



- (51) **International Patent Classification:**
C10G 3/00 (2006.01)
- (21) **International Application Number:**
PCT/US2013/054162
- (22) **International Filing Date:**
8 August 2013 (08.08.2013)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
61/681,141 8 August 2012 (08.08.2012) US
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- (81) **Designated States** (*unless otherwise indicated, for every
kind of national protection available*): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,

BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM,
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KN, KP, KR,
KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME,
MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ,
OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA,
SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM,
TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM,
ZW.

- (84) **Designated States** (*unless otherwise indicated, for every
kind of regional protection available*): ARIPO (BW, GH,
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ,
UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ,
TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK,
EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV,
MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,
TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,
KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- *as to applicant's entitlement to apply for and be granted a
patent (Rule 4.17(ii))*
- *as to the applicant's entitlement to claim the priority of the
earlier application (Rule 4.17(iii))*

Published:

- *without international search report and to be republished
upon receipt of that report (Rule 48.2(g))*

(54) **Title:** PROCESS FOR THE PRODUCTION OF HYDROCARBONS FOR FUELS, SOLVENTS, AND OTHER HYDRO-
CARBON PRODUCTS

(57) **Abstract:** Catalytic processes for converting carboxylic acids obtained from biomass and other natural or industrial sources into
paraffinic or olefinic hydrocarbons through decarboxylation, along with products formed from such hydrocarbons, in which the car-
bon chain length, the ratio of carbon-14 to carbon-12, and the ratio of odd number to even number of carbons in the chain are among
factors which are indicative or otherwise useful for the detection of hydrocarbons formed by undergoing the claimed processes



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(AS PCT RECEIVING RECEIVING OFFICE)

**PROCESS FOR THE PRODUCTION OF HYDROCARBONS FOR
FUELS, SOLVENTS, AND OTHER HYDROCARBON PRODUCTS****Cross Reference to Related US Application**

[0001] This international patent application claims priority to U.S. Provisional Application No. 61/681,141 filed on August 8, 2012.

TECHNICAL FIELD

[0002] The invention relates to the conversion of carboxylic acids obtained from biomass and other natural or industrial sources into paraffinic and olefinic hydrocarbons suitable for use as other hydrocarbon products, including but not limited to fuels, solvents, and other derivatives and products.

BACKGROUND OF THE INVENTION

[0003] Hydrocarbons are an energy source for internal combustion engines, for turbines in jet aircraft, and for other kinds of engines, as well as for other applications that require a source of fuel. Some hydrocarbon fuels, such as diesel fuels, are linear, paraffinic hydrocarbons. Some hydrocarbon products, such as, for example, kerosene, some jet fuels, and some solvents, have branched-chain hydrocarbons and number 10-to-15 carbon atoms in their molecular structure. By comparison, diesel fuels are typically straight-chained and have between 15-to-22 carbon atoms.

[0004] Hydrocarbon fuels and other petrochemical products typically are obtained from crude petroleum oil through a series of conventional steps. These steps include, but are not necessarily limited to, distillation followed by additional refining. Attempts are being made, however, to produce hydrocarbon fuels, solvents, and other hydrocarbon products from

alternative, renewable sources, including but not limited to feedstocks of biological origin. A common objective of such attempts has been to develop hydrocarbon fuels with similar chemical and functional properties to the fuels and other products that are obtained from crude petroleum, but made from alternative sources and without having to utilize the conventional steps such as those mentioned above. Moreover, because of their similar chemical properties and functional properties, some hydrocarbon fuels from alternative, renewable sources are compatible with and, therefore, acceptable for use with, the kinds of engines for which petroleum-derived hydrocarbon fuels are intended. The same is true in regards to other hydrocarbon products as noted above.

[0005] More specifically, hydrocarbon fuels and other hydrocarbon products from alternative, renewable sources other than petroleum (i.e., a fossil fuel) include those products which are obtained from a process according to multiple embodiments and alternatives as described and claimed herein. In some cases, such products are capable of being stored and transported through existing infrastructure (e.g., storage tanks and pipelines) as with petroleum-derived hydrocarbon fuels. This increases the feasibility of using such products as replacements for petroleum-derived hydrocarbon products in applications such as transportation fuels, as well as other applications.

[0006] Neither linear nor branched paraffinic hydrocarbons occur naturally in large quantities from renewable as opposed to fossil sources. However, one route for the production of hydrocarbons is through decarboxylation of carboxylic acids, which are readily available in the lipid portion of biomass raw materials. The fact that biomass raw materials are in relatively large supply increases the desirability of this approach. For example, the lipid portions of plant oils, animal fats, animal oils and algae oils are a ready source of triglyceride esters, which may be converted to carboxylic acids through methods known to persons of ordinary skill in the art, e.g., thermal hydrolysis or acid hydrolysis.

[0007] Through such methods, carboxylic acids are obtained from biomass raw materials, and are used as starting materials in the conversion to linear, paraffinic hydrocarbons. As a non-limiting example, stearic acid, with a chemical formula of $C_{17}H_{35}COOH$ (or, $C_{18}H_{36}O_2$), is a common carboxylic acid derived from biomass raw materials. Various routes exist for the conversion of stearic acid to a linear, paraffinic hydrocarbon, which require the removal of the two oxygen atoms of the carboxylate group. One approach previously studied and reported on, known as hydrodeoxygenation, accomplishes this but requires the use of hydrogen as a reactant. An alternative approach is decarboxylation, which involves removal of the carboxylate group as carbon dioxide. In this approach, the alkane product has one carbon atom less than the carboxylic acid starting material. A decarboxylation reaction does not require the consumption of hydrogen as a reactant.

[0008] Accordingly, decarboxylation produces hydrocarbons with a linear structure in which the alkyl group of the carboxylic acid is preserved, and the carboxylate group (i.e., one carbon atom and two oxygen atoms) is removed as carbon dioxide. Decarboxylation of carboxylic acids is generally less expensive than hydrodeoxygenation, which requires a large supply of hydrogen as a necessary reactant.

[0009] Decarboxylation yields normal, linear, hydrocarbons, without having to use hydrogen as a reactant. These hydrocarbons then may be isolated and separated by fractional distillation or other methods known to persons of ordinary skill in the art into appropriate fractions for use as kerosene, jet fuel, diesel fuel, automobile fuel or other kinds of fuel, solvents, and/or other kinds of hydrocarbon products as desired by an end user.

DISCLOSURE OF THE INVENTION

[00010] A process for producing linear, paraffinic hydrocarbons converts fatty acids (a.k.a. carboxylic acids) containing 6-to-24 carbon atoms into linear, paraffinic hydrocarbons, which can be used as fuels and other hydrocarbon products. Generally, the linear, paraffinic

hydrocarbons contain one less carbon atom than the starting carboxylic acids. As a non-limiting example, decarboxylation of stearic acid (18 carbons) produces heptadecane (17 carbons, C₁₇H₃₆).

[00011] A process for producing linear, olefinic hydrocarbons converts fatty acids containing 6-to-24 carbon atoms into linear, olefinic hydrocarbons. Generally, the linear, olefinic hydrocarbons contain one less carbon atom than the starting carboxylic acids.

