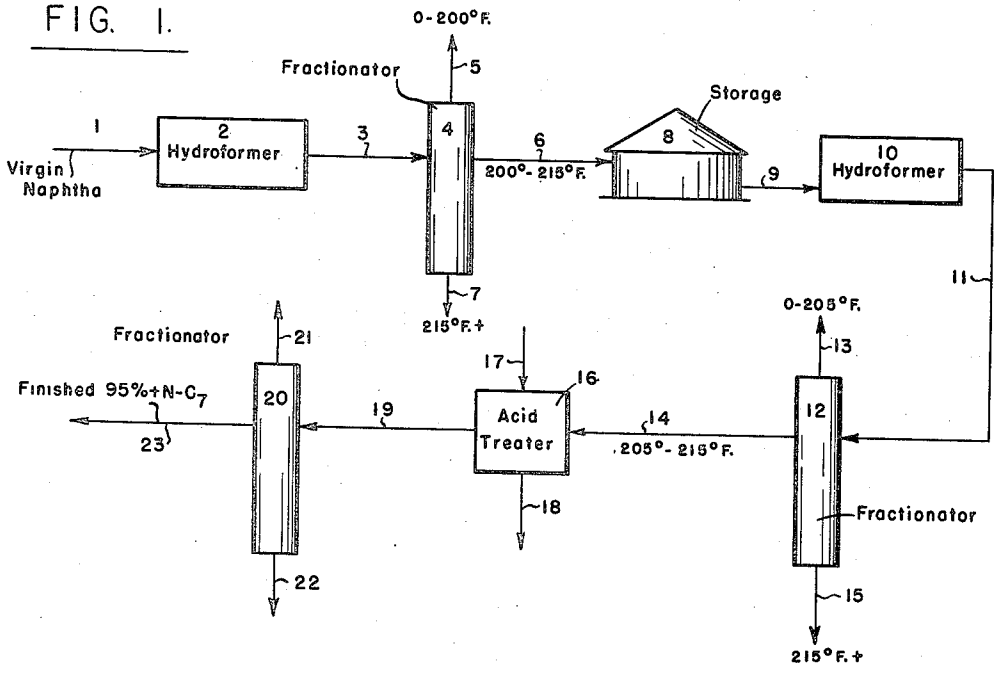
Jan. 10, 1950 K. J. F. DUTSON 2,494,335

METHOD FOR PRODUCING HIGH PURITY NORMAL HEPTANE

Filed Sept. 29, 1947

FIG. 1.



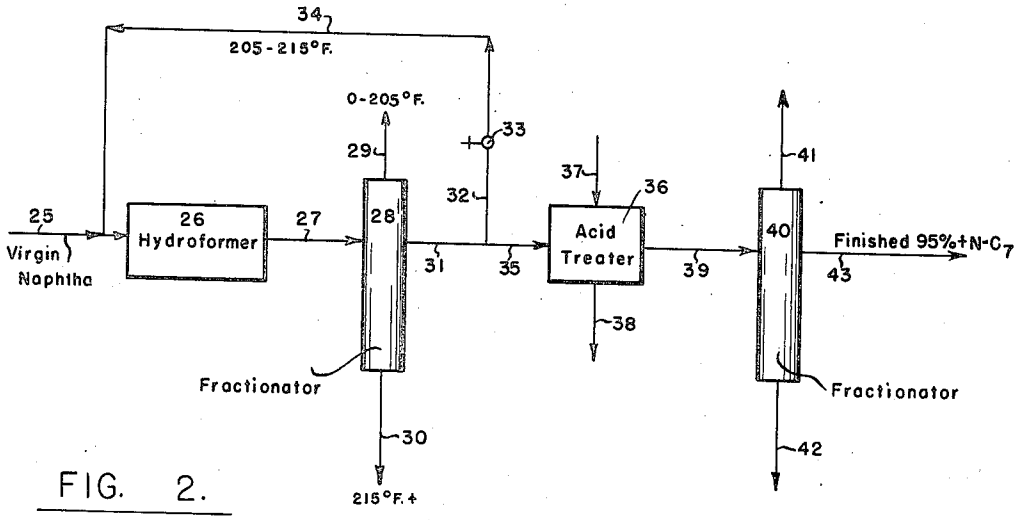


FIG. 2.

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METHOD FOR PRODUCING HIGH PURITY NORMAL HEPTANE

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7 Claims. (Cl. 260—676)

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The present invention relates to an improved method for producing normal heptane. More particularly, it is concerned with a method of hydroforming petroleum hydrocarbons to obtain high yields of substantially pure normal heptane.

In the process of the present application, either straight-run gasolines or catalytically or thermally cracked gasolines or any other hydrocarbon mixture containing normal heptane may be employed as the feed stock. It is well known that normal heptane is present in different amounts in gasolines from different sources. In general, normal heptane is present in higher concentrations in some straight-run gasolines than in catalytically or thermally cracked gasolines. However, in many catalytically or thermally cracked gasolines, normal heptane is present in substantial amounts, the amount which is present depending on the nature of the feed stock cracked, and the cracking conditions maintained. Usually, however, normal heptane will be present in larger quantities in straight-run distillates and in the process hereinafter described I prefer to utilize as a feed stock a straight-run gasoline rich in normal heptane although any petroleum hydrocarbon fraction containing normal heptane may be utilized.

As is well known, in addition to containing normal heptane as well as other paraffinic hydrocarbons, gasolines also contain various quantities of olefins, naphthenes and aromatics in addition to small amounts of contaminating compounds containing sulfur, nitrogen, oxygen, etc. For example, a gasoline containing normal heptane will normally also contain methylcyclohexane. Such gasolines often contain olefinic hydrocarbons boiling at the same temperature as normal heptane. Of course, the relative amounts of each of these several types of hydrocarbons present in a gasoline will depend on a number of factors including the source of the crude from which it is derived and the prior treatment to which it has been subjected.

One of the chief difficulties in the manufacture of normal heptane from gasoline is the separation of normal heptane from other hydrocarbons that are mixed therewith. One of the methods most commonly used for the separation of hydrocarbons is fractional distillation. This method of separation depends for its effectiveness upon the difference in boiling points of the hydrocarbons to be separated. When the boiling points of two or more hydrocarbons are substantially identical, separation by fractionation is impractical if not impossible. In preparing normal heptane from gasoline this difficulty is encountered. For example, there are several heptenes whose boiling points are very close to the boiling point of normal heptane. Of the naphthenes, methylcyclohexane boils within two degrees centigrade of normal heptane. These small differences in boiling points are indicated below in the following tabulation:

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Hydrocarbon	Boiling Point, C.	°F.
n-Heptane	98.4	209.1
Heptene-1	92.8	199.2
Heptene-2	98.1	208.5
Heptene-3	95.8	204.6
Methylcyclohexane	110.3	213.0

It will be seen from the above tabulation that if normal heptane is to be secured in a relatively pure form, methods of separation other than fractional distillation or in addition thereto must be employed.

With the development of high octane motor fuels, normal heptane has become an important and costly material which is used in relatively large quantities as a standard for evaluating the octane rating of motor fuels. Normal heptane is used as the low octane number standard while iso-octane is used as the high octane number standard in this evaluation, and in order to be of value for this purpose both constituents must be available in relatively pure form. Iso-octane is now available in commercial quantities but normal heptane is still difficult to secure in adequate quantities. By the practice of my invention, large quantities of normal heptane can be made available at relatively low cost.

In the process of my invention for preparing relatively pure normal heptane from gasoline fractions, I utilize several steps. Basically I employ the hydroforming reaction as it is conventionally carried out. As is well known in the art, the hydroforming process is characterized by chemical reactions which take place when hydrocarbon oils, particularly hydrocarbons boiling in the gasoline range, are reacted at a temperature in excess of 500° F. in the presence of hydrogen and a reforming catalyst. These reactions involve a net effect of removing hydrogen from the hydrocarbon molecules. Although some olefins are formed in the process the chemical reactions involved are complex and are generally considered to consist mainly of dehydrogenation and cyclization although other side reactions may and do occur. The catalysts utilized in the hydroform-

ing reaction may be selected from a wide variety of materials. Especially satisfactory catalysts for this reaction comprise major portions of aluminum oxide and minor portions of oxides or sulfides of metals of the IV and V, VI and VIII groups of the periodic system. The oxides and sulfides of vanadium, molybdenum, chromium, tungsten and nickel are particularly effective. The aluminum oxide incorporated in the catalyst may be used in its various forms such as activated alumina, bauxite, aluminum hydroxide, alumina gels and peptized alumina gels. As examples of the type of catalyst found suitable in the hydroforming reactions which may be mentioned are alumina or peptized alumina gels containing from 1 to 20% by weight of certain molybdenum oxides or chromium oxides.

The hydroforming reaction is endothermic and consequently heat must be supplied to the reaction zone. In my process this may be accomplished by any of the conventional methods which are well known to the art. Although temperatures as low as 500° F. and pressures as low as atmospheric pressures may be employed, I prefer to conduct the hydroforming reaction at a temperature range of about 900° to 950° F. and at pressures of about 180 to 250 pounds per square inch gauge.

Although the hydroforming reaction is essentially a dehydrogenation reaction in which hydrogen is produced, it is well known that the presence of excess hydrogen results in higher yields of desired products and, consequently, in practicing my invention, I introduce hydrogen into the hydroforming zone.

Heptenes are also sometimes present in the gasolines utilized as feed stocks. Further, small quantities of heptenes may be produced during the hydroforming reaction. Such olefins will, therefore, appear in the distillate fraction recovered from the hydroforming operation and cannot be readily separated from normal heptane by fractional distillation. Consequently, I remove such olefins from this fraction by acid treating with sulfuric acid in a manner well known to the art. In this step, the distillate fraction may be agitated with concentrated sulfuric acid at a temperature between about 140° F. and 210° F. after which the mixture is allowed to separate into an acid layer and a hydrocarbon layer. This hydrocarbon layer contains few, if any, olefins boiling at or near the boiling point of normal heptane and consequently a normal heptane fraction substantially free of heptenes may be distilled therefrom.

As previously pointed out, both normal heptane and methylcyclohexane are present in typical feeds to a hydroforming unit. Under the conditions maintained in the hydroforming unit in my process, methylcyclohexane is converted to toluene while normal heptane is affected relatively little during the reaction. Since the boiling point of toluene is 110.8° C., any toluene formed in the process may be easily separated from the normal heptane by fractional distillation. In my invention, I utilize the marked difference in boiling points of normal heptane and toluene as one of the factors in producing the relatively pure normal heptane.

One specific embodiment of the present invention comprises a process whereby a hydrocarbon mixture containing normal heptane is subjected to the hydroforming reaction and the products from the reactor are separated by fractionation into three fractions, namely, a fraction boiling

below 200° F., a fraction boiling between about 200° and 215° F., and a fraction boiling above about 215° F. The fraction boiling between 200° and 215° F. contains normal heptane, methylcyclohexane, the heptenes and small amounts of other hydrocarbons. In order to prepare a relatively pure normal heptane, this fraction is subjected to a second hydroforming step for the purpose of converting the remaining methylcyclohexane contained in this fraction to toluene. In this step the hydroforming conditions employed are such as will convert all or substantially all of the methylcyclohexane present to toluene and this may be accomplished without materially affecting the normal heptane present. The products from this second hydroforming step are again fractionated into three fractions, namely, materials boiling below about 205° F., a fraction boiling between about 205° and 215° F. and a fraction boiling above about 215° F. The fraction boiling between about 205° F. and 215° F. now contains only normal heptane and olefins boiling in this range. This fraction is subjected to acid treatment under such conditions as to leave the normal heptane relatively unaffected while at the same time polymerizing and otherwise converting the olefins present to compounds having boiling points materially removed from the boiling point of normal heptane. The acid treated product is again fractionated and separated into three fractions, namely, a fraction boiling below about 208° F., a fraction boiling between about 208° F. and about 211° F., and a fraction boiling above about 211° F. The fraction boiling between about 208° and 211° F. constitutes the finished product and consists of normal heptane of 95% purity or better. Normal heptane of very high purities, for example, 99% or better, may be obtained in my process by closely controlled fractionation and by proper control of hydroforming conditions. In stocks containing a very high percentage of methylcyclohexane it may be necessary to introduce an additional hydroforming and fractionation step just prior to the acid treating step. It is understood that it is meant to include such additional hydroforming and fractionation steps in this process where the nature of particular feed stocks requires that such additional steps be employed. However, it is normally unnecessary in the practice of my invention to employ such additional steps since, except in unusual cases, substantially all of the methylcyclohexane present in the fraction boiling between 200° and 215° F. from the hydroforming unit may be converted to toluene with one hydroforming stage.

In another embodiment of my invention, relatively pure normal heptane may be produced from hydrocarbon feed containing n-heptane by recycling a portion of the material which boils between 200° to 215° F. in the product from the unit used to hydroform the virgin feed back to the virgin feed hydroforming unit. The portion of the fraction boiling between 200° and 215° F. which is not recycled is then acid treated to polymerize or otherwise convert the olefins to compounds having boiling points materially removed from the boiling point of normal heptane. This acid treated fraction is then fractionated, three fractions being removed, namely, a fraction boiling below about 208° F., a fraction boiling between about 208° and about 211° F. and a fraction boiling above about 211° F. The fraction boiling between about 208° and 211° F. consists of substantially pure normal heptane, that is, of 95% or greater purity. The purity of this finished normal

heptane is regulated in this embodiment of my invention by proper adjustment of the recycle ratio of the fraction from the hydroforming unit which boils between 200° and 215° F.; the greater the recycle ratio, the greater the purity of the finished normal heptane although it will not usually be necessary to exceed a recycle ratio of 10:1. This second embodiment of my invention possesses the advantage over the first embodiment discussed above of utilizing only one hydroforming unit although it possesses the disadvantage over the first embodiment of reducing over-all through-puts through the hydroforming unit.

The practice of the present invention will now be described further in conjunction with the drawing, in which

Fig. 1 is in the form of a diagrammatic flow sheet showing one modification of the present invention; and

Fig. 2 is in the form of a diagrammatic flow sheet showing another embodiment of the present invention.

Referring to Fig. 1, a virgin naphtha or other normal heptane containing hydrocarbon feed is introduced through line 1 into the hydroforming unit of conventional design 2 where said feed is contacted with a hydroforming catalyst. The treated vapors are withdrawn through line 3 into fractionator 4 of conventional design in which the products from the hydroformer are separated into three fractions, the fraction boiling below about 200° F. being withdrawn through line 5, the fraction boiling between about 200° to 215° F. being withdrawn through line 6 and the fraction boiling above about 215° F. being withdrawn through line 7. The fraction withdrawn through line 6 contains substantially all of the normal heptane and methylcyclohexane, in addition to some olefins. This fraction may be placed in storage in a conventional storage tank 8 for further finishing if desired. When desired, the material stored in tank 8 is withdrawn through line 9 and discharged into a second hydroformer 10 where these materials are brought in contact with a hydroforming catalyst under hydroforming conditions. The reaction product from the second hydroformer is withdrawn through line 11 and discharged into fractionator 12 where a fraction boiling below about 205° F. is withdrawn through line 13, a fraction boiling between about 205 to 215° F. is withdrawn through line 14 and a fraction boiling above about 215° F. is withdrawn through line 15. The fraction withdrawn through line 14 consists of a major portion of normal heptane, with minor amounts of olefins boiling within this range but contains substantially no methylcyclohexane. The material withdrawn through line 15 consists essentially of toluene. The materials in line 14 are discharged to acid treater 16 where they are contacted with sulfuric acid introduced through line 17. Spent acid may by withdrawn through line 18 if desired. In acid treater 16 the olefins which were introduced with the normal heptane through line 14 are polymerized and otherwise converted to products which have a boiling point materially different from that of normal heptane. Conditions maintained in acid treater 16 are such as to substantially convert the olefins present to higher boiling polymers. The treated mixture is withdrawn from acid treater 16 through line 19 from which it is discharged into fractionator 20 of conventional design where materials boiling below about 208° F. are withdrawn through line 21, materials boiling from about 208° to about 211° F. are withdrawn through line 23 and materials boiling above about 211° F. are withdrawn through line 22. The fraction withdrawn through line 23 is the final product and consists of substantially pure normal heptane.

Referring to Fig. 2, a virgin naphtha or other normal heptane-containing hydrocarbon feed is introduced through line 25 into hydroformer 26 where the introduced feed is contacted with a hydroforming catalyst in the hydroforming unit 26 under hydroforming conditions. The reaction products from the hydroforming unit 26 are withdrawn through line 27 and discharged into fractionator 28 of conventional design in which the mixture is separated into a fraction boiling below about 205° F. which is withdrawn through line 29, a fraction boiling above about 215° which is withdrawn through line 30 and a fraction boiling between about 205° F. and 215° F. which is withdrawn through line 31. The fraction withdrawn through line 31 consists essentially of normal heptane, plus some olefins and other hydrocarbons boiling between 205° and 215° F. A portion of the fraction passing through line 31 is withdrawn from line 31 through line 32 and valve 33 and discharged into line 34. The amount of material withdrawn from line 31 into line 32, valve 33 and line 34 is controlled by the manipulation of valve 33 and the amount so withdrawn is determined by the purity of normal heptane desired in the finished product. The material in line 34 is admixed with the feed stock entering the hydroformer 26 through line 25. The portion of the fraction in line 31 which is not recycled through line 32, valve 33 and line 34 flows through line 35 and is discharged into acid treater 36. The fraction discharge into acid treater 36 consists essentially of normal heptane plus some olefins and other hydrocarbons but contains relatively little methylcyclohexane. Fresh acid may be introduced into the acid treater by means of line 37 and spent acid may be removed from acid treater 36 by means of line 38. In acid treater 36 the olefins introduced through line 35 are converted to polymers and other products by properly controlling the conditions of the acid treatment in a manner well known to the art. The hydrocarbon products leaving acid treater 36 by means of line 39 now consist essentially of normal heptane plus olefin polymers. The materials in line 39 are discharged into fractionator 40 of conventional design from which a fraction boiling below about 208° F. is withdrawn through line 41, a fraction boiling above about 211° F. is withdrawn through line 42, and a fraction boiling between about 208° and 211° F. is withdrawn through line 43. The material withdrawn through line 43 is the finished normal heptane and is substantially a pure product.

It will be seen from the examples given herein that relatively pure normal heptane cannot be produced from petroleum distillates by means of ordinary distillation, whereas, according to my process, normal heptane of high purity can readily be obtained.

I claim as my invention:

1. A process for preparing substantially pure normal heptane from a naphtha containing normal heptane in admixture with hydrocarbons having similar boiling points including methylcyclohexane which includes the steps of contacting the said naphtha in the presence of hydrogen with a catalyst capable of dehydrogenating methylcyclohexane at a temperature in the range between 900° and 950° F. and at a pressure in

the range between 180 and 250 pounds per square inch under conditions favorable to the dehydrogenation of methylcyclohexane and removing a product from the reaction zone, contacting at least a portion of said product in the presence of hydrogen with a catalyst capable of dehydrogenating methylcyclohexane at a temperature in the range between 900° and 950° F. and at a pressure in the range between 180 and 250 pounds per square inch under conditions favorable to the dehydrogenation of methylcyclohexane and recovering a product from said latter contacting step, acid treating the said last mentioned product with sulfuric acid and redistilling the acid treated product to recover a hydrocarbon fraction boiling between about 208° F. and 211° F. consisting of substantially pure normal heptane.

2. A process for preparing substantially pure normal heptane from a naphtha containing normal heptane in admixture with hydrocarbons having similar boiling points including methylcyclohexane which includes the steps of contacting said naphtha in the presence of hydrogen in a first stage with a catalyst effective in dehydrogenating napthenes at a temperature in the range between 900° and 950° F. and at a pressure in the range between 180 and 250 pounds per square inch under conditions favorable to the dehydrogenation of naphthenes to form a product, distilling the product from said first stage to separate a fraction boiling between about 200° and 215° F., contacting said separated fraction in the presence of hydrogen in a second stage with a catalyst effective in dehydrogenating naphthenes under substantially the same conditions prevailing in said first stage to form a second product, distilling the product from said second stage to separate a fraction boiling between about 205° F. and 215° F., acid treating the said fraction boiling between about 205° and 215° F. with sulfuric acid and redistilling the acid treated fraction to recover a fraction boiling between about 208° and 211° F. consisting of substantially pure normal heptane.

3. A process for preparing substantially pure normal heptane from a naphtha containing normal heptane in admixture with hydrocarbons having similar boiling points including methylcylohexane which includes the steps of subjecting the vapors of the said naphtha in a first stage to contact with a catalyst effective in dehydrogenating naphthenes at a temperature in the range between 900° and 950° F. and at a pressure in the range between 180 and 250 pounds per square inch, separating from the contacted vapors a fraction boiling between about 200° and 215° F., contacting said fraction in a second stage with a catalyst effective in dehydrogenating naphthenes at a temperature in the range between 900° and 950° F. and at a pressure in the range between 180 and 250 pounds per square inch to form a reaction product, separating from the reaction product of said second stage a fraction boiling between about 205° and 215° F., contacting the fraction boiling between about 205° and 215° F. with sulfuric acid and recovering substantially pure normal heptane from said acid contacted fraction.

4. A process in accordance with claim 2 in which the catalyst employed in the first and second stages is aluminum oxide containing from 1 to 20% by weight of molybdenum oxide.

5. A process for preparing subtantially pure normal heptane from naphtha containing normal heptane in admixture with other hydrocarbons having similar boiling points including methylcyclohexane which includes the steps of contacting said naphtha in the presence of hydrogen with a catalyst effective in dehydrogenating naphthenes at a temperature in the range between 900° and 950° F. and at a pressure in the range between 180 and 250 pounds per square inch, separating a reaction product from said catalyst, distilling the reaction product therefrom to separate a fraction boiling between about 205° and 215° F., separating said fraction into a first and second portion, admixing said first portion with said feed naphtha, acid treating the said second portion with sulfuric acid, distilling the acid treated second portion to recover a fraction boiling between about 208° and 211° F. consisting of substantially pure normal heptane.

6. A process for preparing substantially pure normal heptane from a naphtha containing said hydrocarbon in admixture with hydrocarbons having similar boiling points including methylcyclohexane which includes the steps of subjecting the vapors of said naphtha to contact with a catalyst effective in dehydrogenating naphthenes at a temperature in the range between 900° and 950° F. and at a pressure in the range between 180 and 250 pounds per square inch, separating from the contacted vapors a fraction boiling between about 205° and 215° F., separating said fraction into a first and second portion, admixing said first portion with said feed naphtha, contacting the said second portion with concentrated sulfuric acid and recovering substantially pure normal heptane from said acid contacted second portion.

7. A process in accordance with claim 5 in which the catalyst employed is aluminum oxide containing from 1 to 20% by weight of molybdenum oxide.

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