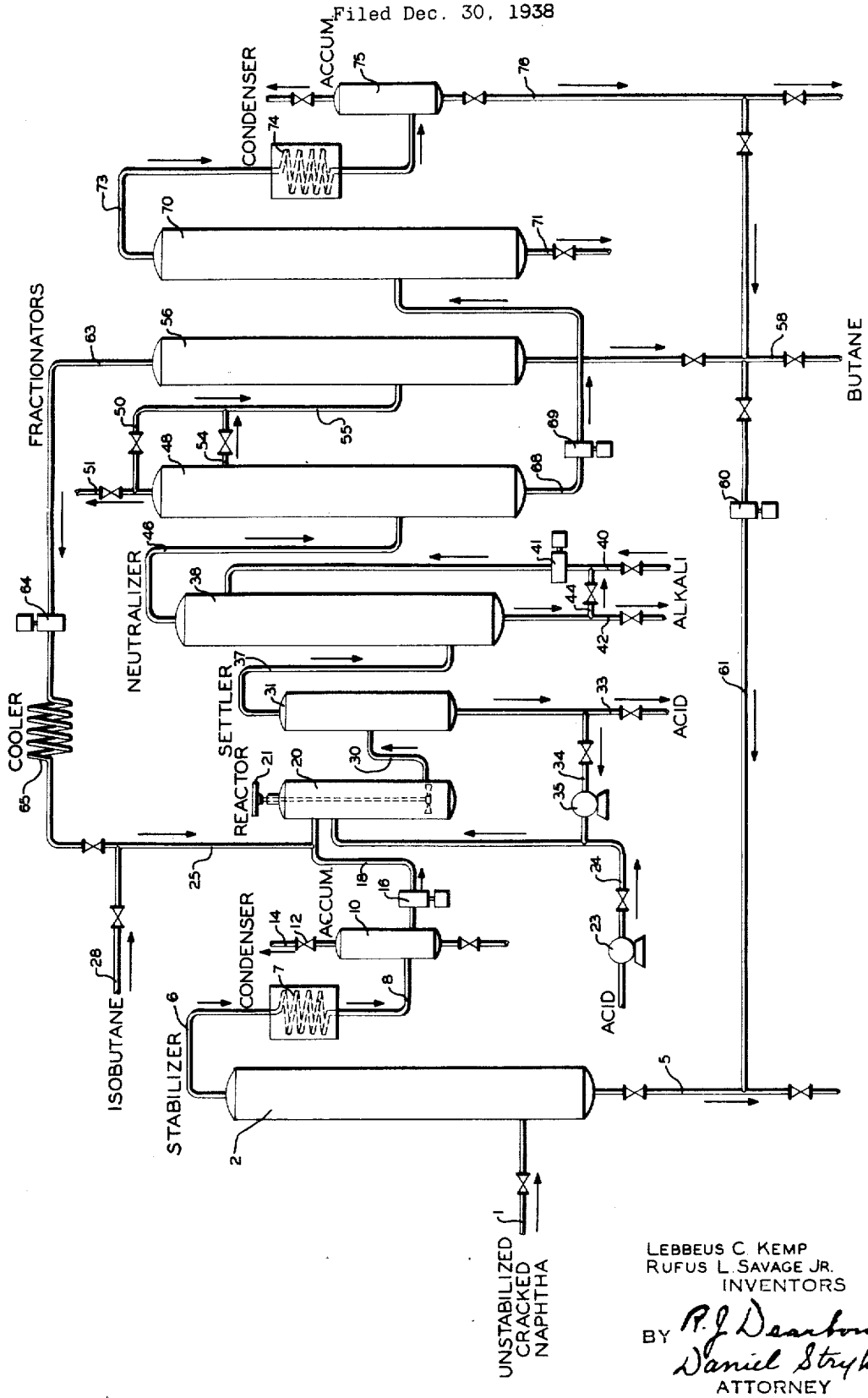
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MANUFACTURE OF MOTOR FUELS

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MANUFACTURE OF MOTOR FUELS

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This invention relates to the manufacture of motor fuels and has to do particularly with the production of high antiknock motor fuels, such as gasoline, by the alkylation of isoparaffins, for example isobutane, with olefins in the presence of an alkylation catalyst, preferably sulfuric acid.

