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ABSTRACT

Hydrocracking studies were performed with two different residual oils. Catalyst fouling by carbon deposition was found to occur at a greater rate than by metals deposition. A mild skin effect was found to be operative on the fresh catalyst. It was concluded that this initial skin effect had little influence on the catalyst performance. Although carbon was deposited relatively uniformily throughout the catalyst, metals deposition predominated at the pellet exterior surface. After long times on stream, prolonged accumulation of metals would narrow the pore mouths to eventually produce a severe skin effect. As the metals concentration and the severity of the catalyst skin effect increase, access of reactant molecules to the catalyst would diminish.

INTRODUCTION

Hydrocracking can be used to convert low grade residual oils, that is carbonaceous materials boiling above 525°C, into useable fuel products. Hydrocracking will probably be used even more extensively as the processing of lower grade (higher residuum content) crude petroleum increases. Unfortunately there are two problems associated with hydrocracking residual oils: hydrogen consumption can be costly; and the catalysts foul rapidly.

Catalyst fouling is known to be caused by the deposition of carbon and metal compounds (1,2,3). A few workers have specifically examined the fouled catalysts. Heimenz (4) has commented briefly on the state of the catalyst after such fouling. In a more detailed study, Silbernagel (5) found that at high concentrations the vanadium deposit in the catalyst was present as V_2S_3. A theoretical model of hydrocracking catalyst fouling has been developed by Newson (6). In this paper we have examined fouling in relationship to the skin effect at the exterior surface of the catalyst pellet.

The catalyst skin is created during the pressing of catalyst powders into catalyst pellets. The particles of powder adjacent to the die wall and punches are compressed more compactly than those in the interior of the pellet. Androutsopoulos and Mann (7) have theoretically described pellets made by this process. They noted that a skin on the catalyst surface, composed of pore mouth constrictions, will decrease accessibility to the catalyst interior. They also concluded that loss in hydrocarbon catalyst activity should be related to the accumulation of carbon layers (physical blocking of pore mouths) and pore structure. It is appropriate to consider the catalyst skin effect in terms of hydrocracking since carbon deposition is one of the phenomena that occur during hydrocracking.

EXPERIMENTAL

The hydrocarbon materials described in Table 1 were hydrocracked using a catalyst containing 3 wt % CoO and 12 wt % MoO_3 on gamma alumina (Harshaw No 0603T). The Leduc pitch, was a vacuum bottoms stream obtained from Imperial Oil Limited at Sarnia, Ontario. The Athabasca bitumen was that separated from the Athabasca Oil Sands by the SUNCOR Company at Fort McMurray, Alberta.

The catalyst pellets were evaluated in a bench-scale fixed bed reactor having a volume of 155 mL and a length to diameter ratio of 12. The hydrocarbon materials, mixed with hydrogen (purity = 99.9 wt %), flowed continuously into the bottom of the reactor and up through the catalyst bed. The product leaving the top of the reactor flowed to receiver vessels where the liquid and vapour separated. Each experiment was performed at a pressure of 13.9 MPa (2000 psig), a liquid volumetric space velocity of 0.58 ks^{-1} (2.0 h^{-1}), and a flow rate of 72 mL/s at STP (5000 cf/bbl).

The catalyst pellets were presulphided and stabilized using the reaction mixture, that is hydrogen and Athabasca bitumen at 430°C or hydrogen and Leduc pitch at 440°C. A fresh batch of catalyst was used for each series of experiments. Series of short term experiments were performed at various temperatures. When an experiment at one temperature was completed, the reactor temperature was changed. Steady state conditions were maintained at the next temperature for 3.6 ks (1 h) prior to, and 10.8 ks (3 h) during, the period in which the sample of liquid product was collected. The same conditions were used for presulphiding and for reaction in catalyst life experiments of longer duration. In these experiments the catalyst was regenerated periodically by passing air through the catalyst bed at 500-550°C for five hours to burn off the carbonaceous deposits.

The liquid product was analyzed for sulphur, nitrogen, and the weight fraction boiling above 525°C. The sulphur content was determined using an x-ray fluorescence technique (8). The nitrogen analyses were performed using a hydrogenation-microcoulometric apparatus (9). A modified version of the U.S. Bureau of Mines Hempel distillation analysis (10) was used to distill the liquid product into ten fractions. The conversion was determined by comparing the amount of pitch, the heaviest fraction (+525°C), in the product with that in the feedstock.

Measurements of the metals and carbon concentration profiles in the pellets and of catalyst pellet porosity were also made. A Micromeritics Model 915-1 mercury porosimeter was used to measure catalyst pore diameter. The contact angle between the mercury and the solid was assumed to be 130 degrees for both penetration and retraction. The concentration profiles were determined with a modified JEOL model JXA-3 electron microprobe having an ORTEC Si(Li) detector. The catalyst pellets were prepared by cutting the

pellets radially, mounting them in trans-optic-organic mounting media, polishing with Linde C (1 μm) silicon carbide paper and Linde A (0.3 μm) alumina at 10 rev/sec in a conventional manner, and finally coating with a 20 nm layer of carbon. The traces were run at 20 KeV and 0.333 μm/sec using 10 μm beam diameter to reduce sample heating and to smooth out the effects caused by catalyst porosity (cracks and holes).

