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71	FULL NAME(S) OF APPLICANT(S)

The Dallas Group of America, Inc.

72	FULL NAME(S) OF INVENTOR(S)

COOKE, Brian S.
BERTRAM, Bryan
ABRAMS, Christopher

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Purification of biodiesel with adsorbent materials

57	ABSTRACT (NOT MORE THAN 150 WORDS)

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The sheet(s) containing the abstract is/are attached.

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(71) Applicant *(for all designated States except US)*: **THE DALLAS GROUP OF AMERICA, INC.** [US/US]; 374 Route 22, P.O. Box 489, Whitehouse, NJ 08888 (US).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **COOKE, Brian, S.** [US/US]; 600 Spicewood Drive, Clarksville, IN 47129 (US). **ABRAMS, Christopher** [US/US]; 3904 Forest Trace, Louisville, KY 40245 (US). **BERTRAM, Bryan** [US/US]; 4105 Doe Ridge Drive, Floyds Knobs, IN 47119 (US).

(74) Agents: **LILLIE, Raymond** et al.; Cella, Byrne, Bain, Gilfillan, Cecchi, Stewart & Olstein, 6 Becker Farm Road, Roseland, NJ 07068 (US).

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(54) Title: PURIFICATION OF BIODIESEL WITH ADSORBENT MATERIALS

(57) **Abstract:** A method of purifying a biodiesel fuel by contacting the biodiesel fuel with at least one adsorbent material, such as magnesium silicate. Such method removes impurities, such as soap, formed during the production of biodiesel fuels.

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PURIFICATION OF BIODIESEL WITH ADSORBENT MATERIALS

This application is a continuation-in-part of, and claims priority based on provisional application Serial No. 60/509,959, filed October 9, 2003, the contents of which are incorporated herein by reference in their entirety.

This invention relates to the purification of biodiesel fuel. More particularly, this invention relates to the purification of biodiesel fuel by contacting the biodiesel fuel with at least one adsorbent material, such as magnesium silicate.

Biodiesel is an alternative diesel fuel source to standard petrochemical diesel fuel. Biodiesel may be employed as an alternative fuel for the same types of engines fueled by petrochemical diesel fuel, such as engines for motorized vehicles, such as automobiles, trucks, buses, boats, airplanes, helicopters, snowmobiles, tractors, plows, and other farm vehicles, as well as locomotives, as well as smaller engines, such as those in lawn mowers and snowblowers. Biodiesel also may be employed in power generators and in heating systems in homes and other buildings. Furthermore, biodiesel may be used in combination with petrochemical diesel fuel.

Biodiesel is derived from triacylglycerides (also called triglycerides), which may be obtained from both plant sources, and animal fat sources, such as, for example, soybean oil, rapeseed oil, palm oil, coconut oil, corn oil, cottonseed oil, mustard oil, used cooking oils, float grease from wastewater treatment plants, animal fats such as beef tallow and pork lard, soapstock, crude oils, "yellow grease," i.e., animal or vegetable oils and fats that have been used or generated as a result of the preparation of food by a restaurant or other food establishment that prepares or cooks food for human consumption with a free fatty acid content of less

than 15%, and white grease, i.e., rendered fat derived primarily from pork, and/or other animal fats, which has a maximum free fatty acid content of 4%.

The production of biodiesel fuel involves reacting triglycerides with an alcohol (such as methanol, or ethanol, or propanol, for example) in the presence of an alkaline catalyst (such as sodium hydroxide or potassium hydroxide, for example), to produce biodiesel, or monoalkyl fatty acid esters. Glycerol is a by-product of the reaction. When the alcohol employed in the reaction is methanol, the biodiesel fuel is a fatty acid methyl ester (FAME). Methyl esters also may be produced via an enzymatic transesterification of triglycerides, with resultant contaminants to be removed.

The alkaline catalyst is present to speed the reaction; however, a soap is formed during the reaction, e.g., a sodium soap is formed when a sodium hydroxide catalyst is employed. The soap must be removed from the biodiesel fuel because the fuel would leave a residual ash if any soap were present. It is normal practice to employ a "water wash" to remove the soap, similar to that employed in edible oil refining. For example, water is sprayed at low velocity on top of the biodiesel. The excess alcohol and catalyst, as well as soaps, become soluble in the water phase. The soap can cause emulsification of the water and methyl ester, which is a common processing problem. The water and any impurities contained therein are separated from the biodiesel either by gravimetric or mechanical means. The biodiesel then is dried to remove any water remaining in the biodiesel subsequent to the initial separation of water therefrom.

When a large amount of soap is present, the water-washing causes emulsion problems, whereby the fatty acid esters, such as fatty acid methyl esters, will not separate from the water. In addition, water-washing does not eliminate effectively some of the other contaminants, such as sulfur, phosphorus, and any remaining free fatty acids. Methyl esters also may be produced via an enzymatic transesterification of triglycerides with resultant contaminants to be removed.

It is an object of the present invention to purify biodiesel to provide a biodiesel product with improved stability, acceptable for use as a fuel, without the

need to use water, and thus avoid the problems resulting therefrom. Another object is to improve the quality of biodiesel produced via the water wash process.

In accordance with an aspect of the present invention, there is provided a method of purifying a biodiesel fuel comprising contacting the biodiesel fuel with at least one adsorbent material.

Adsorbent materials which may be employed in the present invention include, but are not limited to, magnesium silicate, magnesium aluminum silicate, calcium silicate, sodium silicates, activated carbon, silica gel, magnesium phosphate, metal hydroxides, metal oxides, metal carbonates, metal bicarbonates, sodium sesquicarbonate, metal silicates, bleaching clays, bleaching earths, bentonite clay, and alumina. Each of the above-mentioned materials may be employed alone or in combination. When the materials are employed in combination, they may be pre-blended before contacting the biodiesel fuel, or they may brought into contact with the biodiesel fuel separately.

