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(54) **SYSTEM AND PROCESS FOR REMOVAL OF ORGANIC CARBOXYLATES FROM MONO ETHYLENE GLYCOL (MEG) WATER STREAMS BY ACIDIFICATION AND VAPORIZATION UNDER VACUUM**

(52) **U.S. Cl.**
CPC **B01D 3/009** (2013.01)

(57) **ABSTRACT**

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A system and method for removing organic carboxylates from a mono ethylene glycol (“MEG”) stream includes a reaction vessel; means for cooling and diluting the MEG stream being routed to the reaction vessel; means for acidifying the cooled and diluted MEG stream during its residence time within the reaction vessel; and means for removing an acetic-rich overhead stream from the reaction vessel. The acidification of the cooled and diluted MEG stream occurs under a vacuum. The reaction vessel may be located downstream of a calcium removal vessel and receive a filtered bottom stream from that vessel, or it may be a single reaction vessel that cycles between a calcium removal mode and an acetate removal mode, with the pressure of the single vessel being greater during the calcium removal mode than during the acetate removal mode.

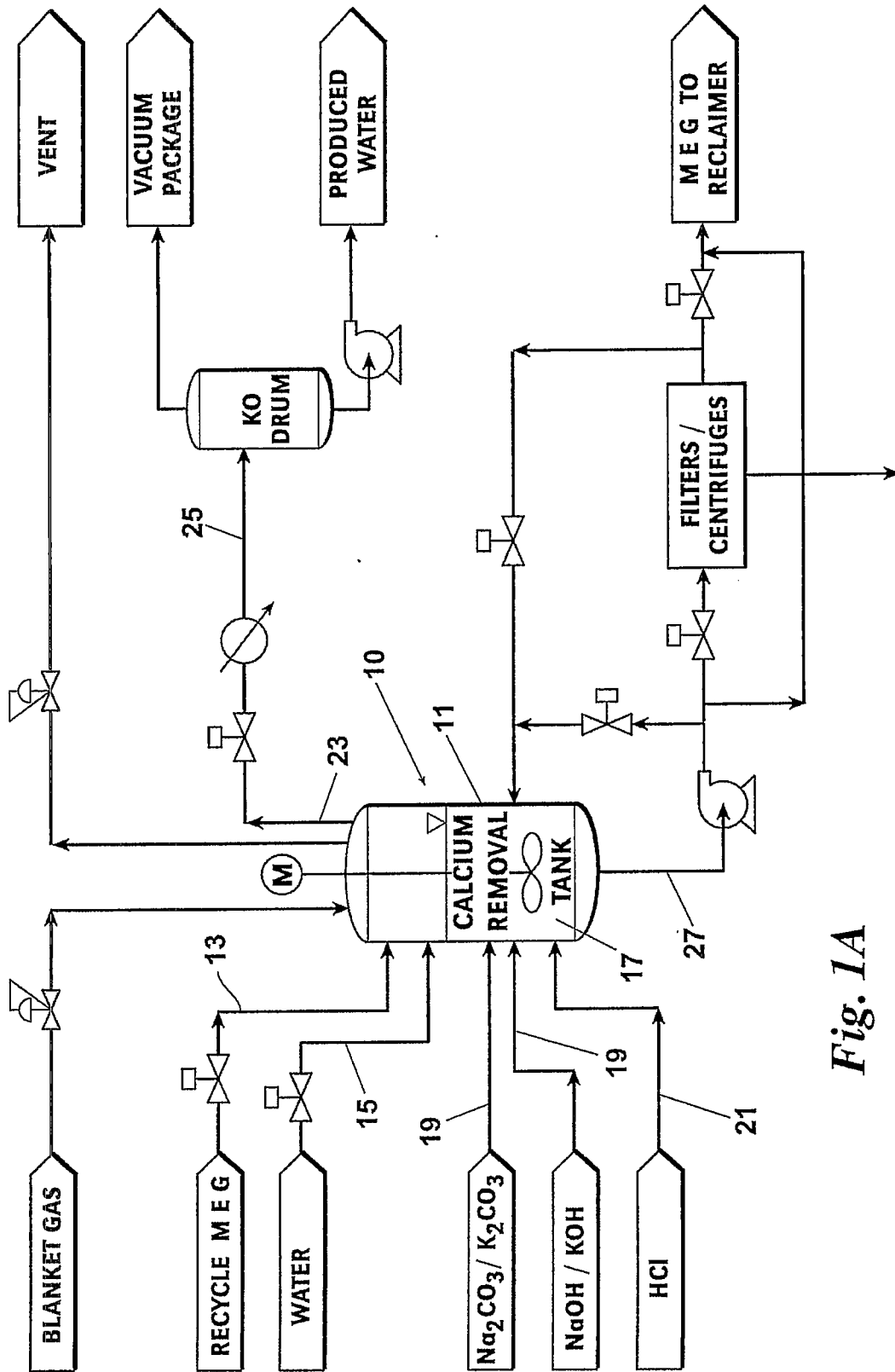


Fig. 1A

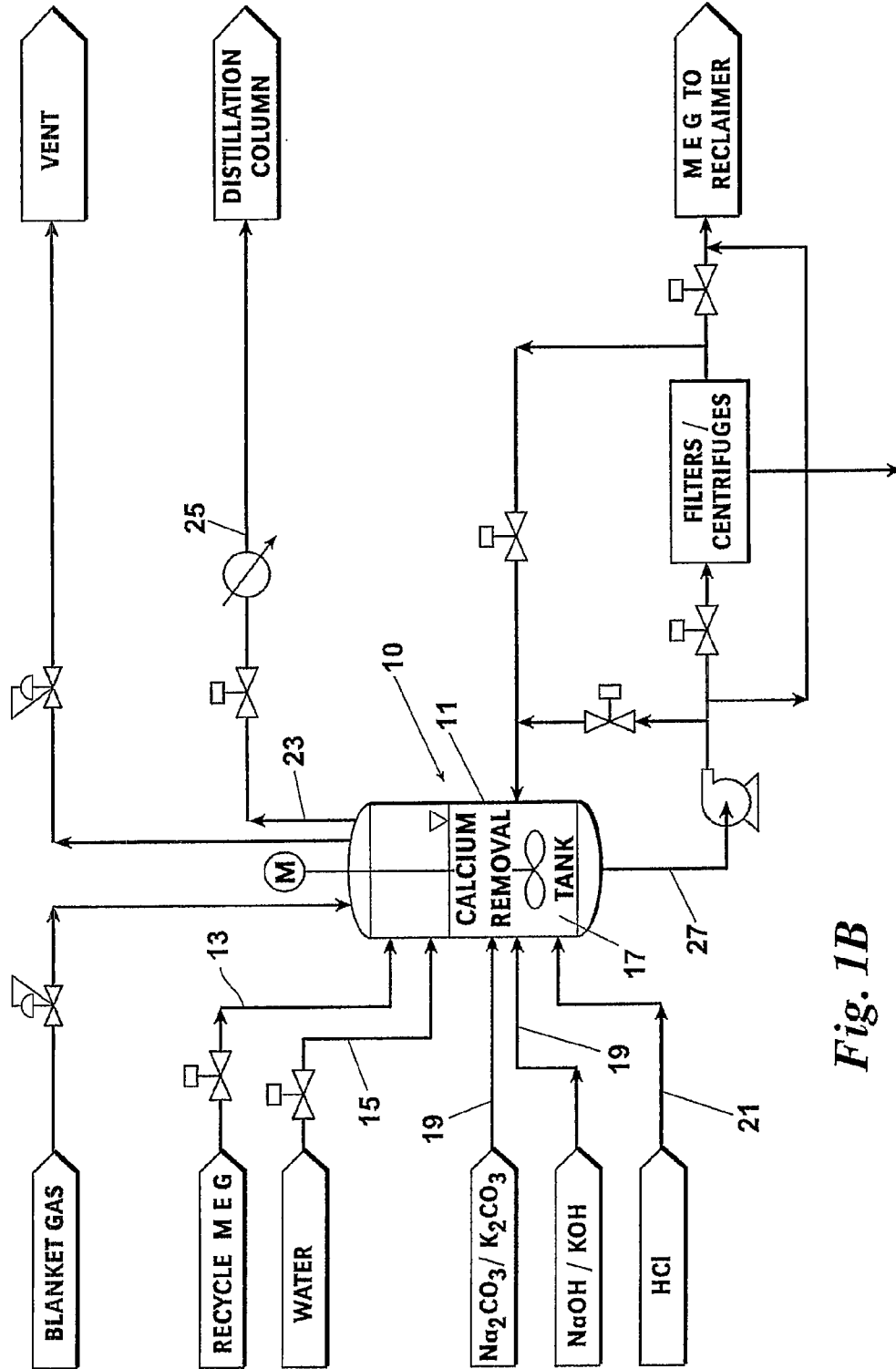


Fig. 1B

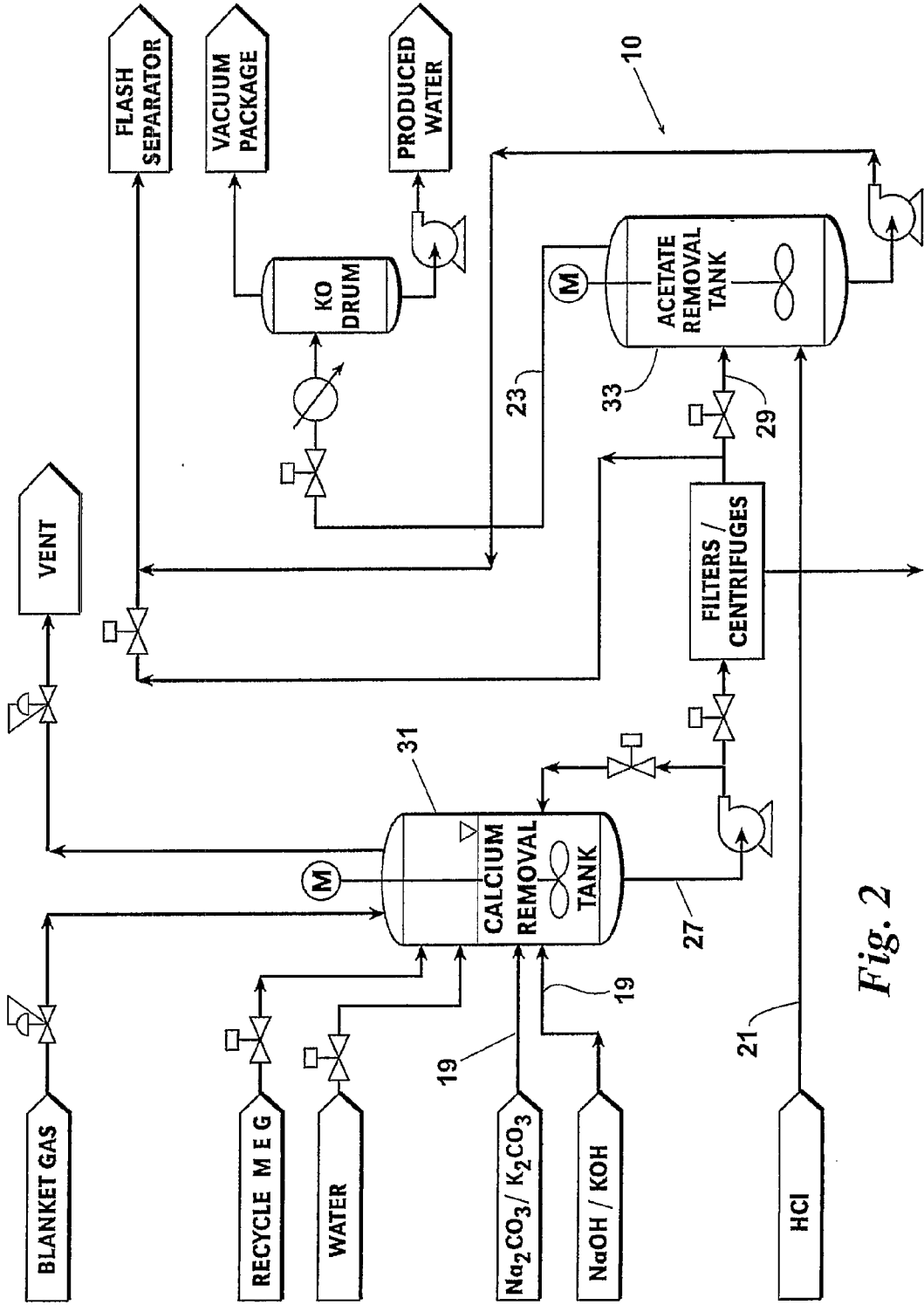


Fig. 2

Figure 3 : Acetate Removal as a function of temperature and pressure

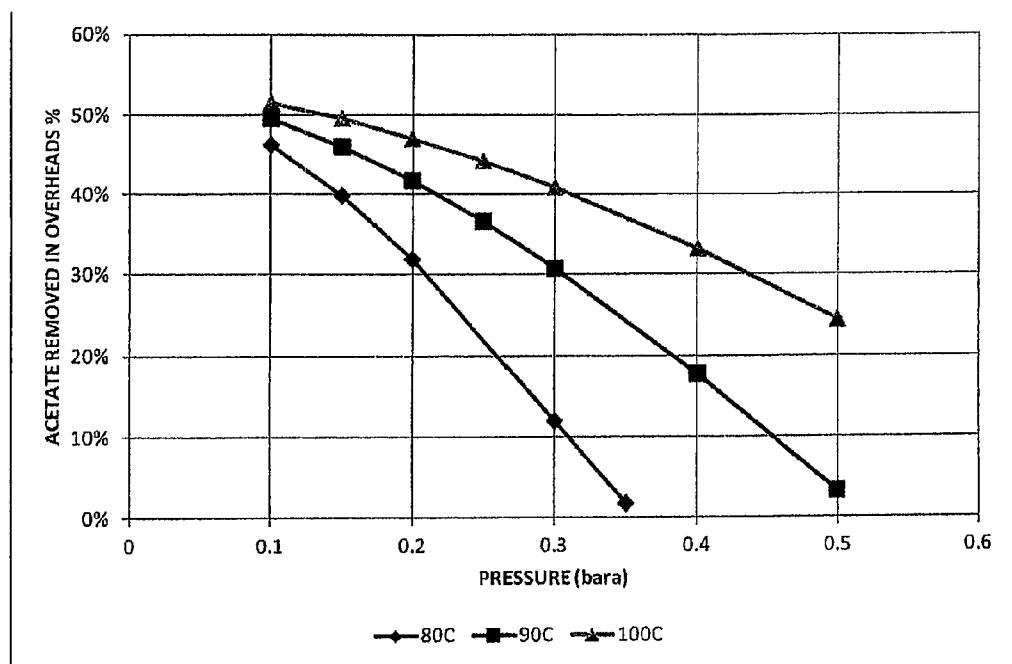


Figure 4 : MEG lost in Reaction vessel overheads as a function of temperature and pressure

