



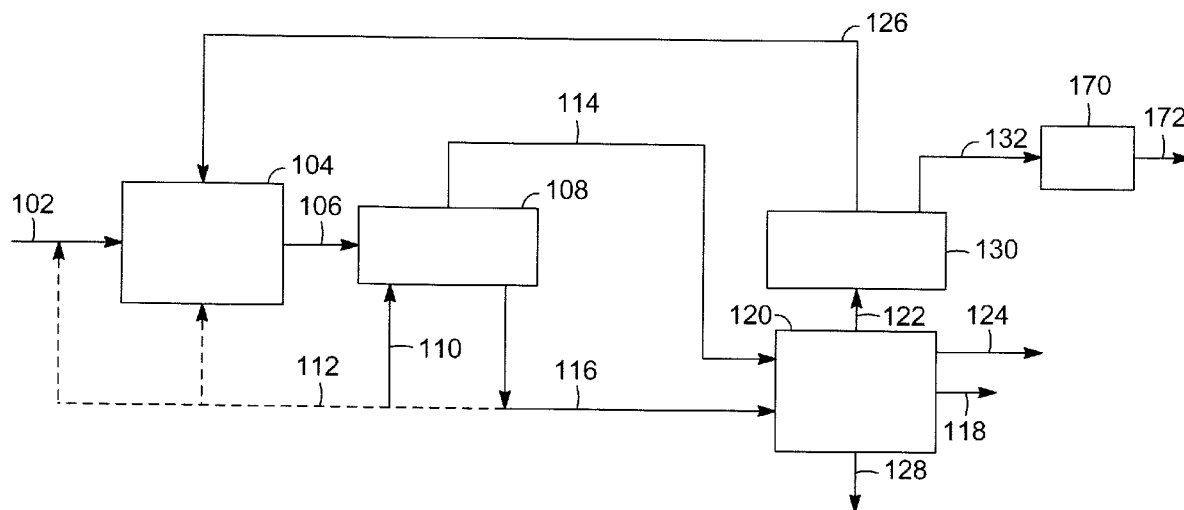
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(19) **United States**(12) **Patent Application Publication**
Marker et al.(10) **Pub. No.: US 2009/0077864 A1**(43) **Pub. Date: Mar. 26, 2009**(54) **INTEGRATED PROCESS OF ALGAE
CULTIVATION AND PRODUCTION OF
DIESEL FUEL FROM BIORENEWABLE
FEEDSTOCKS**(22) Filed: **Aug. 18, 2008****Related U.S. Application Data**(60) Provisional application No. 60/973,806, filed on Sep.
20, 2007.**Publication Classification**(51) **Int. Cl.**
C10L 1/04 (2006.01)(52) **U.S. Cl.** **44/307**(57) **ABSTRACT**

An integrated process has been developed for producing diesel boiling range fuel from renewable feedstocks such as plant and animal fats and oils and for cultivating algae or greenhouse plants. The process involves catalytically treating a renewable feedstock by hydrogenating and deoxygenating to provide a hydrocarbon fraction useful as a diesel boiling range fuel. A selective separation may be used to remove at least the carbon dioxide from the first zone effluent.

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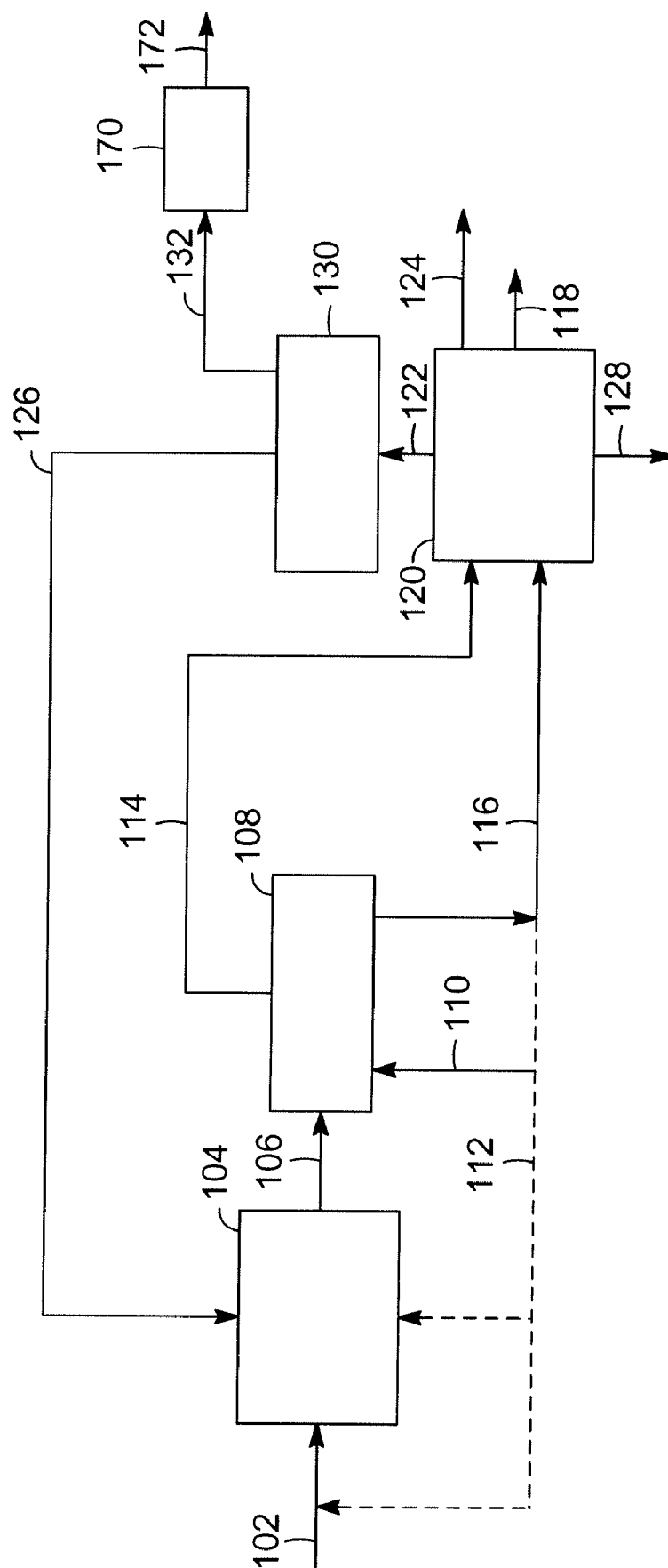


