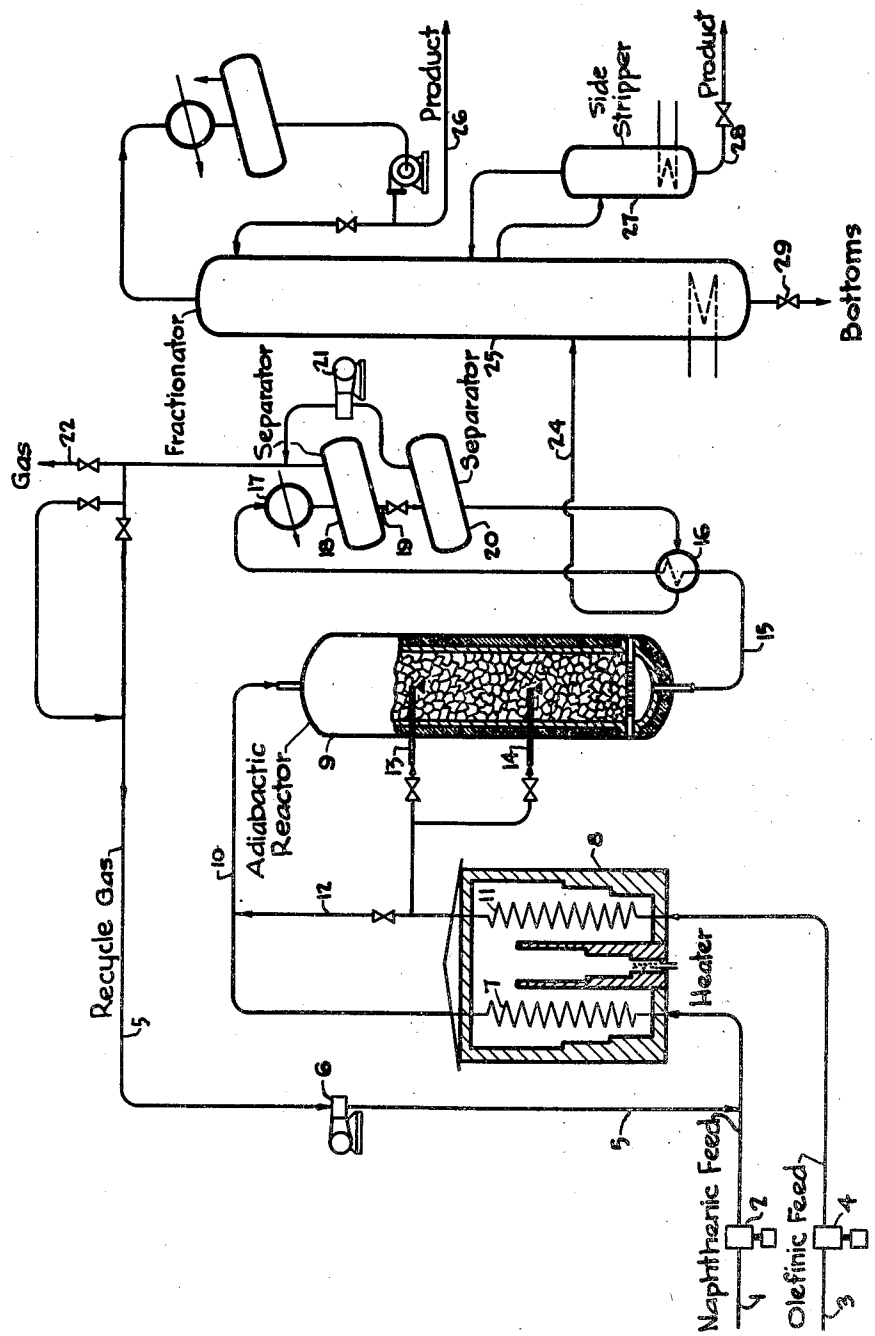
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PRODUCTION OF AROMATIC HYDROCARBONS
BY DEHYDROGENATION OF NAPHTHENES
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PRODUCTION OF AROMATIC HYDROCARBONS BY DEHYDROGENATION OF NAPHTHENES

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13 Claims. (Cl. 260—668)

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This application is a continuation of my copending application Serial No. 457,682, filed September 8, 1942, now abandoned.

The present invention relates to an improved process for the production of aromatic hydrocarbons from naphthenic hydrocarbon fractions, such in particular as straight run petroleum fractions of the nature of gasoline. More particularly the invention relates to an improved process for the production of aromatic hydrocarbons such as toluene from naphthenic hydrocarbon fractions by the use of special catalysts under special conditions.

As is known, the various petroleums obtained from different regions and from different geologic horizons differ in the proportions of the various types of hydrocarbons of which they are constituted. The straight run fractions obtained from petroleums of naphthenic character contain appreciable concentrations of naphthenic hydrocarbons (cycloparaffin hydrocarbons) and in the fraction of the nature of gasoline the naphthenic hydrocarbons are largely monocyclic. The nucleus may consist a ring of 3 up to 8 or more carbon atoms. However, it is known that the naphthenic hydrocarbons found in such petroleum distillates consist about exclusively of those having rings of five and six carbon atoms and that these are present in approximately equal proportions. Those having six-membered rings are sometimes referred to as hydroaromatic naphthenes since they can be conceived as the products of hydrogenation of aromatic hydrocarbons. Those having other than six-member rings may be called non-hydroaromatic naphthenes. By way of example, the concentrations of toluene (T), dimethyl cyclopentanes (DMCP) and methyl cyclohexane (MCH), in naphthenic petroleums are given in the following table:

Table I

Crude	Liquid, Volume Per Cent		
	T	DMCP	MCH
Ten Section	0.58	2.60	1.72
Kettleman	1.00	3.94	1.60
Eocene	0.59	2.17	0.69

The concentrations of toluene (T), methyl cyclohexane (MCH), dimethyl cyclopentanes (DMCP) and paraffins (P) in 85–110° C. straight run fractions from some further typical crude petroleums are shown in the Table II.

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Table II

	Weight Per Cent			
	T	MCH	DMCP	P
West Texas	11	27	25	37
Ventura	7	23	44	26
San Joaquin Valley	9	24	43	24

A more detailed partial analysis of two typical naphthenic petroleums are as follows:

Table III

Component	Boiling Point, °F.	Concentration in per cent by volume	
		Ventura	Los Angeles Basin
Methyl cyclopentane	161.2	0.518	0.359
Cyclohexane	177.4	0.555	0.385
1,1-dimethyl cyclopentane	189.5	0.211	0.146
1,3-dimethyl cyclopentane (trans)	195.3	0.554	0.384
1,2-dimethyl cyclopentane (trans)	197.2	1.210	0.839
1,3-dimethyl cyclopentane (cis)	207	0.230	0.159
1,2-dimethyl cyclopentane (cis)	210.6	0.176	0.122
Ethyl cyclopentane	217.4	0.165	0.144
Methyl cyclohexane	213.4	1.134	0.786

As will be apparent from the boiling points given in the above table, it is not possible by commercial fractionation to effect a separation between the naphthenes of hydroaromatic and non-hydroaromatic type. However, a fairly clean cut separation of fractions according to the total number of carbon atoms can be made. Straight run gasoline fractions from petroleum of naphthenic character, such for instance as just illustrated (referred to hereinafter as naphthenic straight run petroleum fractions), have, in general, relatively poor anti-knock properties, and are therefore not well suited for blending in gasolines having a high octane number. On the other hand, aromatic hydrocarbons such in particular as toluene, the xylenes, etc., are in demand.

