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LARGE PORE CATALYSTS FOR VISCOSITY REDUCTION OF HEAVY FEEDS

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Summary

A number of alumina supported Co/Mo catalysts were evaluated for their efficiency in reducing the viscosity of a Canadian oil sands bitumen to levels low enough for direct pipelining. The supports for the catalysts were prepared by modifying commercial alumina to produce a range of large pores. The resultant catalysts had bimodal pore size distributions, with macropore diameters typically of the order of a 1000 Å or more and small pore diameters of the order of a 100 Å. The experiments were conducted using a fixed bed upflow reactor at the following processing conditions - 400°C, 13.9 MPa and between 0.5 - 0.75 LHSV. The data were collected over 250 hours of time on stream. The performance of the catalysts was assessed in terms of the pentane insolubles content and the viscosity of the hydrocracked product. Even a 25 wt % removal of the pentane insolubles resulted in a remarkable reduction in the viscosity, from about 18 900 cSt to 2000 cSt at 40°C. About 80% removal of the asphaltenes was necessary to reduce the viscosity to levels compatible with pipelining requirements. These results were related to the presence of large pores and their distribution in the catalysts. Used catalysts were examined for changes in the pore structure in order to interpret the moderate deactivations observed.

Introduction

One of the major constraints in the utilization of oil sand bitumen is its high viscosity. The viscosity often dictates that the bitumen can only transported short distances in heated pipes or that it be diluted with an aromatic naphtha which is recovered after the mixture reaches its destination. Once transported to a processing site, the bitumen can be upgraded into usable products using a variety of technologies. Alternatively, it may be advantageous to consider mild upgrading at the production site so that the bitumen can be pipelined to a processing site for more extensive upgrading. The present work reports the results of our investigations of such a process.

Viscosity is known to be strongly dependent on the composition of the fluid. In the case of bitumen its viscosity can be related to the presence of high molecular weight asphaltene species (Speight, 1981). Conversion of these large molecular weight entities into smaller molecular weight fragments would then result in a lowering of the viscosity. With these observations, it was decided to test a number of alumina based Co/Mo catalysts for the viscoisty reduction reaction scheme. Since the large molecular weight species generally may be expected to have large molecular dimensions as well, the cataysts used in this work were designed to have large pore diameters for a more efficient utilization of the catalysts. The specific objective in this work was to reduce the viscosity of Athabasca bitumen by a factor of about 450, from an initial value of about 18900 cSt, measured at 38°C to about 40 cSt .

Experimental

The catalyst supports were prepared from commercially available alpha alumina monohydrate (Catapal SB from Conco, Peterboro, N.J.) using a pretreatment technique developed in our laboratory (Ternan et al., 1982). Briefly it involved treating the alumina with varying quantities of concentrated nitric acid and water, mixing the slurry for a fixed time, followed by drying at 60°C. The dried mixture is either calcined as is or extruded into small cylindrical extrudates of nominal diameter of 3 mm. The materials were then calcined at 500°C for 16 h. The supports pretreated in this fashion have a range of large pore diameters and surface areas of the order of 100 m^2/g or more. The preparation of the catalysts from these supports involved two impregnation steps. In the first, the support was mixed with ammonium hepta molybdate in an aqueous solution, equal in volume to the total pore volume, followed by drying at 60°C and calcining at 500°C. The impregnation, drying and calcining were repeated in the second step with an aqueous solution of cobalt nitrate. After the final calcination, the catalysts were sieved and particle sizes from 290 to 838 microns (10 to 30 mesh) were used for the reactivity tests. The catalysts were prepared to have a bulk composition of 15 m% MoO_3 and 3 m% CoO.

The Athabasca bitumen used in this study was obtained from Great Canadian Oil Sands Limited (now SUNCOR) at Fort McMurray, Alberta. Some pertinent properties of the bitumen are given in Table 1. The equipment employed in this work was previously described in detail (Ternan, 1983.) The catalyst bed was about 0.70 m long with pre and post-reactor sections of 0.37 m and 0.45 m in length respectively. The stainless steel reactor was 0.0175 m I.D. and was equipped with a thermowell (O.D. 0.0063 m) . The temperature was monitored by a set of six thermocouples placed equidistent from each other inside the thermowell. The bitumen mixed with the hydrogen was pumped through the bottom of the reactor and the product was collected from the top.