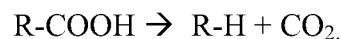
[00012] In some embodiments, surface basicity of the catalyst and its dispersibility over the support are factors for selecting a reaction catalyst. Porosity and/or mesoporosity, as well hydrophobicity, are factors for selecting a support.

[00013] Processes disclosed and claimed herein are for producing linear hydrocarbons which can be used in various ways. In some applications, these products are used as hydrocarbon fuels. Alternatively, these products are starting materials, which are converted to branched-chain paraffinic hydrocarbons through processes known to persons of ordinary skill in the art, and which are suitable for use as hydrocarbon fuels. Alternatively, these products are starting materials for the production of various petrochemicals, through methods which are known to persons of ordinary skill in the art. Non-limiting examples of such petrochemicals include linear alpha olefins, alpha olefin sulfonates, and linear alkyl benzenes. Such petrochemicals are used in the manufacture of various end products. For example, linear alkyl benzenes are used in the manufacture of detergents. Other examples of petrochemicals used in the manufacture of various end products include high viscosity index star polymers. The forgoing are non-limiting examples of a broad scope in which products of the subject process are used.

MODES FOR CARRYING OUT THE INVENTION

[00014] A process for producing linear hydrocarbons comprises (1) obtaining a supply of at least one carboxylic acid; (2) selecting a reaction catalyst and a support as described

herein; and (3) contacting the at least one carboxylic acid with the catalyst over the support, under conditions as described herein, resulting in the decarboxylation reaction:



[00015] In some embodiments, linear, paraffinic hydrocarbons are then isolated from the end products of the reaction. The linear, paraffinic hydrocarbons obtained as the end products of the decarboxylation reaction are fully saturated hydrocarbons, which are appropriate to be used in the various applications described above.

[00016] In some embodiments, the at least one carboxylic acid is a carboxylic acid having 6-to-24 carbon atoms. Optionally, the at least one carboxylic acid is a mixture of at least two carboxylic acids, each having 6-to-24 carbon atoms. In some embodiments, triglyceride esters contained in various sources as described below are converted to carboxylic acids through methods known to persons of ordinary skill in the art. In some embodiments, the at least one carboxylic acid is obtained from a renewable feedstock of biological origin (i.e., biomass raw materials), such as, for example, plant oils; animal fats and oils; algae oils; waste vegetable oils; or oils from heterotrophic microbes. Illustrative, non-limiting examples of heterotrophic microbes are heterotrophic algae, oleaginous yeasts, and various bacteria. Optionally, the source of the at least one carboxylic acid consists of a mixture of two or more members of this group. Alternatively, the at least one carboxylic acid is obtained from an industrial or other non-biological source, such as, for example industrial greases, and waxes obtained from solid wastes, and paper mills.

[00017] In some embodiments, the renewable feedstock includes, but is not necessarily limited to, plant oils from a non-food oil crop such as jatropha oil, camelina oil, pennycress oil, pongamia oil, and carinata oil. Such non-food oil crops are generally less expensive to produce or obtain, are more sustainable, and are significantly lower in lifecycle greenhouse gas emissions than, for example, soybean oil, rapeseed oil, or beef tallow. The use of such

lower-cost, more sustainable oils for decarboxylation processes as described herein, according to multiple embodiments and alternatives, provides increased production flexibility and cost-effectiveness for hydrocarbon fuels, chemicals, and other products because production facilities can be distributed and in closer proximity to locations where these oil crops are grown. By comparison, known hydrodeoxygenation techniques and processes generally require significantly greater economies of scale, and are largely limited to being carried out at or near existing oil refineries with large supplies of hydrogen.

[00018] In some embodiments, starting materials used in a process for producing linear, paraffinic hydrocarbons are saturated carboxylic acids. Alternatively, the starting materials are unsaturated carboxylic acids. In the latter case, it is an option to reduce the unsaturated carboxylic acids to saturated carboxylic acids by reaction with hydrogen, through methods known to persons of ordinary skill in the art, before undergoing decarboxylation, or simultaneously during decarboxylation.

[00019] The decarboxylation reaction (also referred to herein as, "decarboxylation") by which carboxylic acids are converted to linear, paraffinic hydrocarbons, is exothermic. Notwithstanding its favorable thermodynamics, however, the energy associated with the transition state of this reaction represents an activation barrier that requires a catalyst for the reaction to proceed under the kinds of conditions disclosed herein. Therefore, in some embodiments, a catalyst is chosen from the group platinum, palladium, nickel, nickel-molybdenum, nickel-tungsten, and platinum-copper. In some embodiments, surface basicity is considered in selecting a catalyst. It will be noted that the presence or absence of various functional groups at the surface of a catalyst influences its surface basicity.

[00020] Further, a support's basicity or acidity influences the kinds of hydrocarbon products resulting from decarboxylation of the carboxylic acids. For example, the presence of acidic sites in the support tend to catalyze certain side reactions, such as cracking,

isomerization, polymerization, and cyclisation of the primary decarboxylation product, i.e., the linear hydrocarbon. Some products of such side reactions tend to diminish the long-term life and activity of the catalyst. Thus, in some embodiments a solid material with known, basicity properties is chosen as a support.

[00021] The surface basicity of the catalyst is determined by measuring the amount of acetic acid adsorbed from a 0.1 N solution of acetic acid in normal hexane, at room temperature, on a sample of the solid catalyst treated previously at high temperatures to remove impurities (e.g., water, carbon dioxide), and is expressed as equivalents of acetic acid adsorbed by the solid. Also, in general, the extent to which the metal catalyst is dispersed over the support influences the yield of the decarboxylation reaction. Stated differently, the hydrocarbon product yield increases as the level of metal dispersion increases. Preferably, the dispersion of the metal catalyst over the support is at least about 50%.

[00022] In some embodiments, a support is selected which is a porous or mesoporous structure formed from basic oxide materials, which are chosen from the group hydrotalcite, magnesium oxide, calcium oxide, a mixed oxide of ceria-zirconia, and lanthanum oxide. In some embodiments, hydrophobicity is considered in selecting a support for the catalyst. Hydrophobicity of the support is determined by measuring adsorption of water vapor by the support under ambient conditions. Preferably, the support adsorbs no more than about 0.5%wt water vapor under ambient conditions. Optionally, hydrophobicity is determined by exposing the support to water vapor at 25° C and corresponding equilibrium pressures, and measuring the percentage of water vapor adsorbed by the support in relation to the weight of the catalyst to be used.

[00023] In some embodiments, carboxylic acid starting materials are diluted in a suitable solvent before commencing the decarboxylation reaction. One purpose of dilution is to assist a pump-induced flow of carboxylic acid reactant into the reaction chamber. As used herein, a

suitable solvent would include hydrocarbons, such as, for example dodecane or hexadecane. In some embodiments, a mixture of two or more hydrocarbons is used as a solvent. In some embodiments, decarboxylation is carried out in a suitable solvent. Alternatively, decarboxylation is carried out in a solvent-free reaction chamber.