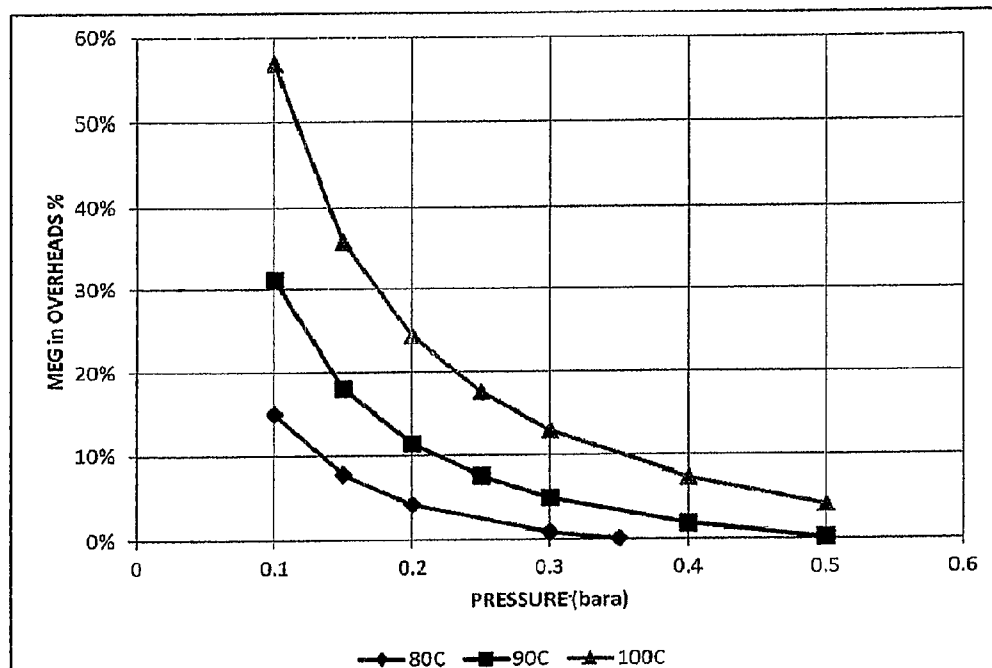


Figure 5 : *Acetate Removal and MEG Losses*

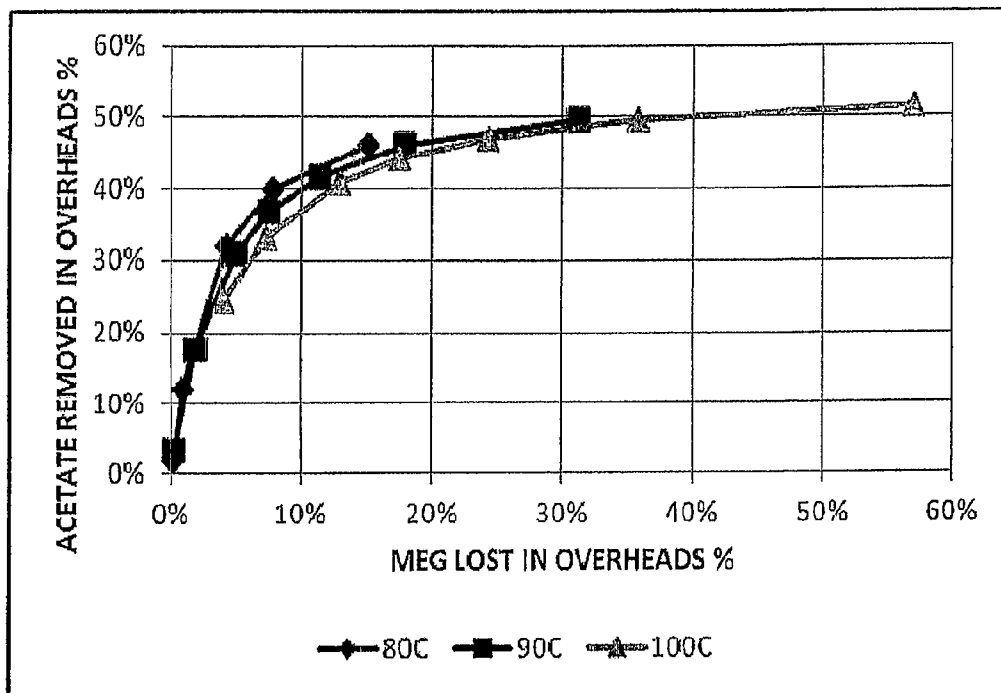
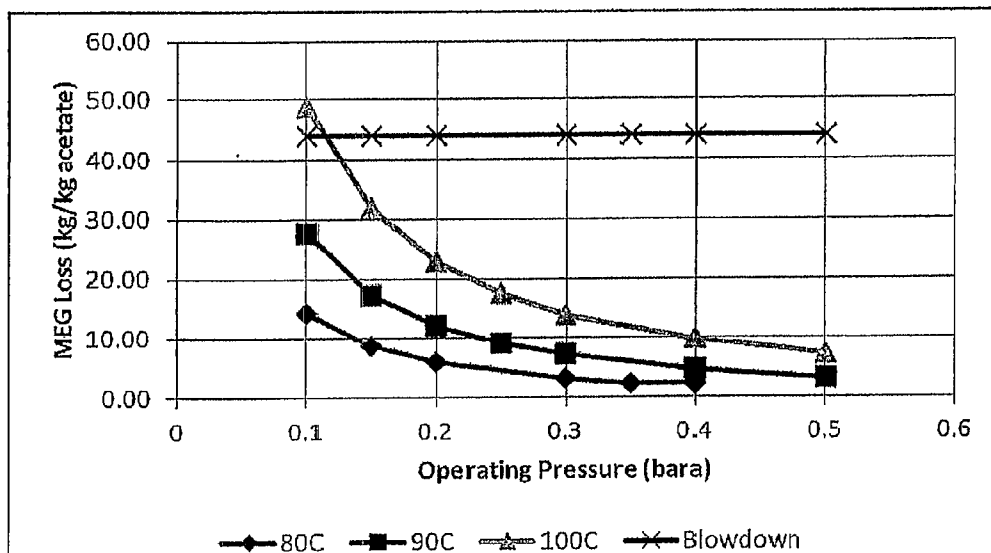


