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(54) Title: SINGLE-STEP PROCESS FOR PRODUCTION OF BRANCHED, CYCLIC, AROMATIC, AND CRACKED HYDRO-
CARBONS FROM FATTY ACIDS

(57) Abstract: A catalytic process is provided which produces in a single reaction branched, cyclic and aromatic hydrocarbons, or
cracked straight-chain hydrocarbons, from fatty acids in which the fatty acids are reacted over a multifunctional catalyst and undergo
both decarboxylation and either conversion or cracking to form reaction products useful as fuels and for other applications that re-
quire a source of energy, or as feedstock for hydrocarbon-based commercial products such as surfactants, solvents and lubricants.



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**SINGLE-STEP PROCESS FOR PRODUCTION OF BRANCHED,
CYCLIC, AROMATIC, AND CRACKED HYDROCARBONS FROM
FATTY ACIDS**

Cross Reference to Related U.S. Application

[0001] This international application claims the benefit of priority to U.S. Provisional Application No. 61/879,272, which was filed on September 18, 2013.

FIELD OF INVENTION

[0002] The invention relates to a single-step process in which carboxylic acids undergo decarboxylation over a supported catalyst along with further transformation through isomerization, cyclization, aromatization, or cracking, to produce hydrocarbon reaction products suitable for fuels, surfactants, solvents, lubricants, and other derivatives and commercial products.

BACKGROUND

[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. Hydrocarbons are also used for a variety of other uses such as surfactants, solvents and lubricants, among other uses. Some hydrocarbon products and fuels are linear, paraffinic hydrocarbons. Others include branched chain hydrocarbons. Some, such as, for example, kerosene and some jet fuels have branched chain hydrocarbons and have 10-to-15 carbon atoms in their molecular structure. By comparison, diesel fuels contain significant amounts of branched and cyclic hydrocarbons and have between 15-to-22 carbon atoms.

[0004] Hydrocarbon fuels and other petrochemical products are obtained from crude petroleum oil through a series of conventional steps. These include, but are not necessarily limited to, distillation followed by additional refining. It is desirable, however, to produce hydrocarbon fuels and 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 fuels and other products that are obtained from crude petroleum, but 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 with other hydrocarbon products as noted above.

[0005] More specifically, hydrocarbon fuels and 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 fuels in their applications as transportation fuels, as well as other applications that require a source of energy or other hydrocarbon products.

[0006] Both linear, and branched, paraffinic hydrocarbons do not occur naturally in large supply. However, one route for the production of these hydrocarbons has been through decarboxylation of carboxylic acids, which are readily available in the lipid portion of biomass raw materials, resulting in linear paraffinic hydrocarbons. The isomerization and

cyclization of the resulting linear paraffins produces branched and cyclic hydrocarbons. 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 are converted to carboxylic acids through methods known to persons of ordinary skill in the art, such as hydrolysis, thermal hydrolysis or acid hydrolysis, all methods well known for decades to practitioners in the field.

[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 are known for the conversion of fatty acids such as stearic acid to a linear, paraffinic hydrocarbon, which require the removal of the two oxygen atoms of the carboxylate group. Such conventional approaches include hydrodeoxygenation, which accomplishes this but requires the use of hydrogen as a starting material in the reaction. However, 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. This decarboxylation reaction does not require a supply of hydrogen as a necessary reactant as in hydrodeoxygenation but is only an optional 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 today than the hydrodeoxygenation approach, in which the manufacturer must also obtain a supply of hydrogen as a reactant and usually a large supply of hydrogen.

[0009] The reaction products of decarboxylation can be isolated and separated by fractional distillation or other methods known to persons of ordinary skill in the art, into appropriate boiling fractions for further conversion and use as kerosene, jet fuel, diesel fuel, automobile fuel or other kinds of fuel, as well as other commercial products which the reaction products can be as starting materials for, such as surfactants, solvents, lubricants, and other derivatives and commercial products, as desired by an end user.

[0010] If the linear paraffinic hydrocarbons obtained by decarboxylation of fatty acids are to be used to an even greater extent as commercial fuels and lubricants, their further transformation into branched, cyclic and aromatic hydrocarbons is needed, for example, to improve the octane number of gasoline, to increase the low temperature performance of diesel and aviation fuels, to obtain high viscosity index lubricant oils. Conversion of the linear paraffins to branched, cyclic and aromatic hydrocarbons plays an important role in the petroleum industry to obtain the aforementioned fuels and lubricants. More stringent specifications pertaining to several characteristics (e.g., volatility, stability, cold flow properties) of automotive engine lubricants have also raised the interest of refining industries in hydroconversion processes of heavy feedstocks and vacuum distillates to meet the market demand.