[00024] If desired, a process for production of paraffinic hydrocarbons, as described herein according to multiple embodiments and alternatives, is carried out in a reactor. In some embodiments, the reactor is a batch reactor. Alternatively, the reactor is a semi-batch reactor. Alternatively, the reactor is a continuous flow reactor. Optionally, the carboxylic acid starting materials are passed over a supported catalyst in a reaction zone contained within the reactor. In some embodiments, decarboxylation is carried out at a temperature in a range of about 200° C – 400 ° C. Alternatively, the temperature is in a range of about 250° C – 350 ° C. In some embodiments, decarboxylation is carried out at a pressure in a range of about 1 bar – 60 bar.

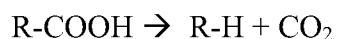
[00025] In some embodiments, decarboxylation produces hydrocarbon products consisting of linear, paraffinic hydrocarbons, which are isolated and separated using techniques known to persons of ordinary skill in the art (e.g., distillation). Alternatively, for feedstocks containing olefinic carboxylic acids, decarboxylation produces hydrocarbon products consisting of linear, olefinic hydrocarbons, which are isolated and separated using such techniques. In this way, the separated reaction products can be put to use according to their intended purpose as selected by a user.

[00026] In some embodiments as described herein, decarboxylation produces only linear, paraffinic hydrocarbons, and carbon dioxide. The lack of cracking, branching, or other side reactions in the decarboxylation reactor may be desirable for the production of certain products, such as, for example, high-cetane diesel blendstock or aromatic-free solvents. The lack of side reactions may also be desirable for increasing the conversion yield of the desired

products. With regard to industrial applications, the lack of side reactions may help to reduce the complexity and cost of downstream separations.

[00027] The combination of certain catalysts and certain supports, according to multiple embodiments and alternatives described herein, may help to reduce unwanted side reactions, including cracking and branching. Further, certain combinations as well as reaction conditions may help to increase single-pass conversion yields. By way of non-limiting illustration, in some embodiments the cracked or branched hydrocarbons are expected to be less than about 5% by mass of the total reaction products. The degree of cracking can be indicated by the ratio of the weighted average carbon chain length of the hydrocarbon products to that of the carboxylic acid feedstock, after accounting for the difference of a single carbon resulting from the decarboxylation itself. In some embodiments, a weighted average chain length of hydrocarbon products greater than 80% of the weighted average chain length of the carboxylic acid feedstock is expected to be a finding indicative of minimal cracking during the decarboxylation reaction.

[00028] Optionally, a process for producing linear hydrocarbons is used for the conversion of unsaturated carboxylic acids to olefinic (unsaturated), linear hydrocarbons. This alternative embodiments comprises (1) obtaining a supply of at least one carboxylic acid; (2) selecting a reaction catalyst and a support as described herein; and (3) contacting the at least one carboxylic acid with the catalyst over the support, under conditions as described herein, resulting in the decarboxylation reaction:



wherein R contains six-to-twenty-four carbons, and has at least one carbon-carbon double bond. Further, in some embodiments, both paraffinic and olefinic carboxylic acids, respectively, are together converted to paraffinic and olefinic linear hydrocarbons in a single reaction chamber, using a catalyst, support, and reaction conditions according to alternative

embodiments as set forth herein. Moreover, in some alternative embodiments, the process converts at least a portion of olefinic carboxylic acids to linear, olefinic hydrocarbons by decarboxylation, which are then converted through hydrogenation, which optionally can be performed in the same reaction chamber or in a separate reaction chamber.

[00029] In those embodiments where the sole or primary hydrocarbon products of decarboxylation are paraffinic hydrocarbons, it will be appreciated by persons of ordinary skill in the art that it is possible to tune the decarboxylation reaction as selectably desired by the practitioner. Depending on the particular product or products desired, reaction conditions and catalyst/support combinations can also be varied in order to favor particular levels of cracking and/or so that the paraffinic hydrocarbons that are produced will meet the specifications of, among other products, high cetane diesel and feedstocks for the downstream production of chlorinated paraffins, alpha olefins, and olefin sulfonates.

[00030] Alternatively, the paraffinic hydrocarbon products of the decarboxylation reaction are subsequently passed over a hydroisomerization catalyst to favor particular levels of cracking and/or branching that meet the specifications of a variety of commercially desirable products, such as, for example various solvents, diesel fuel, aviation turbine fuel, gasoline, and aviation gas. Accordingly, the paraffinic hydrocarbons produced by decarboxylation according to multiple embodiments and alternatives described herein, which can then undergo hydroisomerization as just previously described, can be used as aliphatic solvents for environmentally friendly cleaning fluids. These solvents may offer improved health and safety conditions during use in the workplace and elsewhere given the significantly lower levels of volatile organic compounds (“VOCs”) and of aromatics, while still meeting other key specifications for degreasing solvents and cleaning fluids, such as flash point and drying time. In still other embodiments, the paraffinic hydrocarbons produced from decarboxylation, or, alternatively, decarboxylation followed by isomerization, have a flash

point above about 140°F, have a VOC content at or below 25 g/L, and meet the specifications of MIL-PRF-32295, the military specification for environmentally friendly cleaning fluids, which is now being required in order to protect workers' health and safety.

[00031] Referring now to embodiments where decarboxylation, according to multiple embodiments and alternatives described herein, is used to produce olefinic hydrocarbons, such products can be used as base stock for lubricants. For example, mid-chain olefins with internal double bonds can be used as base stock for lubricants with desired levels of viscosity index, lubricity, and oxidative stability.

[00032] In some embodiments, and as further discussed in the examples below, the paraffinic hydrocarbon products of decarboxylation undergo subsequent hydroisomerization to form branched paraffinic hydrocarbons, which are useful as aviation turbine fuel and which meet the specifications of ASTM D7566, the standard for Jet-A aviation turbine fuel produced from renewable sources. One of the key specifications of that standard is the boiling point range of 180°C-300°C, which can be achieved with the correct balance of cracking and isomerization. The process for the production of these hydrocarbons, as described herein according to multiple embodiments and alternatives, can be tuned as selectably desired by a user to achieve the same boiling point range and other specifications using different feedstock sources with different carbon chain length distributions, and varying degrees of cracking and branching.

[00033] In some embodiments, the paraffinic hydrocarbon products of decarboxylation and subsequent hydroisomerization, as described herein according to multiple embodiments and alternatives, are useful as a high-octane motor gasoline meeting the specifications of ASTM D4814-11B, including a boiling point range of about 35°C-200°C, and these products will also have an octane rating greater than about 90. The decarboxylation process described herein allows for higher-octane gasoline because it can be tuned to convert the (linear)

carboxylic acid feedstocks preferentially into specific paraffinic hydrocarbons, with a minimum of side reactions. For example, some branched paraffinic hydrocarbons have higher octane values than multicyclic paraffinic hydrocarbons with similar volatility. By way of non-limiting illustration, some C9 naphthenes have an octane rating of approximately 35, whereas some types of C12 branched paraffins have an octane rating of approximately 85, yet both molecules have boiling points within about 5°C – 10°C of one another.

