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(54) Title: PRODUCTION OF DIESEL FUEL FROM RENEWABLE FEEDSTOCKS CONTAINING PHOSPHORUS

(57) Abstract: A process has been developed for producing diesel fuel from renewable feedstocks such as plant oils, animal oils and greases. The process involves treating a renewable feedstock by hydrogenating and deoxygenating to provide a diesel boiling range fuel hydrocarbon product. If desired, the hydrocarbon product can be isomerized to improve cold flow properties. A portion of the hydrocarbon product is recycled to the reaction zone to increase the hydrocarbon content of the reaction mixture. The renewable feedstock comprises from 1 to 20 wt. ppm phosphorus measured as elemental phosphorus.

FIG. 1

(58) References Cited

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PRODUCTION OF DIESEL FUEL FROM RENEWABLE FEEDSTOCKS CONTAINING PHOSPHORUS

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims priority from Provisional Application Serial No. 61/076,605 filed June 27, 2008, the contents of which are hereby incorporated by reference in its entirety.

FIELD OF THE INVENTION

[0002] This invention relates to a process for producing diesel boiling range hydrocarbons useful as fuel from renewable feedstocks such as the glycerides and free fatty acids found in materials such as plant oils, animal oils, animal fats, and greases. The process involves hydrogenation, decarboxylation, decarbonylation, and/or hydrodeoxygenation and hydroisomerization in two or more steps. The process is operated with a volume ratio of recycle product to feedstock from 2:1 to 8:1. The process is operated at a total pressure of from 1379 kPa absolute (200 psia) to 4826 kPa absolute (700 psia). The renewable feedstock contains from 1 to 20 wt. ppm phosphorous.

BACKGROUND OF THE INVENTION

[0003] As the demand for diesel boiling range fuel increases worldwide there is increasing interest in sources other than petroleum crude oil for producing diesel fuel. One such source is what has been termed renewable sources. These renewable sources include, but are not limited to, plant oils such as corn, rapeseed, canola, soybean and algal oils, animal fats such as tallow, fish oils and various waste streams such as yellow and brown greases and sewage sludge. The common feature of these sources is that they are composed of glycerides and Free Fatty Acids (FFA). Both of these classes of compounds contain aliphatic carbon chains having from 8 to 24 carbon atoms. The aliphatic carbon chains in the glycerides or FFAs can be fully saturated or mono-, di-, or poly-unsaturated. Phosphorus is a common contaminant in these types of feedstocks.
[0004] There are reports in the art disclosing the production of hydrocarbons from oils. For example, US 4,300,009 discloses the use of crystalline aluminosilicate zeolites to convert plant oils such as corn oil to hydrocarbons such as gasoline and chemicals such as para-xylene. US 4,992,605 discloses the production of hydrocarbon products in the diesel boiling range by hydroprocessing vegetable oils such as canola or sunflower oil. Finally, US 2004/0230085 A1 discloses a process for treating a hydrocarbon component of biological origin by hydrodeoxygenation followed by isomerization.

[0005] Applicants have developed a process which comprises two or more steps to hydrogenate, decarboxylate, decarbonylate, and/or hydrodeoxygenate and then hydroisomerize the feedstock, and which can be successfully operated when the feedstock contains from 1 to 20 wt. ppm of phosphorus. Employing a volume ratio of recycle hydrocarbon to feedstock ranging from 2:1 to 8:1 additionally serves to dilute the phosphorus that is in the feedstock and also provides a mechanism to increase the hydrogen solubility in the reaction mixture sufficiently so that the operating pressure of the process may be lowered. The range of successful volume ratios of recycle to feedstock is based upon the desired hydrogen solubility in the reaction mixture. The reaction zone may be operated at a pressure in the range of 1379 kPa absolute (200 psia) to 4826 kPa absolute (700 psia).

SUMMARY OF THE INVENTION

[0006] The process is for producing a hydrocarbon fraction useful as a diesel boiling range fuel or fuel blending component from a renewable feedstock wherein the renewable feedstock comprises from 1 to 20 wt. ppm phosphorus. The process comprises treating the renewable feedstock, including the 1 to 20 wt. ppm phosphorus, in a reaction zone by hydrogenating and deoxygenating the renewable feedstock at reaction conditions to provide a reaction product comprising a hydrocarbon fraction comprising n-paraffins useful as a diesel boiling range fuel, or fuel blending component. A portion of hydrocarbon fraction is recycled to the reaction zone wherein the volume ratio of recycle to feedstock is in the range of 2:1 to 8:1. The hydrogenation and deoxygenation reaction product, without employing steps to remove phosphorus, is isomerized to provide an isomerized reaction product.
BRIEF DESCRIPTION OF THE DRAWINGS

[0007] FIG. 1 is a general flow scheme of one embodiment of the invention.
[0008] FIG. 2 is a more detailed flow scheme of one embodiment of the invention.

