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**HYDROCRACKING ATHABASCA BITUMEN USING Co-Mo CATALYSTS
SUPPORTED ON WIDE PORE CARBON EXTRUDATES**

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HYDROCRACKING ATHABASCA BITUMEN USING Co-Mo CATALYSTS

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by

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ABSTRACT

In recent years, the use of carbon material as a catalyst support has been considered along with alumina and silica. An experimental investigation has been carried out on the utilization of a wide pore, high surface area, carbon extrudate as a catalyst support for the hydrocracking of Athabasca bitumen. A carbon supported cobalt-molybdenum catalyst was prepared by impregnating the carbon extrudate with an aqueous solution, then calcining it to form the oxide precursor. The experiments were carried out in a high pressure fixed bed tubular reactor. After the catalyst was sulphided the experiments were conducted between 425 - 450 °C and between 6.9 - 20.7 MPa. Liquid hourly space velocities ranged between 0.5 and 1.5 h⁻¹. Similar tests were carried out on an alumina supported cobalt-molybdenum catalyst. Results showed that conversions using the Co-Mo/C catalyst were lower than those obtained using the Co-Mo/Al₂O₃ catalyst. However when the results were compared on the basis of unit catalyst surface area, the pseudo turnover numbers were larger for the carbon supported catalyst than for the alumina supported one.

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INTRODUCTION

A number of studies have been performed in which sulphided hydroprocessing catalysts supported on carbon have been compared with the same catalysts supported on alumina. Stevens and Edmonds (1979) found greater thiophene conversions when sulphided Co-Mo was supported on carbon than when it was supported on alumina. Similarly, Duchet et al. (1983) reported greater thiophene hydrodesulphurization (HDS) when sulphided Mo was supported on carbon rather than on alumina. In addition, HDS with Co alone was vastly superior (deBeer et al., 1981) to Mo alone when supported on carbon. Bridgewater et al. (1982) found that carbon was slightly better than alumina for supported Co-Mo. In contrast Daly et al. (1984) and Brinen et al. (1986) found that alumina was a considerably better support than carbon for benzothiophene HDS. Eisch et al. (1985) found the two supports to be roughly equivalent in HDS experiments with coal derived liquids from an SRC process.

Work in our laboratory has been directed at upgrading the +525°C portion of oil sands bitumen and heavy oils. The present investigation was performed to determine whether carbon supports would also be beneficial for hydrocracking bitumen, which contains molecules that are much larger than the ones used in the previous experiments. Some carbon based materials have very small pores which would probably exclude the larger molecules in bitumen. Therefore a carbon support with particularly large pores was chosen.

EXPERIMENTAL

Two catalysts with the same bulk composition (3 wt % CoO and 15 wt % MoO₃) were used in this investigation. The alumina supported catalyst, type HT 400 E, (3.2 mm diameter extrudates) was purchased from the Harshaw Chemical Company. The carbon support, type S-170, was purchased from the American Cyanamid Company. It was in the form of 7.68 mm extrudates, having relatively wide pores. The catalysts' properties are shown in Table I. A Micromeritics

Autopore II-9220 mercury intrusion porosimeter was used to determine pore size. BET surface areas were determined using nitrogen adsorption measurements with a Carlo-Erba instrument.

The Co-Mo/C catalyst was prepared by crushing the carbon extrudates into relatively smaller sizes before impregnation and discarding particles smaller than 2.83 mm (7 mesh). This was done so that the average size of the carbon particles would be similar to the diameter of the alumina extrudates. Prior to use, the carbon support was analyzed and the following impurities were found, Fe < 0.45 wt %, S < 0.12 wt %, V < 0.004 wt %, Mg < 0.002 wt %, and Mn < 0.002 wt %. The support was then pre-treated with boiling diluted HCl, washed with boiling water and dried in air overnight at 423 K (Duchet et al 1983). The carbon support was dry impregnated with an aqueous solution of ammonium heptamolybdate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$. The impregnated carbon support was dried overnight under reduced pressure at 100°C (Visser et al. 1987B). A second impregnation of the sample was made with an aqueous solution of cobalt nitrate $(\text{Co}(\text{NO}_3)_2)\cdot 6\text{H}_2\text{O}$ and dried at the same conditions. Analytical grade reagents were used. The sample was then calcined in air at 450°C for 6 h. The calcining temperature program was 4°C/min from 20°C to 150°C, 4 h at 150°C, then 4°C/min to 450°C, and 6 h at 450°C. These preparation conditions changed the support properties. For example, a 28 % weight loss was observed when the carbon extrudate was dried and calcined at these temperatures. Brinen et al. (1986) have also noted that drying and calcining conditions influence the catalyst. Finally the finished catalyst was then analyzed for metal content.

The experimental equipment is illustrated in Figure 1. A 152 mL fixed bed tubular reactor having a length to diameter ratio of 12 was used. Three heating zones controlled the reactor temperature and a pre-heating zone was used to heat the bitumen to 250°C, prior to its introduction into the reactor. Equipment details are given elsewhere (Kelly and Ternan, 1979). The reactor was filled completely with catalyst. The bitumen and hydrogen mixture was fed continuously into the bottom of the reactor. The feedstock was Athabasca bitumen from Fort McMurray, Alberta. Its properties are shown in Table II.

Experiments were performed at temperatures from 400 to 450°C, pressures from 6.9 to 20.7 MPa, and liquid hourly space velocities (LHSV) from 0.5 to 1.5 h⁻¹. Examples of the axial temperature profiles in the reactor are shown in Figure 2. A relatively uniform temperature profile was maintained throughout each experiment. The hydrogen flow rate was maintained at 890 mL H₂/mL bitumen (5000 scf H₂ / Bbl of bitumen) in every case. The sequence of experiments is shown in Table III. Catalyst sulphiding was performed in experiment 1, using bitumen and hydrogen.

A weight average molecular weight of 800 for the whole bitumen was taken from published molecular weight distribution measurements (Champagne et al, 1985). An average molecular weight of 7600 for the asphaltenes (pentane insolubles) was determined using the method of Chung et al (1979). Molecular weight determinations were made using a Knauer type 11.00 vapour pressure osmometer. The asphaltene molecular weight was used to calculate turnover frequencies. In this calculation, the weight per cent asphaltenes reacted is transformed to the number of asphaltene molecules reacted.

