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**EUROPEAN PATENT SPECIFICATION**

⑬ Date of publication of patent specification: **16.08.90**

⑭ Int. Cl.<sup>5</sup>: **B 01 J 37/00**

⑮ Application number: **84111374.9**

⑯ Date of filing: **24.09.84**

⑰ **Immobilization of vanadia deposited on sorbent materials during visbreaking treatment of carbo-metallic oils.**

⑱ Date of publication of application:  
**02.04.86 Bulletin 86/14**

⑲ Publication of the grant of the patent:  
**16.08.90 Bulletin 90/33**

⑳ Designated Contracting States:  
**AT BE DE FR GB IT NL SE**

㉑ References cited:  
**EP-A-0 063 683**  
**US-A-3 506 594**  
**US-A-3 932 268**  
**US-A-4 213 882**  
**US-A-4 243 514**  
**US-A-4 263 128**

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## Description

This invention relates to a method of producing a more suitable grade of oil feed material, i.e. having lowered metals and Conradson carbon values, for use as feedstock in a reduced crude conversion (RCC) process or a present day modern FCC process, from extremely low grade crudes.

More particularly, this invention relates to an improvement in the method disclosed in EP-A-0 063 683, and more particularly, the sorbent used therein.

In the catalytic cracking of hydrocarbon and crude oil feedstocks using zeolitic cracking catalysts, it is well known that catalytic activity is severely affected by metal contamination in the feedstock, and by asphaltenes and other Conradson carbon producing values. Reduced crude conversion (RCC) processes have been developed able to cope with reduced crude and other feeds having a degree of metal contamination and Conradson carbon producing components, but there are certain crude oils, such as Mexican Mayan or Venezuelan crude oils, which contain abnormally high metals and Conradson carbon values. If these poor grades of crude are used directly in a catalytic cracking process, even in an RCC process, they will lead to uneconomical operation because of the high burning load which is imposed on the catalyst regenerator to remove carbonaceous deposits from the catalyst before recycling, and will lead to rapid deactivation of the catalyst, both resulting in a high catalyst addition rate to maintain catalyst activity and selectivity. It is thus desirable to develop and identify an economical means of processing more of the poor grade crude oils, such as Mexican Mayan, because of their availability and relative cost, as compared to Middle East crudes.

The literature suggests many processes for the reduction of the metals content and Conradson carbon values of reduced crudes and other contaminated oil fractions. One such process is that described in US-A-4,243,514 and DE-A-29 04 230 both assigned to Engelhard Minerals and Chemicals Inc. Basically, these prior art processes involve contacting a reduced crude fraction or other contaminated oil, with a sorbent material at elevated temperatures in a sorbing zone, such as a fluid bed, to produce a product of reduced metal and reduced Conradson carbon value. One of the sorbents described in US-A-4,243,514 is an inert solid initially composed of kaolin, which has been spray dried to yield microspherical particles having a surface area below 100 m<sup>2</sup>/g and a catalytic cracking microactivity (MAT) value of less than 20 which material is subsequently calcined at high temperature so as to achieve better attrition resistance.

However, as the vanadia content on such sorbents increases above 5,000 ppm and into the range of 10,000 to 30,000 ppm, the sorbent begins to have fluidization problems. For example, it has been found that as vanadium pentoxide and/or sodium vanadate builds up on the sorbent particles, the elevated temperatures encountered in the sorbent regeneration zones to remove carbonaceous deposits cause significant levels of vanadia deposits to flow and form a liquid coating on the sorbent particles. Under this condition an interruption or decrease in particle flow results in coalescence between the liquid coated sorbent particles. Once coalescence occurs, fluidization is interrupted and becomes difficult to reinstate. This condition results for example in stoppage of particle flow in cyclone diplegs, ineffective operation of cyclones, rapid increases in the loss of the sorbent, and will finally result with unit shutdown.

In accordance with the disclosure of EP-A-0 063 683, the problem of vanadia deposition on the sorbent can be tackled in either of two ways. In one, a metallic promoter is incorporated into the sorbent, either directly, or via the reduced crude or crude oil feedstock, which, it is believed, results in the formation of intermetallic vanadium compounds or complexes which are of higher melting point than vanadium pentoxide, and which therefore avoid the formation of liquid vanadia during regeneration of the sorbent particles, and thus avoid the problems of coalescence of the particles, and resultant clogging of the apparatus. In a second method, vanadia (vanadium pentoxide) formation is reduced by close control over the conditions pertaining in the sorbent regeneration zone, in particular the maintenance therein of reducing conditions which result in the formation of vanadium oxide materials of lower oxidation state than the pentoxide, and which are of higher melting point.

In accordance with the present invention, processes of the foregoing type, i.e. processes which involve contacting the reduced crude or crude oil feedstock under visbreaking conditions with a particulate sorbent material having little or no catalytic cracking activity, particularly microspherical particles of kaolinite clay, with or without the metallic promoter as taught in EP-A-0 063 683, in order to reduce metal contamination and Conradson carbon producing components in the feedstock prior to catalytic cracking, are improved still further in that there is used as the sorbent a highly porous microspherical kaolinite clay, i.e. having a pore volume of at least 0.4 cc/g, and obtained by slurring a kaolinite clay in water, said slurry optionally containing a binder for the clay particles, a thermally decomposable, dispersant pore forming material, and optionally said metallic promoter, spray drying the slurry to form microspherical particles comprising the kaolinite clay and, if present in the slurry, the pore forming material, binder and promoter, calcining the microspherical particles at an elevated temperature in the range 548 to 1148°C (1000 to 2100°F) and for a period of up to about 3 hours, and thereafter slowly cooling the particles to a temperature of about 149°C (300°F) over a period of about 16 hours, and optionally thereafter impregnating the particles with said metallic promoter, if not already present in the particles.

More particularly, the high pore volume of the sorbent is such as to provide, in the visbreaking zone, a total pore volume that is substantially in excess of the volume of those components of the feedstock that remain liquid and non-vaporized at the visbreaking temperature, that excess volume being such as to

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provide a volume ratio (total sorbent pore volume:liquid, non-vaporized feedstock) in the range 4:1 to 3:2, or, in other words, that the filling of the pores of the sorbent by the liquid, non-vaporized components of the reduced crude or crude oil feed is theoretically limited to between 1/4 and 2/3 of the total pore volume available within the sorbent particles.

5 The improved solid sorbent particulate material used in this invention, i.e. a high pore volume microspherical kaolinite clay having a pore volume of at least 0.4 cc/g. used with or without one or more metal additive molecules for immobilizing liquidized vanadia, provides greater absorbence characteristics for heavy oil components and greater sorbent stability at the temperature conditions employed up to 871°C (1600°F). In yet another aspect, the improved sorbent material is of a pore size and volume which readily  
10 absorbs high levels of metal deposits and high boiling components of the residual oil feed within its pores in preference to surface deposition contributing to particle agglomeration. Surface deposition of metals, particularly vanadia, contributes to reducing the absorption characteristics of the sorbent by blocking pore openings and causing coalescence of particles as herein described. Thus the improved high pore volume sorbent material used in this invention and the limited feedstock:pore volume ratio allows more  
15 contaminating metal components such as vanadium and asphaltenes to be absorbed within the sorbent pores rather than collect on the particle outer surface. This in turn considerably reduces the tendency for particle coalescence due to high metals bonding as observed with low pore volume sorbent material, and prolongs the life of the sorbent. Furthermore, relatively large volumes of the heavy bottoms boiling above 552°C (1025°F) result in particle coating of low pore volume material with a tacky asphaltic material which  
20 also facilitates coalescence of particles, resulting in plugging and coking within a riser reactor and product separator lines. However, by employing the larger pore volume material in conjunction with restricting the volume of the pores occupied by the heavy oil feed as herein provided, i.e. to between 1/4 and 2/3, the capacity for asphaltic materials in the feedstock to cause particle coalescence is considerably reduced, and the sorbent is usable over an extended operating period.

