+524°C) to lower boiling-point fractions was found by distillation (6).

The catalyst decay was studied at pressures of 7.0, 13.9 and 20.8 MPa. The reaction temperature, space velocity, hydrogen flow rate and hydrogen recycle gas purity were maintained constant for all experiments at 450°C, 1 h⁻¹, 0.042 m³/h and 85% respectively. The hydrogen consumption was measured as described in a previous report (6).

RESULTS AND DISCUSSION

Reproducibility of Catalyst Decay Studies

Two experiments carried out at 13.9 MPa indicate that the experimental results are reproducible (Figure 2). The deviations in sulphur values are within ± 0.04 wt %. The increase in sulphur content (decrease in catalyst activity) with operating time occurred in two stages; a rapid deactivation followed by a slower deactivation. This trend is similar to the coke formation on a platinum/alumina reformer catalyst (7). Butt (8) also observed a rapid initial deposition of coke on the very active surface, forming a well-defined outer shell, for cumene cracking on H mordenite catalyst. He reported that, subsequent to this period, diffusion through the shell appeared to control the rate of coke deposition and activity decline. For the results shown in Figure 2, the activity decline is not only due to coke, but also due to the deposition of mineral matter and strong chemisorption of heavy aromatic hydrocarbons containing metals. The initial deactivation period probably includes the formation of a shell on the external surface of catalyst particles by coke, metals and mineral matter.

Effect of Pressure on Catalyst Decay

The variations in sulphur content and specific gravity at various pressures for heavy oil, light oil and total liquid product are shown in Figures 3 to 5. These results show that the sulphur values were generally more responsive to deactivation than the specific gravity values which for light oil were significantly affected by different pressures. The specific gravity values showed an unexpected pattern at high reaction pressures, where the specific gravity of the light-oil was higher than that at lower pressures. This was probably caused by the effect of pressure on the conversion of heavier fractions into lower boiling range fractions. At higher pressures more heavy oil is converted, which increases

the specific gravity of the light oil. In the case of sulphur, such an anomaly was not observed. Increasing reaction pressure resulted in a decrease of sulphur content in the light oil. The percentage weight of sulphur clearly showed that, with increasing reaction pressure, the rate of deactivation (slope of the isotherm) decreased. Figure 5 shows that the two stages of deactivation, namely rapid and slow deactivation, are obtained at all pressures. The second stage of deactivation is affected significantly by increasing pressure; however, the initial rate of rapid deactivation is not significantly affected by variations. The rates of deactivation in the first and second stage at 7.0 MPa pressure, differ only slightly compared with differences at higher pressures. Hence at pressures lower than 7.0 MPa, the catalyst deactivation process will be a single rapid deactivation process instead of the two-stage deactivation.

The results obtained for Athabasca bitumen were slightly different from the catalyst deactivation isotherms for coker distillate derived from Athabasca bitumen. Aitken et al. (9) found that the rapid deactivation was absent at 20.8 MPa. This is probably due to the fact that the ash content in coker distillate was only 0.03 wt % compared to 0.56 wt % in Athabasca bitumen. Hence, the deactivation in the case of coker distillate is primarily caused by coke. It is clear that the deactivation process for Athabasca bitumen is further complicated by the presence of metals and mineral matter.

The hydrogen consumption and pitch conversion in the liquid products show trends similar to sulphur (Figure 6). The hydrogen consumption and pitch conversion decreased with operating time; with higher reaction pressure the pitch conversion increased with a corresponding increase in hydrogen consumption. The decrease in pitch conversion with operating time indicated that hydrocracking activity of the catalyst was also being lost.

The product samples collected were distilled and analyzed to determine the sulphur, unsaturates, saturates and the distribution of the different boiling-range fractions. The catalyst deactivation affected the sulphur content in the heavier fractions more than in the lighter fractions (Figure 7). This may be due to the fact that the sulphur compounds in the higher boiling fractions are more difficult to remove (10). The product distribution shown in Table 2 indicates that the contents of 250-333°C and 333-418°C fractions are not changed by deactivation. However, there was a slight drop in light fractions and an increase in heavy fractions during the initial deactivation

period. The reaction pressure did not have any effect on the composition of the middle fractions (Table 3) but it did have significant effects on the wt % sulphur of all fractions. The sulphur content in all fractions decreased with increasing pressure. A slight decrease in saturates of both IBP-200°C and 200-250°C fractions was observed with operating time (Figure 8). The changes in pressure surprisingly did not affect the amount of saturates in these fractions. It is possible that the effects of pressure would be more noticeable for higher boiling fractions since it has been reported in literature (11) that for hydrogenation of three-ring aromatics, the equilibrium limitations are important at pressures of about 7.0 MPa and temperatures above 400°C.

Comparison of Fixed- and Fluidized-Bed Reactors

It is reasonable to expect that the catalyst deactivation patterns will be different from those of a fixed-bed system in fluid-bed catalytic hydrocracking of heavy oils. The reaction temperature in the fluid-bed reactor is more uniform and bed plugging due to interstitial deposition is completely eliminated. Further, in a fixed-bed reactor, the catalyst particles in the upstream section are more rapidly deactivated than the catalyst particles in the downstream area. This non-uniform catalyst deactivation would pose problems in optimizing catalyst replacement. Backmixing would be significant in a fluid-bed reactor compared to a trickle-bed reactor, thereby reducing the conversion levels. However, in heavy-oil hydrocracking it has been reported (12,13) that a fixed-bed reactor system with the upflow scheme, where backmixing is present, is more effective in sulphur and metals removal than a down-flow fixed-bed reactor.

The mechanism of catalyst deactivation in heavy-oil hydrocracking supports the idea that full use of the catalyst is made in a fluid-bed reactor. It has been reported that the major cause for deactivation is pore-mouth blocking (14). It has also been reported in coal liquefaction studies that the inorganic deposits penetrated into the catalyst pores only to a depth of about 0.1 mm (15) and the metals penetrated to only about 0.15 mm. These observations suggested that when 1.6-3.2 mm (1/16"-1/8") size catalyst pellets are used, a considerable portion of the internal surface is lost because of pore blocking. Hence, in a fluid-bed reactor, where the particles of 0.2 mm size could be used, a large external surface area is

available for asphaltenes and coke precursors. As the particles are small, the pore-mouth blocking would result in less significant catalyst deactivation.

