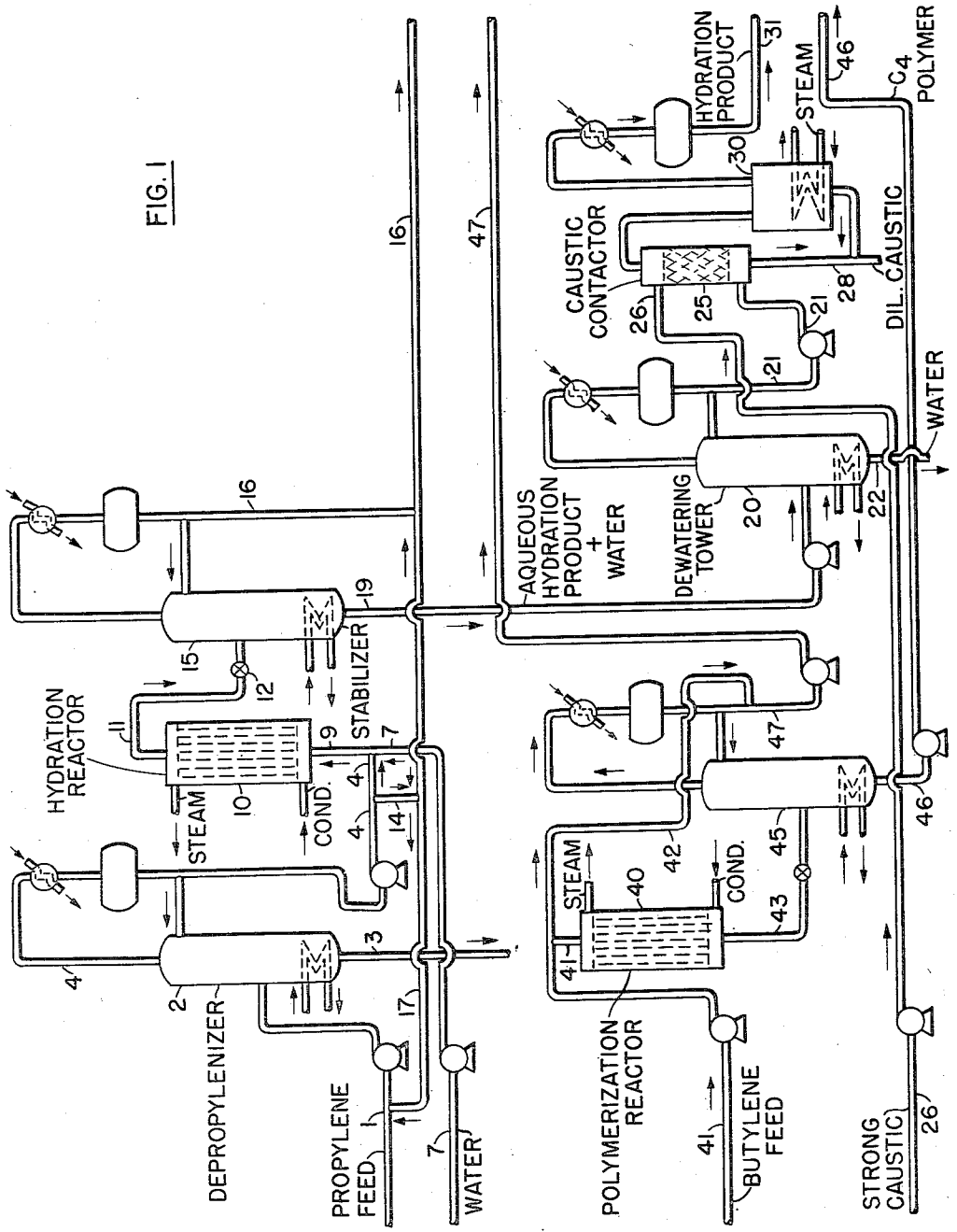
March 18, 1958 W. P. BLOECHER, JR., ET AL 2,827,500