In one embodiment, the at least one adsorbent material comprises magnesium silicate.

In one embodiment the magnesium silicate has the following properties:

Loss on Ignition	15% max (dry basis)
% MgO	15% min. (ignited basis)
% SiO_2	67% min. (ignited basis)
Soluble salts	3% max.
Mole ratio MgO:SiO_2	1:1.36 to 1:3.82

In another embodiment, the magnesium silicate is an amorphous, hydrated, precipitated, synthetic magnesium silicate having a surface area of at least 300 square meters per gram, and preferably has a surface area from about 400 square meters per gram to about 700 square meters per gram, and more preferably has a surface area from about 400 square meters per gram to about 600 square meters per gram. In addition, such magnesium silicate is preferably employed as coarse

particles, with at least 75%, and preferably at least 85% of the particles having a particle size which is greater than 400 mesh, and with no more than 15%, and preferably no more than 5%, all by weight, having a particle size greater than 40 mesh. In most cases, the average particle size of the magnesium silicate employed in accordance with the present invention is in the order of but not limited to 20-175 microns. It is to be understood, however, that the magnesium silicate may have a particle size different than the preferred size.

In addition, the amorphous, hydrated, precipitated magnesium silicate which is employed in accordance with a preferred embodiment of the present invention generally has a bulk density in the order of from 15-35 lbs./cu. ft., a pH of 3-10.8 (5% water suspension) and a mole ratio of MgO to SiO_2 of 1:1.0 to 1:4.0.

The following is a specification and typical value for a magnesium silicate which is employed in accordance with an embodiment of the present invention:

TABLE

Parameter	Specification	Typical Value
Loss on Ignition at 900°C:	15% max.	12%
Mole Ratio MgO:SiO_2	1:2.25 to 1:2.75	1:2.60
pH of 5% Water Suspension	9.5 ± 0.5	9.8
Soluble Salts % by wt.	3.0 max.	1.0%
Average Size, Microns		55
Surface Area (B.E.T.)	300 M^2/g(min.)	400
Refractive Index		Approx. 1.5

A representative example of such an amorphous, hydrated, precipitated synthetic magnesium silicate having a surface area of at least 300 square meters per gram is available as Magnesol® Polysorb 30/40, a product of the Dallas Group of America, Inc., Whitehouse, N.J., and also is described in U.S. Pat. No. 4,681,768.

In another embodiment, the magnesium silicate is a magnesium silicate which has a surface area of no more than 150 square meters per gram, preferably from about 50 square meters per gram to about 150 square meters per gram. Preferably, such a magnesium silicate has a mole ratio of MgO to SiO_2 of from

about 1:3.0 to about 1:3.8, and a pH (5% water suspension) of from about 9.5 to about 10.5. An example of such a magnesium silicate is available as Magnesol® HMR-LS, a product of the Dallas Group of America, Inc., Whitehouse, N.J.

In another embodiment, the magnesium silicate is an amorphous, hydrous, precipitated synthetic magnesium silicate, which has a pH less than about 9.0. As used herein, the term "precipitated" means that the amorphous hydrated precipitated synthetic magnesium silicate is produced as a result of precipitation formed upon the contact of a magnesium salt and a source of silicate in an aqueous medium.

For purposes of the present invention, the pH of the magnesium silicate is the pH of the magnesium silicate as measured in a 5% slurry of the magnesium silicate in water. The pH of the magnesium silicate in a 5% slurry preferably is from about 8.2 to about 8.9, and more preferably from about 8.5 to about 8.8, and most preferably is about 8.5. Examples of such amorphous hydrous precipitated synthetic magnesium silicates are described in U.S. Pat. No. 5,006,356, and also are available as Magnesol® R30 and Magnesol® R60, products of the Dallas Group of America, Inc., Whitehouse, N.J. Magnesol® R30 has an average particle size of 30 microns, and Magnesol® R60 has an average particle size of 60 microns.

In a further embodiment, the magnesium silicate has a pH (5% water suspension) of from about 9.0 to about 9.5.

In another embodiment, the magnesium silicate may be in the form of talc.

It is to be understood, however, that the scope of the present invention is not to be limited to any specific type of magnesium silicate or method for the production thereof.

In general, the biodiesel fuel is contacted with the at least one adsorbent material, such as magnesium silicate as hereinabove described, in an amount effective to remove impurities from the biodiesel fuel. For example, the biodiesel fuel may be contacted with the at least one adsorbent material in an amount of from about 0.01

wt. % to about 20.0 wt.%, based on the weight of the biodiesel fuel, preferably from about 0.5 wt. % to about 4.0 wt. %.

The biodiesel fuel may be derived from any source of triglycerides, including, but not limited to, plant sources, and animal fat or oil sources, including, but not limited to, crude soy, crude oils, used oils, yellow grease, float grease, white grease, soap stock, and any other source of fatty acids.

As stated hereinabove, triacylglycerides are reacted with an alcohol, such as, for example, methanol, ethanol, or propanol, in the presence of a catalyst to produce a mixture of Fatty Acid Methyl Ester (FAME), Fatty Acid Ethyl Ester, and Fatty Acid Propyl Ester, respectively, and by-products described herein. The fatty acid esters are separated from the mixture and heat stripped to remove the residual alcohol.

The fatty acid ester(s) is (are) contacted with the at least one adsorbent material in an amount, such as hereinabove described, effective to remove impurities therefrom. Impurities which may be removed include, but are not limited to, soap, colors, odors, unreacted catalyst, metals and metallic compounds, sulfur, phosphorus, calcium, iron, monoglycerides, diglycerides, polymeric triglycerides, acidic compounds, free and total glycerin, methanol, chlorophyll, water, and sediment, as listed in the specifications for ASTM 6751 for biodiesel, and the European Standard EN14214. The purified biodiesel also will have improved oxidative stability.

