CLAIMS

What is claimed is:

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

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

    b) contacting the bio-ethylene feed with a first oligomerization catalyst system to form a first oligomerization product comprising at least one C_4 to C_{16} alpha-olefin;

    c) contacting a first portion of the first oligomerization product with a second oligomerization catalyst system to provide a second oligomerization product comprising C_{16}-olefins;

    d) separating a second portion of the first oligomerization product prior to contacting the first portion of the first oligomerization product with the second oligomerization catalyst system;

    e) combining the second portion of the first oligomerization product from step (d) with the second oligomerization product from step (c) to form a mixture; and

    f) hydrogenating the mixture of the second portion of the first oligomerization product and the second oligomerization product in the presence of a first hydrogenation catalyst to provide a first C_{16}-paraffin stream.

2. The process for making a sustainable jet fuel according to claim 1, further comprising using the first C_{16}-paraffin stream as a component to form the sustainable jet fuel.

3. The process for making a sustainable jet fuel according to claim 1, wherein the at least one C_4 to C_{16} alpha-olefin comprises C_4 to C_{14} alpha-olefins, C_6 to C_8 alpha-olefins, C_6 plus C_{10} alpha-olefins, C_6 to C_{10} alpha-olefins, or any combination thereof.

4. The process for making a sustainable jet fuel according to claim 1, wherein the steps of contacting the bio-ethylene feed with the first oligomerization catalyst system and contacting the first oligomerization product with the second oligomerization catalyst system are carried out in the same reactor.

5. The process for making a sustainable jet fuel according to claim 1, wherein the steps of contacting the bio-ethylene feed with the first oligomerization catalyst system and contacting the first oligomerization product with the second oligomerization catalyst system are carried out in different reactors.

6. The process for making a sustainable jet fuel according to claim 1, further comprising:

   certifying the sustainable jet fuel as compliant with the Carbon Offsetting and Reduction Scheme for International Jet (CORSIA) sustainability criteria in accordance with the International Sustainability and Carbon Certification (ISCC) CORSIA certification system;

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

7. The process for making a sustainable jet fuel according to claim 1, further comprising:

   certifying the sustainable jet fuel as a Lower Carbon Jet Fuel (LCAF) in accordance with the International Sustainability and Carbon Certification (ISCC) LCAF certification system;

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

8. The process for making a sustainable jet fuel according to claim 1, wherein the first oligomerization catalyst system and the second oligomerization catalyst system, independently, comprise a chromium-based catalyst, a metallocene-based catalyst, a Ziegler-Natta based catalyst, 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, 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.

9. The process for making a sustainable jet fuel according to claim 8, wherein the first oligomerization catalyst system and the second oligomerization catalyst system, independently, further comprise an organoaluminum compound, an organoaluminoxane, an organoboron compound, an organozinc compound, an organomagnesium compound, an organolithium compound, or any combination thereof.

10. The process for making a sustainable jet fuel according to claim 1, wherein the first oligomerization catalyst system and the second oligomerization catalyst system, independently, comprise a chromium-based catalyst, and the chromium-based catalyst comprises (a) a chromium-containing compound, (b) a heteroatomic ligand, and (c) optionally, a diluent;

wherein the heteroatomic ligand is a separate component of the first oligomerization catalyst system or the second oligomerization catalyst system or is a ligand complexed to the chromium-containing compound of the first oligomerization catalyst system or the second oligomerization catalyst system.

11. The process for making a sustainable jet fuel according to claim 1, wherein the bio-ethylene feed is derived from the dehydration of the biomass ethanol or the bio-syngas ethanol in the presence of a dehydration catalyst under conditions suitable to form bio-ethylene, and 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.

12. The process for making a sustainable jet 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;

    wherein (i) the Group 8-12 metal of the heterogeneous catalyst is selected from Fe, Co, Ni, Cu, Zn, Ru, Rh, Pd, Ir, or Pt; (ii) the Group 6-10 metal of the homogeneous catalyst is selected from Ni, Co, Fe, or

Cr; or (iii) the Group 4 metal organometallic compound is selected from a Group 4 metallocene compound.

13. The process for making a sustainable jet fuel according to claim 1, wherein:

contacting the bio-ethylene feed with the first oligomerization catalyst system occurs at a total bio-ethylene pressure of from 50 psig (344 KPa) to 2,500 psig (17.3 MPa);

contacting the first oligomerization product with the second oligomerization catalyst system occurs at a total pressure of from 0 psig (0 KPa) to 2,500 psig (17.3 MPa); and

contacting the bio-ethylene feed with the first oligomerization catalyst system and contacting the first oligomerization product with the second oligomerization catalyst system occur at a temperature selected independently within a range of from 0° C. to 180° C.

