

PATENT SPECIFICATION

(11) 1 523 343

1 523 343

- (21) Application No. 39291/75 (22) Filed 25 Sept. 1975
(31) Convention Application No. 7 412 761
(32) Filed 27 Sept. 1974 in
(33) Netherlands (NL)
(44) Complete Specification published 31 Aug. 1978
(51) INT CL² C10G 23/02, 23/16
(52) Index at acceptance CSE 21H4
(72) Inventors FRANS GOUDRIAAN and KAREL MAARTEN
ADRIANUS PRONK



(54) PROCESS FOR THE UPGRADING OF HEAVY HYDROCARBON OILS

(71) We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V., a company organised under the laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, 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 present invention relates to a process for the upgrading of heavy hydrocarbon oils by contacting these oils with a catalyst at elevated temperature and pressure and in the presence of hydrogen.

High-boiling hydrocarbon oils, such as residual oils obtained in the distillation of crude oils at atmospheric or reduced pressure, as well as certain heavy crude oils, in particular those originating from South America, contain considerable amounts of asphaltenes and have a high viscosity. To reduce the asphaltenes content and the viscosity these oils may be contacted with a suitable catalyst at elevated temperature and pressure and in the presence of hydrogen. In such processes, which are often referred to as processes for the upgrading of heavy oils, oils having a C₃-asphaltenes content about 5%w and a V_{k₂₁₀}

above 30 cSt are contacted with a catalyst at a temperature of at least 400°C, a hydrogen partial pressure of at least 100 bar and a space velocity of at most 2.0 l.l⁻¹.h⁻¹, in order to reduce the C₃-asphaltenes content by at least 30% and the V_{k₂₁₀} by at least 50% (C₃-asphaltenes content and V_{k₂₁₀} of the feed com-

pared with that of the liquid reaction product obtained). Suitable catalysts for this purpose are catalysts comprising one or more metals having hydrogenation activity on a carrier.

An investigation by the Applicants into the upgrading of heavy oils with the aid of catalysts comprising one or more metals having hydrogenation activity on a carrier, has revealed that optimum catalysts for this purpose should meet a number of requirements with regard to their particle diameter and porosity. An optimum catalyst for the upgrading of heavy hydrocarbon oils should be taken to mean in this patent application a catalyst whose activity as well as stability are of a sufficiently high level for this purpose.

It has been found that for the upgrading of heavy hydrocarbon oils the requirements with respect to particle diameter and porosity which an optimum catalyst should meet are as follows. In the first place the catalysts should have a total pore volume above 0.40 ml/g, while the percentage of the total pore volume that consists of pores with a diameter above 100 nm(v) should be smaller than 50. The catalysts should further have such a specific average pore diameter (p in nm) and specific average particle diameter (d in nm) that the quotient p/d meets the requirements: p/d > 3.5–0.02 v. Finally, the catalysts should have a specific surface area larger than 100 m²/g.

In cases where the catalysts have such a p and d that the quotient p/d is larger than 3.5–0.02 v, but is at most 10.0–0.15 v, the catalysts have to meet the following additional requirements:

- (1) the nitrogen pore volume should be larger than 0.60 ml/g,
- (2) the specific surface area should be larger than 150 m²/g, and
- (3) p should be larger than 5 nm.

The above-mentioned values of p and d have been defined as follows on the basis of their method of determination.

The way in which d is determined depends on the shape of the catalyst particles. If the shape is such that the particle diameter distribution of the catalyst can be determined with the aid of a sieve analysis, d is determined as follows. After a complete sieve analysis of a representative catalyst sample has been carried out, d is read from a graph in which for each successive sieve fraction the percentage by weight, based on the total weight of the catalyst sample, has been cumulatively plotted as a function of the linear average particle diameter of the relevant sieve fraction; d is the particle diameter corresponding to 50% of the total weight. This method can be used to determine d of spherical and granular materials and of materials with a similar shape, such as extrudates and pellets having a length/diameter ratio between 0.9 and 1.1. The determination of d of extrudates and pellets having a length/diameter ratio smaller than 0.9 or larger than 1.1 and of similar cylindrically shaped materials, whose particle diameter distribution cannot be determined with the aid of a sieve analysis, is carried out as follows. After a complete length distribution analysis (if the length/diameter ratio is smaller than 0.9) or after a complete diameter distribution analysis (if the length/diameter ratio is larger than 1.1) of a representative catalyst sample has been carried out, d is read from a graph in which for each successive length and diameter fraction, respectively, the percentage by weight, based on the total weight of the catalyst sample, has been cumulatively plotted as a function of the linear average size of the relevant fraction; d is the value corresponding to 50% of the total weight.

After the complete pore diameter distribution of a catalyst sample has been determined, p is read from a graph in which for the pore diameter range of 0—100 nm, for each successive pore volume increment smaller than or equal to 10% of the pore volume, the quotient of the pore volume increment and the corresponding pore diameter interval has been cumulatively plotted as a function of the linear average pore diameter over the relevant pore diameter interval; p is the pore diameter corresponding to 50% of the total quotient at 100 nm.