Figure 6 : *Calculated MEG Loss per kg acetate rejected*



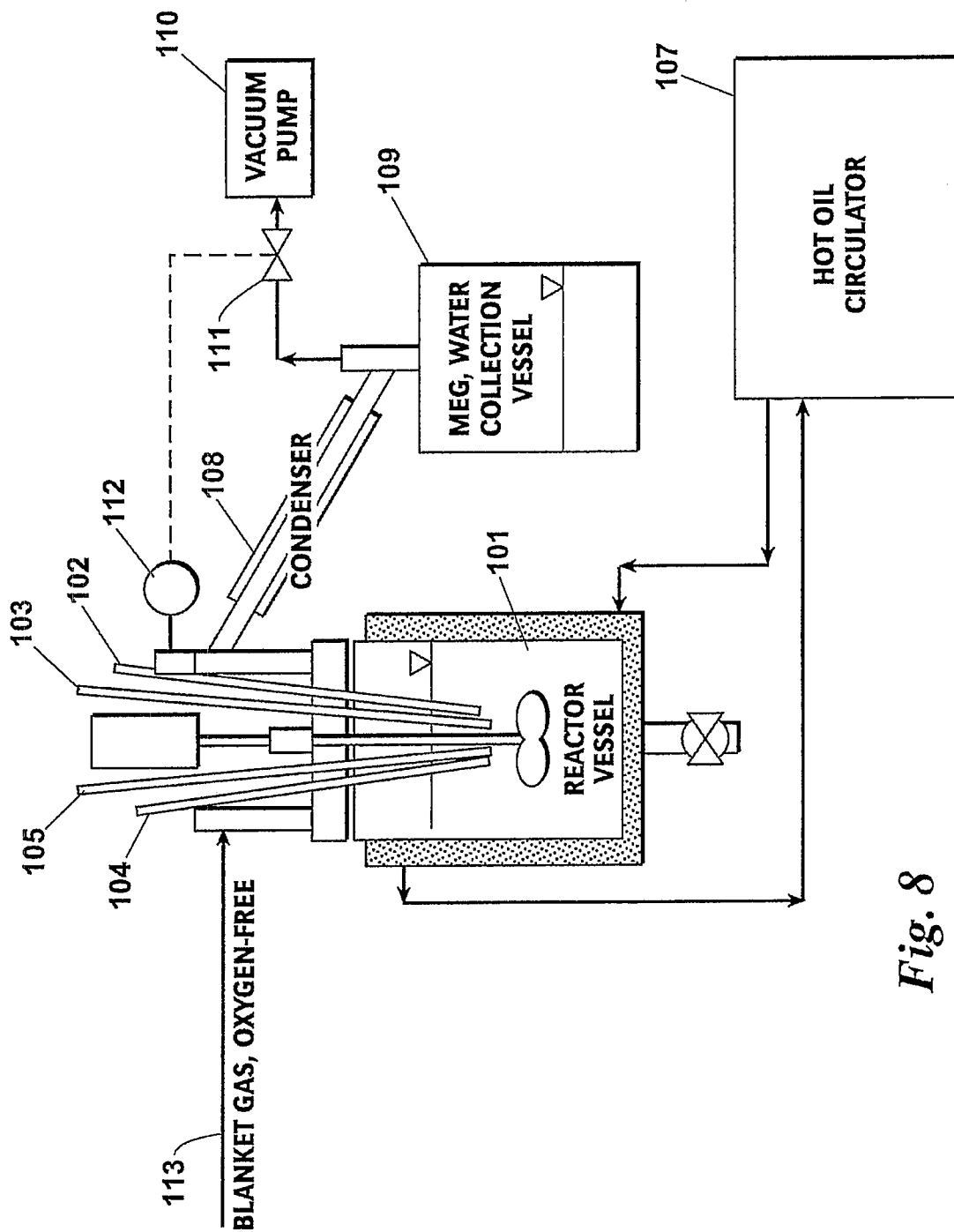


Fig. 8

SYSTEM AND PROCESS FOR REMOVAL OF ORGANIC CARBOXYLATES FROM MONO ETHYLENE GLYCOL (MEG) WATER STREAMS BY ACIDIFICATION AND VAPORIZATION UNDER VACUUM

BACKGROUND OF THE INVENTION

[0001] This invention relates to systems and methods designed to treat mono ethylene glycol ("MEG") streams used in the oil and gas industry to control hydrates formation in the production pipeline. More particularly, the invention relates to systems and processes which allow for removal of carboxylates from the MEG water stream of a MEG reclamation and regeneration package to reduce MEG losses.

[0002] In the oil and gas industry, dry (lean) MEG is injected into the production pipeline to control the formation of hydrates within the produced stream. The MEG injection is part of a MEG loop of a gas production facility. The loop typically includes a reclamation and regeneration package to treat the wet (rich) MEG and reclaim as much MEG as possible for reinjection into the pipeline.

[0003] The formation waters and condensed waters, which arrive at the gas production facility along with the raw hydrocarbon products, contain organic acids. Because these organic acids are highly soluble in MEG-water mixtures, they tend to follow the MEG-water stream. Additionally, in order to protect production pipelines against corrosion, and to remove dissolved divalent cations from the MEG stream, the pH of the MEG-water in the pipeline is elevated by the addition of bases such as sodium hydroxide. At elevated pH, the organic acids are present as a carboxylate salt (e.g., sodium acetate).

[0004] The low volatility of the carboxylate salts results in their accumulation in MEG process streams within the MEG loop. This accumulation, in turn, results in increased viscosity and density, making the MEG streams more difficult to pump.

[0005] To control the carboxylate levels in the MEG loop, the carboxylate-rich MEG is periodically discharged. However, this results in loss of MEG from the system and requires replacement to ensure the MEG inventory of the loop is maintained. Therefore, a need exists for systems and processes which control the carboxylate levels and reduce or eliminate MEG loss in the loop.

[0006] Carboxylate accumulation (either as the organic acid or as the corresponding salt) is an issue for MEG reclamation and regeneration packages due to the high solubility of these species in the water-MEG aqueous phase.

[0007] In order to minimize corrosion issues, the MEG Loop is operated at relatively high pH whereby the carboxylic acids are present predominantly as the carboxylate salts which have low volatility and, thus, are not removed in the overheads (produced water) stream from the regenerators or reclaimers of the MEG Recovery Package. Their high solubility in alkaline MEG solutions means that they do not precipitate when the pH is raised to remove the calcium, magnesium and other divalent cations.

[0008] Accumulation of acetates can lead to elevated density and viscosity in MEG streams which, in turn, lead to operational difficulties. Therefore, a need exists for a system and process to remove organic carboxylates from the MEG water stream.

SUMMARY OF THE INVENTION

[0009] By employing a system and process made and practiced according to this invention, the problems discussed in the above background section are minimized because the acetate levels are controlled to a manageable level while MEG losses associated with the acetate removal process are kept to a minimum when compared to the alternative.

[0010] A system and process for removing organic carboxylates from a mono ethylene glycol ("MEG") stream includes a reaction vessel; means for cooling and diluting the MEG stream being routed to the reaction vessel; means for acidifying the cooled and diluted MEG stream during its residence time within the reaction vessel; and means for removing an acetic-rich overhead stream from the reaction vessel. The acidification of the cooled and diluted MEG stream occurs under a vacuum.