25 In accordance with the present invention, the adverse conditions herein identified with respect to pore plugging, particle sintering and particle coalescence is substantially reduced through the use of a large pore volume microspherical kaolinite clay material having a pore volume of at least 0.4 cc/g and preferably in the range of 0.5 cc/g to 0.8 cc/g.

The sorbent material used for demetallizing high boiling residual oils and reduced crudes in  
30 accordance with this invention is a dehydrated kaolin clay. According to analysis, a kaolin clay contains about 51 to 53% (wt%)  $\text{SiO}_2$ , 41 to 45%  $\text{Al}_2\text{O}_3$  and 0 to 1%  $\text{H}_2\text{O}$ , the remainder consisting of small amounts of originally present impurities. Although these impurities may include titanium, this titanium is bound up in the clay and is not in a form capable of tying up significant amounts of vanadium. In order to facilitate spray drying, the powdered dehydrated kaolinite clay is dispersed in water under conditions to form a  
35 suspension or a slurry of solids, optionally containing other ingredients already indicated which will provide random orientation contributing to large pore volume. In preferred preparation cases in order to achieve attrition resistance and a greater pore volume and avoid expensive calcination, a binder material consisting of silica, alumina, calcium, boria, magnesia or titania may be added. The slurry is then spray dried to provide substantially microspherical particles of kaolinite clay. The spray driers used can have  
40 countercurrent or cocurrent or a mixed countercurrent-cocurrent movement of the suspension and the hot air for the production of microspheres. The air can be heated electrically or by other indirect means. Combustion gases, such as those obtained in the air from the combustion of hydrocarbon heating oils, can also be used.

If a cocurrent drier is used, the air inlet temperature can be as high as 649°C (1200°F) and the clay  
45 should be charged at a rate sufficient to guarantee an air outlet temperature of about 121 to 316°C (250 to 600°F). At these temperatures the free moisture of the suspension is driven away without removing the water of hydration (water of crystallization) from the crude clay component. Dehydration of part of all of the crude clay during the spray drying may be envisioned. The product of the spray drier can be separated in order to obtain microspheres of the desired particle size. Calcination of the particles can be completed  
50 before or after the addition of one or more metal components herein identified.

Although it is advantageous in some cases to calcine the microspheres at temperatures of from 871 to 1149°C (1600 to 2100°F) in order to obtain particles of maximum hardness, it is also possible to dehydrate the microspheres by calcining at lower temperatures. Temperatures of from 548 to 1149°C (1000 to 1600°F) can be used to transform the clay into a material known as "metakaolin". After calcination, the  
55 microspheres should be cooled down and, if necessary, fractionated to obtain the desired particle size range.

A particularly desired high pore volume clay sorbent material may be attained during preparation thereof by the incorporation in the clay slurry of a thermally decomposable, dispersant pore forming material such as carbon black, sugar, other thermally decomposable organic materials such as  
60 methylcellulose, starch, nylon, polyacrylonitrile, polybutene, polystyrene, or thermally decomposable inorganic salts such as nitrates, nitrites, carbonates, sulfites of various molecular weights, which pore forming materials decompose during calcination to give the desired pore size following decomposition.

The process of the present invention may be carried out in apparatus similar to that disclosed in EP-A-0 063 683, but under operating conditions specifically recited herein, in which operation the solids are  
65 employed for a greatly extended on stream operating time thereby contributing measurably to the

economics and efficiency of the operation. Other advantages contributed by the solid sorbent materials of this invention will become more apparent from the following discussion.

The sorbent particulate material used in this invention may be prepared in a specific case by mixing one or more of carbon black, a polymeric material decomposable during high temperature drying or subsequent high temperature treatment, sugar, etc. in a slurry of kaolinite clay which mixture if thereafter spray dried yields a microspherical sorbent particulate of a size in the range of about 20 to about 150 microns ( $\mu\text{m}$ ) and preferably within the fluidizable particle range of 40 to 80 microns. Calcination of the spray dried material may be accomplished in the regeneration step of the process or separately effected before use at a temperature sufficient to remove carbon black by burning or decompose organic material whichever to yield the desired large pore sorbent material. Thus the pore size of the sorbent material is determined essentially by the size of the occluded material removed by calcination and/or burning. A required pore volume of the finished microspherical sorbent is at least 0.4 cc/g and preferably is within the range of 0.5 to about 0.8 cc/g. Thus when one employs a sorbent/oil ratio of 7:1, the total pore volume of the sorbent will be within the range of about 2.8 cc/cc of feed up to about 5.6 cc/cc of feed. With this larger sorbent pore volume than employed heretofore, the pores will not be over filled with deposited high boiling carbon producing component materials and metal contaminants for a much longer period of operating time, deposited hydrocarbonaceous material is removed by burning, and deposited vanadia will be discouraged from flowing from the pores with or without additive metals to accumulate on the outer surface of the solids particle and cause pore plugging and coalescence.

In addition to the substantially increased pore volume provided by the sorbent material used in this invention being a deterrent to short term operation, the increased pore volume in combination with immobilizing metal additives further enhances the hydrothermal visbreaking operation of this invention by permitting an even much larger accumulation of metal contaminants on the sorbent material before discard thereof is required.

The large pore sorbent material used in this invention may be modified as suggested above by the inclusion of one or more vanadia immobilizing metal additives as taught by EP-A-0 063 683 and which may be added to the sorbent material during or after manufacture or during the oil processing cycle, so as to immobilize for example sodium vanadates, and/or vanadium pentoxide deposited on the sorbent during processing of the oil for metals and/or Conradson carbon removal. With the large pore volume sorbent material, however, there is less need for providing the additive metal in the virgin sorbent material. Addition after considerable accumulation of vanadia will suffice.

It is not necessary here to go into any great detail concerning the metallic vanadium immobilization component, since reference may be made to EP-A-0 063 683 for full details. It is sufficient herein to say that the preferred metal additive compounds are magnesium, calcium, barium, titanium, zirconium, manganese, indium, lanthanum, or a mixture of the compounds of these metals. Where the additive is introduced directly into the high pore volume sorbent demetallizing process, that is into a riser contact zone or a falling particle contact zone, into the regenerator or into any intermediate section thereof, the metal additives are preferably organometallic compounds soluble in the hydrocarbon feed or in a hydrocarbon solvent miscible with the feed. Examples of preferred organo-metallic compounds are tetraisopropyltitanate,  $\text{Ti}(\text{C}_3\text{H}_7\text{O})_4$ , available as TYZOR from the DuPont Company; methylcyclopentadienyl manganese tricarbonyl (MMT),  $\text{Mn}(\text{CO})_3\text{C}_6\text{H}_7$ ; zirconium isopropoxide,  $\text{Zr}(\text{C}_3\text{H}_7\text{O})_4$ ; barium acetate,  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ ; calcium oxalate,  $\text{Ca}(\text{C}_2\text{O}_4)$ ; magnesium stearate,  $\text{Mg}(\text{C}_{18}\text{H}_{35}\text{O}_2)_2$ ; indium 2,4, pentanedionate,  $\text{In}(\text{C}_5\text{H}_7\text{O}_2)_3$ ; tantalum ethoxide,  $\text{Ta}(\text{C}_2\text{H}_5\text{O})_5$ ; and zirconium 2,4, pentaenionate,  $\text{Zr}(\text{C}_5\text{H}_7\text{O}_2)_4$ . Other preferred process additives include titanium tetrachloride and manganese acetate, both of which are relatively inexpensive. These additives are only a partial example of the various materials available and others would include alcoholates, esters, phenolates, naphthenates, carboxylates, dienyl sandwich compounds, and various inorganic compounds soluble in hydrocarbon solvents.

