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(54) Title: SELECTIVE ISOMERIZATION AND OLIGOMERIZATION OF OLEFIN FEEDSTOCKS FOR THE PRODUCTION OF TURBINE AND DIESEL FUELS

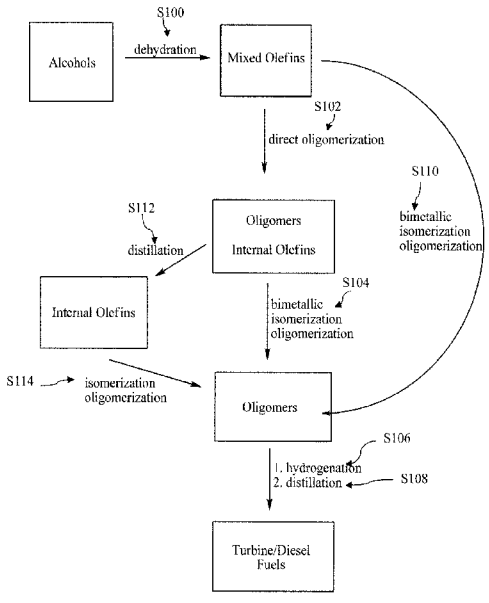

FIGURE 1

(57) Abstract: A process from converting alcohol feedstock to diesel/turbine fuels includes providing an alcohol-based feedstock and dehydrating the alcohol with at least one solid catalyst at a temperature ranging from about 200 °C to about 400 °C to produce an olefin mixture. The mixture is directly oligomerized with a Ziegler Natta catalyst and a cocatalyst to produce an oligomer mixture comprising oligomers and unreacted olefins. An isomerization catalyst is introduced to the oligomer mixture to produce, in situ, a bimetallic isomerization/oligomerization catalyst which converts the unreacted olefins to oligomers through 1,2-addition. The oligomers can be hydrogenated and distilled in producing the diesel/turbine fuels. In other aspects, in a one step process, the olefin mixture is oligomerized with at least one bimetallic isomerization/oligomerization catalyst that includes a metallocene based catalyst in conjunction with an isomerization catalyst to produce oligomers formed through 1,2-addition.

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SELECTIVE ISOMERIZATION AND OLIGOMERIZATION OF OLEFIN FEEDSTOCKS FOR THE PRODUCTION OF TURBINE AND DIESEL FUELS

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0001] The invention described herein may be manufactured and used by or for the government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

FIELD OF THE INVENTION

[0002] The invention generally relates to processes for converting alcohol feedstocks to diesel/turbine fuels, and more specifically, using catalytic methods to efficiently convert biofeedstocks into diesel/turbine fuels.

SUMMARY

[0003] In accordance with one aspect of the invention, a process for manufacturing turbine and/or diesel fuels is provided. The process includes providing an alcohol feedstock that includes at least one alcohol. The alcohol is dehydrated with at least one solid catalyst at a temperature ranging from 200 °C to 400 °C to produce an olefin mixture. The mixture is oligomerized directly with at least one metallocene-based Ziegler Natta catalyst and a methylaluminoxane (MAO) cocatalyst to produce an oligomer mixture that includes oligomers and unreacted olefins. An isomerization catalyst is introduced to the oligomer mixture to produce, *in situ*, a bimetallic isomerization/oligomerization catalyst which converts the unreacted olefins to oligomers through 1,2-addition. The process further includes hydrogenating and distilling the oligomers to produce a fully saturated diesel or turbine fuel.

[0004] In some embodiments, the alcohol can be selected from the group consisting of single alcohols, mixed alcohols, and complex mixtures including alcohols. The alcohol can be selected from the group having a formula $C_nH_{(2n+1)-x}(OH)_x$, where n and x are real integers greater than or equal to one. The alcohol may be a C_1-C_{10} alcohol, such as methanol, ethanol, propanol, butanol,

pentanol, combinations thereof, and the like.

[0005] The olefin mixture can include at least 5 wt. %, or at least 10 wt. %, or at least 20 wt. %, or at least 40 wt. %, or at least 80 wt. % primary olefins, and can be up to 100 wt. %, or up to 90 wt. % primary olefins. The olefin mixture can be 20-80 wt. % primary olefins, which is considered moderately rich in primary olefins. The alcohol feedstock can be greater than 80 wt. % primary olefins, which is considered rich in primary olefins.

[0006] The alcohol feedstock can contain less than 20% primary olefins.

[0007] The alcohol feedstock can include a total of at least about 10 wt. %, or at least about 20 wt. %, or at least 40 wt. %, or at least 80 wt. % of the at least one alcohol and can be up to 90% or up to 100% alcohol.

