

[54] **HYDROCARBON CONVERSION PROCESS**

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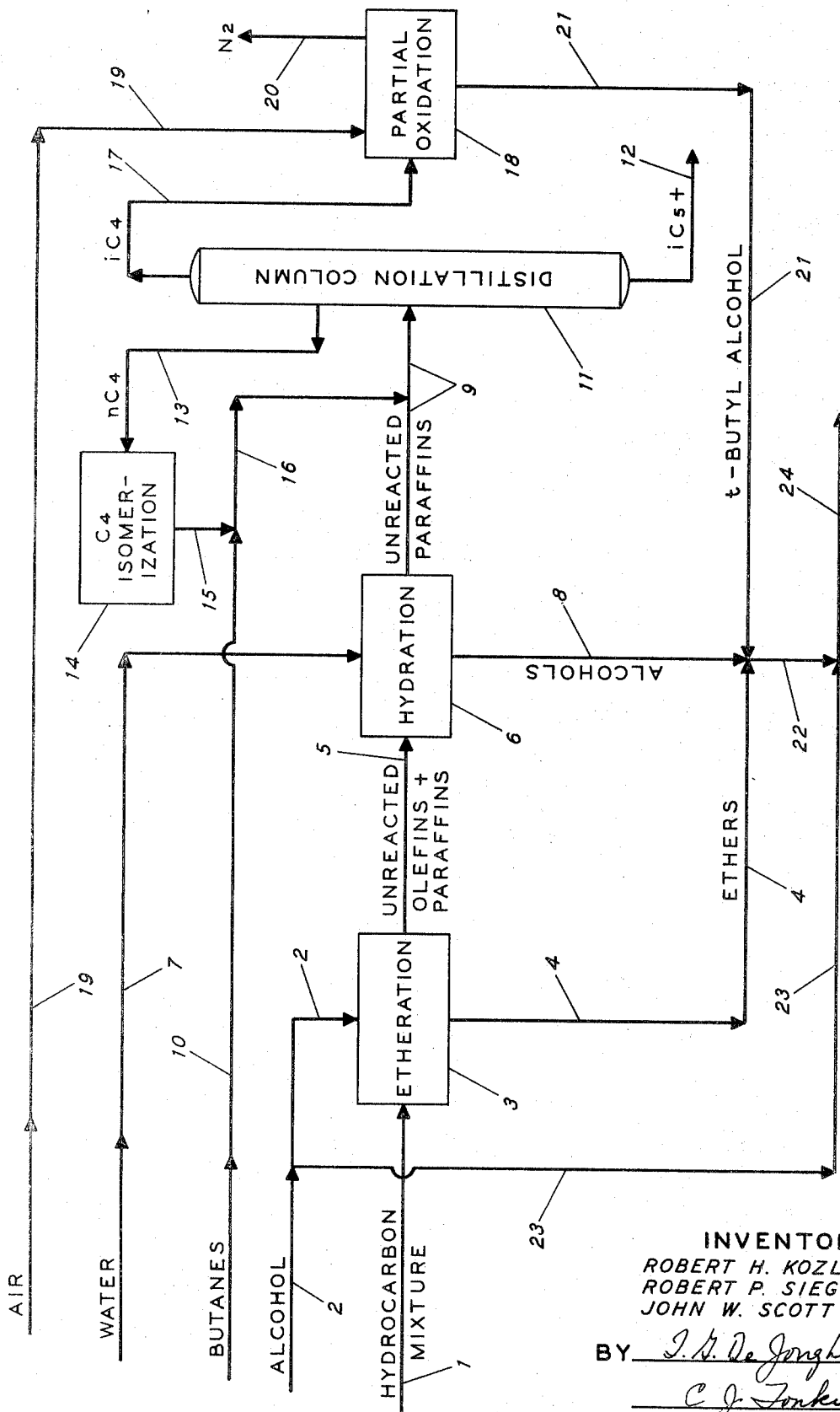
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[57] **ABSTRACT**

A process for producing gasoline blending stock which comprises (a) feeding an alcohol and a light hydrocarbon mixture containing at least tertiary olefins, linear olefins and isobutane to an etheration zone, (b) reacting the alcohol with the tertiary olefins in the etheration zone to obtain an ether and unreacted linear olefins and isobutane, (c) separating the ether from the linear olefins and isobutane, (d) feeding water and at least the linear olefins to a hydration zone, (e) reacting the water with the linear olefins in the hydration zone to obtain at least a secondary alcohol, (f) oxidizing the isobutane to obtain t-butyl alcohol, and (g) blending at least portions of the ether, secondary alcohol and t-butyl alcohol to produce a gasoline blending stock.

