

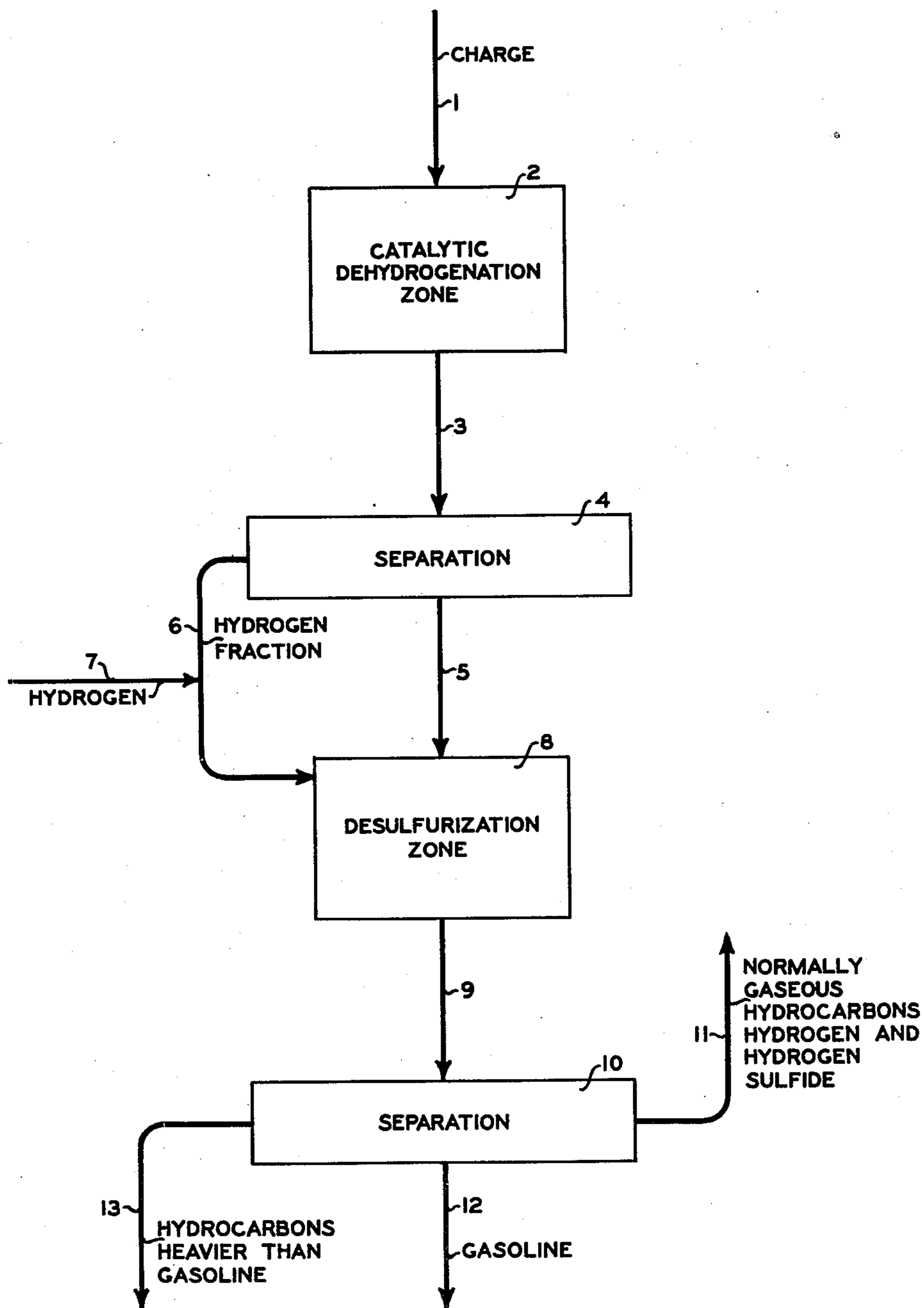
March 30, 1943.

