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(54) **FUEL PRODUCTS FROM PLANT OR ANIMAL LIPIDS**

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(57) **ABSTRACT**

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A novel method for producing fuel products from plant or animal lipids is provided. The carbon-carbon bonds in the molecules of plant or animal lipids are cracked into the molecules with smaller molecular weights. The mixed fuel is formed after chemical treatments. Then the mixed fuel (biopetroleum) is processed by a distillation process to produce fuel products according to their boiling points. The method is particularly advantageous to produce the energy source from agricultural products, which provides a solution for energy crisis with a significant potential.

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FUEL PRODUCTS FROM PLANT OR ANIMAL LIPIDS

BACKGROUND OF THE INVENTION

[0001] This present invention relates to a novel processing method for producing fuels from plant or animal lipids by cracking carbon and carbon bonds in plant or animal lipids and distilling the mixing fuels after chemical treatments.

[0002] The energy crisis of recent years has been a significant challenge. Petroleum is a complex mixture of organic compounds, most of which are alkanes and aromatic hydrocarbons. Petroleum also contains small amounts of oxygen, nitrogen, and sulfur-containing compounds. The primary use of alkanes is as an energy source. Different fraction products are obtained after a distillation process. Most fuels that we use are natural gas, petroleum ester, ligroin, gasoline, kerosene/jet fuel, fuel oil/diesel oil, and lubrication oil. Natural gas fraction contains 1-4 carbons in the molecular formula with the boiling point below 20 degree C. Petroleum ester fraction contains 5-6 carbons in the molecular formula with the boiling point range at 20-60 degree C. Ligroin fraction contains 6-7 carbons in the molecular formula with the boiling point range at 60-100 degree C. Gasoline fraction contains 5-10 carbons in the molecular formula with the boiling point range at 40-200 degree C. Kerosene and jet fuel fraction contains 12-18 carbons in the molecular formula with the boiling point range at 175-325 degree C. Fuel oil and diesel oil fraction contains 12 and more carbons in the molecular formula with the boiling point range at 250-400 degree C. Lubrication oil fraction contains 20 and more carbons in the molecular formula with a much high boiling point. Fuels with lower molecular weights usually have lower boiling points. As we all know that the world's supply of petroleum will run out sometime in the future. It is a hard fact that our societies are so largely organized around machines depending on petroleum-based fuels, which continues the energy challenge. The solution to the energy crisis is to develop alternate sources of energy.

[0003] One area of particular interest relates to fuels for commercial and agricultural vehicles is biodiesel after converting vegetable or animal oils into ester products. Another area is to use vegetable or animal oils and their blended oils with other fuel products for partial replacement for diesel and burning oils. But there are some important issues such as viscosity, boiling point, pollution, and burning performance because there are still mixed compounds in the fuels with high boiling points, sulfur-containing compounds, and nonvolatile compounds. Over the years, various attempts have been made to make biodiesel and lubricant oils. A number of patents have been issued for the processes. U.S. Pat. No. 6,712,867 (2004) discloses a process for production of fatty acid methyl esters as biodiesel from fatty acid triglycerides with the ratio of alcohol to triglycerides at 15:1 to 35:1. Very high level alcohol is needed in the process. U.S. Pat. No. 6,532,918 (2003) discloses a method and device for lubricating and simultaneously supplying fuel in a vegetable oil-operated combustion engine. Fresh vegetable oil and additive-treated vegetable oil are used. U.S. Pat. No. 6,399,800 (2002) discloses a process for producing fatty acid alkyl esters by esterifying the dried saponified feedstock with an alcohol and an inorganic acid catalyst. U.S. Pat. No. 6,015,440 (2000) discloses a process for producing

