

METHOD OF PRODUCING A FUEL ADDITIVE

BACKGROUND

[0001] Commercial gasoline, which is fuel for internal combustion engines, is a refined petroleum product that is typically a mixture of hydrocarbons (base gasoline), additives, and blending agents. Additives and blending agents are added to the base gasoline to enhance the performance and the stability of gasoline, for example octane boosters.

[0002] When used in high compression internal combustion engines, gasoline has the tendency to “knock.” Knocking occurs when combustion of the air/fuel mixture in the cylinder does not start off correctly in response to ignition because one or more pockets of air/fuel mixture pre-ignite outside the envelope of the normal combustion front. Anti-knocking agents, also known as octane boosters, reduce the engine knocking phenomenon, and increase the octane rating of the gasoline

[0003] Hydrocarbon cracking processes are important conversion processes used in petroleum refineries. For example, fluid catalytic cracking (FCC) is widely used to convert the high-boiling, high-molecular weight hydrocarbon fractions of petroleum crude oils to more valuable gasoline, olefinic gases, and other products. Thermal cracking of naphtha and gas oil is also widely used in the petrochemical industry to produce a variety of olefins and aromatics. For example, hydrocarbon feed stocks can be mixed with steam and subjected to elevated temperatures (e.g., 700-900°C) in a steam cracker furnace wherein the feed stock components are cracked into various fractions. The effluent of the steam cracker can contain a gaseous mixture of hydrocarbons, for example, saturated and unsaturated olefins and aromatics (C1-C35). The effluent can then be separated into individual olefins (for example, ethylene, propylene, and C4's) and pyrolysis gasoline. Recycle streams of crude hydrocarbons are often formed as by-products during these cracking processes.

[0004] The presence of isobutylene, butadiene, 1-butene, 2-butene, and other components within the crude hydrocarbon streams can allow for the formation of valuable alcohols and fuel additives. However, the conversion of crude hydrocarbon streams to fuel additive products can often be inefficient and costly. Furthermore, the final product specifications for such alcohols can be undesirable and can fail to meet market quality requirements. For example, alcohol products can have high levels of impurities, high Reid vapor pressures, e.g., greater than 2.0 pounds per square inch (psi) (greater than 10 kilopascals, greater than 12 kilopascals, greater than 13 kilopascals, greater than 14 kilopascals), and low octane numbers (e.g., 82 Research Octane Number (RON)), all of

which correlate with poor product quality. Any improvement in these specifications and/or the efficiency of the process can provide a more valuable fuel additive product.

[0005] Thus, there is a need for an efficient method of producing fuel additives that can make use of crude hydrocarbon streams and produce final products with lower impurities and higher performance specifications.

SUMMARY

[0006] Disclosed, in various embodiments, are methods of producing fuel additives.

[0007] A method of producing a fuel additive comprises: passing a feed stream comprising C4 hydrocarbons through a butadiene extraction unit producing a first process stream; passing the first process stream through a methyl tertiary butyl ether unit producing a second process stream and a methyl tertiary butyl ether product; passing the second process stream through a hydration unit producing the fuel additive and a recycle stream; passing the recycle stream through a hydrogenation unit; and recycling the recycle stream to a steam cracker unit and/or to the feed stream.

[0008] A method of producing a fuel additive, comprising: passing a feed stream comprising C4 hydrocarbons through a catalytic cracking unit; passing the feed stream through a butadiene extraction unit producing a first process stream, wherein the butadiene extraction unit comprises extractive distillation, solvent degassing, solvent regeneration, solvent recovery, or a combination thereof; withdrawing a butadiene product from the butadiene extraction unit; passing the first process stream through a methyl tertiary butyl ether unit producing a second process stream and a methyl tertiary butyl ether product; withdrawing the methyl tertiary butyl ether product from the methyl tertiary butyl ether unit; passing the second process stream through a hydration unit producing the fuel additive and a recycle stream, wherein a temperature within the hydration unit is 30°C to 250°C, a pressure within the hydration unit is 500 kiloPascals to 20,000 kiloPascals, and wherein greater than or equal to 1.0 % by weight of any butenes present in the second process stream is converted to butanol within the hydration unit; withdrawing the fuel additive from the hydration unit, wherein the fuel additive comprises 2-butanol, tert-butyl alcohol, di-isobutene, or a combination thereof; passing the recycle stream through a hydrogenation unit, wherein greater than or equal to 0.001% by weight of any butene present in the recycle stream is converted to butane within the hydrogenation unit; and recycling the recycle stream to the catalytic cracking unit.