[0011] The reaction vessel may be located downstream of a calcium removal vessel and receive a filtered bottom stream from that vessel, or it may be a single reaction vessel that cycles between a calcium removal mode and an acetate removal mode, with the pressure of the single vessel being greater during the calcium removal mode than during the acetate removal mode.

[0012] Preferably, the cooling and diluting means results in the incoming MEG stream to be 50 wt % MEG at a temperature in a range of 80° to 100° C. In the acetate removal mode, the pressure is sub-atmospheric, preferably in a range of 0.1 to 0.3 bar. The acidifying means, which may be hydrochloric acid, results in the cooled and diluted MEG stream during its residence time within the reaction vessel to have a pH in a range of 3.5 to 5.5.

[0013] Objects of the invention include providing a system and process which: (1) can be retrofitted into existing MEG loops; (2) controls and reduces the amount of acetates in the MEG water stream; (3) extends the length of the production run; (4) reduces MEG loss; and (5) increases MEG recovery for re-use.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] FIG. 1A is a preferred embodiment of a system and process practiced according to this invention. A single reaction vessel is used for the removal of calcium and carboxylates from a mono ethylene (MEG) water stream. The reaction vessel swings or cycles between those two removal modes. The acetate-rich overhead stream is routed directly to a knock-out drum.

[0015] FIG. 1B is another preferred embodiment of a system and process practiced according to this invention. A single reaction vessel is used for the removal of calcium and carboxylates from a mono ethylene (MEG) water stream. Similar to FIG. 1A, the vessel cycles between those two removal modes. The acetate-rich overhead stream is routed directly to a distillation column where it is mixed with a MEG-water overhead stream from a reclaimer.

[0016] FIG. 2 is yet another preferred embodiment of a system and process practiced according to this invention. One reaction vessel is used for the removal of calcium from the MEG-water stream and another reaction vessel is used for the removal of carboxylates. The high pH stream generated in the calcium removal vessel is filtered to remove solids and then treated with hydrochloric acid in the acetate removal vessel operated at sub-atmospheric pressure.

[0017] FIGS. 3 to 7 show simulated results of a system and process made according to FIGS. 1A, 1B and 2 for acetate removal from a model solution where solution pH was reduced to 4.5 prior to raising temperature and reducing pressure.

[0018] FIG. 3 is a graph of acetate removal as a function of temperature and pressure.

[0019] FIG. 4 is a graph of MEG losses in the reaction vessel overheads as a function of temperature and pressure.

[0020] FIG. 5 is a graph of acetate removal against MEG loss for three temperatures (80, 90 and 100° C.).

[0021] FIG. 6 is a graph of calculated MEG loss per kg of acetate rejected as a function of operating pressure.

[0022] FIG. 7 is a graph of calculated acetate removed from the reaction vessel as a function of initial pH (3.5, 4.5, 5.5), temperature (60-100° C.), and operating pressure (0.1-0.3 bara).

[0023] FIG. 8 is schematic of an apparatus used to test preferred embodiments of the system and process of this invention.

ELEMENTS AND ELEMENT NUMBERING USED IN THE DRAWING FIGURES

- [0024] 10 System
- [0025] 11 Reaction vessel
- [0026] 13 Incoming carboxylates-rich MEG stream
- [0027] 15 Water stream
- [0028] 17 Cooled and diluted MEG water stream
- [0029] 19 Precipitating means
- [0030] 21 Acidifying means
- [0031] 23 Acetate-rich overhead stream
- [0032] 25 Condensed acetate-rich overhead stream
- [0033] 27 Calcium carbonates bottoms stream
- [0034] 29 Filtered calcium carbonates bottoms stream

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0035] A system and process made and practiced according to this invention allows a target salt (in this case acetate) to accumulate in a reaction vessel and then removes the acetate from a concentrated liquor within the reaction vessel, thereby keeping vessel size and inventory to a minimum.

[0036] Referring to the drawings and first to FIGS. 1A and B, a system 10 for removing organic carboxylates like acetates from a MEG water stream includes a reaction vessel 11 as part of the MEG loop of a MEG reclamation and regeneration package. The MEG reclamation unit (not shown) is typically operated at a temperature in a range of about 120°-140° C. and at sub-atmospheric pressure (about 0.1-0.3 bara). The recycle loop within the reclamation unit is operated at elevated pressure (about 4 bar). The reaction vessel 11 is closely coupled to the recycle loop of the package.

[0037] The incoming carboxylate-rich MEG stream 13 is typically at 80-90 wt % MEG and high pH (>9.5). The incoming MEG stream 13 is cooled and diluted with water 15 to yield a cooled and diluted MEG water stream 17 which enters and resides within reaction vessel 11 as a MEG water mixture. The cooled and diluted MEG stream 17 is preferably at a temperature of about 80-100° C. and 50 wt % MEG.

[0038] The reaction vessel 11 can be switched between a calcium removal mode (high pH, atmospheric pressure) and an acetate removal mode (low pH, sub-ambient pressure). The frequency of calcium removal cycles and acetate removal

cycles can be varied to control the levels of calcium and organic acids in the MEG loop depending on the composition of the MEG feed entering the MEG regeneration package.

[0039] When reaction vessel 11 is in a calcium removal mode or cycle, the vessel 11 operates at atmospheric pressure and removes calcium and other divalent cations from the incoming MEG water stream by elevating pH. Precipitating means 19 such as sodium or potassium carbonate or sodium or potassium hydroxide are introduced to the reaction vessel 11. Salts residing in the MEG water mixture—such as calcium chloride and, commonly, lesser amounts of other divalent salts like magnesium, barium and strontium chlorides—react with the precipitant agent and precipitate out of the MEG water mixture as solid crystals. The solid crystals are removed as a bottom stream 27.

