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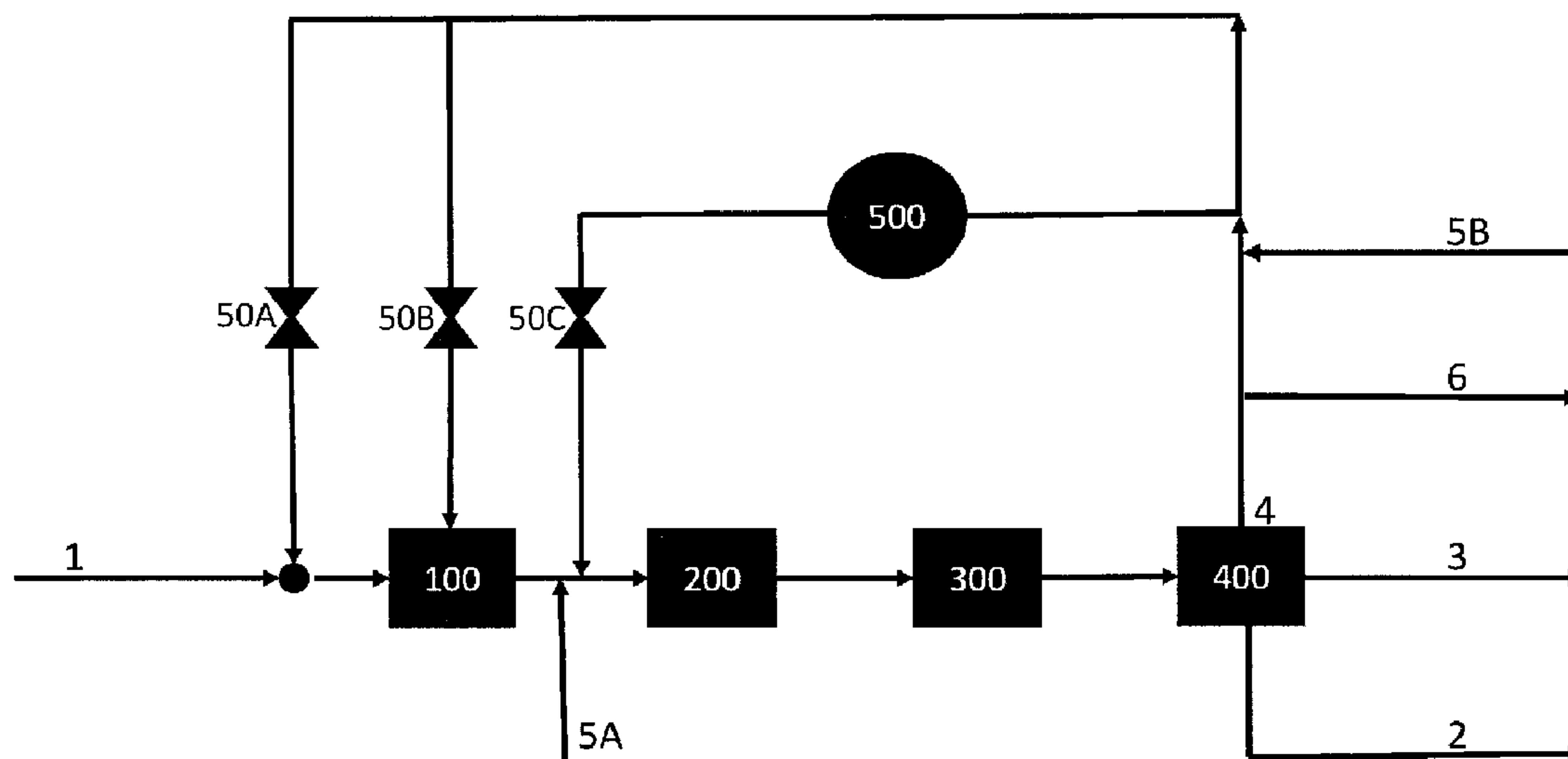
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(57) **Abrégé/Abstract:**

A method of removing oil from oily water is provided, comprising providing water containing a first amount of oil; adding a refrigerant that is oil-soluble at a temperature and pressure at which the refrigerant exists in liquid form, mixing the liquid to ensure contact between the oil and refrigerant and condensed vapour; separating the lower density liquid droplets without reducing pressure or depressuring the mixture to allow the condensed vapour that has dissolved in the oil to re-vapourize forming bubbles directly on and within the oil droplets; and separating and removing a these bubbles as a froth from the water, the water product containing a second amount of oil that is less than the first amount of oil.