6 Claims, 1 Drawing Figure



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HYDROCARBON CONVERSION PROCESS

BACKGROUND OF THE INVENTION

The present invention relates to a combination process to produce a gasoline blending stock. More particularly, the present invention relates to a process combination involving etheration, hydration, and partial oxidation to produce a gasoline blending stock.

Previously, high octane gasoline has generally been produced by blending lead compounds as, for example, tetra methyl lead or tetra ethyl lead, with gasoline. However, it is presently believed that lead compounds in gasoline contribute to air pollution or that lead compounds in the gasoline increase the difficulty of controlling emissions from internal combustion engines.

Components such as ethers have been suggested as blending components for gasoline, but few overall processes have been suggested for producing etherated gasolines. U.S. Pat. No. 3,482,952 suggests a process for producing etherated gasoline.

According to the process disclosed in U.S. Pat. No. 3,482,952, etherated gasoline is produced by reacting C_4 - C_6 tertiary olefins obtained from a cracking reactor with a lower alcohol to obtain ethers. These ethers are then blended with at least one other hydrocarbon stream.

SUMMARY OF THE INVENTION

According to the present invention, a process is provided for producing a gasoline blending stock which process comprises (a) feeding an alcohol and a light hydrocarbon mixture containing at least tertiary olefins, linear olefins and isobutane to an etheration zone, (b) reacting the alcohol with the tertiary olefins in the etheration zone to obtain an ether and unreacted linear olefins and isobutane, (c) separating the ether from the linear olefins and isobutane, (d) feeding water and at least a portion of the linear olefins to a hydration zone, (e) reacting the water with the linear olefins in the hydration zone to obtain a secondary alcohol, (f) oxidizing the isobutane to obtain at least t-butyl alcohol, and (g) blending at least portions of the ether, secondary alcohol and t-butyl alcohol to produce a gasoline blending stock.

According to a preferred embodiment of the present invention, both the isobutane and linear olefins are fed to the hydration zone and unreacted isobutane is withdrawn from the hydration zone and is oxidized to obtain t-butyl alcohol.

In the present specification, the term "tertiary olefin" is used to mean those olefins containing a carbon atom bonded to three other carbon atoms with one of the bonds being a double bond. The term "linear olefin" is used in the present specification to mean olefins other than tertiary olefins and thus to include branched chain olefins wherein the branching does not result in a tertiary olefin. Thus, the term linear olefin includes propylene, butene-2, etc.

According to a particularly preferred embodiment of the present invention, the light hydrocarbon mixture which is fed to the etheration zone contains normal butane in addition to tertiary olefins, linear olefins and isobutane, and, after passing through the etheration and hydration zones, the normal butane is isomerized to obtain isobutane and at least a portion of the isobutane obtained by isomerization is oxidized to t-butyl alcohol.

The alcohol fed to the etheration zone for reaction with the tertiary olefins in accordance with the process of the present invention can be one or a mixture of alcohols ranging from C_1 alcohols up to high alcohols such as C_{10} alcohols. However, it is preferred that the alcohol or alcohol mixture fed to the etheration zone be a lower alcohol such as methanol up to about the amyl alcohols. It is particularly preferred in the process of the present invention to feed methanol to the etheration zone. Methanol is a relatively inexpensive alcohol and we have also determined that methanol can be produced in an overall refinery combination process including the basic steps of the present invention. As is discussed in more detail hereinbelow, one of the important advantages of the present invention is its versatility and ability to combine with other refinery process steps. The methanol feed to the process of the present invention can be obtained from a combination hydrogen-methanol production plant with the hydrogen produced in the combined hydrogen-methanol plant being used in a hydrocracking plant which hydrocracking plant in turn supplies at least a portion of the isobutane for reaction in the isobutane oxidation step according to the present invention. Combined hydrogen and methanol production is discussed in more detail in the commonly assigned applications entitled "Gasoline Production," application Ser. No. 46,264, "Production of Gasoline," Ser. No. 46,230, and "Manufacture of Gasoline," Ser. No. 46,217, all of which were filed on June 15, 1970. The three aforementioned patent applications are incorporated by reference into the present patent application.

