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METHOD OF MANUFACTURING HIGH ANTI-KNOCK SYNTHESIS GASOLINE

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This invention relates to the manufacture of high antiknock gasoline hydrocarbons from carbon oxides and hydrogen.

The catalytic synthesis reaction of a carbon oxide and hydrogen to form higher molecular weight hydrocarbons, both normally gaseous and normally liquid, is well-known. However, the gasoline produced by this known process is of inferior character, being of lower antiknock value than cracked gasolines or straight-run gasolines from petroleum. Also, there is an appreciable loss in yield of the desired gasoline hydrocarbons, since the synthesis products are of wide boiling range including a substantial proportion of normally gaseous hydrocarbons from C_2 to C_4 inclusive, and also a substantial proportion of normally liquid hydrocarbons of lower boiling range than Diesel fuel but of higher boiling range than desired for aviation gasoline.

One of the principal objects of this invention is to produce high antiknock gasoline hydrocarbons suitable for aviation gasoline base stock and high quality motor fuel in good yields from carbon oxides and hydrogen.

A further object is to provide a combination process including hydrocarbon synthesis, alkylation, isomerization and catalytic conversion for producing a high yield of unusually high octane gasoline within the aviation fuel boiling range from carbon oxides and hydrogen.

Another object of the invention is to provide a unitary or self-contained process for accomplishing the foregoing objects, wherein any substantial amounts of extraneous hydrocarbons other than those produced in the system are not required, so that the plant can be located near the source of supply of the carbon oxide and hydrogen and is not dependent on an outside supply of petroleum hydrocarbons.

Other objects and advantages of the invention will be apparent from the following description when taken in conjunction with the appended claims and the accompanying drawing.

In my prior Reissue No. 22,205 of Patent No. 2,257,074, a process is disclosed wherein carbon oxide and hydrogen are catalytically reacted, the resulting synthesis products are separated into a normally gaseous fraction and a normally liquid naptha fraction, and the said fractions are separately subjected to catalytic alkylation with an isoparaffin, such as isobutane. While this process increases the yield and antiknock value of the gasoline hydrocarbons so produced, the alkylation step on the normally liquid fraction is not as effective as desired since the resulting alkylate is diluted with a large proportion of unconverted normal paraffin hydrocarbons originally present in the synthesis products.

In accordance with the present invention, the carbon oxide and hydrogen synthesis products are fractionated to separate a C_4 fraction, a light naphtha fraction boiling below C_9, a heavy naphtha fraction from about C_8 up to 400–450° F. end point, a Diesel fuel fraction and wax. The C_4 fraction is subjected to catalytic alkylation to produce gasoline alkylate, and unreacted normal butane of the C_4 fraction is catalytically isomerized to form isobutane to supply isobutane for the said alkylation step. The light naphtha fraction is subjected to absorption with an acid to convert the normally liquid olefins to the corresponding esters of said acid. The acid-olefin extract is separated from the unabsorbed paraffin raffinate, and the absorbed olefins are then subjected to catalytic alkylation separately from the paraffins, utilizing isobutane produced in the above-mentioned isomerization step, thereby forming additional gasoline alkylate of high quality. The paraffin affinate is in turn subjected to catalytic isomerization, preferably in the presence of an added butane obtained from the synthesis products, under conditions to form a gasoline isomate of paraffins of increased branched chain structure and of substantially improved antiknock quality, while concomitantly producing isobutane. The net production of isobutane in this latter step further makes up any deficiency of isobutane charge for the mentioned catalytic alkylation steps.

The heavy naphtha fraction is in turn subjected to catalytic conversion, such as hydroforming, cyclization, or reforming, under conditions to lower the boiling distribution range and increase the antiknock value of said naphtha, and concomitantly produce additional C_4 hydrocarbons including butanes. The said C_4 hydrocarbons produced in the catalytic conversion are separated and returned to the system, whereby normal butane is supplied to the normal butane isomerization step, and isobutane is utilized in the charge to the catalytic alkylation steps. In this manner, sufficient butanes are produced in the system to supply the isobutane requirements of the alkylation steps and the butane requirement of the paraffin raffinate isomerization step. Aviation gasoline fractions from the resulting alkylates, isomate and hydroformate or other catalytic conversion product may be blended to thereby obtain a high yield of aviation gasoline of high antiknock value; while heavier fractions of said

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products may be blended to produce motor gasoline. Catalyst discharged from the C₄ alkylation step may be employed as at least a portion of the catalyst for the absorbed olefin alkylation step. Likewise, catalyst discharged from the normal butane isomerization step may be used as catalyst for the paraffin raffinate isomerization step. A self-contained process is thereby provided which gives a high yield of aviation gasoline of good quality, while avoiding the necessity of securing extraneous supplies of petroleum hydrocarbons for the system.

The invention is more particularly illustrated in the attached drawing wherein the single figure is a flow diagram of a preferred form of the invention.