RESULTS AND DISCUSSION

Catalyst fouling was readily observed when attempts were made to reproduce sequentially catalytic reaction data. Conversions for nitrogen removal, sulphur removal and +525°C pitch removal are shown in Figure 1. After presulphiding the catalyst, a series of experiments at different temperatures were performed in the following order: 440°C, 450°C, 460°C and 440°C for Athabasca bitumen and 450°C, 460°C, 470°C and 450°C for Leduc pitch. The first experiments (solid data points) were performed at the same conditions as the fourth experiments (open data points). The lower conversions obtained during the fourth experiments indicate catalyst fouling.

Figure 1 also shows the expected increase of all reaction rates with temperature. All of the reactions occur more readily with Athabasca bitumen than with Leduc pitch. The severe hydrocracking conditions produced the high +525°C residuum conversions (molecular weight reduction).

To define catalyst fouling more thoroughly, the catalysts were tested for longer times. These results are shown in Figure 2. The data with Athabasca bitumen were obtained at 450°C while those with Leduc pitch were obtained at 460°C. The catalysts were regenerated with air at 500-550°C after 180 ks (50 h), 328 ks (91 h) and 475 ks (132 h). It was obvious that the catalyst was deactivated rapidly by both Athabasca bitumen and Leduc pitch. With Leduc pitch the catalyst returned to approximately its original value after each regeneration. In contrast, with Athabasca bitumen the initial catalyst activity was lower after each regeneration.

The results can be explained in terms of three types of fouling. Inorganic clay particles may lodge on or in the catalyst. Metal complexes in the feed may decompose to become insoluble materials and may be deposited at the reaction site. Organic species may react to form solid carbonaceous deposits (coke) via polymerization and dehydrogenation routes.

To a first approximation both Athabasca bitumen and Leduc Pitch are expected to have similar coke forming tendencies. The similarity of the Conradson Carbon Residue values in Table 1 suggest that the coking tendency of both feedstocks would be of the same order of magnitude. However, Athabasca bitumen has a much higher content of metals (Ni, V, Fe) and clay (ash) than Leduc pitch. During regeneration the coke is removed from the catalyst but the metals and clay are not. As can be seen in Figure 2, coke removal restores the catalyst activity in the case of Leduc pitch and makes a marked improvement in the case of Athabasca bitumen. Thus the rapid decline in catalyst activity with both feedstocks can be attributed to carbonaceous deposits. Since there are minor amounts of metals and clay in the Leduc pitch, removal of the coke deposit restores catalyst activity to its initial level. With Athabasca bitumen there was a progressive decline in the initial catalyst activity after each regeneration. It can be attributed to deposits of metals and clay, that are not removed during regeneration. The slope of a line drawn through the initial sulphur conversions, measured after each regeneration of the Athabasca bitumen catalyst, as shown in Figure 2, would represent catalyst fouling caused by metals and clay. The slope of such a line would be substantially less than the slope of the line through the experimental data points in Figure 2. This shows that catalyst fouling caused by carbon deposition was quite severe, at least for the times on stream studied here.

Visual inspection of the regenerated catalyst provided additional evidence regarding clay and metals deposition. In the case of the catalyst used with Athabasca bitumen, massive deposits on the surface of the catalyst pellets were evident. In contrast, the regenerated catalyst which was used with Leduc pitch did not appear to be very much different than the fresh catalyst (11).

Individual pellets were examined for metal deposits with the electron microprobe and the results are shown in Figures 3 and 4. The 72 ks (20 h) and 475 ks (132 h) results were obtained respectively from the catalyst pellets used in the temperature series shown in Figure 1 and the longer reaction time series shown in Figure 2. In general the amount of metals tended to be high on the exterior of the pellets and to decrease toward the pellet interior. The iron profile is different from the other two metal deposits in that it is concentrated almost exclusively on the pellet exterior. The iron is probably present as an inorganic clay as ferric ion complexes (12) and as iron sulphide species. In contrast the nickel and vana-

dium are probably present in the feedstock as organometallic complexes such as porphyrins (13). The difference in the concentration profiles of the metal deposits (Fe versus Ni and V) is probably caused by the iron being present as solid inorganic particles while nickel and vanadium are present as organometallic complexes which are soluble.

The deposition of all three metals near the pellet surface is a form of pore mouth plugging. It will contribute to the skin effect described by Androutsopoulos and Mann (7). All the profiles suggest that either the rate of reaction of each metal containing species was different or that the rates were limited by diffusion toward a reaction site. Other results (14) have shown the presence of diffusion limitations. Figure 3 shows that nickel was deposited farther from the pellet surface than iron or vanadium. This suggests that the nickel species may have been less limited by diffusion and may have had the smallest geometric size.

The catalysts which could be used for coke measurements were restricted to the temperature series shown in Figure 1. The coke had already been removed from the regenerated catalysts shown in Figure 2. The procedure used for the measurement of total catalyst coke was as follows. The catalyst pellets were placed in a flowing stream of hydrogen at 525°C for 3.6 ks (1 hour) to remove any oil adhering to the pellets. Subsequently they were placed in a muffle furnace at 500°C. The change in weight after the catalyst had been removed from the furnace was corrected for the conversion of the catalyst molybdenum and cobalt species from the sulphide form to the oxide form. The fesulting weight change was considered to be due to coke. The catalyst used to process Athabasca bitumen and Leduc pitch contained 8.9 and 14.8 wt % coke respectively after reaction.