INTEGRATED HYDRATION AND ALKYLATION OF GASEOUS OLEFINS

Filed Oct. 14, 1954 2 Sheets-Sheet 1

FIG. 1



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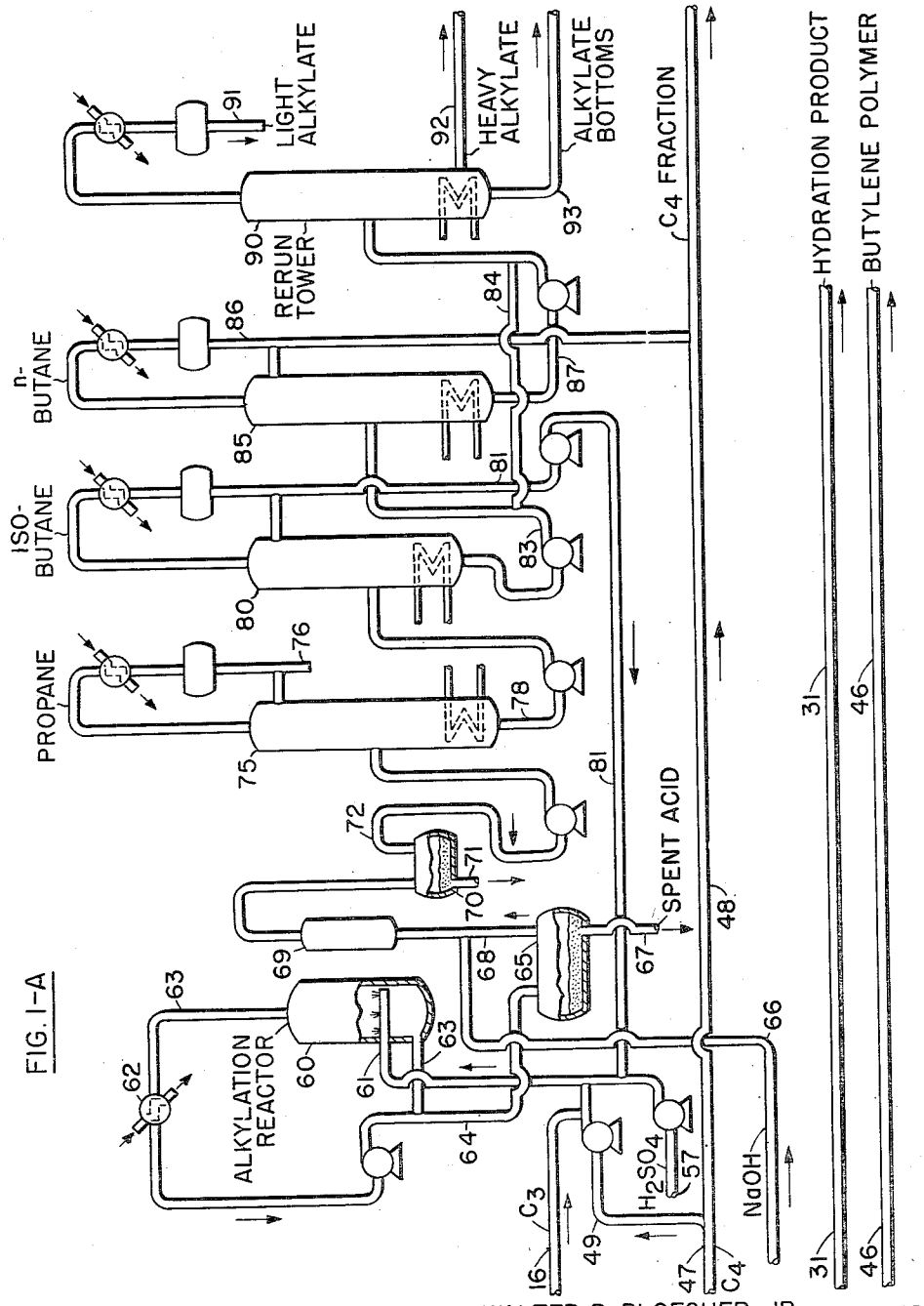


FIG. I-A

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2,827,500

Patented Mar. 18, 1958

2,827,500

INTEGRATED HYDRATION AND ALKYLATION OF GASEOUS OLEFINS

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Application October 14, 1954, Serial No. 462,201

6 Claims. (Cl. 260—641)

This invention relates to the conversion of gaseous olefins to a liquid fuel of balanced volatility and superior anti-knock characteristics. More specifically, it relates to a flexible combination process wherein a C_3—C_4 olefin-containing light hydrocarbon feed is catalytically converted to a high octane liquid motor fuel in two stages, first being partially hydrated to produce an oxygenated motor fuel while the unconverted remainder is alkylated in a subsequent stage to produce gasoline-range hydrocarbons. It also relates to the fuel compositions produced in the process.

In the blending of motor gasoline the quantity of high volatility components which can be included is limited by specifications which are based on Reid vapor pressure and the percentage distilling below 158° F. If these specifications are exceeded, the undue front-end volatility of the gasoline blend tends to cause vapor lock in the combustion engine. Consequently a surplus of propylene, butanes and butylenes is usually available at most refineries and must be either disposed of in low-priced products such as fuel gas or must be converted into a less volatile gasoline blending stock. Such upgrading has been heretofore accomplished mostly by catalytic polymerization of the C_3—C_4 olefins. However, this has not constituted a fully satisfactory use of available light ends since such polymerization makes no use of saturates and the resulting polymer possesses only a moderately good motor octane rating whereas with the advent of automatic transmissions motor octane specifications have been becoming increasingly critical. Therefore, a real need has developed for a refining process capable of producing a gasoline blend having a high motor octane rating while making economical use of available light ends.

It is well known that olefins such as propylene can be directly hydrated in the presence of suitable catalysts such as phosphoric or sulfuric acid or tungstic oxide, to produce oxygenated products such as alcohol, acetone and ether, all of which greatly improve the motor octane rating of gasoline blends when added thereto. However, such addition also results in an increased volatility of the gasoline so that compensating amounts of inexpensive butanes and other light naphtha constituents must be left out of the blend. Consequently, the addition of the oxygenated hydration products may result in a substantial increase in cost of the blended gasoline product and further aggravates, rather than relieving the problem of properly utilizing the surplus light ends. This light ends surplus may become particularly troublesome

in the summertime when a relatively less volatile gasoline is required. Furthermore, the hydration of propylene is in itself rather difficult to accomplish and accordingly requires feeds having as high a concentration of the olefin as possible. But since conversion tends to be rather low and so usually makes stage-wise conversion of unreacted feed imperative, the latter must be purified or separated from the hydration products before it is further hydrated.

It is also known that a premium grade gasoline component can be obtained by alkylation in which olefins such as propylene, butenes or pentenes are combined with isoparaffins such as isobutane or isopentane. Such alkylation can be done thermally at high temperatures and very high pressures, but is preferably done at low temperatures in the presence of catalysts such as concentrated sulfuric acid, hydrofluoric acid, aluminum chloride or boron trifluoride. Such catalytic alkylation proceeds quite readily and, as long as a sufficient excess of the C_4 or C_5 isoparaffin is present, results in substantially complete conversion of the olefinic feed constituents into valuable C_7 to C_9 branched chain paraffins of high anti-knock value and relatively low volatility.

Heretofore, however, when a refinery was required to rely upon such alkylation to any great extent for the purpose of raising the octane level of gasoline, a critical shortage of necessary pressurizing stocks tended to develop. This resulted from the fact that the alkylate product had such low volatility that it had to be supplemented by substantial amounts of butanes to give satisfactory start-up characteristics, but the alkylation itself consumed a large proportion of isobutane from the light ends pool normally available for pressurizing. Consequently, the adoption of alkylation in the production of motor fuel has not always been economically attractive, despite its intrinsic merits. On the contrary, because of the excess supply of olefins with respect to available butanes, notably isobutane, alkylation has been heretofore limited largely to the most desirable olefins, namely the butenes, although C_3 and C_5 olefins can also be alkylated to give a superior gasoline constituent. Moreover, even the alkylation of butenes has often resulted in upsetting the volatility distribution of a given gasoline pool. Here again, the fact that the gasoline product is normally required to meet substantially different volatility specifications in the summer than in the winter has represented an additional complication.

