ABSTRACT

Disclosed is a process for removing solids, metals, phosphorus compounds and other impurities from low quality triglyceride containing feedstock. The final treated triglyceride containing feedstock may be converted to fuel range hydrocarbons via hydrotreating process.
REMOVAL OF IMPURITIES FROM OILS AND/OR FATS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a non-provisional application which claims benefit under 35 USC §119(e) to both U.S. Provisional Application Ser. No. 61/238,338 filed Aug. 31, 2009, entitled “SOLVENT EXTRACTION FOR THE REMOVAL OF IMPURITIES FROM OILS AND/OR FATS” and U.S. Provisional Application Ser. No. 61/238,351 filed Aug. 31, 2009, entitled “REMOVAL OF IMPURITIES FROM OILS AND/OR FATS” which are incorporated herein in their entirety.

STATEMENT OF FEDERALLY SPONSORED RESEARCH

[0002] None

FIELD OF THE INVENTION

[0003] The present invention relates generally to the process for removing impurities from triglycerides, especially prior to the conversion of triglycerides to fuel range hydrocarbons.

BACKGROUND OF THE INVENTION

[0004] There is a national interest in the discovery of alternative sources of fuels and chemicals, other than from petroleum resources. As the public discussion concerning the availability of petroleum resources and the need for alternative sources continues, government mandates will require transportation fuels to include, at least in part, hydrocarbons derived from sources besides petroleum. As such, there is a need to develop alternative sources for hydrocarbons useful for producing fuels and chemicals.

[0005] One possible alternative source of hydrocarbons for producing fuels and chemicals is the natural carbon found in plants and animals, such as for example, oils and fats. These so-called “natural” carbon resources (or renewable hydrocarbons) are widely available, and remain a target alternative source for the production of hydrocarbons. For example, it is known that oils and fats, such as those contained in vegetable oil, can be processed and used as fuel. “Bio Diesel” is one such product and may be produced by subjecting a base vegetable oil to a transesterification process using methanol in order to convert the base oil to methyl esters. After processing, the products produced have some what similar combustion properties as compared to petroleum-derived hydrocarbons. However, the use of Bio-Diesel as an alternative fuel has not yet been proven to be cost effective. In addition, Bio-Diesel often exhibits “gelling” thus making it unable to flow, which limits its use in pure form in cold climates.

[0006] Unmodified vegetable oils and fats have also been used as additives in diesel fuel to improve the qualities of the diesel fuel, such as for example, the lubricity. However, problems such as injector coking and the degradation of combustion chamber conditions have been associated with these unmodified additives. Since cetane (C15H32), heptadecane (C17H36) and octadecane (C18H36) by definition have very good ignition properties (expressed as cetane rating), it is often desired to add paraffinic hydrocarbons in the C15-C18 range, provided that other properties of the additive (such as for example, viscosity, pour point, cloud point, etc., are congruent with those of the diesel fuel.

[0007] Laboratory and commercial tests have demonstrated that vegetable oils and animal fats can be added to a refinery hydrotreater to produce hydrocarbon/transportation fuels. For example, contacting a diesel/vegetable oil mixture with a hydrotreating catalyst. However, the feedstock price accounts for -85% of operational cost for renewable diesel production, and there has been a rapid price increase for the biorenewable feeds currently used (e.g. refined soybean oil and technical tallow). Thus, it is now more economically attractive to use lower quality and less expensive feeds (e.g. inedible tallow, choice white grease and etc.) for making renewable diesel. For example, inedible tallow is about 20% cheaper than technical tallow, so for 1,000 BPD renewable diesel production, an annual feedstock saving of $4 millions can be realized by using the inedible tallow instead of technical tallow.

[0008] The problem associated with hydrotreating these lower priced and poorer quality oils/fats is, however, that these low quality oils/fats, such as, inedible tallow, choice white grease, etc., contain high concentration of solids, metals, phosphorus compounds and other impurities, which can potentially cause reactor fouling and poison the hydrotreating catalysts.

[0009] Therefore, development of an effective process for removing solids, metals, phosphorus compounds and other impurities from low quality oils and fats would be a significant contribution to the art.