All experiments were performed at a pressure of 13.9 MPa and a hydrogen flow of 0.89 m^3/l of feed at STP (5000 ft^3/bbl). Presulphiding of the catalyst was caried out with bitumen in the presence of hydrogen from 250°C to 400°C using the procedure described earlier (Sekhar, 1985). Five catalysts were tested and are referred to as catalyst A, B, C, D and E. In the case of catalysts B and C the bed was dilued with silicon carbide particles of the same size range as the catalyst. The total bed volume was maintained at about 140 to 150 mL. Within the bed the catalyst to diluent volumetric ratio was varied from about 0.25 at the bottom to about 1 at the top. The amounts of the catalyst and the diluents used are listed in Table 2.

A number of properties of the products were measured to evaluate the performance of the catalysts. Sulphur analyses were performed by a LECO SL 32 analyzer and the asphaltene contents were determined by a modified ASTM procedure developed at our laboratoreis. Viscosities were measured at 38°C using ASTM D-445 method.

Results and Discussion

The strong correlation between asphaltene content and the viscosity alluded to earlier is clearly evident from Figure 1. As the asphaltene content decreases the viscosity decreases almost exponentially. The data for this figure was obtained with five different catalysts and over a temperature range of 400 to 440°C and space velocities between 0.5 - 3. The spread in the data is due to the wide variation in the operating conditions and hence a wide variation in the composition of the product. At higher temperatures and lower space velocities the severity of hydrocracking increases resulting in a lower asphaltene content. However, the viscosity reduction is less dramatic. Figure 2 shows the relationship between product viscosity and hydrocracking severity expressed in terms of the conversion of the residuum fraction. In spite of the spread in the data the trend is consistent with the generally accepted fact that the breaking of larger species into smaller ones causes a lowering of the viscosity in the product.

Since the objective of this work was to determine if viscosities could be reduced low enough under mild conditions, attention has been focused on results obtained at 400 °C and a volumetric space velocity of approximately 0.5 v/v/h. Figure 3 shows the product viscosities as a function of time on stream for three catalysts. The experimental conditions were generally constant except that the weight of the catalysts in each case was different. However, the total volume of the catalyst bed was essentially the same.

For catalyst C viscosities appear to level off at about 100 h on stream and beyond. Some data were collected between 100 - 200 h on stream by changing the reaction temperature as well as the space velocity in order to estimate the variations in the product viscosity as a function of these variables. Figure 4 shows the viscosities as a function of space velocities at various temperatures. Some general assumptions and observations are in order at this point. The bitumen feed and the product could be considered to consist of two hypothetical species, termed A and B. Viscosity reduction involves the fragmentation of high molecular weight species A into smaller ones, species B by the breaking of bonds. The high viscosity in the feed arises mainly due to the presence of the high molecular species A in a certain initial weight fraction. The bonds in the species A are broken to form species B which have a lower viscosity. The product obtained under a given set of conditions can also be considered to be a mixture of the two hypothetical species in a certain weight fraction. The relative concentrations of species A and B give rise to the observed viscosity of the product. As the reaction conditions or the catalyst are changed the relative concentrations of A and B in the final product change resulting in the observed variations in the viscosity.

As the conversion increases with contact time t, the weight fraction of A in the mixture decreases and at infinite contact time, all of the species A are converted into species B and the viscosity of the product reduces to a limiting value characteristic of species B. In a flow system a space velocity of zero would correspond to infinite contact time. Therefore an extrapolation of the linear relationships to zero space velocity shown in Figure 4 would give an estimate of the limiting viscosity of the product under conditions of 100% conversion. These limiting viscosities and the corresponding reaction temperatures are given in Table 3. Similar limiting viscosities have been reported in the thermal visbreaking of a Cold Lake bitumen (Shu and Venkatesan, 1984). These limiting values could be used in judging the operating conditions required for achieving a given reduction in viscosity using this particular catalyst. It is important to note that species B are very likely to be different for various temperatures since the nature of the bonds that are broken will likely be different with variation in the temperature.