The light hydrocarbon mixture fed to etheration zone 3 preferably boils between about propylene and 400°F. More preferably, the light hydrocarbon stream comprises hydrocarbons within the range of about C_3 to C_7 . The hydrocarbon mixture fed to the etheration zone can be produced or obtained in a variety of ways. Different streams produced in a refinery, for example, can be combined to obtain the light hydrocarbon mixture for feeding to etheration zone 3. It is particularly preferred in the process of the present invention to feed an olefin-rich C_4 - C_5 stream from a hydrocarbon cracking process to etheration zone 3. The C_4 - C_5 stream from the cracking process can be a relatively pure olefin stream containing only a few tenths percent or so paraffins such as isobutane, or the C_4 - C_5 stream may contain substantial amounts of paraffins such as 5 - 50 weight percent paraffins. One of the important advantages of the present invention is that both the etheration and hydration steps in the present invention operate as serial separation steps, i.e., in the etheration zone, tertiary olefins are converted to ethers which ethers are then easily separated from the remaining olefins and paraffins compared to the difficulty in separating tertiary olefins directly from the linear olefins. And in hydration zone 6, the linear olefins are reacted with water to form alcohols which alcohols are usually relatively easily separated from the remaining paraffins compared to the difficulty of separating the C_4 - C_5 paraffins from the C_4 - C_5 linear olefins.

The preferred olefin-rich C_4 - C_5 stream for feeding to etheration zone 3 in the process of the present invention can be obtained, for example, from a light hydrocarbon cracking process or a cracking process applied to a relatively heavy hydrocarbon such as gas oil. The cracking process can be thermal or catalytic. Suitable

cracking processes operated at cracking temperatures between about 900° and 1200°F. are described in U.S. Pat. No. 3,482,952 at column 3, line 22 to line 46, which disclosure is incorporated by reference into the present specification. It is preferred to obtain the olefin-rich light hydrocarbon mixture for feeding to the etheration zone in the present invention from a catalytic cracking process such as a fluid catalytic cracking process applied to relatively heavy hydrocarbons such as gas oils.

Although C₄ - C₅ olefin-rich streams are advantageous feedstocks for the etheration reaction in the process of the present invention, streams containing mostly C₄ olefins are the most preferred feedstock for the etheration reaction in the process of the present invention. Preferably, the C₄ olefin-rich feed stream is obtained by distilling a C₄ rich cut from the effluent from a hydrocarbon cracking process such as a fluid catalytic cracking process. The C₄ olefin-rich cut is a particularly preferred feedstock for the etheration reaction in the process of the present invention because the isobutene in the C₄ cut has a relatively high reaction rate with alcohols such as methanol to form ethers compared to the reaction rates of higher tertiary olefins with alcohols to form ethers. Furthermore, we have determined that the methyl t-butyl ether formed in reacting isobutene with methanol has relatively high octane blending numbers when blended with gasoline boiling range hydrocarbons. Still further, the olefin-rich C₄ stream provides a relatively high concentration of olefins compared to wider cuts such as C₃ - C₆ olefin-rich hydrocarbon fractions and this higher concentration of olefins contributes to the efficiency of the process of the present invention. In the process of the present invention, unreacted linear olefins and paraffins are removed from the etheration zone and passed at least in part to the hydration reaction step of the present invention. The preferred olefin-rich C₄ fraction provides a relatively high concentration of linear butenes for hydration to produce at least secondary butyl alcohol in the hydration step of the present invention. The secondary butyl alcohol has a relatively high blending octane number compared to higher secondary alcohols. Unreacted isobutane (iC₄) withdrawn from the hydration reaction step in the process of the present invention is oxidized in the partial oxidation step of the present invention to form t-butyl alcohol which has a relatively high blending octane number when blended with gasoline boiling range hydrocarbons.

