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PROCESS FOR THE PRODUCTION OF AROMATIC HYDROCARBONS

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The present invention relates to a process for the production of aromatic hydrocarbons from naphthenic hydrocarbon fractions of the nature of gasoline. By "naphthenic hydrocarbon fractions of the nature of gasoline" is meant hydrocarbon fractions from various sources boiling predominantly within the gasoline boiling range and containing appreciable concentrations, such as 10% or more, of naphthenic hydrocarbons in admixture with paraffin hydrocarbons and also frequently containing appreciable concentrations of olefinic hydrocarbons and/or aromatic hydrocarbons. More particularly, the invention relates to a process for the production of aromatic hydrocarbons from such petroleum fractions wherein maximum yields of aromatic hydrocarbons may be the most economically produced by a combination of three separate catalytic treatments. The invention also relates to the production of aromatic hydrocarbons from such fractions by two sub-combination treatments involving the use of two catalysts which may advantageously be employed in certain cases.

Many hydrocarbon fractions of the nature of gasoline derived from naphthenic base petroleums and from certain conversion processes and hydrocarbon syntheses contain appreciable concentrations of naphthenic hydrocarbons. These various fractions usually contain appreciable concentrations of paraffin hydrocarbons and many of them also contain in addition appreciable concentrations of olefinic hydrocarbons and/or aromatic hydrocarbons. The paraffin hydrocarbons generally are predominantly the normal isomers, the monomethyl isomers being next in frequency of occurrence. The naphthenic hydrocarbons in such distillates consist, in general, of complex mixtures of naphthenic hydrocarbons haxing six-membered rings and naphthenic hydrocarbons having five-membered rings. The naphthenic hydrocarbons having six-membered rings (that is, cyclohexane and its homologues) may be easily converted by dehydrogenation to benzene and the corresponding alkyl benzenes.

In view of the relative ease with which hydroaromatic naphthenic hydrocarbons may be dehydrogenated to corresponding aromatic hydrocarbons, numerous processes have been developed for the catalytic treatment of such distillates under dehydrogenation conditions to produce distillates of more aromatic character. In certain instances where the catalytic dehydrogenation treatment is sufficiently efficient, it has proved practical to produce substantially pure aromatic hydrocarbons by such treatment. These various processes all involve contacting the naphthenic fraction in the vapor phase with a dehydrogenating contact mass. In such cases where it is desired, the aromatic hydrocarbons formed by the treatment are removed or concentrated by one of the various well-known methods such as fractional distillation, solvent extraction, extractive distillation, or by a combination of treatments such as alkylation, followed by fractionation, extraction, etc.

Since the primary reaction involved in the proposed processes is the dehydrogenation of certain of the naphthenic hydrocarbons into the corresponding aromatic hydrocarbons, it is not surprising that nearly all of the many known dehydrogenation catalysts have been found to be effective for this treatment. Thus, it has been proposed to effect such treatment with various compounds such as the oxides, halides, sulfides, chromates, tungstates, molybdates, phosphates, borates, phosphites, chromites, manganates, etc., of such metals as Cu, Mg, Ca, Zn, Cd, Ba, B, Al, La, Tl, Si, Ti, Zr, Sn, Pb, Pt, Th, V, Nb, Sb, Ta, Bi, Cr, Se, Mo, Te, W, U, Mn, Re, Fe, Co, Ni, Ru, Pd, Rh, Ce, Pr and others. Also, many special catalysts containing one or more of these dehydrogenating compounds usually in combination with one or more other materials have been developed for this purpose and the relative merits of these various catalysts have been studied. The appraisal of these various proposed catalysts has been based upon such factors as the increase in octane number of the distillate, the increase in the aromaticity of the distillate, the reaction conditions required to effect these improvements in octane number and aromaticity, the thermal stability of the catalyst, the case with which the catalyst can be prepared, the ease with which the catalyst can be regenerated when spent, the carbon-forming tendency under the reaction conditions, the susceptibility of the catalyst to be poisoned by sulfur compounds, nitrogen bases, etc., found in such distillates, and similar practical aspects of their use. It has not been generally appreciated, however, that many of these catalysts, although they give substantially equivalent end results, are quite distinct in their manner of action. Thus, aside from one or two instances of dehydrogenating compounds exerting a promoting effect upon the catalytic activity of an apparently similar compound when combined therewith, it has not been appreciated that certain of these catalysts are complementary rather than competitive to one another.

We have studied the actions of various of these catalysts upon typical naphthenic fractions and

have now found that by the application of certain combinations of two or three types of dehydrogenation catalysts in series much greater conversions to aromatic hydrocarbons may be obtained than by the use of any one type of dehydrogenation catalyst alone. In fact, by the process of the present invention, it is possible to convert naphthenic fractions of the class described and consisting of hydrocarbons having six or seven carbon atoms entirely into benzene or toluene, respectively. Furthermore, the desirable result may be obtained while realizing much better catalyst life and process efficiency than has been possible in most of the hitherto-proposed processes.