[0011] In conventional practice, long chain linear carboxylic acids containing more than seven carbon atoms can, in principle, be converted to a mixture of branched, cyclic and aromatic hydrocarbons by a two stage process: the fatty acids can be deoxygenated, in a first step, to linear hydrocarbons. The products from this first stage have to be subjected to a separation process wherein the unconverted fatty acids are isolated and recycled back to the first stage while the linear reaction products are sent to a second stage of the process. In the second stage, the linear hydrocarbons from the first stage are converted by isomerization,

cyclisation and aromatization reactions to a mixture of branched, cyclic and aromatic hydrocarbons. This two stage process is, however, not economical in commercial practice due to the high cost of the two different catalysts needed in the two stages and the complexity of the separation and recycle equipment.

[00012] In previous attempts by others, the support for the metal has been inert material (like carbon) or non-acidic components, like silica. The influence of acidic supports in modifying the carbon skeleton of the linear C₁₆- C₁₈ paraffins, which are among the initial products of the decarboxylation of the fatty acid, had not been documented. If the deoxygenation of the fatty acid and isomerization / hydrocracking of the resulting C₁₇- C₁₈ linear paraffins to branched and aromatic hydrocarbons in the gasoline-range C₅- C₁₀ hydrocarbons with lower pour points and higher octane numbers can be accomplished by a single catalyst in a single stage, it will represent a significant advance in the process of conversion of biomass to ' drop-in' transport fuels. The ability to do so reduces the amount of time it takes to obtain the desirable products, increases efficiency, and increases cost-effectiveness. Hence, there is a need for a process which can convert , in a single stage, carboxylic fatty acids directly to a mixture of branched, cyclic and aromatic hydrocarbons that can be used in the manufacture of fuels, solvents surfactants and lubricants. The present embodiments provide these features and advantages.

SUMMARY OF INVENTION

[00013] A process using a catalyst according to multiple embodiments and alternatives for producing in a single reaction branched, cyclic and aromatic hydrocarbons from fatty acids containing 7-to-24 carbon atoms. The reaction products are useful as fuels and for other applications that require a source of energy, or as starting materials for hydrocarbon-based commercial products such as surfactants, solvents and lubricants. The steps of the

process comprise contacting the fatty acids with a solid catalyst containing at least one metal in addition to at least one acidic oxide and wherein the metal is chosen from platinum, palladium or nickel and the acidic oxide is chosen from alumina, silicoalumina, aluminosilicate zeolite, silicoaluminophosphate or their mixtures. Generally, these hydrocarbons contain one or more carbon atoms less than the starting material. Herein, “single-step” refers to a single reaction, having at least one intermediate; “conversion” refers to chemical changes of an intermediate by isomerization, cyclization, or aromatization; “reaction products” refers to products (i.e., what is obtained) from such a single reaction; “commercial products” refers to items manufactured or produced using reaction products as starting materials; “supported catalyst” and “catalyst” are synonymous, and refer to a catalyst with a metal component over a support which can be an acidic oxide; “fatty acid” and “carboxylic acid” are synonymous; “fatty acid” is not included within the meaning of “hydrocarbon”; and cracking refers to a reaction that produces at least one hydrocarbon having a carbon chain shorter by at least three carbons than the fatty acid from which it was derived, and includes both primary and secondary cracking.

MULTIPLE EMBODIMENTS AND ALTERNATIVES

[00014] In certain embodiments, a process for a catalytic reaction for the production of hydrocarbons, from at least one fatty acid forming hydrocarbon reaction products, comprises the steps of:

[00015] contacting fatty acids reactants with a supported catalyst, the catalyst comprising a metal component over a support, the metal being chosen from the group platinum, palladium and nickel, the support being chosen from the group alumina, silicoalumina, aluminosilicate zeolite, and silicoaluminophosphate, and mixtures thereof; and

[00016] isolating hydrocarbon reaction products,

[00017] wherein the metal comprises about 3% - 5% (i.e., about 3% to about 5%) by weight of the catalyst, and the surface area of the support is about 50 m²/g – 480 m²/g (i.e., about 50 m²/g to about 480 m²/g).

