[제 2차 정보제공]

Electrolyte Module을 사용한 MEG Regeneration Unit에 대한 전체공정에 대한 전산모사

2016년 7월 21일(목)

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조 정 호

목 차

1 MEG Regeneration Unit의 기초

What is MEG?: (Introduction)

➢ What is MEG?

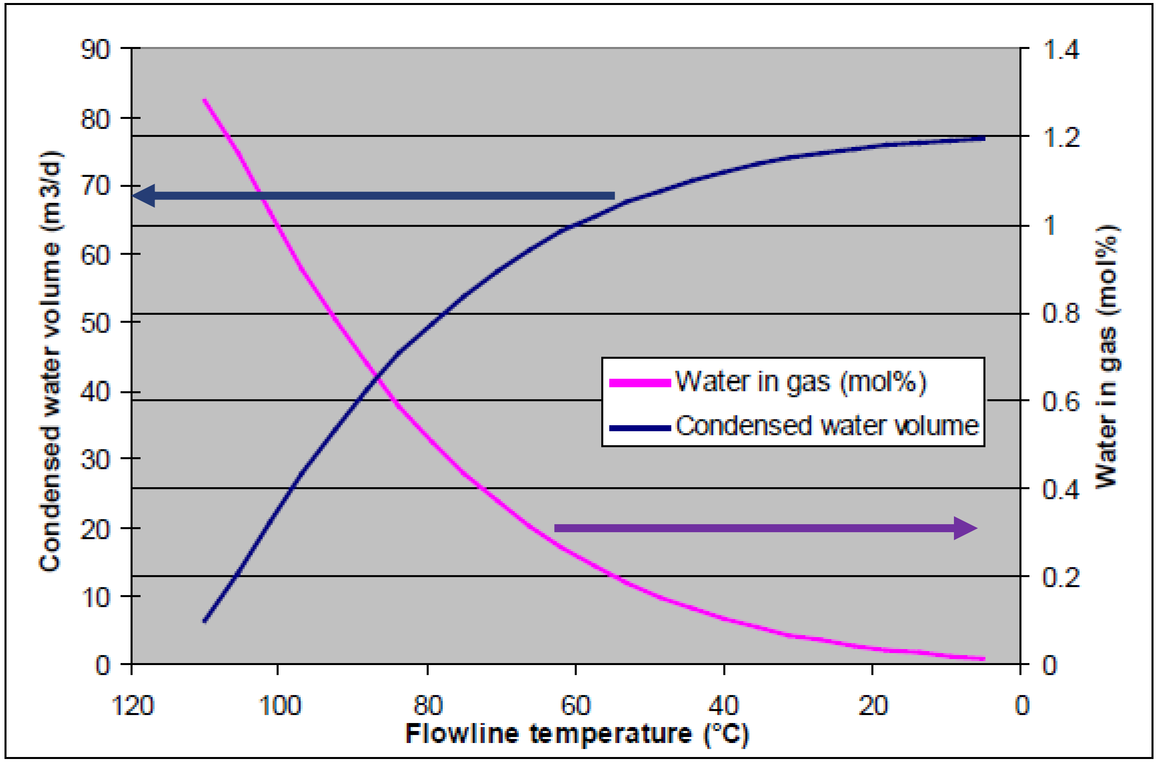
- Mono ethylene glycol
- A thermodynamic inhibitor for prevention of hydrates
- Risk of hydrate formation
  - Natural Gas
  - Free Water present
  - Low T – High P

MEG is preferred hydrate inhibitor for medium to long multiphase flow lines

Water Condensation:

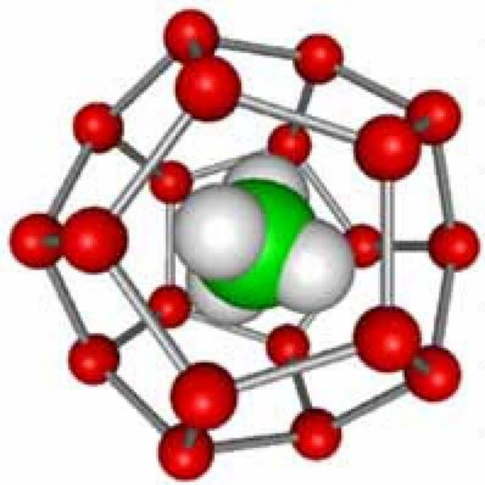
- Water in Gas:
  - Water condenses at low temperature.
  - Water condenses at high pressure.
- At 5^{o}C:
  - 95~99% of water has condensed.

Vegas example:	
Gas	7 Sm^3/day
Flowrate	10 m^3/day
Pressure	150~80 bar
Temperature	110~5^{o}C