It is the main object of the present invention to provide a flexible process for the conversion of light ends, and especially propylene, to a high quality blending agent, the volatility of which can be readily varied to meet operating needs. Another object is to convert C_3—C_4 hydrocarbons to compounds suitable for increasing the motor octane rating of gasoline blends without upsetting their volatility requirements, particularly in the blending of motor fuels having research octane numbers of 96 to 100 or higher and ASTM motor octane numbers in the range of about 83 to 100, and especially those having motor octane numbers between about 85 and 95 or higher. A more specific object is to hydrate and alkylate a propylene feed substantially completely in an integrated process whereby liquid fuels having a

superior octane rating and balanced volatility are produced, with a minimum of recycling or handling of inert diluents. A still further object is to hydrate gaseous olefins in a non-corrosive system to produce oxygenated products suitable as motor fuels, and to achieve substantially complete utilization of the feed with a minimum of recompression and purification. Still another object is to provide blending stocks suitable for raising the volatility and octane characteristics of other streams which may include virgin naphtha, thermally or catalytically cracked naphtha, hydroformate, and so forth. These and other objects as well as the general nature and operation of the invention, will become more clearly apparent from the subsequent description and accompanying drawing.

It has now been discovered that light olefins can be essentially completely converted to valuable gasoline-range constituents of balanced, predetermined volatility in a surprisingly effective manner. This is done by first passing the olefin-rich feed through a catalytic hydration step and then completing the conversion by alkylation of the unconverted olefins. Furthermore, a combination process particularly adapted to optimum utilization of propylene and C_4 hydrocarbons will include direct hydration of propylene, propylene/butylene alkylation, and polymerization of butylenes. According to the present invention these individual processes are combined and integrated so as to complement each other in maintaining a flexible and unusually effective balance among the several reactants, especially propylene, butylenes, and isobutane, and in maximizing conversion of propylene.

Unless otherwise indicated, all ratios and percentages stated in the subsequent description and claims are on a weight basis.

Useful as hydration feeds in the present process are refinery streams containing about 30 to 100 mole percent of a C_3 and/or C_4 olefin, which may further contain minor amounts of ethylene and higher olefins, usually in addition to at least 5 mole percent of inert gases such as hydrogen, methane, ethane, propane, butanes, nitrogen, carbon dioxide, etc. The preferred olefinic feed to the hydration stage is a C_3 hydrocarbon cut consisting essentially of about 70 to 95 mole percent propylene and correspondingly 30 to 5 mole percent propane, that is, a cut containing about 2.3 to 9 moles of propylene per mole of propane. Another likely feed may be a C_3—C_4 cut containing a mixture of propylene and butylenes together with propane and butanes, and usually also some ethylene. In most cases the feed is preferably first purified to remove sulfur compounds, notably hydrogen sulfide, e. g. by washing with diethanolamine or a similar organic base. Alkaline compounds and heavy oils may also desirably be removed from the feed in any known manner and such purification steps do not as such form a part of the present invention.

In the direct hydration step the olefin-rich feed is mixed with 0.2 to 5 moles, preferably 1.5 to 2 moles, of water per mole of olefin. The mixture is then passed over any suitable solid or liquid hydration catalyst, preferably of the low acid, non-corrosive type suitable for use in regular steel equipment. Accordingly, the catalyst may be of the so-called "modified UOP" type containing about 40% of phosphoric acid baked into a solid support such as kieselguhr, clay, silica gel, alumina, titania, char coal, coke, activated carbon, and the like. Other suitable catalysts include adipic, maleic or similar organic dibasic acids, adsorbent silica-aluminia gels of the type commonly used for catalytic cracking, silver sulfate, as well as copper sulfate or phosphate or copper pyrophosphate of the type heretofore used in polymerization. Another suitable catalyst is reduced tungsten pentoxide.

The hydration reactor may be a heat-exchanger type of vessel consisting of catalyst-filled tubes jacketed by condensate and steam for removing the heat of reaction.

Hydration conditions may include pressures of about 500 to 5000 p. s. i. g., preferably 800 to 1500 p. s. i. g., and temperatures of about 120 to 300° C., preferably 200 to 235° C. Above about 235° C. the selectivity to hydrated products may decrease fairly markedly at the expense of polymer formation. The hydrocarbon feed is usually present in the reaction zone as a supercritical mixture. Conversion varies essentially in direct proportion to pressure. The reaction is carried out with space velocities of 0.5 to 5 volumes of liquid olefin feed per volume of reactor per hour, velocities of 1 to 3 v./v./hr. being preferred. At these velocities about 20 to 70%, e. g. 30% of the olefin present in the feed can be readily converted to a liquid mixture of alcohol, ether, some liquid polymer of gasoline boiling range, and usually also some ketone. Such a mixture will have a research octane number of about 110 to 112 to 116 unleaded, a motor octane number of about 93, a specific gravity of about 0.71 to 0.75 and an atmospheric boiling range essentially between about 50 and 95° C., though it may have an end-point as high as about 220° C. due to the presence of some polymer formed in the reaction. It is apparent from these properties, as well as from actual engine tests, that this hydrated mixture represents a valuable, clean burning fuel which is suitable for use in either aviation or motor gasolines. Such a hydration product, on an anhydrous basis, will normally contain about 55 to 96 volume percent of alcohol, 3 to 35 volume percent ether, 0 to 10 volume percent acetone, and about 1 to 25 volume percent polymer.