Referring to the drawing, the numeral 10 indicates the hydrocarbon synthesis reactor, wherein hydrogen and a carbon oxide, preferably carbon monoxide, are reacted in the ratio of two mols of hydrogen to one of carbon monoxide in the presence of a suitable synthesis catalyst in well-known manner. The usual catalyst, comprising a metal of the eighth group of the periodic system, particularly cobalt, nickel and iron, together with activating constituents such as oxides of magnesium, thorium, aluminum and combinations thereof, may be employed, either alone or preferably in conjunction with a contact mass of the character of filter cel, in a vapor phase fixed bed operation. The carbon monoxide and hydrogen gases are passed through the catalyst bed at temperatures of 325–550° F., preferably about 360–400° F., and under a pressure from atmospheric up to 100 atmospheres but preferably near or not substantially above atmospheric pressure for preferential production of hydrocarbons of motor fuel boiling range, utilizing a space velocity of about 10–150 and preferably around 100. It will be understood that the catalyst beds may be prepared, reduced, and conditioned in the usual manner, and may be employed in a cyclic process in which unreacted carbon monoxide and hydrogen are recycled.

With catalysts such as cobalt, nickel or iron, synthesis products are formed in which normal paraffin and olefin hydrocarbons predominate from C₂ up to and including heavy paraffin waxes. However, it is known that under certain special conditions, the resulting synthesis products may contain both normal and isoparaffins, normal and isoolefins, and even naphthenes and aromatics. The present invention is particularly applicable to the upgrading of the usual synthesis products consisting essentially of normal paraffins and olefins. However, it will be understood that the invention can be applied with advantage to synthesis products containing other constituents including aromatics, taking certain precautions as hereinafter specified. The naphtha fraction from the usual operation may run around 25–40 CFRM octane number; while the naphtha fraction from the special operations may be of substantially improved octane number.

Under the conditions set forth above, the synthesis products may contain about 10–15% by volume of normally gaseous C₂—C₄ hydrocarbons, of which about 5–8% on the basis of the total products may be C₄ with an olefin content of around 50–55% by volume. The naphtha fraction up to about 400° F. end point may amount to around 60% by volume with about 30–35% olefin content. Where cobalt or nickel catalysts are employed in the usual manner, the balance will

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comprise mainly high cetane Diesel fuel and paraffin wax.

The synthesis products pass to a fractionating system indicated at 11 from which the unreacted gases together with C₃ and lighter may be removed from a stabilizer and passed by line 12 to a suitable absorption oil recovery system for the recovery of C₂ and C₃ hydrocarbons, and separation of unreacted carbon monoxide and hydrogen for recycling in the system in the manner set forth above. A stream of C₄ hydrocarbons, or C₄ containing a light cut of C₅ so as to eliminate most of the normal pentane, is removed by line 13 and passed to the catalytic alkylation step 14. A light naphtha cut boiling below C₉, which is preferably C₅—C₇ although it may be C₅—C₈ or even C₅—C₆, is removed by line 15 and passed to the absorption step 16. A heavy naphtha fraction, which includes the balance of the naphtha up to about 400–450° end point or up to the initial boiling point of the Diesel fuel fraction, is removed by line 17 to the catalytic conversion step 18. The remaining bottoms of the synthesis products are passed by line 19 to fractionator 20, where Diesel fuel and paraffin wax are removed as final products by lines 21 and 22 respectively.

In the absorption step 16, the normally liquid olefins of the light naphtha fraction are absorbed by contact with an acid, such as strong sulfuric acid, introduced by line 24. This operation is preferably carried out in liquid phase at low temperatures of the order of 0–40° F. by passing a stream of the light naphtha together with a stream of the acid through a suitable mixer and thence into a settler, where the acid-olefin extract separates as a lower layer from the upper hydrocarbon raffinate containing unabsorbed paraffin hydrocarbons. Where the synthesis products are prepared with cobalt, nickel or iron catalyst, and consist mainly of paraffin and olefin hydrocarbons substantially free from aromatics, the absorption operation is not as critical and various strengths of sulfuric acid above about 85% may be employed. However, where the synthesis products contain a substantial proportion of aromatics, the light naphtha fraction removed by line 15 may be one boiling below about 180° F. so as to be substantially free from aromatics. Or, in the case of a wider boiling range fraction containing aromatics, it is treated in the manner disclosed in my copending application Serial No. 375,918, filed January 25, 1941, now Patent No. 2,383,056 dated August 21, 1945, to selectively absorb the olefins in the presence of aromatics and without any substantial absorption of the latter. As set forth therein, this is accomplished by contacting the naphtha with strong sulfuric acid of 96–100% strength at a temperature of about 10–30° F., employing a time of contact of about 30–60 seconds. This serves to extract the bulk of the olefins without any substantial absorption of aromatics, particularly where a large excess of strong acid to naphtha is employed in the cold acid contacting step.

The resulting acid-olefin extract is removed from the lower layer of the settler, or from the outer layer where centrifuge separation is employed, and passed by line 25 to either of branch lines 26 and 27 leading to the ester extraction zone 28 and the catalytic alkylation zone 29 respectively. In the ester extraction zone 28, the acid-olefin extract is contacted with a low boiling isoparaffin, such as isobutane, introduced by line 30, which serves to dissolve ester from the acid. Preferably a large excess of isobutane to acid-

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olefin extract is employed at temperatures of about 30–60° F., and the mixture then allowed to stratify into an upper isoparaffin or isobutane layer containing the dissolved olefin ester, and a lower acid layer which is removed by line **31**. The isoparaffin layer is then passed by line **32** to the catalytic alkylation step, where fresh alkylation catalyst is introduced by line **33**. Where the three-stage operation of absorption, ester extraction and alkylation is employed, the absorption step is preferably carried out with a lower ratio of acid to naphtha which is conducive to the formation of the diester. The acid esters of the lower molecular weight olefins are less soluble in isobutane than the corresponding diesters. Consequently, by coordinating the absorption step to produce mainly the diester, a lower ratio of isobutane to extract may be employed in **28** with satisfactory ester extraction. While diester formation is particularly important in connection with absorbed C₄ olefins, it is not so vital in the case of C₅ and higher olefins, and the absorption step may be carried out under conditions to produce largely the acid esters of the light naphtha olefins, even where the three-stage operation is employed. Where sulfuric acid is employed as the alkylation catalyst, it is generally preferred to use two-stage operation wherein the acid olefin extract is passed directly by line **27** to the catalytic alkylation zone **29**. In such case, the absorption step is preferably carried out with the use of a large excess of acid to olefin, such as about 20–100:1, thereby producing mainly the acid ester.

