Patented Nov. 6, 1951

2,574,450

UNITED STATES PATENT OFFICE

2,574,450

DESULFURIZATION OF HYDROCARBON EXTRACTS

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No Drawing. Application February 7, 1950, Serial No. 142,942. In Great Britain December 14, 1948

5 Claims. (Cl. 196—28)

1

The invention relates to the desulphurisation of hydrocarbons, and more particularly to the catalytic desulphurisation of hydrocarbons derived from mineral oil distillates or residues by means of selective solvents of a polar character such as SO_2, SO_2-benzol mixtures, alcohols, furfural and phenols. Such hydrocarbons will hereinafter be referred to as "aromatic extracts," although it will be appreciated that they do not consist entirely of aromatic hydrocarbons but include varying proportions of other types of hydrocarbons such, for example, as paraffins and naphthenes.

It is known to desulphurise hydrocarbons by passing them with hydrogen over a sulphur-resistant hydrogenation catalyst at elevated temperature and elevated pressure, whereby organic sulphur compounds present in the hydrocarbons are hydrogenated to form hydrogen sulphide which can readily be removed from the treated hydrocarbons. The process as normally carried out involves a net consumption of hydrogen, and the cost of supplying the hydrogen is a major factor in the economics of the process. Furthermore, in order to secure the necessary partial pressure of hydrogen it has generally been considered necessary to operate at elevated pressure ranging from 500–1000 lb./sq. in. or more, and a plant to withstand such pressure has to be made from special steels which are relatively expensive. Thus, the usual method for reducing the sulphur content of aromatic extracts, either as such, or blended with other hydrocarbon materials, such as kerosine, is heavy treatment with oleum (up to 5%).

In the specifications of the co-pending British applications Nos. 17,620/48, 23,583/47, 33,120/47, 17,085/48 and 14,834/48, there are described processes for the catalytic desulphurisation of petroleum fractions ranging from light distillates, such as light naphtha, to heavy distillates, such as wax distillates, in which the feedstock is passed to a catalytic desulphurisation zone where it is treated in the presence of a sulphur-resistant hydrogenation catalyst, as specified, under conditions of temperature and pressure such that sufficient hydrogen is produced by dehydrogenation of naphthene hydrocarbons contained in the feedstock to effect the conversion of sulphur compounds contained in the feedstock into hydrogen sulphide and to provide a hydrogen-rich gaseous fraction which is recycled to the catalytic desulphurisation zone in order to maintain the necessary partial pressure of hydrogen therein. It will thus be appreciated that such processes are carried out without the necessity of using extraneous hydrogen and it is convenient to designate such processes as "autofining" processes, to distinguish them from similar catalytic desulphurisation processes carried out with the aid of extraneous hydrogen, the latter processes being commonly called "hydrofining" processes.

2

The principal object of the present invention is to provide a process whereby aromatic extracts may be desulphurised by conversion of the sulphur contained therein into hydrogen sulphide without the use of hydrogen added from an external source. It is also an object of the invention to enable such a process to be carried out at pressures low enough to avoid the use of special pressure-resisting steels, thereby reducing the cost of the plant. It is a further object of the invention to provide a catalystic desulphurisation process which is effective without further treatment of the products beyond a light soda wash to remove dissolved hydrogen sulphide.

According to the invention the desulphurisation of an aromatic extract is effected by passing the extract in vapour form in admixture with hydrogen over a catalyst which combines activity for dehydrogenation of naphthenes to aromatics, with activity for the conversion of organically combined sulphur to hydrogen sulphide, and which is not poisoned as a catalyst by the presence of sulphur compounds, at a temperature and pressure sufficient to effect the conversion of a considerable proportion of the sulphur contained in the extract into hydrogen sulphide, and to produce a hydrogen-rich gas mixture which is separated from the treated extract and recycled to the reaction zone at a rate sufficient to maintain the necessary partial pressure of hydrogen therein.

The invention may be applied to aromatic extracts as such, or in the form of blends with other hydrocarbon fractions, such as tractors vapourising oil which consists of a blend of aromatic extract and kerosine.

