

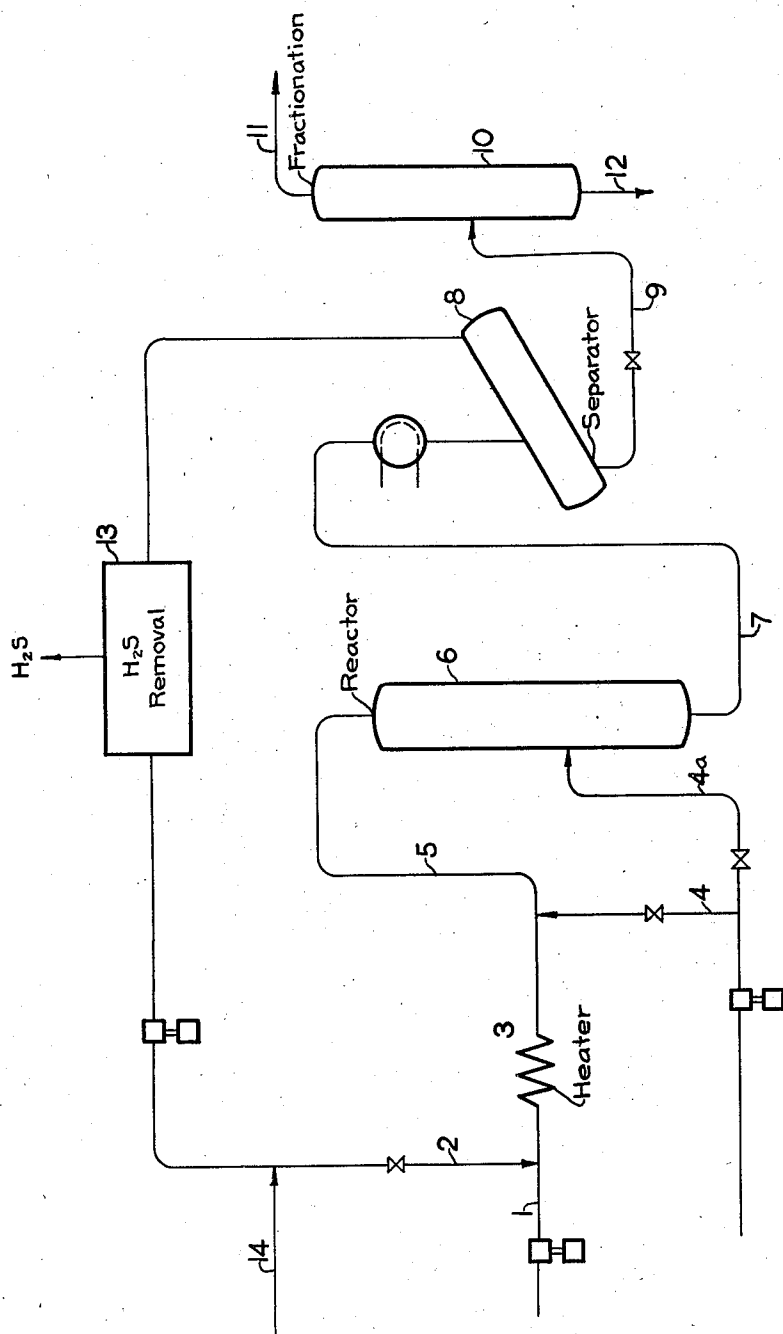
Feb. 12, 1946.

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2,394,751

DESULPHURIZATION OF AROMATIC HYDROCARBONS

Filed Dec. 19, 1944



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UNITED STATES PATENT OFFICE

2,394,751

DESULPHURIZATION OF AROMATIC
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Application December 19, 1944, Serial No. 568,843

4 Claims. (Cl. 260—674)

This invention relates to a process for removal of sulphur compounds from aromatic hydrocarbon fractions by catalytic decomposition of said sulphur compounds under the combined action of hydrogen and catalysts.

It is well known that various aromatic hydrocarbon fractions such as benzol, toluol, xylol and solvent naphtha obtained by the distillation of coal contain appreciable amounts of sulphur compounds. The sulphur compounds in these various aromatic materials are mostly cyclic sulphur compounds of aromatic nature such as thiophene and its homologs and thiophenols. More recently large quantities of so-called synthetic benzene, toluene and xylene have been produced from petroleum sources by extraction and/or dehydrogenation processes. These materials also contain small to appreciable amounts of sulphur compounds. In the unrefined products obtained from petroleum sources there may also be present appreciable amounts of open chain sulphur compounds. Since the open chain sulphur compounds are not aromatic in character and are relatively easily removed by various methods these latter materials are usually substantially absent in the refined products from either of these sources. The cyclic sulphur compounds on the other hand, are very difficult to remove. Attempts to remove them by known methods invariably result in large losses of valuable material.