In the catalytic alkylation step **29**, the extract containing absorbed light naphtha olefins in the form of esters is agitated with a large excess of isobutane introduced by line **34**, together with alkylation catalyst introduced by line **33**. A molar ratio of isobutane to olefin equivalent of the order of 3:1 to 6:1 is preferably employed, and emulsion or hydrocarbon recycle may also be used to materially increase the internal ratio to above about 100:1 as is well understood. Where sulfuric acid is employed as the catalyst, the makeup acid to this step is at least about 88% and preferably about 90% concentration or higher, whereby the strength of the acid in the system is maintained above about 85% with a water content below 4%, the balance being mainly organic matter. The operation is carried out at a temperature of about 30–60° F. and under sufficient pressure to maintain the reactants in liquid phase, employing a volume ratio of acid to hydrocarbons in the reaction zone of about 0.8:1 up to about 2:1 and preferably about 1:1. Efficient agitation is employed, whereby isobutane is alkylated with the absorbed olefins to produce a high yield of alkylate consisting of highly branched or isoparaffinic hydrocarbons within the gasoline boiling range and of high antiknock value. The resulting alkylation products are passed to a settler where the hydrocarbon phase separates from a lower acid phase, the latter being removed and recycled by line **35** to the absorption step.

While sulfuric acid has been particularly described as the alkylation catalyst, it will be understood that this is merely preferred and that other conventional alkylation catalysts may be employed, such as HF, BF₃.H₂O complex, aluminum chloride or aluminum choloride-hydrocarbon complex, chlorosulfonic acid, etc. Moreover, other acids than sulfuric acid can be ultilized in the absorption step, such as phosphoric acid, the various halogen acids including HF, and even

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strong organic acids, to produce the corresponding olefin esters. Where a different acid or catalyst is employed in the alkylation step than is used in the absorption step, it will be understood that the three-stage process is utilized to extract the ester from the acid-olefin extract before the former is passed to the alkylation step.

The hydrocarbon phase from catalytic alkylation step **29** is caustic neutralized and washed in conventional manner, and then passed by line **36** to a stabilizing and fractionating system indicated at **37**. Here, excess isobutane is recovered and recycled by line **38** to lines **34** and **30**. A stabilized aviation fraction of the alkylate is passed by line **39** to the aviation fuel blending tank **40**. The higher boiling or heavy alkylate is passed by line **41** to the motor fuel blending tank **42**.

The C₄, or C₄ plus light C₅ fraction, of the synthesis products may be alkylated directly in the alkylation zone **14**, and this operation is illustrated. However, where the said fraction contains too high a proportion of normal butane, it can be subjected to two-stage or three-stage operation, as described above for the light naphtha fraction, to absorb the olefins and separate them from the diluting paraffins prior to alkylation. As shown, this C₄ alkylation step is carried out in conventional manner with isobutane introduced by line **45** and sulfuric acid catalyst added by line **46**. Here again, various alkylation catalysts, such as hydrofluoric acid, BF₃.H₂O complex, etc. can be employed in place of sulfuric acid, although the latter is preferred. The conditions of this operation are essentially those described for the catalytic alkylation step **29**. While the C₄ fraction from line **13** can be supplied to the ester alkylation **29**, it is preferred to conduct these alkylation steps separately with independent control, thereby enabling better quality alkylates to be produced. Fresh acid, such as 98–100% H₂SO₄ is introduced into the system by line **46** to provide makeup acid for the alkylation zone **14**, and maintain the system acidity above about 88% and preferably about 90–93%. A portion of the acid separated from the hydrocarbon phase of the settler may be recycled by line **47**, and the balance is passed by line **48** to serve as makeup catalyst for the catalytic alkylation step **29**. In this manner, the acid requirements for the system may be minimibed and the most efficient utilization of the catalyst obtained. For optimum results a higher system acidity is employed for the C₄ alkylation than is required for the C₅ and higher olefin alkylation. Consequently, acid discharged from the C₄ alkylation step **14** at an acidity of about 88% or higher is quite satisfactory as makeup for the light naphtha olefin alkylation step **29**, where the acid is further spent to a system acidity of about 85%.

The resulting hydrocarbon alkylation products, after conventional neutralization and washing, are passed by line **50** to stabilizer **51** where C₄ and lighter are removed by line **52** to a butane fractionator **53**. Here, isobutane and lighter is removed overhead by line **54** to a depropanizer **55**, while normal butane is separated as bottoms and passed by line **56** to isomerization zone **57**. In depropanizer **55**, propane and any lighter are removed by line **58** to prevent buildup in the system, thereby obtaining an isobutane rich fraction which is recycled by line **59** to line **45** to serve as the charge for alkylation step **14**, and

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also by line 60 to serve as charge for alkilation step 29 and ester extraction 28.

