The present invention relates to an improved method for obtaining valuable products boiling largely within the gasoline range from gaseous or low boiling hydrocarbons. The invention will be fully understood from the following description and the drawing.

The drawing is a diagrammatic view in sectional elevation of an apparatus for carrying out the process and indicates the flow of materials.

It has been known for some time that valuable products which boil largely within the gasoline range and are endowed with superior anti-detonation qualities, can be produced by polymerization or condensation of low boiling hydrocarbons, and several methods for accomplishing this are now known. The most suitable feed stock available to refiners is a cut rich in hydrocarbons of the butane-butylene range ordinarily obtained by the stabilization of cracked naphthas. Such material has too low a boiling point to be employed in gasoline with the exception of perhaps a few per cent and it is therefore desirable to convert the excess of such material into a higher boiling product which can be used in gasoline.

The C4 stabilizer cut ordinarily available to refiners consists of about 10 to 14% of isobutylene, about 20 to 25% of mixed normal butylenes, alpha and beta, with about 10 or 12% of isobutane, while the remainder consists of normal butane with various amounts of propane, propylene, pentane and amylene, depending on the sharpness of the fractionation.

Processes are known for converting iso-olefins alone to dimers and trimers, but the yield is relatively small, being approximately 10% of the feed stock. Other processes convert normal along with the iso-olefins into cross or copolymers, but the yield of the gasoline-like product is limited to about twice the yield of the iso-olefin present, that is to say roughly 20% of the C4 cut. It has been found that under certain conditions the yield of gasoline-like materials can be increased even more. It is likewise found that the product is not so highly unsaturated as before and, indeed, if care is taken a product may be obtained the lower fractions of which are substantially saturated.

Referring to the drawing, the feed stock which is described generally as a C4 cut of the approximate composition disclosed above is fed by a pipe 4, preferably in a liquid condition, into a purifying tower 2 which is filled with a suitable packing material. Pipe 3 brings the purifying liquid, for example caustic soda solution, into the top of tower 2 and the solution is withdrawn from the lower portion of the tower by pipe 4 and recirculated by pump 5 so that it may be repassed through the tower in contact with the hydrocarbon feed stock.

The purified C4 cut now passes by pipe 6 into a contacting chamber 7 which is filled with sulfuric acid of a concentration and under pressure and temperature as will be disclosed below. This chamber may be any suitable design adapted to bring the liquid hydrocarbon and the acid into intimate contact. For this purpose sprays, jets, perforated or baffle plates or other mixing devices may be employed. The temperature is maintained at the appropriate range by cooling means which are not shown, but which may be a jacket containing a cooling coil. Under the preferred conditions isobutylene is absorbed in the acid along with whatever isoamylene may be present, with little or no effect on normal olefins. The acid along with its dissolved constituents is drawn from the chamber by a pipe 8 and the remaining hydrocarbons flow out of the chamber by a pipe 9 to an acid trap 10, a cooler 11 and thence into a second acid contacting chamber 11. This chamber may be similar in design to chamber 7 and is provided with similar means for bringing the acid and hydrocarbon into intimate contact and to maintain temperature in the prescribed range which will be disclosed below. The reaction conditions, prevailing in this reaction chamber are relatively more vigorous and are adapted to bring about a reaction of the more unreactive hydrocarbon constituents.

The acid with its dissolved constituents flows out of pipe 12 and preferably joins the acid from the first chamber 7 in a pipe 13. Water may be added by a pipe 13 so as to bring the acid concentration below about 70%. The mixed acid and the dissolved constituents then flow through a heater 14 wherein temperature is rapidly raised to cause reaction of the dissolved hydrocarbon constituents. The reaction mixture is then discharged into a separator 16, the acid settles as a lower layer and is drawn off by a pipe 17. Part of this acid may be recycled by pipe 18 and pump 19 to chamber 7 and the remainder may be re-concentrated in suitable apparatus not shown, and returned to chamber 11 by a pipe 20. Additional or make up acid is added from time to time.