A determination of the complete pore diameter distribution of the catalyst may very suitably be carried out with the aid of the nitrogen adsorption/desorption method (as described by E. V. Ballou and O. K. Doolen in *Analytical Chemistry* 32, 532 (1960)) combined with the mercury penetration method (as described by H. L. Ritter and L. C. Drake in *Industrial and Engineering Chemistry, Analytical Edition* 17, 787 (1945)), applying mercury pressures of 1—2000 bar. In this case, the pore diameter distribution of the catalyst in the pore diameter range below and including 7.5 nm is calculated from the nitrogen desorption isotherm (assuming cylindrical pores) according to the method described by J. C. P. Broekhoff and J. H. de Boer in *Journal of Catalysis* 10, 377 (1968) and the pore diameter distribution of the catalyst in the pore diameter range above 7.5 nm is calculated with the aid of the formula:

$$\text{pore diameter (in nm)} = \frac{15000}{\text{absolute mercury pressure (in bar)}}$$

The nitrogen pore volume and the total pore volume mentioned in this patent application are determined as follows. The nitrogen pore volume of a catalyst is the pore volume determined with the aid of the above-mentioned nitrogen adsorption/desorption method. The total pore volume of a catalyst is the sum of the nitrogen pore volume present in pores with a diameter below and including 7.5 nm (determined with the aid of the above-mentioned nitrogen adsorption/desorption method) and the mercury pore volume present in pores with a diameter above 7.5 nm (determined with the aid of the above-mentioned mercury penetration method). The specific surface areas mentioned in this patent application have been determined according to the B.E.T. method.

The present patent application therefore relates to a process for the upgrading of a heavy hydrocarbon oil, in which process the C_5 -asphaltenes content and the $V_{k_{210}}$ of an oil with a C_5 -asphaltenes content above 5%w and a $V_{k_{210}}$ above 30 cSt, are reduced by at least 30% and at least 50%, respectively, by contacting the oil, at a temperature of at least 400°C, a hydrogen partial pressure of at least 100 bar and a space velocity of at most 2.0 l.l⁻¹.h⁻¹, with a catalyst

comprising one or more metals having hydrogenation activity on a carrier, which catalyst meets the following requirements:

- (1) $p/d > 3.5-0.02 v$, in which p is the specific average pore diameter in nm, d is the specific average particle diameter in mm and v is the percentage of the total pore volume that consists of pores with a diameter larger than 100 nm,
- (2) the total pore volume is larger than 0.40 ml/g,
- (3) v is smaller than 50, and
- (4) the specific surface area is larger than 100 m²/g; if the catalyst has such a p and d that the quotient p/d is larger than 3.5-0.02 v , but at most 10-0.15 v , the catalyst has to meet the following additional requirements:
 - (a) the nitrogen pore volume is larger than 0.60 ml/g,
 - (b) the specific surface area is larger than 150 m²/g, and
 - (c) p is larger than 5 nm.

The catalysts applied according to the invention are characterized, among other things, by a given relation between their average pore diameter and average particle diameter. It is essential that the average pore diameter and the average particle diameter used for the characterization of the catalysts should be determined according to the methods specified above for the specific average pore diameter and specific average particle diameter, because, if for the characterization of the catalysts use is made of an average pore diameter or an average particle diameter determined by a method other than those one specified above for the specific average pore diameter and specific average particle diameter (for example an average pore diameter calculated as four times the quotient of the pore volume and the specific surface area or an average particle diameter calculated as the linear average), entirely different results may be obtained.

The relation between p and d makes it possible at a given d of the catalyst particles to determine a minimum value above which the p of the catalyst particles should be selected to obtain an optimum catalyst. Consequently, it is also possible to derive from the relation found the maximum value below which the d of catalyst particles having a certain p should be selected to obtain an optimum catalyst. The most suitable values for p and d , respectively, within the ranges found are determined by, among other factors, the composition of the hydrocarbon oil to be treated. According as the hydrocarbon oil to be treated has a higher C₇-asphaltenes content, a catalyst with a higher p/d is preferred.

The upgrading of heavy hydrocarbon oils according to the invention is preferably carried out in the presence of a catalyst comprising 0.1-15 pbw metals having hydrogenation activity per 100 pbw carrier. The metals having hydrogenation activity are preferably selected from nickel, cobalt, molybdenum, vanadium and tungsten. It is further preferred that the catalyst should comprise at least one metal selected from nickel and cobalt and at least one metal selected from molybdenum, vanadium and tungsten and further that the atomic ratio between nickel and/or cobalt on the one hand and molybdenum, vanadium and/or tungsten on the other hand is between 0.05 and 3.0. Suitable metal combinations are nickel-vanadium, cobalt-molybdenum, nickel-molybdenum and nickel-tungsten.