The specifications from ASTM 6751 are as follows:

Free Glycerin %	0.020 maximum
Total Glycerin, %	0.240 maximum
Flash Point, °C	130 °C maximum
Water and Sediment, Vol. %	0.050 maximum
Carbon Residue, %	0.050 maximum
Sulfated Ash, mass %	0.020 maximum
Kinematic Viscosity, cSt at 40°C	1.9-6.0
Total Sulfur, mass %	0.05 maximum

Cetane Number	47 minimum
Copper Corrosion	No. 3 maximum
Acid Number, mg KOH/gram	0.80 maximum
Phosphorus, Mass %	0.001 maximum

The specifications from EN 14214 are as follows:

Property	Unit	Limits		Test method
		Minimum	Maximum	
Ester content	% (m/m)	96.5		EN 14103
Density at 15°C	kg/m^3	860	900	EN ISO 3675 EN ISO 12185
Viscosity at 40°C	mm^2/s	3.50	5.00	EN ISO 3104
Flash Point	°C	120	_	prEN ISO 3679
Sulfur content	mg/kg	_	10.0	prEN ISO 20846 prEN ISO 20884
Carbon residue (on 10% distillation residue)	% (m/m)	_	0.30	EN ISO 10370
Cetane number		51.0		EN ISO 5165
Sulfated ash content	% (m/m)	_	0.02	ISO 3987
Water content	mg/kg	_	500	EN ISO 12937
Total contamination	mg/kg	_	24	EN 12662
Copper strip corrosion (3h at 50°C)	rating	class 1		EN ISO 2160
Oxidation stability, 110 °C	hours	6.0	_	EN 14112
Acid value	mg KOH/g		0.50	EN 14104
Iodine value	gr iodine /100gr		120	EN 14111
Linolenic acid methyl ester	% (m/m)		12.0	EN 14103
Polyunsaturated (>=4 double bonds) methyl esters	% (m/m)		1	
Methanol content	% (m/m)		0.20	EN 14110
Monoglyceride content	% (m/m)		0.80	EN 14105
Diglyceride content	% (m/m)		0.20	EN 14105
Triglyceride content	% (m/m)		0.20	EN 14105
Free glycerol	% (m/m)		0.02	EN 14105

				EN 14106
Total glycerol	% (m/m)		0.25	EN 14105
Group I metals (Na+K)	mg/kg		5.0	EN 14108 EN 14109
Group II metals (Ca+Mg)	mg/kg		5.0	prEN 14538
Phosphorus content	mg/kg		10.0	EN 14107

Source: European Standard EN 14214: Automotive fuels-Fatty acid methyl esters (FAME) for diesel engines-Requirements and test methods (approved on 14 February 2003)

The invention now will be described with respect to the examples; however, the scope of the present invention is not intended to be limited thereby.

Example 1

Biodiesel fuel samples of 3,733g (4,440 ml) each, including 20 wt. % fatty acid methyl esters derived from corn oil and 80 wt. % fatty acid methyl esters derived from crude soy oil, were treated with either (i) 1 wt. % Magnesol® R60, or (ii) 2 wt. % Magnesol® R60 at 200°F for 20 minutes. Unwashed and treated samples were tested for the presence of various impurities, as well as for flash point, kinematic viscosity, cetane number, cloud point, and copper corrosion. The results are given in Table 1 below.

Table 1

ASTM Spec.	ASTM method of Analysis	Unwashed Methyl Ester	1% R60	2%R60
Free Glycerin, %	D6584	0.170	0.039	0.003
Total Glycerin ,%	D6584	0.321	0.197	0.148
Flash Point, °C	D93	NA	92	141
Water and Sediment, vol %	D2709	0.60	0.005	0
Carbon Residue, %	D524	0.020	<0.010	<0.010
Sulfated Ash, mass %	D874	0.025	0.000	0.00
Kinematic Viscosity, cSt@40°C	D445	3.904	4.22	4.156
Total Sulfur, Mass %	D5453	0.00016	0.00025	0.00008

Cetane Number	D613	51.8	53.2	55.0
Cloud Point, °C	D2500	-1.0	-3.0	0.0
Copper Corrosion	D130	1A	1A	1A
Acid Number, mg KOH/gram	D664	0.23	0.48	0.40
Phosphorus, Mass %	D4951	0.0005	0.0002	0.0000
ppm Soap	NA	2411	27	0

Example 2

Biodiesel fuel samples of 100 grams each, including 20 wt.% fatty acid methyl esters derived from corn oil and 80 wt.% fatty acid methyl esters derived from crude soy oil, were treated with either (i) 1 wt % Magnesol®R30 or (ii) from 1 wt.% up to 1.8 wt.% Magnesol® R60 at 200°F for 20 minutes. Unwashed and treated samples were tested for the presence of free glycerin and total glycerin according to ASTM method D6584. The results are given in Table 2 below.

TABLE 2

Sample Description	Free Glycerin %	Total Glycerin%
Unwashed Methyl Ester	0.170	0.321
1% Magnesol R30	0.029	0.156
1% R60	0.037	0.185
1.1% R60	0.027	0.173
1.2% R60	0.016	0.136
1.4%R60	0.008	0.133
1.8% R60	0.003	0.122

Example 3

Biodiesel fuel samples of 150 grams each, including fatty acid methyl ester derived from corn oil, were treated with either (i) 1 wt.% Magnesol® R60 or (ii) 2 wt. % Magnesol® R60 at 200°F for 20 minutes. Unwashed and treated samples were tested for the presence of soap (AOCS method Cc17-79), and free glycerin and total glycerin according to ASTM method D6584. The results are given in Table 3 below.