The electron microprobe was used to measure the distribution of carbon within the catalyst pellets. The results are shown in Figure 5. With Leduc pitch the carbon content varied from 14 per cent at the edge of the catalyst to 12 per cent at the centre. With Athabasca bitumen the carbon content varied from 15 per cent at the edge of the catalyst to 9 per cent at the centre. These results obtained with the electron microprobe are similar to the total catalyst coke results described above. The profiles for the regenerated pellets indicated that virtually all the coke was removed.

The carbon profiles are considerably different than the profiles of deposited metals. The large metal concentrations at the catalyst exterior indicated the metal containing species in the feedstock did not reach the centre of the catalyst. In contrast the carbon profiles indicate that coke is formed at

the centre of the catalyst as well as the edge. This means that the smaller molecules which have access to the catalyst interior must, form coke almost as readily as the larger ones which are excluded from it. The experimental observation of relatively uniform carbon deposition does not support the assumption of Androutsopoulos and Mann (7) that carbon is preferentially deposited at the catalyst pellet exterior.

The metals and carbon profiles suggested that some skin effect might be present in the catalyst. The pellets had a slightly greater carbon concentration at the edge. The metals concentration in the pellets was much greater at the edge.

The skin effect could also be detected in several other ways. When the catalyst pellets were cut with a razor blade it was difficult to push the razor blade through the exterior surface of the pellet. However, once the surface had been penetrated the rest of the pellet was cut like butter. Second, when the pellets were observed under the microscope using crossed nicols or certain filters the edge area of the pellet appeared to be anisotropic. Third, when the pellets were observed under the microscope the particles at the edge of the pellet were considerably smaller than those just a short distance away towards the centre of the particle. Undoubtedly these smaller particles were made when the powder was compressed in the die. It is possible that higher compressive forces are experienced by those particles adjacent to the die wall and the punches.

Mercury porosimetry measurements were made in an attempt to demonstrate this skin effect quantitatively. Figure 6 shows mercury penetration and retraction curves for whole pellets and for pellets which had been cut radially in half. If the catalyst had a skin, the pores within the catalyst would be larger than those at the surface. The whole pellets would have catalyst skin around their entire exterior. In contrast the cut surface in the halved pellets would not have a skin. Mercury should penetrate and retract through the large pore mouths at the cut surface using lower pressures than through the smaller pore mouths at the uncut surfaces where the catalyst skin is present. Figure 6 shows that penetration occurred at slightly lower pressures in the halved pellets and at significantly lower pressures during retraction. These results demonstrate that the catalyst did have a skin. Furthermore the curves in Figure 6 show the differences

predicted by Androutsopoulos and Mann (7).

Figure 6 shows that the pore size in the pellet skin is only slightly smaller than the pore size in the pellet interior. The curve for the whole pellets show median pore diameters of approximately 7.5 nm and 38 nm for penetraction and retraction respectively. The curve for the halved pellets show median pore diameters of approximately 8.0 nm and 57 nm respectively. In general these pores should be classified (15) as mesopores (2-50 nm). They are smaller than the macropores discussed by Androutsopoulos and Mann (7). However the general model presented by Androutsopoulos and Mann should be applicable to pores of any size.

Figure 6 indicates that mechanical forming of the pellet causes a small difference between the size of the interior pores and the pore mouth. Androutsopoulos and Mann refer to this as a mild skin effect. Qualitatively one can suggest that carbon and metal profiles would not be changed much by a mild skin effect. Small molecules which diffuse rapidly through interior pores, would not be greatly inhibited by slightly smaller pore mouths. The relatively uniform carbon profile suggests that the molecules which form coke were only slightly influenced by diffusion. Large molecules which diffuse slowly through pore mouths would also diffuse slowly through interior pores which were only slightly larger than the pore mouths. The metal profiles indicate that the organometallic compounds may have been limited by diffusion. On this basis a mild skin effect would have only a secondary influence on diffusion rates and catalyst fouling.

Alumina and most other materials frequently used as catalyst supports are relatively incompressible. The results observed in this study with alumina are probably typical of most industrial catalysts. On this basis it is expected that mechanically forming or tabletting most types of catalyst pellets will cause only a mild skin effect.

After hydrocracking residual oils for long times on stream there would be an extensive accumulation of metal deposits near the pellet exterior surface (the pore mouths). Eventually the pore mouth diameters would be much smaller than those of the interior pores. Thus the metal deposits would create what Androutsopoulos and Mann (7) term a severe skin effect. In this situation the dimensions of the pore mouths would cause diffusion limitations for the reactant molecules. Eventually these deposits could accumulate to the extent that all molecules would be excluded from the catalyst interior.

CONCLUSIONS

Catalyst fouling caused by carbon deposits was found to be more rapid than that caused by metals deposits, at reasonably short times on stream. The catalyst pellets which were used had been mechanically formed by tabletting alumina, which is relatively incompressible. Mercury porosimetry measurements on fresh catalyst pellets indicated that the pore mouths were only slightly smaller than the interior pores. At short times on stream this mild skin effect was considered to be a secondary influence on catalyst fouling. The profile of carbon deposition within the catalyst was relatively uniform indicating that coke-forming molecules had access to the catalyst interior. In contrast the concentration of metals at the catalyst exterior was much greater than that within the catalyst, indicating that the metal containing species did not have access to the catalyst interior. It was hypothesized that at much longer times on stream, the accumulation of metals at the catalyst exterior would produce pore mouths which were substantially smaller than the interior pores. This would ultimately create a severe skin effect which would decrease the effectiveness of the catalyst interior.

