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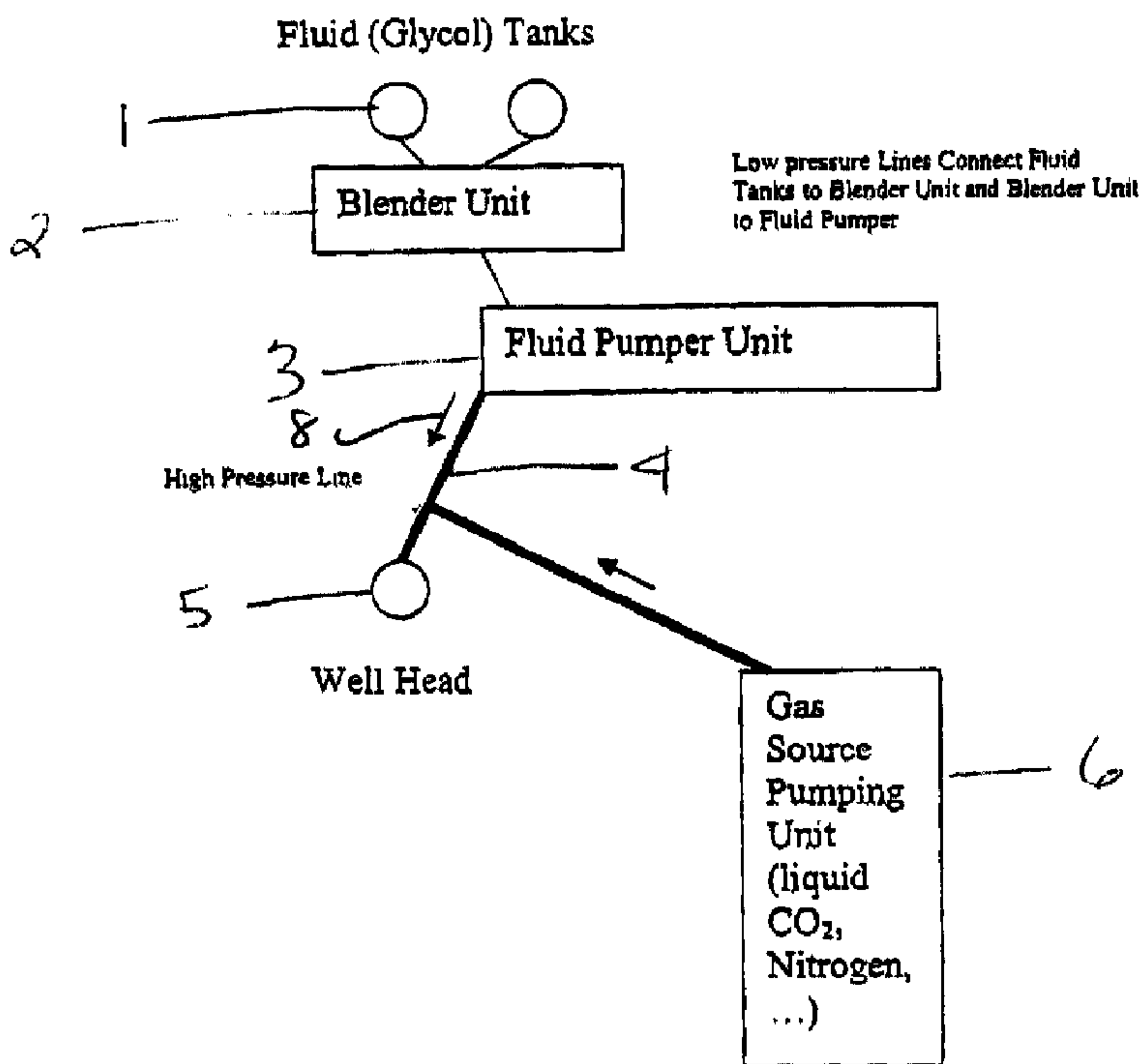
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(54) Title: WELL STIMULATION FLUID AND WELL STIMULATION FLUID RECYCLING PROCESS

**Surface Equipment Rig Up for Glycol Fluid System  
Fracture Treatment**



(57) Abrégé/Abstract:

A glycol-based well stimulation fluid and a process for recycling a glycol-based well stimulation fluid, comprising the steps of filtration and heating.

**ABSTRACT**

A glycol-based well stimulation fluid and a process for recycling a glycol-based well stimulation fluid, comprising the steps of filtration and heating.

## WELL STIMULATION FLUID AND WELL STIMULATION FLUID RECYCLING PROCESS

### Field of the Invention

5 This invention relates to the field of oil and gas production, and more specifically to the improvement of the properties and/or performance of well stimulation fluids and the recycling and re-use of well stimulation fluids.

### Background of the Invention

10 Well stimulation is the treatment of a formation in order to restore or enhance the production of oil or gas. One commonly used method for enhancing productivity is to subject the formation to hydraulic fracturing. Typically, a fracturing fluid or well stimulation fluid is injected into the well at a rate sufficient to open a fracture in the exposed formation. Continued pumping of fluid into the well at a high rate extends the fracture.