Table 3

SAMPLE	ppm Soap	Free Glycerin	Total Glycerin
unwashed M.E.	3382	0.339	0.531
1% R60	244	0.058	0.268
2% R60	10	0.024	0.227

Example 4

Biodiesel fuel samples of 100 grams each, including fatty acid methyl ester derived from crude soy oil, were treated by either (i) washing with water, followed by drying, or by contacting the samples with (ii) 1 wt. Magnesol®R30 ; (iii) 2 wt.% Magnesol®R30 or (iv) 4 wt.% Magnesol®R30 at 160°F for 20 minutes. Unwashed, washed and dried, and Magnesol® treated samples were tested for the presence of soap, and free glycerin and mass percent glycerin according to ASTM method D6584, volume percent water and sediment according to ASTM method D2709, and mass percent sulfated ash according to ASTM method D874. The results are given in Table 4 below.

Table 4

Sample	ppm soap	% Free Glycerin	mass % Glycerin	% water and sediment	Sulfated
unwashed M.E.	1722	0.292	0.402	0.2	0.03
washed and dried M.E.	11	0	0.147	0.1	0
1% Treatment Magnesol R30	48				
2% Treatment Magnesol R30	0	0.031	0.145	0.06	0.00
4% Treatment Magnesol R30	0				

Example 5

Biodiesel fuel samples of 100 grams each, including fatty acid methyl ester derived from crude soy oil, were treated by contact with either (i) 1 wt.% Magnesol® R60; or (ii) 1 wt.% Magnesol®R30 at 170°F or 250°F for 20 minutes. Unwashed and treated samples were tested for the presence of soap, and free and total glycerin according to ASTM method D6584. The results are given in Table 5 below.

Sample	Treatment temp.	Treatment time.	ppm soap	Free Glycerin	Total Glycerin
unwashed methyl ester			1900	0.086	0.204
1% R60	170°F	20 minutes	20	0.011	0.123
1% R60	250°F	20 minutes	18	0.013	0.127
1% Magnesol®R30	170°F	20 minutes	20	0.012	0.127

Example 6

Biodiesel fuel samples of 100 grams each, including fatty acid methyl ester derived from yellow grease, were treated either (i) by washing with water, followed by drying; or by contacting the samples with (ii) 1 wt. % Magnesol®R30; (iii) 2 wt. % Magnesol®R30; or (iv) 4 wt. % Magnesol®R30 at 160 °F for 20 minutes. Unwashed, washed and dried, and Magnesol® treated samples were tested for the presence of soap. The results are given in Table 6 below. In this example, there was a significant amount of unreacted methanol boiling off while heating the samples to treatment temperature. This methanol should have been removed during the heat stripping step.

Table 6

Sample	Ppm Soap
Unwashed M.E.	5971
Washed and dried M.E.	77
1% treatment Magnesol®R30	3723
2% treatment Magnesol®R30	2381
4% treatment Magnesol®R30	1914

The excess methanol may have interfered with the ability of the Magnesol®R30 to adsorb soap. Therefore, the experiment was repeated after removing the excess methanol (See Example 7 below).

Example 7

Biodiesel fuel samples of 100 grams each, including fatty acid methyl ester derived from yellow grease (used in Example 6), were treated after boiling for 2 hours to remove excess methanol by contacting the samples with (i) 2 wt. % Magnesol®R30; (ii) 4 wt.% Magnesol®R30; or (iii) 8 wt.% Magnesol®R30 at 160°F for 20 minutes. Unwashed, and Magnesol®R30 treated samples were tested for the presence of soap. The results are given in Table 7 below.

Table 7

Sample	ppm Soap
unwashed M.E.	4986
2% Treatment Magnesol®R30	1490
4% Treatment Magnesol®R30	79
8% Treatment Magnesol®R30	9

The results confirmed that the excess methanol interfered with the purification of biodiesel sample.

Example 8

cedure and Reaction Conditions

I. Biodiesel Production

60 gallons of both crude soybean oil methyl esters and yellow grease methyl esters were produced at the biodiesel pilot plant located at the Biomass Energy Conversion Facility (BECON) in Nevada, IA. The biodiesel pilot plant is operated by Iowa State University and was constructed using major biodiesel manufacturing facilities as the model. The procedure for making the soybean and yellow grease methyl esters is described below.

Soybean Feedstock

The reaction process for the soybean oil based methyl ester was completed in three steps. Step One involved adding 80% of the methanol and catalyst and removing the glycerin after reaction completion. During Step Two, the remaining 20% of methanol and catalyst were added and the glycerin was separated after reaction completion. Step Three was the stripping of methanol from the reacted biodiesel.

STEP ONE: Primary Reaction

Crude dried and partially degummed soybean oil containing 0.70% FFA weighing 520 lb. (approximately 69 gallons) was added to the reaction tank. 95.68 lb of methanol and 6.37 lb. of sodium methoxide were added and the materials were mixed and heated until the reaction temperature reached 140°F after 30 minutes. The reaction was allowed to continue at 140°F for an additional 1.5 hours (total of 2 hours reaction time) and then the mixing and heating were stopped. After 8 hours of separation time, the glycerin phase was separated from the methyl ester phase. The amount of glycerin removed was 82.7 lb.

STEP TWO: Secondary Reaction

To the remaining methyl ester/soybean oil an additional 23.92 lb. of methanol and 1.59 lb. of sodium methoxide were added and the reaction conditions in step one were repeated. The amount of glycerin removed was 9.8 lb.

STEP THREE: Methanol Stripping

The remaining methyl esters were passed through the flash evaporator to remove the excess methanol. The flash tank vacuum was maintained at 25-26 mm Hg and the spray temperature in the flash tank was 240°F. The condenser water flow rate was 3 gpm and the recirculation time was 45 minutes. The final flash point of the methyl esters was 143°F.

