

DESULFURIZATION OF PETROLEUM

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NOYES DATA CORPORATION

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INTRODUCTION

In recent years, an increasing awareness of environmental pollution has become manifest, particularly with respect to air pollution. This awareness has, in turn, led to the recognition of pollution sources. A chief source of air pollution is the exhaust vapor emanating from internal combustion engines, i.e., automobiles. Much effort has been expended to control this pollutant, including legislation requiring reduced pollutant levels in exhaust vapor emanating from new cars. Although air pollution caused by cars has received considerable attention, air pollution by emissions from other sources has not been overlooked.

Significant contributors to air pollution are the emissions which arise in the combustion of heating oils used in furnaces. Such emissions contain oxides of sulfur which are toxic and reactive. Sulfur arises in these oils as a result of its presence in the crude oil source. The increasing shortages of energy supplies have created an acute shortage of heating oils. To relieve this shortage, resort must be had to inferior sources of heating oils which have increased sulfur contents. Such resort can give rise to increased pollution problems unless catalytic treatment of the heating oil sources can reduce the sulfur content effectively.

Recently, legislation has been enacted to limit the content of sulfur in heating oils to 0.3%. Since the sulfur present in heating oils is that which remains after catalytic treatment of the feedstocks from which heating oils are derived, a critical need for more active catalysts for treatment of feedstocks is apparent.

The feedstocks from which heating oils are derived are light catalytic cycle oils and light virgin gas oils, which are generally used in admixture. The terms used to describe the feedstocks refer more specifically to the manner by which they arise and indicate their boiling range. Typically, the blend of feedstocks has a boiling range of 240° to 730°F, a gravity of about 28 to 32 in accordance with the method of reporting specified by the American Petroleum Industry, a basic nitrogen content of 30 to 50 ppm, and a sulfur content of 1.3 to 1.5 weight percent.

However, the current trend to secondary feedstocks has apparently resulted in a considerable increase in sulfur content. Because of the high sulfur content of the feedstock blend and the adverse levels of pollutants generated by combustion thereof, it is subjected to catalytic hydrotreatment which reduces sulfur content as well as basic nitrogen content, so as to qualify the blend as an acceptable heating oil.

The actual extent to which sulfur removal is effected will depend upon many factors, primarily the original sulfur content of the feedstock, the temperature at which treatment

is effected, and the activity value of the catalyst employed in the hydrodesulfurization reaction. Although sulfur removal in the past was at the discretion of those converting feedstocks to heating oils, the recent legislation requires a high level of removal which is becoming increasingly difficult to achieve. Although easing of this requirement is sought by suppliers of heating oils, the increasing presence of air pollutants in the atmosphere would indicate a contrary trend.

The catalytic hydrodesulfurization of residual hydrocarbon oils or oil fractions involves certain problems which do not arise when this process is used for hydrocarbon oil distillates. These problems result from the fact that most residual hydrocarbon oils, such as residues obtained in the distillation of crude oils under atmospheric or reduced pressure, comprise high-molecular weight nondistillable compounds, such as asphaltenes, resins, polyaromatics and metal compounds. When the residual hydrocarbon oils are exposed to high temperatures, as is usual in hydrodesulfurization, the asphaltenes which are colloiddally dispersed therein tend to flocculate and deposit on the catalyst particles. The flocculation of the asphaltenes during catalytic hydrodesulfurization is further promoted by the fact that the aromaticity of the liquid phase in which the asphaltenes are colloiddally dispersed falls as a result of hydrogenation and hydrocracking.

The principal high-molecular weight metal compounds present in residual hydrocarbon oils are nickel and vanadium compounds. The metal compounds are present in the oils as, among others, organometallic complexes, such as metalloporphyrins, and are for a considerable part bound to the asphaltenes. Like the asphaltenes, the high-molecular weight metal compounds tend to deposit on the catalyst particles during hydrodesulfurization.

A portion of the high-molecular weight compounds which deposit on the catalyst particles are converted into coke. As a result of the increasing concentration of heavy metals and coke on the active sites of the catalyst, a very rapid deactivation of the catalyst occurs in the catalytic hydrodesulfurization of residual hydrocarbon oils. As the activity of the catalyst decreases, a higher temperature must be applied in order to maintain the desired degree of desulfurization. In practice, a procedure that is often followed is to start the process at the lowest possible temperature at which the desired degree of desulfurization can just be obtained.