RESULTS AND DISCUSSION

Table I compares the geometrical properties of the carbon support, as received, and the Co-Mo/C catalyst. The surface area obtained by mercury porosimetry is the surface area in the pores larger than 3 nm, since the maximum pressure used will not force mercury into smaller pores. In contrast the surface area determined by nitrogen adsorption is the surface area for pores both larger and smaller than 3 nm. It is apparent from Table I that considerable total surface area was lost during the procedure used to prepare the carbon catalyst. Furthermore, most of the surface area loss occurred in pores smaller than 3 nm. It is likely that the heat treatment caused sintering which occurred preferentially in the small pores. Another indication of sintering is the slight increase in the median pore diameter, as determined by mercury porosimetry.

Table I also compares the geometrical properties of the alumina

supported catalyst with those of the carbon supported catalyst. Since the surface areas determined by nitrogen adsorption and by mercury porosimetry are similar, it is apparent that both catalysts have most of their surface area in pores larger than 3 nm. The carbon supported catalyst has a smaller surface area and a larger median pore diameter than the alumina catalyst.

Table III, shows that experiment 2 was repeated periodically. The change in conversion with increasing time on stream, of these repeated experiments, indicates catalyst deactivation. For this type of reaction, catalyst fouling is caused by the formation of carbonaceous material and by the deposition of metal compounds, which originate from organometallic species (eg., Ternan and Kriz, 1980) in the bitumen feedstock.

Deactivation of the two catalysts is shown in Figure 3. Over a period of 40 hours there is generally less than a 10 % decrease in conversion. It indicates that the Co-Mo/Al₂O₃ catalyst was superior, both for sulphur and for asphaltene conversion. This is likely caused by its higher surface area, which is about double that of the Co-Mo/C catalyst. The rate of loss in activity is higher for both catalysts during the first 24 h of deactivation. Figure 3 also shows a significantly higher ratio of asphaltene conversion to sulphur conversion for the Co-Mo/C catalyst, than for the Co-Mo/Al₂O₃ catalyst. A mathematical procedure was used to eliminate the influence of deactivation, when comparing the effects of various processing variables (eg., temperature). The calculations were performed by proportioning the deactivation between the repeated experiments among the number of other experiments performed between the repeated experiments. The results obtained approximate the performance of a freshly sulphided catalyst.

Figure 4 shows the effect of temperature on the activity of both carbon and alumina supported catalysts. Variation of the temperature from 400 to 450°C produced a pronounced effect on the extent of sulphur and asphaltene conversions. Figure 4 is consistent with Figure 3 in that the total conversion is higher for the Co-Mo/Al₂O₃ catalyst than for the Co-Mo/C catalysts, especially for sulphur conversion.

The turnover frequency is defined as the number of reactions per second per reaction site. Usually it is extremely difficult to measure accurately the number of reaction sites. Furthermore, it is likely that some of the reaction sites on heterogeneous catalysts have greater turnover frequencies than others. To avoid these difficulties, the pseudo turnover frequency (PTOF) can be defined as the number of reactions per second per $(\text{nm})^2$ of total catalyst surface area. It is easier to determine the total surface area than the total number of reaction sites. On average there will be a certain number of reaction sites per unit of surface area for each catalyst. On this basis the PTOF will differ from the true turnover frequency by this number. It is expected that the number of reaction sites per unit of surface area will change with catalyst composition, structure, and preparation conditions.

In Figure 4 the PTOF for sulphur and asphaltene conversion increase more steeply with increasing temperature for the Co-Mo/C than for the Co-Mo/ Al_2O_3 catalyst. There are two well known phenomena which would be expected to cause an increase in turnover frequency with temperature. One is that kinetics increase with temperature, as indicated by the Arrhenius equation. The other is that the diffusivity increases with temperature. In general both of these effects will apply to both the carbon and the alumina supported catalysts.

The larger increase in PTOF with temperature for the carbon supported catalyst might be explained if the reaction sites on the carbon supported catalyst were different than those on the alumina catalyst. This may be the case since it is known that all of the Mo on carbon supports can be sulphided at low temperature (Vissers et al. 1987A). Some of the Mo on alumina catalysts can be sulphided at low temperature, but the balance requires high temperature (Arnoldy et al. 1985) for sulphiding. This indicates that the Mo is different on carbon than on alumina. Duchet et al., (1983) found that there were more S atoms associated with each Mo atom on carbon than on alumina. By using controlled atmospheric electron microscopy, Hayden et al. (1987) found that MoO_3 was mobile on carbon but disappeared on alumina. This is also evidence for the Mo reaction sites being different on the two supports.

Another kinetic factor results from the feedstock being a mixture of many compounds. Some of these compounds will react more easily than others. In the case of desulphurization the alumina catalyst achieved approximately 90 % conversion. The carbon catalyst achieved approximately 50 % conversion. In general, the individual compounds that are converted up to the 50 % level probably react more easily than those being converted at the 90 % level. For example, at the 90 % level the geometry of the reacting molecules probably causes a greater extent of steric hindrance between the sulphur atoms and the catalyst surface. More reactive compounds (ie., those remaining at 50 % conversion) may cause a greater increase in PTOF when the reaction temperature is increased, than the less reactive compounds (ie., those remaining at 90 % conversion).

Diffusion effects are another explanation for the greater increase in PTOF with temperature for the carbon catalyst. The carbon catalyst had much larger pores than the alumina catalyst. At higher temperatures, as very large molecules (or large micelles of molecules) become reactive, they will have much higher diffusion rates in the large pores of the carbon catalyst.

The change in pressure from 6.9 to 20.7 MPa (1000 - 3000 psig) shown in Figure 5 was found to have much less effect than the other variables on the conversion of both sulphur and asphaltene. For example, the experimental results with the Co-Mo/C catalyst at 698 K and a LHSV of 1 h^{-1} , show that as the pressure increased from 6.9 to 20.7 MPa there was an increase of 6.6 % and 7.9 % for sulphur and asphaltene conversions respectively. The alumina catalyst in Figure 5, as well as other catalysts reported in the literature (Mann et al, 1987), gave similar results.