The 60 gallons of methyl esters produced from soybean feedstock were placed into a 70-gallon capacity-mixing tank. The methyl esters were recirculated for about 10 minutes to ensure that the mixture was uniform. Approximately 3 gallons of the methyl ester were placed into a 5-gallon container to be tested at a later time.

Yellow Grease Feedstock

The reaction process for the yellow grease based methyl esters was completed in four steps. Step One was the pre-treatment to convert the FFA to methyl esters. Step Two involved adding 80% of the methanol and catalyst and removing the glycerin after reaction completion. During Step Three the remaining 20% of methanol and catalyst were added and the glycerin was separated after reaction completion. During Step Four the methanol was stripped from the reacted biodiesel.

STEP ONE: Pretreatment

Yellow grease, weighing 480 lb. (approximately 64 gallons) and containing 11.6% FFA, was added to the reaction tank. Methanol (125.04 lb.) and Sulfuric acid (2.78 lb.) were added to the yellow grease and the materials were mixed and heated until the reaction temperature reached 140°F after 30 minutes. The reaction continued for an additional 1.5 hours. The mixture was allowed to separate for 8 hours in order to confirm the effective conversion of the FFA to methyl esters. The upper phase contained methanol, sulfuric acid and methyl esters and weighed approximately 147.82 lb. The lower phase, consisting of yellow grease, weighed about 460 lb. and contained 1.67% FFA.

STEP TWO: Primary Reaction

To the pre-treated grease from Step One, 84.64 lb. of methanol and 8.21 lb. of sodium methoxide were added. The materials were mixed and heated until the reaction reached 140°F after 30 minutes. The reaction was allowed to continue at 140°F for an additional 1.5 hours (total of 2 hours reaction time) and then the mixing and heating were stopped. After 8 hours of separation time,

the glycerin phase was separated from the methyl ester phase. The amount of glycerin removed was 102 lb. Approximately 10 lb. of the yellow grease/methyl ester was lost.

STEP THREE: Secondary Reaction

To the remaining 450 lb. methyl ester/yellow grease an additional 21.16 lb. of methanol and 2.05 lb. of sodium methoxide were added and the reaction conditions in step one were repeated. The amount of glycerin removed was 10 lb.

STEP FOUR: Methanol Stripping

The remaining methyl esters were passed through the flash evaporator to remove the excess methanol. The flash tank vacuum was maintained at 25-26 mm Hg and the spray temperature in the flash tank was 240°F. The condenser water flow rate was 3 gpm and the recirculation time was 45 minutes.

The 60 gallons of methyl esters produced from yellow grease feedstock was placed into a 70-gallon capacity-mixing tank. The methyl ester was recirculated for about 10 minutes to ensure that the mixture was uniform. Approximately 3 gallons of the methyl ester were placed into a 5-gallon container to be tested at a later time.

II Water Wash Procedure

Soybean Feedstock

Twenty gallons of crude soybean biodielsel were water washed using four successive washes at 140°F soft water wash tank. Each wash was performed using 50% of the volume of the biodiesel (see Table 8). The first two water washes were performed using no agitation (just spraying water into tank) while the third and forth washes were performed using agitation. The water from each wash was removed by gravity separation and discarded

The washed biodiesel then was placed through the flash evaporator to remove excess water. The flash tank vacuum was maintained at 27-28 mm Hg and the spray temperature of the tank was 240°F. The condenser flow rate was 1 gpm, the throttling pressure was 25 psig and the recirculation

time was 30 minutes. The finished biodiesel was then collected into 5-gallon containers and saved for further analysis.

TABLE 8: Water Washed Soybean Biodiesel

Sample Description	*# Water Washes*	*Amount Water/Wash*	*% H_2O*
Water Washed ME	4	220lb.	0.017

Yellow Grease Feedstock

Twenty gallons of the yellow grease biodiesel were water washed using a total of five successive washes at 140°F using soft water in the water wash tank. Each wash was performed using 50% of the volume of the biodiesel (see Table 9). The first three water washes were performed using no agitation while the forth and fifth washes were performed using agitation. The water from each wash was removed by gravity separation and discarded (separation time was 45 minutes/water wash).

TABLE 9: Water Washed Yellow Grease Biodiesel

Sample Description	*# Water Washes*	*Amount Water/Wash*	*% H_2O*
Water Washed ME	5	220lb.	0.019

The washed biodiesel the was placed through the flash evaporator to remove excess water. The flash tank vacuum was maintained at 27-28 mm Hg and the spray temperature of the tank was 240°F. The condenser flow rate was 1 gpm, the throttling pressure was 25 psig and the recirculation time was 30 minutes. The finished biodiesel was then collected into 5-gallon containers and saved for further analysis.

III. Adsorbent Purification with Synthetic Magnesium Silicate

Soybean Methyl Esters

In order to confirm an appropriate treatment level, a 200g sample of the biodiesel was treated in the laboratory with 1% by weight (2g) of MAGNESOL® R60 at 160°F. The material was gravity filtered after 5 minutes contact time was achieved. The acid value and soap content were checked on the sample before and after the treatment (see Table 10 below).

TABLE 10: Initial Soybean Biodiesel Laboratory Testing

Sample Description	Flash Point (°C)	Acid Value (mg KOH/g)	Soap Content (ppm)
Initial ME	143	0.61	651
After 1% R60	NT	0.40	9

Twenty gallons of methyl esters produced from the soybean feedstock (not water washed) were placed into a 70-gallon capacity-mixing tank. The 20 gallons were circulated through a heat exchanger until the tank temperature was 170°F (77°C). MAGNESOL® R60 was added to the methyl esters at the predetermined level of 1% by weight (1.5lb. MAGNESOL®) and the material was mixed for 10 minutes. The methyl ester/MAGNESOL® mixture was recirculated through a sock filter that contained a 5-micron polypropylene filter sock (approximately 6" diameter by 3' length. The filtrate appeared clear after about 10 minutes of circulation through the filter and a sample was taken and checked for soap (See Table 11). The filtrate was collected into 5-gallon containers and saved for further analysis.

