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(54) PROCESS FOR HYDROTREATING HEAVY HYDROCARBON OIL

(71) We, CHIYODA CHEMICAL ENGINEERING AND CONSTRUCTION COMPANY, LIMITED of 1580, Tsurumi-cho, Tsurumi-ku, Yokohama-shi, Kanagawa-Pref., Japan a Japanese company, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

The invention relates to a process for hydrotreating heavy hydrocarbon oils containing asphaltene and heavy metal impurities in large quantities (hereinafter referred to as heavy oils) continuously to convert them into substantially asphaltene-free, demetallised oils.

The heavy oils suitable for processing according to the invention include petroleum crude oils, residues obtained by distilling crude oil under atmospheric or reduced pressure, crude oils extracted from tar sands or mixtures thereof. These contain large quantities of high molecular weight hydrocarbon compounds, whose structures consist of several fragments of condensed aromatics and connecting paraffinic chains and/or naphthenic fragments, and which are usually called asphaltenes. They are generally colloidally dispersed in the oil, and usually contain about from 4 to 8% by weight of sulphur and from 500 to 7000 ppm of heavy metals like vanadium. The term "asphaltene" is used herein to mean *n*-heptane insoluble material as determined by the I.P. method.

The heavy oils most suitable for processing according to the invention are those which contain asphaltenes and vanadium in large quantities. Examples of such heavy oils are Venezuelan crude oil of specific gravity ($D_{15/4°C}$) 1.004 containing as much as 11.8% by weight of asphaltenes, as much as 1240 ppm of vanadium, 5.36% by weight of sulphur, and 5800 ppm of nitrogen, topped crude from Middle-Near East crude of specific gravity ($D_{15/4°C}$) 0.987 containing 6.5% by weight of asphaltenes, 95 ppm of vanadium, 4.45% by weight of sulphur and 3000 ppm of nitrogen, and vacuum residue from other Middle-Near East crude oils of specific gravity ($D_{15/4C}$) 1.038 containing 8.2% by weight of asphaltenes, 270 ppm of vanadium, 3.53% by weight of sulphur and 7300 ppm of nitrogen.

As above described, the heavy oils contain extremely large quantities of contaminants such as sulphur and nitrogen compounds, and organometallic compounds containing vanadium or nickel. As these contaminants are concentrated in the asphaltene-rich, high molecular weight hydrocarbon fraction, catalytic hydrotreatment is difficult. Nevertheless, heavy oils containing asphaltenes in large quantities are abundantly present in nature and are regarded as promising hydrocarbon resources for the future. At present, however, they are utilised merely as extremely low grade fuel oils or as asphalt for road paving. The conversion of such heavy oils into more valuable demetallised and substantially asphaltene-free oils is therefore being investigated extensively.

One method presently adopted for, purifying heavy oils comprises separating the asphaltenes from the heavy oils by a physical process such as solvent deasphalting, and hydrotreating the deasphalted oils, thus avoiding the aforesaid difficulties. The asphaltene-containing fraction produced as by-product may reach 10 to 20% by weight, and in some cases over 30% by weight, of the total oil, varying depending upon the quality of the extracted oil obtained by deasphalting. This process is therefore very wasteful of raw material.

Two hydrotreatment processes for purifying heavy oils have been proposed. One is a process wherein a heavy oil is subjected to catalytic hydrocracking in the presence of a catalyst having metal compound(s) supported on a carrier such as solid acid, or the like, and the other is a process wherein a heavy oil is subjected to catalytic hydrotreating in the presence of a catalyst consisting of non-supported metal compound(s).

In the former process the reaction system adopted is usually of a fixed or ebullated bed type. Two techniques of treatment are disclosed in United States Patent Specification No. 2559285 and Japanese Laid-Open Patent Application No. 32003/1977. In these, it has been proposed to recycle a part of the liquid reaction products separated as a heavy fraction. In these processes, however, the presence of asphaltenes and heavy metals in the charge stock would cause many economical disadvantages, which can be fully understood by those skilled in petroleum refining technology.

That is, the asphaltenes colloidally dispersed in the charge stock are huge molecules that consequently do not readily reach the active sites in the pores of the catalyst. Therefore, the hydrocracking is seriously inhibited. In addition, the presence of asphaltenes extremely accelerates the formation of coke and carbonaceous materials, which leads to rapid reduction of catalyst activity.

Another serious problem is the presence of significant amounts of metals in the charge stock. They accumulate on the surface of the catalyst, exert poisoning action on the catalyst, and seriously shorten the catalyst life.

As a result, when a heavy oil is treated according to this conventional catalytic hydrotreating process, the amount of catalyst consumption per unit volume of oil treated becomes exceedingly large. Furthermore, even if the above described defects were obviated, the conventional catalysts would obviously require severe reaction conditions for the purpose of selective asphaltene-cracking to obtain a light oil, and the reduction of the catalyst activity would be still further accelerated. In addition, there also occurs rapid gasification due to the secondary decomposition reaction of the cracked oil, and hence the light oil fraction cannot be obtained in a high yield and the hydrogen consumption increases. Thus, this conventional process is not very economical.

The second of the two processes referred to above has recently been described in United States Patent Specification No. 3723294. In this process a heavy oil is hydrotreated in a state slurried with catalyst in order to remove metals therefrom and the resulting product is separated into a light oil fraction and a heavy oil fraction slurried with catalyst, which latter fraction is then recycled to the preceding reaction step. This process, however, appears to cause new serious difficulties due to the use of a colloidally slurried mixture of oil-catalyst. In general, procedures become seriously complicated as compared with a fixed-bed process or the like; smooth transportation of the slurry-state reactants and reaction products is difficult under high temperature and pressure; a heat exchanger for heating and cooling the slurry-state reactants and reaction products shows less heat exchanging efficiency as compared with a slurry-free case and is liable to cause troubles such as blocking of the flow-path; gas-liquid separation is hardly feasible for the slurry-state reaction product; in particular, an apparatus and a method for continuously detecting the slurry-state interface under high temperature and pressure are technically difficult to devise; since a control valve for reducing the pressure of the slurry-state reaction product under high temperature and pressure suffers extreme corrosion, it requires special technical considerations from the viewpoint of safety and reliability; stable operation becomes difficult by the contamination with the slurry in the solvent deasphalting step; in a case in which the slurry contains a large quantity of asphaltenic material to be discharged from the reaction system, the solid removing procedure is complicated, and moreover the disposal of the discharged material itself causes a problem; and a special pump with special reliability and durability is necessary for recycling transportation and boosted feeding of the slurry-state reactants and reaction products.

The invention provides a process for hydrotreating heavy hydrocarbon oils containing asphaltene and heavy metal impurities continuously to convert them into substantially asphaltene-free, demetallised oils, the process comprising the steps of

(a) hydrotreating reactor feed oil at a hydrogen to fed oil ratio of from 100 to 200 normal litre/litre, 350 to 450°C, a reaction pressure of from 30 to 250 kg/cm^{2}G and a liquid hourly space velocity of from 0.1 to 10 hour^{-1} in the presence of a catalyst comprising a carrier containing magnesium silicate (as herein defined) as a major component and having supported thereon a metal of Group Va, VIa or VIII of the Periodic Table according to Mendeleev or an oxide thereof, the reactor feed oil being a said heavy hydrocarbon oil and/or oil recycled from the step (c), and withdrawing the hydrotreated product without entraining the catalyst therein,

(b) separating the withdrawn hydrotreated product into a hydrogen-rich gas and a liquid product;

(c) separating the liquid product of step (b), or separating a mixture of the liquid product of step (b) with a said heavy hydrocarbon oil fed directly to this step, into a substantially asphaltene-free, demetallised light fraction and a heavy fraction containing asphaltenes and heavy metals, and

(d) recycling the heavy fraction separated in step (c) to step (a), while maintaining the condition that the reactor feed oil to be hydrotreated in step (a) contains at least 5% by weight of asphaltenes and at least 80 ppm of vanadium.