McColgan and Parsons (3) investigated the deactivation of a cobalt-molybdenum catalyst (Harshaw 0603T, 3 wt % CoO-12 wt % MoO₃/alumina) in a fixed-bed reactor at 7.0 MPa, 440°C and space velocity of 1.05 h⁻¹. Their results showed that the catalyst deactivation followed a pattern similar to that in a fluidized-bed reactor; an initial rapid deactivation followed by a slow deactivation. However, the magnitudes of rates of deactivation in the two reactor systems can not be compared as the catalysts are different. Inoguchi et al. (16) have shown that the deactivation rates were different even for slight variations in catalyst properties. Hence, similar catalysts should be studied in fixed- and fluidized-bed reactors for making quantitative comparisons on deactivation rates. The results reported by Ohtsuka et al. (2) showed that with decreasing particle size (1/4" to 32 mesh) the sulphur removal was higher and the deactivation rates appeared lower. It is conceivable that in a fluidized-bed reactor where catalyst particles are about 0.1-0.2 mm diameter, the deactivation rates will be less than the rates in a fixed-bed reactor where normally at least 1.5-mm size particles are used.

Weekman (17) showed that, with higher values of catalyst decay, fluid-bed reactor conversions were significantly higher than for a fixed-bed reactor. The higher rates of decay would generally be expected for residual feedstocks containing metals, mineral matter and high molecular weight aromatics. It is conceivable that the performance of a fluidized-bed reactor would be better than a fixed-bed reactor for residuum hydrocracking.

Models for Catalyst Deactivation

Several models (8,18) have been presented for catalyst deactivation in the references. Butt (8), Zinkov et al. (19) and Levinter et al. (7) proposed models with two stages of deactivation. Aitken et al. (9) proposed a linear model for catalyst deactivation in coker distillate hydrocracking. The coker distillate contained only 0.03 wt % ash compared to 0.56 wt % in Athabasca bitumen. A model containing two stages of deactivation would be more appropriate for Athabasca bitumen.

An attempt was made to fit the deactivation data obtained in this work (Figure 5) to an exponential equation for each reaction pressure, however, it was found that the deviation from the equation increased with increasing reaction time. This was especially true at higher reaction pressures of 13.9 and 20.8 MPa. Further, the sulphur data presented by Inoguchi et al. (16) for a deactivation test of 3000 hours indicated that after an initial period, the sulphur removal could be represented by a linear equation. It appears from the deactivation results obtained in our work, McColgan and Parsons (3), and in that of Inoguchi et al. (16), that the rapid catalyst deactivation is present up to about 40-hours of operating time. Above this arbitrarily chosen 40 hours of operating time, the deactivation is slow and can be fitted to a linear model; below this the data can be fitted to an exponential equation. It should be noted that the transition from rapid to slow deactivation would depend on the properties of catalyst and feedstock. The empirical model and the results are given in Table 4. It is seen that, in the second stage deactivation, the slope of the equation (proportional to rate of deactivation) is significantly affected by reaction pressure. The slope increases by a factor of 5 with a decrease in pressure from 20.8 MPa to 7.0 MPa. The slope of the equation in the first stage is only slightly affected by reaction pressure. Further studies should be carried out to determine the dependence of these empirical constants on the properties of catalysts and feedstocks.

It should be noted that in this study the reactor was used as a batch fluidized-bed whereas in industrial operations, the catalyst would be continuously added and removed in order to maintain a constant conversion. For such a case, the average residence time of the catalyst would be determined, based on the rates of deactivation obtained using a batch fluidized-bed system or a fixed bed reactor in a pilot plant.

SUMMARY

The catalyst decay studies showed that two stages of deactivation occurred during hydrocracking of Athabasca bitumen. Initially, a rapid deactivation of the catalyst occurred possibly because of the deposition of mineral matter and strong chemisorption of heavy aromatic hydrocarbons. This stage was followed by a slow deactivation of the catalyst. The rates of deactivation during the slow deactivation stage decreased with increasing pressure. The rates of deactivation during the rapid deactivation stage appeared to be relatively independent of pressure.

A comparative discussion of catalyst decay in fluidized- and fixed-bed reactors pointed out some advantages in using fluidized-bed reactors for hydrocracking residual feedstocks. It is recommended that further studies be carried out using catalysts containing the same active metal compositions so that quantitative comparisons of catalyst decay in the two types of reactors can be made.

An empirical model was fitted to the sulphur content. The slow deactivation stage was fitted to a linear equation and the rapid deactivation stage was fitted to an exponential equation.

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REFERENCES

1. Delcos, J., Presson, R.D., Shaw, W.G. and Strecker, H.A. "Fluid-bed hydrocracking of residual stocks"; Amer. Chem. Soc. preprints, Div. Petrol. Chem.; v. 11, no. 3, pp 185-191; Sept. 1966.
2. Ohtsuka, T., Hasegawa, Y. and Takanari, N. "Hydrodesulphurization of Khafii crude oil"; Bull. of Jap. Petrol. Inst.; v. 10, pp 14-19; May 1968.
3. McColgan, E.C. and Parsons, B.I. "The hydrocracking of residual oils and tars"; Mines Branch research report R253; 30 p; Aug. 1972.
4. Soutar, P.S., McColgan, E.C. and Parsons, B.I. "The hydrocracking of residual oils and tars"; Mines Branch Research Report R256; 18 p; Nov. 1972.
5. McColgan, E.C. and Parsons, B.I. "The hydrocracking of residual oils and tars"; Mines Branch Research Report R273; 21 p; May 1974.
6. Merrill, W.H., Logie, R.B. and Denis, J.M. "A pilot scale investigation of thermal hydrocracking of Athabasca bitumen"; Mines Branch Research Report R281; 25 p; Dec. 1973.
7. Levinter, M.E., Berkovich, L.M., Kurchatkina, T.V. and Panfilov, N.A. "Kinetics of coke formation in catalytic reforming, kinetics and catalysis"; v. 16, no. 3, 688 pp; May 1975.
8. Butt, J.B. "Progress toward the apriori determination of catalytic properties"; AIChE Journal; v. 22, no. 1, p 24; Jan. 1976.
9. Aitken, A.R., Merrill, W.H. and Pleet, M.P. "Hydrogenation of a coker distillate derived from Athabasca bitumen"; Can. J. Chem. Eng.; v. 42, pp 234-238; Oct. 1964.
10. Schuit, G.C.A. and Gates, B.C. "Chemistry and engineering of catalytic hydrodesulphurization"; AIChE Journal; v. 19, no. 3, pp 417-438; May 1973.
11. Gully, A.J. and Ballard, W.P. "Hydrogenation of catalytic cracking charge stocks"; Adv. in Pet. Chem. and Ref.; v. 7, pp 241-282; 1963.
12. Takematsu, T. and Parsons, B.I. "A comparison of bottom-feed and top-feed reaction systems for hydrodesulphurization"; Mines Branch Technical Bulletin TB161; 18 p; Sept. 1972.
13. Montagna, A. and Shah, Y.T. "Backmixing effect in an upflow cocurrent hydrodesulphurization reactor"; Chem. Eng. J. (Lausanne); v. 10, no. 2 pp 99-105; 1975.