[00018] In certain embodiments, the fatty acids are decarboxylated and further modified over a multifunctional catalyst containing a metal and a support which in certain embodiments is an acidic oxide, either to shorter-chain hydrocarbons produced from cracking or to branched, cyclic and aromatic reaction products. One function associated with the catalyst is decarboxylation and another function occurring in the same reaction process is either cracking of hydrocarbon intermediates or conversion of hydrocarbon intermediates. In certain embodiments, the reaction products are useful as fuels, motor gasoline, kerosene, diesel, aviation gasoline, aviation turbine fuel, and solvents, or as desired they are useful as starting materials for the production of commercial products such as high-viscosity lubricants, chlorinated paraffins, and detergents. Alternately, these products can also be 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 branched and cyclic hydrocarbons, linear alkyl benzenes, and other surfactants, lubricants and solvents. Such petrochemicals are used in the manufacture of various commercial products. For example, linear alkyl benzenes are used in the manufacture of detergents. Other examples of petrochemicals used in the manufacture of various commercial products include high viscosity index star polymers. The foregoing are non-limiting examples of a broad scope in which reaction products of the subject process are used.

[00019] In certain embodiments, a process is provided for converting linear carboxylic acids into a mixture of branched hydrocarbons. The process comprises contacting a feedstock having at least one carboxylic acid reactant of the chemical formula represented by

R-COOH with a catalyst comprising at least one metal and at least one acidic oxide, wherein at least one reaction product comprising one or more branched hydrocarbons is produced as part of a mixture. In certain embodiments, the support is alumina. In certain embodiments, R has at least six and no more than twenty-four carbon atoms. The process further includes isolating the at least one reaction product from other reaction products in the mixture. In certain embodiments, the catalyst is solid and contains at least one metal chosen from the group platinum, palladium and nickel; and the acidic oxide is chosen from the group alumina, silicoalumina, aluminosilicate zeolite (including but not limited to crystalline materials zeolite Y, mordenite, zeolite beta or MCM-22), and silicoaluminophosphate (including but not limited to SAPO-11), or their mixtures. In certain embodiments, the silicoalumina is an amorphous silicoalumina.

[00020] In certain embodiments, the at least one reaction product comprising one or more branched hydrocarbons is cyclic. Alternatively, this product is aromatic. In certain embodiments, the at least one reaction product comprises branched hydrocarbons, cyclic hydrocarbons and aromatic hydrocarbons. In certain embodiments, the at least one reaction product is suitable for use as motor gasoline, kerosene, aviation gasoline, diesel, aviation turbine fuel, and/or lubricant base oil.

[00021] In certain embodiments, the at least one carboxylic acid reactant is derived from a feedstock, which is chosen from the group plant oils, animal fats, animal oils, algae oils, and oils from heterotrophic microbial organisms.

[00022] In certain embodiments, the solid catalyst is a metal over a support which can be an acidic oxide. Optionally, the at least one carboxylic acid reactant is contacted with the catalyst in the presence of hydrogen or nitrogen. In certain embodiments, the reaction occurs at a temperature between about 200°C to about 500°C and a pressure above about 2 bar. It

has been observed that conducting the reaction at a pressure of about 20 bar and a temperature of 325° C will increase the rate of decarboxylation compared to lower pressures and temperatures.

[00023] In certain embodiments, a process is provided for producing branched, cyclic and aromatic hydrocarbons comprising (1) obtaining a supply of at least one fatty acid; (2) selecting a catalyst as described herein; and (3) contacting the at least one carboxylic acid with the catalyst, under conditions as described herein, resulting in both the decarboxylation of the at least one fatty acid and further conversion of that decarboxylated hydrocarbon by cyclization, isomerization, or aromatization.

[00024] In certain embodiments, the at least one carboxylic acid is a carboxylic acid having 7-to-24 carbon atoms. Optionally, the at least one carboxylic acid is a mixture of at least two carboxylic acids, each having 7-to-24 carbon atoms. Through conventional methods and techniques which are known, triglyceride esters are converted to carboxylic acids, e.g., hydrolysis, thermal hydrolysis, or acid hydrolysis. In certain 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.

[00025] In certain 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 greenhouse gas emissions than, for example, soy, rapeseed oil, or beef tallow. The use of such lower-cost, more sustainable oils with 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 more evenly 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 existing oil refineries.

[00026] In certain embodiments, the solid catalyst contains a metal component exemplified by platinum, palladium or nickel central to the decarboxylation of the fatty acid feedstock materials into a linear hydrocarbon intermediate.

[00027] In certain embodiments, the solid catalyst contains an acidic oxide component exemplified by alumina, silicoalumina, aluminosilicate zeolite, silicoaluminophosphate or their mixture. The acidic oxide plays a major role in the cracking or conversion of the linear hydrocarbon intermediates to reaction products. The choice of the acidic oxide component is influenced by the nature of the desired products. For example, high isomerization and low cracking/ aromatization functionalities may be needed in an acidic oxide in the production of highly branched isoparaffins needed in low temperature diesels, aviation turbine fuels and high viscosity index lubricant base stocks. On the other hand, sufficient cracking and aromatization sites are needed to produce the lower boiling, high octane motor gasolines.