[0008] The isomerization catalyst can include/be at least one Lewis acid that promotes isomerization without affecting the oligomerization process. The isomerization catalyst can include at least one metal selected from nickel, platinum, palladium, and combinations thereof. The isomerization catalyst can include a transition metal with the metal in the +2 to +6 oxidation state which is selected from Ni, Zn, Pd, Pt, Cr, Cr, Fe, Fe, Mn, Co, and combinations thereof. The isomerization catalyst can include at least one ligand, attached to the metal.

[0009] The bimetallic catalyst can have a Lewis acid:metallocene ratio ranging from 0.1 to 10, by weight, or 0.5 to 2, by weight.

[0010] The metallocene based Ziegler Natta catalyst and the methylaluminoxane (MAO) cocatalyst can have/be prepared with a molar ratio of Al:Zr of from 1:1 to 1000:1, or from 1:1 to 100:1.

[0011] The dehydration catalyst can be a heterogeneous catalyst. The dehydration catalyst can be selected from gamma alumina, transition metal oxides, aluminum phosphate, and other heterogeneous catalysts having moderate acidity.

[0012] The olefin mixture can include at least one of 1-butene and 2-butene. The unreacted olefin can include an internal olefin, i.e., an olefin which is saturated at the beta or higher position. The internal olefin can include/be 2-butene. The oligomers can include a chain derived from 1-butene. The forming of oligomers through 1,2-addition can include forming butene oligomers through 1,2-addition. In some embodiments, the process includes separating the unreacted olefins by temperature controlled distillation.

[0013] In various aspects the oligomerizing of the mixture and the introducing an isomerization catalyst can be performed in a one step process which includes oligomerizing the mixture with at least one bimetallic isomerization/oligomerization catalyst having a metallocene based catalyst in conjunction with an isomerization catalyst to produce oligomers formed through 1,2-addition.

[0014] In another embodiment of the invention, a process for manufacturing turbine and/or diesel fuels includes providing an alcohol feedstock comprising at least one alcohol, dehydrating the at least one alcohol with at least one solid acid catalyst at temperatures ranging from 200 °C to 400 °C to produce an olefin mixture, and, in a one step process, oligomerizing the mixture with at least one bimetallic isomerization/oligomerization catalyst having a metallocene based catalyst in conjunction with an isomerization catalyst to produce oligomers formed through 1,2-addition.

[0015] The process can further include hydrogenating and distilling the oligomers to produce fully saturated diesel and turbine fuels.

[0016] The process can be further characterized as for the process described above.

[0017] In another aspect, a process for manufacturing turbine and/or diesel fuels includes providing an alcohol feedstock, dehydrating the alcohol in the feedstock with at least one solid catalyst at temperatures ranging from 200 °C to 400 °C to produce an olefin mixture, oligomizering the mixture directly with at least one metallocene based Ziegler Natta catalyst and methylaluminoxane (MAO) cocatalyst to produce an oligomer mixture including unreacted internal olefins and oligomers, separating the unreacted olefins by temperature controlled distillation, converting the unreacted olefins to a distribution of oligomers with a bimetallic isomerization/oligomerization catalyst having a metallocene based catalyst in conjunction with an isomerization catalyst to produce oligomers formed through 1,2-addition, and hydrogenating and distilling the oligomers to produce fully saturated diesel and turbine fuels.

[0018] The process can be further characterized as for the processes described above.

BRIEF DESCRIPTION OF THE DRAWING

[0019] **FIG. 1** is a generic diagram for the conversion of mixed olefin feedstocks to turbine and diesel fuels, according to embodiments of the invention.

[0020] It is to be understood that the foregoing general description and the following detailed description are exemplary and explanatory only and are not to be viewed as being restrictive of the invention, as claimed. Further advantages of this invention will be apparent after a review of the following detailed description of the disclosed embodiments, which are illustrated schematically in the accompanying drawings and in the appended claims.

DETAILED DESCRIPTION OF THE EMBODIMENTS OF THE INVENTION

[0021] Embodiments of the invention generally relate to processes for converting alcohol feedstocks to diesel/turbine fuels.

[0022] Several technologies exist for the oligomerization of short chain olefins. Oligomerizations catalyzed by Ziegler Natta catalysts have been shown to result in desired distributions of isomers. One drawback of this approach is that these catalysts are only effective with primary olefins. The use of a bimetallic catalyst system to isomerize internal olefins with concomitant conversion of primary olefins to oligomers allows for efficient conversion of mixed olefin feedstocks to fuels suitable for both jet and diesel propulsion.

