EVEN CARBON NUMBER PARAFFIN COMPOSITION AND METHOD OF MANUFACTURING SAME

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0001] Not applicable.

CROSS-REFERENCE TO RELATED APPLICATIONS

[0002] Not applicable.

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0003] The present invention relates to producing specialty materials and chemical intermediates from bio-renewable feedstocks such as animal fats, plant oils, algal oils, bio-derived greases, and tall oil fatty acid (hereafter referred to as biological feedstocks, or alternatively, fatty acids and/or glycerides depending upon the composition of the feedstock). Specifically, the present invention relates to predominantly even carbon number paraffin compositions in the C12-C24 range, and the catalytic hydrogenation/hydrogenolysis method used for its manufacture.

[0004] Paraffins in the C12-C24 range have useful applications as phase change material (PCM). The paraffins undergo solid-liquid phase transition in the about -9 °C (15 °F) to about 50°C (120 °F). Heat is absorbed as the PCM paraffin melts and heat is released later when the PCM freezes. Fabricated systems that use PCM's as such are referred to as passive thermal storage devices. Due to relatively high latent heats of solid-liquid

phase transition (referred to simply as latent heats hereafter), as well as compatibility with common material of construction and high stability, paraffins are considered particularly well-suited for PCM applications. Wall boards of a house impregnated with a PCM are an example of a passive thermal storage device. During a hot day, the PCM will absorb heat as it melts. Since there is no temperature change during phase transition, the surface in contact with the thermal storage device stays at constant temperature until all PCM therein has melted. The heat that would have made the house hot has thus been stored in the molten PCM. At night, as the temperatures get cooler, the molten PCM freezes and releases the heat thus preventing the home from getting cold. The melting-freezing cycles moderate the temperature of the space enclosed within the passive thermal storage device despite extreme night-day temperature swings outside. In general, PCMs are an effective way of storing thermal energy (e.g. solar, off-peak electricity, industrial waste heat), and reducing energy demand (e.g. for heating and air-conditioning).

[0005] The thermal storage capacity of the PCM is dictated by its latent heat. The higher the latent heat, the higher the thermal storage capacity of the PCM, and the smaller the required thermal storage device size/cost.

[0006] Table 1 provides the latent heats and melting points of paraffins. As observed therein, the latent heat for even carbon number paraffins is higher than the latent heat for odd carbon number paraffins of similar

transition temperature. For example, n-heptadecane (carbon number 17) and n-octadecane (carbon number 18) melt in the 22 – 28 °C range. Whereas the latent heat of n-heptadecane is 215 kJ/kg and the latent heat for n-octadecane is 245 kJ/kg or 14% higher. In general, the even carbon number paraffin heats of fusion in the C14-C24 range are 10-16% higher than odd carbon number paraffins.

Table 1. Latent Heats and Solid-Liquid Transition Temperatures of Selected Paraffins

Name	Carbon Number	Melting Point (°C)	Latent Heat (kJ/kg)
n-Tetradecane	14	4.5 – 5.6	231
n-Pentadecane	15	10	207
n-Hexadecane	16	18.2	238
n-Heptadecane	17	22	215
n-Octadecane	18	28.2	245
n-Nonadecane	19	31.9	222
n-Eicosane	20	37	247
n-Heneicosane	21	41	215
n-Docosane	22	44	249
n-Tricosane	23	47	234
n-Tetracosane	24	51	255

[0007] In addition to PCM applications, even carbon number C12-C24 paraffins are also used as chemical intermediates for linear alkyl benzene (C12, C14) and alkyenyl succinate (C16, C18), as well as lubricant/wax additives.

2. Brief Description of the Related Art

[0008] The commercially practiced synthesis of even carbon number n-paraffins involves ethylene oligomerization. Depending on the catalyst and reactor operating conditions, this process produces a distribution of linear alpha olefins in the C4 to C20+ range. Linear alpha olefins in the C4-C8 range are the main products of this process and are separated. These olefins are in high demand, mainly as comonomers for film-grade polyethylene. The C10+ even carbon number olefins are sold as intermediates for specialty chemicals, or hydrogenated to produce even carbon number n-paraffins.

[0009] This ethylene oligomerization process for producing even carbon number paraffins is highly dependent on crude oil and natural gas prices. Furthermore, n-paraffins have to be sold at a premium to the olefins to justify the added cost of hydrogenating. These factors make the price and availability of n-paraffins thus produced highly variable.