The term "magnesium silicate" is used herein to encompass naturally occurring clay minerals such as the preferred carrier, sepiolite, and synthesized equivalents thereof. Sepiolite may be considered to have the formula $Mg_8H_2(Si_4O_{11}).3H_2O$, but this is a simplistic view; the composition of these clay minerals varies according to the source, and some of the magnesium atoms may be substituted by atoms or iron, aluminium, calcium or other metals. Si-O tetrahedron layers predominate in their crystal structure, but again irregularities may occur. Their compositions are usually expressed in terms of their magnesium and silicon contents and their contents of the impurity substituents, expressed as simple oxides. This does not imply that the simple oxides are present in admixture. This understood, their composition may be generally expressed as SiO_2, 30 to 60% by weight; MgO, 10 to 30% by weight; Al_2O_3, less than 8% by weight; Fe_2O_3, less than 25% by weight; FeO, less than 5% by weight; and CaO, less than 3% by weight.

Unlike the prior art processes described above, the use of the magnesium silicate carried in the catalyst used in step (a) is effective to crack asphaltenes and to effect a hydrodemetallisation. Furthermore, the heavy metals removed by the demetallisation, in accumulating on the catalyst, do not poison it but surprisingly appear to enhance its activity.

The kind or amount of the metal or oxide to be supported on the carrier may be selected depending upon the properties of the reactor feed oil or the characteristics of the metals. For example, it is desirable to support Group VIII metals in an amount of 1 to 10% by weight as oxides and the Group VIa metals in an amount of 4 to 15% by weight. Most preferable metals to be supported include Co, Mo, W, Ni and V. These metals may be used in any combination.

As the carrier, use can be made of any magnesium silicate having neso-structure, ino-structure or phyllo-structure, but preferable carriers are inosilicates containing hydroxy radicals and fibrous phyllosilicates. More particularly, use can be made of natural products such as anthophyllite, tremolite, actinolite, edenite, riebeckite, chrysolite, sepiolite and attapulgite and synthetic products closely related thereto in composition and structure.

A particularly effective carrier for the catalyst used in the invention is a natural mineral, sepiolite. This is inexpensively available, and its characteristic physical structure is such as to enhance the reaction activity of the catalyst.

It has surprisingly been discovered that, when a heavy oil containing asphaltenes and heavy metals in large amounts is hydrotreated in the presence of a catalyst comprising a carrier containing mainly magnesium silicate and supported catalytic metals, there occurs the selective cracking of asphaltenes as well as hydrodemetallisation. More surprisingly, in spite of the fact that the metals removed from the reactor feed oil by the hydrodemetallisation accumulate on the outer surface of the catalyst, the catalyst is not poisoned but shows enhanced activity in the selective cracking of asphaltenes as well as in the removal of heavy metals.

The reason for this enhanced catalyst activity has not been fully clarified at present, but it is presumed that, in addition to the hydrodemetallisation activity obtained by supporting metals such as Co and Mo on a carrier composed mainly of magnesium silicate, the activity in the cracking of asphaltenes newly appears as a result of the interaction between a composition of V-Ni-Co-Mo-S, which contains V, Ni and S removed from the heavy oil and accumulated on the catalyst, along with Co and Mo as the initial catalytic components, and the catalyst carrier.

It should be mentioned that the asphaltene cracking activity of the catalyst appears to increase with increasing asphaltene and heavy metal, especially vanadium, content in the reactor feed oil. The reactor feed oils preferably hydrotreated in step (a) are therefore those which contain not less than 5% by weight of asphaltenes and not less than 80 ppm of vanadium. More preferably, they are those containing not less than 10% by weight of asphaltenes and not less than 150 ppm of vanadium. With less than 5% by weight of asphaltenes and less than 80 ppm of vanadium in the reactor feed oil, the asphaltene cracking activity of the catalyst is not fully exhibited and the process is therefore not effective.

This relationship is illustrated by Figure 1 of the drawings, which is a plot of the rate of conversion of asphaltenes and the rate of removal of vanadium against the time on stream for the three charge stocks detailed in Table 1 hydrotreated according to the invention under the reaction conditions given in Table 2. The catalyst used was prepared by supporting cobalt and molybdenum on a Spanish natural ore, sepiolite, as carrier (its chemical composition is shown in Table 3), and then by extrusion moulding. The catalyst had the chemical and physical properties shown in Table 4. The reaction was conducted in a fixed bed isothermal reactor of gas-liquid cocurrent upward flow type.

It is clear from Figure 1 that, when the charge stock A containing asphaltenes and heavy metals in large quantities was hydrotreated, the asphaltene cracking activity of the catalyst increased shortly after the start of the experiment until the conversion of asphaltenes reached 90% by weight. Constant activity was then shown for a long period. The hydrodemetallisation rate initially decreased, but became constant almost simultaneously with the achievement of constant asphaltene cracking activity, and remained constant for a long period. Similar results were obtained when the charge stock B was hydrotreated, although it took longer for the catalyst to reach constant activity, so that there was a less useful initial period, and the rate of vanadium removal was slightly lower than with charge stock A. The results obtained using charge stock C, containing lesser amounts of asphaltenes and heavy metals, were quite different. Cracking of the asphaltenes present did not occur even after 800 hours, and the vanadium removal rate more or less decreased with time, although starting at a high level. It is thus clear that the different contents asphaltenes and vanadium in the charge stocks exerted considerable influence on the asphaltene cracking and demetallisation.

The analyses of the asphaltenes in the charge stocks and in the product oils, as shown in Figure 1 and in Table 1, were carried out in accordance with standard method IP 143/57 of the Institute of Petroleum, Great Britain.

A further noteworthy point is that the mean molecular weight of the asphaltenes in charge stocks A and B was reduced by the hydrotreatment, from 5600 in charge stock A and 3700 in charge stock B to 1400 and 1200 in the respective product oils. On the other hand, the asphaltene mean molecular weight actually increased during the hydrotreatment of charge stock C, from 4150 to 4200. The product oil mean molecular weights were taken from oils produced after 200 hours operation. The lowering of the asphaltene mean molecular weights further simplifies subsequent hydrodesulphurisation of the product oils.

Insight into the difference in catalyst activity for different oils is given by analyses of the spent catalysts. The vanadium and carbon accumulated on the spent catalysts used with charge stocks A and C were analysed, and the results are shown in Table 5. These data are average values throughout all the catalyst layers. The spent catalyst used with charge stock A had a large amount of deposited heavy metals, and a lower than expected amount of deposited carbon. The catalyst used with charge stock C, on the other hand, showed high carbon deposition but little accumulation of heavy metals.

The spent catalyst used for 800 hours with charge stock A was subjected to X-ray analysis to discover the distribution of magnesium, vanadium, sulphur, nickel, cobalt and molybdenum deposited thereon. Figure 2 shows the results obtained. These indicate that the heavy metals removed from the oil by the hydrotreatment, hitherto believed to accumulate mostly within the catalyst, were found overwhelmingly on the outer surface of the catalyst. The supported catalytic metals, cobalt and molybdenum, were also shown to have migrated from the interior to the outer surface of the catalyst. In Figure 2, the intensities of magnesium, cobalt and molybdenum are shown on the same scale, that of vanadium is shown on 1/10 scale, that of sulphur on 1/20 scale and that of nickel on half scale. The metals on the outer surface of the catalyst form a complicated composition of V-Ni-Co-Mo-S. The accumulation of the heavy metals and sulphur on the outer surface of the catalyst in the form of this complicated composition appears to exert a novel catalytic function improperly understood as yet. It is the very same heavy metals and sulphur which poison conventional catalysts for hydrotreatment processes.

Similar X-ray analysis of the spent catalyst used with charge stock C, lower in asphaltene and vanadium contents, showed the heavy metals to have accumulated on the inner surfaces of the catalyst. This is similar to what has been observed with conventional catalysts used in conventional hydrotreatment processes. High asphaltene and heavy metal contents in the oil to be processed therefore plays an important role in the processing.

