

ALIEN PROPERTY CUSTODIAN

PROCESS FOR TREATING NAPHTHENIC HYDROCARBON DISTILLATES

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The present invention relates to a process for treating naphthenic hydrocarbon distillates and particularly such distillates as comprise appreciable concentrations of naphthenic hydrocarbons in admixture with normally liquid paraffinic hydrocarbons having normal boiling points above 67°C.

In the production of certain premium fuels and in certain processes employing naphthenic crude oils, hydrocarbon distillates containing substantial proportions of naphthenic hydrocarbons in admixture with normally liquid paraffinic hydrocarbons having normal boiling points above 67°C. are obtained. These fractions are not of great value per se and have hitherto usually been subjected to a dehydrogenation treatment to convert the naphthenic hydrocarbons to aromatic hydrocarbons. The aromatic fractions thus produced, however, generally have a low lead susceptibility and are now falling into disfavor. I have found that these various naphthenic distillates may generally be considerably improved by subjecting them to a suitable treatment to selectively isomerize certain naphthenic hydrocarbons therein. In order to obtain the desired improvements it is necessary, however, to avoid as far as possible the degradation of the paraffinic hydrocarbons and the various condensation and alkylation reactions which tend to take place to form undesirable high molecular weight hydrocarbons.

It is known that butane, and to a certain extent pentane, may be isomerized with the aid of aluminum halide catalysts provided that the concentration of the aluminum halide is kept sufficiently low, and only small amounts of hydrogen halides are present. The higher paraffin hydrocarbons, such as those containing six or more carbon atoms, on the other hand, cannot be economically isomerized to any appreciable extent under the employed conditions without excessive degradation. Therefore, although it has long been known that certain of the lower simple naphthenic hydrocarbons per se could be isomerized with the aid of acid-acting metal halide isomerization catalysts, it was to be expected that the treatment of these hydrocarbons when in admixture with higher paraffinic hydrocarbons in commercial distillates with isomerization catalysts would lead primarily to degradation reactions, condensation reactions and the like, and that isomerization of the naphthenic hydrocarbons would not take place to any appreciable extent. As a matter of fact, it is known that under the usual isomerizing conditions the presence of

naphthenic hydrocarbons tends to increase the already great tendency of higher paraffinic hydrocarbons to decompose under the influence of aluminum chloride. Thus, one of the foremost authorities on aluminum chloride catalysis states in U. S. Patent No. 2,088,598, "It has been observed that if paraffinic hydrocarbons are heated alone in the presence of aluminum chloride only a very limited amount of decomposition occurs while, if ring hydrocarbons are present, to act as acceptors, extensive decomposition of the paraffins is evidenced from the formation of large quantities of alkylated ring compounds." By treating mixtures of naphthenic hydrocarbons and paraffinic hydrocarbons with aluminum chloride and hydrogen chloride at temperatures in the neighborhood of 175°C., a large amount of degradation of the paraffinic hydrocarbons occurs and a product having a wide boiling range and consisting of lower paraffinic hydrocarbons and higher boiling alkylated naphthenic hydrocarbons is produced.

I have found that although naphthenic hydrocarbons when in admixture with normally liquid paraffinic hydrocarbons having normal boiling points above 67°C. tend to promote the degradation of the paraffinic hydrocarbons by acid-acting metal halide isomerization catalysts, such as aluminum chloride, this is only the case at temperatures ranging from about 150°C. to about 200°C. and above. At temperatures below about 150°C., usually between about 40 and about 130°C., I have found that the effect of naphthenic hydrocarbons in such mixtures is exactly opposite to that expected. Under suitable conditions and at these temperatures, the naphthenic hydrocarbons tend, I have found, to inhibit the normal decomposition of paraffinic hydrocarbons by aluminum chloride and to undergo a clean-cut isomerization. Thus, contrary to expectation, it is actually possible to effect a selective isomerization of the naphthenic hydrocarbons when in admixture with higher paraffinic hydrocarbons under conditions where the higher paraffinic hydrocarbons alone would normally undergo substantial degradation.