It has been known for a long time that naphthenes such as methylcyclohexane, dimethylcyclohexane, etc., may be dehydrogenated comparatively easily to their corresponding aromatic hydrocarbons. With the above-mentioned considerations as a basis, a great deal of effort has been given over the past several years to the development of a suitable process whereby aromatic hydrocarbons could be produced from the naphthenes in such distillates in practical large scale operations. Although several processes have

been suggested, only two of these, as far as known, have developed into practicable and workable processes. The most important by far is that known in the petroleum industry as hydroforming. This process involves the treatment of selected cuts of gasoline at relatively high temperatures with certain metal oxide catalysts. The oxides of Ti, V, Cr, Mn, Mo, W and U can be used as catalysts in this process. However in practice molybdenum oxide or chromium oxide, and particularly molybdenum oxide, are used because in this process the production of aromatic hydrocarbons from the paraffinic constituents of such fractions by dehydrocyclization is an important reaction and these catalysts are particularly active in catalyzing dehydrocyclization. Very special and suitable molybdenum oxide catalysts for the process have been developed. Processes using catalysts of this type, however, require costly equipment and are relatively expensive to operate. This is due to several disadvantages which are inherent in operations with this type of catalyst. One most important disadvantage of this type of process is that under the dehydrogenation conditions necessarily employed appreciable amounts of tarry or coke-like carbonaceous material (often referred to loosely as carbon) are formed and deposit on the catalyst. As a consequence it is necessary to operate the process in short periods of a few hours with periodic removal of the carbonaceous deposits. The practicable method of effecting this removal, and the only method in use, is to burn off the deposited carbonaceous material with a gas containing a low and controlled concentration of oxygen. The numerous disadvantages and difficulties encountered in the practical application of processes of this type are believed to be so well known to those familiar with this art that they do not need to be mentioned in detail. Another undesirable feature of such processes is that the catalysts are both expensive and relatively short-lived. This is in part due to the above-mentioned periodic (regenerative) method of operation necessitated and in part to the inherent nature of the available catalysts.

The process of the present invention provides a means whereby naphthenic fractions may be catalytically aromatized in a most practicable and economic manner while avoiding the above-mentioned disadvantages and while realizing the further important advantages pointed out below. The present process, in its broader outline, comprises subjecting a naphthenic fraction, such for example as a C_7 fraction of a naphthenic straight run gasoline, to catalytic dehydrogenation with a catalyst comprising a sulfide of a metal of the iron group and tungsten sulfide in the presence of added hydrogen and certain concentrations of unsaturated hydrocarbons. More specifically it comprises the substantially continuous aromatization of naphthenic fractions of the character described with the specified catalyst in the presence of controlled concentrations of olefins.

The process of the invention may be employed for the aromatization of hydroaromatic naphthene hydrocarbons or mixtures of naphthene hydrocarbons with other hydrocarbons. Thus, it may be employed to aromatize substantially pure materials such as methyl cyclohexane obtained from any source. The most important application of the process, however, is in the aromatization of naphthenic straight-run fractions of the nature of gasoline, such as described. The process may be applied with the object of converting

the naphthenic fraction into an aromatic-containing fraction with a consequent increase in octane number, kauri-butanol number, etc., or it may be applied with the object of producing relatively pure individual aromatic hydrocarbons, such as nitration grade toluene. In each of these applications, as will be more fully pointed out below, the process affords certain important additional advantages.

When the naphthenic fraction is treated for the purpose of improving its properties with no intention of recovering substantially pure aromatic hydrocarbons, the fraction treated may be a narrow boiling fraction, such as a 205° F.–230° F. fraction, but it will usually be a somewhat broader fraction containing a substantial proportion boiling above 175° F. Fractions boiling up to and including the gasoline end-point, for instance 400° F.–450° F., may be suitably employed. (All boiling ranges herein given refer to the 5% and 95% points in a precision distillation over at least 30 theoretical plates and with a reflux ratio of at least 20 to 1.)

When the process is applied with the primary object of producing a substantially pure aromatic hydrocarbon or a mixture of substantially pure hydrocarbons such, for instance, as benzene, toluene, or a mixture of the xylenes, the process may be applied with any of the above-described fractions, but will be more advantageously applied with relatively narrow boiling fractions in which the naphthenes of the desired number of carbon atoms are more or less concentrated. Thus, for example, for the production of substantially pure benzene, a desirable fraction boils between about 165° F. and 185° F. For the production of nitration grade toluene, a desirable fraction boils between about 185° F.–200° F. and about 240° F.–250° F. This fraction not only contains substantially all of the methylcyclohexane and ethyl cyclopentane, but also includes the major portion of the dimethyl cyclopentanes and the naturally-existing toluene usually found to be present in small concentrations in most straight run gasolines. For the production of xylenes a desirable fraction is, for instance, one boiling between about 245° F. and 270° F.

As pointed out above, the most important application of the process of the invention is in the aromatization of naphthenic hydrocarbon fractions of the nature described. These fractions are substantially saturated in character. Thus, they have bromine numbers below 8 and usually about 0 to 2. Such fractions are treated in the process of the invention in the presence of an added unsaturated hydrocarbon. As will be more fully described, the addition of unsaturated materials such as olefins to the naphthenic gasoline fraction to be treated results in several important advantages. In the process, the olefin or other added unsaturated material is hydrogenated substantially completely. Any vaporizable olefinic hydrocarbon, mixture of olefinic hydrocarbons, or hydrocarbon fraction containing appreciable concentrations of olefins or other unsaturated hydrocarbons may be suitably employed. Such materials are hereinafter collectively referred to as olefinic materials. As will be more particularly pointed out, certain olefinic materials are more desirable addition agents than others, depending upon the particular naphthenic fraction employed and the purpose of the process. Although the gaseous olefinic hydrocarbons such as ethylene, propylene, the butylenes, butadiene, etc., may be used, it is usually more advan-

tageous to use normally liquid olefins. Thus, any of the vaporizable olefinic hydrocarbon fractions such as the usual thermally cracked and/or reformed gasolines, once-run catalytically cracked gasoline stocks, isoformed stocks, and fractions thereof, may be suitably employed. Olefinic hydrocarbons having a branched or iso structure are exceptionally suitable. These olefinic hydrocarbons are generally more easily hydrogenated than their corresponding straight chain isomers. Their use therefore allows the easy production of a product having a low bromine number. This, as will be explained, is desirable both in the production of high octane fuels and in the production of substantially pure aromatic hydrocarbons. The corresponding paraffin hydrocarbons produced in the process when using olefinic hydrocarbons of branched chain structure have higher octane numbers and lower boiling points than the corresponding normal paraffins and this is particularly desirable both in the production of high octane fuels and in the production of substantially pure aromatic hydrocarbons. While the various applicable olefinic hydrocarbon fractions may contain considerable amounts of non-olefinic hydrocarbons, it is generally desirable to employ olefinic hydrocarbon fractions which are relatively highly unsaturated, for example having bromine numbers of 50 or more. The use of such highly olefinic materials allows a high throughput of the naphthenic fractions per volume of catalyst. The various olefinic polymers produced by the polymerization of one or more of the normally gaseous olefins and boiling in the gasoline boiling range are particularly suitable since they offer a very concentrated source of olefins having highly branched structure. Thus, for example, a particularly suitable olefinic material to be employed is the dimer produced by the polymerization of butylenes.