15 The fluid may contain a propping agent, so that fluid injection leads to the build up of a bed of propping agent particles between the fracture walls. These particles prevent complete closure of the fracture as the fluid subsequently leaks off into the adjacent formations or is recovered back to the surface and results in a permeable channel extending from the well bore into the formation.

20 The fluids used in hydraulic fracturing operations must have fluid loss values sufficiently low to permit build up and maintenance of the required pressures at reasonable injection rates. This normally requires that such fluids either have adequate viscosities or other fluid loss control properties which will reduce leak-off from the fracture into the pores of the formation.

Oil and gas well stimulation fluids are used for a variety of reasons to increase the mobility of the reservoir fluid toward the wellbore. Acids are used for their reactivity with the hydrocarbon bearing formation to increase permeability by removing formation material. Solvents and other reactive agents are used to remove precipitates due to the production of reservoir fluids (asphaltines, waxes, scale). Methanol and other surface reactive agents (surfactants) are used to reduce problems associated with water blockage within the formation. Fracture stimulation employs a variety of fluids and gases individually or in combination to propagate an initiated fracture and as a medium to transport the proppants required to provide the permeability contrast to increase production rates from the reservoir to the wellbore. The ideal stimulation fluid would perform the functions required of it and then be recoverable with no residuals left in the reservoir.

The most common fracture fluid is water, due to its relatively low cost, safety and availability. Water however can be trapped within the reservoir rock to reduce permeability, thereby not providing a stimulation to the full potential. Surfactants can be added to the water to reduce its surface tension, but increase cost and safety concerns (flammability). Other chemicals are also used to enhance properties such as viscosity, but can also leave residuals. Water adds costs when used in cold weather as it requires heating to the 20 C range for optimum blending with chemical additives.

Hydrocarbons, crudes, reformates and diesels, are also used as fracture fluids but at higher cost of fluids and safety. Again chemicals can be added to enhance properties but have been seen to cause problems in downstream facilities such as refineries.

Gases and liquid gases such as nitrogen, liquid carbon dioxide, and propane have been used as energizers, fillers, and principle fluids for stimulations. Nitrogen is basically inert, and its properties as a gas provide a method to enhance stimulation fluid recovery due to its relatively low specific gravity. Liquid carbon dioxide works in the same manner, but is pumped as a liquid and is recovered as a gas. Liquid carbon dioxide also

acts as a solvent and surfactant. Liquid carbon dioxide has been used as a principle fluid and in combination with nitrogen as a filler, but requires specialty equipment to perform the operation. Liquid carbon monoxide and nitrogen are not flammable and therefore reduce the safety concerns but the gases are not recyclable. Propane has  
5 also been used for its solvent properties and as a principle fluid, but is a high safety risk.

Methanol is used as an additive, filler and as a principle fluid. Methanol works as a surfactant, reducing surface tension of water, and is fairly cost effective. It can be used to reduce the freezing temperature of a water solution and as a filler to reduce the amount of water used in an operational treatment. Methanol however increases safety  
10 concerns proportional to the concentrations used. Chemicals have been used to increase its viscosity, but methanol vaporizes at formation temperatures making the recovery of the chemicals very difficult.

Liquid CO<sub>2</sub> is used as a non damaging fully recoverable fracture fluid. Gaseous nitrogen has been added as a filler to help reduce the costs of the treatment. And a treatment  
15 was patented that used a chemical to foam the liquid CO<sub>2</sub> - nitrogen gas mixture. This process require specialty equipment and the fracture fluids are not recyclable.

As discussed above, one problem encountered in fracturing operations is the difficulty of total recovery of the well stimulation fluid. Fluids left in the reservoir rock as immobile residual fluids impede the flow of reservoir gas or fluids to the extent that the benefit of  
20 fracturing is decreased or even eliminated. The removal of the well stimulation fluid may require the expenditure of a large amount of energy and time, consequently the reduction or elimination of the problem of fluid recovery and residue removal is highly desirable.

25 One way of addressing this problem is to reduce the friction between the fluids and solids introduced into the well during drilling or subsequent treatment and the formation

fluids and solids. This has entailed the use of surfactants to reduce surface tension between, for example, liquid/liquid and liquid/solid interfaces.

Another problem is that even after the well stimulation fluid is recovered, it may not be easily and economically recyclable. The inability to reuse stimulation fluid increases treatment costs by necessitating the disposal of used fluid and the purchase of new fluid.

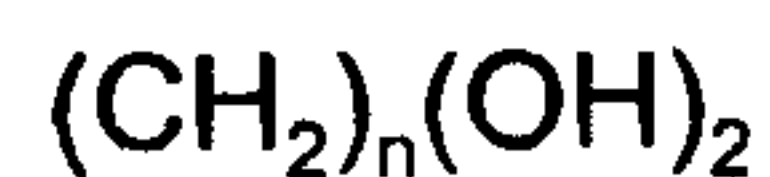
Well stimulation fluids are commonly water-based or oil-based, and often contain a range of additives such as surfactants, fillers, and proppants. The disadvantage of water as aforesaid is that it must be heated to 20°C, resulting in higher costs when drilling takes place under cold conditions. In addition, it is not always easily recovered. Also, as is well known, water is simply incompatible with certain formations and can cause swelling, particularly in the clays. Oil creates safety concerns, due to its flammability. Neither water-based fluids nor oil-based fluids are recyclable at a reasonable cost.