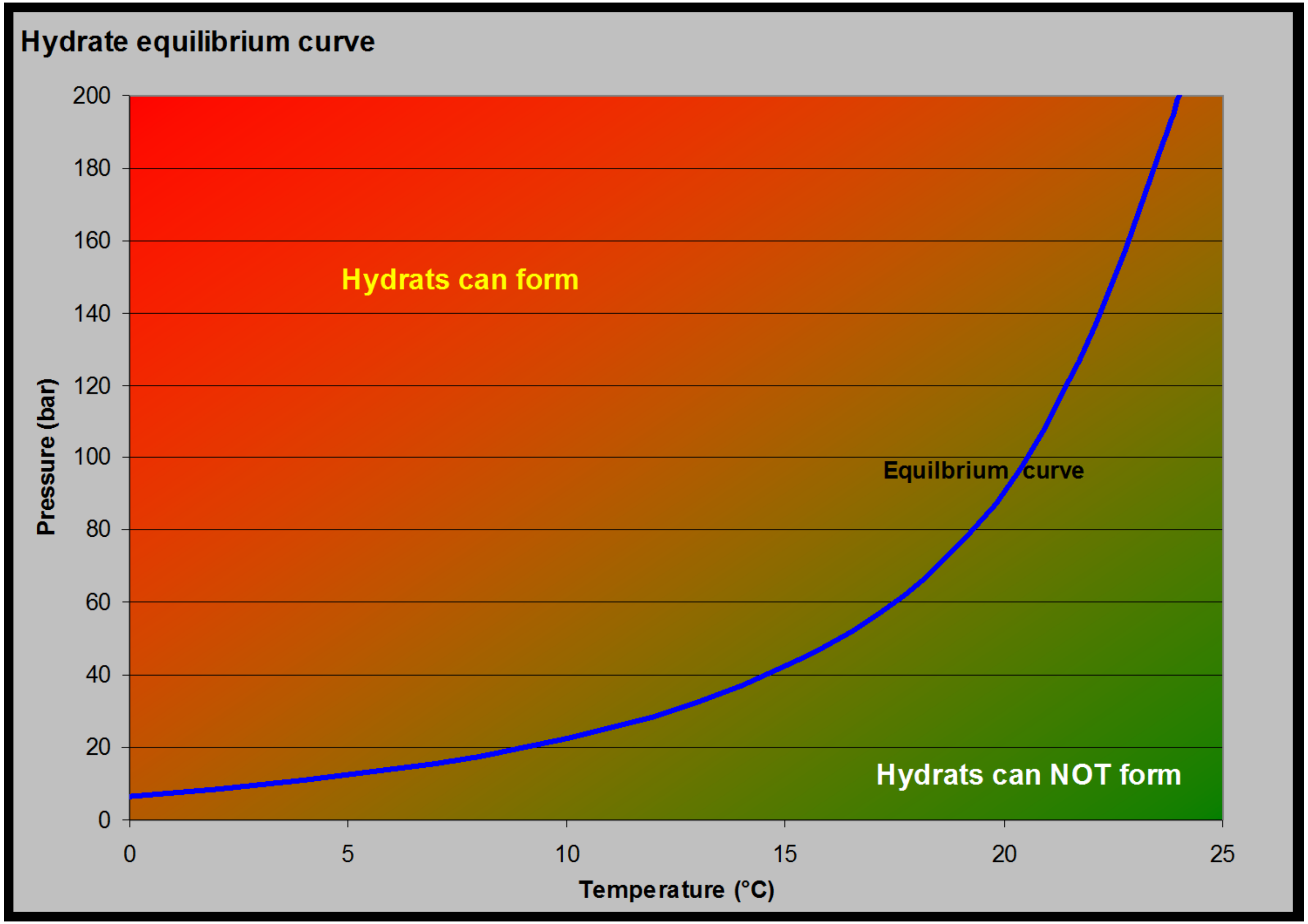
Hydrates:

- Hydrate is water in a solid structure with small gas molecules in cavities.
  - Much like snow/ice
    - Water freezes at 0°C, what about hydrates?
- Requirements for hydrate formation:
  - Low temperature
  - High pressure
  - Free water
  - Small gas molecules (N_2, CO_2, CH_4, C2, and C3, etc….)



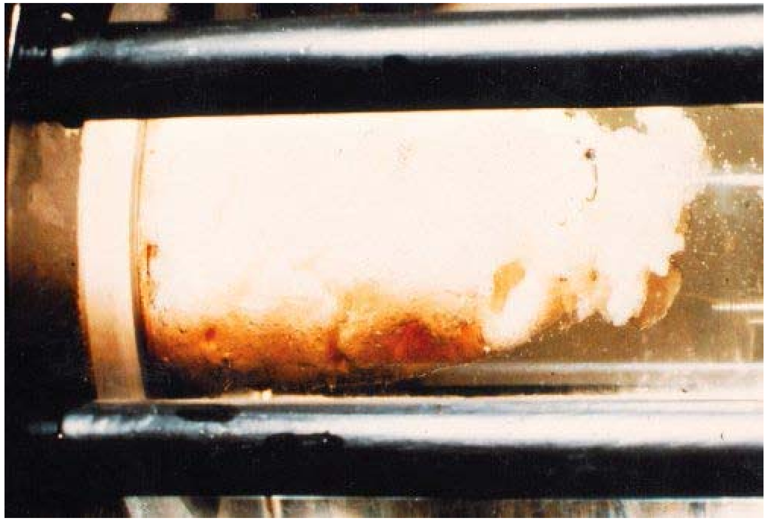
Hydrate phase diagram:

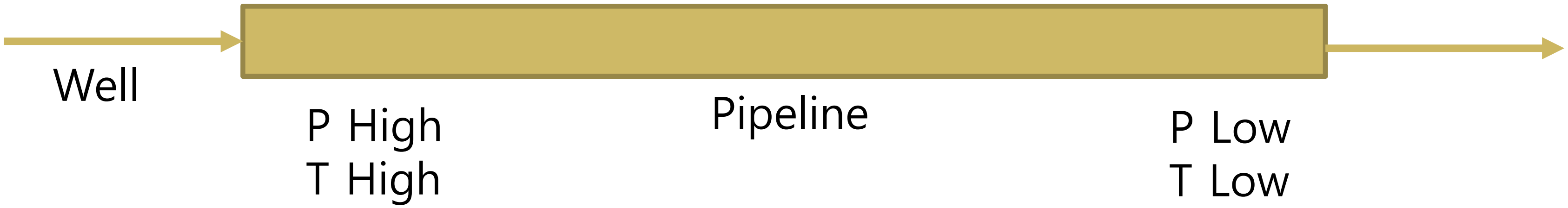
- Water + Gas = Hydrate



Water in Pipeline: Problems

- Water condensates
- Low T, High P and Free Water
  - Hydrate formation

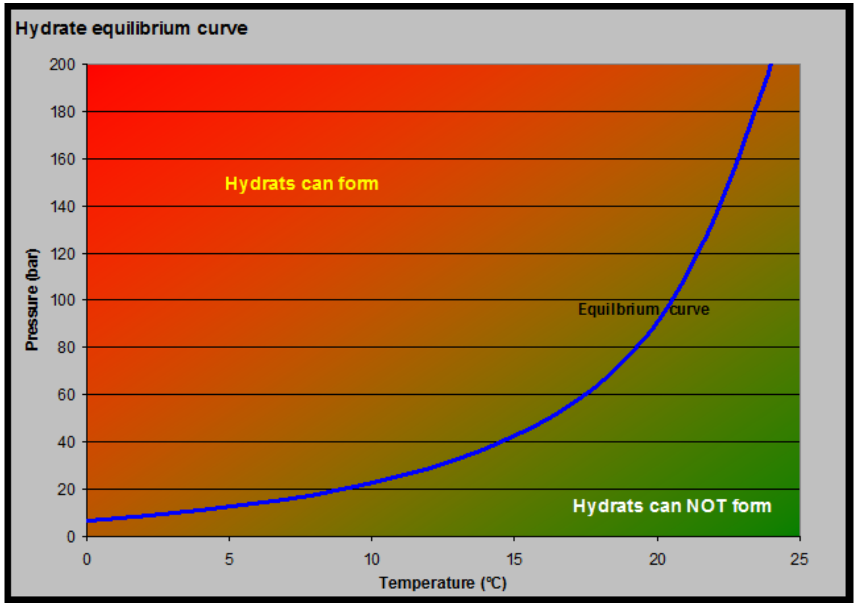




Hydrate Prevention:

- How to avoid hydrate formation
  - Keep temperature high
  - Keep pressure low
  - Dilute water

- Dilute water means separating water molecules and make it more difficult for them to react.