It is believed that the reaction proceeds by dehydrogenation of some of the naphthenes present

in the extract to produce hydrogen in excess of that required to convert the combined sulphur present into hydrogen sulphide and the reaction conditions must therefore be determined having regard to any limiting conditions imposed by these two reactions. Thus, there is a lower temperature of about 700° F. below which little dehydrogenation would occur, and below which the reaction would not be self-supporting in hydrogen. This lower temperature depends to some extent on the sulphur content, and the higher the sulphur content, the higher the temperature necessary to provide sufficient hydrogen. At temperatures above about 800° F. the on-stream time is reduced. The preferred temperature of operation is also to some extent dependent upon the pressure employed which is preferably between 50 and 250 lb./sq. in. As the pressure is increased, the minimum temperature at which satisfactory dehydrogenation of the naphthenes can be obtained increases, and if at a fixed temperature the pressure is sufficiently increased, the reverse reaction of hydrogenation of aromatics begins to occur. Thus, when operating at the higher pressures it is preferable to use higher temperatures. Similarly, it is desirable to avoid the combination of high temperature and low pressure since such conditions lead to a short on-stream time for satisfactory operation.

The space velocity may be varied according to the degree of desulphurisation required and the activity of the catalyst, but space velocities above 10 v./v./hr. result in a low degree of desulphurisation.

Among the catalysts that may be used are metal sulphides and oxides especially those of the 6th group either alone (for example chromium oxide and tungsten sulphide) or in admixture with other sulphides or oxides (for example pellets consisting of two parts tungsten sulphide and one part nickel sulphide) or in combination with other oxides or sulphides (for example cobalt molybdate or thiomolybdate) or mixed with or deposited on a porous support such as natural or processed bauxite, activated alumina and kieselguhr. Natural and processed bauxites may themselves be used as catalysts. The preferred catalyst, however, consists of cobalt molybdate supported on alumina.

An effective pelleted catalyst was prepared by mixing powdered cobalt oxide, molybdenum oxide and alumina, and pelleting with 1% graphite into $\frac{3}{16}$'' pellets which were then treated for two hours at 550° C. The catalyst may also be prepared by extrusion.

An effective supported molybdate catalyst was prepared by the impregnation of roasted Indian bauxite with a cobalt molybdate solution so that the molybdenum content of the material stable at 1000° F. was 3.6% by weight while the cobalt content of the material stable at 1000° F. was 1.0% weight.

The autofining process may be operated by setting the pressure in the autofining zone at a predetermined level and thereafter withdrawing from the system gas in excess of that required to maintain the predetermined pressure. In this case, there is a continuous make of hydrogen indicating that the hydrogen produced in the dehydrogenation reaction is not being fully utilised in the desulphurisation reaction. An improved method of operation was therefore developed in which the hydrogen-containing gaseous fraction is recycled to the reaction zone and the pressure therein allowed to rise to an equilibrium pressure at which the hydrogen evolved equals the hydrogen consumed. This method of operation is fully described in the specification of the co-pending No. 9,672/49 and results in a greater degree of desulphurisation and increased on-stream hours for a product of given sulphur content.

The preferred catalyst for use in the autofining process is of the so-called cobalt molybdate type which consists of the oxides of cobalt and molybdenum deposited on or incorporated with a support, preferably alumina. It has been found that there is a period at the commencement of each run during which the gas make is negligible or non-existent and the desulphurisation is not at its maximum. This low dehydrogenating activity of the catalyst is more noticeable at low feedstock velocities and with the heavier feedstocks. It was discovered that the inactivity of the catalyst during the early hours on-stream could be largely overcome by subjecting the cobalt molybdate catalyst to the action of hydrogen sulphide or hydrogen sulphide-containing gases prior to its use in the autofining process. An autofining process using such a catalyst is described in the specification of the co-pending application No. 24,330/49.

The following are examples of the process of the invention.

EXAMPLE 1

An SO_2 extract of Iranian origin having a sulphur content of 0.69% weight was passed at a temperature of 780° F. and a pressure of 100 lb./sq. in. over a catalyst consisting of cobalt molybdate supported on alumina. The space velocity was maintained at 2 v./v./hr. and the process was continued satisfactorily for a period of 100 hours during which time there was an average gas make of 15 cu. ft./bbl. This gas contained 80% by volume of hydrogen and was recycled to the reaction zone at a rate of 2000 cu. ft./bbl.

The product represented 99% weight on feed and the inspection data of the feedstock and product are set out in the following table, No. 1.