[0009] These and other features and characteristics are more particularly described below.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] The following is a brief description of the drawings wherein like elements are numbered alike and which are presented for the purposes of illustrating the exemplary embodiments disclosed herein and not for the purposes of limiting the same.

[0011] The FIGURE is a schematic diagram representing a unit sequence for producing fuel additives.

DETAILED DESCRIPTION

[0012] Disclosed herein is an efficient method of producing fuel additives that can make use of crude hydrocarbon streams and produce final products with low impurities and high performance specifications. For example, the method disclosed herein can provide a unique sequence of unit operations that converts crude hydrocarbons into valuable alcohol fuel additives. This unique sequence can significantly improve the efficiency of the process, thereby reducing total capital costs. The final fuel additive products can have levels of 2-butanol, tert-butyl alcohol, C4-dimer, or a combination thereof, for example, the final fuel additive products can have levels of the C4-dimer comprising trimethylpentane, di-isobutylene, 2,2,4 trimethylpentane, 2,3,3 trimethylpentane, or a combination thereof in an amount of 0.01 weight % to 50 weight%, based on the total weight of the fuel additive, high octane numbers (e.g., greater than or equal to 85 RON, or greater than or equal to 87 RON), and low Reid vapor pressures of greater than or equal to 55 Kilopascals. For example, the trimethylpentane can be present in an amount of 0.1 to 25 weight percent, for example, 1 to 20 weight %. Any one or all of these properties can correlate with high performance and high market value. The method disclosed herein can also produce secondary products along with the fuel additive product. For example, methyl tertiary butyl ether (MTBE) products can be produced along with the fuel additive, thus maximizing the efficiency and productivity of the process.

[0013] The method can include passing a feed stream of crude hydrocarbons through a butadiene extraction unit producing a first process stream. This butadiene extraction unit can remove the butadiene present in the feed stream. The minimization of butadiene in the process increases desirable product specifications. The first process stream can then be passed through a MTBE unit. The MTBE unit can convert isobutylene present in the first

process stream to a MTBE product and a second process stream. The second process stream can then be passed through a hydration unit to produce a fuel additive, for example, an alcohol fuel additive. A recycle stream can also be produced in the hydration unit. The recycle stream can be recycled through an additional hydrogenation unit and returned to a point in the process before the MTBE unit. For example, the recycle stream can be recycled to a steam cracker unit and/or to the feed stream. The present process can maximize product quality for a fuel additive product while also producing additional MTBE products in an efficient manner.

[0014] The method disclosed herein can include passing a feed stream through an olefin production unit, for example, a hydrocarbon cracking unit, for example, a catalytic and/or steam cracking unit, such that a source of the feed stream can include a product of an olefin cracking process and/or an olefin production process. The feed stream can comprise hydrocarbons, for example, C4 hydrocarbons. Additional hydrocarbons, for example, C2 and C3 hydrocarbons, can also be fed to the olefin production unit. The feed stream can be withdrawn from the olefin production unit as a crude C4 hydrocarbon stream. The stream produced by the olefin production unit can comprise propane, propylene, ethyl acetylene, vinyl acetylene, 1,3-butadiene, 1,2-butadiene, isobutylene, cis-2-butene, trans-2-butene, 1-butene, isobutane, n-butane, or a combination thereof. The total C4 olefin content of the feed stream when withdrawn from a steam cracking unit can be greater than or equal to 90% by weight and the feed stream can comprise greater than or equal to 40% by weight isobutylene. The total C4 olefin content of the feed stream when withdrawn from a fluid catalytic cracking unit can be greater than or equal to 50% by weight and the feed stream can comprise greater than or equal to 30% by weight isobutane.

