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(54) **SYSTEM FOR REMOVAL OF METHANOL  
FROM CRUDE BIODIESEL FUEL**

**Publication Classification**

(76) Inventor: **Joseph P. Lastella**, Bakersfield, CA  
(US)

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Correspondence Address:

**LAW OFFICES OF DAVID L. HOFFMAN**  
**27023 MCBEAN PKWY**  
**SUITE 422**  
**VALENCIA, CA 91355 (US)**

(57) **ABSTRACT**

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**Related U.S. Application Data**

(60) Provisional application No. 60/540,751, filed on Jan.  
31, 2004.

A method of removing methanol and other substances from crude biodiesel, includes mixing a silicone based adsorbent with the crude biodiesel. The silicone based adsorbent may be a magnesium silicate adsorbent with a formula of  $2\text{MgO}:65:02\text{ nH}_2\text{O}$ . A plant for making biodiesel fuel has a first section for making crude biodiesel fuel methanol therein, and a second section for removing the methanol from the crude biodiesel, the second section has a tank for mixing the crude biodiesel and the silicone based adsorbent for the methanol, and a filter for filtering the adsorbent mixed with methanol from the crude biodiesel thereby producing biodiesel.

FIG. 1

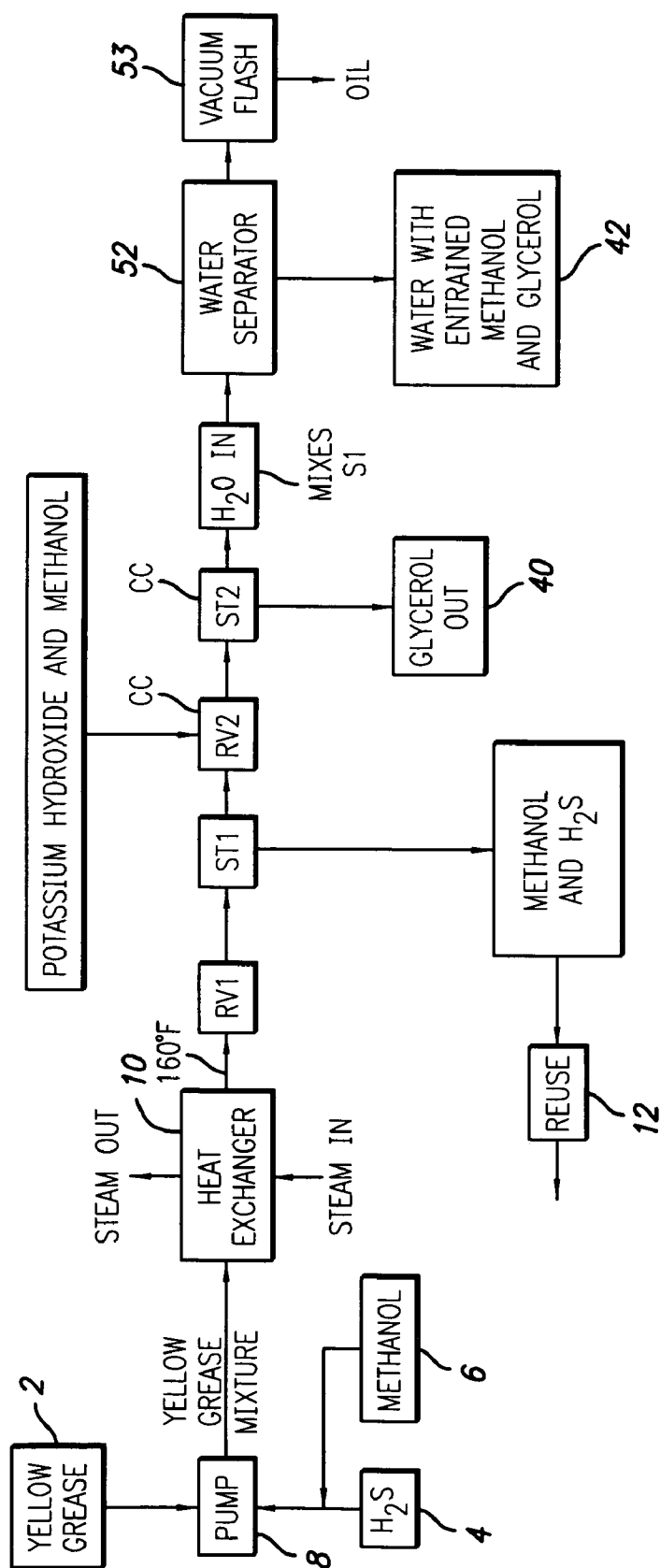


FIG. 2

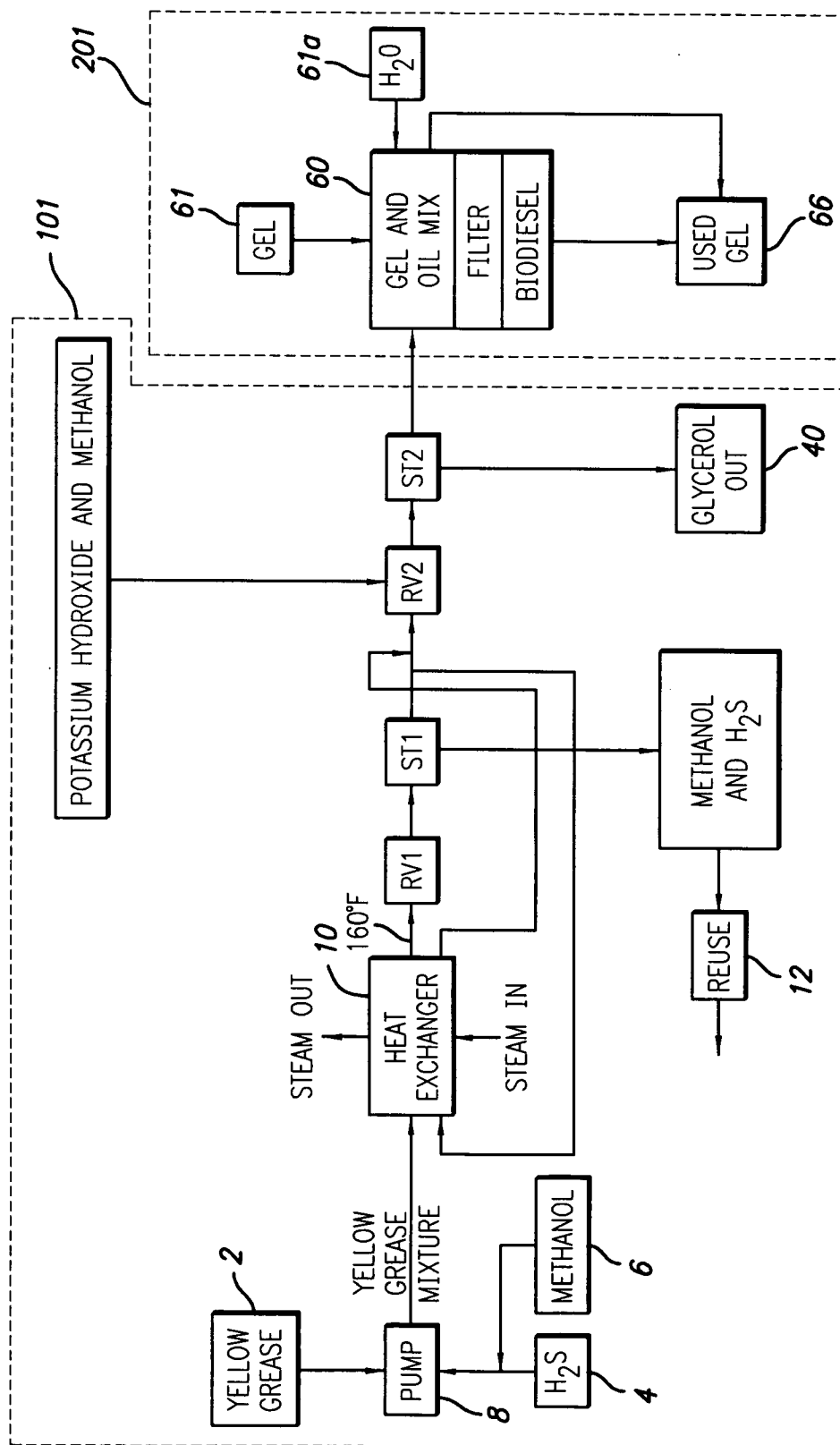


FIG. 3

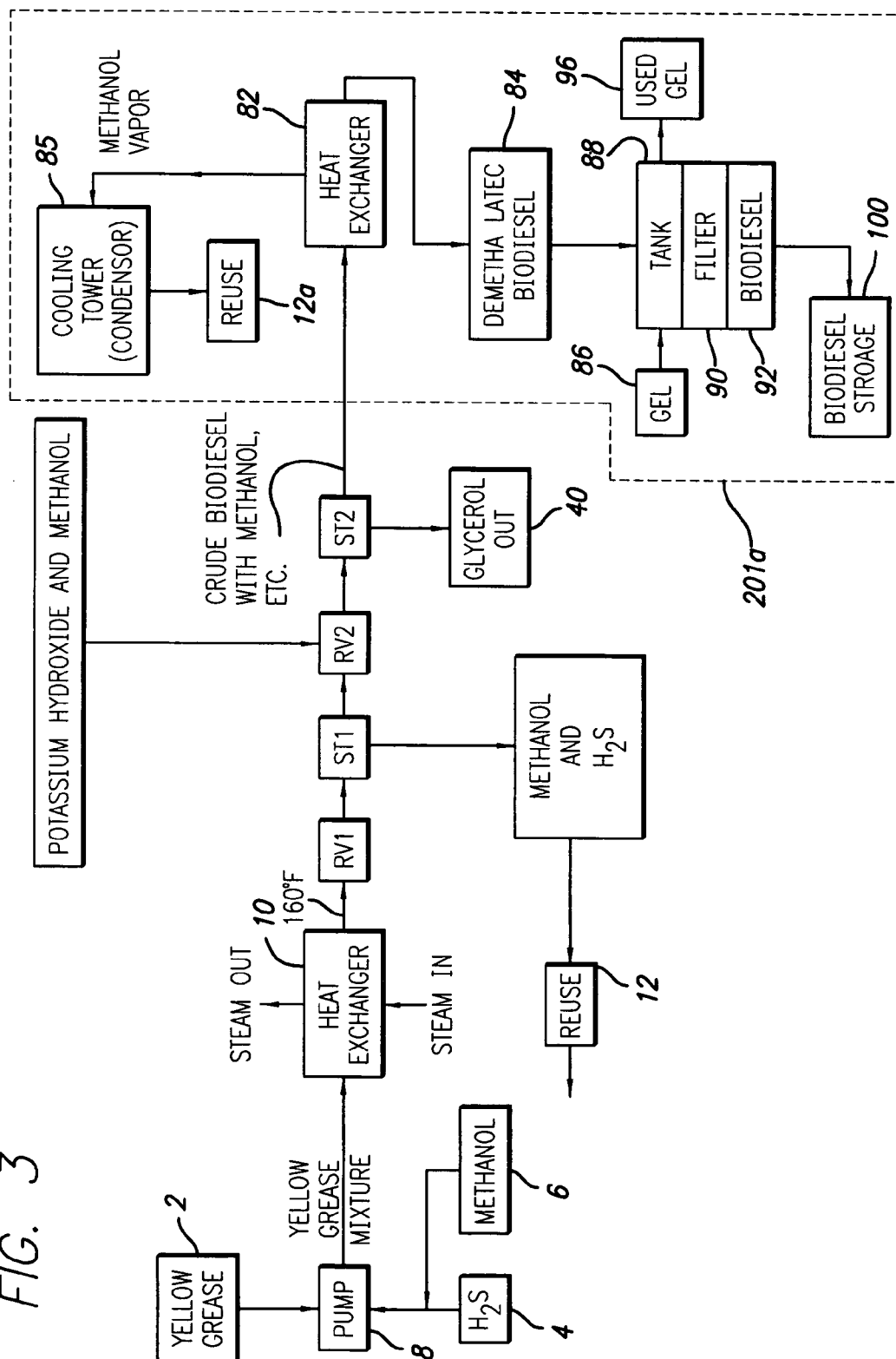


FIG. 4

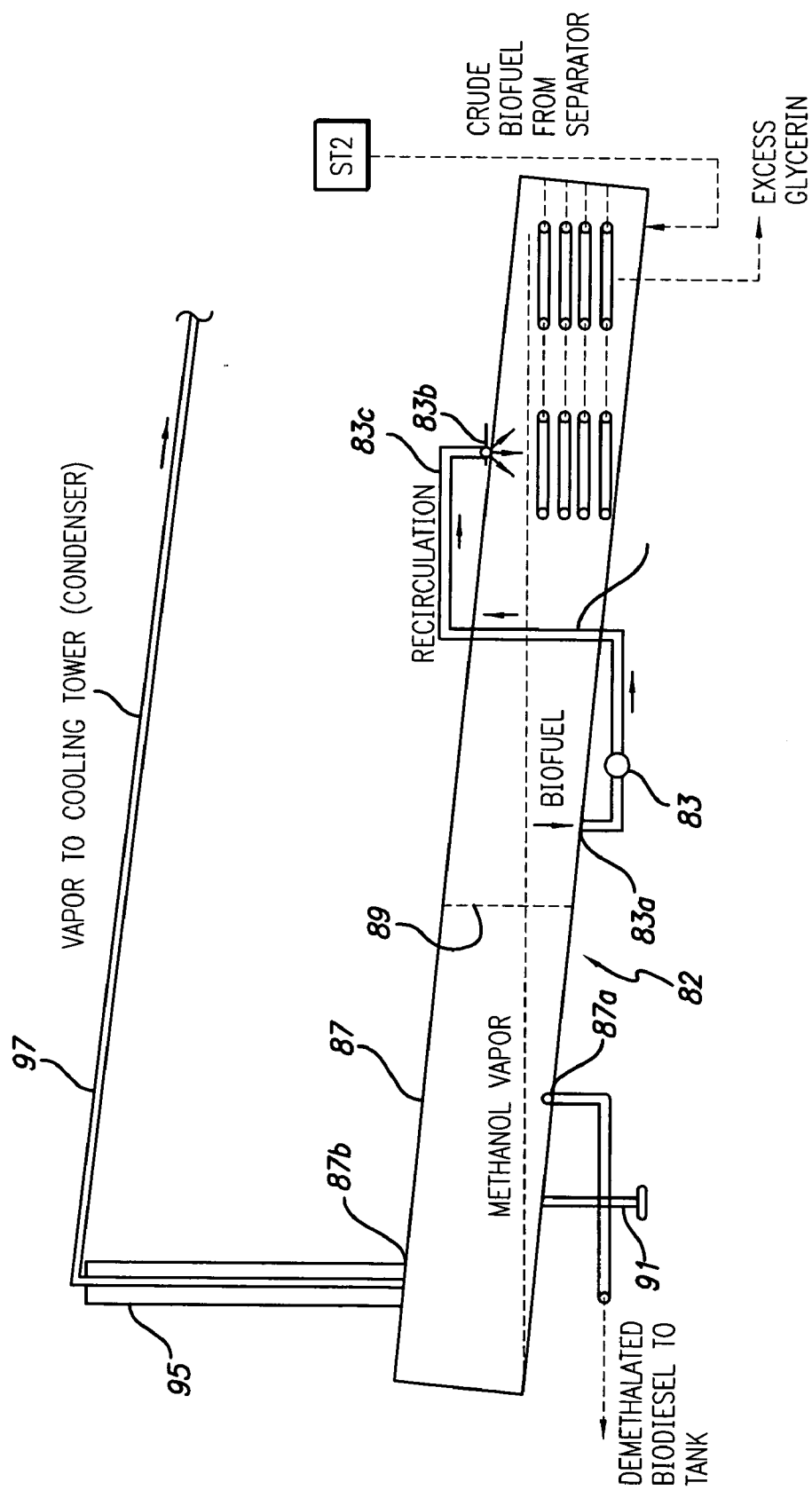


FIG. 4A

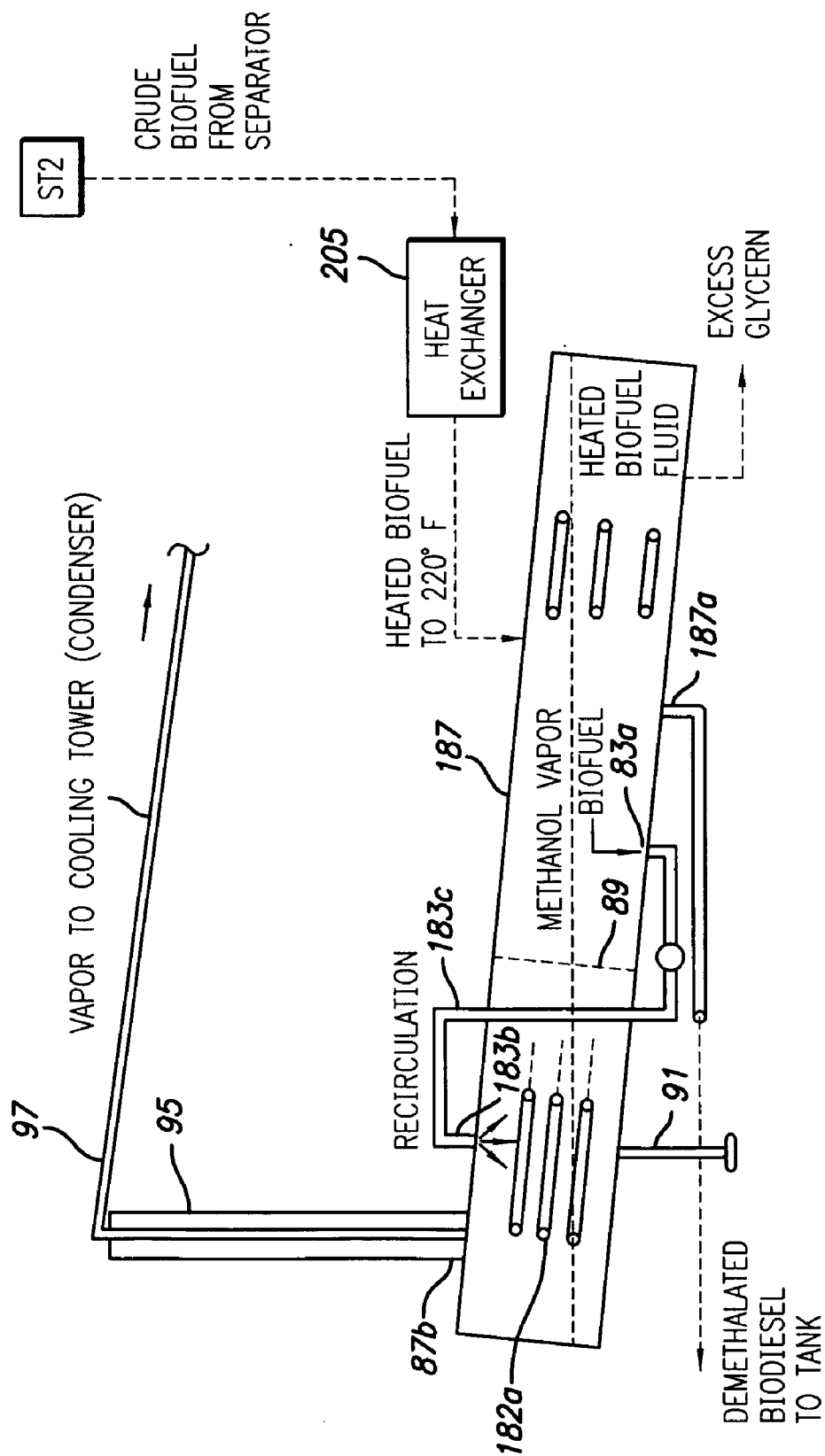


FIG. 5

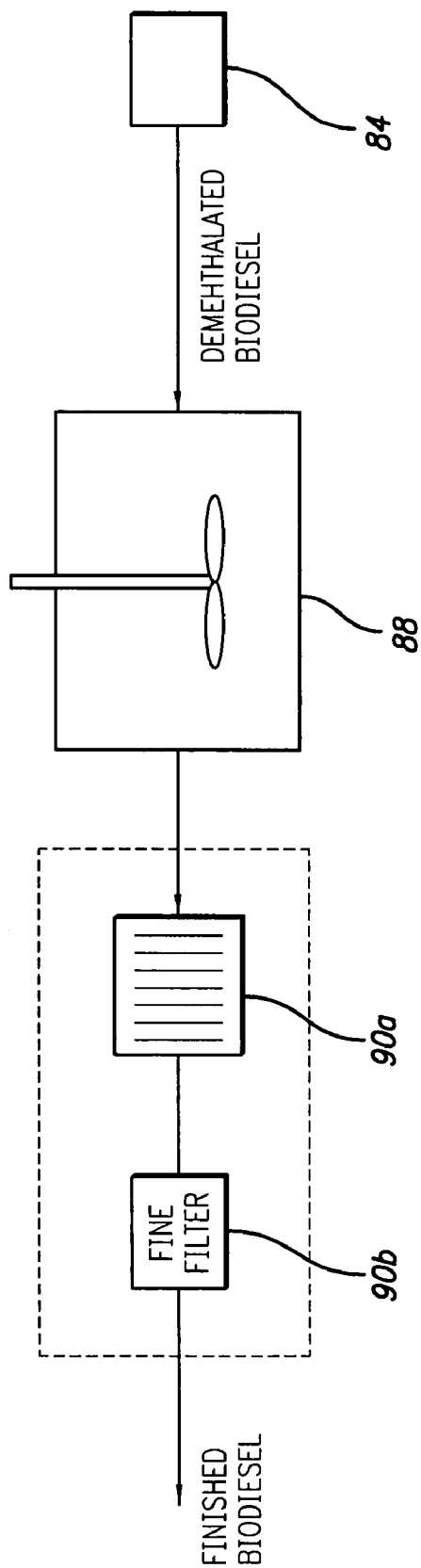
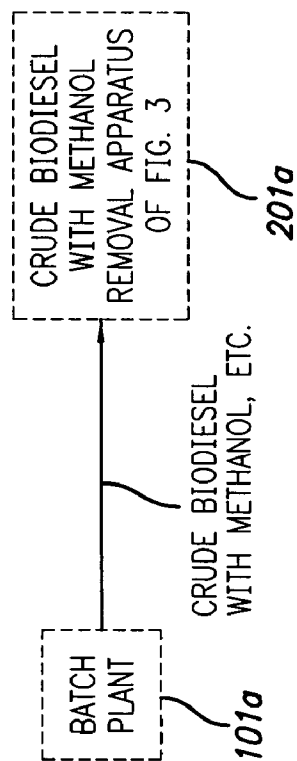