[0023] The fermentation of sugars derived from biomass to alcohols is a proven and effective method for the conversion of sustainable feedstocks to fuels. Although fuels such as ethanol, n-butanol and more recently, n-pentanol have utility as gasoline replacements, certain applications (e.g. jet aircraft propulsion, military vehicles) require fully saturated hydrocarbon fuels. Alcohols can be dehydrated to olefins with modest energy inputs and the olefins can subsequently be oligomerized to produce saturated fuels. The use of specific Ziegler Natta catalysts under controlled conditions has been shown to be an effective route for conversion of primary olefins to jet fuels. In part, the suitability of such fuels is due to their well-controlled branching coupled with chain length selectivity. Dehydration of longer chain alcohols (e.g. C4-C20) typically produces a mixture of internal, external and branched chain olefins. To address this issue, embodiments of the invention combine an isomerization catalyst with the Ziegler-Natta oligomerization catalyst. The isomerization catalyst produces an equilibrium mixture of olefins including a significant amount of primary olefins. The Ziegler Natta catalyst can then convert the primary olefin to oligomer which then allows for the further conversion of remaining internal olefins. In summary, the synergistic

effect of the bimetallic system allows for internal olefins to be effectively converted to specific distributions of oligomers.

[0024] Solid acid catalysts including, but not limited to, zeolites, cation exchange resins, polyphosphoric acid and aluminosilicate clays can effectively oligomerize mixed olefin feedstocks. These methods are in general far less selective than the current approach. An isomerization-polymerization catalyst based on a titanium trichloride-nickel chloride-triethylaluminum catalyst has been described in the literature. Catalyst systems in embodiments of the invention do not produce high molecular weight polymer, but instead are selective for well-defined oligomer distributions.

[0025] Selective isomerization/oligomerization of olefin precursors allows for the custom synthesis of saturated, hydrocarbon fuels from renewable feedstocks. This in turn reduces the carbon footprint of the fuel production process without sacrificing vehicle performance.

[0026] Pure or mixed alcohol feedstocks (e.g. ethanol, propanols, butanols, pentanols...) are derived from renewable sources, and are subsequently dehydrated with a solid acid catalyst at elevated temperature, in the range between about 200 °C and about 400 °C. Potential catalysts include, but are not limited to; gamma alumina, transition metal oxides, aluminum phosphate, and other heterogeneous catalysts of modest acidity. In an embodiment, catalysts that produce mainly (>80%) primary olefins are utilized. In the case of alcohol feedstocks that only include internal alcohols, the choice of catalyst is dictated by overall conversion efficiencies and not by selectivity to primary olefins.

[0027] In embodiments, the mixed olefin feedstock can be converted to oligomers by two routes. When the feedstock is sufficiently rich in primary olefins (20-80%), or >80%, the olefins can be directly oligomerized by a metallocene based Ziegler Natta catalyst with methylaluminoxane (MAO) cocatalyst Al:Zr = 100:1 as described in US Patent Application Serial Number 12/511,796 which is hereby in its entirety incorporated by reference. This transformation results in the quantitative conversion of the normal olefins to an oligomer mixture, while internal olefins are untouched. The unreacted olefins can be separated by a low temperature distillation and then converted to a specific distribution of oligomers through the use of a bimetallic isomerization/oligomerization catalyst comprised of a metallocene based catalyst in conjunction

with an isomerization catalyst.

[0028] In alternative embodiments, the isomerization catalyst can be added directly to the reaction mixture without separation. The isomerization catalyst can be selected from a list of modest Lewis acids that promote isomerization without affecting the oligomerization process. Examples include, but are not limited to transition metal catalysts based on; Ni(II), Zn(II), Pd(II), Pt(II), Cr(II), Cr(III), Fe(II), Fe(III), Mn(II), V(II), V(III), and Co(II). These catalysts can be added with or without ligands, typically with a Lewis Acid:metallocene ratio in the range of from about 0.1 to about 10, or alternatively from about 0.5 to about 2. The isomerization catalyst and oligomerization catalyst are slurried or dissolved in a non-coordinating solvent and are then activated with MAO. In embodiments, the isomerization/oligomerization reaction can be carried out at similar temperatures and pressures as the direct oligomerization process.

[0029] In another alternate embodiment, the approach that is particularly useful for olefin feedstocks with modest amounts of primary olefins (< ~20%) is to forego the direct oligomerization and subject the original olefin mixture to the isomerization/oligomerization catalyst. Oligomerization mixtures are upgraded through hydrogenation and distillation as described in US patent application Serial Number 12/511,796 which is hereby in its entirety incorporated by reference to produce fuels suitable for use in turbine or diesel engines.