The unconverted hydrocarbons withdrawn from the hydration step will contain about 15 to 70 mole percent and preferably only about 20 to 50 mole percent of propylene or C_3—C_4 olefin. The reaction mixture from the hydration stage is desirably first passed through a fractionating column where water and the valuable hydrated products are withdrawn as a liquid bottoms fraction and only the unconverted feed mixture containing primarily the olefin diluted with paraffins or other inert gases is taken overhead and passed to the alkylation stage unit.

The previously mentioned fractionating column or stabilizer is operated at a suitable pressure, e. g. 200 to 400 p. s. i. g., and the olefinic overhead stream is condensed to permit its being pumped to the second-stage reactor. Alternatively, the hydrated products can be separated from the unconverted feed by cooling the hydration zone effluent so as to form a water layer and a hydrocarbon layer separable therefrom.

In the alkylation step the unconverted olefin is combined with an isoparaffin-containing C_4 or C_5 stream such as a butane-butylenes stream coming from a C_4 catalytic polymerization plant and normally containing 50 to 85% isobutane. The combined alkylation feed is of such composition that the isoparaffin contained therein, e. g. isobutane, is sufficient to alkylate the olefin, after incurring any processing losses. As a minimum, for instance, the feed to the alkylation plant should contain 1.6 volumes of isobutane per volume of propylene, or 1.2 volumes of isobutane per volume of butylenes. An isoparaffin/olefin ratio in the total reactor feed of about 3/1 to 10/1 is desirable, a ratio of about 8/1 being preferred. Considerably higher isoparaffin/olefin ratios are normally maintained in the reaction zone proper, ratios of about 150/1 to 1000/1, e. g. 250/1, being suitable. The alkylation may be catalyzed in a conventional manner, e. g. by mixing with sulfuric acid of about 88 to 98% strength. Such an alkylation may be conducted in the acid phase of the resulting oil-acid emulsion, maintained at about 30 to 70° F. by refrigeration. As is otherwise well known, the heat of reaction can be removed from an emulsion recycle, the volume of which is large relative to the fresh feed. For instance, an emulsion/olefin volume ratio of 60/1 to 100/1 is advisable. Recycling of the emulsion also provides the energy required for mix-

ing the contents of the reactor to maintain the emulsion and to eliminate localized concentrations of olefin. The reactor pressure is sufficient to maintain a liquid phase, e. g. 100 to 200 p. s. i. g. The emulsion will consist of 20 to 60% acid by volume, and operations will be maintained so that 40 to 70% by volume of the oil phase will be isoparaffin, the remainder being alkylate, normal paraffins and olefins. Acid strength in the reactor is maintained by fortifying it with 98% acid and withdrawing a corresponding amount of weaker acid from the process.

A portion of the emulsion recycle may be diverted to an acid settler. The oil phase from this vessel is preferably caustic washed and fed to a tower which will remove and purge any residual light hydrocarbons. Since the conversion of olefin in the alkylation plant is essentially 100%, the purge will normally be free of olefin. The bottoms, consisting of isoparaffin, normal paraffin and alkylate are fractionated further. The isoparaffin is split out in a deisobutanizer column and recycled to the alkylation reactor while normal butane is taken overhead in a debutanizer tower, mixed with any by-passed C_4 streams, and sent to gasoline blending for vapor pressure control. Since alkylate and normal butane are remixed in the final gasoline blend, the debutanizer can be bypassed entirely if the combined product happens to meet volatility specifications for motor fuel. The alkylate bottoms from the debutanizer tower may then be rerun to a 330° F. endpoint overhead suitable for aviation gasoline, a 430° F. endpoint sidestream for motor gasoline, and a +430° F. bottoms for heating oil.

Of course, instead of using the sulfuric acid emulsion system described, the alkylation may be conducted in a variety of other ways without departing from the present invention. For instance, gaseous catalyst such as boron trifluoride, other liquid catalyst such as hydrogen fluoride, or a solid catalyst such as aluminum chloride may alternatively be used in suitably modified alkylation processes which are otherwise well known.

In accordance with the preferred embodiment of the invention the process also contains a catalytic polymerization step for maximum versatility. Such polymerization may be of the UOP-type using a tubular reactor packed with a catalyst consisting of kieselguhr impregnated with phosphoric acid. Alternatively, California-type polymerization may be used in which phosphoric acid on quartz chips is placed in a tower-like vessel cooled by recycle quench streams. Both types of plant operate at about 300 to 450° F. and at elevated pressure, e. g. 1000 p. s. i. g. The feed to this unit is an olefinic stream in the C_3—C_4 hydrocarbon range, e. g. a refinery C_4 stream containing 20 to 60% butylenes with 20 to 50% isobutane, preferably washed with caustic soda and water. Propylene may also be fed to the polymerization unit, especially in the summer time when a motor fuel of relatively low volatility is required. The percentage of olefins converted in the polymerization stage can be varied from 0 to 95% either by varying reactor conditions or by bypassing the reactor. Olefin polymer, unreacted olefin, and saturated hydrocarbons can then be separated in a suitable fractionation tower, e. g. at 150 to 200 p. s. i. g. pressure, from which the polymer is removed as bottoms. The overhead may then be sent to gasoline blending and to supply the isoparaffin to the alkylation stage as required.

A specific operation illustrative of the present invention will now be described with reference to the schematic flow plan shown in Figures 1 and 1–A of the accompanying drawing. In the illustrated embodiment a light olefin feed is hydrated and alkylated in sequence, in combination with an olefin polymerization step which further helps in balancing product volatility and thus further increases the flexibility of the process.