[0040] When reaction vessel 11 is in an acetate removal mode, the vessel 11 operates under a vacuum (preferably in a range of about 0.1-0.3 bar) and removes carboxylates by lowering pH (preferably in a range of about 3.5-5.5). The stream 17 is acidified within the reaction vessel 11 using acidifying means 21 such as hydrochloric acid (e.g., 30 w % HCl in water) to achieve a pH in a range of about 3.5-5.5. The pressure in reaction vessel 11 is then reduced to 0.1-0.3 bar and acetates are evolved along with water, some carbon dioxide and some MEG. Means well known in the art are employed to remove the acetic-rich overhead stream 23 from the vessel 11.

[0041] The composition of the overhead stream 23 from the reaction vessel 11 is primarily a function of temperature and pressure (see FIGS. 3 & 4). Ideally, the overhead stream 23 contains the maximum quantity of acetic acid and a minimum quantity of MEG. The results reported below in FIGS. 3 & 4 can be applied to determine an optimum initial pH, temperature and pressure regime whereby the maximum yield of acetic acid is combined with a reduced yield of MEG in the stream 23.

[0042] In the system of FIG. 1A, the overhead stream 23 is condensed and the condensed stream 25 (low pH<3) may be routed to water treatment equipment or neutralized in a knock-out drum. In the system of FIG. 1B, the overhead stream 23 is condensed and the condensed stream 25 is routed directly to the distillation column where it is mixed with a MEG-water overhead stream from the reclaimer. The acetates partition between the aqueous phase (produced water) and the lean MEG phase. Routine experimentation can be used to determine the partitioning of acetic acid between water and lean MEG to determine the preferred routing of acetic acid-MEG-water stream from the acetate removal process.

[0043] Referring now to FIG. 2, separate vessels 31, 33 are used for calcium removal and carboxylates removal, respectively. During simultaneous production of calcium and carboxylic acids the calcium (and other divalent cations) are precipitated in vessel 31 at approximately 80° C. and 1.0 bar by raising the pH using precipitating means 19 and filtering the resulting calcium carbonates stream 27. The centrate/filtrate stream 29 is acidified using acidifying means 21 at 80-100° C. and at sub-atmospheric pressure (about 0.1 to 0.3 bar) in vessel 33 to remove the organic acids and water as an overhead stream 23. The calcium-free and organic acid-free MEG can be returned to the production process.

[0044] However, the same calcium removal process as that described for vessel 11 (see FIGS. 1A and 1B) is employed within vessel 31, as is the same acetate removal process for vessel 33.

Simulated Results

[0045] Simulated results were obtained employing OLI STREAM ANALYZER™ software (OLI Systems, Inc., Cedar Knolls, N.J. A model feed representing a high pH, 50% MEG solution with 3 wt % dissolved sodium acetate and excess sodium hydroxide and sodium bicarbonate was reacted with hydrochloric acid (as HCl) to reduce the pH to 3.5-5.5. The temperature of the solution and the reaction pressure were adjusted and the composition of the predicted overhead stream was calculated. The acetate content of the reaction mixture was fixed at 30 kg sodium acetate.

[0046] FIG. 3 shows acetate removed as a function of temperature and pressure. The highest levels of acetate are removed at elevated temperature and low pressure. FIG. 4 shows that MEG losses are highest at elevated temperature and reduced pressure. Therefore, an optimum temperature/pressure condition is required to maximize acetate removal while reducing or minimizing MEG losses to acceptable levels.

[0047] FIG. 5 plots acetate removal against MEG loss for three temperatures (80, 90 and 100° C.). Lower temperatures and low pressure are preferred to maximize acetate removal. FIG. 6 plots MEG loss as a function of acetate rejected from the MEG Loop. Using simple blowdown, 950 kg of MEG will be ejected with every 30 kg of sodium acetate (44 kg MEG per kg of acetate).

[0048] FIG. 7 plots acetate removal as a function of temperature and pressure for three initial pH conditions: 3.5, 4.5, 5.5). Acetate removal efficiency is increased as the starting solution pH is reduced. For a starting pH of 3.5, 89% of the acetate in the reaction vessel is removed in the overhead stream at 100° C. and 0.1 bara compared to 48.3% for an initial solution pH of 4.5 and 8.8% for an initial solution pH of 5.5.

[0049] Using the acidification/vaporization scheme practiced according to this invention can significantly reduce this MEG loss. At 80° C. and 0.15 bar, the simulation software predicts 73.8 kg of MEG in the overhead stream along with 8.75 kg of acetic acid (8.58 kg MEG per kg acetate). At 80° C. and 0.15 bar only 40% of the acetate is removed per batch with the acetate remaining in the liquid phase being routed back to the reclaiming for re-processing.

Experimental Results

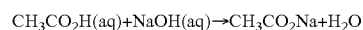
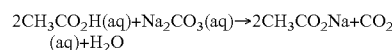
[0050] The apparatus used in the test is shown in FIG. 8. A double skinned 5L glass reactor vessel **101**—fitted with a pH probe **102** (a Hamilton Polilyte Plus ARC 425), a dissolved oxygen probe **103** (Hamilton Oxygold G ARC 425), a RedOx probe **104** (Hamilton Polilyte Plus ORP ARC 425), a electrical conductivity probe **105** (Hamilton Conducell 4USF ARC PG425), and a stirrer **106**—was heated by means of a hot oil circulator bath and heater **107**. The reactor vessel **101** was connected to a condenser **108** and a distillate collection vessel **109**. The reactor vessel **101**, condenser **108**, and distillate collection vessel **109** were evacuated using a vacuum pump **110**, a pressure control valve **111** and a pressure transducer **112**. An oxygen-free nitrogen supply **113** was connected to the reactor vessel **101** to provide gas blanketing function.