14. Newson, E.J. "Demetallation, deactivation and bed plugging in residuum hydrodesulphurization"; Amer. Chem. Soc. Div. Petrol. Chem; preprints, A 141; Sept. 1970.
15. Stanulonis, J.J., Gates, B.C. and Olson, J.H. "Catalyst aging in a process for liquefaction and hydrodesulphurization of coal"; AIChE Journal; v. 22, no. 3, pp 576-581; May 1976.
16. Inoguchi, M., Inaba, K., Satomi, Y., Mizutori, T., Sakurada, S., Kagaya, H., Nishiyama, R., Tate, K., Onishi, S. and Nagari, T. "Study on the hydrodesulphurization catalyst of residual fuel (part 2)"; Bull. Jap. Petrol, Inst.; v. 13, no. 1, p 11; May 1971.
17. Weekman, V.W. "A model of catalytic cracking conversion in fixed, moving and fluid-bed reactors"; I and E.C.; Process Des. Dev.; v. 7, no. 1, pp 90-95; Jan. 1968.
18. Butt, J.B. "Catalyst deactivation"; Advan. Chem.; v. 109, p 259; 1972.
19. Zinkov, L.M., Eigenson, S.A., Bobkouskii, E.I., Manshilin, V.V. and Yu, K. "Method of treating experimental data obtained in hydrodesulphurization of residual petroleum feedstocks"; Int. Chem. Eng.; v. 16, no. 3, pp 446-447; July 1976.

TABLE 1

Properties of Bitumen Feed Stock

Specific Gravity, 15/15°C		1.010
Sulphur	wt %	4.77
Ash	wt %	0.56
Benzene insoluble	wt %	0.56
Pentane insoluble	wt %	15.6
Conradson Carbon residue	wt %	13.8
Vanadium	ppm	196
Nickel	ppm	68
Carbon	wt %	82.59
Hydrogen	wt %	10.82
Nitrogen	wt %	0.40
Oxygen	wt %	0.86

Distillation Analysis

Temperature		Distillate		Sulphur in Distillate
°C	°F	Wt %	Sp Gr	wt %
RT-200	RT-392	1.4	0.815	1.58
200-250	392-482	2.2	0.856	1.03
250-334	482-634	9.7	0.902	1.75
334-419	634-787	17.7	0.952	2.97
419-524	787-975	17.5	0.988	3.83
+524	+975	51.5	1.073	6.39

TABLE 2

Product Distribution in Catalytically Hydrocracked
Bitumen (wt % Yields Based on Feed)
 (13.9 MPa, LHSV = 1.0, 450°C)

Time					
Group		4 hrs	28 hrs	60 hrs	92 hrs
IBP-200°C	wt %	16.6	14.1	14.6	13.9
200-250°C	wt %	15.3	9.4	9.9	9.5
250-333°C	wt %	24.6	25.1	24.6	24.9
333-418°C	wt %	23.3	24.2	23.9	24.8
418-524°C	wt %	10.1	12.1	12.0	12.0
524°C +	wt %	3.0	6.2	6.5	6.7

TABLE 3

Effect of Pressure on Distillate
Fractions and Sulphur

Group	Yield, wt % (based on feed)		Sulphur, wt %		
	13.9 MPa pressure	20.8 MPa pressure	7.0 MPa pressure	13.9 MPa pressure	20.8 MPa pressure
IBP-200°C	14.1	13.6	0.35	0.22	0.13
200-250°C	9.4	11.0	0.88	0.38	0.23
250-333°C	25.1	22.8	1.43	0.83	0.56
333-418°C	24.2	23.7	1.85	1.24	0.88
418-524°C	12.1	14.3	3.00	1.59	1.00
524°C +	6.2	5.4	-	2.50	-

TABLE 4

Empirical Model for Deactivation of
Catalyst in a Fluidized Bed Reactor

First Stage "Rapid Deactivation" (t < 40)

$$s = a_1 e^{a_2 t} \quad (\text{Eq. 1})$$

$$\text{i.e., } \log s = \log a_1 + a_2 t \quad (\text{Eq. 2})$$

where

s = sulphur content, wt %

t = operating time, h

a_1, a_2 = empirical constants

Second Stage "Slow Deactivation" (t > 40)

$$s = a_3 t + a_4$$

where

a_3, a_4 are empirical constants

Pressure MPa	Empirical Constants by Regression Analysis			
	First Stage		Second Stage	
	Slope (a_2)	Intercept ($\log a_1$)	Slope (a_3)	Intercept (a_4)
7.0	0.399	-1.0341	0.0107	1.132
13.9	0.498	-1.6245	0.005	0.962
20.8	0.479	-1.8247	0.002	0.874

