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(54) **LIQUEFACTION OF CARBONACEOUS MATERIAL AND BIOMASS TO PRODUCE A SYNTHETIC FUEL**

(52) **U.S. Cl.**
USPC **585/240; 44/281**

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(57) **ABSTRACT**

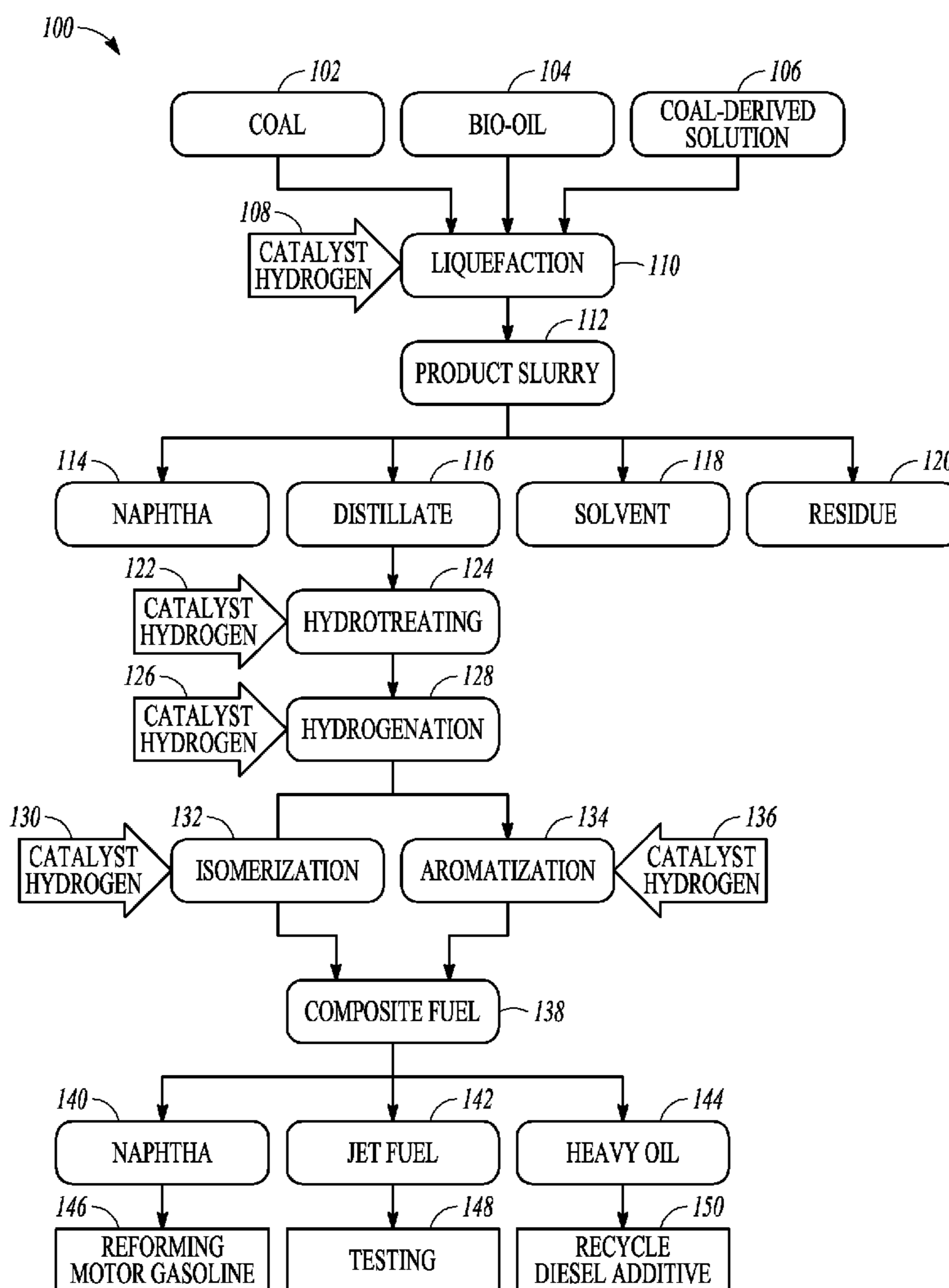
The present invention relates to production of fuels from carbonaceous material and biomass. In some examples, the carbonaceous material is nonpetroleum fossil fuel or petroleum residuals. Various embodiments of the present invention provide a method of liquefaction of carbonaceous material and biomass. The method includes providing or obtaining a feed mixture, the mixture including carbonaceous material and biomass. The method also includes subjecting the feed mixture to liquefaction, to provide a product slurry. Various embodiments of the present invention provide a method of fuel production from carbonaceous material and biomass. The method includes separating the product slurry from the liquefaction, to give a conversion component. The method also includes processing the conversion component, to give a fuel.

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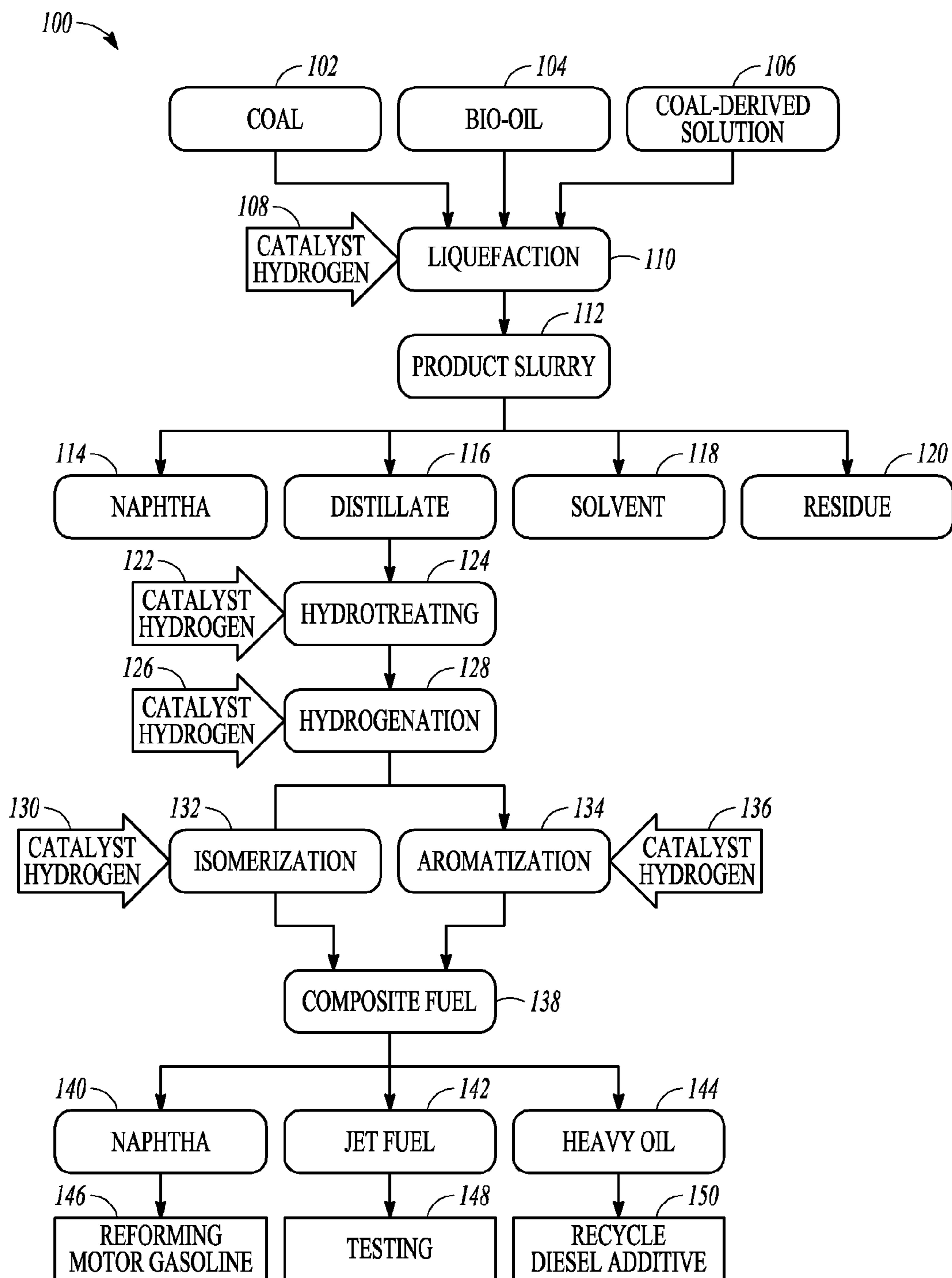