FIG. 1

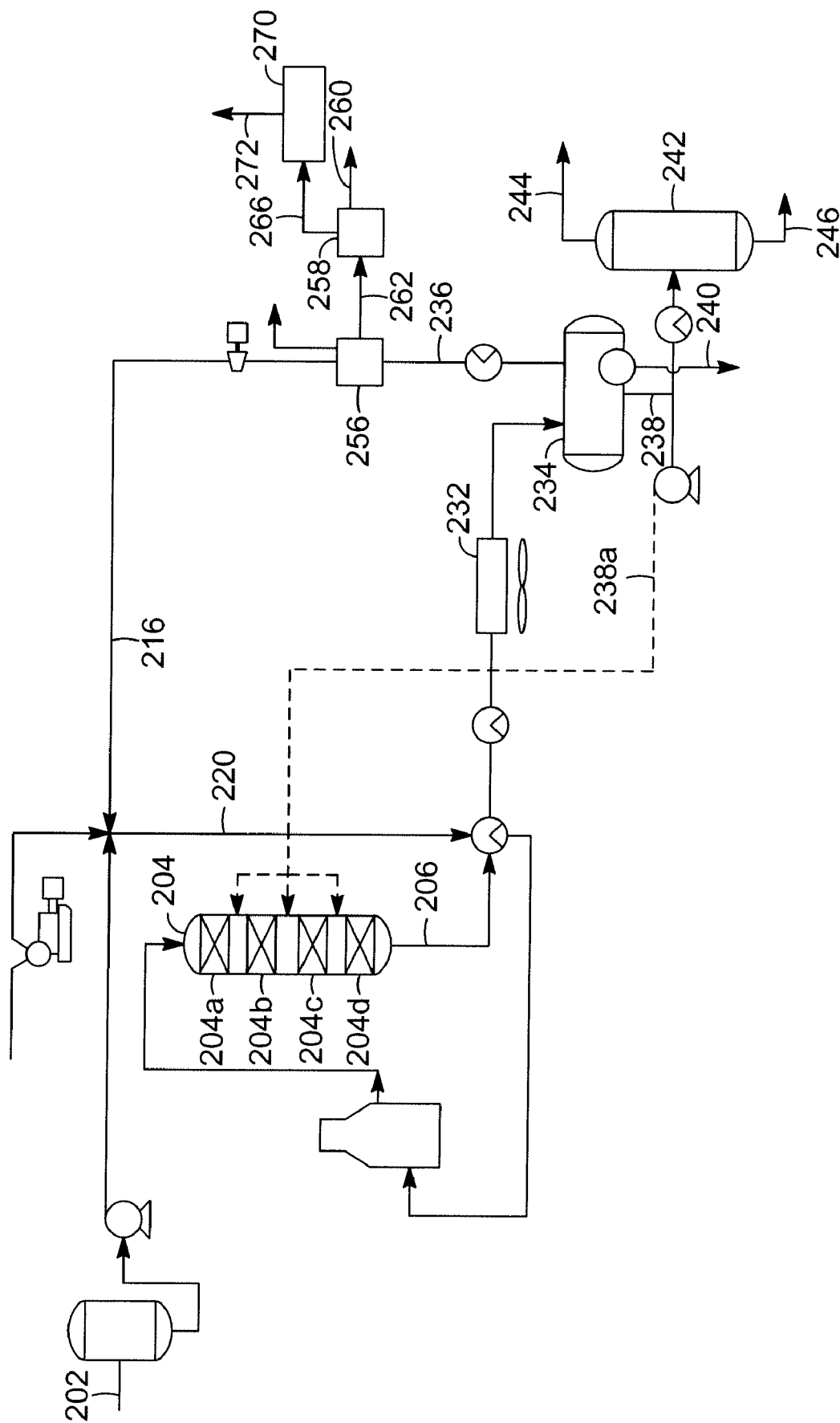


FIG. 2

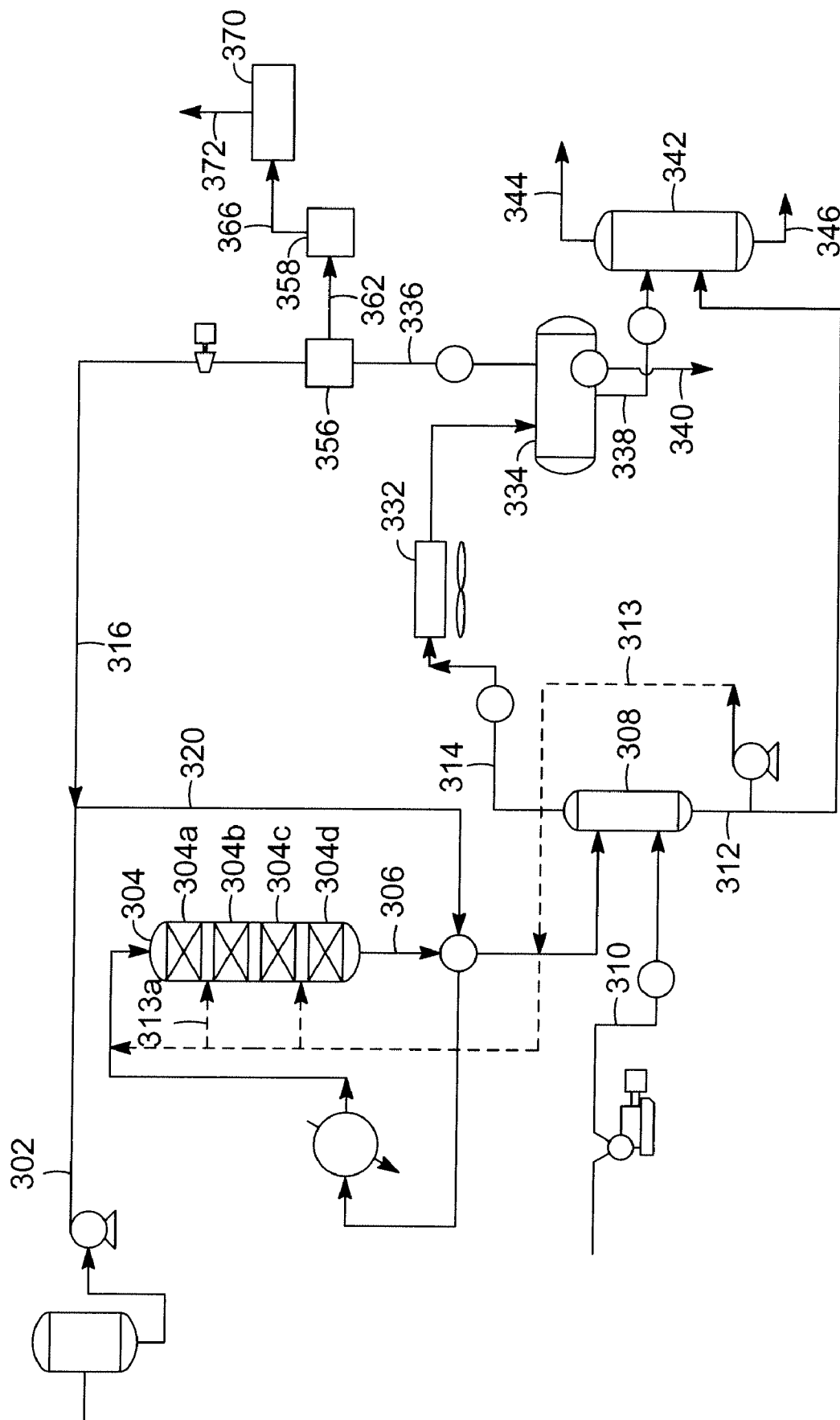


FIG. 3

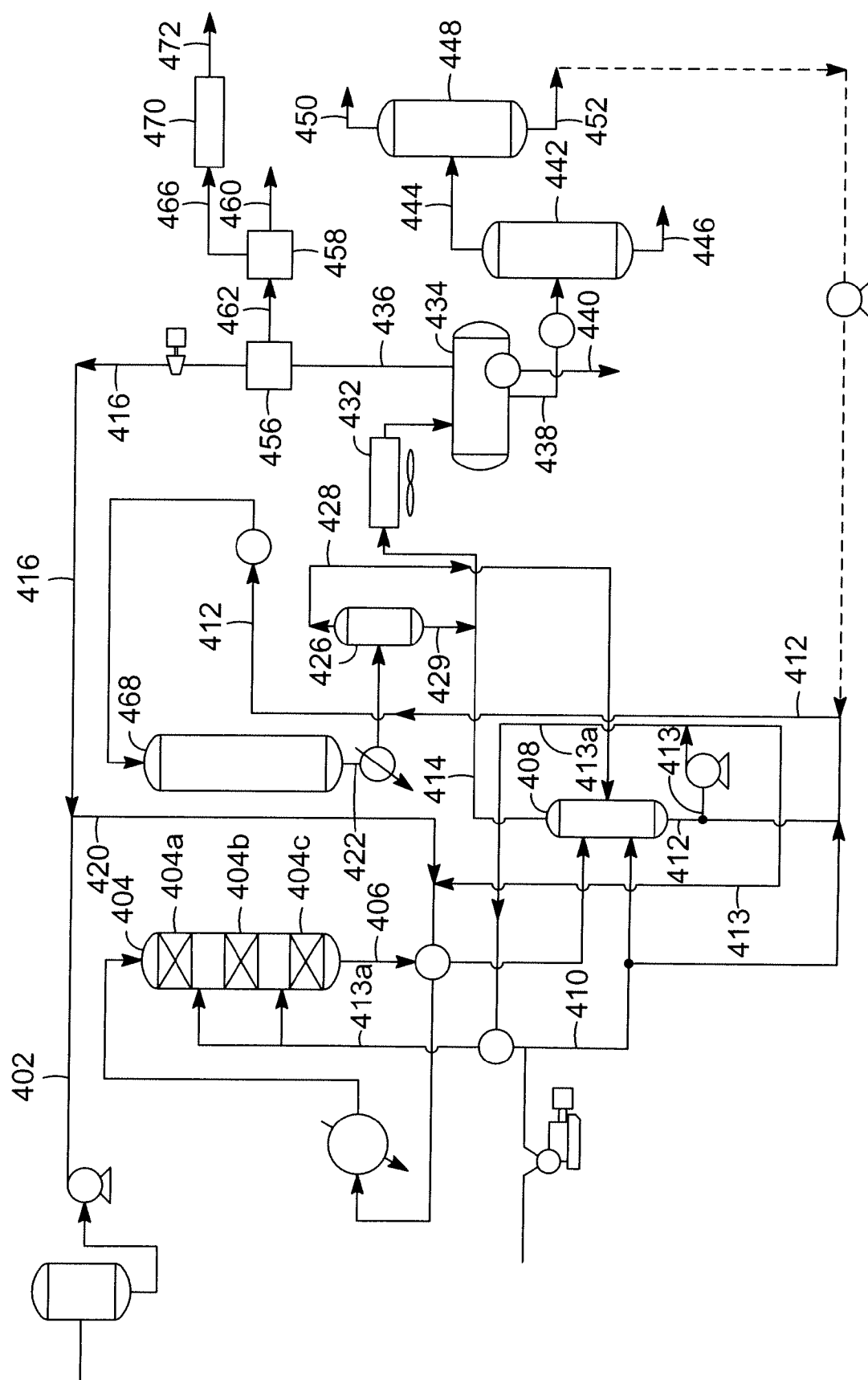


FIG. 4

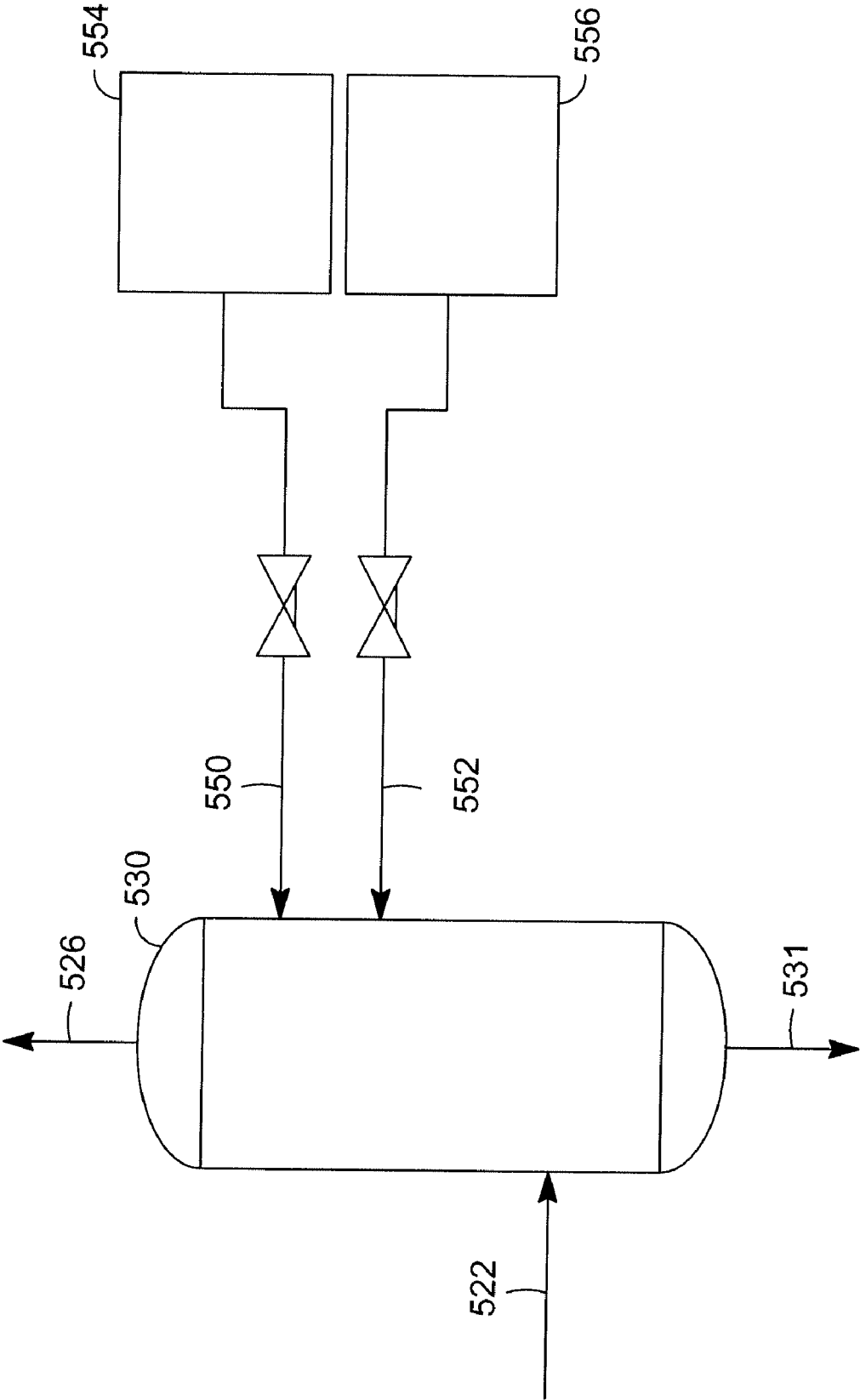


FIG. 5

INTEGRATED PROCESS OF ALGAE CULTIVATION AND PRODUCTION OF DIESEL FUEL FROM BIORENEWABLE FEEDSTOCKS

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims priority from Provisional Application Ser. No. 60/973,806 filed Sep. 20, 2007, the contents of which are hereby incorporated by reference in its entirety.