Of the numerous applicable olefinic fractions containing considerable amounts of non-olefinic hydrocarbons, those which contain appreciable concentrations of aromatic hydrocarbons are particularly suitable. The aromatic hydrocarbons in such distillates may appreciably augment the yield of aromatics obtained in the process and may produce a product containing a minimum amount of non-aromatic materials. This is particularly advantageous when the process is operated for the purpose of producing substantially pure aromatic hydrocarbons and olefinic fractions containing appreciable concentrations of the desired aromatic hydrocarbons are available. Particularly suitable olefinic stocks of this type are the highly reformed cracked gasoline stocks such as produced by subjecting thermally reformed straight run fractions to a severe thermal reforming treatment, preferably in the presence of added gaseous hydrocarbons.

Where the process is operated for the purpose of improving straight run naphthenic gasolines, the olefinic hydrocarbon material added may, if desired, boil over a wide range, for example up to the final boiling point of the desired product. When the process is operated to produce substantially pure aromatic hydrocarbons, such materials of wide boiling range may be employed, but it is generally more advantageous to employ olefinic materials which may be easily separated from the desired aromatic hydrocarbons by simple fractional distillation. Thus, in the production of benzene it is advantageous to employ an olefinic material boiling above about 185° F. or below about 165° F. In the production of toluene it is advantageous to employ an olefinic material boiling above about 235° F. or below about 225° F. In the production of xylene it is advantageous to employ an olefinic material boiling below about 270° F. In such cases, however, where the olefinic material contains appreciable concentrations of the desired aromatic hydrocarbon, as in the case of cracked gasolines, a coextensive fraction comprising the desired aromatic hydrocarbon may be advantageously employed.

The optimum amount of olefinic material depends upon several factors, the most important of which are the degree of unsaturation of the olefinic material employed, the concentration of naphthenes in the naphthenic fraction to be treated, and the amount of fixed gases such as methane produced in the process, and therefore can only be stated to lie within certain limits.

When employing a material relatively concentrated in olefins, the addition of the olefinic material is beneficial up to a concentration of about 3 mols of olefin per mol of hydroaromatic naphthenes in the feed. This is equivalent to about 1.5 mols per mol of total naphthenes in the feed. Although the process may be operated with a net consumption of hydrogen, it is desirable to operate with a net production of hydrogen. The maximum concentration of olefin in the feed mixture is therefore preferably somewhat less than the maximum of 1.5 mols per mol of naphthenes specified above. Suitable mol ratios of olefins to naphthenes are, for instance, between about 0.9:1 and 1.4:1. These ratios correspond to ratios of 1.8:1 and 2.8:1 with respect to the hydroaromatic portion of the naphthenes.

When the concentration of naphthenes is low, for instance 15% or less, even lower ratios down to about one mol of olefin to two mols of naphthene or one mol of hydroaromatic naphthene may be advantageously employed.

Also when the degree of unsaturation of the olefinic material is less (i. e. the olefinic material contains appreciable amounts of non-olefinic diluents), the amount of olefinic material required to afford a ratio of olefin to naphthene of say 1:1 is usually sufficient to materially lower the throughput of the naphthenic fraction. In such cases, as with most cracked gasoline fractions, it is more advantageous to employ somewhat lower concentrations of olefins, for instance a mol ratio of olefin to hydroaromatic hydrocarbons between about 0.5:1 and about 2:1 or about 0.25:1 and 1:1 based on the total naphthenes.

Within these preferred limits the ratio is preferably adjusted so that, with a small withdrawal of recycle gas to prevent lowering of the hydrogen concentration to below about 80% by volume by dilution with fixed gases such as methane, there will be neither a net consumption nor production of hydrogen, i. e. the system operates continuously with a substantially constane quantity of recycle gas containing 80% or more of hydrogen; no gas is added, and the only gas withdrawn is the small amount required to maintain the specified hydrogen concentration in the recycle gas. The amount of olefinic material added is preferably adjusted to afford this method of operation.

The dehydrogenation of the naphthenes is endothermic whereas the hydrogenation of the olefinic hydrocarbons is exothermic. The amount of olefinic hydrocarbons may be adjusted to give a favorable heat balance, taking into consideration the type and thermal efficiency of the catalytic reactors employed. Thus, if the reacted olefins and reacted hydroaromatic naphthenes

are in a mol ratio of about 1.8:1 (this ratio varies somewhat depending upon the particular olefin and hydroaromatic naphthene), an overall reaction results which is neither endothermic nor exothermic.

In order to realize the full advantages of the use of the above-described feed, it is essential that the dehydrogenation be effected with a specific type of mixed sulfide catalyst. Suitable catalysts comprise a sulfide of a metal of the iron group, i. e. iron, cobalt and/or nickel, in intimate mixture with tungsten sulfide. The mol ratio of iron, cobalt and/or nickel to tungsten may vary widely but is usually between about 0.4:1 and 2.5:1. Within this range of ratios, the catalysts containing a major amount of a sulfide of iron, cobalt and/or nickel and a minor amount of tungsten sulfide are somewhat superior in certain respects to those containing a major amount of tungsten sulfide and are also considerably less expensive. One preferred catalyst of the general type comprises nickel sulfide and tungsten sulfide, preferably in a mol ratio of about 2:1.

The catalysts may be prepared by any method whereby the desired metal sulfides are produced or incorporated in intimate association with each other in the desired ratios. In general, the suitability of the catalyst is more or less proportional to the intimacy of the mixture. One suitable method for preparing a nickel sulfide-tungsten sulfide catalyst is, for example, to grind together the requisite quantities of dry nickel carbonate and dry tungstic acid, heat the mixture to decompose the nickel carbonate, thoroughly sulfide the mixture with a stream of hot hydrogen sulfide, and finally form the product into pellets of suitable size, if desired, with binder and/or a relatively inert extender. The activity of catalysts prepared in this manner is best when the components are exceptionally well ground together. In general, however, catalysts prepared in the wet way are more active. Very excellent catalysts may be prepared, for example, as follows:

Tungstic acid is dissolved in aqueous ammonia to form a solution of ammonium tungstate. A suitable procedure in preparing the solution is to suspend the tungstic acid in plain water with stirring and then add aqueous ammonia. Certain commercial tungstic acids are most readily dissolved by this procedure. When soluble tungstic acid is used, however, the order of adding the ingredients is immaterial. The ammonium tungstate is then converted to ammonium thiotungstate by reaction with hydrogen sulfide. The hydrogen sulfide may, if desired, be simply bubbled into the liquid in an open container. It is preferably, however, to react the solution with hydrogen sulfide in a closed pressure-tight vessel, preferably provided with stirring means. In order to form ammonium thiotungstate rather than ammonium di-thictugnstate, the temperature is preferably maintained somewhat above about 35° C. This condition is ordinarily provided automatically by the heat of reaction. Excess ammonium sulfide is preferably present in this solution. A second solution containing a soluble nickel salt is added to the ammonium thiotungstate solution whereupon nickel sulfide (and possibly small amounts of nickel thiotungstate) is precipitated. Most of the remaining tungsten is then precipitated from the solution as tungsten trisulfide by the addition of an acid, for instance, 25% sulfuric acid. The acid is preferably added until the pH of the liquid is between about 1 and 2. This gives a minimum loss of both constituents since tungsten trisulfide is soluble in less acidic solutions while nickel sulfide is soluble in more acidic solutions. If desired, the acid may be combined with the solution of the nickel salt before it is added to the ammonium thiotungstate solution. Also, if desired, the solution of ammonium thiotungstate and acid solution of the nickel salt may be continuously mixed in small streams to effect a continuous co-precipitation. The precipitated sulfide mixture is separated from the solution, and dried. The precipitated sulfides separated from the solution sometimes become warm on standing in air, probably due to oxidation. Prolonged exposure to air, however, does not appear to have any deleterious effects upon the activity of the catalyst. The separated mixed sulfides may, if desired, be washed to remove soluble salts such as ammonium sulfate. Such washing is, however, not essential. The precipitated and dried sulfide mixture is then heated, preferably in a rotating drum at a temperature of about 482° F.–842° F. in the presence of a stream of hydrogen or a mixture of hydrogen and hydrogen sulfide. This treatment is preferably continued to reduce the tungsten trisulfide and produce a material which may be readily pilled. For a forty-pound batch of catalyst, treatment for about six hours is sufficient. There appears to be three stages through which the catalyst passes as this treatment is continued. Insufficient treatment results in material which is somewhat difficult to pill. Further treatment results in a material that yields very hard and shiny pills without recourse to the use of a pilling lubricant or binder. Excessive or prolonged treatment yields a material which produces pills which are hard and shiny but somewhat brittle. The material is then ground and compressed into pellets for use. If desired, the catalyst may be pilled with a binder and/or a relatively inert extender and/or a small proportion, for example 0.25% to 0.5%, of one of the conventional lubricants. The actual valence states of the metals in the active catalysts are not known, but it is believed that the tungsten is present as the disulfide and nickel as some sub-sulfide or mixture of elementary nickel and sulfides in which the average valence of the nickel is about unity. It is found that the above-described reduction treatment, if carried to the indicated extent, may give exceptionally active and suitable catalysts which are magnetic, i. e. attracted by a magnet.

The above-described catalysts, and particularly those prepared by the described wet method, are especially active and selected to the dehydrogenation of naphthenes. Furthermore, they have exceptionally long active lives. Whereas the usual oxide catalysts require regeneration several times per day during use, the above-described catalysts when used to treat the above-described hydrocarbons may be continuously employed over long periods of time, for instance 1000 hours or more, before the conversion drops to a level making regeneration advisable. Thus, the necessity of frequently regenerating the catalyst is entirely eliminated. This is an important feature of the process of the invention. Furthermore, when after a long period of use it becomes advisable to regenerate the catalyst, this may be done simply, without resort to the customary burning with

oxygen-containing gases (although this customary method can, if desired, be employed), by passing a stream of sulfur dioxide (preferably diluted with an inert gas) through the catalyst bed for a short time. This regeneration which may be conveniently executed in situ at the reaction temperature (thus eliminating temperature adjustment of the catalytic converters) may be repeated at intervals to maintain the excellent catalytic activity over exceedingly long periods of time.

A further characteristic feature of the process of the invention is that the treatment of the naphthenic hydrocarbon fraction in the presence of the described concentrations of unsaturated hydrocarbons is effected in the presence of appreciable concentrations of added hydrogen. Thus, there is added to the reaction zone a volume of hydrogen (or more preferably a recycle gas rich in hydrogen) at least equivalent to, and preferably in excess of, the volume of hydrocarbon vapors. Although mol ratios of hydrogen to hydrocarbon as high as 30 to 1 may be suitably employed, it is usually more advantageous to employ ratios between about 3:1 and 12:1, for instance 7:1. In such cases when the composition of this feed is such that there is a hydrogen consumption and when first starting the process, it is necessary to provide hydrogen or hydrogen-containing gas from a separate source. As described above, however, the process is usually effected with a net hydrogen production. The hydrogen required in the process is therefore usually produced by the process and is continuously recycled through the reaction zone.

The recycle of the hydrogen-containing gas separated from the product is particularly advantageous not only in allowing large ratios of hydrogen to be more economically employed but also in providing a recycle gas of more desirable characteristics. Most hydrocarbon feeds, regardless of their history contain traces to appreciable amounts of sulfur compounds. In the present process a part at least of these sulfur compounds is reduced to hydrogen sulfide which then concentrates in the recycled gas to a certain extent. The presence of these small amounts of hydrogen sulfide in the recycle gas may increase the activity and life of the catalyst.

During operation of the process small amounts of normally gaseous hydrocarbon such as methane, ethane and propane, formed by side reactions, gradually accumulate in the recycled gas and tend to dilute the hydrogen. In the preferred embodiment of the process of the invention sufficient recycle gas is continuously or intermittently withdrawn to maintain the concentration of hydrogen above 80% by volume, and the composition of the hydrocarbon feed is adjusted to produce a net production of gas equivalent to the amount withdrawn. If desired, the recycle gas withdrawn from the system may be treated by known means (for instance, by scrubbing or high temperature cracking) to remove hydrocarbon diluents and the hydrogen then returned to the reaction system.

The contacting of the hydrocarbon and hydrogen with the catalyst may be effected in any of the manners conventionally employed for effecting other dehydrogenation and hydrogenation reactions. Thus, for example, the catalyst may be employed in the form of a finely divided powder which may be circulated through the reaction zone concurrent or countercurrent to the reactant vapors, or it may, if desired, be disposed in a continuously or intermittently renewed bed through which reactant vapors and hydrogen are caused to pass. Since, however, the active lives of the described catalysts are very long and frequent regeneration of the catalyst is unnecessary, it is not necessary to resort to these more complicated methods of effecting the contact. On the other hand, the catalyst may be advantageously supported as a fixed bed, or a plurality of beds, in one or more suitable catalytic converters, or catalyst cases through which the reactant vapors are passed. In this method of operation, catalyst converters, or catalyst cases, of conventional design may be employed. Thus, for example, the catalyst may be disposed in suitable reaction tubes, in catalyst cases such as used in catalytic cracking, etc. An important advantage of the process of the present invention is, however, that the catalysts may be employed in large beds in converters or catalyst cases of simple and inexpensive design. In such cases where the concentration of unsaturated hydrocarbons in the feed is adjusted to give an overall reaction which is neither appreciably endothermic nor exothermic, it is also possible and advantageous to employ a converter or catalyst case of the adiabatic type, i. e. a converter or catalyst case, preferably well insulated, which operates without the addition or removal of heat through the walls, or heating or cooling devices such as heating tubes or the like. Even in insulated converters there is usually a small loss of heat by radiation, etc. When employing such converters it is therefore advantageous to adjust the mol ratio of olefinic hydrocarbon to hydroaromatic naphthenes to slightly above 1.8 to 1 (0.9:1 based on total naphthenes) to afford a slightly exothermic reaction.

