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# (54) METHOD OF DISSOLVING A GASEOUS HYDROCARBON INTO A LIQUID HYDROCARBON

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#### **Related U.S. Application Data**

(63) Continuation of application No. 12/185,677, filed on Aug. 4, 2008, which is a continuation of application No. 10/973,007, filed on Oct. 25, 2004, now abandoned. (60) Provisional application No. 60/514,392, filed on Oct. 24, 2003.

# **Publication Classification**

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# (57) **ABSTRACT**

The present invention is directed to a method of dissolving a gaseous hydrocarbon into a liquid hydrocarbon to re-circulate gaseous components, which have separated from the liquid fuel mixture, back into the liquid fuel mixture, as well as, a method for making batch or continuous process amounts of mixed hydrocarbon fuels. The mixed hydrocarbon fuel is produced by introducing a volume of a liquid hydrocarbon into a vessel, and introducing a volume of a gaseous hydrocarbon into the liquid hydrocarbon at a gravitational low point of the vessel such that the bubbled gaseous hydrocarbon is dissolved into the liquid hydrocarbon to produce a liquid fuel solution. The vessel may be a mixing tank from which the liquid fuel is pumped into a vehicle fuel tank, or the vessel may be the vehicle fuel tank.













# METHOD OF DISSOLVING A GASEOUS HYDROCARBON INTO A LIQUID HYDROCARBON

# CROSS-REFERENCE TO RELATED APPLICATIONS

**[0001]** This application is a continuation of U.S. Ser. No. 12/185,677 filed on Aug. 4, 2008, which is a continuation of the U.S. Ser. No. 10/973,007 filed on Oct. 25, 2004, which claims the benefit of U.S. Provisional Application No. 60/514,392, filed Oct. 24, 2003. The entire contents of each application is hereby expressly incorporated herein by reference.

#### BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

**[0003]** The present invention relates generally to methods of producing liquid fuel solutions, and more particularly, but not by way of limitation, to an improved method of dissolving a gaseous hydrocarbon into a liquid hydrocarbon to produce a liquid fuel mixture and to recirculate gaseous components, which have separated from the liquid fuel mixture, back into the liquid fuel mixture.

[0004] 2. Brief Description of the Related Art

**[0005]** Most hydrocarbon fuels are composed of multiple hydrocarbons with varying degrees of volatility. Even gasoline has a composite of several hydrocarbons that vary between refineries and between locations to account for cold or hot conditions, or differences in altitude. Current fuels may be stored and handled in liquid, liquid plus vapor, or vapor phases. The liquid phase of a liquid or liquid plus vapor mixture tends to stratify or separate out with increasingly heavier components migrating toward the bottom of the storage vessel when the fuel mixture remains stationary over an extended period of time.

[0006] Examples of common fuels that have liquid plus vapor components are commercial propane (LPG) and commercial liquid natural gas (LNG). Commercial propane contains propane, ethane, butanes, and other hydrocarbons in a liquid plus vapor form due to the pressure at which these compounds are stored and handled (about 150 psig). Commercial liquid natural gas contains mostly methane in liquid plus vapor phase, with five percent or more of various heavier hydrocarbons contained mostly in the liquid parts of the fuel stored at cryogenic conditions (about  $-200^{\circ}$  F.) in insulated tanks. Finally, commercial compressed natural gas (CNG) contains mostly methane with varying degrees of other compounds, such as nitrogen or carbon dioxide, and is completely gaseous, thus remaining fairly well mixed.

**[0007]** Liquid and liquid plus vapor fuels have higher energy densities (energy content per unit volume) than gaseous fuels. This allows the storage of a greater quantity of useful energy in the fuel tank of a vehicle. However, the more volatile compounds, which are the lighter compounds such as methane, will tend to slowly leave the liquid mixture as a gas primarily due to heat transfer into the fuel tank. If the fuel tank remains stationary for a long period of time, significant stratification of the liquid combined with the vapor leaving the liquid tends to result in the various liquid components to stratify with the heavier components migrating to the bottom of the tank and the lighter components migrating toward the top of the tank. This phenomena is commonly referred to as "weathering". Weathering occurs for all mixed hydrocarbon fuels with a liquid phase under certain thermodynamic conditions which are specific to the composition of the particular fuel mixture. The problems associated with weathering have generally been overcome by reprocessing the fuel. However, this requires significant handling of the fuel and thus significantly increases the production cost of the fuel.