Table 4 gives some properties of the products at selected hours on stream using the various catalysts. All data correspond to a bed temperature of 400°C. Using the data in Table 4 and with reference to Figure 3, a number of observations can be made. At about 95 h on stream, the product obtained using catalyst C has a higher viscosity than that obtained using catalyst D. There was a difference in the mass of the catalysts in the two series of experiments hence a difference occurred in the mass of active metals in the bed, which may partially account for the poor performance of catalyst C compared with catalyst D . But more importantly, as shown in Figures 5 and 6 the pore structures of the two catalysts are different. There are no pores present between about 900 - 150 A for catalyst C. Although this catalyst had macropores and could provide large channels for penetration of the large molecular species, once inside the channels these species did not have access to the pore space where reactions could occur. For catalyst D on the other hand, penetration of mercury occurred almost at every mercury pressure therefore a wide of range of pores was present in this catalyst. This is further confirmed by comparing the product properties of these two catalysts with respect to sulphur and asphaltene removal. Using the data in Figure 4 and Table 3 one might say that even at infinite contact time, the viscosity of the product using catalyst C would always remain high. Unfortunately, it was not possible to directly compare the initial activities of these two catalysts since the experimental conditions were not the same.

A comparison of the two catalysts D and E shows a different picture. At 52 and 95 h on stream, both the catalysts had about the same activity for viscosity reduction and sulphur removal. For asphaltene conversion however, catalyst E performed better . This wass at first surprising since catalyst E was less macroporous than catalyst D as is evident from Figures 6 and 7. Reference to the sulphur and asphaltene contents of the products from catalyst E could explain this apparent anomaly. The very low values of the asphaltene amd the sulphur contents should have produced a product having a viscosity lower than about 100 cSt if the catalyst were capable of breaking down some of the larger species that contribute to high viscosity. Since the reactor bed in the case of catalyst E contained nearly one and a half times the mass of catalyst compared with the series of runs with catalyst D , the presence of higher amounts of active metals could reasonably explain the better conversions for asphaltene removal. That the product viscosities were about the same in fact points to the superior performance of the macroporous catalyst D. A molecular weight determination would perhaps show that the product from catalyst E had a higher average molecular weight than that of the product from catalyst D.

Figures 5 to 7 also show the pore structure of the aged catalysts. The aged catalyst specimens were removed from both ends of the reactor and analysed separately. The specimens were washed with toluene and dried in vacuum at room temperature before analysis by mercury porosimetry. In all cases except catalyst E the upstream samples suffered a higher loss of both the pore volumes and the surface areas compared with the downstream specimens. Also the upstream samples showed a greater loss of micropore volumes than the downstream samples. The lack of loss of surface area in the case of aged samples of catalyst E is somewhat surprising, although there is a loss of pore volume . This could perhaps be due to the shifting of the micropore size distribution to lower pore sizes as is evident from Figure 7, since the surface area increases with the square of the pore diameter. It is very likely that this catalyst would have suffered a dramatic loss both in the surface area and the pore volume had the experiment been continued for a little longer time on stream due to the continuous shift of the micropore size distribution to lower pore sizes.

In summary, the pipelineability of the bitumen requires that its viscosity be reduced to about 40 cSt at 38°C (Riceroglu et al 1982). The data presented in this work indicated that using a catlyst such as D at about 0.5 LHSV and 400°C the viscosity could be reduced to approximately 100 cSt and this activity could be maintained over 225 h on stream. Since catalyst D was shown to be superior to catalyst C, based on the results obtained at higher severities using Caatalyst C, i is estimated that a reactor temperature of about 425 °C would be required to reduce the viscosity to 40 cSt, compatible with pipelining requirements.

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Table 1. Properties of Athabasca bitumen feedstock

Reletive Density	(15/15°C)	1.008
+524 °C Residuam	(m/m%)	51.5
Penatane Insolubles	(Asphaltenes)	18.2
Sulphur		4.6
Kinematic Viscosity @ 38°C	(cSt)	18 900

Table 2. Mass and volumes of catalysts and diluents

Type	Catalyst Mass (g)	Catalyst Volume (mL)	Diluent Mass (g)	Diluent Volume (mL)	Reactor Volume (mL)
A	99	150	nil	nil	150
B	27	50	88	105	155
C	28	48	75	93	141
D	46	140	nil	nil	140
E	74	140	nil	nil	140

Table 3. Limiting viscosities and Reaction Temperatures

Average Temperature °C	Limiting Viscosity cSt @ 38°C	Linear Correlation Coefficient
400	151	0.9788
413	128	0.8843
422	44	0.8371
435	4.5	0.9717

Data collected using Catalyst C between 100 and 200 h on stream.