Although this procedure results in a product having a constant sulfur content, other properties of the product, such as viscosity, change continuously as a result of the rising temperature. As higher temperatures are used hydrocracking reactions become more prevalent and the oil to be desulfurized is increasingly converted to gas and low-boiling fractions, such as gasoline, naphtha, kerosene and the like.

Consequently, a fuel oil is obtained the quality of which is not constant. Moreover, catalyst life is relatively short in this mode of operation, since the deposition of asphaltenes and other high-molecular weight compounds on the catalyst is highest at the low temperatures which are used at the beginning of the process.

When a desulfurization process is operated at the highest possible temperature excessive catalyst activity results in too high a degree of desulfurization, and the fuel oil yield is poor as a result of drastic hydrocracking. Moreover, such a process is very difficult to control, since hydrogen consumption is not constant because the degree of desulfurization falls as catalyst activity decreases during operation.

To prolong catalyst life, removing the asphaltenes from the feed before desulfurizing and subsequently remixing the separated asphaltenes with the desulfurized product has been considered. Apart from the fact that this mode of operation requires an additional process step, namely deasphaltenizing, this method of desulfurization involves another drawback, which is particularly important if a product with a very low sulfur content is desired. Since asphaltenes generally have a fairly high sulfur content, mixing of the desulfurized product with the separated asphaltenes may result in a final product having an unacceptably high sulfur content. If the separated asphaltenes are only partly mixed with the de-

sulfurized product or if mixing is entirely omitted to avoid the drawback, the final product yield may consequently be so adversely affected that the process is no longer economic. Therefore, preference is given to a method of catalytic hydrodesulfurization in which the total feed, i.e., including the asphaltenes, is processed. However, this type of process requires catalysts having greater resistance to deactivation than those which are now generally recommended for this purpose.

The most widely used catalysts in the hydrodesulfurization reaction as it applies to heating oils are composites comprising cobalt oxide, molybdenum oxide and alumina, where alumina is the support carrying the other agents as promoters. Typically, such catalysts are effective in removing from about 70 to 90% of the sulfur present in primary feedstocks. However, such removal can still leave sulfur levels above current limitations, especially when secondary feedstocks are considered. Although the more active of current catalyst materials can provide the required sulfur removal in primary feedstocks, the temperature required for effecting such removal is higher than is desirable.

In addition, to achieve the necessary sulfur removal, peak activity must be maintainable over extended operating times and catalyst activity declines upon continued use, especially at high operating temperatures. The ever-decreasing availability of raw material sources and the ever-increasing shortage of heating oils have combined to make reliance upon secondary feedstocks essential and thus have complicated the problems of sulfur removal.

A number of conventional methods have been employed to prepare the catalyst composites useful in hydrotreating. A preferred procedure is to prepare a formed alumina support and thereafter impregnate the support with the desired levels of promoter sources. Upon activation of the impregnated support, the catalyst composite is obtained. The particular procedures followed and specific materials employed, however, can greatly influence catalytic activity of the composite obtained.

This book describes over 250 processes relating to the desulfurization of residual hydrocarbon oils and middle distillates as described in the U.S. patent literature since 1970. Most of the research and development activity on the part of the major oil companies, and others, has focused on increasing the efficiency of sulfur removal from total feed systems, particularly those residuals which have a high asphaltene content.

Thus the first five chapters largely reflect the processing and hydrodesulfurization of residual oils as obtained from the crude sources in the United States, Venezuela, Canada and in the Arab nations. Improved highly efficient catalysts of the conventional alumina-supported nickel, cobalt and molybdenum type and vanadium based catalytic systems are described in detail in the first two chapters. The critical reactor design and processing variables for fixed beds, ebullated catalyst beds, slurry processes and others are discussed in the next three chapters. The desulfurization of light oils and middle distillates leading to gasoline, jet fuels and specialty lubricants are described in the final chapter.

The desulfurization of waste gases is the subject of another Noyes publication *Sulfur Dioxide Removal from Waste Gases*, 1975 by A.V. Slack and G.A. Hollinden.