The process of my invention may be applied to improve any hydrocarbon distillate containing an appreciable concentration of naphthenic hydrocarbons in admixture with normally liquid paraffinic hydrocarbons having normal boiling points above 67°C. It is particularly suited and advantageous for the treatment of such of these stocks as boil predominantly between about 40°C. and 205°C., and becomes increasingly advanta-

geous as the ratio of naphthenic hydrocarbons to higher paraffinic hydrocarbons increases. Thus the process may be advantageously employed with stocks containing as low as about 5-10% naphthenic hydrocarbons, but is much more advantageous when the naphthenic hydrocarbon concentration is at least 20% or higher, for instance 70%. This appears to be due to the greater inhibition of degradation of the higher paraffinic hydrocarbons exerted by the higher concentrations of naphthenic hydrocarbons. Also, although the process is advantageous and may be employed to treat hydrocarbon stocks containing relatively high molecular weight hydrocarbons having normal boiling points in the neighborhood of 150 to 250°C., it is most advantageous and is preferably employed with such distillates as have a substantial content of hydrocarbons boiling in the range of from about 67-150°C. The reason for this is that the most important advantage realized when treating naphthenic distillates according to the process is due to the isomerization of certain naphthenic hydrocarbons boiling in this range. Particular naphthenic hydrocarbons which may undergo isomerization in the process are for example, cyclopentane, the various alkylated cyclopentanes, cyclohexane, the various alkylated cyclohexanes, and cycloheptane and its various alkylated derivatives.

In order to obtain the best results using the present process, it is preferable that the stock treated be substantially free of olefins. The reason for this is that olefins, if present in substantial quantities, tend to polymerize and undergo various other reactions which are, in general, detrimental. Aromatic hydrocarbons also, if present in appreciable quantities (for example about 12% or above), or undesirable since they tend to react with the naphthenic hydrocarbons under the reaction conditions to form high boiling products of little value. If the stock to be treated contains substantial quantities of olefinic or aromatic hydrocarbons these may be first removed or reduced to unobjectionable concentrations by a suitable treatment, such, for instance, as selective solvent extraction, hydrogenation, etc. Any other minor impurities in the distillate to be treated which are known to be detrimental to the activity of aluminum chloride and other acid-acting metal halide isomerization catalysts, may be removed, if present, by a conventional hydrogenation or refining treatment.

The various naphthenic stocks are treated, according to the present invention, by contacting them at a suitable temperature in the liquid phase, and in the presence of a hydrogen halide with an acid-acting metal halide isomerization catalyst. Of the various applicable acid-acting metal halide isomerization catalysts, anhydrous aluminum chloride is by far the most efficient and preferred. Other acid-acting metal halide isomerization catalysts, such as the halides of Zr, Zn, Sn, Be, Nb, Ta, Sb, B, Co, Ni, Cu, and Cd may also be employed, if desired in conjunction with aluminum chloride. The anhydrous aluminum chloride, if this catalyst is used, may be employed in a number of ways. One suitable method of employing this catalyst is to suspend the finely-divided aluminum chloride in the reaction mixture; for this method of operation the reactor system described in copending application (Ser. No. 298,594 filed October 9, 1939) may be advantageously employed. Another method of applying aluminum chloride is as complex double compounds of the type known as the "Gustavson

Compounds." Still another advantageous way to employ aluminum chloride is to apply it to an adsorptive carrier material and pass the hydrocarbon thereover.

5 The catalyst may be employed in any amount ranging from about 1% to about 25%, depending upon the stock treated, the activity of catalyst, the amount of hydrogen halide present, and the temperature. In general, the effectiveness of the catalyst under any given set of conditions is a linear function of the concentration up to a concentration at which degradation is promoted. If, therefore, under any given set of conditions excessive degradation tends to take place, this may usually be remedied, if the temperature is not too high, by decreasing the concentration of catalyst.

10 In order to avoid substantial degradation of the higher paraffinic hydrocarbons and the production of undesirable higher alkylated naphthenic hydrocarbons, it is essential that the process be executed at a temperature not higher than about 130° C. and at the very most 150° C. In general, the most applicable temperatures are from about 60-130° C. Since the rates of the desired reactions increase rapidly with the temperature up to the point where substantial degradation and alkylation begin, it is advantageous to adjust the temperature to just below that at which substantial degradation begins. The reaction can, however, be executed, if desired, at lower temperatures, but requires longer contact times (which are not generally practical) to obtain an appreciable improvement; for example, if a naphthenic hydrocarbon distillate containing less than about 5% of aromatic hydrocarbons is treated at 20° C., a contact time of from several hours to several days may be required, depending upon the feed, catalyst, etc.

25 The treatment, according to the present process, is always executed in the presence of at least a small amount of free hydrogen halide. Although small amounts of free hydrogen halide are sufficient to promote the desired reactions, I have found that much better results are obtained by employing larger amounts. Thus, for example, according to a preferred embodiment of my invention, the process is executed under a pressure of hydrogen halide at least equivalent to one atmosphere and preferably equivalent to at least three atmospheres when measured at 25° C.