DETAILED DESCRIPTION OF THE INVENTION

[0009] As stated, the present invention relates to a process for producing a hydrocarbon stream useful as diesel boiling range fuel from renewable feedstocks such as those feedstocks originating from plants or animals. The term renewable feedstock is meant to include feedstocks other than those derived from petroleum crude oil. The renewable feedstocks that can be used in the present invention include any of those which comprise glycerides and free fatty acids (FFA). Most of the glycerides will be triglycerides, but monoglycerides and diglycerides may be present and processed as well. Examples of these renewable feedstocks include, but are not limited to, canola oil, corn oil, soy oils, rapeseed oil, soybean oil, colza oil, tall oil, sunflower oil, hempseed oil, olive oil, linseed oil, coconut oil, castor oil, peanut oil, palm oil, mustard oil, cottonseed oil, jatropha oil, tallow, yellow and brown greases, lard, train oil, fats in milk, fish oil, algal oil, sewage sludge, and the like. Additional examples of renewable feedstocks include non-edible vegetable oils from the group comprising Jatropha curcas (Ratanjoy, Wild Castor, Jangli Erandi), Madhuca indica (Mohuwa), Pongamia pinnata (Karanji Honge), and Azadiracta indica (Neem). The glycerides and FFAs of the typical vegetable or animal fat contain aliphatic carbon chains in their structure which have 8 to 24 carbon atoms, with a majority of the fats and oils containing a high concentration of 16 and 18 carbon atom chains. Mixtures or co-feeds of renewable feedstocks and petroleum derived hydrocarbons may also be used as the feedstock. Other feedstock components which may be used, especially as a co-feed component in combination with the above listed feedstocks, include, spent motor oils and industrial lubricants, used paraffin waxes, liquids derived from the gasification of coal, biomass, natural gas followed by a downstream liquefaction step such as Fischer-Tropsch technology (including pyrolysis oils), liquids derived from depolymerization, thermal or chemical, of waste plastics such as polypropylene, high density polyethylene, and low density polyethylene; and other synthetic oils generated as byproducts from petrochemical and chemical processes. Mixtures of the above feedstocks may also be used as co-feed components. One advantage of using a co-feed component is the transformation of may have
been considered to be a waste product from a petroleum based or other process into a valuable co-feed component to the current process.

[0010] Renewable feedstocks that can be used in the present invention may contain a variety of impurities. For example, tall oil is a by product of the wood processing industry and tall oil contains esters and rosin acids in addition to FFAs. Rosin acids are cyclic carboxylic acids. The renewable feedstocks may also contain contaminants such as alkali metals, e.g. sodium and potassium, phosphorous as well as solids, water and detergents. Phosphorus can be problematic as it may be present in the form of phospholipids which can form gums and plug the pre-heaters and reactors. An optional first step is to remove at least some of these contaminants. One possible pretreatment step involves contacting the renewable feedstock with an ion-exchange resin in a pretreatment zone at pretreatment conditions. The ion-exchange resin is an acidic ion exchange resin such as Amberlyst™-15 and can be used as a bed in a reactor through which the feedstock is flowed through, either upflow or downflow. Another possible means for removing contaminants is a mild acid wash. This is carried out by contacting the feedstock with an acid such as sulfuric, nitric or hydrochloric acid in a reactor. The acid and feedstock can be contacted either in a batch or continuous process. Contacting is done with a dilute acid solution usually at ambient temperature and atmospheric pressure. If the contacting is done in a continuous manner, it is usually done in a counter current manner. Yet another possible means of removing metal contaminants from the feedstock is through the use of guard beds which are well known in the art. These can include alumina guard beds either with or without demetallation catalysts such as nickel or cobalt. Filtration and solvent extraction techniques are other choices which may be employed. Hydroprocessing such as that described in USAN 11/770,826 is another pretreatment technique which may be employed.

[0011] However, pretreatment techniques add cost to the overall process and from an economic perspective, it is desirable to minimize their use. On the other hand, higher purity feedstocks that do not need pretreatment are generally more costly than those with higher levels of contaminants. For example crude and refined vegetable oils are significantly more costly than tallow and greases, but tallow and greases contain greater quantities of impurities.

The present process takes advantage of the lower cost feedstocks which contain phosphorus, while at the same time, minimizes the use of pretreatment techniques. The feedstock to the
present invention may contain up to 20 wt. ppm phosphorus, measured as elemental phosphorus. In another embodiment, the renewable feedstock may contain from 10 to 20 wt. ppm phosphorus measured as elemental phosphorus. This allows for lower cost, less refined, feedstocks to be utilized. Pretreatment techniques are also minimized since only phosphorus in excess of 20 wt. ppm needs to be removed.