**ABSTRACT**

A method of removing oil from oily water is provided, comprising providing water containing a first amount of oil; adding a refrigerant that is oil-soluble at a temperature and pressure at which the refrigerant exists in liquid form, mixing the liquid to ensure contact between the oil and refrigerant and condensed vapour; separating the lower density liquid droplets without reducing pressure or depressuring the mixture to allow the condensed vapour that has dissolved in the oil to re-vapourize forming bubbles directly on and within the oil droplets; and separating and removing a these bubbles as a froth from the water, the water product containing a second amount of oil that is less than the first amount of oil.

## **REMOVAL of HYDROCARBON AND OIL FROM WATER**

The present invention relates to methods and systems for removal of hydrocarbon and oil from water to increase the potential for reuse of de-oiled water or enable discharge of de-oiled water to surface water bodies.

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### **BACKGROUND OF THE INVENTION**

Water that contains significant amounts of hydrocarbon and oil is commonly referred to as oily water. Oily water can occur from a number of different industrial processes as well as occurring in flowback and produced water from oil and gas operations including hydraulic fracturing operations. Oily water can emit harmful vapours and odours. Oily water stored in open tanks or ponds represents a hazard to waterfowl. Oily water also presents a potential deleterious substance if released to waterbodies including streams or ponds. Oily water also entraps dissolved and suspended compounds that can be deleterious to the reuse of water.

It would be desirable to be able to use de-oiled water for a number of beneficial uses. However conventional methods of de-oiling water do not cost-effectively reduce the hydrocarbon or oil content to levels that are low enough to meet surface discharge criteria . Likewise, conventional methods of de-oiling water do not achieve low enough concentrations of oil or hydrocarbons to meet standards for other beneficial uses including feed water softening, boiler feed water, once-through steam generation plants for steam assisted gravity drainage processing or oil sand mining and separation facilities.

There are a number of ways of separating oil and hydrocarbon from water but many do not achieve low enough levels of oil or hydrocarbon. These methods do not sufficiently remove tiny (sub-micron) oil droplets to allow reuse or discharge and consist of either filtration or flotation. Filtration systems rely on hydrophobic membranes that are vulnerable to plugging and do not remove the smallest (submicron) oil droplets. Flotation systems rely on the addition of large numbers of small

bubbles that collide with oil droplets, combine and rise to the surface. Conventional flotation systems struggle to remove the tiniest (submicron) oil droplets because gas bubbles need to be of similar size to collide and attach to the oil and hydrocarbon droplets. Conventional air bubble generators do not produce sufficient quantity of submicron sized or larger air bubbles nor do they achieve sufficient  
5 number of air-oil bubble collisions plus attachments to achieve full removal of oil and hydrocarbon.

Thus, there is a need for an efficient and less-costly method and system for removing oil and hydrocarbon from water.

### **SUMMARY SPECIFICATION OF THE INVENTION**

In the first aspect, a method of removing oil from oily water is provided, comprising providing  
10 water containing a first amount of oil; adding a refrigerant that is oil-soluble at a temperature and pressure at which the refrigerant exists in liquid form, mixing the liquid to ensure contact between the oil and condensed vapour; separating the lower density liquid droplets without reducing the pressure or de-pressuring the mixture to allow the condensed vapour that has dissolved in the oil to re-vapourize forming bubbles directly on or within the oil droplets; allowing these bubbles to rise to the surface to  
15 accumulate as a scum or skim or froth referred to as a float; and separating this layer from the water, the water product containing a second amount of oil that is less than the first amount of oil.

In the second aspect, a system for removing oil from oily water is provided comprising a feed inlet for supplying water containing a first amount of oil; raising its pressure to allow the addition of a refrigerant that exists as a liquid; at least one mixer for mixing the oily water and refrigerant while  
20 holding pressure to preserve the liquid phase; at least one separator downstream at the same or lower pressure to separate the oily froth from the water produced.