[00028] In another embodiment, the acidic oxide component catalyses the skeletal isomerization, cyclisation and cracking reactions of the linear hydrocarbons resulting from

the decarboxylation of the fatty acid. Both the metal component and the acidic oxide are important to the activity and selectivity of these catalysts, and thus their ratios vary according to multiple embodiments and alternatives as discussed herein. The catalyst should have suitable compositional and structural characteristics, mainly, proper balance between metal and acid sites, medium pore size, high dispersion of metal on surface of catalyst, mild acidity, and strength distribution of acid sites. Isomerization of the linear paraffins resulting from decarboxylation of the fatty acids occurs first and cracking is a consecutive reaction, which is favored for multibranched alkanes. Monobranched paraffins are less susceptible to cracking than multibranched paraffins. Thus, when commercial products with a large number of carbon atoms, such as lubricant base oils, are desired, multibranching reactions must be limited, which can be done by selection of supports having a suitable pore size. The pore opening of the acidic oxide component can also affect the selectivity toward certain reaction products. In certain embodiments, the choice of supported catalyst as well as the determination of spatial consideration related to pore size increase the benefits of the process by allowing a user to favor certain reaction products. To illustrate, catalysts with relatively smaller pore size create spatial restrictions upon the size and shape of molecules which can access the reactive acidic sites within the pore, favoring cracking of linear hydrocarbons over conversion to branched isomers. By comparison, a catalyst having a medium pore size, e.g., SAPO-11, a 10-membered ring zeolite, favors conversion to branched paraffin reaction products which are useful as aviation fuels and other fuels with reduced pour points. Accordingly, the results achieved are not a simple matter of metal over support, but require a full understanding of the chemical, physical, and spatial effects occurring during the reaction. In view of the above, if converted reaction products are desired (i.e., branched, cyclic, or aromatic), then an acidic oxide support with at least medium pore sizes are preferred, in order to accommodate the spatial characteristics of the desired reaction products.

[00029] In certain embodiments, starting materials used in the process of the present invention are saturated carboxylic acids. Catalysts with a high hydrogenation activity and a weak acidity are usually more favorable for skeletal isomerization than for cracking. Alternatively, the starting materials are unsaturated carboxylic acids. Catalysts with a low hydrogenation activity and strong acidity are more suitable for obtaining aromatic and olefinic hydrocarbons. 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. It is also possible to carry out the decarboxylation reaction in the presence of hydrogen to simultaneously perform decarboxylation and saturation in the presence of the catalysts of this invention.

[00030] In certain embodiments, carboxylic acid starting materials are diluted in a suitable solvent before commencing the decarboxylation reaction in some cases to assist the flow of the carboxylic acid via a pump, among other purposes. As used herein, a suitable solvent would include hydrocarbons, such as, for example dodecane or hexadecane. In certain embodiments, a mixture of two or more hydrocarbons is used as a solvent. In certain embodiments, decarboxylation is carried out in a suitable solvent. Alternatively, decarboxylation is carried out in a solvent-free reaction chamber.

[00031] In certain embodiments, a process for production of paraffinic hydrocarbon is carried out in a reactor, which may be 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 catalyst of this invention in a reaction zone contained within the reactor. In certain embodiments, the reactions are carried out at a temperature in a range of 200° – 450 ° (temperatures are understood to be in Celsius unless

otherwise noted). Alternatively, the temperature is in a range of 250° – 350°. In certain embodiments, decarboxylation is carried out at a pressure in a range of 1 bar – 60 bar.

[00032] In certain embodiments, the reaction products consist of branched, cyclic and aromatic hydrocarbons, which are isolated and separated using techniques known to persons of ordinary skill in the art (e.g., distillation). In this way, the separated reaction products can be put to use according to their intended purpose as selected by a user, or further derived and manufactured into commercial products.