FIG. 8







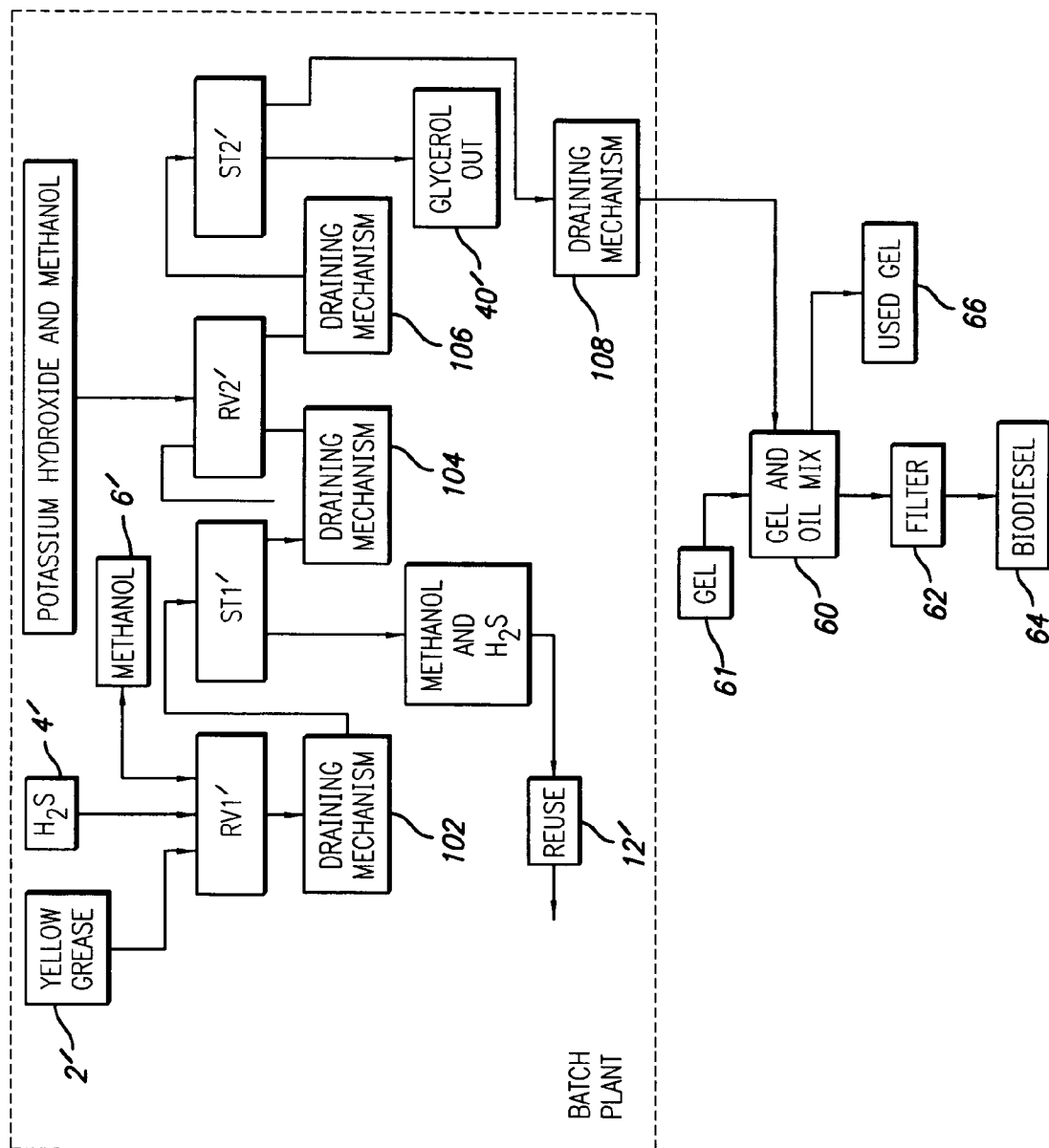


FIG. 7

## SYSTEM FOR REMOVAL OF METHANOL FROM CRUDE BIODIESEL FUEL

### CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims priority under 35 U.S.C. § 119(e) from U.S. Provisional Patent Application No. 60/540,751 filed Jan. 31, 2004, incorporated by reference herein.

### BACKGROUND OF THE INVENTION

[0002] The present invention relates to a system for removal of methanol and other substances from crude biodiesel fuel.

### SUMMARY OF THE INVENTION

[0003] In a process of making biodiesel fuel from soy bean oil, yellow grease or other raw material containing fatty acid esters, generally the raw material is processed with about ten percent methanol and about one percent potassium hydroxide or sodium hydroxide.

[0004] In U.S. patent application Ser. No. 10/235,065, filed Sep. 4, 2002, in the name of the present inventor (referred to herein as "Continuous Flow Application"), and incorporated by reference herein, there is disclosed a continuous flow process for forming biodiesel from yellow grease, vegetable oil, soy bean oil, or other raw material having fatty acid esters. The Continuous Flow Application also contains a description of the conventional batch process.

[0005] In either the continuous or batch process, or any other process for making biodiesel, the raw material is processed with methanol and preferably with a catalyst such as sulfuric acid ( $H_2S$ ) in a reaction vessel, such as RV1 shown in the attached FIG. 1. FIG. 1 is a schematic diagram of a biodiesel plant in accordance with the Continuous Flow Application.

[0006] The methanol reacts with the fatty acid in the oil and produces a methyl ester material. Then, the methyl ester material (treated raw material) is sent to a settling tank ST1 where the sulfuric acid, methanol and water can be removed by gravity separation, settle to the bottom and may be drained, refined and reused. The treated raw material is then reheated in a batch process, or kept heated in a continuous process, and mixed in a second reaction vessel RV2 with more methanol, and also with a catalyst, such as potassium hydroxide (KOH) or sodium hydroxide (NaOH). A reaction known as esterification takes place, creating a mixture of raw or crude biodiesel fuel, and excess methanol, and catalyst. This mixture is sent to a second settling tank ST2. In that tank, the crude biodiesel fuel rises to the top, while the methanol, glycerol and some fatty acid soap sink to the bottom of the tank.

[0007] To minimize the amount of soap, excessive methanol is typically used. That is, more methanol is used than is necessary to react with the amount of raw material. It is desirable to recover this methanol. Moreover, it is desirable to remove any entrained methanol and any other unreacted substances from the crude biodiesel. This is done conventionally by mixing the crude biodiesel with water at mixer 51, then separating out the water having methanol and glycerol from the biodiesel at separator 52 (e.g., a centrifuge or a separator tank).