Thus in the present application a system for removing oil from water is provided. Water containing oil is pressurized and combined with a refrigerant, for example, butane, pentane, propane,

freons, liquefied petroleum gas, refrigerants or other vapours or combinations of vapours that are oil-soluble when condensed to form a mixture. There is a preference to refrigerants that are partially water soluble to enhance the absorption of the condensed vapour into the oil droplets. The refrigerant may be added before, during or after the pressuring stage as either a vapour or a liquid. When the refrigerant is added as a vapour, the oily water absorbs the latent heat of condensation and condenses the vapour. The vapour may be added to the oily water stream either through a compressor or introduced through the suction of the oily water pump.

The mixture is pumped through a pressurized mixer stage to apply sufficient turbulence and time to allow the condensed vapour to be diluted and diffused into the oil droplets. Mixing may be accomplished using pipes, coalescing elements, static mixers, throttling valves or mechanically-driven mixer. The mixture is then maintained at pressure or depressurized into at least one three-phase separator. The de-pressuring may be achieved by reduction in static head, control valve or the mixing elements themselves. The depressurizing separator operates at a lower pressure that allows the condensed vapour to grow out of the oil droplet as a bubble thereby ensuring intimate contact between the bubble and the oil droplet, thereby lifting the oil droplets to the surface of the water. The system benefits from the enormous change in volume when a condensed liquid changes phase into a vapour.

The system operates with a once-through flow of refrigerant or a combination of once-through flow of refrigerant supplemented by refrigerant recovered from the three phase separator.

The method allows for the use of one or more refrigerants in combination or separately to achieve optimum removal, depending upon the physical and chemical characteristics of the oily water including temperature, salinity, density or other compounds that are present.

### BRIEF DESCRIPTION OF THE DRAWINGS

Referring to the drawings wherein like reference numbers indicate similar parts throughout the several views, several aspects of the present invention are illustrated by way of example, and not by way of limitation, in detail in the figures, wherein:

5           Figure 1 is a process diagram of a system for removing oil from water.

### DESCRIPTION OF VARIOUS EMBODIMENTS

The detailed description set forth below in conjunction with the appended drawing is intended as a description of the various embodiments of the present invention and is not intended to represent the only embodiment contemplated by the inventor. The detailed description includes specific details  
10 for the purpose of providing a comprehensive understanding of the present invention. However, it will be apparent to those skilled in the art that the present invention may be practiced without these specific details.

Figure 1 is a schematic illustration of a system for removing oil from water. The system includes an oily water feed inlet 1, a oily water pressurizer 100, a mixer 200, a pressure reducer 300, a three  
15 phase separator 400, a vapour re-compressor 500, a number of valves 50A, 50B and 50C, a de-oiled water outlet 2, an oily float outlet 3, a refrigerant vapour outlet 4, a refrigerant makeup inlet 5A or 5B, and a refrigerant purge 6.

Oily water (water containing a first amount of hydrocarbon and oil) is introduced into the system through the feed inlet 1. The oily water can be from an industrial process such hydraulic  
20 fracturing, primary oil extraction, groundwater extraction for steam injection, medicine formulation, food processing, refinery, hydrocarbon upgrading process.

The oily water may first pass through a pressurizer 100 that increases the pressure high enough to allow the refrigerant to exist as a liquid.

In one embodiment, the pressurizer is a centrifugal pump. The refrigerant can be fed into the oily water through 50A, one of three valves. Valve 50A allows the refrigerant to be injected upstream  
5 of the pressurizer 100. The pressurizer therein increases the pressure of both the oily water and refrigerant as a two phase mixture.

In another embodiment, the pressurizer is a microbubble generator. Valve 50B allows the refrigerant to be injected directly into the pressurizer. The pressurizer therein increases the pressure of both the oily water and refrigerant as a two phase mixture.

10 In another embodiment, refrigerant is injected into the pressurized oily water through Valve 50C downstream of pressurizer 100 where it condenses.

The combined oily water and refrigerant is thoroughly mixed in Mixer 200. The mixer can be any type of mixer for sufficiently agitating the mixture so as to provide adequate turbulence and time for refrigerant to blend into the oil droplets. The mixer can be static mixers that are used for mixing two  
15 fluids and typically contain mixer elements or baffles that agitate the two fluids as they are passed through the static mixer. An example of a static mixer that can be used is Sulzer™ Mixer SMV but other static mixers known in the art can be used. The oily water and refrigerant can also be blended by simultaneously coalescing them onto a oil-wettable surface of a coalescing element. The mixer can be a length of pipe that offers sufficient residence time. The mixer can be a mechanical mixer. The mixer can  
20 be a valve.

