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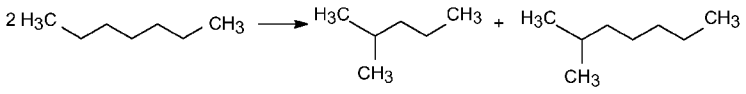


FIG. 1

(57) Abstract: A process for refining naphtha and upgrading butanes is described. The process involves separating a hydrotreated heavy naphtha feed into a C_7 -rich fraction and a C_8+ -rich fraction in a separation zone and then reacting the C_7-rich fraction with C_4 paraffins to form to a low aromatic gasoline blendstock. The C_8+ -rich fraction is sent to a reforming zone to form a reformed product with higher octane and lower RVP than a reformed product derived from heavy naphtha.

WO 2015/164083 A1

COMBINED NAPHTHA REFINING AND BUTANE UPGRADING PROCESS

STATEMENT OF PRIORITY

This application claims priority to U.S. Application No. 14/257,789 which was filed April 21, 2014, the contents of which are hereby incorporated by reference in its entirety.

BACKGROUND OF THE INVENTION

High octane gasoline is required for modern gasoline engines. Previously, it was common to achieve octane number improvement by the use of various lead-containing additives. As lead has been phased out of gasoline for environmental reasons, it has become increasingly necessary to rearrange the structure of the hydrocarbons used in gasoline blending in order achieve higher octane ratings. Catalytic reforming and catalytic isomerization are two widely used processes for this upgrading.

The traditional gasoline blending pool normally includes C_4 and heavier hydrocarbons having boiling points of less than 205°C (400°F) at atmospheric pressure. This range of hydrocarbons includes C_4-C_6 paraffins, and especially the C_5 and C_6 normal paraffins which have relatively low octane numbers. The C_4-C_6 hydrocarbons have the greatest susceptibility to octane improvement by lead addition and were formerly upgraded in this manner. With the phase out of lead additives, octane improvement was obtained by using isomerization to rearrange the structure of the paraffinic hydrocarbons into branched-chain paraffins or reforming to convert the C_6 and heavier hydrocarbons to aromatic compounds. Normal C_5 hydrocarbons are not readily converted into aromatics; therefore, the common practice has been to isomerize these lighter hydrocarbons into corresponding branched-chain isoparaffins. Although the C_6 and heavier hydrocarbons can be upgraded into aromatics through dehydrocyclization, the conversion of C_6 hydrocarbons to aromatics creates higher density species and increases gas yields with both effects leading to a reduction in liquid volume yields. Moreover, the health concerns related to benzene have lead to restrictions on benzene and aromatics. Therefore, it is preferred to change the C_6 paraffins to an isomerization unit to obtain C_6 isoparaffin hydrocarbons. Consequently, octane upgrading commonly uses isomerization to convert C_6 and lower boiling hydrocarbons.

The Reid vapor pressure (RVP) of gasoline has been utilized by the Environmental Protection Agency as a means of regulating volatile organic compounds emissions by transportation fuels and for controlling the formation of ground level ozone. As these regulations become more stringent and as more ethanol (which has a high vapor pressure) is blended into gasoline, C_5 paraffins need to be removed from the gasoline pool. Moreover, the need to remove components may also extend to some C_6 paraffins. This may result in refiners being oversupplied with C_5 paraffins and possibly C_6 paraffins, forcing them to sell these products at prices lower than gasoline blendstock.

Commercial refiners face a number of problems utilizing hydrocarbons with molecular weights less than 90 in gasoline. Some refiners are limited in the amount of light naphtha, particularly pentanes, they can add to gasoline in the summer months because of more stringent regulations on vapor pressure. In addition, some refiners cannot blend all of the high octane reformate they produce into gasoline because of new regulations limiting the total aromatics to 35 vol%. The growth of shale crude oil production has increased the amount of low value butanes and pentanes produced in refineries. Finally, some refiners need to purchase isobutane as feedstock for C_3 and C_4 olefin conversion to gasoline in existing alkylation units.

Therefore, there is a need for processes which allow better utilization of heavy naphtha in refineries.

SUMMARY OF THE INVENTION

One aspect of the invention is a process for refining naphtha and upgrading butanes. In one embodiment, a hydrotreated heavy naphtha feed is separated into a C_7 –rich fraction and a C_8+ –rich fraction in a separation zone. The C_7 –rich fraction is introduced into a reaction zone, and a stream comprising C_4 paraffins is also introduced into the reaction zone. A first portion of the C_7 –rich fraction is disproportionated by contacting the first portion of the C_7 –rich fraction with a catalyst in the reaction zone and a second portion of the C_7 –rich fraction and the C_4 paraffins are reverse disproportionated by contacting the second portion of the C_7 –rich fraction and the C_4 paraffins with the catalyst in the reaction zone under reaction conditions suitable for disproportionation and reverse disproportionation to form a reaction product mixture. The reaction product mixture is separated in a second

separation zone into at least a C_{3-} -rich stream, an iso-C_4 -rich stream, and a C_{6+} -rich stream. The C_{6+} -rich stream is introduced into a hydrocarbon pool.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 illustrates the disproportionation reaction of a normal heptane paraffin.

Fig. 2 illustrates the reverse disproportionation reaction of n-butane and n-heptane.

Fig. 3 illustrates one embodiment of a disproportionation and reverse disproportionation process.

DETAILED DESCRIPTION OF THE INVENTION

The present invention meets this need by providing a process for gasoline refineries. The process involves separating a heavy naphtha feed into a C_7 –rich fraction and a C_8+ –rich fraction. The C_7 –rich fraction and butanes are reverse disproportionated to a product mixture comprising, C_{5-}, and C_{6+} hydrocarbons. The isohexane-rich product has good octane and a lower RVP than pentane. In some cases, the process also produces an isopentane-rich co-product. The process forms primarily isoparaffins, and very few naphthenes, aromatics, and alkenes are formed. The C_{8+} –rich fraction can be reformed in a reforming zone to form a higher octane reformed products.

The process also forms an isobutane-rich product which can be converted to low RVP gasoline blendstock by reaction with propylenes and butenes in a downstream alkylation unit.

