

[54] **HYDROTREATMENT METHOD FOR A PETROLEUM RESIDUE OR HEAVY OIL WITH A VIEW TO REFINING THEM AND CONVERTING THEM TO LIGHTER FRACTIONS**

4,054,508 10/1977 Milsun ..... 208/210  
4,118,310 10/1978 Frayer et al. .... 208/210  
4,925,554 5/1990 Sato et al. .... 208/210

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**FOREIGN PATENT DOCUMENTS**

0113297 7/1984 European Pat. Off. .  
2124252 7/1983 United Kingdom .

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[57] **ABSTRACT**

[22] Filed: **Apr. 14, 1993**

The invention concerns a hydro treatment method in at least two stages, for a heavy hydrocarbon fraction containing asphaltenes, sulphur impurities and metallic impurities, wherein:

**Related U.S. Application Data**

[63] Continuation of Ser. No. 677,179, Mar. 29, 1991, abandoned.

a) in at least one first stage described as hydrodemetallization, the hydrocarbon charge and hydrogen are passed over a hydrodemetallization catalyst,

**Foreign Application Priority Data**

Mar. 29, 1990 [FR] France ..... 90 04153

b) in at least one subsequent stage described as hydrodesulphurization, the product of stage a) and hydrogen are passed over a hydrodesulphurization catalyst.

[51] Int. Cl.<sup>6</sup> ..... **C10G 23/02**

[52] U.S. Cl. .... **208/210; 208/251 H; 208/211; 208/212**

[58] Field of Search ..... **208/210, 211, 89, 212, 208/251 H**

The invention, in which the hydrodemetallization stage comprises one or more zones each containing hydrodemetallization catalyst operating in a fixed bed, is characterised in that this zone or these zones are preceded by two protective zones arranged in parallel, each containing a fixed bed of a hydrodemetallization catalyst, the two protective zones operating alternately.

[56] **References Cited**

**U.S. PATENT DOCUMENTS**

3,716,479 2/1973 Weisy et al. .... 208/210  
3,809,644 5/1974 Johnson et al. .... 208/210  
3,900,390 8/1975 Adams et al. .... 208/210  
3,901,792 8/1975 Walk et al. .... 208/210  
3,968,026 7/1976 Frayer et al. .... 208/210  
4,053,391 10/1977 Paraskos et al. .... 208/210

