

(43) International Publication Date
13 December 2012 (13.12.2012)

(51) International Patent Classification:

C10G 69/00 (2006.01) *C07C 49/88* (2006.01)
C10L 1/08 (2006.01) *C07C 45/87* (2006.01)
C10G 3/00 (2006.01)

(21) International Application Number:

PCT/US2012/037767

(22) International Filing Date:

14 May 2012 (14.05.2012)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

13/157,921 10 June 2011 (10.06.2011) US

(71) **Applicant** (for all designated States except US): **CHEVRON U.S.A. INC.** [US/US]; 6001 Bollinger Canyon Road, San Ramon, California 94583 (US).

(72) **Inventors; and**

(75) **Inventors/Applicants** (for US only): **ZHAN, Bi-Zeng** [CA/US]; 6001 Bollinger Canyon Road, San Ramon, California 94583 (US). **HOMMELTOFT, Sven Ivar** [DK/US]; 6001 Bollinger Canyon Road, San Ramon, California 94583 (US).

(74) **Agents:** **MCQUISTON, Jeffrey M.** et al.; Chevron Corporation, Law Department, P.O. Box 6006, San Ramon, California 94583-0806 (US).

(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, 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, KM, 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, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, 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, ML, MR, NE, SN, TD, TG).

Published:

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

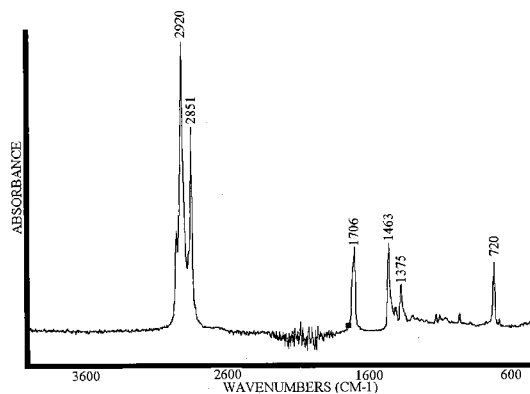
(54) **Title:** CONVERSION OF FATTY ACIDS TO BASE OILS AND TRANSPORTATION FUELS

FIG. 1

(57) **Abstract:** The present invention is directed to methods for processing fatty acids to provide for base oil and transportation fuels, wherein decarboxylation-coupling dimerization of fatty acids provides dimer ketones from which the base oils and transportation fuels may be produced.

CONVERSION OF FATTY ACIDS TO BASE OILS AND TRANSPORTATION FUELS

TECHNICAL FIELD

[001] The invention relates generally to lubricants and fuels derived from renewable
5 resources, and specifically to methods for efficiently making base oils and transportation fuels
from fatty acids.

BACKGROUND

[002] Due to a variety of environmental and energy concerns, there has been a high
10 interest in promoting the use of renewable resources (e.g., biomass) in the manufacture of
lubricants and transportation fuels. Fatty acids are a readily available renewable resource.

[003] Conventional processes for hydroprocessing fatty acids generally involve
hydrotreating. A disadvantage of direct hydrotreating of fatty acids is its high hydrogen
consumption. In addition, the molecular weight of some fatty acids by themselves is too low to
15 prepare base oils.

[004] Additional processes for producing high quality lubricants and transportation
fuels from renewable resources are still sought.

SUMMARY OF THE INVENTION

[005] In one aspect, the invention relates to a method comprising: contacting a fatty acid
20 feed with a decarboxylation-coupling dimerization catalyst in a decarboxylation-coupling
dimerization zone under decarboxylation-coupling dimerization conditions to yield a dimer
ketone; hydrocracking the dimer ketone with a hydrocracking catalyst in a hydrocracking zone
under hydrocracking conditions to yield a mixture of paraffins comprising a heavy waxy oil
25 component and a diesel fuel component; and distilling the mixture to yield a heavy waxy oil and
a diesel fuel.

[006] In another aspect, the invention relates to a method comprising: contacting a fatty
acid feed with a decarboxylation-coupling dimerization catalyst in a decarboxylation-coupling
dimerization zone under decarboxylation-coupling dimerization conditions to yield a dimer
30 ketone; and hydroisomerization dewaxing the dimer ketone with a hydroisomerization dewaxing

catalyst in a catalytic hydroisomerization zone under hydroisomerization dewaxing conditions to yield a lubricating base oil.

BRIEF DESCRIPTION OF THE DRAWINGS

5 [007] FIG. 1 is an FT-IR spectrum of a dimer ketone of Example 2.

DETAILED DESCRIPTION

[008] The following terms will be used throughout the specification and will have the following meanings unless otherwise indicated.

10 [009] The prefix “bio” refers to an association with a renewable resource of biological origin, such resources generally being exclusive of fossil fuels.

[010] “Fatty acid” refers to an aliphatic mono-carboxylic acid having at least 4 carbon atoms. The fatty acid can be saturated or unsaturated, branched or unbranched.

15 [011] “Decarboxylation-coupling dimerization” refers to a chemical reaction in which two molecules, each having a carboxylic acid functional group, combine to form one single molecule having a ketone functional group, with concurrent loss of carbon dioxide and water.