In addition, when the product oil was filtered to separate it into an oil fraction and a residue, and the residue was washed with benzene, there was found only a trace of insoluble matter. This indicates that the product oil contains almost no inorganic compounds, and hence the heavy metals removed from the heavy oil are substantially wholly deposited on the catalyst.

The shape of the particles of the catalyst used in the invention is not particularly limited, but the size is desirably not less than 0.8 mm nominal diameter. The catalyst need not be used in a particulate form, but can be prepared by supporting the metal components on a magnesium silicate layer on a solid plate, pipe wall or the like.

Because the impurities removed from the heavy oil become fixed on the catalyst surface, and are not entrained in the reaction products, reaction systems such as a fixed bed, a moving bed and an ebullating bed can all be used. Reactants may be fed to the reaction zone either at the upper part or at the lower part of the reactor. That is, the gas-liquid flow in the reactor may be passed either upwardly or downwardly in parallel.

The accumulation of the heavy metals removed from the heavy oil on the outer surface of the catalyst makes their recovery from the spent catalysts extremely easy.

As previously stated, the hydrotreatment is carried out at a temperature of from 350 to 450°C. A preferred reaction temperature is from 390 to 420°C. If the reaction temperature is lower than 350°C, sufficient catalytic activity cannot be obtained and the conversion of reactants in the hydrotreatment step does not reach a practical level. On the other hand, if the reaction temperature is higher than 450°C, undesirable side reactions such as coking become marked and cause deterioration of the product oil as well as the loss of the catalytic activity.

The hydrotreatment is carried out under a pressure of from 30 to 250 kg/cm^{2}G, as previously stated. If the pressure falls below 30 kg/cm^{2}G, the formation of coke becomes so serious that normal catalyst activity can hardly be maintained, whereas if it rises above 250 kg/cm^{2}G, the hydrocracking reaction becomes so severe that the hydrogen consumption increases with a decreased yield of the product oil, and hence the rapid increase in the cost of the reactor as well as other related apparatus makes the process entirely impractical from an economic viewpoint. The preferred reaction pressure is from 80 to 160 kg/cm^{2}G.

The liquid hourly space velocity (LHSV) has previously been given as from 0.1 to 10 hour^{-1}, but is preferably from 0.2 to 5 hour^{-1}. If the LHSV is less than 0.1 hour^{-1}, the residence time of the feed oil becomes so long that the heavier components deteriorate by the action of heat resulting in the degradation of the product quality, whereas if the LHSV is more than 10 hour^{-1}, the conversion of reactants per pass becomes too low to be practical.

The hydrogen or the hydrogen-containing gas being supplied to the reaction zone and the reactor feed oil are, as stated, mixed in the proportion of 100 to 2000 volumes of hydrogen (0°C, 1 atm) to 1 volume of reactor feed oil (15°C), that is 100 to 2000 normal litre/litre (Nl/l). The preferred mixing proportion is 500 to 1000 Nl/l. If the proportion is less than 100 Nl/l, hydrogen becomes so deficient in the reaction zone and at the same time the transfer of hydrogen into the liquid phase becomes so poor that coking reactions take place exerting detrimental effects on the catalyst and on the properties of the product oil. On the other hand, if the proportion is more than 2000 Nl/l, no additional improvement is seen in the process of the present invention, though no trouble is caused in the reaction. Nevertheless, since the cost of compression required for circulating hydrogen increases with the amount of the hydrogen being circulated, 2000 Nl/l is the practical upper limit for circulating hydrogen.

Also, even if hydrogen sulphide is contained in the hydrogen-rich circulating gas to be fed to the reaction zone, it not only has no detrimental effect on the reaction, but also tends to accelerate the reaction when contained in a suitable amount. This is because the catalyst used in the present invention undergoes some interaction with hydrogen sulphide under the above described reaction conditions and plays some role in maintaining the catalytic activity. Thus it is within the scope of the present invention that the hydrogen gas to be fed to the reaction zone contains up to 10% of hydrogen sulphide.

The catalyst-free reaction product after having been processed under the above described reaction conditions in the hydrotreating step is transferred to the gas-liquid separation step to separate it into a hydrogen-rich gas and a substantially liquid reaction product.

This gas-liquid separating method and the device therefor may be similar to those which are employed in a conventional desulphurization processes such as a usual fixed bed or an ebullating bed, and are not particularly specified. Since solids like the catalyst are not entrained in the reaction product, the separation and transfer of the liquid products can be performed with ease and therefore, after the pressure has been reduced in a routine manner, it can be sent to the subsequent separation step.

In the subsequent separation step, the liquid products are further separated into a substantially asphaltene- and heavy metal-free light fraction and an asphaltene- and heavy metal-containing heavy fraction. The separation can be performed according to commonly well utilized methods such as distillation, and solvent deasphalting. Special procedures are unnecessary. Any combination of separation methods can be employed. Since substantially no solids are contained in the liquid products, the separation step can be smoothly operated.

If the solvent deasphalting method is employed for the separation step, the solvent is suitably a low molecular weight hydrocarbon such as propane, butane, isobutane, pentane, isopentane, neopentane, hexane or isohexane or a mixture of such low molecular weight hydrocarbons. These solvents are countercurrently brought into contact with the liquid products.

The solvent deasphalting step may be operated at from 10 to 250°C, preferably from 50 to 180°C, under a pressure of from 3 to 100 atmospheres, preferably from 10 to 50 atmospheres.

The heavy fraction obtained from the solvent deasphalting step contains unconverted asphaltenes and heavy metals. This heavy fraction is recycled to the hydrotreating step. However the heavy fraction does not contain solids such as the catalyst or metal sulphides, so that no special devices and methods are necessary for recycling and transferring it.

By virtue of this recycling of the unconverted asphaltenes, the conversion of the asphaltenes per pass need not be taken to an extremely high level. If the reaction conditions are made severe in order to obtain an extremely high conversion per pass, there will be degradation of the product oil quality due to the occurrence of undesirable side reactions. There will also be increases in the hydrogen consumption and the catalyst consumption, and therefore this is economically disadvantageous. The desirable conversion of the asphaltenes per pass ranges from 40% to 90%, which may be decided by considering together the properties of the heavy oil, the efficiency in the separation step, and the hydrogen consumption.

The solvent and the asphaltene- and heavy metal-free oil obtained from the solvent deasphalting step are transferred to a solvent recovering section to recover the solvent. The asphaltene- and heavy metal-free oil obtained thus has, in most cases, a molecular weight of no more than 1000. Further, this oil can be hydrodesulphurised quite easily by subjection to conventional hydrotreatment on a fixed bed or an ebullating bed, for example, to obtain a more valuable hydrocarbon oil. Since the oil obtained according to the invention contains neither heavy metals like vanadium nor asphaltenes, it is most suitable as a raw oil for fluid catalytic cracking processes or the like to produce high grade gasoline.

Reference is now made to Figure 3 of the drawings, which is a flow diagram of one embodiment of the invention. A charge stock is fed through line 1 and mixed with a hydrogen-rich gas fed through line 14. The hydrogen-rich gas is a mixture of make-up hydrogen fed through line 2 and recycles gas from a gas-liquid separation step 15 described below fed through line 13.

The charge stock mixed with the hydrogen-rich gas is fed through line 3 and further mixed with at least a portion of a heavy fraction containing asphaltenes and heavy metals in large amounts, which heavy fraction was separated in a separation step 8 described below. The heavy fraction is fed through lines 10 and 11. The mixed charge stock, heavy fraction and hydrogen-rich gas is fed through line 4 to a hydrotreatment reaction step 5 in which asphaltenes are cracked and heavy metals are removed. The product of the reaction step 5 is sent to the afore-mentioned gas-liquid separator 15 through a line 6, and there separated into the hydrogen-rich gas fed through line 13 and a liquid reaction product.