The disproportionation of paraffins (e.g., n-heptane (n-C_7)) involves reacting two moles of hydrocarbon to form one mole each of two different products, one having a carbon count greater than the starting material and the other having a carbon count less than the starting material (e.g., hexane and octane), as shown in Fig. 1. The total number of moles in the system remains the same throughout the process, but the products have different carbon counts from the reactants.

The microscopic reverse of heptane disproportionation is the combination of one mole of octane and one mole of hexane to form two moles of heptane. This type of reaction is referred herein as reverse disproportionation. Reverse disproportionation-type

reactions can occur in which two paraffins having different carbon numbers react to form two different paraffins having different carbon numbers from those of the feed where the total number of product and moles of carbon and hydrogen in the products does not change from the total number in the feed (e.g., pentane and octane reacting to form hexane and heptane). These reactions are sometimes referred to as comproportionation or molecular averaging reactions. These paraffin rearrangements have also been called alkane metathesis. The use of any of these terms is meant to illustrate that paraffins can react with other paraffins to form additional paraffins different from the original feed. Another example of reverse disproportionation involves heptane and butane reacting to form pentane and hexane, as illustrated in Fig. 2. Utilizing the equilibrium among the various species, the concentration of the product can be controlled by varying the relative ratios of the species. Consequently, two different paraffinic feed sources of varying carbon count can be reacted to obtain a product containing paraffins of intermediate carbon count

Fig. 3 illustrates the disproportionation and reverse disproportionation process 100 which involves upgrading butanes to C_{5+} hydrocarbons. This process also can reduce the amount of feed going to the reformer. It also can result in a lower fraction of aromatics in the refinery gasoline pool.

A hydrotreated heavy naphtha feed 105 is used. Heavy naphtha is a hydrocarbon mixture typically comprising seven, eight and nine carbon hydrocarbon molecules with the majority of the hydrocarbon molecules being saturates as opposed to unsaturates. Heavy naphtha is often defined by a nominal boiling point range of 71°C (160°F) to 204°C (400°F), or 82°C (180°F) to 204°C (400°F), or 93°C (200°F) to 182°C (360°F). Carbon chain length can extend from C_6-C_{10} in the broadest sense depending on how the distillation column operates.

The hydrotreated heavy naphtha feed can be formed by separating a full range hydrotreated naphtha feed into a light naphtha stream and a heavy naphtha stream in a naphtha splitter, for example. Hydrotreated full range naphtha is a hydrocarbon mixture typically comprising five, six, seven, eight and nine carbon hydrocarbon molecules with the majority of the hydrocarbon molecules being saturates as opposed to unsaturates. It typically has less than 10 wt-ppm sulfur and less than 1 wt-ppm nitrogen. Full range naphtha is often defined by a nominal boiling point range 21°C (70°F) to 204°C (400°F), or 27°C (80°F) to

182°C (360°F). Carbon chain length can extend from C_4-C_{10} in the broadest sense depending on how the distillation column operates.

The hydrotreated heavy naphtha feed 105 is sent to a separation zone 110 where it is separated into a C_7 –rich fraction 115 and a C_{8+} -rich fraction 120. The separation can take place in a heavy naphtha splitter, for example.

The C_{8+} -rich fraction 120 (e.g., with a boiling point range of 99°C (210°F) to 204°C (400°F)), which can include some aromatic compounds, can be sent to a reformer for further processing as discussed below, and the reformate can be sent to a hydrocarbon pool, such as a gasoline pool.

The C_7 –rich fraction (e.g., with a boiling point range of 82°C (180°F) to 99°C (210°F))115 is sent to reaction zone 125. A stream 130 comprising C_4 paraffins is also introduced into the reaction zone 125. The C_4 paraffins can include n-C_4 paraffins, iso-C_4 paraffins, or mixtures thereof. In some embodiments, a liquid catalyst stream 132 is also introduced into the reaction zone 125. In other embodiments, the catalyst will be contained in the reaction zone.

A portion of the C_7 –rich fraction is contacted with a catalyst in the reaction zone 125 and disproportionated. The C_4 paraffins and at least a second portion of the C_7 –rich fraction are contacted with the catalyst in the reaction zone 125 and reverse disproportionated. By a portion of the C_7 –rich fraction we mean that some of the C_7 –rich fraction reacts in the stated way. The portions are not physically separated. There will also be some disproportionation of the C_4 paraffins. In addition, other reactions will occur, such as isomerization of the various paraffins. If the C_4 paraffins are present in excess of their equilibrium amount, equilibrium favors the reverse disproportionation reaction.

The molar ratio of C_4 to C_7 is at least 0.055, or at least 0.1, or at least 0.2, or at least 0.5, or at least 0.75, or at least 1, or at least 5, or at least 10, or at least 15. As the C_4 to C_7 ratio increases, additional butanes are consumed and the reaction product becomes richer in pentanes and hexanes. If the ratio is too low, C_4 paraffins will be generated by disproportionation of C_7.

Where a liquid catalyst is used, a spent liquid catalyst stream 134 is removed from the reaction zone 125. It can be regenerated and recycled to the reaction zone 125.

The reaction mixture 135 includes the disproportionation products and reverse disproportionation products. The reaction mixture 135 is separated in a second separation zone 140 into at least a C_{3-}-rich stream 145, an iso-C_4-rich stream 150, and a C_{6+} -rich stream 155. Additional product streams can be taken, if desired. One example of a suitable separation process is distillation.

When a liquid catalyst is used, the liquid catalyst is also present in the reaction mixture. The liquid catalyst can be separated from the reaction mixture by phase separation due to the density difference between the hydrocarbons and the liquid catalyst before separation into the various hydrocarbon streams.

The C_{3-} -rich stream 145 can be recovered and further processed. The C_{3-}-rich stream can be used in a variety of processes. It can be used as a refinery fuel instead of natural gas. Alternatively, it could be purified and recovered as a high purity liquid propane product. It could be used as a feedstock for a hydrogen plant. It could also be used as a feedstock for a chemical plant, such as an ethylene cracker, although this would be less common.

The iso-C_4-rich stream 150 can be recovered. In some embodiments, a portion 160 of the iso-C_4-rich stream 150 is recycled to reaction zone 125 and used in the reverse disproportionation reaction. The iso-C_4-rich product can be used in alkylate production as discussed below

In some embodiments, a n-C_4-rich stream is recovered and recycled to the reaction zone 125 (not shown).