[012] “Diesel fuel” refers to hydrocarbons having boiling points in the range of from 250°F to 700°F (121°C to 371°C).

20 [013] “Base oil” refers to a hydrocarbon fluid to which other oils or substances are added to produce a lubricant.

[014] “Group III base oil” refers to a base oil which contains greater than or equal to 90% saturates and less than or equal to 0.03% sulfur and has a viscosity index greater than or equal to 120 using the ASTM methods specified in Table E-1 of American Petroleum Institute Publication 1509.

25 [015] “Viscosity index” (VI) is an empirical, unit-less number indicating the effect of temperature change on the kinematic viscosity of the oil. The higher the VI of an oil, the lower its tendency to change viscosity with temperature. Viscosity index is measured according to ASTM D 2270-10.

30 [016] “Pour point” is a measurement of the temperature at which a sample will begin to flow under certain carefully controlled conditions, which can be determined as described in ASTM D 5950-02 (reapproved 2007).

[017] "Cloud point" represents the temperature at which a fluid begins to phase separate due to crystal formation, which can be determined as described in ASTM D 5771-10.

[018] The Periodic Table of Elements referred to herein is the Table approved by IUPAC and the U.S. National Bureau of Standards, an example of which is the Periodic Table of the Elements by Los Alamos National Laboratory's Chemistry Division of October 2001.

Fatty Acid Feed

[019] The fatty acid feed can be from a bio-based source (e.g., biomass) or can be derived from Fischer-Tropsch alcohols via oxidation. The fatty acid feed can be a bio-derived fatty acid formed by hydrolysis of one or more triglyceride-containing vegetable oils such as, but not limited to, coconut oil, corn oil, linseed oil, olive oil, palm oil, palm kernel oil, rapeseed oil, safflower oil, soybean oil, sunflower oil, and the like. Other sources of triglycerides, for which hydrolysis can yield fatty acids, include, but are not limited to, algae, animal tallow, and zooplankton.

[020] In some embodiments, wherein the above-mentioned hydrolyzed triglyceride sources contain mixtures of saturated fatty acids, mono-unsaturated fatty acids, and polyunsaturated fatty acids, one or more techniques may be employed to isolate, concentrate, or otherwise separate the desired fatty acids from the other fatty acids in the mixture (see, e.g., U. S. Patent Application Publication No. 2009/0285728).

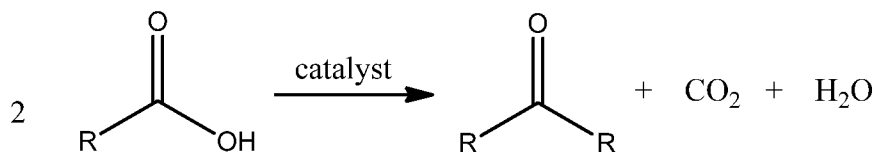
[021] Generally, the fatty acid feed comprises at least 50 wt. % saturated fatty acids, typically at least 75 wt. % saturated fatty acids, and more typically at least 90 wt. % saturated fatty acids.

[022] Non-limiting examples of suitable saturated fatty acids include caproic acid (C₆), caprylic acid (C₈), capric acid (C₁₀), lauric acid (C₁₂), myristic acid (C₁₄), palmitic acid (C₁₆), stearic acid (C₁₈), arachidic acid (C₂₀), palm kernel oil acid (a mixture of C₈ to C₂₂ fatty acids, primarily lauric acid and myristic acid), coconut oil acid (a mixture of C₈ to C₂₂ fatty acids, primarily lauric acid and myristic acid), and any combination of the foregoing.

Decarboxylation-coupling Dimerization

[023] Dimer ketones may be prepared by decarboxylation-coupling of fatty acids. Without wishing to be bound by any particular theory, a ketone is formed in the decarboxylation-coupling process from two moles of fatty acid. Carbon dioxide and water are produced as by-

products. The following reaction scheme illustrates this proposed scheme for a single fatty acid source:



[024] The fatty acid raw material, together with a diluent, when used, is contacted with a catalyst in a so-called reaction zone. Such a zone may, for example, be contained within a fixed bed reactor, a fluid bed reactor, or a slurry reactor. The decarboxylation-coupling processes can also be conducted in a glass-lined stainless steel or similar type reaction equipment. In one preferred embodiment, the reaction zone may be fitted with one or more internal and/or external heat exchangers in order to control the temperature.

[025] Suitable decarboxylation-coupling dimerization conditions comprise generally a temperature in the range between 437°F and 932°F (225°C and 500°C), typically between 572°F and 752°F (300°C and 400°C); a pressure in the range between 10 and 3000 psig (0.07 and 20.7 MPa), typically between 100 and 2500 psig (0.7 and 17.2 MPa); a liquid hourly space velocity (LHSV) of from 0.1 to 50 h⁻¹, typically from 0.5 to 10 h⁻¹.