**16 Claims, 2 Drawing Sheets**

FIG.1

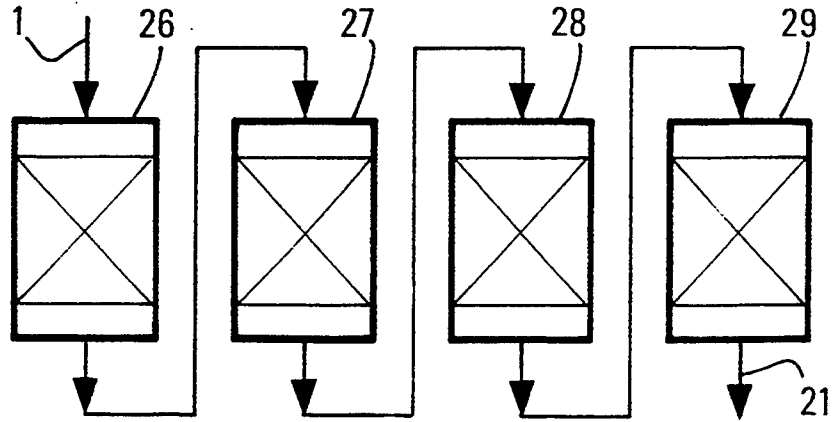


FIG.2

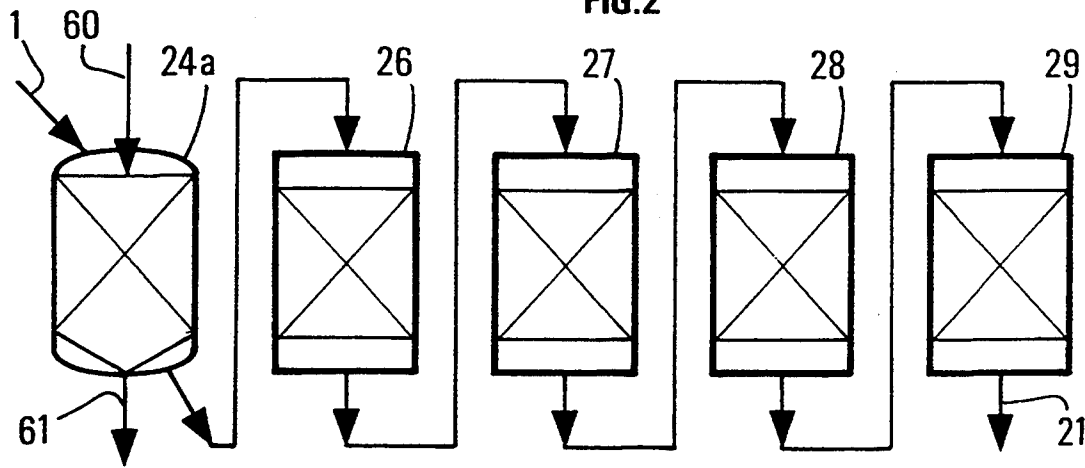


FIG.3

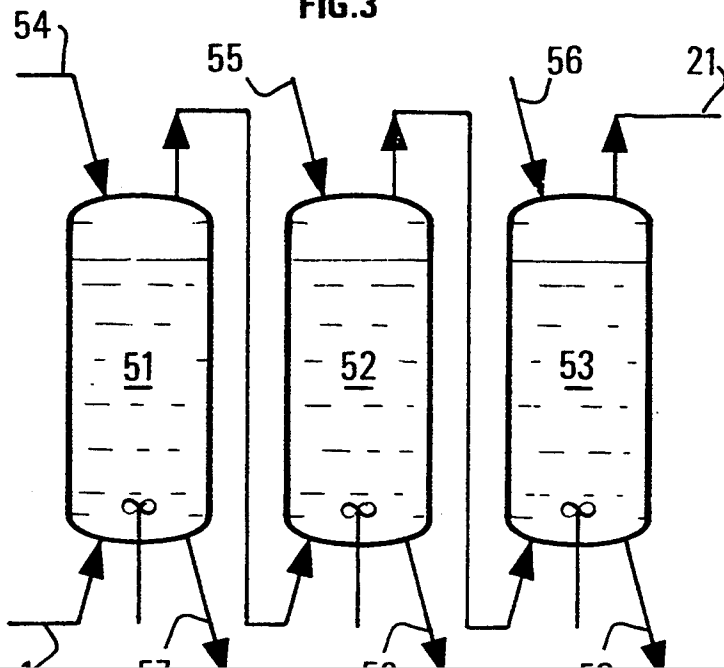


FIG 4

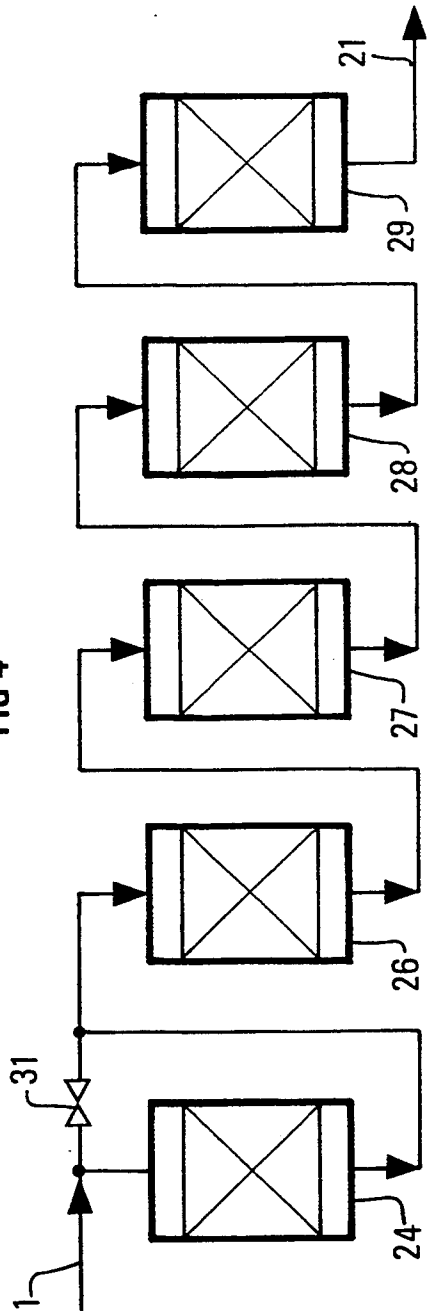
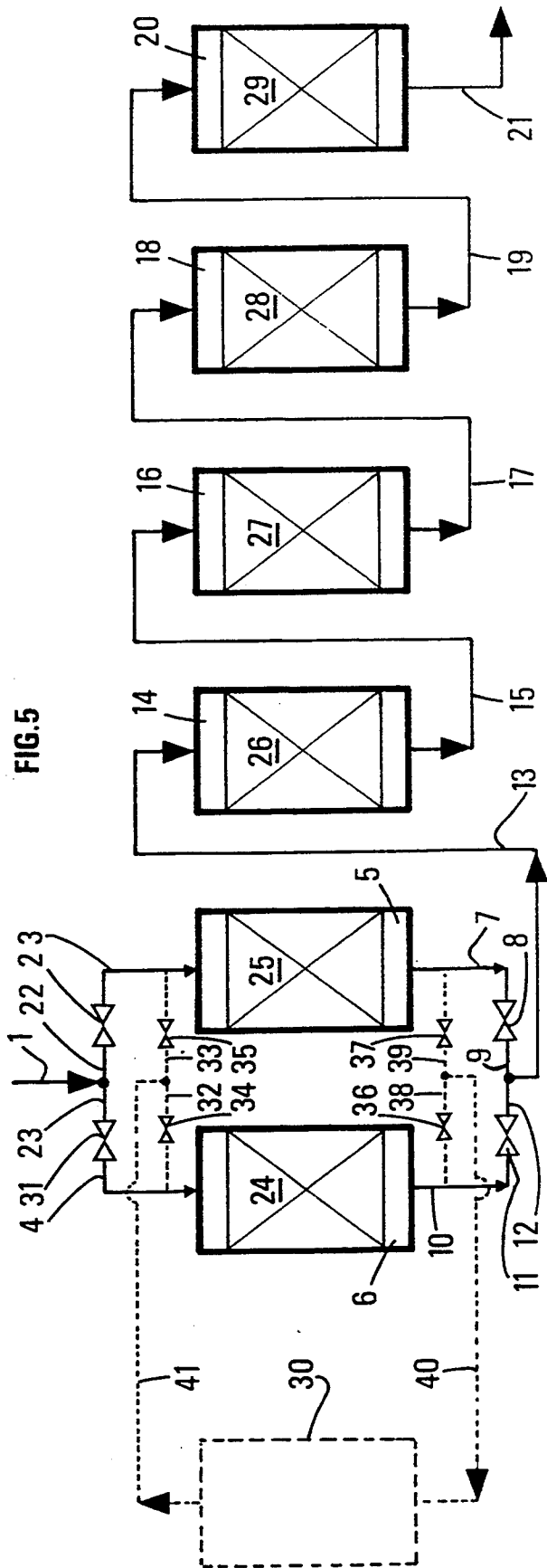


FIG 5



## HYDROTREATMENT METHOD FOR A PETROLEUM RESIDUE OR HEAVY OIL WITH A VIEW TO REFINING THEM AND CONVERTING THEM TO LIGHTER FRACTIONS

This is a continuation of U.S. Ser. No. 07/677,179, filed Mar. 29, 1991, now abandoned.

### BACKGROUND OF THE INVENTION

The invention concerns refining and conversion of heavy liquid hydrocarbon fractions containing inter alia asphaltenes and sulphur and metallic impurities, such as atmospheric residues, vacuum residues, deasphalted oils, pitches, asphalts mixed with an aromatic distillate, coal hydrogenates or heavy oils from any source and particularly from asphaltic sands or oil shales.

These charges which can be treated according to the invention generally contain at least 100 ppm by weight of metals (nickel and/or vanadium), at least 1% by weight of sulphur and at least 2% by weight of asphaltenes.

The object of the catalytic hydrotreatment of these charges is both to refine, i.e. substantially reduce, their content of asphaltenes, metals, sulphur and other impurities, while at the same time improving the hydrogen to carbon ratio (H/C) and converting them more or less partially to lighter cuts. The various effluents thus obtained can act as bases for the production of high quality fuel, gas oil and petrol, or charges for other units such as residue cracking.

The problem posed by the catalytic hydrotreatment of these charges stems from the fact that the impurities are deposited bit by bit on the catalyst in the form of metals and coke, and tend to deactivate and rapidly clog the catalytic system, necessitating a stoppage for its replacement.

Methods of hydrotreatment for this type of charge must therefore be designed to allow the longest possible operating cycle without stopping the unit. The objective is to achieve a one year operating cycle at the minimum, or a minimum of eleven months' continuous operation plus a maximum of one month's stoppage to replace the whole catalytic system.