Referring to the drawing, the equipment shown is subdivided into three principal sections: a catalytic hydration plant and a catalytic polymerization plant, both of which are shown in Figure 1, and a connected alkylation plant shown in Figure 1–A. Two hydrocarbon streams, both being obtained from a C_3—C_4 cut from a catalytic cracking plant, are fed to this combination of units. One stream is a C_3 stream consisting essentially of about 65 mole percent of propylene and 35 mole percent of propane, desulfurized by scrubbing with diethanolamine; and the other is a caustic and water washed C_4 stream consisting essentially of about 48.5 mole percent isobutane, 8 mole percent normal butane, 16 mole percent isobutylene and 27.5 mole percent of normal butylenes. The entire C_3—C_4 cut from which these two feeds were obtained contained about 42.5 mole percent of C_3 hydrocarbons and 57.5 mole percent of the C_4 hydrocarbons.

Referring to Figure 1, the C_3 stream is liquefied and fed to the hydration plant via line **1** to depropylenizer tower **2**. This tower is operated at 300 p. s. i. g. and splits the feed into an olefin concentrate consisting essentially of 90 mole percent propylene and 10 mole percent propane, and a bottoms product consisting essentially of 90 mole percent propane and 10 mole percent propylene. The bottoms stream is withdrawn from the system via line **3** and can be used as fuel or finished to commercial liquefied petroleum gas. The propylene concentrate is removed from tower **2** via overhead line **4**, condensed and mixed with 1.5 moles of water of hydration per mole of propylene. This water is introduced via line **7**. The liquid mixture of olenfinic feed and water is passed through line **9** into hydration reactor **10**. This reactor is a heat-exchange type vessel as previously described, the vertical tubes of which are packed with a pelletized hydration catalyst consisting essentially of reduced tungsten pentoxide prepared as described in British Patent No. 622,937 (1949). The reactor is kept at a temperature of about 225° C., the heat of reaction being removed by cooling water which is circulated through and evaporated in the cooling jacket which surrounds the reactor tubes. The reaction pressure is maintained at about 1700 p. s. i. g. The hydrocarbon feed is passed into tower **10** at a space velocity corresponding to about 0.5 volume of cold liquid feed per reactor volume per hour. A conversion of about 40% of the olefin feed is obtained, yielding a mixture of isopropanol, diisopropyl ether, liquid polymer of gasoline boiling range, and a small quantity of acetone.

The wet crude reaction product is withdrawn from the hydration zone through line **11**, throttled through a valve **12** to a pressure of about 300 p. s. i. g. and fractionated at that pressure in stabilizer tower **15**. Here unreacted propylene and propane are taken as a liquid overhead stream **16** while the hydrated olefin and unreacted water are taken as bottoms through line **19**.

Tie-ins are provided between stabilizer overhead line **16** and depropylenizer feed line **1** and reactor feed line **4**. This permits recycling unconverted propylene from line **16** through line **17** back to hydration reactor **10**, or conversely, if more propylene is available than is required for hydration, surplus olefin may be diverted around reactor **10** from line **1** via line **17**, or from line **4** via lines **14** and **17**. Any unhydrated propylene finally leaves the hydration plant as stabilizer overhead via line **16** and is fed to the alkylation plant as hereafter described.

The stabilizer bottoms **19**, consisting of water and hydrated product, is fed to finishing facilities for removal of water. This may be accomplished by a series of two or more azeotropic distillations conducted at different pressures so as to break the azeotrope formed in the preceding distillation stage. Alternately, as illustrated in the drawing, water may be removed by azeotropic distillation in dewatering tower **20** followed by caustic treatment.

Tower **20** separates the crude hydration product into water bottoms and an azeotropic distillate containing

about 91% organic liquid and 9% water. The water bottoms separated in tower 20 is sent to the sewer via line 22 while the azeotropic distillate 21 is made essentially anhydrous by scrubbing in caustic contactor 25 with a 50% aqueous caustic solution introduced through line 26. Dilute caustic solution is withdrawn via line 28. The final product is taken as an overhead stream 31 from steam evaporator 30 to remove any residual caustic and will contain 3% or less water by volume. For instance, a typical dry product may boil between about 55 and 92° C. at 760 mm. Hg and consist essentially of 85% isopropyl alcohol, 5% diisopropyl ether, 2% acetone, 5% polymer and 3% water, all on a volume basis. This composition is characterized by a clear research octane number of 114 and constitutes a highly effective motor fuel. Thus about 91% of oxygen-containing motor fuel is obtained based on converted propylene, or, depending on the extent of recycle, about 24 to 82% based on total propylene in the feed.

For instance, during winter operations when high volatility is desired, the propylene may be recycled through the hydration plant to extinction, resulting in a hydrated product yield of about 82%. In the summer time when gasoline volatility is to be kept fairly low, the hydration plant may best be operated on a once-through basis, resulting in a hydrated product yield of about 24% based on propylene feed.

If desired, the hydration product can be used directly as a motor fuel, but preferably it will be blended with various hydrocarbon base stocks boiling in the gasoline range. Such base stocks, it is well known, may contain virgin naphtha, thermally or catalytically cracked gasoline, reformed or hydroformed naphtha, polymer gasoline, hydrocodimer, or various mixtures thereof. Furthermore, in accordance with the present invention it is particularly advantageous to balance the increased volatility due to the hydration product by blending in a suitable amount of alkylate produced in a later described part of the present process. Typically, the gasoline base stocks may have a clear research octane rating of about 85 to 103, usually between about 85 and 90 in the case of motor fuel, and a motor octane rating (leaded) which may range from about 85 in summer to 100 in winter. Of course, usual anti-knock agents, e. g. 1 to 5 cc. of tetraethyl lead per gallon, other additives such as lauryl p-aminophenol, 4-methyl-2,6-di-tert-butyl phenol or other anti-oxidants, gum-inhibiting agents, phosphorus containing surface ignition inhibitors such as tricresyl phosphate or chloropropyl thionophosphate, and other conventional materials may also be added. Of course, instead of blending the hydration product into gasoline, it can also be added to diesel fuel, e. g. to improve its cold starting properties.

