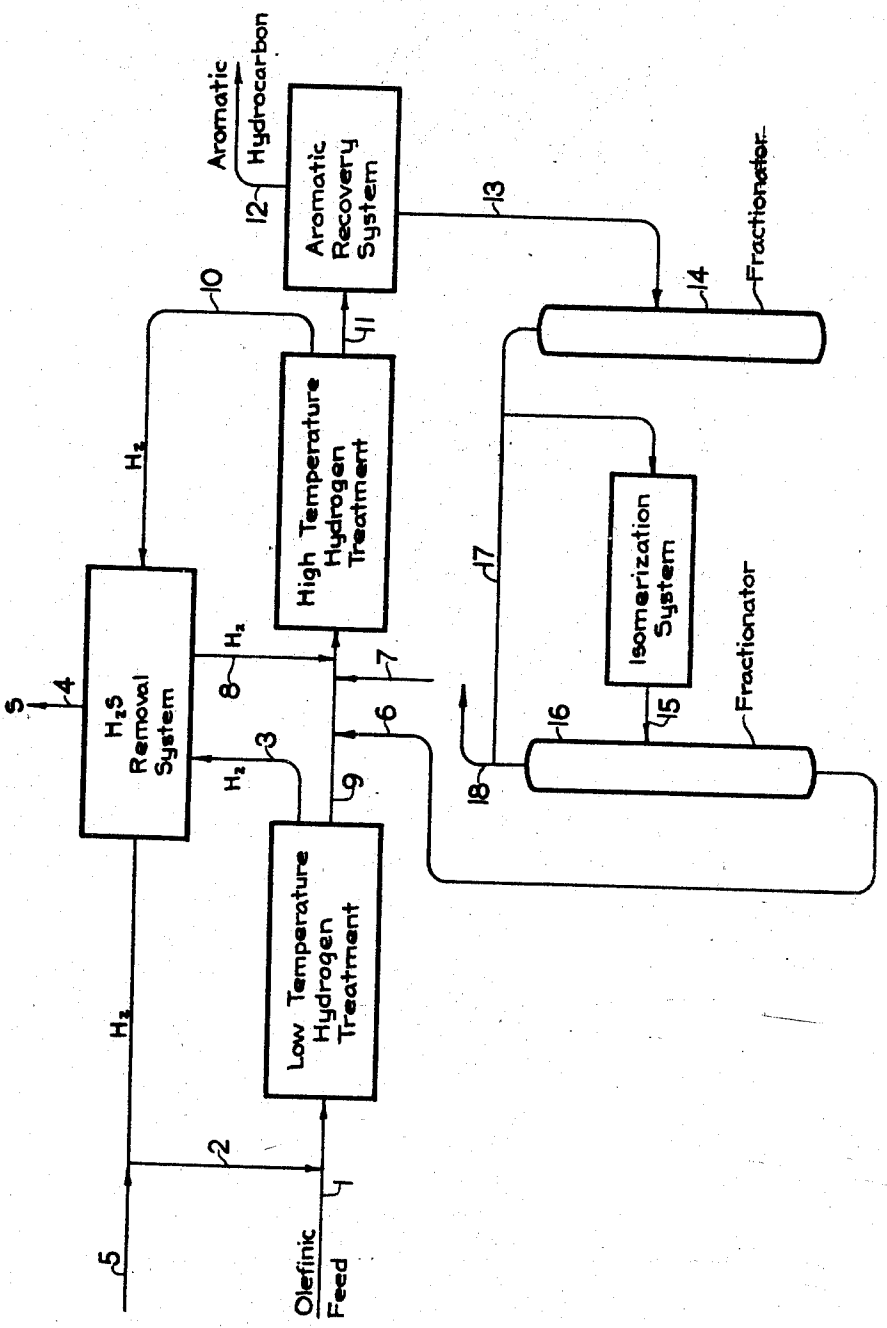
July 1, 1947. R. M. COLE 2,423,176

PRODUCTION OF AROMATIC HYDROCARBONS

Filed Jan. 26, 1945



Inventor: Robert M. Cole

By his Attorney: C. J. Ott

Patented July 1, 1947 2,423,176

UNITED STATES PATENT OFFICE

2,423,176

PRODUCTION OF AROMATIC HYDROCARBONS

Robert M. Cole, Oakland, Calif., assignor to Shell Development Company, San Francisco, Calif., a corporation of Delaware

Application January 26, 1945, Serial No. 574,756

5 Claims. (Cl. 260—668)

1

This invention relates to a process for the production of aromatic hydrocarbons from cracked gasoline stocks and similar stocks containing sulfur compounds and olefins.