SUMMARY OF THE INVENTION

[0010] Disclosed is a process for removing solids, metals, phosphorus compounds and other impurities from low quality triglyceride containing feedstock. The final treated triglyceride containing feedstock may be converted to fuel range hydrocarbons via hydrotreating processes.

[0011] In the first embodiment of the present invention, a process comprising (a) providing a feedstock comprising at least one triglyceride and one type of impurities; (b) admixing an organic solvent with the feedstock for a contacting time to form a mixture; (c) settling the mixture for a retention time to form a layer of treated feedstock, a layer of impurities, and a layer of organic solvent; and (d) recovering the layer of treated feedstock from the mixture, wherein the treated feedstock comprises less than 50% of the amount of the impurities than which is in the feedstock.

[0012] In the second embodiment of the present invention, a process is disclosed comprising contacting the treated feedstock from the first embodiment of the invention with a hydrotreating catalyst in a reaction zone under a condition sufficient to produce a reaction product containing diesel boiling range hydrocarbons, such condition includes a pressure of less than about 2000 psig and a temperature in the range of from about 260° C. to about 430° C.

[0013] In the third embodiment of present invention, a process comprising (a) providing a feedstock comprising at least one triglyceride and one type of impurities; (b) subjecting the feedstock to a first separation device to remove at least 25% of the impurities from the feedstock and to produce a first effluent stream; (c) admixing an acid or acid anhydride with the first effluent stream for a first contact time to form a second mixture; (d) admixing water with the first mixture for a second contact time to form a second mixture; (e) subjecting the second mixture to a second separation device to form an
aqueous phase and oil phase; and (f) subjecting the oil phase to a third separation device to remove another portion of the impurities from the oil phase to produce a treated feedstock.

[0014] In the forth embodiment of the present invention, a process is disclosed comprising contacting the treated feedstock from the third embodiment of the invention with a hydrotreating catalyst in a reaction zone under a condition sufficient to produce a reaction product containing diesel boiling range hydrocarbons, such condition includes a pressure of less than about 2000 psig and a temperature in the range of from about 260°C to about 430°C.

DETAILED DESCRIPTION OF THE INVENTION

[0015] Refer to all four embodiments of the invention, triglycerides or fatty acids of triglycerides, or mixtures thereof, may be converted to form a hydrocarbon mixture useful for liquid fuels and chemicals. The term, “triglyceride,” is used generally to refer to any naturally occurring ester of a fatty acid and/or glycerol having the general formula \( \text{CH}_2 (\text{OCOR}_1\text{OCOR}_2\text{OCOR}_3) \), where \( R_1, R_2, \) and \( R_3 \) are the same or different, and may vary in chain length. Examples of triglycerides useful in the present invention include, but are not limited to, animal fats (e.g. poultry grease, edible or inedible beef fat also referred to as tallow, milk fat, and the like), vegetable oils (e.g. soybean, corn oil, peanut oil, sunflower seed oil, coconut oil, babassu oil, grape seed oil, poppy seed oil, almond oil, hazelnut oil, walnut oil, olive oil, avocado oil, sesame, oil, tall oil, cottonseed oil, palm oil, ricebran oil, canola oil, cocoa butter, shea butter, butyrospermum, wheat germ oil, illipe butter, meadowfoam, seed oil, rapeseed oil, borage seed oil, linseed oil, castor oil, vernonia oil, tung oil, jojoba oil, onagracea oil, algae oil, jatropha oil, yellow grease such as those derived from used cooking oils, and the like), mixtures and combinations thereof.

[0016] Generally, the triglyceride comes with impurities such as phosphorus, metals (e.g. Alkalai metals, alkali earth metals, or etc), solids, proteins and bone materials, or any combinations thereof. The amounts of these elements/compounds are generally in the range of from about 0 ppmw to about 10,000 ppmw.

[0017] Now refer to the first and second embodiments of the invention, the feedstock is generally kept in the range of the lowest temperature at which the feedstock remains as a liquid to 150°C for at least 1 minute. After this step, an organic solvent is added to this feedstock. Any organic solvent may be used, in one embodiment of the invention, any type of polar organic solvent, such as ethylene glycol, may be used.