[00034] For practical purposes, petroleum naturally contains many different species, making it economically impractical, if not impossible, for petroleum refineries to separate hydrocarbons with better anti-knock characteristics (higher octane) from those with poorer anti-knock characteristics (lower octane) when they are of the same or similar molecular weight or boiling points, such as in the previous illustration. Consequently, products obtained from decarboxylation processes according to multiple embodiments and alternatives disclosed herein may produce higher-octane gasoline with lower conversion and separation costs than petroleum refineries typically can achieve.

[00035] In some embodiments, the paraffinic hydrocarbon products of decarboxylation and subsequent hydroisomerization, as described herein according to multiple embodiments and alternatives, are useful as aviation gasoline after the addition of monocyclic aromatics, such as benzene, toluene, and xylene, which can be used to increase the octane to 100 or more. One advantage of this process for producing aviation gas is that the branched paraffinic hydrocarbons resulting from decarboxylation and subsequent hydroisomerization will be very similar species and may have a significantly higher starting octane, as described above – before the addition of any aromatics or tetraethyl lead – compared to paraffinic hydrocarbons obtained from petroleum. Consequently, the aviation gasoline specifications of ASTM D7719, including the requirement of an octane rating of 100 and a boiling point range of 20°C-175°C, can be met without the use of tetraethyl lead, which is prohibited by ASTM

D7719 (the standard for lead-free test aviation gas), with the use of less or no aromatics. Likewise, the specifications of D910 (the standard for leaded aviation gas) can be met with the addition of less or no lead and less or no aromatics. In particular, it is possible to meet the D910 specifications for Grade 100 Low Lead (LL) and Grade 100 Very Low Lead (VLL) aviation gas, which limit tetraethyl lead content to 0.53 and 0.43 mL/L of fuel, respectively. The significance is the high cost of adding tetraethyl lead or aromatics to aviation gas, as well as pressure placed upon producers of aviation gasoline to reduce the amount of lead they use due to the fact that over half the air emissions of lead in the U.S. now come from combustion of aviation gas.

[00036] In some embodiments, the paraffinic hydrocarbon products of decarboxylation are used as feedstocks for downstream processes to produce mid-chain or long-chain chlorinated paraffins. Mid-chain chlorinated paraffins have carbon chain lengths of between 14 and 18 carbons and long-chain chlorinated paraffins have carbon chain lengths greater than 20 carbons.

[00037] In still other embodiments, the paraffinic hydrocarbon products of decarboxylation, as described herein, are capable of being distinguished from paraffinic hydrocarbons produced by petroleum refineries or by hydrodeoxygenation of triglycerides. For example, in many embodiments, the products of decarboxylation are expected to be very low in sulfur, are expected to significantly exceed the Ultra Low Sulfur Diesel (ULSD) specification of no more than 15 ppm sulfur, and actually are expected to have less than about 5 ppm sulfur. Similarly, in many embodiments, the hydrocarbon products of decarboxylation followed by subsequent hydroisomerization are expected to have less than about 5 ppm sulfur.

[00038] It is also possible to distinguish the hydrocarbon products of decarboxylation and/or of subsequent hydroisomerization, according to multiple embodiments and

alternatives described herein, from those of hydrocarbon products produced using conventional techniques at a petroleum refinery based on the molar ratio of linear hydrocarbons to branched or cyclic hydrocarbons. Specifically, this molar ratio is expected to be higher for products obtained by decarboxylation according to embodiments and alternatives described herein. In some embodiments, this molar ratio is expected to be greater than about five, and in some embodiments greater than about ten, compared to a molar ratio of about less than five and possibly less than one for hydrocarbons from petroleum refining. Further, and as discussed above, these embodiments would lead to higher octane gasoline or aviation gas because of the higher ratio of linear or branched to cyclic hydrocarbons.

[00039] It is also possible to distinguish the hydrocarbon products of decarboxylation and/or of subsequent hydroisomerization, according to multiple embodiments and alternatives described herein, from hydrocarbon products produced using conventional techniques at a petroleum refinery based on the ratio of radioactive isotope Carbon-14 to Carbon-12. Specifically, this ratio is expected to be orders of magnitude higher for products obtained by decarboxylation of carboxylic acids from renewable sources according to embodiments and alternatives described herein, than for hydrocarbon products obtained from petroleum. Accordingly, testing methods regarding the ratio of Carbon-14 to Carbon-12 could be used to determine if particular paraffinic hydrocarbons came from renewable feedstocks according to multiple embodiments and alternatives, or whether they came from petroleum sources. Typically, the Carbon-14 to Carbon-12 ratio in contemporary carbon sources, such as renewable triglycerides, is about 10^{-12} , whereas the Carbon-14 to Carbon-12 ratio in petroleum (or hydrocarbons derived from petroleum) is 100 times lower, at a value of about 10^{-14} .

[00040] It is also possible to distinguish the hydrocarbon products of decarboxylation and/or of subsequent hydroisomerization, according to multiple embodiments and alternatives described herein, from those of hydrocarbon products produced using the known technique of hydrodeoxygenation based on the ratio of molecules having even-numbered carbon chain lengths to those having odd-numbered carbon chain lengths. This is possible because renewable triglycerides, which are in large supply and which are generally of the kind that can be subjected to either decarboxylation (according to present embodiments and alternatives) or hydrodeoxygenation, routinely have even-numbered carbon chain lengths in nature. Decarboxylation removes one carbon from each carboxylic acid, such that the products of decarboxylation will typically have odd-numbered carbon chain lengths. Hydrodeoxygenation, by contrast, does not remove carbon from the carboxylic acid, so the products of hydrodeoxygenation typically will have even-numbered carbon chain lengths, although allowing for some cracking, they may not be exclusively even-numbered. Consequently, the hydrocarbon products of decarboxylation are expected to have a ratio of odd-numbered to even-numbered carbon chain lengths significantly above one to one (i.e., 1:1), and generally above about four to one (i.e., 4:1), whereas the hydrocarbon products of hydrodeoxygenation are expected to have a ratio significantly below one. The ratio of odd-numbered to even-numbered chain lengths can be estimated by analyzing the hydrocarbon products of these processes using a Gas Chromatograph-Mass Spectrometer (GC-MS), which will show the proportion by mass of the hydrocarbons at different chain lengths. This mass proportion can then be converted to a molar proportion.

[00041] By way of further illustration, the decarboxylation of stearic acid, $C_{18}H_{36}O_2$, according to multiple embodiments herein, yields predominantly heptadecane, $C_{17}H_{36}$, a linear paraffinic hydrocarbon containing only 17 carbon atoms. Conversely, hydrodeoxygenation of stearic acid yields predominantly octadecane, $C_{18}H_{38}$, containing the

same number of carbon atoms (18) as the starting carboxylic acid (stearic acid), with the oxygen atoms being removed as water. Thus, in this illustration, the presence of heptadecane, having an odd number of carbon atoms, is a factor indicative of decarboxylation of the stearic acid feedstock. In general, the predominance of odd-numbered carbons over even-numbered carbons, at a ratio of about 4:1, indicates that decarboxylation is the predominant reaction occurring.