[0015] The feed stream can be passed through a butadiene extraction unit. The butadiene extraction unit can be an optional component that can be used in addition to the extraction unit if excess butadiene slippage occurs. The butadiene extraction unit can comprise a butadiene extractive distillation column and other components in series. For example, the butadiene extraction unit can comprise a butadiene extractive distillation column, followed by solvent degassing, solvent regeneration, and solvent recovery. The butadiene unit can be operated at a temperature of less than or equal to 150° (300°F) and a pressure of 700 kilopascals (100 pounds per square in gauge). A liquid solvent selected from a single compound or a mixture of aromatic or aliphatic solvents, preferably toluene, benzene, ethylbenzene, cumene, xylenes, mesitylene, hexane, octane, cyclohexane, olefins, preferably, hexene, heptane, octane, or ethers, preferably diethylether, tetrahydrofurane,

dimethylformamide, n-methyl-pyrrolidone, acetonitrile, furfural, N-methyl-2-pyrrolidone, acetone, dimethylacetamide, cuprous ammonium acetate or β -methoxypropionitrile, more preferably an aromatic solvent, most preferably n-methyl-pyrrolidone can be used. This butadiene extraction unit can remove butadiene present in the process stream. Accordingly, a first product stream, i.e., a butadiene product stream, can be withdrawn from the butadiene extraction unit. The butadiene product can be withdrawn with a purity of greater than or equal to 90%. The first process stream, now with reduced butadiene content, can be withdrawn from the butadiene extraction unit and transferred to another unit. The process stream being withdrawn from the butadiene extraction unit can comprise less than or equal to 5% butadiene by weight, for example, less than or equal to 3%, for example, less than or equal to 1%.

[0016] The first process stream can then be passed through a hydrogenation unit, for example, a selective hydrogenation unit. For example, the hydrogenation unit can be a selective butadiene hydrogenation unit. The hydrogenation unit can convert butadiene present in the first process stream to 1-butene, cis-2-butene, and trans-2-butene. The conversion rate from butadiene to 1-butene, cis-2-butene, and trans-2-butene can be greater than or equal to 90%. Propylene, ethyl acetylene, and vinyl acetylene present in the first process stream can also undergo hydrogenation within the hydrogenation unit. The selective hydrogenation catalyst can comprise palladium with an aluminum base. The hydrogenation catalyst can comprise platinum, rhodium, palladium, ruthenium, cobalt, nickel, copper, or a combination thereof. Hydrogen can be injected into the first process stream prior to passing through the reactor.

[0017] The first process stream exiting the hydrogenation unit can then be passed through a MTBE unit. Methanol can be fed through the MTBE unit via a methanol stream. The MTBE unit can convert isobutylene present in the first process stream to a MTBE product. The first process stream can be contacted with the methanol and a catalyst, for example, an acidic ion-exchange resin catalyst, within the MTBE unit. Methanol and isobutylene can be present within the MTBE unit in a molar ratio of 1.0 mole of isobutylene to 0.05 moles to 10.0 moles of methanol, for example, one mole of isobutylene to 0.1 moles to 5.0 moles of methanol, for example, one mole of isobutylene to 0.5 moles to 2.0 moles of methanol. The MTBE product can be withdrawn from the MTBE unit via a MTBE product stream. The purity of the MTBE product can be greater than or equal to 95%. The conversion rate from isobutylene to MTBE within the MTBE unit can be greater than or equal to 75%, for example, greater than or equal to 85%, for example, greater than or equal to

95%. The second process stream can then be withdrawn from the MTBE unit with reduced isobutylene content. For example, the second process stream exiting the MTBE unit can comprise less than or equal to 5% isobutylene. A temperature within the MTBE unit can be 15°C to 150°C, for example, 35°C to 125°C. A pressure within the MTBE unit can be 500 kiloPascals to 2800 kiloPascals, for example, 1000 kiloPascals to 2000 kiloPascals, for example, 1500 kiloPascals. The MTBE unit can also produce a second process stream.

[0018] The second process stream exiting the MTBE unit can then be passed through a hydration unit to produce a fuel additive, for example, an alcohol fuel additive. The second process stream entering the hydration unit can comprise less than or equal to 5% butadiene by weight, for example, less than or equal to 3%, for example, less than or equal to 1%. The fuel additive product can be withdrawn from the hydration unit via a product stream. Water can be fed to the hydration unit via a water stream. The hydration unit can comprise an oscillating baffle reactor, a fixed bed reactor, a membrane integrated reactor, or a combination thereof. The hydration unit can convert butene present in the process stream to butanol. For example, greater than or equal to 90% of the butene present in the feed stream can be converted to butanol within the hydration unit. The second process stream can be contacted with water and a catalyst within the hydration unit. For example, the catalyst can comprise phosphoric acid, hypophosphorous acid, an ion-exchange resin, sulfur, polystyrene, polymer, niobium oxide, or a combination thereof. Water and butene can be present within the hydration unit in a molar ratio of 1.0 mole of water to 1 mole to 20 moles of butene, for example, one mole of water to 5 moles to 10 moles of butene. A temperature within the hydration unit can be 30°C to 250°C, for example, 100°C to 200°C. A pressure within the hydration unit can be 500 kiloPascals to 20,000 kiloPascals, for example, 5000 kiloPascals to 10,000 kiloPascals, for example, 7500 kiloPascals.