[026] The decarboxylation-coupling dimerization reaction can be conducted in the presence of at least one inert liquid diluent. Dilution can help minimize the corrosivity of the fatty acid feed. The liquid diluent should be a good solvent for the starting materials and easily separable from the ketone product. Suitable diluents include, but are not limited to, hydrocarbon solvents (e.g., benzene, toluene, xylene, ethylbenzene, heptane, octane, nonane, decane, dodecane, tridecane, and the like) and oxygenated solvents such as alcohols, ethers and ketones. When liquid diluents are used, the feed comprises generally between 1 and 95 wt. % of fatty acid, or between 5 and 50 wt. % of fatty acid.

[027] Suitable catalysts for fatty acid decarboxylation-coupling dimerization include alumina, silica, silica-alumina, titania, zirconia, and combinations thereof, and supported metal carbonates or hydroxides. Typical metals include Mg, Ca, Sr, Ba, and Mn. The support for metal carbonates or hydroxides can be chosen from any refractory material such as alumina, silica, silica-alumina, titania, zirconia, zinc oxide, magnesium oxide, and combinations thereof, or even naturally-occurring materials such as pumice. In one embodiment, the decarboxylation-coupling dimerization catalyst is alumina.

[028] The decarboxylation-coupling dimerization process can be carried out in batch or continuous mode, with recycling of unconsumed starting materials if required.

[029] Dimer ketones derived by the above-described process can be separated from by-products (such as oligomeric or polymeric species and low molecular weight “fragments” from the fatty acid chains) by distillation. For example, the crude reaction product can be subjected to a distillation-separation at atmospheric or reduced pressure through a packed distillation column.

[030] The decarboxylation-coupling dimerization product is generally a wax at room temperature and pressure. In order to prevent clogging of the apparatus in which decarboxylation-coupling dimerization is performed, it may be necessary to heat those tubes by which the decarboxylation-coupling dimerization product is removed from the reaction zone and any vessel into which the dimer ketone is to be collected.

Hydrocracking

[031] Hydrocracking is generally accomplished by contacting, in a hydrocracking reactor or reaction zone, the feedstock to be treated with a suitable hydrocracking catalyst under conditions of elevated temperature and pressure. Hydrocracking reactions reduce the overall molecular weight of the heavy feedstock to yield upgraded (that is, higher value) products including transportation fuels (e.g., diesel fuel), kerosene, and naphtha. These upgraded products that are converted in the hydrocracking reaction zone are typically separated from the total hydrocracker effluent as lower boiling fractions, using one or more separation and/or distillation operations. A remaining higher boiling fraction, containing heavy waxy feedstocks (referred herein as a “heavy hydrocarbon intermediate” or a “heavy waxy oil”) suitable for upgrading to lubricating base oils by hydroisomerization to improve its cold flow properties, is always generated in the fractionators. The heavy waxy oil has a boiling range of approximately 650°F to 1300°F (343°C to 704°C).

[032] The temperature in the hydrocracking zone is within the range of from 500°F to 900°F (260°C to 482°C), typically within the range of from 600°F to 800°F (316°C to 427°C), more often with 650°F to 750°F (343°C to 399°C). A total pressure above 1000 psig (6.89 MPa) is used. For example, the total pressure can be above 1500 psig (10.34 MPa), or above 2000 psig (13.79 MPa). Although greater maximum pressures have been reported in the literature and may be operable, the maximum practical total pressure generally will not exceed 3000 psig (20.68

MPa). In some embodiments, more severe hydrocracking conditions such as higher temperature or pressure will result in producing an original base oil product with a higher viscosity index.

[033] The LHSV generally falls within the range of from 0.1 to 50 h⁻¹, typically from 0.2 to 10 h⁻¹, more often from 0.5 to 5 h⁻¹. The supply of hydrogen (both make-up and recycle) is preferably in excess of the stoichiometric amount needed to crack the target molecules and generally falls within the range of from 500 to 10000 standard cubic feet (SCF)/barrel, typically from 1000 to 5000 SCF/barrel. Note that a feed rate of 10000 SCF/barrel is equivalent to 1781 L H₂/L feed. In general, hydrocracking conditions are sufficient to convert the dimer ketone to hydrocarbon.

[034] The catalysts used in the hydrocracking zone are composed of natural and synthetic materials having hydrogenation and dehydrogenation activity and cracking activity. These catalysts are well known in the art and are pre-selected to crack the target molecules and produce the desired product slate. Exemplary commercial cracking catalysts generally contain a support consisting of alumina, silica, silica-alumina composites, silica-alumina-zirconia composites, silica-alumina-titania composites, acid treated clays, crystalline aluminosilicate zeolitic molecular sieve (e.g., zeolite A, faujasite-Y, zeolite beta), and various combinations of the above. The hydrogenation/dehydrogenation components generally consist of a metal or metal compound of Group VIII or Group VIB of the Periodic Table of the Elements. Metals and their compounds such as, for example, Co, Ni, Mo, W, Pt, Pd and combinations thereof are known hydrogenation components of hydrocracking catalysts.