In isomerization step 57, the normal butane feed is preferably contacted in liquid phase with a suitable isomerization catalyst, such as aluminum halide together with hydrogen halide. An aluminum chloride-hydrocarbon complex liquid fortified by the addition of aluminum chloride so as to have a heat of hydrolysis of about 320–350 calories per gram constitutes an excellent catalyst for this purpose. The isomerization reaction may be carried out in conventional manner at a temperature of about 190–250° F. and preferably 210–230° F. and under sufficient pressure to maintain the normal butane in liquid phase, and in the presence of about 1–3% of HCl based on the hydrocarbon charge. This operation is preferably conducted in a tower reactor in known manner, wherein the normal butane is dispersed in the form of small droplets into the base of the tower containing a deep body of the complex liquid catalyst, the droplets rising through the maintained catalyst layer and coalescing upon reaching the upper surface to form a superposed hydrocarbon layer. During passage through the catalyst liquid, a substantial conversion of normal butane to isobutane on the order of about 40–55% or somewhat higher is obtained. The hydrocarbon isomerization products, consisting essentially of isobutane and normal butane, are returned in major part by line 60' to the butane fractionator 53, where the isobutane is separated from unconverted normal butane in the manner previously described. In this manner, high conversion of the normal butane content of the synthesis products to isobutane is ultimately obtained, whereby the produced isobutane supplies a substantial proportion of the charge to the catalytic alkylation operations 14 and 29.

The stabilized alkylate is removed as bottoms from stabilizer 51 and passed by line 61 to alkylate fractionator 62, where separation is made of aviation alkylate passed by line 63 to blending tank 40, and heavy alkylate passed by line 64 to blending tank 42.

The paraffin raffinate from absorption step 16 is passed by line 66 to treater 67. In the event that the light naphtha fraction of the synthesis products is substantially free from aromatics, the paraffin raffinate from line 66 is given a mild treat with strong sulfuric acid in treater 67 to remove any residual olefin content. The resulting acid-olefin extract is passed by line 68 to the absorption step 16 for recovery of the olefin content. It will be understood that a portion of the acid-olefin extract from line 25 can also be recycled to the absorption step 16, although once-through operation with short contact time of the order of about 1–10 minutes is preferred for absorption step 16.

When the synthesis products contain a substantial proportion of aromatics, and the light naphtha fraction supplied by line 15 includes naphtha within the boiling range of the aromatics, then the absorption step 16 is carried out to selectively remove olefins and leave the aromatics in the paraffin raffinate as described above. In such case, the paraffin raffinate from line 66 is preferably treated with a selective solvent for aromatics, such as liquid sulfur dioxide. This removes not only the residual olefin content but also the aromatics in the solvent extract from treater 67. This extract is passed by line 69 to still 70 where the solvent is removed over-

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head by line 71 for recycling to the treater 67. Bottoms from still 70 consisting of the aromatic concentrate may be supplied by line 72 to blending tank 40 to serve as a constituent of the aviation fuel, or can be used for toluene recovery, paint solvent or other purpose as desired. The solvent extraction may be operated to leave a residual aromatic content of about 0.5–1.0%, which functions as a cracking inhibitor in the subsequent isomerization step.

The paraffin raffinate from treater 67, which is substantially free from olefins and aromatics, or contains the controlled amount of residual aromatics as specified above, is passed by line 74 to isomerization zone 75. Here the normally liquid paraffins, or paraffins plus naphthenes, are subjected to catalytic isomerization under mild cracking conditions to convert the said raffinate into a gasoline isomate of paraffins of increased branched chain structure, and concomitantly produce a substantial yield of isobutane. This operation may be carried out in well-known manner by the use of an aluminum halide catalyst and hydrogen halide promoter at a temperature of about 210–250° F. and preferably about 230° F., and under sufficient pressure of the order of 100–150 pounds per square inch to maintain butanes in the liquid phase. Preferably, an aluminum chloride-hydrocarbon complex liquid fortified with aluminum chloride to have a heat of hydrolysis of about 310–350 calories per gram is employed, together with about 1–3% HCl on the basis of the hydrocarbon charge.

Sufficient butanes may be added by line 76 to provide a volume ratio of butanes to liquid raffinate of the order of about 0.5:1 to 6:1 and preferably about 1:1 to 3:1. The presence of the butanes inhibits severe or objectionable cracking and side reactions which result in rapid catalyst deterioration. In this isomerization step 75, a substantially saturated paraffinic naphtha of increased branched chain structure and greatly improved antiknock value is produced in good yield. Also there is a net production of isobutane over and above that added in the feed, although there is little breakdown to C₃ and lighter. It is preferred to carry out this isomerization step in a tower reactor of the character described above for the normal butane isomerization step 57, wherein the paraffin raffinate charge from line 74, together with the butanes from line 76 and the HCl from line 77, are dispersed into the lower portion of a maintained body of the fortified complex liquid of substantial height, the dispersed bubbles then rising through the catalyst liquid and coalescing into a hydrocarbon layer at the upper surface thereof. To effect further economy in the catalyst requirements of the system, the complex liquid discharged from isomerization step 57 is preferably supplied by line 78 to serve as the catalyst for the isomerization step 75. This liquid may be fortified, if required, by aluminum chloride added by line 79.