The oily water and refrigerant mixture is de-pressured in Pressure Reducer 300 to allow the refrigerant to re-vapourize and grow bubbles both within and outside the oil droplets. One embodiment of the pressure reducer is a simple throttling valve. Another embodiment is a reduction in static head

within a pipe or vessel. One embodiment of the pressure reducer is to utilize Mixer 200 to both mix and reduce pressure.

Another embodiment is not to reduce the pressure once the refrigerant has been added to the oily water, but to let the lower density liquid droplets separate naturally.

5           The depressurized oily water and refrigerant mixture is routed into Separator 400 where it separates into three phases. The de-oiled water phase is removed from the bottom of the Separator through Outlet 2. The float phase containing oil and residual refrigerant is skimmed from the surface through either simple weir, floating weir, bucket and weir assembly, skim box, mechanical paddles. The float phase is then routed through Oily Float Outlet 3. The vapourized refrigerant is removed through  
10 Refrigerant Vapour Outlet 4 for recovery through recycling.

One embodiment of the Separator is to utilize a horizontal or vertical cylindrical vessel. A pressure vessel allows for the separation of oil and refrigerant from high-temperature water or the use of a high pressure refrigerant at lower temperatures.

One embodiment of the Separator is to use a vertical cylindrical tank.

15           One embodiment of the Separator is to use a rectangular tank at atmospheric pressure.

The recovered refrigerant vapour can be recycled into the oily water through Valve 50A or 50B. The recovered refrigerant vapour can be compressed in Re-Compressor 500 and recycled into the oily water through Valve 50C. An example of the Re-Compressor can be a liquid-ring compressor or sliding vane compressor or scroll compressor.

20           During normal operation, some refrigerant is dissolved in the water and is lost through De-oiled Water Outlet 2. During normal operation, some refrigerant remains in the float and is lost through Oily Float Outlet 3. During normal operation, some refrigerant may be recovered from the de-oiled water

and float by passing each through a flash vessel operating under partial vacuum, compressed and added to the refrigerant vapour recovered in Separator 400.

During normal operation, some refrigerant may be contaminated with non-condensable components and require purging through Refrigerant Purge 6.

- 5 To compensate for the loss of refrigerant, replacement refrigerant may be added through Refrigerant Makeup Inlets at 5A, 5B or combination thereof.

Example 1.

An example of 1 liter of oily water containing 100 mg/l of API 14 oil present as micron-sized droplets at a temperature of 4 to 12 degrees centigrade is fed into Oily Water Feed Inlet 1 and  
10 pressurized to 11 psig. A refrigerant quantity of 100 m/l butane is injected through valve 50A, compressed to 11 psig and injected into the oily water where it condenses. The condensing temperature of butane at this pressure is 15 degrees centigrade, therefore it condenses within the oily water. The combined oily water and refrigerant mix is fed through a static mixer and the oil droplets become saturated with butane. The water-oil-refrigerant mix is then depressurized to atmospheric  
15 pressure (0 psig) where the refrigerant inside the oil droplets partially re-vapourizes. The vapour pressure of pure butane at 4 degrees centigrade is 2.7 psig, therefore at atmospheric pressure approximately 50% of the butane will re-vapourize and expand. At 1 atmosphere pressure, the density of butane liquid is 0.601 kg/litre and the density of butane vapour is .0027 kg/litre, therefore the volume occupied by butane increases by 221 times when it re-vapourizes increasing the droplet size by 6 times  
20 and reducing its density to that of butane vapour, therefore allowing the larger and less dense oil droplet to float to the surface. The resultant de-oiled water can contain as little as 5 mg/l or less oil.

The previous description of the disclosed embodiments is provided to enable any person skilled in the art to make or use the present invention. Various modifications to those embodiments will be

readily apparent to those skilled in the art, and the generic principles defined herein may be applied to other embodiments without departing from the spirit or scope of the invention. Thus, the present invention is not intended to be limited to the embodiments shown herein, but is to be accorded the full scope consistent with the claims, wherein reference to an element in the singular, such as by use of the article “a” or “an” is not intended to mean “one and only one” unless specifically so stated, but rather “one or more”. The invention described herein can be applied as a single stage or one of multiple stages with each further reducing the oil content of the de-oiled water. In a multi-stage installation, for example, the makeup refrigerant can be added to the last stage while the most-contaminated refrigerant can be purged at the first stage.