The C_{6+} -rich stream 155 is sent to the hydrocarbon pool, such as a gasoline pool.

In some embodiments, the reaction mixture 135 is separated into at least a C_{3-} -rich stream 145, an iso-C_4-rich stream 150, a C_{6+} -rich stream 155, and a C_5 –rich stream 165, which can be recovered. In some embodiments, a portion 170 of the C_5 –rich stream 165 is mixed with the C_{6+} -rich stream 155 and sent to the hydrocarbon pool. In some embodiments, all or a portion of the C_5-rich stream 165 could be recycled to the reaction zone 125 (not shown). Alternatively, all or a portion of the C_5-rich stream 165 could be recovered and used a feedstock for a chemical plant.

If a separate C_5 –rich stream is not recovered, the C_5 hydrocarbons will be included in the C_{6+} –rich stream.

In some embodiments, the vapor pressure of the C_{6+} –rich stream can be controlled by controlling the amount of the C_5 –rich stream included in the C_{6+} -rich stream. By forming a separate C_5 –rich stream and mixing only a portion of the C_5 –rich stream (or none) with the C_{6+} –rich stream, the vapor pressure can be controlled as needed.

In some embodiments, the gasoline product yield can be maximized by mixing at least a portion of the C_5 –rich stream with the C_{6+} -rich stream.

The iso-C_4-rich stream and at least one olefin containing stream (containing olefins such as an ethylene, propylene, or butene stream, or mixtures thereof) can be introduced into an alkylation reaction zone to produce additional gasoline blendstock.

Suitable reaction conditions include a temperature of 200°C or less, or 175°C or less, or 150°C or less, or 125°C or less, or 100°C or less, or 90°C or less, or 80°C or less, or 70°C or less, or 60°C or less, or in the range of 0°C to 200°C, or 0°C to 175°C, or 0°C to 150°C, or 10°C to 150°C , or 25°C to 150°C, or 30°C to 150°C, or 40°C to 150°C, or 50°C to 150°C , or 55°C to 150°C.

The pressure in the reaction zone is typically in the range of 0 MPa to 13.8 MPa, or 0 MPa to 8.1 MPa, or 0 MPa to 5 MPa, or 0 MPa to 3.5 MPa. The pressure should be sufficient to ensure that the reaction product is in a liquid state. Small amounts of vapor may also be present, but this should be minimized.

The reaction can take place in the presence of a gas. Suitable gases include, but are not limited to methane, ethane, propane, hydrogen, hydrogen chloride, nitrogen, and the like.

The residence time in the reaction zone is generally less than 12 hr, or less than 10 hr, or less than 7 hr, or less than 5 hr, or less than 4 hr, or less than 3 hr, or less than 2 hr, or less than 1 hr. The reaction time can be selected so that a predetermined conversion can be obtained. When the catalyst is an ionic liquid, the reaction time is a function of the degree of mixing, and the reaction temperature. Where a liquid catalyst is used, the reaction time is also a function of the concentration of the carbocation promoter (if present), the molar ratio of the catalyst promoter (if present) to liquid catalyst, and the mass/volume ratio of

liquid catalyst to hydrocarbon being reacted. Generally, increasing any of these conditions will increase the reaction rate.

When a liquid catalyst is used, the reaction will proceed simply by contacting the hydrocarbon feed and the liquid catalyst, the reaction rate is generally too slow to be commercially viable. When mass transfer rate is controlling, the reaction rate can be substantially increased by increasing the mixing intensity of hydrocarbon feed and liquid catalyst. After a certain point, increasing the mixing intensity will not provide any additional benefit. Mixing intensity can be controlled using pumps, flow configurations, and baffles. Baffles help to prevent a vortex from forming in the reactor, which would reduce the amount of mixing.

The contacting step may be practiced in laboratory scale experiments through full scale commercial operations. The process may be operated in batch, continuous, or semi-continuous mode. The contacting step can take place in various ways, with both concurrent and co-current flow processes being suitable. The order of addition of the reactants may not always be critical. For example, the reactants can be added individually, or some reactants may be combined or mixed before being combined or mixed with other reactants.

Suitable catalysts include, but are not limited to, HF, sulfated zirconias, $AlCl_2/SiO_2$, zeolites, ionic solids, platinum on chlorided Al_2O_3/Ga_2O_3 supports, supported ionic liquids, $Pt/W/Al_2O_3$, HF/TiF_4, ionic liquids, or combinations thereof.

If the catalyst is an ionic liquid, when the ionic liquid catalyst is separated from the reaction product mixture, it can include deactivated catalyst after being used in the process. The ionic liquid catalyst can become deactivated as a result of the buildup of a heavy hydrocarbon, which will be referred to as conjunct polymer herein. This conjunct polymer is a byproduct of the disproportionation and reverse disproportionation reactions. The deactivated catalyst can be regenerated using any known regeneration process. Suitable regeneration methods include, but are not limited to the following. The ionic liquid containing the conjunct polymer could be contacted with a reducing metal (e.g., Al), an inert hydrocarbon (e.g., hexane), and hydrogen and heated to 100°C. The deactivating polymer will be transferred to the hydrocarbon phase, allowing for the conjunct polymer to be removed from the ionic liquid phase. See e.g., US 7,651,970; US 7,825,055; US 7,956,002;