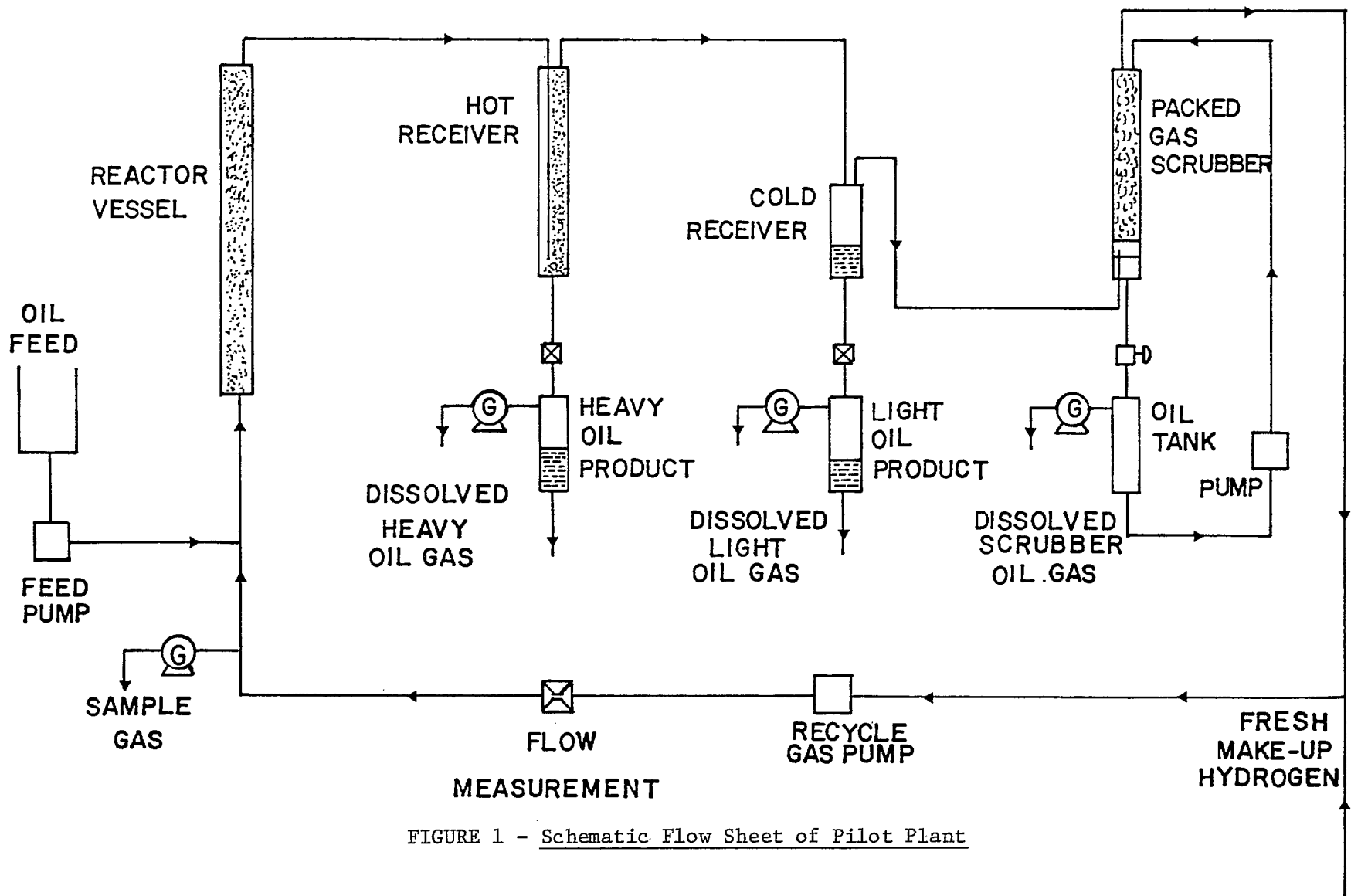
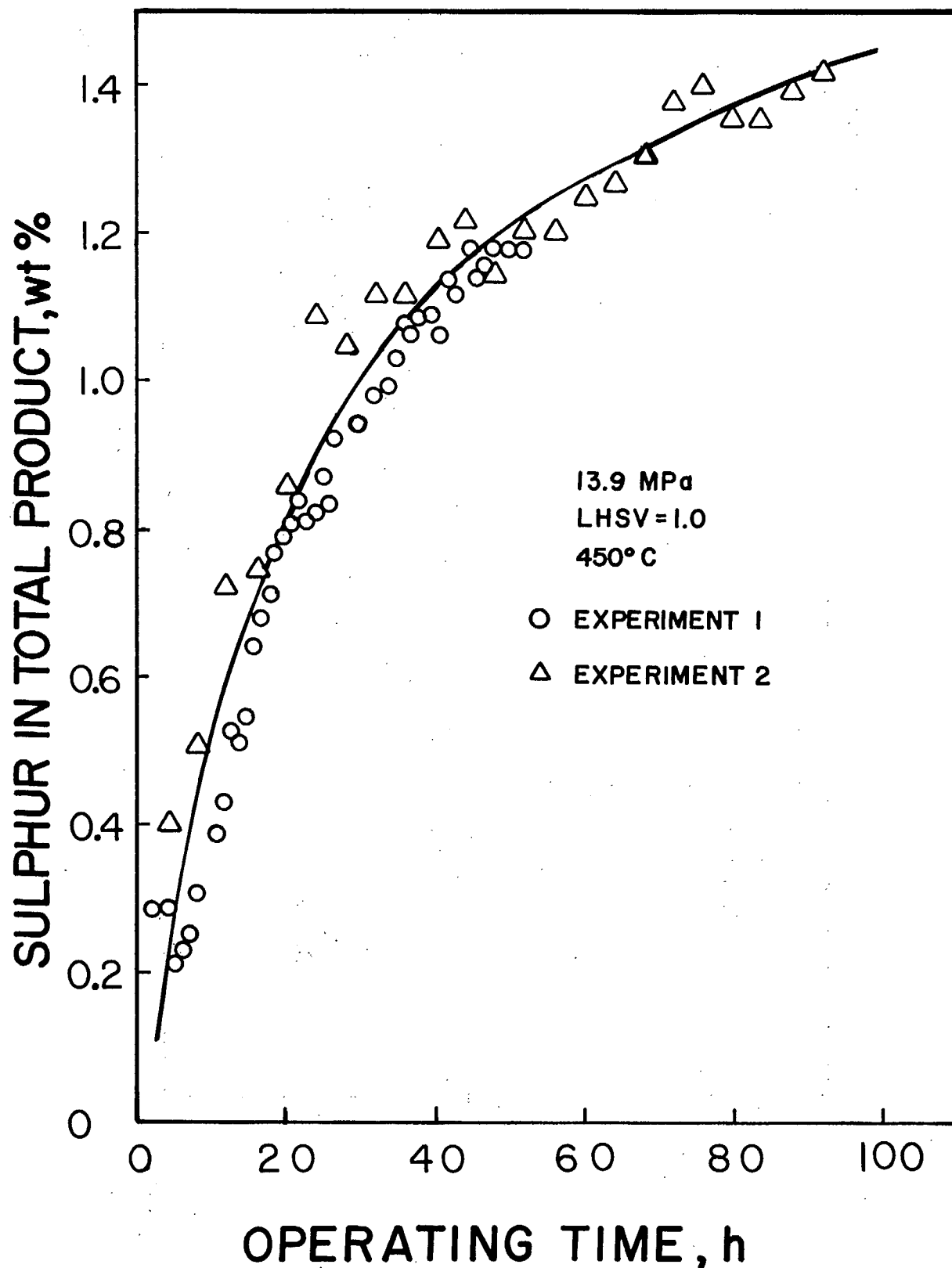