### PRESENT STATE OF THE ART

There are various existing treatments for this type of charge. They have so far been carried out:

- either in methods with fixed beds of catalyst, for example, the HYVAHL-E process of Institut Français du Pétrole;
- or in methods comprising at least one reactor allowing for quasi continuous replacement of catalyst, such as the HYVAHL-M fluidized bed method of IFP.

### BRIEF DESCRIPTION OF THE DRAWINGS

Various other objects, features, and attendant advantages of the present invention will be more fully appreciated as the same becomes better understood when considered in conjunction with the accompanying drawings, in which like reference characters designate the same or similar parts throughout the several views and wherein:

FIGS. 1-4 are flowsheets or prior art systems for hydrotreating the above-described charges, and

FIG. 5 is a flowsheet illustrating a preferred comprehensive embodiment of the present invention.

### a) FIXED BED METHODS

This method is an improvement to the methods with fixed beds of catalyst. In such methods (see FIG. 1), the charge arriving along line 1 circulates through a plurality of fixed bed reactors arranged in series, the first reactor or reactors 26 or 27 being used chiefly for hydrodemetallization of the charge (so-called HDM stage) and a hydrodesulphurization part, the last reactor or reactors 28 or 29 being used for deep refining and particularly hydrodesulphurization of the charge (so-called HDS stage). The effluents are drawn off from the last HDS reactor 29 through the pipe 21.

Such methods most frequently use specific catalysts adapted to each stage, under mean operating conditions of about 150 to 200 bars pressure and about 370° to 420° C. temperature.

For the HDM stage the ideal catalyst must be capable of treating charges rich in asphaltenes, while at the same time having a high demetallizing power associated with a high capacity for retaining metals and great resistance to coking. Such a catalyst has been developed on a particular macroporous carrier (with a "sea urchin" structure) which gives it the precise properties required at this stage (Patents EP-B-113297 and EP-B-113284):

Demetallization rate of at least 80 to 90% at the HDM stage;

Metal retaining capacity of over 60% relative to the weight of new catalyst, enabling longer operating cycles to be obtained;

Great resistance to coking even at temperatures over 400° C., thus helping to lengthen the cycle, which is often limited by an increase in the pressure drop and loss of activity due to coke production, and enabling the essential part of the heat conversion to be obtained at this stage.

For the HDS stage the ideal catalyst must have strong hydrogenating power so as to carry out deep refining of the products: desulphurization, continued demetallization, lowering of the Conradson carbon and the asphaltene content. Applicants have developed such a catalyst (Patents EP-B-113297 and EP-B-113284) which is particularly well adapted to treating this type of charge.

The disadvantage of this type of catalyst with high hydrogenating power is that it is deactivated rapidly in the presence of metals or coke. Therefore if an appropriate HDM catalyst, capable of functioning at relatively high temperature to carry out the essential part of the conversion and demetallization, is associated with an appropriate HDS catalyst—which, being protected from metals and other impurities by the HDM catalyst, can be operated at a relatively low temperature, thereby encouraging deep hydrogenation and limitation of coking—the global refining performance finally obtained is better than that obtained with a single catalytic system and better than that obtained with a similar HDM/HDS arrangement using an increasing temperature profile, which leads to rapid coking of the HDS catalyst.

The importance of fixed bed methods is that a good refining performance is obtained due to the great catalytic effectiveness of fixed beds. On the other hand, when the charge has more than a certain metal content (e.g. 100 to 150 ppm), in spite of using the best catalytic systems, the performance and above all the operating time of the process is found to become inadequate: the reactors (particularly the first HDM reactor) rapidly

become charged with metals and thus deactivated. Temperatures are increased to compensate for the deactivation, thus encouraging coke formation and an increase in the pressure drop. Moreover the first catalytic bed is known to be liable to clog fairly rapidly due to the asphaltenes and sediments contained in the charge or as a result of operating trouble.

Consequently the unit has to be stopped every 3 to 6 months at the minimum to replace the first catalytic beds which are deactivated or clogged. This operation may take up to 3 weeks, with a corresponding reduction in the operating factor of the unit.

#### b) FLUIDIZED BED OR BOILING BED METHODS

Attempts have been made to deal with these disadvantages of fixed bed arrangements in different ways.

Thus one idea has been to install one or more 24-A fluidized bed reactors at the head of the HDM stage (see e.g. FIG. 2) (Patents U.S. Pat. No. 3,910,834 or GB-B-2124252A). The fluidized beds may operate co-currently (e.g. SHELL's HYCON process) or counter-currently (e.g. HYVAHL-M process). In this way fixed bed reactors are protected, while carrying out part of the demetallization and filtering the particles contained in the charge which may lead to clogging. In addition the quasi continuous replacement of catalyst in the fluidized bed reactor or reactors (with spent catalyst drawn off through pipe 61 and fresh catalyst introduced through pipe 60) avoids stopping the unit every 3 to 6 months.