In accordance with the invention, an unstabilized cracked naphtha from any well known or preferred type of cracking operation, is stabilized to separate therefrom substantially all hydrocarbons of lower boiling point than C_5 hydrocarbons, including normal butane, isobutane, butylenes and, in some cases, lower molecular weight paraffins and olefins, such as propane and propylene. The stabilizer overhead is then subjected to an alkylation operation in the presence of concentrated sulfuric acid, whereby the isobutane is alkylated by the olefins to produce high antiknock saturated hydrocarbons within the gasoline boiling range. The normally liquid hydrocarbons are separated from the reaction products and excess normal butane returned to the stabilized cracked naphtha to increase the volatility thereof and the unconsumed isobutane recycled to the alkylation operation.

The invention will be more fully understood from the following description read in connection with the accompanying drawing which is a diagrammatical sketch of one form of apparatus for carrying out the process of the invention.

Referring to the drawing, an unstabilized cracked naphtha from a suitable source of supply, not shown, such as an adjacent cracking still, is passed through the line 1 into a stabilizer or fractionator 2. The unstabilized naphtha may contain essentially C_4 hydrocarbons, including normal butane, isobutane and butylene, or it may contain in addition to the C_4 hydrocarbons a substantial amount of C_3 hydrocarbons, for example, propane and propylene. It may be advantageous in some cases to use an unstabilized cracked naphtha containing essentially C_4 hydrocarbons, whereby on alkylation of the stabilizer overhead a somewhat improved product, particularly with respect to antiknock value may be obtained. Ordinarily, either C_4 or a mixture of C_4 and C_3 hydrocarbons is suitable for alkylation and consequently the unstabilized naphtha may contain various amounts of C_4 or C_3 hydrocarbons or both.

It is contemplated, although not shown in the drawing, that the stabilizer overhead, in case it contains both C_3 and C_4 hydrocarbons, may be fractionated to separate the C_3 from the C_4 hydrocarbons. The C_4 hydrocarbons may then be subjected to the alkylation operation, and the C_3 hydrocarbons used for other purposes, for example, as a charge to a polymerization process.

In the stabilizer 2 the naphtha is stabilized or fractionated to separate therefrom substantially all hydrocarbons of less than five carbon atoms per molecule. The stabilized naphtha is drawn off from the lower portion of the stabilizer through the line 5. The stabilized naphtha will be of lower volatility than commercial gasoline and ordinarily requires the addition of butane to bring the volatility up to commercial gasoline specifications.

The stabilizer overhead is removed as vapors from the upper portion of the stabilizer through the vapor line 6 and condenser coil 7 wherein condensable hydrocarbons, such as C_3 and C_4 hydrocarbons, are condensed to liquids.

Ordinarily the stabilizer will be operated under sufficient pressure to effect condensation of the condensable hydrocarbons on cooling in the coil 7. However, if insufficient pressure is maintained on the stabilizer, it may be necessary to compress the vapors by a compressor, not shown, prior to cooling the vapors in condenser 7. The mixture of condensate and uncondensable gases is passed through the run-down line 8 to accumulator 10. Uncondensable or fixed gases, such as methane, ethane and ethylene, and some of the C_3 hydrocarbons, may be released from the accumulator through the relief valve 12 in line 14.

The liquid hydrocarbons are pumped from the accumulator 10 by the pump 16 through the line 18 to the reactor or alkylation chamber 20, provided with a stirring mechanism 21. Strong sulfuric acid of about 90 to 100% concentration and preferably about 94 to 96% concentrations, is forced by the pump 23 through the line 24 into the reactor 20. The hydrocarbons introduced into the reactor should contain sufficient isobutane whereby the ratio of isobutane to olefins in the feed is at least about 1: 1 and preferably between about 2:1 and 5:1. The excess isobutane may be obtained by introducing additional isobutane through the line 25, from an extraneous source as by line 28, or by recycling excess isobutane in the system, or bath.

In the reactor 20 the hydrocarbons are intimately contacted with the sulfuric acid at a temperature around room temperature, such as 60 to 90° F. although temperatures ranging from 0° to 120° F. may be used. The reaction is continued for sufficient time to effect substantial alkylation of the isobutane with the olefins.

Under proper conditions substantially all the olefins may be consumed. A sufficient pressure is maintained in the reactor to keep the hydrocarbons substantially in the liquid phase.