biodiesel fuel from triglycerides with methanol and a homogeneous basic catalyst. U.S. Pat. No. 5,885,946 (1999) discloses a process for preparing a synthetic ester from a vegetable oil by a two-stage transesterification process. U.S. Pat. No. 5,713,965 (1998) discloses a method to produce biofuels by utilizing lipases to transesterify triglyceride-containing substances and to esterify free fatty acids to alkyl esters using short chain alcohols. U.S. Pat. No. 5,697,986 (1997) discloses a process to produce biofuels by carrying out the enzymatic transesterification of fatty acid-containing materials directly in automotive fuels. U.S. Pat. No. 5,525,126 (1996) discloses a process for producing esters from a fat or an oil with an alcohol and non-alkaline catalyst. The catalyst includes a mixture of calcium acetate and barium acetate. The reaction mixture is heated at a temperature effective to make esters. U.S. Pat. No. 5,116,546 (1992) discloses a process for producing fatty acid esters by transesterification, esterification, and recovery steps. U.S. Pat. No. 4,698,186 (1987) discloses a process for reducing the free fatty acid content of fats and oils by esterifying the free fatty acids with a lower monoalcohol in the presence of an acidic cation exchange resin as a solid esterification catalyst. U.S. Pat. No. 4,695,411 (1987) discloses a process for manufacturing fatty acid esters useful for combustion in diesel engines. There are three processing steps are involved in the esterification process. U.S. Pat. No. 4,557,734 (1985) discloses a process for producing microemulsions from vegetable oil, methanol or ethanol, a straight-chain isomer of octanol, and optionally water. The fuels are characterized by a relatively high water tolerance, acceptable viscosity, and performance properties comparable to No. 2 diesel fuel. U.S. Pat. No. 4,371,470 (1983) discloses a method for manufacturing fatty acid esters by a two-step transesterification from a natural oil or fat with methyl alcohol. The trace amounts of the colored or chromogenic impurities are removed by admixing an absorbent. U.S. Pat. No. 4,164,506 (1979) discloses a process for producing lower alcohol esters of fatty acids by esterifying free fatty acids of unrefined fats with a lower alcohol.

[0004] The principle of preparing biodiesel is transesterification or esterification, which is described in Organic Chemistry (Solomons, 1984). Transesterification or alcoholysis of triglycerides of vegetable oils and animal fats in the presence of an alcohol leads to the formation of fatty acid esters, which is also described in European Pat. No. 127,104 and U.S. Pat. No. 4,164,506. After the transesterification or esterification reactions, the viscosity and boiling points for the esters from vegetable or animal oils are reduced compared with vegetable or animal oils. But ester products still have 17-19 carbons in the molecular formula. Also the final fuel products still contains other compounds such as sulfur-containing compounds, nonvolatile compounds, and non-reacted triglycerides and fatty acids, which affects the burning performance and causes pollution.

DESCRIPTION OF THE INVENTION

[0005] This present invention provides a novel processing method for producing mixing fuels from plant or animal lipids by cracking carbon and carbon bonds in plant or animal lipids, chemical treatments, and distilling the mixing fuels. Then the issues such as viscosity, molecular weight, boiling point, pollution, and burning performance with biodiesel can be resolved.

[0006] Plant or animal lipids are such as glyceryl trialkanoates (is also called triglycerides), carboxylic acids (free fatty acids), phospholipids, glycolipids, and terpenes. A glyceryl trialkanoate is made by three fatty acids and one glycerol in the molecular formula. There are saturated and unsaturated fatty acids. For unsaturated fatty acids, there are unsaturated (double) carbon-carbon bonds. A phospholipid is made by two fatty acids, one phosphoric acid, and one glycerol in the molecular formula. Terpenes such as essential oil and natural rubber have unsaturated carbon-carbon bonds and branched methyl groups in the molecular formula. The lipids, which include such as raw materials, products, intermediate products, byproducts, and waste products from plant or animal lipid sources, are used in this process. Most common lipids such as oils and fats from plant or animal origin are glyceryl trialkanoates, which are usually have long-chain alkyl groups for fatty acids. Those glyceryl trialkanoates that are liquids at room temperature are generally as oils; those that are solids are usually called fats. The fats become oils after heat. Table 1 shows major fatty acid composition obtained by hydrolysis of common fats and oils