[0008] In this water rinse and dry cycle, the water attracts excess methanol and glycerol. Therefore, the biodiesel (oil) comes out with "impurities" removed or minimized, and water with entrained methanol and glycerol 42 also comes out of the rinse/dry process. The rinse/dry process may be performed multiple times, typically two to four times, on the biodiesel (oil), each time producing more contaminated water.

[0009] Water with methanol is not easily disposable, since the methanol therein makes the water contaminated, i.e., a hazardous material, e.g., under EPA standards. The contaminated water can be boiled and condensed (distilled) to remove the methanol. This distillation process is expensive, because of the relatively high amount of methanol and the large amount of water.

### BRIEF DESCRIPTION OF THE DRAWINGS

[0010] FIG. 1 is a schematic diagram of a biodiesel plant in accordance with a continuous flow process, one type of process to which the system of the present invention may be applied;

[0011] FIG. 2 is a view similar to FIG. 1 showing a modification of the plant in accordance with a first embodiment of the invention;

[0012] FIG. 3 is a view similar to FIG. 2 showing a modification of the plant in accordance with a second embodiment of the invention;

[0013] FIG. 4 is a partial schematic view of a condenser and related equipment in the embodiment of FIG. 3;

[0014] FIG. 4A is a partial schematic view of a condenser and related equipment similar to FIG. 4 with modifications;

[0015] FIG. 5 is a schematic view of a mixing tank and related equipment in the embodiment of FIG. 3;

[0016] FIG. 6 is a schematic view of an overall biodiesel plant structure in accordance with a third embodiment of the invention;

[0017] FIG. 7 is a schematic view of a batch process plant having crude biodiesel, methanol and other impurity separation structure similar to that of the first embodiment of the invention; and

[0018] FIG. 8 is a schematic view of a batch process plant having crude biodiesel, methanol and other impurity separation structure similar to that of the second embodiment.

### DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

[0019] With reference to FIG. 1, it has been proposed to use a methanol removing substance in place of the water rinse (separator 52) to remove methanol from the biodiesel, e.g., a silicone based gel adsorbent of a type explained below, previously used to reclaim oils in the food industry. FIG. 2 shows such an arrangement. After settling in ST2, crude biodiesel with entrained impurities including methanol and glycerol (glycerin) leaves the crude biodiesel portion 101 of the plant and enters the crude biodiesel with methanol separation portion 201 of the plant. Specifically, the crude biodiesel with methanol and other impurities enters a tank 60 where it mixes and reacts with silicone gel 61. The biodiesel fuel, after about ten to fifteen minutes or more, is

then passed through a filter **62** and is finished biodiesel **64** ready for use. It may then be cleaned, stored, shipped, or otherwise handled, as is conventional.

[0020] The present inventor has experimented with such silicone based gel, and found that this process removes methanol and glycerol. However, in doing so, a relatively large amount of gel must be used, making the process relatively expensive.

[0021] As explained above, after settlement in tank **ST2**, the crude biodiesel still has some methanol entrained in it. It is better to err on the side of too much methanol in the crude biodiesel portion **10'**, rather than too little, because if there is too little the process makes a lot of soap. Generally, two to four percent methanol is entrained in the biodiesel. The methanol is relatively valuable, and can be reused in the transesterification process. To meet ASTM standards, currently D6751, the biodiesel is conventionally processed by vacuum distillation, which is very expensive and in some cases may still not be sufficient to meet the standards.

[0022] More specifically, the conventional process of removing methanol from crude biodiesel is to perform wash and dry cycles as explained above and further explained below.

[0023] The crude biodiesel is mixed with ten to thirty percent water which has an affinity for the trapped methanol. The water grabs the methanol and any glycerin (which is a small amount). Then, the water with the methanol (and any glycerin) is separated from the biodiesel, e.g., by centrifuge or gravity separation. Alternatively, separation of the biodiesel is achieved by putting the biodiesel and water in a settling tank to sit for several hours or more. The water with methanol and glycerin dropout from the biodiesel, which goes to the top.

[0024] Typically, two or four cycles of this process are performed. To remove the methanol (and glycerin and sometimes other by products) from the water, a large and complex condensing system must be used. The water cannot be disposed of without a special permit, because the water is contaminated.

[0025] The biodiesel also still has entrained water, so it must still be heated and run through a vacuum evaporator to get rid of the remaining water.

[0026] Use of water washing and a vacuum "flash" evaporator ("falling film vacuum flash evaporator") is very expensive, yet it is still industry standard.

[0027] In accordance with a preferred embodiment of the present invention as shown in **FIG. 3**, the crude biodiesel (formed at the separator **ST2**) is sent to crude biodiesel with methanol removal apparatus **201a** which starts with a heat exchanger **82** which boils off the entrained methanol. With reference to **FIGS. 3 and 4**, crude biodiesel is heated in the exchanger to at or about 240° F. or more, e.g., most preferably about 240° F. to about 280° F., well above the boiling point of 149° F. (at one atmosphere) of methanol alone.

[0028] At this high temperature, the methanol evaporates and is sent to a condenser **85**, and may then be reused (at **12a**). In the heat exchanger, the crude biodiesel is preferably heated by numerous pipes **82a**, and is re-circulated from an outlet **83a** via a pump **83**. The biodiesel is sprayed on to any

exposed heated pipes **82a** by a spray nozzle **83b** after traveling through recirculation pipe **83c**. The heated fluid in the pipes is preferably at about 250° F. or higher, i.e., at least a temperature high enough to boil methanol from crude biodiesel. This temperature is well above the normal methanol boiling point of about 149° F.

[0029] Remaining liquid is continuously re-circulated, preferably by a high volume pump at about eight to about ten times the speed that the crude biodiesel is entering the heat exchanger. The heat exchanger is preferably an elongated tank, and preferably is set at an angle, such as shown in **FIG. 4**. The angle is selected to maintain most of the biodiesel near the bottom end so it has sufficient residence time to be heated by the pipes located at and near the low end.