[00033] In certain embodiments as described herein, the reaction products obtained by practicing the present embodiments contain predominantly linear, paraffinic hydrocarbons which may be desirable for the production of certain commercial products. Among commercial products contemplated as being obtainable from present embodiments are, for example, high-cetane diesel blendstock or aromatic-free paraffinic solvents. The lack of hydrocracking reactions may also be desirable for increasing the conversion yield of the reaction products used as feedstocks for obtaining such commercial products. With regard to industrial applications, the lack of side reactions may help to reduce the complexity and cost of downstream separations. In still other embodiments, leveraging operating conditions that increase hydrocracking and/or branching can reduce downstream process steps for certain end products, for example by providing naphtha and other higher-value, lower molecular weight feedstocks obtained as reaction products. As a further example, it is expected that increased reaction temperatures would lead to higher yields of isomerized reaction products. It will be appreciated that the lower molecular feedstocks obtained from cracking are suitable as starting materials for certain kinds of commercial products (e.g., paraffinic solvents), while isomerized reaction products are more suitable for different kinds of commercial products (e.g., winter diesel and aviation fuel).

[00034] Certain embodiments of the present invention take advantage of the ability to vary the reaction conditions and to vary the proportions of the metal- acidic oxide combination. In doing so, one may significantly control the level of cracking or branching seen in the reaction products. In certain embodiments, the ratio of metal : support is about 3 – 5% by weight. The choice of reaction conditions such as temperature and pressure can depend upon the particular reaction product(s) desire to favor particular levels of cracking and/or branching so that the paraffinic hydrocarbons that are produced will meet the specifications of, among other products, high cetane diesel, “winter” diesel (including biofuels blended with petrodiesel). For example, it is expected that increasing the metal content of the supported catalyst will provide higher yields of hydrocarbon reaction products by favoring decarboxylation, while increasing temperature and pressure will tend to favor shorter-chain reaction products due to cracking. On the other hand, conversion will be favored over cracking at lower pressures, with cyclization and aromatization occurring at higher rates as the reaction temperature is raised, as such conversions have a higher activation energy needed to overcome ring strain. Such reaction products which are usable either as “winter diesel” or as a blended component of winterized diesel include iso-paraffins having 9-18 carbons. In still other embodiments, the reaction products are usable as feedstocks for the downstream production of alpha olefins and olefin sulfonates.

[00035] In another embodiment, the products of the process of the present invention can be used as aliphatic solvents for environmentally friendly cleaning fluids. These solvents are generally associated with 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 a flash point above about 140°, sufficiently low water content at 50 ppm or less for limited drying time, and VOC content at or below 25 g/L.

Additionally, in certain embodiments the reaction products can be manufactured into commercial products usable as cleaning fluids and meeting the specifications of MIL-PRF-32295, such as flash point above about 140° F; vapor pressure <0.5 mm Hg at 20°; specific gravity between 0.950-0.960; VOC Content <25 grams/liter; and distillation range within approximately 185 - 205° C. MIL-PRF-32295 is the military specification for environmentally friendly cleaning fluids, which is now being required in order to protect workers' health and safety.

[00036] Referring now to embodiments where decarboxylation and hydrocracking, according to multiple embodiments and alternatives described herein, is used to produce olefinic hydrocarbons which are usable as feedstock for the manufacture of 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.

[00037] Additionally, certain branched isoparaffin reaction products according to the embodiments herein are useful as aviation turbine fuel, which meets the specifications of ASTM D1655 and/or ASTM D7566, the standards for Jet-A aviation turbine fuel. One of the key specifications of these standards 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 the reaction products, 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 or branching.

[00038] In certain embodiments, these reaction products exhibit a boiling point range of about 35°C-200°C, have an octane rating greater than about 90, and are otherwise usable as high-octane motor gasoline meeting the specifications of ASTM D4814-11B. Reducing the

ratio of metal-to-support is expected to increase the selectivity toward isomerization over cracking. Further, the use of multifunctional catalysts according to embodiments herein allows reactions to occur at reduced temperature which also favors isomerization over cracking, the latter of which tends to be favored with increasing reaction temperature and pressure. In this way, present embodiments allow for higher-octane gasoline because it can be tuned to convert the (linear) carboxylic acid feedstocks preferentially into branched isomers while reducing cracking. For example, branched paraffinic hydrocarbons have higher octane values than multi cyclic paraffinic hydrocarbons. By way of non-limiting illustration, a C9 naphthene has an octane rating of approximately 35, whereas a C12 branched paraffin has an octane rating of approximately 85, yet both molecules have boiling points within about 5° C – 10° C of one another. This scenario illustrates that for some uses, isomerized reaction products have advantages over cyclic reaction products. It is expected that at reduced temperature isomerization will tend to be favored over cyclization and aromatization, the latter of which are associated with greater activation energies needed to overcome ring strain. In turn, as reaction temperature is increased, a higher yield of cyclic and aromatized reaction products will be provided, along with a higher percentage of cracked hydrocarbons. 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. Consequently, products obtained from fatty acids according to multiple embodiments and alternatives disclosed herein produce higher-octane gasoline with lower conversion and separation costs than petroleum refineries typically can achieve.

