

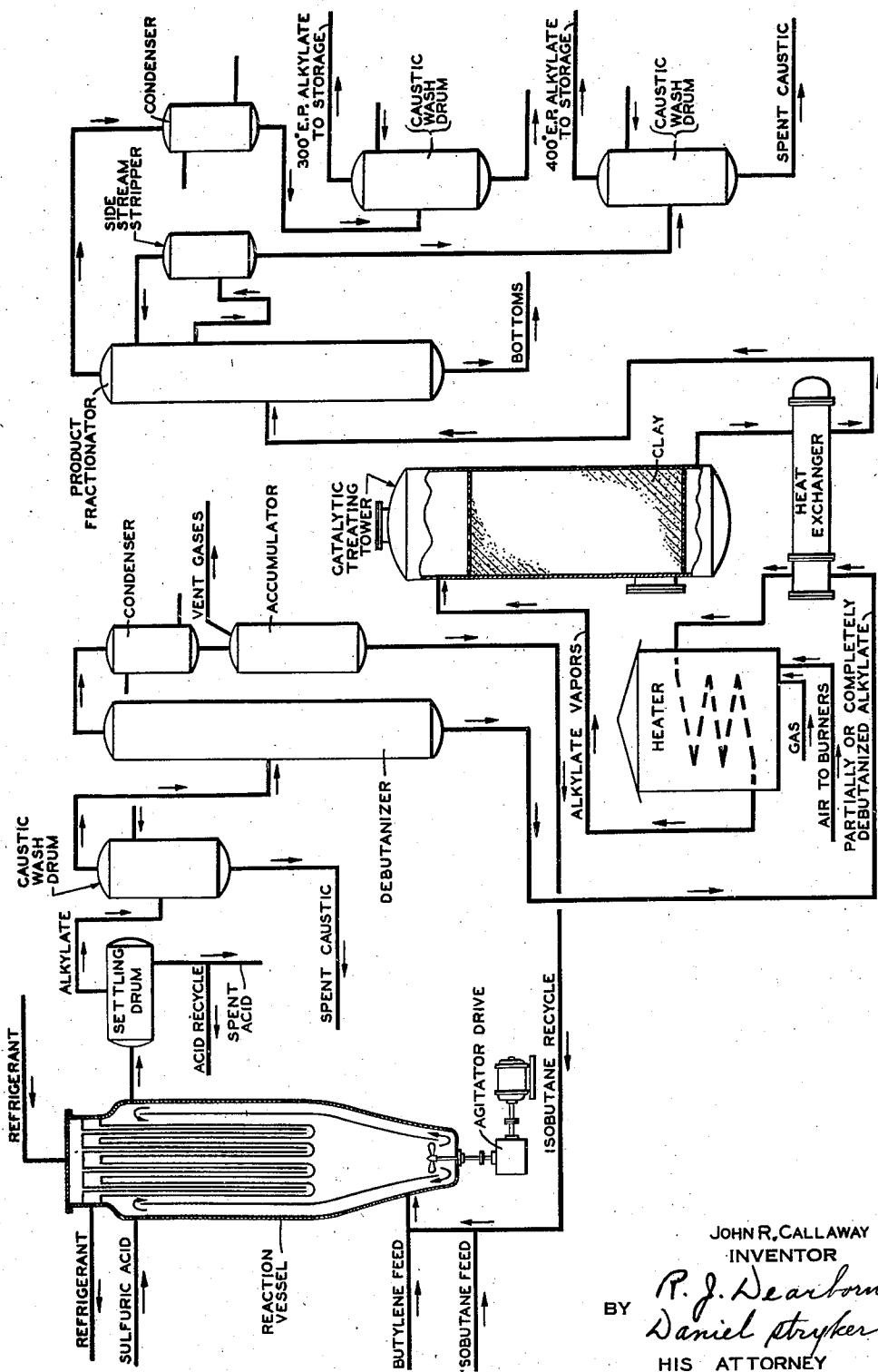
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PROCESS FOR TREATING HYDROCARBON FRACTIONS

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PROCESS FOR TREATING HYDROCARBON FRACTIONS

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My application relates to the improvement of alkylation gasolines, and especially to a catalytic process for improving the quality of alkylates obtained by the alkylation of paraffinic hydrocarbons with olefinic hydrocarbons.