One explanation for hydrogen having little effect on the desulphurization reaction is that the reaction is controlled by the concentration of sulphur species and that hydrogen is present in excess. Another explanation would be that the catalyst is fully saturated with hydrogen (Langmuir type isotherm) at 6.9 MPa. Therefore increasing the hydrogen pressure would not change the amount of hydrogen adsorbed.

Figure 6 shows the effect of the liquid feed rate on the performance of both catalysts, for LHSV between 0.5 and 1.5 h⁻¹. As the LHSV increased, a significant decrease occurred in both sulphur and asphaltene conversions. As the LHSV increases, more feedstock will flow over a unit of catalyst per unit time. Therefore the contact time between a particular molecule and the catalyst will decrease and the conversion will decrease as shown in Figure 6. However the PTOF for both sulphur and asphaltene reactions increased with increasing LHSV. This is caused by the feedstock being a mixture of hydrocarbon components. Some types of molecules are easier to convert than others. When the LHSV increases, each reaction site will be contacted by a larger number of "easy to convert" molecules. Although the number of molecules converted per reaction site increases, the total per cent converted decreases because there are more molecules contacting each unit of catalyst.

The PTOF is related to the LHSV and the conversion (X) by a constant, C₁, as shown in Equation 1.

$$\text{PTOF} = C_1 \text{ LHSV } X \quad (1)$$

C₁ is calculated to convert the units on one side of Equation 1 to the units on the other side. The following information is required for the conversion: volume and mass of catalyst in the reactor, specific surface area of the catalyst, liquid feed rate, 4.8 wt % S in feed, 18.7 wt % asphaltenes (pentane insolubles) in feed, and 7600 asphaltene molecular weight. Values of C₁ for each catalyst and reaction are shown in Table IV.

The conversion obtained in a first order reaction can be expressed (Smith, 1970) by Equation 2.

$$X = 1 - \exp(-kt) \quad (2)$$

where k is the first order rate constant, with units of [s⁻¹], and t is the

reaction time in [s]. An approximate relationship between the reaction time and LHSV can be developed. It is assumed that there is plug flow of the liquid upward through the reactor. Then Equation 3 can be written:

$$t = \frac{3600}{f_v \text{ LHSV}} = \frac{C_2}{\text{LHSV}} \quad (3)$$

where f_v is the void fraction of reactor volume (void volume between the catalyst pellets plus the catalyst pore volume). It is calculated from the empty reactor volume, the catalyst pellet density, and the catalyst pore volume. $C_2 = 4760$ for alumina and 4980 for carbon.

By substituting Equations 2 and 3 into Equation 1, the PTOF can be expressed in terms of LHSV.

$$\text{PTOF} = C_1 \text{ LHSV} \left(1 - \exp\left(\frac{-C_2 k}{\text{LHSV}}\right) \right) \quad (4)$$

The curves for PTOF in Figure 6 were derived from Equation 4, by adjusting the value of k to give the best fit of the experimental data. It is apparent that they represent the data reasonably well. The values of the rate constants for each combination of reaction and catalyst are listed in Table IV. The hydrodesulphurization rate constants are similar to those reported in the literature for petroleum feedstocks. Mohammed et al. (1986) reported a rate constant of $6.9 \times 10^{-4} \text{ s}^{-1}$ for HDS of an atmospheric resid at 400°C and 6.1 MPa. Mann et al. (1987) reported a rate constant of 5.8×10^{-4}

s^{-1} for HDS of a heavy gas oil at $450^{\circ}C$ and 7 MPa.

The above development shows that data for PTOF versus LHSV in Figure 6, can be represented in terms of a rate constant, k . All other terms in Equation 4 are constants. Furthermore, the value of k has been shown to be consistent with other first order rate constants reported in the literature.

Both sulphur and asphaltene conversions in Figures 3 to 6 are lower for the carbon supported catalyst than for the alumina supported one. This is consistent with the HDS data for benzothiophene reported by Daly et al. (1984). The lower conversions with the carbon supported catalyst can probably be attributed to its substantially lower surface area as shown in Table I. When the catalysts are compared on a unit surface area basis, it is seen that the PTOF are always greater for the carbon supported catalysts.

The Co-Mo/C catalyst did have its surface area in pores which were large enough for bitumen molecules. However, its combined surface area, pore diameter and pore volume were not optimized for bitumen molecules. For alumina catalysts it has been shown (Ternan, 1983) that maximum conversions are often obtained using catalysts with the largest surface areas. If a carbon supported catalyst could be made with sufficient surface area in large pores, so that it was comparable to the alumina catalyst, then its conversion might be even greater than the alumina catalyst if the value of the PTOF could be maintained. Methods for making such catalysts have been described (Walker, 1978)

CONCLUSIONS

All of these results consistently show that greater conversions are obtained with alumina supported catalysts rather than carbon supported catalysts. This is consistent with the benzothiophene HDS results of Daly et al. (1984). However, when the reaction results are compared on a unit surface area basis, the PTOF were greater for the carbon supported catalysts. This is consistent with the results for thiophene HDS (Stevens and Edmonds, 1979; deBeer et al., 1981; Bridgewater et al., 1982; Duchet et al., 1983). If a wide pore carbon supported catalyst having as much surface area as alumina could be

developed, then perhaps conversions which equal or exceed those of the alumina supported catalyst could be obtained.

LITERATURE CITED

Arnoldy, P., J.A.M. van den Heijkant, G.D. deBok, and J.A. Moulijn, *J. Catal.* 92, 35 (1985).

Bridgewater, A.J., R. Burch and P.C.H. Mitchell, "Carbon Supported Hydrodesulphurization Catalysts", *App. Catal.* 4, 267-283 (1982).

Brinen, J.S., L.F. Allard, and F.P. Daly, "XPS and AEM Studies of Carbon Supported HDS Catalysts", *Surf. Interf. Anal.* 9 227-236 (1986).

Champagne, P.J., E. Manolakis and M. Ternan, "Molecular Weight Distribution of Athabasca Bitumen", *Fuel* 64, 423-425 (1985).