As indicated above, preferably at least a portion of the paraffinic C₄ feed for the process of the present invention is obtained from a hydrocracking process. Hydrocracking using Group VIB and/or Group VIII components on acidic supports such as silica-alumina produces substantial quantities of isobutane. The isobutane is advantageously oxidized in the partial oxidation step of the present invention to form the relatively high blending octane number component t-butyl alcohol.

The hydrocracking or other hydroconversion step such as hydrotreating or hydrofining can advantageously be combined with fluid catalytic cracking to produce at least a portion of the feedstock for the catalytic cracking process. According to a preferred overall embodiment of the present invention, hydroconversion is used to provide at least a portion of the isobutane which is converted to t-butyl alcohol, at least a portion of the effluent from the hydroconversion step is fed to

a catalytic cracking process which provides at least a portion of the C₄ olefins fed to the etheration step of the present invention and preferably, at least a portion of the ethers and alcohols produced in the etheration, hydration and/or partial oxidation steps of the present invention are blended with at least a portion of the gasoline boiling range hydrocarbons produced in the hydroconversion and/or catalytic cracking steps.

According to one preferred alternate overall process embodiment in accordance with the present invention, a process is provided for producing a gasoline blending stock which comprises (a) feeding an alcohol and a C₄ - C₅ stream, containing at least tertiary olefins, linear olefins, isobutane, n-butane and isopentane, to an etheration zone, (b) reacting the alcohol with the tertiary olefins in the etheration zone to obtain an ether, (c) separating the ether from unreacted linear olefins and paraffins, (d) feeding water and the unreacted linear olefins and paraffins to a hydration zone, (e) reacting the water with the unreacted linear olefins in the hydration zone and withdrawing at least a secondary alcohol and unreacted paraffins from the hydration zone, (f) separating the secondary alcohol from the unreacted paraffins, (g) separating the unreacted paraffins into at least isobutane and isopentane, (h) oxidizing the isobutane to obtain t-butyl alcohol, (i) blending at least a portion of the ether, secondary alcohol and t-butyl alcohol to produce a gasoline blending stock.

The gasoline blending stock produced in accordance with the present invention can be blended with various gasoline boiling range hydrocarbons to obtain an unleaded relatively high octane gasoline.

BRIEF DESCRIPTION OF THE DRAWING

The drawing is a schematic process flow diagram illustrating a preferred embodiment of the process of the present invention.

DETAILED DESCRIPTION OF THE DRAWING

Referring now more particularly to the drawing, a hydrocarbon mixture containing tertiary olefins, linear olefins, and isobutane is fed via line 1 to etheration zone 3. In etheration zone 3, the tertiary olefins are reacted with alcohol fed via line 2 to obtain an ether which is withdrawn from the etheration zone via line 4. It is, of course, to be understood that distillation facilities will be operated in conjunction with the etheration reactor in etheration zone 3.

To catalyze the ether synthesis reaction in zone 3, solid acidic or homogeneous acidic catalysts can be used. Preferred temperatures for use in the ether synthesis reactor are between 70 and 225°F. and preferred pressures are between 10 and 600 psig. Preferred catalysts for use in the ether synthesis reactor are relatively high molecular weight, water-insoluble, carbonaceous materials containing at least one -SO₃H group as the functional group. These catalysts are exemplified by the sulfonated coals (Zeo-Karb H, Nalcite X, and Nalcite AX) produced by the treatment of bituminous coals with sulfuric acid and commercially marketed as zeolitic water softeners or base exchangers. These materials are usually available in a neutralized form and, in this case, must be activated to the hydrogen form by treatment with a mineral acid, such as hydrochloric acid, and water washed to remove sodium and chloride ions prior to use. Also suitable are the sulfonated resin type catalysts which include the reaction products of