[0012] The renewable feedstock, containing from 1 to 20 wt. ppm of phosphorus, measured as elemental phosphorus, is flowed to a reaction zone comprising one or more catalyst beds in one or more reactors. The term feedstock is meant to include feedstocks that have not been treated to remove contaminants as well as those feedstocks purified in a pretreatment zone to remove phosphorus in excess of 20 wt. ppm. Feedstocks containing phosphorus in excess of 20 wt. ppm formed gums in the pre-heater or in the reactor which lead to plugging of the pre-heater or the reactor. However, feedstocks containing less than 20 wt. ppm phosphorus did not cause gum formation in the pre-heater or in the reactor, see the example below.

[0013] In the reaction zone, the renewable feedstock is contacted with a hydrogenation or hydrotreating catalyst in the presence of hydrogen at hydrogenation conditions to hydrogenate the olefinic or unsaturated portions of the n-paraffinic chains. Hydrogenation or hydrotreating catalysts are any of those well known in the art such as nickel or nickel/molybdenum dispersed on a high surface area support. Other hydrogenation catalysts include one or more noble metal catalytic elements dispersed on a high surface area support. Non-limiting examples of noble metals include Pt and/or Pd dispersed on gamma-alumina. Hydrogenation conditions include a temperature of 200°C to 300°C and a pressure of 1379 kPa absolute (200 psia) to 4826 kPa absolute (700 psia). Other operating conditions for the hydrogenation zone are well known in the art.

[0014] The hydrogenation and hydrotreating catalysts enumerated above are also capable of catalyzing decarboxylation, decarbonylation, and/or hydrodeoxygenation of the feedstock to remove oxygen. Decarboxylation, decarbonylation, and hydrodeoxygenation are herein collectively referred to as deoxygenation reactions. Decarboxylation and decarbonylation conditions include a relatively low pressure of 3447 kPa (500 psia) to 6895 kPa (1000 psia), a temperature of 288°C to 345°C and a liquid hourly space velocity of 1 to 4 hr\(^{-1}\). Since hydrogenation is an exothermic reaction, as the feedstock flows through the catalyst bed the
temperature increases and decarboxylation and hydrodeoxygenation will begin to occur. Thus, it is envisioned and is within the scope of this invention that all three reactions occur simultaneously in one reactor or in one bed. Alternatively, the conditions can be controlled such that hydrogenation primarily occurs in one bed and decarboxylation and/or hydrodeoxygenation occurs in a second bed. Of course if only one bed is used, then hydrogenation occurs primarily at the front of the bed, while decarboxylation, decarbonylation and hydrodeoxygenation occurs mainly in the middle and bottom of the bed. Finally, desired hydrogenation can be carried out in one reactor, while decarboxylation, decarbonylation, and/or hydrodeoxygenation can be carried out in a separate reactor.

[0015] Hydrogen is a reactant in the reactions above, and to be effective, a sufficient quantity of hydrogen must be in solution to most effectively take part in the catalytic reaction. Past processes have operated at high pressures in order to achieve a desired amount of hydrogen in solution and readily available for reaction. If hydrogen is not available at the reaction site of the catalyst, the coke forms on the catalyst and deactivates the catalyst. To solve this problem, the pressure is often raised to insure enough hydrogen is available to avoid coking reactions on the catalyst. However, higher pressure operations are more costly to build and to operate as compared to their lower pressure counterparts. One advantage of the present invention is the operating pressure is in the range of 1379 kPa absolute (200 psia) to 4826 kPa absolute (700 psia) which is lower than that found in other previous operations. In another embodiment the operating pressure is in the range of 2413 kPa absolute (350 psia) to 4481 kPa absolute (650 psia), and in yet another embodiment operating pressure is in the range of 2758 kPa absolute (400 psia) to 4137 kPa absolute (600 psia). Furthermore, the rate of reaction is increased resulting in a greater amount of throughput of material through the reactor in a given period of time. Lower operating pressures provide an additional advantage in increasing the decarboxylation reaction while reducing the hydrodeoxygenation reaction. The result is a reduction in the amount of hydrogen required to remove oxygen from the feedstock component and produce a finished product. Hydrogen can be a costly component of the feed and reduction of the hydrogen requirements is beneficial from an economic standpoint.

[0016] The desired amount of hydrogen is kept in solution at lower pressures by employing a large recycle of hydrocarbon. Other processes have employed hydrocarbon
recycle in order to control the temperature in the reaction zones since the reactions are exothermic reactions. However, the range of recycle to feedstock ratios used herein is set based on the need to control the level of hydrogen in the liquid phase and therefore reduce the deactivation rate. The amount of recycle is determined not on temperature control requirements, but instead, based upon hydrogen solubility requirements. Hydrogen has a greater solubility in the hydrocarbon product than it does in the feedstock. By utilizing a large hydrocarbon recycle the solubility of hydrogen in the liquid phase in the reaction zone is greatly increased and higher pressures are not needed to increase the amount of hydrogen in solution and avoid catalyst deactivation at low pressures. In one embodiment of the invention, the volume ratio of hydrocarbon recycle to feedstock is from 2:1 to 8:1 or from 2:1 to 6:1. In another embodiment the ratio is in the range of 3:1 to 6:1 and in yet another embodiment the ratio is in the range of 4:1 to 5:1. The determination of the ranges of suitable volume ratios of hydrocarbon recycle is shown in USAN 12/193,149, hereby incorporated by reference in its entirety.