The other main feed to the process is a C_4 stream from a catalytic cracking unit. This stream may contain, as an example, 55% butylenes, 36% isobutane and 9% normal butane. After caustic and water washing this C_4 stream is fed via line 41 to a tubular UOP type polymerization reactor 40 filled with a catalyst consisting essentially of kieselguhr impregnated with phosphoric acid. This reactor is operated at about 1000 p. s. i. g. and 380° F. A butylene conversion of about 70% is obtained in reactor 40. However, if desired, a lower overall conversion of butylenes can be obtained by diverting butylenes from line 41 around reactor 40 via by-pass line 42. Of course, lower or higher butylenes conversion can also be obtained by proper variation of reaction conditions in reactor 40.

Butylene polymer, unreacted butylenes and butanes are separated from the polymerization product 43 in debutanizer 45 which is operated at 175 p. s. i. g. pressure. Here a C_4 to 430° F. butylene polymer is removed as bottoms via line 46. Butylenes and butanes are taken as an overhead product 47 and, after mixing with by-passed reactor feed 42, if any, sent to gasoline blending and the alkylation plant as required. For instance, referring to Figure 1-A, an increased amount of the C_4 cut can be sent via line 48 to gasoline blending when C_4 hydrocarbons are in relatively short supply with respect to the vapor pressure requirements of the gasoline product pool. Conversely, when C_4 hydrocarbons are in long supply, all or most of the C_4 cut from the polymer plant is sent through line 49 to the alkylation plant and little or none is withdrawn through line 48. In such cases any need for raising the volatility of the gasoline pool can be satisfied by using the normal butane separated in the alkylation plant as hereafter described.

Again referring to Figure 1-A, the feed to the alkylation reactor may comprise the butane-butylenes stream 49 from the polymerization plant, the propylene-rich stream 16 from the hydration plant and a stream 57 of 98% sulfuric acid which serves as a catalyst. For example, in the summer the C_4 stream 49 may contain about 82.7 vol. percent isobutane, 13.7 vol. percent n-butane and 3.6 vol. percent butylenes, and C_3 stream 16 may contain about 86.3 vol. percent propylene and 13.7 vol. percent propane. The combined feed in line 61 is of such composition that the isobutane is just adequate to alkylate the olefin. For example, about 1.6 volumes of isobutane are used to alkylate one volume of propylene, and additional isobutane should be present so as to also allow complete alkylation of any butylenes present. Thus, in the summer, streams 16 and 49 are mixed in a ratio of about 0.6 to 1 volume of C_3 hydrocarbons per volume of C_4 hydrocarbons, or specifically about 0.78/1 for the particular example given. On the other hand, no propylene will normally be sent to alkylation in winter. Consequently, the alkylation feed will consist of the C_4 stream 49 which then may be somewhat leaner in isobutane, e. g., it may contain 50 vol. percent isobutane, 8.4 vol. percent n-butane, and 41.6% butylenes. Fresh acid is added to the hydrocarbon feed at about the rate at which it is consumed, that is, about 1 to 1.5 gals./gal. olefin. The mixture is maintained in reactor 60 in liquid phase at about 35° F. and a pressure of 150 p. s. i. g. Heat of reaction is removed by refrigeration from emulsion recycle line 63 which passes through heat exchanger 62 at a rate of about 100 volumes of emulsion per volume of olefin feed. The emulsion consists of about 50% acid by volume. The oil phase of the emulsion contains about 55% isobutane by volume.

A fraction equal to about 3 to 5 percent of the emulsion is diverted from recycle line 63 via line 64 to acid settler 65. Here the spent acid layer is removed via line 67, while the oil phase is removed via line 68 and washed in scrubber 69 with strong caustic introduced via line 66. After settling in tank 70 the spent caustic is discarded via line 71 while the scrubbed oil phase is sent via line 72 to stabilizer tower 75. There any residual C_3 hydrocarbon, that is, essentially pure propane, is removed and sent via line 76 for use in liquefied petroleum gas. The bottoms from depropanizer tower 75 are pumped via line 78 to deisobutanizer tower 80 where isobutane is split out and recycled via line 81 to alkylation reactor 60. The bottoms from tower 80 are pumped via line 83 to debutanizer tower 85 where normal butane is split out and sent via line 86 to gasoline blending for vapor pressure control. Where necessary, some of this normal butane may also be isomerized to increase the supply of isobutane required in the alkylation. The alkylate bottoms stream 87 from the debutanizer may then be rerun in tower 90. There a light alkylate having a 330° F. endpoint suitable for aviation gasoline is produced as an overhead stream 91, a heavy alkylate having a 430° F. endpoint suitable for motor gasoline is removed via line 92, and alkylate bottoms suitable for heating oil are removed via line 93. Of course, since alkylate and normal butane are eventually remixed in the final gasoline blend, alkylate debutanizer 85 can be partially or entirely bypassed via line 84, if

the combined products meet the desired volatility specifications.

Substantially complete conversion of the olefin is thus obtained in the alkylation, with about 91% selectivtity to a gasoline fraction boiling between about C_4 and 350° F. and consisting largely of C_7 and C_8 hydrocarbons, together with some C_5 and C_6 hydrocarbons. This gasoline will have a clear research octane number of about 92 to 93 and a motor octance number of about 90.

EXAMPLE

The products of the present invention can be used for formulating various gasoline blends which will meet the customary voatility specifications with respect to both Reid vapor pressure and percent distilling at 158° F. Thus, Tables I and II illustrate winter- and summer-grade gasolines, respectively, formulated by blending all of the various products of the novel combination process.

Table I

WINTER-GRADE GASOLINE

	Vol./100 vol. Total C_3-C_4 Feed	Composition of Blend, Vol. Percent
C_3 Hydration Product	25.3	35.6
C_3 Alkylate	0	0
C_3 Polymer	0	0
C_4 Alkylate	38.1	53.6
C_4 Polymer	2.1	3.0
Isobutane	0.9	1.3
Normal Butane	4.6	6.5
Total	71.0	100.0

Anti-knock qualities of gasoline:

CFR Research Octane Number (with 2.6 cc. tetraethyl lead) ---------- 105.5

ASTM Motor Octane Number (with 2.6 cc. tetraethyl lead) ---------- 98.9

Table I shows that the novel process can be adjusted so that the entire feed is converted into gasoline constituents which, upon being combined, produce a gasoline blend which has excellent anti-knock properties and possesses enough volatility to satisfy winter requirements. 71 volumes of gasoline product are obtained in this manner per 100 volumes of C_3—C_4 feed, the difference in volume being due to the fact that the product is considerably denser than the light hydrocarbon feed.