The disadvantage of these fluidized bed technologies is finally that their performance and effectiveness are rather lower than those of fixed beds of the same size, that they cause wear on the circulating catalyst which may lead to blockage of downstream fixed beds, and that—particularly under the operating conditions used—the dangers of coking and thus of the formation of conglomerates of catalyst is far from negligible in these heavy charges, particularly if there is operating trouble; this may prevent circulation of the catalyst either in the reactor or in the lines for tapping spent catalyst, and finally lead to stoppage of the unit to clean the reactor and tapping lines.

Another idea has been to use one or more boiling or "bubbling" beds arranged in series (the H-OIL process of the Hydrocarbon Research Institute or the LC-FINING process) of Ste Lymmus, U.S. Pat. No. 3,809,644. The carrying out of this technology has now been mastered and, particularly to a certain degree, the formation of aggregates due to coking does no harm since the grains of catalyst are always in motion. The catalyst is replaced quasi continuously without stopping the unit. On the other hand, the movement of catalyst causes serious wear, which makes it impossible to have any fixed bed reactor downstream of the boiling bed. Above all, the mixing of fresh and spent catalyst and the mixing of effluents with charge make the performance substantially worse than that of the fixed bed (quality of products), and make the catalyst ineffective (high catalyst consumption). FIG. 3 illustrates 3 reactors 51, 52, 53 in series, the arrival of fresh charge through the pipe 1 at the bottom of the first reactor 51 through which the charge passes, the discharge of effluent drawn off at the top of the last reactor 53 through which the charge passes, and the respective catalyst inlets 54, 55 and 56 and outlets 57, 58 and 59 in the 3 reactors in the figure.

#### c) EXISTING IMPROVEMENTS IN FIXED BED METHODS

In order to preserve the excellent performance of fixed beds while maintaining an acceptable operating factor, a fixed bed protective reactor (reacteur de garde) (space velocity VVH=2 to 4) has been added before the HDM reactors U.S. Pat. Nos. 4,118,310 and 3,968,026). The protective reactor 24 can most frequently be short-circuited, particularly by using a valve 31 (see FIG. 4). This gives the main reactors temporary protection from clogging. When the protective reactor is clogged it is short-circuited, but the next main reactor (26) may then become clogged in turn and lead to stoppage of the unit. In addition the small size of the protective reactor (24) does not produce good demetallisation of the charge, so the main HDM reactors (reactors 26 and 27) are ill-protected from metal deposits in the case of charges rich in metals (over 150 to 200 ppm). There is consequent accelerated deactivation of the reactors, leading to over-rapid stoppages of the unit, and hence the operating factors are still inadequate.

#### SUMMARY OF THE INVENTION

In the present invention it has finally been discovered that, in order to associate the high performance of the fixed bed with a high operating factor for treating charges with a high metal content (100 to 400 ppm but preferably 100 to 300 ppm) an excellent method consists of:

using a fixed bed arrangement comprising an HDM stage then an HDS stage, the HDM stage being made up of one or more fixed bed HDM zones, preceded by two protective HDM zones, also fixed bed but arranged in parallel so that they can be used alternately; a single protective zone being in operation and gradually becoming charged with metals, coke, sediments and various other impurities, while the other protective zone is disconnected from the unit and standing by, filled with fresh HDM catalyst;

exchanging the protective zones when the first is completely saturated with metals and various impurities, that is to say, putting the protective zone containing the fresh catalyst into operation while disconnecting the protective zone previously in operation, containing the spent catalyst saturated with metals and various impurities;

preferably using a special processing section enabling the protective zones to be exchanged while in operation, that is to say, without stopping the unit: firstly a system operating at moderate pressure (from 10 to 50 bars but preferably from 15 to 25 bars) enables the following operations to be carried out on the disconnected protective reactor: washing, stripping, cooling before the spent catalyst is discharged, then heating and sulfurization when the fresh catalyst has been charged; next another pressurizing/depressurizing, valve/tap system with the appropriate technology effectively enables the protective zones to be exchanged without stopping the unit, that is to say, without affecting the operating factor, since all the operations of washing, stripping, discharging the spent catalyst, recharging the fresh catalyst, heating and sulphurization take place in the disconnected protective reactor or zone;

preferably also using the following space velocities per hour (VVH):

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