[0017] Another benefit of the recycle ratio employed is that the recycle material operates to dilute the amount of phosphorus that is present in the reaction mixture. While the feedstock may contain up to 20 wt. ppm phosphorus, the feedstock is mixed with the hydrocarbon recycle effectively diluting the concentration of phosphorus in the reaction mixture. With the feedstock being limited to less than 20 wt. ppm phosphorus, and then being diluted with the hydrocarbon recycle, the phosphorus containing compounds do not form gums in the pre-heater or in the reactor. Furthermore, the resulting concentration of phosphorus in the reaction mixture can be tolerated by the catalyst in the hydrogenation and deoxygenation zone. The hydrogenation and deoxygenation catalyst appears to remove the phosphorus from the reaction mixture without severely deactivating the catalyst. Even though the feedstock contained up to 20wt. ppm phosphorus, and gums were not formed in the pre-heaters or in the reactor, the effluent of the hydrogenation and deoxygenation reactor contains little phosphorus. Therefore it is not necessary to remove phosphorus from the hydrogenation and deoxygenation zone effluent before passing the effluent to the isomerization zone.

[0018] The reaction product from the deoxygenation reactions in the deoxygenation zone will comprise a liquid portion and a gaseous portion. The liquid portion comprises a hydrocarbon fraction which is essentially all n-paraffins and having carbon numbers in the
range of C8 to C24. Different feedstocks will result in different distributions of paraffins. A portion of this hydrocarbon fraction, after separation, may be used as the hydrocarbon recycle described above. Although this hydrocarbon fraction is useful as a diesel boiling range fuel, or a fuel blending component, because it comprises essentially all n-paraffins, it will have poor cold flow properties. To improve the cold flow properties of the liquid hydrocarbon fraction, the liquid hydrocarbon fraction is contacted with an isomerization catalyst under isomerization conditions to at least partially isomerize the n-paraffins to branched paraffins such as isoparaffins. Catalysts and conditions for isomerization are well known in the art. See for example US 2004/0230085 A1 which is incorporated by reference in its entirety.

Isomerization can be carried out in a separate bed of the same reaction zone, i.e. same reactor, described above or the isomerization can be carried out in a separate reactor.

[0019] The product of the hydrogenation and deoxygenation reaction zone is contacted with an isomerization catalyst in the presence of hydrogen at isomerization conditions to isomerize the normal paraffins to branched paraffins. Only minimal branching is required, enough to overcome cold-flow problems of the normal paraffins. Since attempting for significant branching runs the risk of high degree of undesired cracking, the predominant isomerized product is a mono-branched hydrocarbon.

[0020] The isomerization of the paraffinic product can be accomplished in any manner known in the art or by using any suitable catalyst known in the art. Suitable catalysts comprise a metal of Group VIII (IUPAC 8-10) of the Periodic Table and a support material. Suitable Group VIII metals include platinum and palladium, each of which may be used alone or in combination. The support material may be amorphous or crystalline. Suitable support materials include amorphous alumina, amorphous silica-alumina, ferrierite, ALPO-31, SAPO-11, SAPO-31, SAPO-37, SAPO-41, SM-3, MgAPSO-31, FU-9, NU-10, NU-23, ZSM-12, ZSM-22, ZSM-23, ZSM-35, ZSM-48, ZSM-50, ZSM-57, MeAPO-11, MeAPO-31, MeAPO-41, MeAPSO-11, MeAPSO-31, MeAPSO-41, MeAPSO-46, ELAPO-11, ELAPO-31, ELAPO-41, ELAPSO-11, ELAPSO-31, ELAPSO-41, laumontite, cancrinite, offretite, hydrogen form of stillbite, magnesium or calcium form of mordenite, and magnesium or calcium form of partheite, each of which may be used alone or in combination. ALPO-31 is described in US 4,310,440. SAPO-11, SAPO-31, SAPO-37, and SAPO-41 are described in US 4,440,871. SM-3 is described in US 4,943,424; US 5,087,347; US 5,158,665; and US 5,208,005. MgAPSO is a MeAPSO, which is
an acronym for a metal aluminumsilicophosphate molecular sieve, where the metal Me is magnesium (Mg). Suitable MeAPSO-31 catalysts include MgAPSO-31. MeAPSOs are described in US 4,793,984, and MgAPSOs are described in US 4,758,419. MgAPSO-31 is a preferred MgAPSO, where 31 means a MgAPSO having structure type 31. Many natural zeolites, such as ferrierite, that have an initially reduced pore size can be converted to forms suitable for olefin skeletal isomerization by removing associated alkali metal or alkaline earth metal by ammonium ion exchange and calcination to produce the substantially hydrogen form, as taught in US 4,795,623 and US 4,924,027. Further catalysts and conditions for skeletal isomerization are disclosed in US 5,510,306, US 5,082,956, and US 5,741,759.