TABLE 11: Treatment of Soybean Biodiesel with MAGNESOL® R60

Sample Description	Methyl Ester Wt.	MAGNESOL® R60 Wt.	% treatment	Treatment Temperature	Soap Content (ppm)
Initial ME R60	146.6 Lb.				651
Treated ME		1.5lb.	1.0	170°F	8

Yellow Grease Methyl Esters

In order to confirm an appropriate treatment level, a 200g sample of the biodiesel was treated in the laboratory with 2% by weight (4g) of MAGNESOL® R60 AT 160°F. The soap and flash point were tested before and after the treatment (see Table 12)

TABLE 12: Initial Yellow Grease Biodiesel Laboratory Testing

Sample Description	Flash Point (°C)	Soap Content (ppm)
Initial ME	140	2600
after 2% R60	145	10

15 Gallons of the methyl ester made from yellow grease feedstock (not water washed) were pumped into the mix tank to be treated with MAGNESOL® R60 . A one-gallon sample was collected. The remaining 14 gallons were treated with MAGNESOL® at 170°F for 10 minutes and then the filter

was started and recirculated for about 20 minutes (Table 13). The biodiesel was collected into 5-gallon containers for further analysis.

TABLE 13: Treatment of Yellow Grease Biodiesel with MAGNESOL® R60

Sample Description	Methyl Ester Wt.	MAGNESOL® *R60 Wt.*	%Treatment	Treatment Temperature	Soap Content (ppm)
Initial ME	102.6lb.				2600
R60 Treated ME		2.05lb.	2.0	170°F	22

IV Analytical Testing of Biodiesel Samples

The biodiesel samples that were collected were labeled as follows:

S1=unwashed, untreated soybean biodiesel

S2=washed and dried soybean biodiesel

S3=1% MAGNESOL® R60 treated soybean biodiesel

Y1=unwashed, untreated yellow grease biodiesel

Y2=washed and dried yellow grease biodiesel

Y3=2% MAGNESOL® R60 treated yellow grease biodiesel

ASTM D6751

All samples were sent to a recognized analytical laboratory for the entire ASTM D6751 testing.

Additional Parameters Tested

All samples were tested for additional parameters, including: metal content (P, Na, Mg, Ca), soap, viscosity and oxidative stability.

Data and Results

Soybean Oil Based Biodiesel

TABLE 14: ASTM D6751 Results for Soybean Biodiesel

ASTM SPECIFICATION	ASTM D6751 specification	Unwashed, Untreated M.E.	1% MAGNESOL® R60	Washed And Dried

				M.E.
Free Glycerin, %	0.020 maximum	0.033	0.005	0.002
Total Glycerin, %	0.240 maximum	0.209	0.191	0.196
Flash Point, ^{0}C	130 minimum	>190	200	163
Water and Sediment, vol. %	0.050 maximum	0.10	0.04	0.00
Carbon Residue, %	0.050 maximum	<0.010	<0.010	0.050
Sulfated Ash, mass %	0.020 maximum	0.000	0.000	0.005
Kinematic Viscosity, cSt@40^{0}C	1.9 – 6.0	4.127	4.097	4.207
Total Sulfur, mass%	0.05 maximum	0.00006	0.00002	0.00007
Cetane Number	47 minimum	51.0	51.3	55.9
Cloud Point, ^{0}C	Report	0.0	0.0	0.0
Copper Corrosion	No. 3 maximum	1a	1a	1a
Acid Number, mg KOH/gram	0.80 maximum	0.32	0.27	0.31
Phosphorus, mass%	0.001	0.0007	0.0005	0.0006

The results from the ASTM D6751 testing for the soybean methyl esters are summarized in Table 14. The untreated, unwashed soybean methyl ester did not meet the ASTM D6751 specifications. The washed and dried methyl ester and the 1% MAGNESOL® treated methyl ester were able to meet all ASTM specifications. The results show that the traditional water washing of the methyl ester could be replaced completely by the adsorptive treatment with MAGNESOL®.

TABLE 15: Additional Parameters Tested for Soybean Biodiesel

Parameter	Method	Unwashed, Untreated M.E.	1% MAGNESOL® R60	Washed And Dried M.E.
Viscosity at 40°C, mm^2/sec	ISO 3104	4.1	4.1	4.2
Oxidation stability at 110°C, hours	EN 14112	0.5	3.7	0.2
Methanol content, %	EN14110	0.113	0.011	<0.001
Metals I Na, mg/kg	AA	3	<1	5
Metals II Ca, mg/kg	EN 14538	0	0	0
Metals II Mg, mg/kg	EN 14538	0	0	0
Phosphorus content, mg/kg	EN 14107	<1	<1	<1
Soap, mg/kg	AOCS Cc17-79	651	4	13

Some additional parameters that were tested on the soybean methyl esters are reported in Table 15. The oxidative stability of biodiesel is a very important parameter that relates to the storage and thermal stability of the biodiesel fuel. The oxidative stability of the biodiesel was improved significantly by treatment with MAGNESOL® when compared to the unwashed, untreated methyl ester and the traditional water wash method (86% and 95% improvement).

There was not any significant amount of metals or soap (4ppm) after the treatment and filtration of the methyl esters with MAGNESOL®, while the water washed biodiesel contained 5ppm sodium and 13 ppm soap.