In such cases where the catalyst is employed in the form of formed pellets, it is sometimes noticed that the mechanical strength of the pellets decreases somewhat over long periods of use and that this is most pronounced in the first-contacted portion of the catalyst. When employing relatively large beds of catalyst, it is therefore advantageous to pass the hydrocarbon and hydrogen down-flow through the catalyst bed. In this method of operation, the first-contacted portion of the catalyst is not subjected to the weight of the catalyst bed.

In general, the olefin or other unsaturated hydrocarbon is introduced into the reaction zone with the naphthenes to be dehydrogenated.

In some cases, however, depending upon the particular naphthene and unsaturated hydrocarbon employed, the hydrogenation of the unsaturated hydrocarbon may take place at a faster rate than the dehydrogenation and may tend to increase the temperature in the first contacted section more than in the last contacted section of the reaction zone. In such cases, it may be advantageous to introduce at least a portion of the olefin or other unsaturated material to one or more points along the length of the reaction zone.

The conditions in the reaction zone are maintained conducive to the simultaneous dehydrogenation of naphthenes and hydrogenation of olefins or other unsaturated hydrocarbon added. With the above-described catalysts and in the presence of the described concentrations of hydrogen, these reactions may be simultaneously effected under a fairly wide range of conditions at temperatures above about 500° F. Applicable

ranges of conditions with respect to the several determining factors are, for example, as follows:

Temperature	°F.	797–977
Pressure	atms.	5–75
Liquid hourly space velocity		0.3–5

These various factors governing the conditions are interdependent, as they are in most all catalytic reactions. The ranges given are therefore not to be taken as rigidly fixed or absolutely limited, but only indicative of bounds outside of which it is ordinarily unnecessary to go in practicing the invention. The conditions with respect to any of the above governing factors which will be optimum under any given set of circumstances will depend upon the conditions with respect to the other factors as well as upon the particular hydrocarbon feed, the ratio of hydrogen employed, etc., but will ordinarily fall within the above limits. In no case are all of the factors made so severe that appreciable destructive hydrogenation takes place. When treating a straight-run naphthenic gasoline fraction in the presence of added olefinic polymer, very suitable conditions giving about optimum results are, for example, as follows:

Temperature	°F.	842–905
Pressure	p. s. i.	400–800
Liquid hourly space velocity		0.5–3
Mol ratio of hydrogen to hydrocarbon		3:1–12:1

The above-described process is superior to the hitherto-employed processes in a number of important respects. One important advantage of the present process is that it may be carried out continuously for long periods of time. Thus, the necessity for regenerating the catalyst every few hours with all its difficulties, inconveniences, expenses, loss of production capacity, etc. is entirely eliminated. A further important advantage of the present process is that the conversion rates and efficiency are generally unexpectedly higher than usual and the production capacity, instead of being materially lowered, is higher than might be expected. It is to be particularly pointed out, however, that the process of the invention differs fundamentally from the various reactions hitherto studied involving the simultaneous treatment of a hydrogen donor and hydrogen acceptor. In these known reactions the effect of the hydrogen acceptor is to decrease the partial pressure of hydrogen in the reaction system, thus disturbing the equilibrium between the hydrogen and the hydrogen donor and causing a more complete reaction. In the process of the present invention this is not the case since the process is executed in the presence of a mol excess of hydrogen which is usually recycled through the reaction zone. Any decrease in the partial pressure of hydrogen caused by the hydrogenation reaction is negligible and altogether insufficient to exert any appreciable effect upon the equilibriums which may be present in the system.

A further important advantage of the described process is that the dehydrogenation of hydroaromatic naphthenes is effected with a small heat of reaction. This particularly advantageous since it allows a hitherto unattainable flexibility in converter design. Simple, inexpensive converters including the highly desirable adiabatic type may be used and complicated furnaces, etc. may be dispensed with. Furthermore, the process may be effected with converters of large size containing beds of catalyst of large cross-section. This advantage allows the process to be effected with important economies in space, investment and thermal efficiency.

Another important advantage of the process is that it allows the production of additional yields of valuable products. For example, when an olefinic cracked or reformed stock is employed, greatly increased yields of valuable aviation base stock are obtained; when polymers of lower olefins, such as di-isobutylene, are employed, considerable quantities of valuable isooctanes are obtained. The additional yields of these various valuable hydrogenated products are furthermore obtained without increase of the capital investment or loss of production capacity; in fact, the production capacity may be increased. Furthermore, the hydrogen required for the production of these additional valuable saturated products is simply and cheaply obtained in the present method since the usual problems of separating, purifying, compressing, and storing hydrogen are reduced or completely eliminated. This is not only an advantage with respect to supplying hydrogen for separate hydrogenation processes but also in the disposal of the usual hydrogen produced in the separate hydrogenation of straight-run fractions.

Aside from the yields of additional valuable products, the process of the invention is advantageous with respect to the yields of the primary aromatic hydrocarbons and its much broader range of applicability. Thus, the production capacity with respect to aromatic hydrocarbons may usually be considerably increased due to an increased conversion efficiency and the recovery of small to appreciable amounts of aromatic hydrocarbons in the olefinic materials employed. (No appreciable amounts of aromatic hydrocarbons are produced in the process from open chain olefins.) This is not only a distinct advantage with respect to the production capacity but also in that it allows relatively small concentrations of aromatic hydrocarbons, such as taluene, to be recovered from various olefinic distillates which would ordinarily be considered too lean to warrant treatment. Conversely, the process also allows fractions containing small concentrations of naphthenes to be economically treated where it would otherwise be uneconomical.

Another advantage of the present process is that sulfur-bearing fractions may be employed. These are substantially desulfurized during treatment. This advantage is two-fold since the dehydrogenation is benefited by the presence of small amounts of such sulfur compounds.

It is furthermore to be pointed out that the treatment of the described hydrocarbon mixtures is more efficient than the separate treatment of olefinic stocks or saturated naphthenic stocks in still other respects.

In the hydrogenation of olefins, such as di-isobutylene, with the present catalysts the catalytic activity declines unless the mol ratio of hydrogen to hydrocarbon is very large, for example, 30:1. In the process of the present invention, however, wherein the olefin is hydrogenated in the presence of substantial concentrations of naphthenes, much lower mol ratios of hydrogen are sufficient to insure a very slow decline in the catalytic activity. Thus, for example, mol ratios of hydrogen to hydrocarbon below 10:1 are suitable and practicable.

The catalysts described above have been tried under the specified conditions for the treatment of cracked gasoline fractions alone. It was found, however, that in the treatment of such stocks alone under these conditions the activity of the catalyst declined at a much faster rate, presumably due to the deposition of carbonaceous deposits. Consequently, the process was not only uneconomical due to the high hydrogen consumption, but the substantially continuous operation which is an important feature of the process of the invention was not attained. In the described process wherein cracked stocks are treated in conjunction with straight run naphthenic stocks and the concentration of cracked stocks limited to give a ratio of olefin to total naphthenes of, for example, 1:1, the expected detrimental effect of the cracked stock is avoided as is also the high hydrogen ratio required for the hydrogenation of olefin polymers, and instead, the process may be carried out substantially continuously with low hydrogen ratios while obtaining an increased dehydrogenation efficiency and the other advantages noted.