**[0008]** To this end, a need exists for an improved method of dissolving a gaseous hydrocarbon into a liquid hydrocarbon to re-circulate gaseous components, which have separated from the liquid fuel mixture, back into the liquid fuel mixture, as well as, a method for making batch or continuous process amounts of mixed hydrocarbon fuels. It is to such methods that the present invention is directed.

# BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING

**[0009]** FIG. **1** is a cross-sectional view of a mixing and storage tank constructed in accordance with the present invention.

[0010] FIG. 2 is a cross-sectional view of a lower portion of a liquid inlet tube looking left to right horizontally in FIG. 1. [0011] FIG. 3 is a cross-sectional view of another embodiment of a mixing and storage tank constructed in accordance with the present invention.

**[0012]** FIG. **4** is a schematic flow diagram of a process for manufacturing a two-phase composite fuel within a vehicle storage tank.

**[0013]** FIG. **5** is a schematic flow diagram of another embodiment of a process for manufacturing a two-phase composite fuel.

**[0014]** FIGS. **6**A and **6**B are a block diagram of a control algorithm for use in the process of FIG. **5**.

### DETAILED DESCRIPTION OF THE INVENTION

[0015] It has been found that a fuel composed of an approximately 50/50 mass mixture of liquid petroleum gas (LPG) and compressed natural gas (CNG) offers a variety of advantages over other types of alternative fuels, such as vehicle mileage range while maintaining both economical and environmental superiority. The composite fuel has been shown to reduce some of the problems associated with the use of commercial compressed natural gas (CNG) or commercial liquid petroleum gas (LPG). For example, the fuel is stored at approximately half the pressure of CNG (approximately 1500 psig), but retains the high energy density of LPG. An example of a fuel composed of a 50/50 mass mixture of liquid petroleum gas (LPG) and compressed natural gas (CNG) is disclosed in U.S. Pat. Nos. 5,900,515 and 6,111,154 issued to Mallinson et al., each of which is hereby incorporated herein by reference. Preferably, the two phase fuel mixture comprises a gaseous methane and at least one other hydrocarbon and a mole percent of methane from about 50 percent to about 80 percent. The mixture of methane and the at least one other hydrocarbon maintained at a temperature of about -1° C. or greater and at a pressure of about 8.0 Mpa or greater. As mentioned above, due to the effects of weathering, problems are encountered when attempts are made to store composite fuels.

**[0016]** Referring now to the drawings, and more particularly to FIG. **1**, a vessel **10** for mixing and storing a two phase fuel composite, such as in a vehicle, in accordance with the present invention is illustrated. The vessel **10** is an example of a standard natural gas storage vessel having a single point of

entry. However, double ended tanks may also be used. The vessel 10 is provided with an inlet tube 12, a liquid outlet tube 14, and a vapor outlet tube 16. In a manner to be discussed in greater detail below, the composite fuel may either be mixed within the vessel 10 or mixed outside the vessel 10 and then conveyed to the vessel 10. In either case, the gaseous fuel component is first introduced into the vessel 10 via the inlet tube 12 to raise the pressure in the vessel 10 above the known vaporization pressure of the liquid fuel component. When the composite fuel is mixed outside the vessel 10, the composite fuel is introduced to the vessel 10.

[0017] When the composite fuel is mixed in the vessel 10, the constituent fuel that is normally liquid at the lowest pressure is then introduced into the vessel 10 via the inlet tube 12. The more volatile, gaseous fuel component is next introduced into the vessel 10 via the inlet tube 12. The inlet tube 12 has a lower portion 18 positioned near the gravitational low point of the vessel 10. The gaseous fuel component is slowly added by bubbling the gaseous fuel component into the liquid fuel component. The bubbles are routed by the inlet tube 12 to the lowest gravitational point, and released downward through a series of openings 20 (FIG. 2) oriented at angles just off straight downward (5 to 45 degrees, depending on the downward velocity). This downward directional release of the bubbles ensures that a dead layer of heavier hydrocarbon does not become fixated in the tank (it is also possible to release the gas from the bottom wall upward, but the key is to avoid dead layers). The openings 20 of the inlet tube 12 should be sufficiently small (or pass to a device such as a porous block that does have sufficiently small orifices) to allow collapse of the bubbles rising from the inlet tube 12 over the available length of liquid height above the inlet tube 12.