FIGURE 1 - Schematic Flow Sheet of Pilot Plant

FIGURE 2 - Reproducibility of Catalyst Decay Studies

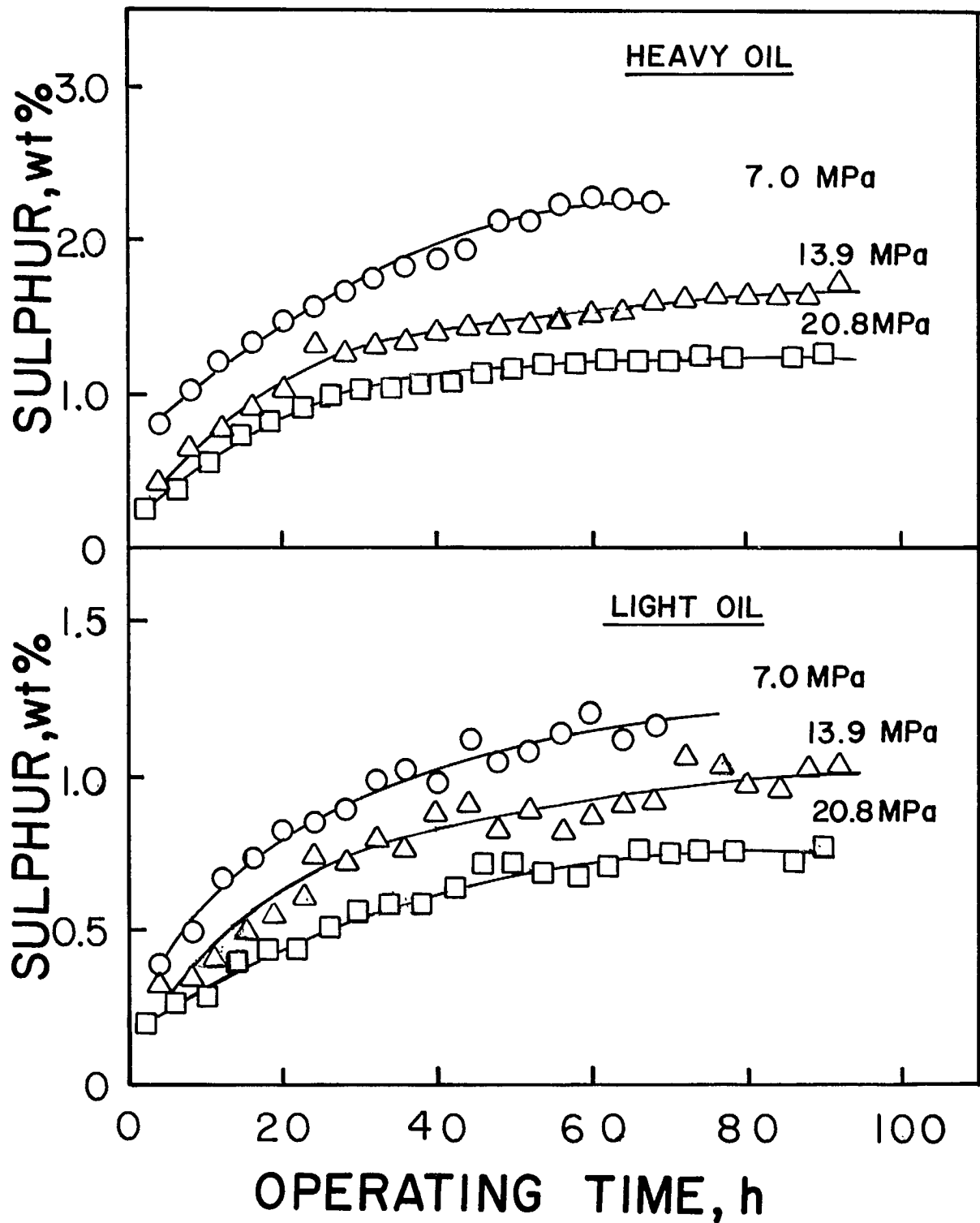


FIGURE 3 - Variations of Sulphur in Heavy and Light Oil Products