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2,315,144

TREATMENT OF HYDROCARBONS

Filed May 11, 1939



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2,315,144

TREATMENT OF HYDROCARBONS

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Application May 11, 1939, Serial No. 272,950

2 Claims. (Cl. 196—24)

This invention relates to a process for converting hydrocarbon oils of relatively high sulfur content into valuable hydrocarbon oils of relatively low sulfur content and which, in addition to being substantially sulfur-free, are also substantially olefin-free. The gasoline obtained as a final product or contained in the final product is particularly valuable for blending in aviation fuel because it contains predominantly aromatic and paraffinic hydrocarbons.

More specifically, it is concerned with a process which involves a novel sequence of steps wherein provisions are made for subjecting the hydrocarbon oil to dehydrogenation treatment followed by desulfurization treatment by hydrogenation to produce a product substantially free of sulfur and containing predominantly paraffinic and aromatic hydrocarbons.

Various processes have been proposed for treating hydrocarbon oils of relatively high sulfur content, a satisfactory one being the hydro refining process. This process involves contacting the hydrocarbon oil with hydrogen in the presence of a suitable catalyzing agent at relatively high temperature and superatmospheric pressure whereby the sulfur, present either in a combined or a free state, is converted to hydrogen sulfide and the hydrocarbon molecule is substantially completely saturated with hydrogen. The process when used alone, however, is relatively expensive to operate, partly because of the high cost of hydrogen and because it reduces the octane number of the finished gasoline produced unless severe operating conditions are employed and, in this case, the yield is materially reduced.

In the present invention in order to produce a valuable product substantially free of sulfur, a dehydrogenation treatment which involves the conversion of paraffins to olefins and/or conversion of naphthenes to aromatics, the former corresponding to the removal of one molecule of hydrogen while the latter corresponds to the removal of three molecules of hydrogen, is combined with the hydro refining treatment which involves the removal of sulfur as hydrogen sulfide by hydrogenation using the hydrogen produced in the dehydrogenation treatment.

In one specific embodiment the invention comprises subjecting hydrocarbon oil to dehydrogenation treatment to convert a substantial portion thereof into unsaturated compounds without materially altering its boiling range, subjecting the dehydrogenated products, together with the hydrogen produced in the dehydrogenation treatment, to desulfurization treatment by hy-

drogenation in the presence of a catalytic mass and under selected conditions of temperature, pressure and contact time whereby the sulfur is removed as hydrogen sulfide and whereby only partial hydrogenation is effected so that the resulting treated hydrocarbon oil is predominantly aromatic and paraffinic.

The term "dehydrogenation treatment" as used throughout the specification and claims refers both to the conversion of paraffinic hydrocarbons into olefinic hydrocarbon and to the conversion of naphthenic hydrocarbons into aromatic hydrocarbons. For example, a paraffinic hydrocarbon, such as normal hexane, may be converted to its corresponding olefinic hydrocarbons by the removal of one molecule of hydrogen, the resulting compound having a single double bond in its structure. This reaction may be accomplished in the presence of the same catalyst and under substantially the same conditions of temperature and pressure as the reaction which involves converting cyclohexane to benzene, which reaction involves the removal of six atoms or three molecules of hydrogen, the resulting compound having three double bonds and retaining its cyclic structure.

The dehydrogenation treatment will ordinarily produce relatively large quantities of olefinic hydrocarbons, the presence of which is undesirable in an aviation gasoline because of the relatively high acid heat test of the gasoline and because of the poor lead susceptibility of the olefinic hydrocarbons. On the other hand, gasoline containing predominantly paraffinic and aromatic hydrocarbons, even though the octane number be lower than the olefinic gasoline unless isomeric compounds are present, has a lower acid heat test and good lead susceptibility. I have found that I can obtain a gasoline product having the properties desirable in an aviation gasoline by subjecting the products of dehydrogenation to desulfurization treatment under selected temperature and pressure conditions and in the presence of selected catalytic masses whereby the sulfur present, either in the combined or free state, is removed as hydrogen sulfide and the olefinic hydrocarbons are hydrogenated to paraffins, while substantially no hydrogenation of the aromatic hydrocarbons is effected.