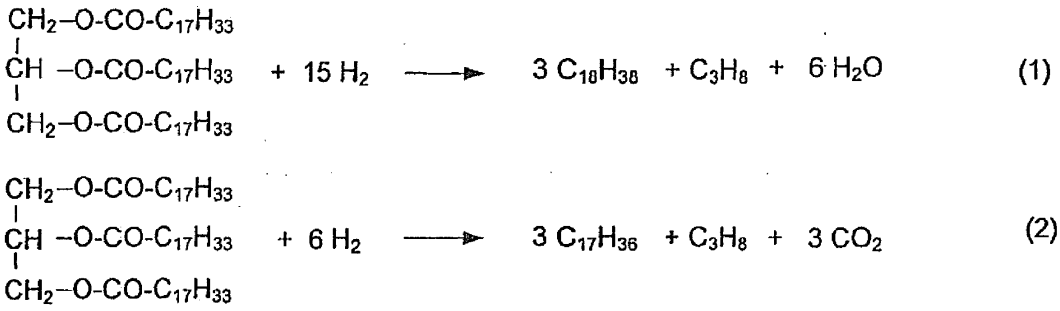
[0010] Another method of producing n-paraffins is Fischer-Tropsch synthesis. The liquid product of this reaction is a broad distribution of even and odd carbon number paraffins, from C5 to C50+.

[0011] Naturally occurring fatty acids and esters may be hydrotreated to produce a hydrocarbon composition including even and odd carbon number paraffins as reported in prior art, namely: Wong, et. al. "Technical and Economic Aspects of Manufacturing Cetane-Enhanced Diesel Fuel from Canola Oil"; Bio-Oils Symposium, Saskatoon, Saskatchewan, Canada; March

1994. Figure 2 of Wong et. al. includes typical gas chromatography/mass spectrometry (GC/MS) trace of hydrotreated canola oil wherein the relative heights of even and odd carbon number paraffins are similar, indicating presence of comparable concentrations of each. The prior art method for converting triglycerides and fatty acids to paraffins employs a fixed-bed catalytic reactor, packed with commercially available hydrotreating catalysts. These catalysts are cylindrical or three-fluted extrudates of alumina with nickel molybdenum or cobalt molybdenum sulfided metal activity. The typical equivalent diameter of these catalysts is from about 1.5 mm to about 2.0 mm.

[0012] The equivalent diameter is used to characterize non-spherical particles by size. Equivalent particle diameter of a non-spherical particle is defined as the diameter of a sphere having the same volume as the non-spherical particle. For a cylindrical catalyst of diameter D and length L, the equivalent particle diameter D_p is expressed as $D_p = 6\ (4/L + 4/D)^{-1}$. For a three-fluted extrudate, the equivalent particle diameter expression is $D_p = 6\ [2/L + 5\pi/(D(\sin(60^\circ)+1.25\pi)]^{-1}$.

[0013] The fatty acid/glyceride feed is hydrogenated and deoxygenated in the fixed bed reactor packed with commercial hydrotreating catalysts. As illustrated by Equations 1 and 2 for the example of triolein (oleic acid triglyceride), the deoxygenation is achieved by oxygen hydrogenolysis, decarboxylation (removal of CO2), and decarbonylation (loss of CO).



(1)

(2)

[0014] In both reactions, the glycerol backbone is converted to propane and double bonds are saturated. Since one carbon is removed from the fatty acids during decarboxylation and decarbonylation reactions (as illustrated in Equation 2), odd carbon number paraffins are formed from even carbon number naturally occurring fatty acids.

[0015] To this end, there is a need for even carbon number paraffin compositions and a selective process for producing even carbon number paraffins. In particular, the present invention is a process for converting biological feedstocks into even carbon number paraffin compositions.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] Fig. 1 is a schematic diagram of an embodiment of an operation of a continuous process in accordance with the present invention.

[0017] Fig. 2 is a schematic diagram of an embodiment of an operation of a series-reactor process in accordance with the present invention.

[0018] Fig. 3 is a schematic diagram of an alternative embodiment of an operation of a series-reactor process in accordance with the present invention.

[0019] Fig. 4 is a schematic diagram of an embodiment of an operation of a batch process in accordance with the present invention.

[0020] Fig. 5 is a bar graph summarizing the results of Example 1.

[0021] Fig. 6 is a bar graph summarizing the results of Example 2.

[0022] Fig. 7 is a McCabe-Thiele diagram for C16-C18 paraffin separation.

DETAILED DESCRIPTION OF THE INVENTION

[0023] The present invention relates to even carbon number paraffin compositions and a method for producing such even carbon number paraffin compositions from biological feedstocks. Paraffin compositions of the present invention have superior properties as phase PCM material.

[0024] It has been discovered that hydrocarbon compositions with very high concentrations of even carbon number paraffins can be obtained from biological feedstocks. The products are produced by a single-step hydrogenation/hydrogenolysis process of biological feedstocks. One embodiment of the process is carried out using a bimetallic catalyst of about 10 to about 500 micron equivalent particle diameter. The shorter diffusion path length, more accessible pores, and lower intra-catalyst temperature gradients in the smaller catalyst system of the present invention reduce

thermal decarboxylation and consequent co-production of odd number paraffins.