In my copending application, Serial No. 569,234, filed December 21, 1944, of which this application is a continuation-in-part, I have described a process for the treatment of sulfur-bearing hydrocarbon fractions of the nature of cracked gasolines for the purpose of removing sulfur compounds therefrom. According to one preferred embodiment of said process the material is subjected to two treatments under hydrogen pressure in the presence of sulf-active hydrogenation-dehydrogenation catalysts, the first treatment being carried out at a temperature below about 850° F. and under such conditions that the sulfur concentration is decreased to slightly below 0.10% while leaving the olefins substantially unaffected, and the second treatment being carried out at a temperature above about 850° F. in order to prevent depreciation of the anti-knock properties of the material being desulfurized. In another embodiment of the invention the desulfurization is carried out without loss of anti-knock properties at temperatures above about 850° F. and the sulfur content of the feed is maintained below about 0.10% by recycling a suitable amount of the desulfurized product. The present invention relates to a process which is designed primarily to obtain maximum production of desirable aromatic hydrocarbons in a relatively pure form rather than to desulfurization (although substantial desulfurization is inherent), in which process various features of the invention described in the above-mentioned copending application are applied in novel combination to afford certain further advantages.

Various processes for the production of aromatic hydrocarbons, for example, synthetic toluene and synthetic xylene have been proposed and two of these are presently used to produce the greater part of the nation's supply of these materials. These processes are designed for and adapted only to the production of these materials from naphthenic straight run petroleum fractions. One of these processes is a specific application of the broader so-called hydroforming process. This process is inexpensive and relatively simple, but operates with a very low efficiency, i. e., the yield of aromatic hydrocarbon based upon the potential aromatic hydrocarbon is poor. This process will therefore not be further discussed. The other process is somewhat more complicated but is quite efficient. In this

2

process the naphthenic straight run gasoline is fractionated in a specific particular manner which cannot be divulged at this time. A part of it is subjected to a catalytic isomerization treatment to convert nonhydroaromatic naphthenes to the corresponding hydroaromatic naphthenes. Certain selected fractions are then subjected to catalytic dehydrogenation to convert hydroaromatic naphthenes to the corresponding aromatic hydrocarbons, and finally the aromatic hydrocarbons are recovered in a substantially pure state by a suitable process such, for instance, as extractive distillation. As stated above, these processes are designed for and are suitable only for the production of aromatic hydrocarbons from naphthenic straight run petroleum fractions. Neither process is suited for the treatment of materials containing substantial amounts of olefins such in particular as cracked and reformed gasoline stocks. In the hydroforming process small amounts of cracked stocks can be tolerated with the straight run feed. In the second more efficient process involving isomerization, even small amounts of cracked stocks would be very detrimental.

The process of the present invention is designed and applicable for the production of aromatic hydrocarbons from olefinic cracked stocks. Gasoline and other stocks obtained by thermal cracking, thermal reforming, catalytic cracking, and certain other high temperature processes usually have the following characteristics: They contain appreciable quantities of olefins and other unsaturated bodies. They contain appreciable quantities of aromatic hydrocarbons and naphthenes. They contain appreciable amounts of sulfur compounds and other impurities. The sulfur content is usually in the order of 0.2% to over 1%. These stocks are a potential source of large amounts of a variety of aromatic hydrocarbons. However, due to the presence of the olefins, sulfur compounds and other impurities the obtaining of the potential aromatic hydrocarbons from such materials has been most difficult and uneconomical. The process of the present invention affords a practical and economical process for the production of aromatic hydrocarbons from such materials.

The process of the present invention in its broader more general aspect comprises treating a stock such as described with hydrogen at a temperature below about 850° F. in the presence of a sulf-active hydrogenation catalyst under conditions selected to reduce the sulfur content of the feed to about 0.10%, or somewhat lower, with

incomplete hydrogenation of olefins; treating the partially desulfurized materials in the presence of a recycled isomerized fraction obtained as hereinafter specified, and if desired in the presence of added straight run material, with hydrogen at a temperature above 850° F. in the presence of a dehydrogenating sulfide of a metal of the iron group under conditions chosen to effect further desulfurization, dehydrogenation of naphthenes and a substantial saturation of olefins; removing aromatic hydrocarbons from the thus-treated material; fractionating the remainder to separate a fraction rich in nonhydroaromatic naphthenes; subjecting said fraction to a catalytic isomerization treatment; and cycling at least a portion of said isomerized material to the second hydrogen treatment.