10 All structural and functional equivalents to the embodiments described throughout the disclosure that are known or later come to be known by those of ordinary skill in the art are intended to be encompassed by the elements of the claims. For example, in a multistage unit, each stage need not be identical with regards to how the refrigerant vapour is recycled. Moreover, nothing disclosed herein is intended to be dedicated to the public regardless of whether such disclosure is explicitly recited in the  
15 claims.

**CLAIMS**

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method of removing oil from oily water, comprising:
  - providing water containing a first amount of oil;
  - adding a refrigerant that is oil-soluble at a temperature and pressure at which the refrigerant exists in liquid form;
  - mixing the liquid to ensure contact between the oil and condensed vapour;
  - separating the less dense oil droplets without depressuring; or,
  - de-pressuring the mixture to allow the condensed vapour that has dissolved in the oil to re-vapourize forming bubbles directly on the oil droplets;
  - allowing these bubbles to rise to the surface to accumulate as a scum or skim or froth referred to as a float; and,
  - separating this layer from the water, the water product containing a second amount of oil that is less than the first amount of oil.
2. The method of claim 1 wherein the refrigerant is butane.
3. The method of claim 1 wherein the refrigerant is propane.
4. The method of claim 1 wherein the refrigerant is pentane.
5. The method of claim 1 wherein the refrigerant is freons.
6. The method of claim 1 wherein the refrigerant is fluorinated hydrocarbons.
7. The method of claim 1 wherein the refrigerant is liquefied petroleum gas.
8. The method of claim 1 wherein the refrigerant is a combination of multiple refrigerants,
9. The method of claim 1 wherein the refrigerant is added to the oily water upstream of the pressurizer.

10. The method of claim 9 wherein the pressurizer is a centrifugal pump.
11. The method of claim 1 wherein the refrigerant is added to the oily water inside the pressurizer.
12. The method of claim 9 wherein the pressurizer is a microbubble generator.
13. The method of claim 1 wherein the refrigerant is added downstream of the pressurizer.
14. The method of claim 13 wherein the refrigerant is compressed with a compressor.
15. The method of claim 14 wherein the compressor is a liquid ring compressor.
16. The method of claim 14 wherein the compressor is a sliding vane compressor.
17. The method of claim 14 wherein the compressor is a scroll compressor.
18. The method of claim 1 wherein the oily water and refrigerant are blended in a mixer.
19. The method of claim 18 wherein the mixer is pipe.
20. The method of claim 18 wherein the mixer is a static mixer.
21. The method of claim 18 wherein the mixer is a coalescer.
22. The method of claim 18 wherein the mixer is a mechanical mixer.
23. The method of claim 18 wherein the mixer is a valve.
24. The method of claim 1 wherein the oily water and refrigerant are de-pressurized.
25. The method of claim 1 wherein the oily water and refrigerant are maintained at pressure.
26. The method of claim 24 wherein the de-pressurizer is a valve.
27. The method of claim 24 wherein the de-pressurizer is a vertical pipe that causes a reduction in static head.
28. The method of claim 24 wherein the de-pressurizer is a vessel that causes a reduction in static head.
29. The method of claim 24 wherein the de-pressurizer is the mixer and is operated to reduce the pressure.
30. The method of claim 1 wherein the oily water and refrigerant is routed into a Separator.

31. The method of claim 30 wherein the Separator is a horizontal or vertical pressure vessel.
32. The method of claim 30 wherein the Separator is an low-pressure cylindrical vertical tank.
33. The method of claim 30 wherein the Separator is low-pressure horizontal rectangular box.
34. The method of claim 30 wherein the de-oiled water is removed.
35. The method of claim 30 wherein the oil and refrigerant float is removed.
36. The method of claim 30 wherein the vapourized refrigerant is recovered for recycling.
37. The method of claim 1 wherein recovered refrigerant is recycled for injection upstream of the pressurizer.
38. The method of claim 1 wherein recovered refrigerant is recycled for injection into the pressurizer.
39. The method of claim 1 wherein recovered refrigerant is recycled to the compressor for injection downstream of the pressurizer.
40. The method of claim 1 wherein the recovered refrigerant contains non-condensable gases or other contaminants and is purged.
41. The method of claim 1 wherein refrigerant is added to replenish refrigerant removed in the de-oiled water, float and purge.
42. The method of claim 1 wherein refrigerant vapour contained in the float or deoiled water is recovered by flashing under partial vacuum and added to the refrigerant recovered in the Separator.
43. The method of claim 1 wherein the invention described herein can be applied as a single stage or one of multiple stages with each further reducing the oil content of the de-oiled water.
44. The method of claim 1 wherein in a multistage unit, the makeup refrigerant can be added to the last stage while the most-contaminated refrigerant can be purged at the first stage.
45. The method of claim 1 wherein in a multistage unit, each stage need not be identical with regards to how the refrigerant vapour is recycled.