The metal load of the catalysts applied according to the invention preferably amounts to 0.5-10 pbw and in particular 2.0-7.5 pbw per 100 pbw carrier. Especially preferred catalysts according to the invention are catalysts comprising about 1/2 pbw nickel and about 2 pbw vanadium per 100 pbw carrier, as well as catalysts comprising about 1 pbw nickel or cobalt and about 4 pbw molybdenum per 100 pbw carrier. The metals may be present on the carrier in the metallic form or in the form of their oxides or sulphides. Preference is given to catalysts in which the metals are present on the carriers in the form of their sulphides. Sulphidation of the present catalysts may be carried out by any technique for the sulphidation of catalysts known in the art. Sulphidation may, for instance, be carried out by contacting the catalysts with a sulphur-containing gas, such as a mixture of hydrogen and hydrogen sulphide, a mixture of hydrogen and carbon disulphide, or a mixture of hydrogen and a mercaptan such as butyl mercaptan. Sulphidation may also be carried out by contacting the catalysts with hydrogen and with a sulphur-containing hydrocarbon oil, such as a sulphur-containing kerosine or gas oil. In addition to the above-mentioned catalytically active metals, the catalysts may contain other catalytically active metals and promoters such as phosphorus, boron and halogens, such as fluorine and chlorine. Very suitable carriers for the catalysts are oxides of the elements of Group II, III or IV of the Periodic Table of

Elements or mixtures of the said oxides, such as silica, alumina, magnesia, zirconia, thoria, boria, hafnia, silica-alumina, silica-magnesia and alumina-magnesia.

Another type of material that is very suitable to serve as the carrier for the present catalyst is soot, in particular a soot obtained as by-product of the partial oxidation of hydrocarbons with air, oxygen or mixtures of air and oxygen, either in the presence or in the absence of steam. Apart from the fact that soot is a suitable carrier for the present catalysts, its use for this purpose has an additional advantage when the catalysts are employed for the upgrading of hydrocarbon oils having a high metal content, which advantage is not achieved when any of the oxidic carriers mentioned hereinbefore is employed. This can be elucidated as follows. Although the present catalysts show a long life when applied in the process according to the invention to hydrocarbon oils having a high metal content, even these catalysts are in the long run deactivated as a result of the deposition of large amounts of metals, in particular vanadium and nickel, and therefore, after a certain time of operation, they have to be replaced. If it is intended to recover the deposited metals from the deactivated catalyst, the use of a catalyst on soot as the carrier offers the considerable advantage over catalysts on other carrier materials that the carrier can simply be removed from the deactivated catalyst by combustion, after which a mixture of the metals concerned is left behind in the form of their oxides for further working up.

The preparations of the catalysts may be carried out by depositing the metals concerned on a carrier having such a pore diameter distribution and specific average pore diameter that after deposition of the metals thereon a catalyst is obtained which meets the requirements of the invention, either as such or after the specific average catalyst particle diameter has been decreased.

The porosity of the finished catalyst depends to a certain extent on the metal load applied. In general, it is true to say that when starting from a carrier with a given porosity, the porosity of the finished catalyst will be lower according as the metal load is higher. This phenomenon plays only a minor role when relatively low metal loads are applied. This means that at the relatively low metal loads which are preferred for the catalysts according to the invention, the porosity of the finished catalyst is mainly determined by the porosity of the carrier applied, so that for the preparation of these catalysts carriers should be selected having a porosity which differs only little from the desired porosity of the finished catalyst. The porosity of a carrier may also be influenced by means of a high-temperature treatment, either in the presence or in the absence of steam.

The porosity of a carrier is mainly determined by the way in which the carrier has been prepared. Catalyst carriers of the metal-oxide type are usually prepared by adding to one or more aqueous solutions of the salts of the metals concerned one or more gelating agents, as a result of which the metals are precipitated in the form of metal hydroxide gels, which are subsequently shaped and calcined. Usually, before being shaped the metal hydroxide gels are allowed to age for some time. During the preparation of the carrier there is ample opportunity to influence the porosity of the carrier. The porosity of the final carrier depends, among other factors, on the rate of addition of the gelating agents, and on the temperature and pH applied during the formation of the gel. The porosity of the final carrier may also be influenced by addition of certain chemicals to the gel, such as phosphorus compounds and/or halogen compounds. If ageing is applied, the porosity of the final carrier also depends on the ageing time and on the temperature and pH applied during ageing. In the preparation of mixed metal oxide carriers a further aspect of importance for the porosity of the final carrier is the way in which the metal hydroxide gels are precipitated: simultaneously or separately, e.g. one gel on top of the other. The porosity of the final carrier further depends on the way in which the carrier particles have been shaped, on the conditions applied during shaping, and on the temperature applied during calcination.

During shaping the porosity of the carrier particles is influenced, for example, by the type and amount of peptizing agents and binders which are usually added during this stage of carrier preparation, by the addition of certain chemicals, and by the addition of small amounts of inert materials. If the carrier particles are shaped by extrusion or tableting, the porosity of the final carrier is influenced by the extrusion or tableting pressure applied. If use is made of the spray-drying technique, the porosity of the carrier is influenced by the spraying temperature and spraying pressure applied.

The catalysts may be prepared by any technique for the preparation of

supported catalysts known in the art. It is not necessary for the catalytically active metals to be deposited on a finished carrier. They may also be incorporated into the carrier material during the preparation thereof, for example, prior to shaping. Incorporating the catalytically active metals into the carrier at an early state of catalyst preparation may also have a considerable influence on the porosity of the finished catalyst.