[0030] In addition, the outlet **83a** is roughly about half way or so up the tank. This helps ensure that the biodiesel will have sufficient residence time in the tank, and be sprayed over and over again onto the heated pipes. A partition **89** placed above the pump has apertures to allow methanol vapor to pass, and to slowly allow liquid biodiesel to pass, and also to help ensure sufficient residence time in the tank.

[0031] It is important to note that while one could remove a lot or perhaps all or virtually all of methanol using the heat exchanger, a more preferred embodiment of the invention allows the biodiesel to exit the tank at outlet **87a** with a small amount of methanol still in it, e.g., less than one percent or other small percent of the entrained methanol.

[0032] The methanol vapor passes through an outlet **87b** condensed by being sent through a tube or pipe to a condenser. Any entrained glycerin, liberated by the heating, falls to the bottom and may be drained, e.g., periodically.

[0033] The demethalated biodiesel **84** is sent to a tank **88** (**FIGS. 3 and 5**) for mixing with a methanol-removing substance, preferably, a magnesium silicate adsorbent, e.g., 2 MgO.65:02 nH<sub>2</sub>O (CAS Number 1343-88-0), referred to above as gel (although it can be in powder form). Suitable compounds, often synthetics, are available commercially, such as Magnesol® (e.g., R60) sold by The Dallas Group in Indianapolis, Ind.

[0034] The adsorbent is mixed with the biodiesel. After a period of time, e.g., about ten to fifteen minutes, is passed through a filter **90** (**FIG. 3**) such as a plate filter **90a**, e.g. a star filter press, and a fine filter **90b** (e.g., about two microns) producing finished biodiesel fuel. While the gel (adsorbent) could be used on crude biodiesel without the heating and condensing of the crude biodiesel to boil off some methanol, the gel might have to be used in a relatively large amount of anywhere from about one to four weight percent of the crude biodiesel. By contrast, by first boiling off some methanol, the gel need only be used in an amount of less than one weight percent, e.g., at or about 0.4 to at or about 0.8 weight percent, or even less, where the biodiesel is at a temperature of at or about 150° F. to 200° F.

[0035] Another overall view of the biodiesel plant process is shown in **FIG. 6**, which is preferably for use of soy bean oil as raw material. If yellow grease is used, an additional stage of treatment with H<sub>2</sub>S and methanol may be provided before entering the reactor where the soybean oil is shown entering.

[0036] Heat exchanger 82 may be a conventional heat exchanger raised at one end and modified as shown in the drawings and described herein, including the angle, which need only be relatively small. For example, stand 91 as shown in FIG. 4 need only raise one end about three feet for a thirty four foot long tank 87. A larger or smaller height will also work, but preferably the height that one end is raised is about the same as the diameter of the tank.

[0037] With this angle, the heat exchanger with separator 89 is filled about one half way with liquid biodiesel and is used herein as a methanol (vapor) extractor. The low end of the tank 87 allows glycerin to collect there (due to its high specific weight relative to the biodiesel). The glycerin thus can be periodically removed as needed.

[0038] The high volume pump circulating and re-circulating the biodiesel fluid serves to mix the fluid and help ensure residence time and thereby sufficient heating. In addition, the spray onto exposed pipes of the heated pipes greatly increases the heating effect and thereby increases the speed of methanol removal.

[0039] The partition upstream from the recirculation outlet and pump enable a partial separation of new biodiesel fluid entering the heat exchanger from the demethalated biodiesel exiting the tank at outlet 87a, deterring mixing and increasing residence time.

[0040] The angling of the vapor tube down to the cooling tower (condenser) enables condensing to start in the tube, as liquid will flow down the tube to the cooling tower. Accordingly, extending the vertical portion of the vapor recovery tube from the vapor outlet 87b of the tank, e.g., about eight or nine feet, provides height for the inclined portion to go down into the cooling tower. To prevent or minimize condensing in the vertical portion, insulation 95 may be used on tube 97.

[0041] FIG. 4a shows a similar structure as FIG. 4 where like reference numerals have been given like numbers, as throughout the drawings. One important variation is that a heat exchanger 205 is added to preheat the crude biodiesel with impurities. This preheating is preferably above 140° F. and may be as much as 220° F. or more. At 220° F., the methanol and glycerin are separated out very quickly, e.g., about seven minutes. The other changes to the structure of FIG. 4 as shown in FIG. 4A mainly concern the positioning of the elements having a corresponding number to FIG. 4 but with one hundred added to it.

[0042] In tank 187, heat exchanger pipes 182a are provided at both the low and high ends of the tank. Recirculation pipe 183c sprays biofuel on the pipes at the high end at nozzle 183b. Demethalated biodiesel is taken at the outlet 187a.

[0043] The present inventor has also found that the esterification reaction creating the crude biodiesel which rises to the top of the reactor RV2, and the glycerin by product which falls to the bottom of RV2 may be sped up by heating RV2 well above the conventional 110° F. In the past, in the batch process, this reaction took several hours at 110° F.

[0044] In the process of the continuous flow Application, whether by batch or continuous flow, the reaction in RV2 takes about one to two hours at 140° F. to 145° F. It has also been found that this process can be accelerated even more,

to only about eighteen minutes, if heated well above 140° F., e.g., from at or about 156° F. to at or about 158° F. Because methanol boils at 149° F., raising the temperature to 140° F. and certainly to 156° F. or more can cause substantial methanol loss. That is extremely undesirable because methanol is a health hazard, and also potentially explosive. If a sealed top is placed on the tank, the pressure build up may be considerable. Therefore, in accordance with another aspect of the invention, the inventor places a condensing coil at the top of the tank, which is connected to a vacuum pump and scrubber. The vacuum pump maintains a slight negative pressure at the top of the tank. Therefore, no methanol fumes can escape. A small amount of fresh air is allowed to enter into the top of the tank which is under negative pressure. Any methanol vapor will be sucked into the condensing coil at the top of the tank along with some fresh air. As the methanol vapors rises, it condenses in the coils and becomes a liquid and returns as a liquid into the top of the reactor, and gets remixed with the incoming soy oil and methanol catalyst. Only very small amounts of methanol vapor will reach the scrubber.