The process of the present invention is applicable to the treatment of any vaporizable hydrocarbon fraction containing, for instance, 10% or more of naphthenic hydrocarbons of both hydroaromatic and non-hydroaromatic character in admixture with paraffin hydrocarbons and/or olefinic hydrocarbons and/or aromatic hydrocarbons. Thus, for example, it is well suited for the treatment of straight run naphthenic petroleum fractions such, in particular, as those boiling in the gasoline boiling range. Particularly suitable fractions to be treated are the so-called C_6 and/or C_7 and/or C_8 fractions from naphthenic straight run, cracked and/or reformed stocks consisting essentially of the hydrocarbons having six and/or seven and/or eight carbon atoms, respectively.

The material to be treated is, according to the present process, treated with two or three separate dehydrogenation catalysts under suitable conditions. According to the one aspect of the invention, the material is treated first under dehydrogenation conditions (with respect to hydroaromatic hydrocarbons) with a dehydrogenating metal sulfide. For this treatment any of the known metal sulfide dehydrogenation catalysts may be employed. Thus, for example, one may apply catalysts consisting largely of one or more sulfides of Fe, Co, Ni, Mo or W. Particularly suitable catalysts, for example, comprise substantial proportions of tungsten sulfide, preferably in combination with a sulfide of a metal selected from group VIII, for example Fe, Co or Ni. These catalysts are employed in the present process under dehydrogenation conditions. Dehydrogenation conditions most suitable for catalysts of this type are different from the conditions used in destructive hydrogenation and are usually different from the conditions most suitable for dehydrogenation with catalysts of the oxide type. Suitable dehydrogenation conditions with respect to temperature, pressure, partial pressure of hydrogen and space velocity depend somewhat upon the particular catalyst but are, in general, within the following limits:

Temperature ____°C__	About 425–550
Pressure ____atmospheres__	About 10–70
Partial pressure of hydrogen atmospheres__	About 8–60
Liquid hourly space velocity____	About 0.5–4.0

Naphthenic gasoline fractions when treated under these conditions with these catalysts are considerably aromatized. Thus, for example, in the case of the treatment of straight run fractions the products from this treatment are usually found to contain between about 20% and 40% aromatic hydrocarbons. Unsaturated hydrocarbons such as olefins, if present in the feed, are substantially completely hydrogenated. The aromatic hydrocarbons formed in this step of the process may be removed from the product, if desired, by any one of the several known methods. For example, the aromatic hydrocarbons may be removed from the product by extraction with one of the many solvents, for example SO_2, aniline, etc., having a selective solvent action for aromatic hydrocarbons, or it may in some cases be simply fractionally distilled to recover a pure or relatively concentrated aromatic fraction, or the aromatic hydrocarbon may be conveniently separated by an extractive distillation in a known manner.

The product from the above-described first step of the process, either with or without subsequent removal of the aromatic hydrocarbons formed, is contacted under dehydrogenation conditions with a molybdenum oxide catalyst. Any of the molybdenum oxide hydroforming catalysts may be employed. Very suitable catalysts, for example, comprise 4% to 30% molybdenum oxide on a suitable adsorptive support such as absorptive alumina, adsorptive magnesia, activated clay, or the like. Molybdenum oxide supported (15%) on adsorptive alumina is an especially good catalyst for this purpose. Suitable dehydrogenation conditions with respect to temperature, pressure, partial pressure of hydrogen and space velocity are chosen within the following approximate limits:

Temperature ____°C__	About 425–550
Pressure ____atmospheres__	About 2–50
Partial pressure of hydrogen atmospheres__	About 1–40
Liquid hourly space velocity____	About 0.1–4.0

The product from the dehydrogenation treatment with molybdenum oxide catalyst may, if desired, be treated to recover the aromatic hydrocarbons formed.