The process will be described in more detail in connection with the schematic flow diagram in the accompanying drawing. Referring to the drawing, the feed entering via line 1 is mixed with a suitable amount of hydrogen entering via line 2 and subjected to a partial desulfurization-hydrogenation treatment. The feed is a sulfur-bearing olefinic petroleum fraction such as a cracked gasoline fraction or the like. As pointed out, these materials ordinarily contain appreciable amounts of sulfur. The treating conditions in this first hydrogen treatment are adjusted to reduce the sulfur content of the material to about 0.10% or less or to such an extent that after adding the recycled isomerized fraction and/or some straight run naphthenic gasoline, the sulfur content of the mixture does not exceed 0.10%. For reasons set forth in the above-mentioned copending application this treatment is carried out at a temperature below about 850° F., for example at a temperature between about 450° F. and 850° F. The treatment is carried out in the presence of an excess of hydrogen, for example, 1 to 30 mols of hydrogen per mol of hydrocarbon and at a superatmospheric pressure of at least 10 atmospheres. Any of the various sulf-active hydrogenation catalysts may be employed. Examples of such suitable catalysts are tungsten sulfide, nickel sulfide, iron sulfide, cobalt sulfide, molybdenum sulfide, cobalt thiomolybdate, zinc chromite, and various combinations of these. Under the chosen conditions a substantial if not the major, part of the olefins in the feed remains intact.

The hydrogen gas recycled in this step tends to become enriched in hydrogen sulfide. Consequently the hydrogen is usually recycled via line 3 to a hydrogen sulfide-removal system such as a Shell phosphate treater or the like. Hydrogen sulfide recovered per se or as a secondary product is removed via line 4. Most of the hydrogen for the treatment is usually supplied by the second hydrogen treatment. Make-up hydrogen for the process is added via line 5.

A substantially saturated isomerized fraction such as hydroaromatic hydrocarbon is added via line 6 to the product from the first, or low temperature, hydrogen treatment. If desired a portion of a substantially saturated straight run naphthenic gasoline may also be added via line 7. The mixture of products containing less than about 0.10% sulfur is mixed with an excess of hydrogen from line 8 and passed via line 9 to the second, or high temperature, treatment. The treating conditions in this treatment are adjusted to afford a substantial dehydrogenation of hydroaromatic naphthenes and a simultaneous hydrogenation of substantially all of the olefins. Under these conditions a further substantial desulfurization is also effected. Thus, the temperature in the second, or high temperature, treatment is between about 850° F. and 1000° F. The treatment is carried out in the presence of a large excess of hydrogen, for example, 4 to 30 mols of hydrogen per mol of hydrocarbon, and at a superatmospheric pressure of at least 10 atmospheres. The catalyst used in this second treatment is a dehydrogenating sulfide of a metal of the iron group and may furthermore advantageously also contain a sulfide of a metal of the group VI of the periodic system of the elements. Particularly suitable catalysts are, for example, a mixture of sulfides of nickel and tungsten corresponding approximately to the formula

$$2WS_2 \cdot 3Ni_2S_3$$

and various combinations of sulfide compounds of cobalt and molybdenum. The first of these is advantageously applied without a carrier and the second is advantageously applied with a carrier such in particular as an Activated Alumina-silica blend.

The hydrogen gas used in the second step may also be recycled via line 10 through a suitable hydrogen sulfide-removal system as illustrated.

The product from the second hydrogen treatment contains substantial amounts of aromatic hydrocarbons. It also contains appreciable amounts of non-hydroaromatic naphthenes which wer epresent in the original feed and/or formed in the preceding steps and which are not dehydrogenated under the present conditions specified. It is, however, substantially free of sulfur compounds and olefins. Consequently, the recovery of aromatic hydrocarbons from this material is much less difficult than the recovery of the aromatics from the original feed. The product from the second hydrogen treatment, or a fraction thereof, is passed via line 11 to an aromatic hydrocarbon-recovery system to remove the aromatic hydrocarbons. Any of the conventional systems involving solvent extraction, distillation, extractive distillation, or azeotropic distillation may be employed. The recovered aromatic hydrocarbon is removed via line 12.

The material remaining after the removal of the aromatic hydrocarbons contains considerable quantities of non-hydroaromatic naphthenes such, for example, as (depending upon the boiling range of the materials charged) methylcyclopentane, dimethylcyclopentanes, ethylcyclopentanes, methyl ethyl cyclopentane, and the like. These materials may be introduced as constituents of the original feed and/or by formation from hydroaromatic naphthenes during one or both of the hydrogen treatments. These non-hydroaromatic naphthenes, it is found, may be easily concentrated by a simple fractionation. The material remaining after the removal of the aromatic hydrocarbon is therefore first subjected to a suitable fractionation to separate a fraction rich in one or more of these non-hydroaromatic naphthenes. For example, if the original feed is a cracked gasoline fraction boiling essentially within the range of 185° F. and 232° F. the aromatic-free raffinate is advantageously passed via line 13 to a fractionator 14 where it is fractionated to recover an overhead fraction boiling essentially between 185° F. and about 210° F. and a higher bottom fraction. The higher boiling bottom fraction is removed via line 15 as a product of the process. The non-hydroaromatic fraction taken overhead is subjected to a catalytic isomerization