and US 7,732,363. Another method involves contacting the ionic liquid containing the conjunct polymer with a reducing metal (e.g., Al) in the presence of an inert hydrocarbon (e.g. hexane) and heating to 100°C. The conjunct polymer will be transferred to the hydrocarbon phase, allowing for the conjunct polymer to be removed from the ionic liquid phase. See e.g., US 7,674,739 B2. Still another method of regenerating the ionic liquid involves contacting the ionic liquid containing the conjunct polymer with a reducing metal (e.g., Al), HCl, and an inert hydrocarbon (e.g. hexane), and heating to 100°C. The conjunct polymer will be transferred to the hydrocarbon phase, allowing for the conjunct polymer to be removed from the IL phase. See e.g., US 7,727,925. The ionic liquid can be regenerated by adding a homogeneous metal hydrogenation catalyst (e.g., $(PPh_3)_3RhCl$) to the ionic liquid containing the conjunct polymer and an inert hydrocarbon (e.g. hexane). Hydrogen would be introduced, and the conjunct polymer would be reduced and transferred to the hydrocarbon layer. See e.g., US 7,678,727. Another method for regenerating the ionic liquid involves adding HCl, isobutane, and an inert hydrocarbon to the ionic liquid containing the conjunct polymer and heating to 100°C. The conjunct polymer would react to form an uncharged complex, which would transfer to the hydrocarbon phase. See e.g., US 7,674,740. The ionic liquid could also be regenerated by adding a supported metal hydrogenation catalyst (e.g. Pd/C) to the ionic liquid containing the conjunct polymer and an inert hydrocarbon (e.g. hexane). Hydrogen would be introduced and the conjunct polymer would be reduced and transferred to the hydrocarbon layer. See e.g., US 7,691,771. Still another method involves adding a suitable substrate (e.g. pyridine) to the ionic liquid containing the conjunct polymer. After a period of time, an inert hydrocarbon would be added to wash away the liberated conjunct polymer. The ionic liquid precursor [1-butyl-1-methylpyrrolidinium][Cl] would be added to the ionic liquid (e.g. [1-butyl-1-methylpyrrolidinium][Al2Cl7]) containing the conjunct polymer followed by an inert hydrocarbon. After a given time of mixing, the hydrocarbon layer would be separated, resulting in a regenerated ionic liquid. The solid residue would be converted to ionic liquid by adding $AlCl_3$. See e.g., US 7,737,363 and US 7,737,067. Another method involves adding the ionic liquid containing the conjunct polymer to a suitable substrate (e.g. pyridine) and an electrochemical cell containing two aluminum electrodes and an inert hydrocarbon. A voltage would be applied and the current measured to determine the extent of reduction. After a given time, the inert hydrocarbon would be separated, resulting in a regenerated ionic liquid. See, e.g., US 8,524,623.

In some embodiments, after the ionic liquid has been regenerated, a carbocation promoter is added to the regenerated ionic liquid so the liquid catalyst can be recycled to the reaction zone.

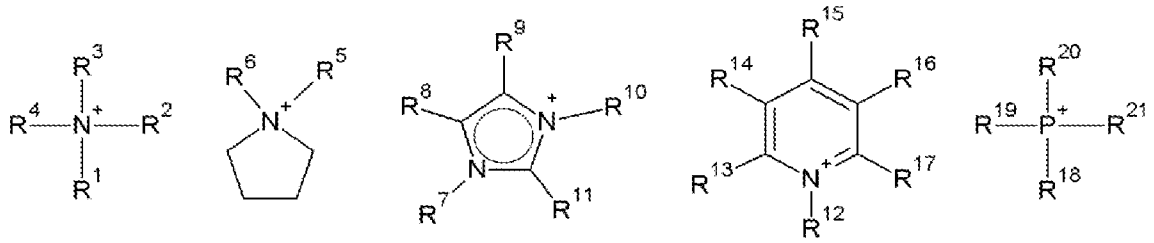
The molar ratio of the carbocation promoter to the ionic liquid in the liquid catalyst is typically in the range of 0:1 to 3:1, or 0.1:1 to 1:1. This relates to forming the carbocation promoter from the halo-alkane or mineral acid. This ratio is important relative to the specific type of anion. For example, if the anion is $AlCl_4^-$, a reaction is unlikely to occur or will be poor because the aluminum is fully coordinated. However, if the anion is $Al_2Cl_7^-$, there is some aluminum present that can coordinate to the carbocation promoter's anion, assisting in generating the carbocation from the carbocation promoter.

When an ionic liquid catalyst is used, the mass or volume ratio of liquid catalyst (ionic liquid and carbocation promoter) to hydrocarbon feed is typically less than 1:1. This is desirable because the ionic liquid is an expensive component in the process. In some embodiments, the mass ratio of ionic liquid to hydrocarbon feed is not more than 0.75:1, or not more than 0.7:1, or not more than 0.65:1, or not more than 0.60:1, or not more than 0.55:1, or not more than 0.50:1. In some embodiments, the volume ratio of ionic liquid to hydrocarbon feed is not more than 0.8:1, or not more than 0.7:1, or not more than 0.6:1, or not more than 0.5:1, or not more than 0.45:1, or not more than 0.4:1, or not more than 0.35:1, or not more than 0.3:1, or not more than 0.25:1. In some embodiments, the mass or volume ratios of liquid catalyst to hydrocarbon feed can be 1:1 or more.

When an ionic liquid catalyst is used, there can be one or more ionic liquids in the liquid catalyst.

In some embodiments, the liquid catalyst comprises an ionic liquid and a carbocation promoter. The ionic liquid is in liquid form. In some embodiments, it is not supported on an oxide support. In addition, in some embodiments, the ionic liquids do not contain Brønsted acids, so the acid concentration within these systems is less than prior art processes using ionic liquids which are Brønsted acidic organic cations. In some embodiments, the acid concentration is less than 2.5 M, or less than 2.25 M, or less than 2.0 M, or less than 1.75 M, or less than 1.5 M.

The ionic liquid comprises an organic cation and an anion. Suitable organic cations include, but are not limited to:



where R^1-R^{21} are independently selected from C_1-C_{20} hydrocarbons, C_1-C_{20} hydrocarbon derivatives, halogens, and H. Suitable hydrocarbons and hydrocarbon derivatives include saturated and unsaturated hydrocarbons, halogen substituted and partially substituted hydrocarbons and mixtures thereof. C_1-C_8 hydrocarbons are particularly suitable.