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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
Iron (ppm)	358	28
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

LIST OF CAPTIONS

Figure 1 Weight Percent Nitrogen Removed, Weight Percent Sulphur Removed and Weight Percent Conversion of +525°C Pitch Versus Temperature. Data for the fourth experiments (open symbols) in each series were obtained at the same temperature as the first experiments in each series. Circles represent Athabasca bitumen, squares represent Leduc Pitch.

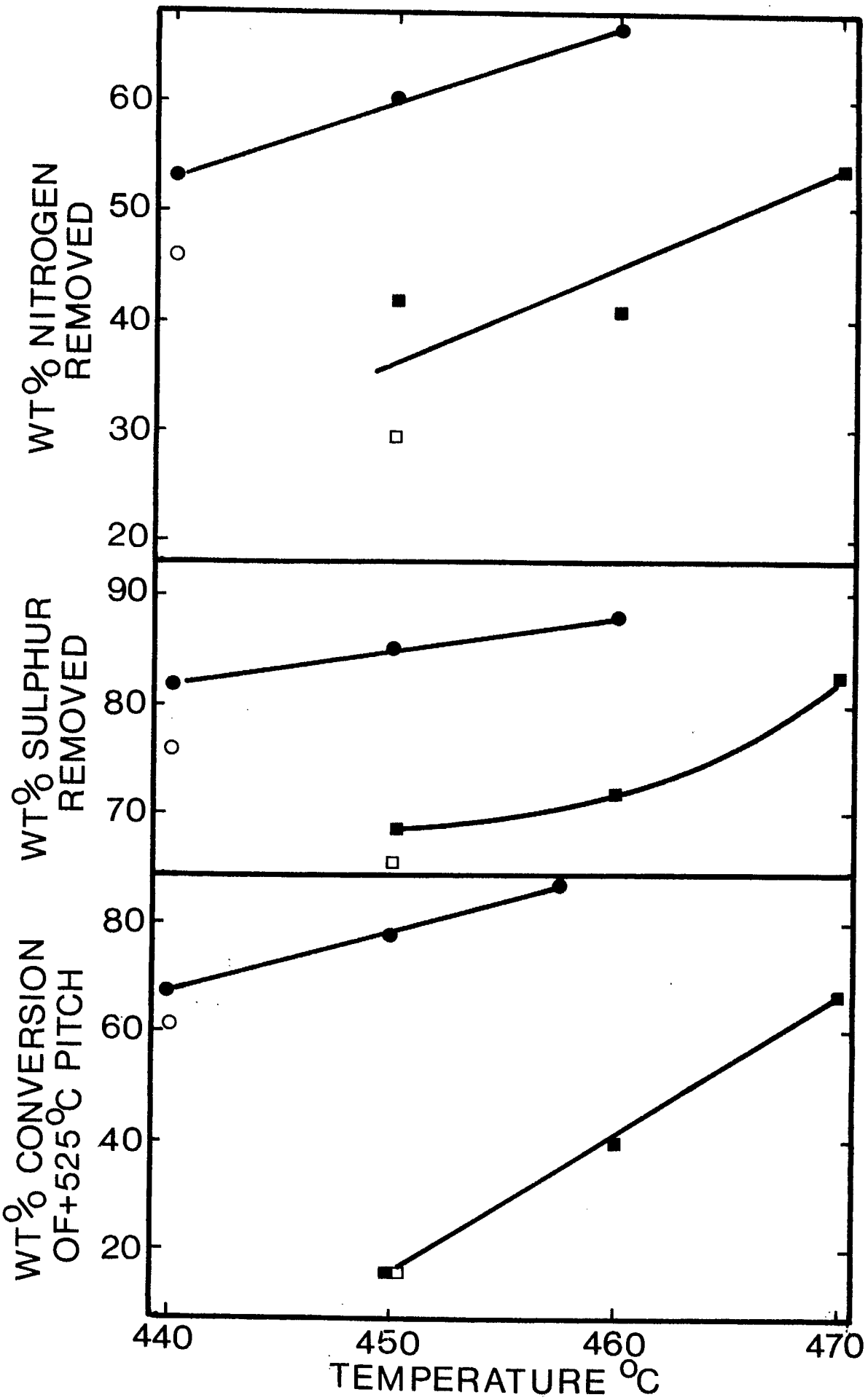
Figure 2 Weight Percent Sulphur Removed Versus Time, for Athabasca Bitumen and Leduc Pitch. Regeneration were performed after 180 ks (50 h), 328 ks (91 h) and 475 ks (132 h). The reaction temperatures were 450°C and 460°C for Athabasca bitumen and Leduc Pitch respectively.