treatment to convert the non-hydroaromatic naphthenes largely to hydroaromatic naphthenes. Such isomerization is itself well known and therefore will not be described in detail. The isomerization is usually carried out in the liquid phase with a Friedel-Crafts type catalyst, for instance as aluminum chloride-hydrocarbon complex, in the presence of a small amount of hydrogen chloride promoter at moderate elevated temperature, for instance 150–300° F. The product from the isomerization treatment may be advantageously passed via line 15 to a fractionator 16 to effect a further concentration of the desired hydroaromatic naphthenes. Thus, for example, in the above-assumed case the isomerized product is advantageously separated in fractionator 16 into a higher boiling fraction boiling above about 210° F. and containing substantially all of the hydroaromatic naphthenes, and a lower boiling fraction containing unisomerized naphthenes and other non-naphthenic constituents. A portion of this lower boiling fraction may be advantageously recycled via line 17 to the isomerization step and the remainder may be withdrawn via line 18 as a product of the process. The isomerized product is cycled by line 6 and added to the olefinic feed stock after the first hydrogen treatment and prior to the second hydrogen treatment.

The process of the invention, it is seen, allows the production of aromatic hydrocarbons (if desired in a substantially pure state) from cracked gasolines and other sulfur-bearing olefinic petroleum fractions. This is made possible by the particular order and combination of the steps described. Some of the fine points contributing to this desired end may be mentioned. The combination of the first, or low temperature, hydrogen treatment and the diluting effect of the recycled isomerized material acts to reduce the sulfur content of the material to the second, or high temperature, hydrogen treatment to below about 0.10%. The diluting effect of the isomerized material makes a less drastic treatment in the first hydrogen treatment necessary in order to reduce the sulfur content to 0.10% or below. This in turn allows the first hydrogen treatment to be carried out with less hydrogenation of olefins. The preservation of the olefins in the first step is desired because the hydrogenation of these olefins in the second, or high temperature, step is desired to offset or counterbalance the large endothermic heat of reaction involved in the production of the aromatics. In the first, or low temperature, hydrogen treatment and also to some extent in the second, or high temperature, hydrogen treatment, there is a tendency for a part of the hydroaromatic naphthenes in the feed to isomerize to non-hydroaromatic naphthenes. In the process described these materials are reisomerized and recycled, thereby avoiding loss through this course. The isomerization step in the present process is also improved since the hydroaromatic naphthenes are dehydrogenated and removed prior to the isomerization. They therefore do not repress the desired isomerization as they do when the isomerization is applied prior to the dehydrogenation.

I claim as my invention:

1. A process for the production of aromatic hydrocarbons from sulfur-bearing olefinic petroleum fractions which comprises treating said petroleum fractions with hydrogen at a temperature between about 450° F. and 850° F. in the presence of a sulf-active hydrogenation catalyst under conditions selected to reduce the sulfur content of the material with incomplete hydrogenation of olefins; admixing with the product of said treatment a saturated isomerized hydroaromatic fraction mentioned below to produce a mixture containing less than about 0.10% sulfur; treating the mixture with hydrogen at a temperature between about 850° F. and 1000° F. in the presence of a dehydrogenating sulfide of a metal of the iron group under conditions chosen to effect further desulfurization, dehydrogenation of naphthenes and a substantial saturation of olefins; removing aromatic products from the thus-treated material; fractionating the remainder to separate a fraction rich in non-hydroaromatic naphthenes; subjecting said non-hydroaromatic fractions to a catalytic isomerization treatment to convert non-hydroaromatic naphthenes to hydroaromatic naphthenes; and cycling at least a portion of said isomerized material to the second hydrogen treatment as above specified.

2. Process according to claim 1 in which the first hydrogen treatment is adjusted to reduce the sulfur content of the feed to about 0.10%.

3. Process according to claim 1 in which the catalyst used in the second hydrogen treatment comprises nickel sulfide.

4. Process according to claim 1 in which the catalyst used in the second hydrogen treatment consists essentially of nickel sulfide and tungsten sulfide.

5. Process according to claim 1 in which the fraction treated boils predominantly within the range of 185° F. and 232° F. and the predominant aromatic product is toluene.

ROBERT M. COLE.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,298,346	Corson et al.	Oct. 13, 1942
2,241,393	Danner	May 13, 1941
2,283,854	Friedman et al.	May 19, 1942
2,288,866	Hoog	July 7, 1942
2,374,175	Burk	Apr. 24, 1945
2,348,557	Mattox	May 7, 1944
2,355,366	Conn	Aug. 8, 1944
2,376,086	Reid	May 15, 1945

FOREIGN PATENTS

Number	Country	Date
296,429	Great Britain	Dec. 16, 1929
418,926	Great Britain	Nov. 2, 1934