Yellow Grease Based Biodiesel

TABLE 16: ASTM D6751 Results for Yellow Grease Methyl Ester

ASTM Specification	ASTM D6751 specification	Unwashed, Untreated M.E.	2% MAGNESOL® R60	Washed And Dried M.E.
Free Glycerin, %	0.020 maximum	0.063	0.004	0.037
Total Glycerin, %	0.240 maximum	0.220	0.147	0.185
Flash Point, °C	130 minimum	179	168	>190
Water and Sediment, vol. %	0.050 maximum	0.70	0.005	0.06
Carbon Residue, %	0.050 maximum	0.060	0.000	0.013
Sulfated Ash, mass %	0.020 maximum	0.007	0.002	0.004
Kinematic Viscosity, cSt@40°C	1.9 – 6.0	5.095	5.060	5.107

Total Sulfur, mass %	0.05 maximum	0.00146	0.00133	0.00139
Cetane Number	47 minimum	57.8	57.4	60.3
Cloud Point, °C	Report	10.0	9.0	9.0
Copper Corrosion	No. 3 maximum	1a	1a	1a
Acid Number, mg KOH/gram	0.80 maximum	0.21	0.32	0.27
Phorphorus, mass %	0.001 maximum	0.0009	0.0008	0.0008

The results from ASTM D6751 testing for the yellow grease methyl esters are summarized in Table 16. The untreated, unwashed soybean methyl ester and the washed and dried methyl esters did not meet the ASTM D6751 specifications. The washed and dried methyl ester did not meet the specification for free glycerin and water and sediment. There was a very high soap content (see Table 17) in the unwashed, untreated methyl ester, which may have led to poor separation and emulsification, which could explain the inability to meet the ASTM specifications.

The 2% MAGNESOL® treated yellow grease methyl ester was able to meet all ASTM D6751 specifications. The results show that the adsorptive treatment of the yellow grease methyl esters yielded a more pure biodiesel than that obtained by the traditional water washing method.

TABLE 17: Additional Parameters Tested for Yellow Grease Biodiesel

EN 14214 Specification	EN 14214 Method	Unwashed, Untreated M.E.	2% MAGNESOL® R60	Washed And Dried M.E.
Viscosity at 40°C (mm^2/sec)	ISO 3104	5.0	4.9	5.1

Oxidation stability at 110°C, hours	EN 14112	0.5	4.3	0.2
Methanol content, %	EN 14110	0.116	0.002	<0.001
Metals I Na, mg/kg	AA	16	<1	3
Metals II Ca, mg/kg	EN 14538	0	<1	0
Metals II Mg, mg/kg	EN 14538	0	1	0
Phosphorus content, mg/kg	EN 14107	<1	<1	1
Soap, mg/kg	AOCS Cc17 – 79	2458	4	91

Some additional parameters that were tested on the yellow grease methyl esters are reported in Table 17. The oxidative stability of the biodiesel was improved significantly by treatment with MAGNESOL® when compared to the unwashed untreated sample (88% Improvement). The oxidative stability was also significantly improved when compared to the traditional water wash method (95% Improvement).

There was not any significant amount of metals (all <1ppm) or soap (4ppm) after the treatment and filtration of the methyl esters with MAGNESOL®, while the water washed biodiesel contained 91 ppm soap.

Example 9

A 400g sample of methyl ester (biodiesel) produced from refined bleached, deodorized (RBD) soybean oil was treated with MAGNESOL® R60, or MAGNESOL® 300R (a blend of 30% sodium

silicate and 70% MAGNESOL® R60), or MAGNESOL® 600R (a blend of 60% sodium silicate and 40% MAGNESOL® R60), or MAGNESOL® 900R (a blend of 90% sodium silicate and 10% MAGNESOL® R60) at 180°F for 20 minutes in the amounts shown in Table 18 below.

Table 18

Adsorbent	Wt. %
MAGNESOL R60	2.0
MAGNESOL 300R	1.0
MAGNESOL 300R	1.25
MAGNESOL 300R	1.5
MAGNESOL 300R	1.75
MAGNESOL 300R	2.0
MAGNESOL 600R	0.75
MAGNESOL 900R	0.50

The samples then were tested for the presence of free fatty acids (FFA) and soap (ppm). The results are given in Table 19 below.

Table 19

Sample	% FFA	Soap (ppm)
Blank	0.88	19

2% MAGNESOL® R60	0.72	0
1.0% MAGNESOL® 300R	0.49	23
1.25% MAGNESOL® 300R	0.36	N/A
1.5% MAGNESOL® 300R	0.29	N/A
1.75% MAGNESOL® 300R	0.20	N/A
2.0% MAGNESOL® 300R	0.24	16
0.75% MAGNESOL® 600R	0.42%	18
0.50% MAGNESOL® 900R	0.41	34

Example 10

A 400g sample of crude methyl ester (biodiesel) produced from soybean oil was treated with MAGNESOL® R60 or MAGNESOL® 700R, a blend of 70% sodium silicate and 30% MAGNESOL® R60, in the amounts shown in Table 20 below for 20 minutes at temperatures from 78°F to 350°F also as shown in Table 20 below. The treated samples then were tested for the presence of free fatty acids (FFA), soap (ppm), and chlorophyll (ppm). The results are given in Table 20 below.

Table 20

Adsorbent	Wt. %	Temp.	Time	% FFA	Soap (ppm)	% Free Glycerin	% Total Glycerin	Chlorophyll (ppm)

MAGNESOL® R60	0.50	200°F	20 min.	0.46	0	---	---	---
MAGNESOL® R60	0.75	200°F	20 min.	0.45	0	---	---	---
MAGNESOL® 700R	0.75	200°F	20 min.	0.28	143	---	---	---
MAGNESOL® 700R	0.75	150°F	20 min.	0.21	56	---	---	---
MAGNESOL® R60	0.75	78°F	20 min.	0.49	6	---	---	2.96
MAGNESOL® R60	0.75	150°F	20 min.	0.48	0	---	---	2.00
MAGNESOL® R60	0.75	200°F	20 min.	0.46	0	---	---	0.91
MAGNESOL® R60	0.75	300°F	20 min.	0.46	0	---	---	1.00
MAGNESOL® R60	0.75	350°F	20 min.	0.46	0	---	---	0.97
Before Treating	---	---	---	0.87	60	0.002	0.195	3.2

The disclosure of all patents and publications (including published patent applications) are hereby incorporated by reference to the same extent as if each patent and publication were incorporated individually by reference.