The organo-metallic additives may be introduced directly into the hydrocarbon treatment or visbreaking zone, preferably near the bottom of a riser reaction zone so that the metal additive will be deposited on the sorbent particulate before or along with the heavy metals in the oil feed. When the additive metal in the sorbent material of the invention reaches the regenerator, its oxide is formed, either by decomposition of the additive directly to the metal oxide or by decomposition of the additive to the free metal which is then oxidized under the regenerator conditions. This provides an intimate mixture of metal additive and undesired heavy metal contaminants in the feed and is believed to be a most effective method for tying up vanadium pentoxide as soon as it is formed in the regenerator. The metal additive may be introduced into the riser visbreaker zone by mixing it with the feed in an amount sufficient to give an atomic ratio between the metal additive and the vanadium in the feed of at least 0.25, preferably in the range of 0.5 to 3.0. The addition of metal additive is preferably delayed until significant levels of metal deposits are accumulated so that the economics of the process will be preserved as long as possible.

If the metal additive is added directly to the sorbent during sorbent manufacture or at some other time before the sorbent is introduced into the riser reactor, the metal additives are preferably water soluble inorganic salts of these metals, such as the acetate, halide, nitrate, sulfate, sulfite, and/or carbonate. If the metal additive is not added to the sorbent before or during particle formation, then it can be added by impregnation techniques to the spray dried microspheres.

Inorganic metal additives may be introduced into the process along with water containing streams,

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such as can be used to directly cool the solids in the regenerator or to lift, fluidize or to strip the sorbent solid material.

The present invention thus provides an improved sorbent and an improved method for treatment of high boiling oil feeds containing significant levels of hydrocarbon materials boiling above 552°C (1025°F) and an amount of vanadium of at least 1.0 ppm. More particularly, the sorbent particulate material of improved high pore volume and metals adsorption capacity reduces also the phenomenon of particle coalescence and loss of fluidization for the reasons herein described and caused in part particularly by vanadium compound contaminants of low melting point. Gas oil and heavier high boiling portions of oil feeds of all types utilized in FCC operations and more particularly in reduced crude cracking operations comprise vanadium, nickel, iron and copper in considerably varying amounts with vanadium quite often being a major portion thereof. The invention described herein is thus particularly useful in the removal of excessive carbo-metallic containing oil components from feeds to be utilized in a process known as a reduced crude cracking (RCC) process possessing hydrocarbon composition of higher metals content than processed in gas oil cracking (FCC) operations.

It is to be understood that the large pore volume sorbent particles used in this invention can be of any size, depending on the size appropriate to the conversion process in which the sorbent is to be employed. Thus, while a fluidizable size is preferred in a riser contact zone, i.e. 20 to 150 microns, preferably 40 to 80, the sorbent particles may be employed as larger size particles in other systems such as moving beds systems in contact with partially vaporized or unvaporized feeds.

The preparation of high pore volume sorbents for use in this invention is illustrated by the following Examples.

### Example 1

1. Into a homogenizing mixer called a Kady Mill was added 12 l of tap water and 25 g of sodium pyrophosphate hydrate. The phosphate is a surface active agent to disperse 22 kg of a fine kaolinite clay named HYDRITE UF. The clay was added over a 15 minute period with vigorous agitation.

The following is a typical chemical analysis of a HYDRITE kaolinite:

Aluminium oxide	38.38	Calcium oxide	0.05
Silicon dioxide	45.30	Magnesium oxide	0.25
Ignition loss at 950°C	13.97	Titanium oxide	1.44
Iron oxide	0.30		

HYDRITE UF kaolinite, the finest kaolinite available, is further identified as follows:

Median particle size (microns)	0.20
Brightness(G.E.% of MgO)	82.0—85.0
pH	4.2—5.2
325 Mesh (0.044mm) Residue Max. (%)	0.20
Oil Adsorption %	47
Aqueous Viscosity	0.4 Pa.s (400 cps)

(58% solids, 0.5% sodium herametaphosphate on weight of kaolinite. Measured at 10 R.P.M. on Brookfield Viscometer.)

2. To the clay slurry was added 2.8 kg of Catapul Alumina and the mixture was stirred for 15 minutes. Catapul Alumina is identified as alpha monohydrate (Boehmite) as comprising:

Al <sub>2</sub> O <sub>3</sub>	74.2%	Na <sub>2</sub> O	0.004%
Ignition loss	25.8%	SiO <sub>2</sub>	0.003%
Carbon	0.36%	Sulfur	Nil
Fe <sub>2</sub> O <sub>3</sub>	0.005%	TiO <sub>2</sub>	0.120%

After calcination for 3 hours at 482°C (900°F) crystal structure is gamma alumina.

3. Over a three minute period, 150 ml of concentrated H<sub>2</sub>SO<sub>4</sub> was dripped into the stirred slurry. Eleven

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litres of H<sub>2</sub>O was added during a 15 minute period with stirring. The resultant slurry had a pH of 3 and a viscosity of 1.1 Pa.s (1100 cps) at 54°C (130°F).

4. The clay slurry was spray dried at an inlet and outlet air temperature of 124°C (255°F) and 399°C (750°F) respectively.

5. The microspherical solid from the spray drier was placed in a furnace at room temperature and heated to 1010°C (1850°F) in 3 hours. Heating was stopped and the material was slowly cooled to 149°C (300°F) over a 16 hour period.

6. This procedure yielded a fluidizable clay adsorbent material with 13wt% alumina binder. The surface area was 31 m<sup>2</sup>/g and the pore volume was 0.51 cc/g with medium pore radius of 56 nm (560Å).

### Example 2

#### Preparation of Clay Adsorbent with Silica Binder B600-142-1C

1. Into a homogenizing mixer (Kady Mill) was placed 17 l of tap water and 160 g of sodium pyrophosphate hydrate. With stirring, 16 kg of HYDRITE UF Kaolinite Clay was added over a 20 minute period.

2. To this stirred clay slurry was added 2 l of "N" Brand sodium metasilicate during a 5 minute period.

3. The resultant thick clay slurry was diluted with 16 l of tap water while mixing at 52°C (125°F).

4. The slurry was spray dried at 399°C (750°F) inlet air temperature and 121°C (250°F) outlet temperature.

5. The microspherical solid was then placed in a furnace at 27°C (80°F) and heated to 1038°C (1900°F) during the next three hours. Heating was stopped and the material cooled to 149°C (300°F) over a 16 hour period.

6. The fluidizable clay adsorbent contained 5wt% silica binder and 93wt% clay. The pore volume of the material was 0.41 cc/g while the surface area was 14 m<sup>2</sup>/g.