The resulting hydrocarbon isomerization products are passed by line 80 to fractionating system 81 where a C₄ and lighter fraction is removed by line 82. A substantial proportion of this fraction is recycled by line 83 to supply the major proportion of the butanes in the feed to the isomerization step. In order to prevent buildup of propane and any lighter in the system and also to recover the net production of isobutane resulting from isomerization step 75, a minor proportion of the C₄ and lighter fraction

from line 82 is supplied by line 84 to the butane fractionator 53. Here, the isobutane and lighter fraction is separated by line 54 and passed to depropanizer 55 for eventual recovery of the isobutane rich fraction in line 59, with elimination of propane and lighter from the system by line 58. In this manner substantial additional isobutane is recovered from the system to further supply the requirements of the alkylation steps 14 and 29. Also, normal butane of the C4 fraction from line 84 is recovered in the butane fractionator 53 and passed by line 56 to the isomerization step 57 as previously described.

A minor proportion of the normal butane from line 56 can be diverted by line 85 to the feed line 86 to supply the butane makeup required for the isomerization step 75. If any additional butanes are needed, they can conveniently be obtained in most instances from natural gasoline and shipped by tank car to the plant, if distantly located from the source of such supply, and introduced by line 86. It will be understood that, while the butane makeup for isomerization step 75 is primarily normal butane, the gases recycled by line 83 will generally consist of about equal proportions of isobutane and normal butane, due to the reactions taking place in zone 75. Since the recycle gases comprise by far the greater proportion of the butane feed to this step, the isomerization of the liquid paraffins takes place in the presence of a substantial excess of isobutane. Under these conditions, the resulting product from step 75 is substantially saturated. The liquid isomate from fractionator 81 is substantially all within the aviation boiling range, and is supplied by line 87 to blending tank 40.

In the special cases where the synthesis products contain a substantial proportion of isoparaffins, and/or aromatics and naphthenes, the raffinate from absorption step 16 may have a CFRM octane of the order of 65 and above. In such case, the raffinate may be blended directly in aviation or motor fuel, without being subjected to isomerization. It will be understood that a branch line from line 66 may be provided for this purpose, leading directly to tank 40 or tank 42, or both.

The heavy naphtha fraction of the synthesis products from line 17 is preferably subjected to hydroforming in known manner in zone 18. This is carried out by mixing the preheated naphtha with heated recycle gas having a hydrogen content of about 60–85%, in the proportion of around 1500–2500 cubic feet of recycle gas per barrel of naphtha, and passing the resulting mixture at a temperature of about 900–1050° F., and preferably 950–1000° F., and under a pressure of about 150–250 pounds per square inch through catalyst beds of hydroforming catalyst, such as molybdena-alumina, at a space velocity of 0.2–0.7 volumes of feed per volume of catalyst per hour, and preferably about 0.4–0.5. As is well-known, a catalyst bed may be kept on stream for about 10–16 hours, and the charge is then diverted to a regenerated catalyst bed, while the previously used catalyst bed is then regenerated by burning out carbon with flue gas and air in well-known manner. Under the conditions set forth above, a yield of about 70–80% by weight, on the basis of the heavy naphtha charged, of a broad boiling range debutanized gasoline line of greatly improved antiknock value, and which is nearly saturated, is obtained. Also, there is a substantial yield of around 6–8% by weight based on the naphtha charge of C4 hydrocarbons consisting largely of

isobutane and normal butane but also containing some butylenes.

The products of hydroforming are passed by line 90 to the stabilizing and fractionating system indicated at 91, where C3 and lighter are removed by line 92 and passed to a conventional absorption system for the recovery of C2 and C3 hydrocarbons, the off-gas from the absorption operation being returned together with hydrogen enrichment, if required, as the recycle gas to the hydroforming step 18. A C4 fraction is removed from fractionator 91 by line 93 and may be passed to line 13 for introduction into the C4 alkylation and isomerization system. In this manner, additional isobutane and butylenes, with the isobutane generally in substantial excess, are supplied to the catalytic alkylation step 14. Also, the normal butane from line 93 is thus eventually utilized in the isomerization step 57. The resulting production of butanes in the hydroforming step 18, coupled with the net make of isobutane in isomerization step 75, and the initial production of butanes in the synthesis products, are generally sufficient to supply the isobutane requirements for the system. Moreover, the plant can readily be balanced by increasing or decreasing the end boiling point of the light naphtha fraction of line 15, to thereby regulate the amount of normally liquid olefins supplied to the catalytic alkylation step 29 in accordance with the isobutane available.

An aviation hydroformate separated in the fractionating system 91 is passed by line 95 to blending tank 40. Heavier naphtha hydroformate is passed by line 96 to blending tank 42. It will be understood that the hydroformates can be treated to recover toluene or other aromatics, if desired, and the residual naphtha then supplied to aviation or motor fuel depending on the octane number thereof.

It is thus seen that a substantial yield of high grade aviation fuel is produced in this process by blending aviation fractions of the alkylates, the isomate and the hydroformate. It will be understood that any two or more of these various fractions can be blended in tank 40, the balance being supplied to motor fuel or other purposes as may be desired. Also, it will be understood that isopentane, 2,3-dimethylbutane, isobutane-ethylene alkylate consisting largely of 2,3-di-methylbutane, as well as various aromatics, amines, or other blending constituents may be added to the aviation fuel in tank 40 in conventional manner, together with the required amount of antiknock additive of the character of tetraethyl lead. The resulting aviation gasoline is passed from tank 40 by line 97 to suitable storage.