Chung, K.E., L.L. Anderson and W.H. Wiser, "New Procedure for Molecular Weight Determination by Vapour Pressure Osmometry", *Fuel* 58, 847-852 (1979).

Daly, F.P., J.S. Brinen, and J.L. Schmitt, "A Wide Pore Carbon Supported Hydrodesulphurization Catalyst", *App. Catal.* 11 161-164 (1984).

deBeer, V.H.J., J.C. Duchet, and R. Prins, "The Role of Cobalt and Nickel in Hydrodesulphurization: Promoters or Catalysts?", *J. Catal.* 72, 369-372 (1981).

Duchet, J.C., E.M. van Oers, V.H.J. deBeer, and R. Prins, "Carbon Supported Sulphide Catalysts", *J. Catal.* 80, 386-402 (1983).

Hayden, T.F., J.A. Dumesic, R.D. Sherwood, and R.T. Baker, "Direct Observation by Controlled Atmosphere Electron Microscopy of the Changes in Morphology of Molybdenum Oxide and Sulfide Supported on Alumina and Graphite", *J. Catal.* 105, 299-318 (1987).

Eisch, J.J., L.E. Hallenbeck, and M.A. Lucarelli, "Desulphurization and Denitrogenation of SRC Liquids by Transition Metals on Solid Supports", *Fuel*, 64, 440-442 (1985).

Kelly, J.F., and M. Ternan, "Hydrocracking Athabasca Bitumen with Alkali Metal Promoted $\text{CoO-MoO}_3\text{-Al}_2\text{O}_3$ Catalysts", *Can. J. Chem. Eng.* 57 726-733 (1979).

Mann, R.S., I.S.S. Sambhi, and K.C. Khulbe, "Catalytic Hydrofining of Heavy Gas Oil", *Ind. Eng. Chem. Res.* 26, 410-414 (1987).

Mohammed, A.A.K., A.A.A. Abbar, and A.K. Al-Maiya, *Chem. Technol. Fuel Oils* 22, 19-21 (1986) English translation pp. 644-648.

Smith, J.M., "Chemical Engineering Kinetics", 2nd ed., McGraw-Hill, New York, 1970, p. 263.

Stevens, G.C., and T. Edmonds, "Preparation and Properties of Thiomolybdate Graphite Catalysts", in "Preparation of Catalysts II", (eds. B. Delmon, P. Grange, P. Jacobs and G. Poncelet). Elsevier, Amsterdam, 1979, pp. 507-517.

Ternan, M., and J.F. Kriz, "Some Effects of Catalyst Composition on Deactivation and Coke Formation when Hydrocracking Athabasca Bitumen", in "Catalyst Deactivation", (eds. B. Delmon and G. Froment), Elsevier, Amsterdam, 1980, pp. 283-293.

Ternan, M., "Catalytic Hydrogenation and Asphaltene Conversion of Athabasca Bitumen", *Can., J. Chem. Eng.* 61, 689-696 (1983).

Vissers, J.P.R., B.Scheffer, V.H.J. deBeer, J.A. Moulijn, and R. Prins, "Effect of the Support on the Structure of Mo-Based Hydrodesulphurization Catalysts: Activated Carbon versus Alumina", *J. Catal.* 105, 277-284 (1987A).

Vissers, J.P.R., S.M.A.M. Bouwens, V.H.J. deBeer, and R. Prins, "Carbon Black Supported Molybdenum Sulphide Catalysts", *Carbon* 25, 485-493 (1987B).

Walker, P.L., "Carbon - A Versatile Catalyst Support", Proc. 5th Ind. conf. on Carbon and Graphite, London, soc. Chem. Ind., (1978), pp. 427 - 436.

CAPTIONS FOR FIGURES

Figure 1. Diagram of Experimental Equipment. 1. pump, 2. preheater, 3. reactor, 4. three zone heater, 5. gas/liquid separator, 6. scrubber, 7. wet test meter, FC flow controller, PC pressure controller, PI pressure indicator, TC temperature controller, TR temperature recorder for 6 thermocouples.

Figure 2. Axial Temperature Profiles on the Reactor Centerline

Figure 3. Catalyst Deactivation - Conversion (wt %) versus Time (h). Solid lines are for hydrodesulphurization and dashed lines are for hydrodeasphalting. Circles and crosses are for alumina supported catalysts and carbon supported catalysts respectively.

Figure 4. Upper - Conversion (wt %) versus Temperature ($^{\circ}\text{C}$). Lower - Pseudo Turnover Frequency (atoms S removed $(\text{nm})^{-2} \text{s}^{-1}$) or (molecules asphaltene converted $(\text{nm})^{-2} \text{s}^{-1}$) versus Temperature ($^{\circ}\text{C}$). Solid lines are for hydrodesulphurization. Dashed lines are for hydrodeasphalting. Circles and crosses are for alumina supported catalysts and carbon supported catalysts respectively.

Figure 5. Upper - Conversion (wt %) versus Pressure (MPa). Lower - Pseudo Turnover Frequency, (atoms S removed $(\text{nm})^{-2} \text{s}^{-1}$) or (molecules asphaltene converted $(\text{nm})^{-2} \text{s}^{-1}$) versus Pressure (MPa). Solid lines are for hydrodesulphurization. Dashed lines are for hydrodeasphalting. Circles and crosses are for alumina supported catalysts and carbon supported catalysts respectively.

Figure 6. Upper - Conversion (wt %) versus Liquid Hourly Space Velocity, (h^{-1}). Lower - Pseudo Turnover Frequency (atoms S removed $(\text{nm})^{-2} \text{s}^{-1}$) or (molecules asphaltene converted $(\text{nm})^{-2} \text{s}^{-1}$) versus Liquid

Hourly Space Velocity (h^{-1}). Solid lines are for hydrodesulfurization. Dashed lines are for hydrodeasphalting. Circles and crosses are for alumina supported catalysts and carbon supported catalysts respectively.