FIG. 1

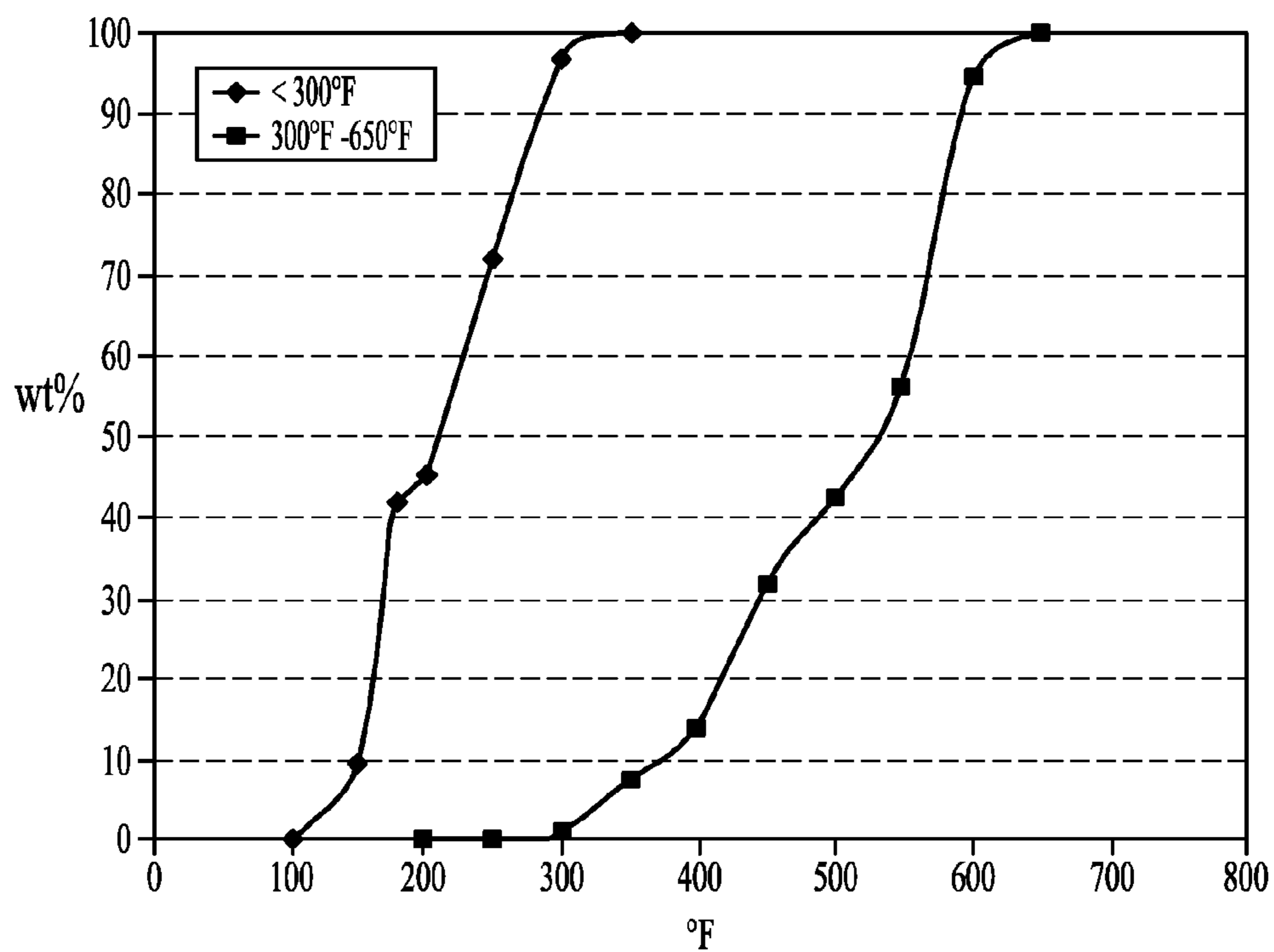


FIG. 2

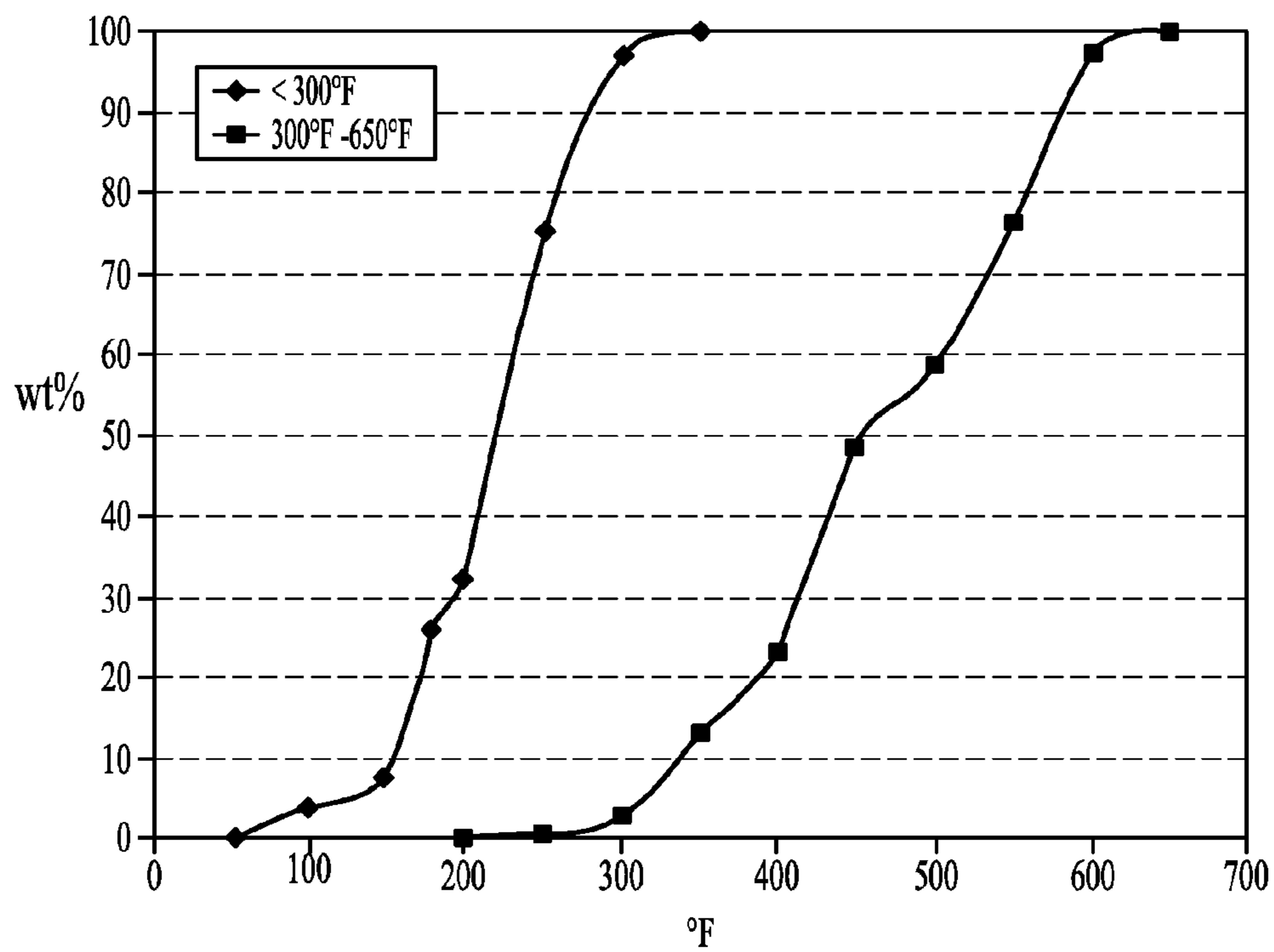


FIG. 3

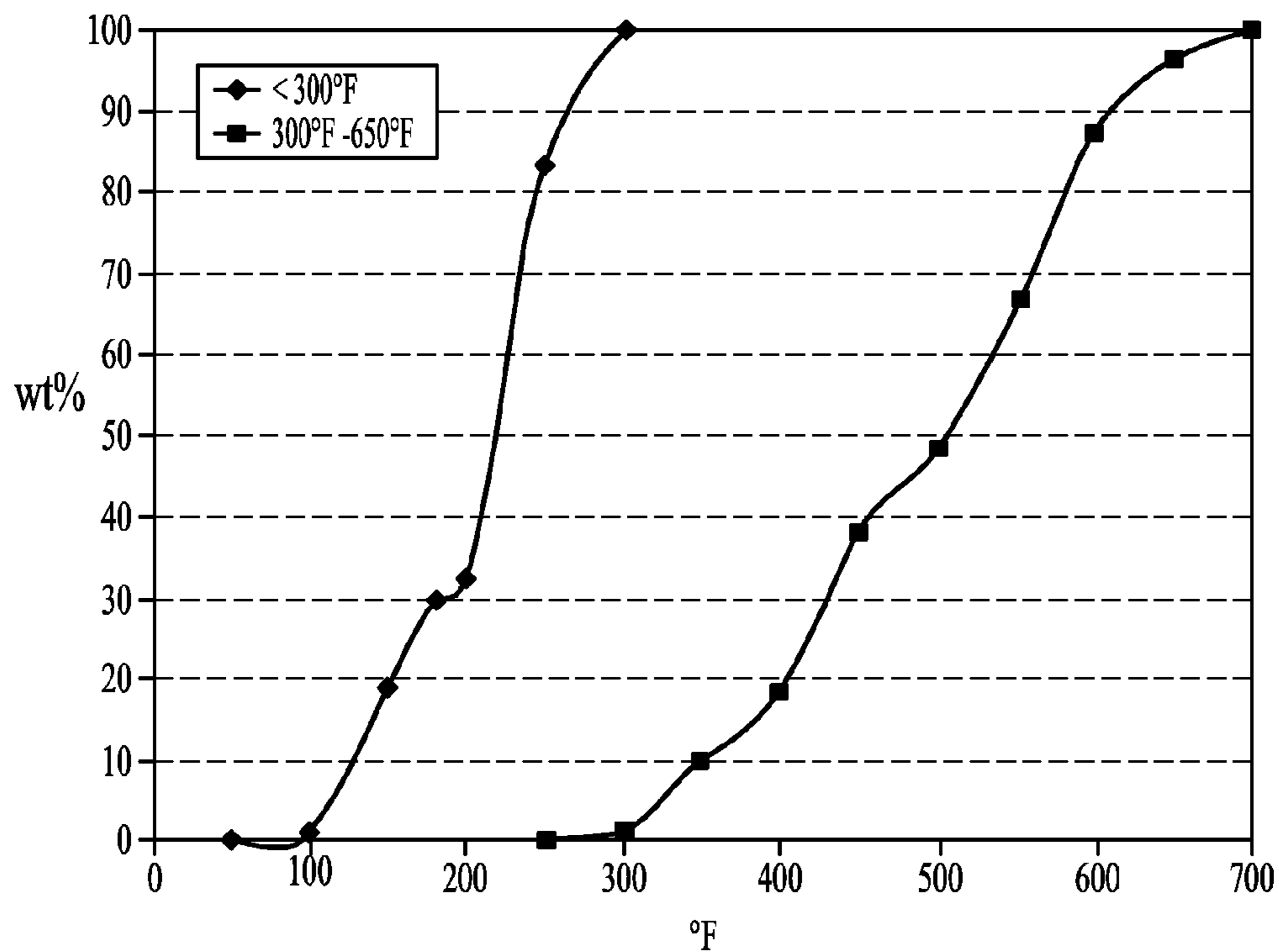


FIG. 4

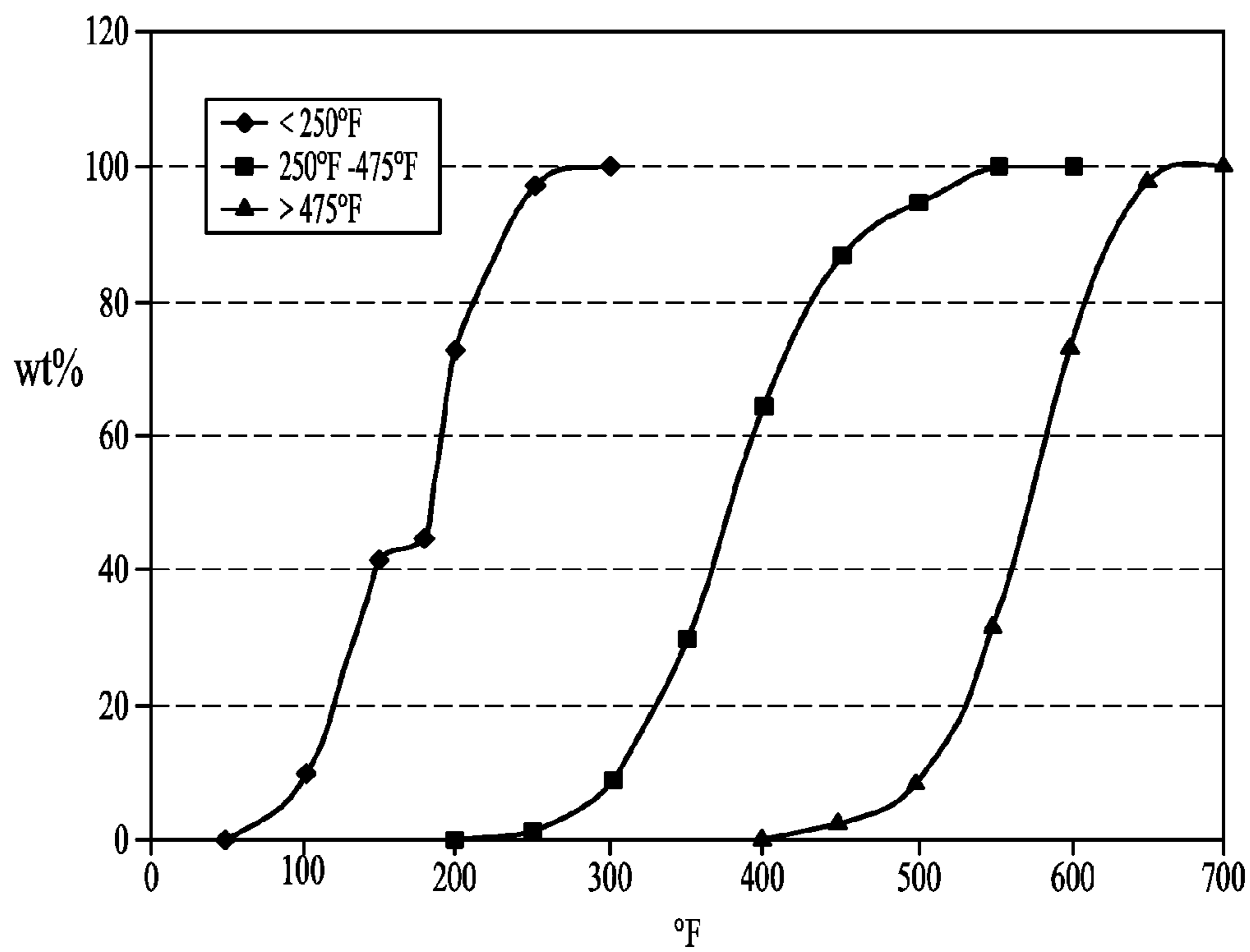


FIG. 5

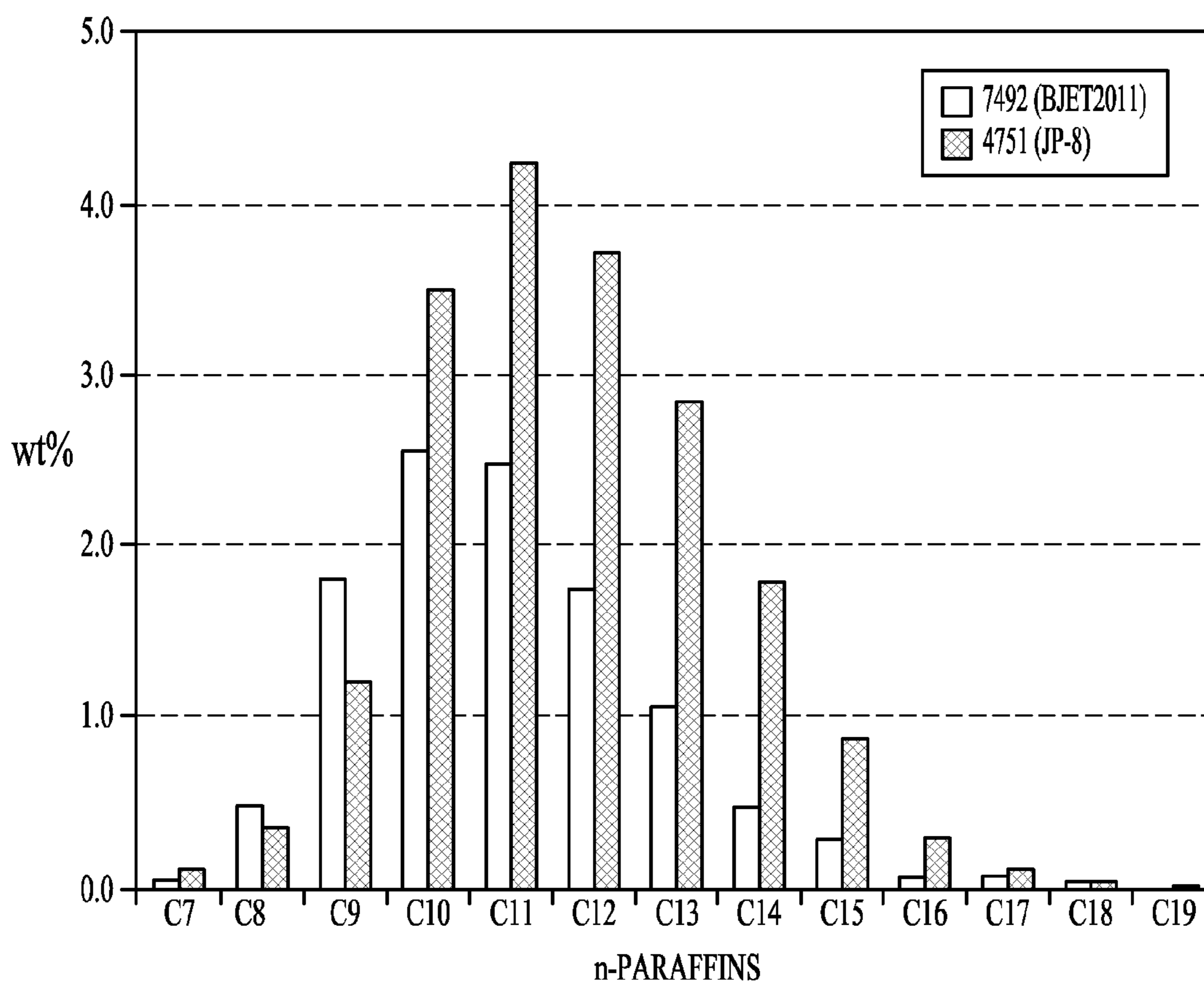


FIG. 6

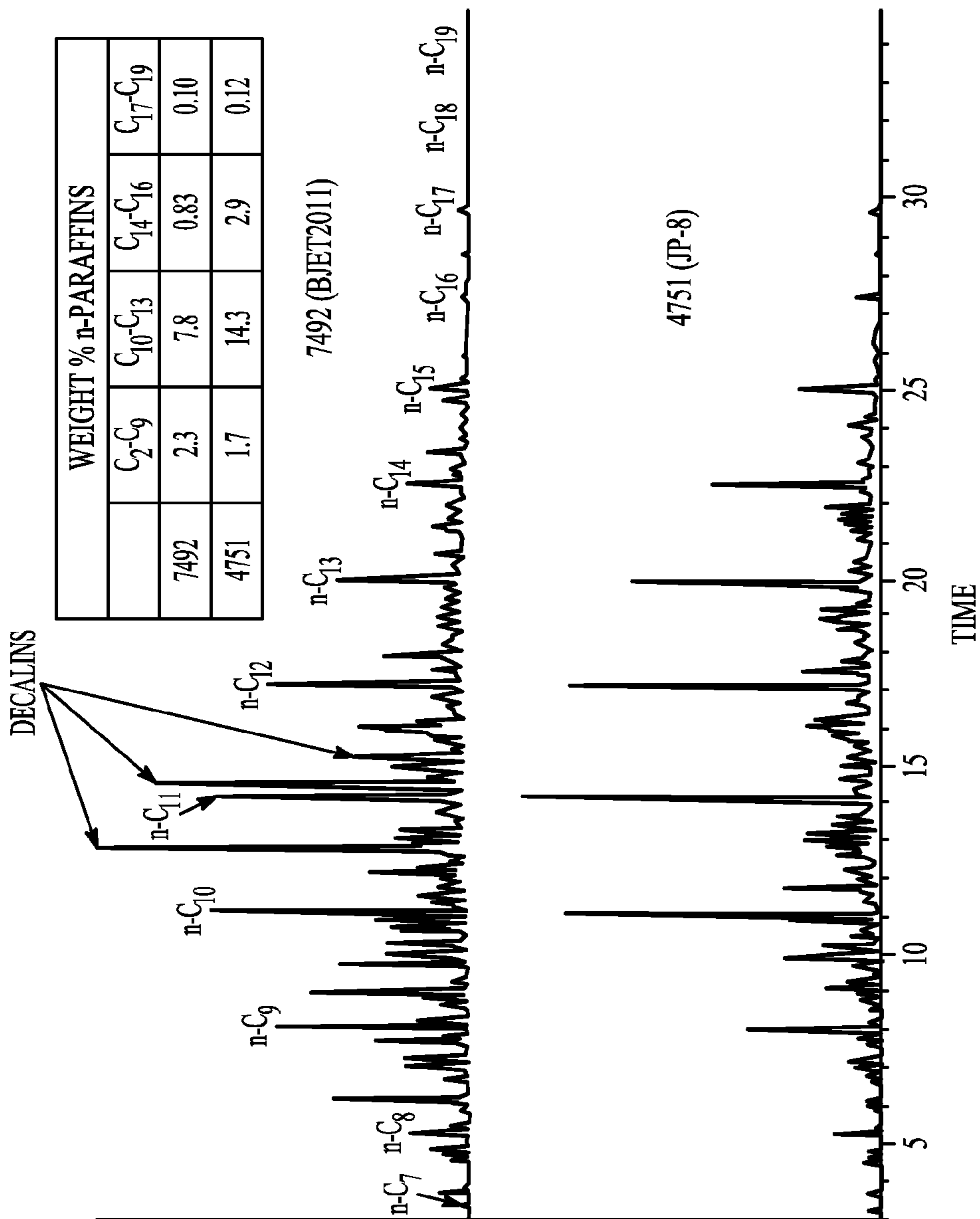


FIG. 7

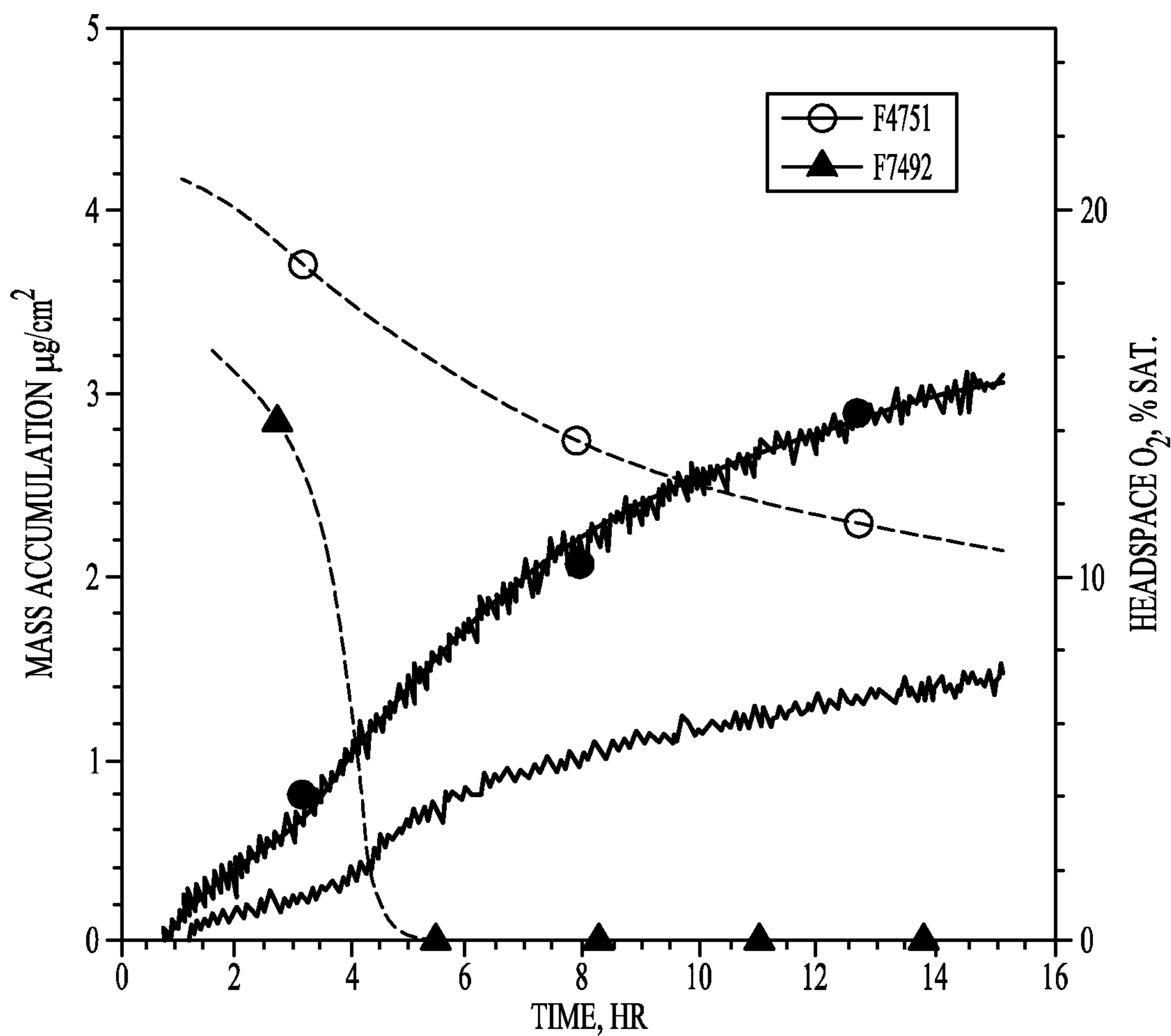


FIG. 8

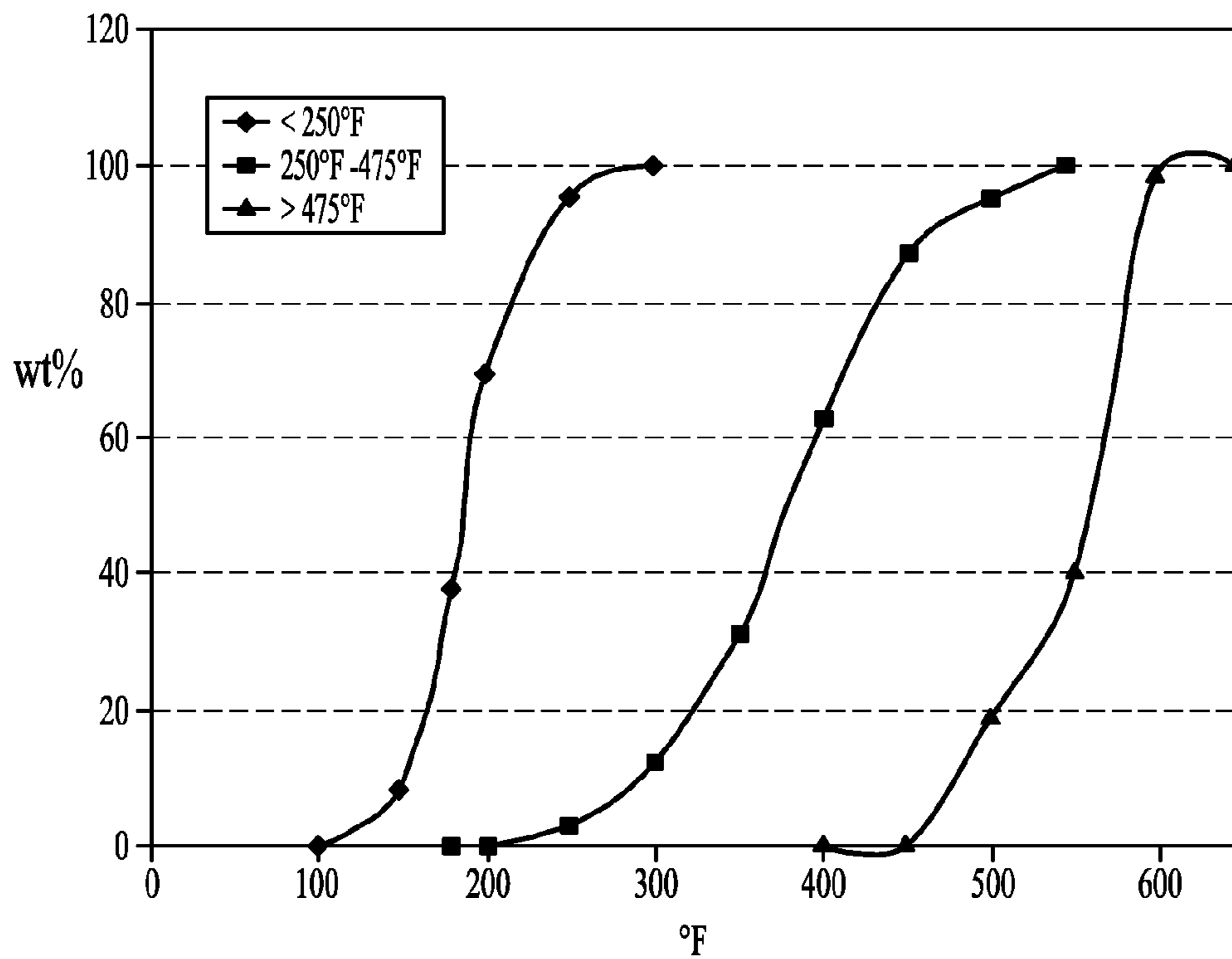


FIG. 9

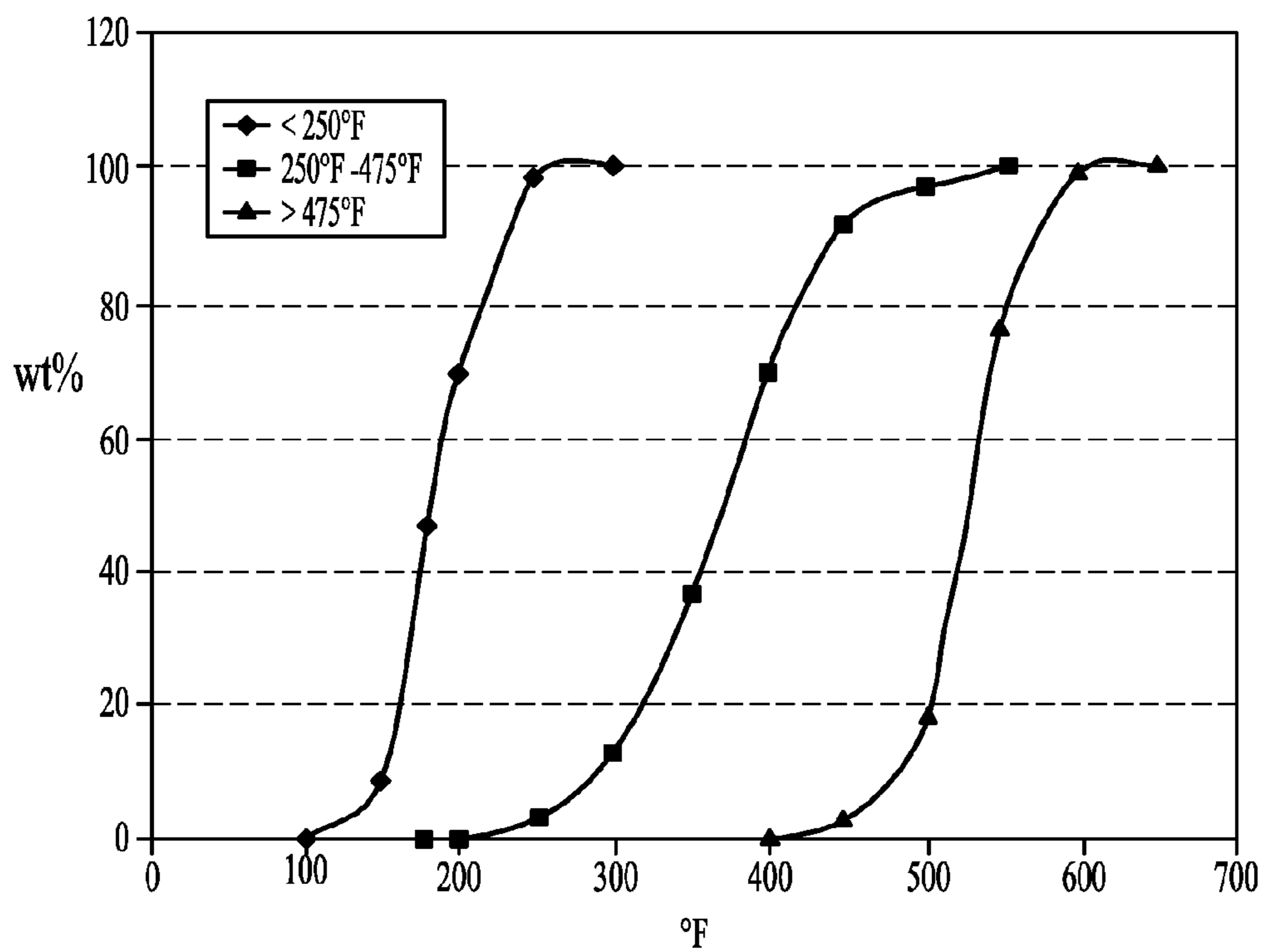


FIG. 10

**LIQUEFACTION OF CARBONACEOUS
MATERIAL AND BIOMASS TO PRODUCE A
SYNTHETIC FUEL**

STATEMENT OF GOVERNMENT SUPPORT

[0001] This invention was made with government support under U.S. Department of Energy (DOE) Cooperative Agreement No. DE-FC26-0SNT43291 entitled "EERC-DOE Joint Program on Research and Development for Fossil Energy-Related Resources," Subtask 3.5 entitled "Catalytic Coal Liquefaction to Produce Transportation Fuels," Energy & Environmental Research Center (EERC) Fund 15159, and U.S. Department of Energy Cooperative Agreement No. DE-FC26-0SNT43291 entitled "EERC-DOE Joint Program on Research and Development for Fossil Energy-Related Resources," Subtask 3.8 entitled "Analysis of Multiple Pathways for Converting Coal to Liquid Transportation Fuels," EERC Fund 16344. The government has certain rights in this invention.

BACKGROUND OF THE INVENTION

[0002] Refining of petroleum crude is the most common pathway for the production of fuels. However, petroleum is a limited and nonrenewable resource, and the extraction, transportation, and refining of petroleum can be problematic from an environmental, political, and energy efficiency standpoint. Several competitive technologies allowing production of synthetic fuels from other sources such as coal or natural gas are currently being developed or are at advanced stages of development. In addition, most competitive technologies do not produce all of the key constituents needed to produce synthetic fuels, such as aviation fuels. At best, they produce blendstocks that need to be mixed with petroleum-derived fuels or blendstocks to meet the key requirements of particular fuels, such as aviation fuels.

[0003] Recently, the U.S. Department of Defense expressed interest in a universal fuel for military use, preferably from a synthetic process to improve energy security. Termed Battlefield Use Fuel of the Future (BUFF), the fuel is very similar to jet fuel in specifications, but has more stringent flash point specifications (60° C.).

SUMMARY OF THE INVENTION

[0004] Various embodiments of the present invention provide a method of liquefaction of carbonaceous material and biomass. The method includes providing or obtaining a feed mixture. The feed mixture includes carbonaceous material and biomass. The method also includes subjecting the feed mixture to liquefaction. The liquefaction provides a product slurry. The carbonaceous material includes a nonpetroleum fossil fuel or a petroleum refinery residue.

[0005] Various embodiments of the present invention provide a method of fuel production from carbonaceous material and biomass. The method includes providing or obtaining a feed mixture. The feed mixture includes carbonaceous material and biomass. The method also includes subjecting the feed mixture to liquefaction. The liquefaction provides a product slurry. The carbonaceous material includes a nonpetroleum fossil fuel or a petroleum refinery residue. The method also includes separating the product slurry. Separating the product slurry provides a conversion component. The method also includes processing the conversion component. Processing provides a fuel.

[0006] Various embodiments of the present invention provide certain advantages of other methods of liquefaction and fuel production. In some embodiments, the ratio of carbonaceous material and biomass can be adjusted to generate a desired mixture of products. Some embodiments of the present invention can provide a synthetic fuel facility that can produce a fully or substantially fully synthetic fuel that meets JP-5/JP-8 specs or JP-5/BUFF specs. Some embodiments of the present method have a smaller carbon footprint than other methods of liquefaction and other methods of fuel production, such as petroleum fuel production or other methods of synthetic fuel production. Some embodiments of the present invention can provide a fully or substantially synthetic kerosene-dominant refinery in which the naphtha and distillate that are coproduced are easily refinable to meet final fuel specs, rather than having to be sold as naphtha or distillate blendstocks. Some embodiments are integrated or substantially integrated with respect to fuel production, such that all or most components of a desired fuel, such as jet fuel, are generated in a single refinery without the need for the addition of other blendstocks, such as petroleum-derived blendstocks. In some embodiments, the ability to generate materials that are fully or substantially fully refinable into a synthetic fuel can be advantageous for refinery locations far from markets for intermediate blendstock products or for refineries used as a strategic asset for the production of fuel for military use, including, for example, for production of synthetic aviation fuels. Some embodiments can refine fuel precursors into a desired fuel more efficiently than other refining techniques, for example with less consumption of energy or valuable materials than other methods. In some embodiments, in the refining process, the proportion of hydrogenated material subjected to a hydroisomerization process or aromatization process can be varied to achieve a desired fuel blend. Various embodiments of the method are flexible, allow tailoring of the secondary products, and can accommodate different refining technology preferences. In some examples, the method can be less complex than other refining techniques and can allow the production of fuels such as aviation fuels, while, in some embodiments, coproducing chemicals or other transportation fuels. In some examples, the present invention can allow elimination of substantial gas cleanup equipment, reducing the overall size of the plant.

[0007] In various embodiments, the present invention provides a method of liquefaction of coal and biomass. The method includes providing or obtaining a feed mixture. The feed mixture includes coal and biomass. The biomass includes plant-derived oil, algae-derived oil, biomass pyrolysis oil, waste oil, yellow grease, brown grease, tar, or animal fat. The method also includes subjecting the feed mixture to liquefaction. The liquefaction provides a product slurry. The liquefaction includes contacting the feed mixture with a liquefaction catalyst and hydrogen gas at a temperature of about 200° to 450° C., at a pressure of about 50 to 450 atm.