Instead of using the two reaction chambers 7 and 11 respectively, a single chamber such as 11 may be employed and in this case the purified C4 cut passes from the pipe 6 by bypass line 26 directly into the chamber 11.
The hydrocarbon constituents which are undissolved in chamber 14 are withdrawn as before by a pipe 21 to an acid trap 22 and in the preferred embodiment of the invention this hydrocarbon mixture is combined with the hydrocarbon layer withdrawn from chamber 18 by a pipe 23. The mixture is then passed through heater 24 and into a fractionating tower 25 from which the unconverted butane and/or butylene is withdrawn by pipe 26 overhead, condensed and collected at 27. The constituents heavier than butane and butylene are withdrawn from the tower by pipe 28 and may be collected as such or redistilled in the tower 29 so as to segregate and collect the lighter distillate at 30 and a heavier liquid at 31.

If desired, instead of adding the hydrocarbon product collected at 18 to the product obtained from 22, the former may be separately distilled in equipment similar to 22. Thus the two products may be collected separately. The product collected at 16 is unsaturated and should be hydrogenated after which it has a good octane blending value. The product collected at 23 is used as a nearly saturated fuel which may be used without hydrogenation but has a slightly lower octane number than the product collected at 16.

In the preferred operation of the present process, the C6 cut, preferably after purification with caustic soda, is first brought into contact with a relatively dilute acid ranging from about 50 to 65% by weight at a temperature below about 100° F. preferably between about 80° and 100° F. It is desirable to avoid polymerization at this point so that acid strength and temperature are both relatively low. It is then possible to extract isomethylene, particularly isobutylene, without any substantial reaction or solution of the other constituents. In the second stage of the process, the feedstock is brought into contact with an acid of about 87% concentration or stronger, preferably of 90 to 100%, in order to bring about a reaction of the less reactive constituents. The temperature in this reactor is preferably maintained between about 30 and 100° F., roughly at room temperature. The reactions taking place are complex and not entirely understood, but it should be sufficient to say that under these conditions a portion of the remaining olefins is dissolved in the acid and is withdrawn therewith. In addition, however, there is a conversion of a portion of the remaining constituents into higher boiling hydrocarbons largely of the gasoline range. These are removed in the hydrocarbon stream.

The above acid contact steps may be carried out at atmospheric pressure, if desired, but it is preferable to carry out the process under a superatmospheric pressure, sufficient to maintain the constituents in liquid condition. The acid extractives from both contact steps are combined and forced under a high pressure, for example 200 to 400 pounds per sq. inch, through a heater so that the temperature is raised to 150 to 300° F., or preferably in the narrower range of 200 to 250° F. Under these conditions the extracted constituents are brought into reaction to produce materials which largely boil within the gasoline range and which are separated as disclosed above.

As indicated in the previous description, it is preferable to use a two stage acid contact process, but it is possible to use the first stage. If desired, and pass the C6 cut directly into the second reaction stage. The two stage process is preferred because of increased yield and superior quality, but the single step process requires less equipment. It will be understood that while each stage is represented by a single chamber, it may often be desirable to substitute two or more vessels operating under substantially the same conditions in order to obtain a substantially complete reaction under the conditions imposed in each stage.

It is preferred to mix the hydrocarbon stream withdrawn from the strong acid reaction chamber 11 with the reaction product obtained from the separation chamber 16. Both constituents contain small amounts of product boiling below the gasoline range and both likewise usually contain constituents heavier than desired. The equipment shown for the purpose of segregating the gasoline cut is diagrammatic and merely suggestive of what may be employed, but variations in the equipment and process are within the scope contemplated by the present inventors.

The mixed product obtained by the present process is considerably more saturated than the polymer products obtained either from isooctenes alone, or by the co- or cross-polymerization of normal and isooctenes. It is usually desirable, however, to hydrogenate this mixed product and that may be accomplished by using either the conventional nickel catalysts at atmospheric or higher pressures or the sulfur resistant catalysts such as the oxides and sulfides of the 6th Group metals; such catalysts are preferably used under high pressure conditions.

As indicated before, when care is taken with the conditions in the strong acid contacting zone, a product may be obtained from the hydrocarbon stream which is substantially saturated and can be used directly as a motor fuel constituent without hydrogenation after stabilization to remove unreacted C6 hydrocarbons and preferably the heavier or higher boiling constituents which are produced to some degree.

As a further aid to a complete understanding of the present invention, the following examples are submitted. It is to be distinctly understood, however, that these examples are purely illustrative and are not definitive of the scope of the present invention.