FIELD OF THE INVENTION

[0002] This invention relates to an integrated process for cultivating algae and for producing diesel boiling range fuel from renewable feedstocks such as the glycerides and free fatty acids found in materials such as plant and animal fats and oils. Hydrogenation and deoxygenation are performed in one or more reactors. A vapor stream is separated from the reaction zone effluent, and carbon dioxide is separated from the vapor stream. The separated carbon dioxide is passed to an algae cultivation operation. The hydrocarbons may be optionally isomerized. Additionally, some algae produce hydrogen which may be employed in the reaction zone in the diesel boiling range fuel process.

BACKGROUND OF THE INVENTION

[0003] As the demand for diesel boiling range fuel increases worldwide there is increasing interest in sources other than crude oil for producing diesel boiling range fuel. One such renewable 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 inedible 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 about 8 to about 24 carbon atoms. The aliphatic chains in the glycerides or FFAs can be fully saturated, or mono, di or poly-unsaturated.

[0004] There are reports in the art disclosing the production of hydrocarbons from oils. For example, U.S. Pat. No. 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. U.S. Pat. No. 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. It is also known that a key component in the cultivation of algae is carbon dioxide.

[0005] Applicants have developed an integrated process that generates and separates a carbon dioxide stream suitable for use in an algae cultivation operation. The carbon dioxide is generated through a diesel boiling range fuel production process and is separated from other vaporous components. The diesel boiling range fuel production process comprises one or more steps to hydrogenate and deoxygenate (via catalytic decarboxylation, decarbonylation and/or hydrodeoxygenation) the renewable feedstock. Sulfur containing components may be naturally present in the feedstock or may be

added to the feedstock or the reaction mixture for various different purposes. Carbon dioxide and water are generated in the reaction zone and need to be at least partially removed from the reactor effluent prior to recycling any excess hydrogen back to the reaction zone. The effluent from the reaction zone is separated into at least a vapor portion and a liquid portion though, for example, cooling and separating. At least some of the liquid portion may be recycled to the reaction zone. The vapor portion is treated using an amine absorber solution to remove at least the carbon dioxide and optionally the sulfur component such as hydrogen sulfide so that the remaining hydrogen can be recycled back to the first reaction zone. The separated carbon dioxide is passed to an algae cultivation operation. The separated hydrogen sulfide may be used for other purposes. Optionally, selective separation unit such as a hot high pressure hydrogen stripper may be employed to selectively separate the majority of the hydrocarbon liquid portion from the vapor portion of the effluent and some of this hydrocarbon liquid portion may be recycled to the reactor. The vapor portion is then cooled to separate any water. Optionally, the hydrocarbons produced by the deoxygenation reactions may be isomerized to produce branched-paraffins.

SUMMARY OF THE INVENTION

[0006] A hydroconversion process for producing at least a diesel boiling range fuel from a renewable feedstock wherein the process comprises treating the renewable feedstock in a catalytic reaction zone by hydrogenating and deoxygenating the feedstock at reaction conditions to provide a reaction product comprising paraffins and a gaseous fraction comprising at least carbon dioxide and hydrogen. The paraffins are optionally isomerized to produce branched paraffins. At least one sulfur containing component may be present in the reaction mixture.

[0007] The carbon dioxide generated in the catalytic reaction zone and any excess hydrogen are selectively removed from the desired reaction product as a vapor stream using, for example, (1) a cooling and separating process or (2) an integrated hot high pressure stripper using a high purity hydrogen stream as the stripping gas followed by the cooling and separating process. The carbon dioxide is then separated from the hydrogen using, for example, at least one selective amine absorber solution. The separated carbon dioxide is passed to an algae cultivation operation. The hydrogen sulfide may be removed from the vapor stream using the amine absorber solution, or the amine absorber solution may be specially chosen to allow the hydrogen sulfide to recycle with the hydrogen to the reactor.

[0008] In another embodiment, hydrogen produced by algae is introduced to the catalytic reaction zone of the diesel boiling range fuel production process.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] FIG. 1 is a general flow scheme diagram of the invention.

[0010] FIG. 2 is a more detailed flow scheme diagram of one embodiment of the invention.

[0011] FIG. 3 is a detailed flow scheme diagram of the embodiment of the invention employing the optional hot high pressure hydrogen stripper.

[0012] FIG. 4 is a detailed flow scheme diagram of the embodiment of the invention employing the optional hot high pressure hydrogen stripper and the optional isomerization reaction zone.

[0013] FIG. 5 is a portion of a flow scheme showing the operation of the flexible absorber embodiment.

DETAILED DESCRIPTION OF THE INVENTION

[0014] As stated, the present invention relates to an integrated process for producing a hydrocarbon stream useful at least as diesel boiling range fuel or a diesel boiling range fuel blending component from renewable feedstocks such as renewable feedstocks originating from plants or animals as well as producing a carbon dioxide stream useful in the cultivation of algae. The term renewable feedstock is meant to include feedstocks other than those obtained from crude oil. Another term that has been used to describe this class of feedstock is biorenewable fats and oils. 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, 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* (Ratanjy, Wild Castor, Jangli Erandi), *Madhuca indica* (Mohuwa), *Pongamia pinnata* (Karanji Honge), and *Azadiracta indica* (Neem). The triglycerides and FFAs of the typical vegetable or animal fat contain aliphatic hydrocarbon chains in their structure which have about 8 to about 24 carbon atoms with a majority of the fats and oils containing high concentrations of fatty acids with 16 and 18 carbon atoms. 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, or natural gas followed by a downstream liquefaction step such as Fischer-Tropsch technology, 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 what has been considered to be a waste product from a petroleum based or other process into a valuable co-feed component to the current process.

[0015] Renewable feedstocks that can be used in the present invention may contain a variety of impurities. For example, tall oil is a byproduct 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. An optional first step is to remove some or all 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. The conditions at which the reactor is operated are well known in the art.

[0016] 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 some of 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 U.S. application Ser. No. 11/770,826, hereby incorporated by reference, is another pretreatment technique which may be employed.

[0017] The renewable feedstock is flowed to a first 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. In the reaction first zone, the feedstock is contacted with a hydrogenation or hydrotreating catalyst in the presence of hydrogen at hydrogenation conditions to hydrogenate reactive component such as the olefinic or unsaturated portions of the aliphatic side chains of a glyceride molecule. Hydrogenation or hydrotreating catalysts are any of those well known in the art such as sulfided 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 about 40° C. to about 400° C. and a pressure of about 689 kPa absolute (100 psia) to about 13,790 kPa absolute (2000 psia). In another embodiment the hydrogenation conditions include a temperature of about 200° C. to about 350° C. and a pressure of about 1379 kPa absolute (200 psia) to about 4826 kPa absolute (700 psia). Other operating conditions for the hydrogenation zone are well known in the art.

[0018] The hydrogenation and hydrotreating catalysts enumerated above are also capable of catalyzing decarbonylation, decarboxylation and/or hydrodeoxygenation of the feedstock to remove oxygen. Decarbonylation, decarboxylation, and hydrodeoxygenation are herein collectively referred to as deoxygenation reactions. Decarbonylation, decarboxylation, and hydrodeoxygenation conditions include a relatively low pressure of about 1379 kPa (200 psia) to about 6895 kPa (1000 psia), a temperature of about 200° C. to about 400° C. and a liquid hourly space velocity of about 0.5 to about 10 hr⁻¹. In another embodiment the decarbonylation, decarboxylation, and hydrodeoxygenation conditions include the same relatively low pressure of about 3447 kPa (500 psia) to about 6895 kPa (1000 psia), a temperature of about 288° C. to about 345° C. and a liquid hourly space velocity of about 1 to about 4 hr⁻¹. Since hydrogenation is an

exothermic reaction, as the feedstock flows through the catalyst bed the temperature increases and decarboxylation, decarbonylation and hydrodeoxygenation will begin to occur. Thus, it is envisioned and is within the scope of this invention that all 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, decarbonylation and/or hydrodeoxygenation occurs in a second bed. Of course if only one bed is used, then hydrogenation may occur 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 and/or hydrodeoxygenation can be carried out in a separate reactor.

[0019] Sulfur containing components are often present in the reaction mixture. Such components may be present in the feedstock naturally, or may be added to the feedstock or the reaction zone. Sulfur-containing components may be organic, inorganic, natural, or synthetic. A single sulfur-containing component may be present or more than one may be present. The sulfur containing component may be present in an amount ranging from about 1 ppm to about 5 mass %. Many sulfur containing components are converted to hydrogen sulfide in the reaction zone. For ease of understanding, the description below will use the term hydrogen sulfide as the primary example of a sulfur containing component, but that is not meant to limit the scope of the claims in any way.

[0020] The reaction product from the deoxygenation reactions comprises both a liquid portion and a gaseous portion. The liquid portion comprises a hydrocarbon fraction which is primarily paraffins and having a large concentration of paraffins in the range of about 9 to about 18 carbon atoms. Different feedstocks will result in different distributions of paraffins. The gaseous portion comprises hydrogen, carbon dioxide, carbon monoxide, water vapor, propane and perhaps sulfur components such as hydrogen sulfide. For the case where there is no isomerization catalyst in the reaction zone, most of the hydrocarbons will be normal paraffins. The hydrogenation/deoxygenation catalyst may catalyze a slight amount of isomerization but it is expected that no more than about 5 or about 10 mass % of the normal paraffins would be isomerized to branched paraffins. The diesel boiling range fuel old flow properties depend on the relative amounts of normal and branched paraffin in the product. In warmer climate regions, poor cold flow properties are not a great concern. In colder climate regions, improvements to cold flow properties are needed and at least some of the normal paraffins are isomerized to branched paraffins. By optimizing the isomerization requirement where appropriate due to the climate, a substantial cost savings in both capital costs and operating costs can be achieved.

[0021] The effluent from the reaction zone is conducted to a selective separation zone comprising, for example, a heat exchanger and a product separator and optionally an air or water cooler. After cooling, a vapor stream containing the hydrogen, hydrogen sulfide, carbon monoxide, and carbon dioxide is readily separated from the liquid phase containing the normal paraffins having from about 8 to about 24 carbon atoms in the product separator. Suitable operating conditions of the separator include, for example, a temperature of about 20 to 80° C. or 45 to 50° C. and a pressure of about 2758 kPa absolute (400 psia) to about 68985 kPa absolute (1000 psia) with a specific embodiment at 3850 kPa absolute (560 psia).