[0008] In various embodiments, the present invention provides a method of fuel production from coal and biomass. The method includes providing or obtaining a feed mixture. The mixture includes coal and biomass. The biomass includes plant-derived oil, algae-derived oil, biomass pyrolysis oil, waste oil, yellow grease, brown grease, tar, or animal fat. The method also includes subjecting the feed mixture to liquefaction. The liquefaction provides a product slurry. The method also includes distilling the product slurry. Distilling provides a distillate. The method also includes hydrotreating the dis-

tillate. Hydrotreating provides a hydrotreated material. The method also includes hydrogenating the hydrotreated material. Hydrogenating provides a hydrogenated material. The method also includes isomerizing at least some of the hydrotreated material. Isomerizing at least some of the hydrotreated material provides an isomerized material. The method also includes aromatizing at least some of the hydrotreated material. The aromatizing provides an aromatized material. The method also includes blending at least some of the isomerized material and at least some of the aromatized material. The blending provides a fuel.

BRIEF DESCRIPTION OF THE FIGURES

[0009] In the drawings, which are not necessarily drawn to scale, like numerals describe substantially similar components throughout the several views. Like numerals having different letter suffixes represent different instances of substantially similar components. The drawings illustrate generally, by way of example, but not by way of limitation, various embodiments discussed in the present document.

[0010] FIG. 1 illustrates a flow sheet of process fuel production from carbonaceous material and biomass, in accordance with various embodiments.

[0011] FIG. 2 illustrates the distillation profile of a coal-canola oil-derived liquid, in accordance with various embodiments.

[0012] FIG. 3 illustrates the distillation profile of a coal-algae oil-derived liquid, in accordance with various embodiments.

[0013] FIG. 4 illustrates the distillation profile of a coal-wax-derived liquid, in accordance with various embodiments.

[0014] FIG. 5 illustrates distillation profiles for coal-canola oil-derived fuels, in accordance with various embodiments.

[0015] FIG. 6 illustrates the wt % of n-paraffins in a fuel sample produced by an embodiment of the method of the present invention, as compared to a JP-8 fuel sample.

[0016] FIG. 7 illustrates a gas chromatography (GC) chromatogram of a fuel sample produced by an embodiment of the method of the present invention, as compared to a JP-8 fuel sample.

[0017] FIG. 8 illustrates quartz crystal microbalance (QCM)-determined mass accumulation and headspace oxygen of a fuel sample produced by an embodiment of the method of the present invention, as compared to a JP-8 fuel sample.

[0018] FIG. 9 illustrates distillation profiles for coal-algae oil-derived fuels, in accordance with various embodiments.

[0019] FIG. 10 illustrates distillation profiles for coal-wax-derived fuels, in accordance with various embodiments.

DETAILED DESCRIPTION OF THE INVENTION

[0020] Reference will now be made in detail to certain claims of the disclosed subject matter, examples of which are illustrated in the accompanying drawings. While the disclosed subject matter will be described in conjunction with the enumerated claims, it will be understood that they are not intended to limit the disclosed subject matter to those claims. On the contrary, the disclosed subject matter is intended to cover all alternatives, modifications, and equivalents, which can be included within the scope of the presently disclosed subject matter as defined by the claims.

[0021] References in the specification to “one embodiment,” “an embodiment,” “an example embodiment,” and the like, indicate that the embodiment described can include a particular feature, structure, or characteristic, but every embodiment may not necessarily include the particular feature, structure, or characteristic. Moreover, such phrases are not necessarily referring to the same embodiment. Further, when a particular feature, structure, or characteristic is described in connection with an embodiment, it is submitted that it is within the knowledge of one of ordinary skill in the art to effect such feature, structure, or characteristic in connection with other embodiments whether or not explicitly described.

[0022] Values expressed in a range format should be interpreted in a flexible manner to include not only the numerical values explicitly recited as the limits of the range, but also to include all the individual numerical values or subranges encompassed within that range as if each numerical value and subrange is explicitly recited. For example, a range of “about 0.1% to about 5%” or “about 0.1% to 5%” should be interpreted to include not only about 0.1% to about 5%, but also the individual values (e.g., 1%, 2%, 3%, and 4%) and the subranges (e.g., 0.1% to 0.5%, 1.1% to 2.2%, 3.3% to 4.4%) within the indicated range.

[0023] In this document, the terms “a,” “an,” or “the” are used to include one or more than one, unless the context clearly dictates otherwise. The term “or” is used to refer to a nonexclusive “or” unless otherwise indicated. In addition, it is to be understood that the phraseology or terminology employed herein, and not otherwise defined, is for the purpose of description only and not of limitation. Any use of section headings is intended to aid reading of the document and is not to be interpreted as limiting; information that is relevant to a section heading may occur within or outside of that particular section. Furthermore, all publications, patents, and patent documents referred to in this document are incorporated by reference herein in their entirety as though individually incorporated by reference. In the event of inconsistent usages between this document and those documents so incorporated by reference, the usage in the incorporated reference should be considered supplementary to that of this document; for irreconcilable inconsistencies, the usage in this document controls.