[0021] The isomerization catalyst may also comprise a modifier selected from the group consisting of lanthanum, cerium, praseodymium, neodymium, samarium, gadolinium, terbium, and mixtures thereof, as described in US 5,716,897 and US 5,851,949. Other suitable support materials include ZSM-22, ZSM-23, and ZSM-35, which are described for use in dewaxing in US 5,246,566 and in the article entitled "New molecular sieve process for lube dewaxing by wax isomerization," written by S. J. Miller, in Microporous Materials 2 (1994) 439-449. The teachings of US 4,310,440; US 4,440,871; US 4,793,984; US 4,758,419; US 4,943,424; US 5,087,347; US 5,158,665; US 5,208,005; US 5,246,566; US 5,716,897; and US 5,851,949 are hereby incorporated by reference.

[0022] US 5,444,032 and US 5,608,134 teach a suitable bifunctional catalyst which is constituted by an amorphous silica-alumina gel and one or more metals belonging to Group VIII A, and is effective in the hydroisomerization of long-chain normal paraffins containing more than 15 carbon atoms. US 5,981,419 and US 5,968,344 teach a suitable bifunctional catalyst which comprises: (a) a porous crystalline material isostructural with beta-zeolite selected from boro-silicate (BOR-B) and boro-alumino-silicate (Al-BOR-B) in which the molar SiO₂:Al₂O₃ ratio is higher than 300:1; (b) one or more metal(s) belonging to Group VIII A, selected from platinum and palladium, in an amount comprised within the range of from 0.05 to 5% by weight. Article V. Calemma et al., App. Catal. A: Gen., 190 (2000), 207 teaches yet another suitable catalyst.

[0023] The isomerization catalyst may be any of those well known in the art such as those described and cited above. Isomerization conditions include a temperature of 150°C to 360°C and a pressure of 1724 kPa absolute (250 psia) to 4726 kPa absolute (700 psia). In another
embodiment the isomerization conditions include a temperature of 300°C to 360°C and a pressure of 3102 kPa absolute (450 psia) to 3792 kPa absolute (550 psia). Other operating conditions for the isomerization zone are well known in the art.

[0024] The final effluent stream, i.e. the stream obtained after all reactions have been carried out, is now processed through one or more separation steps to obtain a purified hydrocarbon stream useful as a diesel boiling range fuel or fuel blending component. Because the final effluent stream comprises both a liquid and a gaseous component, the liquid and gaseous components are separated using a separator such as a cold separator. The separated liquid component comprises the product hydrocarbon stream useful as a diesel fuel. Further separations may be performed to remove naphtha and LPG from the product hydrocarbon stream. The separated gaseous component comprises mostly hydrogen and the carbon dioxide from the decarboxylation reaction. The carbon dioxide can be removed from the hydrogen by means well known in the art, reaction with a hot carbonate solution, pressure swing absorption, etc. Also, absorption with an amine in processes such as described in co-pending applications USAN 12/193,176 and USAN 12/193,196, hereby incorporated by reference, may be employed. If desired, essentially pure carbon dioxide can be recovered by regenerating the spent absorption media. The hydrogen remaining after the removal of the carbon dioxide may be recycled to the reaction zone where hydrogenation primarily occurs and/or to any subsequent beds/reactors.

[0025] Finally, a portion of the product hydrocarbon is recycled to the hydrogenating and deoxygenating reaction zone. The recycle stream may be taken from the product hydrocarbon stream after the hydrogenating and deoxygenating reactor(s) and separation form gaseous components, and recycled back to the hydrogenating and deoxygenating reactor(s). Or the recycle stream may be taken from the effluent of a separation unit, such as a hot high pressure separator, located between the deoxygenation reaction zone and the isomerization reaction zone. Although possible, it is less preferred to take the recycle stream from the isomerized product since isomerized products are more susceptible to cracking than the normal paraffins in the hydrogenating and deoxygenating reaction zone. A portion of a hydrocarbon stream from, for example, a hot high pressure separator or a cold high pressure separator, may also be cooled down if necessary and used as cool quench liquid between the beds of the deoxygenation reaction zone to further control the heat of reaction and provide quench liquid.
for emergencies. The recycle stream may be introduced to the inlet of the deoxygenation reaction zone and/or to any subsequent beds or reactors. One benefit of the hydrocarbon recycle is to control the temperature rise across the individual beds. However, as discussed above, the amount of hydrocarbon recycle herein is determined based upon the desired hydrogen solubility in the reaction zone. Increasing the hydrogen solubility in the reaction mixture allows for successful operation at lower pressures, and thus reduced cost. Operating with high recycle and maintaining high levels of hydrogen in the liquid phase helps dissipate hot spots at the catalyst surface and reduces the formation of undesirable heavy components which lead to coking and catalyst deactivation. Furthermore, high hydrocarbon recycle operates to dilute the phosphorus in the feedstock and avoid formation of gums which plug pre-heaters and the reactor.