TABLE 1

Major fatty acid composition of common fats and oils (mole, %)						
	Saturated		Unsaturated			
	C16	C18	C16	C18/oleic	C18/linoleic	C18/linolenic
Vegetable Oils						
Soybean	6-10	2-4		20-30	50-58	5-10
Corn	7-11	3-4	1-2	25-35	50-60	
Linseed	4-7	2-4		14-30	14-25	45-60
Olive	5-15	1-4		67-84	8-12	
Animal Fats						
Lard	25-30	12-18	4-6	48-60	6-12	
Beef tallow	24-34	15-30		35-45	1-3	

[0007] (Solomons, 1984). For saturated fatty acids, C16 is palmitic acid and C18 is stearic acid. For unsaturated fatty acids, C16 is palmitoleic acid and C18 is oleic acid (cis-9-octadecenoic acid with one double carbon-carbon bond —HC=CH—), linoleic acid (cis, cis-9,12-octadecenoic acid with two double carbon-carbon bonds $\text{—HC=CH—CH}_2\text{—HC=CH—}$) or linolenic acid (cis, cis, cis-9, 12, 15-octadecenoic acid with three double carbon-carbon bonds $\text{—HC=CH—CH}_2\text{—HC=CH—CH}_2\text{—HC=CH—}$). To crack double carbon-carbon bonds of the unsaturated fatty acids in plant or animal lipids is technically feasible and practical with several chemical reactions and processes such as (1) oxidative cleavage of alkenes with an oxidant under base/acid and heat, (2) ozonization of alkenes with ozone, zinc, and water or (3) hydroxylation of the double bond using osmium tetroxide, dilute aqueous potassium permanganate, or a peroxy acid and subsequent cleavage of the glycol using periodic acid. The chemical reactions are as follows:

[0008] (1) Oxidative cleavage: $\text{—HC=CH—} \rightarrow \text{—COOH}$
(under base and acid conditions)

[0009] (2) Ozonization: $\text{RHC=CHR}' \rightarrow \text{RHCO} + \text{R}'\text{HCO}$

[0010] (R and R' are long-chain alkyl groups with or without glycerol)

[0011] (3) Hydroxylation: $\text{RHC=CHR}' \rightarrow \text{RHCOH—CO—HHR}'$

[0012] $\text{RHCOH—COHHR}' \rightarrow \text{RHC=O} + \text{O=CHR}'$
(with HIO_4)

[0013] After cracking the double carbon-carbon bonds of the unsaturated fatty acids in plant or animal lipids, the products are the mixtures. The carbon numbers in the molecular formulas and molecular weights in the mixtures are reduced significantly, which changes the viscosity, boiling points, and burning performance for the fuels. Cracking the double carbon-carbon bonds of the unsaturated fatty acids can be done before or after the glycerol in the lipids is dissociated from the lipid molecules. Glycerol is water soluble and has a boiling point 290°C . and a density 1.26, which can also be separated by centrifugation process. The carbon number range for fuel products in the mixed products is usually from C3 to C18 such as C3 C6, C7, C8, C9, C12, and C18, which likes petroleum with wide carbon number range. There are also some compounds with carbon number more than 18 from the raw materials or intermediate products.