[0024] In the methods of manufacturing described herein, the steps can be carried out in any order without departing from the principles of the invention, except when a temporal or operational sequence is explicitly recited.

[0025] Furthermore, specified steps can be carried out concurrently unless explicit claim language recites that they be carried out separately. For example, a claimed step of doing X and a claimed step of doing Y can be conducted simultaneously within a single operation, and the resulting process will fall within the literal scope of the claimed process.

DEFINITIONS

[0026] The term “about” as used herein can allow for a degree of variability in a value or range, for example, within 10%, within 5%, or within 1% of a stated value or of a stated limit of a range. When a range or a list of sequential values is given, unless otherwise specified any value within the range or any value between the given sequential values is also disclosed.

[0027] The term “substantially” as used herein refers to a majority of, or mostly, as in at least about 50%, 60%, 70%,

80%, 90%, 95%, 96%, 97%, 98%, 99%, 99.5%, 99.9%, 99.99%, or at least about 99.999% or more.

[0028] The term “organic group” as used herein refers to but is not limited to any carbon-containing functional group. For example, an organic group may be an oxygen-containing group such as alkoxy groups, aryloxy groups, aralkyloxy groups, oxo(carbonyl) groups, carboxyl groups including carboxylic acids, carboxylates, and carboxylate esters; a sulfur-containing group such as alkyl and aryl sulfide groups; and other heteroatom-containing groups.

[0029] The term “substituted” as used herein refers to an organic group as defined herein or a molecule in which one or more hydrogen atoms contained therein are replaced by one or more non-hydrogen atoms. The term “functional group” or “substituent” as used herein refers to a group that can be or is substituted onto a molecule or onto an organic group.

[0030] The term “alkyl” as used herein refers to straight chain and branched alkyl groups and cycloalkyl groups having from 1 to 40 carbon atoms, 1 to about 20 carbon atoms, 1 to 12 carbons or, in some embodiments, from 1 to 8 carbon atoms. Examples of straight-chain alkyl groups include those with from 1 to 8 carbon atoms such as methyl, ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, n-heptyl, and n-octyl groups. Examples of branched alkyl groups include, but are not limited to, isopropyl, isobutyl, sec-butyl, t-butyl, neopentyl, isopentyl, and 2,2-dimethylpropyl groups. As used herein, the term “alkyl” encompasses n-alkyl, isoalkyl, and anteisoalkyl groups as well as other branched chain forms of alkyl. Representative substituted alkyl groups can be substituted one or more times with any of the groups listed herein, for example, amino, hydroxy, cyano, carboxy, nitro, thio, alkoxy, and halogen groups.

[0031] The term “alkenyl” as used herein refers to straight- and branched-chain and cyclic alkyl groups as defined herein, except that at least one double bond exists between two carbon atoms. Thus alkenyl groups have from 2 to 40 carbon atoms, or 2 to about 20 carbon atoms, or 2 to 12 carbons or, in some embodiments, from 2 to 8 carbon atoms. Examples include, but are not limited to, vinyl, $-\text{CH}=\text{CH}(\text{CH}_3)$, $-\text{CH}=\text{C}(\text{CH}_3)_2$, $-\text{C}(\text{CH}_3)=\text{CH}_2$, $-\text{C}(\text{CH}_3)=\text{CH}(\text{CH}_3)$, $-\text{C}(\text{CH}_2\text{CH}_3)=\text{CH}_2$, cyclohexenyl, cyclopentenyl, cyclohexadienyl, butadienyl, pentadienyl, and hexadienyl among others.

[0032] The term “alkynyl” as used herein refers to straight- and branched-chain alkyl groups, except that at least one triple bond exists between two carbon atoms. Thus, alkynyl groups have from 2 to 40 carbon atoms, 2 to about 20 carbon atoms, or from 2 to 12 carbons or, in some embodiments, from 2 to 8 carbon atoms. Examples include, but are not limited to $-\text{C}\equiv\text{CH}$, $-\text{C}\equiv\text{C}(\text{CH}_3)$, $-\text{C}\equiv\text{C}(\text{CH}_2\text{CH}_3)$, $-\text{CH}_2\text{C}\equiv\text{CH}$, $-\text{CH}_2\text{C}\equiv\text{C}(\text{CH}_3)$, and $-\text{CH}_2\text{C}\equiv\text{C}(\text{CH}_2\text{CH}_3)$ among others.

[0033] The term “acyl” as used herein refers to a group containing a carbonyl moiety wherein the group is bonded via the carbonyl carbon atom.

[0034] The term “cycloalkyl” as used herein refers to cyclic alkyl groups such as, but not limited to, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, and cyclooctyl groups. In some embodiments, the cycloalkyl group can have 3 to about 8-12 ring members, whereas in other embodiments, the number of ring carbon atoms ranges from 3 to 4, 5, 6, or 7.

[0035] The term “aryl” as used herein refers to cyclic aromatic hydrocarbons that do not contain heteroatoms in the ring. Thus aryl groups include, but are not limited to, phenyl,

azulenyl, heptalenyl, biphenyl, indacenyl, fluorenyl, phenanthrenyl, triphenylenyl, pyrenyl, naphthacenyl, chrysenyl, biphenylenyl, anthracenyl, and naphthyl groups. In some embodiments, aryl groups contain about 6 to about 14 carbons in the ring portions of the groups. Aryl groups can be unsubstituted or substituted, as defined herein. Representative substituted aryl groups can be mono-substituted or substituted more than once, such as, but not limited to, 2-, 3-, 4-, 5-, or 6-substituted phenyl or 2-8 substituted naphthyl groups, which can be substituted with carbon or noncarbon groups such as those listed herein.

[0036] The term “heterocyclyl” as used herein refers to aromatic and nonaromatic ring compounds containing 3 or more ring members, of which one or more is a heteroatom such as, but not limited to, N, O, and S. Thus a heterocyclyl can be a cycloheteroalkyl, or a heteroaryl, or if polycyclic, any combination thereof. In some embodiments, heterocyclyl groups include 3 to about 20 ring members, whereas other such groups have 3 to about 15 ring members.

[0037] The term “heteroaryl” as used herein refers to aromatic ring compounds containing 5 or more ring members, of which one or more is a heteroatom such as, but not limited to, N, O, and S; for instance, heteroaryl rings can have 5 to about 8-12 ring members. A heteroaryl group is a variety of a heterocyclyl group that possesses an aromatic electronic structure.

[0038] The terms “halo” or “halogen” or “halide,” as used herein, by themselves or as part of another substituent mean, unless otherwise stated, a fluorine, chlorine, bromine, or iodine atom.

[0039] The term “haloalkyl” group, as used herein, includes mono-halo alkyl groups, poly-halo alkyl groups wherein all halo atoms can be the same or different, and per-halo alkyl groups, wherein all hydrogen atoms are replaced by halogen atoms, such as fluoro. Examples of haloalkyls include trifluoromethyl, 1,1-dichloroethyl, 1,2-dichloroethyl, 1,3-dibromo-3,3-difluoropropyl, perfluorobutyl, and the like.

[0040] The term “monovalent” as used herein refers to a substituent connecting via a single bond to a substituted molecule. When a substituent is monovalent, such as, for example, F or Cl, it is bonded to the atom it is substituting by a single bond.

[0041] The term “solvent” as used herein refers to a liquid that can dissolve a solid, liquid, or gas. Nonlimiting examples of solvents are silicones, organic compounds, water, alcohols, ionic liquids, and supercritical fluids.

[0042] The term “independently selected from” as used herein refers to referenced groups being the same, different, or a mixture thereof, unless the context clearly indicates otherwise. Thus, under this definition, the phrase “ X^1 , X^2 , and X^3 are independently selected from noble gases” would include the scenario where, for example, X^1 , X^2 , and X^3 are all the same, where X^1 , X^2 , and X^3 are all different, where X^1 and X^2 are the same but X^3 is different, and other analogous permutations.

[0043] The term “air” as used herein refers to a mixture of gases with a composition approximately identical to the native composition of gases taken from the atmosphere, generally at ground level. In some examples, air is taken from the ambient surroundings. Air has a composition that includes approximately 78% nitrogen, 21% oxygen, 1% argon, and 0.04% carbon dioxide, as well as small amounts of other gases.

[0044] The term “room temperature” as used herein refers to ambient temperature, which can be, for example, between about 15° and about 28° C.

[0045] The term “brown grease” as used herein includes waste vegetable oil, animal fat, grease, and the like, such as trap grease (e.g., grease recovered from wastewater), sewage grease (e.g., from a sewage plant), and black grease. Brown grease from traps and sewage plants is typically unsuitable for use as animal feed. The term brown grease also encompasses other grease having a free fatty acid (FFA) content greater than 20% and being unsuitable for animal feed.

[0046] The term “yellow grease” as used herein includes for example used frying oils such as, for example, those from deep fryers. It also encompasses lower-quality grades of tallow from rendering plants.

[0047] The term “renewable” as used herein refers to non-petroleum-derived. A feedstock can be considered renewable if it contains a proportion of materials derived from nonpetroleum sources, for example, about 1, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 95, or about 99 wt % of the feedstock can include materials derived from nonpetroleum sources. Likewise, a fuel can be considered renewable if it contains a proportion of hydrocarbons derived from nonpetroleum sources, for example about 1, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 95, or about 99 wt % of the fuel can include hydrocarbons derived from nonpetroleum sources. Nonpetroleum sources can include, for example, any biological source, such as plants, animals, or organisms such as algae.

[0048] The term “blendstock” as used herein refers to a composition that can be blended with any other suitable composition to form a fuel. A blendstock can form any suitable proportion of the final fuel product, for example about 1, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 95, or about 99 wt % of the final product. In some examples, distillation can be used to form distinct blendstocks (e.g., having a particular range of hydrocarbon chain lengths or particular proportions of certain types of hydrocarbon compounds) from a product mixture, and any number of different distinct blendstock forms from one or different products can be blended in suitable proportions to form a fuel.

[0049] Generally, psi pressures given herein are gauge pressures unless otherwise indicated.

[0050] The term “fuel” as used herein can refer to a hydrocarbon mixture, such as, for example, a distillate fuel, jet fuel, diesel fuel, compression ignition fuel, gasoline, spark ignition fuel, rocket fuel, marine fuel, or other fuel, qualifying as such by virtue of having a set of chemical and physical properties that comply with requirements delineated in a specification developed and published by ASTM International (ASTM), European Standards Organization (CEN), and/or the U.S. military. In some examples, a fuel can be a liquid transportation fuel, for example, for surface or air transport. Surface transport includes both terra firma and oceanic transport. Fuels of this type are included, but not limited to, ASTM specifications D975 (Diesel Fuel Oil), D1655 (Aviation Turbine Fuels), D4814 (Automotive Spark Ignition Fuel); military specifications MIL-DTL-83133G (Turbine Fuel, Aviation, Kerosene Type), MIL-DTL-25576D (Propellant, Rocket-Grade Kerosene), MIL-DTL-38219D (Turbine Fuel, Low Volatility), MIL-DTL-5624U (Turbine Fuel, Aviation), MIL-DTL-16884L (Fuel, Naval Distillate), and other such specifications for similar fuels.

[0051] As used herein, “kerosene” indicates a mixture including hydrocarbons having a carbon number range from about C9 to C16 and having a boiling point range of from about 149° to 288° C.

[0052] As used herein, “integrated” in terms of an integrated process or an integrated method with respect to a feature such as fuel production can indicate that the method or process can produce a fuel without the addition of any blendstocks from outside the process. For example, an integrated process for fuel production that is integrated with respect to the fuel can produce a synthetic fuel without the need for any petroleum-derived blendstocks. In another example, an integrated process that is integrated with respect to a solvent used as a starting material can use solvent that is generated as a product of the process and recycled back to the beginning. In another example, an integrated process that is integrated with respect to hydrogen gas that is used as a starting material can use hydrogen gas that is generated as a by-product of the process and recycled back or hydrogen gas that is purposefully generated as a side product and recycled back. A process integrated with respect to a particular feature can require the feature during a start-up period before an integrated steady state is achieved.

[0053] As used herein, “vacuum bottoms” refers to the residual material left behind after vacuum distillation of hydrocarbon mixtures and can include, for example, hydrocarbon waxes, heavy oils, and petroleum residuals. Vacuum bottoms can be obtained from, for example, a petroleum refinery. Vacuum bottoms can be, for example, a viscous tarry sludge.

Description

[0054] Embodiments of the present invention are not limited to any particular mechanism of action. Petroleum-derived aviation fuels include paraffinic/isoparaffinic, aromatic, and naphthenic hydrocarbons. The hydrocarbons derived from plants are primarily paraffinic and from coal are mainly aromatics and naphthenes; thus generally hydrocarbons from these sources can only be used as blendstocks to generate other fuels. However, by deriving hydrocarbons from a suitable combination of coal and plant- or animal-derived material, various embodiments of the present invention advantageously allow the integrated or substantially integrated generation of a synthetic aviation fuel.

[0055] Various embodiments of the present invention provide a method of producing a synthetic fuel, for example, an aviation fuel, from a combination of carbonaceous material, such as coal, and renewable material. The method can include liquefaction coupled with an upgrading process to give the fuel. In some examples, the overall process can include a) liquefaction; b) catalytic hydrotreating of carbonaceous material liquids, such as coal liquids, to remove heteroatoms; c) saturation to hydrogenate the aromatics to naphthenes; d) aromatization of at least part of the saturated product stream; and e) catalytic isomerization of at least part of the saturated product stream to produce isoparaffins. In one example, blending the products from Steps d and e together in the appropriate ratios can allow control over the composition of the product fuel. In another example, adjusting the ratios of the carbonaceous material and the biomass can allow control over the composition of the product fuel. By controlling the composition of the product fuel, various fuels can be produced, such as, for example, gasoline, naphtha, kerosene, jet fuel, or diesel fuel.

[0056] In various examples, the fuels produced by the present method can not only meet but even exceed the military aviation fuel-screening criteria, advantageously providing a pathway to energy security to the U.S. military and the entire nation. In some examples, fuels produced by the method of the present invention can meet or exceed the specification parameters for JP-8, a petroleum-based jet fuel widely used by the U.S. military, including parameters such as freeze point, density, and flash point. In some examples, the fuel can meet or exceed the thermal stability specification of JP-8 fuel as determined by a QCM test. In various examples, the present method can produce fuels that can look and act identically or superiorly to petroleum-derived fuels and that can thus be used interchangeably without any special requirements, providing renewable options across the spectrum of fuel needs. In some examples, superior qualities of the fuels of the method as compared to petroleum-derived equivalent fuels can include cleaner burning with less particulate emissions and having a lower concentration of sulfur-containing compounds and aromatics.

[0057] Herein the invention has been described with what feedstocks are presently considered the preferred embodiments; however, it is to be understood that the invention is not limited to the disclosed embodiments, but rather is intended to cover various other readily available feedstocks within the scope of the appended claims. For example, adding tank bottoms or petroleum residuals, which are generally considered as waste streams (for example in the petroleum refining industry), as a feedstock for liquefaction can provide a pathway for producing the key components of the transportation fuels, for example, aviation fuels. In various embodiments, the present method can be used to recover salable hydrocarbons from tank bottoms or petroleum residuals, thus reducing the volume of waste. Various examples of the liquefaction method provided by the present invention can provide major economic and environmental benefits to oil producers, while reducing their economic and environmental liabilities.

Liquefaction of Carbonaceous Material and Biomass

[0058] Various embodiments of the present invention provide a method of liquefaction of carbonaceous material and biomass. The method includes providing or obtaining a feed mixture. The feed mixture includes carbonaceous material and biomass. The method also includes subjecting the feed mixture to liquefaction. The liquefaction provides a product slurry. The carbonaceous material includes a nonpetroleum fossil fuel or a petroleum refinery residue.

[0059] The feed mixture includes a carbonaceous material. The carbonaceous material can be any suitable carbonaceous material that is either not provided from petroleum products or that is a waste product from petroleum refining. For example, the carbonaceous material can be a nonpetroleum fossil fuel or a petroleum refinery residue, including petroleum waste greases and other by-products of petroleum refining and other industrial processes. Examples of nonpetroleum fossil fuels can include coal, coal tar, wax from a Fischer-Tropsch (FT) process, petroleum refinery residue, tar sand, or bitumen. Examples of coal can include lignite, brown coal, jet coal, subbituminous coal, bituminous coal, steel coal, anthracite, and graphite. In some examples, the coal can be Illinois No. 6 coal. The coal can be in any suitable form, such as pulverized coal, coal powder, or coal dust. A single carbonaceous material can be used, or a combination of carbonaceous materials can be used.

[0060] The feed mixture includes biomass. The biomass can be any suitable biomass from which fuel components can be derived. The biomass can be renewable. For example, the biomass can be an oil derived from a biomaterial, such as an oil derived from plants such as crops or an oil derived from algae. The crops represent a major renewable resource that can be converted into hydrocarbons. If crops or oils derived therefrom are added to coal as a feed for direct liquefaction, in some examples, substantial reduction in greenhouse gases can be achieved. The biomass or bio-oil can be derived from any suitable biomaterial, such as, for example, straw, stalks, cobs, beets, beet pulp, seed hulls, bagasse, algae, corn starch, potato waste, sugar cane, or fruit waste. The biomass can be biomass pyrolysis oil. The biomass can be waste oils or waste grease that is produced as a waste stream from food industry and industrial processes. The biomass can be animal fat. The biomass can be grease, such as brown grease or yellow grease. The biomass can be a tar. In some examples, mixing biomass or biomass-derived fuel with carbonaceous materials such as coal potentially enhances the liquid fuel yield and improves fuel quality to meet specifications of transportation fuel.