The product from the above treatment, either with or without subsequent removal of aromatic hydrocarbons, is then contacted under dehydrogenation conditions with a chromium oxide catalyst. Any of the chromium oxide dehydrogenation catalysts may be employed. Thus, for example, one may use precipitated and pilled catalysts consisting of Cr_2O_3, Cr_2O_3—Al_2O_3,

Cr_2O_3—Al_2O_3—K_2O, Cr_2O_3—SiO_2, Cr_2O_3—ZrO_2

Cr_2O_3—MgO, etc. Also, one may use chromium oxide catalysts of the impregnated type such as Cr_2O_3 supported upon an adsorptive support such as alumina, magnesia, clay, carbon, etc. Very suitable catalysts comprise adsorptive alumina impregnated with 16% Cr_2O_3 and promoted by 1.3% K_2O and 1% CeO_2. Suitable conditions to be employed in the treatment with the chromium oxide catalysts are chosen within the following approximate limits:

Temperature ____°C__	About 425–550
Pressure ____atmospheres__	About 0.1–7
Partial pressure of hydrogen atmospheres__	0.5
Liquid hourly space velocity____	About 0.1–3.0

The product from the treatment with the chromium oxide catalyst may, if desired, be used per se or may be treated to recover aromatic hydrocarbons in a pure or more concentrated form. The aromatic content of this product depends upon whether or not aromatic hydrocarbons have been removed after the first or second of the above-described dehydrogenation treatments. If aromatic hydrocarbons have been removed from the product after the first and/or second dehydrogenation treatment, this product usually contains about 50% aromatic hydrocarbons. If aromatic hydrocarbons have been removed only after

the first dehydrogenation step, aromatic contents of about 70% are usually present. If aromatic hydrocarbons have not been removed after either the first or second of the above-described dehydrogenation steps, the aromatic content of this product is much higher, for example 80%. If the aromatic hydrocarbons formed are removed from the product after the chromium oxide treatment, the non-aromatic fraction may, if desired, be recycled back to the chromium oxide treatment. In this way substantially complete conversion of the naphthenic fraction to aromatic hydrocarbons may be obtained.

In the above, the process has been described as comprising three separate dehydrogenation treatments under three definite dehydrogenation conditions with three separate types of dehydrogenation catalyst. This three-step process gives optimum results. It is not necessary, however, that the complete efficiency of the above-described three-step process be utilized. The invention also contemplates two sub-combinations of this three-step process which, while not as efficient as the three-step process, are nevertheless superior to any of the single-step processes heretofore proposed and may be profitably employed, for example, where it is desired to avoid the cost of providing three separate dehydrogenation units. The first of these alternative two-step processes involves contacting the naphthenic hydrocarbon fraction first with a metal sulfide dehydrogenation catalyst as above described in the first step of the three-step process and then contacting the product, either with or without subsequent removal or concentration of aromatic hydrocarbons, with a molybdenum oxide catalyst as described in the second step of the three-step process. It will be observed that this alternative process is the same as the above-described three-step process except that the dehydrogenation treatment with a chromium oxide catalyst is omitted.

According to the second alternative two-step process, the naphthenic petroleum fraction, preferably a straight run gasoline fraction, is first contacted with a molybdenum oxide catalyst as described in the second step of the three-step process and the product, either with or without subsequent removal or concentration of aromatic hydrocarbons, is treated with a chromium oxide catalyst as described in the third step of the three-step process. It will be observed that this alternative process is the same as the three-step process except that the dehydrogenation with the metal sulfide catalyst is omitted.

It is to be particularly pointed out that the above combination of treatments, except for the two above-described two-step processes, will not give the same or comparable high efficiency if the various treatments are combined in other manners. Thus, the product from the dehydrogenation treatment with the metal sulfide catalyst contains, in general, about 30% aromatic hydrocarbons. If the aromatic hydrocarbons formed are removed from this product and the product recycled, no appreciable additional yields of aromatic hydrocarbons are obtained. When, however, the product from the dehydrogenation treatment with the metal sulfide catalyst is contacted under dehydrogenation conditions with the molybdenum oxide catalyst as described, the product contains considerable additional aromatic hydrocarbons, for example 20%–40%. Again, if the aromatic hydrocarbons are removed from this product and the aromatic-free product recycled to the first dehydrogenation treatment with the metal sulfide, no appreciable further amounts of aromatic hydrocarbons are formed. By contacting this product, however, under dehydrogenation conditions with the chromium oxide catalyst as described, additional amounts (for example, 10%–70%) of aromatic hydrocarbons are formed. It is also to be noted that if the material is contacted with the various dehydrogenation catalysts in any other way, appreciable increase in yield of aromatic hydrocarbons over that obtained by the conventional one-step process is not obtained. Thus, if the naphthenic fraction is contacted with the molybdenum oxide or chromium oxide catalyst first, only very small amounts of aromatic hydrocarbons are formed by subsequent contacting of this material under dehydrogenation conditions with the metal sulfide catalyst, or if the material is contacted with the chromium oxide catalyst prior to contacting it with the molybdenum oxide catalyst, the dehydrogenation with the molybdenum oxide catalyst gives much lower yields of aromatic hydrocarbons than those obtained with the chromium oxide catalyst in the last step of the described process, and the catalytic life of the chromium oxide catalyst is found to be very poor.