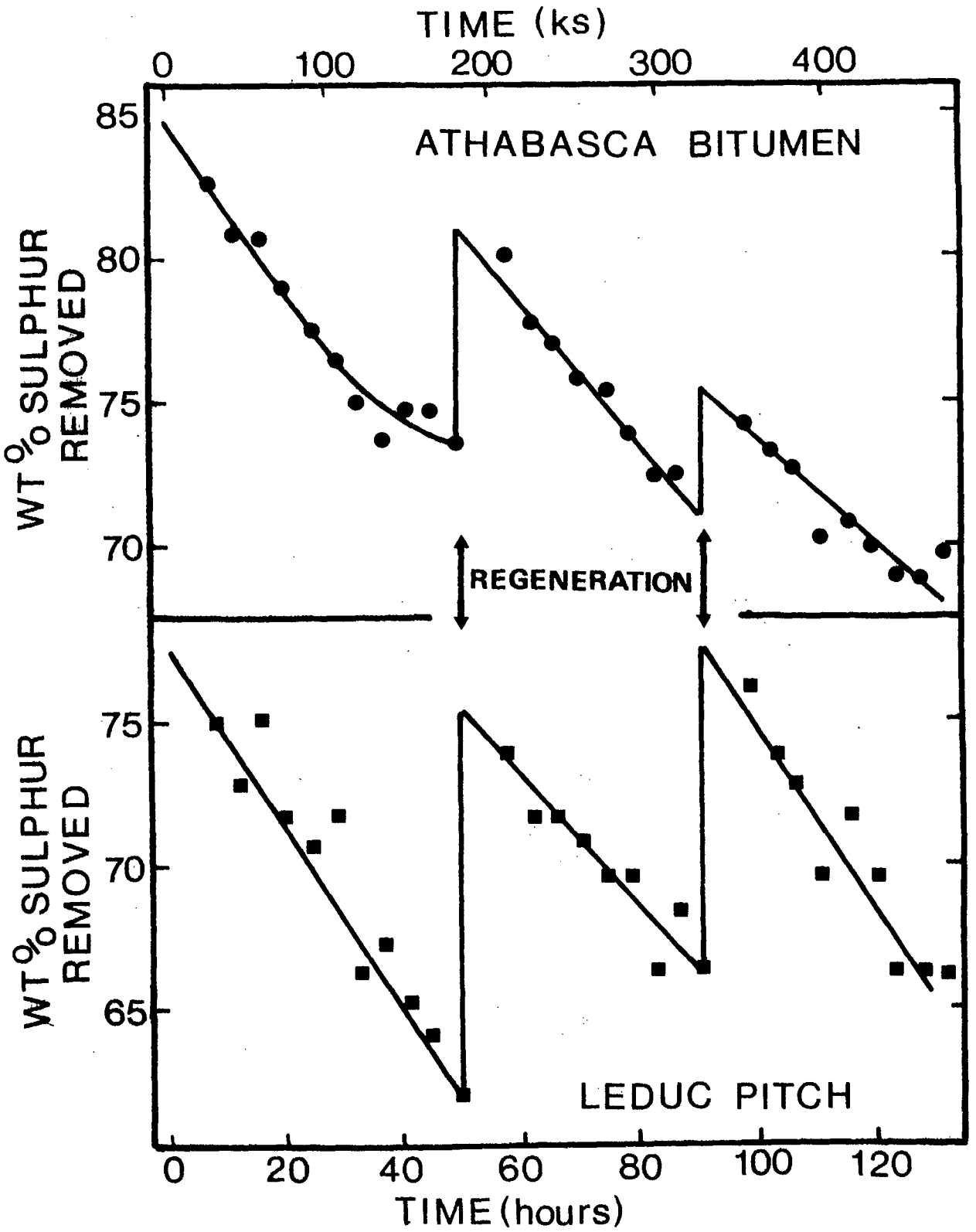
Figure 3 Iron, Vanadium and Nickel Concentrations Versus Radial Position in Catalyst Pellets Used to Process Athabasca bitumen.