The reaction products are transferred from the reactor **20** through the line **30** to a settler **31** wherein the acid is allowed to settle out in the lower portion thereof. The used or spent acid is withdrawn from the settler through the line **33** and may be discharged from the system. It is ordinarily advantageous to recycle all or a portion of the acid for further use to the reactor through the line **34** by the pump **35**.

The hydrocarbons separate as an upper layer in the settler **31** and are withdrawn from the upper portion thereof through the line **37** to a neutralizer **38** wherein acid hydrocarbons are contacted with a neutralizing agent introduced through the line **40** by the pump **41**. The neutralizing agent may be any alkaline solution suitable for neutralizing the acidity of the hydrocarbons, for example dilute caustic or caustic soda solution. The alkaline solution, after intimate contact with the hydrocarbons, settles out in the lower portion of the neutralizer and may be withdrawn through the line **42**. Any portion or all of the alkaline solution may be by-passed through the line **44** for recycling and reuse in the system.

The neutralized hydrocarbons collecting in the upper portion of the neutralizer are passed through the line **46** to a fractionator **48**. In the fractionator **48** the normally liquid hydrocarbons are separated from the excess normally gaseous hydrocarbons. The operation of the fractionator **48** will depend somewhat upon whether it is intended to manufacture aviation gasoline or ordinary motor fuel gasoline.

For the manufacture of aviation gasoline, it is desirable to retain in the normally liquid products only sufficient normal butane to meet the volatility requirements of the aviation fuel. The remainder of the normally gaseous hydrocarbons is separated as vapors in the upper portion of the fractionator. If the vapors consist essentially of isobutane and normal butane, these hydrocarbons may be withdrawn as one cut from the upper portion of the fractionator through the line **50**. In the vapors contain a substantial amount of propane, which may build up in the system, then it is advantageous to fractionate out and release the propane and any uncondensable gases from the upper portion of the fractionator through the line **51**. In the latter case, the normal butane and isobutane may be removed from the fractionator as a liquid side stream through the line **54**.

The butanes passed through the line **50** or **54** as the case may be, are conducted through the line **55** to a fractionator **56** wherein a separation is made between the normal butane and the isobutane. The normal butane is separated out as a liquid in the lower portion of the fractionator from which it may be withdrawn through the line **59**. Sufficient of the normal butane, which may be all or a portion thereof, is preferably passed through the pump **60** and line **61** to the line **5**, wherein it is combined with the stabilized cracked naphtha, referred to heretofore, in sufficient amount to bring the naphtha up to about commercial gasoline volatility. The isobutane is removed as vapors overhead from the fractionator **56** through the line **63** in which is located a compressor **64**. The vapors are compressed, if necessary, to sufficiently high pressure whereby on cooling in the cooling coil **65**, the vapors are condensed. The condensate is then passed through the line **25** referred to heretofore, to the reactor **20**.

The liquids containing the aviation gasoline, are withdrawn from the lower portion of the fractionator **48** through the line **68** and forced by the pump **69** to a fractionator or still **70**, wherein the product is subjected to fractional distillation. The aviation gasoline is separated from the higher hydrocarbons which are withdrawn as bottoms from the lower portion of the fractionator through the line **71**. The vapors are removed overhead from the upper portion of the fractionator **70** through the line **73** and condenser **74** to the accumulator **75**.

For the production of motor fuel gasoline, fractionator **48** is operated to produce normally liquid hydrocarbons which contain substantially all the normal butane, that is sufficient normal butane to satisfy the requirements of the product obtained when the alkylation gasoline is blended with the stabilized cracked naphtha from stabilizer **2**. These normally liquid hydrocarbons, together with the normal butane are withdrawn from the lower portion of fractionator **48** through line **68** and pump **69** to the fractionator **70**, wherein the products are fractionated to produce a fraction of substantially gasoline boiling range as an overhead product, while the high boiling range hydrocarbons are withdrawn from the lower portion of the fractionator as bottoms through the line **71**. The gasoline vapors are passed overhead through the vapor line **73** and condenser **74** and the liquid product collected in the accumulator **75**. This product containing excess normal butane is withdrawn through the line **76** and branch line **61**, and combined with the stabilized naphtha withdrawn from the bottom of stabilizer **2** through line **5**. The addition of the alkylation gasoline to the stabilized naphtha not only provides sufficient normal butane to bring the volatility up to commercial gasoline specifications, but also imparts to the blend a substantial increase in anti-knock value.