Hydrate Prevention:

- How to avoid hydrate formation
  - ~~Keep temperature high~~
  - ~~Keep pressure low~~
  - Dilute water

$$Water + Gas \leftrightarrow Hydrate$$

- Dilute water means separating water molecules and make it more difficult for them to react.

- We need to add something:
  - Salts: Words
  - Alcohol: Works (Example: methanol)
  - Glycol: Works (Example: MEG and TEG)

Hydrate Prevention:

- Hydrate formation reaction (simplified)
- Chemical potential
  - If $\Delta\mu < 0$ reaction will go spontaneously.
- Chemical potential of gas is mainly given by pressure and temperature and can normally not be changed.
- Chemical potential of hydrate can not be changed.
- Chemical potential of water

$$\mu_{H_2O}^{l} = \mu_{H_2O}^{\circ} + RT\ln a_{H_2O} = \mu_{H_2O}^{\circ} + RT\ln \gamma_{H_2O} x_{H_2O}$$

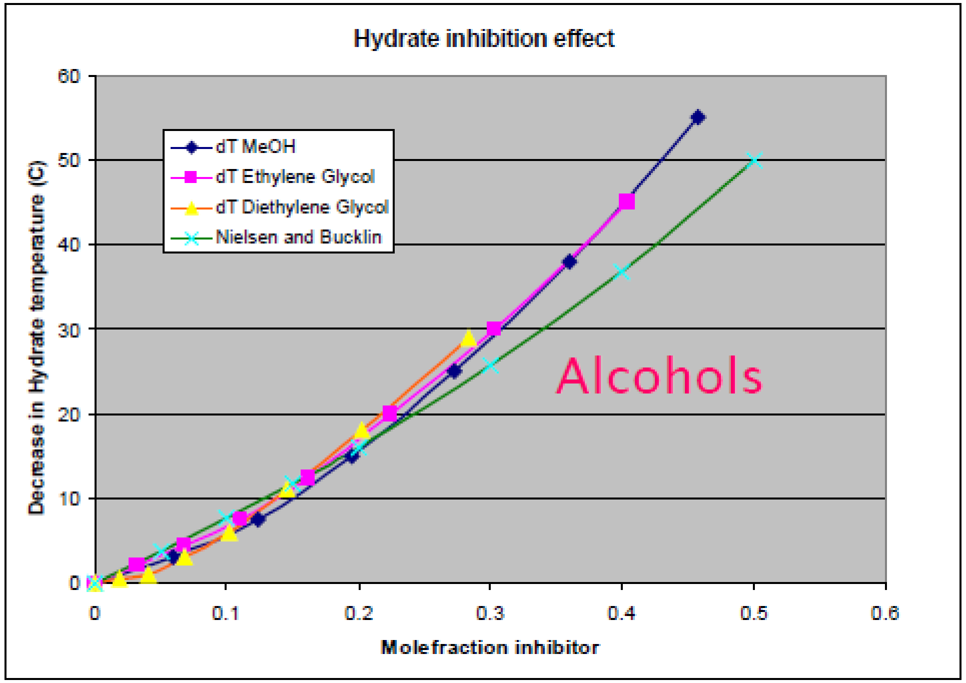
  - If we dilute water to get x_{H2O} lower, the chemical potential of water will be lower and the reaction is shifted to the left → "No Hydrates"

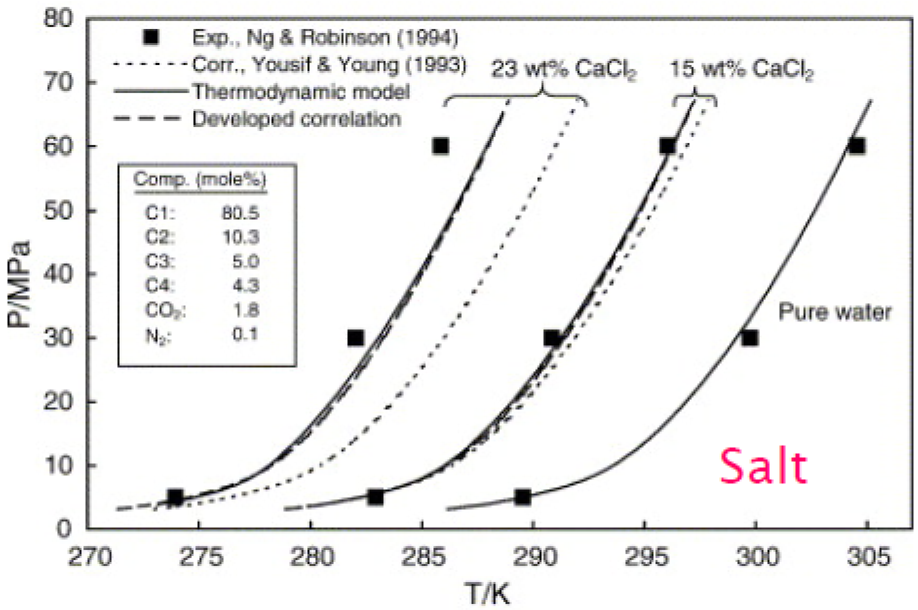
$$H_2O(l) + gas \leftrightarrow H_2O(hyd)$$

$$\Delta\mu = \cancel{\mu_{H_2O}^{hyd}} - \mu_{H_2O}^{l} - \cancel{\mu_{gas}}$$

Hydrate Prevention: Diluting the Water

- Hydrates can be prevented with "anything" that reduces the mole fraction of water.