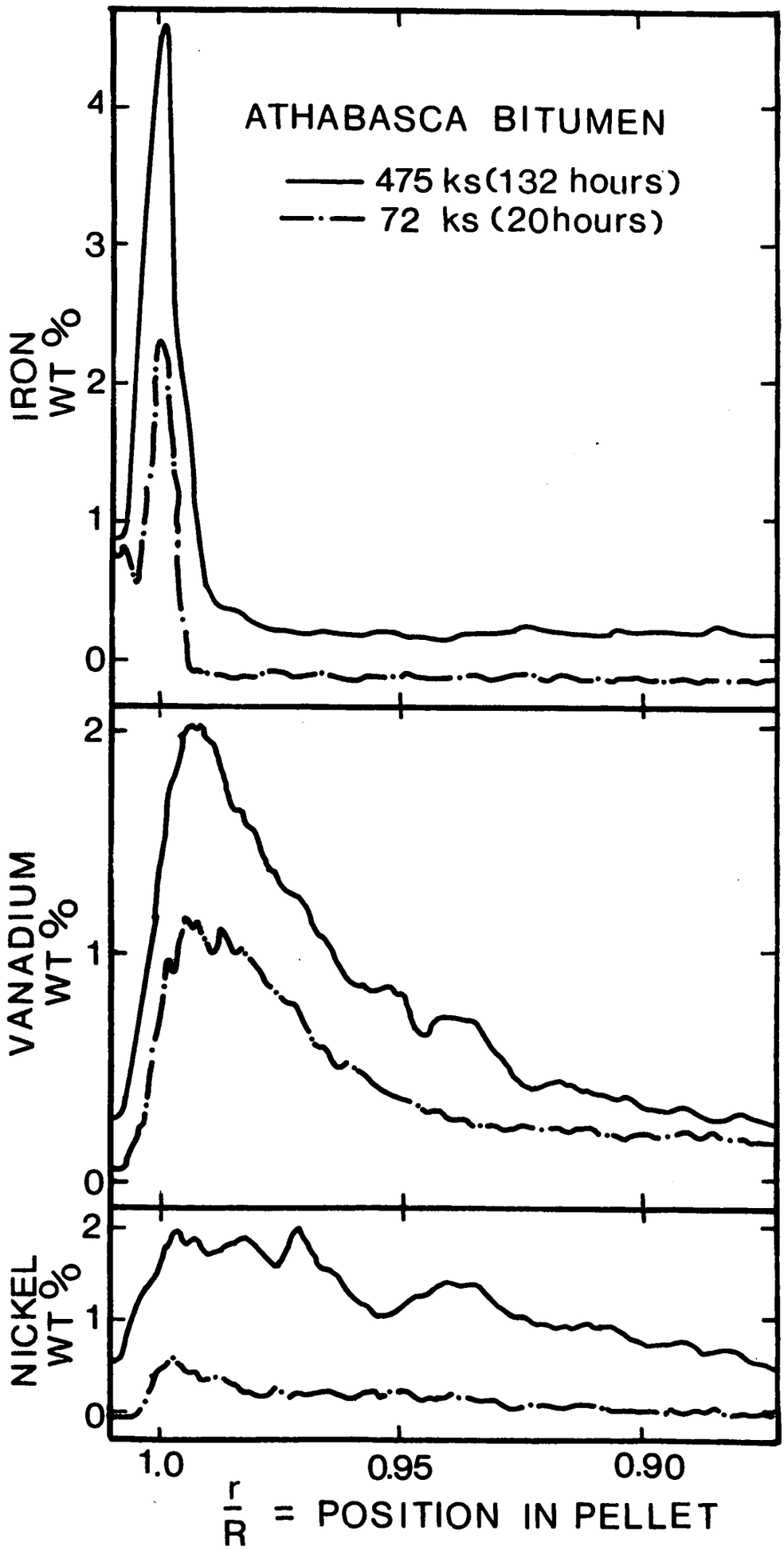
Figure 4 Iron, Vanadium and Nickel Concentrations Versus Radial Position in Catalyst Pellets Used to Process Leduc Pitch.

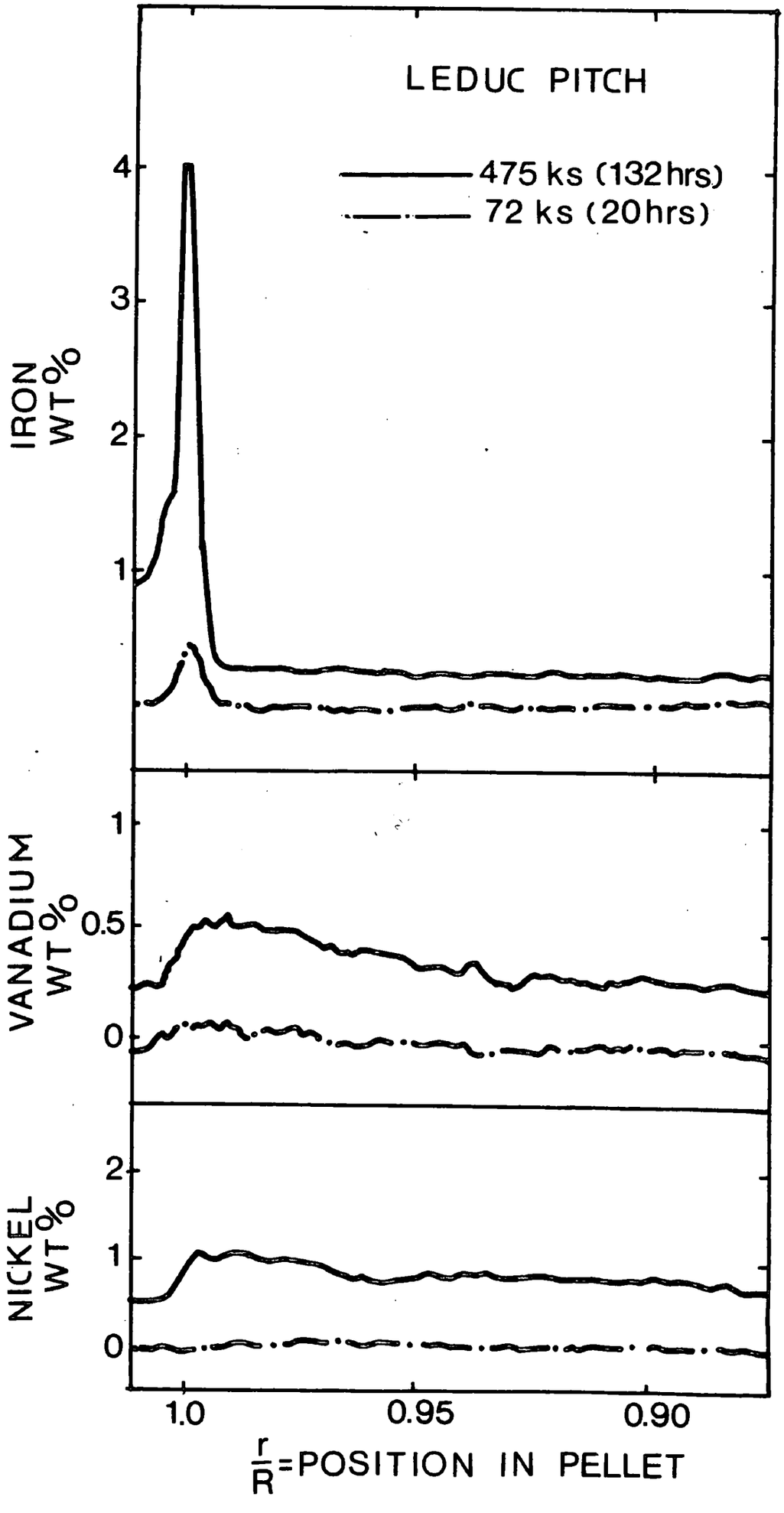
Figure 5 Carbon Concentration Versus Radial Position in the Catalyst Pellet.