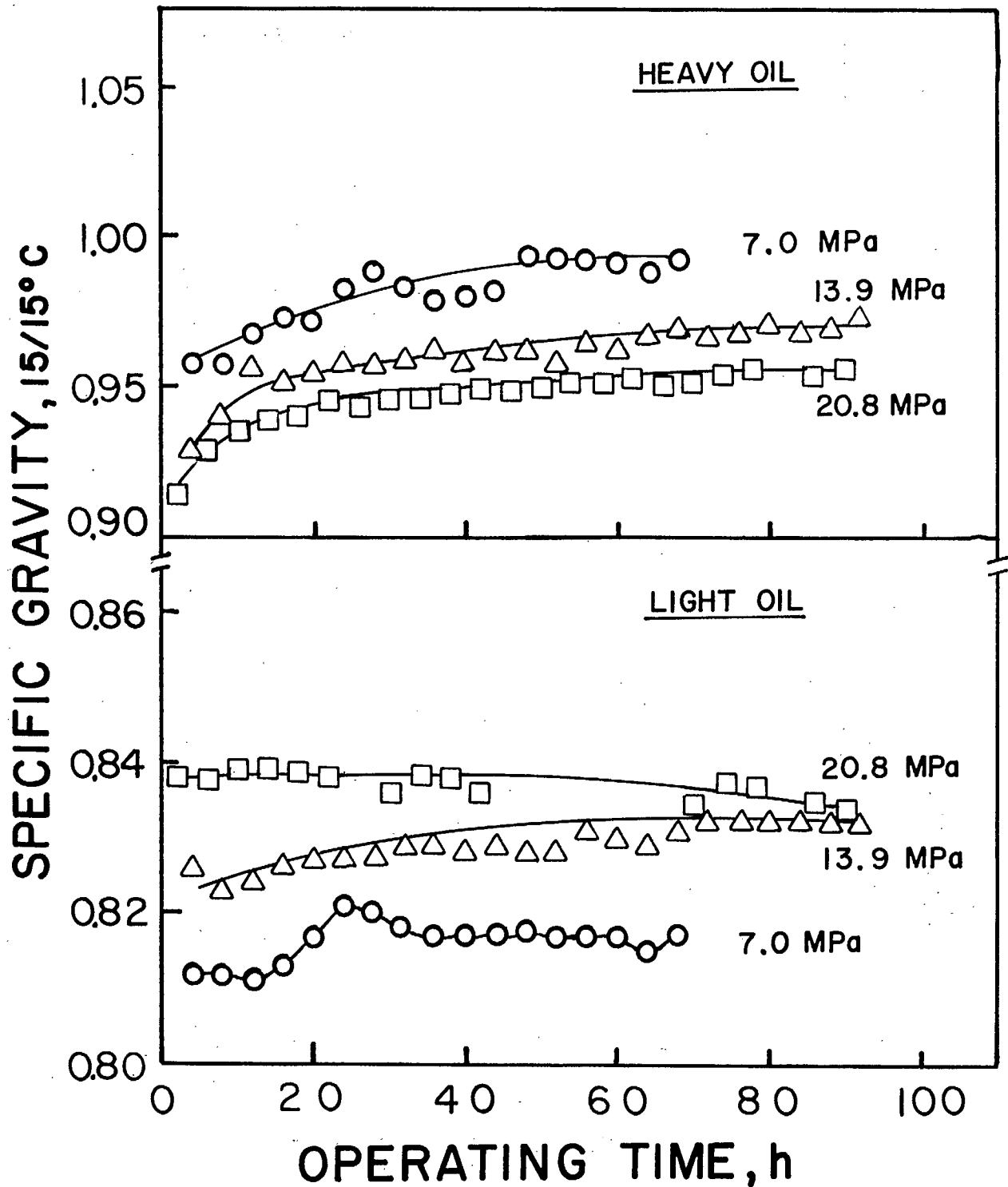


FIGURE 4 - Variations of Specific Gravity in Heavy and Light Oil Products

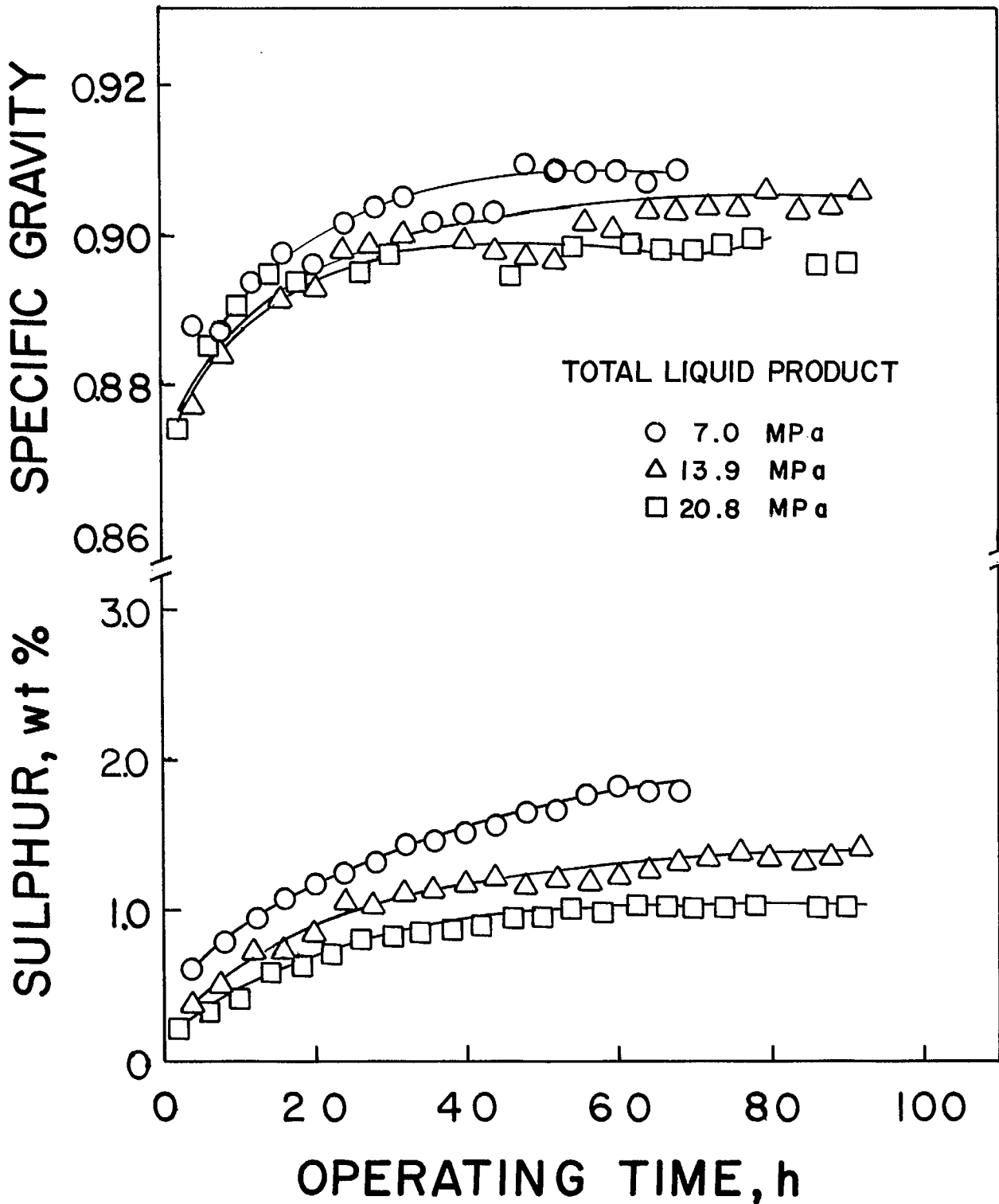


FIGURE 5 - Variations of Sulphur and Specific Gravity