An attractive way in which the present catalysts may be prepared is by single or multistep coimpregnation of a carrier with an aqueous solution comprising one or more nickel and/or cobalt compounds and one or more molybdenum, vanadium and/or tungsten compounds, followed by drying and calcining. If the impregnation is carried out in several steps, the material may be dried and calcined, if desired, between the successive steps of impregnation. Drying and calcining are preferably carried out at temperatures between 50 and 150°C and between 150 and 550°C, respectively. Examples of suitable water-soluble compounds of nickel, cobalt, vanadium, molybdenum and tungsten which may be applied in the preparation of the present catalysts are nitrates, chlorides, formates and acetates of nickel and cobalt, vanadyl oxalate, vanadyl sulphate, ammonium vanadate and vanadyl acetyl acetonate, ammonium molybdate and ammonium tungstate. In order to increase the solubility of these compounds and to stabilize the solutions, certain compounds, such as ammonium hydroxide, monoethanolamine and sorbitol, may be added to the solutions.

As carriers for the present catalysts aluminas, silicas and silica-aluminas are preferred. Very suitable carriers are alumina particles or silica particles prepared by spray-drying of an alumina or silica gel, followed by shaping of the spray-dried micro particles into larger particles, e.g. by extrusion, and spherical alumina particles or silica particles obtained by the well-known oil drop method. The latter method comprises formation of an alumina or silica hydrosol, combining the hydrosol with a suitable gelating agent and dispersing the mixture as droplets into an oil which may be kept at an elevated temperature; the droplets are allowed to remain in the oil until they have solidified to spherical hydrogel particles, which are subsequently isolated, washed, dried and calcined. Very suitable silica-alumina carriers for the present catalysts are cogels of aluminium hydroxide gel on silica hydrogel.

In addition to extrusion and tableting, which have already been mentioned hereinbefore as attractive shaping techniques for the present catalysts and catalyst carriers, another attractive shaping technique is the well-known nodulizing (also called agglomeration) technique. According to this technique catalyst particles or catalyst-carrier particles having a diameter of, for example, at most 0.1 mm are agglomerated with the aid of a granulation liquid to larger particles having a diameter of, for example, at least 1.0 mm. In actual practice catalyst preparation according to the nodulizing technique usually takes place as follows. Catalyst-carrier material having a diameter of at most 0.1 mm is placed on a rotating disc provided with a raised edge and a scraping device. The disc is disposed at a specific angle to the horizontal plane. A granulation liquid is sprayed onto the carrier material, which is in continuous motion on the disc. In practice, when alumina is used as the carrier, a dilute aqueous solution of acetic acid or citric acid is usually employed as the granulation liquid. During the residence of the small particles on the disc, larger particles are formed from the small ones by agglomeration. The nodulizing technique may be carried out either batchwise or continuously. When the continuous process is used finely divided material is continuously supplied to the rotating disc and agglomerated material continuously leaves the disc via the top of the raised edge when this is in its lowest position. After the agglomerated particles have left the disc a sieve fraction with the desired diameter is separated from it. Particles with a diameter smaller than that of the desired sieve fraction may be recycled to the disc. If the agglomerated material contains particles with a diameter larger than that of the desired sieve fraction, these particles, after reduction of the particle size, for instance by grinding, may also be recycled to the disc. The conversion of the agglomerated material with the desired particle size into a suitable carrier material takes place by drying and calcination. The emplacement of one or more metals with hydrogenation activity on the carrier material thus prepared is usually effected by impregnation with an aqueous solution of compounds of the respective metals, followed by drying and calcination of the impregnated material.

If in the process according to the invention use is made of a catalyst prepared

according to the nodulizing technique, preference is given to a catalyst that meets one or more of the following conditions.

- (1) The pore volume of the catalyst that consists of pores with a diameter larger than 50 nm should be at least 0.2 ml/g and preferably at least 0.3 ml/g.
- (2) The catalyst comprises alumina as the carrier and has been prepared using dilute nitric acid as the granulation liquid.
- (3) In the preparation of the catalyst the starting material from which larger particles are formed by nodulizing, has been mixed with a certain amount of glass powder, preferably 0.5—15%w based on the amount of starting material with which it is mixed, and the particles formed by nodulizing are subjected to a calcination at a temperature above the softening temperature of glass.
- (4) The catalyst comprises phosphorus, preferably in an amount of 0.5—5 pbw per 100 pbw carrier material.
- (5) In the preparation of the catalyst the particles formed have been rotated for some time after they have left the rotating disc, but before drying and calcination and preferably for a period of time at least equal to the residence time of the material on the rotating disc.
- (6) In the preparation of the catalyst a granulation liquid has been applied into which one or more compounds of metals with hydrogenation activity have been incorporated.

The relationship found between p and d makes it possible to prepare catalysts having optimum properties for the upgrading of heavy hydrocarbon oils. If a catalyst or catalyst carrier is available of which d is too large in relation to p, it is possible to prepare therefrom an optimum catalyst or catalyst carrier by adapting d to p. This can be effected in a simple way by reducing the particle size of the catalyst or catalyst carrier, for example by grinding the particles.