What is needed is a well stimulation fluid that is suitable for use under typical temperature ranges, has low flammability, is easily recovered from the formation, and is easily recycled for reuse at a reasonable cost.

A method for recycling the well stimulation fluid is also needed.

### **Summary of the Invention**

The present invention relates to a well stimulation fluid comprising glycol. The term "glycol" is used herein to refer to a dihydric alcohol in which two hydroxyl groups are bonded to different carbon atoms. The general formula takes the form:



Any glycol may be used in the fluids of the present invention. Generally, the larger the glycol molecule, the higher its viscosity. Larger glycol molecules also tend to be more costly.

The simplest glycol is ethylene glycol:



Ethylene glycol is commonly used as antifreeze in automobiles because of its relatively high boiling point (197 C), low freezing point, miscibility with water and low corrosive activity.

10                    Environmental aspects of ethylene glycol show well relative to other products used in oil and gas production. Ethylene glycol reacts with hydroxyl radicals with a half life of the reaction estimated at 0.3 to 3.5 days.

15                    Historically glycol has been used in gas production as a product to help eliminate water in gas pipelines. Glycol is injected prior to a dehydration unit, where the glycol water solution is heated to remove the water and then re-injected for the same purpose. In some cases, hydrocarbon condensate is also a by product and is used as a fuel for heating the solution. In recent years glycol has been used as a heat transfer agent replacing the conventional use of boilers and steam for winter heating operations. The glycol system is more efficient as it is a closed loop system, reusing the fluid.

20                    Glycol has also been used as an additive or carrying agent for additives used in stimulation fluids. The surfactant nature of the product has been used for foaming and defoaming aerated fluids and as a non aqueous carrier for solid particles such as cement.

The high boiling point of glycols means that fewer vapours are generated during well stimulation. Glycol reduces the freezing point of aqueous solutions; this is particularly

important when gas/oil production is taking place at sub-zero temperatures. It also reduces the surface tension of aqueous solutions, which improves fluid recovery. It is soluble in many substances commonly used in stimulation fluids, such as water, methanol and toluene. Glycol has a high flash point, meaning that it is non-flammable and safe to use. Its viscosity is inversely related to temperature, so it is not necessary to heat the fluid in order to increase viscosity.

Glycol may be used on its own as a stimulation fluid, or in combination with additives. For example, because of its high density, energizers such as N<sub>2</sub> and CO<sub>2</sub> may be used to improve recovery. Fillers and solvents such as water, methanol and toluene may be added to reduce the amount of glycol needed, thus reducing costs. Surfactants such as Surfynol™ 124, available from Air Products, may be added to reduce surface tension. Various chemicals may be added to enhance characteristics such as viscosity or foaming, or to reduce side effects such as damage to the formation. None of these additives would affect the recoverability and recyclability of glycol.

Although the glycol-based fluids of the present invention are to be used mainly for well stimulation, they may also be used for any application in which it is advantageous to recover and recycle the fluid. For example, glycol-based fluids may be used as kill fluids, where it is desirable to stop the flow of reservoir fluids. Glycol-based fluids may be used as workover fluids, where the well is being repaired or restored. In addition, the fluids of the present invention may be used to transport solids, such as mineral processing wastes, backfill for open pits, clay for lining storage ponds, substances for sealing coal fires, and materials for filling mined cavities to prevent surface subsidence.

The present invention also relates to a process for recycling a well stimulation fluid comprising glycol. Upon recovery from the well, the well stimulation fluid is channelled into a separation vessel where solids fall to the bottom of the vessel, liquids are drained off, and gases are removed through the top of the vessel. The liquids are then filtered to further remove any solids. The liquids are heated in a regeneration vessel to a point



where water and hydrocarbons are vaporized, yet glycol remains in a liquid state. The gaseous materials are removed from the top of the vessel. This process may be repeated until the desired purity of glycol is achieved. It can then be removed to storage, awaiting reuse.

- 5 Glycols are relatively more expensive than fluids such as water, methanol, liquid CO<sub>2</sub>, and hydrocarbon fluids. Glycol is approximately double the cost of methanol and liquid CO<sub>2</sub>. The cost benefit to utilizing glycol is the relative ease in recapturing and recycling it after the stimulation.

### **Brief Description of the Drawings**

- 10 Figure 1 is a schematical view of the equipment to be used for blending and pumping the well stimulation fluid.

Figure 2 is a cross section of a well bore illustrating the flow of well stimulation fluid into the formation.

- 15 Figure 3 is a cross section of a well bore illustrating the flow of well stimulation fluid and gas or oil out of the formation.

Figure 4 is a cross section of a separation vessel.