phenolformaldehyde resins with sulfuric acid (Amberlite IR-1, amherlite IR-100, and Nalcite MX). Also useful are the sulfonated resinous polymers of coumarone indene with cyclopentadiene, sulfonated polymers of coumarone indene with furfural, sulfonated polymers of coumarone indene with cyclopentadiene and furfural, and sulfonated polymers of cyclopentadiene with furfural. The most preferred cationic exchange resins are strongly acidic exchange resins consisting essentially of sulfonated polystyrene resin, for instance, a divinylbenzene cross-linked polystyrene matrix having about 0.5 to 20 percent, preferably about 4 to 16 percent, of copolymerized divinylbenzene therein to which are attached ionizeable or functional nuclear sulfonic acid groups. These resins are manufactured and sold commercially under various trade names; e.g., Dowex 50, Nalcite HCR, and Amberlyst 15. As commercially obtained, they have solvent contents of about 50 percent and can be used in the instant process in this form or can be dried and then used.

Particularly preferred as a catalyst for use in the ether synthesis zone is Amberlyst 15 which is a divinylbenzene cross-linked polystyrene matrix, having between 0.5 - 20 percent of copolymerized divinylbenzene by weight of the resin catalyst to which is attached sulfonate groups, and having a macroreticular structure. More specifically, Amberlyst 15 has the following properties:

Property	Amberlyst 15
Appearance	Hard, spherical, dark-brown particles, toluene-saturated
Typical particle size distribution, percent retained on:	
16 mesh U.S. Standard Screens	2.4
-16 + 20 mesh U.S. Standard Screens	24.2
-20 + 30 mesh U.S. Standard Screens	47.9
-30 + 40 mesh U.S. Standard Screens	18.8
-40 + 50 mesh U.S. Standard Screens	5.7
Through 50 mesh, percent	1.0 max.
Whole bead content, %	100
Bulk density, g/l as supplied	850
lbs./cu. ft.	54
True density, g/ml as supplied	1.4
Mositure, % by weight	less than 1%
Solids, %	55-60
Percentage swelling from dry state to solvent-saturated state —	
hexane	12
toluene	15
ethylene dichloride	17
ethyl acetate	35
ethyl alcohol (95%)	66
water	66
Hydrogen ion concentration	
meq./g. dry	4.9
meq./ml. packed column	2.4
Surface Area, m ² /g.	40 - 50
Porosity, ml. pore/ml. bead	.30 - .35
Average Pore Diameter, A	200 - 600

As can be seen from the properties given above, Amberlyst 15 is generally obtained with a hydrogen ion concentration ($-\text{SO}_3\text{H}$ concentration) of about 4.9 meq. per gram of catalyst.

The term "macroreticular" is used herein to connote a resin catalyst pore structure having a high degree of true porosity, that is, pores which are rigid and fixed within the resin beads. The high porosity gives rise to a large surface area which is conducive to high catalytic activity. The macroreticular structure in Amberlyst 15

permits ready access of reactants to the sulfonate groups or ions present throughout the resin catalyst beads. This accessibility is not generally found in conventional ion-exchange resins.

The olefin hydration in zone 6 can be catalyzed by mildly acidic solid catalysts or homogeneous acidic catalysts. Preferred temperatures for the hydration of olefins in hydration zone 6 are between about 70 and 325°F. and preferred pressures are between about 50 and 500 psig. Preferred catalysts for use in the hydration zone include those mentioned above for use in the ether synthesis zone, but somewhat reduced acidity is preferred for the hydration catalysts compared to the ether synthesis catalyst. Thus, Amberlyst 15 with the acidity adjusted to between about 0.5 and 2.5 meq. H⁺/g. of catalyst is a particularly preferred catalyst for use in the hydration zone.

Distillation facilities are an included part of hydration zone 6. In the distillation facilities, unreacted paraffins are separated from the secondary alcohol. The unreacted isobutane and other paraffins such as normal butane and isopentane are fed to distillation column 11.

According to a preferred embodiment of the present invention, additional butanes are also fed to distillation column 11 as indicated by line 10 in the drawing. Isopentane and, in general, hydrocarbons with less volatility than normal butane, are fractionated downward in distillation column 11. An isopentane-rich stream is withdrawn from the bottom of the distillation column via line 12. This isopentane-rich stream is advantageously used as a gasoline blending component as isopentane itself has a relatively high octane number.