The process according to the invention is preferably carried out by passing the hydrocarbon oils together with hydrogen in upward, downward or radial direction through one or more vertically disposed reactors containing a fixed or moving bed of the catalyst particles concerned. The process may, for instance, be carried out by passing the hydrocarbon oils together with hydrogen through a vertically disposed catalyst bed in the upward direction, the liquid and gas velocity used being such that expansion of the catalyst bed occurs (processing in ebullated bed operation). If several reactors are used in series for the process, the catalysts present in these reactors may differ from each other, for instance with respect to their p, d and/or chemical composition. A very attractive embodiment of the present process is one in which the hydrocarbon oil is passed through a vertically disposed catalyst bed in which during operation fresh catalyst is periodically introduced at the top of the catalyst bed and spent catalyst is withdrawn at the bottom thereof (processing in bunker flow operation). Another very attractive embodiment of the present process is one in which a plurality of reactors each containing a fixed catalyst bed are used, which reactors are alternately used for the process; while the process is carried out in one or more of these reactors, the catalyst in the other reactors is replenished (processing in fixed-bed swing operation). If desired, the process may also be carried out by suspending the catalyst in the hydrocarbon oil to be demetallized (processing in slurry phase operation).

For the upgrading of heavy hydrocarbon oils use is generally made of catalyst particles having a d of 0.4—5.0 mm. Catalyst particles having a d of 0.5—4.0 mm and in particular of 0.6—3.0 mm are preferred for this purpose.

The catalyst particles preferably have a total pore volume of at least 0.50 ml/g, while the specific surface area is above 150 m²/g.

The process according to the invention is preferably carried out at a temperature of 400—500°C, a hydrogen partial pressure of 100—300 bar and a space velocity of 0.2—2.0 l.l⁻¹.h⁻¹.

Examples of heavy hydrocarbon oils which can be upgraded by application of the process according to the invention are crude oils and residues obtained from the distillation of crude oils at atmospheric or reduced pressure, such as topped crude oils and long and short residues.

The invention will now be further elucidated with the aid of the following example.

Example

Seven catalysts were tested for the upgrading of a residual hydrocarbon oil having a C₃-asphaltenes content of 11.0%w, and a V_{k210} of 183 cSt, which oil had

been obtained as residue in the atmospheric distillation of a crude oil originating from South America. To this end the oil, together with hydrogen, was passed downwards through a cylindrical, vertically disposed fixed catalyst bed at a temperature of 410°C, a hydrogen partial pressure of 125 bar, a space velocity of 0.4 l.l⁻¹.h⁻¹ and an exit gas rate of 250 NI/kg of feed. The catalysts were applied in the form of their sulphides. The preparation of the seven catalysts is described hereinafter. The results of the upgrading experiments as well as the properties of the catalysts have been collected in the table.

Catalyst preparation

10 Catalyst A

As starting material use was made of an alumina obtained by spray-drying with a d smaller than 0.09 mm, this alumina having a pore volume of 1.2 ml/g consisting of pores with a diameter larger than 50 nm. Of this alumina 100 g was mixed with 2 g glass powder with a d smaller than 0.09 mm; the mixture was put on a rotating disc and 100 ml of an aqueous solution containing 3.5 g citric acid was gradually sprayed onto it. The rotating disc, which was provided with a raised edge of 10 cm high, had a diameter of 40 cm. The disc made 40 revolutions per minute and was disposed at an angle of 45° to the horizontal plane. After 15 minutes' residence time the nodules formed were removed from the disc. After drying at 120°C a sieve fraction with a d of 2.0 mm was isolated from the dried material. After 1 hour's calcination at 600°C followed by calcination for 1 hour at 800°C the particles were impregnated with an aqueous solution containing nickel nitrate, ammonium molybdate and NH₄H₂PO₄. Finally, the impregnated material was dried at 120°C and calcined for 1 hour at 500°C. The catalyst thus prepared contained 1 pbw nickel, 4 pbw molybdenum and 1 pbw phosphorus per 100 pbw alumina.

Catalyst B

The starting material was a soot with a d smaller than 0.1 mm, which soot had a pore volume of 0.58 ml/g consisting of pores with a diameter larger than 50 nm. The soot had been obtained as a by-product of the partial oxidation of hydrocarbons with air. The soot, being available in the form of a slurry in water, was isolated from it by filtration, drying of the filter cake and grinding of the dried material to the particle size mentioned. From the soot nodules were prepared. The preparation of the nodules from the soot was carried out in substantially the same way as that of the nodules from alumina as described for catalyst A, the difference being, however, that in the present case no glass powder was used and that an aqueous solution of ligno sulphonate was used as the granulation liquid. After 15 minutes' residence time the nodules formed were removed from the disc. After drying at 120°C a sieve fraction with a d of 1.8 mm was isolated from the dried material. After 1 hour's calcination in a nitrogen stream at 700°C these particles were impregnated with an aqueous solution containing nickel nitrate and vanadyl oxalate. Finally, the impregnated material was dried at 120°C and calcined for 1 hour at 500°C in a nitrogen stream. The catalyst thus prepared contained 0.5 pbw nickel and 2 pbw vanadium per 100 pbw soot.