The liquid reaction product is then sent through line 7 to the aforementioned separation step 8, in which it is separated into a substantially asphaltene-free, demetallised light fraction and the asphaltene and heavy metal-rich heavy fraction fed through lines 10 and 11. The light fraction is withdrawn from the system through line 9. A portion of the heavy fraction may be withdrawn from the system through line 12, if necessary.

Instead of feeding the charge stock directly to the hydrotreatment step (a), as described with reference to Figure 3 (hereinafter called embodiment [X]), the charge stock may be fed initially to one of the separation steps, most suitably step (c). This embodiment will be called embodiment [Y]. The choice between embodiments [X] and [Y] depends upon the properties of the charge stock, especially those of the lighter component which can be separated therefrom, and the quality of the oil it is desired to produce. Embodiment [Y] in which the concentrated impurities are hydrotreated is preferable from the viewpoint of reaction kinetics. However, in cases where the lighter fraction of the charge stock contains high levels of impurities and/or it is economically disadvantageous because of reduced yield or otherwise to choose separation consitions such that the lighter fraction is not so contaminated, the adoption of embodiment [X] is desirable.

For example, the relationship of the vanadium and nickel contents to the yield of the lighter fraction obtained by solvent extracting Venezuelan crude oil, charge stock A in Table 1, is as follows:

Yield (% by weight)	40	50	60
vanadium (ppm)	35	60	100
nickel (ppm)	5	3	11

Even when the yield is reduced to a comparatively low level, the metal content is so high that the light oil thus obtained is entirely unsuitable for fluid catalytic cracking.

Thus, in this case, embodiment [X] is preferable. On the other hand, if charge stock B of Table 1 is solvent extracted in the same manner, the following yield to impurities relationship is found:

Yield (% by weight)	40	50	60
vanadium (ppm)	trace	3	6
nickel (ppm)	trace	1	3

Here the amount of metal impurities is so low that it is economically desirable to adopt embodiment [Y], in which the lighter component is preliminarily separated and recovered as product, rather than being subjected to hydrotreatment together with the heavier component.

It has already been seen that when a charge stock having asphaltene and vanadium contents falling short of 5% by weight and 80 ppm respectively is treated as in embodiment [X], the catalyst does not exhibit effective activity. Nevertheless, such charge stocks may be effectively treated in embodiment [Y]. Pretreating the charge stock C of Table 1 containing less than 5% by weight of asphaltenes and less than 80 ppm of vanadium in separation step (c) of embodiment [Y], it is possible to make the oil fed to reaction step (a) contain at least 5% by weight of asphaltenes and 80 ppm of vanadium. This is enough for the catalyst to exhibit its effective activity.

In a further embodiment of the invention, the heavy hydrocarbon oil is fed to a separately provided step (a') in which it is hydrotreated in the presence of a catalyst of the kind used in step (a) under reaction conditions within the limits set out for step (a) and is thereafter withdrawn without entraining the catalyst and is fed to step (b). In this case step (a') is substantially fulfilling the pretreatment function of embodiment [Y].

The choice of embodiments may be decided on consideration of the properties of the charge stock and of the desired product oil, of equipment and operation and of economy.

The invention is illustrated by the following Examples.

Example 1

Venezuelan crude oil containing asphaltenes and vanadium in large quantities (fuller details of this oil are given under A in Table 1) was hydrotreated according to the invention in a fixed-bed isothermal reactor of gas-liquid cocurrent upward flow type. The reaction conditions were as given in Table 2. The catalyst used as catalyst (I) which has the composition and properties given in Table 4.

For comparison, the same oil was hydrotreated under the same conditions using catalyst (II) as the catalyst. Catalyst (II) is a typical catalyst used in conventional fixed-bed hydrodesulphurisation processes. Its composition and properties are given in Table 6.

The results are shown in Figure 4. It is clear that the activity of catalyst (II) rapidly declined. Additionally, Table 7 gives details of product oils obtained using catalysts (I) and (II). To give an oil of similar asphatlene content, the process using catalyst (II) consumed more than twice as much hydrogen at the process using catalysts (I) and (II). To give an oil of similar asphaltene content, the process using product oil of the process using catalyst (II) was three times that of the product of the process using catalyst (I).

For further comparison, the catalysts (I) and (II) were withdrawn from the reactor after 800 hours use, and were photographed by a scanning electron microscope. Figure 8 is a reproduction of a photograph of catalyst (I) before use and Figure 9 is a reproduction of the photograph of catalyst (I) after 800 hours use. It will be observed that minute fibrous crystals have grown on the surface of catalyst (I) during use. The fibrous crystals are complicated compositions of V-Ni-Co-Mo-S as already stated, and although it is not yet clearly known what role this composition plays in the catalysis, it is believed that these minute fibrous crystals do contribute to the cracking of asphaltenes.

Figure 10 is a reproduction of the photograph of catalyst (II) after 800 hours use. It is observed that no fibrous crystals are present but instead granular crystals are found on the catalyst surface, which is similar to that of the unused catalyst (I).

Example 2

The hydrotreatments described in Example 1 were repeated, save that the reaction conditions were as given in Table 8. In order to clarify the difference in the selectivity between both the reactions, the same operating conditions were employed and the hydrogen consumption per pass was chosen so as to be equal, although in the case of catalyst (II) the decrease in the hydrogen consumption accompanying the decrease in the catalytic activity varied largely depending on the lapse of the reaction time.

After the lapse of about 450 hours the hydrogen consumption had become equal in both cases. It was found that even under the same conditions with the same hydrogen consumption per pass the cracking of asphaltenes and the removal of vanadium can be achieved more selectively in the treatment using the catalyst (I).

Figure 5 shows molecular weight distribution curves for the charge oil and the two product oils measured by Gel Permeation Chromatography using polystyrene as packing and chloroform as developer. Figure 6 shows the distillation curves of the charge oil and the two product oils measured according to ASTM-D1160. It is clear that using catalyst (I) in a process according to the invention enables much more effective conversion of the heavy fraction into the light fraction than using the conventional catalyst (II). This is irrespective of the hydrogen consumption.

Example 3

Charge stock A (Table 1), containing asphaltene in large quantities, was mixed at a flow rate of 300 cc/hour with a hydrogen-rich gas in a hydrogen/oil ratio of 1000 Nl/1, i.e. at a hydrogen flow rate of 300 Nl/hour. The mixture was preheated and sent to a hydrotreatment step in a fixed-bed isothermal reactor of gas-liquid cocurrent upward flow type filled with catalyst (I) (Table 4). The reaction conditions were those given in Table 8.

The reaction product was separated into a hydrogen-rich gas and a substantially liquid product in a gas-liquid separator operated at a pressure substantially equal to that in the hydrotreatment reactor and at a temperature of 150°C.

The hydrogen-rich gas was scrubbed in an amine scrubber to remove impurities such as excess hydrogen sulphide and ammonia, and after having been mixed with make-up hydrogen, was recycled to the hydrotreatment step. To avoid excessive build-up of light hydrocarbon gases in the mixture with the make-up hydrogen about 10% of the hydrogen-rich gas was continuously withdrawn from the system.

The liquid product was solvent deasphalted using butane at an average tower temperature of about 130°C under a pressure sufficient to maintain liquid phase operation (40 kg/cm^{2}G). About 75% by volume of the liquid product transferred into the solvent phase, which was sent to a solvent-recovering unit to recover the solvent.

The remaining heavy fraction, which contained a large amount of asphaltene and which did not transfer into the solvent phase, was recycled at about 200°C to the hydrotreatment step. The amount recycled was 100 cc/hr. The charge point of the recycled oil on the charge stock feeding line was upstream of the point where the oil was mixed with the hydrogen-rich gas.

Continuous operation over a period of 600 hours was attained. The product oil was an oil of excellent quality, extremely low in asphaltene and heavy metal contents. Its properties are given in Table 9. The yield of the product was not less than 96% by weight, and the chemical hydrogen consumption was 430 SCF/BBL.