Hydrocarbons heavier than gasoline, which may be included in the charging stock to the dehydrogenation treatment, may consist of hydrocarbon oils, such as, for example, cracked or straight-run kerosene or gas-oil fractions, which after desulfurization and hydrogenation are par-

ticularly valuable because of their saturated character, since the Diesel fuels derived from said gas-oil fraction are of relatively high cetane number.

In the accompanying diagrammatic drawing, in order to illustrate the process of the invention without complicating it with unnecessary details of each specific step, the general practice of illustrating each specific step in detail has been departed from and the flow diagram used instead.

Referring to the accompanying flow diagram, the hydrocarbon oil charging stock, which may consist of straight-run or cracked or reformed gasoline, cracked or straight-run kerosene, or gas-oil fractions, or, when desired, a mixture of the above named fractions, is introduced through line 1 to dehydrogenation treatment in zone 2 wherein a substantial portion of the hydrocarbons are converted to unsaturated hydrocarbons consisting essentially of olefins or aromatics or both. In the dehydrogenation treatment naphthenes are converted to aromatics as well as paraffins to olefins simultaneous to the production of hydrogen which is used in the desulfurizing treatment, and in subsequent steps of the process conditions are preferably regulated so that the aromatics remain as such in the final product.

Catalysts which have been found to be highly efficient in the dehydrogenation of paraffinic or naphthenic hydrocarbons to unsaturated hydrocarbons consist in general of pellets or granules of magnesium oxide composited with a chromate of a metal selected from the group consisting of lead, zinc, magnesium, cadmium, iron, nickel, cobalt, copper, aluminum, and the alkali metals, and/or a metallic oxygen-containing salt selected from the group consisting of sulfates, nitrates, and acetates of zinc, copper and aluminum. Although these catalysts are the preferred catalysts they are not to be considered as a limiting feature, for catalysts, such as, for example, those consisting of alumina or other inert siliceous and refractory materials composited with compounds of the elements selected from the group consisting of the elements in the left hand columns of groups 4, 5, and 6 in the periodic table, and others known to those skilled in the art may be employed within the broad scope of the invention. Temperatures ranging, for example, from 750 to 1400° F., but preferably from 900 to 1100° F. may be employed when utilizing atmospheric or sub-atmospheric pressures to 100 pounds or more per square inch superatmospheric.

The conversion products from zone 2, together with the hydrogen produced therein, are directed through line 3 to separation zone 4 wherein the hydrogen and any normally gaseous hydrocarbons present are separated from the normally liquid conversion products.

When desired, separation zone 4 may be dispensed with and all of the conversion products from zone 2 introduced directly to zone 8 for desulfurization treatment. However, since the desulfurization treatment is ordinarily carried out in a plurality of reactors and since the practice is to introduce hydrogen between the various reactors, the preferred method is to separate the hydrogen as previously described. The conversion products from separation zone 4, in the case here illustrated, are directed through line 5 to desulfurization treatment in zone 8. Hydrogen separated in zone 4 is directed through

line 6 to zone 8 and, when desired, fresh hydrogen introduced through line 7 may be commingled with the hydrogen separated in zone 4 in line 6. The dehydrogenated products are subjected to contact with a suitable catalyzing agent in zone 8 in the presence of hydrogen to convert the sulfur to hydrogen sulfide and, in addition, to effect hydrogenation of the olefinic hydrocarbons to paraffinic hydrocarbons while employing selected conditions so that the aromatics remain unaffected.