The usual method of treating the commercial aromatic fractions is to effect a partial desulphurization by a conventional sulphuric acid treatment. This treatment has certain shortcomings which are well known. More recently certain catalytic processes have been proposed in which the sulphur compounds are removed by hydrogenation. The difficulty invariably encountered in these processes is, however, that the cyclic sulphur compounds are aromatic in character and any treatment which affects them likewise tends to affect the aromatic hydrocarbons proper. Thus, if it is attempted to obtain a substantially complete desulphurization a considerable amount of the aromatic hydrocarbon is also hydrogenated. This difficulty is partly overcome by effecting only a partial desulphurization by a mild treatment. The importance of this problem is attested to by the large amount of work done in attempts to develop sulph-active catalysts with the hope that one might be found which is more selective in its action. The use of such catalysts has afforded a slight advantage under particular low temperature conditions, but has not afforded a solution to the problem.

I have now found that this difficulty may be

substantially overcome in a simple and practical manner by effecting the catalytic hydrogenation of the sulphur compounds in the presence of certain concentrations of olefins. It is found that by maintaining a small concentration of olefins in the material being treated the aromatic hydrocarbons may be protected while the desulphurization may be carried as near to completion as desired. Further advantages of this method are that any sulph-active hydrogenation catalyst may be used and higher temperatures up to about 325° F. may be employed, at which temperatures certain secondary refining effects may usually be obtained.

The minimum amount of olefin found to be necessary to protect the aromatic hydrocarbon is about 1% of the product. The preferred concentration range is between about 2% and about 5% of the product. The concentration in the initial feed may be higher by the amount of olefin hydrogenated during the desulphurization.

The protection of aromatic hydrocarbons desulphurizing hydrogenation conditions by the presence of such amounts of an olefin that the olefin concentration of the product is between about 1% and 5% is illustrated by the following:

Straight toluene and toluene to which had been added various minor amounts of diisobutylene (D. I. B.) were treated under the following conditions:

Catalyst—tungsten-nickel sulphide, corresponding approximately to the formula $WS_2 \cdot 1.5 NiS_2$
Temperature—700° F.

Pressure—700 p. s. i. g.

Liquid hourly space velocity (L. H. S. V.)—as shown.

The following results were obtained:

Feed	L. H. S. V.	Vol. percent D. I. B. in product	Vol. percent toluene hy- drogenated
Toluene	5.7	0.38	29
Toluene+D. I. B.	5.2	0.26	25.9
Do.	4.7	0.26	31.2
Toluene	16	1	7.7
Toluene+D. I. B.	16	2.2	3.5
Do.	16	2.2	2.6

It is seen that by effecting the treatment in the presence of such an amount of olefin that the olefin content of the product is 1% or above, and the hydrogenation of the toluene is substantially inhibited.

Further experiments indicated that the minimum necessary olefin concentration for effective inhibition of hydrogenation of the aromatic hydrocarbons varies somewhat in the following

manner: (1) The lower the boiling range of the material treated, the higher the minimum olefin content should be; (2) the higher the sulphur content of the material treated, the lower the minimum olefin content may be; (3) the more drastic the treating conditions the higher the minimum olefin content must be.

The maximum olefin content is not so critical. However, if large amounts of olefin are used these will necessarily result in a large consumption of hydrogen and increased distillation costs. Large amounts may also depress to a certain extent the desired hydrogenation of thiophene and similar sulphur compounds. On the other hand, if a small controlled concentration of olefin is maintained the increased hydrogen consumption is negligible, very little material has to be subsequently separated, and a more complete and generally satisfactory desulphurization may be obtained. In such cases where the conditions are conducive to the hydrogenation of excessive amounts of olefins, for example when desulphurizing under severe conditions, it is advantageous to add the olefin in increments along the length of the reaction zone. In such cases where the feed contains large amounts of sulphur, for instance over 0.5%, all of the olefin added may be added at one or more points along the reaction zone since it is found that the hydrogenation of the aromatics does not proceed at an appreciable rate until the sulphur content is reduced to about 0.2%.