in Total Liquid Product

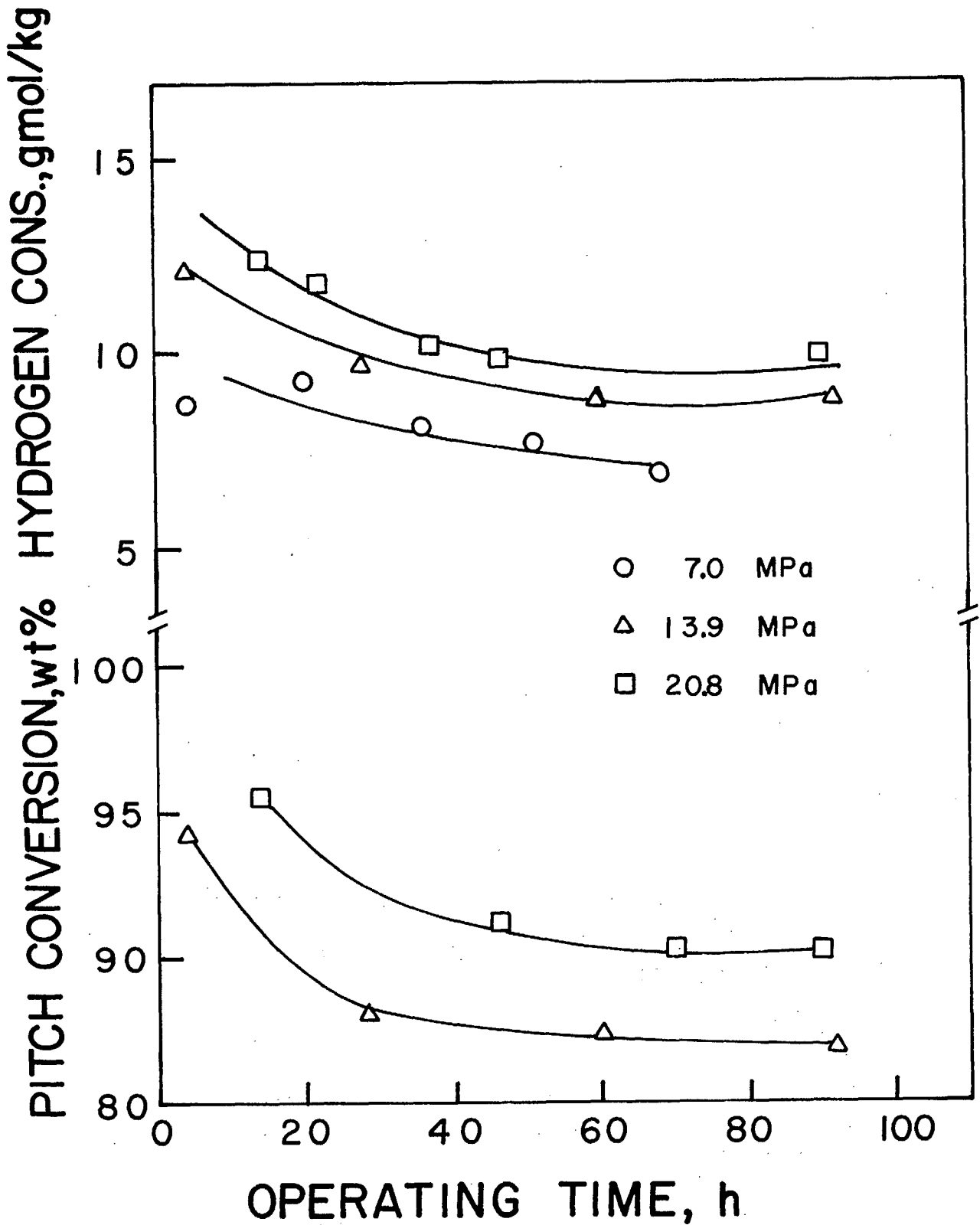


FIGURE 6 - Effect of Catalyst Decay on Hydrogen Consumption and Pitch Conversion

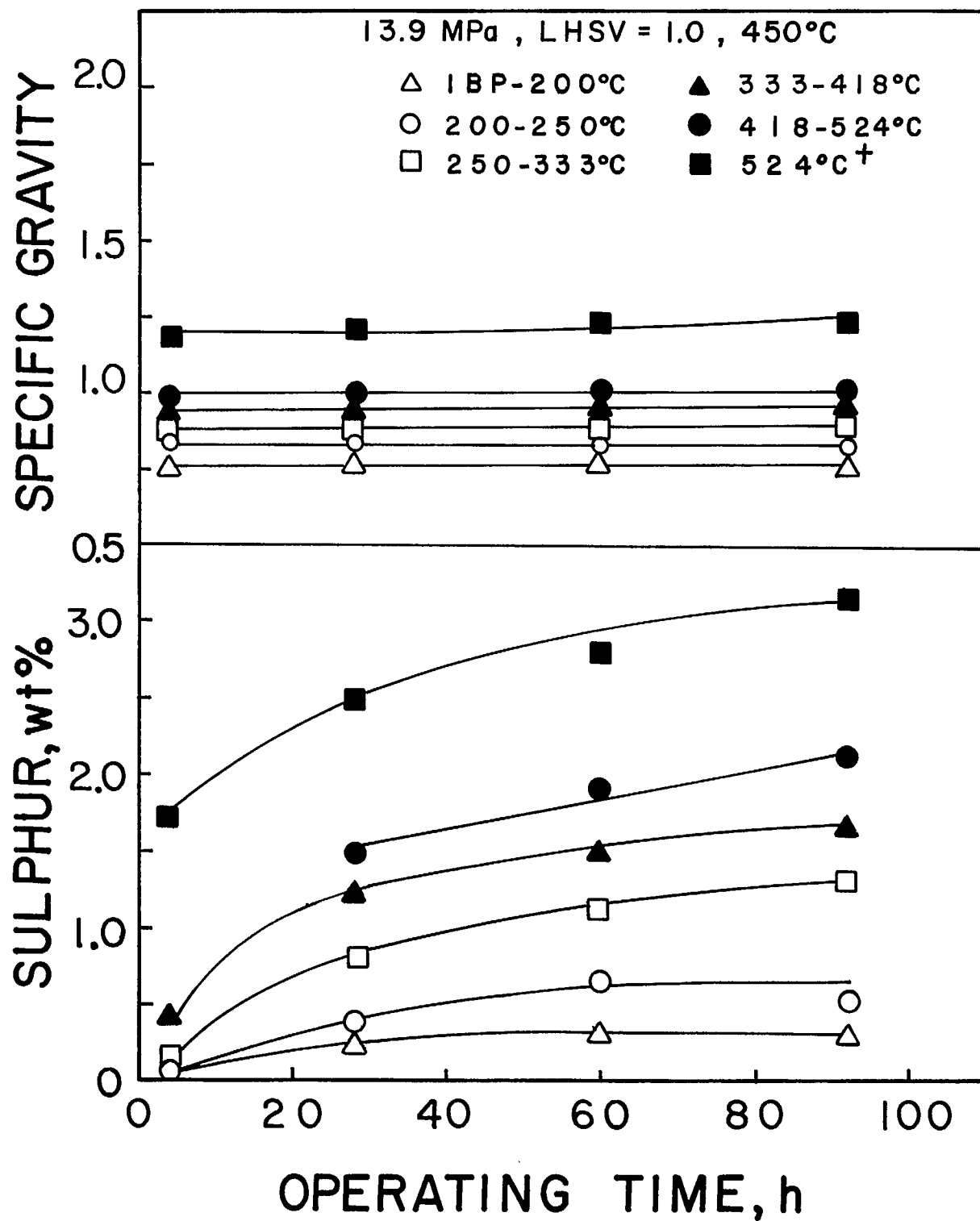