**[0018]** The entire mixture is blended by bubbling until the pressure exists at a point sufficiently over the critical pressure for the mixture to overcome pressure losses that might occur in handling the mix. For example, a 50/50 molar percent mix of methane and propane would be mixed to about 1350 psig at standard temperature conditions; a projected ultimate pressure for the mix would be to exceed 1265 psig. All bubbles tend to collapse above the critical pressure, enforcing a uniform resultant mixture. The bubbling serves to avoid large deviation in additional heavy hydrocarbon by avoiding unmixed regions in the tank.

[0019] If the mixture may be fully utilized at above the critical pressure of the mixture, then the feed from the vessel 10 should be located at the lowest gravitational point on the vessel 10. If the contents of the vessel 10 involves only pressures below the critical pressure, then several extraction points may be needed. To this end, the extraction tube 14 is provided with a series of openings 22 extending along a portion of the extraction tube 14. The inlet tube 12 and the liquid outlet tube 14 may be combined, although this may restrict the process time and flow rate. Preferably, the extraction tube 14 extends to nearly touch the bottom of the vessel 10.

**[0020]** As the vessel **10** is emptied by extracting liquid, vapor will be produced in the handling process. Some vapor may be utilized to maintain the necessary pressure conditions in the vessel **10**. Additionally, vapor may be periodically captured by the vapor outlet tube **16** positioned at gravitationally high points in the vessel **10** and circulated back into the vessel **10** by bubbling the vapor into the liquid via the inlet

tube **12** to maintain a uniform composition. Alternatively, the captured vapor may be metered to a vehicle engine (not shown).

**[0021]** FIG. 3 illustrates another embodiment of a vessel 10a for mixing and storing a two phase composite fuel in accordance with the present invention. The vessel 10a is similar to the vessel 10 described above with the exception that the vessel 10a has a horizontal configuration as opposed to a vertical configuration. The vessel 10a is provided with an inlet tube 12a, and a liquid outlet tube 14a, and a vapor outlet tube 16a. The bubbles are routed by the inlet tube 12a to the lowest gravitational point, and released downward at angles just off straight downward (5 to 45 degrees, depending on the downward velocity). This downward directional release of the bubbles ensures that a dead layer of heavier hydrocarbon does not become fixated in the tank (it is also possible to release the gas from the bottom wall upward, but the key is to avoid dead layers).

**[0022]** The holes 20a of the inlet tube 12a direct flow downward and should be sufficiently small (or pass to a device such as a porous block that does have sufficiently small orifices) to allow collapse of the bubbles rising from that tube over the available length of liquid height above the inlet tube 12a.

**[0023]** As the vessel 10a is emptied by extracting liquid, vapor will be produced in the handling process. Some vapor may be utilized to maintain the necessary pressure conditions in the vessel 10a. This vapor may be captured by the vapor outlet tube 16a positioned at gravitationally high points in the vessel 10a. The captured vapor may then be fed back into the vessel 10a if captured at a high enough pressure or metered to a vehicle engine (not shown)if captured on board a vehicle at lower pressure.

[0024] FIG. 4 is a schematic illustration of a process of making a mixed composite fuel within a vehicle fuel tank, such as the vessels 10 and 10a described above, in accordance with the present invention. This process depends on the thermodynamic end state required relative to the mixed phase. The pressure associated with the usual state of individual constituents does not match the end state of the mixed fuel. To use the contents of vessels 10 or 10a fully down to lowest pressure, the volatile component of the mixture is first injected, if the tank/vessel pressure is lower than the thermodynamic vaporization point of the liquid constituent. Once the vaporization pressure of the liquid is reached, the constituent fuel that is normally liquid at the lowest pressure is first introduced into a sufficiently high pressure, vented vessel, such as the vessels 10 and 10a described above. The more volatile, gaseous fuel is next introduced at the gravitational low point of the vessel as described above. The more volatile fuel is usually stored at higher pressure than the final mixture, thus simple mixing of the gas into the liquid is possible. Positive compression is only needed if the gaseous component is at a pressure less than or equal to the final required state (target pressure). As the higher pressure, gaseous component is slowly added, the pressure is allowed to build up in the mixture, until the final pressure that is required is met. After manufacture of the mixture, re-circulation is then performed periodically to maintain a uniform composition using the concepts described above.