PREPARATION OF GROUP VIb AND VIII SUPPORTED CATALYSTS

Many catalysts are formed by compositing various transition metals or compounds with solid supports, the metals or compounds acting as hydrogenation-dehydrogenation components. The most prevalent of supports are refractory inorganic oxides such as alumina, silica, silica-alumina, kieselguhr, magnesia, thoria, boria, zirconia, titania, various types of spinels and even zeolites or the so-called molecular sieve bases. In preparation of a catalyst, the refractory inorganic oxide is usually pilled, pelleted, beaded, or extruded, alone or in mixture with other materials, then dried and crushed to particles of desired size. The solid is generally treated by contact with an aqueous solution or a salt containing the desired metal, or metals.

The salts can be added in mixture or in a sequence of contacts with different solutions. The so-treated solids can be dried, calcined and then contacted with hydrogen, in situ or ex situ, to reduce the salt to the desired metal, or, e.g., oxidized or sulfided to produce a compound of the metal. Illustrative of such catalysts are those typically used in hydrofining or hydrodesulfurization reactions where a support, e.g., an alumina, is composited with a metal, or metals, or compounds thereof, of Group VIb and the nonnoble Group VIII metals such as molybdenum, tungsten, cobalt, nickel and mixtures of these and other metals. Reforming catalysts are also typical of such catalysts.

These generally comprise the noble metals of Group VIII, e.g., the most significant of which is platinum, or mixtures of these and other metals as hydrogenation-dehydrogenation components, also typically composited with alumina or other inorganic oxide support. In reforming catalysts, a small amount of an acidic substance is generally composited with the alumina and metal to provide acidity to effect isomerization reactions as well as hydrogenation-dehydrogenation reactions. Hydrocracking catalysts are formed by incorporation of such metals, or compounds thereof, as hydrogenation-dehydrogenation components with crystalline aluminosilicate zeolite or molecular sieve bases.

ALUMINA CARRIER

Large Orifice Pore Structure

R.D. Christman, G.E. Elliott, Jr., J.D. McKinney and G.R. Wilson; U.S. Patent 3,814,682; June 4, 1974; assigned to Gulf Research & Development Company describe a process for hydrodesulfurization of metal-containing crude petroleum oil or residual oil employing catalysts whose pore structure possesses relative dimensions adapted to provide a prede-

terminated balance between catalyst activity on the one hand and long catalyst life on the other hand.

A high proportion of the sulfur content of crude and residual petroleum oils is contained in the heavy fractions of the oil, such as the propane-insoluble asphaltene and resin fractions which contain substantially the entire metal content of the oil. The hydrodesulfurization process is directed towards the removal of sulfur present in these oils in the presence of Group VI and Group VIII metal-containing catalysts supported on a suitable support, such as alumina which contains less than 5% silica, generally, and preferably less than 1% of silica. If desired, other porous oxides and/or mixed oxide supports can be used, such as alumina-magnesia, silica-magnesia, etc. Preferred catalysts are nickel-molybdenum, cobalt-molybdenum or nickel-cobalt-molybdenum on alumina. Tungsten can replace molybdenum in such combinations.

The metal-impregnated supported catalysts have a high pore volume, i.e., a pore volume of at least about 0.4 or at least 0.45 or 0.5 cc/g. This pore volume is made up predominantly of relatively large pore sizes which are particularly adapted to admission of the relatively large size molecules in which the sulfur is concentrated. It is shown below that the pores are provided with inlet orifice restrictions which are sufficiently large to admit the sulfur-containing molecules but which are small enough to tend to reject the metal-containing molecules which are the largest molecules contained in the crude. The metal-containing molecules are larger than the molecules requiring desulfurization and tend to rapidly deactivate the catalyst by depositing metals in the pores.

A highly critical feature of the process is the method utilized to determine the size of catalyst pores. Catalyst pore size is a function in large part of the temperature, water content and other conditions of calcination used in preparing both the support and the catalyst. In determining catalyst pore size the method of isothermal nitrogen adsorption at liquid nitrogen temperature is commonly employed. This method measures milliliters of nitrogen (at standard temperature and pressure) adsorbed per gram in terms of relative pressure P/P_0 . P is the pressure at which the gas is adsorbed and P_0 is the vapor pressure of the nitrogen at the adsorption temperature.