[0026] The following embodiment is presented in illustration of this invention and is not intended as an undue limitation on the generally broad scope of the invention as set forth in the claims. First an embodiment is described in general as with reference to FIG. 1. Then an embodiment is described in more detail with reference to FIG. 2.

[0027] Turning to FIG. 1 renewable feedstock 102 enters deoxygenation reaction zone 104 along with recycle hydrogen 126. Renewable feedstock contains from 1 to 20 wt. ppm phosphorus, measured as elemental phosphorus. Deoxygenated product 106 is stripped in hot high pressure hydrogen stripper 108 using hydrogen 114a. Carbon oxides and water vapor are removed with hydrogen in overhead 110. Selectively stripped deoxygenated product is passed to isomerization zone 116 along with recycle hydrogen 126a and make-up hydrogen 114b. Isomerized product 118 is combined with overhead 110 and passed to product recovery zone 120. Carbon oxide stream 128, light ends stream 130, water byproduct stream 124, hydrogen stream 126, and branched paraffin-rich product 122 are removed from product recover zone 120. Branched paraffin-rich product 122 may be collected for use as diesel fuel and hydrogen stream 126 is recycled to the deoxygenation reaction zone 104.

[0028] Turning to FIG. 2, the process begins with a renewable feedstock stream 2 which may pass through an optional feed surge drum. Renewable feedstock stream 2 contains from 1 to 20 ppm phosphorus, measured as elemental phosphorus. The feedstock stream is combined with recycle gas stream 68 and recycle stream 16 to form combined feed stream 20, which is heat exchanged with reactor effluent and then introduced into deoxygenation reactor 4. The heat
exchange may occur before or after the recycle is combined with the feed. Deoxygenation reactor 4 may contain multiple beds shown in FIG. 2 as 4a, 4b and 4c. Deoxygenation reactor 4 contains at least one catalyst capable of catalyzing decarboxylation and/or hydrodeoxygenation of the feedstock to remove oxygen. Deoxygenation reactor effluent stream 6 containing the products of the decarboxylation and/or hydrodeoxygenation reactions is removed from deoxygenation reactor 4 and heat exchanged with stream 20 containing feed to the deoxygenation reactor. Stream 6 comprises a liquid component containing largely normal paraffin hydrocarbons in the diesel boiling range and a gaseous component containing largely hydrogen, vaporous water, carbon monoxide, carbon dioxide and propane.

Deoxygenation reactor effluent stream 6 is then directed to hot high pressure hydrogen stripper 8. Make up hydrogen in line 10 is divided into two portions, stream 10a and 10b. Make up hydrogen in stream 10a is also introduced to hot high pressure hydrogen stripper 8. In hot high pressure hydrogen stripper 8, the gaseous component of deoxygenation reactor effluent 6 is selectively stripped from the liquid component of deoxygenation reactor effluent 6 using make-up hydrogen 10a and recycle hydrogen 28. The dissolved gaseous component comprising hydrogen, vaporous water, carbon monoxide, carbon dioxide and at least a portion of the propane, is selectively separated into hot high pressure hydrogen stripper overhead stream 14. The remaining liquid component of deoxygenation reactor effluent 6 comprising primarily normal paraffins having a carbon number from 8 to 24 with a cetane number of 60 to 100 is removed as hot high pressure hydrogen stripper bottom 12.

A portion of hot high pressure hydrogen stripper bottoms forms recycle stream 16 and is combined with renewable feedstock stream 2 to create combined feed 20. Another portion of recycle stream 16, optional stream 16a, may be routed directly to deoxygenation reactor 4 and introduced at interstage locations such as between beds 4a and 4b and/or between beds 4b and 4c in order, or example, to aid in temperature control. The remainder of hot high pressure hydrogen stripper bottoms in stream 12 is combined with hydrogen stream 10b to form combined stream 18 which is routed to isomerization reactor 22. Stream 18 may be heat exchanged with isomerization reactor effluent 24.