46. A method of claim 1 wherein in a multistage unit, separators can be combined into a single large separator.

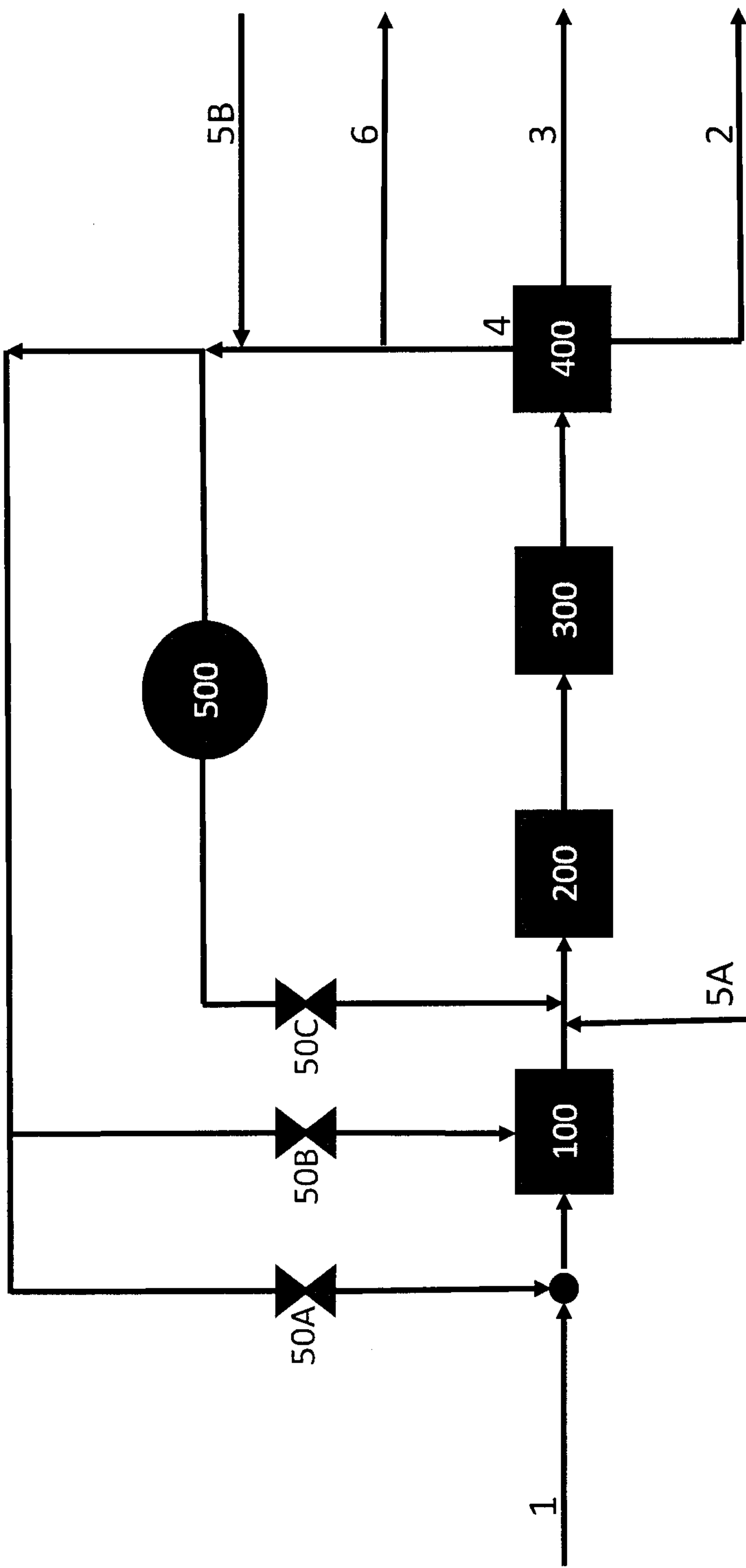


Figure 1.