The vapors in the fractionator **48** are fractionated to obtain a fraction rich in isobutane together with any normal butane which may not have been fractionated out. The fraction rich in isobutane is withdrawn through line **50** or line **54** depending on whether it is necessary to separate and remove propane through the line **51**. The product is passed through the line **55** to the fractionator **56** wherein further fractionation may be effected to more completely separate the normal butane from isobutane. The normal butane is withdrawn from the lower portion of fractionator **56** through the line **58** and may, in part or entirely, be passed into the line **61** to be added to the blend of stabilizer naphtha and alkylation gasoline. The isobutane fraction is removed overhead from the fractionator **56** through the line **63** and recycled, as described above, to the alkylation reactor **20**.

As an example of the operation of the invention, an unstabilized cracked naphtha was stabilized to separate all the hydrocarbons of lesser number of carbon atoms than five. A stabilized naphtha of lower volatility than commercial gasoline was withdrawn as a liquid from the stabilizer. The stabilizer overhead was condensed to produce a liquid fraction comprising C_3 and C_4 hydrocarbons, which were subjected to alkylation in the liquid phase, in the presence of

sulfuric acid of about 94% concentration and at a temperature of about 90° F. Sufficient isobutane, essentially a recycle stock, was added to bring the ratio of isobutane to olefins in the reaction mixture to around 2:1 to 3:1. The reaction products were separated to remove the acid and the hydrocarbons neutralized by scrubbing with dilute caustic soda solution. The neutralized hydrocarbons were then fractionated to produce a liquid hydrocarbon fraction comprising normally liquid hydrocarbons and a major portion of normal butane. The lighter hydrocarbons were fractionated to produce a fraction rich in isobutane which was recycled to the alkylation operation. The liquid fraction was distilled to separate higher boiling hydrocarbons and to produce a fraction of about gasoline endpoint. This fraction, containing excess normal butane was added to the stablized naphtha to produce a motor fuel of about gasoline specifications, and having a high antiknock value.

As another example of the operation of the invention, a cracked naphtha was subjected to stabilization to produce a stabilized naphtha containing substantially no hydrocarbons lighter than C_5. The stabilizer overhead or reflux containing C_4 and all or a portion of C_3 hydrocarbons, if any, were subjected to alkylation, substantially as described above, whereby the isobutane was alkylated with the olefins. A liquid fraction containing sufficient normal butane to meet the volatility requirements of the alkylation gasoline was separated and the liquid fraction distilled to produce a distillate of substantially aviation gasoline characteristics and having an antiknock value of about 92. The uncondensed vapors were fractionated to separate the normal butane from the isobutane, the isobutane was recycled to the alkylation operation and the normal butane was added to the stabilized cracked naphtha to bring the volatility up to about commercial gasoline specifications.

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.

We claim:

1. A process for the manufacture of high antiknock motor fuel, which comprises stabilizing cracked naphtha to remove therefrom substantially all hydrocarbons of less than five carbon atoms thereby producing a stabilized cracked naphtha of lower volatility than commercial gasoline and a normally gaseous hydrocarbon fraction containing n-butane, isobutane and olefins, subjecting said fraction to the action of concentrated sulfuric acid whereby the isobutane is alkylated by the olefins to produce high antiknock normally liquid hydrocarbons within the gasoline boiling range, separating the normally liquid hydrocarbons from residual normally gaseous hydrocarbons, fractionating said residual normally gaseous hydrocarbons to produce a fraction rich in normal butane and a fraction rich in isobutane, combining the fraction rich in normal butane with said stabilized naphtha to increase the volatility thereof and recycling the fraction rich in isobutane to the alkylation operation.

2. A process for the manufacture of high antiknock motor fuel, which comprises stabilizing cracked naphtha to remove therefrom substantially all hydrocarbons of less than five carbon atoms thereby producing a stabilized cracked naphtha of lower volatility than commercial gasoline and a normally gaseous hydrocarbon fraction containing n-butane, isobutane and olefins, subjecting said fraction to the action of concentrated sulfuric acid whereby the isobutane is alkylated by the olefins to produce high antiknock normally liquid hydrocarbons within the gasoline boiling range, fractionating the resulting product to obtain a normally gaseous fraction rich in isobutane and a fraction containing normally liquid hydrocarbons within the gasoline boiling range and containing a substantial amount of normal butane, recycling said fraction rich in isobutane to the alkylation operation and combining the fraction containing normally liquid hydrocarbons and ni-butane with said stabilized naphtha.