However, it is an important feature of the process that the method of nitrogen adsorption to determine pore size distribution cannot be employed by itself, especially in catalysts whose pores have a pronounced orifice, as explained below. Many catalysts of the process yield widely dissimilar pore size distribution data when tested at liquid nitrogen temperatures by the method of nitrogen adsorption as compared to the method of nitrogen desorption. The nitrogen adsorption tests tend to indicate a relatively uniform distribution of pores over the entire range of pore sizes in the catalyst, with the most frequent pore size ranges appearing at deceptively high pore sizes. The nitrogen desorption tests indicate a much less uniform distribution of pore sizes and a relatively high concentration of the total pore volume in a relatively narrow range of relatively smaller pore sizes. This feature of nitrogen adsorption and desorption test measurements is shown more fully in U.S. Patent 3,814,683.

The reason for the disparate results when using the nitrogen adsorption method as compared to the nitrogen desorption method is evidently due to the configuration of the pores. When the pores tend to have a relatively uniform diameter throughout or are below 35 to 40 Å in radius, the nitrogen adsorption and desorption methods tend to produce equivalent or comparable results.

However, when the pores are above 35 to 40 Å in radius and the shape of the pores deviate from a uniform, cylindrical configuration so that an ink bottle or balloon shape pore configuration becomes manifest with the opening or orifice of the pore at the surface of the catalyst having a relatively narrow neck and the main body of the pore being enlarged, the described discrepancy in apparent pore size distribution when employing the adsorption and desorption methods becomes apparent. The discrepancy in the apparent pore size distributions as determined by the adsorption and desorption methods becomes larger

as the body of the pore becomes larger compared to the neck or orifice of the pore.

The differing results obtained between adsorption and desorption pore size methods are accounted for by the fact that during the adsorption portion of the test the nitrogen enters the pore relatively easily upon an increase in nitrogen pressure until pore saturation occurs. However, upon subsequently reducing nitrogen pressure at the same temperature in the desorption portion of the same test, the nitrogen does not always escape from the pores as easily as it entered so that the amount of nitrogen contained within the catalyst at a given relative pressure of nitrogen in the desorption isotherm portion of the test can be greater than the amount of nitrogen contained in the catalyst at the same nitrogen relative pressure in the preceding adsorption portion of the test. In fact, a residual amount of nitrogen can remain trapped within the catalyst pores even at the conclusion of the desorption portion of the test at zero relative nitrogen pressure at liquid nitrogen temperatures.

The narrower that the neck of the pore is relative to the body of the pore the more difficult it is for the nitrogen within a pore to escape during the desorption portion of the isotherm test. On the other hand if the pore opening were unobstructed by an orifice, the liquid nitrogen adsorbed would be able to escape from the pore with the same ease with which it entered the pore, in which case the adsorption and desorption portions of the isotherm test would tend to indicate the same pore size distribution.

Table 1 contains detailed physical characteristics data for five catalysts. The data in Table 1 represent the characteristics of finished catalysts each containing about the same quantity of nickel, cobalt and molybdenum impregnated on an alumina support containing less than 1% of silica. The metals can be impregnated on the support before or after forming the support with similar results. The adsorption-desorption data reported were obtained by the use of an Aminco Adsorptomat, Model No. 4-4680.