Figure 5 is a cross section of a regeneration vessel.

### **Detailed Description of the Drawings**

- 20 The present invention proposes the use of glycol as a stimulation fluid additive or as a principle fluid utilizing conventional equipment. Further, the processes would utilize

recapture and recycling operations to reduce the overall cost of the operation and reduce the volume of fluids requiring additional disposal costs.

5 Ideally a glycol would be used as the sole stimulation fluid without the addition of chemicals. This type of stimulation would be comparable to a liquid CO<sub>2</sub> treatment, but not require the specialized equipment needed to add proppants to the fluid. Viscosity limitations of liquid CO<sub>2</sub> (about 0.1 cP) are not a problem, and glycol viscosity increases with lowered temperatures (no heating required). Post treatment, the glycol is easily and safely collected where it can be recycled by heating to remove any absorbed water and other impurities.

10 Due to the density of glycols, it is envisioned that energizers such as nitrogen and liquid CO<sub>2</sub> will sometimes be used to help in the recovery of the treatment fluid. The use of liquid CO<sub>2</sub> could enhance the viscosity properties of the glycols as liquid CO<sub>2</sub> is pumped at -20 C. Again the recovered fluid would be easily captured and heated for recycling.

15 Spacers (fillers) and/or solvents and/or surfactants, water, methanol, toluene or other commonly used stimulation fluids may be used to reduce costs or enhance the required characteristics of the glycol. Still the glycols would be recoverable and recyclable.

Glycol could also be used as a spacer (filler) to enhance the properties of other commonly used stimulation fluids.

20 It is also envisioned that chemical additives can be used to enhance the properties of glycols (for example: viscosity) or reduce the risks of potential damaging side effects caused by non pure recycled products (examples biocides, clay swelling ...). Chemical additives could be created to optimize the foaming characteristics when used with gases or liquid gases.

Figure 1 illustrates that glycol is stored in tanks 1 prior to use. When the glycol is needed, it is directed through a blender unit 2 where it is blended to ensure that the glycol and any additives and proppants are thoroughly mixed. A fluid pumper unit 3 then pumps the glycol fluid through a high pressure line 4 to the well head and into the formation being treated at a pressure sufficient to cause fracturing as is well known in the art. Energizers such as liquid CO<sub>2</sub> and N<sub>2</sub> may also be pumped from a gas source pumping unit 6 into high pressure line 4 along with the glycol fluid. Pumping the CO<sub>2</sub> or N<sub>2</sub> from a separate source permits independent control of the timing and rates at which these fluids are introduced into the glycol stream.

Figure 2 illustrates the flow of the well stimulation fluid 8 down through the well bore 7 into formation 9 to instigate and propagate fractures into the formation.

Figure 3 illustrates the flow back of well stimulation fluid, along with water and gas or oil from formation 9, back up through well bore 7 to the surface.

Figure 4 illustrates that as the well stimulation and other materials flow out of well head 5, they are diverted into a separation vessel 10. Gaseous materials are removed through the top 11 of the vessel and may be either flared off or channelled to a pipeline for further processing. The presence of glycol in any recovered gas is not a problem as the industry typically uses glycol in any event to remove water from flowing gas. Solid materials fall to the bottom 12 of the vessel. The remaining liquids may be drained out for further purification as shown in Figure 5.

Figure 5 illustrates that after leaving separation vessel 10, the liquid may be passed through a filter 13 to further remove any remaining entrained solids. The filtered liquid is then collected in a regeneration vessel 14. The liquid is circulated between regeneration vessel 14 and a combined heater and circulation pump 15. As the liquid is heated, water and hydrocarbon materials having a boiling point lower than that of glycol will vaporize. The vaporized materials are evacuated through a valve 16 at the

top of vessel 14. Circulation of the liquid continues until the desired purity of glycol is achieved, at which point, the purified glycol 18 is channelled off for storage and reuse.