[00039] In certain embodiments, the reaction products are suitable for commercial uses such 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 the branched hydrocarbon reaction products resulting from decarboxylation and subsequent conversion have a significantly higher starting octane, as described above, before the addition of any aromatics or tetraethyl lead, than paraffinic hydrocarbons obtained from petroleum. Consequently, certain aviation gasoline specifications (e.g., ASTM D7719) requiring an octane rating of 100 and a boiling point range of 20° -175° can be satisfied without the addition of tetraethyl lead, which is prohibited by ASTM D7719 (the standard for lead-free test aviation gas), and with the addition of lesser amounts or no amounts of aromatics. Likewise, the specifications of D910 (the standard for leaded aviation gas) can be met with the addition of lesser amounts of lead and with lesser amounts or no amounts of 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. Advantageously, this reduces the cost of adding tetraethyl lead or aromatics to aviation gas.

[00040] In certain embodiments, the paraffinic reaction products are used as feedstocks for downstream processes to produce commercial products such as mid-chain (9-18) or long-chain (>18) chlorinated paraffins. Such commercial products are produced from these feedstocks according to reactions and methods which are known in the art. 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.

[00041] In certain embodiments, the paraffinic reaction products, as described herein according to multiple embodiments and alternatives, are useful as feedstocks for downstream processes to produce commercial products such as alpha olefins and poly alpha olefins. The appropriate carbon chain lengths of paraffinic hydrocarbons for this application would be

between 9-18 carbons. Surfactants are compounds that reduce the surface tension between liquid- liquid and liquid- solid phases and are used as detergents, dispersants and emulsifiers. Alpha olefin sulfonates (AOS) and linear alkyl benzenes(LAB) are typical examples of detergents that are made from linear hydrocarbons containing 9 to 18 carbon atoms. AOS are olefins with the double bond located adjacent the terminal part of the carbon chain which, by sulfonation according to known methods, generate AOS with surfactant properties. Conventionally, the linear hydrocarbons used as starting materials for such commercial products as mentioned above are obtained by separation from petroleum fractions, like kerosene, using molecular sieves. In certain embodiments of the present invention, however, these linear hydrocarbons are obtained from carboxylic acids derived from renewable, biological sources such as those described hereinabove. Accordingly, it will be appreciated that the ability to obtain linear olefin reaction products according to present embodiments is advantageous. For example, there are no known practical alternatives as starting materials for the production of commercial AOS aside from linear olefins. In this regard, the present embodiments offer advantages and benefits compared to obtaining them by separation from petroleum fractions.

[00042] In still other embodiments, the reaction products as described herein, are advantageously capable of being distinguished from hydrocarbons produced by petroleum refineries or by hydrodeoxygenation of triglycerides. For example, in many embodiments, the products obtained by the process of the present invention 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. It is also possible to distinguish the reaction products of this invention according to multiple embodiments and alternatives described herein, from those of paraffinic hydrocarbons 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 higher for products obtained by processes according to embodiments and alternatives described herein, than for the same products obtained from petroleum. This is generally because 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 fossil fuels such as petroleum (or hydrocarbons derived from petroleum) is 100 times lower, at a value of about 10^{-14} . 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.

Examples:

[00043] The following non-limiting examples are offered to further illustrate various embodiments according to the above teachings. However, it is to be understood that these are illustrative only and not to be construed as limiting the scope of the subject matter described and claimed herein, or in future application(s) claiming priority to this application.

[00044] Example 1: This example illustrates the preparation of the catalysts of this invention. The catalysts were metals (Pt, Pd or Ni) / supports (5% / 95% by wt.) were prepared by conventional dry impregnation of the acidic oxide samples with nitrate solutions of Pt, Pd or Ni nitrates, respectively. The catalysts were then dried in air at 120 C and calcined in air at 400 C for 5 hrs. Prior to use in catalytic reactions , they were reduced in dry hydrogen at 150 C for 3 hrs.

[00045] Example 2 : This example illustrates the process of the present invention for converting long chain carboxylic fatty acids exemplified by oleic acid (90%, Alfa-Aesar), into branched, cyclic and aromatic hydrocarbons. The decarboxylation reactions were

conducted in a 250 mL stainless steel high pressure Parr reactor (model 4576A). Oleic acid and catalyst were loaded into the reactor with a mass ratio of 20:1. Before the reaction started, CO₂ or H₂ was passed through the reactor until reaching the desired reaction pressure (usually 20 bar). Then, the reactor was heated at a temperature rate of 10°C/min to reaction temperature and continuously stirred during the reaction time. The reaction temperature was kept constant during the reaction (200-325°C). After the reaction, the catalyst particles were separated from the liquid product.