TABLE 1: ADSORPTION-DESORPTION DATA FOR FRESH RESIDUE HDS FINISHED CATALYSTS

Compacted density, g/cc	Catalyst 1 0.728		Catalyst 2 0.736		Catalyst 3 0.688		Catalyst 4 0.792		Catalyst 5 0.820	
	N ₂ ad- sorption	N ₂ de- sorption	N ₂ ad- sorption	N ₂ de- sorption	N ₂ ad- sorption	N ₂ de- sorption	N ₂ ad- sorption	N ₂ de- sorption	N ₂ ad- sorption	N ₂ de- sorption
Surface area, m ² /g	185.2	169.7	148.7	144.3	151.1	149.2	214.6	210.3	153.8	151.5
Pore volume, cc/g	0.94	0.90	0.51	0.52	0.65	0.66	0.48	0.5	0.591	0.583
Pore radius, A., avg.										
Pore radius at which 1/2 total pore vol. is filled with liquid nitrogen	76.8	56.4	98.0	84.7	114.6	80.3	65.9	53.7	101.1	77.8
2X10 ³ pore volume/surface area	66.3	69.6	69.3	72.5	85.5	89.0	45.0	43.9	76.8	77.3
Pore size dist., percent of pore volume:										
250-300 A. radius	1.3	0.3	1.0	0.2	1.3	0.4	1.1	0.2	2.0	0.7
200-250	2.4	0.6	3.7	0.4	3.3	0.7	2.3	0.4	4.7	1.8
150-200	4.0	1.0	10.0	0.7	16.2	1.1	3.8	0.6	10.5	3.1
100-150	13.5	2.6	31.9	3.3	42.5	10.1	19.3	1.3	33.9	12.4
90-100	8.3	1.0	7.3	3.6	8.1	14.8	6.5	0.9	9.2	8.2
80-90	14.6	1.5	8.8	13.6	7.2	23.5	7.4	4.6	10.5	14.7
70-80	17.2	4.7	7.7	18.7	5.8	19.0	6.8	9.3	8.4	18.4
60-70	14.7	23.6	7.2	22.0	5.1	14.1	9.3	22.8	7.0	18.8
50-60	9.8	38.6	5.9	15.4	3.7	8.1	8.6	17.6	4.5	14.4
45-55	3.5	12.3	3.3	6.1	1.3	3.0	3.7	5.1	2.3	5.2
40-50	3.6	7.9	2.6	5.4	1.7	2.6	4.5	7.4	1.7	2.4
35-40	2.5	4.5	3.1	3.4	1.3	1.1	4.8	6.1	2.0	0.0
30-35	2.0	1.4	2.3	2.4	1.2	0.8	4.4	5.7	1.1	0.0
25-30	2.3	0.0	2.9	2.8	1.2	0.6	5.4	6.9	1.7	0.0
20-25	0.3	0.0	2.2	2.1	0.1	0.0	5.4	6.7	0.6	0.0
15-20	0.0	0.0	0.0	0.0	0.0	0.0	6.5	1.4	0.0	0.0
10-15	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.0	0.0
7-10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

The data of Table 1 show for each of the catalysts measured a difference in average pore radius depending upon whether the measurement is made during the adsorption or desorption of the isotherm. Table 1 shows that the method used for measuring pore radius is critical since the described difference appears in determining average pore radius as that pore radius at which one-half of the total pore volume is filled with liquid nitrogen. No comparable difference appears when employing the method of dividing 20,000 times the pore volume in cc/g by the surface area in m²/g because Table 1 shows that the pore vol-

ume and surface area values do not change significantly when measured by adsorption or desorption.

It has been discovered in hydrodesulfurization tests employing hydrocarbon feedstocks including the metal-containing components of the feed, particularly vanadium- and nickel-containing molecules, that the relative size of the neck of the pore has a very great effect upon catalyst activity and aging characteristics when treating a residual oil comprising the metal-containing molecules, which are concentrated in the asphaltene and resin fractions of the crude and are the highest boiling materials in the crude oil. The average pore radius as obtained in desorption isotherm tests tends to be representative of the size of the neck or orifice of the pores while the average pore radius as determined by the adsorption isotherm tests tends to be representative of the size of the larger body of the pore.

Since the metal-containing molecules tend to be the largest molecules in a petroleum oil, a relatively small pore orifice size tends to be a barrier or sieve preventing the admission of these large molecules to the interior of the catalyst pores. In the hydrosulfurization reaction, most of the reaction occurs within the pores of the catalyst and if the metal-containing molecules are permitted easy access to the interior of the pores there is a high lay-down of vanadium and nickel contaminants upon the pore walls and the catalyst tends to become deactivated. On the other hand, if the pore orifice is small it can serve as a membrane or a sieve, barring access of the very large metal-containing compounds to the interior of the pore of the catalyst, enabling the pore surfaces to retain high catalyst desulfurization activity for a prolonged throughput duration.

For this reason, a small pore orifice will tend to maintain high surface activity within the body of the pore by preventing access to the pores of the larger size metal-containing molecules. However, a correlative disadvantage in terms of decreased catalyst life occurs in the case of a catalyst whose pores have a small size orifice. This disadvantage arises when the metal-containing molecules which are barred from access to the body of the pore react sufficiently within the pore opening near the outer catalyst surface and deposit metals within the pore opening to abruptly substantially close off the already restricted opening. When the pore orifice becomes blocked, the life of the catalyst is substantially terminated because the smaller sulfur-containing molecules are then prevented access to the body of the pore, even though the surface of the body of the pore is still highly active.