[0018] Further referring to the first and second embodiments of the invention, the amount of organic solvent added to the feedstock may vary depending upon the amount of the feedstock to be mixed. According to the present invention, the amount of the organic solvent added is in the range from 0.1 to 50 wt %, calculated on the weight of triglyceride containing feedstock.

[0019] Further referring to the first and second embodiments of the invention, the organic solvent added to the feedstock is given sufficient contacting time to mix with the feedstock to thereby forming a mixture. The contacting time required for mixing the organic solvent with the feedstock may be affected by temperature of the feedstock as well as the types of device for mixing. In one embodiment, such contacting time is at least 1 minute under dynamic mixing action provided by devices such as stirrer or high shear mixers. The temperature of the mixture is maintained in the range of from the lowest temperature at which the mixture remains as a liquid to 150°C during the mixing of organic solvent with the feedstock.

[0020] After the contacting time mentioned above, the mixture is allowed to set for a sufficient retention time, usually without any mixing action, to thereby form a layer of treated feedstock, a layer of impurities, and a layer of organic solvent. The retention time required in this step may be affected by the temperature of the mixture. In one embodiment, such retention time is at least 1 minute. The temperature of the mixture is maintained in the range of from the lowest temperature at which the mixture remains as a liquid to 150°C during the setting of the mixture.

[0021] Further refer to the first and second embodiments of the invention, the layer of the treated feedstock is recovered but not limited by separation funnel.

[0022] Further refer to the first and second embodiments of the invention, the treated feedstock after the inventive process comprises less than 50% of the amount of the impurities than it is in the feedstock prior to the inventive process. In one embodiment where a polar organic solvent (e.g. ethylene glycol) is used, the treated feedstock after the inventive process comprises less than 80% of the amount of the impurities than it is in the feedstock prior to the inventive process.

[0023] Additionally, in both first and second embodiment of the invention, the layer of organic solvent may also be recycled for using in the treating of additional feedstock.

[0024] Now referring to the third and forth embodiments of the current invention, a feedstock comprising triglyceride and impurities is subject to a first separation device where in at least 25% of the impurities may be removed from the feedstock. Any suitable separation device capable of separating the solid from an oil phase feed may be used. A first separation device according to one embodiment of the current invention is a commercially available bag or cartridge filter with a pore size of at least 0.1 µm. In another embodiment with the feedstock being the inedible tallow, the first separation device of choice is a commercially available bag or cartridge filter with a pore size anywhere from 2 to 7 µm, which removes at least 50% of the impurities from the inedible tallow feedstock to produce the first effluent stream.

[0025] Further refer to the third and forth embodiments of the invention, the acid or acid anhydride, in principle all inorganic and organic acids having a pH of from 0-6 as measured at 20°C in a one molar aqueous solution, may be used. For example: phosphoric acid, sulfuric acid, acetic acid, citric acid, tartaric acid, succinic acid, etc., or mixtures of such acids.

[0026] The acids or acid anhydride may be added in any concentration, in one embodiment of this invention, an aqueous solution of the acid added contains 0.1 to 99.9% of the acid in H₂O.

[0027] Further refer to the third and forth embodiments of the invention, after the acid or acid anhydride being added to the first effluent stream, it is given a sufficient contacting time to mix with the first effluent stream to form the first mixture. The contacting time required for homogeneously mixing the acid or acid anhydride with the first effluent stream may be affected by temperature of the first effluent stream as well as the type of device for mixing. In one embodiment, such contacting time is at least 0.1 minute under dynamic mixing action provided by devices such as stirrer or high shear mixers. In another embodiment, such contacting time is about 0.1
tion, ion exchange and vapor deposition. In an embodiment of the present invention, the catalyst contains molybdenum and cobalt supported on alumina or molybdenum and nickel supported on alumina.

Still refer to the second and the forth embodiments of the invention, this process in accordance with an embodiment of the present invention can be carried out in any suitable reaction zone that enables intimate contact of the treated feed and control of the operating conditions under a set of reaction conditions that include total pressure, temperature, liquid hourly space velocity, and hydrogen flow rate. The catalyst can be added first to the reactants and thereafter, fed with hydrogen.

