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HYDROCATALYTIC DESULFURIZATION
OF GAS OIL

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1 Claim. (Cl. 208—216)

This invention relates to the hydrocatalytic desulfurization of petroleum hydrocarbons, more particularly relatively high boiling petroleum distillates such as gas oils.

It is well-known that organically combined sulfur contained in petroleum hydrocarbons may be removed by contacting the hydrocarbons in the presence of added hydrogen at elevated temperature and pressure with a sulfur-resistant hydrogenation catalyst whereby the organically combined sulfur is converted into hydrogen sulfide which may readily be removed from the treated hydrocarbons. Such processes are commonly called hydrofining processes and are usually carried out at temperatures within the range 750° to 800° F. which is considered to be optimum for the hydrogenation reaction.

It is known however, that temperatures within this range promote cracking and adversely affect catalyst activity, and it has therefore been considered necessary to operate at pressures within the range 500 to 1000 p.s.i.g. in order to ensure a satisfactory catalyst activity and life. For the same reason it has been considered necessary to operate at relatively high gas recycle rates of at least 4000 s.c.f./b.

Large quantities of hydrogen are now available from catalytic reforming processes, and as this hydrogen is not normally available at pressures above 450 p.s.i.g., it would be an advantage to be able to operate the hydrofining process at pressures below 500 p.s.i.g. with the additional advantage that a plant built to operate at such pressures would be less expensive, since it would not require the use of such expensive pressure-resisting steels. It would also be economically advantageous to be able to operate with low gas recycle rates as the energy required for circulating and heating the gas would be reduced. It has already been disclosed in United States application Serial No. 501,168, filed April 13, 1955, now U.S. Patent No. 2,837,465, granted June 3, 1958, that reduction of the gas recycle rate from 4000 s.c.f./b. to approximately 1000 s.c.f./b. has no adverse effect on catalyst activity or life when operating at pressures of the order of 1000 p.s.i.g.

It has now been discovered that relatively low gas recycle rates may equally well be used at pressures not exceeding 500 p.s.i.g. and that a satisfactory catalyst life can be achieved at such pressures by operating at temperatures in the region of 700° F. The desired degree of desulfurization under these relatively mild conditions may be achieved by lowering the space velocity of the feedstock as compared with operation at higher temperatures and pressures.

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According to the present invention therefore, a process for the hydrocatalytic desulfurization of petroleum hydrocarbons, particularly relatively high boiling petroleum hydrocarbons such as gas oils, comprises contacting the hydrocarbons at a temperature within the range 650° to 750° F. and at a pressure within the range 200–500 p.s.i.g. with a sulfur-resistant hydrogenation catalyst in the presence of not more than 2000 s.c.f./b. of hydrogen.

The space velocity of the liquid feedstock will be selected to give the desired degree of desulfurization. In the case of gas oils containing in the region of 1.0% weight sulfur, 90% desulfurization can generally be achieved with a space velocity between 1 and 2 v./v./hr.

The preferred catalyst consists of, or comprises, the oxides of cobalt and molybdenum, either as such or in combined form, preferably incorporated with a metal oxide support, preferably alumina, although other sulfur-resistant hydrogenation catalyst known in the art may be used. The preferred catalyst may also contain a small amount e.g. 0.1 to 6% wt., of fluorine.

The process according to the invention may be operated with pure hydrogen or with hydrogen-rich gases from a catalytic reforming process or from any other source.

The process of the invention is illustrated by the following examples:

Example 1

A straight run Kuwait gas oil of 0.8435 specific gravity, 248° to 359° C. ASTM distillation range and 1.30% wt. sulfur was hydrofined over a catalyst consisting of the mixed oxides of cobalt and molybdenum on alumina. The catalyst contained 15.6% wt. molybdenum and 2.9% wt. cobalt, expressed as MoO₃ and CoO.

The operating conditions employed were as follows:

Pressure----- 220 p.s.i.g.
Temperature----- 680° F.
Space velocity----- 1.35 v./v./hr.
Gas recycle rate----- 535 s.c.f./b.