3. A process for the manufacture of high antiknock motor fuel, which comprises stabilizing cracked naphtha to remove therefrom substantially all hydrocarbons of less than five carbon atoms thereby producing a stabilized cracked naphtha of lower volatility than commercial gasoline and a normally gaseous hydrocarbon fraction containing n-butane, isobutane and olefins, subjecting said fraction to the action of concentrated sulfuric acid whereby the isobutane is alkylated by the olefins to produce high antiknock normally liquid hydrocarbons within the gasoline boiling range, separating from the reaction products an unstabilized alkylation naphtha containing high antiknock hydrocarbons essentially within the gasoline boiling range and normal and isobutane, stabilizing said alkylation naphtha to separate the isobutane and produce a stabilized alkylation naphtha of high antiknock value and containing a substantial amount of normal butane, recycling said isobutane to the alkylation operation and combining said stabilized alkylation naphtha with the first mentioned stabilized cracked naphtha.

4. A process according to claim 3 in which sufficient normal butane is retained in the alkylation naphtha to meet the volatility requirements of both the alkylation naphtha and the cracked naphtha.

5. A process for the manufacture of high antiknock hydrocarbons suitable for the manufacture of aviation gasoline, which comprises stabilizing cracked naphtha to produce a stabilized product deficient in normal butane for commercial gasoline, and an overhead fraction predominating in hydrocarbons lighter than C_5 and containing isobutane, normal butane and olefins between 2 and 5 carbon atoms, subjecting the stabilizer overhead to an alkylation operation in the presence of concentrated sulfuric acid whereby the isobutane is condensed with the olefins to form high antiknock saturated hydrocarbons within the gasoline boiling range, recovering from the reaction products a naphtha fraction suitable for the manufacture of aviation gasoline, stabilizing said fraction to remove isobutane and excess normal butane, fractionating the normally gaseous hydrocarbons to separate the isobutane from the normal butane, recycling said isobutane to the alkylation operation and combining the normal butane with said stabilized cracked naphtha.

6. A process for the manufacture of high antiknock motor fuel, which comprises stabilizing cracked naphtha to remove therefrom substantially all hydrocarbons of less than five carbon atoms thereby producing a stabilized cracked naphtha of lower volatility than commercial gas-

oline and a normally gaseous hydrocarbon fraction containing isobutane, n-butane and olefins, subjecting said fraction to an alkylation operation in the presence of an excess of isobutane and an alkylation catalyst whereby the isobutane is alkylated by the olefins to produce high antiknock normally liquid hydrocarbons within the gasoline boiling range, separating from the reaction products the normally liquid hydrocarbons, excess normal butane and isobutane, recycling the excess isobutane to the alkylation operation and recombining the excess normal butane with the stabilized naphtha to impart volatility thereto.

7. A process according to claim 6 in which the catalyst is sulfuric acid of about 90 to 100% concentration.

LEBBEUS C. KEMP.
RUFUS L. SAVAGE, JR.

CERTIFICATE OF CORRECTION.

Patent No. 2,172,560. September 12, 1939.

LEBBEUS C. KEMP, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, first column, line 38, for the word "butylene" read butylenes; and second column, line 19, for "cndensed" read condensed; line 38, for "concentrations" read concentration; line 48, for "bath" read both; page 2, first column, line 49, for "In" read If; line 65, for the reference numeral "59" read 58; page 3, second column, line 17, claim 2, for "ni-butane" read n-butane; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 14th day of November, A. D. 1939.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.

oline and a normally gaseous hydrocarbon fraction containing isobutane, n-butane and olefins, subjecting said fraction to an alkylation operation in the presence of an excess of isobutane and an alkylation catalyst whereby the isobutane is alkylated by the olefins to produce high antiknock normally liquid hydrocarbons within the gasoline boiling range, separating from the reaction products the normally liquid hydrocarbons, excess normal butane and isobutane, recycling the excess isobutane to the alkylation operation and recombining the excess normal butane with the stabilized naphtha to impart volatility thereto.

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