[0061] Algae or algae oil can be advantageously selected as the biomass in embodiments of the present invention. Algae is one of the fastest-growing renewable resources. Algae is increasingly studied as feed for fuel production. Microalgae can be used as a CO₂ avoidance approach that can be applied to coal-fired utility plants. The carbon dioxide generated from coal and biomass combustion as well as other industrial processes, including liquefaction processes, can be used as a nutrient for microalgae growth. As a result, for example, carbon-neutrality can be increased, and the coal industry can reduce its carbon footprint. Therefore, the use of algae as an additive to coal for fuel production is also attractive as it can reduce the carbon footprints of the liquefaction process or even make it carbon-neutral.

[0062] The feed mixture is a mixture of at least the carbonaceous material and the biomass. The mixture can be mixed to any suitable extent, and by any suitable method, provided that the mixture is suitable for liquefaction as described herein. The mixture can be any suitable proportion of carbonaceous material and biomass. For example, the mass ratio of carbonaceous material to biomass can equal to or less than about 0.001:1, 0.002:1, 0.004:1, 0.008:1, 0.01:1, 0.02:1, 0.04:1, 0.08:1, 0.1:1, 0.2:1, 0.3:1, 0.4:1, 0.5:1, 0.6:1, 0.7:1, 0.8:1, 0.9:1, 1:1, 1.1:1, 1.2:1, 1.3:1, 1.4:1, 1.5:1, 1.6:1, 1.7:1, 1.8:1, 1.9:1, 2:1, 5:1, 10:1, 25:1, 50:1, 75:1, 100:1, 250:1, 500:1, 750:1, or less than or equal to about 1000:1. In some embodiments, the mass ratio of carbonaceous material to biomass can be about 0.00001-99,999 to 1, about 0.01-10 to 1, or about 0.05-0.7 to 1.

[0063] The feed mixture can further include a solvent. The solvent can be any suitable solvent, provided the feed mixture can be subjected to the liquefaction process described herein. For example, the solvent can be any suitable organic solvent. In some examples, the solvent can be a carbonaceous material-derived heavy liquid, such as a coal-derived heavy liquid, such as a mixture of hydrocarbons derived from coal having a boiling point of about 343° to 538° C. In some embodiments, the solvent is derived from nonpetroleum fossil fuel or from a petroleum refinery residue. In some examples, the solvent can be derived at least in part or wholly from the product of the liquefaction method or from the product of the fuel-production method, as described herein. By deriving the solvent from the products of the process, the process can be

integrated with respect to solvent requirements. In other examples, the solvent can be in whole or in part derived from materials not produced by embodiments of the present method. The amount of solvent can be any suitable amount. For example, the mass ratio of solvent to carbonaceous material and biomass can be less than or equal to about 0:1, 0.001:1, 0.002:1, 0.004:1, 0.008:1, 0.01:1, 0.02:1, 0.04:1, 0.08:1, 0.1:1, 0.2:1, 0.3:1, 0.4:1, 0.5:1, 0.6:1, 0.7:1, 0.8:1, 0.9:1, 1:1, 1.1:1, 1.2:1, 1.3:1, 1.4:1, 1.5:1, 1.6:1, 1.7:1, 1.8:1, 1.9:1, 2:1, 5:1, 10:1, 25:1, or less than or equal to about 50:1. In some examples, the mass ratio of solvent to carbonaceous material and biomass can be about 0-2 to 1, or about 0.1-1.6 to 1.

[0064] The method includes subjecting the feed mixture to liquefaction. The liquefaction can be any suitable liquefaction, such that a product mixture is formed from which fuel can be derived. The liquefaction can be a direct liquefaction, wherein the feed mixture is converted directly into a liquid fuel that can be upgraded to meet specific fuel specifications. In some examples, the liquefaction can be a carbonization liquefaction, such as including coking coal between about 360° and 750° C. In some examples, the liquefaction can be a hydrogenation liquefaction, such as a Bergius process, solvent refined coal-I or -II processes, consil synthetic fuels process, H-coal process, Exxon donor solvent process, integrated two-stage liquefaction, multistage slurry phase liquefaction, or NUS Corporation hydrogenation process. In some embodiments, subjecting the feed mixture to liquefaction can include contacting the feed mixture with a liquefaction catalyst and hydrogen gas. In some embodiments, the temperature during the contacting of the feed mixture and the liquefaction catalyst during the liquefaction can be about 200° to 700° C., about 200° to 600° C., about 300° to 600° C., about 350° to 500° C., about 400° to 500° C., about 450° C., or about 400° C. In some embodiments, the pressure during the contacting of the feed mixture and the liquefaction catalyst during the liquefaction can be about 50 to 450 atm, about 100 to 350 atm, about 150 to 250 atm, or about 200 atm.

[0065] The liquefaction catalyst can be any suitable liquefaction catalyst. For example, the liquefaction catalyst can be iron-based catalysts such as a nickel catalyst, cobalt catalyst, a molybdenum catalyst, or any combination thereof. In some examples, the liquefaction catalyst is a nickel-molybdenum catalyst or a cobalt-molybdenum catalyst, and can be sulfided or unsulfided. In some examples, the concentration of the catalyst can be about 250-350 ppm, about 100-500 ppm, or about 10-1000 ppm.

[0066] The hydrogen gas can be provided from any suitable source of hydrogen gas. For example, the hydrogen gas can be partially or fully commercially obtained. In other examples, the hydrogen gas can be generated on-site. The hydrogen gas can be partially or fully generated from the liquefaction process or from the fuel upgrading method; for example, the hydrogen can be generated from a by-product of the liquefaction or fuel-upgrading process, such that the method of fuel production or liquefaction is integrated with respect to hydrogen gas.

[0067] The product of the liquefaction is a product slurry. The product slurry contains the unupgraded fuel derived from the carbonaceous material and the biomass, along with any solids remaining from the carbonaceous material and the biomass. The fuel in the product slurry generally contains significant amounts of contaminants such as sulfur, oxygen,

and nitrogen, which can be removed via an upgrading process, such as the fuel production process described herein. Method of Fuel Production from Carbonaceous Material and Biomass

[0068] Various embodiments of the present invention provide a method of fuel production from carbonaceous material and biomass. The method includes providing or obtaining a product slurry or a material having similar qualities thereto, which can be a product of embodiments of the liquefaction process herein, or which can be obtained or provided in any suitable fashion. The method also includes separating the product slurry. Separating the product slurry provides a conversion component. The method also includes processing the conversion component. Processing provides a fuel. In some embodiments, the method of making a fuel from carbonaceous material and biomass is substantially or fully integrated.

[0069] In some embodiments, the present invention provides a method of fuel production from carbonaceous material and biomass. In other embodiments, the present invention provides a method of fuel production from a product slurry or similar mixture derived from carbonaceous material and biomass.

[0070] The method of fuel production can include separation of the product slurry. The separation can be any suitable separation, such that a fraction or part of the product slurry is provided that is suitable for upgrading to a fuel that meets a fuel specification. In some examples, the separating can include filtering, such as using gravity or pressure to drive the product slurry through a filter medium, for example a frit or filter aid, to separate the solids from the liquid. In some examples, the separating can include a distillation with any suitable number of stages and at any suitable temperature and pressure. The distillation can produce a distillate, and any suitable fraction of the distillate can be brought forward in the method. In some examples, a distillation can be performed to provide a fraction having a boiling point of about 110° to 390° C., or about 149° to 343° C. The separated fraction that proceeds to later steps of the fuel production method can be referred to as the conversion component.

[0071] The conversion component resulting from the separation of the product slurry can be processed to give a fuel. The fuel that results from the method can be any suitable fuel. The processing can clean the fuel of contaminants such as sulfur, oxygen, and nitrogen and can cause the fuel to have the proper mixture of hydrocarbons such that the properties of the fuel are in accordance with any of various fuel specifications.

[0072] The fuel that results from the processing can be any suitable fuel. The fuel can be a liquid transportation fuel. For example, the fuel can be gasoline, naphtha, kerosene, jet fuel, or diesel fuel. The fuel can comply with any suitable fuel standard. In some embodiments, a fuel produced by the process has a composition that complies with JP-5, JP-8, or BUFF requirements.

[0073] In some embodiments, the method of fuel generation can be fully integrated with respect to the fuel produced, such that the fuel produced from the process without any additives or added blendstocks is sufficient to meet a particular fuel specification. In some examples, the method can be substantially or partially integrated, such that the method of fuel generation produces a fuel that only requires a small amount of additives or blendstocks to meet a particular fuel specification, such that the final fuel that meets the specification includes equal to or less than about 99.999 wt % of the

product of the method of fuel generation, 99.99, 99.9, 99, 98, 97, 96, 95, 94, 93, 92, 91, 90, 85, 80, 75, 50, or about 25 wt % of the product of the method of fuel generation.

Processing

[0074] The processing can be any suitable processing that provides a fuel that meets a particular fuel specification from the conversion component. The processing can be any suitable processing that provides at least part of a fuel that meets a particular fuel specification (e.g., in some examples, the process can provide a blendstock) from the conversion component. In some examples, the processing can be any suitable method of fuel upgrading and preparation that is known to one of ordinary skill in the art. For example, the processing can include any one or any combination of hydrotreating, hydrogenating, isomerizing, aromatizing, and blending in any suitable order.

[0075] In some embodiments, the processing can include first hydrotreating, next hydrogenating, next either isomerizing or aromatizing or a combination thereof, and next blending. In some examples, one portion of the hydrogenated product can be isomerized, one portion of the hydrogenated product can be aromatized, and the products or product of isomerization, aromatization, or both can be suitably blended to produce a fuel meeting a particular specification. In some embodiments, a portion or all of the hydrogenated product can be isomerized, but no portion of the hydrogenated product be subjected to aromatization. In some embodiments, a portion or all of the hydrogenated product can be aromatized, but no portion of the hydrogenated product subjected to isomerization. For example, the mass ratio of hydrogenated product that is isomerized to hydrogenated product that is aromatized can be equal to or less than about 0.001:1, 0.002:1, 0.004:1, 0.008:1, 0.01:1, 0.02:1, 0.04:1, 0.08:1, 0.1:1, 0.2:1, 0.3:1, 0.4:1, 0.5:1, 0.6:1, 0.7:1, 0.8:1, 0.9:1, 1:1, 1.1:1, 1.2:1, 1.3:1, 1.4:1, 1.5:1, 1.6:1, 1.7:1, 1.8:1, 1.9:1, 2:1, 5:1, 10:1, 25:1, 50:1, 75:1, 100:1, 250:1, 500:1, 750:1, or less than or equal to about 1000:1. In some examples, the mass ratio of hydrogenated product that is isomerized to hydrogenated product that is aromatized can be about 0 to about 99, 999:1.

[0076] Between any of hydrotreating, hydrogenating, isomerizing, aromatizing, and blending, a separation can occur to selectively only bring particular products forward to the next step. For example, a distillation can be performed to only bring a particular fraction of the distillate forward.

[0077] In any of hydrotreating, hydrogenating, isomerizing, and aromatizing, the liquid hourly space velocities (LHSV) can be about 0.01 reactor volumes/hr (e.g., hr^{-1}) to 20 hr^{-1} , about 0.1 to 8 hr^{-1} , about 0.5 to 4 hr^{-1} , or about 0.8 to 1.2 hr^{-1} . Any suitable time of reaction and hydrogen flow rate can be used depending on the space velocity conditions, pressure, temperature, and other conditions, suitable to bring about the desired chemical transformation.

Hydrotreating the Conversion Component

[0078] In some embodiments, the processing can include hydrotreating. For example, the conversion component can be hydrotreated. Hydrotreating gives a hydrotreated material. The hydrotreating can be any suitable hydrotreating that provides a material suitable for moving forward in the processing to produce all or at least part of a fuel that meets a particular

fuel specification. In some examples, the hydrotreating can be any suitable method of hydrotreating that is known to one of ordinary skill in the art.

[0079] The term “hydrotreatment” as used herein is used to refer to a catalytic process performed in the presence of hydrogen that includes reductive chemical reactions, such as, for example, reduction of unsaturated bonds and reduction of carbon to lesser oxidation states via removal of bonds to oxygen or other heteroatoms, including, for example, carboxylate reduction, carboxylate decarboxylation, carboxylate decarbonylation, alkene reduction, reduction of conjugated or aromatic unsaturated bonds, reduction of any carbon-oxygen bond including, for example, conversion of glycerine to propane, or other reactions including carbon-carbon bond cracking and cycloparaffin formation via cyclization, or cycloparaffin formation via cyclization followed by hydrogenation/saturation of conjugated or nonconjugated C—C bonds, or aromatization. For example, hydrotreatment can include a catalytic process whereby oxygen is removed from organic compounds, for example as water (hydrodeoxygenation); sulfur from organic sulfur compounds, for example as dihydrogen sulfide (hydrodesulfurization); nitrogen from organic nitrogen compounds, for example as ammonia (hydrodenitrogenation); and halogens from organic compounds, for example, as chlorine from organic chloride compounds as hydrochloric acid (hydrodechlorination).

[0080] In some embodiments, hydrotreating can include contacting the conversion component with a hydrotreatment catalyst and hydrogen gas. The contacting can be any suitable contacting. For example, the hydrotreatment catalyst and hydrogen gas can be contacted with the conversion component in a reactor. The hydrotreating can occur at any suitable temperature, pressure, and for any suitable time such that the hydrotreating generates suitable hydrotreated material for moving forward in the processing. The temperature can be about 150° to 800° C. , about 250° to 600° C. , about 200° to 500° C. , about 250° to 450° C. , about 300° to 550° C. , about 300° to 400° C. , or about 340° to 530° C. Reactor pressures can be about 1 to 750 atm, about 10 to 500 atm, about 10 to 300 atm, or about 100 to 150 atm. In some embodiments, reactor pressures can be about 25 to 250 atm, while in some embodiments, reactor pressures can be about 60 to 200 atm.

[0081] The hydrotreating catalyst can be any suitable hydrotreating catalyst. The hydrotreating catalyst can include one or more metals from IUPAC groups 6, 8, 9, and 10 of the periodic table of the elements. In some examples, the one or more metals can be selected from palladium (Pd), platinum (Pt), nickel (Ni), and combinations thereof. In embodiments, the catalyst is a nickel-molybdenum (NiMo) catalyst including nickel and molybdenum. In some embodiments, the catalyst is a cobalt-molybdenum (CoMo) catalyst. The hydrotreating catalyst can include supported or unsupported metals. In various embodiments, the catalyst includes a support. In applications, the support includes alumina, silica, or a combination thereof. The catalyst can be a supported NiMo or CoMo catalyst. In embodiments, NiMo/ Al_2O_3 — SiO_2 or CoMo— Al_2O_3 catalyst is utilized. In some embodiments, a Ni catalyst is utilized. In some embodiments, a molybdenum catalyst is utilized. In some embodiments, a catalyst with any suitable proportion of Ni and Mo is utilized.

[0082] Catalysts having any suitable type or combination of active sites or structures can be used as the hydrotreating catalyst. In various examples, catalysts with Type I active

sites or structures can be utilized; in other examples, catalysts without Type II active sites or structures can be utilized. In various examples, catalysts with Type II active sites or structures can be utilized; in other examples, catalysts without Type II active sites or structures can be utilized.

Hydrogenating the Hydrotreated Material

[0083] In some embodiments, the processing can include hydrogenating. For example, the hydrotreated material can be hydrogenated. Hydrogenation gives a hydrogenated material. The hydrogenating can be any suitable hydrogenating that provides a material suitable for moving forward in the processing to produce all or at least part of a fuel that meets a particular fuel specification. In some examples, the hydrogenating can be any suitable method of hydrogenating that is known to one of ordinary skill in the art. Hydrogenation can include the reaction of hydrogen with unsaturated bonds, including aromatic or conjugated bonds, such as carbon-carbon unsaturated bonds, carbon-heteroatom unsaturated bonds, or heteroatom-heteroatom unsaturated bonds, to form a saturated bond.

[0084] Any suitable proportion of the hydrotreated material can be hydrogenated in the hydrogenation step. For example, about 1, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90 or about 95 wt % of the hydrotreated material can be hydrogenated. In some examples, multiple contactings, or passes, can be performed to elicit a desired proportion of hydrogenation. In some example, each contacting or pass provides about 1, 5, 10, 20, 30, 40, 50, or about 60 wt % hydrogenation of the hydrocarbon. Any suitable number of contacting or passes can be conducted, for example, 1, 2, 3, 4, 5, 6, or 7 contactings or passes can be conducted.

[0085] In some embodiments, hydrogenating can include contacting hydrotreated material with a hydrogenation catalyst and hydrogen gas. The contacting can be any suitable contacting. For example, the hydrogenation catalyst and hydrogen gas can be contacted with the hydrotreated material in a reactor. The hydrogenating can occur at any suitable temperature, pressure, and for any suitable time such that the hydrogenation generates suitable hydrogenated material for moving forward in the processing. In some examples, during the hydrogenating the temperature can be about 50° to 400° C., about 50° to 300° C., about 100° to 250° C., about 100° to 150° C., about 150° to 200° C., about 200° to 250° C., or about 250° to 300° C. In some examples, during the hydrogenating, the pressure can be about 10 to 250 atm, about 25 to 175 atm, or about 68 to 136 atm.