**[0025]** Again, in order to use the contents of vessels **10** or **10***a* fully down to lowest pressure, the volatile component of the mixture is first injected, if the tank/vessel pressure is lower than the thermodynamic vaporization point of the liquid constituent. Once the vaporization pressure of the liquid is

reached, the system then operates by first pumping LPG, such as propane, into the vessel **10** from a storage tank **30** via a liquid stream **32**. Once the desired amount of LPG is pumped into the vessel **10**, CNG is allowed to flow from a storage tank **34** into the vessel **10** via a gas stream **36** bubbling through the LPG that is already disposed in the vessel **10**. By these means, the fuel is formulated on board the vehicle. The desired amount varies depending on the size of the vessel **10**.

**[0026]** The storage tanks **30** and **34** are located at a fueling site and are constructed to be watertight to ensure maximum isolation. The storage tanks **30** and **34** are preferably enclosed in an insulated housing (not shown).

[0027] As shown in FIG. 4, the system includes a pump 38 and a compressor 39. The pump 38 is an 8 gpm Hydra-Cell D10 pump or other positive displacement pumping device similar to that shown and described in reference to FIG. 5, driven by an explosion proof motor 40. A pressure relief loop 41 is installed to protect against over pressurization of the pump 38. A fill line 42 is provided with a coupling 43 for connection with the vessel 10.

**[0028]** A controller (not shown) is used to monitor and control all functions of the system in a manner well known in the art. An example of a suitable controller is a Direct Logic 205 programmable logic computer (PLC). The controller monitors a pair of axial turbine flow meters **45** and **46** or other precision flow devices, such as coriolis flow meters, and controls two valves **47** and **48**, the pump **38**, a pressure switch **50**, and a pressure transducer **52**. The pressure switch **50** is used to indicate to the controller when the required pressure has been reached. The pressure transducer **52** is used to keep track of the pressure in the CNG storage tank **34** in order to maintain correct flow meter calibration. The storage tanks **30** and **34** should be electrically isolated, and all wiring enclosed in rigid conduit and sealed junction boxes.

**[0029]** It has been found that fueling times are greatly reduced when the pressure in the vessel **10** is low (e.g., <100 psig). The fueling time has been greatly reduced when this condition is present since the pump **38** functions as a transfer pump. Also, the methane and propane content of the mixture is greatly enhanced due to turbulent convection mass transfer produced by the fast bubbling of CNG into the propane. To improve the speed of propane delivering to the vessel **10**, the inlet downstream piping is preferably at least about 0.75 inches. The FIG. **4** process is termed a "bubble-on-board" process because the mixed fuel is processed onboard a vehicle. This processing method may be suitable for lost fuel handling for small captive vehicle fleets or where the constituent fuel compositions added to a vehicle are regulated.

[0030] FIG. 5 is a schematic illustration of a process for making and storing a mixed two-phase composite fuel for fueling of a vehicle storage tank constructed in accordance with the present invention. The process illustrated in FIG. 5 is termed a "fast-fill" process because the constituent components are premixed, allowing for faster transfer to a vehicle. The process also allows the filling of a vehicle that has any residual fuel onboard the vehicle, at any pressure within the design of the present invention. The process involves three primary steps: (1) pumping a liquid hydrocarbon, such as propane, from a storage tank 60 into a mixing tank 62, (2) passing a gaseous hydrocarbon, such as compressed natural gas, from a storage tank 64 into the mixing tank 62, and (3) pumping the composite fuel from the mixing tank 62 to a vehicle fuel tank 66. This is accomplished through a series of valves and sensors illustrated in FIG. 5. A secondary process is the identification of the contents of the vehicle tank to be filled, after sufficient inventory of mixed fuel is available.

[0031] Propane, which is stored in the storage tank 60 at approximately 150 psig, is conveyed from the propane storage tank 60 to the mixing tank 62 with a pump 70. A 3-way valve 72 positioned upstream of the pump 70 and a 3-way valve 74 positioned downstream of the pump 70 cooperate to direct the propane to the mixing tank 62 along a conduit 76. Upstream of the valve 72, the propane is passed through a filter 78 to remove debris and a flow meter 80.