[0025] One embodiment of the process of the present invention is preferably carried out with the catalyst in the slurry phase. Commercially available catalyst extrudates may be ground and sieved to reduce the catalyst size to the preferred range of the present invention, from about 10 microns to about 400 microns, most preferably from about 30 microns to about 80 microns. Examples of the catalyst include but are not limited to nickel-molybdenum (NiMo), cobalt-molybdenum (CoMo), or nickel-tungsten (NiW) on alumina or alumina phosphate supports. Pre-ground catalyst extrudates are commercially available in both oxide and active sulfide forms. The metal oxide catalysts are activated by sulfiding.

[0026] Commercial bimetallic catalysts are also available as slurry grades and well-suited for the invention disclosed herein. Preferred examples include sponge metal catalysts such as Mo promoted Raney® Ni and Co (Raney® is the trade name of the Grace Davison sponge metal catalyst). Sponge metal catalysts are formed by leaching nickel-aluminum or cobalt-aluminum alloys with concentrated caustic (sodium hydroxide) solution to form hydrogen active metal of high surface area. These slurry catalysts are active as received, but may be sulfided to achieve the desired selectivity.

[0027] Supported slurry catalysts suitable for the process of this invention may be prepared by impregnating spray-dried alumina or modified alumina supports with solutions containing nickel, cobalt, molybdenum and/or tungsten compounds before calcining.

[0028] It should be understood by one of ordinary skill in the art that any such catalyst may be utilized in the present invention so long as the catalyst operates as described herein.

[0029] Referring now to the drawings and more particular to Fig. 1, shown therein is one embodiment of an operation of a process utilizing a continuous flow reactor constructed in accordance with the present invention. A biological feedstock 101 is pressurized to reactor pressure of about 200 psig to about 2,000 psig via pump 102. Preferred operating pressures for the slurry bubble column reactor are from about 400 to about 1,000 psig. The feed 101 comprises of vegetable oils, animal fats/greases, plant oils, tall oil fatty acid, and algal oils. Algal oils can be naturally occurring or produced in bioreactors. Pressurized liquid stream 103 enters a reactor 104.

[0030] The slurry reactor 104 is preferably a bubble column. The reactor catalyst loading is between about 1% and about 30% (dry bulk catalyst volume per total slurry volume), preferably between about 2% and about 20%. The catalyst particle size is from about 10 to about 400 microns, preferably from about 30 to about 80 microns. The throughput of

the pressurized biological feed stock, 103, is between about 0.1 and about 10 LHSV (volume feed per volume catalyst per hour), preferably between about 0.5 and about 5 LHSV. These parameters set the slurry reactor 104 volume for the design feed rate.

[0031] The pressurized liquid stream 103 reacts therein with hydrogen 105 which is optionally preheated through heater 116. The hydrogen-rich gas 105 preferably has a hydrogen concentration between 70 and 100 mol %, preferably between 80 and 99 mol %. The hydrogen-rich gas 105 is supplied at a rate of about 3,000 to about 10,000 SCF/bbl (volume gas per volume biological feedstock). The gas to feedstock ratio is preferably from about 4,000 SCF/bbl to about 8,000 SCF/bbl. The diameter of bubble column reactor vessel 104 is selected such that the gas flow rate is in the churn-turbulent regime from about 7 cm/s to about 40 cm/s, preferably from about 8 cm/s to about 12 cm/s. A heated hydrogen-rich gas 105A is dispersed through a sparger 119. The sparger may be of various configurations including but not limited to a ring-type sparger with multiple orifices, a sintered metal plate or sintered metal distributing pipe(s) or co-fed with the biological feedstock via a simple pipe distributor. In some embodiments the catalyst is dispersed in the slurry phase by mechanical agitation. The gas flow through the reactor 104 produces a uniform catalyst slurry 106. Alternatively, a side arm/downcomer (not shown) can also be deployed to recirculate de-gassed slurry to the reactor 104 which also aides

catalyst distribution in the reactor 104. The biological feedstock converts into mainly even carbon number paraffins as it is diluted within the catalyst-paraffin slurry 106.

[0032] The heat of reaction is in part removed by evaporation of a boiler feed water 117 in cooling tubes/coils 120, producing steam 118. At the hydrodynamic regimes described herein, high heat removal may be achieved with cooling coil device 120 immersed in the reactor 104. Typical heat transfer coefficient for a steam-generating cooling coil is in the 40 to 200 Btu/hr-ft^2-°F range. The reactor temperature is thus controlled between about 450 °F (232 °C) to about 750 °F (399 °C), preferably between about 600 °F (315 °C) and about 650 °F (343 °C). At these preferred temperatures, high pressure steam (greater than about 400 psig, and preferably greater than about 600 psig) may be produced and used for driving motors, generating electricity, and/or supplying process heat.