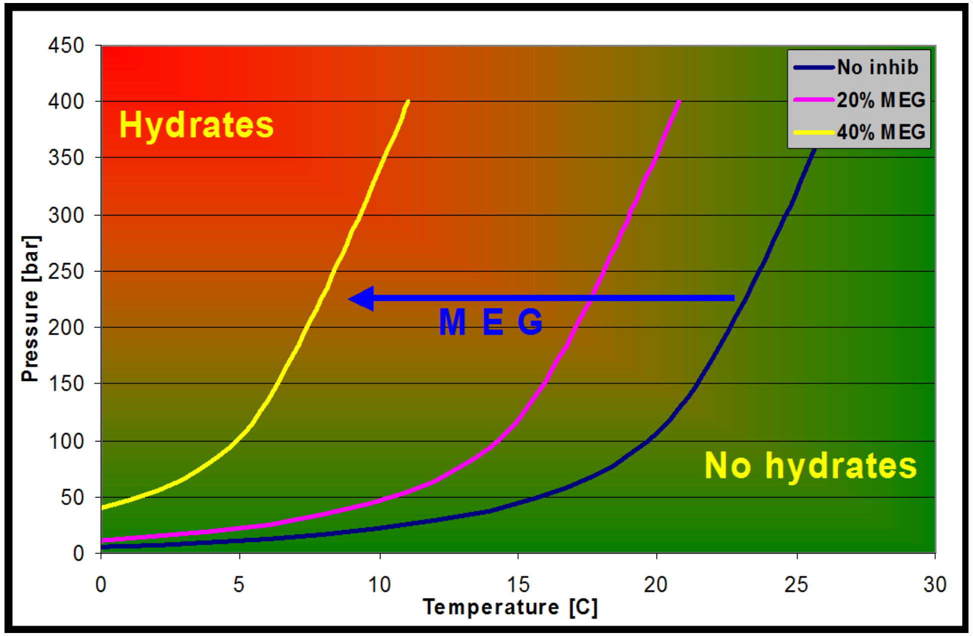




$$\Delta T = -72 \ln\left(1 - x_{Inhib}\right)$$

Thermodynamic Hydrate Inhibitors:

- MEG (Mono Ethylene Glycol) inhibits hydrate formation.
  - Freezing point lowered

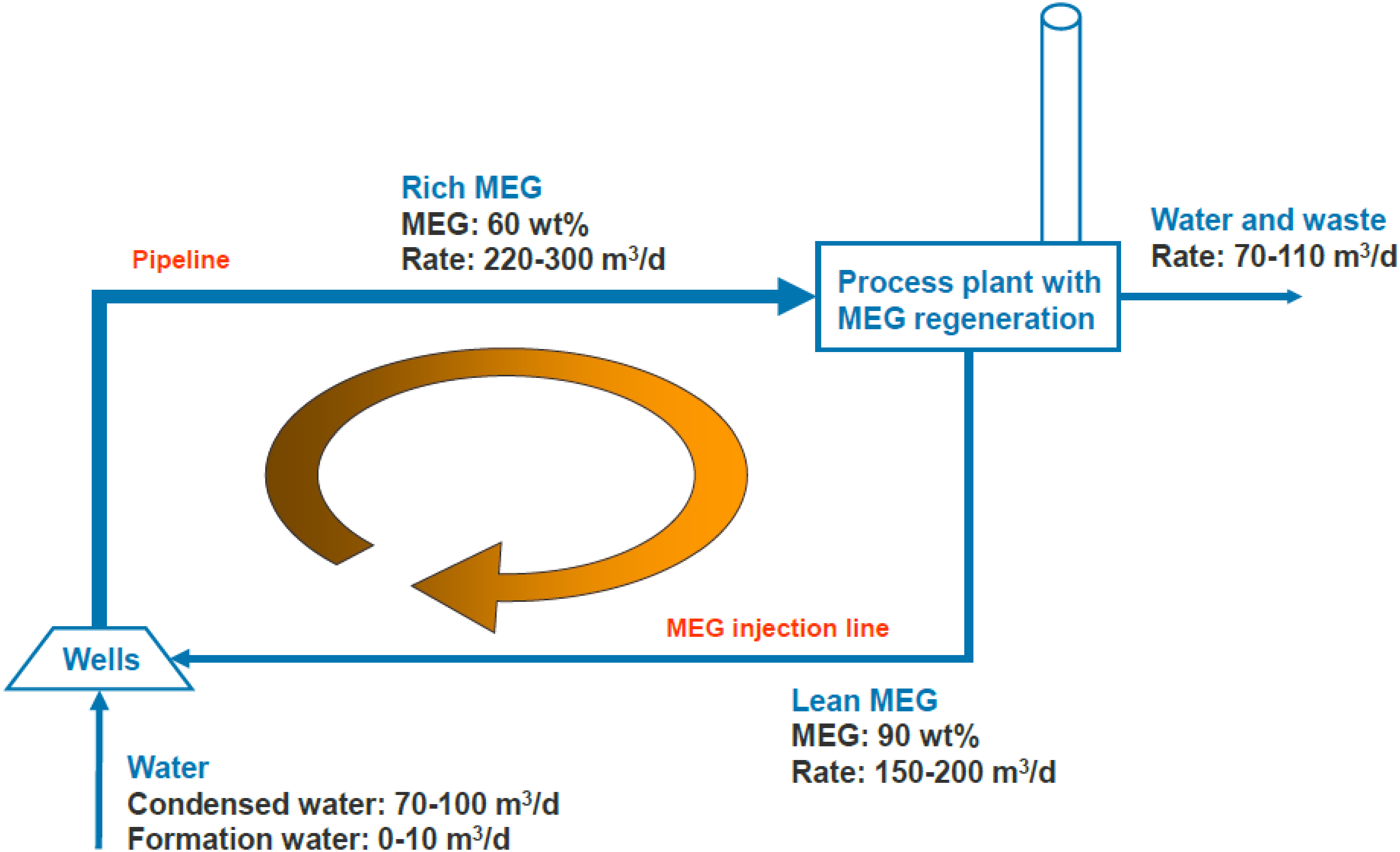


Inhibitor	Water	MeOH	MEG	TEG
Density	1.0	0.79	1.11	1.12
Viscosity (cP @25°C)	0.89	0.5	18	36
Freezing Point	0°C	-94°C	-13°C	-5°C
Boiling Point	100°C	65°C	198°C	278°C