[0019] The fuel additive product can comprise 2-butanol, tert-butyl alcohol, C4-dimer, or a combination thereof, for example, the C4-dimer can comprise di-isobutylene, 2,2,4 trimethylpentane, 2,3,3 trimethylpentane, or a combination thereof. The fuel additive product can comprise greater than or equal to 0.1% by weight trimethylpentane, for example, greater than or equal to 0.5% by weight, for example, greater than or equal to 1.0% by weight. An octane number of the fuel additive product can be greater than or equal to 80 for example, greater than or equal to 82, for example, greater than or equal to 85, for example, greater than or equal to 87, for example, greater than or equal to 90 according to the Anti-Knock Index, for example, greater than or equal to 85, for example, 90.

[0020] The octane number is a standard measurement used to gage the performance of an engine or fuel. The higher the octane number, the more compression the fuel is able to withstand before igniting. Fuels with higher octane ratings are generally used in high performance gasoline engines that need higher compression ratios. Fuels with lower octane numbers can be desirable for diesel engines because diesel engines do not compress the fuel, but rather compress only air and then inject fuel into the air which is heated by compression. Gasoline engines rely on ignition of air and fuel compressed together as a mixture, which is ignited at the end of the compression stroke using spark plugs. As a result, high compressibility of fuel is a consideration for gasoline engines.

[0021] The Anti-Knock Index is measured by adding the research octane number and the motor octane number and dividing by two, i.e., $(RON+MON)/2$. The Research Octane Number is determined by running the fuel in a test engine at a speed of 600 revolutions per minute with a variable compression ratio under controlled conditions, and comparing the results with those for mixtures of iso-octane and n-heptane. Motor Octane Number is determined by testing a similar test engine to that used in determining the Research Octane Number but at a speed of 900 revolutions per minute with a preheated fuel mixture, higher engine speed, and variable ignition timing. Depending on the composition, the Motor Octane Number can be about 8 to 12 octanes lower than the Research Octane Number. The research octane number can be greater than or equal to 80, for example, greater than or equal to 85, for example, greater than or equal to 90. The motor octane number can be greater than or equal to 70, for example, greater than or equal to 75, for example, greater than or equal to 80, for example, greater than or equal to 82. Higher octane ratings can give higher amounts of energy needed to initiate combustion. Fuels with higher octane ratings are less prone to auto-ignition and can withstand a greater rise in temperature during the compression stroke of an internal combustion engine without auto-igniting.

[0022] Reid vapor pressure is used to measure the volatility of gasoline defined as the absolute vapor pressure exerted by a liquid at 37.8°C as determined by ASTM D-323. The measures the vapor pressure of gasoline volatile crude oil, and other volatile petroleum products, except for liquefied petroleum gases. Reid vapor pressure is measured in kiloPascals and represents a relative pressure to atmospheric pressure since ASTM D-323 measures the gage pressure of the sample in a non-evacuated chamber. High levels of vaporization are desired for winter starting and operation and lower levels are desirable in avoiding vapor lock during summer heat. Fuel cannot be pumped when vapor is present in the fuel line and winter starting will be difficult when liquid gasoline in the combustion

chambers has not vaporized. This means that the Reid vapor pressure is changed accordingly by oil producers seasonally to maintain gasoline engine reliability. The Reid vapor pressure of the fuel additive product can be less than or equal to 25 kiloPascals, for example, less than or equal to 15 kiloPascals, for example, less than or equal to 10 kiloPascals. The fuel additive product can also comprise less than or equal to 10% impurities formed by dimerization of C4 olefins such as isobutylene, 1-butene, 2-butene or combinations thereof.