The process described above is illustrated diagrammatically in the attached drawing. Referring to the drawing the naphthenic fraction to be treated, for instance, the 204–226° F. naphthenic straight-run gasoline fraction of Example I is introdumed via line 1 and pump 2. The olefinic feed, for example, the 157–225° F. olefinic cracked gasoline fraction of Example I is introduced via line 3 and pump 4. Recycled product gas containing at least 80% hydrogen is introduced via line 5 and compressor 6. The amount of recycled product gas is, for example, approximately 7 mols per mol of combined hydrocarbon feed. The naphthenic feed and recycled product gas are preheated to about 900° F. in coil 7 of furnace 8 and then passed into the top of reactor 9 via line 10. Reactor 9 is a vertically disposed downflow adiabatic reactor containing a fixed bed of the pelleted nickel sulfide-tungsten sulfide catalyst described above. The conditions in reactor 9 are, for example, maintained as follows:

Temperature, °F.	900
Pressure, p. s. i.	720
Liquid hourly space velocity	about 1.5
Recycled gas, cu. ft. per barrel	about 6,500

The olefinic feed, after being preheated to the reaction temperature in coil 11, is passed via line 12 and co-mingled with the remaining feed in line 10. Part of this olefinic feed may be introduced at spaced points in the reactor by means of lines 13 and 14, as described, to maintain a more even temperature throughout the length of the catalyst bed.

The product leaves the reactor 9 via line 15 and, after being cooled in heat exchanger 16 and condenser 17, it is passed to the high pressure separator 18. The liquid condensate is then passed via line 19 to a low pressure separator 20. The product gas from the low pressure separator is compressed by compressor 21 and recombined with the product gas from the high pressure separator. Some of the recycled gas is withdrawn from the system via line 22 to maintain the pressure constant, the amount withdrawn being dependent upon the ratio of the two feeds applied and being adjusted such that the concentration of hydrogen in the recycled gas is maintained above 80% by volume. As indicated in Example I, for example, when the naphthenic feed and the olefinic feed are applied in a ratio of about 1.74 to 1, the mol ratio of olefins to naphthenes is about 0.31 to 1, the amount of gas withdrawn is about 310 cu. ft. per barrel of feed, and the concentration of hydrogen in the recycled gas is maintained at about 94%.

The liquid product from separator 20 is passed via line 24 to a fractionating column 25. In the fractionator 25 the product is separated into a fully saturated non-aromatic overhead product removed via line 26 and a toluene fraction which is removed via side stripper 27 and line 28. A bottom fraction of heavy ends is removed via line 29.

The following examples which, it is to be understood, are not intended to limit the invention in any way are submitted for the purpose of illustrating various aspects of the invention.

Example I

A naphthenic fraction boiling between about 204° F. and 226° F. was separated from a straight-run gasoline. This was a saturated fraction containing about 41.5% methyl cyclohexane. When this fraction was dehydrogenated with a nickel sulfide-tungsten sulfide catalyst containing the nickel and tungsten in a mol ratio of about 2:1 under the following approximate conditions:

Temperature, °F.	900
Pressure, p. s. i.	720
Volume of catalyst, cu. ft.	1.22
Volume of hydrocarbon charge per hour, gal./hr.	13.5
Volume of gas recycled per hour, cu. ft.	2100

there was a hydrogen production of about 200 cu. ft. per hour and the reaction was so endothermic that the desired conditions could be maintained only with difficulty with a small bed of catalyst with means provided for supplying the necessary heat.

To 635 parts of this naphthenic fraction there were added 365 parts of a cracked fraction boiling between about 157° F. and 255° F. and containing about 3.8% by volume of aromatic hydrocarbons and 44% by volume olefins (bromine number, 67). The approximate composition of the blend was as follows:

Olefins, percent by volume	16
Aromatics, do	8.5
Methyl cyclohexane, do	30
Mol ratio of olefins to naphthenes	0.31:1

When this blend was treated in place of the unblended naphthenic fraction, the hydrogen production dropped to about 100 cu. ft. per hour and the endothermic heat of reaction was neutralized to such an extent that with the reactor employed there was no difficulty in maintaining a temperature of 900° F. throughout the conversion zone. The hydrogen concentration of the recycle gas was maintained at about 94%.

Example II

A naphthenic straight-run gasoline was subjected to a fractional distillation and a fraction boiling between about 197° F. and 226° F. was separated. This was a saturated fraction containing 38% by volume methyl cyclohexane and 0.7% by volume toluene. This fraction was treated with a nickel-tungsten sulfide catalyst

prepared by the above-described wet method under the following approximate conditions:

Temperature, °F.	880
Pressure, p. s. i.	426
Liquid hourly space velocity	3.27
Mol ratio of hydrogen-containing gas (93% hydrogen) to hydrocarbon	7:1

The catalyst had been in use for 606 hours prior to this use and was approximately 75% as efficient as the fresh catalyst. The conversion efficiency was about 39.7%, i. e. about 39.7% of the available methyl cyclohexane was dehydrogenated to the corresponding toluene.

One volume of the above-described naphthenic fraction was blended with an equal volume of octylenes (obtained by the hot acid polymerization of butylenes) to produce a blend in which the mol ratio of olefins to hydroaromatic naphthenes was about 3:1. The blend was treated with the same catalyst under the same conditions (as near as they could be held—liquid hourly space velocity, 3.42), and the conversion efficiency immediately increased to 63.2%. The product was a substantially saturated toluene fraction.

A portion of the original unblended naphthenic fraction was again treated with the same catalyst under the same conditions (liquid hourly space velocity, 3.24). The conversion efficiency dropped again to 39.7%. This example illustrates, among other things, the increased conversion efficiency realized in the process of the invention.

Example III

A methyl cyclohexane fraction containing 96% methyl cyclohexane was dehydrogenated with a nickel sulfide-tungsten sulfide catalyst containing the nickel and tungsten in a mol ratio of about 2:1 under the following approximate conditions.

Temperature, °F.	862
Pressure, p. s. i.	426
Liquid hourly space velocity	2.03
Mol ratio of hydrogen-containing gas (93% hydrogen) to hydrocarbon	7:1

The catalyst had been used for 396 hours prior to this use. The conversion efficiency was 64%.

A portion of the methyl cyclohexane fraction was blended with 1.00 volume of a butylene dimer fraction to produce a blend in which the mol ratio of olefins to methyl cyclohexane was about 0.865:1. This blend was treated under the same conditions (liquid hourly space velocity of 2.08) with the same catalyst. The conversion efficiency was 70%.

In the above the process of the invention has been described with reference to the treatment of naphthene fractions in the presence of certain concentrations of unsaturated hydrocarbon with the particular type of catalyst employed. It will be appreciated that this novel treating step may be employed in various combinations with such steps as thermal cracking, catalytic cracking, iso-forming, destructive hydrogenation, thermal reforming, catalytic reforming, olefin isomerization, alkylation, catalytic isomerization of paraffins, solvent extraction, fractionation, and the like to produce novel and advantageous unit processes for the more economical production of various refinery products.

One improved refining operation leading to increased yields of substantially saturated aviation base stock involves fractionating a naphthenic base petroleum to separate a light naphtha and a heavy naphtha or gas oil, catalytically cracking the heavy naphtha, separating the cracked product into a light naphtha and a heavy naphtha, and subjecting the cracked light naphtha in admixture with the straight naphtha to the above-described treatment.