[0033] The extent of back-mixing within the bubble column depends to a large extent on the height-to-diameter ratio of the reactor. Typical columns have successfully been modeled as 1.1 -1.9 ideal CSTR's in series. At the preferred reactor design conditions, the reactor liquid composition is mainly the paraffin, and the temperature very close to uniform.

[0034] The vapor product 107 from bubble column reactor 104 is cooled in air cooler 108 wherein byproduct water and light hydrocarbons condense. At operating pressures below 500 psig and temperatures above about 315 °C

(600 °F), more than about 50% of the $C18^-$ paraffin reaction product will vaporize and is condensed overhead with water and light hydrocarbons.

[0035] A three phase composition 109 is separated in separator drum 110. The water stream 111B and hydrocarbon 111A are thus separated from recycle hydrogen-rich gas 111C. In some embodiments, the hydrogen-rich gas 111C may be purified to remove some or all of the minor reaction byproducts such as ammonia, hydrogen sulfide, and carbon oxides. Recycle hydrogen-rich gas may then be combined with makeup hydrogen to form the reactor hydrogen-rich gas 105.

[0036] The slurry 106 is transported through conduit 112 to filter 113 to separate the catalyst from the reactor product. In some embodiments filter 113 is a cross-flow filter. In other embodiments, a hydrocyclone followed by a filter is used. It should be understood by one of ordinary skill in the art that any device capable of separating suspended solids from liquid may be used in the present invention. The catalyst slurry concentrate stream 114 returns to reactor 104, while the filtered paraffin product 115 exits the reactor system. Product streams 115 and 111B include equal to or greater than about 75 wt % even carbon number paraffins in the C12-C24 range. Preferably, the product streams comprise of equal to or greater than about 80 wt % even carbon number paraffins. In some embodiments, the product stream may undergo further processing such as distillation to recover the even carbon number paraffin products.

[0037] In other embodiments of the present invention, a plurality of reactors are employed to divide the hydrogenation/hydrogenolysis load over two or more reactors. Those skilled in the art will recognize that the reactors-in-series configuration is used in back-mixed reactor systems to achieve higher conversion at same or lower total reactor volume.

[0038] Referring now to Figure 2, biological feedstock 201 is pressurized to the reactor system pressure in pump 202. The reactor system pressures are in the same range previously specified herein. The reactor system further contains catalyst of type and size specified in the detailed description of the invention. The pressurized feed 203 is optionally heated in heater 240. The preheated feed 203A enters the first stage reactor 204 wherein partial conversion occurs in the catalyst slurry phase. Hydrogen-rich gas 205 is introduced into slurry bubble column reactor 204 through a sparger device (not shown) at the rates previously specified herein. Reactor 204 is equipped with cooling coils 210 to maintain the reactor at the desired temperature range previously specified. The extent of feed conversion in reactor 204 is about 10% to about 90%, preferably about 30% to about 60%. Stream 206, the partially converted product including paraffin, biological feedstock, and reaction intermediates such as fatty alcohols, fatty acids, and olefins, is filtered through filter 207 to separate the catalyst. The catalyst rich slurry 209 is returned to the reactor 204 while the filtered, partially converted product 208 flows to second stage reactor 211.

[0039] Typically, a reactor 211 operates under the same temperature and gas-to-oil ratio as the reactor 204. In some embodiments the reactor 211 operates at a higher temperature than the reactor 204. In some embodiments, the pressure in reactors 211 and 239 are lower than the reactor 204 to facilitate filtrate flow from the reactor 204 to the reactor 211, and from the reactor 211 to the reactor 239. After undergoing reaction with hydrogen provided by gas stream 212, a partially converted slurry 213 undergoes solid-liquid separation in a filter 214. A catalyst rich slurry 216 is returned to the reactor 211 while the partially converted stream 215 is transferred to the reactor 239. The total extent of feed conversion in the reactor 211 is about 30% to about 95%, preferably between about 50% and about 80%.

[0040] Hydrogen is supplied to the reactor 239 from the gas stream 217. The total feed conversion achieved in this slurry bubble column reactor is between about 80% and about 100%, preferably at or very near about 100% feed conversion. The temperature, pressure, and gas-to-oil ratio are in the same range described previously. However in some embodiments, the reactor 239 is operated at a higher temperature than the reactors 204 and 211. A paraffin-catalyst slurry stream 218 is filtered in a filter 219 to supply a product stream 221 and returning high-solids slurry stream 220 to the reactor 239. The product 221 includes equal to or greater than about 75 wt % even carbon number paraffins in the C12-C24 range. Preferably, the

product stream 221 comprises of equal to or greater than about 80 wt % even carbon number paraffins in the C12-C24 range.