[00042] Examples 1, 3, 4, 5, 6, 7, 10, 11, 12 and 13, which are described below, are alternative embodiments of a process for producing linear, paraffinic hydrocarbons. Examples 2, 8, and 9 are offered as comparative examples. Example 14 illustrates one application for the products of the subject process, namely as starting materials for conversion of paraffinic hydrocarbons to aviation turbine fuel (i.e., jet fuel).

[00043] In the examples, the catalytic run was carried out continuously over 150 hours. The liquid products contained two layers: a hydrocarbon top layer and a bottom layer containing unconverted carboxylic acids, which were condensed and collected in a product receiver at the end of 50 and 150 hours. The identity of the hydrocarbon products was determined by gas chromatography using a Hewlett Packard 4890 gas chromatograph. The acid number of the products of the hydrocarbon layer were determined, and compared to the acid number of the carboxylic acid feedstock. Based upon that comparison, the conversion of the carboxylic acid feedstock to paraffinic hydrocarbons was determined, as further described below. Iodine number is an indicator of unsaturation and presence of carbon-carbon double bonds, which serves as indicator of process effects on saturation of carbon-carbon double bonds.

Example 1

A palladium metal catalyst supported on a basic hydrotalcite oxide support

[00044] The surface area of the support was approximately 99.5 m² per gram; the pore volume of the support was approximately 0.3 ml per gram of catalyst. The support was dried overnight at 150° C. The average pore width of the catalyst was approximately 9.5 nm (nanometers); basicity of the catalyst, as determined by titration with 0.1 normal acetic acid, was approximately 0.15 mEq (milliequivalent) acetic acid per gram.

[00045] An aqueous solution of palladium nitrate containing a sufficient amount of palladium metal for 5 wt% of palladium in the final catalyst was prepared. A suspension of the hydrotalcite support in the palladium nitrate solution was prepared. A 0.1 normal aqueous solution of sodium hydroxide, of volume at least equal to the pore volume of the catalyst, was added to that suspension. The palladium compound was reduced to the metallic state by addition of a sufficient amount of sodium borohydride. The catalyst was dried in a flow of nitrogen at 200° C for 5 hours.

[00046] The reduced catalyst was loaded in a downflow, fixed bed reactor. A feedstock consisting of a mixture of oleic acid and normal hexadecane in equal weight proportions was passed over the catalyst with a HPLC pump at a temperature of 330° C, hydrogen pressure of 20 bar, a hydrogen to oleic acid ratio of 600 (V/V) and a weight hourly space velocity of oleic acid of 1.0. The gaseous product of the reaction was carbon dioxide.

[00047] In the liquid phase, the conversion of the oleic acid to hydrocarbon products was 94 wt% after 50 hours and 92 wt% after 150 hours. The hydrocarbon layer contained penta-, hexa, hepta- and octa-decanes. The iodine number of these products was negligible, indicating that the product contained only saturated paraffinic hydrocarbons. From the ratio of heptadecane to (heptadecane + octadecane), i.e., C17/(C17+C18)), the selectivity for decarboxylation was calculated to be 92% after 50 hours and 94% after 150 hours. The catalyst was evaluated according to conventional methods and determined not to have been deactivated.

Example 2

A palladium metal catalyst supported on a non-basic support material, i.e., activated carbon

[00048] The surface area of the support was approximately 778 m² per gram; the pore volume of the support was approximately 0.45 ml per gram of catalyst. The support was dried overnight at 150° C. The average pore width of the catalyst was approximately 3.3 nm; basicity of the catalyst, as determined by titration with 0.1 normal acetic acid, was approximately 0.02 mEq acetic acid per gram.

[00049] An aqueous solution of palladium chloride containing a sufficient amount of palladium metal for 5 wt% of palladium in the final catalyst was prepared and deposited on the carbon by incipient deposition. The catalyst was dried in a flow of nitrogen at 200° C for 5 hours. The dried catalyst was loaded in a downflow, fixed bed reactor and reduced in flowing hydrogen at 250° C, 20 bar pressure for 6 hours. A feedstock consisting of a mixture of oleic acid and normal hexadecane in equal weight proportions was passed over the catalyst with a HPLC pump at a temperature of 330° C, hydrogen pressure of 20 bar, a hydrogen to oleic acid ratio of 600(V/V) and a weight hourly space velocity of oleic acid of 1.0. The gaseous product of the reaction was carbon dioxide.

[00050] In the liquid phase, the conversion of the oleic acid to hydrocarbon products was 98 wt% at the end of 50 hours and 69 wt% after 150 hours. The hydrocarbon layer contained penta-, hexa-, hepta- and octa decanes. The iodine number of these products was negligible, indicating that the product contained only saturated paraffinic hydrocarbons. From the ratio of heptadecane (C17) to octadecane (C18), the selectivity for decarboxylation was calculated to be only 43% after 50 hours. Thus, even though this catalyst was active for the deoxygenation reaction, it deactivated at the end of 150 hours and most of the oxygen of the carboxyl group was removed as H₂O rather than as CO₂. As a consequence, hydrogen consumption during the process was relatively high.

Example 3

A palladium metal catalyst supported on a basic hydrotalcite oxide support; reaction not carried out under hydrogen pressure

[00051] Process conditions were the same as for Example 1, except that the reaction was not carried out under hydrogen; the pressure within the reactor remained at 20 bar of nitrogen throughout the reaction. The gaseous product of the reaction was carbon dioxide.

[00052] The hydrocarbon layer contained penta-, hexa-, hepta- and octa decanes. The iodine number of these products was negligible, indicating that the product contained only saturated paraffinic hydrocarbons. The conversion of the oleic acid to hydrocarbon products was 94 wt% at the end of 50 hours. From the ratio of heptadecane to (heptadecane + octadecane), the selectivity for decarboxylation was calculated to be 93%.

Example 4

A palladium metal catalyst supported on a magnesium oxide support

[00053] The surface area of the support was approximately 99.5 m² per gram; the pore volume of the support was approximately 0.23 ml per gram of catalyst. The support was dried overnight at 250° C. The average pore width of the catalyst was approximately 3.4 nm; basicity of the catalyst, as determined by titration with 0.1 normal acetic acid, was approximately 0.11 mEq acetic acid per gram.

[00054] An aqueous solution of palladium nitrate containing a sufficient amount of palladium metal for 5 wt% of palladium in the final catalyst was prepared. A suspension of the magnesium oxide support in the palladium nitrate solution was prepared. A 0.1 normal aqueous solution of sodium hydroxide, of volume at least equal to the pore volume of the solid, was added to that suspension. The palladium compound was reduced to the metallic state by addition of a sufficient amount of sodium borohydride. The catalyst was dried in a flow of nitrogen at 200° C for 5 hours.