[0023] A recycle stream, e.g., a hydrocarbon recycle stream, can be withdrawn from the hydration unit and recycled to a steam cracker unit and/or the initial feed stream. The recycle stream can comprise 1-butene, 2-butene, isobutane, n-butane, or a combination thereof. The recycle stream can optionally be passed through a drying unit for trace water removal and a recycle hydrogenation unit prior to returning to the initial feed stream. The recycle hydrogenation unit can convert the 1-butene and 2-butene present in the recycle stream to n-butane and isobutane. For example, greater than or equal to 90% of any butene present in the hydrocarbon recycle stream can be converted to butane within the hydrogenation unit.

[0024] A more complete understanding of the components, processes, and apparatuses disclosed herein can be obtained by reference to the accompanying drawings. These figures (also referred to herein as “FIG.”) are merely schematic representations based on convenience and the ease of demonstrating the present disclosure, and are, therefore, not intended to indicate relative size and dimensions of the devices or components thereof and/or to define or limit the scope of the exemplary embodiments. Although specific terms are used in the following description for the sake of clarity, these terms are intended to refer only to the particular structure of the embodiments selected for illustration in the drawings, and are not intended to define or limit the scope of the disclosure. In the drawings and the following description below, it is to be understood that like numeric designations refer to components of like function.

[0025] Referring now to the FIGURE, this simplified schematic diagram represents a unit sequence 10 used in a method for producing fuel additives. The sequence 10 can include passing a feed stream comprising hydrocarbons through a hydrocarbon cracking unit 14. For example, the hydrocarbon cracking unit 14 can be a steam cracking and/or a catalytic cracking unit.

[0026] A first process stream 16 can then be withdrawn from the cracking unit 14 and sent to a butadiene extraction unit 18. The first process stream 16 can comprise crude hydrocarbons, for example, C4 hydrocarbons. The butadiene extraction unit 18 can comprise

a butadiene extractive distillation column and other components in series. This butadiene extraction unit 18 can remove butadiene present in the first process stream 16. Accordingly, a butadiene product stream 19 can be withdrawn from the butadiene extraction unit 18.

[0027] A second process stream, now with reduced butadiene content, can be withdrawn from the butadiene extraction unit 18. The second process stream 24 can then be passed through an MTBE unit 26. Methanol can be fed through the MTBE unit 26 via stream 20. The MTBE unit 26 can convert isobutylene present in the second process stream 24 to an MTBE product. This MTBE product 22 can be withdrawn from the MTBE unit 24. A third process stream 28 can then be withdrawn from the MTBE unit 26, now comprising a reduced isobutylene content.

[0028] The third process stream 28 can then be passed through a hydration unit 30 to produce a fuel additive product 46, for example, an alcohol fuel additive. The fuel additive product 46 can be withdrawn from the hydration unit 30. Water can be fed to the hydration unit 30 via stream 44.

[0029] A recycle stream 32, for example, a hydrocarbon recycle stream, can be withdrawn from the hydration unit 30 and recycled to the initial feed stream 12. The recycle stream 32 can be passed through a recycle hydrogenation unit 42 prior to returning to the feed stream 12. The resulting hydrogenated recycle stream 48 can then be combined with the feed stream 12.

[0030] The methods disclosed herein include(s) at least the following aspects:

[0031] Aspect 1: A method of producing a fuel additive, comprising: passing a feed stream comprising C4 hydrocarbons through a butadiene extraction unit producing a first process stream; passing the first process stream through a methyl tertiary butyl ether unit producing a second process stream and a methyl tertiary butyl ether product; passing the second process stream through a hydration unit producing the fuel additive and a recycle stream; passing the recycle stream through a hydrogenation unit; and recycling the recycle stream to a steam cracker unit and/or to the feed stream.

[0032] Aspect 2: The method of Aspect 1, wherein a source of the feed stream comprises a product of an olefin cracking process and/or an olefin production process.

[0033] Aspect 3: The method of any of the preceding aspects, wherein the feed stream comprises propane, propylene, ethyl acetylene, vinyl acetylene, 1,3-butadiene, 1,2-butadiene, isobutylene, cis-2-butene, trans-2-butene, 1-butene, isobutane, n-butane, or a combination thereof.

[0034] Aspect 4: The method of any of the preceding aspects, wherein the butadiene extraction unit comprises extractive distillation, solvent degassing, solvent regeneration and/or solvent recovery.