Table 4. Product properties at selected hours on stream and at 400°C

Catalyst	TOS (h)	Viscosity cSt @ 38 °C	Asphaltenes m/m%	Sulphur m/m%	LHSV v/v/h	WHSV g/g/h
D	52	99	4.72	1.02	0.50	1.52
E	52	122	3.54	0.95	0.50	0.95
C	97	369	7.76	1.96	0.53	2.64
D	95	117	5.92	1.13	0.50	1.52
E	93	95	3.71	0.89	0.50	0.95

Table 5. Mercury Porsosimetry Data

		Surface Area (m^2/g)			Pore Volume (mL/g)		
Catalyst	TOS (h)	Fresh	Aged Inlet	Aged Exit	Fresh	Aged Inlet	Aged Exit
A	45	88	18		0.39	0.20	
B	100	149	33	49	0.34	0.19	0.19
C	329	106	28	36	0.30	0.14	0.17
D	273	129	22	37	0.32	0.18	0.29
E	95	100	83	73	0.32	0.19	0.19

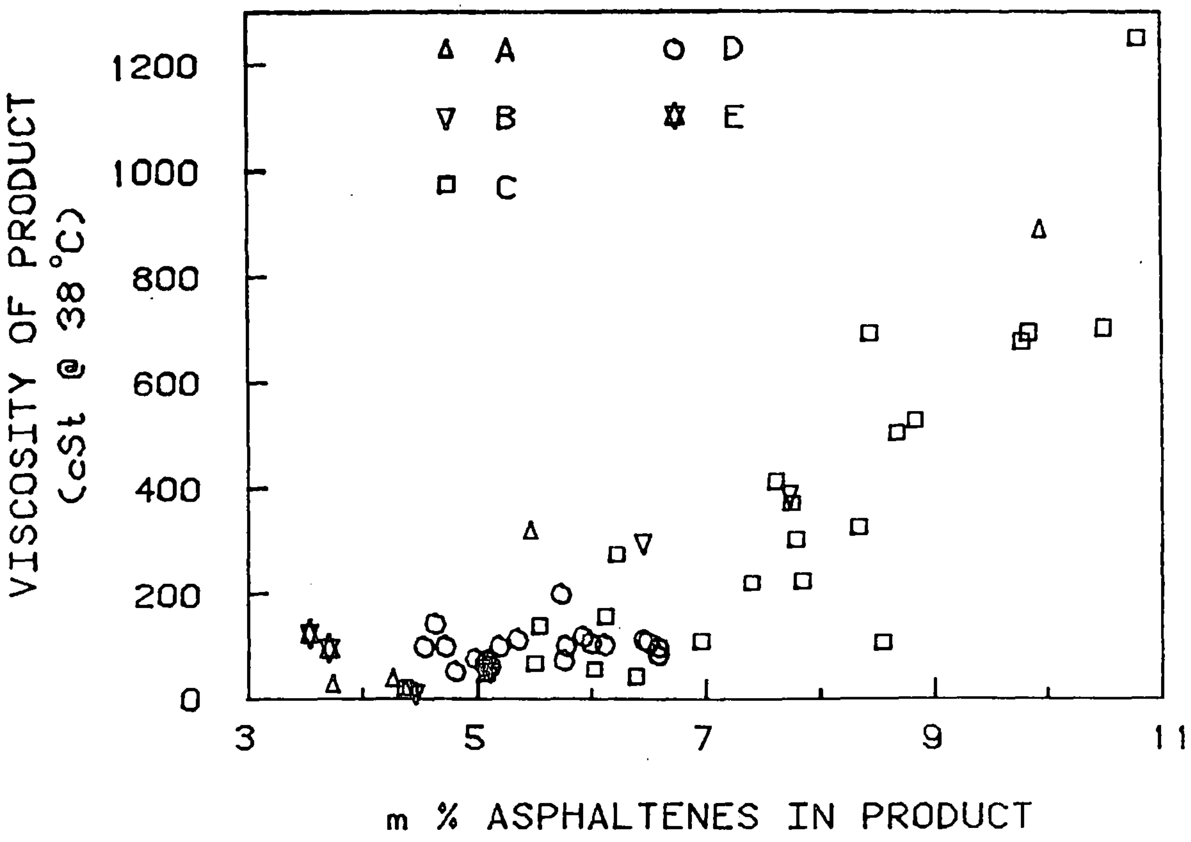

Figure 1. Viscosity vs asphaltene content

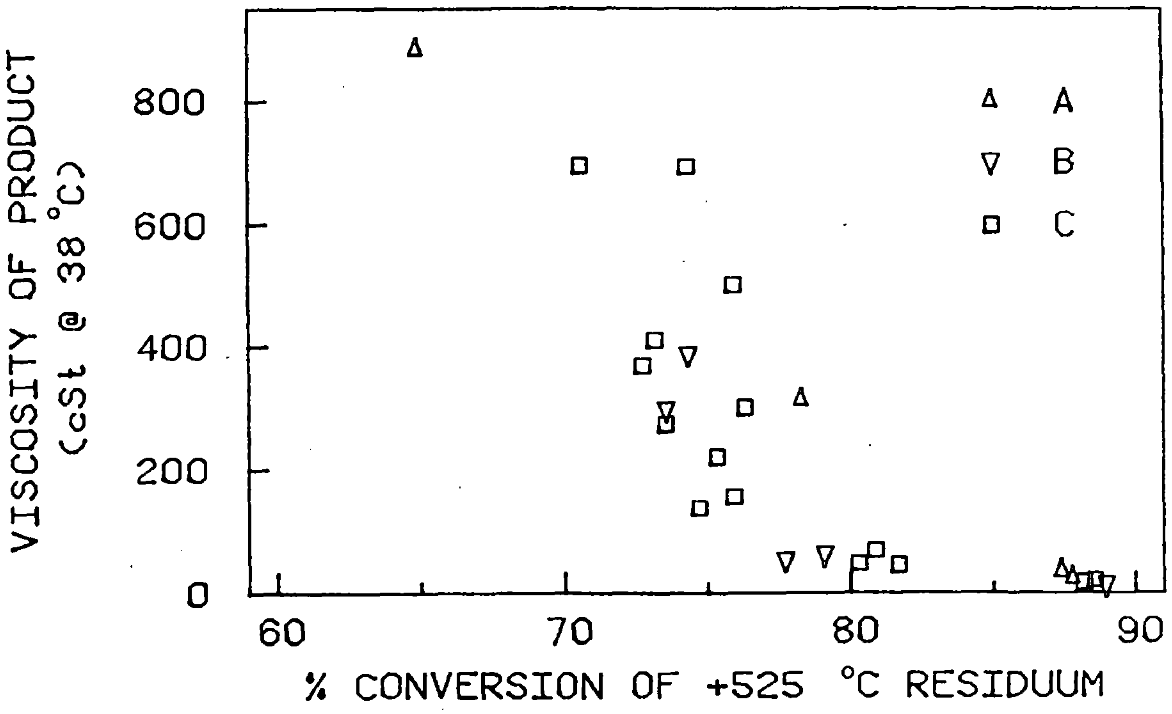