A side-stream rich in normal butane is preferably withdrawn from the upper part of the distillation column as a liquid draw from a sump tray or the like at some position intermediate between the top of the column and the feed point to the column, or a normal butane-rich stream can be withdrawn from the lower part of the distillation column as a vapor side stream withdraw. In accordance with a preferred embodiment of the present invention, the normal butane is isomerized in C₄ isomerization zone 14 to produce additional butane. The isomerization of normal butane in zone 14 can be carried out using, for example, a platinum on silica alumina or platinum on chlorided alumina catalyst. Preferred operating temperatures for the normal butane isomerization are between about 200° and 750°F. and preferred pressures are between about 100 and 1000 psig. In a typical normal butane isomerization process, a deisobutanizer is operated in conjunction with the isomerization reactor. However, in the process of the present invention, it is preferred to use distillation column 11 in conjunction with C₄ isomerization zone 14 rather than to use a separate deisobutanizer column to further purify the normal butane feed passed via line 13 to zone 14. Zone 14 will, however, contain some separating and heating equipment operating in conjunction with the normal butane isomerization reactor. A typical normal butane isomerization process is described in the *Oil and Gas Journal*, Volume 56, No. 13, Mar. 31, 1958, at pages 73 - 76.

The normal butane feed to zone 14 is largely converted to isobutane which is withdrawn from zone 14 via line 15 and fed to distillation column 11 via line 16 and 9. Isobutane is distilled overhead in distillation column 11 and is withdrawn via line 17. The isobutane-

rich stream withdrawn via line 17 is fed to partial oxidation zone 18 wherein the isobutane is oxidized preferably with molecular oxygen or oxygen present in ordinary air introduced to zone 18 via line 19. In those cases where air is used to supply the oxidizing gas for zone 18, a nitrogen-rich stream is removed from zone 18 via line 20. A number of methods can be employed to effect the oxidation of the isobutane feedstock to zone 18 to form tertiary butanol.

Preferably, the oxidation is carried out in the presence of a catalyst containing cobalt, copper or nickel or combinations thereof. According to recent laboratory work, it has been found that high conversions of liquid isobutane to tertiary butanol can be obtained while using reaction conditions including a tempera-

components, it is preferred to use a mixture of these components as a high octane gasoline blending stock. In accordance with an alternate embodiment of the present invention, a portion of the alcohol, such as methanol, fed to the process of the present invention via line 2, is passed via line 23 for blending with one or more of the ether, alcohol or tertiary butanol streams produced in accordance with the process of the present invention. In this instance, the product gasoline blending stock is withdrawn from the process via line 24.

EXAMPLE

Table 1 below summarizes the feed and products obtained according to an example embodiment of the present invention.

TABLE 1

Feed		Product	
Mixed Butanes	12,000 BPD	Tertiary Butyl Methyl Ether	5,800 BPD
Water	500 do.	Secondary Butyl Alcohol	2,500 do.
Methanol	2,300 do.	Tertiary Butyl Alcohol	11,000 do.
C ₄ Olefins	7,500 do.	Total	19,300 do.
Air	—		

ture between 150° and 500°F. and a pressure between 200 and 1000 psig by contacting the liquid isobutane with a catalyst comprising at least one of the elements copper, nickel, cobalt, iron, and manganese. Preferred operating temperatures are between 150° and 400°F. and preferred pressures are between 100 and 500 psig for the oxidation of isobutane to obtain high yields of tertiary butanol. Air or pure oxygen can be used as the oxidant.

In particular, in laboratory experiments at 200°F. and 600 psig, a conversion of 91.7 percent of feed liquid isobutane to tertiary butanol was obtained. The product analysis was as follows:

Isobutane	7.18	weight percent
Water	9.33	weight percent
t-Butanol	81.7	weight percent
t-Butyl Hydroperoxide	0.67	weight percent
Di-t-Butyl Peroxide	0.75	weight percent

Molecular oxygen was used as the oxidant and the reaction was carried out in a Monel reactor which provided copper and nickel catalytic surfaces.