Table 2 shows that as a result of hydrodesulfurization of a reduced crude oil with catalysts 1, 2 and 3 of Table 1, substantial amounts of metal, particularly vanadium, but also nickel, are deposited on the catalyst.

TABLE 2: FRESH AND SPENT MID-BED CATALYST METALS ANALYSIS

	Catalyst 1	Catalyst 2	Catalyst 3
Fresh catalyst (weight percent):			
Nickel.....	0.5	0.6	0.6
Cobalt.....	1.0	1.1	1.1
Molybdenum.....	8.0	9.9	7.5
Silicon.....		0.13	
Sulfur.....		0.67	
Spent (EOR) mid-bed catalyst:			
Nickel.....	3.0	3.8	4.1
Cobalt.....	0.58	0.47	0.35
Molybdenum.....	5.7	4.6	3.6
Vanadium.....	11.7	17.3	18.6
Carbon.....	3.74	5.78	5.16
Sulfur.....	17.3	20.9	22.0
Weight of spent catalyst equivalent to 1 gram of fresh catalyst (gram).	1.577	1.803	2.024

Table 3 shows the average pore radius and pore volume data for catalysts 1, 2, and 3 of Table 2 after they have become spent.

TABLE 3: ADSORPTION-DESORPTION DATA FOR SPENT CATALYSTS^a FROM HDS PROCESS

	Catalyst 1		Catalyst 2		Catalyst 3	
	N ₂ adsorption	N ₂ desorption	N ₂ adsorption	N ₂ desorption	N ₂ adsorption	N ₂ desorption
Surface area, m ² /g.....	100.9	88.3	81.0	78.7	76.8	74.5
	b(64.0)	b(56.0)	b(42.8)	b(41.6)	b(38.0)	b(36.8)
Pore volume, cc./g.....	0.27	0.29	0.20	0.19	0.22	0.22
	b(0.17)	b(0.19)	b(0.11)	b(0.10)	b(0.11)	b(0.11)
Pore radius, A., avg.: Pore radius at which 1/2 total pore vol. is filled with liquid nitrogen. 2X10 ⁸ X pore volume/surface area.....	64.7	43.5	66.3	49.1	72.0	52.0
	53.4	66.5	49.4	49.4	56.9	60.2
Pore size dist., percent of pore volume:						
200-300 A. radius.....	5.9	1.2	2.3	1.8	3.2	1.1
100-200.....	17.6	4.0	15.8	2.2	19.6	4.4
80-100.....	11.2	3.5	18.4	1.2	17.6	3.0
50-80.....	34.1	22.2	36.0	42.7	34.9	46.0
Total:						
50-300 A. radius.....	68.9	34.3	70.5	47.9	75.3	54.5
80-300.....	34.8	8.7	34.5	5.2	40.4	8.5

^a Data corrected to a fresh catalyst weight basis.^b Data expressed per gram of spent catalyst.

Comparing the average pore radius and the pore volume of the spent catalysts from an HDS process as shown in Table 3 with the comparable fresh catalysts shown in Table 1, it is seen that there is a considerable decrease in pore volume and average pore radius following hydrodesulfurization of residual petroleum oils, due to deposits of metals such as vanadium and nickel. Although Table 2 shows that other materials, such as carbon and sulfur, are deposited at the same time as vanadium and nickel, carbon and sulfur are materials that could be removed by regeneration while vanadium and nickel, being metals, cannot be removed by conventional regeneration so that once these metallic deposits become excessive the catalyst is permanently deactivated and must be discarded.