[0014] When cracking the double carbon-carbon bonds of the unsaturated fatty acids is done before the glycerol in the lipids is dissociated from the lipid molecules, a transesterification is further processed to form ester products. When cracking the double carbon-carbon bonds of the unsaturated fatty acids is done after the glycerol in the lipids is dissociated and removed from the lipid molecules, an esterification is further processed to form ester products. The boiling points of ester products are much lower than fatty acids such as ethyl methyl ester ($\text{C}_2\text{H}_5\text{OCH}_3$) has the boiling point at 8°C . and propanoic acid ($\text{C}_2\text{H}_5\text{COOH}$) has the boiling point at 141°C . even both products have the same carbon numbers (3). After the cracking the double carbon-carbon bonds of the unsaturated fatty acids, aldehyde products (with —CHO groups) such as hexanal are formed. Aldehyde products can be used directly. Aldehyde products can also be converted into alkane products (with —CH_3 group) by such as hydrazones, which is called the Wolff-Kishner reduction. After hexanal is converted into hexane, the boiling point is reduced from 128°C . (for hexanal $\text{CH}_3(\text{CH}_2)_4\text{CHO}$) to 69°C . (for hexane $\text{CH}_3(\text{CH}_2)_4\text{CH}_2$). Besides glyceryl trialkanoates, carboxylic acids (fatty acids), phospholipids, glycolipids, and terpenes can be similarly treated as above. The most valuable products as fuels are the organic or carbohydrate products with smaller carbon numbers such as less than 15 in the molecular formula and lower boiling points such as lower than 300°C .

[0015] To crack saturated (single) carbon-carbon bonds of the saturated acids in plant or animal lipids is difficult. When a mixture of alkanes from the gas oil materials (C12 and higher) are heated to very high temperature in the presence of a variety of catalysts, then the molecular break apart and rearrange to smaller, more highly branched alkanes containing 5 to 10 carbons. The cracking can also be done at very high temperature without a catalyst. But this process to crack saturated single carbon-carbon bonds tends to have alkanes with unbranched chains (Solomons, 1984).

[0016] After the cracking carbon-carbon bonds and the chemical reactions to convert such as from the fatty acids into their ester products with chemicals and catalysts, the mixed products with carbon numbers from C3 to C18 and higher in the molecular formulas processed from plant or animal lipids with carbon numbers about C45 to C57 in the

molecular formula may be considered as biopetroleum. Then a distillation process is applied to produce the fraction products according to their boiling points, which is similar to the distillation process of normal petroleum. The products with low boiling points are used as better fuels. The products with high boiling points are used as oils. The nonvolatile products are used for other applications. The products as fuels are obtained from distillation process, which are totally different from current processes for biodiesel products. The products from distillation process have low molecular weight, low boiling points, and low viscosity. The method in this invention produces better products after distillation process.

What is claimed is:

1. A method of producing a fuel composition comprising cracking unsaturated carbon and carbon bonds in plant or animal lipids, converting into a mixed fuel, and distilling the mixing fuel to form the fuel products.

2. The method of claim 1 wherein the unsaturated carbon and carbon bonds are cracked chemically.

3. The method of claim 1 wherein the unsaturated carbon and carbon bonds are cracked before or after dissociating glycerol from plant or animal lipids.

4. The method of claim 1 wherein esterification or transesterification with the alcohol consisting carbon 1 to 4 is used to convert fatty acids into esters.

5. The method of claim 4 wherein an enzyme is used for the transesterification.

6. The method of claim 1 wherein the aldehydes are converted into alkanes.

7. The method of claim 1 wherein a catalyst is used.

8. The method of claim 1 wherein heat or cooling process is used.

9. The method of claim 1 wherein the products are used as fuel products.

10. The method of claim 1 wherein the products are used as organic products.

11. A method of producing a fuel composition comprising cracking carbon and carbon bonds in plant or animal lipids, converting into a mixed fuel, and distilling the mixing fuel to form the fuel products.

12. The method of claim 11 wherein the carbon and carbon bonds are cracked by catalyst and pressure cooker.

13. The method of claim 11 wherein the method the carbon and carbon bonds are cracked before or after dissociating glycerol from the plant or animal lipids.

14. The method of claim 11 wherein esterification or transesterification with the alcohol consisting carbon 1 to 4 is used to convert fatty acids into esters.

15. The method of claim 14 wherein an enzyme is used for the transesterification.

16. The method of claim 11 wherein the aldehydes are converted into alkanes.

17. The method of claim 11 wherein a catalyst is used.

18. The method of claim 11 wherein heat or cooling process is used.

19. The method of claim 11 wherein the products are used as fuel products.

20. The method of claim 11 wherein the products are used as organic products.

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