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Johnson et al.

[11] **3,870,623**

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[54] **HYDROCONVERSION PROCESS OF RESIDUUM OILS**

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Related U.S. Application Data

[63] Continuation of Ser. No. 210,436, Dec. 21, 1971, abandoned.

[52] **U.S. Cl.**..... **208/108,** 208/48 R, 208/112, 208/157, 208/251 H

[51] **Int. Cl.**..... **C10g 13/02,** C10g 9/16, B01j 11/74

[58] **Field of Search** ..... 208/108, 112, 164, 251 H

[56] **References Cited**

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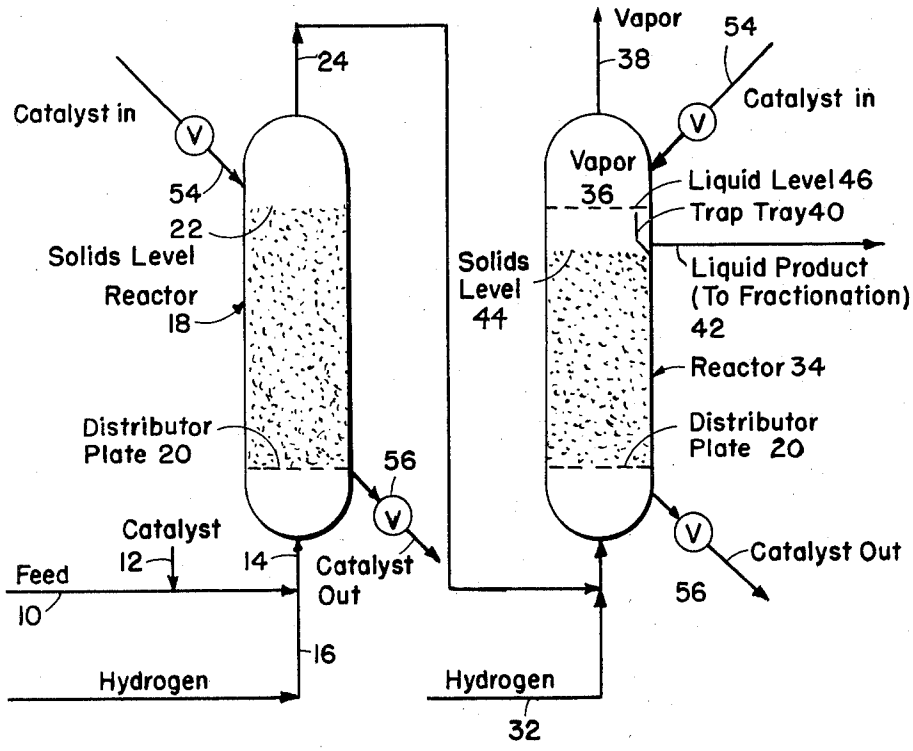
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3,547,809	12/1970	Ehrlich et al.	208/143
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Primary Examiner—Delbert E. Gantz
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[57] **ABSTRACT**

In processing high metals Venezuelan residuum, higher conversion of the 975°F plus fraction and improved operability can be obtained by maintaining a high catalyst addition rate to obtain reduced metals loading on the catalyst; it being determined that for a macroporous catalyst there is a limiting factor of metals deposition.