This selective separation zone is operated at essentially the same pressure as the reaction zone. By “essentially” it is meant that the operating pressure of the selective separation zone is within about 1034 kPa absolute (150 psia) of the operating pressure of the reaction zone. For example, the selective separation zone is no more than 1034 kPa absolute (150 psia) less than that of the reaction zone. The vapor stream and the liquid stream are both removed from the product separator. A portion of the liquid stream may be recycled to the reaction zone, at the feed location or at one or more intermediate locations. A water byproduct stream is also removed. The liquid stream may be recovered or may be routed to a product recovery column to separate the light ends from the diesel and naphtha products.

[0022] Optionally, the effluent from the deoxygenation reaction zone is conducted to a hot high pressure hydrogen stripper before at least a portion of the effluent is cooled and conducted to the cold product separator. One benefit of this embodiment is that a liquid stream of paraffins is generated at or near to the temperature and pressure of the reaction zone, and a portion of that stream may be recycled to the reaction zone with minimal pumping energy and minimal additional heating. Saving the utilities of pumping and reheating can significantly reduce the cost of the overall process and if the recycle stream is large enough would more than offset the additional capital cost of the hot high pressure hydrogen stripper. Likewise the net liquid going to the product recovery column needs less heating to separate light byproducts. Another benefit is the liquid stream is essentially dry and therefore does not pass carry water back to the reactor. In addition, the separation in the cold product separator becomes more efficient since the phase separation does not include the heavy hydrocarbons having from about 8 to about 24 or more carbon atoms. Furthermore, any unreacted tri-, di- and or mono-glycerides or free fatty acids present in the reactor effluent during a unit start-up or unit upset are selectively removed in the hot separator liquid and do not come into contact with a condensed water phase where they could contaminate the byproduct water.

[0023] The reaction zone effluent enters the hot high pressure stripper and the water and normally gaseous components, are carried with the hydrogen stripping gas and separated into an overhead stream. By using a dry hydrogen stream as the stripping gas, water, carbon monoxide, carbon dioxide, and any ammonia or hydrogen sulfide are selectively separated from the hydrocarbon liquid product in the hot high pressure hydrogen stripper. The hydrogen stripping gas can be hydrogen make-up gas that is effectively free of carbon oxides and water. By effectively free, it is meant that the hydrogen make-up gas is free of carbon oxides and water, or if carbon oxides or water are present they are in such a small amount so as not to effect the stripping. The remainder of the deoxygenation effluent stream is removed as hot high pressure hydrogen stripper bottoms and contains the liquid hydrocarbon fraction having components such as normal hydrocarbons having from about 8 to about 24 carbon atoms. A portion of this liquid hydrocarbon fraction in hot high pressure hydrogen stripper bottoms may be used as the hydrocarbon recycle described below, and the stripper bottoms are already at or near the operating conditions of the reaction zone thereby saving the costs involved with pumping or heating of the recycle portion. The stripper bottoms are conducted to a product recovery column.

[0024] The temperature of the hot high pressure hydrogen stripper may be controlled in a limited range to achieve the desired separation and the pressure may be maintained at approximately the same pressure as the reaction zone to minimize both investment and operating costs. The hot high pressure hydrogen stripper may be operated at conditions ranging from a pressure of about 689 kPa absolute (100 psia) to about 13,790 kPa absolute (2000 psia), and a temperature of about 40° C. to about 350° C. In another embodiment the hot high pressure hydrogen stripper may be operated at conditions ranging from a pressure of about 1379 kPa absolute (200 psia) to about 4826 kPa absolute (700 psia), or about 2413 kPa absolute (350 psia) to about 4882 kPa absolute (650 psia), and a temperature of about 50° C. to about 350° C. The hot high pressure hydrogen stripper may be operated at essentially the same pressure as the reaction zone. By “essentially” it is meant that the operating pressure of the high pressure hydrogen stripper is within about 1034 kPa absolute (150 psia) of the operating pressure of the reaction zone. For example, the pressure of the hot high pressure hydrogen stripper separation zone is no more than 1034 kPa absolute (150 psia) less than that of the reaction zone.

[0025] One purpose of the hot high pressure hydrogen stripper is to separate the gaseous portion of the effluent from the liquid portion of the effluent. As hydrogen is an expensive resource, to conserve costs, the separated hydrogen is ultimately recycled to the deoxygenation reactor. Hydrogen is a reactant in at least one of the deoxygenation reactions, 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 that is readily available for reaction. 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 ability to operate in a pressure range of about 1379 kPa absolute (200 psia) to about 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 about 2413 kPa absolute (350 psia) to about 4481 kPa absolute (650 psia), and in yet another embodiment operating pressure is in the range of about 2758 kPa absolute (400 psia) to about 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.

[0026] In one embodiment, 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 determined not on temperature control requirements, but instead, based upon feedstock composition and 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. In one embodiment of the invention, the volume ratio of hydrocarbon recycle to feedstock is from about 2:1 to about 8:1, or about 2:1 to about 6:1. In another embodiment the ratio is in the range of about 3:1 to

about 6:1 and in yet another embodiment the ratio is in the range of about 4:1 to about 5:1.

[0027] The gaseous portion of the reaction zone effluent in the overhead from the hot high pressure hydrogen stripper is cooled, by techniques such as heat exchange, air cooling, or water cooling and passed to a cold separator where liquid components are separated from the gaseous components by phase separation. Suitable operating conditions of the cold separator include, for example, a temperature of about 20 to 80° C. or 45 to 50° C. and a pressure of relatively low pressure of about 3447 kPa (500 psia) to about 6895 kPa (1000 psia), with one embodiment at 3850 kPa absolute (560 psia). A water byproduct stream is also separated. The gaseous component stream from the cold separator comprises hydrogen, carbon monoxide, carbon dioxide, and hydrogen sulfide while the liquid component stream from the cold separator comprises naphtha and LPG. Again, this separation may be operated at essentially the same pressure as the reaction zone. By “essentially” it is meant that the operating pressure of the cold separator is within about 1034 kPa absolute (150 psia) of the operating pressure of the reaction zone. For example, the pressure of the separator is no more than 1034 kPa absolute (150 psia) less than that of the reaction zone.

[0028] Either the hot high pressure hydrogen stripper bottoms or the liquid component from the cold product separator in the embodiment with no hot high pressure hydrogen stripper may be recovered as diesel boiling point range product. However, the liquid component from the product separator and the hot high pressure hydrogen stripper bottoms, if present, collectively contain the hydrocarbons useful as diesel boiling range fuel or diesel boiling range fuel blending component as well as smaller amounts of naphtha and LPG and may be further purified in a product recovery column. The product recovery column fractionates lower boiling components and dissolved gases from the diesel product containing C₈ to C₂₄ paraffins. Suitable operating conditions of the product recovery column include a temperature of from about 20 to about 200° C. at the overhead and a pressure from about 0 to about 1379 kPa absolute (0 to 200 psia).

[0029] Although this hydrocarbon fraction is useful as a diesel boiling range fuel or a diesel boiling range fuel blending component, because it comprises essentially n-paraffins, it will have poor cold flow properties. To improve the cold flow properties of the liquid hydrocarbon fraction, the paraffins produced in the first reaction zone are optionally contacted with an isomerization catalyst under isomerization conditions to at least partially isomerize the n-paraffins to branched paraffins. The effluent of the second reaction zone, the isomerization zone, is a branched-paraffin-rich stream. By the term “rich” it is meant that the effluent stream has a greater concentration of branched paraffins than the stream entering the isomerization zone, and preferably comprises greater than 50 mass-% branched paraffins. It is envisioned that the isomerization zone effluent may contain 70, 80, or 90 mass-% branched paraffins. Isomerization can be carried out in a separate bed of the same reaction zone, i.e. same reactor, described above for the deoxygenation reactions or the isomerization can be carried out in a separate reactor. For ease of description the following will address the embodiment where a second reactor is employed for the isomerization reaction. The hydrogen stripped product of the 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 the 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 paraffin.

[0030] 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. One or more beds of catalyst may be used. It is preferred that the isomerization be operated in a co-current mode of operation. Fixed bed, trickle bed down flow or fixed bed liquid filled up-flow modes are both suitable. See also, for example, US 2004/0230085 A1 which is incorporated by reference in its entirety. 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, mesoporous silica alumina, 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 U.S. Pat. No. 4,310,440. SAPO-11, SAPO-31, SAPO-37, and SAPO-41 are described in U.S. Pat. No. 4,440,871. SM-3 is described in U.S. Pat. No. 4,943,424; U.S. Pat. No. 5,087,347; U.S. Pat. No. 5,158,665; and U.S. Pat. No. 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 U.S. Pat. No. 4,793,984, and MgAPSOs are described in U.S. Pat. No. 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 U.S. Pat. No. 4,795,623 and U.S. Pat. No. 4,924,027. Further catalysts and conditions for skeletal isomerization are disclosed in U.S. Pat. No. 5,510,306, U.S. Pat. No. 5,082,956, and U.S. Pat. No. 5,741,759.

[0031] 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 U.S. Pat. No. 5,716,897 and U.S. Pat. No. 5,851,949. Other suitable support materials include ZSM-22, ZSM-23, and ZSM-35, which are described for use in dewaxing in U.S. Pat. No. 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 U.S. Pat. No. 4,310,440; U.S. Pat. No. 4,440,871; U.S. Pat. No. 4,793,984; U.S. Pat. No. 4,758,419; U.S. Pat. No. 4,943,424; U.S. Pat. No. 5,087,347; U.S. Pat. No. 5,158,665; U.S. Pat. No. 5,208,005; U.S. Pat. No. 5,246,566;

U.S. Pat. No. 5,716,897; and U.S. Pat. No. 5,851,949 are hereby incorporated by reference.

[0032] U.S. Pat. No. 5,444,032 and U.S. Pat. No. 5,608,968 teach a suitable bifunctional catalyst which is constituted by an amorphous silica-alumina gel and one or more metals belonging to Group VIIIA, and is effective in the hydroisomerization of long-chain normal paraffins containing more than 15 carbon atoms. U.S. Pat. No. 5,981,419 and U.S. Pat. No. 5,908,134 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 SiO_2 : Al_2O_3 ratio is higher than 300:1; (b) one or more metal(s) belonging to Group VIIIA, selected from platinum and palladium, in an amount comprised within the range of from 0.05 to 5% by weight. Article V. Calemme et al., *App. Catal. A: Gen.*, 190 (2000), 207 teaches yet another suitable catalyst.

[0033] 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 about 150° C. to about 360° C. and a pressure of about 1724 kPa absolute (250 psia) to about 4726 kPa absolute (700 psia). In another embodiment the isomerization conditions include a temperature of about 300° C. to about 360° C. and a pressure of about 3102 kPa absolute (450 psia) to about 3792 kPa absolute (550 psia). Other operating conditions for the isomerization zone are well known in the art.