In the second and forth embodiments of the present invention, either fixed bed reactors or fluidized bed reactors can be used. As used herein, the term “fluidized bed reactor” denotes a reactor wherein a fluid feed can be contacted with solid particles in a manner such that the solid particles are at least partly suspended within the reaction zone by the flow of the fluid feed through the reaction zone and the solid particles are substantially free to move about within the reaction zone as driven by the flow of the fluid feed through the reaction zone. As used herein, the term “fluid” denotes gas, liquid, vapor and combinations thereof.

The reaction conditions at which the reaction zone is maintained generally include a temperature in the range of from about 260°C to about 430°C. Preferably, the temperature is in the range of from about 310°C to about 370°C.

In accordance with the second and forth embodiments of the present invention, regardless of whether a fixed or fluidized bed reactor is used, the pressure is generally in the range of from about 100 pounds per square inch gauge (psig) to about 2000 psig. Generally, in a fixed bed reactor, the pressure is in the range of from about 100 psig to about 1500 psig. In a fluidized bed reactor, the pressure can also be about 600 psig. In a fluidized bed reactor, the pressure is generally in the range of from about 400 psig to about 750 psig, and can also be about 500 psig.

The following example is presented to further illustrate the present invention and is not to be construed as unduly limiting the scope of this invention.

**Example 1**

Comparison Study on Impurities Removal from Tallow Using Ethylene Glycol Vs. Water

A comparison study was performed on impurities removal from tallow using ethylene glycol vs. water. The same procedure is followed. A 100 grams of tallow feedstock is added in a container and heated at a temperature of 90°C for 0.5-1 hour. A 10 ml of ethylene glycol or water was added to the container and stirred with the tallow feedstock at a temperature of 90°C for 2-3 hours. The mixture was then kept at 55-60°C overnight without stirring. Three layers were formed comprising a layer of treated tallow, a brown color layer of impurities, and a layer of ethylene glycol. The result of the experiment has shown that the under the same procedure and condition, less brown color layer of impurities were found in the container with water than it was in the container with ethylene glycol.

**Example 2**

An inedible tallow feed stock is provided. Such feedstock was subject to a commercially available sintered
metal filter with a pore size of 2 μm to remove solids from the feedstock. The filtered feedstock was then mixed with phosphoric acid at the concentration of 75-85% for about 3 minutes followed by the addition of 5 wt % H₂O. The tallow/phosphoric acid/water was further mixed for 60 minutes followed by a centrifugal step in which an aqueous phase and oil phase were separated. Sample of feedstock at the various stages were obtained and measured. As shown in Table 1, the results of this experiment indicates that there are a significant (more than 50%) reduction of the metals, phosphorus and solids concentration achieved by just after passing the feedstock through a sintered metal filter with pore size of 2 μm alone.

<table>
<thead>
<tr>
<th>Impurities (ppm)</th>
<th>Pre-treated indible tallow</th>
<th>Indible tallow after mixing with phosphoric acid and centrifugal separation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metals</td>
<td>146</td>
<td>48</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>129</td>
<td>60</td>
</tr>
<tr>
<td>Solids</td>
<td>1400</td>
<td>210</td>
</tr>
</tbody>
</table>

The oil phase feed is further subject to a commercially available sintered metal filter with a pore size of 0.5 μm to remove some solids from the feedstock. Thereby, significantly purified indible tallow is obtained.

While this invention has been described in detail for the purpose of illustration, it should not be construed as limited thereby but intended to cover all changes and modifications within the spirit and scope thereof.

That which is claimed:

1. A process comprising:
(a) providing a feedstock comprising at least one triglyceride and one type of impurities;
(b) admixing an organic solvent with said feedstock for a contacting time to form a mixture;
(c) settling said mixture for a retention time to form a layer of treated feedstock, a layer of impurities, and a layer of organic solvent; and
(d) recovering said layer of treated feedstock from said mixture, wherein said treated feedstock comprises less than 50% of the amount of said impurities than which is in said feedstock.

2. The process in accordance with claim 1 further comprising the step of
(e) contacting said treated feedstock with a hydrotreating catalyst in a reaction zone under a condition sufficient to produce a reaction product containing diesel boiling range hydrocarbons, wherein said condition includes a pressure of less than about 2000 psig and a temperature in the range of from about 260°C to about 430°C.