TABLE 1

Inspection Data	Feedstock	Product
S.G. @ 60° F	0.868	0.864
Vol. to 160° C.....per cent	2	5
Vol. to 260° C.....do	100	100
Aromatics, per cent wt	73	75
Color Lovibond (6" cell)	27Y+4.3R	15Y+0.3R
Sulphur, per cent wt	0.69	0.045
Sulphur removal, per cent		93.5

It will be seen that a product containing 0.05% weight sulphur was obtained from an extract containing 0.69% weight sulphur, representing a sulphur removal of 93.5%. Except for a light soda wash to remove dissolved hydrogen sulphide, no further treatment of the product was required.

EXAMPLE 2

A mixture of 45% by volume of SO_2 extract of Iranian origin having a sulphur content of 0.9% wt., and 55% by volume of kerosine of Iranian origin boiling between 160° C. and 260° C., the mixture having a total sulphur content of 0.55% wt., was passed at a temperature of 780° F. and a pressure of 100 lb./sq. in. over a catalyst consisting of cobalt molybdate supported on alumina.

The space velocity was maintained at 5.0 v./v./hr. and the process was continued satisfactorily for a period of 200 hours during which time there was an average gas make of 20 cu. ft./bbl. This gas contained 85% by volume of hydrogen and was recycled to the reaction zone at the rate of 2000 cu. ft./bbl.

The product represented 99% weight on feed and the inspection data of the feedstock and product are set out in the following table, No. 2.

TABLE 2

Inspection Data	Feedstock	Product
S. G. @ 60° F	0.829	0.825
Vol. to 160° C.....per cent	Nil	2
Vol. to 260° C.....do	100	100
Colour, Saybolt	−8	+12
Sulphur, per cent wt	0.55	0.045
Sulphur removal, per cent		92
Octane No. M. M	52.0	54.0

It was only necessary to give the product a light soda wash: it will be seen that a product having a sulphur content of 0.45% weight was obtained from a feedstock having a sulphur content of 0.55% weight, representing a sulphur removal of 92% by weight. The product showed a gain of two octane numbers and was satisfactory for use as a tractor vapourising oil without further treatment.

EXAMPLE 3

This example illustrates the application of the equilibrium pressure method of operation which is described in the specification of the co-pending application No. 9,672/49.

The feedstock was a crude kerosine SO_2 extract prepared from mixed Iranian and Iraqi crudes of boiling range 161 to 288.5° C. (A. S. T. M.).

Autofining conditions

Catalyst, cobalt molybdate on alumina
Temperature (average), 800° F.
Pressure, equilibrium (100–68 p. s. i. ga.)
Space velocity, 3.0 v./v./hr.
Recycle rate, 2000 c. f./b. (at 1000 p. s. i. ga.)
Duration of run, 174 hrs.

Inspection Data	Feedstock	Bulked Product
S. G., 60° F./60° F	0.8675	0.8630
I. B. P. ° C	161	155
10% Vol. @ ° C	171	170
50% Vol. @ ° C	190	191
90% Vol. @ ° C	241	235
F. B. P., ° C	288.5	279
Bromine No	3	6
Octane No. (M. M.)	76.8	79.2
Sulphur, % wt	1.00	0.36
Sulphur Removal, %		64.0

EXAMPLE 4

The feedstock was a benzine SO_2 extract of 115 to 162.5° C. A. S. T. M. boiling range containing approximately 75 per cent aromatics prepared from mixed Iranian crudes.

Autofining conditions

Catalyst, cobalt molybdate on alumina
Temperature, 780° F.
Pressure, 100 p. s. i. ga.
Space velocity, 3.0 v./v./hr.
Recycle rate, 2000 c. f./b.
Duration of run, 60 hours.
Average gas make, 5 c. f./b.

Inspection Data	Feedstock	Bulked Product
S. G., 60° F./60° F	0.836	0.835
I. B. P., ° C	115	110
10% Vol. @ ° C	120	119
50% Vol. @ ° C	129	127
90% Vol. @ ° C	145	144
F. B. P., ° C	162.5	164
Bromine No	2	1
Colour, Saybolt	+15	+21
Gum Existence, mg./100 ml	1	1
Gum (E + B), mg./(120 min)	1	1
Octane No. (M. M.)	85.3	87.2
Sulphur, per cent wt	0.295	0.004
Sulphur Removal, per cent		98.6

EXAMPLE 5

Feedstock components

45% vol. Iranian/Iraqi kerosine SO_2 extract, 163 to 293° C. A. S. T. M.
35% vol. Iranian/Iraqi kerosine, 162 to 301° C. A. S. T. M.
20% vol. Iranian/Iraqi naphtha, 143 to 184° C. A. S. T. M.