Product analysis:

[00046] The liquid product from the reactor was analyzed with a gas chromatograph (GC, 7820 A) equipped with a HP-5 MS column (with dimensions of 30 m × 250 μm × 0.25 μm) and a 5975 MSD detector. A sample of 0.2 μL was injected into the GC column (150°C, 10.5 psi) with a split ratio 20:1, and the carrier gas (helium) flow rate was 1 mL/min. The injector and detector temperature were set at 150°C. The following temperature profile was used for analysis: 100°C for 5 min, 300°C (20°C/min, for 2 min). Quantitative analysis was accomplished by generating and using calibration curves for each compound of interest. The product identification was validated with a gas chromatograph - mass spectrometer (GC-MS). The amount of carboxylic acid groups remained in the products after the reaction was evaluated by quantifying the acid number. Acid number is the mass of potassium hydroxide (KOH) in milligrams that is required to neutralize one gram of either the reactant or the product. To quantify the acid number, a known amount of sample (about 0.1g) is dissolved in solvent (ethanol + Petroleum ether), then titrated with a solution of sodium hydroxide (NaOH, 0.1N) and with phenolphthalein as a color indicator.

[00047] Acidity number is calculated from this equation:

$$\text{Acidity} = 56.1 \frac{NV}{W}$$

N= 0.1 (N)

V= volume of NaOH consumed (ml)

W= mass of the sample (g)

[00048] The decarboxylation % was calculated using the acid number of oleic acid and acid number of the product using the following relation:

[00049] % Decarboxylation= (acid number of oleic acid- acid number of the product) / acid number of oleic acid × 100%.

[00050] 2g of Pt-SAPO 11, prepared as described in Example 1, were reacted, for 2 hr, with 40 g of oleic acid at 325 C, 20 bar H₂ pressure for 2 hr. The conversion of oleic acid was 90% and the liquid hydrocarbon layer contained 60% (wt) of dodecyl benzene. The other constituents of the liquid were branched hydrocarbons and alkyl cyclohexanes.

[00051] Example 3: 1g of Pd-alumina prepared as in Example 1, was contacted with 40 g of oleic acid at 300 C and 20 bar hydrogen pressure for 2 hrs, under conditions described in Example 2 . The acid number of the product was 9.2 corresponding to 72.0 % conversion of oleic acid to hydrocarbons. The iodine number of the product was 36.0. The concentration (wt%) of the various cracked or converted reaction products (by carbon number) are :

C₉⁻ = 11.8; C₉ = 12.0; C₁₀ = 11.6; C₁₁= 10.8; C₁₂= 9.9 ; C₁₃= 8.2; C₁₄= 7.2; C₁₅= 7.4; C₁₆= 4.7; C₁₇= 13.1; C₁₈= 1.3; C₁₈⁺ =1.7.

[00052] Example 4 . 1g of Pt-alumina prepared as in Example 1, was contacted with 40 g of oleic acid at 250 C and 20 bar hydrogen pressure for 2 hrs, under conditions described in Example 2 . The acid number of the product was 2.2 corresponding to 97.5 % conversion of oleic acid to hydrocarbons. The iodine number of the product was 0.95. The concentration (wt%) of the various branched, isomerized, aromatized and cracked hydrocarbons (by carbon number) are :

C10 = 1.4; C11= 1.9; C12= 2.7 ; C13= 2.9; C14= 3.2; C15= 6.0; C16= 5.7;
C17= 62.7; C18= 6.8; C18⁺=4.1.

[00053] 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.

[00054] 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.

[00055] 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 a catalytic reaction for the production of hydrocarbons from at least one fatty acid forming hydrocarbon reaction products, comprising the steps of:

contacting fatty acids reactants with a supported catalyst, the catalyst comprising a metal component over a support, the metal being chosen from the group platinum, palladium and nickel, the support being chosen from the group alumina, silicoalumina, aluminosilicate zeolite, and silicoaluminophosphate, and mixtures thereof; and

isolating hydrocarbon reaction products;

wherein the metal comprises about 3% - 5% by weight of the catalyst, and the surface area of the support is about 50 m²/g -- 480 m²/g.

2. The process of claim 1, wherein decarboxylation and cracking both occur during the catalytic reaction to yield at least one reaction product having a carbon chain shorter by at least three carbons than the fatty acid from which it was derived.

3. The process of claim 1, wherein decarboxylation and conversion both occur during the catalytic reaction to yield at least one branched reaction product.