[00055] The reduced catalyst was loaded in a downflow, fixed bed reactor. A feedstock consisting of a mixture of oleic acid and normal hexadecane in equal weight proportions was passed over the catalyst with a HPLC pump at a temperature of 330° C, hydrogen pressure of 30 bar, a hydrogen to oleic acid ratio of 600 (V/V) and a weight hourly space velocity of oleic acid of 1.0. The gaseous product of the reaction was carbon dioxide.

[00056] In the liquid phase, the conversion of the oleic acid to hydrocarbon products was 95 wt% at the end of 50 hours and 94 wt% after 150 hours. The hydrocarbon layer contained penta-, hexa-, hepta- and octa-decanes. From the ratio of heptadecane to (heptadecane + octadecane), the selectivity for decarboxylation was calculated to be 86% after 50 hours and 90% after 150 hours. The catalyst was evaluated according to conventional methods and determined not to have been deactivated.

Example 5

A palladium metal catalyst supported on a basic hydrotalcite oxide support; reaction carried out under nitrogen pressure

[00057] Process conditions were the same as for Example 1, except that the reaction was carried out under nitrogen; the pressure within the reactor remained at 20 bar of nitrogen throughout the reaction. The gaseous product of the reaction was carbon dioxide. In the liquid phase, the conversion of oleic acid was 97 wt%, and its selectivity ($C_{17}/(C_{17}+C_{18})$) value was 91%.

Example 6

A nickel metal catalyst supported on a mixed oxide support of ceria-zirconia

[00058] A ceria-zirconia mixed oxide support was prepared by coprecipitation of the mixed hydroxides of cerium and zirconium from an aqueous solution of the nitrates using sodium hydroxide as the precipitating agent. The support had a surface area of approximately 163 m² per gram; the pore volume of the support was approximately 0.165 ml per gram of catalyst.

[00059] The support was then impregnated with a nickel nitrate solution by the incipient wetness method to yield 41.54 wt% of nickel oxide in the final catalyst. The material was dried in air at 120° C for 12 hours and calcined in air at 400° C for 12 hours. Basicity of this catalyst, as determined by titration with 0.1 normal acetic acid, was approximately 0.21 mEq acetic acid per gram. The contents of cerium and zirconium oxides in the final catalyst were 25.6 wt% and 32.8 wt%, respectively. Surface area of the final catalyst was 134 m² per gram, and its pore volume was 0.12 ml per gram.

[00060] Except as stated above, process conditions were the same as for Example 1. In the liquid phase, the conversion of the oleic acid to hydrocarbon products was 85 wt% at the end of 50 hours and 81 wt% after 150 hours. The selectivity (C17/(C17+C18)) value was 84% after 50 hours and 89% after 150 hours.

Example 7

A palladium metal catalyst supported on basic hydrotalcite catalyst as in Example 1, from a mixture of dodecanoic acid and oleic acid

[00061] This example used the catalyst and support of Example 1 with the same process conditions as Example 1, except as noted with respect to temperature and pressure. An equimolar mixture of dodecanoic acid (C₁₂H₂₄O₂) and oleic acid (C₁₈H₃₄O₂) – with a weight hourly space velocity of the combined fatty acids of 1.0 – underwent decarboxylation in hexadecane solvent, at 295 ° C, and a hydrogen pressure of 10 bar. The conversion of dodecanoic acid (as determined by gas chromatography) was 90%, and the conversion of oleic acid (as determined by gas chromatography) was 96%. The selectivity in the conversion of dodecanoic acid (C11/(C11+C12)) value was 86%, and the corresponding value for the selectivity in the conversion of oleic acid (C17/(C17+C18)) was 91%.

Example 8

A palladium metal catalyst supported on a non-basic support material, i.e., activated acidic aluminum oxide

[00062] The surface area of the support was approximately 178 m² per gram; the pore volume of the support was approximately 0.35 ml per gram of catalyst. The support was dried overnight at 150° C.

[00063] The average pore width of the catalyst was approximately 2.3 nm; basicity of the catalyst, as determined by titration with 0.1 normal acetic acid, was approximately 0.03 mEq acetic acid per gram. An aqueous solution of palladium chloride containing a sufficient amount of palladium metal for 5 wt% of palladium in the final catalyst was prepared and deposited on the support by incipient deposition. The catalyst was dried in a flow of nitrogen at 200° C for 5 hours.

[00064] The dried catalyst was loaded in a downflow, fixed bed reactor and the palladium metal was reduced in flowing hydrogen at 350° C, 20 bar pressure for 6 hours. A feedstock consisting of a mixture of oleic acid and normal hexadecane in equal weight proportions was passed over the catalyst with a HPLC pump at a temperature of 350° C, hydrogen pressure of 30 bar, a hydrogen to oleic acid ratio of 600 (V/V) and a weight hourly space velocity of oleic acid of 1.0. The gaseous products of the reaction were carbon dioxide, ethane, propane, butane, as well as propylene and butane.

[00065] In the liquid phase, the conversion of the palmitic acid to hydrocarbon products was 78 wt% at the end of 50 hours and 39 wt% after 150 hours. The hydrocarbon layer contained penta-, hexa-, hepta- and octa-decanes as well as olefins. The iodine number of the product, an indicator of unsaturation and presence of carbon-carbon double bonds, was 35 indicating that the product contained some olefins in addition to the saturated paraffinic hydrocarbons. From the ratio of heptadecane to octadecane, the selectivity for decarboxylation was calculated as 42% at the end of 50 hours. The catalyst was evaluated according to conventional methods, and was found to have sustained severe catalytic deactivation. Thus, even though this catalyst was active for the deoxygenation reaction, it

deactivated fast and most of the oxygen of the carboxylate group was removed as H₂O rather than as CO₂. As a consequence, hydrogen consumption during the process was relatively high.

Example 9

A nickel oxide-molybdenum oxide catalyst supported on a non-basic support material

[00066] The surface area of the support was approximately 212 m² per gram; the pore volume of the support was approximately 0.23 ml per gram of catalyst. The catalyst was prepared by the deposition of ammonium molybdate and nickel nitrate on aluminum oxide, drying at 120° C and calcining it further in air at 500° C. The average pore width of the catalyst was approximately 2.5 nm; basicity of the catalyst, as determined by titration with 0.1 normal acetic acid, was approximately 0.03 mEq acetic acid per gram.

[00067] The catalyst was loaded in a downflow, fixed bed reactor and dried overnight at 150° C to remove adsorbed matter like water and carbon dioxide. The catalyst was then sulfided for 24 hours at 200° C in a stream of hexadecane containing 100 ppm of dimethyl disulfide.

[00068] A feedstock consisting of a mixture of oleic acid and normal hexadecane in equal weight proportions was then passed over the catalyst with a HPLC pump at a temperature of 330° C, hydrogen pressure of 45 bar, a hydrogen to oleic acid ratio of 1200 (V/V) and a weight hourly space velocity of oleic acid of 1.5. The gaseous product of the reaction was carbon dioxide.

[00069] In the liquid phase, the conversion of the oleic acid to hydrocarbon products was 90 wt% at the end of 50 hours and 85 wt% after 150 hours. The hydrocarbon layer contained penta-, hexa-, hepta- and octa-decanes. The iodine number of these products, indicating that the product contained only saturated paraffinic hydrocarbons and no olefins. From the

ratio of heptadecane to octadecane, the selectivity for decarboxylation was calculated to be 60%.