FIGURE 7 - Effect of Catalyst Decay on Properties of Different Fractions

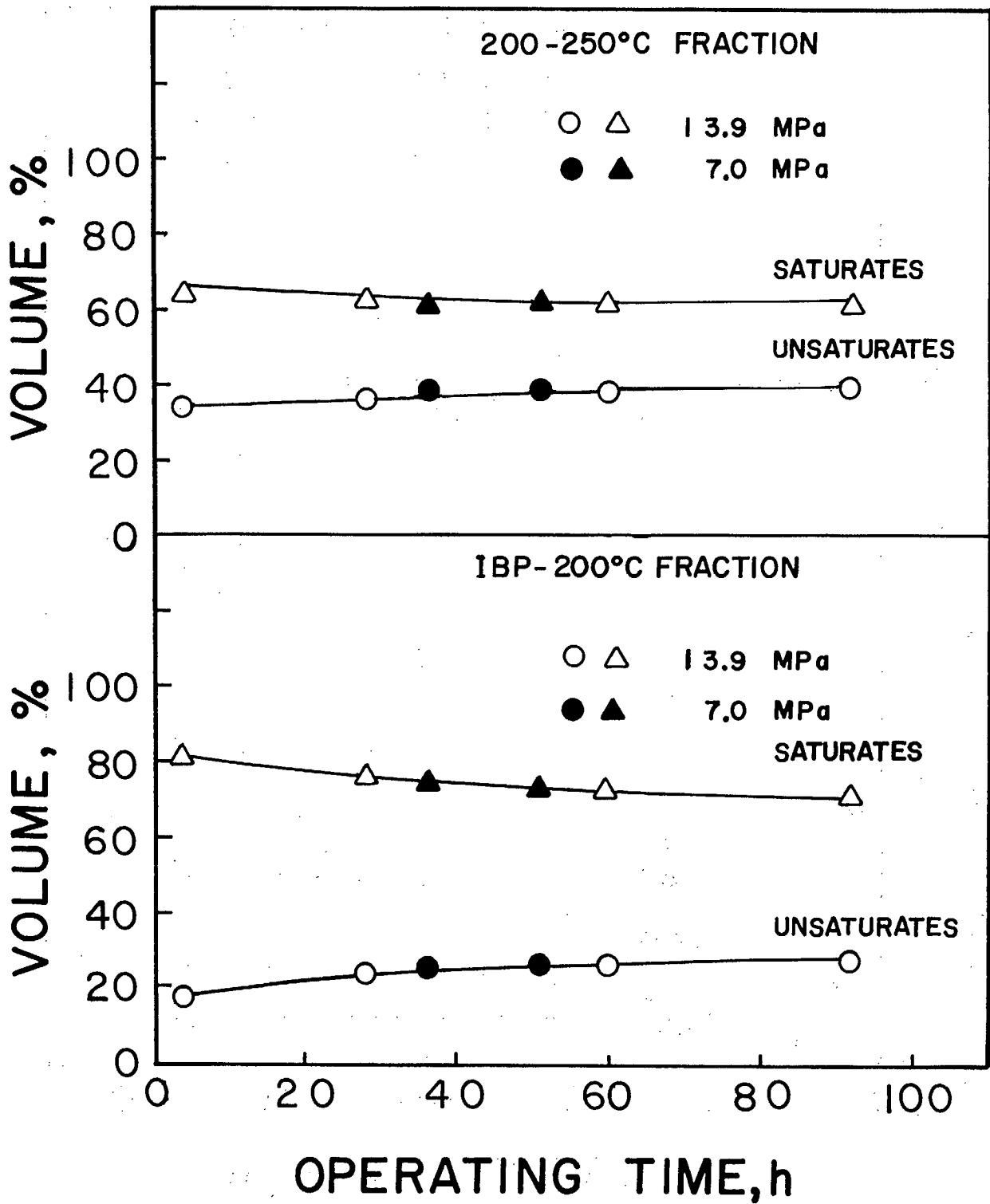


FIGURE 8 - Effect of Catalyst Decay on Saturates and Unsaturates

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