[0034] At least a portion of the hydrogen in the isomerization zone effluent may be separated in an optional isomerization effluent separator with the separated hydrogen being removed in an overhead stream. Suitable operating conditions of the isomerization effluent separator include, for example, a temperature of 230° C. and a pressure of 4100 kPa absolute (600 psia). If there is a low concentration of carbon oxides, or the carbon oxides are removed, the hydrogen may be recycled back to the hot high pressure hydrogen stripper for use both as a stripping gas and to combine with the remainder as a bottoms stream. The remainder may be passed to the isomerization reaction zone and thus the hydrogen becomes a component of the isomerization reaction zone feed streams in order to provide the necessary hydrogen partial pressures for the reactor.

[0035] The hydrogen is also a reactant in the deoxygenation reactors, and different feedstocks will consume different amounts of hydrogen. The isomerization effluent separator allows flexibility for the process to operate even when larger amounts of hydrogen are consumed in the first reaction zone. Furthermore, at least a portion of the remainder or bottoms stream of the isomerization effluent separator may be recycled to the isomerization reaction zone to increase the degree of isomerization. Suitable operating conditions of the isomerization effluent separator include, for example, a temperature of 230° C. and a pressure of 4100 kPa absolute (600 psia).

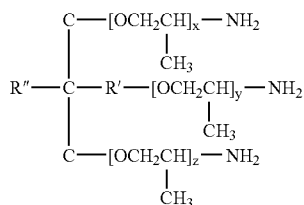
[0036] The remainder of the final effluent, after the removal of at least a portion of the hydrogen, still has liquid and gaseous components and is cooled, by techniques such as air cooling or water cooling and passed to a cold separator where the liquid component is separated from the gaseous component as discussed above. A water byproduct stream is also separated.

[0037] The LPG/Naphtha stream may be further separated in a debutanizer or depropanizer in order to separate the LPG into an overhead stream, leaving the naphtha in a bottoms

stream. Suitable operating conditions of this unit include a temperature of from about 20 to about 200° C. at the overhead and a pressure from about 0 to about 2758 kPa absolute (0 to 400 psia). The LPG may be sold as valuable product or may be used as feed to a hydrogen production facility. Similarly, the naphtha may be used as feed to a hydrogen or gasoline production facility, or may be blended into the gasoline pool.

[0038] The gaseous component separated in the product separator of any of the embodiments above comprises mostly hydrogen and the carbon dioxide from the decarboxylation reaction. Other components such as carbon monoxide, propane, and hydrogen sulfide or other sulfur containing component may be present as well. It is desirable to recycle the hydrogen to the reaction zone, but if the carbon dioxide was not removed, its concentration would quickly build up and effect the operation of the reaction zone. Usually, carbon dioxide would be removed from the hydrogen by means well known in the art such as absorption, along with hydrogen sulfide, using an amine, reaction with a hot carbonate solution, pressure swing absorption, etc. and if desired, essentially pure carbon dioxide could be recovered by regenerating the spent absorption media. However, the separation of carbon dioxide from hydrogen may be complicated by the sulfur containing component such as hydrogen sulfide which is sometimes present to maintain the sulfided state of the deoxygenation catalyst or to control the relative amounts of the decarboxylation reaction and the hydrogenation reaction that are both occurring in the deoxygenation zone. Because the hydrogen sulfide serves a useful purpose in the deoxygenation reaction zone, it is desirable to recycle the hydrogen sulfide to the reaction zone as opposed to purchasing additional hydrogen sulfide or sulfur components. In some applications, there may be a need to control the level of hydrogen sulfide being recycled which may require removing the substantially all the hydrogen sulfide in order to control the amount of separated hydrogen sulfide that is recycled to the reaction zone. Therefore, the techniques for removing the carbon dioxide also need to provide the sulfur management in the process.

[0039] In one embodiment of the invention an amine absorber is used to selectively remove carbon dioxide while allowing hydrogen and hydrogen sulfide to pass to recycle. In this embodiment the gaseous stream from the cold product separator is routed through an amine absorber containing an aqueous solution of a polyoxypropylene triamine having the formula:



Where R' represents a methylene group and R'' represents hydrogen or methyl or ethyl and wherein the sum of X+Y+Z is a positive integer having a value of from about 4 to about 6. These amines are fully described in U.S. Pat. No. 4,710,362 which is hereby incorporated by reference in its entirety. The amine is in an aqueous solution containing about 35 to about 55

wt. % of the polyoxypropylene triamine, and the absorption in the absorber may be conducted at about 20° C. to about 50° C.

[0040] In another embodiment, two amine absorbers are employed. The first amine scrubber removes both carbon dioxide and hydrogen sulfide allowing hydrogen to pass to recycle. The amine chosen to be employed in first amine absorber is capable of 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). The promoter may be piperazine, and the promoted amine may be used as an aqueous solution. See U.S. Pat. No. 6,337,059, hereby incorporated by reference in its entirety. Suitable amines for the first amine absorber 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 absorber to be recycled to the first reaction zone. The amine is regenerated and the carbon dioxide and hydrogen sulfide are released and removed. The regenerated amine may be recycled and reused. The released carbon dioxide and hydrogen sulfide are passed through a second amine absorber 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, HS102, HS103, HS104, HS115. Therefore the carbon dioxide passes through second amine absorber and is available for use elsewhere. The amine may be regenerated which releases the hydrogen sulfide to be recycled. A portion of the hydrogen sulfide may be sent to a Claus plant. Regenerated amine is then recycled and reused. The hydrogen sulfide recycle to the reaction zone may be controlled so that the appropriate amount of sulfur is maintained in the reaction zone. Conditions for the first scrubber zone includes a temperature in the range of 30 to 60° C. At least 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 absorber is within about 1034 kPa absolute (150 psia) of the operating pressure of the reaction zone. For example, the pressure of the absorber is no more than 1034 kPa absolute (150 psia) less than that of the reaction zone. Also, at least the first absorber is operated at a temperature that is at least 1° C. higher than that of the separator. Keeping at least the first absorber 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. Conditions for the second amine solution absorber zone may include from about 20 to about 60° C. and a pressure in the range of about 138 kPa (20 psia) to about 241 kPa (35 psia).

[0041] The gaseous component stream from the cold product separator has a total volume that is much greater than the combined volume of carbon dioxide and hydrogen sulfide. Typically, the amount of hydrogen sulfide in vapor stream **36** ranges from about 0.01 to about 2 volume-%. In the configurations shown in the figures, the first amine absorber zone is sized to accommodate the flow of the entire vapor stream from the cold product separator. However, the second amine absorber zone is greatly reduced in size as compared to the first since the flow of material to the second amine absorber zone is only a fraction of vapor stream from the cold product

separator. The reduction in the size of the second amine absorber zone allows for reduced capital and operating costs.

[0042] In yet another embodiment, the process may be equipped with a flexible solvent absorber. Processes discussed herein require sulfur management steps to control the sulfur component used in the process. However, not all diesel boiling range processes using renewable feedstock require sulfur management. Therefore, to provide the greatest degree of flexibility from the process units, a flexible absorber may be employed as the amine absorber. A flexible absorber allows for at least two different amine solvents to be supplied to the flexible absorber. For example, when sulfur management is required, amines as discussed above may be supplied to the flexible absorber. In applications where sulfur management is not required, other amines may be supplied to the flexible absorber. Or, the flexible absorber may be used to supply the carbon dioxide selective amine in one application, and the carbon dioxide and hydrogen sulfide selective amine in another application. For example The purpose of the flexible absorption system is to (a) selectively remove carbon dioxide from the recycle gas when feed sulfur content is low, for example refined soybean oil, and it is advantageous to allow hydrogen sulfide to build up in the recycle gas to maintain the required hydrogen sulfide partial pressure in the hydrodeoxygenation reaction zone and (b) remove both carbon dioxide and hydrogen sulfide from the recycle gas when the sulfur content in the reaction zone of the feed is high, for example brown grease, it is undesirable for hydrogen sulfide to build up in the recycle gas to the deoxygenation reaction zone. A polyoxypropylenetriamine-rich solvent may be used for case (a) and a formulated MDEA-based solvent such as UCARSOL[®], may be used for case (b). The choice of solvent will be dictated by the sulfur content in the reaction zone, the hydrodeoxygenation catalyst active metals loading and the target hydrogen sulfide concentration in the reaction zone.

[0043] Two separate solvent make-up systems and recycle reservoirs are required. The gas to the absorber enters the absorber zone and is sent to the bottom of the absorber vessel. The gas flows upward through the acid gas absorption section and then passes through a demisting pad. The absorber is equipped with multiple trays, or packing where the feed gas counter-currently contacts either the carbon dioxide selective polyoxypropylenetriamine-type solvent or the MDEA-based non-selective solvent. In both cases, the cooled lean solvent enters near the tower top through a liquid distributor and flows down through the packing, absorbing either the carbon dioxide while letting the hydrogen sulfide pass through or absorbing both the carbon dioxide and the hydrogen sulfide to the required product specification. This lean solvent line is equipped with an antifoam injection point to allow for the injection of anti-foam when needed. A solvent reservoir is maintained in the bottom of the absorber via liquid level control. High and low level alarms are provided since loss of liquid level can cause high-pressure gas to exit the absorber bottom. The product gas passes through a demisting pad at the top of the absorber to minimize entrainment of liquid. The product gas exiting the absorber leaves the zone water saturated.

[0044] As the effluent gas stream from the flexible absorber is recycled to the reaction zone it is typically required that the gas be first cooled and any condensable liquids removed in an appropriate separator. If separated, the condensable aqueous phase liquid recovered could contain solvent and to reduce solvent make-up requirements for the flexible unit, the aqueous

phase from this downstream separator should be routed back to the absorber zone. The rich solvent may be regenerated as is known in the art. Two separate regeneration systems may be required, one for each of the different amine solvents that may be used.

[0045] The flexible absorber is operated at essentially the same pressure as the reaction zone pressure and near ambient temperature. By "essentially" it is meant that the pressure of the flexible absorber is within 1034 kPa absolute (150 psia) of the pressure of the product separator. The pressure of the flexible absorber is no more than 1034 kPa absolute (150 psia) less than the pressure of the product separator. Lean solvent should enter the absorber slightly warmer than the acid gas stream so as to prevent condensation of any light product hydrocarbons in the amine solvent.

[0046] For the amine solvent which selectively removes only carbon dioxide, the absorber effluent gas will contain from about 100 to about 1000 ppm carbon dioxide and >50% of the hydrogen sulfide present in the gas entering the absorber. For the amine solvent which selectively removes both carbon dioxide and hydrogen sulfide, the absorber effluent gas will contain <1 ppm hydrogen sulfide and from about 100 to about 1000 ppm carbon dioxide.