Likewise, it is seen that an appreciable yield of high grade motor fuel blending stock is also obtained in tank 42 by the blending of two or more of the heavier fractions, or the heavier and lighter fractions specified above. It will be understood that various cracked or straight run naphthas can also be added in tank 42, together with other usual constituents, to produce a balanced motor fuel which is discharged by line 98 to suitable storage.

While isobutane has been specifically described above as the isoparaffin employed in the catalytic alkylation steps 14 and 29, and the ester extraction step 28, it will be understood that other low-boiling isoparaffins, such as isopentane, can be used for this purpose. For example, the paraffin raffinate from line 66 or line 74 can be fractionated to separate a normal pentane fraction, and the latter separately isomerized to produce

isopentane to form a part of the isoparaffin charge to either or both of the catalytic alkylation steps. Also, while the aviation fractions from the various steps can be blended to form a composite aviation fuel in the manner shown, it will be understood that certain of the fractions can be separately utilized to produce various grades of aviation fuel, depending on the antiknock characteristics.

While fixed bed hydroforming has been specifically described for step 18, it will be understood that any other type of operation can be employed, such as fluid catalyst operation. Also, any other suitable hydroforming catalyst may be used, such as chromic oxide-alumina. Moreover, while hydroforming constitutes the preferred treatment for the heavy naphtha fraction, any other suitable type of catalytic conversion may be employed which results in some breakdown or cracking to produce a C_4 yield and also lower the boiling distribution range and increase the antiknock value of the naphtha. Thus, catalytic cyclization or catalytic reforming may be used, both steps being conducted in conventional manner. For example, catalytic cyclization may be carried out by passing the heavy naphtha in vapor form through catalyst beds of chromic oxide-alumina at temperatures of about 900–1100° F. and under relatively low pressures of several atmospheres, thereby producing a naphtha of substantially increased aromatic content and which is more unsaturated, with the concomitant production of a substantial yield of C_4 and lighter. Catalytic reforming may be conducted with a silica-alumina catalyst, either with or without fixed gas or C_1—C_2 hydrocarbon recycle, at temperatures of the order of 900–1100° F. and at pressures from slightly above atmospheric up to about 250 pounds per square inch, thereby resulting in considerable cracking and production of C_4 and lighter, and the formation of a more highly unsaturated naphtha of broad boiling range. In all of these processes the heavy naphtha is substantially reduced in boiling range distribution and concomitantly upgraded in antiknock value, while at the same time there is a net production of C_4 hydrocarbons which augment the charge to the C_4 alkylation step and increase the production of this high grade alkylate.

The following specific example is listed by way of illustration. A mixture of one part by volume of carbon monoxide and two parts by volume of hydrogen, heated to a temperature of about 370° F., was passed continuously through a contact mass of catalyst having a composition of approximately 32% cobalt, 64% filter cel and 4% thorium and magnesium oxides. The catalyst mass was maintained within a temperature range of 374 to 385° F., and a feed gas space velocity of about 100 was employed. An average yield of liquid condensate from C_4 to about 750° F. end point of about 0.85 gallon per 1,000 cubic feet of feed gas was obtained. Separation of the condensate into fractions provides about 8% by volume of C_4 hydrocarbons, about 25% by volume of a light C_5—C_7 naphtha fraction having a clear CFRM octane of about 25, about 35% by volume of a C_8–400° F. end point heavy naphtha fraction having a clear CFRM octane of about 35, and about 20% by volume of a Diesel fuel having a cetane value of around 90 with the balance being essentially paraffin wax.

The light naphtha fraction is contacted at 25° F. with ten volumes of 90% H_2SO_4 (having a water content of about 2%, the balance being mainly organic matter) per volume of naphtha with a contact time of about two minutes, with about 97% removal of the olefins. The acid-olefin extract is alkylated with isobutane in a molar ratio of 5:1 on the equivalent olefin content, at a temperature of 50° F., utilizing an acid to hydrocarbon ratio in the reactor of 1:1 and a contact time of twenty minutes. An aviation alkylate of 350° F. end point having a clear CFRM octane of about 84 is produced in a yield equivalent to about 80% by volume on the basis of the light naphtha charged to the absorption step, or about 190% by weight of the equivalent olefin content converted to C_4.

The remaining paraffin raffinate is given a mild acid treatment with 98% H_2SO_4 at 60° F. in a proportion of 10 pounds of acid per barrel, providing a paraffin raffinate of substantially zero bromine number. This is subjected to isomerization in the presence of a fortified aluminum-chloride-kerosene complex liquid having a heat of hydrolysis of 340 calories per gram, and with 2% HCl on the weight of the paraffin raffinate, together with one volume of mixed butanes per volume of raffinate, at a temperature of 235° F. A net production of 9% by weight of isobutane on the weight of the raffinate charge is obtained, together with a yield of about 88% of a 110–297° F. gasoline isomate having a clear CFRM of about 73.