In the above described hydrotreatment step, considerable hydrodesulphurization (about 55%) also took place in addition to asphaltene-cracking and hydrodemetallization. The theoretical hydrogen consumption for this hydrodesulphurization was about 400 SCF/BBl on the assumption that 3 moles of hydrogen per g atom of sulphur is consumed.

Example 4

Vacuum residue of Middle Near East Oil, the properties of which are shown in Table 12, was used as charge stock in hydrotreatments according to the above described embodiment (Y) of the invention. The catalyst was catalyst (I) (Table 4).

The charge stock was first mixed with the liquid products obtained in the reaction step and then sent to the deasphalting section, where deasphalting was effected using butane at an average tower temperature of 125°C under a pressure of 40 kg/cm^{2}G. In this deasphalting section about 48% by volume of the liquid mixture transferred into the solvent phase, which was sent to a solvent-recovering unit to recover the solvent. The heavy fraction which did not dissolve in the solvent contained a large amount of asphaltenes and was fed at about 200°C to the reaction step. In the reaction step the hydrotreatment was carried out under the reaction conditions shown in Table 13.

The hydrotreated product was separated into a gaseous reaction product and liquid products in a gas-liquid separator. The separation conditions were such that the pressure was substantially the same as in the reactor and the temperature was about 150°C. The liquid product was mixed with the charge stock fed to the deasphalting section by recycling it to the feed line of the charge stock as above described. The flow rates of the main stocks in this experiment are as follows.

Charge stock	476 g/hr
Product oil	449 g/hr
Recycled liquid products	486 g/hr

Continuous operation was successfully carried out for a period of about 1200 hours. The product was an asphaltene- and heavy-metal free oil of superior quality. The yield of the product oil was 97% by weight on the basis of hydrocarbon, and the chemical hydrogen consumption was 370 SCF/BBL.

Example 5

In this Example it is shown that, even when the amounts of asphaltenes and vanadium contained in the charge stock are unfavourably small, good results can be achieved by the adoption of the embodiment [Y].

The charge stock used was an atmospheric residue of Middle Near East crude whose asphaltene and vanadium contents fell short of 5% by weight and 80 ppm respectively. The charge stock had the properties shown in Table 1 (Charge Stock C).

As described in Example 4, the charge stock was first mixed with the liquid products from the reaction step, and then sent to a deasphalting section, where deasphalting was effected using butane at an average tower temperature of 128°C under a pressure of 40 kg/cm^{2}G. In the deasphalting section about 75% by volume of the above described liquid mixture was separated and transferred into the solvent phase, which was sent to a solvent recovering unit to recover the solvent.

On the other hand, the heavy fraction containing a large amount of asphaltenes which was not dissolved by the solvent was fed at about 200°C to the reaction step. In the reaction step the hydrotreatment was carried out by the use of the catalyst (I) under the reaction conditions shown in Table 13, which are the same as those in Example 4.

The hydrotreated products were separated into a gaseous product and liquid products in a gas-liquid separator. The separation conditions were such that the pressure was substantially the same as in the reactor, and the temperature was 150°C.

The liquid products were mixed with the charge stock fed to the deasphalting section by recycling to the feeding line the charge stock as above described. The flow rates of the main stocks in this Example were as follows:

Charge stock	410 g/hour
Product oil	390 g/hour
Recycling liquid products	110 g/hour

This Example also recorded successfully a continuous operation over a period of 1000 hours. The product was an asphaltene- and heavy metal-free oil of superior quality containing only minor amounts of asphaltene and vanadium, ideal for subsequent subjection to conventional fixed bed hydrodesulphurisation, hydrocracking or fluid catalytic cracking. The yield of the product oil was about 98% by weight on the basis of hydrocarbon, and the hydrogen consumption was 310 SCF/BBL.

Example 6

In this Example there are shown the results of a series of hydrotreating experiments, carried out in accordance with the flow diagram of Figure 7.

The charge stock used was a vacuum residue of Middle Near East crude, the same as that used in Example 4, having the properties shown in Table 12, and the catalyst used in both the reaction steps (a) and (a') was the catalyst (I).

The charge stock was mixed with a portion of the hydrogen-rich gas recycled from the gas-liquid separation step (b) and then sent to reaction step (a'). The operation conditions employed in reaction step (a') are shown in Table 16. The products from step (a') were then mixed with the products from treatment in step (a) of the heavy fraction separated in the deasphalting step (c), and sent to the gas-liquid separation step (b). The separation conditions in step (b) were such that the pressure was substantially the same as in the reactor and the temperature was 150°C.

The hydrogen-rich gas separated in the gas-liquid separation step was recycled after purification partly to reaction step (a) and partly to reaction step (a'). The liquid products separated in the gas-liquid separation step were fed to the above described deasphalting step, in which deasphalting was effected using butane at an average tower temperature of 145°C under a pressure of 40 kg/cm^{2}G.

In the deasphalting step about 61% by volume of the above described liquid mixture was separated and transferred into the solvent phase, which was sent to a solvent recovering unit to recover the solvent as well as the product asphaltene- and heavy metal-free oil. The fraction which did not dissolve in the solvent (i.e. that containing large amounts of asphaltenes and heavy metals) was mixed with the hydrogen-rich gas recycled from the gas-liquid separation step, and then hydrotreated in reaction step (a). The operation conditions in step (a) are shown in Table 17. The products from step (a) were mixed for recycling with the products from step (a').

The flow rates of the main stocks in this Example were as follows:

Charge stock fed to step (a')	476 g/hour
Product oil	452 g/hour
Charge stock recycled to step (a)	360 g/hour

This Example also successfully recorded stable and continuous operation over a period of about 1000 hours. The product was an asphaltene- and heavy metal-free oil of superior quality containing only minor amounts of asphaltenes and heavy metals as shown in Table 18, and almost comparable to that obtained in Example 4 as shown in Table 14. The yield of the product oil was about 97% by weight on the basis of hydrocarbon, and the hydrogen consumption was 369 SCF/BBL.

As seen from these results, the same quantity of charge stock can produce a product oil comparable to that of Example 4 even though the operation conditions are not the same. Indeed, in Example 4 the amount of the catalyst used in step (a) was 1530 cc, while in this Example the amounts of the catalyst used in steps (a) and (a') were 570 cc and 740 cc respectively, rather less in total than in Example 4. This suggests that by the adoption of this embodiment the amount of recycling oil can be reduced, and that by providing steps (a) and (a') separately, the reaction in step (a) can be made more effective.

TABLE 1

Charge Stock

Charge stock	A*	B*	C*
Specific gravity ($D_{15/4°C}$)	1.004	1.025	0.948
Asphaltenes (wt%)	11.8	8.7	2.5
Sulfur (wt%)	5.4	3.53	3.77
Vanadium (ppm)	1240	270	50
Nitrogen (ppm)	5800	7000	2200
Average molecular weight of asphaltene	5600	3700	4150

A* Venezuelan crude oil
B* Vacuum residue of Middle Near East crude
C* Atmospheric residue of Middle Near East crude

TABLE 2

Hydrotreating Conditions

Reaction temperature (°C)	405
Reaction pressure (kg/cm².G)	140
LHSV (Hr^{-1})	0.3
H_2/oil ratio (Nl/l)	1000

TABLE 3

Composition of Sepiolite

Al_2O_3 (wt%)	1.3
SiO_2 (wt%)	56.7
MgO (wt%)	23.9
Fe_2O_3 (wt%)	0.4

TABLE 4

Properties of Catalyst (I)

Chemical Composition	
Al_2O_3 (wt%)	5.5
MoO_3 (wt%)	6.9
CoO (wt%)	1.9
SiO_2 (wt%)	48.8
MgO (wt%)	18.6
Physical Properties	
Surface Area (m²/g)	171
Pore Volume (cc/g)	0.79
Pore Distribution	
0—100 Å (cc/g)	0.031
100—200 Å (cc/g)	0.094
200—400 Å (cc/g)	0.387
400—600 Å (cc/g)	0.278

