CLAIMS

What is claimed is:

1. A process for making a sustainable aviation fuel, the process comprising:

    a) providing a bio-ethylene feed, at least a portion of which is derived from dehydration of biomass ethanol;

    b) contacting the bio-ethylene feed with a first catalyst system comprising a first oligomerization catalyst to form an oligomerization product comprising at least one C_4-C_8 alpha-olefin and a mixture of decenes;

    c) separating the mixture of decenes from the oligomerization product;

    d) (i) contacting the mixture of decenes with at least one C_{6-} alpha-olefin in the presence of a second catalyst system comprising a second oligomerization catalyst, or (ii) contacting the mixture of decenes with at least one C_{8-} alpha-olefin in the presence of a second catalyst system comprising a metathesis catalyst, to provide a C_{16-} olefin stream;

    e) hydrogenating the C_{16-} olefin stream in the presence of a first hydrogenation catalyst to provide C_{16-} paraffins; and

    f) using the C_{16-} paraffins as a component to form a sustainable aviation fuel.

2. The process for making a sustainable aviation fuel according to claim 1, wherein the at least one C_{6-} alpha-olefin comprises ethylene, propylene, 1-butene, 1-pentene, 1-hexene, or a combination thereof.

3. The process for making a sustainable aviation fuel according to claim 1, wherein the at least one C_{8-} alpha-olefin comprises propylene, 1-butene, 2-butene, isobutylene, 1-pentene, 1-hexene, 3,3-dimethyl-1-butene, 1-octene, or a combination thereof.

4. The process for making a sustainable aviation fuel according to claim 1, wherein the oligomerization product comprises 1-butene, 1-hexene, 1-octene, dodecenes, tetradecenes, or any combination thereof.

5. The process for making a sustainable aviation fuel according to claim 1, wherein:

    a) the sustainable aviation fuel is certified as compliant with the Carbon Offsetting and Reduction Scheme for International Aviation (CORSIA)

sustainability criteria in accordance with the International Sustainability and Carbon Certification (ISCC) CORSIA certification system; or

b) the sustainable aviation fuel is certified as a Lower Carbon Aviation Fuel (LCAF) in accordance with the International Sustainability and Carbon Certification (ISCC) LCAF certification system;

wherein the certification is based upon the weight or fraction of the sustainable aviation fuel attributable to the biomass ethanol determined by mass balance and a free attribution method.

6. The process for making a sustainable aviation fuel according to claim 1, wherein the oligomerization product comprises:

at least 60 mol % 1-hexene, at least 60 mol % 1-octene, or at least 60 mol % 1-hexene and 1-octene combined; or

from 70 wt. % to 99.8 wt. % hexene or from 70 wt. % to 99.8 wt. % octene, and at least 0.2 wt. % of the mixture of decenes.

7. The process for making a sustainable aviation fuel according to claim 1, wherein the mixture of decenes comprises 1-decene, 2-butyl-1-hexene, 3-propyl-1-heptene, 4-ethyl-1-octene, 5-methyl-1-nonene, 4-decene, 5-decene, or any combination thereof.

8. The process for making a sustainable aviation fuel according to claim 1, wherein the mixture of decenes comprises from 76 mol % to 95 mol % C_{10} monoolefins.

9. The process for making a sustainable aviation fuel according to claim 1, wherein the first catalyst system, the second catalyst system, or both comprise independently a chromium-based catalyst, a metallocene-based catalyst, a Ziegler-Natta based catalyst, a metal-oxide supported Group 6-10 transition metal-based catalyst, or a combination thereof.

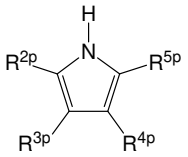
10. The process for making a sustainable aviation fuel according to claim 9, wherein the first catalyst system, the second catalyst system, or both further comprise a metal alkyl compound selected from an organoaluminum compound, an organoaluminoxane, an organoboron compound, an organozinc compound, an organomagnesium compound, an organolithium compound, or any combination thereof.