[0086] The hydrogenation catalyst can be any suitable hydrogenation catalyst. The catalyst can include one or more metals from IUPAC groups 6, 8, 9, and 10 of the periodic table of the elements. The hydrogenation catalyst can be any hydrogenation catalyst known to one of ordinary skill in the art. For example, the catalyst can be a palladium catalyst, a platinum catalyst, a nickel catalyst, or a catalyst including any combination of at least two of palladium, platinum, and nickel. The hydrogenation catalyst can be unsupported. In some embodiments, the hydrogenation catalyst can be supported on any suitable support, for example, on alumina or silica-alumina. In some examples, the hydrogenation catalyst is a platinum-zeolite catalyst.

Isomerizing the Hydrotreated Material

[0087] In some embodiments, the processing can include isomerizing. Isomerizing gives an isomerized material. For

example, at least some of the hydrogenated material can be isomerized. The isomerizing can be any suitable isomerizing that provides a material suitable for moving forward in the processing to produce all or at least part of a fuel that meets a particular fuel specification. In some examples, the isomerizing can be any suitable method of isomerizing that is known to one of ordinary skill in the art. Isomerizing can be an optional step. In some embodiments, isomerizing is performed. In other embodiments, isomerizing is not performed. In some examples, at least one of aromatizing and isomerizing is performed. In some embodiments, both aromatizing and isomerizing are performed. In some embodiments, aromatizing and isomerizing are performed simultaneously, sequentially, or any combination thereof.

[0088] Isomerizing can include breaking and reforming carbon-carbon bonds to create branched hydrocarbons from straight-chain hydrocarbons or to increase the branching of already-branched hydrocarbons. In some embodiments, depending on the process conditions, such as the type of catalyst, temperature, and pressure used, some aromatization can occur in the isomerizing step, although the isomerization step substantially causes isomerization as compared to aromatization. In other embodiments, the isomerizing step causes predominantly or only isomerization as compared to aromatization.

[0089] In some examples, the isomerization step can include a dewatering step. The dewatering step can include removal of water from the starting material for the isomerization step. The dewatering step can include any suitable procedure that removes a suitable amount of water from the hydrocarbon starting material. In some examples, the dewatering step can include cooling the hydrocarbon mixture to any suitable temperature; for example the hydrocarbon mixture can be cooled to ambient temperature (e.g., 20°-30° C.). The dewatering step can include allowing the less polar hydrocarbon-containing phase to separate from a more polar water-containing phase. The water-containing phase can then be physically separated from the hydrocarbon-containing phase. In some examples, the hydrocarbon can be placed in contact with molecular sieves, for instance 4-Å molecular sieves, which can further remove water. Generally, for larger amounts of water, a phase separation can be performed first, then a second step contacting with molecular sieves.

[0090] In some examples, the isomerization step can include a deacidification step. The deacidification step can include removal of acid from the starting material for the isomerization step. Any suitable method of acid removal can be used for the deacidification step. In one example, removal of the water-containing phase during a dewatering step can substantially remove the acid, because of preference of the acid to reside in the more polar water-containing phase, advantageously combining dewatering with deacidification. In some examples, treatment of the undewatered or dewatered hydrocarbons with a basic material can allow for deacidification. In some embodiments, contacting the hydrocarbons with molecular sieves can further deacidify the hydrocarbons, because of basic properties of certain molecular sieves, advantageously combining dewatering with deacidification.

[0091] In some embodiments, isomerizing can include contacting hydrogenated material with a isomerization catalyst and hydrogen gas. The contacting can be any suitable contacting. For example, the isomerization catalyst and hydrogen gas can be contacted with the hydrogenated material in a reactor. The isomerization can occur at any suitable tempera-

ture, pressure, and for any suitable time such that the isomerization generates suitable isomerized material for moving forward in the processing. Any suitable proportion of the hydrogenated material can be isomerized in the isomerization step. For example, about 1, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90 or about 95 wt % of the hydrogenated material can be isomerized. In some examples, multiple contactings, or passes, can be performed to elicit a desired proportion of isomerization of the hydrogenated material. In some example, each contacting or pass provides about 1, 5, 10, 20, 30, 40, 50, or about 60 wt % isomerization of the hydrogenated material. Any suitable number of contacting or passes can be conducted, for example, 1, 2, 3, 4, 5, 6, or 7 contactings or passes can be conducted.

[0092] Any suitable isomerization catalyst can be used to effect the isomerization. For example, catalysts which possess a suitable balance of catalytic metal dehydrogenation/hydrogenation activity and support acidity can be used. Support acidity can be a controlling feature, along with operational temperature, which can determine the amount of carbon chain cracking that will occur. Strongly acidic supports can result in greater amounts of chain cracking at a given temperature than a weakly acidic support at the same temperature. Support acidity can be controlled by the silica-alumina ratio in the support. Additionally, the silica-alumina ratio in the support can control the pore size of the support. Pore size can also control cracking to a certain degree, again based upon operational temperature. Isomerization catalysts with strong dehydrogenation/hydrogenation activity and weak support acidity may find greater utility in the production of diesel fuel fractions. Isomerization catalysts with moderate acidity and strong dehydrogenation/hydrogenation activity may find greater utility in the production of jet fuel fractions. Isomerization catalysts with strong acidity may find greater utility in production of naphtha fractions. Suitable isomerization catalysts include any suitable isomerization catalyst known to one of ordinary skill in the art, such as those having two or more catalytic metals and a silica-alumina support, wherein the metals and support can be present in any suitable proportion. The catalyst can include one or more metals from IUPAC Groups 6, 8, 9, and 10 of the periodic table of the elements. The isomerization catalyst can be any isomerization catalyst known to one of ordinary skill in the art. For example, the catalyst can be a palladium catalyst, a platinum catalyst, a nickel catalyst, a molybdenum catalyst, or a catalyst including any combination of at least two of palladium, platinum, nickel, and molybdenum. The isomerization catalyst can be unsupported. In some embodiments, the isomerization catalyst can be supported on any suitable support, for example, on alumina or silica-alumina. In various embodiments, the isomerization catalyst can include a nickel-molybdenum catalyst.

[0093] Any suitable temperature can be used during the isomerization. For example, operation of an isomerization catalyst at a moderately low temperature, such as about 280° to 380° C. or about 320° to 340° C., may find utility in the production of diesel fuel, especially low-cloud-point diesel fuel. Operation of an isomerization catalyst at moderate temperature may find utility in the production of jet fuel. Operation of an isomerization catalyst at high temperature, such as about 320° to 420° C. or about 360° to 380° C., may find utility in the production of naphtha and gasoline-blendstock fuels. Suitable temperature ranges can include, for example,

about 100° to 500° C., about 200° to 450° C., about 250° to 400° C., about 300° to 360° C., or about 330° to 400° C.

[0094] Any suitable pressure can be used during the isomerization. For example, operation of an isomerization catalyst at high hydrogen pressure, such as about 600 to 900 psig or about 700 to 800 psig, may suppress the dehydrogenation activity of the catalyst, resulting in only slight isomerization, but potentially significant cracking. Operation of an isomerization catalyst at moderate hydrogen pressure, such as about 250 to 700 psig, may provide high isomerization with only slight cracking. Operation of an isomerization catalyst at low hydrogen pressure, such as about 150 to 250 psig, may suppress the hydrogenation activity of the catalyst, resulting in significant cracking as well as alkene production. Suitable hydrogen pressures can include about 100 to 900 psig. Suitable isomerization pressures can include about 1 to 200 atm, about 5 to 150 atm, about 10 to 100 atm, or about 30 to 70 atm.

[0095] Any suitable liquid flow rate can be used during the isomerization. For example, a liquid flow rate of about 0.1 to 20 reactor volumes per hour or about 0.5 to 10 reactor volumes per hour can be a suitable flow rate.

[0096] Any suitable amount of the hydrogenated material can be subjected to isomerization, such that sufficient isomerized material is generated to form a desired fuel blend. For example, equal to or less than about 1%, 5%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, or about 100% of the hydrogenated material can be subjected to the isomerization. For example about 50%-95%, about 75%-95%, about 80%-90%, or about 85% of the hydrogenated material can be subjected to the isomerization.

Aromatizing the Hydrotreated Material

[0097] In some embodiments, the processing can include aromatizing. Aromatizing gives an aromatized material. For example, at least some of the hydrogenated material can be aromatized. The aromatizing can be any suitable aromatizing that provides a material suitable for moving forward in the processing to produce all or at least part of a fuel that meets a particular fuel specification. In some examples, the aromatizing can be any suitable method of aromatizing that is known to one of ordinary skill in the art. Aromatizing can be an optional step. In some embodiments, aromatizing is performed. In other embodiments, aromatizing is not performed. In some examples, at least one of aromatizing and isomerizing is performed. In some embodiments, both aromatizing and isomerizing are performed. In some embodiments, aromatizing and isomerizing are performed simultaneously, sequentially, or any combination thereof.

[0098] Aromatization includes the removal of hydrogen atoms to produce aromatic unsaturated in carbon-carbon bonds. Depending on the process conditions, such as the type of catalyst, temperature, and pressure used, some isomerization can occur in the aromatization step, although the aromatization step substantially causes aromatization as compared to isomerization. In some embodiments, the aromatizing step causes predominantly or only aromatization as compared to isomerization.

[0099] In some examples, the aromatization step can include a dewatering step. The dewatering step can include removal of water from the starting material for the aromatization step. The dewatering step can include any suitable procedure that removes a suitable amount of water from the hydrocarbon starting material. In some examples, the dewatering

tering step can include cooling the hydrocarbon mixture to any suitable temperature, for example the hydrocarbon mixture can be cooled to ambient temperature (e.g., 20°-30° C.). The dewatering step can include allowing the less polar hydrocarbon-containing phase to separate from a more polar water-containing phase. The water-containing phase can then be physically separated from the hydrocarbon-containing phase. In some examples, the hydrocarbon can be placed in contact with molecular sieves, for instance 4-Å molecular sieves, which can further remove water. Generally, for larger amounts of water, a phase separation can be performed first, then a second step contacting with molecular sieves.

[0100] In some examples, the aromatization step can include a deacidification step. The deacidification step can include removal of acid from the starting material for the aromatization step. Any suitable method of acid removal can be used for the deacidification step. In one example, removal of the water-containing phase during a dewatering step can substantially remove the acid, because of the preference of the acid to reside in the more polar water-containing phase, advantageously combining dewatering with deacidification. In some examples, treatment of the undewatered or dewatered hydrocarbons with a basic material can allow for deacidification. In some embodiments, contacting the hydrocarbons with molecular sieves can further deacidify the hydrocarbons, because of basic properties of certain molecular sieves, advantageously combining dewatering with deacidification.

[0101] Any suitable proportion of the hydrocarbon can be aromatized in the aromatization step. For example, about 1, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90 or about 95 wt % of the hydrocarbon can be aromatized. In some examples, multiple contactings, or passes, can be performed to elicit a desired proportion of aromatization of the hydrocarbon. In some examples, each contacting or pass provides about 1, 5, 10, 20, 30, 40, 50, or about 60 wt % aromatization of the hydrocarbon. Any suitable number of contacting or passes can be conducted, for example, 1, 2, 3, 4, 5, 6, or 7 contactings or passes can be conducted.

[0102] In some embodiments, aromatizing can include contacting hydrogenated material with an aromatization catalyst and hydrogen gas. The contacting can be any suitable contacting. For example, the aromatization catalyst and hydrogen gas can be contacted with the hydrogenated material in a reactor. The aromatization can occur at any suitable temperature, pressure, and for any suitable time such that the aromatization generates suitable aromatized material for moving forward in the processing. In some examples, during the aromatization, the temperature can be about 100° to 1000° C., about 350° to 750° C., or about 500° to 550° C. In some examples, during the aromatization, the pressure can be about 50 to 750 psig, about 100 to 500 psig, about 250 to 350 psig, about 1 to 200 atm, about 5 to 150 atm, about 10 to 100 atm, or about 20 to 40 atm.

[0103] The aromatization catalyst can be any suitable aromatization catalyst. The catalyst can include one or more metals from IUPAC Groups 6, 8, 9, and 10 of the periodic table of the elements. The aromatization catalyst can be any aromatization catalyst known to one of ordinary skill in the art. For example, the catalyst can be a palladium catalyst, a platinum catalyst, a nickel catalyst, or a catalyst including any combination of at least two of palladium, platinum, and nickel. The aromatization catalyst can be unsupported. In some embodiments, the aromatization catalyst can be sup-

ported on any suitable support, for example, on alumina or silica-alumina. In some examples, the aromatization catalyst is platinum on zeolite.

[0104] Any suitable amount of the hydrogenated material can be subjected to aromatization, such that sufficient aromatized material is generated to form a desired fuel blend. For example, equal to or less than about 1%, 5%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, or about 100% of the hydrotreated material can be subjected to the aromatization. For example about 50%-95%, about 75%-95%, about 80%-90%, or about 85% of the hydrogenated material can be subjected to the isomerization.

Blending the Isomerized Material and the Aromatized Material

[0105] In some embodiments, the processing can include blending. Blending gives a fuel. For example, at least some of the isomerized material and at least some of the aromatized material can be blended. The blending can be any suitable blending that provides all or at least part of a fuel that meets a particular fuel specification. In some examples, the blending can be any suitable method of blending that is known to one of ordinary skill in the art.

[0106] Any suitable proportion of isomerized material and aromatized material can be blended to generate a fuel having a particular specification. In order to achieve a desired mass ratio of isomerized material and aromatized material, any suitable amount of the isomerized material or aromatized material can be used to form the blend. For example, in the blend, the mass ratio of the isomerized material blended to the aromatized material blended can be equal to or less than about 0.001:1, 0.002:1, 0.004:1, 0.008:1, 0.01:1, 0.02:1, 0.04:1, 0.08:1, 0.1:1, 0.2:1, 0.3:1, 0.4:1, 0.5:1, 0.6:1, 0.7:1, 0.8:1, 0.9:1, 1:1, 1.1:1, 1.2:1, 1.3:1, 1.4:1, 1.5:1, 1.6:1, 1.7:1, 1.8:1, 1.9:1, 2:1, 5:1, 10:1, 15:1, 20:1, 25:1, 50:1, 75:1, 100:1, 250:1, 500:1, 750:1, or less than or equal to about 1000:1, depending on the type of fuel desired. In some examples, the blend includes the mass ratio of the isomerized material in a mass percent of about 50%-95%, with the remainder aromatized material, for example, 80-90 wt % isomerized material, about 83-88 wt % isomerized material, or about 85% isomerized material. In some examples, the blended material is sufficient to fulfill a particular fuel specification. In other embodiments, the blended fuel is combined with a suitable blendstock to generate a fuel that fulfills a particular fuel specification.

[0107] A flowchart corresponding to one embodiment of the present invention is illustrated in FIG. 1. The present invention provides a method of fuel production from coal and biomass. The method (100) includes providing or obtaining a feed mixture (102, 104, and 106). The mixture can include coal (102) and bio-oil (104). The mixture can also include a coal-derived solvent (106). The method also includes subjecting the feed mixture to liquefaction (110). The liquefaction can include contacting the feed mixture with hydrogen gas and a catalyst (108). The liquefaction provides a product slurry (112). The method also includes distilling the product slurry. Distilling provides distillate fractions, such as naphtha (114), distillate fraction (116, conversion component), solvent (118), and residue (120). The method also includes hydrotreating the distillate (124). The hydrotreating (124) can include contacting the distillate with hydrogen gas and a hydrotreating catalyst (122). Hydrotreating provides a hydrotreated material. The method also includes hydrogenat-

ing the hydrotreated material (128). Hydrogenating can include contacting the hydrotreated material with hydrogen gas and a hydrogenation catalyst (126). Hydrogenating (128) provides a hydrogenated material. The method also includes isomerizing at least some of the hydrotreated material (132). Isomerizing can include contacting the hydrotreated material with hydrogen gas and an isomerization catalyst (130). Isomerizing at least some of the hydrotreated material (132) provides an isomerized material. The method also includes aromatizing at least some of the hydrotreated material (134). Aromatizing can include contacting the hydrogenated material with hydrogen gas and an aromatization catalyst (136). The aromatizing provides an aromatized material. The method also includes blending at least some of the isomerized material and at least some of the aromatized material. The blending provides a composite fuel (138). The composite fuel can include naphtha (140) which can be reformed or used as motor gasoline (146). The composite fuel can include jet fuel (142) which can be tested (148) to demonstrate if it meets jet fuel specifications. The composite fuel can include heavy oil (144) which can be recycled or used as a diesel additive. Alternatively, the isomerized and aromatized products can be distilled and appropriately blended to give a composite fuel that only or predominately includes jet fuel or another desired fuel fraction.

EXAMPLES

[0108] The present invention can be better understood by reference to the following examples which are offered by way of illustration. The present invention is not limited to the examples given herein.

[0109] General Methods.

[0110] The liquefaction of coal-biomass mixtures was performed, producing a volume of middle distillate for further hydroprocessing/product quality testing to produce liquid fuels. The tests for producing middle distillate were carried out in a 2-gallon autoclave rated at 347 atm at 340° C. with an ability to provide for hydrogen flow. The coal used was Illinois No. 6 coal.

Example 1

Production of Solvent

[0111] Initial tests were performed to produce test coal-derived solvent for the liquefaction runs. A slurry including coal tar-derived solvent (b.p., 343°-538° C.) was formed with predried pulverized coal. The slurry was contacted with a commercial presulfided CoMo catalyst under a hydrogen pressure in the autoclave. The experiment was run at 450° C., a pressure of 78 atmo, and under a constant flow of 13 scfh hydrogen for 60 minutes. The product slurry was distilled to produce test coal-derived solvent (b.p., 343°-538° C.). The

liquefaction procedure was repeated using the solvent generated to produce solvent using a recycled solvent.