14. A process for making a sustainable jet fuel, the process comprising:

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

b) contacting the bio-ethylene feed with a first oligomerization catalyst system to form a first oligomerization product comprising at least one C_4 to C_{16} alpha-olefin;

c) contacting a first portion of the first oligomerization product with a second oligomerization catalyst system to provide a second oligomerization product comprising C_{16}-olefins;

d) hydrogenating the second oligomerization product in the presence of a first hydrogenation catalyst to provide a first C_{16}-paraffin stream;

e) separating a C_6 to C_8 aliphatic hydrocarbon stream comprising at least one C_6 to C_8 alpha-olefin and/or C_6 to C_8 paraffin from the first oligomerization product;

f) contacting the C_6 to C_8 aliphatic hydrocarbon stream with a reforming catalyst to provide a C_6 to C_8 aromatic hydrocarbon stream; and

g) hydrogenating at least a portion of the C_6 to C_8 aromatic hydrocarbon stream in the presence of a third hydrogenation catalyst to form a C_6 to C_8 cycloparaffin stream.

15. The process for making a sustainable jet fuel according to claim 14, further comprising:

h) using the C_6 to C_8 cycloparaffin stream, the C_6 to C_8 aromatic hydrocarbon stream, or both as components to form the sustainable jet fuel.

16. The process for making a sustainable jet fuel according to claim 14, wherein:

step (e) of separating the C_6 to C_8 aliphatic hydrocarbon stream from the first oligomerization product provides an alpha-olefin raffinate comprising at least one C_4 and C_{10}-C_{16} alpha-olefin; and

step (c) of contacting the first portion of the first oligomerization product with the second oligomerization catalyst system comprises contacting the alpha-olefin raffinate with the second oligomerization catalyst system to provide the second oligomerization product comprising C_{16}-olefins.

17. The process for making a sustainable jet fuel according to claim 14, wherein the reforming catalyst comprises:

a) an inorganic support selected from a crystalline inorganic oxide or an amorphous inorganic oxide, and a Group 8-10 metal; or

b) an inorganic support selected from a crystalline inorganic oxide or an amorphous inorganic oxide, a Group 8-10 metal, and one or more of fluoride, chloride, bromide, or iodide.

18. The process for making a sustainable jet fuel according to claim 14, wherein the reforming catalyst comprises an inorganic support, which is selected from a zeolite, a silica-bound zeolite, a clay mineral, silica, alumina, silica-alumina, aluminum phosphate, a heteropolytungstate, titania, zirconia, magnesia, boria, zinc oxide, mixed oxides thereof, or any combination thereof.

19. The process for making a sustainable jet fuel according to claim 14, wherein the reforming catalyst comprises L-zeolite, K/L-zeolite, X-zeolite, Y-zeolite, omega zeolite, beta zeolite, ZSM-4, ZSM-5, ZSM-10, ZSM-11, ZSM-12, ZSM-20, REY, USY, RE-USY, LZ-210, LZ-210-A, LZ-210-M, LZ-210-T, SSZ-24, SSZ-26, SSZ-31, SSZ-33, SSZ-35, SSZ-37, SSZ-41, SSZ-42, SSZ-44, MCM-58, mordenite, mazzite, faujasite, or combinations thereof.

20. The process for making a sustainable jet fuel according to claim 17, wherein the reforming catalyst comprises a binder selected from an inorganic solid oxide different from the inorganic support, a clay, or a combination thereof, and the binder is present in a concentration of from about 3 wt % to about 35 wt %, based on the total weight of the reforming catalyst.

21. The process for making a sustainable jet fuel according to claim 14, wherein the reforming catalyst comprises a Group 8-10 metal selected from iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, platinum, or any combination thereof.

22. The process for making a sustainable jet fuel according to claim 14, wherein the reforming catalyst comprises platinum and L-zeolite, and wherein:

the platinum is present in the reforming catalyst from about 0.5 wt % to about 2.5 wt %;

the reforming catalyst comprises either (a) from about 0.7 wt % to about 6.0 wt % fluoride relative to the weight of the catalyst prior to reduction; or (b) from about 1.5 wt % to about 6.0 wt % chloride relative to the weight of the catalyst prior to reduction.

23. The process for making a sustainable jet fuel according to claim 14, further comprising:

separating a second portion of the first oligomerization product prior to contacting the first portion of the first oligomerization product with the second oligomerization catalyst system.

24. The process for making a sustainable jet fuel according to claim 14, wherein the at least one C_4 to C_{16} alpha-olefin comprises C_4 to C_{14} alpha-olefins, C_6 to C_8 alpha-olefins, C_6 plus C_{10} alpha-olefins, C_6 to C_{10} alpha-olefins, or any combination thereof.

25. The process for making a sustainable jet fuel according to claim 24, further comprising using the first C_{16}-paraffin stream as a component to form the sustainable jet fuel.

26. The process for making a sustainable jet fuel according to claim 25, wherein the steps of contacting the bio-ethylene feed with the first oligomerization catalyst system and contacting the first oligomerization product with the second oligomerization catalyst system are carried out in the same reactor.