[0047] At least one flexible absorber would be used in the place of a traditional absorber, but it is within the scope of the invention to replace all traditional absorbers with flexible absorbers. FIG. 5. shows a drawing of a sample flexible absorber. Vapor stream 522 from the cold product separator enters flexible absorber 556. Liquid amine absorber is introduced through either line 550 or 552. Line 550 is connected to first solvent source 554 and line 552 is connected to second solvent source 556. Each of the two solvent sources provide a solvent of differing selectivity. For example, first solvent source 554 may provide a solvent of the type disclosed in U.S. Pat. No. 4,710,362 and second solvent source 556 may provide a solvent such as the UCARSOL[™] AP series solvents from DOW such as AP802, AP804, AP806, AP810 and AP814. As an example, when an application calls for only carbon dioxide to be removed from the stream 522, the solvent from the first solvent source 554 would be directed to flexible absorber 530. However, when an application requires both carbon dioxide and hydrogen sulfide to be removed from the stream 522, solvent from the second source would be directed to flexible absorber 530. In either case, solvent is removed from flexible absorber 530 via line 531 and conducted to a regeneration zone.

[0048] The techniques exemplified here for the separation of the carbon dioxide are not limiting, and other known techniques for the separation of the carbon dioxide may be used. The hydrogen stream remaining after the removal of the carbon oxides may be recycled to the reaction zone. The hydrogen stream may contain the hydrogen sulfide being recycled to the reaction zone, or the separated hydrogen sulfide may be recycled independently such as in controlled amounts. The hydrogen recycle stream may be introduced to the inlet of the reaction zone and/or to any subsequent beds/reactors.

[0049] The carbon dioxide stream is conducted to an algae cultivation operation. Algae require three primary components to grow: sunlight, carbon dioxide and water. Algae grow through photosynthesis where sunlight energy is converted to chemical energy to drive, for example, the formation of sugars or the fixation of nitrogen into amino acids. Often algae cultivation is performed in open ponds such as raceway ponds, open air bioreactors, photobioreactors and combina-

tions thereof. Raceway ponds are shallow ponds which have the algae and the nutrients circulating around a track with paddlewheels stirring the pond solution and providing the fluid flow. The algae is suspended in the water of the pond and are circulated to the surface with regular frequency. If contamination, pH control, temperature control, and other parameters are an issue, the algae cultivation operation may be closed off or covered, such as a greenhouse. Carbon dioxide and nutrients are continuously fed to the ponds and an excess of carbon dioxide is thought to increase algae production. Often, the carbon dioxide is bubbled through the pond. Algae-containing water is removed and processed to obtain algae oil. The carbon dioxide stream from the diesel boiling range fuel generation process may be utilized in any algae cultivation operation, since carbon dioxide is a key component in the cultivation operations. The term algae is meant to include microalgae. Some strains of microalgae may be cultivated under saline conditions

[0050] Algae strains typically cited in the literature for algae oil production are Chlorophyceae, Bacilliarophy (diatom algae), *Botryococcus braunii* and *Dunaliella tertiolecta*. Algal strains such as *Botryococcus braunii* can produce long chain hydrocarbons representing 86% of its dry weight. The green alga *Botryococcus* is unique in the quality and quantity of the liquid hydrocarbons it produces. Some scientists consider the ancestors of *Botryococcus* to be responsible for many of the world's fossil fuel deposits. The *Dunaliella tertiolecta* strain is reported to have oil yield of about 37% (organic basis). *D. tertiolecta* is a fast growing strain and that means it has a high CO₂ sequestration rate as well. A favored strain of algae includes Chlorophyceae (green algae). Green algae tend to produce starch, rather than lipids, and green algae have very high growth rates at 30° C. and high light in a water solution of type I at 55 mmho/cm. Another favored algae strain is Bacilliarophy (diatom algae). However, the diatom algae needs silicon in the water to grow, whereas green algae requires nitrogen to grow. Under nutrient deficiency the algae produced more oils per weight of algae, however the algae growths also were significantly less.

[0051] Some green algae, such as *Chlamydomonas reinhardtii* and *Chlamydomonas moewusii*, are known to sometimes switch from the production of oxygen to the production of hydrogen. If the algae culture medium is deprived of sulfur the algae will switch from the production of oxygen via normal photosynthesis to the production of hydrogen through the enzyme hydrogenase. If the algae is able to produce hydrogen, then another integration with the diesel boiling range fuel production process becomes available. The hydrogen produced by the algae may be introduced to the reaction zone of the diesel boiling range fuel production process. The hydrogen may be combined with other sources of hydrogen, and may be combined with the feedstock to the reaction zone.

[0052] The carbon dioxide from the diesel boiling range fuel process described above may be integrated with the algae cultivation operation, the hydrogen produced from an algae cultivation process may be integrated with the diesel boiling range fuel process, or both integrations may be simultaneously employed providing multiple points of integration between the diesel boiling range fuel process and the algae cultivation process. In each case, a byproduct of one process is being used as a valuable component of another process.

[0053] The algae can be used to also utilize waste carbon dioxide from other processes such as power plants burning coal or other fossil fuels. The algae eliminate the need for

sequestering the carbon dioxide made from power plants and actually use all the carbon dioxide byproduct to make oil which can be turned into valuable fuel as described herein.

[0054] The following embodiments are presented in illustration of this invention and are not intended as an undue limitation on the generally broad scope of the invention as set forth in the claims. First the process without the optional isomerization zone is described in general as with reference to FIG. 1. Then the process without the optional isomerization reaction zone is described in more detail with reference to FIG. 2. The process is described in detail employing the optional hot high pressure hydrogen stripper, but not the optional isomerization reaction zone with reference to FIG. 3. The process is described in detail employing the optional isomerization reaction zone with reference to FIG. 4.

[0055] Turning to FIG. 1 renewable feedstock 102 enters deoxygenation reaction zone 104 along with recycle hydrogen and hydrogen sulfide stream 126 and optional product recycle 112. Contacting the renewable feedstock with the deoxygenation catalyst generates deoxygenated product 106 which is directed to optional first selective separation zone 108 which comprises a hot high pressure hydrogen stripper. Hydrogen-rich make-up gas 110 and optionally recycle hydrogen is added to optional first selective separation zone. The hydrogen in the reaction zone or the hydrogen-rich make-up gas may be produced by particular strains of algae.

[0056] Carbon oxides and water vapor are removed with hydrogen in optional first selective separation zone overhead 114 and separated deoxygenated liquid product are removed in optional first selective separation zone bottoms 116. Both streams are passed to product recovery zone 120. Product recovery zone 120 comprises at least a cooler, a cold product separator, and a product recovery column. Carbon dioxide and hydrogen stream 122, light ends stream 124, water byproduct stream 128, and paraffin-rich product 118 are all removed from product recovery zone 120. Paraffin-rich product 118 may be collected for use as diesel boiling range fuel. Carbon dioxide and hydrogen stream 122 is directed to second selective separation zone 130 which contains one or more selective amine absorbers. At least carbon dioxide is removed from stream 122 via line 132. Carbon dioxide stream 132 is conducted to algae cultivation operation 170 and algae is collected from stream 172. Hydrogen recycle stream 126 is removed from second selective separation zone and recycled to the deoxygenation reaction zone 104.

[0057] Turning to FIG. 2, the process begins with a renewable feedstock stream 202 which may pass through an optional feed surge drum. The feedstock stream is combined with recycle stream 216 to form combined feed stream 220, which is heat exchanged with reactor effluent and then introduced into catalytic deoxygenation reactor 204. The heat exchange may occur before or after the recycle is combined with the feed. Deoxygenation reactor 204 may contain multiple beds shown in FIG. 2 as 204a, 204b, 204c and 204d. Deoxygenation reactor 204 contains at least one catalyst capable of catalyzing decarboxylic and/or hydrodeoxygenation of the feedstock to remove oxygen. Deoxygenation reactor effluent stream 206 containing the products of the decarboxylic and/or hydrodeoxygenation reactions is removed from deoxygenation reactor 204 and heat exchanged with stream 220 containing feed to the deoxygenation reactor. Stream 206 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.

[0058] Deoxygenation reactor effluent stream 206 is directed to air cooler 232 and then introduced into product separator 234. In product separator 234 the gaseous portion of the stream comprising hydrogen, carbon monoxide, hydrogen sulfide, carbon dioxide and propane are phase separated and removed in stream 236 while the liquid hydrocarbon portion of the stream is removed in stream 238. A portion of the liquid hydrocarbon stream 238a is recycled to the reaction zone 204. A water byproduct stream 240 may also be removed from product separator 234. Stream 238 is introduced to product recovery column 242 where components having higher relative volatilities are separated into stream 244 with the remainder, the diesel range components, being withdrawn from product recovery column 242 in line 246. Stream 244 is optionally introduced into a fractionator which operates to separate LPG into an overhead leaving a naphtha bottoms stream (not shown).

[0059] The vapor stream 236 from product separator 234 contains the gaseous portion of the reaction zone effluent which comprises at least hydrogen, carbon monoxide, carbon dioxide and propane and is directed to a system of at least one amine absorber and regenerator 256 to separate carbon dioxide and optionally hydrogen sulfide (if present) from the vapor stream. Because of the cost of hydrogen, it is desirable to recycle the hydrogen to deoxygenation reactor 204, but it is not desirable to circulate the carbon dioxide or an excess of sulfur containing components. In one embodiment, vapor stream 236 is passed through a system of one amine absorber 256, also called a scrubber. The amine chosen to be employed in the single amine absorber 256 is capable of selectively removing carbon dioxide while allowing hydrogen and hydrogen sulfide to pass through the absorber. Suitable amines for use in are described in U.S. Pat. No. 4,710,362. The amine absorber may be operated at from about 20 to about 60 C and a pressure in the range of about 3447 kPa (500 psia) to about 6895 kPa (1000 psia).

[0060] In another embodiment, to separate both the sulfur containing components and the carbon dioxide from the hydrogen, vapor stream 236 is passed through a system of at least two amine absorbers 256 and 258. The amine employed in amine scrubber 256 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). The promoter may be piperazine, and the promoted amine may be used as an aqueous solution. See U.S. Pat. No. 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 216 to be recycled to reaction zone 204. The amine is regenerated and the carbon dioxide and hydrogen sulfide are released and removed in line 262. Within the first amine absorber zone, regenerated amine may be recycled for use again. The released carbon dioxide and hydrogen sulfide in line 262 are passed through optional second amine scrubber zone 258 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, HS102, HS103, HS104, HS115. Therefore the carbon dioxide passes through second amine scrubber zone 258 and into line 266. The carbon dioxide in line 266 is passed to an algae cultivation operation 270 and used, along with nutrients and sunlight, to cultivate the algae. Algae is removed in line 272. The amine may be regenerated which releases the hydrogen sulfide into line 260. At least a portion of the hydrogen sulfide in line 260 may be recycled to the reaction zone 204, possibly in measured controlled amount. Excess hydrogen sulfide may be directed to a Claus plant. Regenerated amine is then reused. Conditions for each scrubber zone include from about 20 to about 60 C. and a pressure in the range of about 3447 kPa (500 psia) to about 6895 kPa (1000 psia).

[0061] In another embodiment, the amine solution absorber zone 256 may contain the amine solution of U.S. Pat. No. 4,710,362 which selectively separates only the carbon dioxide and allows the hydrogen sulfide to pass with the hydrogen into recycle line 216. In this embodiment, the second amine absorber zone 258 is not necessary.