2 Claims, 1 Drawing Figure



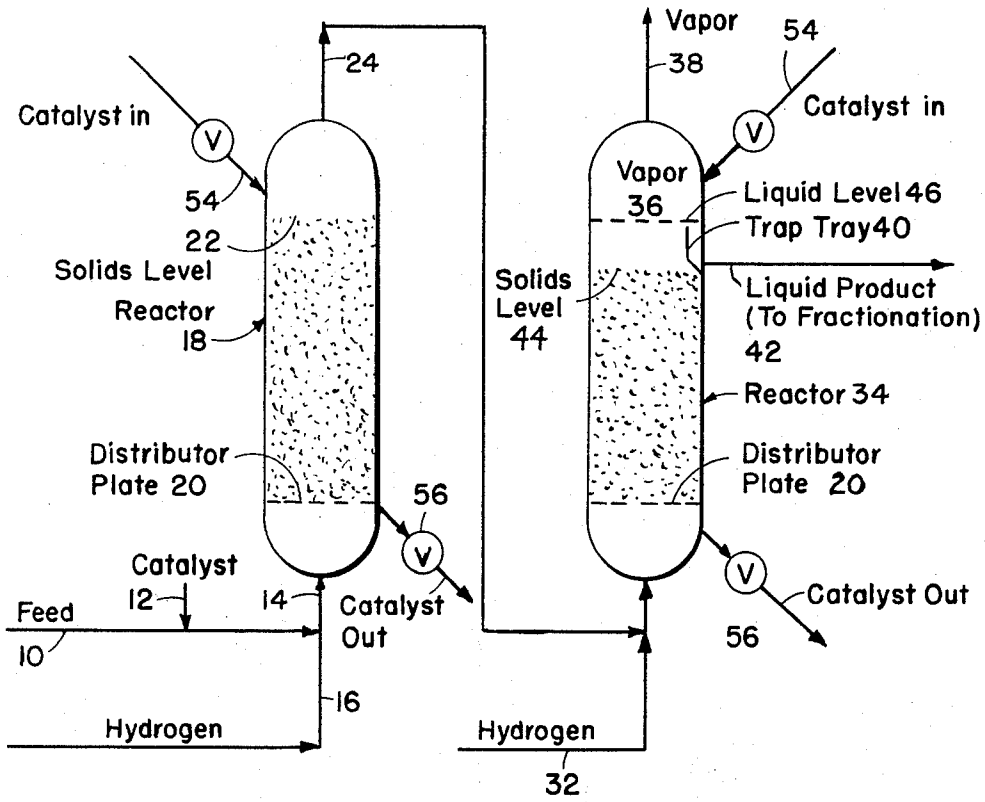

Catalyst in
54
22
Solids Level
Reactor
18
24
Distributor
Plate 20
56
Catalyst
12
Feed
10
14
Catalyst
Out
16
Hydrogen
Vapor
38
54
Catalyst in
Vapor
36
Liquid Level 46
Trap Tray 40
Solids
Level
44
Liquid Product
(To Fractionation)
42
Reactor 34
Distributor
Plate 20
Catalyst Out
56
Hydrogen
32

FIG. 1

HYDROCONVERSION PROCESS OF RESIDUUM OILS

RELATED APPLICATION

This is a continuation of application Ser. No. 210,436, filed Dec. 21, 1971, and now abandoned.

BACKGROUND OF THE INVENTION

The ebullated bed system described by Johanson in U.S. Reissue Pat. No. 25,770 has proved successful in hydrogenation, including hydrocracking and hydrodesulfurization, of a wide variety of petroleum stocks. The advantages of high throughput, uniform temperature, low pressure drop and non-plugging characteristics have been of great benefit to residuum processors. Liquid phase conditions assure good catalyst contact with no substantial attrition.

In processing vacuum residuum, such as Lagunillas, which contain in excess of 500 ppm of vanadium, conversion was limited to about 50 percent of the feed boiling above 975 F to lower boiling products in a non-replacement catalyst system. The high metals levels and high asphaltene content of Venezuelan residuum makes them difficult to convert due to the rapid poisoning of catalyst. This results in a short onstream time and, therefore, low conversion rates are obtained. As the amount of metals deposition on the catalyst increases the residuum begins to coke in the reactor. The coking then causes the rapid defluidization of the catalyst bed and this requires that the reactor be then shut down. However, a catalyst replacement reactor system utilizing a catalyst replacement rate such that not more than about 23 percent of vanadium was deposited on the catalyst showed long term successful operations even in the 70–80 percent conversion range.