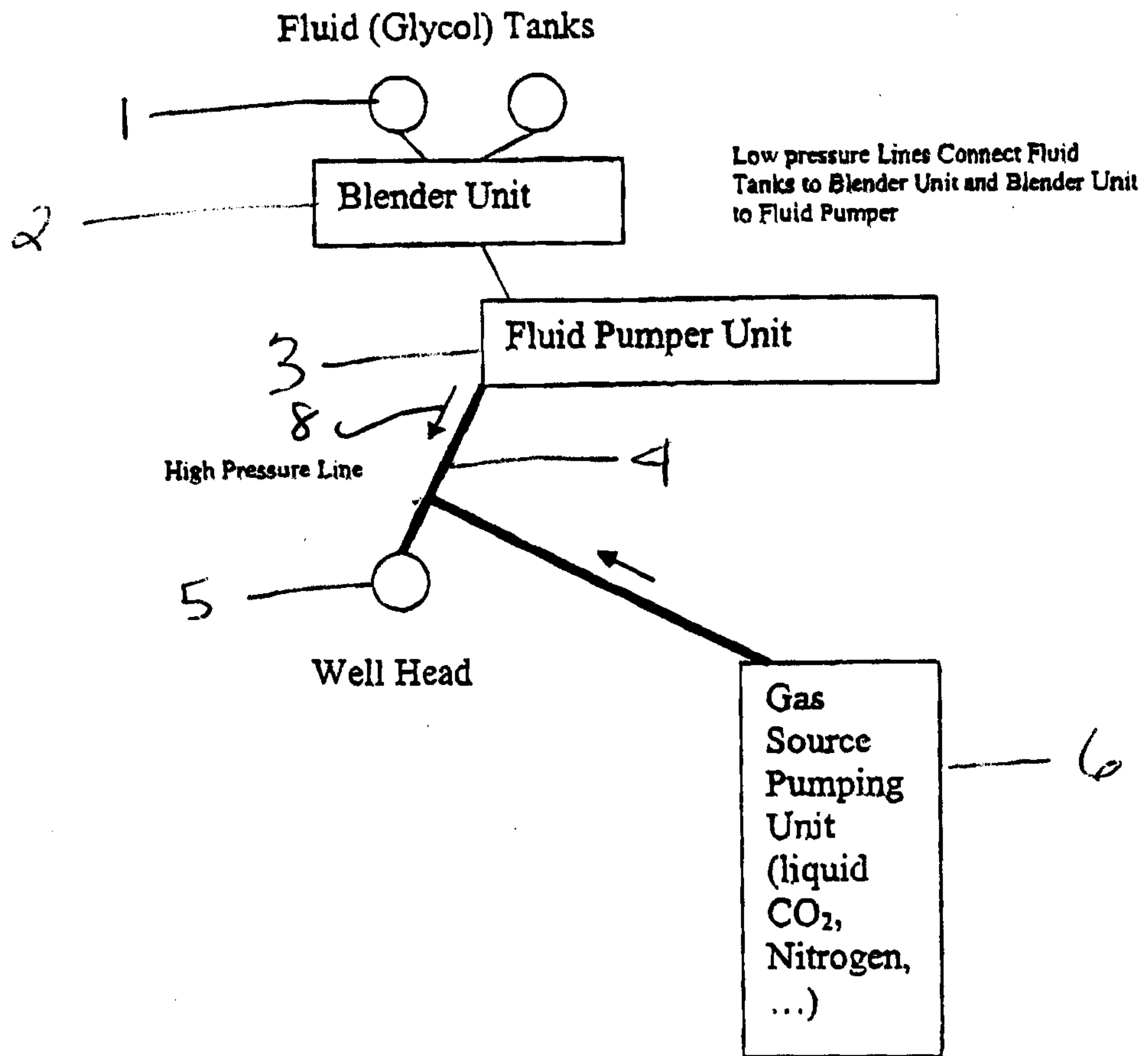
5 Although it is contemplated that ethylene glycol will be used most commonly in the context of the present invention, other glycols can also be used including, but not limited to diethylene, triethylene, tetraethylene, propylene, dipropylene and tripropylene glycol.

10 The above-described embodiments of the present invention are meant to be illustrative of preferred embodiments of the present invention and are not intended to limit the scope of the present invention. Various modifications, which would be readily apparent to one skilled in the art, are intended to be within the scope of the present invention. The only limitations to the scope of the present invention are set out in the following appended claims.