[0030] Example: Cp_2ZrCl_2 and $NiCl_2$ are added to a reactor and activated by addition of 100 molar equivalents of MAO in toluene. The solution is allowed to react for one hour and the solvent along with residual $AlMe_3$ is removed under reduced pressure. Dry trans-2-butene is condensed onto the catalyst, the reactor is then sealed, and the solution is stirred for several hours at room temperature. The reaction is quenched with water, filtered, and the resultant distribution of oligomers is upgraded through hydrogenation and distillation.

[0031] **Figure 1** illustrates a method for the conversion of alcohol feedstocks to fully saturated turbine and diesel fuels. In the initial step (S100), pure alcohols or mixtures are dehydrated to produce an olefin feedstock. This mixed feedstock can then be either directly oligomerized with an appropriate Ziegler Natta catalyst (S102) and any internal olefins oligomerized with a bimetallic isomerization/oligomerization catalyst, which can be produced in situ (S104). Or, depending on the distribution of olefins, the mixture of olefins can be isomerized and oligomerized with a bimetallic

isomerization/oligomerization catalyst to produce a specific distribution of oligomers (S110). In the case of direct oligomerization, residual olefins are optionally separated by distillation (S112) and then subjected to isomerization/oligomerization conditions (S114) to further improve the yield of the process. Oligomer mixtures are then hydrogenated (S106) and distilled (S108) to produce fuels suitable for use in both turbine and diesel engines.

[0032] Where a range of values is provided, it is understood that each intervening value, to the tenth of the unit of the lower limit unless the context clearly dictates otherwise, between the upper and lower limits of that range is also specifically disclosed. Each smaller range between any stated value or intervening value in a stated range and any other stated or intervening value in that stated range is encompassed within the invention. The upper and lower limits of these smaller ranges may independently be included or excluded in the range, and each range where either, neither or both limits are included in the smaller ranges is also encompassed within the invention, subject to any specifically excluded limit in the stated range. Where the stated range includes one or both of the limits, ranges excluding either or both of those included limits are also included in the invention.

CLAIMS

What is Claimed is:

1. A process for manufacturing turbine and/or diesel fuels, comprising:

providing an alcohol feedstock comprising at least one alcohol;

dehydrating said alcohol with at least one solid catalyst at a temperature ranging from 200 °C to 400 °C to produce an olefin mixture;

oligomerizing said mixture directly with at least one metallocene-based Ziegler Natta catalyst and a methylaluminoxane (MAO) cocatalyst to produce an oligomer mixture comprising oligomers and unreacted olefins;

introducing an isomerization catalyst to the oligomer mixture to produce in situ, a bimetallic isomerization/oligomerization catalyst which converts said unreacted olefins to oligomers formed through 1,2-addition; and

hydrogenating and distilling said oligomers to produce a fully saturated diesel or turbine fuel.

2. The process according to claim 1, further characterized by said alcohol being selected from the group consisting of single alcohols, mixed alcohols, and complex mixtures including alcohols.

3. The process according to claim 1, further characterized by said alcohol being selected from the group having a formula $C_nH_{(2n+1)-x}(OH)_x$, where *n* and *x* are real integers greater than or equal to one.

4. The process according to claim 1, further characterized by said olefin mixture comprising at least 5 wt. %, or at least 10 wt. %, or at least 20 wt. %, or at least 40 wt. %, or at least 80 wt. % primary olefins.

5. The process according to claim 1, further characterized by said olefin mixture comprising 20-80 wt.% primary olefins.

6. The process according to claim 1, further characterized by said alcohol feedstock comprising greater than 80% primary olefins.

7. The process according to claim 1, further characterized by said alcohol feedstock comprising less than 20% primary olefins.

8. The process according to claim 1, further characterized by said alcohol feedstock comprising a total of at least 20 wt. %, or at least 40 wt. %, or at least 80 wt. % of said at least one alcohol.

9. The process according to claim 1, further characterized by said isomerization catalyst comprising at least one Lewis acid that promotes isomerization without affecting said oligomerization process.

10. The process according to claim 1, further characterized by said isomerization catalyst comprising at least one metal selected from the group consisting of nickel, platinum, palladium, and combinations thereof.

11. The process according to claim 1, further characterized by said isomerization catalyst comprising a transition metal with the metal in the +2 to +6 oxidation state selected from the group consisting of Ni, Zn, Pd, Pt, Cr, Cr, Fe, Fe, Mn, Co, and combinations thereof.