Isobutane can also be oxidized to form mixtures of tertiary butanol and t-butyl hydroperoxide wherein the amount of t-butyl hydroperoxide relative to t-butanol is substantial, i.e., above about one part t-butyl hydroperoxide per seven parts t-butanol. In the process of the present invention, when isobutane is oxidized to form substantial amounts of t-butyl hydroperoxide in addition to the t-butanol formed, it is preferred to convert the t-butyl hydroperoxide by thermal decomposition or to convert it by reaction with an olefin to form additional t-butanol. For example, the t-butyl hydroperoxide can be reacted with propylene to form t-butanol and propylene oxide.

The tertiary butanol produced in zone 18 is withdrawn via line 21 and preferably is blended with ethers and alcohols withdrawn from zones 3 and 6, respectively, to produce a relatively high octane gasoline blending component in line 22. Although any one or more of the respective ether, secondary alcohol and tertiary butanol streams produced in the present invention can advantageously be used as gasoline blending

The 2,300 barrels per day of methanol feed indicated in Table I is fed to etheration zone 3 wherein the methanol is reacted with tertiary olefins present in an olefin-rich stream fed to etheration zone 3 via line 1. The olefin-rich stream contains a minor amount of normal and isobutane and about 67 weight percent of the C₄ olefins is isobutene. Thus, the primary product produced in zone 3 is tertiary butyl methyl ether.

Unreacted linear olefins and paraffins are withdrawn from zone 3 via line 5 and fed to hydration zone 6. In hydration zone 6, the linear olefins are reacted with about 500 barrels per day of water introduced via line 7 to produce about 2,500 barrels per day of secondary butyl alcohol which is withdrawn from zone 6 via line 8. The small amount of butanes present in the feed to etheration zone 3 remain unreacted after etheration zone 3 and hydration zone 6. These butanes are fed to distillation column 11 along with additional mixed butanes fed via lines 10 and 16 to column 11. The additional mixed butane stream introduced via line 10 is withdrawn from various refinery processes including hydrocracking. Distillation column 11 is operated in conjunction with C₄ isomerization zone 14 to produce an isobutane-rich stream which is withdrawn via line 17 from column 11 and fed to partial oxidation zone 18.

Only a relatively small amount of hydrocarbons and oxygenated components less volatile than normal butane are withdrawn via line 12 from the bottom of column 11.

The isobutane withdrawn from the top of column 11 is oxidized in zone 18 to produce approximately 11,000 barrels per day of tertiary butyl alcohol which is withdrawn via line 21. The combined tertiary butyl methyl ether, secondary butyl alcohol and tertiary butyl alcohol is about 19,300 barrels per day. The combined gasoline blending stock of about 19,300 barrels per day has a boiling range of about 130° to 210°F. and a research clear blending octane number of about 110 - 115 in 90 - 95 octane gasoline.

The process of the present invention is particularly advantageous in its flexibility and ability to combine

with basic refinery processing steps such as catalytic cracking, hydrocracking and alkylation.

For example, the basic process of the present invention can be combined with alkylation as follows: A mixed hydrocarbon stream containing, for example, mostly C_4 hydrocarbons such as isobutane, normal butane, isobutene and normal butene is fed to etheration zone 3 via line 1. The isobutene is reacted with methanol introduced to zone 3 via line 2 to produce tertiary butyl methyl ether. Also, a portion of the isobutene is reacted in etheration zone 3 with isopropyl alcohol to produce tertiary butyl isopropyl ether which is a particularly good high octane gasoline blending component. The isopropyl alcohol can be produced in hydration zone 6 from propylene introduced as a separate stream to hydration zone 6. However, according to a preferred embodiment of the present invention, propylene contained in the mixed hydrocarbon feed to etheration zone 3 is used as the reactant to form isopropyl alcohol in hydration zone 6. Because the propylene does not contain a tertiary carbon atom, it does not react to form an ether to any appreciable extent in etheration zone 3 and thus, etheration zone 3 serves to increase the linear olefin (including propylene) content of the mixed hydrocarbon stream originally fed to the etheration zone.