Example 1

Fourteen hundred liters of refinery C6 cut containing 12.4% of isobutylene and 18.6% of normal butylene, the remainder being a mixture of iso- and normal butanes, was passed at atmospheric pressure and at a temperature between about 40 and about 60° F. through two absorbing units arranged in series. These units contained sulfuric acid of 96 and 98% concentration respectively each unit holding 300 ccs. of acid. The refinery C6 cut was passed through frosted glass dispersion plates placed in the bottom of the sulfuric acid absorbers at a rate between about 19 and about 45 liters per hour. As the concentration of the sulfuric acid dropped during the reaction, fresh acid was added to bring the concentration to about that originally used. The resulting liquid product was drawn off the acid layers of each of the absorbers. This product was then debutanized and 700 gms. of debutanized liquid product was obtained having a boiling point between about 100° F. and about 600° F., and representing a yield of 36% based on total feed. Above the liquid the product boiled in the gasoline boiling range.

The product was subjected to an analytical distillation. The C6 fraction boiling between 214° F. and 270° F. constituted about 20% of the product.
This Cs cut consisted of about nine individual fractions separated from each other in boiling point by some 5 to 10° F. and each constituting about 10% of the total Cs cut. This Cs cut had a refractive index ranging from 1.3882 to 1.3970. The total product has a bromine number of 17, while the Cs fraction had a bromine number of 0.

**Example II**

Using the same absorbing units and catalyst and under the same reaction conditions as described in the preceding example, a refinery Cs cut containing 8.6% of isobutylene, 14.9% of normal butylene and 12% of isobutane was continuously bubbled through the acid in the absorbers at the rate of about 51 liters/hr. After 4½ hours the product was obtained with a yield of about 28.5% based upon the total feed. The Cs fraction of this product, which amounted to 28.4% of the total product, had a zero bromine number.

**Example III**

In another experiment, duplicating the above experiment except that the feed rate was 27.4 liters per hour, the product contained a Cs fraction of 31.4% of the total final product and this fraction had a bromine number of 0.6. The octane number of the Cs fraction measured as a 10% blend with iso-octane was 94.

**Example IV**

(a) 6 liters of Cs cut, which contained 5% propane, 9% iso-butylene, 20% N-butylene, 15% iso-butane and 51% N-butene, was maintained as a liquid under a pressure of 50 pounds per sq. in. and passed through a two litre bath of sulfuric acid of 65% strength maintained at about room temperature. About 10% of the feed stock was dissolved by the acid and the remaining hydrocarbon was then passed through a second two litre bath containing 50% sulfuric acid which was also maintained at about room temperature. The two extracts were withdrawn and mixed and heated to 200° F., then cooled and a hydrocarbon layer separated from the acid. This hydrocarbon layer was mixed with the hydrocarbon stream from the second acid bath and the mixture distilled to remove the remaining butane and butylene. The yield of the liquid product obtained was found to be about 19.8 volume per cent of the original feed stock. It had a bromine number of 12. The fraction distilling below 300° F. amounted to 83.8% of the total product and showed an octane number of 86.4 without hydrogenation, bromine number of 3.4, gravity of 72.6° A. P. I. and boiled over the range of 10° F. to 274° F. The higher boiling fraction had a bromine number of 21.5, boiled from 310° to 653° F. and had a gravity of 80.5° A. P. I.

(b) In a similar process, the undissolved hydrocarbon fraction from the second acid reaction zone was distilled alone to remove butane and butylene. The liquid product boiling above this range was found to amount to about 18.3 volume percent of the original feed stock. It had a bromine number of 16.4. The fraction distilling below 300° F. constituted 48.4% of total product and had an octane number of 85.6 without hydrogenation, gravity 73° A. P. I., bromine number of 5.5 and distillation range 107° to 275° F. The higher boiling part had a gravity of 50.6° A. P. I., bromine number of 26.5 and boiled from 310° to 660° F.

The present application is a continuation in part of the prior application Serial No. 56,914 filed December 31, 1933.

The nature and scope of the invention having been thus fully described, what is claimed as new and useful and desired to be secured by Letters Patent is:

1. A process for converting hydrocarbons of a refinery Cs cut to higher boiling products suitable for motor fuel, comprising passing the hydrocarbons through sulfuric acid of 50 to 65% concentration at temperature below about 100° F., separating the undissolved hydrocarbons, passing the latter through sulfuric acid of at least 87% at a temperature from 30 to 103° F., separating the undissolved hydrocarbons, then contacting the two acid products and heating the same to 150 to 300° F., separating the hydrocarbons from the acid, admixing the hydrocarbons so produced with the said lastly separated undissolved hydrocarbons, and distilling the unconverted lighter fraction from the mixture.