[0035] Aspect 5: The method of any of the preceding aspects, wherein less than or equal to 50% by weight of any butadiene present in the feed stream is extracted by the butadiene extraction unit, preferably wherein 20 to 50% by weight of any butadiene present in the feed stream is extracted by the butadiene extraction unit.

[0036] Aspect 6: The method of any of the preceding aspects, further comprising contacting the first process stream with a catalyst within the methyl tertiary butyl ether unit, wherein the catalyst comprises an acid-type ion-exchange resin.

[0037] Aspect 7: The method of any of the preceding aspects, wherein a temperature within the methyl tertiary butyl ether unit is 15°C to 150°C and a pressure within the methyl tertiary butyl ether unit is 500 kiloPascals to 2800 kiloPascals.

[0038] Aspect 8: The method of any of the preceding aspects, wherein methanol and isobutylene are present in the methyl tertiary butyl ether unit in a molar ratio of one mole of isobutylene to 0.05 moles to 10 moles of methanol, preferably wherein the molar ratio is 0.1 to 5.

[0039] Aspect 9: The method of any of the preceding aspects, wherein greater than or equal to 1.0% by weight of any isobutylene present in the first process stream is converted to methyl tertiary butyl ether within the methyl tertiary butyl ether unit, preferably wherein 5 to 35% by weight is converted.

[0040] Aspect 10: The method of Aspect 9, further comprising withdrawing a methyl tertiary butyl ether product from the methyl tertiary butyl ether unit.

[0041] Aspect 11: The method of any of the preceding aspects, wherein the second process stream comprises less than or equal to 3.0% butadiene by weight prior to passing through the hydration unit.

[0042] Aspect 12: The method of any of the preceding aspects, further comprising contacting the second process stream with a catalyst within the hydration unit, wherein the catalyst comprises phosphoric acid, hypophosphorous acid, ion-exchange resin, sulfur, polystyrene, polymer, niobium oxide, or a combination thereof.

[0043] Aspect 13: The method of any of the preceding aspects, wherein a temperature within the hydration unit is 30°C to 250°C and a pressure within the hydration unit is 500 kiloPascals to 20,000 kiloPascals.

[0044] Aspect 14: The method of any of the preceding aspects, wherein greater than or equal to 1.0 % by weight of any butene present in the second process stream is converted to butanol within the hydration unit, preferably wherein 1 to 50% by weight is converted.

[0045] Aspect 15: The method of any of the preceding aspects, further comprising withdrawing a fuel additive product from the hydration unit.

[0046] Aspect 16: The method of Aspect 15, wherein the fuel additive product comprises 2-butanol, tert-butyl alcohol, di-isobutene, or a combination thereof.

[0047] Aspect 17: The method of Aspect 15 or Aspect 16, wherein an octane number of the fuel additive product is greater than 85 in accordance with the Anti-Knock Index.

[0048] Aspect 18: The method of any of Aspects 15-17, wherein a Reid vapor pressure of the fuel additive product is less than or equal to 15 kiloPascals.

[0049] Aspect 19: The method of any of the preceding aspects, wherein greater than or equal to 0.001 % by weight of any butene present in the recycle stream is converted to butane within the hydrogenation unit, preferably wherein 0.001 to 2% by weight is converted.

[0050] Aspect 20: A method of producing a fuel additive, comprising: passing a feed stream comprising C4 hydrocarbons through a catalytic cracking unit; passing the feed stream through a butadiene extraction unit producing a first process stream, wherein the butadiene extraction unit comprises extractive distillation, solvent degassing, solvent regeneration, solvent recovery, or a combination thereof; withdrawing a butadiene product from the butadiene extraction unit; passing the first process stream through a methyl tertiary butyl ether unit producing a second process stream and a methyl tertiary butyl ether product; withdrawing the methyl tertiary butyl ether product from the methyl tertiary butyl ether unit; passing the second process stream through a hydration unit producing the fuel additive and a recycle stream, wherein a temperature within the hydration unit is 30°C to 250°C, a pressure within the hydration unit is 500 kiloPascals to 20,000 kiloPascals, and wherein greater than or equal to 1.0 % by weight of any butenes present in the second process stream is converted to butanol within the hydration unit; withdrawing the fuel additive from the hydration unit, wherein the fuel additive comprises 2-butanol, tert-butyl alcohol, di-isobutene, or a combination thereof; passing the recycle stream through a hydrogenation unit, wherein greater than or equal to 0.001% by weight of any butene present in the recycle stream is converted to butane within the hydrogenation unit; and recycling the recycle stream to the catalytic cracking unit.