Example 2

Runs 1-3: Liquefaction of Canola Oil and Coal

[0112] After a desired quantity of the test coal-derived solvent was generated using the recycled solvent, a slurry including coal, canola oil, vacuum bottoms (e.g., hydrocarbon waxes similar to petroleum residue left after refining of crude oil) and coal-derived solvent (having a mass ratio of 0.8:0.2:1.0:1.0), and 0.03 wt % of commercial presulfided CoMo catalyst was placed in the autoclave. The sulfur in the coal was enough to keep the catalyst sulfided during the run. The reactor was charged with 70 atm hydrogen pressure and placed in the heating jacket. The reactor was heated to 350° C. to convert triglycerides into paraffins via hydrolysis and decarbonylation and then heated and pressurized to the temperature and pressure shown in Table 1, which also shows other operating conditions. A constant hydrogen flow was maintained throughout the run. The runs were carried out in hydrogen flow-through mode (13.18 scfh). At the end of the run, the reactor was cooled to room temperature and degassed. The gas was metered into a gas bag, and total volume of the gas was recorded. The reactor was opened, and the contents of the reactor were distilled to obtain the following fractions: naphtha (b.p., <149° C.), distillate (b.p., 149°-343° C.), heavy oil (b.p., 343°-538° C.), and residue (b.p., >538° C.).

TABLE 1

Operating Conditions for Liquefaction Tests.										
Run No.	AC Size, cm ³	Pressure, atm	Temp., ° C.	Run Time, min	Agitation, rpm	Catalyst, ppm	Coal Charge, g	Bio-oil, g	Solvent, g	Vac. Bottoms, g
1-3	7570	225	450	60	900	300	600	200	800	800
4-5	7570	218	450	60	900	300	600	200	800	800
6-7	7570	176	450	60	900	300	600	200	800	800

[0113] Upon standing, the naphtha fraction separated into two layers: the upper oily layer and the aqueous bottom layer. The oily layer was saved for further analysis, and the aqueous layer was rejected. A complete mass balance was obtained, and the yields are shown in Table 2. The conversion is based on the wt % of dry ash-free coal and bio-oil or wax used for liquefaction. All of these fractions were analyzed by gas chromatography-mass spectroscopy (GC-MS), as discussed in Example 5.

TABLE 2

Composition of the Distillate.				
Run No.	Conversion	Water, wt %	Naphtha (<149° C.), wt %	Middle Distillate (149°-343° C.), wt %
1-3	73.3	14.7	12.0	46.6
4-5	71.5	15.4	14.1	42.0
6-7	75.5	11.3	13.2	51.0

Example 3

Runs 4-5: Liquefaction of Algae Oil and Coal

[0114] Coal, algae oil, and catalyst were slurried in a coal-derived solvent. A similar procedure to that used in Example 2 was used. Operating conditions and yield data are given in Tables 1 and 2.

Example 4

Runs 6-7: Liquefaction of Waxes and Coal

[0115] Waxes from FT synthesis of syngas, coal, and catalyst were slurried in a coal-derived solvent. A similar procedure

to that used in Example 2 was used. The operating conditions and yield data are given in Tables 1 and 2.

Example 5

Analysis of Examples 2-4, Runs 1-7

[0116] The raw coal liquids produced from the fractional distillation of liquefaction slurry were analyzed by elemental analysis, density, gas chromatographic distillation (GCD) and GC-MS to determine product quality of the distillates. These data are needed to design an appropriate upgrading scheme to produce specification-compliant fuels. The yield data and hydrocarbon types are presented in Tables 3-5. The distillation profiles of coal-canola oil-derived, coal-algae oil-derived, and coal-wax-derived middle distillates are shown in FIGS. 2, 3, and 4, respectively.

TABLE 3

Distillation Data for Coal-Biomass-Derived Fuels						
Sample Identification	Coal-Canola, <149° C.	Coal-Canola, 149°-343° C.	Coal-Algae, <149° C.	Coal-Algae, 149°-343° C.	Coal-FT Resid, <149° C.	Coal-FT Resid, 149°-343° C.
Yield	9.0%	58.2%	9.2	56.5	10.8	59.8
GC Distillation wt % Off at ° C.						
38			3.67		0.8	
65	9.24		7.75		18.46	
82	41.23	0	26.17	0	29.14	
93	45.13	0	32.61	0	31.71	
121	72.60	0.16	75.56	0.60	82.95	0
149	96.64	0.86	96.69	2.85	100	1.22
177	100	7.41	100	13.00		9.53
204	0	14.28		23.31		18.12
232	0	32.47		48.51		37.61
260	0	42.44		58.44		48.24
288	0	56.38		76.17		66.48
315	0	94.67		96.94		87.03
343	0	100.00		100		95.74
343 +	0	0.00		0		100
wt % Off						
149° C.-	96.64	0.86	96.69	2.85	100	0
177° C.-	100	7.41	100	13.00	—	9.53
232° C.-	—	32.47	—	48.51	—	37.61
343° C.+	—	0	—	0.0	—	4.26

TABLE 4

Hydrocarbon-Type Analysis of Raw Distillate from Coal Biomass Liquefaction						
	Coal-Canola		Coal-Algae		Coal-FT Resid	
	<149° C.	149°-343° C.	<149° C.	149°-343° C.	<149° C.	149°-343° C.
Paraffins	64.1	47.86	51.4	31.73	45.8	56.59
Naphthenes	19.09	2.02	35.82	7.96	33.09	3.44
Aromatics	16.81	50.12	12.78	60.31	21.11	39.96

TABLE 5

Hydrocarbon Type Analysis of Raw Coal-Canola Oil-Derived Distillate	
Composition, wt % by MS	Middle Distillate
Paraffins	5.43
1-R Naphthenes	2.40
2-R Naphthenes	0.00
3-R Naphthenes	0.00
4+-R Naphthenes	0.00
Total Naphthenes	7.83
1-R AR	41.84
2-R AR	45.76
3-R AR	4.57
4+-R AR	0.00
Total AR	92.17
Total	100

Example 6

Upgrading of the Products of Liquefaction

[0117] The coal liquids (distillate fraction having b.p. 149°-343° C.) obtained from the liquefaction of coal and bio-oil or wax mixtures were upgraded to produce JP-8-compliant fuel. Upgrading can remove heteroatoms such as nitrogen, sulfur, and oxygen along with hydrocracking and hydrogenation to produce distillate fuels including paraffins/isoparaffins, aromatics, and naphthenes, which are key constituents of jet fuel. The upgrading scheme is described below.

[0118] Stage 1—Hydrotreating.

[0119] The catalytic hydrotreatment of the coal liquids was carried out using a commercial hydrotreating catalyst to produce JP-8-compliant jet fuel. Initial tests were conducted using coal liquid produced from the distillation of coal tar to validate the catalyst and reactor system and optimize the conditions. The hydrotreatment was carried out in a tubular reactor packed with a nickel-molybdenum hydrotreating catalyst on a silica-alumina support diluted with an equal volume of glass beads in a small continuous reactor (SCR), with a temperature of about 365°-370° C. and a pressure of about 136 atm, with a space velocity of about 0.3/h (e.g. 0.3 reactor volumes per hour). The catalyst was presulfided using n-dodecane spiked with 1.5 wt % dimethyl disulfide (DMDS). The presulfidation was carried out by passing the sulfiding solution through the catalyst bed until H₂S breakthrough was observed in the product gas as indicated by an online laser analyzer.

[0120] After the desired amount of coal liquid was hydrotreated, the hydrotreated product was washed twice with water to remove chlorine that may have been present, and nitrogen was passed through the washed oil to expel any dissolved ammonia and hydrogen sulfide that may have been present. The resulting product was passed through a tubular reactor packed with acidic clay to remove residual nitrogen compounds. The hydrotreated liquid was fractionally distilled to remove the naphtha fraction (b.p. room temperature—121° C.). Each fraction was analyzed using ASTM International standards to evaluate the efficacy of the process.

[0121] Stage 2—Hydrogenation.

[0122] The hydrotreated product (b.p. >121° C.) was hydrogenated using a commercial platinum-zeolite catalyst to saturate the aromatic rings to produce naphthenic fuel. The

hydrogenation was carried out in a tubular packed-bed reactor using SCR as described earlier, with a temperature of about 150° C. and a pressure of about 100 atm, and a space velocity of about 1.1/h. The catalyst was preactivated prior to hydrogenation of the fuels. The hydrogenation was carried out until complete saturation of the aromatics was achieved as indicated by GC-MS.

[0123] Stage 3—Aromatization.

[0124] Aromatization can generate lubricity, which is desired for a synthetic jet fuel. A portion of the hydrogenated product from Stage 2 was aromatized (about 20 wt %) using commercial catalyst to convert the naphthenes into aromatic hydrocarbons. The catalyst and process conditions were selected in order to maximize the yield of aromatic hydrocarbons and minimize the coke and gas, using a temperature of about 520° C., a pressure of about 34 atm, a space velocity of about 0.3/h, and a platinum-zeolite catalyst. The aromatized product was fractionally distilled to produce the following fractions: naphtha (b.p. <135° C.), jet fraction (b.p., 135°-212° C.), heavy oil (b.p. >212° C.).

[0125] Stage 4—Hydroisomerization.

[0126] GC-MS analysis of the fuel generated by liquefaction of the coal-bio-oil mixture and upgraded by Stages 1 and 2 hydroprocessing indicated only straight-chain paraffins and naphthenes. In order to improve the resulting fuel properties further, a portion of the hydrogenated product was isomerized (about 80 wt %) using a commercial nickel-molybdenum catalyst to produce branched paraffins using a temperature of about 350° C. and a pressure of about 50 atm, with a space velocity of about 3/h. The GC-MS data were used to determine the n-paraffin/isoparaffin ratio. The resulting product was fractionally distilled to generate the following fractions: naphtha (b.p. <121° C.), jet fraction (b.p., 121-246° C.), diesel (b.p. >246° C.).

Example 7

Preparation of Jet Fuel Sample

[0127] The jet fractions from Stage 3 (135°-212° C.) and Stage 4 (121°-246° C.) were analyzed by GC-MS to determine the hydrocarbon types. Based on the GC-MS data, the desired volumes of these jet fractions were blended together to produce composite fuels that contains at least 8 vol % aromatic compounds. The final fuel mixture was approximately 85 wt % isomerized product and approximately 15% aromatized product.

Example 8

Testing of Jet Fuel Sample

[0128] The jet fuel produced above was analyzed using a set of ASTM International standard tests to evaluate the fuel properties. The fuel properties were compared with the specification for JP-8 fuels to determine specification compliance.

Example 9

Fuel from Coal and Canola Oil

[0129] Fuels were produced from the liquefied product of the coal and canola oil combination of Runs 1-3 using the procedure of Example 7. The fuels were tested using ASTM International standards, and the results are given in Tables 6-8. The data indicate that the jet fuel meets the key compo-

nents and exceeds military specifications for JP-8 fuel. The distillation profiles for the coal-canola oil-derived fuels are given in FIG. 5.

TABLE 6

Distillation Data for Coal-Canola Oil-Derived Fuels			
Distillation Profile (GCD)	<121° C.	121°-246° C.	+246°
	wt % Off at ° F.		
100	9.24		
150	41.23		
180	45.13	0	
200	72.60	0	
250	96.64	1.21	
300	100	8.43	
350	0	29.83	
400	0	64.59	
450	0	86.78	2.56
500	0	94.57	8.40
550	0	99.80	31.91
600	0	100	73.36
650	0		97.79
650+	0		0.21
wt % Off at ° F.			
<300° F.	100	8.43	0
350° F.	—	29.83	0
450° F.	—	86.78	2.56
+650° F.	—	100	0.21

TABLE 7

Hydrocarbon Type Analysis of Coal-Canola Oil-Derived Fuels	
Sample Identification	121°-246° C. wt %
Total Paraffins	38.74
n-Paraffins	18.33
isoParaffins	20.41
Naphthenes	50.22
1R-Naphthenes	18.33
2R-Naphthenes	28.56
3R-Naphthenes	3.33
Aromatics	11.04
1R-Naphthenes	8.01
2R-Naphthenes	3.03
3R-Naphthenes	0

TABLE 8

Fuel Properties of Coal-Canola Oil-Derived Jet Fuel		
Grade: Specifications	JP-8 MIL-DTL-83133F	EERC CB Jet2011 121-246° C.
Color, Saybolt	No limit	Clear, colorless
Aromatics, vol %	25.0 max.	7.2
Sulfur, wppm	3000 max.	—
Nitrogen, wppm	—	—
Thermal Stability Tube Rating, Color	<3 visual	1.4
Density, g/cm ³ at 15° C. or API Gravity	0.775-0.840	0.804 at 15° C.
Gravity at 60° F.	51.0-37.0	43.6
Flash Point, ° C.	38 min	46
Freeze Point, ° C.	-47 max.	-62
Naphthalene, vol %	3.0 max.	<0.3

TABLE 8-continued

Fuel Properties of Coal-Canola Oil-Derived Jet Fuel		
Grade: Specifications	JP-8 MIL-DTL-83133F	EERC CB Jet2011 121-246° C.
Heat of Combustion, MJ/kg	42.8	43.2
Hydrogen Content, wt %	13.4 min.	—

[0130] A 500-mL sample of coal-canola oil-derived jet-fuel (EERC CB Jet2011) was tested at the Fuels Branch, U.S. Air Force Research Laboratory (AFRL). The fuel underwent evaluations for use as a propulsion fuel for military aviation systems according to Tier I as outlined in the "Alternative and Experimental Jet Fuel and Jet Fuel Blend Stock Evaluation" protocol developed by AFRL. The fuel sample was evaluated in comparison to a representative petroleum-derived propulsion fuel. Results from testing with EERC CB Jet2011 and the representative JP-8 fuel are shown in Table 9-11, along with JP-8 specification limits. The results indicate that this fuel meets the JP-8 specifications. It has lower aromatics (7 vol %) by JP-8 specification method D1319, as compared to the JP-8 specification limit (maximum 25 vol %) and the representative JP-8 value (19 vol %). FIG. 6 shows the wt % of n-paraffins (C7-C19) in the sample, as compared to the representative sample of JP-8. FIG. 7 shows GC results of the sample, as compared to the representative sample of JP-8.

TABLE 9

Results of Testing			
Specification Test	MIL-DTL-83133G Spec. Requirement	7492 BJet2011	4751 JP-8
Aromatics, vol %	≤25	6.6	18.8
Olefins, vol %		0.6	0.8
Heat of Combustion (measured), MJ/kg	≥42.8	43.2	43.3
Distillation:			
IBP, ° C.		153	159
10% recovered, ° C.	≤205	171	182
20% recovered, ° C.		178	189
50% recovered, ° C.		196	208
90% recovered, ° C.		235	244
EP, ° C.	≤300	260	265
Residue, % vol	≤1.5	1.3	1.3
Loss, % vol	≤1.5	0.4	0.8
Flash Point, ° C.	≥38	46	51
Freeze Point, ° C.	≤-47	-62	-50
API Gravity at 60° F.	37.0-51.0	43.3	44.4
Density at 15° C., kg/L	0.775-0.840	0.809	0.804

TABLE 10

Hydrocarbon Type Analysis by D2425 for Coal-Canola Oil-Derived Jet Fuel and JP-8 Fuel		
D2425 (mass %)	EERC CB Jet2011	JP-8
Paraffins (normal + iso)	39	49
Cycloparaffins	54	30
Alkylbenzenes	5.4	13
Indans and Tetralins	1.5	5.8
Indenes and C _n H _{2n-10}	<0.3	0.6
Naphthalene	<0.3	<0.3
Naphthalenes	<0.3	1.0
Acenaphthenes	<0.3	<0.3
Acenaphthylenes	<0.3	<0.3

TABLE 10-continued

Hydrocarbon Type Analysis by D2425 for Coal-Canola Oil-Derived Jet Fuel and JP-8 Fuel		
D2425 (mass %)	EERC CB Jet2011	JP-8
Tricyclic Aromatic	<0.3	<0.3
Total	100	100

TABLE 11

Weight Percent of Paraffins for Coal-Canola Oil-Derived Jet Fuel and JP-8 Fuel		
n-Paraffins, wt %	7492 CB Jet2011	4751 JP-8
n-Heptane	0.036	0.10
n-Octane	0.44	0.34
n-Nonane	1.79	1.21
n-Decane	2.53	3.48
n-Undecane	2.47	4.24
n-Dodecane	1.73	3.71
n-Tridecane	1.05	2.84
n-Tetradecane	0.46	1.79
n-Pentadecane	0.30	0.87
n-Hexadecane	0.068	0.27
n-Heptadecane	0.074	0.089
n-Octadecane	0.023	0.024
n-Nonadecane	<0.001	0.008
Total n-Paraffins	11.0	19.0

[0131] Thermal stability characteristics of this fuel were assessed using QCM under typical experimental conditions (i.e., 140° C., air-saturated fuel, 15 hours). QCM results for the fuels (see Table 12 and FIG. 8) show that the biofuel produces a level of deposits (1.4 µg/cm²) that is below that of the representative JP-8 fuel (3.0 µg/cm²) and below the average range of JP-8 fuels of 2 to 6 g/cm². In FIG. 8, solid curves and closed markers illustrate mass accumulation, and dashed curves and open markers illustrate headspace oxygen profiles. With regard to oxygen consumption in the biofuel, the oxygen is consumed at a fairly rapid rate (within 5 hours), indicating that it contains no antioxidant.