Table I: CATALYST SPECIFICATIONS

Identification	Co-Mo/Al ₂ O ₃	Co-Mo/C	carbon support as received
support type	Al ₂ O ₃	Wide pore-C	Cyanamid wide pore-C extrudate
Amount of catalyst used,g	115.0	65.7	
Catalyst bulk density,g/mL	0.766	0.438	_____
Catalyst pellet density,g/mL	1.32	0.74	_____
MoO ₃ , wt %	15.0	15.0	_____
CoO , wt %	3.0	3.0	_____
N-adsorption			
S _{BET} , m ² /g (N ₂)	210.0	116.0	221.1
Mercury porosimetry			
S _{poros} , m ² /g	207.3	100.0	143.7
V _{pore} , cm ³ /g	0.44	0.72	0.92
D _{pore} , nm	8.5	28.6	25.5

Table II: PROPERTIES OF ATHABASCA BITUMEN

Specific gravity at 15°C	1.008
Carbon wt %	83.9
Hydrogen wt %	10.7
Nitrogen wt %	0.365
Sulphur wt %	4.8
Oxygen wt %	0.95
Pentane Insolubles wt %	18.7
Ash wt %	0.57
Vanadium ppm	213
Nickel ppm	67
Iron ppm	358
+525°C Residue wt %	51.0
Conradson carbon residue wt % ..	13.3

TABLE III: SEQUENCE OF EXPERIMENTS

Experiment No	Pressure MPa	Temperature °C	LHSV h ⁻¹
1	13.8	400	1
2	13.8	425	1
3	13.8	425	1.5
4	13.8	450	1
5	6.9	425	1
6	13.8	425	1
7	20.7	425	1
8	13.8	425	0.5
9	13.8	425	1

TABLE IV: CONSTANT FOR EQUATION (4)

Catalyst type	Reaction type	Conversion constant		Rate constant
		C_1^*	C_1^{**}	k, s^{-1}
Co-Mo/Al ₂ O ₃	HDS	1.5×10^{-3}	-----	5×10^{-4}
	HDA	-----	2.56×10^{-5}	3.75×10^{-4}
Co-Mo/C	HDS	4.94×10^{-3}	-----	0.94×10^{-4}
	HDA	-----	8.10×10^{-5}	2×10^{-4}