11. The process for making a sustainable aviation fuel according to claim 1, wherein the first catalyst system, the second catalyst system, or both comprise independently a chromium-based catalyst, and the chromium-based catalyst

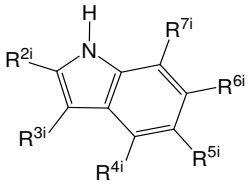
comprises (a) a chromium-containing compound, (b) a heteroatomic ligand, (c) a metal alkyl compound, and (d) optionally, a diluent.

12. The process for making a sustainable aviation fuel according to claim 11, wherein the heteroatomic ligand is selected from a pyrrole compound, a diphosphino aminyl compound, an N^2-phosphinyl amidine compound, an N^2-phosphinyl formamidine compound, or combinations thereof.

13. The process for making a sustainable aviation fuel according to claim 11, wherein the heteroatomic ligand is selected from a pyrrole compound having the Formula P1 or Formula I1:



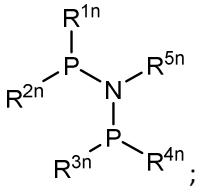
Formula P1



Formula I1

wherein R^{2p}, R^{3p}, R^{4p}, and R^{5p} of Formula P1 and R^{2i}, R^{3i}, R^{4i}, R^{5i}, R^{6i}, and R^{7i} of Formula I1 are selected independently from a C_1 to C_{18} organyl group, a C_1 to C_{18} hydrocarbyl group, or a C_3 to C_{60} silyl group.

14. The process for making a sustainable aviation fuel according to claim 11, wherein the heteroatomic ligand is a diphosphino aminyl moiety having Structure PNP2:



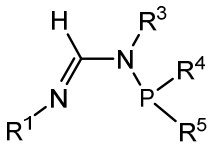
;

Structure PNP2

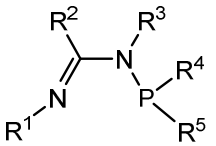
wherein the R^{1n}, R^{2n}, R^{3n}, R^{4n}, and R^{5n} independently are: a C_1 to C_{30} organyl group; a C_1 to C_{30} organyl group comprising inert functional groups; a C_1 to C_{30} hydrocarbyl group; a C_1 to C_{30} alkyl group; a C_6 to C_{30} aromatic group; a phenyl group or a C_6 to C_{30} substituted phenyl group; or a substituted or an unsubstituted C_1 to C_{20} alkyl group.

15. The process for making a sustainable aviation fuel according to claim 14, wherein any substituent of a substituted group is selected from a halide, a C_1 to C_{10} hydrocarbyl group, or a C_1 to C_{10} hydrocarboxy group.

16. The process for making a sustainable aviation fuel according to claim 11, wherein the heteroatomic ligand is selected from an N^2-phosphinyl formamidine compound having Structure NPF1, or an N^2-phosphinyl formamidine compound having Structure NPA1:



Structure NPF1



Structure NPA1

wherein R^1, R^2, R^3, R^4, and R^5 are independently a C_1 to C_{30} organyl group, a C_1 to C_{30} organyl group consisting essentially of inert functional groups, or a C_1 to C_{30} hydrocarbyl group.

17. The process for making a sustainable aviation fuel according to claim 11, wherein the diluent comprises a hydrocarbon, a halogenated hydrocarbon, or combinations thereof.

18. The process for making a sustainable aviation fuel according to claim 1, wherein the first catalyst system, the second catalyst system, or both comprise independently:

    a) a chromium-containing compound, a pyrrole compound, an organoaluminum compound, and optionally a halide containing compound;

    b) a chromium-containing compound, a diphosphino aminyl compound, and an organoaluminum compound;

    c) a chromium-containing compound complexed to a diphosphino aminyl compound, and an organoaluminum compound;

    d) a chromium-containing compound, an N^2-phosphinyl amidine compound, and an organoaluminum compound;

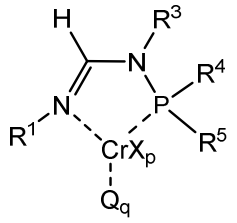
    e) a chromium-containing compound complexed to an N^2-phosphinyl amidine compound, and an organoaluminum compound;

    f) a chromium-containing compound, an N^2-phosphinyl formamidine compound, and an organoaluminum compound;

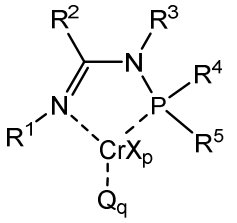
    g) a chromium-containing compound complexed to an N^2-phosphinyl formamidine compound, and an organoaluminum compound; or

h) any combinations thereof.