Distilling

[035] In some embodiments, the step of distilling employs a distillation column (unit) to separate the heavy waxy oil and the diesel fuel into individual fractions. Generally, the heavy waxy oil is collected in a high-boiling fraction and the diesel fuel is collected in a low-boiling fraction. In some particular embodiments, a fractional bifurcation occurs at or around 650°F (343°C), in which case the diesel fuel is largely contained within a 650°F- fraction (boiling below 650°F) and the heavy waxy oil is contained within a 650°F+ fraction (boiling above 650°F). Those of skill in the art will recognize that there is some flexibility in characterizing the high and low boiling fractions, and that the products may be obtained from "cuts" at various temperature ranges.

[036] In some embodiments, the diesel fuel has a cetane index of at least 65, or at least 70, as determined by ASTM D 4737-10. In some or other such embodiments, the diesel fuel has a pour point of less than 0°C.

Hydroisomerization dewaxing

5 [037] Heavy intermediate feedstocks are characterized by high pour points and high cloud points. In order to prepare commercially useful lubricating base oils from heavy intermediate feedstocks, the pour point and cloud point must be lowered without compromising the desired viscosity characteristics. Hydroisomerization dewaxing is intended to improve the cold flow properties of the heavy intermediate feedstocks by the selective addition of branching
10 into the molecular structure. Hydroisomerization dewaxing ideally will achieve high conversion levels of the waxy oil to non-waxy iso-paraffins while at the same time minimizing cracking.

[038] Hydroisomerization dewaxing is achieved by contacting a feed with a hydroisomerization dewaxing catalyst in a hydroisomerization zone under hydroisomerization dewaxing conditions. The hydroisomerization catalyst preferably comprises a shape selective
15 intermediate pore size molecular sieve, a noble metal hydrogenation component, and at least a refractory oxide support. The shape selective intermediate pore size molecular sieve is preferably selected from the group consisting of SAPO-11, SAPO-31, SAPO-41, SM-3, SM-7, ZSM-22, ZSM-23, ZSM-35, ZSM-48, ZSM-57, SSZ-32, ferrierite, and combinations thereof. SAPO-11, SM-3, SM-7, SSZ-32, ZSM-23, and combinations thereof are often used. The noble metal
20 hydrogenation component can be Pt, Pd, or combinations thereof.

[039] The hydroisomerization dewaxing conditions depend on the feed used, the hydroisomerization dewaxing catalyst used, whether or not the catalyst is sulfided, the desired yield, and the desired properties of the product. Preferred hydroisomerization dewaxing conditions useful in the current invention include temperatures of 260°C to 413°C (500°F to
25 775°F); a total pressure of 15 to 3000 psig (0.10 to 20.68 MPa); a LHSV of 0.25 to 20 h⁻¹; and a hydrogen to feed ratio from about 200 to 30000 SCF/barrel. In some embodiments, the hydrogen to feed ratio can be from 500 to 10000 SCF/barrel, in others from 1000 to 5000 SCF/barrel, and in still others from 2000 to 4000 SCF/barrel. Typically, hydrogen will be separated from the product and recycled to the hydroisomerization zone. In general, hydroisomerization dewaxing
30 conditions are sufficient to convert dimer ketones to hydrocarbon.

[040] Additional details of suitable hydroisomerization dewaxing processes are described in U.S. Pat. Nos. 5,135,638; 5,282,958; and 7,282,134.

[041] In some embodiments, the base oil has a viscosity index of at least 140, typically at least 170, and often at least 200. In some embodiments, the base oil is a Group III base oil. In
5 some embodiments, the base oil produced has a pour point of less than 0°C.

Hydrofinishing

[042] Hydrofinishing may be used as a step following hydroisomerization in the process of this invention to make base oils with improved properties. This step is intended to improve the oxidation stability, UV stability, and appearance of the product by removing traces of olefins and
10 color bodies. A general description of hydrofinishing may be found in U.S. Pat. Nos. 3,852,207 and 4,673,487. In one embodiment, the isomerized product from the hydroisomerization reactor passes directly to the hydrofinishing reactor.

[043] As used in this disclosure, the term UV stability refers to the stability of the lubricating base oil when exposed to ultraviolet light and oxygen. Instability is indicated when
15 the lubricating base oil forms a visible precipitate or darker color upon exposure to ultraviolet light and air which results in a cloudiness or floc in the product. Usually lubricating base oils prepared by hydrocracking followed by hydroisomerization require UV stabilization before they are suitable for use in the manufacture of commercial lubricating oils.

[044] EXAMPLES: The following examples are given to illustrate the present
20 invention. It should be understood, however, that the invention is not to be limited to the specific conditions or details described in these examples.

EXAMPLE 1

Fatty Acid Feeds

[045] Fatty acid feeds were obtained with properties shown below in Table 1. Diluent
25 was added to the fatty acids to lower the total acid number (TAN) to less than 20 mg-KOH/g feed.