The anion can be derived from halides, sulfates, bisulfates, nitrates, sulfonates, fluoroalkanesulfonates, and combinations thereof. The anion is typically derived from metal and nonmetal halides, such as metal and nonmetal chlorides, bromides, iodides, fluorides, or combinations thereof. Combinations of halides include, but are not limited to, mixtures of two or more metal or nonmetal halides (e.g., $AlCl_4^-$ and BF_4^-), and mixtures of two or more halides with a single metal or nonmetal (e.g., $AlCl_3Br^-$). In some embodiments, the metal is aluminum, with the mole fraction of aluminum ranging from $0 < Al < 0.25$ in the anion. Suitable anions include, but are not limited to, $AlCl_4^-$, $Al_2Cl_7^-$, $Al_3Cl_{10}^-$, $AlCl_3Br^-$, $Al_2Cl_6Br^-$, $Al_3Cl_9Br^-$, $AlBr_4^-$, $Al_2Br_7^-$, $Al_3Br_{10}^-$, $GaCl_4^-$, $Ga_2Cl_7^-$, $Ga_3Cl_{10}^-$, $GaCl_3Br^-$, $Ga_2Cl_6Br^-$, $Ga_3Cl_9Br^-$, $CuCl_2^-$, $Cu_2Cl_3^-$, $Cu_3Cl_4^-$, $ZnCl_3^-$, $FeCl_3^-$, $FeCl_4^-$, $Fe_3Cl_7^-$, PF_6^-, and BF_4^-.

The ionic liquid is typically combined with one or more carbocation promoters. In some embodiments, the carbocation promoter is added to the ionic liquid. In other embodiments, the carbocation promoter is generated in situ. However, in situ production might not provide reproducible results if it is not controlled.

Suitable carbocation promoters include, but are not limited to, halo-alkanes, mineral acids alone or combined with alkenes, and combinations thereof. Suitable halo-alkanes include but are not limited to 2-chloro-2-methylpropane, 2-chloropropane, 2-chlorobutane, 2-chloro-2-methylbutane, 2-chloropentane, 1-chlorohexane, 3-chloro-3-

methylpentane, perchloroethylene, hydrogen chloride, or combinations thereof. In some embodiments, the carbocation promoter is not a cyclic alkane.

Suitable mineral acids include, but are not limited to, HCl, HBr, H_2SO_4, and HNO_3. Although HF can also be used, it is less desirable due to safety issues. If the mineral acid is not strong enough to protonate off a hydrogen from a C-H bond, isobutene or another alkene can be added with the mineral acid to produce the desired carbocation promoter. The mineral acid can be generated in situ by the addition of a compound that reacts with the ionic liquid. In situ acid generation can also occur as a result of reaction with water present in the system. The mineral acid may also be present as an impurity in the ionic liquid.

The C_{8+} -rich fraction can be sent to a reforming zone. The reforming zone upgrades the octane number of the reforming feed stream through a variety of reactions including naphthene dehydrogenation and paraffin dehydrocyclization and isomerization.

Reforming operating conditions may include a pressure of from atmospheric to 6080 kPa(a), with the preferred range being from atmospheric to 2026 kPa(a) and a pressure of below 1013 kPa(a) being especially preferred. Hydrogen is generated within the reforming zone, but additional hydrogen may be directed, if necessary, to the reforming zone in an amount sufficient to correspond to a ratio of from 0.1 to 10 moles of hydrogen, both generated and added, per mole of hydrocarbon feedstock. The volume of the contained reforming catalyst corresponds to a liquid hourly space velocity of from 1 to 40 hr^{-1}. The operating temperature generally is in the range of 260° to 560°C.

Reforming catalysts may comprise a supported platinum-group metal component which comprises one or more platinum-group metals, with a platinum component being preferred. An illustrative platinum component generally comprises from 0.01 to 2 mass % of the catalytic composite, preferably 0.05 to 1 mass %, calculated on an elemental basis. Reforming catalysts may contain other metal components known to modify the effect of the preferred platinum component. Such metal modifiers may include Group IVA (14) metals, other Group VIII (8-10) metals, rhenium, indium, gallium, zinc, uranium, dysprosium, thallium and mixtures thereof. A preferred metal modifier is a tin component. Catalytically effective amounts of such metal modifiers may be incorporated into the catalyst by any means known in the art.

The reforming catalyst may be a dual-function composite containing a metallic hydrogenation-dehydrogenation component on a refractory support which provides acid sites for cracking and isomerization. The refractory support of the reforming catalyst should be a porous, adsorptive, high-surface-area material which is uniform in composition without composition gradients of the species inherent to its composition. Examples of suitable refractory supports are those containing one or more of: (1) refractory inorganic oxides such as alumina, silica, titania, magnesia, zirconia, chromia, thoria, boria or mixtures thereof; (2) synthetically prepared or naturally occurring clays and silicates, which may be acid-treated; (3) crystalline zeolitic aluminosilicates, either naturally occurring or synthetically prepared such as FAU, MEL, MFI, MOR, MTW (IUPAC Commission on Zeolite Nomenclature), in hydrogen form or in a form which has been exchanged with metal cations; (4) non-zeolitic molecular sieves as disclosed in US 4,741,820, incorporated by reference; (5) spinels such as $MgAl_2O_4$, $FeAl_2O_4$, $ZnAl_2O_4$, $CaAl_2O_4$; and (6) combinations of materials from one or more of these groups.

Reforming catalysts may optimally contain a halogen component. The halogen component may be fluorine, chlorine, bromine or iodine or mixtures thereof. Chlorine is the preferred halogen component.

The reforming catalyst may comprise a large-pore molecular sieve such as a molecular sieve having an effective pore diameter of 7 angstroms or larger. Examples of large-pore molecular sieves which might be incorporated into the present catalyst include LTL, FAU, AFI and MAZ (IUPAC Commission on Zeolite Nomenclature) and zeolite-beta. Or, the reforming catalyst may contain a nonacidic L-zeolite (LTL) and an alkali-metal component as well as a platinum-group metal component. It is often necessary to composite the L-zeolite with a binder in order to provide a convenient form. Any refractory inorganic oxide binder is suitable. One or more of silica, alumina or magnesia may be preferred binder materials. The L-zeolite and binder may be composited to form the desired catalyst shape by any method known in the art. An alkali metal component is part of the alternative reforming catalyst. One or more of the alkali metals, including lithium, sodium, potassium, rubidium, cesium and mixtures thereof, may be used, with potassium being preferred. The alkali metal optimally will occupy essentially all of the cationic exchangeable sites of the nonacidic L-zeolite.