[0041] The off gas from the three slurry bubble column reactors in series, streams 222, 223 and 224, are combined to form a vapor stream 225. The vapor stream 225 is cooled in a condenser 226 to a temperature from about 60°F (15.5 °C) to about 160°F (71 °C), preferably from about 80°F (27 °C) to about 140 °F (60 °C). A three phase stream 227 enters drum 228 where the stream 227 is separated into a water phase 229, a light hydrocarbon phase 230 and a gas phase 231. The gas phase 231 is rich in hydrogen. The other components of the gas phase 231 include propane, other light hydrocarbons, and minor byproducts described previously. The hydrogen-rich gas stream may be partially purged (stream 232) with the rest recycled as stream 233. The aforementioned impurities may be removed in a hydrogen purification unit 234. The hydrogen purification unit 234 is typically a scrubber used to remove ammonia and hydrogen sulfide. A purified hydrogen-rich stream 235 is then combined with makeup hydrogen 238 in recycle compressor 236. A recompressed hydrogen-rich gas 237 is used to supply each of the slurry bubble column reactors.

[0042] In an alternative embodiment of an operation of a reactors-in-series process of the present invention, a slurry bubble column reactor containing catalyst of the type and size previously described herein may be followed by a fixed-bed reactor. Referring to Fig. 3, the biological feedstock

251 is pressurized by pump 252 to the reactor system pressure previously specified herein. The pressurized biological feedstock is heated by the reactor feed-effluent exchanger 254. A heated stream 255 enters a slurry bubble column reactor 257 where a catalyst of the type and size-range previously described herein is suspended in the slurry phase by sparging of hydrogen-rich gas 258. Reactor 257 is equipped with cooling coils 256 to control the temperature at target value within the range previously specified herein. A partially converted effluent slurry 259 is processed through filter 260. A catalyst rich slurry 262 is returned to the reactor 257 while a filtered partially converted product 261 is transferred to a fixed-bed reactor 264 for achieving full conversion. Before entering the reactor 264, the liquid feed is mixed with optionally preheated hydrogen 286. A combined feed 263 trickles through the fixed-bed reactor 264 wherein the partially converted feedstock and reaction intermediates are fully converted to a predominately even carbon number paraffin composition. The fixed-bed reactor 264 is operated adiabatically and the temperature is allowed to rise within the preferred range previously specified herein. A reactor effluent 265 is partially cooled in exchanger 254. A partially cooled product 266 enters high pressure separator 267 wherein the hydrogen-rich vapor stream 270 is separated from a mainly even carbon number paraffinic liquid product 268. The liquid product 268 may be further processed through distillation to

recover the desired even carbon number paraffin composition previously specified herein.

[0043] The hydrogen-rich gas streams 270 and 269, from the high pressure separator 267 and the slurry bubble column reactor 257 respectively, are combined to form vapor stream 271. Water 271A is added to vapor stream 271 to wash any deposits that may form upon condensation in a condenser 272. A cooled stream 273 is a three phase composition which is separated in drum 274. The liquid fractions include byproduct water 275 and light hydrocarbons 276. A hydrogen-rich gas 277 is partially purged as stream 278. The rest of the gas, stream 279 is optionally treated in purification unit 290 to remove ammonia, hydrogen sulfide, and other byproducts of the hydrogenation/hydrogenolysis reaction. A purified hydrogen-rich gas 280 is combined with makeup hydrogen 282 in recycle compressor 281. A recompressed hydrogen-rich gas 283 is optionally heated in heater 284 before supplying the slurry bubble column 257 and the fixed-bed reactor 264.

[0044] The slurry catalyst reaction may also be conducted in batch mode. This may be a preferable embodiment when large volume production is not sought, or when the paraffin products from different feed stocks need to be segregated.

[0045] Referring to Fig. 4, a biological feedstock 301 is charged to a batch stirred reactor 302. The reactor 302 is equipped with an agitator

assembly 303 for suspending solids and dispersing gas, and a jacket 304 for heat transfer. A slurry catalyst 306 is then added to the reactor 302. The catalyst is of the type and size-range previously described herein. The reactor is then purged and pressurized with hydrogen 307 to the target operating pressure. Pressure ranges described previously for the continuous flow reactor embodiments are applicable to the batch reactor embodiment as well. These preferred pressures are from about 400 psig to about 1,000 psig.

[0046] The reactor 302 is then heated to a target operating temperature in the range previously described for the continuous reactor embodiments, preferably between 450 °F (232 °C) and 650 °F (343 °C). The operating temperatures may be achieved by circulation of a heat transfer fluid 308 through the reactor jacket 304. Once at target temperature, the heat transfer fluid 308 is used for cooling. The hydrogen 307 supply rate is used to limit the release of reaction heat through a temperature control loop 309. In some embodiments, the hydrogen flow rate is maintained constant and the reactor pressure is controlled through a back pressure control loop 310, while temperature is controlled through circulation rate of the heat transfer fluid. In some embodiments, reactor 302 is equipped with a cooling coil (not shown) to increase heat removal and shorten batch cycle.