19. The process for making a sustainable aviation fuel according to claim 18, wherein the chromium-containing compound complexed to an N^2-phosphinyl formamidine compound and the chromium-containing compound complexed to an N^2-phosphinyl amidine compound have the following structures:



Structure NPFCr1



Structure NPACr1

wherein X is an anionic ligand, p is from 2 to 6, Q is a neutral ligand, and q is from 0 to 6; and

wherein R^1, R^2, R^3, R^4, and R^5 are independently a C_1 to C_{30} organyl group, a C_1 to C_{30} organyl group consisting essentially of inert functional groups, or a C_1 to C_{30} hydrocarbyl group.

20. The process for making a sustainable aviation fuel according to claim 18, wherein the chromium-containing compound is selected from chromium(II) nitrate, chromium(II) sulfate, chromium(II) fluoride, chromium(II) chloride, chromium(II) bromide, chromium(II) iodide, chromium(III) nitrate, chromium(III) sulfate, chromium(III) fluoride, chromium(III) chloride, chromium(III) bromide, chromium(III) iodide, a chromium(II) carboxylate, a chromium(II) alkoxide, chromium(II) aryloxide, a chromium(II) beta-dionate, a chromium(III) carboxylate, a chromium(III) alkoxide, chromium(III) aryloxide, or a chromium(III) beta-dionate.

21. The process for making a sustainable aviation fuel according to claim 1, wherein the first catalyst system, the second catalyst system, or both independently comprise a chromium carboxylate, wherein each carboxylate group of the chromium carboxylate is independently selected from acetate, propionate, n-butyrate, isobutyrate, valerate (n-pentanoate), neo-pentanoate, capronate (n-hexanoate), n-heptanoate, caprylate (n-octanoate), 2-ethylhexanoate, n-nonanoate, caprate (n-decanoate), n-undecanoate, laurate (n-dodecanoate), or stearate (n-octadecanoate).

22. The process for making a sustainable aviation fuel according to claim 1, wherein the first catalyst system, the second catalyst system, or both independently comprise a chromium carboxylate selected from chromium(II) acetate,

chromium(II) propionate, chromium(II) butyrate, chromium(II) isobutyrate, chromium(II) neopentanoate, chromium(II) oxalate, chromium(II) octanoate, chromium(II) 2-ethylhexanoate, chromium(II) laurate, chromium(II) stearate, chromium(III) acetate, chromium(III) propionate, chromium(III) butyrate, chromium(III) isobutyrate, chromium(III) neopentanoate, chromium(III) oxalate, chromium(III) octanoate, chromium(III) 2-ethylhexanoate, chromium(III) 2,2,6,6,-tetramethylheptanedionate, chromium(III) naphthenate, chromium(III) laurate, or chromium(III) stearate.

23. The process for making a sustainable aviation fuel according to claim 1, wherein the first catalyst system, the second catalyst system, or both independently comprise an organoaluminum compound selected from a triorganoaluminum compound, a diorganoaluminum halide, an organoaluminum dihalide, a diorganoaluminum alkoxide, an organoaluminum dialkoxide, an aluminoxane, or combinations thereof.