## I CLAIM:

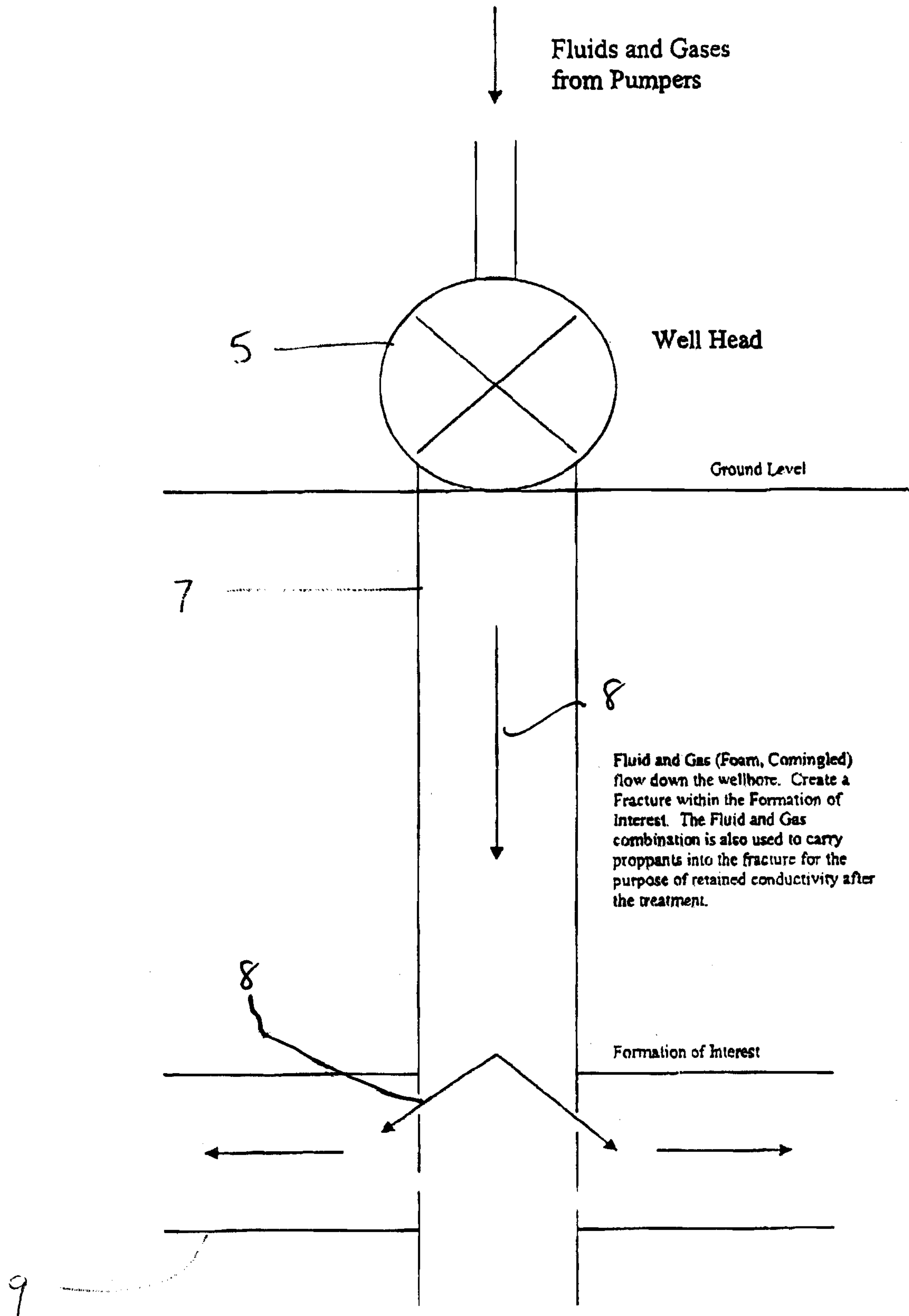
1. A well stimulation fluid comprising a glycol, said a glycol representing between 51 and 100% of said fluid, by weight.
2. A well stimulation fluid as claimed in claim 1, in the form of a foam including a liquefied gas selected from the group consisting of N<sub>2</sub>, CO<sub>2</sub>, and air.
3. A well stimulation fluid as claimed in claim 1, further comprising a solvent selected from the group consisting of water, methanol, and toluene.
4. A well stimulation as claimed in claim 1, wherein said glycol is ethylene glycol.
5. A kill fluid comprising glycol.
6. A workover fluid comprising glycol.
7. A fluid for transporting solids, comprising glycol.
8. A method for recycling a well stimulation fluid comprising a glycol, said method comprising the steps of:
  - a) filtering said fluid; and
  - b) heating said fluid to vaporize materials having a lower boiling point than said fluid.
9. A method as claimed in claim 8, wherein said glycol is ethylene glycol.