4. The process of claim 1, wherein decarboxylation and conversion both occur during the catalytic reaction to yield at least one cyclic reaction product.

5. The process of claim 1, wherein at least one fatty acid is unsaturated, and decarboxylation and conversion both occur during the catalytic reaction to yield at least one aromatic reaction product.

6. The process of claim 1, carried out at a reaction temperature between about 200 ° C and about 325 ° C.

7. The process of claim 1, carried out at a reaction temperature no greater than about 350 ° C.

8. The process of claim 1, wherein the silicoaluminophosphate is SAPO-11, and the aluminosilicate zeolite is chosen from the group zeolite Y, mordenite, zeolite beta and MCM-22.

9. The process of claim 1, wherein at least about 72.0% of fatty acids are converted to hydrocarbon reaction products.

10. The process of claim 1, wherein the at least one fatty acid is obtained from a renewable source chosen from the group plant oils; animal fats, animal oils; algae oils; waste vegetable oils; and oils from heterotrophic microbes, and mixtures thereof.

11. The process of claim 10, wherein the heterotrophic microbe is chosen from the group heterotrophic algae and oleaginous yeast.

12. The process of claim 10, wherein the plant oil is chosen from the group jatropha oil, camelina oil, pennycress oil, pongamia oil, and carinata oil, and mixtures thereof.

13. A process for generating a feedstock for the manufacture of at least one commercial product, comprising the steps of:

contacting fatty acids reactants with a supported catalyst, the catalyst comprising a metal component over a support, the metal being chosen from the group platinum, palladium

and nickel, the support being chosen from the group alumina, silicoalumina, aluminosilicate zeolite, and silicoaluminophosphate, and mixtures thereof; and

isolating hydrocarbon reaction products,

wherein the metal comprises about 3% - 5% by weight of the catalyst, and the surface area of the support is about 50 m²/g – 480 m²/g; and

wherein decarboxylation and conversion both occur during the catalytic reaction to yield at least one reaction product chosen from the group branched hydrocarbon reaction product, cyclic hydrocarbon reaction product, and aromatic hydrocarbon reaction product.

14. The process of claim 13, wherein the at least one commercial product is chosen from the group: (i) gasoline having an octane rating greater than about 85; (ii) aviation fuel meeting the standard set forth in ASTM D1655; (iii) cleaning fluid having a flash point above about 140° F and VOC Content less than about 25 grams/liter; (iv) AOS detergent having between 9 and 18 carbons; (v) LAB detergent having between 9 and 18 carbons; (vi) lubricant; (vii) surfactant; and (viii) solvent.

15. A process for generating a feedstock for the manufacture of at least one commercial product chosen from the group diesel fuel, aviation fuel, solvents, and cleaning fluids, comprising the steps of:

contacting fatty acids reactants with a supported catalyst, the catalyst comprising a metal component over a support, the metal being chosen from the group platinum, palladium and nickel, the support being chosen from the group alumina, silicoalumina, aluminosilicate zeolite, and silicoaluminophosphate, and mixtures thereof; and

isolating hydrocarbon reaction products,

wherein the metal comprises about 3% - 5% by weight of the catalyst, and the surface area of the support is about 50 m²/g – 480 m²/g; and

wherein decarboxylation and cracking both occur during the catalytic reaction to yield at least one reaction product having a carbon chain shorter by at least three carbons than the fatty acid from which it was derived.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 14/56288

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C07C 7/163 (2014.01)

CPC - C07C 5/10; C07C 2/74; C07C 2523/755

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC(8): C07C 7/163 (2014.01)

CPC: C07C 5/10; C07C 2/74; C07C 2523/755

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

USPC: 585/268; 585/260; 585/269; 585/270

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

PatBase; FreePatentsOnline; GoogleScholar. Search Terms: catalytic reaction hydrocarbons production fatty acid contacting fatty acids supported catalyst metal component support platinum palladium nickel alumina silicoalumina aluminosilicate zeolite silicoaluminophosphate

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 2009/0300970 A1 (Perego et al.) 10 December 2009 (10.12.2009) para [0001]; [0011]; [0012]; [0015]; [0016]; [0026]; [0047]; [0074-0078]	1-7, 9, 10, 13 and 15 ----- 8, 11, 12 and 14
Y	US 2011/0099891 A1 (Kaul et al.) 05 May 2011 (05.05.2011) para [0018]; [0023]; [0028]; [0084]	8, 11 and 12
Y	US 2012/0323051 A1 (Powell) 20 December 2012 (20.12.2012) para [0008]; [0017]; [0117]	14

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

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

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