The heavy naphtha fraction of about 198–397° F. end point was subjected to hydroforming with a molybdena-alumina catalyst, employing a recycle gas containing about 70% hydrogen content at a recycle gas rate of around 2,300 cubic feet per barrel of naphtha feed, at a temperature of about 975° F. and a pressure of around 200 pounds per square inch, utilizing a space velocity of about 0.5. A yield of about 78% by weight based on the naphtha charged of debutanized aviation hydroformate having an end boiling point of 364° F. and a clear CFRM octane of about 74 was obtained, said hydroformate naphtha being nearly saturated with a bromine number of 8. In addition, 8% by weight of C_4 hydrocarbons, consisting mainly of normal butane and isobutane, was produced.

In the alkylation of the C_4 fraction of the synthesis products with isobutane, charging 99% H_2SO_4 to maintain a titratable acidity within the system of 90–93%, employing a 5:1 molar ratio of isobutane to butylenes, at a temperature of 40° F. With a 1:1 volume ratio of acid to hydrocarbons in the reaction zone, a yield of about 190% by weight based on the olefins charged of aviation alkylate of 350° F. end point is obtained, said alkylate having a clear CFRM octane of about 92.

A blend of the aviation alkylates, isomate and hydroformate in the ratio of production provides a composite aviation gasoline having a clear CFRM of about 80. The gasoline has good lead susceptibility, such that about 4.5 cc. of tetraethyl lead per gallon produces 100 octane aviation gasoline.

Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. A process for the manufacture of high antiknock gasoline from carbon oxides and hydrogen,

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which comprises reacting a carbon oxide and hydrogen in the presence of a synthesis catalyst under conditions effective to produce normally gaseous and normally liquid paraffin and olefin hydrocarbons containing a substantial proportion of normally liquid hydrocarbons within the gasoline boiling range, separating from the resulting synthesis products a light naphtha fraction containing normally liquid olefin and paraffin hydrocarbons from C_5 up to and including at least C_7 but below C_9 and also a heavy naphtha fraction above C_7, extracting olefins from said light naphtha fraction by contacting the same with an acid alkylation catalyst under conditions to absorb the olefins, separating the acid-olefin extract from the remaining unabsorbed paraffin hydrocarbons, alkylating a low-boiling isoparaffin with said absorbed normally liquid olefins in the presence of an alkylation catalyst under conditions to produce alkylate within the gasoline boiling range, subjecting said heavy naphtha fraction to catalytic conversion under conditions including an elevated temperature of about 900-1100° F. effective to lower the boiling points of a substantial proportion thereof and produce a broad boiling range gasoline of substantially improved antiknock value, and combining a gasoline fraction from said conversion step with said gasoline alkylate.

2. A process for the manufacture of high antiknock gasoline from carbon monoxide and hydrogen which comprises reacting the carbon monoxide and hydrogen in the presence of a synthesis catalyst under conditions effective to produce normally gaseous and normally liquid paraffin and olefin hydrocarbons containing a substantial proportion of C_4 and C_{12} hydrocarbons, separating from the resulting synthesis products a fraction consisting essentially of C_4 hydrocarbons containing a substantial proportion of butylenes with not more than the lighter portion of the C_5 hydrocarbons, and also a fraction containing remaining C_5 through at least C_7 hydrocarbons but boiling below C_9 hydrocarbons having a substantial proportion of normally liquid olefins, catalytically alkylating isobutane with butylenes of said C_4 containing fraction to produce normally liquid gasoline alkylate, subjecting said C_5 and heavier fraction to contact with an acid alkylation catalyst to absorb the normally liquid olefins therefrom, separating the resulting acid-olefin extract from remaining unabsorbed paraffin hydrocarbons, catalytically alkylating isobutane with absorbed normally liquid olefins of said extract to produce additional gasoline alkylate, combining said alkylates, also separating from said synthesis products a heavy naphtha fraction above C_7, subjecting said heavy naphtha fraction to catalytic conversion under conditions including an elevated temperature of about 900-1100° F. effective to lower the boiling points of a substantial proportion thereof and produce a broad boiling range gasoline of substantially improved anti-knock value, as well as additional C_4 olefin containing hydrocarbons, separating said C_4 olefin containing hydrocarbons and supplying them to said C_4 catalytic alkylation step, combining a gasoline fraction from said heavy naphtha conversion step with said gasoline alkylates, and supplying catalyst discharged from said C_4 alkylation step to furnish makeup catalyst for said extract alkylation step.

3. A unitary process for the manufacture of high antiknock gasoline from carbon monoxide and hydrogen, which comprises reacting carbon

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monoxide and hydrogen in the presence of a synthesis catalyst under conditions effective to produce normally gaseous and liquid paraffin and olefin hydrocarbons including a substantial proportion of butanes and butylenes and also normally liquid paraffin and olefin hydrocarbons within the gasoline boiling range, recovering normal butane from said synthesis products, subjecting at least a part of said recovered normal butane to catalytic isomerization to produce isobutane, recovering an isobutane-rich fraction from said isomerization products, also separating from said synthesis products a light naphtha fraction containing normally liquid paraffin and olefin hydrocarbons, absorbing normally liquid olefins from said light naphtha fraction by contact with an acid alkylation catalyst, separating the resulting acid-olefin extract from the unabsorbed paraffin raffinate, utilizing at least a portion of said isobutane-rich fraction for alkylating said absorbed olefins in the presence of an alkylation catalyst to produce gasoline alkylate, subjecting said paraffin raffinate to catalytic isomerization in the presence of added butane, utilizing another part of said recovered normal butane as the butane charged to said last-mentioned isomerization step, and blending resulting gasoline isomate from said last-mentioned isomerization step with said gasoline alkylate.