* $(ml_{cat} \text{ h/ml}_{fd}) / (\text{atom } S_{fd}/nm^2 \text{ s})$

** $(ml_{cat} \text{ h/ml}_{fd}) / (\text{molecule } A_{fd}/nm^2 \text{ s})$

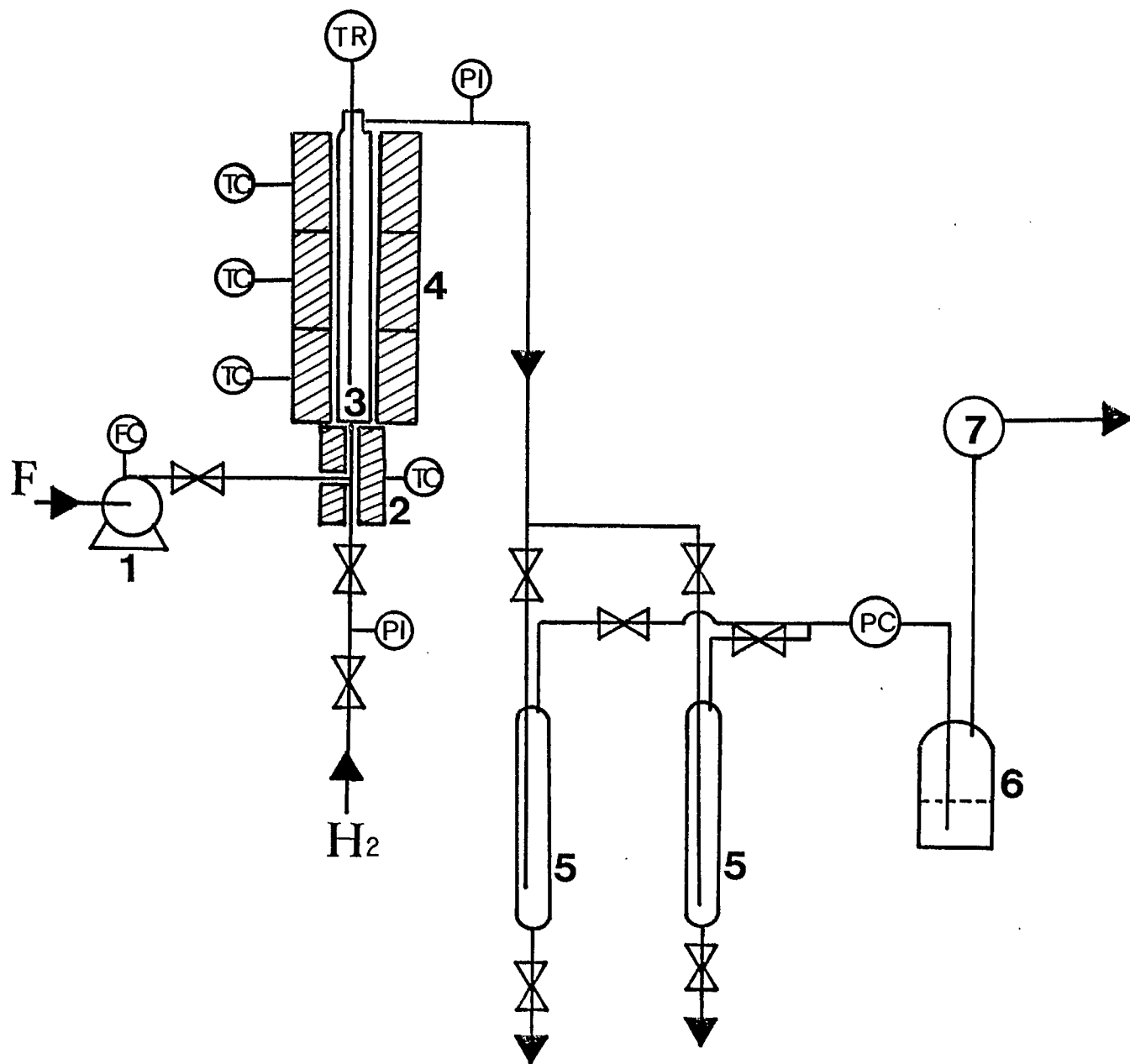


Fig 1

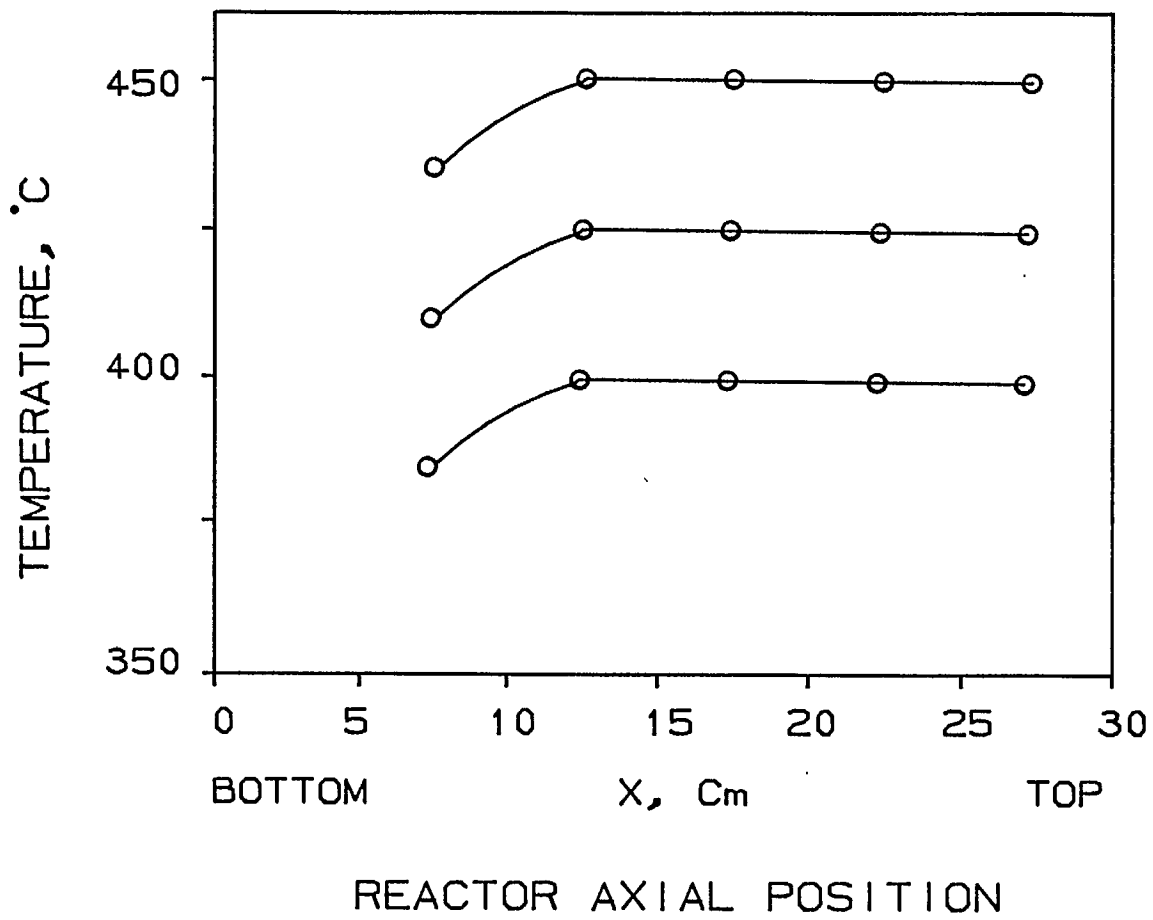


FIG 2

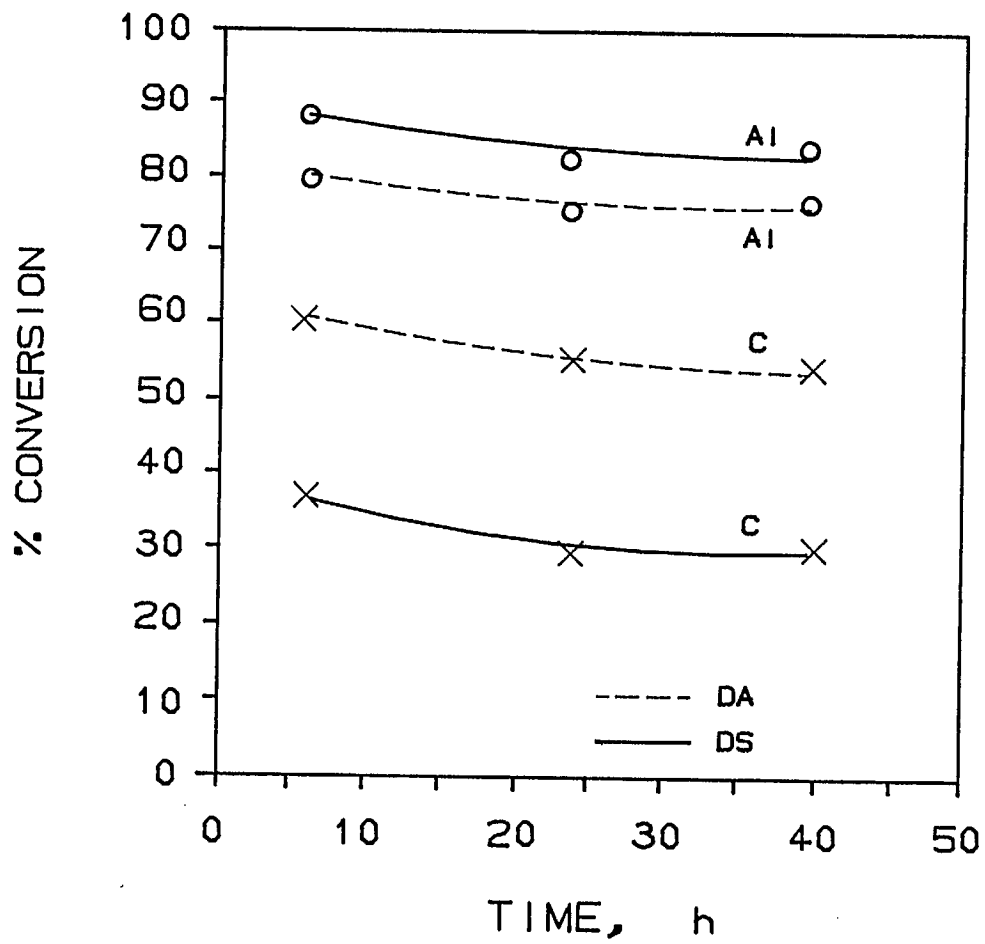


Fig 3