[0062] In yet another embodiment, amine scrubber zone 256 may contain the flexible amine scrubber such as shown in FIG. 5 and described in detail above. In this embodiment, the amine solvent best suited for the separation required is provided to the absorber.

[0063] Another embodiment of the invention employs a hot high pressure hydrogen stripper. Turning to FIG. 3, the process begins with a renewable feedstock stream 302 which may pass through an optional feed surge drum. The feedstock stream is combined with recycle stream 316 to form combined feed stream 320, which is heat exchanged with reactor effluent and then introduced into deoxygenation reactor 304. The heat exchange may occur before or after the recycle is combined with the feed. Deoxygenation reactor 304 may contain multiple beds shown in FIG. 3 as 304a, 304b, 304c and 304d. Deoxygenation reactor 304 contains at least one catalyst capable of catalyzing decarboxylic and/or hydrodeoxygenation of the feedstock to remove oxygen. Deoxygenation reactor effluent stream 306 containing the products of the decarboxylic and/or hydrodeoxygenation reactions is removed from deoxygenation reactor 304 and heat exchanged with stream 320 containing feed to the deoxygenation reactor. Stream 306 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.

[0064] Deoxygenation reactor effluent stream 306 is directed to hot high pressure hydrogen stripper 308. Make up hydrogen in stream 310 is also introduced to hot high pressure hydrogen stripper 308. In hot high pressure hydrogen stripper 308, the gaseous component of deoxygenation reactor effluent 306 is stripped from the liquid component of deoxygenation reactor effluent 306 using make-up hydrogen 310 and optional recycle hydrogen (not shown). The gaseous component comprising hydrogen, vaporous water, carbon monoxide, carbon dioxide and possibly some propane, is separated into hot high pressure hydrogen stripper overhead stream 314. The remaining liquid component of deoxygenation reactor effluent 306 comprising primarily normal paraffins having a carbon number from about 8 to about 24 with a cetane

number of about 60 to about 100 is removed as hot high pressure hydrogen stripper bottoms **312**.

[0065] A portion of hot high pressure hydrogen stripper bottoms forms recycle stream **313** and is combined with renewable feedstock combined stream **320**. Another portion of recycle stream **313**, optional stream **313a**, may be routed directly to deoxygenation reactor **304** and introduced at inter-stage locations such as between beds **304a** and **304b** and/or between beds **304c** and **304d** in order, for example, to aid in temperature control. The remainder of hot high pressure hydrogen stripper bottoms in stream **312** is routed to product recovery column **342**.

[0066] Hydrogen stripper overhead stream **314** is air cooled using air cooler **332** and introduced into product separator **334**. In product separator **334** the gaseous portion of the stream comprising hydrogen, carbon monoxide, hydrogen sulfide, carbon dioxide and propane are removed in stream **336** while the liquid hydrocarbon portion of the stream is removed in stream **338**. A liquid water byproduct stream **340** may also be removed from product separator **334**. Stream **338** is introduced to product recovery column **342** where components having higher relative volatilities are separated into stream **344** with the remainder, the diesel range components, being withdrawn from product recovery column **342** in line **346**. Stream **344** may be introduced into a fractionator which operates to separate LPG into an overhead and leaving a naphtha bottoms (not shown).

[0067] The vapor stream **336** from product separator **334** contains the gaseous portion of the isomerization effluent which comprises at least hydrogen, carbon monoxide, carbon dioxide and propane and is directed to a system of amine absorbers to separate carbon dioxide and optionally hydrogen sulfide (if present) from the vapor stream. The separation of the carbon dioxide and the optional separation of any hydrogen sulfide is described with reference to FIG. 2 and is not repeated here. Note that the carbon dioxide in line **366** is passed to an algae cultivation operation **370** and used, along with nutrients and sunlight, to cultivate the algae. Algae is removed in line **372**. Other separation systems are possible, such as adsorbents and treating processes.

[0068] Turning to FIG. 4, the process begins with a renewable feedstock stream **402** which may pass through an optional feed surge drum. The feedstock stream is combined with recycle stream **416** to form combined feed stream **420**, which is heat exchanged with reactor effluent and then introduced into deoxygenation reactor **404**. The heat exchange may occur before or after the recycle is combined with the feed. Deoxygenation reactor **404** may contain multiple beds shown in FIG. 4 as **404a**, **404b**, and **404c**. Deoxygenation reactor **404** contains at least one catalyst capable of catalyzing decarboxylic and/or hydrodeoxygenation of the feedstock to remove oxygen. Deoxygenation reactor effluent stream **406** containing the products of the decarboxylic and/or hydrodeoxygenation reactions is removed from deoxygenation reactor **404** and heat exchanged with stream **420** containing feed to the deoxygenation reactor. Stream **406** 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.

[0069] Deoxygenation reactor effluent stream **406** is directed to hot high pressure hydrogen stripper **408**. Make up hydrogen in stream **410** is also introduced to hot high pressure hydrogen stripper **408**. In hot high pressure hydrogen stripper

408, the gaseous component of deoxygenation reactor effluent **406** is stripped from the liquid component of deoxygenation reactor effluent **406** using make-up hydrogen **410** and optional recycle hydrogen **411**. The gaseous component comprising hydrogen, vaporous water, carbon monoxide, carbon dioxide and possibly some propane, is separated into hot high pressure hydrogen stripper overhead stream **414**. The remaining liquid component of deoxygenation reactor effluent **406** comprising primarily normal paraffins having a carbon number from about 8 to about 24 with a cetane number of about 60 to about 100 is removed as hot high pressure hydrogen stripper bottoms **412**.

[0070] A portion of hot high pressure hydrogen stripper bottoms forms recycle stream **413** and is combined with renewable feedstock combined stream **420**. Another portion of recycle stream **413**, optional stream **413a**, may be routed directly to deoxygenation reactor **404** and introduced at inter-stage locations such as between beds **404a** and **404b** and/or between beds **404b** and **404c** in order, for example, to aid in temperature control. The remainder of hot high pressure hydrogen stripper bottoms in stream **412** is routed to isomerization zone **468** where it contacts an isomerization catalyst to convert normal paraffins to branched paraffins. Stream **412** may be heat exchanged with isomerization reactor effluent **422**.

[0071] 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 **422**, and after optional heat exchange with stream **412**, is introduced into hydrogen separator **426**. The overhead stream **428** from hydrogen separator **426** contains primarily hydrogen which may be recycled back to hot high pressure hydrogen stripper **408**. Bottom stream **429** from hydrogen separator **426** is air cooled using air cooler **432** and introduced into product separator **434**. In product separator **434** the gaseous portion of the stream comprising hydrogen, carbon monoxide, hydrogen sulfide, carbon dioxide and propane phase separate and are removed in stream **436** while the liquid hydrocarbon portion of the stream is removed in stream **438**. A liquid water byproduct stream **440** may also be removed from product separator **434**. Stream **438** is introduced to product recovery column **442** where components having higher relative volatilities are separated into stream **444** with the remainder, the diesel range components, being withdrawn from product recovery column **442** in line **446**. Stream **444** is introduced into fractionator **448** which operates to separate LPG into overhead **450** leaving a naphtha bottoms **452**.

[0072] The vapor stream **436** from product separator **434** contains the gaseous portion of the isomerization effluent which comprises at least hydrogen, carbon monoxide, carbon dioxide and propane and is directed to a system of at least one amine solution absorber to separate carbon dioxide and optionally hydrogen sulfide from the vapor stream. The separation of the carbon dioxide and the optional separation of any hydrogen sulfide is described with reference to FIG. 2 and is not repeated here. Note that the carbon dioxide in line **466** is passed to an algae cultivation operation **470** and used, along with nutrients and sunlight, to cultivate the algae. Algae is removed in line **472**. Other separation systems are possible, such as adsorbents and treating processes.

[0073] Other techniques of separating the carbon dioxide generated in the deoxygenation reaction zone may be employed, with the separated carbon dioxide being provided for use in an algae cultivation operation.

[0074] In an alternate embodiment, the carbon dioxide generated in the deoxygenation reaction zone may be employed in enclosed green houses to grow plants. The plants may then become a source of renewable feedstock to the diesel boiling range fuel production process. In this embodiment, upon separation of the carbon dioxide as discussed above, the carbon dioxide may be conducted to one or more enclosed green houses in order to cultivate plants being grown in the enclosed green houses.

[0075] In yet another alternate embodiment of the invention, the carbon dioxide generated in the deoxygenation reaction zone may be employed in supercritical extraction processes. In this embodiment, upon separation of the carbon dioxide as discussed above, the carbon dioxide may be conducted to one or more supercritical extraction operations to be used as an extractant in the supercritical extraction operations in order to separate at least two components from a mixture.

1. An integrated process for producing a paraffin-rich diesel boiling range product from a renewable feedstock and for cultivating algae, said integrated process comprising:

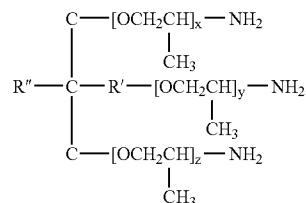
- a) treating the renewable feedstock in a reaction zone by hydrogenating and deoxygenating the feedstock using at least one catalyst at reaction conditions in the presence of hydrogen to provide a reaction zone product stream comprising hydrogen, carbon dioxide, water and a paraffins having from about 8 to about 24 carbon atoms;
- b) cooling the reaction zone product stream and separating to provide:
 - i) a gaseous component comprising at least hydrogen and carbon dioxide;
 - ii) a hydrocarbon product comprising the paraffins; and
 - iii) a water component;
- c) recovering the hydrocarbon product;
- d) separating the gaseous component comprising at least hydrogen and carbon dioxide into a stream comprising hydrogen and a stream comprising carbon dioxide; and
- e) passing the stream comprising carbon dioxide to an algae cultivation operation and using the carbon dioxide stream to cultivate algae.

2. The process of claim 1 wherein the separating step 1(d) is at essentially the same pressure as the reaction pressure and at a temperature that is at least about 1° C. above the separation temperature of step (b), and comprises passing the gaseous component through at least one amine absorber zone to produce the hydrogen stream and the carbon dioxide stream.

3. The process of claim 2 wherein the amine absorber zone comprises an aqueous solution of methyldiethanolamine and piperazine.

4. The process of claim 1 wherein the algae cultivation operation is selected from the group consisting of an open pond, a covered pond, a raceway pond, a bioreactor, a photobioreactor, and combinations thereof.

5. The process of claim 2 wherein the amine is an aqueous solution of a polyoxypropylene triamine having the formula:



where R' represents a methylene group and R'' represents hydrogen or methyl or ethyl and wherein the sum of X+Y+Z is a positive integer having a value of from about 4 to about 6.