Table II

SUMMER-GRADE GASOLINE

	Vol./100 vol. Total C_3-C_4 Feed	Composition of Blend, Vol. Percent
C_3 Hydration Product	6.0	9.3
C_3 Alkylate	29.4	45.3
C_3 Polymer	3.4	5.2
C_4 Alkylate	2.0	3.1
C_4 Polymer	19.5	30.0
Isobutane	0	0
Normal Butane	4.6	7.1
Total	64.9	100.0

CFR Research O. N. (with 2.6 cc. tetraethyl lead)- 103.1

ASTM Motor O. N. (with 2.6 cc. tetraethyl lead)- 88.9

Table II shows a product obtained from essentially the same feed in an alternative operation. Here the combination process was operated so as to convert the feed into a gasoline blend of excellent anti-knock characteristics and sufficiently low vapor pressure suitable for summer use.

By comparison with Table I it will be observed that, to meet summer specifications, it is desirable to hydrate only a minor proportion of the propylene while alkylating most of it. Some butylenes are also alkylated to reduce volatility further. The remaining C_3 and C_4 olefins which cannot be alkylated because of insufficient isoparaffin are then converted into gasoline by polymerization. Conversely, to meet winter specifications, most or all of the propylene can be diverted to the hydration step while being replaced in the alkylation step with butylenes so as to make full use of the isoparaffin available. In either case the polymerization step serves as a kind of fly wheel which keeps gasoline production at a maximum by utilizing the olefins left unconverted in the hydration and alkylation steps.

Tables I and II illustrate the unusual flexibility of the novel process in that they demonstrate that this process is entirely self-sufficient to produce gasoline blends meeting a wide variety of specifications. Thus, gasolines can be produced which have Reid vapor pressures of about 7.5 to 13.0 p. s. i. g. and distillation characteristics such that 18 to about 60 percent will be volatile at 158° F. Such gasolines may contain, for instance, about 5 to 36 volume percent of the hydration product, about 2 to 40 volume percent of gasoline-range polymer of a C_3—C_4 olefin, about 35 to 60 volume percent of an alkylate having 7 to 8 carbon atoms per molecule, and about 5 to 10 parts of butanes. Of course, the process can also be operated in conjunction with conventional refining operations. In such a case the final gasoline blend may contain various amounts of extraneous constituents such as virgin, catalytic and reformed naptha, the process of the invention being operated under conditions adjusted to satisfy the volatility specifications of the final blend while maximizing the particularly desirable constituents such as hydration product and alkylate.

In summary, the foregoing shows that the main value of the integrated process lies in its ability to provide maximum yields of products which are very high in certain critical motor gasoline inspections, notably octane number and volatility. Furthermore, the integrated process is unusualy flexible and thereby adapted to meet fluctuations due to seasonal product quality requirements or available feed supply. According to this invention superior products are obtained from the light ends which are available in any normal fuel products refinery, particularly in one which includes catalytic cracking facilities.

Secondly, the integrated process is valuable in that it provides compensations for certain limitations which characterize the several component steps individually. For instance, the relatively high volatility of the hydration product tends to offset the relative lack of volatility of the alkylate, thereby making more paraffins available for valuable alkylate production. The relatively poor octane blending factor which normally characterizes polymer gasoline is kept to a minimum since in the present invention polymerization can be largely or even totally replaced by hydration which produces a fuel component of greatly superior blending value. Polymerization is used here only as a means of controlling the isoparaffin/olefin ratio for alkylation. Where surplus olefins can be used elsewhere, the present process need not contain any polymerization step at all.

Finally, the drawback of low conversion which normally characterizes olefin hydration is overcome in the integrated process in that the desired conversion is completed in the efficient alkylation stage, rather than attempting to complete conversion by recycling to the hydration stage. Consequently, the present process maximizes conversion in a particularly advantageous manner. In addition, the process has an advantage in that the olefin feed which is sent to alkylation from the hydration step contains a greater concentration of olefins than a catalytically cracked C_3 cut ordinarily used for alkylation.

The characteristics of the individual stages of the process are summarized in Table III.

Table III

LIGHT ENDS CONVERSION

Process	Catalytic Polymerization	Direct Hydration	Alkylation	
Olefin Feedstock	$C_4^=$	$C_3^=$	$C_3^=$	$C_4^=$.
Maximum conversion—percent on olefin feed	95	20–50	100	100.
Other Feedstocks	None	None	$iC_4°$	$iC_4°$.
Products	Motor Gaso. Poly.; C_4 stream of variable olefin content (3–55%).	Propylene hydration product plus C_3 stream of variable olefin content (18–90%).	Light alkylate; Alkylate Btms.; iC_4 concentrate; nC_4 concentrate.	Heavy alkylate;
	$C_4^=$ Polymer	C_3 Hydr. Product	$C_3^=$ Alky.	$C_4^=$ Alky.
Motor Gasoline Quality:				
Effective Blending RVP,[1] p. s. i. g	1.5	19.2	2.5	2.5.
Proportion Distilled at 158° F. (D+L) Percent.	−6	134	0	0.
Research Blending No.—				
(clear)	72; 101.2 ON	70; 99.5 ON	63; 92.2 ON	65.1; 94.5 ON.
(+2.6 cc. TEL)	76; 103.8 ON	79; 105.1 ON	73; 102.3 ON	74.3; 102.9 ON.
Blending ASTM Motor ON—				
(clear)	83		91	92.5.
(+2.6 cc. TEL)	86	135	93–94	93–94.
Vapor Lock Constant [2]	0	230	12.5	12.5.