4. The method according to claim 3, wherein a heavy naphtha fraction is also separated from said synthesis products, said heavy naphtha fraction is subjected to catalytic conversion under conditions including an elevated temperature of about 900-1100° F., effective to lower the boiling points of a substantial proportion thereof and produce a broad boiling range gasoline of improved antiknock value and also additional C_4 hydrocarbons including a substantial proportion of normal butane and isobutane, utilizing normal butane from said conversion products as a portion of the charge to said normal butane isomerization step, utilizing isobutane from said conversion products as a portion of the charge to said catalytic alkylation step, and blending a gasoline fraction from said conversion step with said gasoline isomate and said gasoline alkylate.

5. A process for the manufacture of high antiknock gasoline from carbon oxides and hydrogen, which comprises reacting a carbon oxide and hydrogen in the presence of a synthesis catalyst under conditions effective to produce normally gaseous and normally liquid paraffin and olefin hydrocarbons containing a substantial proportion of normally liquid hydrocarbons within the gasoline boiling range, separating from the resulting synthesis products the following three fractions, namely, (1) a normally gaseous fraction containing butylenes and butanes, (2) a light naphtha fraction containing normally liquid olefin and paraffin hydrocarbons including at least C_5 and C_6 but below C_9, and (3) a heavy naphtha fraction above C_7, alkylating olefins including the butylenes of fraction (1) above with a low-boiling isoparaffin in the presence of an alkylation catalyst to produce gasoline alkylate, subjecting fraction (2) above to absorption with a mineral acid to produce an acid extract of absorbed normally liquid olefins, separating the acid extract from the resulting unabsorbed paraffin raffinate, alkylating the absorbed olefins of the said extract with a low-boiling isoparaffin in the presence of an alkylation catalyst to produce additional gasoline alkylate, subjecting the said paraffin raffinate to catalytic isomerization to convert the normally

liquid paraffin hydrocarbons to a gasoline isomate of paraffins of increased branched chain structure, subjecting said heavy naphtha fraction to catalytic conversion under conditions including an elevated temperature of the order of 900–1100° F. effective to reduce the boiling points of a substantial proportion thereof and produce a broad boiling range gasoline of substantially improved antiknock value, and combining a gasoline fraction from said conversion step with said gasoline isomate and said gasoline alkylates.

6. The method according to claim 5, wherein said catalytic conversion step also produces a substantial yield of butanes and butylenes which are combined with said fraction (1), normal butane is recovered from the alkylation products resulting from the alkylation of said fraction (1), at least a portion of said normal butane is subjected to catalytic isomerization to produce isobutane, and resulting isobutane is utilized as at least a portion of the low-boiling isoparaffin charge to both of said alkylation steps.

7. The method according to claim 5, wherein said catalytic conversion step also produces a substantial yield of butylenes and butanes, the last-mentioned butylenes are combined with the butylenes from said fraction (1) and the combined butylenes subjected to said catalytic alkylation, normal butane is recovered from both said products of conversion of fraction (3) and from said fraction (1), a portion of said normal butane is supplied to said paraffin raffinate isomerization step, another portion of said normal butane is subjected to catalytic isomerization to produce isobutane, and resulting isobutane is utilized as the low-boiling isoparaffin charge to both of said alkylation steps.

8. A unitary process for the manufacture of high anti-knock gasoline from carbon monoxide and hydrogen, which comprises reacting carbon monoxide and hydrogen in the presence of a synthesis catalyst under conditions effective to produce normally gaseous and liquid paraffin and olefin hydrocarbons including a substantial proportion of C_4 hydrocarbons containing normal butane and butylenes, and also normally liquid hydrocarbons within the gasoline boiling range, separating from said synthesis products a C_4 fraction containing butylenes and normal butane, and also a light naphtha fraction containing normally liquid paraffin and olefin hydrocarbons from C_5 up to and including C_7, but below C_9, agitating isobutane obtained from a source hereinafter defined with said C_4 fraction in the pres-

ence of an alkylation catalyst under conditions effective to alkylate isobutane with said butylenes to produce gasoline alkylate, separating from the resulting alkylation products a gasoline alkylate fraction and also a fraction consisting essentially of normal butane, subjecting said normal butane fraction to catalytic isomerization to convert a substantial proportion thereof to isobutane, separating an isobutane-rich fraction from the resulting isomerization products, supplying a portion of isobutane-rich fraction to said C_4 alkylation step to serve as the isobutane charge thereto, absorbing normally liquid olefins from said light naphtha fraction by contact with an acid alkylation catalyst, separating the resulting acid-olefin extract from the unabsorbed hydrocarbon paraffin raffinate, mixing another portion of said isobutane-rich fraction with absorbed olefins recovered from said light naphtha fraction and agitating the mixture in the presence of an alkylation catalyst under conditions to alkylate isobutane with said absorbed olefins to produce additional gasoline alkylate, combining said gasoline alkylates, subjecting said paraffin raffinate to catalytic isomerization to form gasoline isomate of paraffins of increased branched chain structure with the concomitant production of isobutane, separating from the isomerization products the gasoline isomate and also the produced isobutane, utilizing said produced isobutane as a portion of the isobutane charge to the alkylation steps, passing catalyst discharged from said normal butane isomerization step to said paraffin raffinate isomerization step, and blending said gasoline isomate with said gasoline alkylates.

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