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HYDROCATALYTIC DESULFURIZATION OF PETROLEUM HYDROCARBONS

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4 Claims. (Cl. 196—24)

This invention relates to the hydrocatalytic desulfurization of petroleum hydrocarbons and is more particularly concerned with the treatment of gas oils.

The hydrocatalytic desulfurization of gas oils in the vapor phase is well known and the process is usually carried out at a pressure of 500–1000 p. s. i. ga., a temperature of 750–820° F., and a high recycle rate e. g. of the order of 4000 S. C. F./B. It is known also to treat gas oils in the liquid phase by allowing the oils to flow in a thin layer over the catalyst at a temperature above 200° C. and a pressure of at least 10 atmospheres. Typical conditions are a temperature of 350° C. and a pressure of 50 atmospheres. It has been suggested that under such conditions, low recycle rates of the order of 250–1250 cu. ft./bbl. are possible.

It has now been found that it is advantageous to operate at the higher temperatures normally associated with vapor phase operation and with lower recycle rates than are customary at such temperatures.

According to the present invention, a process for the hydrocatalytic desulfurization of petroleum hydrocarbons is carried out at a temperature of 750–820° F., a pressure of above 300 p. s. i. ga. and preferably within the range 500–1000 p. s. i. ga., a space velocity of the liquid feedstock of 0.5–20 v./v./hr., and a hydrogen recycle rate not exceeding 2000 S. C. F./B.

The preferred catalyst consists of or comprises the oxides of cobalt and molybdenum, either as such or in combined form, incorporated with a metal oxide support, preferably alumina.

The process is particularly suitable for the desulfurization of gas oils and the preferred recycle rate is of the order of 1000 S. C. F./B. When desulfurizing gas oils under such conditions a considerable portion of the oil in the reactor is in the liquid phase, but the process of the invention has an advantage over the conventional liquid phase process since a higher space velocity can be employed due to the higher temperature. The process of the invention is also superior to the conventional vapor phase process in that the reduction in recycle rate from 4000 S. C. F./B. results in a reduction in the capital cost of the plant.

The invention will be illustrated by the following examples:

Example 1

A straight-run Middle East gas oil containing 1.25% wt. sulfur was desulfurized at 8 v./v./hr., 780° F., 1000 p. s. i. ga. pressure, and 1250 S. C. F./B. gas recycle over a cobalt oxidemolybdenum oxide on alumina catalyst, using catalytic reformer exit gases containing 70% mol. hydrogen. The product contained 0.1% wt. sulfur and the hydrogen consumption was 130 S. C. F./B. The catalyst only required regenerating at intervals of 12 months.

Example 2

A blend of 80% by volume straight-run Middle East gas oil and 20% by volume Middle East catalytic cracker light cycle oil, containing 1.6% wt. sulfur, was desulfurizated at 8 v./v./hr., 780° F., 1000 p. s. i. ga. pressure and 1250 S. C. F./B. gas recycle over a Co–Mo oxide on alumina catalyst, using catalytic reformer exit gases containing 70% mol. hydrogen. The product contained 0.1% wt. sulfur and the hydrogen consumption was 200 S. C. F./B. The catalyst only required regenerating at intervals of 6 months.

We claim:

1. A process for the hydrocatalytic desulfurization of petroleum hydrocarbons boiling in the gas oil range, which comprises passing the hydrocarbons at a space velocity of the liquid feedstock within the range 0.5 to 20 v./v./hr. and in admixture with up to 2000 S. C. F./B. of hydrogen over a sulfur-resistant hydrogenation catalyst at a temperature of 750–820° F. and a pressure of above 500 p. s. i. ga. and not exceeding 1000 p. s. i. ga., whereby organically combined sulfur in the hydrocarbons is converted into hydrogen sulfide, and removing hydrogen sulfide from the treated hydrocarbons.

2. A process for the hydrocatalytic desulfurization of petroleum hydrocarbons boiling in the gas oil range, which comprises passing the hydrocarbons at a space velocity of the liquid feedstock within the range 0.5 to 20 v./v./hr. and in admixture with up to 2000 S. C. F./B. of hydrogen over a catalyst consisting of the oxides of cobalt and molybdenum incorporated with a metal oxide support, at a temperature of 750–820° F. and a pressure of above 500 p. s. i. ga. and not exceeding 1000 p. s. i. ga., whereby organically combined sulfur in the hydrocarbons is converted into hydrogen sulfide, and removing hydrogen sulfide from the treated hydrocarbons.

2. A process for the hydrocatalytic desulfurization of petroleum hydrocarbons boiling in the gas oil range, which comprises passing the hydrocarbons at a space velocity of the liquid feedstock of the order of 8 v./v./hr. and in admixtunre with up to 2000 S. C. F./B. of hydrogen over a catalyst consisting of the oxides of cobalt and molybdenum incorporated with a support consisting essentially of alumina, at a temperature of 750–820° F. and a pressure of about 1000 p. s. i. ga., whereby organically combined sulfur in the hydrocarbons is converted into hydrogen sulfide, and removing hydrogen sulfide from the treated hydrocarbons.

4. A process for the hydrocatalytic desulfurization of petroleum hydrocarbons boiling in the gas oil range, which comprises passing the hydrocarbons at a space velocity of the liquid feedstock of the order of 8 v./v./hr. and in admixture with approximately 1000 S. C. F./B. of hydrogen over a catalyst consisting of the oxides of cobalt and molybdenum incorporated with a support consisting essentially of alumina, at a temperature of 750–820° F. and a pressure of about 1000 p. s. i. ga., whereby organically combined sulfur in the hydrocarbons is converted into hydrogen sulfide, and removing hydrogen sulfide from the treated hydrocarbons.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,837,465 June 3, 1958

Frederick William Bertram Porter et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, lines 5 and 6, for "desulfurizated" read -- desulphurised --; line 38, for "2. A process" read -- 3. A process --; same column 2, line 42, for "admixtunre" read -- admixture --.

Signed and sealed this 23rd day of August 1960.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents