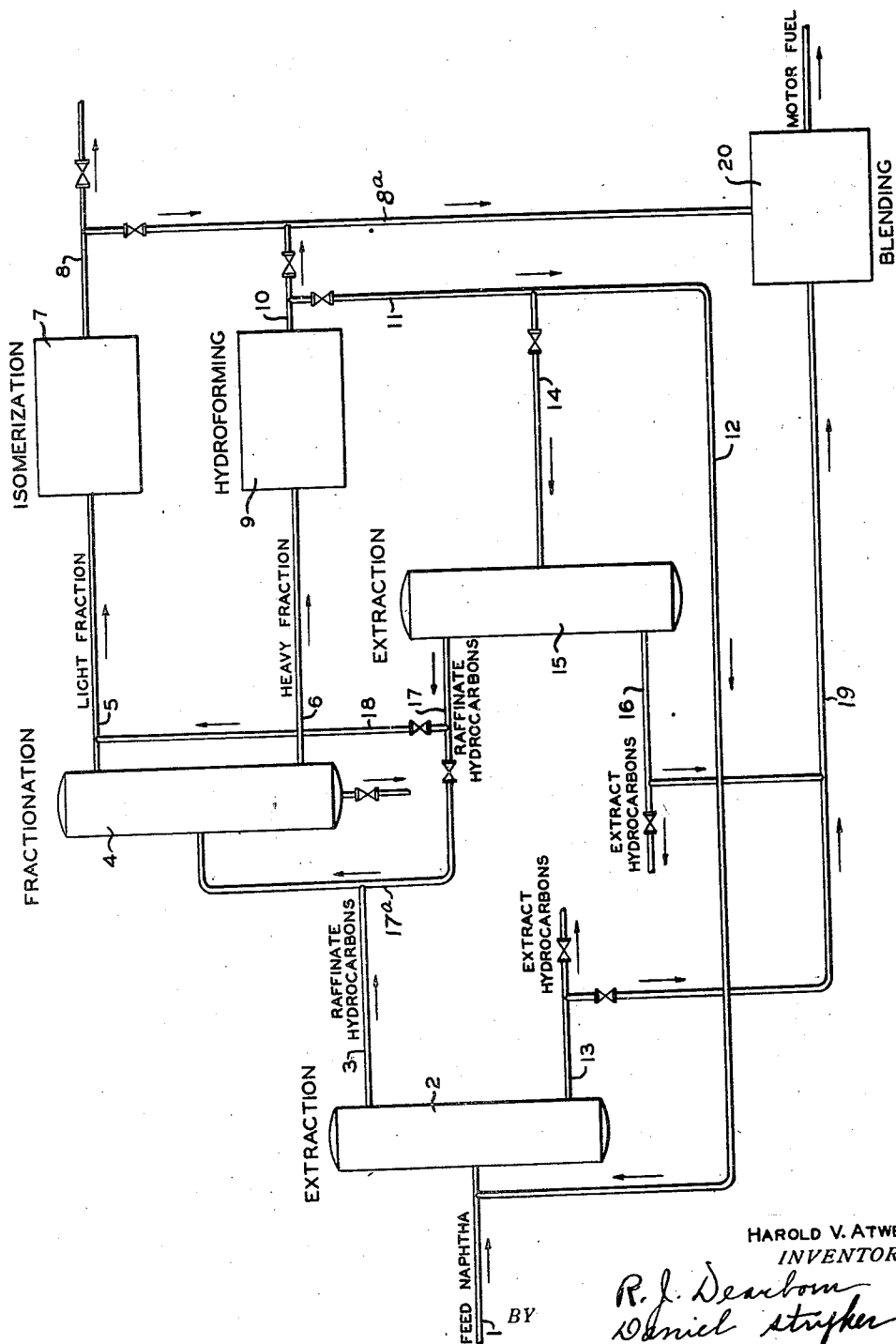


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MANUFACTURE OF MOTOR FUEL

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MANUFACTURE OF MOTOR FUEL

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This invention relates to the manufacture of motor fuel and has to do with the conversion of naphtha hydrocarbons to gasoline hydrocarbons of improved antiknock value.

The invention contemplates a process for the manufacture of motor fuel which involves subjecting a naphtha hydrocarbon mixture rich in aliphatic hydrocarbons to contact with a conversion catalyst maintained under hydroforming conditions such that there is substantial conversion to aromatic hydrocarbons. The aromatic hydrocarbons are removed from the hydroformed naphtha mixture and the remaining hydrocarbons or lower boiling portions thereof are subjected to isomerization. Where the lower boiling hydrocarbon constituents only are subjected to isomerization, the higher boiling constituents may be recycled to the hydroforming reaction for further conversion into aromatic hydrocarbons.

In accordance with the invention a naphtha hydrocarbon mixture such as straight run naphtha is passed to an extraction zone wherein aromatic constituents are extracted from the naphtha by means of a suitable selective solvent. The resulting raffinate portion of the naphtha rich in paraffinic constituents is withdrawn and advantageously subjected to fractionation into light and heavy fractions. The light fraction advantageously comprises hydrocarbons boiling in the range 100 to about 200° F. while the heavy fraction comprises naphtha hydrocarbons boiling above about 200° F.

The light fraction is passed to an isomerization reaction zone wherein straight chain hydrocarbons are converted to branched chain hydrocarbons of improved antiknock value. The heavy fraction, on the other hand, is passed to a catalytic conversion zone maintained under hydroforming conditions so as to convert at least a substantial portion of the hydrocarbons into aromatic hydrocarbons suitable as constituents of motor fuel.

The hydroformed mixture is withdrawn and all or in part recycled to the aforesaid solvent extraction zone wherein it is subjected to solvent extraction along with fresh feed naphtha for the purpose of removing aromatic constituents therefrom. That portion of the hydroformed mixture not recycled may be used as blending stock for blending with the previously mentioned isomerized hydrocarbons for the purpose of producing a motor fuel of desired characteristics.

Instead of recycling the hydroformed mixture to the extraction zone wherein aromatic con-

stituents are extracted from the feed naphtha the hydroformed mixture may be subjected to a separate solvent treatment for the purpose of separating it into a fraction rich in aromatics and a fraction rich in non-aromatic constituents. The non-aromatic fraction rich in paraffin hydrocarbons may be passed directly to an isomerization reaction, or if desired only the lower boiling constituents may be passed to such isomerization reaction, while the higher boiling constituents are recycled to the hydroforming reaction.

In any case the aromatic constituents separated from the feed naphtha and from the hydroformed naphtha hydrocarbons may be blended in any suitable proportion with isomerized hydrocarbons for the production of motor fuel of desired characteristics.

Advantageously, aromatic constituents are separated from the feed naphtha or from the hydroformed naphtha hydrocarbon mixture by extraction with water or a solvent consisting essentially of water at elevated temperature and pressure such that the solvent exerts preferential solvent action upon aromatic hydrocarbons. The extractive treatment with water or a solvent consisting essentially of water may be effected at a temperature of about 500° F., or in the range about 400 to 600° F. The treatment is effected under sufficient pressure to maintain the solvent substantially in the liquid phase and this pressure may range from about 1000 to 5500 pounds per square inch gauge.

Under such conditions it has been found that water exerts a preferential solvent action upon aromatic hydrocarbon constituents of naphtha so that these constituents can be extracted from naphtha without effecting substantial removal of naphthenic and paraffinic constituents of the naphtha.

This is of advantage as concerns the subsequent isomerization step, since it has been found that the presence of naphthene hydrocarbons in a naphtha undergoing isomerization is beneficial from the standpoint of suppressing undesired side reactions and catalyst deterioration, particularly where the isomerization reaction is carried out in a liquid phase operation with aluminum chloride dissolved or suspended in metallic halide-hydrocarbon complex and at relatively high temperatures, for example, in the range about 160 to 300° F. or higher.

It has also been found that water by itself exerts relatively low solvent action upon olefinic constituents of naphtha, although it appears that

a water-aromatic mixture exerts considerable solvent action upon olefinic constituents. Accordingly, in the event that the feed naphtha contains olefins it is contemplated that the extraction will be carried out under conditions such that olefinic constituents are substantially removed. Other selective solvents exerting substantial solvent action upon olefinic as well as aromatic constituents may be employed, particularly if the naphtha mixture has a large content of olefins.

In order to describe the invention more fully reference will now be made to the accompanying drawing, which comprises a diagram of flow illustrating one method of practicing the process of the invention.

Referring to the drawing a feed naphtha such as straight run naphtha is conducted from a source not shown through a pipe 1 to an extraction unit 2 wherein it is extracted with a selective solvent.

The extraction unit may comprise a tower or extraction zone packed with a suitable contact material such as Raschig rings. The unit will also include means, not illustrated, for withdrawing extract and raffinate phases, and for separate treatment of the withdrawn phases to separate the solvent from the hydrocarbons. When using water as the extraction solvent the naphtha feed at a temperature of about 500 to 575° F. is introduced to the lower portion of the tower and caused to flow upwardly therethrough countercurrently to a body of water. The water is continuously introduced to the upper portion of the tower at substantially this same temperature.

As a result extract and raffinate phases will be formed. The raffinate phase will comprise non-aromatic constituents, including paraffins and naphthenes mixed with a relatively small amount of the water while the extract phase will comprise the bulk of the water having aromatic constituents of the naphtha dissolved therein.

The extract and raffinate phases are continuously withdrawn and separately subjected to cooling while maintained under substantially the same pressure prevailing within the extraction tower. Thus, the withdrawn phases may be cooled to a temperature in the range about 70 to 250° F., for example, so that separation occurs between water and hydrocarbons. The water layers are continuously drawn off, and after heating to the desired extraction temperature, recycled to the extraction tower for reuse. The remaining hydrocarbon layers, namely, raffinate hydrocarbons and extract hydrocarbons respectively are separately withdrawn for further treatment.

Thus, the raffinate hydrocarbons are conducted through a pipe 3 to a fractionation unit 4 wherein they are separated into low boiling and high boiling fractions respectively.

For example, a low boiling fraction comprising hydrocarbons boiling in the range about 100 to 200° F. is drawn off through a pipe 5 while a high boiling fraction comprising hydrocarbons boiling above about 200° F. is drawn off through a pipe 6.

If the fresh feed naphtha is relatively low boiling, it may be unnecessary to fractionate the raffinate, and in that case the fractionation unit 4 may be by-passed.

The low boiling hydrocarbons are conducted through the pipe 5 to an isomerization unit 7. Isomerization may be effected by any suitable isomerizing process, as for example, subjecting the hydrocarbons to contact with a metallic halide-hydrogen halide catalyst such as alumi-

num chloride and hydrogen chloride, employing a reaction temperature in the range about 160 to 300° F. In such cases the reaction may be carried out in either vapor or liquid phase and the catalyst may be used in solid fragmentary form or in the form of a suspension or solution in metallic halide-hydrocarbon complex liquid.

As previously indicated the reaction is advantageously effected in the presence of naphthene hydrocarbons so as to substantially suppress cracking and catalyst deterioration. Provision may be included for recycling unreacted hydrocarbons through the reaction zone and also for effecting the reaction in the presence of extraneous gases including isobutane, carbon monoxide and hydrogen, etc., which may be continuously recycled through the reaction for the purpose of prolonging catalyst life.

The isomerization unit 7 advantageously includes provision for fractionating the reaction mixture so as to segregate the desired fraction or fractions of isomerized hydrocarbons, and remove other materials for recycling to the reaction.

Thus, the desired isomerized hydrocarbons will be discharged from the isomerization unit through a pipe 8 and may be disposed of all or in part as blending stock for motor fuel.

The high boiling naphtha hydrocarbons produced from the fractionation unit 4 are conducted through the previously mentioned pipe 6 to a hydroforming unit 9. In this unit the hydrocarbons are subjected to contact with a hydroforming catalyst such as the oxides of chromium, molybdenum and vanadium supported upon alumina. The treatment is effected at a temperature in the range about 950 to 1050° F. and under a pressure in the range about 200 to 400 pounds. The reaction is effected in the presence of a relatively large amount of hydrogen containing gas.

For example, the feed hydrocarbons in the vapor phase together with a large amount of recycled hydrogen containing gas are passed through a solid contact mass with a space velocity of about 0.5 or 2.0. The recycled gas contains about 30 to 50% of hydrogen and is usually recycled to the extent of about 2500 cubic feet of gas per barrel of charge naphtha.

Under these conditions a product is obtained which may contain 40 to 50% of aromatic hydrocarbons within the gasoline boiling range and the gasoline fraction so obtained will have an octane number of about 77 to 80. The product usually contains a little or no naphthene hydrocarbons and may contain about 5% or more of olefinic hydrocarbons. On the other hand, it contains a considerable amount of paraffinic material, lower boiling than the charge to the hydroforming reaction, and which upon separation from the hydroformate is advantageously converted by isomerization into gasoline hydrocarbons of improved antiknock value.

The hydroformed naphtha mixture is discharged through a pipe 10 and at least a substantial portion thereof is conducted through a branched pipe 11 for further treatment.

According to one modification the portion of hydroformate conducted through the pipe 11 may be recycled through a pipe 12 to the previously mentioned extraction unit 2 wherein it undergoes extraction together with fresh entering feed naphtha for the purpose of having aromatic constituents extracted therefrom. The resulting aromatic extract including aromatics extracted from fresh feed naphtha are discharged from the extraction unit through a pipe 13.

Instead of recycling to the extraction unit the hydroformed naphtha mixture may be conducted through a pipe 14 to a separate extraction unit 15 wherein the mixture is separately extracted with water or other suitable selective solvent for the purpose of extracting therefrom an aromatic and olefin fraction which is withdrawn through a pipe 16. If desired the mixture passing through pipe 14, may be subjected to fractionation prior to extraction so as to remove constituents higher boiling than about 250 to 300° F., such higher boiling material advantageously being disposed of as blending stock for motor fuel.

The remaining raffinate hydrocarbon fraction is discharged through a pipe 17 and may be recycled directly through a branch pipe 17a to the previously mentioned fractionation unit 4 wherein the lighter components are segregated for the subsequent isomerization treatment while the heavier components are segregated for recycling to the hydroforming reaction.

In some cases it may be advantageous to pass the entire raffinate hydrocarbon fraction from the pipe 17 through a branched pipe 18 to the isomerization unit 7 so that all of the paraffin hydrocarbon constituents of the raffinate fraction may be subjected to the isomerization treatment.

The aromatic hydrocarbons discharged through pipes 13 and 16 may be passed all or in part through a pipe 19 to a blending type tank 20 wherein they may be blended in any suitable proportion with isomerized hydrocarbons discharged through the pipe 8 and branch pipe 8a and also with any suitable proportion of hydroformed mixture discharged through the pipe 10.

One advantage in subjecting the hydroformed mixture to separate extraction in the extraction unit 15 is that the extraction may be carried out with a different solvent or under different conditions than prevail in the extraction unit 2. For example, the hydroformed mixture may contain a large amount of olefinic constituents in addition to aromatic constituents. In such case it is desirable to extract olefins as well as aromatics from the hydroformed mixture so that that portion of the hydroformed hydrocarbons which is being recycled to the isomerization unit 7 will be substantially free from olefinic constituents or at least of substantially reduced olefin content. Removal of olefins is desirable from the standpoint of avoiding substantial catalyst deterioration when using an aluminum chloride type of isomerization catalyst.

In such case the extraction solvent employed in the extraction unit 15 may comprise water employed under conditions substantially different from those prevailing in the extraction unit 2. As previously indicated the water-aromatic mixture has some solvent action on olefins. The solvent may comprise a different type such as sulfur dioxide or furfural and the like which solvents exert substantial solvent action upon olefins as well as aromatic constituents.

It will be seen that an important advantage of the process of the invention involves recycling to the hydroforming reaction heavier hydrocarbons of relatively low antiknock value, and also the conversion of the lower boiling normal paraffin constituents of the hydroformed mixture by an isomerizing reaction so as to increase their antiknock value. In this way a substantially larger proportion of the feed naphtha is converted into gasoline hydrocarbons with high antiknock value.

As previously intimated the hydroformate contains a substantial amount of paraffin material of lower boiling range than the charge to the hydroforming reaction and this lower boiling material is advantageously converted into valuable hydrocarbons by isomerization. The substantial absence of naphthenes from this relatively low boiling material as segregated for feed to the isomerization reaction is compensated at least in part by the presence of naphthenes in that portion of the fresh freed naphtha passing to the isomerization reaction. Thus, a further advantage of the process involves isomerizing the lower boiling paraffinic constituents of the hydroformate in the presence of naphthenes contained in the virgin feed naphtha.

As already mentioned the solvent employed in the extraction units may consist entirely of water or essentially of water. Thus, it is contemplated that water may contain a suitable auxiliary substance for the purpose of increasing the solubility of aromatic hydrocarbons in the solvent mixture without substantially reducing the selectivity of the mixture as between aromatic and non-aromatic constituents of the hydrocarbon mixture undergoing extraction. Suitable auxiliary substances comprise hydroxy and polyhydroxy organic compounds which are substantially completely soluble in water at least at temperatures of the order of 70 to 600° F. Dihydroxy saturated and unsaturated alcohols such as ethylene and polyethylene glycols have been found effective for this purpose. The di, tri and hexa ethylene glycols may also be used as well as the halogenated derivatives of the dihydroxy alcohols such as trimethylene chlorohydrine, glycerol b-di-chlorohydrine and a-chloroglycerol.

Other organic compounds which may be used include polyolefin glycols, polyvinyl alcohols, polyhydroxyl alcohols such as glycerine, manitol and sorbitol. Phenolic compounds such as resorcinol, phloroglucinol and pyrogallol may be used. Still other compounds include the hydroxy acids such as salicylic and lactic acids, and the aliphatic alcohols including amino and nitro derivatives thereof, such as mono, di and tri ethanol amines and 2-nitro ethanol.

The proportion of added substance which may be employed is such that the mixture of water and secondary solvent will exert substantial solvent action upon aromatic hydrocarbons at temperatures of substantially above 250° F. but will exert substantially little solvent action upon aromatic hydrocarbons at ordinary temperatures, for example, from about room temperature to about 250° F. In other words, the proportion of secondary solvent and water in the solvent mixture is such that when the solution of desired aromatic hydrocarbons in the solvent is separated from the extraction zone the desired aromatic hydrocarbons can be substantially entirely separated from the solvent merely by reducing the temperature of the solution to a temperature in the range about 70 to 250° F.

Thus, the proportion of above-mentioned hydroxy material contained in the water may range from a fraction of a per cent to 50% or more by weight of the solvent mixture and preferably will range from about 5 to 25% by weight.

Instead of using an extraction tower as specifically mentioned previously, the extraction may be effected in other types of apparatus including mixers and settlers arranged in stages.

Obviously many modifications and variations of the invention as above set forth may be made

without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated by the appended claims.

I claim:

1. A process for the manufacture of motor fuel of high antiknock value from a naphtha hydrocarbon mixture containing aromatic hydrocarbons and non-aromatic hydrocarbons including paraffins and naphthenes which comprises passing said feed naphtha to an extraction zone, subjecting the naphtha to contact with a solvent consisting essentially of water at a temperature in the range 400 to 600° F. and under elevated pressure such that a fraction rich in aromatics is separated from the feed naphtha without effecting substantial removal of naphthenes, removing the separated aromatics, removing the remaining portion of said feed naphtha from which aromatics have been removed, fractionating said portion to form a low boiling fraction and a high boiling fraction, subjecting said low boiling fraction containing naphthenes to contact with a metallic halide-hydrogen halide isomerization catalyst maintained under isomerizing conditions such that there is substantial conversion to isomerized hydrocarbons, subjecting said heavy fraction to contact with a hydroforming catalyst maintained under conditions such that there is substantial conversion to aromatic hydrocarbons, recycling at least a portion of said hydroformed heavy fraction to said extraction zone, and blending aromatics removed from said separating zone with isomerized hydrocarbons to form motor fuel.

2. The method according to claim 1 in which a portion of said hydroformed heavy fraction is blended directly as such with isomerized hydrocarbons to form motor fuel.

3. The method according to claim 1 in which the naphtha hydrocarbon mixture remaining after separation of aromatics is fractionated into a low boiling fraction boiling in the range about

100 to 200° F. and a heavy fraction boiling above about 200° F.

4. A process for the manufacture of motor fuel of high antiknock value from a naphtha hydrocarbon mixture containing aromatic hydrocarbons and non-aromatic hydrocarbons including paraffins and naphthenes which comprises passing said feed naphtha to an extraction zone, subjecting the naphtha mixture to extractive contact therein with a solvent consisting essentially of water under conditions such that aromatic constituents are extracted therefrom without effecting substantial removal of naphthenes, removing the extracted aromatics, removing said feed naphtha from which aromatics have been removed, fractionating the removed naphtha to form a low boiling fraction and a high boiling fraction, subjecting said low boiling fraction containing naphthenes to contact with a metallic halide-hydrogen halide isomerization catalyst maintained under isomerizing conditions such that there is substantial conversion to isomerized hydrocarbons, subjecting said heavy fraction to contact with a hydroforming catalyst maintained under conditions such that there is substantial conversion to aromatic hydrocarbons, recycling at least a portion of said hydroformed heavy fraction to said extracting zone, and blending aromatics removed from said extracting zone with isomerized hydrocarbons to form motor fuel.

5. The method according to claim 4 in which a portion of said hydroformed heavy fraction is blended directly as such with isomerized hydrocarbons to form motor fuel.

6. The method according to claim 4 in which the naphtha hydrocarbon mixture remaining after separation of aromatics is fractionated into a low boiling fraction boiling in the range about 100 to 200° F. and a heavy fraction boiling above about 200° F.

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