Numerous processes have been developed for the production of gasoline range hydrocarbons from normally gaseous hydrocarbons, by effecting alkylation of the paraffinic components, and especially the isoparaffins, by means of olefinic components. These processes include thermal alkylation and various liquid phase alkylation processes involving the use of catalysts, such as sulfuric acid, hydrofluoric acid, aluminum chloride, and the like. Generally, all of these processes produce alkylates which are superior to straight run gasolines in anti-knock properties. However, in view of the continuing demand for higher and higher octane number gasolines, it is desirable to improve the quality of the alkylates produced by any of the present alkylation procedures. This is especially true if the alkylation process is carried out under conditions favorable to maximum throughput, rather than under optimum conditions for the highest quality alkylate. In such cases, the octane number of the alkylate produced may be from 1 to 3 points, or even more, below the octane number which could be obtained under optimum reaction conditions.

An object of the present invention is to provide a process for the treatment of hydrocarbon fractions obtained by the alkylation of paraffinic hydrocarbons with olefinic hydrocarbons to improve the motor fuel characteristics of such fractions.

Another object of the present invention is to provide a catalytic process for the treatment of alkylates to effect an improvement in their anti-knock characteristics.

A further object of this invention is to provide an alkylation process in which decreased alkylate quality, resulting from inferior charge stocks, or from throughput in excess of optimum reaction conditions for maximum product quality, is offset by catalytic treatment of the alkylate thus produced.

Other objects and advantages of the present invention will be apparent from the following description:

In accordance with the present invention, the alkylation reaction product, free from alkylation catalyst, is subjected to contact with an adsorption type catalyst at elevated temperatures, preferably not greatly below the cracking temperature range. This treatment will decompose mercaptans and other sulfur compounds which may

be present in the alkylates, but the application of my process to most alkylates would not be economically warranted for this improvement alone. My catalytic treatment effects other improvements which will generally be of much more relative importance than any desulfurization effected. Such improvements include the reduction of the unsaturated hydrocarbon content of low quality alkylates, the decomposition of esters formed from inorganic acid alkylation catalysts, and other improvements in alkylate quality presumably due to molecular rearrangement of the saturated hydrocarbons. The mechanism of the process with respect to improvement of the saturated hydrocarbons is not understood, but may be partially due to direct isomerization, and partially a result of depolymerization of olefin polymers in the alkylate and catalytic vapor phase alkylation of isoparaffins in the alkylate by means of the depolymerized olefins thus produced. In any event, it is to be understood that my invention is not to be limited to any particular theory with respect to its operation.

The catalysts which may be employed in my process comprise any of the adsorption type catalysts which are employed in other types of hydrocarbon treating operations, such as the clay catalysts used in decolorizing, desulfurizing, and cracking operations. These catalysts, which are commonly referred to as "clay type catalysts" or "adsorption type catalysts," include the diatomaceous earths (commonly known as fuller's earth, kieselguhr, etc.) and the aluminum silicate clays, such as bauxites, bentonites, and the like. Among these catalysts, the most effective comprise the acid treated bentonites, and especially those from selected natural deposits which are particularly suited for the production of highly activated products by acid treating. The material sold under the trade name "Super-Filtrol," is an example of the latter type of catalyst. Satisfactory results may be obtained in my process with any of these catalysts, but I prefer to use a highly activated catalyst, such as "Super-Filtrol," in any case where the improvement of product quality is sufficient to warrant the differential in catalyst cost.