It is to be understood, however, that the scope of the present invention is not to be limited to the specific embodiments described above. The invention may be practiced other than as particularly described and still be within the scope of the accompanying claims.

WHAT IS CLAIMED IS:

1. A method of purifying a biodiesel fuel, comprising:

   contacting said biodiesel fuel with at least one adsorbent material.

2. The method of Claim 1 wherein said at least one adsorbent material comprises magnesium silicate.

3. The method of Claim 2 wherein said magnesium silicate has a surface area of at least 300 square meters per gram.

4. The method of Claim 3 wherein said magnesium silicate has a surface area of at least 400 to about 700 square meters per gram.

5. The method of Claim 3 wherein said magnesium silicate has a particle size of from about 20 microns to about 175 microns.

6. The method of Claim 3 wherein said magnesium silicate has a bulk density of from about 15 to about 35 pounds per cubic foot.

7. The method of Claim 2 wherein said magnesium silicate is an amorphous hydrous precipitated synthetic magnesium silicate, said magnesium silicate having been treated to reduce the pH thereof to less than about 9.0.

8. The method of Claim 7 wherein said magnesium silicate has a pH in a 5% slurry of from about 8.2 to about 8.9.

9. The method of Claim 8 wherein said magnesium silicate has a pH in a 5% slurry of from about 8.5 to about 8.8.

10. The method of Claim 2 wherein said magnesium silicate has a surface area of no more than 150 square meters per gram.

11. The method of Claim 10 wherein said magnesium silicate has a surface area of from about 50 square meters per gram to about 150 square meters per gram.

12. The method of Claim 11 wherein said magnesium silicate has a mole ratio of MgO to SiO_2 of from about 1:3.0 to about 1:3.8 and a pH in a 5% water suspension of from about 9.5 to about 10.5.

13. The method of Claim 2 wherein said magnesium silicate has a pH of from about 9.0 to about 9.5.

14. The method of Claim 1 wherein said biodiesel fuel is contacted with said at least one adsorbent material in an amount of from about 0.01 wt.% to about 20.0 wt%, based on the weight of said biodiesel fuel.

15. The method of Claim 14 wherein said biodiesel fuel is contacted with said at least one adsorbent material in an amount of from about 0.5 wt.% to about 4.0 wt.%, based on the weight of said biodiesel fuel.

16. The method of Claim 1 wherein free fatty acids are removed from said biodiesel fuel.

17. The method of Claim 1 wherein chlorophyll is removed from said biodiesel fuel.

18. Biodiesel fuel purified according to the method of Claim 1.

19. The method of Claim 1 wherein methanol is removed from said biodiesel fuel.

20. The method of Claim 19 wherein said methanol is trace methanol.

21. The method of Claim 1 wherein glycerin is removed from said biodiesel fuel.

22. The method of Claim 1 wherein unreacted catalyst is removed from said biodiesel fuel.

23. A method for treating biodiesel fuel, said biodiesel fuel having been prepared by reacting methanol with triglycerides in the presence of a catalyst, said method comprising:

treating said biodiesel fuel with at least one adsorbent material to remove soap, unreacted catalyst, sulfur, phosphorus, calcium, iron, monoglycerides, diglycerides, acidic compounds, glycerin, chlorophyll, water, sediment, and remaining methanol.

24. The method of Claim 23 wherein said at least one adsorbent material is magnesium silicate.

25. The method of Claim 24 wherein said magnesium silicate has a surface area of at least 300 square meters per gram.

26. The method of Claim 25 wherein said magnesium silicate has a particle size of from about 20 microns to about 175 microns.

27. The method of Claim 24 wherein said magnesium silicate is an amorphous hydrous precipitated synthetic magnesium silicate, said magnesium silicate having been treated to reduce the pH thereof to less than about 9.0.

28. The method of Claim 23 wherein said biodiesel fuel is contacted with said at least one adsorbent material in an amount of from about 0.01 wt.% to about 20.0 wt.%, based on the weight of said biodiesel fuel.

29. The method of Claim 28 wherein said biodiesel fuel is contacted with said at least one adsorbent material in an amount of from about 0,5 wt.% to about 4.0 wt. %, based on the weight of said biodiesel fuel.

30. The method of Claim 1 wherein said at least one adsorbent material is magnesium aluminum silicate.

31. The method of Claim 1 wherein said at least one adsorbent material is calcium silicate.

32. The method of Claim 1 wherein said at least one adsorbent material is silica gel.

33. The method of Claim 1 wherein said at least one adsorbent material is a metal silicate.

34. The method of Claim 1 wherein said at least one adsorbent material is a bleaching clay.

35. The method of Claim 1 wherein said at least one adsorbent material is a bleaching earth.

36. The method of Claim 1 wherein said at least one adsorbent material is bentonite clay.

37. The method of Claim 23 wherein said at least one adsorbent material is magnesium aluminum silicate.

38. The method of Claim 23 wherein said at least one adsorbent material is calcium silicate.

39. The method of Claim 23 wherein said at least one adsorbent material is silica gel.

40. The method of Claim 23 wherein said at least one adsorbent material is metal silicate.

41. The method of Claim 23 wherein said at least one adsorbent material is a bleaching clay.

42. The method of Claim 23 wherein said at least one adsorbent material is a bleaching earth.

43. The method of Claim 23 wherein said at least one adsorbent material is bentonite clay.

44. A method as claimed in Claim 1 or Claim 23, substantially as herein described with reference to and as illustrated in any of the examples.

45. Fuel as claimed in Claim 18, substantially as herein described with reference to and as illustrated in any of the examples.