30 The advantages realized by treating commercial naphthenic hydrocarbon distillates according to the present process are manifold and depend somewhat upon the use or treatment to which the treated stock is to be subsequently applied. Thus, suitable stocks may be treated according to the present process to improve their stability and ignition properties; they may be treated and fractionated with a view of obtaining various close fractions having a high concentration of a particular type of hydrocarbon or specific properties; or they may be treated with a view of rendering the stock more suitable for a subsequent treatment. For example, by treating naphthenic stocks according to the present process and then by a dehydrogenation treatment, much higher yields of aromatic hydrocarbon may generally be produced than with the same stock untreated.

35 In order to illustrate the process the following examples, showing results obtained with comparatively simple hydrocarbon mixtures, are presented. Other more complex mixtures and commercial naphthenic fractions of various compositions have also been treated successfully, and

It is therefore to be understood that the following examples are not to be considered as limiting the invention in any manner.

Example I

A hydrocarbon mixture consisting essentially of 80% by weight of normal heptane and 20% by weight methyl cyclopentane was treated with 5% by weight of anhydrous aluminum chloride and 5% by weight hydrogen chloride at about 100° C. for five hours. The product analyzed as follows:

	Per cent
Heptane	78.2
Cyclohexane	16.8
Methyl cyclopentane.....	5.0

Thus, under conditions where normal heptane itself would normally be predominantly decomposed, no appreciable degradation took place and the labile and thermally less stable methyl cyclopentane was approximately $\frac{3}{4}$ converted into the more desirable cyclohexane.

Example II

A naphthenic gasoline was fractionated and a fraction boiling between 65°C. and 75°C. collected. This fraction which consisted of about

	Per cent by weight
Naphthenic hydrocarbons.....	60
Aromatic hydrocarbons.....	10
Paraffinic hydrocarbons.....	30

was treated with 1% by weight of aluminum chloride and 5% by weight of HCl in an autoclave at 80°C. for ten hours.

After decantation from the AlCl₃ the product obtained was washed with lye and water and then dried. The reaction product was subsequently subjected to a sharp rectification, whereupon 45% by weight of a cyclohexane fraction boiling between 78 and 80.5°C., having a refractive index of 1.4265-20/0, was obtained.

Example III

750 grams of a Borneo gasoline fraction boiling between 85°C. and 104°C. and consisting approximately of

	Per cent
Naphthenic hydrocarbons.....	74
Aromatic hydrocarbons.....	3
Paraffinic hydrocarbons.....	23

was treated with 40 grams of anhydrous aluminum chloride, and 100 grams anhydrous HCl for ten hours at 80°C. in a 2 liter stirring autoclave. The product, after washing and drying, consisted approximately of

	Per cent
Naphthenic hydrocarbons.....	73
Aromatic hydrocarbons.....	2
Paraffinic hydrocarbons.....	25

This treated gasoline fraction, when subjected to a dehydrogenation treatment, was found to give much superior yields of aromatic hydrocarbons.

Example IV

A fraction of a straight-run gasoline from a Venezuelan crude boiling between 85°C. and 104°C., and consisting approximately of

	Per cent
Aromatic hydrocarbons.....	6
Hydroaromatic cycloparaffinic hydrocarbons.....	29
Non-hydroaromatic cycloparaffinic hydrocarbons.....	25
Paraffinic hydrocarbons.....	40

was treated as follows: 4% of anhydrous HCl was dissolved in the distillate and the mixture forced at a rate of 1 liter per hour under a pressure of about 15 atmospheres through a 2 liter stirring autoclave containing 500 grams of aluminum chloride and maintained at a temperature of 80°C. After treating about 140 liters, small quantities of aluminum chloride were intermittently added to the autoclave to maintain the catalytic activity. At the very beginning a portion of the small amount of aromatic hydrocarbons contained in the feed was consumed to produce a complex compound of the Gustavson type with the aluminum chloride. The product, after washing with caustic, washing with water, and drying, consisted approximately of

	Per cent
Aromatic hydrocarbons.....	6
Hydroaromatic cycloparaffinic hydrocarbons.....	46
Non-hydroaromatic cycloparaffinic hydrocarbons.....	8
Paraffinic hydrocarbons.....	40

Thus, it is seen that the content of non-hydroaromatic hydrocarbons was reduced from about 25% to about 8% while the concentration of valuable aromatic hydrocarbons was not appreciably altered and degradation of the paraffinic hydrocarbons was substantially avoided. This treated distillate is exceptionally suited for a conventional reforming treatment.

The present application is a continuation-in-part of my copending application, Serial No. 270,655 filed April 28, 1939.

While I have described my invention in its preferred embodiments and indicated certain variations thereof, these are not to be construed as limiting the invention. It is to be understood that no limitations other than those imposed by the scope of the appended claims are intended.

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