TABLE 1

Feed Name	Coconut fatty acid in n-tridecane	Stearic acid in n-octane
API Gravity	53.2	65.4
TAN, mg-KOH/g feed	12.70	10.2
<u>SimDis, wt %</u>		
0.5/5	455/457	250/262
10/30	458/461	265/268
50/	463/	269/
70/90	464/465	271/272
95/99.5	466/590	273/689

EXAMPLE 2

Decarboxylation-coupling Dimerization of Coconut Fatty Acid over an Alumina Catalyst

[046] The decarboxylation-coupling dimerization of coconut fatty acid over an alumina catalyst was conducted at conditions of 680°F to 730°F, about 0.45 to 1.0 h⁻¹ LHSV and 45 to 60 psig unit pressure. Both whole liquid product (WLP) and Wasson gas samples were taken periodically for inspections. The WLP was also submitted for total acid number test to check the conversion of fatty acid. The results are set forth in Table 2.

TABLE 2

Run time, h	45	141	165	189	957	981
CAT, °F	680	680	680	680	730	730
LHSV, h ⁻¹	0.98	0.46	0.44	0.48	0.50	0.51
Pressure, psig	45	50	50	60	50	50
<u>No-loss Yield, wt.%</u>						
C ₁₋₄	0	0.04	0.03	0.02	0.04	0.03
C _{5-250°F}	0.01	0.01	0.01	0	0.08	0
250-550°F	96.71	95.54	95.36	95.63	96	95.97
550-700°F	0.45	0.43	0.42	0.37	0.5	0.55
700°F+	2.12	2.49	2.62	2.52	2.38	2.44
<u>WLP</u>						
TAN, mg-KOH/g	4.34	1.01	1.05	1.76	0.24	0.26
<u>SimDis, wt.%</u>						
0.5/5	454/458	455/458	455/458	455/459	445/460	449/459
10/30	460/463	460/463	460/464	460/464	462/465	460/464
50/	465/	465/	466/	466/	467/	466/
70/90	467/469	467/468	468/469	468/469	469/470	467/469
95/99.5	469/844	469/819	470/819	470/819	471/820	469/819

[047] Table 2 shows that the TAN was reduced from 12.7 mg-KOH/g of the diluted coconut fatty acid feed to about 1 mg-KOH/g of the decarboxylated product at catalyst temperature (CAT) of 680°F and 0.5 h⁻¹ LHSV and further reduced to about 0.3 mg-KOH/g at conditions of 730°F CAT and 0.5 h⁻¹ LHSV, indicating catalytic conversion of fatty acid on alumina catalyst. Simulated Distillation or SimDis data (ASTM D 6352-04, reapproved 2009) indicate the formation of a heavy product with a boiling point of about 800°F+, much higher than

the boiling point of the coconut fatty acid (590°F). The FT-IR of the heavy product indicates ketone formation as evidenced by a C=O stretching band at 1706 cm⁻¹ (see FIG. 1).

[048] Table 3 sets forth the concentration of CO and CO₂ in the off-gas of the decarboxylation-coupling dimerization process. The results demonstrate that carbon dioxide and water are the major side products, supporting ketone formation via decarboxylation-coupling dimerization.

TABLE 3

Run time, h	45	141	165	189
CAT, °F	680	680	680	680
LHSV, h ⁻¹	0.98	0.46	0.44	0.48
<u>Gas composition, vol. %</u>				
CO	1.68	3.04	4.80	4.51
CO ₂	92.83	86.17	85.45	84.32
<u>Water formation, g</u>	2.84	-	3.47	3.75

EXAMPLE 3

Decarboxylation-coupling Dimerization of Stearic Acid over an Alumina Catalyst

[049] The decarboxylation-coupling dimerization of stearic acid over an alumina catalyst was conducted at conditions of 680°F to 730°F, about 1 to 2 h⁻¹ LHSV and 30 to 50 psig unit pressure. Both whole liquid product (WLP) and Wasson gas samples were taken periodically for inspections. The WLP was also submitted for total acid number test to check the conversion of fatty acid. The results are set forth in Table 4.

TABLE 4

Run Time, h	117	213	861	1029	1053
CAT, °F	680	680	730	730	730
LHSV, h ⁻¹	0.97	0.97	1.94	1.95	1.95
Pressure, psig	50	45	30	30	30
<u>No-loss</u> <u>Yield, wt. %</u>					
C ₁₋₄	0.01	0.02	0	0	0
C ₅ -250°F	0.78	0.73	0.39	0.55	0.57
250-550°F	98.02	97.67	97.11	96.63	97.43
550-700°F	0.93	0.97	1.17	1.17	1.29
700°F+	1.43	1.83	2.48	2.95	1.95
<u>WLP</u>					
TAN, mg-KOH/g	< 0.05	< 0.05	2.97	2.59	2.88
<u>SimDis,</u> <u>wt. %</u>					
0.5/5	246/260	249/262	251/264	250/264	250/264
10/30	262/265	264/266	265/268	265/268	265/268
50/	266/	268/	270/	270/	269/
70/90	268/269	269/271	271/273	271/272	271/272
95/99.5	269/910	271/912	273/936	273/936	273/935

[050] Table 4 shows reduced TAN of the stearic acid solution from 10.2 to less than 0.05 – 3.0 mg-KOH/g after contact with the alumina catalyst at conditions of about 1 – 2 h⁻¹ LHSV and 680°F/730°F CAT. The major product via decarboxylation-coupling dimerization showed a boiling point of about 900°F+, slightly higher than that in Example 2. This is consistent with the higher molecular weight of stearic acid in comparison to coconut fatty acid.