3. The process in accordance with claim 1, wherein said triglyceride is selected from the group consisting of vegetable oils, animal fats, and any combination thereof.

4. The process in accordance with claim 1 wherein said impurities is selected from the group consisting of phosphorus, metals, solids, proteins and bone materials, and any combination thereof.

5. The process in accordance with claim 1 wherein said organic solvent is polar organic solvent, wherein said treated feedstock comprises less than 80% of the amount of said impurities than which is in said feedstock.

6. The process in accordance with claim 5 wherein said polar organic solvent is ethylene glycol.

7. The process in accordance with claim 1 wherein the amount of said organic solvent is in the range from 0.1 to 50 wt %, calculated on the weight of triglyceride.

8. The process in accordance with claim 1, wherein the temperature of said feedstock is kept in the range of the lowest temperature at which said mixture remains as a liquid to 150°C for at least 1 minute prior to admixing with said solvent;

9. The process in accordance with claim 1 wherein said contacting time is at least 1 minute; and wherein said retention time is at least 1 minute.

10. The process in accordance with claim 1 further comprising a step of recycling said layer of organic solvent after step c.

11. The process of claim 2, wherein said hydrotreating catalyst comprises nickel and molybdenum.

12. The process of claim 2, wherein said hydrotreating catalyst comprises cobalt and molybdenum.

13. A process comprising:
(a) providing a feedstock comprising at least one triglyceride and one type of impurities;
(b) subjecting said feedstock to a first separation device to remove at least 25% of said impurities from said feedstock and to produce a first effluent stream;
(c) admixing an acid or acid anhydride with said first effluent stream for a first contact time to form a mixture;
(d) admixing water with said first mixture for a second contact time to form a second mixture;
(e) subjecting said second mixture to a second separation device to form an aqueous phase and oil phase; and
(f) subjecting said oil phase to a third separation device to remove another portion of said impurities from said oil phase to produce a treated feedstock.

14. The process in accordance with claim 13 further comprising the step of
g) contacting said treated feedstock with a hydrotreating catalyst in a reaction zone under a condition sufficient to produce a reaction product containing diesel boiling range hydrocarbons, wherein said condition includes a pressure of less than about 2000 psig and a temperature in the range of from about 260°C to about 430°C.

15. The process in accordance with claim 13, wherein said triglyceride is selected from the group consisting of vegetable oils, animal fats, and any combinations thereof.

16. The process in accordance with claim 13 wherein said impurities is selected from the group consisting of phosphorus, metals, solids, proteins and bone materials, and any combinations thereof.

17. The process in accordance with claim 13 wherein said acid or acid anhydride having a pH of from 0 to 6 as measured at 20°C in a one molar aqueous solution.

18. The process in accordance with claim 13 wherein said acid is phosphoric acid.

19. The process in accordance with claim 13 wherein an aqueous solution of said acid containing 0.1 to 99.9% of the acid in H₂O is used.
20. The process in accordance with claim 13 wherein the amount of water added is in the range from 0.1 to 10 wt %, calculated on the oil.

21. The process in accordance with claim 13 wherein said first contacting time is at least 0.1 minute, and where in said second contacting time is at least 1 minute.

22. The process in accordance with claim 13 wherein the temperature of said first mixture is maintained in the range of the lowest temperature at which said first mixture remains as a liquid to 150°C during said first contacting time.

23. The process in accordance with claim 13 wherein said first separation device is a filter with a pore size of at least 0.1 μm.

24. The process in accordance with claim 13 wherein said first separation device is a filter with a pore size from 2 to 7 μm, where in said filter removes at least 50% of said impurities from said feedstock to produce said first effluent stream.

25. The process in accordance with claim 13 wherein said second separation device is a centrifuge.

26. The process in accordance with claim 13 wherein said third separation device is a filter with pore size of at least 0.1 μm.

27. The process of claim 14 wherein said hydrotreating catalyst comprises nickel and molybdenum.

28. The process of claim 14, wherein said hydrotreating catalyst comprises cobalt and molybdenum.

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