SUMMARY OF THE INVENTION

A system for obtaining in excess of a 70 percent conversion of the 975 F plus fraction in high metals residuums is disclosed using an ebullated bed reactor system. This system operates by replacing the demetalization catalyst at a rate sufficient to limit vanadium deposition, thereby assuring continuous operability. The process for this invention is carried out at temperatures from 750 to 850 F, pressures of 1,000 to 3,000 psig, space velocity of 0.2 to 2.0 V /hr/V (volume of feed per hour per volume of reactor) and a hydrogen circulation of 4,000 to 10,000 SCF of hydrogen per barrel of liquid product.

DESCRIPTION OF THE DRAWING

The drawing is a schematic drawing of the preferred embodiment of the process for the hydroconversion of high metals content residua using a continuous demetalization catalyst replacement.

PREFERRED FORM OF EMBODIMENT

In the drawing, a high metals containing residuum feed **10** is preferably combined with a catalyst **12** and fed by line **14** with hydrogen from line **16** in upflow through a reactor generally designated **18.** Residua containing high metals are exemplified by Lagunillas vacuum bottoms, Venezuelan atmospheric bottoms, Tia Juana vacuum bottoms and the like with metals levels of at least 100 ppm and preferably 500 ppm. The metals are basically vanadium and nickel. The reactor

may have a liquid distributor and catalyst support **20** so that the liquid and gas passing upwardly through the reactor **18** will tend to place the catalyst in random motion in the liquid.

The catalyst particle size range is usually of a narrow size range for uniform expansion and random motion of the catalyst bed under controlled liquid and gas flow conditions. While the overall range of sizes that can be used is usually between 3 and 325 mesh (USS), a once through operation uses catalyst in the 60 to 325 mesh range with a liquid velocity in the order of 1 to 10 gallons per minute per square foot of horizontal reaction space. Alternatively, larger catalyst, usually in the 3 to 60 mesh size, can be used by adequate recycle of oil to provide from about 10 to 60 gallons total liquid velocity per minutes per square foot of horizontal reactor space. The lifting effect of the hydrogen and oil are factors in the buoyancy of the catalyst.

High metals containing residua are considered heavy hydrocarbon oils. Such oils are most preferably hydrogenated with the use of catalytic macroporous microspheres. These macroporous microspheres are composed of platinum, palladium, molybdenum, nickel or cobalt and the oxides or sulfides thereof or mixtures thereof supported on an alumina or silica carrier or mixtures thereof as a carrier.

A macroporous microsphere catalyst according to this invention should be of a type and fall within a given size range as hereinbefore described. At the same time the macroporous microspheres have a pore volume of from about 0.10 cc/g to 0.60 cc/g comprising pores larger than 250A and a pore volume of from about 0.30 cc/g to 0.50 cc/g comprising pores with a diameter of less than 250A. The total pore volume of the macroporous microspheres is between about 0.40 cc/g and about 1.10 cc/g. A preferred macroporous microsphere catalyst would have a pore volume of from about 0.2 to about 0.4 cc/g in pores with a diameter larger than 250A and a pore volume from about 0.35 to about 0.45 cc/g in pores with a diameter of less than 250A and the total pore volume is between about 0.55 and about 0.85 cc/g.

The macroporous microspheres have an average size such that 80 weight percent fall within a narrow size range and are ebullated by the upward flow of oil and hydrogen through the reactor during hydroconversion. The pore volume of the microspheres is critical as there must be a penetration of the hydrocarbon oil into the catalyst for at least a 3 percent gain in weight. These microspheres are more specifically disclosed in U.S. Pat. No. 3,622,500.

By the control of the microspherical catalyst particle size and density and the liquid and gas velocities and taking into account the viscosity of the liquid under the operating conditions, the catalyst bed may be expanded to have a definite solids level or interface indicated at **22** in the liquid. The settled or static level of the catalyst is considerably lower than level **22.** Normally, bed expansion should be at least 10 percent and seldom over 300 percent of the static level.

The entire effluent is removed overhead at **24** and passed with such hydrogen as may be required from line **32** into the second stage reactor **34.** This reactor is similar to the first stage reactor except that a vapor separating space **36** is provided at the top. The vapors, substantially solids-free and liquid-free are removed at **38** and a liquid is removed over trap tray **40** through

line **42**. The upper solids level is indicated at **44** and the upper liquid level is indicated at **46**.