Another improved process leading to increased yields of substantially saturated aviation base stocks involves thermally cracking a heavy naphtha fraction, iso-forming the cracked light naphtha and subjecting the iso-formed light naphtha in admixture with a straight-run naphthenic naphtha to the above-described treatment. Thus, for example, a heavy straight-run naphtha may be thermally cracked by one of the conventional methods, for instance, the Dubbs process or the TVP process. The product is fractionated to separate an olefinic light naphtha fraction boiling, for instance, up to about 225° F. The cracked light naphtha is then subjected to an iso-forming treatment. In iso-forming the naphtha is passed in contact with a catalyst having olefin isomerizing activity at a temperature slightly below that giving appreciable cracking (for instance, 750° F.). The catalyst is usually the same as or very similar to the clay-type catalysts commonly employed in catalytic cracking. (See U. S. Patent No. 2,400,431.) A very suitable catalyst is, for example, the synthetic alumina-silica composite cracking catalyst now in common use as a cracking catalyst. The iso-forming process which is a process developed by the Standard Oil Company of Indiana is described in detail in U. S. Patents Nos. 2,326,703, 2,347,299 and 2,410,908 to Thiele et al., to which patents reference is made for various details. The iso-formed product, preferably after rerunning to remove small amounts of polymers or tars which may be formed, is then mixed with a straight-run naphthenic gasoline fraction such as described above to produce a blend in which the mol ratio of olefins to naphthenes is, for example, between 0.5:1 and 1:1. The blend is then treated with the described tungsten sulfide-nickel sulfide composite catalyst under the following conditions:

Temperature, °F.	842–905
Pressure, p. s. i.	400–800
Liquid hourly space velocity	0.5–3
Mol ratio of hydrogen to hydrocarbon	3:1–12:1

The product is a particularly valuable blending component in high octane 150° C. end point aviation gasoline.

Still another novel advantageous application of the process of the invention which leads to the production of high yields of aromatic hydrocarbons and a substantially saturated aromatic-free naphtha of exceptionally high octane number involves subjecting a blend of a low octane straight-run naphthenic distillate and an olefinic distillate, such as cracked stock, high-temperature once-run catalytically cracked stock, hydroformed stock, reformed stock or the like, to the above-described treatment, separating aromatic hydrocarbons from the product, and subjecting the substantially saturated remainder to a catalytic isomerization treatment.

It is also possible to produce the desired concentration of unsaturated hydrocarbons in the saturated naphthenic fractions to be treated by a suitable combination of steps. For instance, a naphthenic straight-run naphtha may be

lightly cracked to produce the desired ratio of olefins to hydroaromatic naphthenes and the product subjected to the described treatment. In this process it is advantageous to employ the recycled hydrogen-containing gas as a cooling medium to bring the temperature of the partially cracked material down to a temperature suitable for the dehydrogenation-hydrogenation treatment. In this process fractions of high octane number are produced since there is a tendency to selectively crack out the low octane components.

The process may also be advantageously applied to produce high yields of aromatic hydrocarbons and lower boiling olefins by subjecting a naphthenic naphtha to the described dehydrogenation-hydrogenation treatment, subjecting the product to a thermal reforming-cracking treatment, recovering lower boiling olefins from the product, and recycling the higher boiling olefins to the dehydrogenation-hydrogenation treatment.

I claim as my invention:

1. In a process for the production of toluene by dehydrogenation of a naphthenic straight run petroleum fraction, the improvement which comprises separating a fraction of naphthenic straight run gasoline containing hydroaromatic naphthenes and non-hydroaromatic naphthenes and boiling predominantly within 195° F. and 250° F., adding to said straight run naphthenic gasoline fraction an olefinic cracked gasoline fraction in such an amount that the mol ratio of olefins to hydroaromatic naphthene in the mixture is between about 0.5:1 and 2:1, and effecting the dehydrogenation of said mixture substantially continuously with a catalyst consisting essentially of a major mol amount of a sulfide of a metal of the iron group and a minor mol amount of tungsten sulfide in the presence of at least 3 mols per mol of hydrocarbon feed of gas containing at least 80% hydrogen under conditions chosen within the following limits,

Temperature	°F.	797–977
Pressure	atmospheres	5–75
Liquid hourly space velocity		0.3–5

thereby to obtain a substantially saturated product rich in toluene.

2. In a process for the production of toluene by dehydrogenation of a naphthenic straight run petroleum fraction, the improvement which comprises employing a naphthenic straight run gasoline fraction boiling predominantly within 195° F. and 250° F., adding to said straight run naphthenic gasoline fraction a cracked gasoline fraction containing a substantial proportion of olefins of branched chain structure, effecting the dehydrogenation of said mixture substantially continuously with a catalyst consisting essentially of a major mol amount of nickel sulfide and a minor mol amount of tungsten sulfide under conditions chosen within the following limits,

Temperature	° F.	797–977
Pressure	atmospheres	5–75
Liquid hourly space velocity		0.3–5

and with a substantially constant volume of gas which is recycled in an amount of at least 3 mols per mol of hydrocarbon feed, substantially continuously withdrawing from said recycle gas stream such an amount of gas that the concentration of hydrogen in said recycle gas is maintained above 80% by volume, the mol ratio of olefins to hydroaromatic naphthenes in the said mixture being adjusted and maintained in the range of about 0.5:1 to 2:1 so as to furnish net production of gas equal to said amount withdrawn.

3. In a process for the production of toluene by dehydrogenation of a naphthenic straight run petroleum fraction, the improvement which comprises employing a naphthenic straight run gasoline fraction boiling predominantly within 195° F. and 250° F., adding to said straight run naphthenic gasoline fraction an olefinic cracked gasoline fraction, effecting the dehydrogenation of said mixture substantially continuously with a catalyst consisting essentially of a major mol amount of nickel sulfide and a minor mol amount of tungsten sulfide in the presence of at least 3 mols per mol of hydrocarbon feed of recycle product gas under conditions chosen within the following limits,

Temperature	° F.	797–977
Pressure	atmospheres	5–75
Liquid hourly space velocity		0.3–5

the amount of said cracked gasoline fraction added to said straight run naphthenic gasoline fraction being adjusted such that the mol ratio of olefins to hydroaromatic naphthenes in the mixture is sufficiently above 0.5:1 but not above 2:1 so that upon operating with a substantially constant quantity of said recycle product gas the concentration of hydrogen in said recycled product gas is maintained above 80% by volume.

4. In a process for the production of toluene by dehydrogenation of a naphthenic straight run petroleum fraction, the improvement which comprises employing a naphthenic straight run gasoline fraction boiling predominantly within 195° F. and 250° F., adding to said straight run naphthenic gasoline fraction an olefinic cracked gasoline fraction in such an amount that the mol ratio of olefins to hydroaromatic naphthenes in the mixture is at least 0.5:1 but not above 2:1, and effecting the dehydrogenation of said mixture substantially continuously with a catalyst consisting essentially of a major mol amount of a sulfide of a metal of the iron group and a minor mol amount of tungsten sulfide in the presence of at least 3 mols per mol of hydrocarbon feed of gas containing at least 80% hydrogen under conditions chosen within the following limits,

Temperature	°F.	797–977
Pressure	atmospheres	5–75
Liquid hourly space velocity		0.3–5

thereby to obtain a substantially saturated product rich in toluene.