12. The process according to claim 1, further characterized by said isomerization catalyst further comprising at least one ligand.

13. The process according to claim 1, further characterized by said bimetallic catalyst having a Lewis acid:metallocene ratio ranging from 0.1 to 10, by weight.

14. The process according to claim 13, further characterized by said bimetallic catalyst having a Lewis acid:metallocene ratio ranging from 0.5 to 2, by weight.

15. The process according to claim 1, further characterized by said metallocene based Ziegler Natta catalyst and said methylaluminoxane (MAO) cocatalyst being prepared with a molar ratio of Al:Zr of from 1:1 to 1000:1.

16. The process according to claim 1, further characterized by said metallocene based Ziegler Natta catalyst and methylaluminoxane (MAO) cocatalyst being prepared with molar ratio of Al:Zr of from 1:1 to 100:1.

17. The process according to claim 1, further characterized by said dehydration catalyst being selected from the group consisting of gamma alumina, transition metal oxides, aluminum phosphate.

18. The process according to claim 1, further characterized by said olefin mixture comprising at least one of 1-butene and 2-butene.

19. The process according to claim 1, further characterized by said unreacted olefin comprising an internal olefin.

20. The process according to claim 1, further characterized by said internal olefin comprising 2-butene.

21. The process according to claim 1, further characterized by said oligomers comprising a chain derived from 1-butene.

22. The process according to claim 1, further characterized by said forming of oligomers through 1,2-addition comprising forming butene oligomers through 1,2-addition.

23. The process according to claim 1, further characterized by oligomerizing said mixture and said introducing an isomerization catalyst comprises a one step process which includes oligomerizing said mixture with at least one bimetallic isomerization/oligomerization catalyst having a metallocene based catalyst in conjunction with an isomerization catalyst to produce oligomers formed through 1,2-addition.

24. A process for manufacturing turbine and/or diesel fuels, comprising:

providing an alcohol feedstock comprising at least one alcohol;

dehydrating said at least one alcohol with at least one solid acid catalyst at temperatures ranging from 200 °C to 400 °C to produce an olefin mixture; and

in a one step process, oligomerizing said mixture with at least one bimetallic isomerization/oligomerization catalyst having a metallocene based catalyst in conjunction with an isomerization catalyst to produce oligomers formed through 1,2-addition.

25. The process according to claim 24, further comprising hydrogenating and distilling said oligomers to produce fully saturated diesel and turbine fuels.

26. The process according to claim 24, further characterized by said alcohol in said feedstock being selected from the group consisting of single alcohols, mixed alcohols, and complex mixtures including alcohols.

27. The process according to claim 24, further characterized by said alcohol being selected from the group having a $C_nH_{(2n+1)-x}(OH)_x$ formula where n and x are real integers greater than or equal to one.

28. The process according to claim 24, further characterized by said olefin mixture having a concentration of primary olefins of less than 20%.

29. The process according to claim 24, further characterized by said isomerization catalyst comprising at least one Lewis acid that promotes isomerization without affecting said oligomerization process.

30. The process according to claim 24, further characterized by said isomerization catalyst comprising at least one metal selected from the group consisting of nickel, platinum, palladium, and combinations thereof.

31. The process according to claim 24, further characterized by said isomerization catalyst comprising a transition metal with the metal in the +2 to +6 oxidation state selected from the group consisting of Ni, Zn, Pd, Pt, Cr, Fe, Mn, V, Co, and combinations thereof.

32. The process according to claim 24, further characterized by said isomerization catalyst comprising ligands.

33. The process according to claim 24, further characterized by said bimetallic catalyst having a Lewis acid:metallocene ratio ranging from 0.1 to 10, by weight.

34. The process according to claim 24, further characterized by said bimetallic catalyst having a Lewis acid:metallocene ratio ranging from 0.5 to 2, by weight.

35. The process according to claim 24, further characterized by said metallocene based Ziegler Natta catalyst and methylaluminoxane (MAO) cocatalyst being in a molar ratio of Al:Zr ranging from 1:1 to 1000:1.

36. The process according to claim 24, further characterized by said metallocene based Ziegler Natta catalyst and methylaluminoxane (MAO) cocatalyst being in an Al:Zr ratio ranging from 1:1 to 100:1.

37. The process according to claim 24, further characterized by said dehydration catalyst being selected from the group consisting of gamma alumina, transition metal oxides, aluminum phosphate, and other heterogeneous catalysts having moderate acidity.

38. The process according to claim 24, further characterized by said olefin mixture comprising at least one of 1-butene and 2-butene.