### Example 3

#### Preparation of Clay Adsorbent with Carbon Black

1. Into a homogenizing mixer (Kady Mill) was added 24 l of water and 350 g (0.35 kg) of lignin (CBO<sub>3</sub>-Carbon Black) as a dispersant. This mixture was agitated to thoroughly mix the dispersant before adding 7 kg of carbon black (United N219L) particle diameter 28 nm (280Å), to the Kady Mill mixture to get the carbon black dispersed in the water. The mixture was agitated for 15 minutes. Then 32.4 kg of HYDRITE UF Clay was added to the mixture in four portions over a mixture period of about 15 minutes. Following the clay addition, the mixture was further agitated for another 15 minutes to form a homogenous slurry.

2. The homogenous slurry was then spray dried at an inlet temperature of about 124°C (255°F) and an outlet temperature of about 399°C (750°F).

The product of the spray drying operation comprising microspherical solids is then calcined by heating in a furnace gradually to an elevated temperature up to 1010°C (1850°F) in about 3 hours. The calcined material is then slowly cooled to about 149°C (300°F) over an extended period of up to 16 hours. During calcination of the spray dried material, the carbon black in the solids comprising about 20% carbon black is burned out to provide a high pore volume clay particle of at least 0.5 cc/g.

This invention is especially effective for the treatment of reduced crudes, residual oils, topped crudes and other high boiling carbo-metallic containing hydrocarbon feed comprising relatively high vanadium to nickel ratios and high Conradson carbon values. The hydrocarbon fractions or high boiling oil feeds having a high level of metal contaminants and Conradson carbon producing components values are preferably initially contacted in a reaction zone such as riser reactor zone with a diluent material such as water, steam or a combination thereof to provide temperature control and hydrocarbon partial pressure reduction upon contact with the solid sorbent particulate material of this invention providing surface area and high pore volume herein defined at temperatures above about 482°C (900°F). Residence time of the oil feed charged will vary with boiling range and generally is below 5 seconds. Preferably the residence time for high boiling residual oils and reduced crude will be in the range of 0.5 to 3 seconds. The preferred high pore volume sorbent material according to this invention of fluidizable particle size is a spray dried composition in the form of microspherical particles generally in the size range of 20 to 150 microns and preferably between about 40 and about 80 microns.

Representative feedstocks contemplated for demetallizing treatment according to this invention include any oil fraction comprising undesired metal levels for catalytic cracking thereof such as whole crude oils, atmospheric gas oils, heavy vacuum gas oils and heavy fractions of crude oils included with topped crude, reduced crude, vacuum fractionator bottoms, other fractions containing heavy residua, coal-derived oils, shale oils, waxes, untreated or deasphalted residua and blends of such fractions with gas oils and the like. Thus, a relatively small amount (5 to 25%) of a demetallized reduced crude or other heavy hydrocarbon feedstock may be mixed with atmospheric or vacuum gas oils to provide a feedstock for catalytic conversion. A high vanadium containing oil feed for FCC processing is one having more than 0.1 ppm vanadium up to about 5.0 ppm. A high vanadium feed for RCC processing on the other hand is one having more than 1.0 ppm vanadium and usually more than about 5.0 ppm.

A carbo-metallic feed to be visbroken and demetallized according to this invention is one in a specific example boiling above 343°C (650°F) having a heavy metal content of at least about 4 ppm nickel

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equivalents, (ppm total metals being converted to nickel equivalents by the formula:  $Ni\ Eq. = Ni + V/4.8 + Fe/7.1 + Cu/1.23$ ), a Conradson carbon residue value greater than about 1.0, and a vanadium content of at least 1.0 ppm. The feedstocks for which the method of this invention is particularly useful will have a heavy metal content of at least about 5 ppm of nickel equivalents, and a vanadium content of at least 2.0.

5 The greater the heavy metal content, the greater the proportion of vanadium in that heavy metal content, and the higher the Conradson carbon content of the material boiling above 552°C (1025°F), the more advantageous is the increased high pore volume solid sorbent material of this invention with and without metal additives and use thereof as herein provided.

A particularly preferred hydrocarbon feedstock for demetallization and upgrading treatment by the method of the invention includes a fraction of crude oil comprising 70% or more of a +343°C (650°F) material having a resid fraction greater than 20% boiling above 552°C (1025°F) at atmospheric pressure, a metals content of greater than 5.5 ppm nickel equivalents of which at least 5 ppm is vanadium, a vanadium to nickel atomic ratio of at least 1.0, and a Conradson carbon residue greater than 4.0. This identified residual oil feed may also have a hydrogen to carbon ratio of less than about 1.8 and coke precursors in an amount sufficient to yield about 4 to 14% or greater coke by weight based on fresh feed.

Sodium vanadates have low melting points and may also flow and cause particle coalescence in a similar manner to vanadium pentoxide. Although it is desirable to maintain low sodium levels in the feed in order to minimize coalescence, as well as to avoid sodium vanadates on the sorbent, the metal additives of the present invention are also effective in forming compounds, alloys or complexes with sodium vanadates so as to prevent these compounds from melting and flowing.

With respect to the tolerance levels of heavy metals on the high pore volume sorbent itself, such metals may accumulate on the sorbent to levels in the range of from about 3,000 to 70,000 ppm of total metals, and more usually to high levels in the range of 10,000 to 30,000 ppm, of which a large proportion thereof is vanadium.

25 The demetallizing decarbonizing and hydrothermal visbreaking process of the invention will produce large amounts of coke initially deposited as hydrocarbonaceous material in amounts up to 14% by weight based on the weight of fresh feed. This carbonaceous material deposit often referred to as coke is laid down on the sorbent particle material in amounts in the range of about 0.3 to 3% by weight of sorbent, depending upon the sorbent to oil ratio (weight of sorbent to weight of feedstock) employed in the demetallizing and decarbonizing zone such as a riser contact zone. The severity of the thermal visbreaking operation affected in the presence of steam and/or water should be sufficiently low however, so that thermal conversion of the feed to gasoline and lighter products is kept relatively low and preferably below 20% by volume. Even at these low levels of conversion severity, whether thermal and/or some catalytic, the hydrothermal visbreaking process is effective for reducing the Conradson carbon value of the feed at least 20%, preferably in the range of 40 to 70%, and reduce the heavy metals content of the residual oil feed by at least 50% and preferably in the range of 75 to 90%.

The high boiling feed to be demetallized and decarbonized by the sorbent material of this invention is introduced in one embodiment into a bottom portion of a riser reaction zone under conditions to form a suspension with hot sorbent particulate material separately introduced and provided in accordance with this invention. Steam, naphtha, water, flue gas and/or some other suitable diluent material such as nitrogen or carbon dioxide is introduced separately to the riser or along with the high boiling feed to aid atomized and vaporized contact of the feed with the solids sorbent particulate material and form a fluidizable suspension therewith. These diluents may be from a fresh source or may be recycled as purity permits from a process stream of a refinery operation in association therewith.

45 Where recycle diluent streams are used, they may contain hydrogen sulfide and other sulfur compounds which may help passivate adverse catalytic activity by heavy metals accumulating on the sorbent material. It is to be understood that water may be introduced either as a liquid or as steam. In the interest of energy conservation, the water is preferably introduced as a liquid.

Water is added primarily as a source of vapor for dispersing the feed in intimate contact with sorbent particles, for reducing the oil partial pressure and for accelerating the feed and sorbent formed suspension to achieve the vapor velocity and hydrocarbon residence time desired in a riser contact zone.