27. The process for making a sustainable jet fuel according to claim 25, wherein the steps of contacting the bio-ethylene feed with the first oligomerization catalyst system and contacting the first oligomerization product with the second oligomerization catalyst system are carried out in different reactors.

28. A process for making a sustainable jet fuel, the process comprising:

    i. providing a bio-ethylene feed, at least a portion of which is derived from a biomass ethanol or a bio-syngas ethanol;

ii. contacting the bio-ethylene feed with a first oligomerization catalyst system to form a first oligomerization product comprising at least one C_4 to C_{16} alpha-olefin;

iii. contacting a first portion of the first oligomerization product with a second oligomerization catalyst system to provide a second oligomerization product comprising C_{16}-olefins; and

iv. hydrogenating the second oligomerization product in the presence of a first hydrogenation catalyst to provide a first C_{16}-paraffin stream;

wherein the first oligomerization catalyst system and
the second oligomerization catalyst system, independently, comprise:

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, 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;

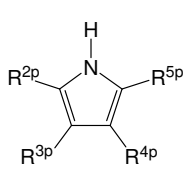
e) a chromium-containing compound complexed to an N^2-phosphinyl amidine compound, and an organoaluminum compound;

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

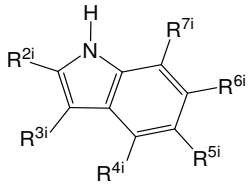
g) a chromium-containing compound complexed to an N^2-phosphinyl formamidine compound, and an organoaluminum compound; or

h) any combinations thereof.

29. The process for making a sustainable jet fuel according to claim 28, wherein the pyrrole compound has the structure of Formula P1 or Formula I1:



P1

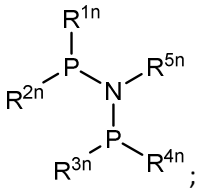


I1

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 independently:

hydrogen, 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.

30. The process for making a sustainable jet fuel according to claim 28, wherein the diphosphino aminyl compound has the Structure PNP2:



;

PNP2

wherein 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, C_5 to C_{20} cycloalkyl group, or C_6-C_{20} aromatic group;

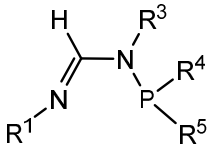
wherein any substituents are selected independently from a C_1 to C_{10} hydrocarbyl group.

31. The process for making a sustainable jet fuel according to claim 30, wherein:

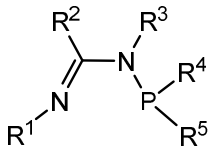
R^{1n} and R^{2n}, and/or R^{3n} and R^{4n} of the diphosphino aminyl compound are joined to form a ring containing a phosphorus atom of the diphosphino aminyl compound; or

R^{1n} and R^{5n}, or R^{4n} and R^{5n} of the diphosphino aminyl compound are joined to form a ring containing a phosphorus atom and the nitrogen atom of the diphosphino aminyl compound.

32. The process for making a sustainable jet fuel according to claim 28, wherein the N^2-phosphinyl formamidine compound has Structure NPF1 or the N^2-phosphinyl formamidine compound has 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; 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 benzyl group or a C_6 to C_{30} substituted benzyl group.

33. The process for making a sustainable jet fuel according to claim 28, wherein the chromium-containing compound is selected from:

chromium(II) nitrate, chromium(II) sulfate, chromium(II) fluoride, chromium(II) chloride, chromium(II) bromide, or 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, a chromium(II) aryloxide, a chromium(II) beta-dionate, a chromium(III) carboxylate, a chromium(III) alkoxide, a chromium(III) aryloxide, or a chromium(III) beta-dionate;

wherein each carboxylate group of the chromium(II) carboxylate and the chromium(III) 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).

34. The process for making a sustainable jet fuel according to claim 28, wherein organoaluminum compound comprises a triorganoaluminum compound, a diorganoaluminum halide, an organoaluminum dihalide, a diorganoaluminum alkoxide, an organoaluminum dialkoxide, an aluminoxane, or combinations thereof.

35. The process for making a sustainable aviation fuel according to claim 28, wherein the organoaluminum compound has a general formula $Al(R^{10})_n(X^{11})_{3-n}$, wherein: n is from 1 to 3 inclusive; each R^{10} is independently a C_1 to C_{20} hydrocarbyl; and X^{11} is independently a halide, a hydride, a C_1 to C_{20} hydrocarbyl, or a C_1 to C_{20} hydrocarbyloxide.

36. The process for making a sustainable jet fuel according to claim 28, wherein:

the at least one C_4 to C_{16} alpha-olefin comprises C_4 to C_{14} alpha-olefins, C_6 to C_8 alpha-olefins, C_6 plus C_{10} alpha-olefins, C_6 to C_{10} alpha-olefins, or any combination thereof, and

the process further comprises using the first C_{16}-paraffin stream as a component to form the sustainable jet fuel.