2. In a process for producing normally liquid hydrocarbons boiling within the gasoline boiling range by condensing at least a portion of the constituents of a refinery Cs cut with sulfuric acid, the steps comprising removing a portion of the more reactive olefins contained therein, thereby reducing the amount of olefins present with respect to the butanes present in the reaction mixture, contacting the hydrocarbon mixture of reduced olefin content with from about 87 to about 100% sulfuric acid at a temperature between about 30 and about 100° F., and separating the hydrocarbons produced from the reacted mixture.

3. In a process for producing normally liquid hydrocarbons boiling within the gasoline boiling range by condensing at least a portion of the constituents of a refinery Cs cut with sulfuric acid, the steps comprising removing a portion of the more reactive olefins contained therein, thereby materially decreasing the amount of olefins present with respect to the amount of butanes present in the reaction mixture, contacting the resulting hydrocarbon mixture with between about 87 and 100% sulfuric acid at about room temperature while maintaining sufficient super-atmospheric pressure to insure liquid phase operation under the reaction conditions, and separating normally liquid hydrocarbons boiling within the gasoline boiling range from the reacted mixture.

4. A process as in claim 3 wherein the preliminary removal of olefins is effected by contacting the refinery Cs cut with between about 50 and about 65% sulfuric acid at a temperature below 100° F. and wherein the resultant acid extract is separated from the refinery Cs cut prior to contacting said refinery Cs cut with the more concentrated sulfuric acid.

5. A process for converting refinery Cs cut containing butanes, isobutylene and normal butylene to hydrocarbons boiling within the gasoline boiling range by condensing constituents of said cut in the presence of sulfuric acid, the steps comprising condensing and distilling the finite components of the said refinery Cs cut by contacting with between about 50 and about 65% sulfuric acid at a temperature between about 80 and about 100° F., separating the acid phase from the undissolved hydrocarbons, further condensing the undissolved hydrocarbons at a temperature between about 30 and about 100° F. In the presence of between about 87 and about 100° F.
sulfuric acid and recovering hydrocarbons boiling within the gasoline boiling range from the reacted mixture.

6. A process as in claim 5 wherein sufficient super-atmospheric pressure is maintained to insure liquid phase operation under the prevailing reaction conditions.

7. In a process for producing normally liquid hydrocarbons boiling within the gasoline range by condensing at least a portion of the constituents of a refinery C4 cut containing iso and normal butylenes and iso and normal butanes in the presence of sulfuric acid wherein substantially only isobutylene is absorbed in sulfuric acid under selective absorption conditions and suitable acid concentration followed by heating the resulting extract to condense the olefinic content thereof, the steps comprising intimately contacting the resultant isobutylene-free refinery C4 cut with sulfuric acid of at least 87% concentration at substantially room temperature, separately withdrawing an acid layer and a hydrocarbon layer, combining the acid layer with the isobutylene-containing acid extract prior to its heat treatment to condense the olefinic content thereof and separating normally liquid hydrocarbons boiling within the gasoline range both from the heat treated acid layer and acid extract and from the hydrocarbon layer.

9. A process as in claim 7 wherein sufficient super-atmospheric pressure is maintained to insure liquid phase operation under the prevailing reaction conditions.

10. A process for the production of normally liquid hydrocarbon condensation products boiling within the gasoline range which comprises selectively absorbing from a refinery C4 cut containing substantial amounts of iso and normal butylenes, iso and normal butanes, under selective conditions of absorption and sulfuric acid concentration substantially only the isobutylene content thereof, intimately contacting the resultant isobutylene-free refinery C4 cut with sulfuric acid of between about 87% and about 100% concentration at a temperature of between about 30°F. and about 100°F., separating the resulting hydrocarbon layer from the acid layer and recovering from the said hydrocarbon layer normally liquid hydrocarbons boiling within the gasoline range.

11. A process as in claim 10 wherein sufficient super-atmospheric pressure is maintained to insure liquid phase operation under the prevailing reaction conditions.

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