[0047] The batch reactor is equipped with piping 312, 312A, and condenser 318. Condensable byproducts of the hydrogenation/

hydrogenolysis reaction which occurred in reactor 302, light hydrocarbons and water, are thus collected in drum 314 after cool-down with coolant 316 in condenser 318. Upon completion of the reaction, when no more H2 consumption is observed, the reactor 302 is cooled to about 140°F (60 °C) to about 160 °F (71 °C) and the products and byproducts are drained out through conduits 320 (water, followed by light hydrocarbons) and 322 (main paraffin product). Most of the catalyst settles to the bottom of reactor 302 after agitation has been turned off, for reuse in the next batch. The suspended catalyst fines are removed from the n-paraffin product through filter 324. Sintered metal or cartridge elements may be used for catalyst filter 324. A filtered product 326 has the same even carbon number paraffin composition previously described in the continuous flow reactor embodiments of the present invention.

[0048] In order to further illustrate the present invention, the following examples are given. However, it is to be understood that the examples are for illustrative purposes and are not to be construed as limiting the scope of the subject invention.

EXAMPLES

[0049] Example 1 – Hydrogenation/hydrogenolysis of canola oil with 1/16" trilobe catalyst extrudates ($D_p \sim 1.2$ mm) in a fixed-bed reactor

[0050] The present example demonstrates the conversion of a biological feedstock, canola oils, into paraffinic compositions using standard-size

catalyst extrudates. A 100 cc isothermal tubular reactor was filled with 80 cc of a commercially available NiMo catalyst (purchased from Catalyst Trading Corporation, Houston, TX) of 1.2 mm equivalent particle diameter, and 70-100 mesh glass beads. The catalyst was sulfided in the presence of hydrogen with dimethyl disulfide at two hold temperatures: 6 hours at 400°F and 12 hrs at 650°F. Hydrogen sulfide break-through was confirmed before the temperature was raised from 400 °F (204 °C) to 650 °F (343 °C) at 50 °F/hr. After sulfiding, the reactor was cooled to 400 °F (204°C).

[0051] Next a fatty triglyceride feed was introduced to the isothermal reactor. The reactor was slowly heated to 650°F to achieve full conversion of the triglyceride feed to a paraffin composition. The reactor temperature was further increased to 700°F (371 °C) to maintain good catalyst activity at 80 cc/hr feed rate (1.0 hr^{-1} LHSV). Canola oil feedstock was then introduced at these reactor conditions.

[0052] The product was analyzed using a gas chromatography (GC) method involving calibration with n-paraffin standards. The results of feed conversion to paraffins are summarized in Fig. 5. As observed therein, a significant percent of C17 paraffins was produced from decarbonylation/ decarboxylation of C18 fatty acids. The overall concentration of even carbon number paraffins was only 61 wt %.

[0053] Example 2 - Hydrogenation/hydrogenolysis of canola oil with crushed and sieved catalyst (D_p = 30-80 micron) in slurry reactor

The catalyst used in Example 1 was discharged from the reactor, crushed, and sieved into a 30-80 micron particle-size cut. Ten (10) grams of the 30-80 micron cut of the ground catalyst was combined with 300 g of canola oil in a 1 liter Autoclave stirred-reactor. The agitation was set at 1000 rpm. The reactor was purged with N2 before starting H2 flow at 3 L/min. The reactor was controlled at 500 psig pressure. The temperature was ramped at 1 °F/min to hold temperatures of 450 °F (232 °C), 500 °F (260 °C), 550 °F (288 °C), and 600 °F (316 °C). Liquid samples were obtained at each hold temperature and analyzed by GC. The hold times were 20 hrs at 450 °F (232 °C), 5 hrs at 500 °F (260 °C), 23 hrs at 550 °F (288 °C), and 19 hrs at 600 °F (316 °C).

The results of the slurry catalyst conversion reaction are summarized in Figure 6. It is thus observed that most of the C18 and C16 fatty acids in the canola oil were converted to C18 and C16 paraffins, suggesting a high selectivity for the oxygen hydrogenolysis mechanism and low decarboxylation/decarbonylation. The overall concentration of even carbon number paraffins was 80 wt %.

[0054] Example 3 - Even Carbon Number Paraffin Composition from Rapeseed Oil

[0055] Rapeseed oil was the third largest source of vegetable oil in the world (USDA year 2000 statistics), behind palm and soybean oils. The oil yield from rapeseed is 40-50%, compared to only 20 percent for soybeans.

Table 2 summarizes the fatty acid profile of representative biological feedstocks.