[0051] In general, the invention may alternately comprise, consist of, or consist essentially of, any appropriate components herein disclosed. The invention may additionally,

or alternatively, be formulated so as to be devoid, or substantially free, of any components, materials, ingredients, adjuvants or species used in the prior art compositions or that are otherwise not necessary to the achievement of the function and/or objectives of the present invention. The endpoints of all ranges directed to the same component or property are inclusive and independently combinable (e.g., ranges of “less than or equal to 25 wt%, or 5 wt% to 20 wt%,” is inclusive of the endpoints and all intermediate values of the ranges of “5 wt% to 25 wt%,” etc.). Disclosure of a narrower range or more specific group in addition to a broader range is not a disclaimer of the broader range or larger group. “Combination” is inclusive of blends, mixtures, alloys, reaction products, and the like. Furthermore, the terms “first,” “second,” and the like, herein do not denote any order, quantity, or importance, but rather are used to denote one element from another. The terms “a” and “an” and “the” herein do not denote a limitation of quantity, and are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. “Or” means “and/or.” The suffix “(s)” as used herein is intended to include both the singular and the plural of the term that it modifies, thereby including one or more of that term (e.g., the film(s) includes one or more films). Reference throughout the specification to “one embodiment”, “another embodiment”, “an embodiment”, and so forth, means that a particular element (e.g., feature, structure, and/or characteristic) described in connection with the embodiment is included in at least one embodiment described herein, and may or may not be present in other embodiments. In addition, it is to be understood that the described elements may be combined in any suitable manner in the various embodiments.

[0052] The modifier “about” used in connection with a quantity is inclusive of the stated value and has the meaning dictated by the context (e.g., includes the degree of error associated with measurement of the particular quantity). The notation “ $\pm 10\%$ ” means that the indicated measurement can be from an amount that is minus 10% to an amount that is plus 10% of the stated value. The terms “front”, “back”, “bottom”, and/or “top” are used herein, unless otherwise noted, merely for convenience of description, and are not limited to any one position or spatial orientation. “Optional” or “optionally” means that the subsequently described event or circumstance can or cannot occur, and that the description includes instances where the event occurs and instances where it does not. Unless defined otherwise, technical and scientific terms used herein have the same meaning as is commonly understood by one of skill in the art to which this invention belongs. A “combination” is inclusive of blends, mixtures, alloys, reaction products, and the like. In a list of alternatively useable species, “a combination thereof” means that the combination can include a

combination of at least one element of the list with one or more like elements not named.

Also, “at least one of” means that the list is inclusive of each element individually, as well as combinations of two or more elements of the list, and combinations of at least one element of the list with like elements not named.

[0053] All cited patents, patent applications, and other references are incorporated herein by reference in their entirety. However, if a term in the present application contradicts or conflicts with a term in the incorporated reference, the term from the present application takes precedence over the conflicting term from the incorporated reference

[0054] While particular embodiments have been described, alternatives, modifications, variations, improvements, and substantial equivalents that are or may be presently unforeseen may arise to applicants or others skilled in the art. Accordingly, the appended claims as filed and as they may be amended are intended to embrace all such alternatives, modifications variations, improvements, and substantial equivalents.

CLAIMS

What is claimed is:

1. A method of producing a fuel additive, comprising:
passing a feed stream comprising C4 hydrocarbons through a butadiene extraction unit producing a first process stream;
passing the first process stream through a methyl tertiary butyl ether unit producing a second process stream and a methyl tertiary butyl ether product;
passing the second process stream through a hydration unit producing the fuel additive and a recycle stream;
passing the recycle stream through a hydrogenation unit; and
recycling the recycle stream to a steam cracker unit and/or to the feed stream.
2. The method of Claim 1, wherein a source of the feed stream comprises a product of an olefin cracking process and/or an olefin production process.
3. The method of any of the preceding claims, wherein the feed stream comprises propane, propylene, ethyl acetylene, vinyl acetylene, 1,3-butadiene, 1,2-butadiene, isobutylene, cis-2-butene, trans-2-butene, 1-butene, isobutane, n-butane, or a combination thereof.
4. The method of any of the preceding claims, wherein the butadiene extraction unit comprises extractive distillation, solvent degassing, solvent regeneration and/or solvent recovery.
5. The method of any of the preceding claims, wherein less than or equal to 50% by weight of any butadiene present in the feed stream is extracted by the butadiene extraction unit, preferably wherein 20 to 50% by weight of any butadiene present in the feed stream is extracted by the butadiene extraction unit.
6. The method of any of the preceding claims, further comprising contacting the first process stream with a catalyst within the methyl tertiary butyl ether unit, wherein the catalyst comprises an acid-type ion-exchange resin.