Figure 2. Viscosity vs severity of hydrocracking

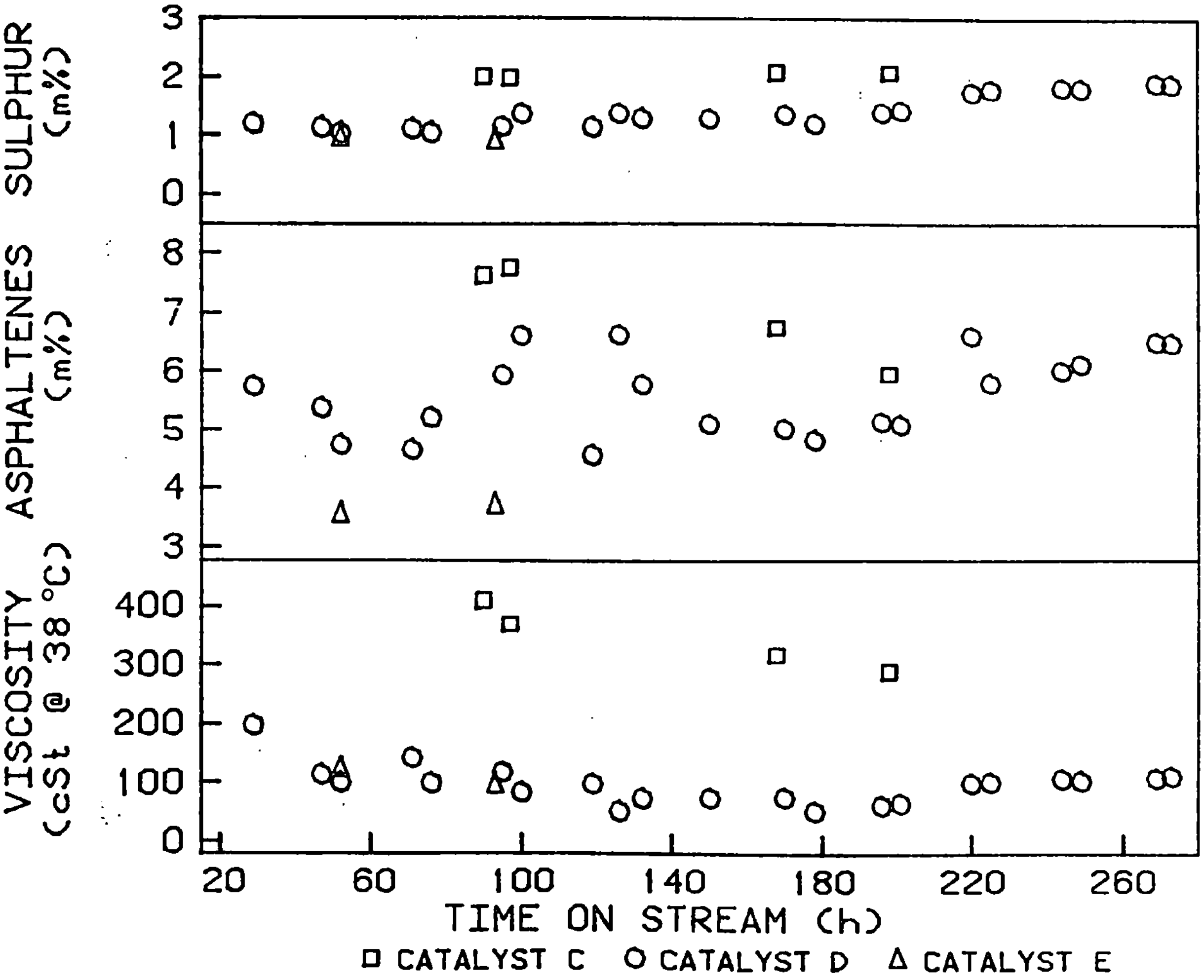

Figure 3. Product properties vs time on stream

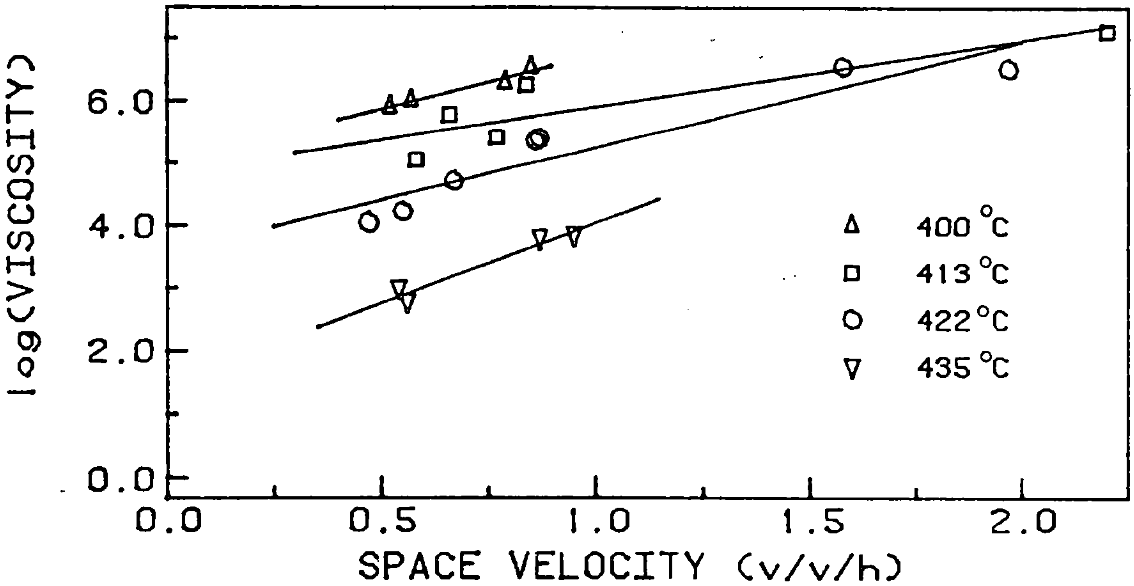

Figure 4. Viscosity vs space velocity for catalyst C