[0051] A MEG-water-acetic acid solution was prepared in the reactor vessel **101** by adding 93 g of acetic acid (99-100% ex Sigma-Aldrich) to a mixture of monoethyleneglycol (1,737 g, Uninhibited CoolFlow MEG ex Hydra Technologies Limited, Fforestfach, Swansea SA5 4AJ, UK) and de-

ionised water (1,710 g). The pH of this solution was measured as 2.61 at 23° C. The acetate content of the solution was calculated as 2.58 wt %.

[0052] The pH of the test mixture was elevated to 10.2 by addition of 100 g of anhydrous sodium carbonate (ex Sigma-Aldrich) and 1 g of sodium hydroxide pellets (ex Sigma-Aldrich). At this high pH, the acetic acid is converted to sodium acetate which is non-volatile and which would not be removed from the reaction vessel by elevating the temperature and reducing the operating pressure.

[0053] In conventional MEG loops the organic acids in the formation water and condensed water are usually present as the sodium salt:



[0054] In order to effectively remove the dissolved acetate the pH of the solution was reduced from 10.2 to 3.5 by addition of 70 g of 37 wt % hydrochloric acid solution (Sigma-Aldrich). The pressure in the reactor vessel **101** was reduced to 0.15 barA and the temperature was raised to 80° C. The reactor vessel **101** was held at 0.15 barA/80° C. for approximately 3.3 hours.

[0055] The reactor vessel **101** was allowed to cool and the residue in the vessel **101** and the distillate collected in the MEG-water collection vessel **109** were weighed and analyzed. The results are shown in Table 1 below.

[0056] Table 1 shows that the MEG level in the reactor vessel **101** rises from 53.6 wt % to 93.7 wt % as the water component is removed in preference to the less volatile MEG at low pressure and elevated temperatures. Table 1 also shows that the acetate component in the reactor vessel **101** is also removed in preference to the MEG component and that the acetate content of the distillate (predominantly water) is higher (29,093 mg/L) than in the original reactor mixture (measured at 20,994 mg/L, calculated from starting composition at 25,396 mg/L).

TABLE 1

Analysis of Reactor and Distillate Vessel Contents					
	Inven- tory (g)	MEG by GC [Note 1] (wt %)	Estimated Density [Note 2] (g/L)	Acetate by IC [Note 3] (mg/L)	Acetate Calculated [Note 4] (g)
Reactor @ t = 0	3,781	53.6	1,065	20,964	75.49
Reactor @ t = 3.33 hrs	2,079	93.7	1,109	17,326	32.75
Distillate @ t = 3.33 hrs	1,580	6.7	1,006	29,093	45.69

[Note 1]:

MEG content measured by Gas Chromatography

[Note 2]:

Density estimated as a function of MEG:water:dissolved salt at 20° C.

[Note 3]:

Acetate content measured using Ion Chromatography

[Note 4]:

Acetate(g) = Acetate (mg/L) × Inventory (g)/Density (g/L)

[0057] Based on a total final acetate measurement of 78.44 g (32.75 g remaining in the reactor vessel **101** plus 45.69 g collected in the distillate), it is calculated that 58.3% in the acetate present as sodium acetate in the reactor vessel at

pH=10.2 was removed as acetic acid by reducing pH to 3.5 then reducing the pressure to 0.15-0.17 barA and raising the temperature to 80° C.

[0058] Experimental results and predicted values from the OLI STREAM ANALYZER™ are shown in Table 2, below. The OLI model predicts 70% removal of acetate at 80oC/1.5 barA.

TABLE 2

Experimental acetate removal compared with simulated results				
	pH	TEMP	PRESSURE	ACETATE
	—	deg C.	barA	REMOVED %
OLI Prediction	3.50	80	0.15	70.0
Experimental	3.34-3.78	66-80	0.14-0.17	58.3

Summary

[0059] The above preferred embodiments of a system and method made and practice according to this invention are not all possible embodiments. The claims listed below define the scope of the invention, including equivalents to the elements listed.

What is claimed:

1. A system for removal of organic carboxylates from a mono ethylene glycol (“MEG”) stream, the system comprising:

- a reaction vessel;
- means for cooling and diluting the MEG stream being routed to the reaction vessel;
- means for acidifying the cooled and diluted MEG stream during its residence time within the reaction vessel; and
- means for removing an acetic-rich overhead stream from the reaction vessel;

wherein the acidification of the cooled and diluted MEG stream occurs under a vacuum.

2. A system according to claim 1 wherein the reaction vessel includes an acetate removal mode and a calcium removal mode, the reaction vessel including means for alternating between the above mentioned modes, the pressure of the reaction vessel being greater during the calcium removal mode than during the acetate removal mode.

3. A system according to claim 1 wherein the reaction vessel is located downstream of a calcium removal vessel within a MEG recycle loop and receives a bottom stream from the calcium removal vessel.

4. A system according to claim 1 further comprising means for raising the alkalinity of the cooled and diluted MEG stream during its residence time within the treatment vessel.

5. A system according to claim 4 wherein the raising alkalinity means is selected from the group consisting of sodium carbonate, potassium carbonate, sodium hydroxide, and potassium hydroxide.

6. A system according to claim 1 further comprising means for removing a calcium-rich bottom stream from the reaction vessel.

7. A system according to claim 1 wherein the reaction vessel is at a pressure in a range of 0.1 to 0.3 bar.

8. A system according to claim 1 wherein the acidifying means results in the cooled and diluted MEG stream during its residence time within the reaction vessel having a pH in a range of 3.5 to 5.5.

9. A system according to claim 1 wherein the acidifying means is hydrochloric acid.

10. A system according to claim 1 wherein the cooled and diluted MEG stream is below 80 wt % MEG.

11. A system according to claim 10 wherein the cooled and diluted MEG stream is about 50 wt % MEG

12. A system according to claim 1 wherein the cooled and diluted MEG stream is at a temperature in a range of 80° to 100° C.

* * * * *