EXAMPLE 4

Decarboxylation-coupling Dimerization of Stearic Acid over a Ti-Modified Silica-Alumina Catalyst

[051] The decarboxylation-coupling dimerization of stearic acid over a silica-alumina catalyst (SIRAL[®]-30 from Sasol) doped with 10 wt. % Ti was conducted at conditions of 630°F to 680°F, about 1 h⁻¹ LHSV and 40 psig unit pressure. Both whole liquid product (WLP) and Wasson gas samples were taken periodically for inspections. The WLP was also submitted for total acid number test to check the conversion of fatty acid. The results are set forth in Table 5.

10

15

20

25

30

TABLE 5

Run time, h	70	142	166	190	214	310	334
CAT, °F	680	680	680	680	630	630	630
LHSV, h ⁻¹	0.99	0.99	0.98	0.99	0.9	0.99	0.99
Pressure, psig	40	40	40	40	40	40	40
<u>No-loss Yield, wt. %</u>							
C ₁₋₄	0.29	0.17	0.11	0.09	0.06	0.02	0.21
C ₅ -250°F	1.76	1.28	1.57	1.43	1.28	1.45	1.55
250-550°F	95.96	95.57	94.86	94.87	94.9	94.22	95.07
550-700°F	0.36	0.68	0.79	0.81	0.66	0.83	0.75
700°F+	0.66	1.32	1.68	1.83	1.8	2.94	1.13
<u>WLP</u>							
TAN, mg-KOH/g	< 0.05	< 0.05	< 0.05	< 0.05	0.74	0.75	< 0.05
<u>SimDis, wt. %</u>							
0.5/5	238/259	245/261	249/263	246/261	248/262	248/262	240/260
10/30	261/264	262/265	265/268	262/265	263/266	263/266	262/264
50/	266/	267/	269/	267/	267/	267/	266/
70/90	267/268	268/269	271/272	268/270	269/270	268/270	267/268
95/99.5	269/795	270/889	270/904	270/903	270/934	270/1056	269/885

[052] The results show significantly reduced TAN of the stearic acid solution from 10.2 to less than 0.05 and 0.75 mg-KOH/g after contact with Ti-modified SIRAL[®]-30 catalyst at 680°F and 630°F, respectively, lower than the required temperature for the alumina catalyst.

[053] Table 6 sets forth a comparison of the activity, yields and product properties in stearic acid decarboxylation-coupling dimerization over the alumina catalyst of Example 3 and the Ti-modified SIRAL[®]-30 catalyst of Example 4. As shown, the acidic sites on the SIRAL[®]-30 lead to cracking resulting in the formation of 1.0 to 1.5 wt. % C₅-250°F, higher than 0.5 to 1.0 wt.

% with the pure alumina catalyst of Example 2 at comparable decarboxylation-coupling dimerization conditions.

TABLE 6

Run time, h	117	213	142	190
Catalyst	Ex. 3	Ex. 3	Ex. 4	Ex. 4
CAT, °F	680	680	680	680
LHSV, h ⁻¹	0.97	0.97	0.99	0.99
Pressure, psig	50	45	40	40
<u>No-loss</u>				
<u>Yield wt. %</u>				
C ₁₋₄	0.01	0.02	0.17	0.09
C ₅ -250°F	0.78	0.73	1.28	1.43
250-550°F	98.02	97.67	95.57	94.87
550-700°F	0.93	0.97	0.68	0.81
700°F+	1.43	1.83	1.32	1.83
<u>WLP</u>				
TAN, mg-KOH/g	< 0.05	< 0.05	< 0.05	< 0.05
<u>SimDis, wt. %</u>				
0.5/5	246/260	249/262	245/261	246/261
10/30	262/265	264/266	262/265	262/265
50/	266/	268/	267/	267/
70/90	268/269	269/271	268/269	268/270
95/99.5	269/910	271/912	270/889	270/903

EXAMPLE 5

Hydrocracking of Dimer Ketone Product

[054] The dimer ketone products from Example 3 were blended together and the n-octane solvent was removed via a rotary evaporator. The physical properties of the feed are set forth in Table 7.

TABLE 7

API Gravity	43.7
TAN, mg-KOH/g	31.8
Bromine Number, g-Br/100g	10
<u>SimDis</u> , wt. %	
0.5/5	323/323
10/30	324/599
50/	692
70/90	930/935
95/99.5	942/1228

[055] Hydrocracking of the dimerized product was performed using a commercial hydrocracking catalyst under the following conditions: 7000 SCF/barrel hydrogen, 1.0 h⁻¹ LHSV and 2000 psig unit pressure. An online stripper operated at a cut point of about 700°F to generate a stripper overhead product or STO (700°F-, diesel fuel) and a stripper bottoms product or STB (700°F+, heavy waxy oil). Table 8 sets forth the activity, yields and product properties for the hydrocracked dimer ketone from stearic acid.