45 Catalyst C

This catalyst, which comprised 0.5 pbw nickel and 2.0 pbw vanadium per 100 pbw alumina carrier was prepared by impregnation of an alumina with an aqueous solution containing vanadyl oxalate and nickel nitrate, followed by drying and calcination of the composition.

50 Catalyst D

This catalyst, which comprised 0.5 pbw nickel and 2.0 pbw vanadium per 100 pbw silica carrier was prepared in substantially the same way as catalyst C, the difference being, however, that in the present case a silica instead of an alumina was used as the carrier.

55 Catalyst E

This catalyst, which comprised 4.0 pbw cobalt and 11.0 pbw molybdenum per 100 pbw alumina carrier was prepared by impregnation of an alumina with an aqueous solution containing cobalt nitrate, ammonium molybdate and hydrogen peroxide, followed by drying and calcination of the composition.

Catalyst F

This catalyst, which comprised 2.5 pbw cobalt and 6.0 pbw molybdenum per 100 pbw alumina carrier, was prepared in substantially the same way as catalyst E.

Catalyst G

This catalyst, which comprised 1.0 pbw nickel and 8.0 pbw molybdenum per 100 pbw alumina carrier, was prepared in substantially the same way as catalyst E, the difference being, however, that in the present case an impregnation liquid was used containing nickel nitrate instead of cobalt nitrate.

TABLE

Catalyst No.	A	B	C	D	E	F	G
Specific surface area, m ² /g	264	450	236	272	353	303	210
Total pore volume, ml/g	1.39	1.50	0.86	0.94	0.74	0.45	0.78
Nitrogen pore volume, ml/g	0.74	0.80	0.72	0.89	0.59	0.45	0.55
Pore volume consisting of pores with a diameter larger than 50 nm, ml/g	0.80	0.36					
v, %	47	8	20	5	25	<0.5	22
d, mm	2.9	1.8	2.0	1.8	1.0	1.5	1.5
p, nm	90	38	14.6	9.4	9.4	4.8	7.6
Experiment No.	1	2	3	4	5	6	7
Reduction in C ₅ —asphaltenes content after processing 2 tons feed/kg catalyst, %	47	33	34	38	43	15	6
Reduction in V _{k₂₁₀} after processing 2 tons feed/kg catalyst, %	89	77	78	82	87	37	16

A catalyst is optimum under the conditons applied during these upgrading experiments when the criterion is met that the catalyst is still capable of reducing the C₅-asphaltenes content and the V_{k₂₁₀} of the oil by at least 30% and at least

50%, respectively, after two tons of the oil have been processed over the catalyst.

Experiments 1—5 (in which catalysts were applied which met the above-mentioned requirements concerning the reduction of asphaltenes content and viscosity) are upgrading experiments within the scope of the present invention.

In experiments 1, 2, 3 and 5, in which catalysts were applied with p/d > 10.0–0.15 v, these catalysts also satisfied the further requirements of the invention concerning v(<50%), total pore volume (>0.40 ml/g) and specific surface area (>100 m²/g). In experiment 4, in which a catalyst was applied with 10.0–0.15 v > p/d > 3.5–0.02 v, this catalyst also satisfied the further requirements of the

invention concerning $v(<50\%)$, $p(>5\text{ nm})$, nitrogen pore volume ($>0.60\text{ ml/g}$) and specific surface area ($>150\text{ m}^2/\text{g}$).

Experiments 6 and 7 (in which the catalysts did not meet the above requirements concerning the reduction of asphaltenes content and viscosity) are experiments outside the scope of the present invention. In experiment 6 a catalyst was applied with $p/d<3.5-0.02\text{ v}$. In experiment 7 a catalyst was applied with $10.0-0.15\text{ v}>p/d>3.5-0.02\text{ v}$, but with a nitrogen pore volume smaller than 0.60 ml/g .