[0032] The propane inlet of the mixing tank 62 is at the bottom of the mixing tank 62. The mixing tank 62 preferably is a tank that is rated for 5000 psig. The mixing tank 62 is provided with an open loop 82 connecting a top cap 84 with a bottom cap 86. Pressure equalizes the liquid level in the mixing tank 62 with the liquid level in the loop 82. A capacitive sensor 88 detects the liquid level of propane. The capacitive sensor 88 is mounted outside the loop 82 at the maximum height of propane needed to prepare the composite fuel. When the liquid level reaches the preselected height, the capacitive sensor 88 produces a signal which causes the valves 72 and 74 to close and operation of the pump 70 to be terminated. Subsequently, a 3-way valve 90 interposed in a conduit 92 opens permitting compressed natural gas (CNG) to pass from the gas storage tank 64 to the mixing tank 62.

[0033] The CNG, which is stored in the gas storage tank 64 at about 3000 psig, flows by regulated pressure (above the critical pressure as described earlier) into the mixing tank 62. The 3-way valve 90 controls the flow of the CNG between a pre-filling conduit 94 and a mixing tank conduit 96. The pre-filling conduit 94 permits the vehicle fuel tank 66 to be pre-filled with CNG before filling the vehicle fuel tank 66 with the composite fuel to avoid flash vaporization. The mixing tank conduit 96 is connected to the top of the mixing tank 62 and is the bubbling line for manufacturing the composite fuel. The mixing tank conduit 96 extends into the mixing tank 62 and down to near the gravitational low point of the mixing tank 62 for bubbling purposes in a manner similar to that described above in relation to the vessel 10. The CNG is passed through a flow meter 98 and bubbled into the mixing tank 62 until it reaches a pressure above 1265 psig, at which time a pressure transducer 100 produces a signal to close the valve 90 and thus terminate the flow of gas from the CNG storage tank. The composite fuel in the mixing tank 62 is now ready to be transferred to the vehicle fuel tank 66.

[0034] The vehicle fuel tank 66, when empty, has a much lower pressure than the mixing tank 62. Therefore, to avoid flashing, the vehicle fuel tank 66 is preferably pre-filled with CNG to a pressure near 1000 psig via the pre-filling conduit 94. A pressure transducer 101 located at the end of the pre-filling conduit 94 produces a signal to start and stop the pre-filling process.

[0035] With the vehicle fuel tank 66 pre-filled with CNG, the pump 70 is actuated and the valves 72 and 74 are operated to cause the composite fuel to pass from the mixing tank 62 via the conduit 76. The composite fuel then travels through a conduit 102, the valve 72, the pump 70, the valve 74, and a conduit 104 and into the vehicle fuel tank 66. A flow meter 106 measures the liquid volume of composite fuel delivered to the vehicle fuel tank 66. When the fuel capacity of the vehicle fuel tank 66 is reached, a capacitive sensor 108 produces a signal to stop the pump 70 and to close the valves 72 and 74.

[0036] For safety purposes, the process preferably includes a venting loop 110 to prevent overfilling of the vehicle fuel tank 66. The venting loop 110 includes a vapor extraction conduit 112 connectable to the vehicle fuel tank 66 for capturing vapor and transferring the captured vapor into a recycle tank 114. The capacitive sensor 108 detects when the vehicle fuel tank 66 is full and overflows into the conduit 112 to the recycle tank 114. The capacitive sensor 108 produces a signal to terminate the pump 70 and to close a valve 116 interposed in the conduit 112. The collected vapor in the recycle tank 114 may then be compressed and bubbled back into the mixing tank 62 via a conduit 118. a valve 119 is interposed in the conduit 118 to control the flow of the vapor. Knowing the target conditions of the thermodynamic mixture (pressure/ temperature, which are unique at this design point), this constitutes the secondary sensing to reliably fill a partially full vehicle tank with a nominal 50/50 molar mix of the composite fuel.

[0037] The mixing tank 62 should be rated for at least 3000 psi. meeting appropriate federal and state standards. The mixing tank 62 might either be U-Stamped for 3000 psi, meet AMSE code for 3000 psi, or be made of rated composite designed to the appropriate standard. The dimensions of the mixing tank 62 may be, by way of example, a length of about 74 inches, an outer diameter of about 16 inches, and a volume of about 30 US gallons (water volume). The mixing tank 62 is preferably a double ended tank.