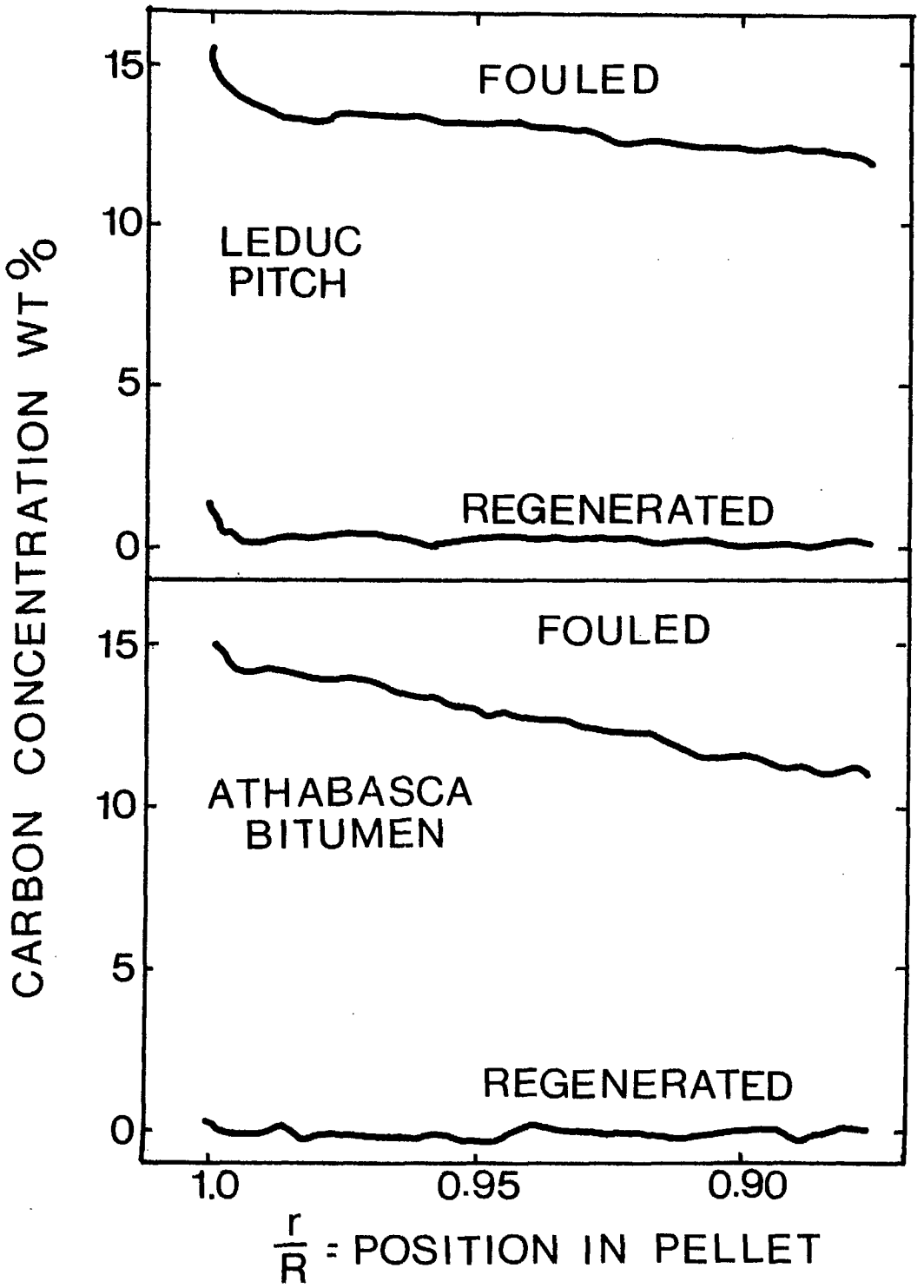
Figure 6 Cumulative Catalyst Pore Volume Versus Catalyst Pore Diameter for Whole Catalyst Pellets (squares) and for Catalyst Pellets which had been Cut in Half (circles).