The iso-C_4-rich product can be sent to an alkylation zone. Alkylation is typically used to combine light olefins, for example mixtures of alkenes such as propylene

and butylene, with isobutane to produce a relatively high-octane branched-chain paraffinic hydrocarbon fuel, including isoheptane and isooctane. Similarly, an alkylation reaction can be performed using an aromatic compound such as benzene in place of the isobutane. When using benzene, the product resulting from the alkylation reaction is an alkylbenzene (e.g. toluene, xylenes, ethylbenzene, etc.). For isobutene alkylation, typically, the reactants are mixed in the presence of a strong acid catalyst, such as sulfuric acid or hydrofluoric acid. The alkylation reaction is carried out at mild temperatures, and is typically a two-phase reaction. Because the reaction is exothermic, cooling is needed. Depending on the catalyst used, normal refinery cooling water provides sufficient cooling. Alternatively, a chilled cooling medium can be provided to cool the reaction. The catalyst protonates the alkenes to produce reactive carbocations which alkylate the isobutane reactant, thus forming branched chain paraffins from isobutane. Aromatic alkylation is generally now conducted with solid acid catalysts including zeolites or amorphous silica-aluminas.

The alkylation reaction zone is maintained at a pressure sufficient to maintain the reactants in liquid phase. For a hydrofluoric acid catalyst, a general range of operating pressures is from 200 to 7100 kPa absolute. The temperature range covered by this set of conditions is from -20°C to 200°C. For at least alkylation of aromatic compounds, the volumetric ratio of hydrofluoric acid to the total amount of hydrocarbons entering the reactor should be maintained within the broad range of from 0.2:1 to 10:1, preferably from 0.5:1 to 2:1

Any suitable alkylation catalyst may be used. Typically, the catalysts are acidic. Suitable alkylation catalysts include, but are not limited to, hydrofluoric acid, sulfuric acid and acidic ionic liquids. Other catalysts include zeolites having a zeolite framework type selected from the groups consisting of beta, MOR, MWW, FAU and NES. Suitable zeolites include mordenite, ZSM-4, ZSM-12, ZSM-20, offretite, gmelinite, beta, NU-87, UZM-8, MCM-22, MCM-36, MCM-49, zeolite Y, zeolite X, and gottardite. Another class of acidic, solid catalysts are acidified refractory oxides such as chlorided, fluorided, or sulfated alumina, gallia, boria, molybdia, ytterbia, titania, chromia, silica, zirconia, and the like and combinations thereof. Clays and amorphous catalysts may also find utility. Further discussion of alkylation catalysts can be found in U.S. Pat. Nos. 5,196,574; 6,315,964B1 and 6,617,481B1. Newer alkylation catalysts can also be used in this process. For example, one

such catalyst comprises a mixture of two types of zeolitic materials, where the zeolites are mixed and produced to have two zeolites within a single catalyst pellet. With the new catalysts, the first zeolite is also characterized by its acidity, wherein the acidity is characterized by having less than 70% of NH_3 desorption off the zeolite at temperatures greater than 400°C. An example of the first zeolite is UZM-8. The second zeolite having a silica to alumina molar ratio less than 8, and includes a rare earth element incorporated into the zeolitic framework in an amount greater than 16.5 wt %. The first zeolite component is in an amount between 10 and 90% by weight of the catalyst, and the second zeolite component is in an amount between 10 and 90% by weight. The zeolites are intermingled into single catalyst particles. An example of the second zeolite is a rare earth substituted X zeolite, Y zeolite, or a zeolite having an EMT/FAU intergrowth. The incorporation of rare earth exchanged ions in a low ratio zeolite reduces the acidity due to an increase in the number of framework alumina at low ratios, and also reduces geometric space in the supercage.

Example

A refinery model was used to estimate the yields that could be achieved when processing a feedstock composed of 50 wt-% butanes and 50 wt-% heptanes at reverse disproportionation conditions that included a pressure of 2.8 MPa(g) (400 psig), a temperature of 100°C, and a residence time of greater than 4 hours using an ionic liquid catalyst. To maximize the combined yield of C6+ blendstock and iC4 for use as alkylation feedstock, the normal butane and pentane co-products produced by the process were recovered and recycled to the reactor. The mass ratio of recycle flow to feedstock was 0.5. Sufficient mechanical mixing was assumed to allow the reactants to approach an equilibrium product mixture. The resultant process mass balance is illustrated in Table 1 below.

Table 1 – Estimated Process Mass Balance

Feed	Wt-%
nC4	50
nC7	50
Products	

C3-	3.0
iC4	40.0
nC4	0.1
C5	0.2
C6+	56.7

SPECIFIC EMBODIMENTS

While the following is described in conjunction with specific embodiments, it will be understood that this description is intended to illustrate and not limit the scope of the preceding description and the appended claims.

A first embodiment of the invention is a process for refining naphtha and upgrading butanes comprising separating a hydrotreated heavy naphtha feed into a C7 –rich fraction and a C8+ –rich fraction in a separation zone; introducing the C7 –rich fraction into a reaction zone; introducing a stream comprising C4 paraffins into the reaction zone; disproportionating a first portion of the C7 –rich fraction by contacting the first portion of the C7 –rich fraction with a catalyst in the reaction zone and reverse disproportionating a second portion of the C7 –rich fraction and the C4 paraffins by contacting the second portion of the C7 –rich fraction and the C4 paraffins with the catalyst in the reaction zone under reaction conditions suitable for disproportionation and reverse disproportionation to form a reaction product mixture; separating the reaction product mixture in a second separation zone into at least a C3- -rich stream, an iso-C4 -rich stream, and a C6+ -rich stream; and introducing the C6+ -rich stream into a hydrocarbon pool. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph further comprising reforming the C8+ –rich fraction in a reforming zone to form a higher octane reformed product and introducing the reformed product into the hydrocarbon pool. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein separating the reaction product mixture comprises separating the reaction product mixture into at least the C3- -rich stream, the iso-C4 -rich stream, a C5 –rich stream, and the C6+ -rich stream. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first