The product of the isomerization reactor containing a gaseous portion of hydrogen and propane and a branched-paraffin-rich liquid portion is removed in line 24, and after optional heat exchange with stream 18, is introduced into hydrogen separator 26. The overhead stream
28. from hydrogen separator 26 contains primarily hydrogen which may be recycled back to hot
high pressure hydrogen stripper 8. Bottom stream 30 from hydrogen separator 26 is air cooled
using air cooler 32 and introduced into product separator 34. In product separator 34 the gaseous
portion of the stream comprising hydrogen, carbon monoxide, hydrogen sulfide, carbon dioxide
and propane are removed in stream 36 while the liquid hydrocarbon portion of the stream is
removed in stream 38. A water byproduct stream 40 may also be removed from product
separator 34. Stream 38 is introduced to product stripper 42 where components having higher
relative volatilities are separated into stream 44 with the remainder, the diesel range
components, being withdrawn from product stripper 42 in line 46. Stream 44 is introduced into
fractionator 48 which operates to separate LPG into overhead 50 leaving a naphtha bottoms 52.
Any of optional lines 72, 74, or 76 may be used to recycle at least a portion of the isomerization
zone effluent back to the isomerization zone to increase the amount of n-paraffins that are
isomerized to branched paraffins.

[0032] The vapor stream 36 from product separator 34 contains the gaseous portion of the
isomerization effluent which comprises at least hydrogen, carbon monoxide, hydrogen sulfide,
carbon dioxide and propane and is directed to a system of amine absorbers to separate carbon
dioxide and hydrogen sulfide from the vapor stream. Because of the cost of hydrogen, it is
desirable to recycle the hydrogen to deoxygenation reactor 4, but it is not desirable to circulate
the carbon dioxide or an excess of sulfur containing components. In order to separate sulfur
containing components and carbon dioxide from the hydrogen, vapor stream 36 is passed
through a system of at least two amine absorbers, also called scrubbers, starting with the first
amine absorber zone 56. The amine chosen to be employed in first amine scrubber 56 is capable
of selectively removing at least both the components of interest, carbon dioxide and the sulfur
components such as hydrogen sulfide. Suitable amines are available from DOW and from
BASF, and in one embodiment the amines are a promoted or activated methyldiethanolamine
(MDEA). See US 6,337,059, hereby incorporated by reference in its entirety. Suitable amines
for the first amine absorber zone from DOW include the UCARSOL™ AP series solvents such
as AP802, AP804, AP806, AP810 and AP814. The carbon dioxide and hydrogen sulfide are
absorbed by the amine while the hydrogen passes through first amine scrubber zone and into
line 68 to be recycled to the first reaction zone. The amine is regenerated and the carbon dioxide
and hydrogen sulfide are released and removed in line 62. Within the first amine absorber zone,
regenerated amine may be recycled for use again. The released carbon dioxide and hydrogen sulfide in line 62 are passed through second amine scrubber zone 58 which contains an amine selective to hydrogen sulfide, but not selective to carbon dioxide. Again, suitable amines are available from DOW and from BASF, and in one embodiment the amines are a promoted or activated MDEA. Suitable amines for the second amine absorber zone from DOW include the UCARSOL™ HS series solvents such as HS101, HS 102, HS103, HS104, HS115. Therefore the carbon dioxide passes through second amine scrubber zone 58 and into line 66. The amine may be regenerated which releases the hydrogen sulfide into line 60. Regenerated amine is then reused, and the hydrogen sulfide may be recycled to the deoxygenation reaction zone.

Conditions for the first scrubber zone includes a temperature in the range of 30 to 60°C. The first absorber is operated at essentially the same pressure as the reaction zone. By “essentially” it is meant that the operating pressure of the first absorber is within 1034 kPa absolute (150 psia) of the operating pressure of the reaction zone. For example, the pressure of the first absorber is no more than 1034 kPa absolute (150 psia) less than that of the reaction zone. The second amine absorber zone is operated in a pressure range of from 138 kPa absolute (20 psia) to 241 kPa absolute (35 psia). Also, at least the first the absorber is operated at a temperature that is at least 1°C higher than that of the separator. Keeping the absorbers warmer than the separator operates to maintain any light hydrocarbons in the vapor phase and prevents the light hydrocarbons from condensing into the absorber solvent.

[0033] The following examples are presented in illustration of this invention and are not intended as undue limitations on the generally broad scope of the invention as set out in the appended claims.

EXAMPLE

[0034] Several renewable feedstocks, each having different levels of phosphorus were hydrogenated and deoxygenated (some were also isomerized), and the occurrence of plugging in the pre-heater or in the reactors was noted. Some of the experiments were conducted with a hydrocarbon recycle and some of the experiments were conducted without a hydrocarbon recycle. The renewable feedstocks tested included vegetable oils, grease, and tallow. For all cases except the yellow grease, the beef tallow, and the cooking oil, the feedstocks were processed at 1 LHSV with respect to fresh feedstock in a down-flow trickle bed reactor.
containing 150 cc of a promoted nickel-molybdenum on alumina catalyst. The feedstocks were continuously added at a rate of 150cc/hr or 1LHSV over a period of 1000 hours at an operating pressure of 3447 kPa absolute (500 psia) and 310 to 332°C (590 to 650°F). The H2/hydrocarbon ratio in the feed was 3700 to 5000 scfb (658 to 889 std m³/m³).