6. The process of claim 2 wherein the gaseous component further comprises hydrogen sulfide and the amine absorber zone contains an amine that removes both carbon dioxide and hydrogen sulfide, said process further comprising regenerating the amine that removes both carbon dioxide and hydrogen sulfide to generate an acid gas stream containing carbon dioxide and hydrogen sulfide; passing the acid gas stream through a second amine absorber zone containing an amine selective to hydrogen sulfide to generate a carbon dioxide stream; regenerating the amine selective to hydrogen sulfide to generate a hydrogen sulfide stream; and recycling at least a portion of the hydrogen sulfide stream to reaction zone.

7. The process of claim 6 wherein the amine absorber zone and the second amine absorber zone comprises aqueous solutions of methyldiethanolamine and piperazine.

8. The process of claim 2 wherein the amine absorber is a flexible amine absorber.

9. The process of claim 1 wherein a portion of the hydrocarbon product is recycled to the reaction zone is at a volume ratio of recycle to feedstock in the range of about 2:1 to about 8:1.

10. The process of claim 1 wherein the reaction conditions in the reaction zone include a temperature of about 40° C. to about 400° C. and a pressure of about 689 kPa absolute (100 psia) to about 13,790 kPa absolute (2000 psia) and the separating of step 1 b) is at a pressure that is no more than 1034 kPa absolute (150 psia) less than the pressure of the reaction zone.

11. The process of claim 1 wherein at least a portion of the hydrogen of step (a) is generated by algae.

12. The process of claim 1 further comprising treating a petroleum derived hydrocarbon in the reaction zone with the renewable feedstock.

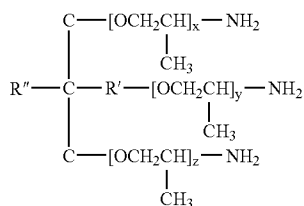
13. An integrated process for producing a paraffin-rich diesel boiling point range product from a renewable feedstock and for cultivating algae, said integrated process comprising:

- a) treating the renewable feedstock in a reaction zone by hydrogenating and deoxygenating the feedstock using at least one catalyst at reaction conditions in the presence of hydrogen to provide a reaction zone product stream comprising hydrogen, carbon dioxide, water, and paraffins having from about 8 to about 24 carbon atoms;
- b) selectively separating the reaction zone product stream into a gaseous stream comprising hydrogen and at least a portion of the water and carbon dioxide from the reaction zone product stream and a remainder stream comprising at least the paraffins;

- c) recycling a first portion of the remainder stream comprising at least the paraffins to the reaction zone;
- d) combining the gaseous stream and a second portion of the remainder stream to form a combined stream and separating the combined stream to provide:
 - a. a gaseous component comprising at least hydrogen, water, and carbon dioxide;
 - b. a hydrocarbon product; and
 - c. a water component;
 and recovering a portion of the hydrocarbon product and recycling a portion of the hydrocarbon product to the reaction zone;
- e) selectively separating the gaseous component using at least one amine absorber zone to produce at least a stream comprising carbon dioxide and a stream comprising at least hydrogen and depleted in carbon dioxide; and
- f) passing the stream comprising carbon dioxide to an algae cultivation operation and using the carbon dioxide to cultivate algae.

14. The process of claim 13 wherein the amine absorber zone contains an amine selective to carbon dioxide, and the stream containing at least hydrogen and depleted in carbon dioxide further comprises hydrogen sulfide.

15. The process of claim 14 wherein the amine is an aqueous solution of a polyoxypropylene triamine having the formula:



Where R' represents a methylene group and R'' represents hydrogen or methyl or ethyl and wherein the sum of X+Y+Z is a positive integer having a value of from about 4 to about 6.

16. The process of claim 13 wherein gaseous component further comprises hydrogen sulfide and the amine absorber zone comprises an amine selective to carbon dioxide and hydrogen sulfide, said process further comprising

regenerating the amine selective to carbon dioxide and hydrogen sulfide to generate an acid gas stream containing carbon dioxide and hydrogen sulfide;

passing the acid gas stream through a second amine absorber zone containing an amine selective to hydrogen sulfide to generate the stream comprising carbon dioxide;

regenerating the amine selective to hydrogen sulfide to generate a stream comprising hydrogen sulfide stream; and

recycling at least a portion of the stream comprising hydrogen sulfide stream to reaction zone.

17. The process of claim 16 wherein the amine absorber zone and the second amine absorber zone comprise aqueous solutions of methyldiethanolamine and piperazine.

18. The process of claim 13 wherein the selectively separating in step 13(b) is performed using a hot high pressure hydrogen stripper operated at a temperature of about 40° C. to

about 300° C. and a pressure of about 689 kPa absolute (100 psia) to about 13,790 kPa absolute (2000 psia).

19. The process of claim 13 wherein the separating in step 13(d) is performed using cooling followed by phase separation.

20. The process of claim 13 wherein the amine absorber is a flexible amine absorber.

21. The process of claim 13 wherein the first portion of the remainder stream is recycled to the reaction zone at a volume ratio of recycle to feedstock in the range of about 2:1 to about 8:1, and wherein the reaction conditions in the reaction zone include a temperature of about 40° C. to about 400° C. and a pressure of about 689 kPa absolute (100 psia) to about 13,790 kPa absolute (2000 psia).

22. The process of claim 13 further comprising introducing a third portion of the remainder stream to a second reaction zone to contact an isomerization catalyst at isomerization conditions to isomerize at least a portion of the n-paraffins into branched paraffins and generate the said second portion of the remainder stream.

23. The process of claim 22 further comprising treating a petroleum derived hydrocarbon in the reaction zone with the renewable feedstock.

24. A process for producing a branched paraffin-rich diesel product from a renewable feedstock comprising;

a. treating the feedstock in a first reaction zone by hydrogenating and deoxygenating the feedstock using a catalyst at reaction conditions in the presence of hydrogen and at least one sulfur containing compound to provide a first reaction zone product stream comprising hydrogen, hydrogen sulfide, carbon dioxide, and a hydrocarbon fraction comprising n-paraffins useful as a diesel boiling range fuel;

b. selectively separating, in a hot high pressure hydrogen stripper, a gaseous stream comprising hydrogen, hydrogen sulfide, and at least a portion of the water and carbon dioxide from the first reaction zone product stream and introducing a remainder stream comprising at least the n-paraffins to a second reaction zone to contact an isomerization catalyst at isomerization conditions to isomerize at least a portion of the n-paraffins and generate a branched paraffin-rich stream;

c. combining the branched-paraffin-rich stream and the gaseous stream to form a combined stream and separating;

i. a gaseous component comprising at least hydrogen and carbon dioxide;

ii. a hydrocarbon component; and

iii. a water component

and recovering at least a portion of the hydrocarbon component;

d. selectively separating the gaseous component using in a first amine solution absorber zone to produce a stream comprising at least hydrogen and depleted in carbon dioxide and a stream comprising carbon dioxide and hydrogen sulfide;

e. selectively separating the stream comprising carbon dioxide and hydrogen sulfide in a second amine solution absorber zone to produce a stream comprising at least hydrogen sulfide and depleted in carbon dioxide and a stream comprising carbon dioxide;

f. recycling at least a portion of the stream comprising at least hydrogen and depleted in carbon dioxide and at

least a portion of the stream comprising at least hydrogen sulfide and depleted in carbon dioxide to the first reaction zone.

25. The process of claim **24** wherein the isomerization conditions in the second reaction zone include a temperature of about 40° C. to about 400° C. and a pressure of about 689 kPa absolute (100 psia) to about 13,790 kPa absolute (2000 psia) and wherein the hot high pressure hydrogen stripper is operated at a temperature of about 40° C. to about 300° C. and a pressure of about 689 kPa absolute (100 psia) to about 13,790 kPa absolute (2000 psia).

26. The process of claim **24** further comprising treating a petroleum derived hydrocarbon in the reaction zone with the renewable feedstock.

27. An integrated process for producing a paraffin-rich diesel product from a renewable feedstock and for cultivating algae, said integrated process comprising:

- a) generating hydrogen using an algae cultivation operation;
- b) treating the feedstock in a reaction zone by hydrogenating and deoxygenating the feedstock using at least one catalyst at reaction conditions in the presence of the hydrogen generated in step (a) to provide a reaction zone product stream comprising hydrogen, carbon dioxide, water and a paraffins having from about 8 to about 24 carbon atoms;
- c) cooling the reaction zone product stream and separating to provide:
 - i. a gaseous component comprising at least hydrogen and carbon dioxide;
 - ii. a hydrocarbon product comprising the paraffins; and
 - iii. a water component; and
- d) recovering the hydrocarbon product.

28. The process of claim **27** further comprising separating the gaseous component comprising at least hydrogen and carbon dioxide into a stream comprising hydrogen and a stream comprising carbon dioxide and passing the stream comprising carbon dioxide to an algae cultivation operation and using the carbon dioxide stream to cultivate algae.

29. The process of claim **27** further comprising treating a petroleum derived hydrocarbon in the reaction zone with the renewable feedstock.

30. An integrated process for producing a paraffin-rich diesel boiling range product from a renewable feedstock and for cultivating plants in an enclosed greenhouse, said integrated process comprising:

- f) treating the renewable feedstock in a reaction zone by hydrogenating and deoxygenating the feedstock using at least one catalyst at reaction conditions in the presence of hydrogen to provide a reaction zone product stream comprising hydrogen, carbon dioxide, water and a paraffins having from about 8 to about 24 carbon atoms;
- g) cooling the reaction zone product stream and separating to provide:
 - i) a gaseous component comprising at least hydrogen and carbon dioxide;
 - ii) a hydrocarbon product comprising the paraffins; and
 - iii) a water component;
- h) recovering the hydrocarbon product;
- i) separating the gaseous component comprising at least hydrogen and carbon dioxide into a stream comprising hydrogen and a stream comprising carbon dioxide; and
- j) passing the stream comprising carbon dioxide to an enclosed green house and using the carbon dioxide stream to cultivate plants growing the enclosed greenhouse.

31. An integrated process for producing a paraffin-rich diesel boiling range product from a renewable feedstock and for separating at least two components by supercritical extraction, said integrated process comprising:

- a. treating the renewable feedstock in a reaction zone by hydrogenating and deoxygenating the feedstock using at least one catalyst at reaction conditions in the presence of hydrogen to provide a reaction zone product stream comprising hydrogen, carbon dioxide, water and a paraffins having from about 8 to about 24 carbon atoms;
- b. cooling the reaction zone product stream and separating to provide:
 - i. a gaseous component comprising at least hydrogen and carbon dioxide;
 - ii. a hydrocarbon product comprising the paraffins; and
 - iii. a water component;
- c. recovering the hydrocarbon product;
- d. separating the gaseous component comprising at least hydrogen and carbon dioxide into a stream comprising hydrogen and a stream comprising carbon dioxide; and
- e. passing the stream comprising carbon dioxide to a supercritical extraction operation and using the carbon dioxide stream as the extractant in the supercritical extraction operation to separate at least a first component from a second component in a mixture.

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