39. The process according to claim 24, further characterized by said unreacted internal olefins comprises at least one of pure *cis*- 2-butene, pure *trans*- 2-butene or a mixture thereof.

40. The process according to claim 24, further characterized by said oligomers comprising a 1-butene-derived chain.

41. The process according to claim 24, further characterized by said oligomers formed through 1,2-addition being butene oligomers.

42. A process for manufacturing turbine and/or diesel fuels, comprising:

providing an alcohol feedstock;

dehydrating said alcohol in said feedstock with at least one solid catalyst at temperatures ranging from 200 °C to 400 °C to produce an olefin mixture;

oligomerizing said mixture directly with at least one metallocene based Ziegler Natta catalyst and methylaluminoxane (MAO) cocatalyst to produce an oligomer mixture including unreacted internal olefins and oligomers;

separating said unreacted olefins by temperature controlled distillation;

converting said unreacted olefins to a distribution of oligomers with a bimetallic isomerization/oligomerization catalyst having a metallocene based catalyst in conjunction with an isomerization catalyst to produce oligomers formed through 1,2-addition; and

hydrogenating and distilling said oligomers to produce fully saturated diesel and turbine fuels.

43. The process according to claim 42, further characterized by said alcohol in said feedstock being selected from the group consisting of single alcohols, mixed alcohols, and complex mixtures including alcohols.

44. The process according to claim 42, further characterized by said alcohol is selected from the group having a formula $C_nH_{(2n+1)-x}(OH)_x$, where *n* and *x* are real integers greater than or equal to one.

45. The process according to claim 42, further characterized by said olefin mixture comprises a mixture moderately rich in primary olefins ranging from 20% to 80%.

46. The process according to claim 42, further characterized by said olefin mixture comprises a mixture rich in primary olefins, greater than 80% primary olefins.

47. The process according to claim 42, further characterized by said isomerization catalyst comprising at least one modest Lewis acid that promotes isomerization without affecting said oligomerization process.

48. The process according to claim 42, further characterized by said isomerization catalyst comprising a metal selected from the group consisting of nickel, platinum, palladium, and combinations thereof.

49. The process according to claim 42, further characterized by said isomerization catalyst comprising a transition metal with the metal in the +2 to +6 oxidation state selected from the group consisting of Ni, Zn, Pd, Pt, Cr, Fe, Mn, V, Co, and combinations thereof.

50. The process according to claim 42, further characterized by said isomerization catalyst comprising ligands.

51. The process according to claim 42, further characterized by said bimetallic catalyst having a Lewis acid:metallocene ratio ranging from 0.1 to 10, by weight.

52. The process according to claim 42, further characterized by said bimetallic catalyst having a Lewis acid:metallocene ratio ranging from 0.5 to 2, by weight.

53. The process according to claim 42, further characterized by said metallocene based Ziegler Natta catalyst and methylaluminoxane (MAO) cocatalyst having a molar ratio of Al:Zr of from 1:1 to 1000:1.

54. The process according to claim 42, further characterized by said metallocene based Ziegler Natta catalyst and methylaluminoxane (MAO) cocatalyst being prepared with the ratio of Al:Zr being from 1:1 to 100:1.