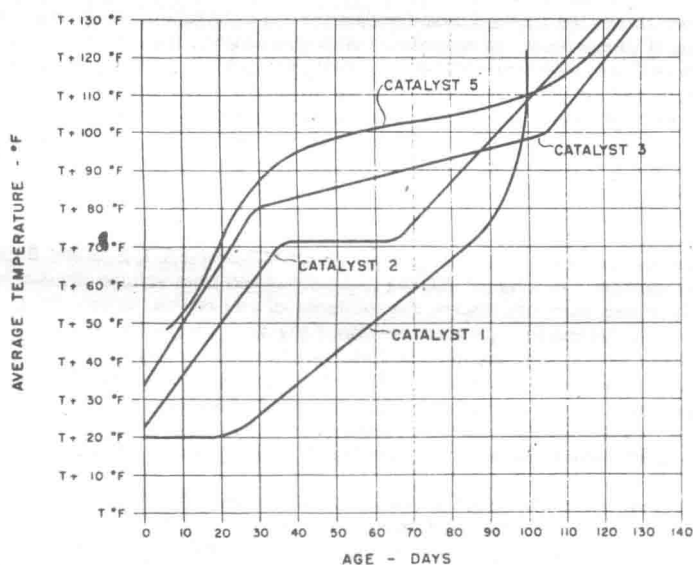
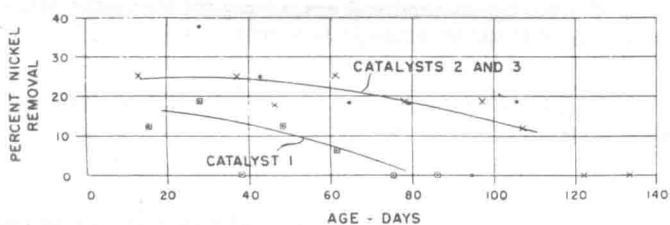
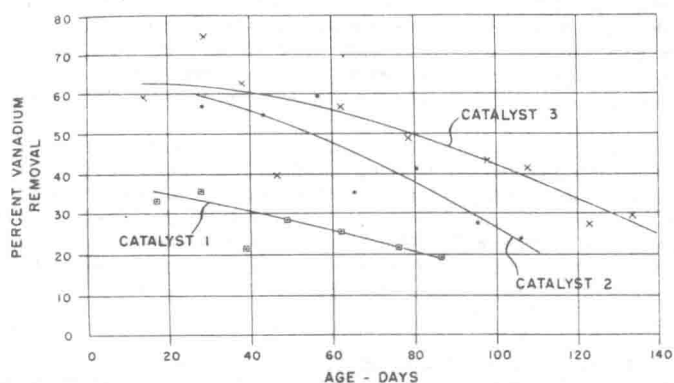
Figures 1.1a, 1.1b and 1.1c illustrate the importance of the pronounced ink bottle configuration of the catalysts 1, 2 and 3 in the treatment of crude and residual oil. The tests were made in a hydrodesulfurization process comprising passing at 650°F residual oil charge downflow over a fixed bed of NiCoMo on alumina hydrodesulfurization catalyst at a 4.0 LHSV to reduce the sulfur content of the feed from about a 4 weight percent level to about a 2.4 weight percent level. The pressure was 2,050 psig and the temperatures were whatever was required to produce a constant effluent sulfur level.

Evidence for the orifice size effect described above is illustrated graphically in Figures 1.1a, 1.1b and 1.1c. Figure 1.1a shows that catalyst 1, having the smallest average pore radius as determined in the desorption isotherm of catalysts 1, 2 and 3, removes the smallest amount of vanadium, while catalyst 2 which has an intermediate average pore radius as determined in the nitrogen desorption isotherm, removes an intermediate amount of vanadium and catalyst 3, which has the largest orifice as determined by the desorption isotherm, remove the greatest amount of vanadium from the feed, at all stages of catalyst aging.

This indicates that the amount of large size metal-containing material admitted to the interior of the catalyst pores is directly proportional to the size of the catalyst orifice as determined by the nitrogen desorption isotherm data. Figure 1.1b shows similar results in terms of nickel removal since Figure 1.1b shows that catalyst 1, having the smallest pore orifice of catalysts 1, 2 and 3, removes a smaller amount of nickel at all stages of catalyst aging as compared to catalysts 2 and 3.

Figure 1.1c represents the results in the same tests of the metal removing effect attributable to the size of the pore orifice restriction in terms of the sulfur-removal activity of the catalyst. Relative temperatures required to maintain a product having a constant level of sulfur were varied as indicated in Figure 1.1c, with higher temperatures generally required with increasing catalyst age.

FIGURE 1.1: CATALYSTS HAVING PORES OF CONTROLLED ORIFICE SIZE



Source: R.D. Christman, G.E. Elliott, Jr., J.D. McKinney and G.R. Wilson; U.S. Patent 3,814,682; June 4, 1974