24. The process for making a sustainable aviation fuel according to claim 1, wherein the first catalyst system, the second catalyst system, or both independently comprise:

    a) molybdenum oxide on alumina (MoO_3/Al_2O_3), tungsten oxide on silica (WO_3/SiO_2), tungsten oxide on silica-alumina ($WO_3/SiO_2/Al_2O_3$), rhenium oxide on alumina (Re_2O_7/Al_2O_3), cobalt oxide and molybdenum oxide on alumina ($CoO/MoO_3/Al_2O_3$), rhenium oxide on alumina activated with tetramethyl tin ($Re_2O_7/Al_2O_3/SnMe_4$), or any combination thereof; or

    b) tungstated zirconium, molybdenum zirconium, nickel and/or cobalt doped tungstated zirconium, nickel and/or cobalt doped molybdenum zirconium catalysts, a Group 3 to Group 12 metal-treated zeolite, or combinations thereof.

25. The process for making a sustainable aviation fuel according to claim 1, wherein the dehydration of the biomass ethanol comprises contacting the biomass ethanol with a dehydration catalyst under conditions suitable to form bio-ethylene, and wherein the dehydration catalyst comprises:

    a) alumina, silica gel, silica-alumina, a crystalline silicate, a dealuminated crystalline silicate, a phosphorus-modified crystalline silicate, a zeolite, a molecular sieve, or anhydrous calcium sulfate; or

    b) a lanthanum-modified H-ZSM-catalyst, a ZSM-5/SAPO-34 composite, a mordenite catalyst, microspherical SAPO-34 catalyst, a phosphorus-modified HZSM-5 catalyst, a lanthanum-phosphorous modified HZSM-5 catalyst, a gallium-modified zeolite, a gallium-modified SAPO-11, a gallium-modified HZSM-5, a ZSM-based catalyst, a heteropolyacid catalyst, or a supported heteropolyacid catalyst.

26. The process for making a sustainable aviation fuel according to claim 1, wherein the first hydrogenation catalyst comprises:

    a) a heterogeneous catalyst selected from a Group 8-12 metal deposited on a carrier selected from carbon, silica, alumina, silica-alumina, a zeolite, or calcium carbonate; or

    b) a homogeneous catalyst selected from (i) a Ziegler catalyst comprising an organic salt of a Group 6-10 metal and an organoaluminum compound, or (ii) a coordination compound of Ru, Rh, or Ir, or (iii) a Group 4 metal organometallic compound.

27. The process for making a sustainable aviation fuel according to claim 26, wherein
(a) the Group 8-12 metal is selected from Fe, Co, Ni, Cu, Zn, Ru, Rh, Pd, Ir, or Pt;
(b) the Group 6-10 metal is selected from Ni, Co, Fe, or Cr; and
(c) the Group 4 metal organometallic compound is selected from a Group 4 metallocene compound.

28. The process for making a sustainable aviation fuel according to claim 1, wherein contacting the bio-ethylene feed with the first catalyst system occurs at a temperature within a range of from 0° C. to 180° C.

29. The process for making a sustainable aviation fuel according to claim 1, wherein the C_{16-} olefin stream comprises:

    2-ethyl-3-propyl-1-heptene, 5-propyl-1-nonene, 2-ethyl-5-methyl-1-nonene, 7-methyl-1-undecene, 2-ethyl-4-ethyl-1-octene, 6-ethyl-1-decene, 2-ethyl-1-decene, and 1-dodecene;

    4-methylene-5-propylnonane, 2-methyl-5-propylnon-1-ene, 7-methyl-4-methyleneundecane, 2,7-dimethylundec-1-ene, 6-ethyl-4-methylenedecane, 6-ethyl-2-methyldec-1-ene, 4-methylenedodecane, and 2-methyldodec-1-ene; 5-methylene-6-propyl decane, 3-methylene-6-propyl decane, 5-methylene-8-methyl dodecane, 3-methylene-8-methyl dodecane, 5-methylene-7-ethyl undecane, 3-methylene-7-ethyl undecane, 2-butyl-1-decene, and 2-ethyl-1-dodecene; or

    6-methylene-5-propyl dodecane, 2-butyl-5-propyl-1-nonene, 2-hexyl-5-methyl-1-nonene, 2-butyl-7-methyl-1-undecene, 6-methylene-4-ethyl tridecane, 2-butyl-6-ethyl-1-decene, 2-hexyl-1-decene, and 4-butyl-1-dodecene.