Any olefin or mixture of olefins may be employed in the present process. In many cases the small amount of residual olefin does no harm and may be left in the product. In other cases the residual olefin is removed by a suitable after-treatment, such for example as a very mild sulphuric acid treatment. In a preferred embodiment of the invention, an olefin is used which boils sufficiently different from the aromatic material treated that the residual olefin, as well as the product of its hydrogenation, may be simply separated from the product by a simple or fractional distillation. Particularly suitable materials of this type are the lower boiling olefins such as propylene and butylene and the higher boiling polymers of these materials, such as diisobutylene, triisobutylene, the cross polymers and the like. As pointed out, some of the olefin added becomes hydrogenated in the process. When using such polymer materials the hydrogenated products may be removed as valuable by-products.

A suitable application of the process of the invention is illustrated in the flow diagram shown in the drawing. Referring to the drawing the feed, which may be for example a coal tar distillate, an aromatic extract or the like, enters via line 1. It is mixed with an excess of hydrogen, for instance from about one to about 30 mol parts, entering via line 2. The mixture passes through a preheater 3 wherein the mixture is completely vaporized and the vapors brought up to about the desired inlet reaction temperature. A regulated amount of an olefin, for instance an olefin polymer, is added to the mixture via line 4. The mixture of aromatic material, olefin and hydrogen then pass via line 5 to a reactor 6. Reactor 6 is filled with a sulph-active hydrogenation catalyst such, for example, as tungsten sulfide, nickel sulfide, molybdenum sulfide, cobalt thiomolybdate or any one of the other known catalysts of this general class. The conditions in re-

actor 6 are adjusted according to the particular feed and the particular catalyst to afford the desired desulphurization. The temperature may range, for example, from about 450° F. up to about 825° F. The pressure is usually above 10 atmospheres but is not sufficiently high to give destructive hydrogenation. The throughput rate, expressed as liquid hourly space velocity, may vary from about 1 to about 20.

An additional small amount of olefin sufficient to maintain the desired residual olefin concentration in the product may be injected into the reaction zone via line 4a. Whether the olefin added should be added via line 4 or 4a depends largely upon the character of the feed. Usually if the feed contains large amounts of sulphur and/or some olefinic materials it is most advantageous to add all of the added olefin into the reaction zone at one or more intermediate points, such as by line 4a. On the other hand, if the material to be treated is quite low in sulphur and is substantially devoid of olefins at least a part of the olefin is advantageously added to the feed material via line 4. The hydrogenated product containing between 1% and about 5% of olefins passes via line 7 from the reactor to a pre-cooler and to a separator 8. The liquid product containing the olefin and the hydrogenated product thereof passes via line 9 to a fractionator 10. Here the desulphurized aromatic product is separated from the olefin and its hydrogenated product. If the olefin employed boils above the aromatic material treated, the aromatic product is recovered via 11 and the olefin and its hydrogenated product are recovered as a small bottom stream via line 12. The gas separated in separator 8 consists largely of hydrogen and contains appreciable amounts of hydrogen sulphide. This gas is usually passed through a hydrogen sulphide removal system 13 to remove a part of the hydrogen sulphide prior to recycling the gas. Any of the conventional systems for removing hydrogen sulphide from such gases may be used. Additional hydrogen is fed to the system via line 14.

I claim as my invention:

1. A process for the catalytic hydrogenation of sulphur-bearing aromatic hydrocarbon fractions to effect a substantial desulphurization thereof with substantially no attack of the aromatics which comprises treating the sulphur-bearing aromatic fraction at a temperature between about 450° F. and 825° F., at a pressure above 10 atmospheres but below that causing destructive hydrogenation and at a liquid hourly space velocity between about 1 and 20 affording the desired sulphur removal with between about one and 30 volumes of hydrogen in the presence of a metal sulphide hydrogenation catalyst and in the presence of such an amount of an added olefin that the olefin concentration in the product remains substantially constant between 1% and about 5%.

2. Process according to claim 1 in which the olefin has a boiling point sufficiently different from that of the aromatic hydrocarbon that the residual olefin may be separated by distillation of the product.

3. Process according to claim 1 in which the olefin is a polymer of a butylene.

4. Process according to claim 1 in which the olefin is injected into the reaction mixture at one or more points along the length of the reaction zone.

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