The treatment of the present process is effected at temperatures sufficiently high to effect substantial isomerization, and below a temperature at which substantial cracking occurs. Temperatures within the range 650–850° F. will usually be satisfactory, and I generally prefer to employ a temperature of 700–750° F. The contact time or space velocity is not critical, except at the

higher temperature ranges, where excessive contact time may cause undue cracking. Space velocities of 0.1 to 1.0 volume of liquid alkylate per apparent volume of catalyst, will generally be satisfactory at temperatures of 700-750° F. The space velocity may be varied, roughly in proportion to the temperature, when operating outside this range. Under these conditions, a catalyst life of from 1000 to 5000 barrels of alkylate per ton of catalyst can usually be expected. The spent catalyst may be subjected to reactivation treatments with solvents, or to reactivation by burning off organic deposits; but, in view of the low cost of this type of catalyst, it will usually be preferred to discard the spent catalyst and replace it with new.

The catalytic treatment may be applied to the entire hydrocarbon reaction product from the alkylation process, or to a specific fraction of the alkylate such as an aviation gasoline fraction, or to a blend of alkylate and other motor fuel hydrocarbons. Since most alkylation processes involve the use of a large excess of paraffinic hydrocarbon reactant, it will usually be desirable to remove the bulk of the unreacted gaseous hydrocarbons, for recycling to the alkylation process, prior to subjecting the alkylate to the present catalytic treatment. In some cases, and especially when low quality alkylates are obtained, having substantial amounts of unsaturated hydrocarbons present, it is desirable to include a small proportion of normally gaseous isoparaffin in the charge to the catalytic treatment, in order to favor vapor phase alkylation, and effect reaction of the olefins, olefin polymers, or depolymerized polymers. For this purpose, the separation of gaseous hydrocarbons for recycle to the alkylation reaction is intentionally made incomplete. Further fractionation of the alkylate, prior to catalytic treatment, may be effected if desired, but it is usually more economical to effect this fractionation subsequent to the catalytic treatment. In the latter case, a single fractionation may serve to separate any high boiling materials formed in the catalytic process, and also to separate the alkylate into desired fractions. The temperature of the vapors leaving the catalytic treatment is more than sufficient to effect this final fractionation, and cooling to the proper fractionator feed temperature may be suitably effected by heat exchange with the alkylate passing to the heater for the catalytic treatment.

The catalyst treatment of the present invention is applicable to alkylation reaction products obtained from any of the known alkylation processes, such as thermal alkylation, and catalytic alkylations employing aluminum halide catalysts or inorganic acid catalysts, such as sulfuric acid or hydrofluoric acid. Alkylates obtained from the alkylation of either normal or isoparaffins may be treated by the present process, and such alkylates may be obtained by the use of monomeric olefins, the lower olefin polymers, or olefin addition products such as alcohols or acid sulfates, as the alkylating agents. However, my process is especially suitable for the treatment of alkylates obtained in the sulfuric acid alkylation of normally gaseous isoparaffins such as isobutane, with normally gaseous olefins, and my process will be further illustrated with specific references to this type of alkylation.

One modification of a sulfuric acid alkylation process including the catalytic treating process

of the present invention is illustrated in the accompanying drawing. Referring to the flow diagram shown in the drawing, it may be seen that the alkylation of isobutane with butylenes, and the separation of the reaction mixture, are effected in a conventional manner. The separated oil phase, after caustic washing to remove residual sulfuric acid, is then subjected to distillation in a debutanizing column in accordance with the customary procedure. In the present process, substantially complete or only partial debutanization is effected, depending on whether or not isobutane is desired in the product to undergo the following catalytic treatment. The partially or completely debutanized alkylate then flows to the heater, which may be any conventional type such as a direct fired tube still. Here, the alkylate is vaporized and heated to a temperature of, say, 750° F. The hot vapors then flow to the top of the catalyst tower, entering at a temperature of about 740° F.

The catalyst tower may contain a single bed of catalyst, as shown, or a plurality of separate beds supported by perforated trays, or the like. The amount of catalyst charged is, of course, dependent upon the throughput of alkylate and the desired space velocity. For average alkylates being treated at the present illustrative temperature, the amount of catalyst may suitably be in the range 250-2500 cu. ft. per 1000 bbl. of alkylate throughput per day.