embodiment in this paragraph further comprising controlling a vapor pressure of the C6+ –rich stream by recovering at least a portion of the C5 –rich stream. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph further comprising maximizing a gasoline product yield by mixing at least a portion of the C5 –rich stream with the C6+ -rich stream. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph further comprising recycling at least a portion of the C5 –rich stream to the reaction zone. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the reaction conditions include a temperature of less than 200°C. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph further comprising introducing the iso-C4 –rich stream and at least one olefin containing stream into an alkylation reaction zone to produce low vapor pressure, high octane gasoline blendstock. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein a molar ratio of C4 to C7 is at least 0.055. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph further comprising recycling at least a portion of the iso-C4 -rich stream to the reaction zone. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein at least one of the first or second catalyst comprises HF, sulfated zirconias, AlCl2/SiO2, zeolites, ionic solids, platinum on chlorided Al2O3/Ga2O3 supports, supported ionic liquids, Pt/W/Al2O3, HF/TiF4, an ionic liquid, or combinations thereof. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, wherein the catalyst is a liquid catalyst comprising an ionic liquid and a carbocation promoter. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the ionic liquid comprises an organic cation and an anion, and wherein the organic cation is selected from the group consisting of where R1-R21 are independently selected from C1-C20 hydrocarbons, C1-C20 hydrocarbon derivatives, halogens, and H. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the ionic liquid comprises an organic cation and an anion, and wherein the

anion is derived from halides, sulfates, bisulfates, nitrates, sulfonates, fluoroalkanesulfonates, or combinations thereof. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the carbocation promoter comprises halo-alkanes, mineral acids, alkenes, or combinations thereof. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph further comprising mechanically mixing while contacting the C7 –rich fraction with the catalyst and while contacting the C7 –rich and the C4 paraffins with the catalyst. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph further comprising separating the catalyst from the reaction product mixture before separating the reaction product mixture; regenerating the separated catalysts; optionally, adding a carbocation promoter to the regenerated catalyst; and recycling at least a portion of the regenerated catalyst to the reaction zone. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein a mass ratio of the catalyst to the C7 fraction and the butanes is less than 0.751. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the hydrotreated heavy naphtha feed is formed by separating a full range hydrotreated naphtha feed into a hydrotreated light naphtha stream and the hydrotreated heavy naphtha feed.

A second embodiment of the invention is a process for refining naphtha and upgrading butanes comprising separating a hydrotreated heavy naphtha feed into a C7 –rich fraction and a C8+ –rich fraction in a separation zone; introducing the C7 –rich fraction into a reaction zone; introducing a stream comprising C4 paraffins into the reaction zone; disproportionating a first portion of the C7 –rich fraction by contacting the first portion of the C7 –rich fraction with a liquid catalyst in the reaction zone and reverse disproportionating a second portion of the C7 –rich fraction and the C4 paraffins by contacting the second portion of the C7 –rich fraction and the C4 paraffins with the liquid catalyst in the reaction zone under reaction conditions suitable for disproportionation and reverse disproportionation to form a reaction product mixture, wherein the liquid catalyst comprises an ionic liquid and a carbocation promoter; separating the liquid catalyst from the reaction product mixture; separating the reaction mixture in a second separation zone into at least a C3- -rich stream, an

iso-C4 -rich stream, and a C6+ -rich stream; introducing the C6+ -rich stream into a hydrocarbon pool; and reforming the C8+ –rich fraction in a reforming zone to form a reformed product and introducing the reformed product into the hydrocarbon pool.

While at least one exemplary embodiment has been presented in the foregoing detailed description of the invention, it should be appreciated that a vast number of variations exist. It should also be appreciated that the exemplary embodiment or exemplary embodiments are only examples, and are not intended to limit the scope, applicability, or configuration of the invention in any way. Rather, the foregoing detailed description will provide those skilled in the art with a convenient road map for implementing an exemplary embodiment of the invention. It being understood that various changes may be made in the function and arrangement of elements described in an exemplary embodiment without departing from the scope of the invention as set forth in the appended claims.

CLAIMS

1. A process for refining naphtha and upgrading butanes comprising:

separating a hydrotreated heavy naphtha feed (105) into a C_7 –rich fraction (115) and a C_8+ –rich fraction (120) in a separation zone (110);

introducing the C_7 –rich fraction (115) into a reaction zone (120);

introducing a stream (130) comprising C_4 paraffins into the reaction zone (125);

disproportionating a first portion of the C_7 –rich fraction (115) by contacting the first portion of the C_7 –rich fraction (115) with a catalyst in the reaction zone (125) and reverse disproportionating a second portion of the C_7 –rich fraction (115) and the C_4 paraffins by contacting the second portion of the C_7 –rich fraction (115) and the C_4 paraffins with the catalyst in the reaction zone (125) under reaction conditions suitable for disproportionation and reverse disproportionation to form a reaction product mixture (135);

separating the reaction product mixture (135) in a second separation zone (140) into at least a C_{3-} -rich stream (145), an iso-C_4 -rich stream (150), and a C_{6+} -rich stream (155); and

introducing the C_{6+} -rich stream (155) into a hydrocarbon pool.

2. The process of claim 1 further comprising reforming the C_{8+} –rich fraction (120) in a reforming zone to form a higher octane reformed product and introducing the reformed product into the hydrocarbon pool.

3. The process of claim 1 wherein separating the reaction product mixture (135) comprises separating the reaction product mixture into at least the C_{3-} -rich stream (145), the iso-C_4 -rich stream (150), a C_5 –rich stream (165), and the C_{6+} -rich stream (155).

4. The process of claim 3 further comprising controlling a vapor pressure of the C_{6+} –rich stream (155) by recovering at least a portion of the C_5 –rich stream (165).

5. The process of claim 3 further comprising maximizing a gasoline product yield by mixing at least a portion of the C_5 –rich stream (165) with the C_{6+} -rich stream (155).

6. The process of claim 3 further comprising recycling at least a portion of the C_5 –rich stream (165) to the reaction zone (125).

7. The process of claim 1 further comprising introducing the iso-C_4 –rich stream (150) and at least one olefin containing stream into an alkylation reaction zone to produce low vapor pressure, high octane gasoline blendstock.

8. The process of claim 1 further comprising recycling at least a portion of the iso-C_4 -rich stream (150) to the reaction zone (125).