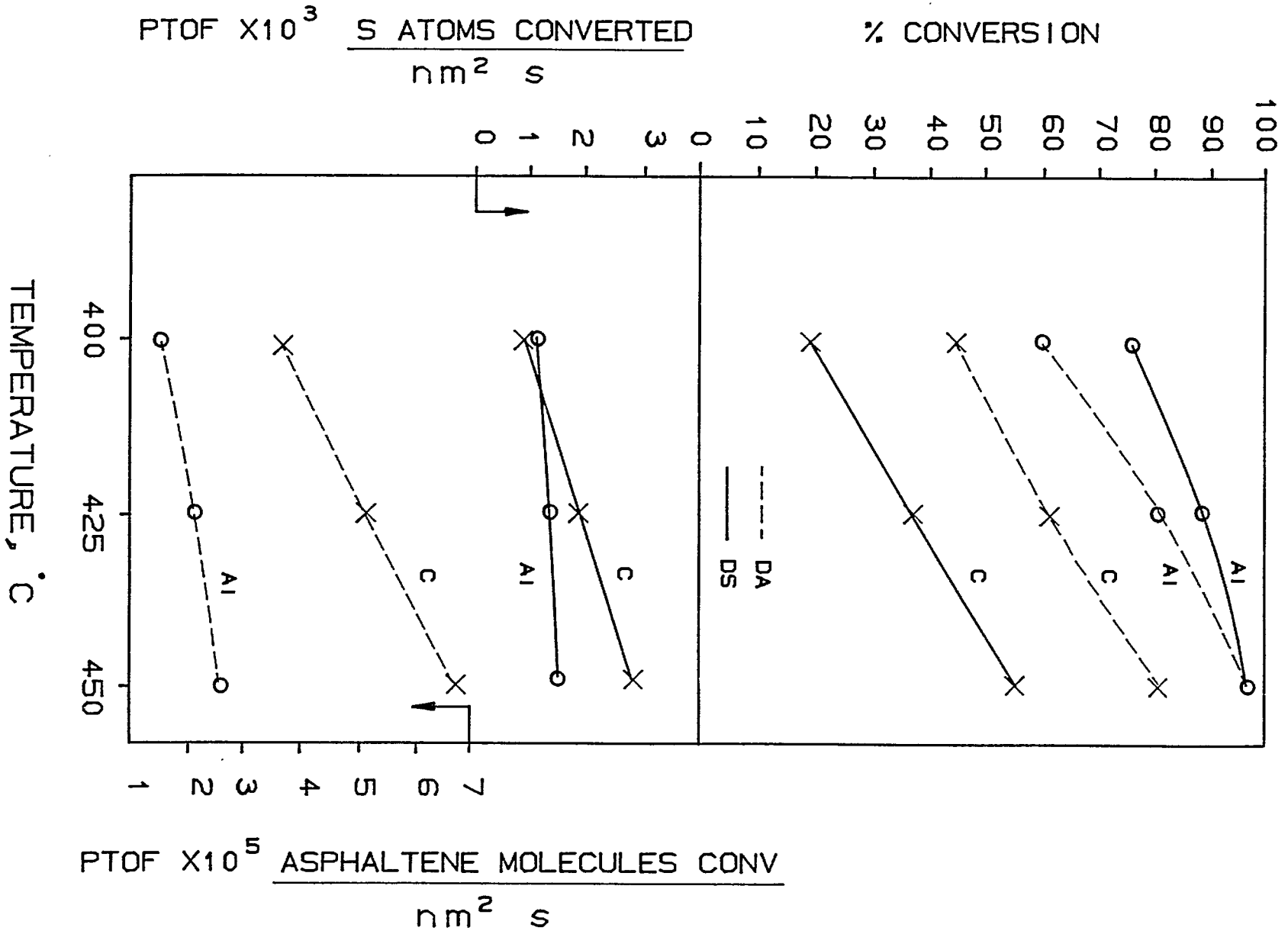


Fig 4

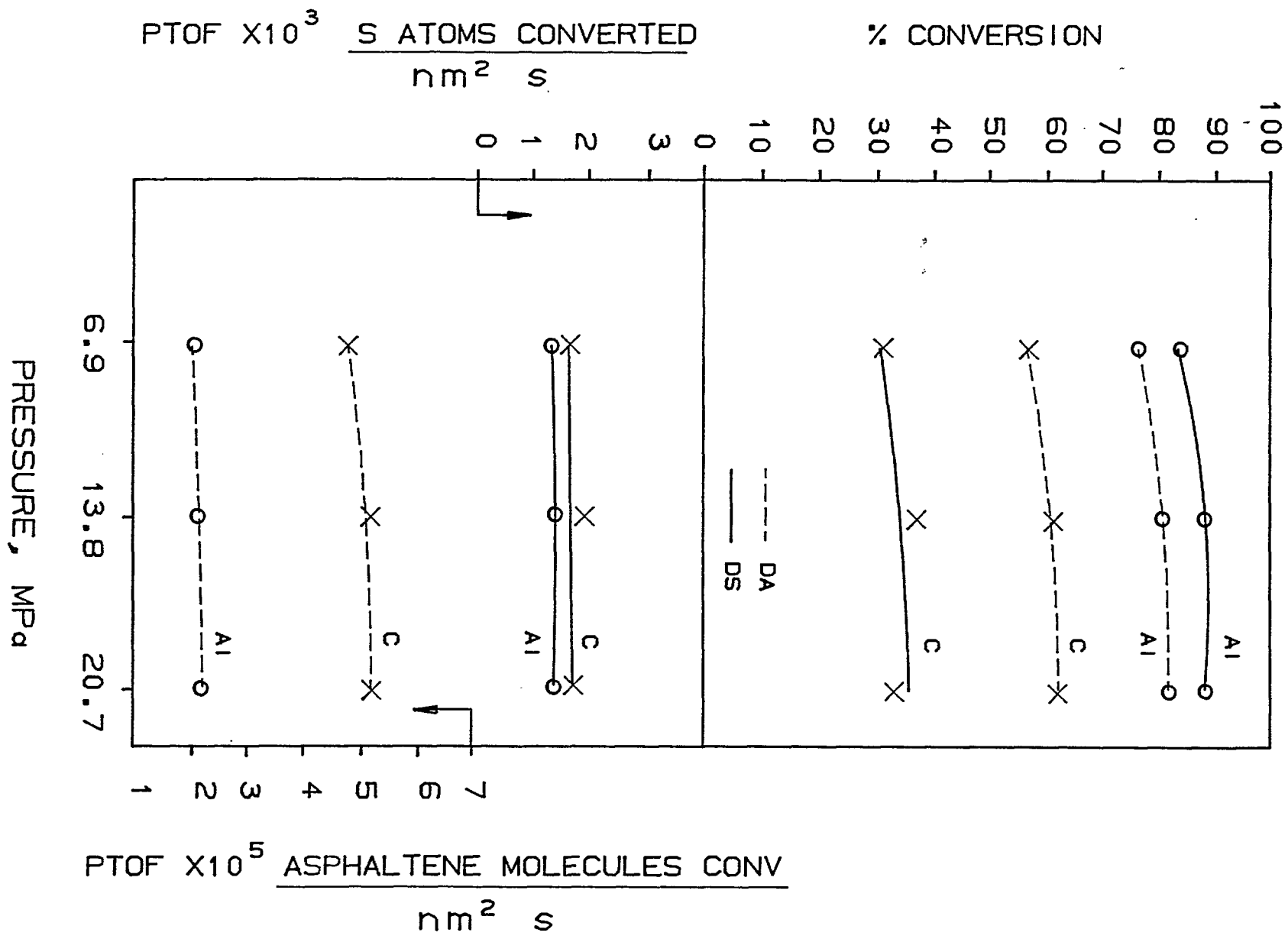


Fig 5

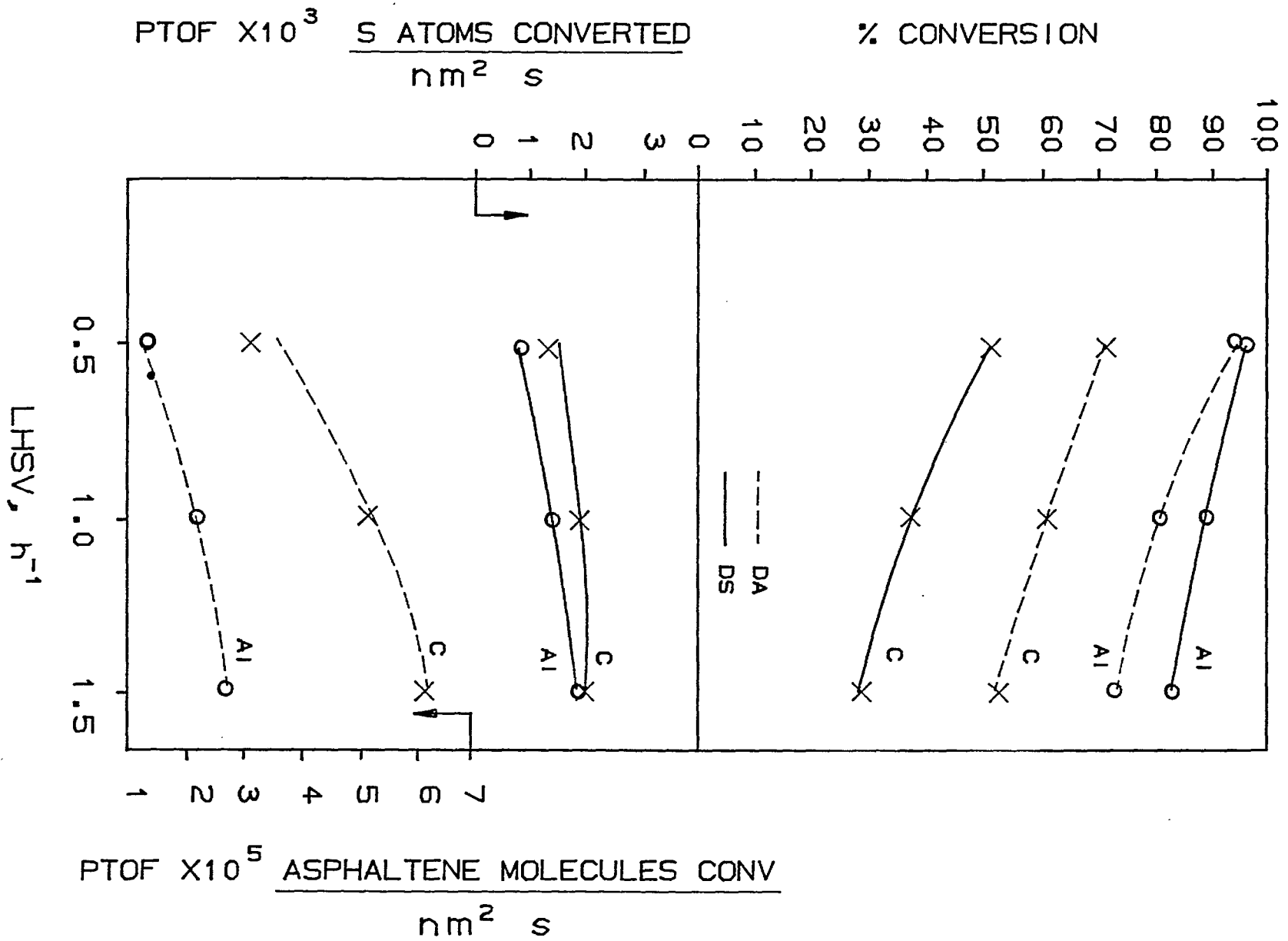


Fig 6