The treated alkylate, leaving the catalyst tower at a temperature of about 720° F., may be cooled in a conventional heat exchanger to a temperature of about 480° F., thereby preheating the alkylate charge for the heater to about 300° F. The vapors leaving the heat exchanger then flow to the product fractionator where the desired fractions of the alkylate may be separated. Any high boiling materials formed in the catalytic treatment may be removed as fractionator bottoms, and any unreacted gaseous hydrocarbons and normally gaseous products may suitably be separated from the fractionator overhead condensate in the accumulator drum. The alkylate fractions are preferably given a finishing treatment with alkali, such as a conventional caustic washing, to remove any residual hydrogen sulfide formed from the decomposition of sulfur compounds in the catalytic treatment.

My invention will be further illustrated by the following specific examples:

Example I

Isobutane is alkylated with mixed refinery butylenes in a conventional manner, as shown in the flow diagram discussed above, using sulfuric acid of 98% initial and 88% spent concentration in a 1/1 volume ratio of acid to hydrocarbon. The reaction is effected in a "Stratco Mixer" reaction vessel at 55° F., with a contact time of 20 min., an external isobutane to olefin ratio of about 6/1, and sufficient emulsion recirculation in the reaction vessel to produce an internal isobutane to olefin ratio of approximately 1000/1. Using isobutane of 90% purity for feed and recycle, the isobutane content of the reactor hydrocarbon mixture is about 67% under these conditions, the production of the unit is about 900 bbl. per day of total alkylate, with the depentanized aviation fraction having a CFRM octane number of 93.5.

The capacity of the unit is increased to 1800 bbl. per day by decreasing the external isobutane to olefin ratio to about 3.6/1 and the contact

time to about 15 minutes for the same over-all liquid circulation. These conditions are further from the optimum than the former conditions, and the CFRM octane number of the aviation fraction obtained is only 91.5.

In order to increase the octane number of the high production alkylate to approximate that of the low production alkylate, the former is subjected to the catalytic treatment of the present invention, in accordance with the procedure of the flow diagram previously discussed. The debutanized alkylate obtained from the debutanizer, at the rate of approximately 1800 bbl. per day, is heated to about 750° F. and passed at a contact temperature of 740–720° F. through "Super-Filtrol" type acid treated bentonite in a single bed 10 ft. in diameter and approximately 15 ft. deep. The space velocity thus obtained is approximately 0.5 volume of liquid alkylate per apparent volume of catalyst per hour.

The CFRM octane number of the depentanized and caustic washed aviation fraction of the treated high production alkylate may be as high as 93.5, or even higher. In addition to the improvement in anti-knock characteristics, the catalytically treated alkylate is superior to untreated alkylate in the substantial elimination of constituents such as alkyl sulfates, other sulfur compounds, and polymerizable compounds, all of which are undesirable in high quality aviation gasoline even when present only in traces.

Example II

Isobutane is alkylated with a mixture of 92 mol per cent propylene and 8 mol per cent isobutylene using 98% sulfuric acid in an acid to hydrocarbon volume ratio of 1/1. The reaction is effected continuously in an agitated reaction vessel at a temperature of about 70° F., with a contact time of 25 minutes. With a paraffin to olefin mol ratio in the charge of about 5/1, the yield of debutanized alkylate amounts to about 190%, based on the weight of the olefin charged. The CFRM octane number of the alkylate thus obtained is about 88.5.

The propylene alkylate obtained as described above is vaporized and passed through fuller's earth at a temperature of about 700° F. and a space velocity of about 0.8 volume of liquid alkylate per apparent volume of fuller's earth per hour. The treated alkylate is fractionated, and a 300° F. end point aviation fraction is taken off, and is caustic washed before exposure to air. The CFRM octane number of this treated alkylate may be as high as 90.0, or even higher. In addition to the improvement in octane number, the treated alkylate is improved by the substantially complete elimination of propyl sulfate and gum-forming constituents, and in its superior stability on storage in the presence of tetraethyl lead.