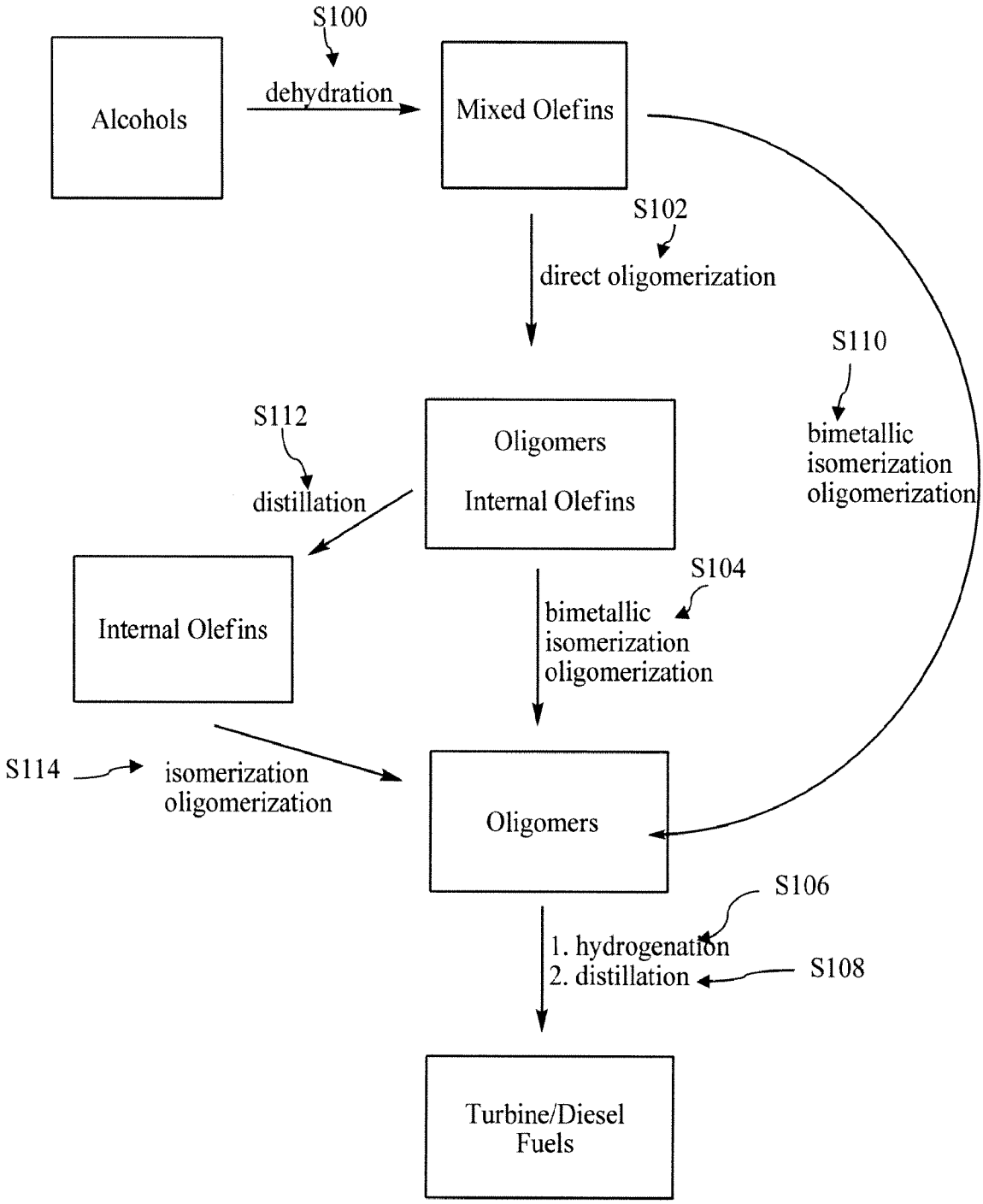
55. The process according to claim 42, further characterized by said dehydration catalyst being selected from the group consisting of gamma alumina, transition metal oxides, aluminum phosphate, and other heterogeneous catalysts having moderate acidity.

56. The process according to claim 42, further characterized by said olefin mixture comprises of 1-butene and 2-butene.

57. The process according to claim 42, further characterized by said unreacted internal olefins comprising pure *cis-* or *trans-* 2-butene or a mixture thereof.

58. The process according to claim 42, further characterized by said oligomers comprising a 1-butene-derived chain.

59. The process according to claim 42, further characterized by said oligomers formed through 1,2-addition being butene oligomers.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Internal Olefins
S104
bimetallic
isomerization
oligomerization
S114
isomerization
oligomerization
Oligomers
S106
1. hydrogenation
2. distillation
S108
Turbine/Diesel
Fuels

FIGURE 1

INTERNATIONAL SEARCH REPORT

International application No.
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A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C07C 2/58; C10L 1/04 (2012.01)
USPC - 208/15, 134
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)
IPC(8)- C07C 2/58; C10L 1/04 (2012.01);
USPC- 208/15, 134

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Patents and NPL (classification, keyword; search terms below)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PubWest (US Pat, PgPub, EPO, JPO), GoogleScholar (PL, NPL), FreePatentsOnline (US Pat, PgPub, EPO, JPO, WIPO, NPL); search terms: oligomerize, isomerize, bimetallic, dehydrate, alcohol, methylaluminoxane, hydrogenate, fuel, diesel