Autofining conditions

Catalyst, cobalt molybdate on alumina
Temperature, 780° F.
Pressure, 100 p. s. i. ga.
Space velocity, 3.0 v./v./hr.
Recycle rate, 2000 c.f./b.
Duration of run, 422 hours
Average gas make, 2.5 c.f./b.

Inspection Data	Feedstock	Bulked Product
S. G. 60° F./60° F	0.824	0.821
I. B. P., ° C	151	149
10% vol. @ ° C	164.5	164
50% vol. @ ° C	185	186
90% vol. @ ° C	243	243.5
F. B. P. ° C	292	283.5
Colour, Saybolt	−6	−9
Sulphur, per cent wt	0.577	0.126
Sulphur Removal, per cent		78
Octance No. (M. M.)	48.1	51.2

EXAMPLE 6

The feedstock was a 50–90% vol. tray cut from a kerosine SO_2 extract prepared from Iraqi crude and had a boiling range of 187–252° C. A. S. T. M.

Autofining conditions

Catalyst, cobalt molybdate on alumina
Temperature, 780° F.
Pressure, 100 p. s. i. ga.
Space velocity, 1.6 v./v./hr.
Recycle rate, 3400–4400 c.f./b.
Duration of run, 300 hours

Inspection Data	Feedstock	Bulked Product
S. G., 60° F./60° F	0.8715	0.8660
I. B. P., ° C	187	169
10% vol. @ ° C	196.5	193
50% vol. @ ° C	210	211
90% vol. @ ° C	233	235
F. B. P., ° C	252	258
Flash Point, ° F	152	128
Copper strip (@ 100° C.)	Brown	Passes
Gum Existent, (mg./100 ml.)	6	5
Gum Potential (mg./100 ml.)	Trace	
Sulphur, per cent wt	1.07	0.189
Sulphur Removal		82.3

We claim:

1. A process for the hydrocatalytic desulphurization of a sulphur-and-naphthene-containing aromatic extract of hydrocarbon oil, which process is self-supporting with respect to the hydro-

gen needed and is productive of a desulphurized aromatic extract having, except for lowered sulphur content, properties and boiling range substantially the same as the feedstock, comprising the steps of: passing a feedstock consisting of the aromatic extract to be desulphurized to a reaction zone and contacting the feedstock therein with a dehydrogenation-hydrogenation catalyst and with hydrogen derived solely from the feedstock, said catalyst being resistant to sulphur poisoning and combining activity for the dehydrogenation of naphthenes in said feedstock to aromatics with activity for the hydrogenation of organically combined sulphur in said feedstock to hydrogen sulphide; maintaining a selected temperature in said zone between about 700° F. to about 800° F. at which hydrogen is continuously produced from said feedstock; maintaining a selected pressure in said zone between about 50 to about 250 lbs./sq. in. gauge, said selected temperature and pressure being correlated to provide, from the dehydrogenation of naphthenes contained in said feedstock, a net production of hydrogen at least sufficient to convert organically combined sulphur in the feedstock into hydrogen sulphide and to maintain said selected pressure; separating hydrogen sulphide and a hydrogen-rich gas mixture from the desulphurized feedstock; recycling said hydrogen-rich gas mixture to the reaction zone to constitute the whole of the hydrogen supplied to said zone, the hydrogen recycle rate being sufficient to maintain the necessary partial pressure of hydrogen in said zone; and, recovering the desired desulphurized aromatic extract from the residue of said separating operation.

2. A process according to claim 1, wherein the feedstock is passed to said reaction zone at a space velocity less than about 10 v./v./hr., wherein the selected temperature is approximately 780° F., wherein the selected pressure is approximately 100 lbs./sq. in. gauge, and wherein said hydrogen-rich gas mixture is recycled to the reaction zone at a rate between about 2000 and 4000 cu. ft./bbl. of feedstock.

3. A process according to claim 1, wherein the catalyst consists of the combined oxides of cobalt and molybdenum supported on alumina.

4. A process according to claim 1, wherein the feedstock consists of a blend of aromatic extract and kerosene.

5. A process according to claim 1, wherein the feedstock consists of a blend of an aromatic kerosene extract, a kerosene fraction, and a naphtha fraction.

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