Oil and hydrogen were passed downflow through the reactor. Pure hydrogen was used as make-up gas and hydrogen sulfide was removed from the recycle gas by adsorption in soda-lime.

In a test of 1000 hours duration the sulfur content of the product remained constant at 0.10% wt. as shown in the table below. The hydrogen consumption averaged 130 s.c.f./b.

Hours on stream..	50	100	250	350	500	600	750	1,000
Organic sulfur in liquid product, percent weight..	0.07	0.09	0.10	0.09	0.10	0.09	0.10	0.10

Example 2

The feedstock and catalyst described in Example 1 were used in an experiment carried out under the following conditions:

Pressure----- 300 p.s.i.g.
Temperature----- 680° F.
Space velocity----- 1.35 v./v./hr.
Gas recycle rate----- 765 s.c.f./b.

Downflow operation was employed. Make-up gas was the exit gas from a catalytic reformer containing approxi-

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mately 75% mol hydrogen. Hydrogen sulfide was removed from the recycle gas by absorption in soda-lime.

In a test of 173 hours duration the sulfur content of the product remained constant at less than 0.1% wt. as shown in the table below. The hydrogen consumption averaged 125 s.c.f./b.

Hours on stream.....	50	75	100	125	150	173
Organic sulfur in liquid product, percent weight.....	0.09	0.09	0.07	0.07	0.06	0.08

Example 3

A blend of 80% by volume of straight run gas oil and 20% by volume of light catalytic cracker cycle oil, from Middle East crudes, having a specific gravity of 0.856 and containing 1.60% wt. sulfur was hydrofined over the catalyst described in Example 1.

The operating conditions employed were as follows:

Pressure..... 400 p.s.i.g.
 Temperature..... 680° F.
 Space velocity..... 1.35 v./v./hr.
 Gas recycle rate..... 1100 s.c.f./b.

Downflow operation was employed. Make-up gas was the exit gas from a catalytic reformer containing approximately 68% mol hydrogen. Hydrogen sulfide was removed from the recycle gas by absorption in soda-lime.

After the catalyst had been used for 275 hours hydrofining the feedstock described above under various process conditions, a test of 550 hours duration was carried out under the conditions described above. The sulfur content of the product remained constant at 0.11% wt. as shown in the table below. The hydrogen consumption averaged 130 s.c.f./b.

Hours on stream.....	300	350	447	575	650	700	725
Organic sulfur in liquid product, percent weight.....	0.08	0.11	0.12	0.10	0.11	0.11	0.09

Example 4

The improved desulfurization obtained by using a fluorine-promoted catalyst in the hydrofining of a gas oil is shown in the following table.

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Catalyst	Co-Mo oxides on alumina	Fluorine promoted Co-Mo oxides on alumina
Analysis of catalyst:		
CoO.....percent weight.....	3.05	2.54
MoO ₃ do.....	19.4	16.1
F.....do.....		3.46
Dimensions of catalyst pellets, inches.....	7/32	7/32
Operating conditions:		
Space velocity.....v./v./hr.....	1.35	1.35
Temperature.....°F.....	680	680
Recycle rate.....s.c.f./b.....	535	535
Pressure.....p.s.i.g.....	220	220
Sulfur content of feedstock, percent weight.....	1.59	1.59
Sulfur content of product, percent weight.....	0.185	0.125

We claim:

A process for the hydrocatalytic desulfurization of gas oil which comprises contacting the gas oil at a temperature within the range of 650° F. to 750° F. and at a pressure within the range 200-500 p.s.i. ga. with a catalyst consisting essentially of the oxides of cobalt and molybdenum incorporated with an alumina support, said catalyst containing between 0.1% and 6.0% wt. of fluorine and in the presence of not more than 2000 s.c.f./b. of hydrogen, the space velocity of the liquid feedstock being between 1.0 and 2.0 v./v./hr.

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