[00070] These results indicated that even though the catalyst was active for the deoxygenation reaction over 150 hours, most of the oxygen of the carboxyl group was removed as H₂O rather than as CO₂. As a consequence, its selectivity for decarboxylation was relatively low, and hydrogen consumption during the process was relatively high.

Example 10

A palladium metal catalyst supported on a basic calcium oxide support

[00071] The support was prepared by the decomposition of calcium carbonate at 650° C in air. The surface area of the support was approximately 76.8 m² per gram; the pore volume of the support was approximately 0.28 ml per gram of catalyst. The support was dried overnight at 200° C. The average pore width of the catalyst was approximately 2.5 nm; basicity of the catalyst, as determined by titration with 0.1 normal acetic acid, was approximately 0.23 mEq acetic acid per gram.

[00072] An aqueous solution of palladium nitrate containing a sufficient amount of palladium metal for 5 wt% of palladium in the final catalyst was prepared. A suspension of the calcium oxide support in the palladium solution was prepared. The palladium compound was reduced to the metallic state by addition of a sufficient amount of sodium borohydride. The catalyst was dried in a flow of nitrogen at 200° C for 5 hours.

[00073] The reduced catalyst was loaded in a downflow, fixed bed reactor. A feedstock consisting of a mixture of palmitic acid and normal dodecane in equal weight proportions was passed over the catalyst with a HPLC pump at a temperature of 335° C, hydrogen pressure of 20 bar, a hydrogen to palmitic acid ratio of 600 (V/V) and a weight hourly space velocity of palmitic acid of 1.0. The gaseous product of the reaction was carbon dioxide.

[00074] In the liquid phase, the conversion of the palmitic acid to hydrocarbon products was 88 wt% at the end of 50 hours and 85 wt% after 150 hours. The hydrocarbon layer contained dodecane, penta- and hexa decanes. The iodine number of these products was negligible, indicating that the product contained mainly saturated paraffinic hydrocarbons. From the ratio of pentadecane to (pentadecane + hexadecane), the selectivity for decarboxylation was calculated to be 93% after 50 hours and 95% after 150 hours.

Example 11

A palladium metal catalyst supported on a basic lanthanum oxide support

[00075] The support was prepared by the decomposition of lanthanum carbonate at 700° C in air. The surface area of the support was approximately 85.7 m² per gram; the pore volume of the support was approximately 0.19 ml per gram of catalyst. The support was dried overnight at 300° C. The average pore width of the catalyst was approximately 3.6 nm; basicity of the catalyst, as determined by titration with 0.1 normal acetic acid, was approximately 0.21 mEq acetic acid per gram.

[00076] An aqueous solution of palladium nitrate containing a sufficient amount of palladium metal for 5 wt% of palladium in the final catalyst was prepared. A suspension of the lanthanum oxide support in the palladium nitrate solution was prepared. The palladium compound was reduced to the metallic state by addition of sufficient amount of sodium borohydride. The catalyst was dried in a flow of nitrogen at 200° C for 5 hours.

[00077] The reduced catalyst was loaded in a downflow, fixed bed reactor. A feedstock consisting of a mixture of palmitic acid and normal dodecane in equal weight proportions was passed over the catalyst with a HPLC pump at a temperature of 335° C, hydrogen pressure of 20 bar, a hydrogen to palmitic acid ratio of 600 (V/V) and a weight hourly space velocity of palmitic acid of 1.0. The gaseous product of the reaction was carbon dioxide.

[00078] In the liquid phase, the conversion of the palmitic acid to hydrocarbon products was 90 wt% at the end of 50 hours and 85 wt% after 150 hours. The hydrocarbon layer contained dodecane, penta- and hexa-decanes. The iodine number of these products was negligible, indicating that the product contained mainly saturated paraffinic hydrocarbons. From the ratio of pentadecane to (pentadecane + hexadecane), the selectivity for decarboxylation was calculated to be 85% after 50 hours and 87% after 150 hours. The catalyst was evaluated according to conventional methods and determined not to have been deactivated.

Example 12

A palladium metal catalyst supported on basic hydrotalcite catalyst -
fatty acids obtained from beef tallow

[00079] The catalyst and support of Example 1 were used, along with the process conditions of Example 1, except as noted with respect to temperature and pressure. Feedstock was a 50:50 wt. % mixture of n-hexadecane and C14-C18 fatty acids, the latter being obtained by hydrolyzing beef tallow supplied by Emery Oleochemicals LLC, Cincinnati, Ohio. The beef tallow was black in color, with a density of 0.86 g/cc; flash point of 185° C; acid number of 198.5; iodine number of 56.9. Fatty acid content of feedstock was 3% C14:0, 22% C16:0, 4% C16:1, 1% C17:0, 20% C18:0, 45% C18:1, and 5% C18:2, wherein “0” represents the saturated hydrocarbon, “1” represents a monounsaturated hydrocarbon, and “2” represents two C=C double bonds in the molecule.

[00080] 80 gm of feedstock was heated in an autoclave with 4 gm of the catalyst of Example 1 at 350° C and 30 bar pressure of nitrogen for 3 hrs. The yield of liquid product was 81 wt%, with the gaseous product being mainly carbon dioxide with 1-3% of methane. The product was light orange in color. The liquid product's acid number was 1.5, and its iodine number was 45. The freezing point of the liquid product was 16° C. Based upon the reduction of acid number, decarboxylation of fatty acids in the beef tallow to linear paraffin

hydrocarbons was calculated at greater than 99 wt% after 3 hours. The hydrocarbon layer contained C8 to C18 saturated and unsaturated hydrocarbons. The hydrocarbon chain length distribution (in wt%) in the liquid product obtained by gas chromatography was as follows: 9.3% C8, 10.5% C9, 11.9% C10, 11.8% C11, 9.3% C12, 8.1% C13, 5.8% C14, 5.9% C15, 17.3% C16, 4.1% C17, 3.5% C18, and 2.4% C19.

Example 13

Palladium catalyst supported on basic lanthanum oxide support -
fatty acids obtained from beef tallow

[00081] 80 gm of feedstock of Example 12 (mixture of fatty acids from beef tallow and n-hexadecane) was reacted with catalyst of Example 11 over support of Example 11, by heating in an autoclave with 4 gm of the aforementioned palladium metal catalyst supported on a basic lanthanum oxide support catalyst at 350° C and 40 bar pressure of nitrogen for 3 hrs. The yield of liquid product was 78 wt%, with the gaseous product being mainly carbon dioxide with 2% of methane. The product was colorless. The acid number of the liquid product was 1.1 and its iodine number was 1.7. The freezing point of the liquid product was 17° C. Based upon reduction of acid number, decarboxylation of fatty acids in beef tallow to hydrocarbon products was calculated at greater than 99 wt% after 3 hours. The hydrocarbon layer contained C10 to C18 saturated and unsaturated hydrocarbons. The hydrocarbon chain length distribution according to gas chromatography (in wt%) of the liquid product obtained was 1.3% C10, 1.7% C11, 2.1% C12, 4.4% C13, 6.5% C14, 18.7% C15, 19.4% C16, and 45.6% C17.