As the high boiling feed travels up the riser under visbreaking conditions herein specified, it forms four products known in the industry as dry gas, wet gas, naphtha and a high boiling demetallized and decarbonized oil product suitable for use as feed to a reduced crude or cracking operation or in some cases the feed may be suitable charged to a conventional FCC operation. At the upper end or discharge end of the riser, the sorbent particles are preferably quickly separated from product vapors to minimize thermal cracking and catalytic to the extent present. The solid sorbent particles which contain metals and carbonaceous deposits formed in the riser contact zone are sent to a regenerator operation to burn off the carbonaceous deposits. The separated product vapors are normally sent to a fractionator for separation to provide the four basic products above identified.

60 The preferred conditions for contacting feed and sorbent in the riser are summarized in Table A, in which the abbreviations used have the following meanings: "Temp" for temperature, "Dil" for diluent, "pp" for partial pressure, "wt" for weight, "V" for vapor, "Res" for residence, "S/O" for sorbent to oil ratios, "sorb" for sorbent, "bbl" for barrel, "MAT" for microactivity by the MAT test using a standard Davison feedstock, "Vel" for velocity, "Cge" for charge, "d" for density and "Reg" for regenerated.

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TABLE A - Sorbent Riser Conditions

	Parameter	Broad Operating Range	Preferred Range
5	Feed Temp	204-427°C (400-800°F)	204-343°C (400-650°F)
	Steam Temp	93-260°C (200-500°F)	149-204°C (300-400°F)
10	Reg Sorb Temp	482-816°C (900-1500°F)	621-760°C (1150-1400°F)
	Riser Exit Temp	427-760°C (800-1400°F)	482-593°C (900-1100°F)
	Pressure	0-690 kPa (0-100 psia)	69-345 kPa (10-50 psia)
15	Water/Feed by wt	0.01-0.30	0.04-0.15
	Dil pp/Feed pp	0.25-3.0	1.0-2.5
	Dil wt/Feed wt	≤0.4	0.1-0.3
20	V Res Time	0.1-5 sec	0.5-3 sec
	S/O wt	3-18	5-12
	Sorb Feed	0.3-11 kg/m <sup>3</sup> (0.1-4 lbs/bbl)	0.6-5.5 kg/m <sup>3</sup> (0.2-2 lbs/bbl)
25	Inlet Sorb MAT	<25 vol%	<20 vol%
	Outlet Sorb MAT	<20 vol%	<10 vol%
	V Vel	7.5-27 m/sec (25-90 ft/sec)	9-18 m/sec (30-60 ft/sec)
30	V Vel/Sorb Vel	≥1.0	1.2-2.0
	Dil Cge Vel	1.5-27 m/sec (5-90 ft/sec)	3-15 m/sec (10-50 ft/sec)
35	Oil Cge Vel	0.3-15 m/sec (1-50 ft/sec)	1.5-15 m/sec (5-50 ft/sec)
	Inlet Sorb d	16-144 kg/m <sup>3</sup> (1-9 lbs/ft <sup>3</sup> )	32-96 kg/m <sup>3</sup> (2-6 lbs/ft <sup>3</sup> )
40	Outlet Sorb d	16-96 kg/m <sup>3</sup> (1-6 lbs/ft <sup>3</sup> )	16-48 kg/m <sup>3</sup> (1-3 lbs/ft <sup>3</sup> )

45 In treating carbo-metallic containing oil feedstocks in accordance with the present invention, the regenerating gas may be any gas which can provide oxygen to convert carbonaceous deposits to carbon oxides. The amount of oxygen in the regeneration gas required per kilogram (pound) of coke for combustion depends upon the carbon dioxide to carbon monoxide ratio desired in the effluent flue gases and upon the amount of other oxidizable materials present in the coke, such as hydrogen, sulfur, nitrogen and other elements capable of forming gaseous oxides at regenerator temperature conditions.

50 The regenerator for the solid sorbent particulate material is operated at temperatures in the range 538 to 871°C (1000 to 1600°F), preferably 621 to 816°C (1150 to 1500°F) to achieve combustion of carbonaceous deposits while keeping sorbent temperatures below that at which significant sorbent degradation can occur. Temperature control in the regeneration zone is exercised by regulating the feed rate of the oxidizing gas employed, and the feed and withdrawal rates of sorbent to and from the regenerator. These parameters may be regulated such that the ratio of carbon dioxide to carbon monoxide in the effluent gases is less than about 4.0 and preferably less than about 1.5 so that the flue gas is CO rich. In addition, water, either as liquid or steam, may be added to the regenerator to help control temperatures therein and to influence CO production in preference to carbon dioxide. On the other hand, only a portion of the separated sorbent material may be passed to the regenerator with the remaining portion thereof recycled directly to the riser reactor following high temperature stripping in admixture with regenerated particulate material passed to the riser.

60 The regenerator carbonaceous material combustion reaction is carried out so that the amount of carbon remaining on regenerated sorbent is less than about 0.50% and preferably less than about 0.25% on a substantially moisture-free weight basis.



When a metal additive is provided with the solid sorbent material it is introduced as an aqueous or hydrocarbon solution or as a volatile compound during the processing cycle. It may be added at any point of sorbent travel in the processing system. This would include, but not be limited to, the addition of the metal additive to a bottom portion of the riser reactor along the riser reactor length to a dense bed of solids in a collector vessel about the upper end of the riser, to the strippers provided in the system, to the regenerator air inlet, separately to the regenerator bed of solids, and to the regenerated sorbent standpipe.

The high pore volume sorbent material of this invention with or without the metal additive is charged for use in a hydrothermal visbreaking operation as herein described in the absence of added molecular hydrogen.

#### Brief Description of the Drawings

Figure 1 is a schematic diagram in elevation of an arrangement of an apparatus for carrying out the visbreaking-demetalizing process of the invention.

Referring now to Figure 1 by way of example, sorbent particle circulation and operating parameters are brought up to process conditions by methods well-known to those skilled in the art. The high temperature sorbent material of regeneration at a temperature in the range 621 to 760°C (1150 to 1400°F) contacts the high boiling residual oil feed charged in a bottom or upper portion of the riser reactor depending on contact time desired therein. A fluidizing gas may initially suspend the sorbent solids before contact with charged oil feed. The oil feed is dispersed with a diluent, steam, water, flue gas or a combination thereof injected at point 2. Water and/or naphtha may be initially injected as required at point 3 to suspend solids and aid in feed vaporization, sorbent fluidization and controlling contact time of a formed suspension of solids and gasiform material in a bottom initial portion of riser 4. The sorbent and gasiform material comprising vaporous and unvaporized high boiling hydrocarbons travel up through riser 4 for a contact time restricted to within the range of 0.1 to 5 seconds, preferably 0.5 to 3 seconds or whatever is required to achieve desired demetallization and decoking in the absence of substantial thermal and/or metals conversion of charged oil. The sorbent comprising hydrocarbonaceous and metal deposits is rapidly separated from vaporous hydrocarbons at the riser outlet 6 at a temperature in the range 482 to 593°C (900 to 1100°F). A gasiform material comprising vaporous hydrocarbons, steam, wet and dry gaseous materials pass through one or more cyclones such as a multi-stage cyclone represented by cyclone 7 wherein entrained sorbent particles are separated and recovered by diplegs provided with the gasiform material comprising hydrocarbon vapors being sent to a fractionator (not shown) via transfer line 8. The sorbent particle material comprising hydrocarbonaceous material decomposition products of the feed components boiling above 552°C (1025°F) and metal deposits are collected as a downwardly flowing fluid bed of solids countercurrent to stripping gas introduced by 21 to stripper 10 for further removal of any entrained or formed hydrocarbon vapors before all or a portion thereof is passed to a regenerator vessel 11 to form a dense fluidized bed of solid 12 to be regenerated. An oxygen containing gas such as air with or without oxygen enrichment or carbon dioxide mixed with an oxygen containing gas is admitted to the dense fluid bed of solids 12 in regeneration vessel 11 maintained under conditions to burn carbonaceous deposits and form carbon oxides and other combustion products as herein identified. The resulting flue gas which may or may not be CO rich, depending on the operation selected, is processed through cyclones 2 and exits from regenerator vessel 11 via line 23. The regenerated solid sorbent particulate containing less than 0.5 weight percent carbon is transferred to stripper 15 for removal as required of any entrained combustible gases and before transfer to a bottom portion of the riser via line 16 to repeat the cycle. The regenerated solids may also be stripped in the withdrawal well in the upper portion of bed 12 by means not shown.