TABLE 8

Run Hours	2036	2060	2084	2108	Product Blend ¹
CAT, °F	640	640	670	670	
LHSV, h ⁻¹	1	1	1.01	1.01	
Total Pressure, psig	2020	2020	2020	2020	
Inlet H ₂ P, psia	1949	1949	1949	1948	
Synthetic Conversion < 700°F, wt%	12.93	14.39	15.8	23.01	
<u>No-loss Yields, wt %</u>					
C ₁₋₄	0.37	0.34	0.34	0.38	
C ₅ -180°F	2.31	2.25	2.30	1.99	
180-250°F	0.18	0.19	0.15	1.24	
250-550°F	31.75	31.94	34.06	35.67	
550-700°F	23.20	23.92	22.93	23.74	
700°F+	42.51	41.70	40.61	37.53	
<u>STO</u>					
API					54.9
Br Index, mg-Br/100g					217
TAN, mg-KOH/g					< 0.05
TPG Dis., wt. %					
0.5/5					247/262
50/					434/
95/99.5					629/750
Cloud Point, °C					24
Pour Point, °C					-1
Cetane Index					73.8
<u>STB</u>					
API					38.9
VI					204
Vis @ 100°C, cSt					5.852
Vis @ 70°C, cSt					10.62
Cloud Point, °C					-
Pour Point, °C					64
Br Index, mg-Br/100g					307
TAN, mg-KOH/g					< 0.05
TPG Dis., wt.%					
0.5/5					731/836
50/					908/
95/99.5					915/1066

¹Product blend from yield periods of 2036 to 2108 hours.

[056] The results in Table 8 show cracking conversion (less than 700°F) increased from
5 15 wt. % to about 23 wt. % when the CAT temperature increased from 640°F to 670°F. Both

STO and STB hydrocarbons are highly saturated as measured by bromine index (ASTM D 2710-09). The hydrocracking process does not generate much gas (about 0.3 wt. %) or naphtha (2.5 to 3.0 wt. %, C₅-250°F). Importantly, high quality diesel fuel was produced. The cetane index for the STO is 73.4 with cloud and pour point of 24°C and -1°C, respectively. The STB product gave a significantly high viscosity index of 204, qualified for Group VI. Its pour point was 64°C. The pour point may be reduced by a subsequent hydroisomerization dewaxing process with a hydroisomerization dewaxing catalyst in a catalytic hydroisomerization zone under hydroisomerization dewaxing conditions to yield a lubricating base oil.

[057] For the purposes of this specification and appended claims, unless otherwise indicated, all numbers expressing quantities, percentages or proportions, and other numerical values used in the specification and claims, are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that can vary depending upon the desired properties sought to be obtained by the present invention.

It is noted that, as used in this specification and the appended claims, the singular forms "a," "an," and "the," include plural references unless expressly and unequivocally limited to one referent. As used herein, the term "include" and its grammatical variants are intended to be non-limiting, such that recitation of items in a list is not to the exclusion of other like items that can be substituted or added to the listed items.

[058] This written description uses examples to disclose the invention, including the best mode, and also to enable any person skilled in the art to make and use the invention. The patentable scope is defined by the claims, and can include other examples that occur to those skilled in the art. Such other examples are intended to be within the scope of the claims if they have structural elements that do not differ from the literal language of the claims, or if they include equivalent structural elements with insubstantial differences from the literal languages of the claims. To an extent not inconsistent herewith, all citations referred to herein are hereby incorporated by reference.

CLAIMS

1. A method comprising:
 - a) contacting a fatty acid feed with a decarboxylation-coupling dimerization catalyst in a decarboxylation-coupling dimerization zone under decarboxylation-coupling dimerization conditions to yield a dimer ketone;
 - b) hydrocracking the dimer ketone with a hydrocracking catalyst in a hydrocracking zone under hydrocracking conditions to yield a mixture of paraffins comprising a heavy waxy oil component and a diesel fuel component; and
 - c) distilling the mixture to yield a heavy waxy oil and a diesel fuel.
2. The method of claim 1, wherein the fatty acid feed is derived from biomass.
3. The method of claim 1, wherein the fatty acid feed comprises at least 75 wt. % saturated fatty acids.
4. The method of claim 3, wherein the saturated fatty acids are selected from the group consisting of caproic acid, caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, arachidic acid, palm kernel oil acid, palm oil acid, coconut oil acid, soy bean oil acid, rape seed oil fatty acid, animal tallow derived fatty acids, and combinations thereof.
5. The method of claim 1, wherein the decarboxylation-coupling dimerization catalyst is selected from the group consisting of alumina, silica, silica-alumina, titania, zirconia, supported metal carbonates, supported metal hydroxides, and combinations thereof.
6. The method of claim 1, wherein the diesel fuel is a biofuel.
7. The method of claim 1, wherein the diesel fuel has a cetane index of at least 65.
8. The method of claim 1, further comprising hydroisomerization dewaxing the heavy waxy oil with a hydroisomerization dewaxing catalyst in a catalytic hydroisomerization dewaxing zone under hydroisomerization dewaxing conditions to yield a lubricating base oil.