WHAT WE CLAIM IS:—

1. A process for the upgrading of a heavy hydrocarbon oil, in which process the C_3 -asphaltenes content and the $V_{k_{210}}$ of an oil with a C_3 -asphaltenes content above $5\%w$ and a $V_{k_{210}}$ above 30 cSt are reduced by at least 30% and at least 50% , respectively, by contacting the oil, at a temperature of at least 400°C , a hydrogen partial pressure of at least 100 bar and a space velocity of at most $2.0\text{ l.l}^{-1}.\text{h}^{-1}$, with a catalyst comprising one or more metals having hydrogenation activity on a carrier, which catalyst meets the following requirements:
 - (1) $p/d>3.5-0.02\text{ v}$, in which p is the specific average pore diameter in nm , d is the specific average particle diameter in mm and v is the percentage of the total pore volume that consists of pores with a diameter larger than 100 nm ,
 - (2) the total pore volume is larger than 0.40 ml/g ,
 - (3) v is smaller than 50 , and
 - (4) the specific surface area is larger than $100\text{ m}^2/\text{g}$;
 if the catalyst has such a p and d that the quotient p/d is larger than $3.5-0.02\text{ v}$, but at most $10-0.15\text{ v}$, the catalyst has to meet the following additional requirements:
 - (a) the nitrogen pore volume is larger than 0.60 ml/g ,
 - (b) the specific surface area is larger than $150\text{ m}^2/\text{g}$, and
 - (c) p is larger than 5 nm .
2. A process according to claim 1, which process is carried out in the presence of a catalyst comprising $0.1-15\text{ pbw}$ metals having hydrogenation activity per 100 pbw carrier.
3. A process according to claim 2, which process is carried out in the presence of a catalyst comprising $0.5-10\text{ pbw}$ and preferably $2.0-7.5\text{ pbw}$ metals having hydrogenation activity per 100 pbw carrier.
4. A process according to any one of claims 1-3, which process is carried out in the presence of a catalyst of which the metals having hydrogenation activity are selected from nickel, cobalt, molybdenum, vanadium and tungsten.
5. A process according to claim 4, which process is carried out in the presence of a catalyst comprising at least one metal selected from nickel and cobalt and at least one metal selected from molybdenum, vanadium and tungsten.
6. A process according to claim 5, which process is carried out in the presence of a catalyst in which the atomic ratio between nickel and/or cobalt on the one hand and molybdenum, vanadium and/or tungsten on the other hand is between 0.05 and 3.0 .
7. A process according to claim 6, which process is carried out in the presence of a catalyst comprising either about $1/2\text{ pbw}$ nickel and about 2 pbw vanadium, or about 1 pbw nickel or cobalt and about 4 pbw molybdenum per 100 pbw carrier.
8. A process according to any one of claims 1-7, which process is carried out in the presence of a catalyst containing the metals with hydrogenation activity in the form of their sulphides.
9. A process according to any one of claims 1-8, which process is carried out in the presence of a catalyst containing a carrier selected from silica, alumina, silica-alumina and soot.
10. A process according to claim 9, which process is carried out in the presence of a catalyst containing soot as the carrier, which soot has been obtained as by-product of the partial oxidation of hydrocarbons with air, oxygen or mixtures of air and oxygen, either in the presence or in the absence of steam.
11. A process according to any one of claims 1-10, which process is carried out in the presence of a catalyst prepared according to the nodulizing technique.
12. A process according to claim 11, which process is carried out in the presence of a catalyst whose pore volume that consists of pores with a diameter larger than 50 nm should at least be 0.2 ml/g and preferably at least 0.3 ml/g .



invention concerning $v(<50\%)$, $p(>5\text{ nm})$, nitrogen pore volume ($>0.60\text{ ml/g}$) and specific surface area ($>150\text{ m}^2/\text{g}$).

Experiments 6 and 7 (in which the catalysts did not meet the above requirements concerning the reduction of asphaltenes content and viscosity) are experiments outside the scope of the present invention. In experiment 6 a catalyst was applied with $p/d<3.5-0.02\text{ v}$. In experiment 7 a catalyst was applied with $10.0-0.15\text{ v}>p/d>3.5-0.02\text{ v}$, but with a nitrogen pore volume smaller than 0.60 ml/g .

WHAT WE CLAIM IS:—

1. A process for the upgrading of a heavy hydrocarbon oil, in which process the C_3 -asphaltenes content and the $V_{k_{210}}$ of an oil with a C_3 -asphaltenes content above $5\%w$ and a $V_{k_{210}}$ above 30 cSt are reduced by at least 30% and at least 50% ,

respectively, by contacting the oil, at a temperature of at least 400°C , a hydrogen partial pressure of at least 100 bar and a space velocity of at most $2.0\text{ l.l}^{-1}\text{.h}^{-1}$, with a catalyst comprising one or more metals having hydrogenation activity on a carrier, which catalyst meets the following requirements:

(1) $p/d>3.5-0.02\text{ v}$, in which p is the specific average pore diameter in nm , d is the specific average particle diameter in mm and v is the percentage of the total pore volume that consists of pores with a diameter larger than 100 nm ,

(2) the total pore volume is larger than 0.40 ml/g ,

(3) v is smaller than 50 , and

(4) the specific surface area is larger than $100\text{ m}^2/\text{g}$;

if the catalyst has such a p and d that the quotient p/d is larger than $3.5-0.02\text{ v}$, but at most $10-0.15\text{ v}$, the catalyst has to meet the following additional requirements:

(a) the nitrogen pore volume is larger than 0.60 ml/g ,

(b) the specific surface area is larger than $150\text{ m}^2/\text{g}$, and

(c) p is larger than 5 nm .

2. A process according to claim 1, which process is carried out in the presence of a catalyst comprising $0.1-15\text{ pbw}$ metals having hydrogenation activity per 100 pbw carrier.

3. A process according to claim 2, which process is carried out in the presence of a catalyst comprising $0.5-10\text{ pbw}$ and preferably $2.0-7.5\text{ pbw}$ metals having hydrogenation activity per 100 pbw carrier.

4. A process according to any one of claims 1-3, which process is carried out in the presence of a catalyst of which the metals having hydrogenation activity are selected from nickel, cobalt, molybdenum, vanadium and tungsten.