### Surface Equipment Rig Up for Glycol Fluid System Fracture Treatment



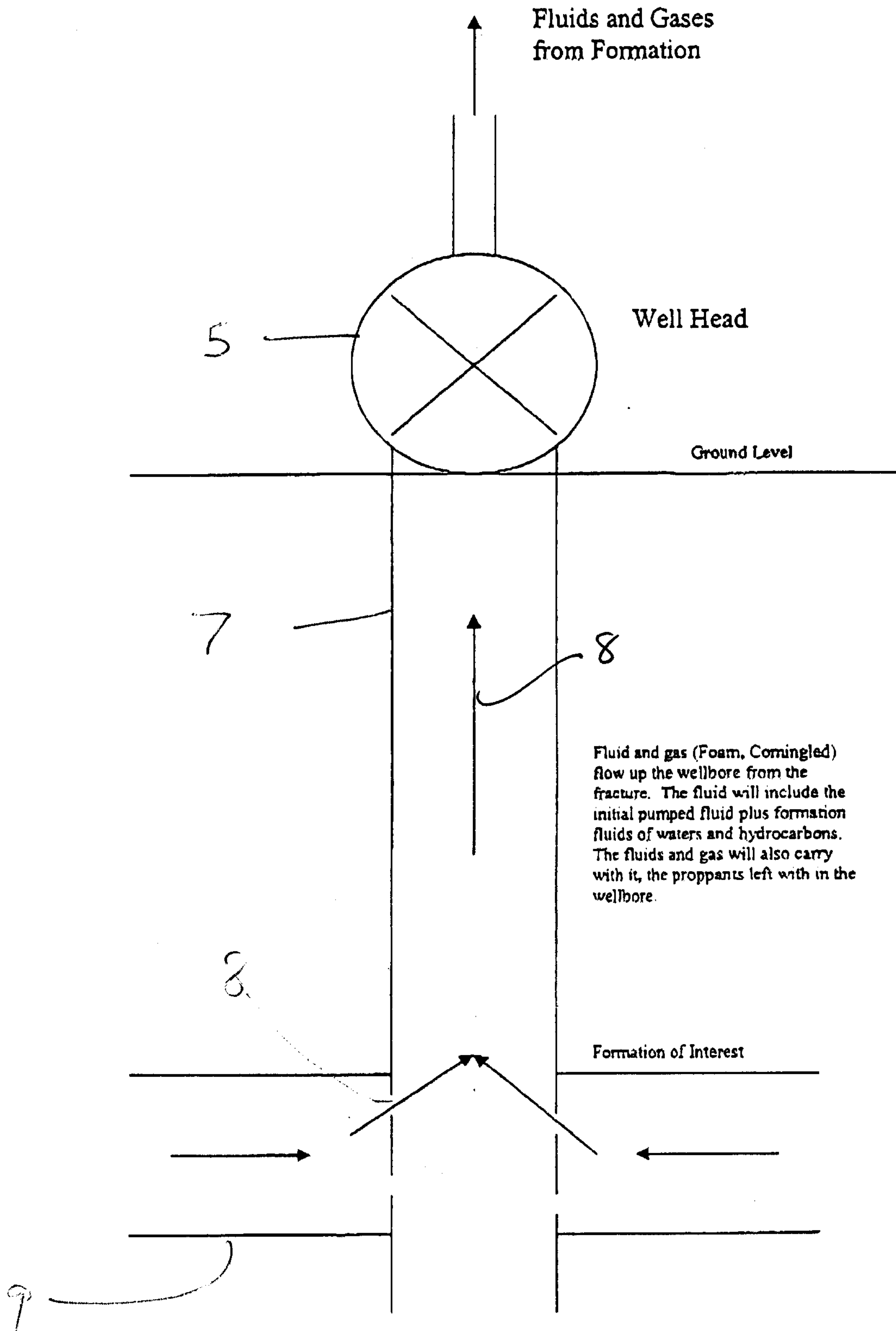
**FIGURE 1**

### Formation Fracturing with Glycol Fluid System



**FIGURE 2**

### Fluid Flow Back After Fracture Treatment



**FIGURE 3**