9. The method of claim 8, wherein the hydroisomerization catalyst comprises a shape selective intermediate pore size molecular sieve, a noble metal hydrogenation component, and at least a refractory oxide support.
10. The method of claim 9, wherein the molecular sieve is selected from the group consisting of SAPO-11, SAPO-31, SAPO-41, SM-3, SM-7, ZSM-22, ZSM-23, ZSM-35, ZSM-48, ZSM-57, SSZ-32, ferrierite, and combinations thereof.
11. The method of claim 8, wherein the base oil has a viscosity index of at least 140.
12. The method of claim 8, wherein the base oil has a viscosity index of at least 170.
13. The method of claim 8, wherein the base oil is a Group III base oil.
14. The method of claim 8, further comprising a step of hydrofinishing the base oil.
15. A method comprising:
 - a) contacting a fatty acid feed with a decarboxylation-coupling dimerization catalyst in a decarboxylation-coupling dimerization zone under decarboxylation-coupling dimerization conditions to yield a dimer ketone; and
 - b) hydroisomerization dewaxing the dimer ketone with a hydroisomerization dewaxing catalyst in a catalytic hydroisomerization zone under hydroisomerization dewaxing conditions to yield a lubricating base oil.

1/1

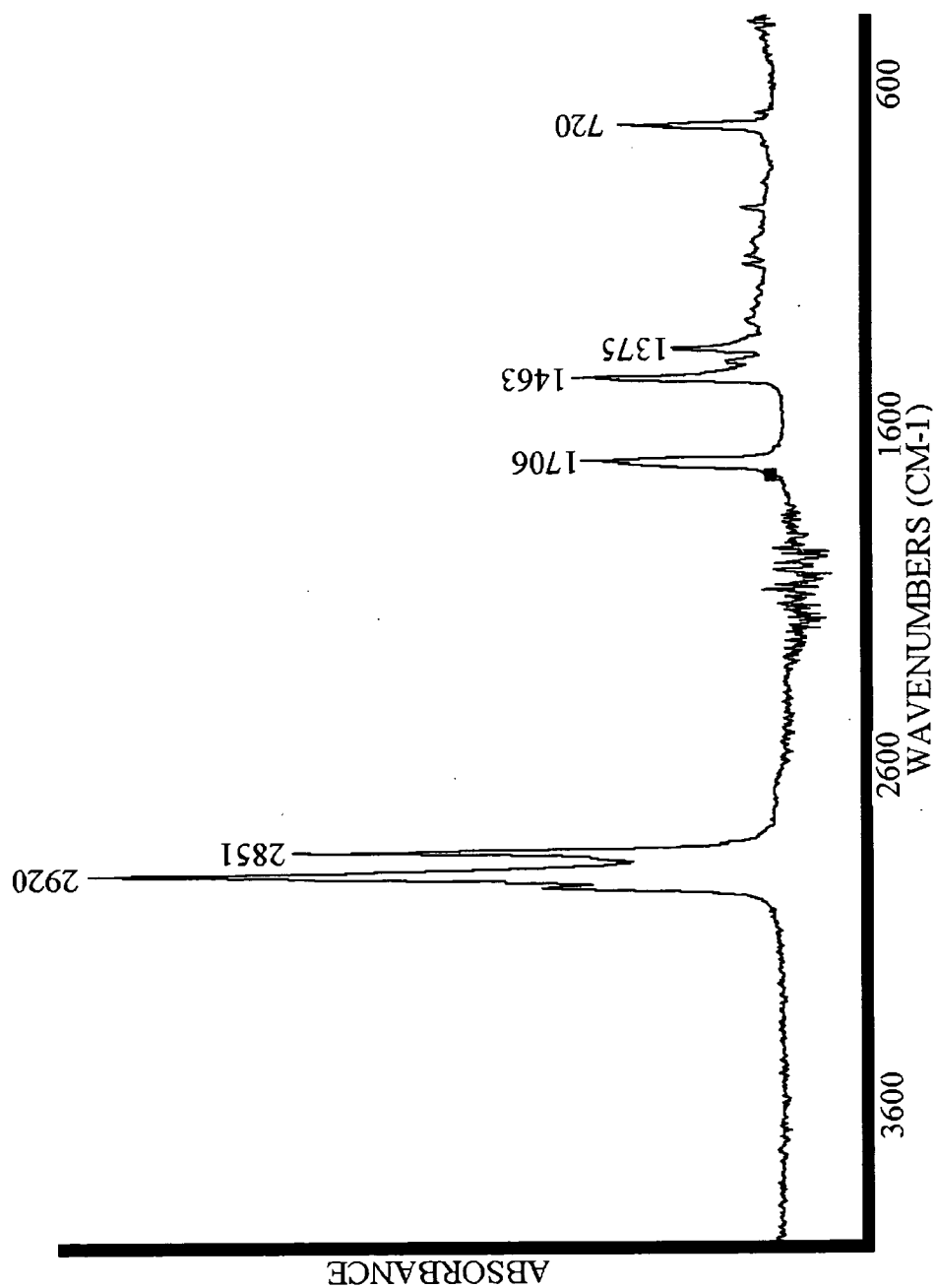


FIG. 1