9. The process of claim 1 wherein at least one of the first or second catalyst comprises HF, sulfated zirconias, $AlCl_2/SiO_2$, zeolites, ionic solids, platinum on chlorided Al_2O_3/Ga_2O_3 supports, supported ionic liquids, $Pt/W/Al_2O_3$, HF/TiF_4, an ionic liquid, or combinations thereof.

10. The process of claim 1 further comprising:

separating the catalyst from the reaction product mixture before separating the reaction product mixture;

regenerating the separated catalysts;

optionally, adding a carbocation promoter to the regenerated catalyst; and

recycling at least a portion of the regenerated catalyst to the reaction zone (125).

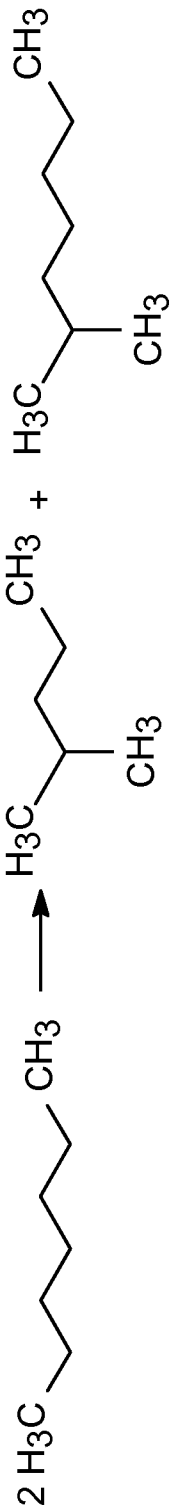

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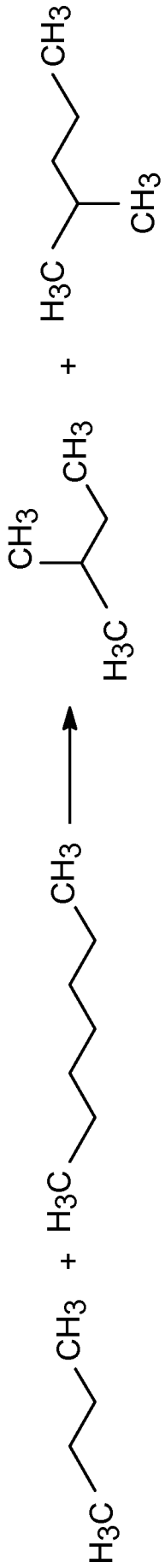
FIG. 1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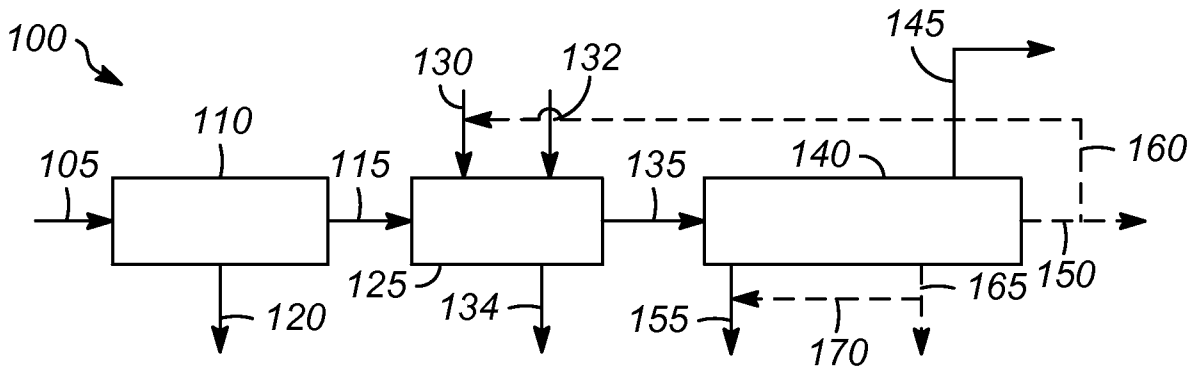
CH3

FIG. 2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140
145
160
120
125
134
155
165
150
170

FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2015/025032

A. CLASSIFICATION OF SUBJECT MATTER

C10G 35/00(2006.01)i, C10G 2/00(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10G 35/00; C10G 39/00; C07C 15/02; C07C 6/08; C07C 5/09; B01J 31/00; B01J 29/28; C10G 2/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & keywords: reverse disproportionation, disproportionation, heptane, butane, iso-butane, hexane, gasoline, high octane rating, ionic catalyst, naphtha

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2005-0033102 A1 (RANDOLPH, B. B. et al.) 10 February 2005 See abstract; paragraphs [0007]-[0016]; claims 12, 18, 19, 22-24, 28.	1-10
A	US 4440967 A (HOBBS, C. F.) 3 April 1984 See abstract; column 2, line 20-column 3, line 33; claims 1, 2, 8.	1-10
A	US 4190519 A (MILLER, S. J. et al.) 26 February 1980 See abstract; column 2, line 64-column 4, line 47; claims 1, 8; figure.	1-10
A	US 2004-0116764 A1 (RANDOLPH, B. B. et al.) 17 June 2004 See abstract; paragraphs [0012], [0013], [0019], [0020]; claims 1, 2, 15, 16.	1-10
A	US 2004-0077914 A1 (ZAVILLA, J. et al.) 22 April 2004 See abstract; paragraphs [0027]-[0037]; claims 1, 8.	1-10
A	US 4975179 A (HARANDI, M. N. et al.) 4 December 1990 See abstract; column 7, lines 1-44; claims 1, 8; figure.	1-10

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
29 June 2015 (29.06.2015)	**29 June 2015 (29.06.2015)**

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2015/025032

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2005-0033102 A1	10/02/2005	WO 2005-016855 A2 WO 2005-016855 A3	24/02/2005 21/07/2005
US 4440967 A	03/04/1984	None	
US 4190519 A	26/02/1980	None	
US 2004-0116764 A1	17/06/2004	US 2005-0131264 A1 US 7214845 B2	16/06/2005 08/05/2007
US 2004-0077914 A1	22/04/2004	EP 1402950 A1 JP 2004-268018 A	31/03/2004 30/09/2004
US 4975179 A	04/12/1990	EP 0414449 A1 EP 0414449 B1 JP 03-109490 A	27/02/1991 29/09/1993 09/05/1991