TABLE 5

Charge stock	A	C
Vanadium (wt%/fresh catalyst)	56.0	1.5
Carbon (wt%/fresh catalyst)	12.8	28.4

TABLE 6

Properties of Catalyst (II)

Chemical Composition	
Al_2O_3 (wt%)	78.4
MoO_3 (wt%)	15.0
CoO (wt%)	4.1
SiO_2 (wt%)	0.3
MgO (wt%)	—
Physical Properties	
Surface Area (m^2/g)	154.5
Pore Volume (cc/g)	0.601
Pore Distribution	
0—100 Å (cc/g)	0.024
100—200 Å (cc/g)	0.499
200—300 Å (cc/g)	0.058
300—600 Å (cc/g)	0.020

TABLE 7

Catalyst	(I)	(II)
Asphaltenes (wt%)	3.1	3.2
Chemical hydrogen consumption (SCF/BBL)	420	980
Vanadium (ppm)	70	210

TABLE 8

Reaction temperature (°C)	405
Reaction pressure (kg/cm^2.G)	140
LHSV (Hr^{-1})	0.5
H_2/Oil ratio (Nl/l)	1000

TABLE 9

	Catalyst (I)	Catalyst (II)
Hydrogen consumption (SCF/BBL)	320	330
Specific gravity ($D_{15/4°C}$)	0.951	0.963
Asphaltenes (wt%)	4.5	10.6
Vanadium (ppm)	104	816
Sulfur (wt%)	3.14	3.03

TABLE 10

Reaction temperature (°C)	405
Reaction pressure (kg/cm^2.G)	140
LHSV *(Hr^{-1})	0.25
H_2/Oil Ratio (Nl/l)	1000

(*) per fresh charge stock

TABLE 11

Specific gravity ($D_{15/4°C}$)	0.941
Sulfur (wt%)	2.40
Nitrogen (wt%)	0.54
Vanadium (ppm)	18
Nickel (ppm)	6
Asphaltenes (wt%)	trace

TABLE 12

Specific gravity ($D_{15/4°C}$)	1.036
Asphaltenes (wt%)	13.5
Sulfur (wt%)	5.27
Vanadium (ppm)	181
Nitrogen (ppm)	3600

TABLE 13

Reaction temperature (°C)	405
Reaction pressure (kg/cm^2.G)	140
LHSV *(Hr^{-1})	0.3
H_2/oil ratio (Nl/l)	1000

*Reactor feed oil base

TABLE 14
Properties of Product Oil

Specific gravity ($D_{15/4^\circ C}$)	0.946
Sulfur (wt%)	2.46
Nitrogen (wt%)	0.24
Vanadium (ppm)	1.7
Nickel (ppm)	1.1
Asphaltenes (wt%)	trace

TABLE 15
Properties of Product Oil

Specific gravity ($D_{15/4^\circ C}$)	0.927
Sulfur (wt%)	2.26
Nitrogen (wt%)	0.18
Vanadium (ppm)	1.4
Nickel (ppm)	11.2
Asphaltenes (wt%)	trace

TABLE 16

Reaction temperature (°C)	405
Reaction pressure (kg/cm^2.G)	140
LHSV (Hr^{-1})	0.8
H_2/oil ratio (Nl/l)	1000

TABLE 17

Reaction temperature (°C)	405
Reaction pressure (kg/cm^2.G)	140
LHSV* (Hr^{-1})	0.42
H_2/oil ratio (Nl/l)	1000

(*) per unit volume of reactor feed oil fed to step (a)

TABLE 18

Specific gravity ($D_{15/4^\circ C}$)	0.943
Sulfur (wt%)	2.42
Nitrogen (wt%)	0.23
Vanadium (ppm)	1.6
Nickel (ppm)	1.2
Asphaltenes (wt%)	trace

WHAT WE CLAIM IS:—

1. A process for hydrotreating heavy hydrocarbon oils containing asphaltene and heavy metal impurities continuously to convert them into substantially asphaltene-free, demetallised oils, the process comprising the steps of

(a) hydrotreating reactor feed oil at a hydrogen to fed oil ratio of from 100 to 2000 normal litre/litre, a reaction temperature of from 350 to 450°, a reaction pressure of from 30 to 250 kg/cm^{2}G and a liquid hourly space velocity of from 0.1 to 10 hour^{-1} in the presence of a catalyst comprising a carrier containing magnesium silicate (as herein defined) as a major component and having supported thereon a metal of Group Va, VIa or VIII of the Periodic Table according to Mendeleev or an oxide thereof, the reactor feed oil being a said heavy hydrocarbon oil and/or oil recycled from the step (c), and withdrawing the hydrotreated product without entraining the catalyst therein;

(b) separating the withdrawn hydrotreated product into a hydrogen-rich gas and a liquid product;

(c) separating the liquid product of step (b), or separating a mixture of the liquid product of step (b) with a said heavy hydrocarbon oil fed directly to this step, into a substantially asphaltene-free, demetallised light fraction and a heavy fraction containing asphaltenes and heavy metals; and

(d) recycling the heavy fraction separated in step (c) to step (a), while maintaining the condition that the reactor feed oil to be hydrotreated in step (a) contains at least 5% by weight of asphaltenes and at least 80 ppm of vanadium.

2. A process according to claim 1 in which the said heavy hydrocarbon oil is fed to step (a).

3. A process according to claim 1 in which the said heavy hydrocarbon oil is fed to step (c).

4. A process according to claim 3 in which heavy hydrocarbon oil is fed to a separately provided step (a′) in which it is hydrotreated in the presence of a catalyst as defined for step (a) under the reaction conditions defined for step (a) and is thereafter withdrawn without entraining the catalyst and is fed to step (b).

5. A process according to any preceding claim in which step (a) is carried out at a hydrogen to fed oil ratio of from 500 to 1000 normal litre/litre, at a temperature of from 390 to 420°C, at a pressure of from 80 to 160 kg/cm^{2}G and at a liquid hourly space velocity of from 0.2 to 5 hour^{-1}.

6. A process according to any preceding claim in which the hydrogen-rich gas separated in step (b) is recycled to step (a).

7. A process according to claim 6 in which the hydrogen-rich gas contains 10% or less of hydrogen sulphide.

8. A process according to any preceding claim in which the carrier comprises from 30 to 60% by weight of SiO_2, from 10 to 30% by weight of MgO, less than 8% by weight of Al_2O_3, less than 25% by weight of Fe_2O_3, less than 5% by weight of FeO and less than 3% by weight of CaO.

9. A process according to any preceding claim in which the carrier is sepiolite.

10. A process according to any preceding claim in which the metal or oxide supported on the magnesium silicate carrier is cobalt, molybdenum, nickel, vanadium, tungsten or an oxide of any thereof or a mixture of any thereof.

11. A process according to any preceding claim in which step (c) is effected by solvent deasphalting.

12. A process according to claim 1, the process being substantially as described herein with reference to any of the Examples.

13. A hydrocarbon oil produced by a process according to any preceding claim.

SERJEANTS,
Chartered Patent Agents,
25 The Crescent,
Leicester.