WT% NITROGEN REMOVED
60
50
40
30
20
WT% SULPHUR REMOVED
90
80
70
WT% CONVERSION OF+525°C PITCH
80
60
40
20
440
450
460
470
TEMPERATURE °C


TIME (ks)
0
100
200
300
400
85
80
75
70
ATHABASCA BITUMEN
WT % SULPHUR REMOVED
REGENERATION
75
70
65
WT % SULPHUR REMOVED
LEDUC PITCH
0
20
40
60
80
100
120
TIME (hours)


ATHABASCA BITUMEN
475 ks(132 hours)
72 ks (20hours)
IRON WT %
VANADIUM WT %
NICKEL WT %
4
3
2
1
0
2
1
0
2
1
0
1.0
0.95
0.90
r/R = POSITION IN PELLET


LEDUC PITCH
475 ks (132hrs)
72 ks (20hrs)
IRON WT%
4
3
2
1
VANADIUM WT%
1
0.5
0
NICKEL WT%
2
1
0
1.0
0.95
0.90
r/R=POSITION IN PELLET


FOULED
LEDUC
PITCH
REGENERATED
FOULED
ATHABASCA
BITUMEN
REGENERATED
CARBON CONCENTRATION WT %
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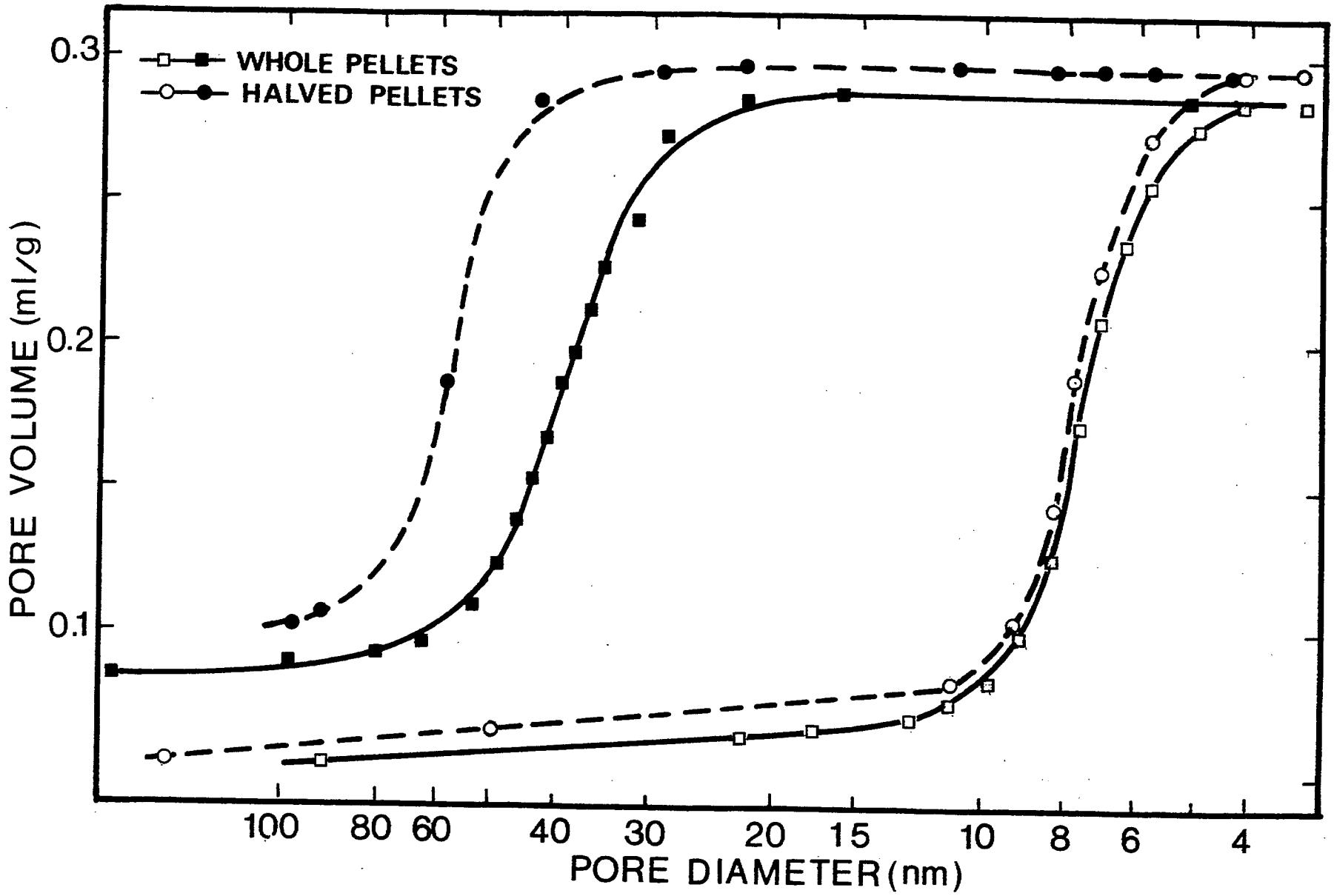
10
5
0
15
10
5
0
1.0
0.95
0.90
r/R = POSITION IN PELLET


WHOLE PELLETS
HALVED PELLETS
PORE VOLUME (ml/g)
0.3
0.2
0.1
100
80
60
40
30
20
15
10
8
6
4
PORE DIAMETER (nm)