7. The method of any of the preceding claims, wherein a temperature within the methyl tertiary butyl ether unit is 15°C to 150°C and a pressure within the methyl tertiary butyl ether unit is 500 kiloPascals to 2800 kiloPascals.
8. The method of any of the preceding claims, wherein methanol and isobutylene are present in the methyl tertiary butyl ether unit in a molar ratio of one mole of isobutylene to 0.05 moles to 10 moles of methanol, preferably wherein the molar ratio is 0.1 to 5.
9. The method of any of the preceding claims, wherein greater than or equal to 1.0% by weight of any isobutylene present in the first process stream is converted to methyl tertiary butyl ether within the methyl tertiary butyl ether unit, preferably wherein 5 to 35% by weight is converted.
10. The method of Claim 9, further comprising withdrawing a methyl tertiary butyl ether product from the methyl tertiary butyl ether unit.
11. The method of any of the preceding claims, wherein the second process stream comprises less than or equal to 3.0% butadiene by weight prior to passing through the hydration unit.
12. The method of any of the preceding claims, further comprising contacting the second process stream with a catalyst within the hydration unit, wherein the catalyst comprises phosphoric acid, hypophosphorous acid, ion-exchange resin, sulfur, polystyrene, polymer, niobium oxide, or a combination thereof.
13. The method of any of the preceding claims, wherein a temperature within the hydration unit is 30°C to 250°C and a pressure within the hydration unit is 500 kiloPascals to 20,000 kiloPascals.
14. The method of any of the preceding claims, wherein greater than or equal to 1.0 % by weight of any butene present in the second process stream is converted to butanol within the hydration unit, preferably wherein 1 to 50% by weight is converted.
15. The method of any of the preceding claims, further comprising withdrawing a fuel additive product from the hydration unit.

16. The method of Claim 15, wherein the fuel additive product comprises 2-butanol, tert-butyl alcohol, di-isobutene, or a combination thereof.
17. The method of Claim 15 or Claim 16, wherein an octane number of the fuel additive product is greater than 85 in accordance with the Anti-Knock Index.
18. The method of any of Claims 15-17, wherein a Reid vapor pressure of the fuel additive product is less than or equal to 15 kiloPascals.
19. The method of any of the preceding claims, wherein greater than or equal to 0.001 % by weight of any butene present in the recycle stream is converted to butane within the hydrogenation unit, preferably wherein 0.001 to 2% by weight is converted.
20. A method of producing a fuel additive, comprising:
passing a feed stream comprising C4 hydrocarbons through a catalytic cracking unit;
passing the feed stream through a butadiene extraction unit producing a first process stream, wherein the butadiene extraction unit comprises extractive distillation, solvent degassing, solvent regeneration, solvent recovery, or a combination thereof;
withdrawing a butadiene product from the butadiene extraction unit;
passing the first process stream through a methyl tertiary butyl ether unit producing a second process stream and a methyl tertiary butyl ether product;
withdrawing the methyl tertiary butyl ether product from the methyl tertiary butyl ether unit;
passing the second process stream through a hydration unit producing the fuel additive and a recycle stream, wherein a temperature within the hydration unit is 30°C to 250°C, a pressure within the hydration unit is 500 kiloPascals to 20,000 kiloPascals, and wherein greater than or equal to 1.0 % by weight of any butenes present in the second process stream is converted to butanol within the hydration unit;
withdrawing the fuel additive from the hydration unit, wherein the fuel additive comprises 2-butanol, tert-butyl alcohol, di-isobutene, or a combination thereof;
passing the recycle stream through a hydrogenation unit, wherein greater than or equal to 0.001% by weight of any butene present in the recycle stream is converted to butane within the hydrogenation unit; and
recycling the recycle stream to the catalytic cracking unit.