### On-Location Fluids/Gas/Solids Separation

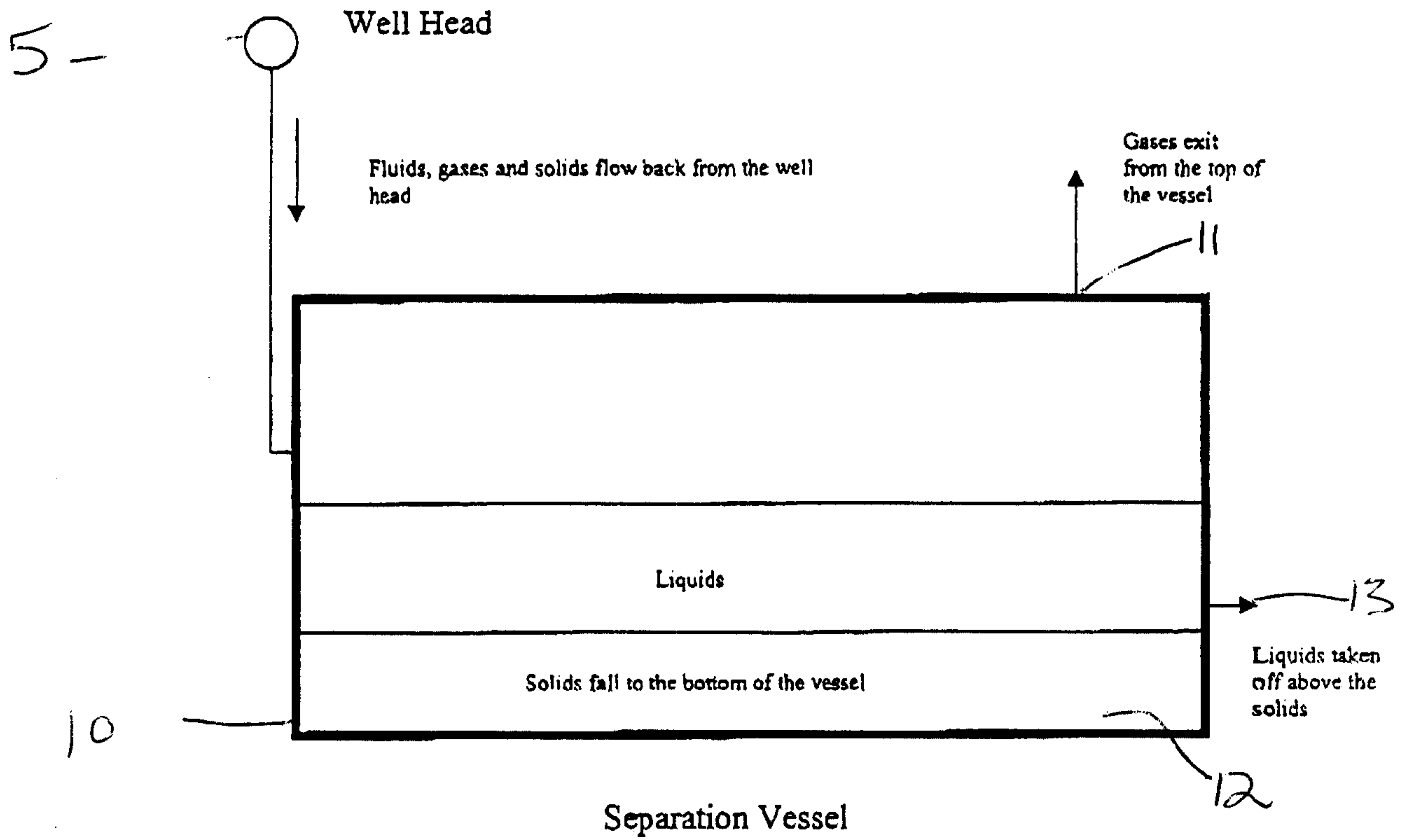


FIGURE 4

### Glycol Fracture Fluid Regeneration

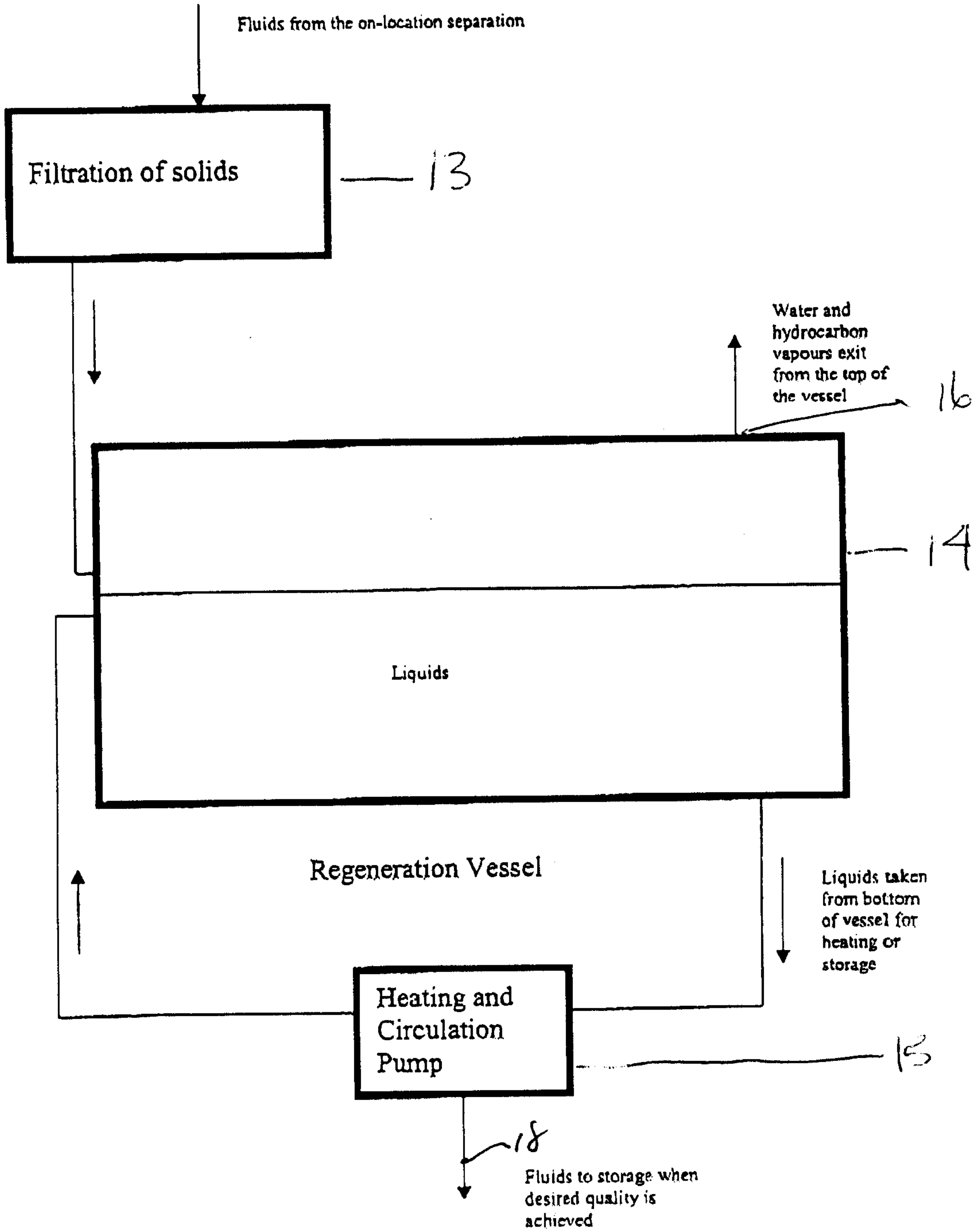


FIGURE 5

# Surface Equipment Rig Up for Glycol Fluid System Fracture Treatment