In one embodiment of this invention, a portion of the recovered solid sorbent material contaminated with hydrocarbonaceous material and metal deposits may bypass the regenerator vessel through conduit 42 for recycle to the riser reactor following high temperature stripping thereof in admixture with hot freshly regenerated catalyst. This method of operation may be relied upon to reduce the regenerated catalyst temperature as well as effect further high temperature visbreaking of deposited hydrocarbonaceous materials. It is even contemplated removing some carbonaceous deposits by reacting with a CO<sub>2</sub> rich gas in such a zone between the regenerator and riser reactor.

The bypass of the regenerator as above identified may be used to reduce vanadium oxidation, to increase thermal decomposition of liquid hydrocarbons as well as reduce regeneration temperatures by reducing the amount of carbonaceous deposits charged to the regenerator. Other advantages will be apparent to those skilled in the art.

In a particular embodiment it is desirable in regeneration of the sorbent material to effect combustion of carbonaceous deposits sufficient to provide a solid sorbent particle containing less than 0.2 weight percent carbon and preferably less than 0.10 weight percent carbon.

At such time that the metal level on the sorbent becomes intolerably high such that sorbent effectiveness drops to an undesired low level or desired equilibrium conditions is exceeded, additional sorbent material can be added to replace deactivated sorbent withdrawn by conduits 42 and 43. Points 18 and 19 can be utilized to add virgin sorbents with or without metal additives. In the case of a virgin sorbent prepared without additive, the metal additive as an aqueous solution or as an organo-metallic compound in aqueous or hydrocarbon solvents can be added at points 18 and 19, as well as at addition points 2 and 3 on feed line 1, addition points 20 and 20<sup>2</sup> in riser 4 and addition point near the bottom of vessel 5 may also be

employed for this purpose. The addition of the metal additive is not limited to these locations, but can be introduced at any point in the oil/sorbent processing cycle. Inlet conduits 20 and 20<sup>1</sup> are also for the purpose of adding feed to be demetallized and decarbonized to obtain different contact times in the riser.

The sorbent materials which may be employed according to this invention include kaolinite clay solids of little or no catalytic activity and may include some catalytically spent cracking catalysts. However, clays prepared in accordance with this invention which are considered relatively inert because of low activity catalytically below about 20 MATS as measured by the ASTM Test Method No. D3907-80 are preferred.

More particularly, in accordance with this invention, the thermal visbreaking operation is initiated with freshly prepared sorbent particle clay material of at least 0.4 cc/g pore volume and a solids to oil ratio so that only about 1/4 up to about 2/3 of the solids pore volume will be initially filled with heavy oil feed comprising tacky asphaltic material to minimize coalescence of particles as discussed above and to effect demetallization and decarbonization of the heavy oil feed.

The relationships herein identified with respect to pore volume, pore openings, zeolite content, catalyst to oil ratio to restrict pore filling, temperature and contact time are not only particularly desirable but a critical relationship in operating, significantly contributing to the efficiency and thus economics of the thermal visbreaking operation of this invention.

The regenerator vessel as diagrammatically illustrated in Figure 1 is a simple one zone dense fluid bed of solids in a single regeneration zone. The regeneration operation of this invention is not necessarily limited to the single stage regeneration operation shown but can comprise two or more separate regeneration zones in stacked or side by side relationship, with internal and/or external circulation transfer lines from zone to zone. Some multistage regenerator arrangements known in the prior art may be used with advantage.

Although the visbreaking process of this invention is preferably conducted in a riser reactor because of desired restricted temperature contact time parameters, other types of reactors may be employed with either upward or downward solid flow. Thus the thermal visbreaking operation may be conducted with a type of downflowing moving bed of sorbent which moves in concurrent relation to liquid (unvaporized) or partially vaporized feedstock under contact conditions of pressure, temperature and weight hourly space velocity as particularly defined herein.

### 30 Claims

1. A method of visbreaking reduced crudes and crude oils high in metal contamination and Conradson carbon producing components, prior to catalytic cracking of the reduced crude or crude oil, which comprises contacting the reduced crude or crude oil in a visbreaking reaction zone at a temperature above about 486°C (900°F) with a sorbent material having little or no catalytic cracking activity and comprising a porous microspherical kaolinite clay having a particle size in the range 20 to 150 microns (μm) and a pore volume of at least 0.4 cc/g and obtained by slurrying a kaolinite clay in water, said slurry optionally containing a binder for the clay particles, a thermally decomposable, dispersant pore forming material, and optionally a metallic promoter for the immobilization on the sorbent of vanadia resulting from vanadium present in the reduced crude or crude oil, spray drying the slurry to form microspherical particles comprising the kaolinite clay and, if present in the slurry, the pore forming material, binder and promoter, calcining the microspherical particles at an elevated temperature in the range 548 to 1148°C (1000 to 2100°F) and for a period of up to about 3 hours, and thereafter slowly cooling the particles to a temperature of about 149°C (300°F) over a period of about 16 hours, and optionally thereafter impregnating the particles with said metallic promoter, if not already present in the particles, and thereafter separating the treated reduced crude or crude oil from the spent sorbent, characterised in that the pore volume of the sorbent particles fed to the visbreaking zone, whether as fresh or regenerated particles, is such as to provide a substantial excess total pore volume relative to the total volume of those components of the reduced crude feed fed to the visbreaking zone that remain liquid and non-vaporised at the visbreaking temperature, that excess total pore volume providing in the reaction zone an initial volume ratio, i.e. the ratio of the total pore volume of sorbent particles as fed to the visbreaking zone relative to the calculated volume of those components of the feed that remain liquid and non-vaporised at the visbreaking temperature, in the range 4:1 to 3:2.

2. A method according to claim 1, characterised in that the slurry used to prepare the sorbent particles contains a binder for the kaolinite clay.

3. A method according to claim 2, characterised in that the binder used is silica, alumina, calcium oxide, boria, magnesia or titania.

4. A method according to claim 3, characterised in that the binder used is alpha alumina monohydrate.

5. A method according to any one of claims 1 to 4, characterised in that the slurry used to prepare the sorbent particles contains a thermally decomposable, dispersant pore forming material, which material decomposes during the calcination step thereby to result in pores of increased size in the calcined product.

6. A method according to claim 5, characterised in that the pore forming material used is sugar, carbon black, a thermally decomposable material other than sugar, or a thermally decomposable inorganic salt.