Thus, unreacted linear olefins in the effluent from the etheration zone are passed to hydration zone 6 wherein they are reacted with water to form secondary butyl alcohol, including isopropyl alcohol in those instances when propylene is present in the mixed hydrocarbon feed to the etheration zone.

Preferably, a portion of the linear olefins in the effluent from the etheration zone are fed to an alkylation process such as a sulfuric acid or HF alkylation process to form a high octane gasoline boiling range alkylate. The isobutane fed to the alkylation step can be obtained directly as an outside isobutane stream, but preferably the isobutane is obtained in part from unreacted isobutane present in the effluent from the etheration zone and in part by nC_4 isomerization to increase the iC_4 content of a mixed butane stream.

A portion of the isobutane withdrawn from distillation column 11 via line 17 is fed to partial oxidation zone 18 for production of tertiary butyl alcohol. Particularly in those instances when there is a shortage of isobutene feed for etheration zone 3, it is advantageous in the process of the present invention to dehydrate at least a portion of the tertiary butyl alcohol to form isobutene which is fed to etheration zone 3.

Thus, the oxygenated components which are produced in this embodiment of the present invention include tertiary butyl methyl ether, tertiary butyl isopropyl ether, isopropyl alcohol, secondary butyl alcohol, and tertiary butyl alcohol. One or more of these relatively high octane gasoline blending components can be blended with the alkylate produced in accordance with this preferred embodiment of the present invention to obtain a high octane unleaded gasoline.

Although various embodiments of the invention have been described, it is to be understood that they are meant to be illustrative only and not limiting. Certain features may be changed without departing from the spirit or scope of the invention. It is apparent that the present invention has broad application to the production of gasoline blending stocks in a combination pro-

cess involving etheration, hydration, and partial oxidation. Accordingly, the invention is not to be construed as limited to the specific embodiments or examples discussed but only as defined in the appended claims.

What is claim is:

1. A process for producing a gasoline blending stock which comprises:

- feeding an alcohol and a light hydrocarbon mixture containing at least tertiary olefins, linear olefins and isobutane to an etheration zone,
- reacting the alcohol with the tertiary olefins in the etheration zone to obtain an ether and unreacted linear olefins and isobutane,
- separating the ether from the linear olefins and isobutane,
- feeding water and at least a portion of the linear olefins to a hydration zone,
- reacting the water with the linear olefins in the hydration zone to obtain a product alcohol,
- oxidizing the isobutane to obtain t-butyl alcohol, and
- blending at least portions of the ether, product alcohol and t-butyl alcohol to produce a gasoline blending stock.

2. A process in accordance with claim 1 wherein both the isobutane and linear olefins are fed to the hydration zone and unreacted isobutane is withdrawn from the hydration zone and is oxidized to obtain t-butyl alcohol.

3. A process in accordance with claim 1 wherein the light hydrocarbon mixture also contains n-butane and the n-butane is isomerized to obtain isobutane and at least a portion of the isobutane obtained by isomerization is oxidized to t-butyl alcohol.

4. A process in accordance with claim 1 wherein the light hydrocarbon mixture comprises C_4 - C_5 hydrocarbons obtained from a hydrocarbon cracking process.

5. A process in accordance with claim 4 wherein the C_4 - C_5 hydrocarbons are obtained from fluid catalytic cracking.

6. A process for producing a gasoline blending stock which comprises:

- feeding an alcohol and a C_4 - C_5 cracking effluent stream, containing at least tertiary olefins, linear olefins, isobutane, n-butane and isopentane, to an etheration zone,
- reacting the alcohol with the tertiary olefins in the etheration zone to obtain an ether,
- separating the ether from unreacted linear olefins and paraffins,
- feeding water and the unreacted linear olefins and paraffins to a hydration zone,
- reacting the water with the unreacted linear olefins in the hydration zone and withdrawing a product alcohol and unreacted paraffins from the hydration zone,
- separating the product alcohol from the unreacted paraffins,
- separating the unreacted paraffins into at least isobutane and isopentane,
- oxidizing the isobutane to obtain t-butyl alcohol,
- blending at least a portion of the ether, product alcohol and t-butyl alcohol to produce a gasoline blending stock.

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