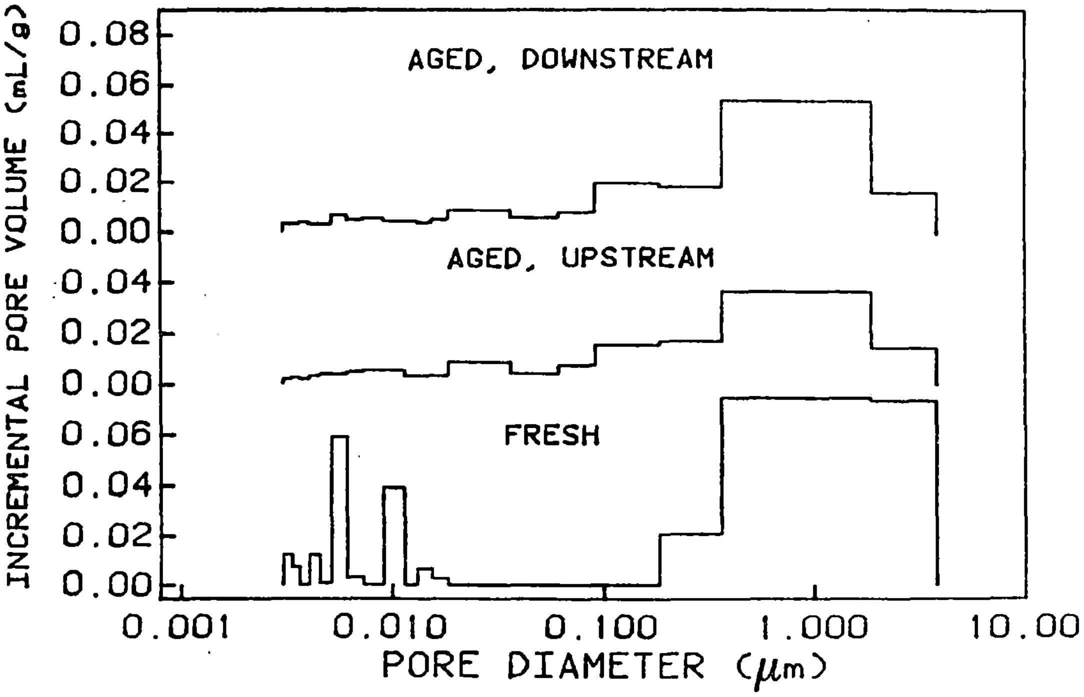

Figure 5. Pore structure of Catalyst C

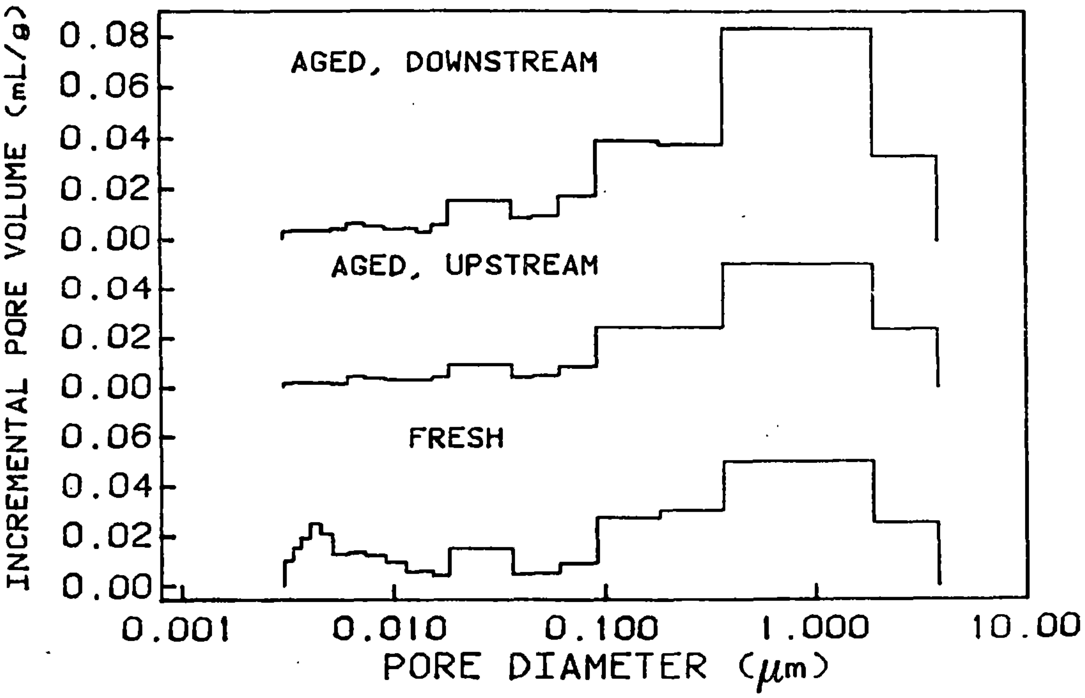

Figure 6. Pore structure of catalyst D

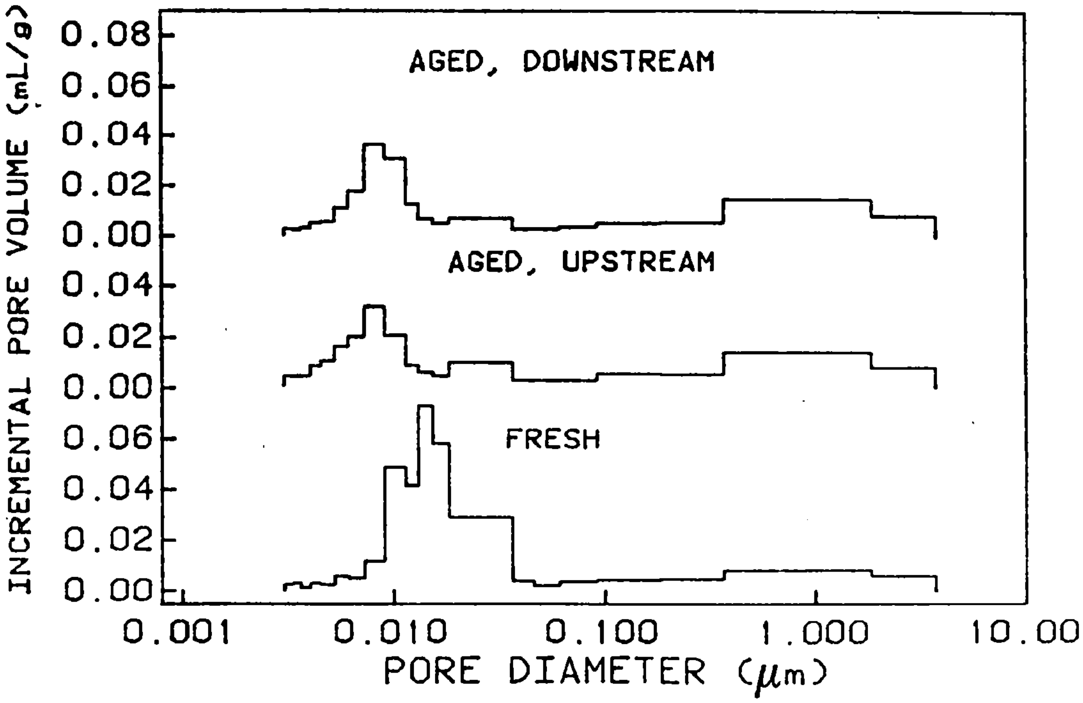

Figure 7. Pore structure of catalyst E