It should be understood, of course, that the above examples are merely illustrative and are not to be construed as limiting the scope of my invention. The procedure of these examples may be modified in numerous respects, such as the substitution of different charge stocks, alkylation catalysts, or alkylating conditions, and the substitution of other adsorption type treating catalysts or different treating conditions. Also, the order of the various steps in the procedures of the examples may be changed, as by fractionating the alkylate and catalytically treating only selected distillate fractions, or by leaving a part or all of the unreacted isoparaffin in the alkylate

until after the catalytic treatment. In general, it may be said that the use of any equivalents or modifications of procedure which would naturally occur to those skilled in the art is included in the scope of my invention. Only such limitations should be imposed on the scope of my invention as are indicated in the appended claims.

I claim:

1. In the manufacture of aviation gasoline the process that comprises charging normally gaseous olefins and isoparaffins to an alkylating zone wherein the olefins and isoparaffins are contacted with sulfuric acid under alkylating conditions to produce normally liquid hydrocarbons in the gasoline boiling range with a limited time of reaction insufficient to support conversion to an alkylate product of maximum anti-knock value, maintaining the proportion of isoparaffins to olefins charged to the alkylating zone below that necessary to produce an alkylate product of maximum anti-knock value and contacting resultant gasoline alkylate with an adsorptive clay catalyst at a temperature of about 650–850° F. with a time of contact adequate to effect molecular rearrangement of saturated hydrocarbons into hydrocarbons of increased anti-knock value but insufficient to effect cracking to thereby increase the anti-knock value of the alkylate and produce a final gasoline product adapted for aviation gasoline.

2. In the manufacture of aviation gasoline the process that comprises charging normally gaseous olefins and isoparaffins to an alkylating zone wherein the olefins and isoparaffins are contacted with sulfuric acid under alkylating conditions to produce normally liquid hydrocarbons in the gasoline boiling range with a limited time of reaction insufficient to support conversion to an alkylate product of maximum anti-knock value, maintaining the proportion of isoparaffins to olefins charged to the alkylating zone below that necessary to produce an alkylate product of maximum anti-knock value and contacting resultant gasoline alkylate with an adsorptive clay catalyst at a temperature of 700–750° F. and a space velocity of 0.1–1.0 to effect molecular rearrangement of saturated hydrocarbons into hydrocarbons of increased anti-knock value to thereby increase the anti-knock value of the alkylate product without the cracking thereof and produce a final gasoline product adapted for aviation gasoline.

3. In the manufacture of aviation gasoline the process that comprises charging normally gaseous olefins and isoparaffins to an alkylating zone wherein the olefins and isoparaffins are contacted with sulfuric acid under alkylating conditions to produce normally liquid hydrocarbons in the gasoline boiling range with a limited time of reaction insufficient to support conversion to an alkylate product of maximum anti-knock value, maintaining the proportion of isoparaffins to olefins charged to the alkylating zone below that necessary to produce an alkylate product of maximum anti-knock value, debutanizing the alkylate product and contacting the debutanized alkylate with an adsorptive clay catalyst at a temperature of about 650–850° F. with a time of contact adequate to effect molecular rearrangement of saturated hydrocarbons into hydrocarbons of increased anti-knock value but insufficient to effect cracking to thereby increase the anti-knock value of the alkylate and produce a final gasoline product adapted for aviation gasoline.

4. In the manufacture of aviation gasoline the process that comprises charging normally gaseous olefins and isoparaffins to an alkylating zone wherein the olefins and isoparaffins are contacted with sulfuric acid under alkylating conditions to produce normally liquid hydrocarbons in the gasoline boiling range with a limited time of reaction insufficient to support conversion to an alkylate product of maximum anti-knock value, maintaining the proportion of isoparaffins to olefins charged to the alkylating zone below that neces-

5 sary to produce an alkylate product of maximum anti-knock value and contacting resultant gasoline alkylate with fuller's earth at a temperature of about 650-850° F. with a time of contact adequate to effect molecular rearrangement of saturated hydrocarbons into hydrocarbons of increased anti-knock value but insufficient to effect cracking to thereby increase the anti-knock value of the alkylate and produce a final gasoline product adapted for aviation gasoline.

10 JOHN RICHARD CALLAWAY.