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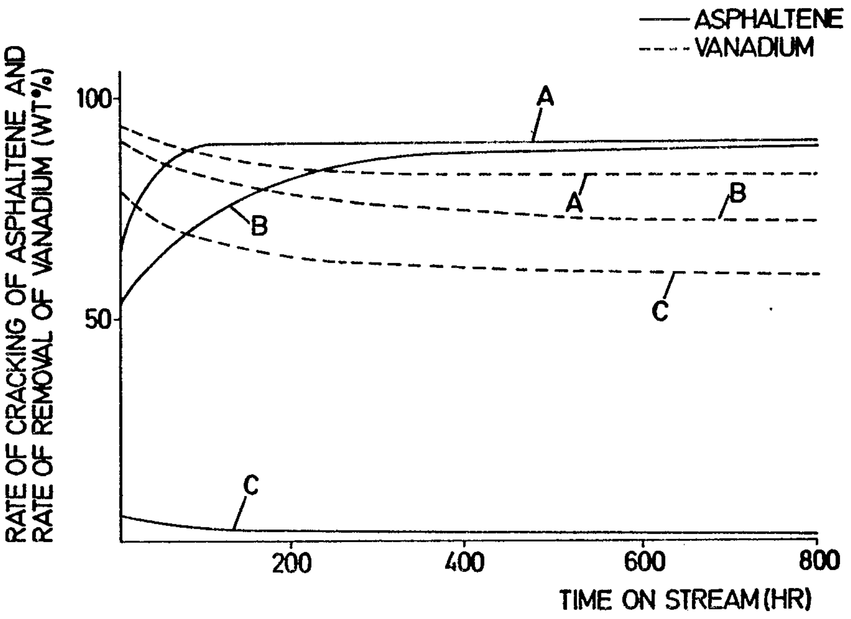
ASPHALTENE
VANADIUM
RATE OF CRACKING OF ASPHALTENE AND RATE OF REMOVAL OF VANADIUM (WT%)
100
50
200
400
600
800
TIME ON STREAM (HR)
A
A
B
B
C
C

FIG.1

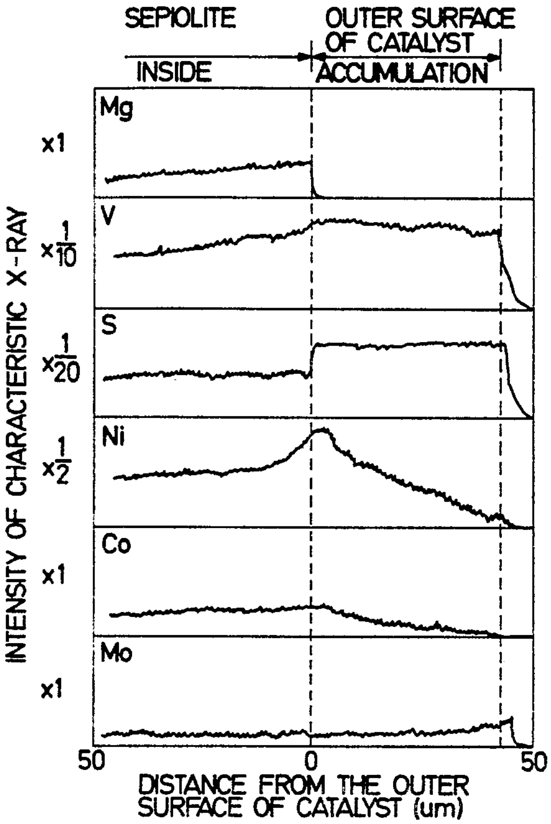
SEPIOLITE
OUTER SURFACE OF CATALYST
INSIDE
ACCUMULATION
Mg
x1
V
x1/10
S
x1/20
Ni
x1/2
Co
x1
Mo
x1
INTENSITY OF CHARACTERISTIC X-RAY
50
0
50
DISTANCE FROM THE OUTER SURFACE OF CATALYST (um)

FIG. 2

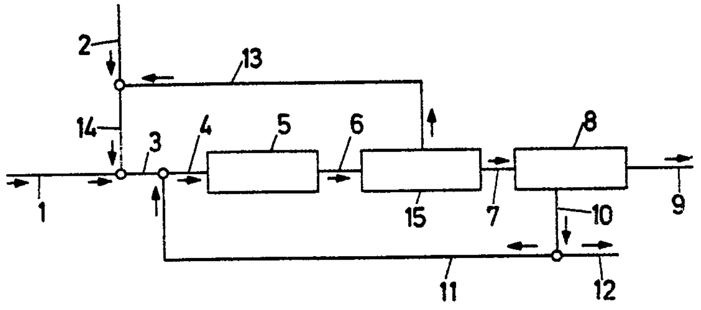
2
13
14
3
4
5
6
8
1
15
7
10
9
11
12

FIG.3

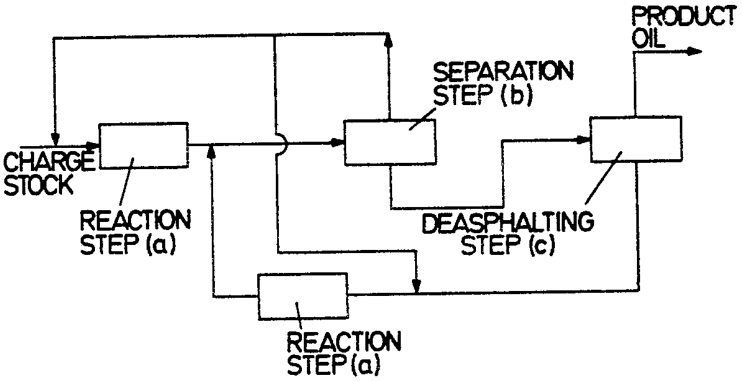
PRODUCT OIL
SEPARATION STEP (b)
CHARGE STOCK
REACTION STEP (a)
DEASPHALTING STEP (c)
REACTION STEP (a)

FIG.7

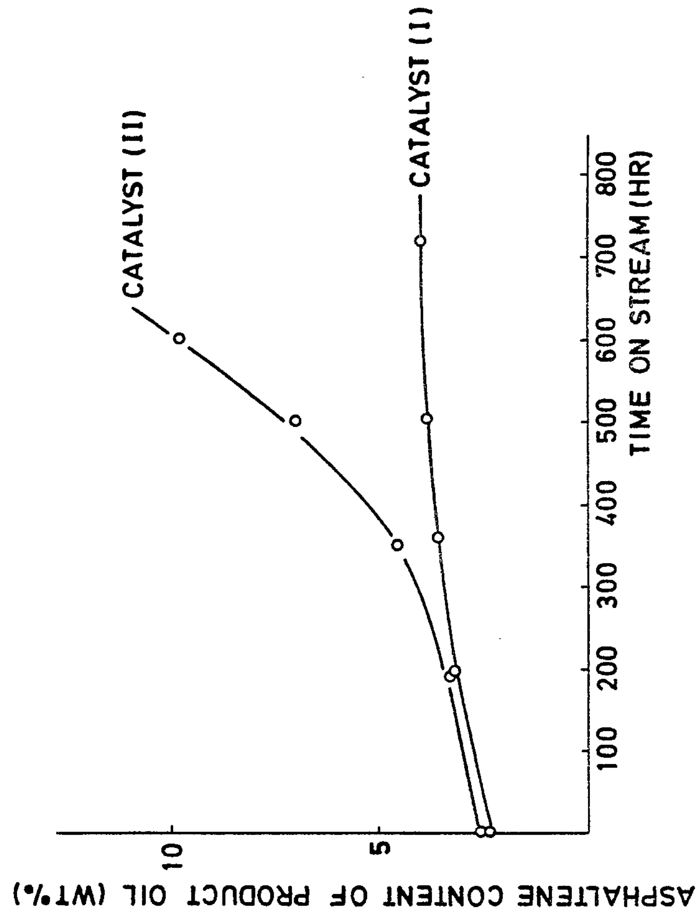
CATALYST (II)
CATALYST (I)
10
5
ASPHALTENE CONTENT OF PRODUCT OIL (WT%)
100
200
300
400
500
600
700
800
TIME ON STREAM (HR)