7. A method according to any one of claims 1 to 6, characterised in that the sorbent has a pore volume in the range 0.5 to 0.8 cc/g.

8. A method according to any one of claims 1 to 7, characterised in that the sorbent particles contain a metallic promoter for the immobilization on the sorbent of vanadia resulting from vanadium contamination present in the reduced crude or crude oil feed.

9. A method according to claim 8, characterised in that the promoter is a compound or mixture of compounds containing one or more of the following metals: magnesium, calcium, barium, titanium, zirconium, manganese, indium or lanthanum.

10. A method according to any one of claims 1 to 9, characterised in that the spray dried, microspherical particles of kaolinite clay, optionally containing the binder, pore forming material and promoter, are calcined for up to 3 hours at a temperature in the range 871 to 1148°C (160 to 2100°F).

11. A method according to any one of claims 1 to 10, characterised in that the reduced crude or crude oil feed is contacted with the sorbent particles in a riser zone in the presence of a lift gas comprising steam, naphtha, flue gas, carbon dioxide or nitrogen or a mixture of two or more thereof, and at a contact time of less than 5 seconds.

12. A method according to claim 11, characterised in that the contact time is from 0.5 to 3 seconds.

13. A method according to claim 11 or 12, characterised in that the spent sorbent particles recovered at the top of the riser are passed to a sorbent regeneration zone wherein they are regenerated by contact with a hot oxygen containing regeneration gas, and thereafter recycled to the bottom of the riser.

14. A method according to claim 13, characterised in that the regenerated sorbent particles are recycled to the riser at a temperature in the range 621 to 760°C (1150 to 1400°F) and the riser operates at an exit temperature in the range 482 to 593°C (900 to 1100°F).

## Patentansprüche

1. Verfahren zur Herabminderung der Viskosität von Reduktionsölen und Rohölen mit einem hohen Gehalt an Metallverunreinigung und Conradson Kohlenstoff produzierenden Komponenten vor dem katalytischen Cracken des Reduktionsöls oder Rohöls, wobei man das Reduktionsöl oder Rohöl in einer Zone zur Herabminderung der Viskosität bei einer Temperatur von größer als etwa 486°C (900°F) mit einem Sorptionsmaterial in Kontakt bringt, das geringe oder keine katalytische Crackaktivität besitzt und einen porösen mikrosphärischen Kaolinitton mit einer Teilchengröße im Bereich von 20 bis 150 Mikrometern ( $\mu\text{m}$ ) und einem Porenvolumen von mindestens 0,4 cc/g umfaßt und das erhalten wurde durch Aufschlännen eines Kaolinittons in Wasser, wobei die Aufschlännung gegebenenfalls ein Bindemittel für die Tonteilchen, ein thermisch zersetzbares, dispergierbares porenbildendes Material und gegebenenfalls einen metallischen Promotor zur Immobilisierung von Vanadiumoxid aus dem Vanadium, das in Reduktionsöl oder Rohöl anwesend ist, auf dem Sorptionsmittel enthält, durch Sprühtrocknen der Aufschlännung zur Bildung mikrosphärischer Teilchen, die den Kaolinitton und, sofern in der Aufschlännung anwesend, das porenbildende Material, das Bindemittel und den Promotor enthalten, durch Kalzinieren der mikrosphärischen Teilchen bei einer erhöhten Temperatur im Bereich von 548 bis 1148°C (1000 bis 2100°F) und für eine Zeitspanne bis zu etwa 3 Stunden und durch anschließendes langsames Abkühlen der Teilchen auf eine Temperatur von etwa 149°C (300°F) über eine Zeitspanne von etwa 16 Stunden und gegebenenfalls durch anschließendes Imprägnieren der Teilchen mit dem genannten metallischen Promotor, sofern er nicht schon in den Teilchen vorhanden ist, und wobei man anschließend das behandelte Reduktionsöl oder Rohöl von dem verbrauchten Sorptionsmittel abtrennt, dadurch gekennzeichnet, daß das Porenvolumen der Sorptionsmittelteilchen, die in die Zone zur Herabminderung der Viskosität, sei es als frische oder regenerierte Teilchen, eingespeist werden, so ist, daß ein wesentlicher Überschuß des Gesamtporenvolumens, gegenüber dem Gesamtvolumen der Komponenten der Reduktionsölbeschickung, die in die Zone zur Herabsetzung der Viskosität eingespeist wird, die flüssig und unverdampft bei der Temperatur zur Herabminderung der Viskosität bleiben, erhalten wird, daß das überschüssige Gesamtporenvolumen in der Reaktionszone ein anfängliches Volumenverhältnis, d.h. das Verhältnis des Gesamtporenvolumens der Sorptionsmittelteilchen, wie sie in die Zone zur Herabminderung der Viskosität eingespeist werden, zu dem berechneten Volumen der Komponenten der Beschickung, die bei der Temperatur zur Herabminderung der Viskosität flüssig und unverdampft bleiben, im Bereich von 4:1 bis 3:2 ergibt.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Aufschlännung, die zur Herstellung der Sorptionsmittelteilchen verwendet wird, ein Bindemittel für den Kaolinitton enthält.

3. Verfahren nach Anspruch 2, dadurch gekennzeichnet, daß das verwendete Bindemittel Siliciumdioxid, Aluminiumoxid, Calciumoxid, Boroxid, Magnesiumoxid oder Titandioxid ist.

4. Verfahren nach Anspruch 3, dadurch gekennzeichnet, daß das verwendete Bindemittel  $\alpha$ -Aluminiumoxidmonohydrat ist.

5. Verfahren nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß die Aufschlännung, die zur Herstellung der Sorptionsmittelteilchen verwendet wird, ein thermisch zersetzbares, dispergierbares porenbildendes Material enthält, das sich während der Kalzinierungsstufe zersetzt, wobei Poren mit vergrößerter Größe im Kalzinierungsprodukt entstehen.

6. Verfahren nach Anspruch 5, dadurch gekennzeichnet, daß das verwendete porenbildende Material Zucker, Ruß, ein thermisch zersetzbares Material außer Zucker oder ein thermisch zersetzbares anorganisches Salz ist.

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7. Verfahren nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß das Sorptionsmittel ein Porenvolumen im Bereich von 0,5 bis 0,8 cc/g besitzt.

8. Verfahren nach einem der Ansprüche 1 bis 7, dadurch gekennzeichnet, daß die Sorptionsmittelteilchen einen metallischen Promotor zur Immobilisierung von Vanadiumoxid aus Vanadiumverunreinigung, die in dem eingespeisten Reduktionsöl oder Rohöl vorhanden ist, auf dem Sorptionsmittel enthält.

9. Verfahren nach Anspruch 8, dadurch gekennzeichnet, daß der Promotor eine Verbindung oder ein Gemisch aus Verbindungen ist, die eine oder mehrere der folgenden Metalle: Magnesium, Calcium, Barium, Titan, Zirkon, Mangan, Indium oder Lanthan enthalten.

10. Verfahren nach einem der Ansprüche 1 bis 9, dadurch gekennzeichnet, daß die sprühgetrockneten mikrosphärischen Teilchen aus Kaolinitton, die gegebenenfalls das Bindemittel, das porenbildende Material und den Promotor enthalten, bis zu 3 Stunden bei einer Temperatur im Bereich von 871 bis 1148°C (1600 bis 2100°F) kalziniert werden.