While we have shown microspherical catalyst addition through line **12**, it is also convenient to add catalyst directly to the upper part of the reactors as through lines **54** and remove it through lines **56** using suitable valves as more particularly disclosed in the Ehrlich, et al., U.S. Pat. No. 3,547,809. The catalyst is added and removed at a high rate in the range of 0.2 to 0.5 lbs. of catalyst per barrel of feed oil so as to maintain the percent vanadium on the spent microspherical catalyst at less than 23 percent. Under these conditions the reactor operates without defluidization or coking.

In a reactor system of this type, the vapor overhead **38** is largerly hydrogen which may be purified by conventional means and after being appropriately reheated and recompressed, can be recyled to the hydrogen feed line **16** and **32** to the reactors.

Although it is preferable to hydrogenate the feeds in a two stage system, a single stage is also suitable.

Table I shows the results of five operations for the hydrogenation of heavy metals containing residuum using macroporous microspheres as the catalyst. From the results it can be seen that the microspherical catalyst must be added and removed at a rate such that the spent catalyst has less than 23 percent vanadium deposited on it. In this manner at least 70 percent conversion of the feed is maintained without the defluidization and coking of the microspherical catalyst bed taking place.

Above 70 percent conversion, 85 percent of vanadium in the feed is removed, 94 percent of which ends up on catalyst. Therefore, 80 percent of vanadium ends up on catalyst.

While we have shown and described the preferred form of embodiment of our invention, it will be apparent that modifications may be made thereto without departing from the scope and spirit of the description herein and of the claims appended hereinafter.

TABLE I

	I	II	III	IV	V
FEED	A*	A	A	B*	C*
°API	4.0	4.0	4.0	18	8
% S	2.75	2.75	2.75	2.2	2.7
ppm V	535	535	535	200	570
Vol. % 975°F+	75	75	75	50	89
OPERATING CONDITIONS					
Temperature °F	830	840	830	825	820
Pressure psig					
Circulation	2250	2250	2250	2000	2000
H_2 SCF/Bbl	5000	9000	5000	6000	6000
Space Velocity $V_f/hr/V_r$	0.6	0.5	0.6	0.5	0.4
CONVERSION**	72%	81%	73%	75%	70%
Cat. Rate No./bbl.	0.36	0.36	0.18	0.18	0.18
% Vanadium on Spent Catalyst	20	21	40	8	23
Reactor Operability	Satisfactory	Satisfactory	Coked	Satisfactory	Coked

*A is Lagunillas Vacuum Bottoms combined with 20% decant oil.
B is a light Venezuelan Atmospheric Bottoms.
C is Tia Juana Vacuum Bottoms.
**Conversion is disappearance of 975°F plus material.

We claim:

1. In a process for the continuous hydrogenation of a Lagunillas vacuum bottoms having in excess of 500 ppm of metals from the group of vanadium and nickel wherein the residuum and hydrogen are passed upwardly through a reaction zone containing a macroporous microspherical particulate catalyst being closely sized within the range of 60 to 325 U.S. Standard mesh at a rate to place the microspherical catalyst in random motion in the liquid without substantial carryover from the reaction zone and wherein the operating conditions are within a pressure range of 1,000 to 3,000 PSIG, and a temperature range of 750° to 850°F and a liquid space velocity of 0.2 to 2.0 $V_f/hr/V_r$ such as to maintain conversion of at least 80 percent of the portion of the residuum boiling above 975°F to material boiling below 975°F wherein the improvement comprises:

adding said catalyst to and removing said catalyst from the reaction zone at a rate between 0.2 and 0.5 pounds of catalyst per barrel of feed oil such that the percent of vanadium on the spent catalyst is less than 23 percent.

2. The process of claim **1** wherein the catalyst addition and withdrawal rate is between 0.4 and 0.5 pounds of catalyst per barrel of feed oil.

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