Table 2. Fatty Acid Composition of Several Common Biological Feedstocks [1-5]

	Saturated Acids							Mono-Unsaturated Acids			Poly-Unsaturated Acids	
	Caprylic	Capric	Lauric	Myristic	Palmitic	Stearic	Eicosenic/ Behenic	Palmeic	Oleic	Eicosenic/ Behenoic	Linoleic	Linolenic
	C8:0	C10:0	C12:0	C14:0	C16:0	C18:0	C20:0/C22:0	C16:1	C18:1	C20:1/C22:1	C18:2	C18:3
	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
Animal fats												
Chicken Fat	-	-	-	-	7	2	-	-	69	-	17	-
Beef Tallow	-	-	0.2	2-3	24-30	21-26	0.4-1	-	39-43	0.3	2-3	1
Yellow Grease	-	3	3	1-11	23-27	10-12	-	1	29-50	-	2-16	1
Choice White Grease	-	7	3	9	25	12	-	-	27	-	1-3	1
Lard (pork fat)	-	-	-	1-2	25-30	12-18	-	2-5	41-51	2-3	4-22	0.2
Vegetable Oils												
Soybean Oil	-	-	-	0.3	7-11	3-6	6-10	0-1	22-34	-	50-60	2-10
Corn Oil	-	-	-	0-2	8-11	1-4	-	1-2	28-50	0-2	34-58	1
Cottonseed Oil	-	-	-	0-3	17-23	1-3	-	-	23-41	2-3	34-55	1
Canola Oil	-	-	-	-	4	2	-	-	62	-	22	10
Coconut Oil	5-9	4-10	44-51	13-18	7-10	1-4	-	-	5-8	-	1-3	-
Sunflower Oil	-	-	-	-	6-7	4-5	1-4	-	19		68-69	0.3-1
Palm Oil	-	-	-	1-6	32-47	1-6	-	-	40-52	-	2-11	-
Palm Kernel Oil	2-4	3-7	46-52	14-19	6-9	1-3	1-2	0-1	10-18	-	1-2	-
Rapeseed (High Eurcic)	-	-	-	-	2-5	1-2	0.9	0.2	10-15	50-60	10-20	5-10

(1) http://www.scientificpsychic.com/fitness/fattyacids.html
(2) Kinast, J.A. March 2003, "Production of Biodiesel from Multiple Feedstocks and Properties of Biodiesel/Diesel Blends, NREL/AR-510-31460
(3) Tyson, K.S., NREL Presentation "Biodiesel for New England" March 26, 2003
(4) Food Fats and Oils, Institute of Shortening and Edible Oils, Ninth Edition 2006
(5) a "-" in a cell means that this constituent is not present

[0056] As observed therein, rapeseed oil consists of 50-60 wt % C22 fatty acids with the balance mainly C18 fatty acids. According to the inventive conversion process disclosed herein, rapeseed oil will produce an even carbon number composition comprising of a ratio of about 1:1 to 1.5:1 C22:C18 n-paraffins. This composition is useful as a PCM in construction or textile/clothing application for high temperatures, including desert climates when day times can surpass 44 °C (melt point of C22 paraffin), and night times below 28 °C (freeze point of C18 paraffin). The high temperature phase transition makes this PCM composition well suited for computer cooling applications (i.e. heat sink or cooling pad under the computer) as well.

[0057] Example 4 – Even Carbon Number Paraffin Compositions from Palm Oil and Palm Kernel Oil

[0058] Palm oil recently surpassed soybean oil as the largest volume plant oil produced in the world. Whereas palm oil itself is derived from the fruit of the palm tree, the palm kernel oil is extracted from the fruit's seeds. Referring to Table 2, palm oil consists of about 40 wt % C16 fatty acids, with the balance mainly C18 fatty acids. According to the method of the present invention, the palm oil is converted to a mainly even carbon number paraffin composition in the C16-C18 range with C18:C16 weight ratio of about 1.5:1. The composition is useful as a PCM for construction and textile/clothing applications in the 18 °C to 28 °C range.

[0059] Referring to Table 2, palm kernel oil has a fatty acid composition of about 45-52 wt % C12, 14-19 wt % C14, 6-9 wt % C16, and 11-17 wt % C18. According to the present invention, the biological feedstock is converted to a mainly even carbon number n-paraffin composition including C12, C14, C16, and C18 components. The n-paraffin composition may be distilled to yield a C12/C14 composition suitable for very low temperature PCM applications (such as for bridge warmers and dive suites) or as chemical intermediates (such as for producing linear alkyl benzenes).

[0060] Example 5 – Separation of even carbon number paraffins derived from the method of the present invention

[0061] The method of the present invention may be used to convert most animal fats into a composition with approximately 30 mol % C16 n-paraffins and the balance mainly C18 paraffin. Vacuum distillation is a well understood and broadly practiced separation technology. At 20 torr pressure, the vapor-liquid equilibrium (VLE) constants ("K-values") for n-octadecane and n-hexadecane are 1.34 and 0.82 respectively (computed using HYSYS simulation software's Peng-Robinson thermodynamic model). These K-values may be used to generate the equilibrium curve of Fig. 7. Distillation column operating lines have been added according to the McCabe-Thiele methodology as disclosed in prior art, namely, Foust et. al. *Principles of Unit Operations,* 2nd Ed.; John Wiley & Sons: New York, 1980; Chapter 7. According to McCabe-Thiele procedure for distillation column design, with a reflux ratio of 6.5, or 30% higher than minimum reflux, a separation yielding 90 mol % purity C18 and C16 n-paraffin products requires 14.5 theoretical stages. Assuming 73% tray efficiency, the vacuum tower requires 20 actual trays.