TABLE 12

Data from QCM Thermal Stability Analysis	
Fuel Description	15-hr Mass Accumulation, µg/cm ²
EERC CB Jet2011	1.4
JP-8	3.0

Example 10

Fuel from Coal and Algae Oil

[0132] Fuels were produced from the liquefied product of the coal and algae oil combination of Runs 4-5 using the procedure of Example 7. The fuels were tested using ASTM International standards, and the results are given in Tables 13-15. The data indicate that the jet fuel meets the key components and specifications of JP-8 fuel. The distillation profiles for the coal-algae oil-derived fuels are given in FIG. 9.

TABLE 13

Distillation Data for Upgraded Coal-Algae Oil-Derived Fuel			
Distillation Profile (GCD)	<121° C.	121°-246° C.	+246° C.
wt % Off at ° F.			
100	0		
150	8.7		
180	37.5	0	
200	68.9	0.17	
250	94.6	3.26	
300	100	12.31	
350	0	31.00	
400	0	62.60	
450	0	86.50	0.50
500	0	94.70	19.10
550	0	100	39.9
600	0		98.2
650	0		100
650+	0		0
wt % Off at ° F.			
<300° F.	100	12.31	0
350° F.-	—	31.00	0
450° F.-	—	62.60	0.5
550° F.-	—	100	39.90
600° F.-	—	—	98.2

TABLE 14

Hydrocarbon Type Analysis of Coal-Algae Oil-Derived Fuel	
Sample Identification	121°-246° C. wt %
Total Paraffins	25.35
n-Paraffins	19.55
isoParaffins	5.80
Naphthenes	60.87
1R-Naphthenes	21.15
2R-Naphthenes	35.64
3R-Naphthenes	4.08
Aromatics	13.78
1R-Aromatics	9.17
2R-Aromatics	4.60
3R-Aromatics	0

TABLE 15

Fuel Properties of Coal-Algae Oil-Derived Fuel		
Grade Specification	JP-8 MIL-DTL-83133F	EERC CAO Jet2011 121°-246° C.
Color, Saybolt	No limit	Clear, colorless
Aromatics, vol %	25.0 max.	10.2
Sulfur, wppm	3000 max.	—
Nitrogen, wppm	—	—
Thermal Stability Tube Rating, color	<3 visual	—
Density, g/cm ³ at 15° C. or gravity	0.775-0.840	0.819 at 15° C.
API at 60° F.	51.0-37.0	45.3
Flash Point, ° C.	38 min	39
Freeze Point, ° C.	-47 max.	-58.6
Naphthalene, vol %	3.0 max.	0
Hydrogen Content, wt %	13.4 min.	—

Example 11

Fuel from Coal and Coal-Wax-Derived Fuels

[0133] Fuels were produced from the liquefied product of the coal and wax combination of Runs 6-7 using the procedure of Example 7. The fuels were tested using ASTM International standards, and the results are given in Tables 16-18. The data indicate that the jet fuel meets the key components and properties of JP-8. The distillation profiles for the coal-wax-derived fuels are given in FIG. 10.

TABLE 16

Distillation Data for Coal-Wax-Derived Fuel			
Distillation Profile (GCD)	<121° C.	121° C.-246° C.	>246° C.
wt& Off at ° F.			
100	0		
150	8.4		
180	46.3	0	
200	69.1	0.10	
250	98.3	2.79	
300	100	12.68	
350	0	36.13	
400	0	69.21	
450	0	91.56	3.00
500	0	97.04	18.02
550	0	100	76.64
600	0		99.34
650	0		100
650+	0		0
wt % Off at ° F.			
<300° F.	100	12.68	0
350° F.-	—	36.13	0
450° F.-	—	91.56	3.00
550° F.-		100	76.64
600° F. (315° C.)-	—	—	99.34

TABLE 17

Hydrocarbon Type Analysis of Coal-Wax-Derived Fuel	
Sample Identification	121°-246° C. wt %
Total Paraffins	40.69
n-Paraffins	22.58
isoParaffins	18.11
Naphthenic	48.69
1R-Naphthenes	22.70
2R-Naphthenes	24.61
3R-Naphthenes	1.38
Aromatics	10.61
1R-Aromatics	8.16
2R-Aromatics	2.45
3R-Aromatics	0

TABLE 18

Fuel Properties of Coal-Wax-Derived Fuel		
Grade Specifications	JP-8 MIL-DTL-83133F	EERC CAO Jet2011 121° C.-246° C.
Color, Saybolt	No limit	Clear, colorless
Aromatics, vol %	25.0 max.	7.90
Sulfur, wppm	3000 max.	—
Nitrogen, wppm	—	—

TABLE 18-continued

Fuel Properties of Coal-Wax-Derived Fuel		
Grade Specifications	JP-8 MIL-DTL-83133F	EERC CAO Jet2011 121° C.-246° C.
Thermal Stability Tube Rating, Color	<3 visual	—
Density, g/cm ³ at 15° C. or gravity	0.775-0.840	0.803 at 15° C.
API at 15° C. (60° F.)	51.0-37.0	43.63
Flash Point, ° C.	38 min	40
Freeze Point, ° C.	-47 max.	-61.6
Naphthalene, vol %	3.0 max.	0
Hydrogen Content, wt %	13.4 min.	14.0

[0134] The terms and expressions which have been employed are used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus it should be understood that although the present invention has been specifically disclosed by preferred embodiments and optional features, modification and variation of the concepts herein disclosed may be resorted to by those of ordinary skill in the art and that such modifications and variations are considered to be within the scope of this invention as defined by the appended claims.

Additional Embodiments

[0135] The present invention provides for the following exemplary embodiments, the numbering of which is not to be construed as designating levels of importance.

[0136] Embodiment 1 provides a method of liquefaction of carbonaceous material and biomass, including providing or obtaining a feed mixture, the mixture including carbonaceous material and biomass, and subjecting the feed mixture to liquefaction, to provide a product slurry; wherein the carbonaceous material includes a nonpetroleum fossil fuel or a petroleum refinery residue.

[0137] Embodiment 2 provides the method of Embodiment 1, wherein the carbonaceous material includes coal, coal tar, wax from a FT process, petroleum refinery residue, vacuum bottoms, tar sand, bitumen, or a combination thereof.

[0138] Embodiment 3 provides the method of Embodiment 2, wherein the coal includes coal powder, pulverized coal, or a combination thereof.

[0139] Embodiment 4 provides the method of any one of Embodiments 2-3, wherein the coal includes lignite, brown coal, jet coal, subbituminous coal, bituminous coal, steel coal, anthracite, graphite, or a combination thereof.

[0140] Embodiment 5 provides the method of any one of Embodiments 1-4, wherein the biomass includes plant-derived oil, algae-derived oil, biomass pyrolysis oil, waste oil, yellow grease, brown grease, tar, or animal fat.

[0141] Embodiment 6 provides the method of any one of Embodiments 1-5, wherein the mass ratio of carbonaceous material to biomass is about 0.01-10 to 1.

[0142] Embodiment 7 provides the method of any one of Embodiments 1-6, wherein the mixture further includes solvent.

[0143] Embodiment 8 provides the method of Embodiment 7, wherein the solvent includes a carbonaceous material-derived heavy liquid.

[0144] Embodiment 9 provides the method of any one of Embodiments 1-8, wherein the liquefaction includes direct liquefaction.

[0145] Embodiment 10 provides the method of any one of Embodiments 1-9, wherein subjecting the feed mixture to liquefaction includes contacting the feed mixture with a liquefaction catalyst and hydrogen gas at a temperature of about 200° to about 600° C., at a pressure of about 50 to about 300 atm.

[0146] Embodiment 11 provides the method of Embodiment 10, wherein the liquefaction catalyst includes a cobalt-molybdenum catalyst.

[0147] Embodiment 12 provides the method of any one of Embodiments 10-11, wherein the hydrogen gas is provided from a supply integrated in the method.

[0148] Embodiment 13 provides the method of any one of Embodiments 10-12, wherein the pressure during the liquefaction is about 150 to about 250 atm.

[0149] Embodiment 14 provides the method of any one of Embodiments 10-13, wherein the temperature during liquefaction is about 400° to about 500° C.

[0150] Embodiment 15 provides a method of fuel production from carbonaceous material and biomass, including performing the method of any one of Embodiments 1-14; separating the product slurry, to give a conversion component; and processing the conversion component, to give a fuel.

[0151] Embodiment 16 provides the method of Embodiment 15, wherein the method is substantially or fully integrated with respect to the fuel production.

[0152] Embodiment 17 provides the method of any one of Embodiments 15-16, wherein separating the product slurry includes distilling, wherein the conversion includes at least part of the distillate from the distilling.

[0153] Embodiment 18 provides the method of any one of Embodiments 15-17, wherein processing the distillate includes hydrotreating the conversion component, to give a hydrotreated material; hydrogenating the hydrotreated material, to give a hydrogenated material; optionally isomerizing at least some of the hydrotreated material, to give an isomerized material; optionally aromatizing at least some of the hydrotreated material, to give an aromatized material; and blending the isomerized material and the aromatized material, to give the fuel; wherein at least one of isomerizing and aromatizing is performed or both isomerizing and aromatizing are performed.

[0154] Embodiment 19 provides the method of Embodiment 18, wherein isomerizing is performed.

[0155] Embodiment 20 provides the method of any one of Embodiments 18-19, wherein aromatizing is performed.

[0156] Embodiment 21 provides the method of any one of Embodiments 18-20, wherein both isomerizing and aromatizing are performed.

[0157] Embodiment 22 provides the method of any one of Embodiments 18-21, wherein the hydrotreating includes contacting the conversion component with a hydrotreatment catalyst and hydrogen gas at a temperature of about 200° to about 500° C., at a pressure of about 10 to about 300 atm, sufficient to give the hydrotreated material.

[0158] Embodiment 23 provides the method of Embodiment 22, wherein the hydrotreatment catalyst includes palladium (Pd), platinum (Pt), nickel (Ni), nickel-molybdenum (NiMo), cobalt-molybdenum (CoMo), or any combination thereof.

[0159] Embodiment 24 provides the method of any one of Embodiments 18-23, wherein the hydrogenating includes contacting the hydrotreated material with a hydrogenation catalyst and hydrogen gas at a temperature of about 50° to about 300° C., at a pressure of about 10 to about 250 atm, sufficient to give the hydrogenated material.

[0160] Embodiment 25 provides the method of Embodiment 24, wherein the hydrogenation catalyst includes a platinum-zeolite catalyst.

[0161] Embodiment 26 provides the method of any one of Embodiments 18-25, wherein the isomerizing includes contacting the hydrotreated material with an isomerization catalyst and hydrogen gas at a temperature of about 200° to about 450° C., at a pressure of about 5 to about 150 atm, sufficient to give the isomerized material.

[0162] Embodiment 27 provides the method of Embodiment 26, wherein the isomerization catalyst includes a nickel-molybdenum catalyst.

[0163] Embodiment 28 provides the method of any one of Embodiments 18-27, wherein the aromatizing includes contacting the hydrotreated material with an aromatization catalyst and hydrogen gas at a temperature of about 350° to about 750° C., at a pressure of about 10 to about 150 atm, sufficient to give the aromatized material.

[0164] Embodiment 29 provides the method of Embodiment 28, wherein the aromatization catalyst includes a platinum-zeolite catalyst.

[0165] Embodiment 30 provides the method of any one of Embodiments 18-29, wherein the mass ratio of hydrotreated material subjected to isomerizing to hydrotreated material subjected to aromatizing is about 1-20 to 1.

[0166] Embodiment 31 provides the method of any one of Embodiments 18-30, wherein the mass ratio of isomerized material blended to aromatized material blended is about 1-20 to 1.

[0167] Embodiment 32 provides the method of any one of Embodiments 15-31, wherein the fuel includes a liquid transportation fuel.

[0168] Embodiment 33 provides the method of any one of Embodiments 15-32, wherein the fuel is gasoline, naphtha, kerosene, jet fuel, or diesel fuel.

[0169] Embodiment 34 provides the method of any one of Embodiments 15-33, wherein the fuel has a composition that complies with JP-5, JP-8, or BUFF requirements.

[0170] Embodiment 35 provides a method of liquefaction of coal and biomass, including providing or obtaining a feed mixture, the mixture including coal and biomass, the biomass including plant-derived oil, algae-derived oil, biomass pyrolysis oil, waste oil, yellow grease, brown grease, tar, or animal fat and subjecting the feed mixture to liquefaction, to provide a product slurry, the liquefaction including contacting the feed mixture with a liquefaction catalyst and hydrogen gas at a temperature of about 350° to about 500° C., at a pressure of about 150 to about 250 atm.

[0171] Embodiment 36 provides a method of fuel production from coal and biomass, including providing or obtaining a feed mixture, the mixture including coal and biomass, the biomass including plant-derived oil, algae-derived oil, biomass pyrolysis oil, waste oil, yellow grease, brown grease, tar, or animal fat; subjecting the feed mixture to liquefaction, to provide a product slurry; distilling the product slurry, to give a distillate; and hydrotreating the distillate, to give a hydrotreated material; hydrogenating the hydrotreated material, to give a hydrogenated material; isomerizing at least

some of the hydrotreated material, to give an isomerized material; aromatizing at least some of the hydrotreated material, to give an aromatized material; and blending at least some of the isomerized material and at least some of the aromatized material, to give a fuel.

[0172] Embodiment 37 provides the apparatus or method of any one or any combination of Embodiments 1-36 optionally configured such that all elements or options recited are available to use or select from.

We claim:

1. A method of liquefaction of carbonaceous material and biomass, comprising:

providing or obtaining a feed mixture, the mixture comprising carbonaceous material and biomass; and
subjecting the feed mixture to liquefaction, to provide a product slurry;

wherein the carbonaceous material comprises a nonpetroleum fossil fuel or a petroleum refinery residue.

2. The method of claim 1, wherein the carbonaceous material comprises coal, coal tar, wax from a FT process, petroleum refinery residue, vacuum bottoms, tar sand, bitumen, or a combination thereof.

3. The method of claim 2, wherein the coal comprises coal powder, pulverized coal, or a combination thereof.

4. The method of claim 2, wherein the coal comprises lignite, brown coal, jet coal, subbituminous coal, bituminous coal, steel coal, anthracite, graphite, or a combination thereof.

5. The method of claim 1, wherein the biomass comprises plant-derived oil, algae-derived oil, biomass pyrolysis oil, waste oil, yellow grease, brown grease, tar, or animal fat.

6. The method of claim 1, wherein the mass ratio of carbonaceous material to biomass is about 0.01-10 to 1.

7. The method of claim 1, wherein the mixture further comprises solvent.

8. The method of claim 7, wherein the solvent comprises a carbonaceous material-derived heavy liquid.

9. The method of claim 1, wherein the liquefaction comprises direct liquefaction.

10. The method of claim 1, wherein subjecting the feed mixture to liquefaction comprises contacting the feed mixture with a liquefaction catalyst and hydrogen gas at a temperature of about 200° to about 600° C., at a pressure of about 50 to about 300 atm.

11. The method of claim 10, wherein the liquefaction catalyst comprises a cobalt-molybdenum catalyst.

12. The method of claim 10, wherein the hydrogen gas is provided from a supply integrated in the method.

13. The method of claim 10, wherein the pressure during the liquefaction is about 150 to about 250 atm.

14. The method of claim 10, wherein the temperature during liquefaction is about 400° to about 500° C.

15. A method of fuel production from carbonaceous material and biomass, comprising:

performing the method of claim 1;

separating the product slurry, to give a conversion component; and

processing the conversion component, to give a fuel.

16. The method of claim 15, wherein the method is substantially or fully integrated with respect to the fuel production.

17. The method of claim 15, wherein separating the product slurry comprises distilling, wherein the conversion comprises at least part of the distillate from the distilling.

18. The method of claim 15, wherein processing the distillate comprises:

hydrotreating the conversion component, to give a hydrotreated material;

hydrogenating the hydrotreated material, to give a hydrogenated material;

optionally isomerizing at least some of the hydrotreated material, to give an isomerized material;

optionally aromatizing at least some of the hydrotreated material, to give an aromatized material; and

blending the isomerized material and the aromatized material, to give the fuel;

wherein at least one of isomerizing and aromatizing is performed, or both isomerizing and aromatizing are performed.

19. The method of claim 18, wherein isomerizing is performed.

20. The method of claim 18, wherein aromatizing is performed.

21. The method of claim 18, wherein both isomerizing and aromatizing are performed.

22. The method of claim 15, wherein the fuel comprises a liquid transportation fuel.

23. A method of liquefaction of coal and biomass, comprising:

providing or obtaining a feed mixture, the mixture comprising coal and biomass, the biomass comprising plant-derived oil, algae-derived oil, biomass pyrolysis oil, waste oil, yellow grease, brown grease, tar, or animal fat; and

subjecting the feed mixture to liquefaction, to provide a product slurry, the liquefaction comprising contacting the feed mixture with a liquefaction catalyst and hydrogen gas at a temperature of about 350° to about 500° C., at a pressure of about 150 to about 250 atm.

24. A method of fuel production from coal and biomass, comprising:

providing or obtaining a feed mixture, the mixture comprising coal and biomass, the biomass comprising plant-derived oil, algae-derived oil, biomass pyrolysis oil, waste oil, yellow grease, brown grease, tar, or animal fat;

subjecting the feed mixture to liquefaction, to provide a product slurry;

distilling the product slurry, to give a distillate; and

hydrotreating the distillate, to give a hydrotreated material;

hydrogenating the hydrotreated material, to give a hydrogenated material;

isomerizing at least some of the hydrotreated material, to give an isomerized material;

aromatizing at least some of the hydrotreated material, to give an aromatized material; and

blending at least some of the isomerized material and at least some of the aromatized material, to give a fuel.