A suitable application of the process is illustrated by the folowing example:

A hydrocarbon fraction consisting essentially of a mixture of normal paraffin and cycloparaffin hydrocarbons of both hydroaromatic and non-hydroaromatic character was treated with a tungsten sulfide-nickel sulfide catalyst under the folowing conditions:

Temperature ° C.	475
Pressure atmospheres	25
Mol ratio of hydrogen to hydrocarbon	8
Liquid hourly space velocity	1.0

The product contained about 27% by weight of aromatic hydrocarbons, chiefly toluene. The aromatic hydrocarbons were extracted from the product and the non-aromatic portion treated with a molybdenum oxide-alumina catalyst (14% Mo) under the following conditions:

Temperature ° C.	490
Pressure atmospheres	10
Mol ratio of hydrogen to hydrocarbon	3
Liquid hourly space velocity	0.6

The product contained about 26% by weight of aromatic hydrocarbons. The aromatic hydrocarbons were extracted from the product. The remaining non-aromatic portion was exceptionally suited for treatment with a chromium oxide-alumina (11% Cr) catalyst under the following conditions:

Temperature ° C.	475
Pressure atmospheres	1
Mol ratio of hydrogen to hydrocarbon	0
Liquid hourly space velocity	0.4

The ultimate yield of aromatic hydrocarbons obtained by the above combination of steps is higher than could be obtained with the said hydrocarbon fraction by the same number of passes with any one of the three catalysts separately or by any other order of the three treatments.

We claim as our invention:

1. A process for the production of aromatic hydrocarbons from naphthenic fractions of the nature of gasoline which comprises contacting the naphthenic gasoline fraction under dehydro-

genation conditions first with a dehydrogenating metal sulfide catalyst, then with a molybdenum oxide catalyst and then with a chromium oxide catalyst.

2. The process according to claim 1 wherein the metal sulfide dehydrogenation catalyst comprises tungsten sulfide.

3. The process according to claim 1 wherein the metal sulfide dehydrogenation catalyst comprises tungsten sulfide and nickel sulfide.

4. The process according to claim 1 wherein the molybdenum oxide catalyst consists essentially of molybdenum oxide supported upon alumina.

5. The process according to claim 1 wherein the chromium oxide catalyst consists essentially of chromium oxide and alumina.

6. A process for the production of aromatic hydrocarbons from naphthenic fractions of the nature of gasoline which comprises contacting the naphthenic fraction with a metal sulfide dehydrogenation catalyst under conditions chosen within the following limits:

Temperature——° C—	About 425–550
Pressure——atmospheres—	About 10–70
Partial pressure of hydrogen atmospheres—	About 8–60
Liquid hourly space velocity——	About 0.5–4.0

to selectively dehydrogenate naphthenes and hydrogenate any olefins present, and then contacting the thus-treated fraction with a molybdenum oxide catalyst under dehydrogenation conditions chosen within the following limits:

Temperature——° C—	About 425–550
Pressure——atmospheres—	About 2–50
Partial pressure of hydrogen atmospheres—	About 1–40
Liquid hourly space velocity——	About 0.1–4.0

7. The process according to claim 6 wherein the metal sulfide dehydrogenation catalyst comprises tungsten sulfide.

8. The process according to claim 6 wherein the metal sulfide dehydrogenation catalyst comprises tungsten sulfide and nickel sulfide.

9. The process according to claim 6 wherein the molybdenum oxide catalyst consists essentially of molybdenum oxide supported upon alumina.

10. The process according to claim 1 wherein the naphthenic fraction consists predominantly of hydrocarbons having seven carbon atoms.

11. The process according to claim 6 wherein the naphthenic fraction consists predominantly of hydrocarbons having seven carbon atoms.

12. The process according to claim 1 wherein aromatic hydrocarbons produced are removed from the product after each of said catalytic treatments.

13. The process according to claim 6 wherein aromatic hydrocarbons produced are removed from the product prior to the treatment with the molybdenum oxide catalyst.

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CERTIFICATE OF CORRECTION.

Patent No. 2,378,209. June 12, 1945.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, second column, line 36, for "case" read --ease--; page 2, second column, line 61, for "0.5" read --0-5--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 2nd day of October, A. D. 1945.

Leslie Frazer

(Seal) First Assistant Commissioner of Patents.

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4. The process according to claim 1 wherein the molybdenum oxide catalyst consists essentially of molybdenum oxide supported upon alumina.

5. The process according to claim 1 wherein the chromium oxide catalyst consists essentially of chromium oxide and alumina.

6. A process for the production of aromatic hydrocarbons from naphthenic fractions of the nature of gasoline which comprises contacting the naphthenic fraction with a metal sulfide dehydrogenation catalyst under conditions chosen within the following limits:

Temperature——° C—	About 425–550
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