[0038] The pump 70 is preferably a hydraulic piston pump powered by a hydraulic power assembly 120 and consists of a hydraulic cylinder 122 and a pump cylinder 124. A suitable pump is commercially available from Parker Hannifin Corporation with the hydraulic cylinder 122 being model no. 2.5 inches CJB2HKTV34AC10 (Parker or equivalent) and the being model no. pump cylinder 3.25 inch JB2HKTV14A101/2 (Parker or equivalent). The example hydraulic cylinder has a 2.50 inch bore, a cushioned head and cap, and a 10 inch stroke. The pump cylinder has a 3.25 inch bore and 10.5 inch stroke. The pump operates using proximity sensors to signal when the cylinders should change direction. In production, larger cylinders and steam/water/hydraulics/ electrics or other driven engines might power the pumping process.

**[0039]** The valves and pump described herein are preferably controlled with a programmable logic controller. Control valves and controllers constructed to operate in the manner described herein are well known in the art. Thus, a detailed description of such components is not believed necessary to enable one skilled in the art to understand the operation of the system of the present invention. An example of a suitable controller is a Direct Logic 205 with a CPU 240 made by Koyo.

[0040] FIG. 6 shows a control algorithm for the process shown in FIG. 5. The control algorithm is written using ladder programming RLL Plus. The program is composed of three main stages: filling propane into the mixing tank 62, injecting CNG into the mixing tank 62 to a pressure of 1500 psi, and transferring the mixture into the vehicle fuel tank.

**[0041]** From the above description it is clear that the present invention is well adapted to carry out the objects and to attain

the advantages mentioned herein as well as those inherent in the invention. While presently preferred embodiments of the invention have been described for purposes of this disclosure, it will be understood that numerous changes may be made which will readily suggest themselves to those skilled in the art and which are accomplished within the spirit of the invention disclosed and as defined in the appended claims.

What is claimed is:

1. A method of mixing a two phase fuel mixture comprising a vapor component and a liquid component in a vessel to reduce stratification of the fuel mixture, the method comprising:

- providing the two phase fuel mixture in the vessel, the two phase fuel mixture comprising a gaseous methane and at least one other hydrocarbon and a mole percent of methane from about 50 percent to about 80 percent, the mixture of methane and the at least one other hydrocarbon maintained at a temperature of about  $-1^{\circ}$  C. or greater and at a pressure of about 8.0 Mpa or greater
- withdrawing at least a portion of the vapor component of the mixture from the vessel; and
- re-introducing the withdrawn vapor component into the vessel by bubbling the withdrawn vapor component into the liquid component of the fuel mixture at a gravitational low point of the vessel such that the bubbled vapor component is dissolved into the liquid component and the fuel mixture is sufficiently agitated to effectively mix the two phase fuel mixture.

**2**. The method of claim **1** wherein the vapor component is bubbled into the liquid component of the fuel mixture at a downward angle of from about 5 degrees to about 45 degrees relative to a vertical axis of the vessel.

**3**. A method of mixing a two phase fuel mixture comprising a vapor component and a liquid component in a vessel to reduce stratification of the fuel mixture, the method comprising the steps of:

- providing the two phase fuel mixture in the vessel, the two phase fuel mixture comprising a gaseous methane and at least one other hydrocarbon and a mole percent of methane from about 50 percent to about 80 percent, the mixture of methane and the at least one other hydrocarbon maintained at a temperature of about  $-1^{\circ}$  C. or greater and at a pressure of about 8.0 Mpa or greater
- withdrawing at least a portion of the vapor component of the mixture from the vessel; and
- re-introducing the withdrawn vapor component into the vessel by bubbling the withdrawn vapor component into the liquid component of the fuel mixture in a downward direction such that the bubbled vapor component is dissolved into the liquid component and the fuel mixture is sufficiently agitated to effectively mix the two phase fuel mixture.

**4**. The method of claim **3** wherein the vapor component is bubbled into the liquid component of the fuel mixture at a downward angle of from about 5 degrees to about 45 degrees relative to a vertical axis of the vessel.

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