[1] Reid vapor pressure.
[2] Vapor lock constant C=(5 RVP+percent distilled at 158° F.).

It can be seen that catalytic polymerization reacts olefins only, over a wide range of conversions, to a relatively nonvolatile gasoline stock of good research but only fair motor octane number. Substantially complete conversion of the olefins can be achieved. This affords a convenient means of completely utilizing the olefins as far as they cannot be used up in the other steps of the process. Also it is an effective way of preparing an isoparaffin concentrate suitable for alkylation.. If desired, the resulting isobutane or isopentane content of the concentrate may be further increased by isomerization.

The direct hydration of propylene and/or butylenes reacts the olefin only, and to a limited degree. The resulting product has good research octane and superb motor octane quality. However, due to azeotropic effects, it is highly volatile in admixture with hydrocarbon gasoline components and this effect must be counterbalanced by other, less volatile constituents.

The alkylation is capable of reacting both propylene and butylenes with a saturate such as isobutane to produce a low volatility product with excellent quality in both motor and research octane. Conversion of the olefin feed is essentially complete. Application of the integrated process to motor fuel production becomes simply a matter of adjusting the characteristics of the individual operations so as to maximize product yield and minimize product giveaway, that is, avoid uneconomical surpassing of required product specifications.

In choosing proper operating conditions for the integrated process, four major variables must be considered: (*a*) Research octane number; (*b*) motor octane number; (*c*) vapor lock; and (*d*) ratio of isoparaffin to olefin fed to alkylation, so as to stay in balance between these two reagents in the alkylation stage.

In practice there are several ways of controlling each variable as summarized in Table IV below. In each case, since the spent hydrocarbon streams from both hydration and polymerization are alkylated the essentially complete olefin conversion obtainable in alkylation is utilized in the clean-up of residual olefin from the two other operations. This allows for maximum flexibility along with high total conversion.

Table IV

CONTROL OF GASOLINE QUALITY

Origin of Gasoline	Case No. 1—Process of Invention Only		Case No. 2—Process of Invention plus Conventional Practice
Desired Increase In	Primary Control	Secondary Control	Conventional Control.
Research Octane No	Diverting olefin feed from alkylation to hydration.		Tetraethyl lead concentration. Usually also reforming or hydroforming.
Motor Octane No	Divert Olefin feed from alkylation to hydration.	Divert olefin from polymerization to alkylation.	Do.
Volatility	Divert propylene from alkylation to hydration. Also divert C_4 hydrocarbons from alkylation to gasoline blending.	Divert butylenes from polymerization to alkylation. Also propane can be blended into gasoline if no C_4 hydrocarbons are available.	Divert C_4 hydrocarbons from conversion steps to gasoline blending. Also thermal reforming of heavy virgin naphtha.
$iC_4°$/olefin balance to alkylation plant	Divert propylene from alkylation to hydration.		Divert butylenes from alkylation to polymerization.

Having described the general nature and specific examples illustrating the invention, it will be understood that the latter can be modified in various ways without departing from the scope and spirit hereof. The novelty of the present invention is particularly pointed out in the appended claims.

What is claimed is:

1. A process for converting a hydrocarbon feed supply of C_3 and C_4 paraffins and olefins into gasoline components of variable predetermined volatility and good anti-knock characteristics, which comprises segregating from said feed hydrocarbons an olefin-rich C_3 fraction containing 70 to 95% propylene and a C_4 fraction containing butylenes and isobutane, feeding at least a portion of said olefin-rich C_3 fraction and water of hydration into a hydration zone containing a hydration catalyst under conditions conducive to producing an oxygenated liquid boiling principally between about 50°

and 95° C., recovering said oxygenated liquid and an unconverted propylene-containing fraction, recycling a portion of said unconverted fraction to said hydration zone, thereby adjusting the ratio of unconverted propylene to propylene converted to oxygenated liquid, passing a sufficient portion of said C_4 fraction through a polymerization zone containing a polymerization catalyst under conditions conducive to the formation of gasoline-range polymer to thereby adjust the butylene content of the remaining unpolymerized C_4 fraction such that the isobutane present therein is just about sufficient to alkylate all the remaining unconverted olefin, recovering said gasoline-range polymer, feeding said unpolymerized C_4 fraction and all the unhydrated C_3 fraction to an alkylation zone containing an alkylation catalyst under conditions conducive to converting said fractions into an alkylate of which at least 90% boils between about 50° and 220° C., recovering said alkylate, and controlling the quality of the resulting gasoline components by increaseing the ratio of hydration zone olefin feed to alkylation zone olefin feed plus polymerization zone olefin feed when increased product volatility is desired, and by decreasing said ratio when decreased product volatility is desired.

2. A process according to claim 1 wherein butylene polymerizaton is increased in relation to butylene alkylation as propylene alkylation is correspondingly increased in relation to propylene hydration, in order to reduce product volatility, and wherein butylene alkylation is increased in relation to butylene polymerization as propylene hydration is correspondingly increased in relation to propylene alkylation, in order to increase product volatility.

3. A process according to claim 1 wherein substantially the entire C_3 fraction is passed through the hydration zone and as much of the unconverted propylene from the hydration zone is mixed with the C_4 fraction as will produce a mixture having a proper isobutane propylene ratio for feeding to the alkylation zone while remaining butylenes are fed to the polymerization zone.

4. A process according to claim 1 for producing a relatively volatile combination of gasoline components, which comprises converting substantially all available propylene in the hydration stage.

5. A process according to claim 1 wherein the hydration catalyst is selected from the group consisting of phosphoric acid catalyst, active silica gel catalysts and reduced tungsten pentoxide catalysts.

6. A process according to claim 1 wherein said alkylation catalyst is selected from the group consisting of 88–98% sulfuric acid, hydrogen fluoride, boron fluoride, and aluminum chloride.

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