[0062] While the C18 product of the separation can be sold as a PCM for narrow temperature control applications, the C16 n-paraffin (n-hexadecane or cetane) has other markets. One large volume application is diesel fuel additive. Another use of linear C16 hydrocarbons is as intermediates for specialty chemicals including alkenyl succinates for paper coatings.

[0063] The analysis of this example shows that the even carbon number compositions of the present invention, such as those derived from animal fats/greases, are well suited for producing chemicals using conventional separation techniques.

[0064] While the compositions and methods of this invention have been described in terms of preferred embodiments, it will be apparent to those of skill in the art that variations may be applied to the process described herein without departing from the concept and scope of the invention. All such similar substitutes and modifications apparent to those skilled in the art are deemed to be within the scope and concept of the invention as it is set out in the following claims.

What is claimed is:

1. A composition comprising paraffins falling in the C_{12}-C_{24} range, wherein:

the composition is undistilled;

at least 75 wt % of the composition comprises even carbon number paraffins;

the paraffins and the even carbon number paraffins are produced from a renewable biological feedstock by a process comprising hydrogenation and hydrogenolysis; and

the even carbon number paraffins comprise n-dodecane and n-tetradecane.

2. The composition of claim 1, wherein the even carbon number paraffins further comprise n-hexadecane and n-octadecane.

3. The composition of claim 1, wherein at least 80 wt % of the composition is even carbon number paraffins.

4. The composition of claim 1, wherein the renewable biological feedstock is selected from the group consisting of vegetable oils, plant oils, algal oils, animal fats, tall oil fatty acid, products of the food industry, and a combination of any two or more thereof.

5. The composition of claim 1, wherein the renewable biological feedstock is selected from the groups consisting of soybean oil, corn oil, cottonseed oil, canola oil, coconut oil, sunflower oil, palm oil, palm kernel oil, rapeseed oil, and a

combination of any two or more thereof.

6. The composition of claim 1, wherein the renewable biological feedstock is selected from the group consisting of soybean oil, canola oil, palm oil, palm kernel oil, rapeseed oil, and a combination of any two or more thereof.

7. The composition of claim 1, wherein the renewable biological feedstock comprises palm oil.

8. A diesel fuel comprising the composition of claim 1.

9. A diesel fuel comprising the composition of claim 2.

10. A diesel fuel comprising the composition of claim 3.

11. A diesel fuel comprising the composition of claim 4.

12. A diesel fuel comprising the composition of claim 5.

13. A diesel fuel comprising the composition of claim 6.

14. A diesel fuel comprising the composition of claim 7.

15. A composition comprising paraffins falling in the C_{12}-C_{24} range, wherein:

the composition is undistilled;

at least 80 wt % of the composition comprises even carbon number paraffins;

the paraffins and the even carbon number paraffins are produced from a renewable biological feedstock by a process comprising hydrogenation and hydrogenolysis over a bimetallic catalyst; and

the even carbon number paraffins comprise n-hexadecane and n-octadecane.

16. The composition of claim 15, wherein the even carbon number paraffins further comprise n-dodecane and n-tetradecane.

17. The composition of claim 15, wherein the renewable biological feedstock is selected from the group consisting of vegetable oils, plant oils, algal oils, animal fats, tall oil fatty acid, products of the food industry, and a combination of any two or more thereof.

18. The composition of claim 15, wherein the renewable biological feedstock is selected from the groups consisting of soybean oil, corn oil, cottonseed oil, canola oil, coconut oil, sunflower oil, palm oil, palm kernel oil, rapeseed oil, and a combination of any two or more thereof.

19. The composition of claim 15, wherein the renewable biological feedstock is selected from the group consisting of soybean oil, canola oil, palm oil, palm kernel oil, rapeseed oil, and a combination of any two or more thereof.

20. The composition of claim 15, wherein the renewable biological feedstock comprises palm oil.

21. A diesel fuel derived from the composition of claim 15.

22. A diesel fuel derived from the composition of claim 16.

EVEN CARBON NUMBER PARAFFIN COMPOSITION AND METHOD OF MANUFACTURING SAME

Abstract

Paraffin compositions including mainly even carbon number paraffins, and a method for manufacturing the same, is disclosed herein. In one embodiment, the method involves contacting naturally occurring fatty acid/glycerides with hydrogen in a slurry bubble column reactor containing bimetallic catalysts with equivalent particle diameters from about 10 to about 400 micron. The even carbon number compositions are particularly useful as phase change material.

[Fig. 7]