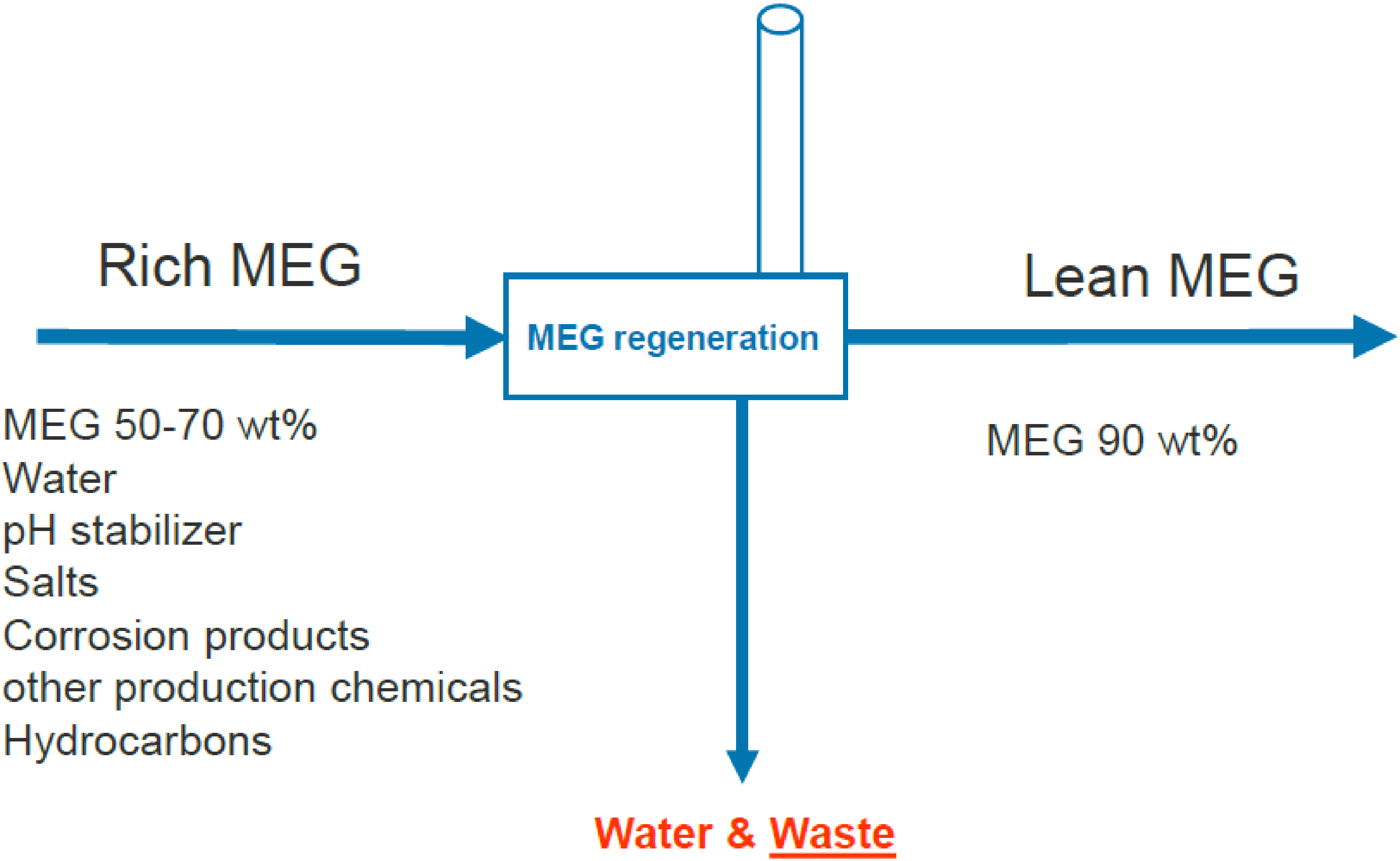
What we have learned:

- Hydrates
  - An ice/snow like solid
  - Forms at low temperature and high pressure
    - Need water (liquid or solid) + small molecules (e.g. N_2, CO_2, C1 & C2)
  - Reversible reaction
    - For example, it can be removed by
- Hydrate formation can be inhibited by:
  - Anything that dilutes water i.e. is mixable with water
    - Salt
    - Alcohol
  - Works because water molecules are separated
- MEG:
  - Used as anti-freezing agent in cars
  - Much used as hydrate inhibitor in oil industry

A Typical MEG Loop:

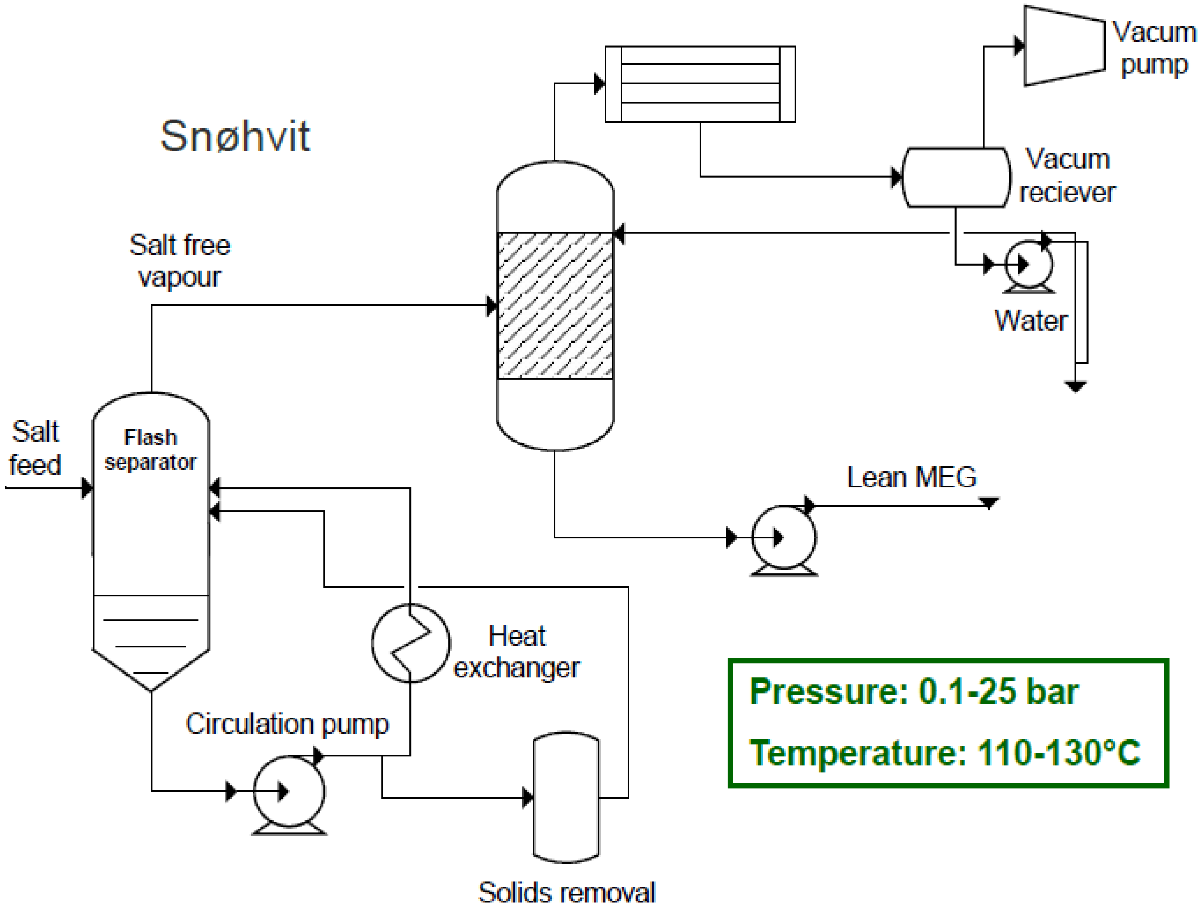


MEG Regeneration:



Salt Removal:

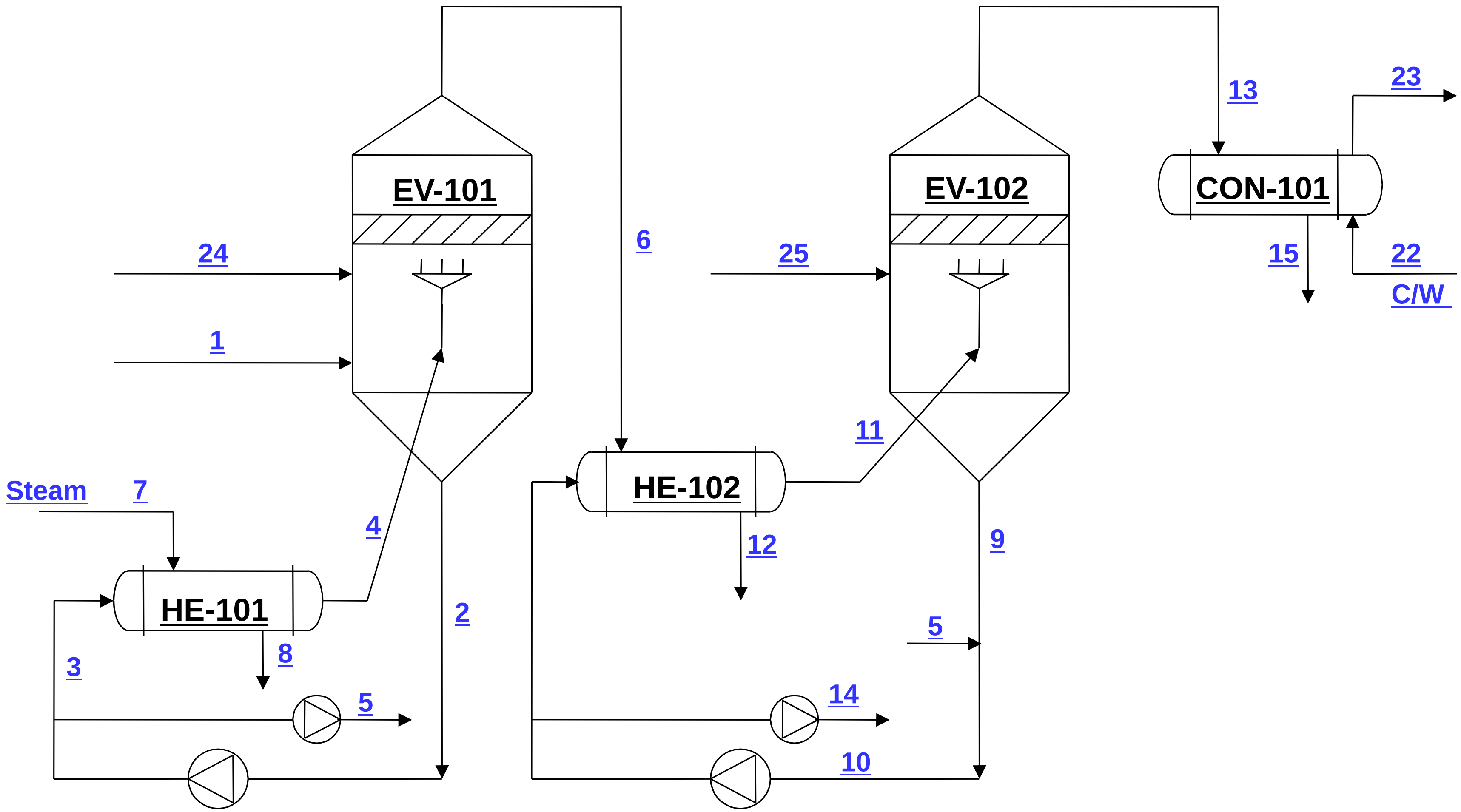
- Need to remove something!
  - Dissolved salt/chemicals etc.
  - Evaporate all water+MEG