Catalysts which may be employed in the desulfurization of hydrocarbon oils consist in general of the oxides of molybdenum, aluminum, chromium, tungsten, and vanadium, the sulfides of molybdenum, calcium, and cobalt, or mixtures of these compounds. In addition such catalysts as metallic nickel or copper, either alone or mixed or as promoters on suitable supports, may be employed. The preferred catalysts, however, consist essentially of the sulfides or oxides of molybdenum, because it has been found that the oxides after prolonged contact with hydrogen sulfide mixtures are converted to the sulfides and remain active for a considerably longer period of time than some of the other catalysts. It is to be understood, however, that the catalysts referred to above are not intended as a limiting feature for other catalysts capable of promoting the desired reaction may be employed within the broad scope of the invention.

When using the preferred catalyst, temperatures on the order of 750 to 1000° F. may be employed with a superatmospheric pressure ranging, for example, from 750 to 5000 pounds or more per square inch.

The desulfurized products from zone 8 containing hydrocarbons boiling in the range of gasoline and heavier unused hydrogen and hydrogen sulfide are directed through line 9 to separation zone 10. Separation zone 10 will ordinarily comprise a fractionating zone wherein hydrocarbons boiling in the range of gasoline and normally gaseous hydrocarbons containing hydrogen sulfide and unused excess hydrogen are separated from the hydrocarbons of a higher average boiling point than that of the gasoline fraction, and condensing and collecting equipment wherein a fraction consisting predominantly of hydrogen sulfide and excess unused hydrogen from zone 8 is separated from the desired gasoline fraction. The fraction containing hydrogen sulfide, in the case here illustrated, is directed through line 11 and may, when desired, be treated for the removal of said hydrogen sulfide and the unused hydrogen returned to zone 8, by well known means not shown. A gasoline fraction is directed through line 12 to cooling and storage or to further treatment as desired. The heavier hydrocarbon oil fraction, whose average boiling point is above that of the desired gasoline fraction, is directed through line 13 to cooling and storage or may, when desired, be subjected to further separation in a second fractionating zone, not shown, to separate desirable fraction, such as, for example, kerosene and Diesel fuel.

The following is an example of one specific operation of the process as it may be accomplished when using the preferred catalyst and the preferred temperature and pressure conditions. It is not, however, intended as a limiting feature, for various other catalysts well known to those versed in the art may be employed within the broad scope of the invention and the op-

erating conditions adjusted to produce the desired result.

The charging stock, a 65° A. P. I. gravity straight-run gasoline of 50 octane number and with a sulfur content of approximately 0.3, was subjected to dehydrogenation treatment in the presence of a catalyst consisting essentially of magnesium oxide admixed with minor proportions of lead chromate and zinc sulfate at a temperature of 932° F. and at substantially atmospheric pressure. The normally liquid conversion products from the dehydrogenation treatment, corresponding to approximately 90% recovery, was subjected to contact with a desulfurization catalyst consisting essentially of molybdenum disulfide (MoS_2) at a temperature of approximately 850° F. and under a superatmospheric pressure of approximately 3000 pounds per square inch in the presence of hydrogen produced in the dehydrogenation treatment. The products from the desulfurization treatment had a sulfur content of approximately 0.03% and contained saturated aliphatic hydrocarbons

and aromatic hydrocarbons. The final product had an octane rating of approximately 60 (motor method).

I claim as my invention:

- 5 1. A process for improving hydrocarbon oil of relatively high sulfur content which comprises subjecting the oil to contact with a dehydrogenating catalyst at dehydrogenating conditions to form olefins and aromatics therein with the simultaneous production of hydrogen, and sub-
10 jecting the sulfur-containing dehydrogenated hydrocarbons to hydrogenation with hydrogen formed in the dehydrogenating step at a temperature of about 750 to 1000° F. and under a
15 pressure of about 750 to 5000 pounds per square inch, thereby converting the sulfur to hydrogen sulfide and effecting substantial saturation of the olefins.

- 20 2. The process as defined in claim 1 further characterized in that said hydrocarbon oil comprises gasoline fractions.

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