11. Verfahren nach einem der Ansprüche 1 bis 10, dadurch gekennzeichnet, daß das eingespeiste Reduktionsöl oder Rohöl mit den Sorptionsmittelteilchen in einer Steigzone in Gegenwart eines Fördergas aus Dampf, Naphtha, Abgas, Kohlendioxid oder Stickstoff oder einem binären oder mehrfachen Gemisch davon und bei einer Kontaktzeit von weniger als 5 Sekunden in Kontakt gebracht wird.

12. Verfahren nach Anspruch 11, dadurch gekennzeichnet, daß die Kontaktzeit 0,5 bis 3 Sekunden beträgt.

13. Verfahren nach Anspruch 11 oder 12, dadurch gekennzeichnet, daß die verbrauchten Sorptionsmittelteilchen, die am oberen Ende der Steigzone wiedergewonnen werden, in eine Zone zur Regeneration des Sorptionsmittels geleitet werden, worin sie durch Kontakt mit einem heißen sauerstoffhaltigen Regenerationsgas regeneriert werden und anschließend wieder an das untere Ende der Steigzone zurückgeführt werden.

14. Verfahren nach Anspruch 13, dadurch gekennzeichnet, daß die regenerierten Sorptionsmittelteilchen in die Steigzone bei einer Temperatur im Bereich von 621 bis 760°C (1150 bis 1400°F) zurückgeführt werden und daß die Steigzone bei einer Ausgangstemperatur im Bereich von 482 bis 593°C (900 bis 1100°F) betrieben wird.

### Revendications

1. Un procédé de viscoréduction de bruts réduits et d'huile brutes réduites, à niveau élevé de contamination par les métaux et à teneur élevée en composants produisant du carbone Conradson, avant le craquage catalytique du brut réduit ou de l'huile brute, qui comprend la mise en contact de brut réduit ou de l'huile brute réduite, dans une zone de réaction de viscoréduction à une température au-dessus d'environ 486°C (900°F), avec une matière sorbante ayant peu ou n'ayant pas d'activité de craquage catalytique et comprenant une argile de type kaolinite, microsphérique, poreuse, ayant une granulométrie dans la plage de 20 à 150 microns (µm) et un volume de pore d'au moins 0,4 cm<sup>3</sup>/g et obtenue par la mise en suspension d'une argile de type kaolinite dans l'eau, ladite suspension contenant facultativement un liant pour les particules d'argile, une matière porogène, dispersante, décomposable par la chaleur, et, facultativement, un promoteur métallique pour l'immobilisation sur le sorbant de l'oxyde de vanadium résultant du vanadium présent dans le brut réduit ou l'huile brute réduite, le séchage par pulvérisation de la suspension pour former des particules microscopiques comprenant l'argile de type kaolinite et, s'ils sont présents dans la suspension, la matière porogène, le liant et le promoteur, la calcination des particules microsphériques à une température élevée dans la plage de 548 à 1148°C (1000 à 2100°F) et pendant une période allant jusqu'à environ 3 heures, puis le refroidissement lent des particules à une température d'environ 149°C (300°F) sur une période d'environ 16 heures, et, facultativement, par la suite, l'imprégnation des particules par ledit promoteur métallique, s'il n'était pas déjà présent dans les particules, puis la séparation du brut réduit traité ou de l'huile brute réduite traitée du sorbant usé, caractérisé par le fait que le volume de pores des particules de sorbant, amenées à la zone de viscoréduction qu'elles se présentent sous la forme de particules fraîches ou de particules régénérées, est tel qu'il crée un volume total de pores en excès sensible par rapport au volume total des composants de la charge de brut réduit amenée à la zone de viscoréduction qui restent liquides et non-vaporisés à la température de viscoréduction, ce volume total de pores en excès créant, dans la zone de réaction, un rapport de volume initial, c'est-à-dire le rapport du volume total de pores des particules de sorbant telles qu'amenées à la zone de viscoréduction, au volume calculé des composants de la charge qui restent liquides et non-vaporisés à la température de viscoréduction, dans la plage 4:1 à 3:2.

2. Un procédé selon la revendication 1, caractérisé en ce que la suspension utilisée pour préparer les particules de sorbant contient un liant pour l'argile de type kaolinite.

3. Un procédé selon la revendication 2, caractérisé en ce que le liant utilisé est la silice, l'alumine, l'oxyde de calcium, l'oxyde de bore, la magnésie ou l'oxyde de titane.

4. Un procédé selon la revendication 3, caractérisé en ce que le liant utilisé est l'alumine alphas-monohydratée.

5. Un procédé selon l'une quelconque des revendications 1 à 4, caractérisé en ce que la suspension

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utilisée pour préparer les particules de sorbant contient une matière porogène, dispersante, décomposable par la chaleur, laquelle matière se décompose pendant l'étape de calcination, pour conduire ainsi à des pores de dimension accrue dans le produit calciné.

5 6. Un procédé selon la revendication 5, caractérisé en ce que la matière porogène utilisée est le sucre, le noir de carbone une matière décomposable par la chaleur autre que le sucre, ou un sel minéral décomposable par la chaleur.

7. Un procédé selon l'une quelconque des revendications 1 à 6, caractérisé en ce que le sorbant présente un volume de pores dans la plage de 0,5 à 0,8 cm<sup>3</sup>/g.

10 8. Un procédé selon l'une quelconque des revendications 1 à 7, caractérisé en ce que les particules de sorbant contiennent un promoteur métallique pour l'immobilisation sur le sorbant d'oxyde de vanadium résultant de la contamination par le vanadium présent dans la charge de brut réduit ou d'huile brute réduite.

9. Un procédé selon la revendication 8, caractérisé en ce que le promoteur est un composé ou un mélange de composés contenant un ou plusieurs des métaux suivants: magnésium, calcium, baryum, 15 titane, zirconium, manganèse, indium ou lanthane.

10. Un procédé selon l'une quelconque des revendications 1 à 9, caractérisé en ce que les particules microsphériques, séchées par pulvérisation, d'argile de type kaolinite, contenant de façon facultative le liant, la matière porogène et le promoteur, sont calcinées pendant une période allant jusqu'à 3 heures, à une température dans la plage de 871 à 1148°C (160 à 2100°F).

20 11. Un procédé selon l'une quelconque des revendications 1 à 10, caractérisé en ce que la charge de brut réduit ou d'huile brute réduite est mise en contact avec les particules de sorbant dans une zone de colonne montante, en présence d'un gaz élévateur comprenant de la vapeur d'eau, du naphta, du gaz de fumée, du dioxyde de carbone ou de l'azote ou un mélange de deux d'entre eux ou davantage et à un temps de contact de moins de 5 secondes.

25 12. Un procédé selon la revendication 11, caractérisé en ce que le temps de contact va de 0,5 à 3 secondes.

13. Un procédé selon la revendication 11 ou 12, caractérisé en ce que qu'on fait passer les particules de sorbant usé, récupérées à la partie supérieure de la colonne montante, dans une zone de régénération de sorbant, dans laquelle elles sont régénérées par contact avec un gaz de régénération chaud, contenant de 30 l'oxygène, puis recyclées vers la partie inférieure de la colonne montante.

14. Un procédé selon la revendication 13, caractérisé en ce que les particules de sorbant régénéré sont recyclées vers la colonne montante, à une température dans la plage de 621 à 760°C (1150 à 1400°F), et la colonne montante fonctionne à une température de sortie dans la plage de 482 à 593°C (900 à 1100°F).

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FIG. 1