Example 14

Production of aviation turbine fuel

[00082] The liquid product of Example 13 was reacted with a hydroisomerization catalyst known in the art at 350° C and a hydrogen pressure of 40 bars for 3 hrs. The product had a

freezing point of -64 C, a total sulfur content of 4 ppm (per ASTM D-1266), a smoke point of 26.7 mm (ASTM D-1322), net heat of combustion of 43.8 MJ/Kg (ASTM D-4809); approximately 10% of the products boiled at a temperature of less than about 254° C and about 90% boiled in a range between about 254° C – 300° C; and the elemental composition by %wt of 85% carbon, 15% hydrogen, and 0% oxygen. The liquid sample obtained by hydroisomerization of linear paraffins obtained in Example 13 meets ASTM D-1655, the standard specification for jet fuel.

[00083] It is to be understood that the embodiments described herein are not limited in their application to the details of the teachings and descriptions set forth herein, or as illustrated in the above examples. Rather, it will be understood that a process for the production of linear, paraffinic hydrocarbons, as described and claimed according to multiple embodiments disclosed herein, is capable of other embodiments and of being practiced or of being carried out in various ways.

[00084] Also, it is to be understood that the phraseology and terminology used herein is for the purpose of description and should not be regarded as limiting. The use herein of “including,” “comprising,” “e.g.,” “such as, for example,” “containing,” or “having” and variations of those words is meant in a non-limiting way to encompass the items listed thereafter, and equivalents of those, as well as additional items.

[00085] Accordingly, the foregoing descriptions are meant to illustrate a number of embodiments and alternatives, rather than to serve as limits on the scope of what has been disclosed herein. The descriptions herein are not intended to be exhaustive, nor are they meant to limit the understanding of the embodiments to the precise forms disclosed. It will be understood by those having ordinary skill in the art that modifications and variations of these embodiments are reasonably possible in light of the above teachings and descriptions.

CLAIMS

What is claimed is:

1. A process for converting fatty acids to paraffinic hydrocarbons, comprising the steps of:

 contacting carboxylic acid reactants with a catalyst over a support; and

 isolating paraffinic hydrocarbon products from other reaction products;

 wherein the carboxylic acid reactants have a chemical formula represented by R-COOH, R has at least six and no more than twenty-four carbon atoms, the basicity of the catalyst is at least approximately 0.1 mEq, the catalyst is chosen from the group platinum, palladium, nickel, nickel-molybdenum, nickel-tungsten, and platinum-copper, and the support is chosen from the group hydrotalcite, magnesium oxide, calcium oxide, a mixed oxide of ceria-zirconia, and lanthanum oxide; and

 wherein carboxylic acid reactants are derived from a feedstock, which is chosen from the group plant oils, animal fats, animal oils, algae oils, and oils from heterotrophic microbial organisms.
2. The process of claim 1, wherein the yeast is an oleaginous yeast.
3. The process of claim 1, wherein the plant oils are chosen from the group jatropha oil, camelina oil, pennycress oil, pongamia oil, and carinata oil.
4. The process of claim 1, wherein branched paraffinic hydrocarbons comprise less than about 5% by mass of the total reaction products, the remainder of the paraffinic hydrocarbon products being linear.
5. A process for converting fatty acids to paraffinic hydrocarbons comprising the steps of claim 4, further comprising a reaction step of contacting at least one of the linear, paraffinic hydrocarbon products with a hydroisomerization catalyst to form at least one branched hydrocarbon.

6. A paraffinic hydrocarbon product formed by the process of claim 1, wherein the weighted average chain length of the paraffinic hydrocarbon products is greater than about 80% of the weighted average chain length of the carboxylic acid feedstock.
7. A paraffinic hydrocarbon product formed by the process of claim 1, wherein the ratio of hydrocarbons having an odd number of carbons to hydrocarbons having an even-number of carbons is about 4:1 or higher.
8. A paraffinic hydrocarbon product formed by the process of claim 1, wherein the ratio of carbon-14 to carbon-12 is about 10^{-12} or higher.
9. A paraffinic hydrocarbon product formed by the process of claim 5 for use as aviation turbine fuel, the paraffinic hydrocarbon product having a boiling point of about 180°C to about 300°C, wherein the paraffinic hydrocarbon product for use as aviation turbine fuel satisfies American Society for Testing and Materials (ASTM) standard D7566.
10. A mixture comprising at least one paraffinic hydrocarbon product formed by the process of claim 5 and at least one monocyclic aromatic hydrocarbon chosen from the group benzene, toluene, and xylene, wherein the mixture is for use as aviation gas having an octane rating of at least about 100 and a boiling point range of about 20°C to about 175°C.
11. The mixture of claim 10, having a tetraethyl lead content no greater than about 0.53 mL/L, wherein the mixture for use as aviation gas satisfies American Society for Testing and Materials (ASTM) standard D7719.
12. A paraffinic hydrocarbon product formed by the process of claim 5 for use as gasoline, the paraffinic hydrocarbon product having a boiling point of about 35°C to about 200°C, wherein the paraffinic hydrocarbon product satisfies American Society for Testing and Materials (ASTM) standard D4814-11B.

13. A paraffinic hydrocarbon product formed by the process of claim 1, wherein such product is capable of being converted to a chlorinated paraffin having an average carbon chain length of at least about 14 carbons.
14. A formulation for an end use chosen from the group solvent, degreaser, and cleaning fluid, comprising a paraffinic hydrocarbon product formed by the process of claim 5.
15. A cleaning fluid comprising a paraffinic hydrocarbon product formed by the process of claim 5, wherein the cleaning fluid has a flash point above about 140°F and a volatile organic content (VOC) no greater than about 25 g/L.
16. A process for converting fatty acids to olefinic hydrocarbons, comprising the steps of:
contacting carboxylic acid reactants with a catalyst over a support; and
isolating olefinic hydrocarbon products from other reaction products;
wherein the carboxylic acid reactants have a chemical formula represented by R-COOH, R has at least six and no more than twenty-four carbon atoms, the basicity of the catalyst is at least approximately 0.1 mEq, the catalyst is chosen from the group platinum, palladium, nickel, nickel-molybdenum, nickel-tungsten, and platinum-copper, and the support is chosen from the group hydrotalcite, magnesium oxide, calcium oxide, a mixed oxide of ceria-zirconia, and lanthanum oxide; and
wherein carboxylic acid reactants are derived from a feedstock, which is chosen from the group plant oils, animal fats, animal oils, algae oils, and oils from heterotrophic microbial organisms.
17. An olefinic hydrocarbon product formed by the process of claim 16, wherein the ratio of hydrocarbons having an odd number of carbons to hydrocarbons having an even number of carbons is about 4:1 or higher.
18. An olefinic hydrocarbon product formed by the process of claim 16, wherein the ratio of carbon-14 to carbon-12 is about 10^{-12} or higher.