30. The process for making a sustainable aviation fuel according to claim 1, wherein the C_{16-} olefin stream comprises:

4-propyl-2-octene, 5-ethyl-2-nonene, 6-methyl-2-decene, 2-undecene, 2-hexene, 2-heptene, and 2-octene;

5-propyl-3-nonene, 6-ethyl-3-decene, 7-methyl-3-undecene, 3-dodecene, 3-heptene, 3-octene, and 3-nonene;

2-methyl-4-propyl-2-octene, 5-ethyl-2-methyl-2-nonene, 2,6-dimethyl-2-decene, 2-methyl-2-undecene, 2-methyl-2-hexene, 2-methyl-2-heptene, and 2-methyl-2-octene;

6-propyl-4-decene, 7-ethyl-4-undecene, 8-methyl-4-dodecene, 4-tridecene, 4-octene, 4-nonene, and 4-decene;

7-propyl-5-undecene, 8-ethyl-5-dodecene, 9-methyl-5-tridecene, 5-tetradecene, 4-nonene, 5-decene, and 5-undecene;

2,2-dimethyl-5-propyl-3-nonene, 6-ethyl-2,2-dimethyl-3-decene, 2,2,7-trimethyl-3-undecene, 2,2-dimethyl-3-dodecene, 2,2-dimethyl-3-heptene, 2,2-dimethyl-3-octene, and 2,2-dimethyl-3-nonene; or

5-propyl-6-tridecene, 5-ethyl-7-tetradecene, 11-methyl-7-pentadecene, 7-hexadecene, 4-undecene, 5-dodecene, and 6-tridecene.

31. A process for making a sustainable aviation fuel, the process comprising:

    a) providing a bio-ethylene feed, at least a portion of which is derived from the dehydration of biomass ethanol;

    b) contacting the bio-ethylene feed with a first catalyst system comprising a first oligomerization catalyst to form an oligomerization product comprising at least one C_4-C_8 alpha-olefin and a mixture of decenes;

    c) separating the mixture of decenes from the oligomerization product;

    d) hydrogenating the mixture of decenes in the presence of a first hydrogenation catalyst to provide a mixture of decanes; and

    e) using the mixture of decanes as a component to form a sustainable aviation fuel.

32. The process for making a sustainable aviation fuel according to claim 31, wherein the mixture of decanes is blended with C_{16-} paraffins and/or cycloparaffins to form the sustainable aviation fuel.

33. The process for making a sustainable aviation fuel according to claim 31, wherein:

a) the sustainable aviation fuel is certified as compliant with the Carbon Offsetting and Reduction Scheme for International Aviation (CORSIA) sustainability criteria in accordance with the International Sustainability and Carbon Certification (ISCC) CORSIA certification system; or

b) the sustainable aviation fuel is certified as a Lower Carbon Aviation Fuel (LCAF) in accordance with the International Sustainability and Carbon Certification (ISCC) LCAF certification system;

wherein the certification is based upon the weight or fraction of the sustainable aviation fuel attributable to the biomass ethanol determined by mass balance and a free attribution method.

34. The process for making a sustainable aviation fuel according to claim 31, wherein the mixture of decenes comprises 1-decene, 2-butyl-1-hexene, 3-propyl-1-heptene, 4-ethyl-1-octene, 5-methyl-1-nonene, 4-decene, 5-decene, or any combination thereof.

35. The process for making a sustainable aviation fuel according to claim 34, wherein the at least one C_4-C_8 alpha-olefin comprises 1-butene, 1-hexene, 1-octene, or any combination thereof.

36. The process for making a sustainable aviation fuel according to claim 35, wherein the oligomerization product comprises:

at least 60 mol % 1-hexene, at least 60 mol % 1-octene, or at least 60 mol % 1-hexene and 1-octene combined; or

from 70 wt. % to 99.8 wt. % hexene or from 70 wt. % to 99.8 wt. % octene, and at least 0.2 wt. % of the mixture of decenes.