[0045] The present inventor has also discovered that the gel attracts methanol first from impurities in the crude biodiesel. After all the methanol has been bonded to the gel, then the free gel attracts glycerin. After all the glycerin has been bonded to the gel, then the free gel attracts potassium (or sodium) hydroxide. By contrast, the biodiesel industry would likely teach that adding water at this stage would be undesirable, because it would form an emulsion.

[0046] Therefore, as shown in FIG. 2, a modification of this embodiment of the invention is to add water 61a to the gel and crude biodiesel mixture in the mixing tank 60. Preferably, the amount of water added is about one percent weight of the contents of tank 60. The result of adding water is that methanol, glycerin and potassium (or sodium) hydroxide are attracted to the water at the same time, and the gel then attracts the water with the methanol, glycerin and potassium (or sodium) hydroxide. For example, the water and gel are added to the tank 60, and then the contents are mixed, e.g., for ten minutes.

[0047] When the water is used, the amount of gel used may be reduced from the amount needed without water, to reach the same level of impurity removal. Therefore, the amount of gel may be reduced below 0.4 to 0.8 weight percent, i.e., below 0.4 weight percent.

[0048] It is noted that the gel will also attract some biodiesel. This biodiesel could be reclaimed, but normally the amount is negligible.

[0049] FIG. 7 shows a biodiesel plant which is a batch process plant. Yellow grease 2', sulfuric acid 4', and methanol 6' are added to a first reaction vessel RV1'. The resultant liquid is drained at draining mechanism 103 after several hours. They are drained first and may be reused at unit 12'. The remaining mixture may be drained at mechanism 104 and added to reaction vessel RV2' along with potassium (or sodium) hydroxide and methanol. After several hours the contents are drained by draining mechanism 106 and added to second settlement tank ST2'. After several hours glycerol 40' is drained out, followed by removing the crude biodiesel with methanol and other impurities at mechanism 108. The remainder of the structure is the same as section 201 of FIG. 2.

[0050] In FIG. 8, batch plant 101 is followed by sending the crude biodiesel to section 201a, which is the same as unit 201a of FIG. 3.

[0051] Due to the fast reaction, glycerin accumulates quickly at the bottom of the reactor tank and/or separator tank. Accordingly, the height of these tanks may be increased to help pressure push the glycerin out of the bottom of RV2 and/or ST2.

[0052] Although the invention has been described using specific terms, devices, and/or methods, such description is for illustrative purposes of the preferred embodiment(s) only. Changes may be made to the preferred embodiment(s) by those of ordinary skill in the art without departing from the scope of the present invention, which is set forth in the following claims. In addition, it should be understood that aspects of the preferred embodiment(s) generally may be interchanged in whole or in part.

What is claimed is:

1. A method of removing methanol and other substances from crude biodiesel, the method including a step of mixing the crude biodiesel with a silicone based adsorbent.

2. The method of claim 1, wherein the silicone based adsorbent comprises a magnesium silicate adsorbent.

3. The method of claim 2, wherein the magnesium silicate adsorbent has the formula  $2 \text{MgO} \cdot 65.02 \text{ nH}_2\text{O}$ .

4. The method of claim 1, further comprising a step of filtering the crude biodiesel and adsorbent to separate the biodiesel from the adsorbent mixed with methanol and other substances.

5. The method of claim 1, wherein the amount of adsorbent mixed with the crude biodiesel is no more than one weight percent.

6. The method of claim 1, wherein the amount of adsorbent mixed with the crude biodiesel is 0.4 to 0.8 weight percent.

7. The method of claim 1, further comprising a step of adding water to the crude biodiesel in addition to the adsorbent.

8. The method of claim 7, wherein the amount of water is about one weight percent.

9. A method of forming crude biodiesel by a process including the steps of adding methanol to a reaction vessel where esterification takes place, and heating the reaction vessel to at least about 140° F, sealing the top of the vessel, placing a condensing coil outside of the vessel and in

communication with an upper portion of the vessel containing methanol vapor, for condensing methanol which escapes from the vessel in the condensing coil.

10. The method of claim 9, wherein a negative pressure is applied to the coil for creating a negative pressure at the top of the vessel, and air is allowed into the top of the vessel.

11. The method of claim 7, wherein the amount of adsorbent is less than 0.4 weight percent.

12. The method of claim 1, wherein the crude biodiesel is formed by a continuous flow process.

13. The method of claim 1, wherein the crude biodiesel is formed by a batch process.

14. The method of claim 1, wherein there is a step of heating the crude biodiesel before mixing in the adsorbent to demethanolate the crude biodiesel.

15. The method of claim 1, wherein in the step of removing methanol, glycerin and one of potassium and sodium hydroxide are removed.

16. A plant for making biodiesel fuel, the plant comprising:

a first section for making crude biodiesel fuel having methanol therein, and a second section for removing the methanol from the crude biodiesel,

the second section comprising a tank for mixing the crude biodiesel and a silicone based adsorbent for the methanol, and a filter for filtering the adsorbent mixed with methanol from the crude biodiesel thereby producing purer biodiesel.

17. The plant of claim 16, wherein there is a means for heating the crude biodiesel to demethanolate it prior to the tank.

18. The plant of claim 17, wherein the means for demethanulating comprises, a chamber disposed at an angle, the chamber comprising means for heating the crude biodiesel fuel proximate a low end of the chamber to create methanol vapor, and having means for condensing methanol vapor, and means for removing the biodiesel, both proximate a high end of the chamber.

19. The plant of claim 18, further comprising means for removing glycerin proximate a low end of the chamber.

20. The plant of claim 18, further comprising means for recirculating biodiesel from above a low end of the chamber back to the low end of the chamber to the means for heating.

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