FIG. 4

1602640 COMPLETE SPECIFICATION

8 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 5

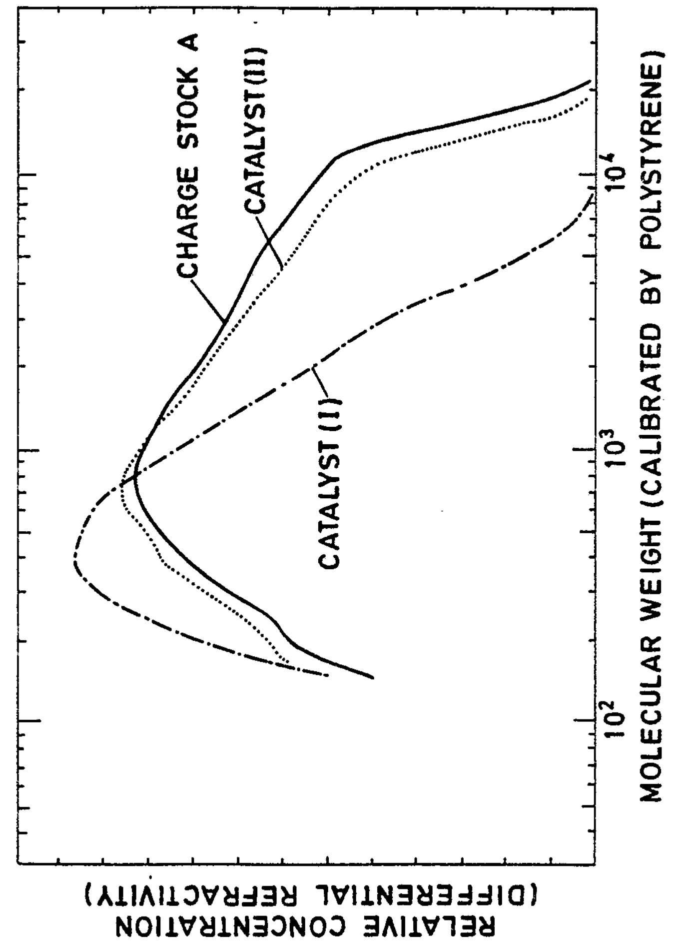

FIG. 5

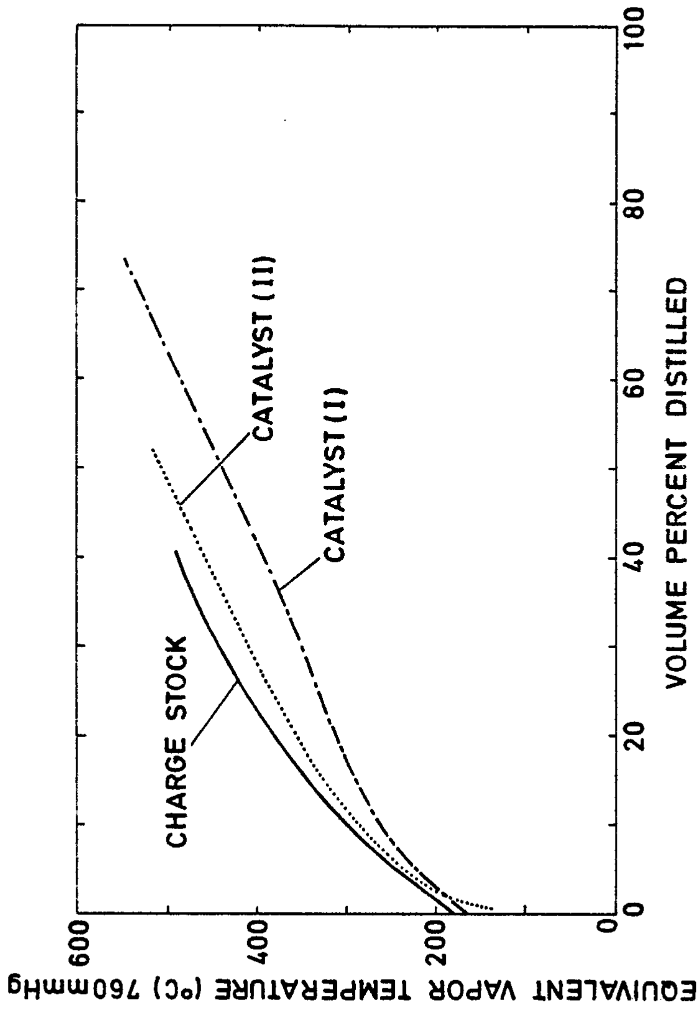
EQUIVALENT VAPOR TEMPERATURE (°C) 760mmHg
600
400
200
0
VOLUME PERCENT DISTILLED
0
20
40
60
80
100
CHARGE STOCK
CATALYST (II)
CATALYST (I)

FIG. 6

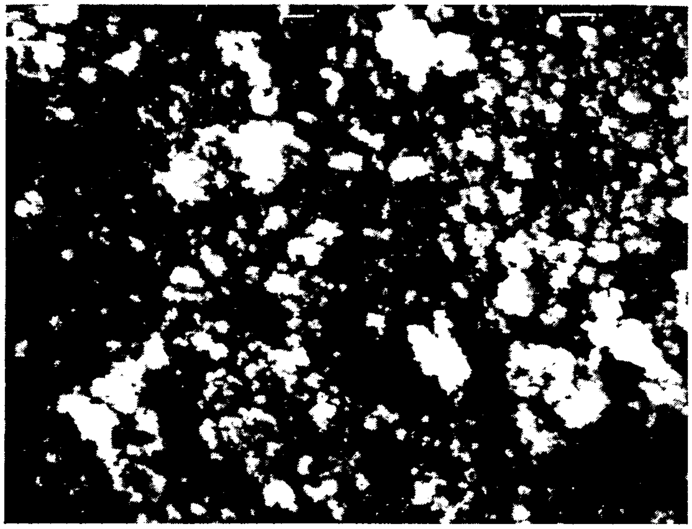

FIG. 8

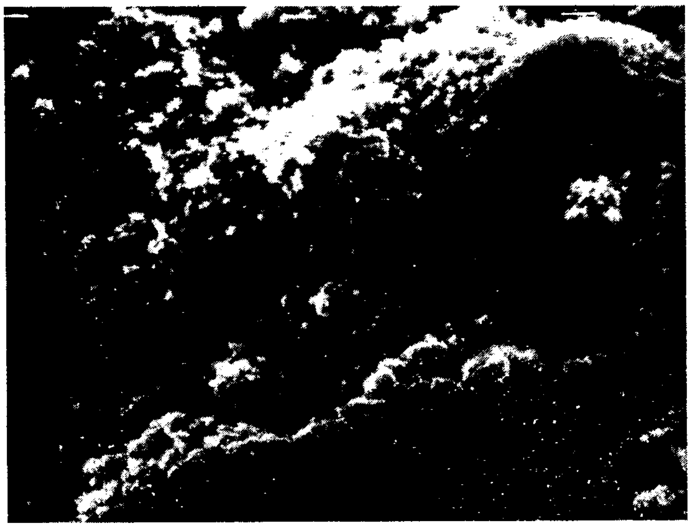

FIG.10

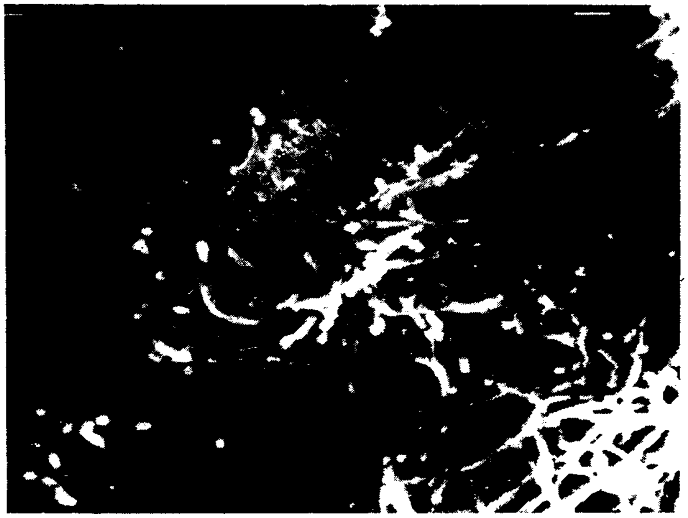

FIG.9