The Table shows the different renewable feedstocks, the concentration of phosphorus in the renewable feedstock in wt. ppm measured as elemental phosphorus, the hydrocarbon recycle to feedstock volume ratio, and the occurrence of plugging in the pre-heater or in a reactor. Plugging includes a stoppage or reduction in fluid flow through the pre-heater or reactor, or may be indicted by a high pressure drop across the pre-heater or reactor.

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Phosphorus, wt. ppm</th>
<th>Hydrocarbon Recycle to Feedstock Volume Ratio</th>
<th>Plugging of Pre-Heater or Reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soybean Oil</td>
<td>5</td>
<td>No Hydrocarbon Recycle</td>
<td>No</td>
</tr>
<tr>
<td>Palm Oil</td>
<td>0.3</td>
<td>No Hydrocarbon Recycle</td>
<td>No</td>
</tr>
<tr>
<td>Cooking Oil</td>
<td>None detected</td>
<td>No Hydrocarbon Recycle</td>
<td>No</td>
</tr>
<tr>
<td>Canola Oil</td>
<td>0.7</td>
<td>4:1</td>
<td>No</td>
</tr>
<tr>
<td>Canola Oil</td>
<td>41</td>
<td>4:1</td>
<td>Yes</td>
</tr>
<tr>
<td>Jatropha Oil</td>
<td>0.1</td>
<td>4:1</td>
<td>No</td>
</tr>
<tr>
<td>Yellow Grease</td>
<td>30</td>
<td>No Hydrocarbon Recycle</td>
<td>Yes</td>
</tr>
<tr>
<td>Beef Tallow</td>
<td>80</td>
<td>No Hydrocarbon Recycle</td>
<td>Yes</td>
</tr>
<tr>
<td>Beef Tallow</td>
<td>16</td>
<td>4:1</td>
<td>No</td>
</tr>
<tr>
<td>Beef Tallow</td>
<td>15</td>
<td>4:1</td>
<td>No</td>
</tr>
<tr>
<td>Beef Tallow</td>
<td>5</td>
<td>4:1</td>
<td>No</td>
</tr>
</tbody>
</table>
CLAIMS:

1) A process for producing a diesel boiling range hydrocarbon product from a renewable feedstock comprising:
   a) treating the renewable feedstock in a reaction zone by hydrogenating and
deoxygenating the feedstock at reaction conditions to provide a reaction product
   comprising paraffins having from 8 to 24 carbon atoms, and recycling a portion of the
   reaction product to the reaction zone wherein the volume ratio of recycle to feedstock
   is in the range of 2:1 to 8:1, wherein the renewable feedstock comprises from 1 to 20
   wt. ppm phosphorus, measured as elemental phosphorus; and
   b) isomerizing at least a portion of the paraffins in the reaction product in an
   isomerization zone by contacting with an isomerization catalyst at isomerization
   conditions to isomerize at least a portion of the paraffins to branched-paraffins.

2) The process of Claim 1 wherein the renewable feedstock comprises from 10 to 20 wt.
   ppm phosphorus, measured as elemental phosphorus.

3) The process of Claim 1 wherein the volume ratio of recycle to feedstock is in the range of
   2:1 to 6:1.

4) The process of Claim 1 wherein the volume ratio of recycle to feedstock is in the range of
   4:1.

5) The process of Claim 1 further comprising pre-treating the renewable feedstock in a
   pretreatment zone at pretreatment conditions to remove phosphorus in excess of 20 wt.
   ppm, measured as elemental phosphorus.

6) The process of Claim 1 where the feedstock is hydrogenated and deoxygenated by
   contacting the feedstock with a hydrogenation and deoxygenation catalyst at a temperature
   of 200°C to 300°C and a pressure of 1379 kPa absolute (200 psia) to 4826 kPa absolute
   (700 psia).

7) The process of Claim 1 wherein the reaction product is passed to the isomerization zone
   without employing phosphorus removal techniques.

8) The process of Claim 1 further comprising treating a petroleum hydrocarbon feedstock in
   the reaction zone.

9) The process of Claim 1 wherein the renewable feedstock comprises at least one
   component selected from the group consisting of canola oil, corn oil, soy oil, rapeseed oil,
soybean oil, colza oil, tall oil, sunflower oil, hempseed oil, olive oil, linseed oil, coconut oil, castor oil, peanut oil, palm oil, mustard oil, cottonseed oil, jatropha oil, tallow, yellow and brown greases, lard, train oil, fats in milk, fish oil, algal oil, sewage sludge.

10) The process of Claim 9 wherein the renewable feedstock further comprises at least one co-feed component selected from the group consisting of spent motor oils, spent industrial lubricants, used paraffin waxes, liquids derived from the gasification of coal, biomass, natural gas followed by a downstream liquefaction step, liquids derived from depolymerization, thermal or chemical, of waste plastics, and synthetic oils generated as byproducts from petrochemical and chemical processes.