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2009/0299109 A1 (GRUBER et al.) 03 December 2009 (03.12.2009), para [0016]-[0019], [0035], [0037], [0079], [0081], [0086], [0100], [0106], [0121], [0122], [0131], [0135]-[0143], [0154]-[0162], [0171]-[0173], [0176], [0179], [0230], [0249], [0250], [0270], [0272]	1-59
Y	US 2003/0125595 A1 (BAGHERI et al.) 03 July 2003 (03.07.2003), para [0012], [0019], [0020], [0022], [0024], [0025], [0027], [0033], [0036], [0044], [0046]	1-59
Y, P	US 2011/0172475 A1 (PETERS et al.) 14 July 2011 (14.07.2011), para [0015]-[0197]	1-59
Y, P	US 2011/0160502 A1 (WU et al.) 30 June 2011 (30.06.2011), para [0023]-[0282]	1-59
Y	LEEUWEN et al. "New processes for the selective production of 1-octene." Coordination Chemistry Reviews [online], Epub 16 October 2010 (16.10.2010) [Retrieved on 2012-07-13], Vol. 255, Iss. 13-14; pp. 1499-1517, Retrieved from the Internet: <URL: http://www.sciencedirect.com/science/article/pii/S0010854510002225>, see entire document, especially Fig; 5, Scheme 1; Table 6	1-59
Y	US 2008/0216391 A1 (CORTRIGHT et al.) 11 September 2008 (11.09.2008), para [0012]-[0190]	1-59
Y	US 2005/0267271 A1 (MINK et al.) 01 December 2005 (01.12.2005), para [0012]-[0256]	1-59
Y	US 2001/0006154 A1 (KRUG et al.) 05 July 2001 (05.07.2001), para [0024]-[0102]	1-59

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

* 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
13 July 2012 (13.07.2012)	20 SEP 2012
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 12/35121

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,830,821 A (ROHRMANN et al.) 03 November 1998 (03.11.1998), col 2-14	1-59
Y	WILLIAMS et al. "Kineticstudies of catalyticdehydration of tert-butanol on zeolite NaH-ZSM-5." Journal of Catalysis [online], January 1991 [Retrieved on 2012-07-09], Vol. 127, Iss. 1, pp 377-392, Retrieved from the Internet: <URL: http://www.sciencedirect.com/science/article/pii/002195179190233T>, see entire document, especially Table 1, Figs 3-6	1-59

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 12/35121

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Group I, Claims 1-23 and 42-59

Group II, Claims 24-41

- - - Please see Extra Sheet - - -

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☒ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 12/35121

Continued from Box No. III, Observations where unity of invention is lacking:

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1.

Group I, Claims 1-23 and 42-59, drawn to a process for manufacturing turbine and/or diesel fuels, comprising
providing an alcohol feedstock comprising at least one alcohol;
dehydrating said alcohol with at least one solid catalyst at a temperature ranging from 200 degC to 400 degC to produce an oletln mixture;
introducing an isomerization catalyst to the oligomer mixture to produce in situ, a bimetallic isomerization / oligomerization catalyst which converts said unreacted olefins to oligomers formed through 1,2-addition;
hydrogenating and distilling said oligomers to produce a fully saturated diesel or turbine fuel.

Group II, Claims 24-41, drawn to a process for manufacturing turbine and/or diesel fuels comprising
providing an alcohol feedstock comprising at least one alcohol;
dehydrating said at least one alcohol with at least one solid acid catalyst at temperatures
ranging from 200 degC to 400 degC to produce an olefin mixture; anda one step process, oligomerizing said mixture with at least one bimetallic isomerization / oligomerization catalyst having a metallocene based catalyst in conjunction with an isomerization catalyst to produce oligomers.

The inventions listed as Groups I and II do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Group I does not include the inventive concept of in a one step process, oligomerizing said mixture, as required by Group II.

Group II does not include the inventive concept of
introducing an isomerization catalyst to the oligomer mixture to produce in situ, a bimetallic isomerization / oligomerization catalyst which converts said unreacted olefins to oligomers formed through 1,2-addition; and
hydrogenating and distilling said oligomers to produce a fully saturated diesel or turbine fuel, as required by Group I.

The inventions of Groups I and II share the special technical feature of manufacturing turbine and/or diesel fuels comprising
providing an alcohol feedstock comprising at least one alcohol;
dehydrating said at least one alcohol with at least one solid acid catalyst at temperatures ranging from 200C to 400C to produce an olefin mixture; and
using isomerization / oligomerization catalyst.

However, this special technical feature US 2009/0299109 A1 to Gruber, et al. (hereinafter 'Gruber') 03 December 2009 (03.12.2009), because Gruber discloses
providing an alcohol feedstock comprising at least one alcohol; (para [0015])
dehydrating said at least one alcohol with at least one solid acid catalyst at temperatures ranging from 200-400 degC to produce an olefin mixture; (para [0024], [0121])
manufacturing turbine and/or diesel fuels (para [0035], [0037], [0100], and [0106]) using an isomerization / oligomerization catalyst (para [0086], [0121], [0123], and [0155]-[0160]).

Groups I and II therefore lack unity under PCT Rule 13 because they do not share a same or corresponding special technical feature.