5. A process according to claim 4, which process is carried out in the presence of a catalyst comprising at least one metal selected from nickel and cobalt and at least one metal selected from molybdenum, vanadium and tungsten.

6. A process according to claim 5, which process is carried out in the presence of a catalyst in which the atomic ratio between nickel and/or cobalt on the one hand and molybdenum, vanadium and/or tungsten on the other hand is between 0.05 and 3.0 .

7. A process according to claim 6, which process is carried out in the presence of a catalyst comprising either about $1/2\text{ pbw}$ nickel and about 2 pbw vanadium, or about 1 pbw nickel or cobalt and about 4 pbw molybdenum per 100 pbw carrier.

8. A process according to any one of claims 1-7, which process is carried out in the presence of a catalyst containing the metals with hydrogenation activity in the form of their sulphides.

9. A process according to any one of claims 1-8, which process is carried out in the presence of a catalyst containing a carrier selected from silica, alumina, silica-alumina and soot.

10. A process according to claim 9, which process is carried out in the presence of a catalyst containing soot as the carrier, which soot has been obtained as by-product of the partial oxidation of hydrocarbons with air, oxygen or mixtures of air and oxygen, either in the presence or in the absence of steam.

11. A process according to any one of claims 1-10, which process is carried out in the presence of a catalyst prepared according to the nodulizing technique.

12. A process according to claim 11, which process is carried out in the presence of a catalyst whose pore volume that consists of pores with a diameter larger than 50 nm should at least be 0.2 ml/g and preferably at least 0.3 ml/g .

20



* C L M S *

10

1,523,343

13. A process according to claim 11 or 12, which process is carried out in the presence of a catalyst that comprises alumina as the carrier and has been prepared using dilute nitric acid as the granulation liquid.

14. A process according to any one of claims 11—13, which process is carried out in the presence of a catalyst in the preparation of which the starting material from which larger particles are formed by the nodulizing technique has been mixed with a certain amount of glass powder, preferably 0.5—15%w based on the amount of starting material with which it is mixed, and in which the particles formed by the nodulizing technique are subjected to a calcination at a temperature above the softening temperature of glass.

15. A process according to any one of claims 11—14, which process is carried out in the presence of a catalyst comprising phosphorus, preferably in an amount of 0.5—5 pbw per 100 pbw carrier material.

16. A process according to any one of claims 11—15, which process is carried out in the presence of a catalyst in the preparation of which the particles formed are rotated for some time after they have left the rotating disc, but before drying and calcination, and preferably for a period of time at least equal to the residence time of the material on the rotating disc.

17. A process according to any one of claims 11—16, which process is carried out in the presence of a catalyst in the preparation of which a granulation liquid is applied into which one or more compounds of metals with hydrogenation activity have been incorporated.

18. A process according to claim 9, which process is carried out in the presence of a catalyst comprising as the carrier alumina particles or silica particles prepared by spray-drying of an alumina or silica gel, followed by shaping of the spray-dried micro particles into larger particles.

19. A process according to claim 9, which process is carried out in the presence of a catalyst comprising as the carrier spherical alumina particles or silica particles prepared with the aid of the oil drop method.

20. A process according to claim 9, which process is carried out in the presence of a catalyst comprising a carrier prepared from a cogel of aluminium hydroxide gel on silica hydrogel.

21. A process according to any one of claims 1—20, which process is carried out by passing the hydrocarbon oil in the presence of hydrogen in upward, downward or radial direction through one or more vertically disposed reactors containing a fixed or moving bed of the catalyst particles concerned.

22. A process according to claim 21, which process is carried out by passing the hydrocarbon oil through a vertically disposed catalyst bed in which during operation fresh catalyst is periodically introduced at the top of the catalyst bed and spent catalyst is withdrawn at the bottom thereof (processing in bunker flow operation).

23. A process according to claim 21, which process is carried out in a plurality of reactors each containing a fixed catalyst bed, which reactors are alternately used for the process; while the process is carried out in one or more of these reactors, the catalyst in the other reactors is replenished (processing in fixed-bed swing operation).

24. A process according to any one of claims 1—23, which process is carried out in the presence of a catalyst having a d of 0.4—5.0 mm.

25. A process according to claim 24, which process is carried out in the presence of a catalyst having a d of 0.5—4.0 mm and preferably of 0.6—3.0 mm.

26. A process according to any one of claims 1—25, which process is carried out in the presence of a catalyst having a total pore volume of at least 0.50 ml/g.

27. A process according to any one of claims 1—26, which process is carried out in the presence of a catalyst having a specific surface area above 150 m²/g.

28. A process according to any one of claims 1—27, which process is carried out at a temperature of 400—500°C, a hydrogen partial pressure of 100—300 bar and a space velocity of 0.2—2.0 l.l⁻¹.h⁻¹.

29. A process for the upgrading of a heavy hydrocarbon oil, which process is carried out substantially as described hereinbefore and with particular reference to the Example as far as it relates to experiments 1—5.



21

1,523,343

11

30. Heavy hydrocarbon oils which have been upgraded according to a process as claimed in claim 29.

ROY C. ROGERS,
Chartered Patent Agent,
Shell Centre,
London, S.E.1.
Agent for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1978.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.