5. In a process for the aromatization of a naphthenic straight run petroleum fraction by dehydrogenation, the improvement which comprises separating from a naphthenic petroleum a straight run fraction of the nature of gasoline containing hydroaromatic naphthenes and non-hydroaromatic naphthenes, adding to the straight run naphthenic fraction an olefinic fraction in such an amount that the mol ratio of olefins to hydroaromatic naphthenes in the mixture is between about 0.5:1 and 2:1, and effecting the dehydrogenation of said mixture substantially continuously with a catalyst consisting essentially of a major mol amount of nickel sulfide and a minor mol amount of tungsten sulfide in the presence of at least 3 mols per mol of hydrocarbon feed of

recycle product gas containing hydrogen under conditions chosen within the following limits,

Temperature	°F.	797–977
Pressure	atmospheres	5–75
Liquid hourly space velocity		0.3–5

to obtain a substantially saturated aromatized product.

6. In a process for the aromatization of a naphthenic straight run petroleum fraction by dehydrogenation, the improvement which comprises separating a naphthenic straight run fraction of the nature of gasoline, adding to said straight run naphthenic fraction an olefinic cracked gasoline fraction in such an amount that the mol ratio of olefin to hydroaromatic naphthene in the mixture is 0.5:1 to 2:1, and effecting the dehydrogenation of said mixture substantially continuously with a catalyst consisting essentially of a major mol amount of nickel sulfide and a minor mol amount of tungsten sulfide in the presence of at least 3 mols per mol of hydrocarbon feed of recycled product gas under conditions chosen within the following limits,

Temperature	°F.	797–977
Pressure	atmospheres	5–75
Liquid hourly space velocity		0.3–5

thereby to obtain a substantially saturated liquid product rich in aromatic hydrocarbons and a product gas rich in hydrogen.

7. A process for the production of substantially saturated aviation base stock from straight run naphthenic naphtha and cracked naphtha which comprises thermally cracking a heavy naphtha, separating from the product an olefinic light cracked naphtha, subjecting the olefinic light cracked naphtha to an isoforming treatment, commingling the isoformed light cracked naphtha with a naphthenic straight run gasoline fraction in such an amount as to give a mol ratio of olefins to hydroaromatic naphthenic hydrocarbons between about 0.5:1 and 2:1, treating the composite with a tungsten sulfide-nickel sulfide composite catalyst in the presence of at least 3 mols of recycled product gas per mol of hydrocarbon feed under conditions chosen within the following limits,

Temperature	°F.	797–977
Pressure	atmospheres	5–75
Liquid hourly space velocity		0.3–5

8. In a process for the dehydrogenation of naphthenes in a straight-run petroleum fraction the improvement which comprises continuously passing the straight-run petroleum fraction along with at least 3 mols of recycled product gas containing at least 80% hydrogen into one end of an unheated elongated reaction zone to pass lengthwise therethrough in contact with a catalyst consisting essentially of a sulfide of a metal of the iron group and tungsten sulfide at a temperature between 797° F. and 977° F. and a pressure between 5 and 75 atmospheres, supplying an olefin in sufficient amount at a plurality of points spaced along the reaction zone to balance heat evolved by hydrogenation of said olefin with heat absorbed by dehydrogenation of said naphthene and thereby maintain a substantially uniform reaction temperature within said limits throughout the reaction zone, the mol ratio of added olefin to hydroaromatic naphthene being between about 0.5:1 and 2:1.

9. In a process for the dehydrogenation of naphthenes in a straight run petroleum fraction the improvement which comprises dehydrogenating the naphthenic straight run fraction in the presence of olefins added in such an amount that the mole ratio of olefins to hydroaromatic naphthenes in the mixture is between 0.5:1 and 2:1, said dehydrogenation being effected with a catalyst consisting essentially of a major mole amount of a sulfide of a metal of the iron group and a minor mole amount of tungsten sulfide in the presence of at least 3 moles per mole of hydrocarbon feed of recycled product gas containing at least 80% hydrogen under conditions chosen within the following limits

Temperature	°F.	797–977
Pressure	atmospheres	5–75
Liquid hourly space velocity		0.3–5

thereby to obtain a substantially saturated liquid product rich in aromatic hydrocarbons in a substantially continuous operation.

10. In a process for the dehydrogenation of naphthenes in a straight run petroleum fraction the improvement which comprises dehydrogenating the naphthenic straight run fraction in the presence of olefin added in such an amount that the mole ratio of olefins to hydroaromatic naphthenes in the mixture is at least 0.5:1 but not above 2:1, said dehydrogenation being effected substantially continuously with a catalyst consisting essentially of a major mole amount of a sulfide of a metal of the iron group and a minor mole amount of tungsten sulfide under conditions chosen within the following limits

Temperature	°F.	797–977
Pressure	atmospheres	5–75
Liquid hourly space velocity		0.3–5

and with a substantially constant volume of gas which is recycled in an amount of at least 3 moles per mole of hydrocarbon feed, substantially continuously withdrawing from the recycle gas stream such an amount of gas that the concentration of hydrogen in said recycled gas is maintained above 80% by volume, the mole ratio of said added olefin to naphthenes in the said mixture being adjusted and maintained to furnish a net product of gas equal to said amount withdrawn.

11. In a process for the dehydrogenation of naphthenes in a straight run petroleum fraction the improvement which comprises dehydrogenating the naphthenic straight run fraction in the presence of olefin added in such an amount that the mole ratio of olefins to hydroaromatic naphthenes in the mixture is 0.5:1 to 2:1, said dehydrogenation being effected with a catalyst consisting essentially of a major mole amount of a sulfide of a metal of the iron group and a minor mole amount of tungsten sulfide in the presence of at least 3 moles per mole of hydrocarbon feed of recycled product gas under conditions chosen within the following limits

Temperature	°F.	797–977
Pressure	atmospheres	5–75
Liquid hourly space velocity		0.3–5

the amount of said added olefin being further adjusted such that upon operating substantially continuously with a substantially constant quantity of said recycled product gas the concentration of hydrogen in said recycled product gas is maintained above 80% by volume.

12. A process for producing aromatic hydrocarbons comprising the steps of admixing a first hydrocarbon fraction comprising naphthenic con-

stituents with a second hydrocarbon fraction comprising olefinic constituents in such proportion that the ratio of naphthenic constituents to olefinic constituents in the admixture is no less than 1 to 1 and contacting said admixture with a bed of a catalyst consisting essentially of a sulfide of a metal of the iron group and tungsten sulfide under a temperature in excess of 500° F. and in the presence of hydrogen under such conditions that there is an overall net production of hydrogen, and subsequently recovering a product rich in aromatic materials.

13. A process for producing aromatic hydrocarbons comprising the steps of maintaining a bed of a catalyst consisting essentially of a sulfide of a metal of the iron group and tungsten sulfide at a temperature ranging from 797° F. to 977° F., contacting said catalyst bed with an admixture of hydrocarbons comprising both olefinic and naphthenic materials with the ratio of olefinic materials to naphthenic materials no greater than 1 to 1 and in the presence of hydrogen, under such conditions that there is an overall net production of hydrogen in the presence of said catalyst, removing the reaction products from contact with said catalyst, and separating an aromatic constituent therefrom.

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