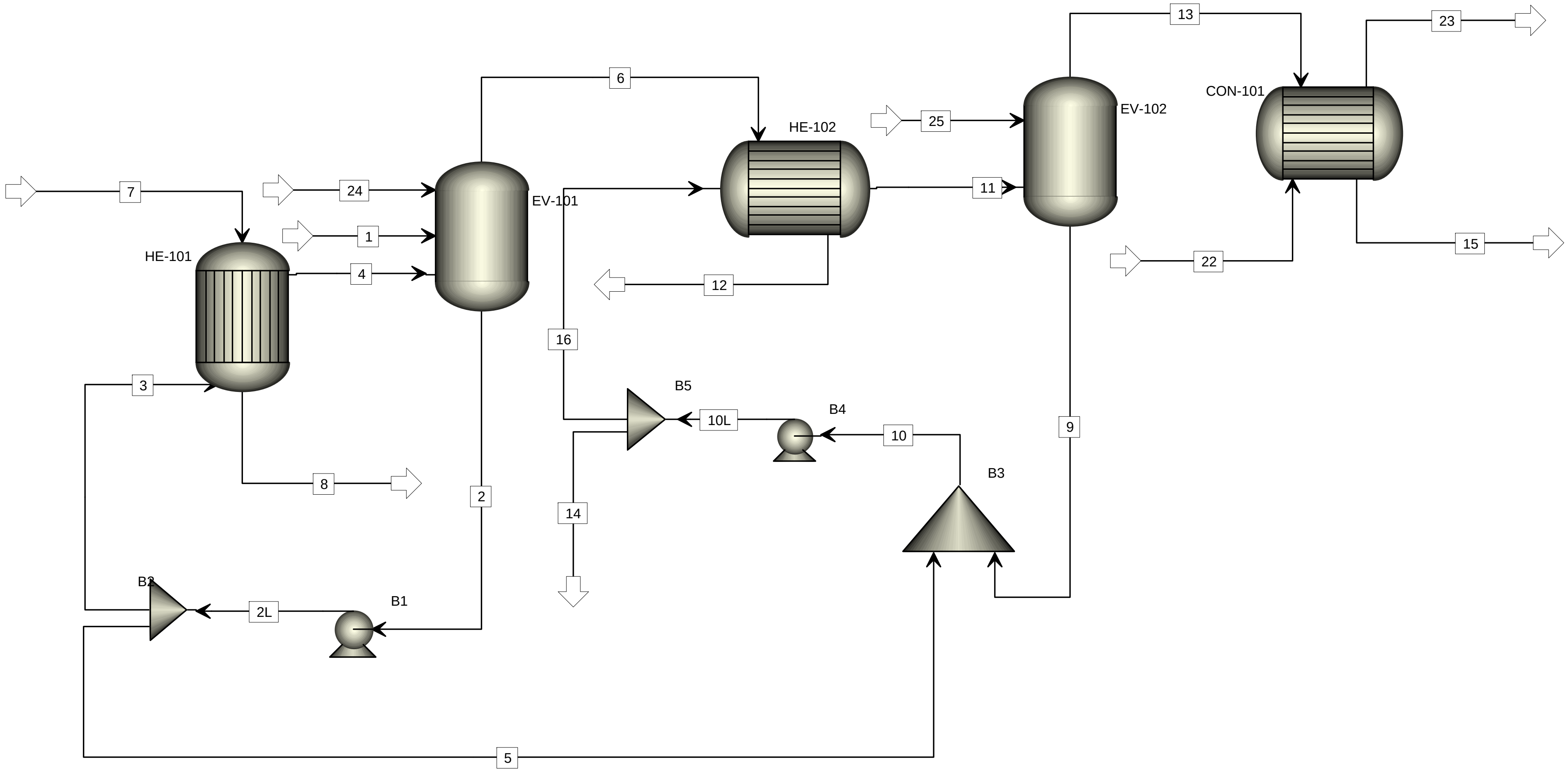
Pressure: 0.1-25 bar

Temperature: 110-130°C

Salt Removal: 유사 프로젝트 수행 경험



Salt Removal: 유사 프로젝트 수행 경험



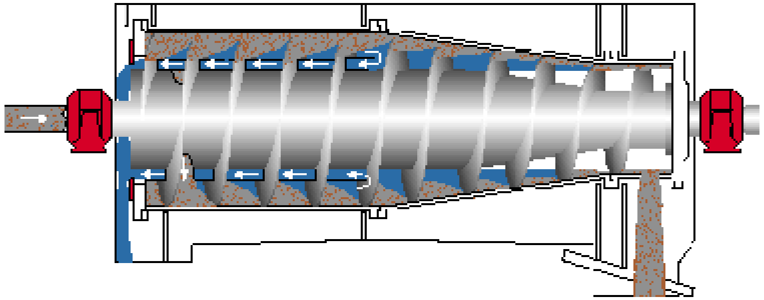
Salt Removal: 유사 프로젝트 수행 경험

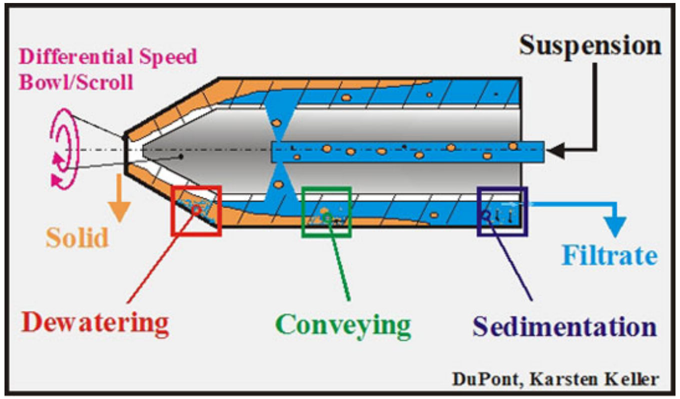
- Feedstock properties are as:

Component	Flow (Kg/hr)	(Wt %)
Water	6,103	74
Soluble Salt	1,732	21
DEG	412	5
Crystal Salt	-	0
Total	8,247	
Temp. (^oC)	45	
Press.	Atmospheric	
Density (Kg/L)	1.16	
Viscosity (cP)	9	
Specific Heat (Kcal/Kg-^oC)	0.83	

Solids Removal:

- Sediment Tanks
  - Onshore
- Centrifuges
  - Offshore

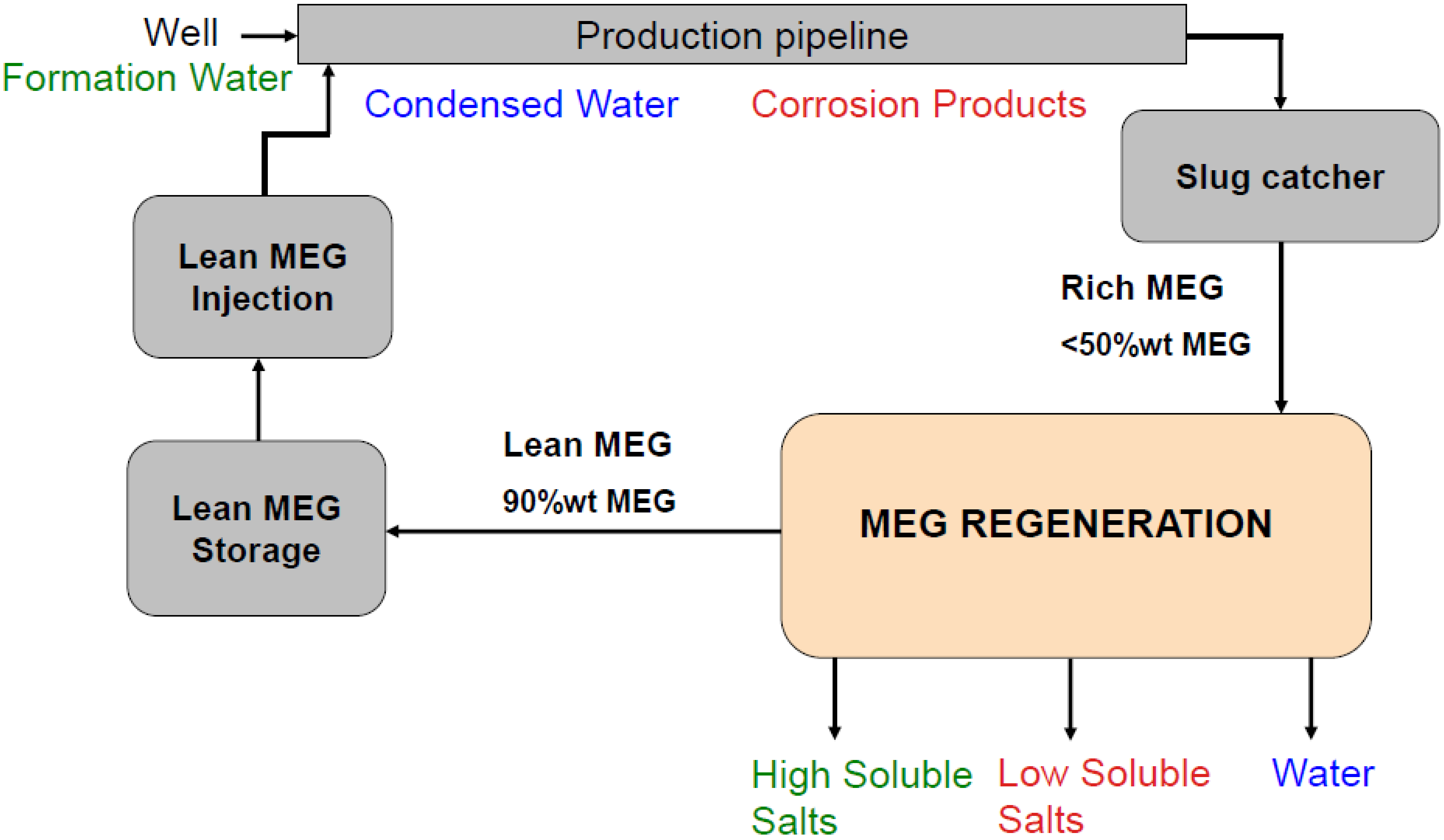




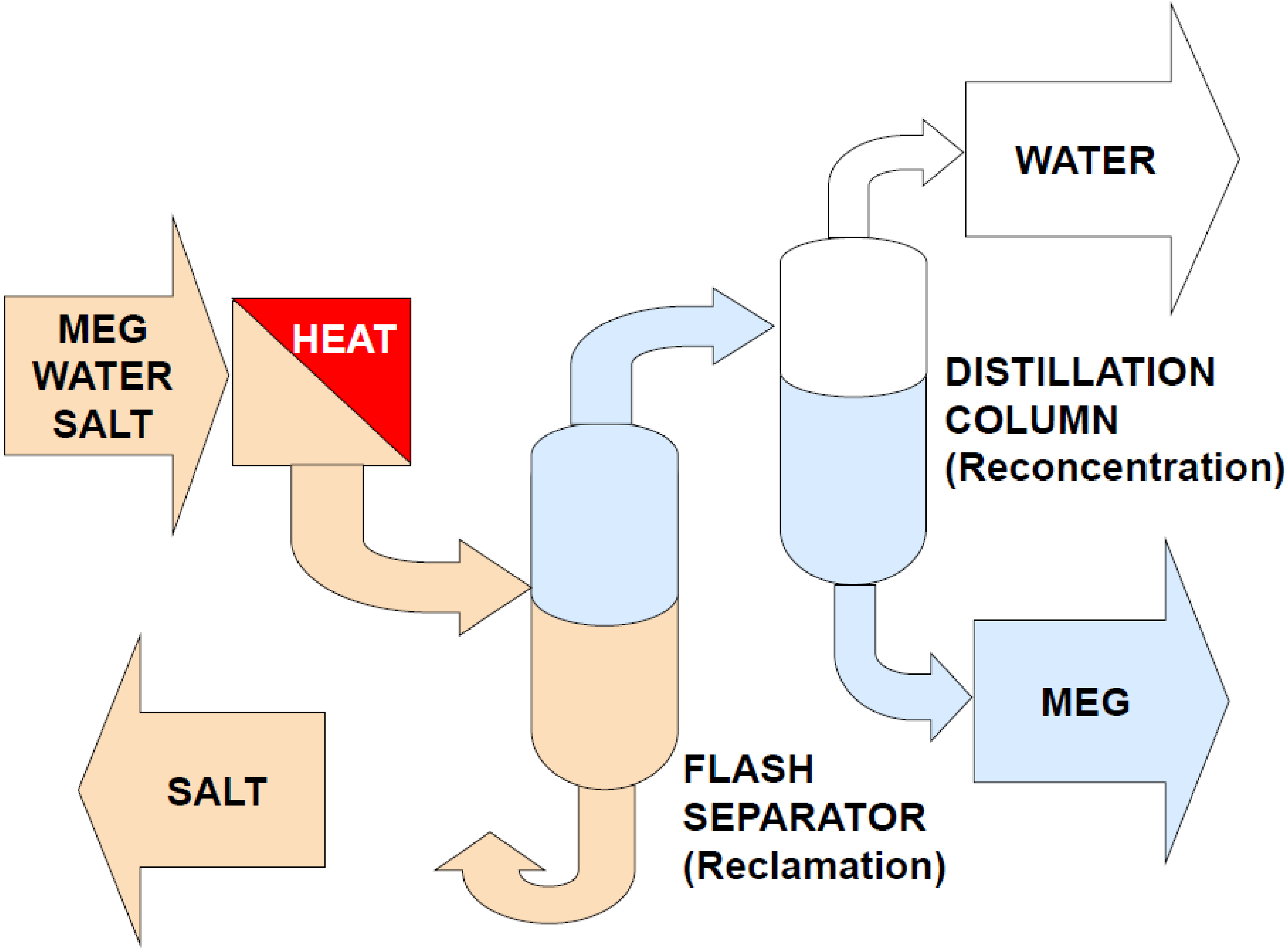
MEG Recovery:

- MEG regeneration:
  - Only water is evaporated.
  - MEG passes through the facility as liquid phase.
  - Any salts, chemicals, etc. remains in the MEG.
  - For example, MEG loop can be “polluted”.
- MEG reclamation:
  - Both water and MEG is evaporated.
  - Salts, chemicals etc. are left behind in the liquid phase.
  - For example, salts/chemicals can be removed.

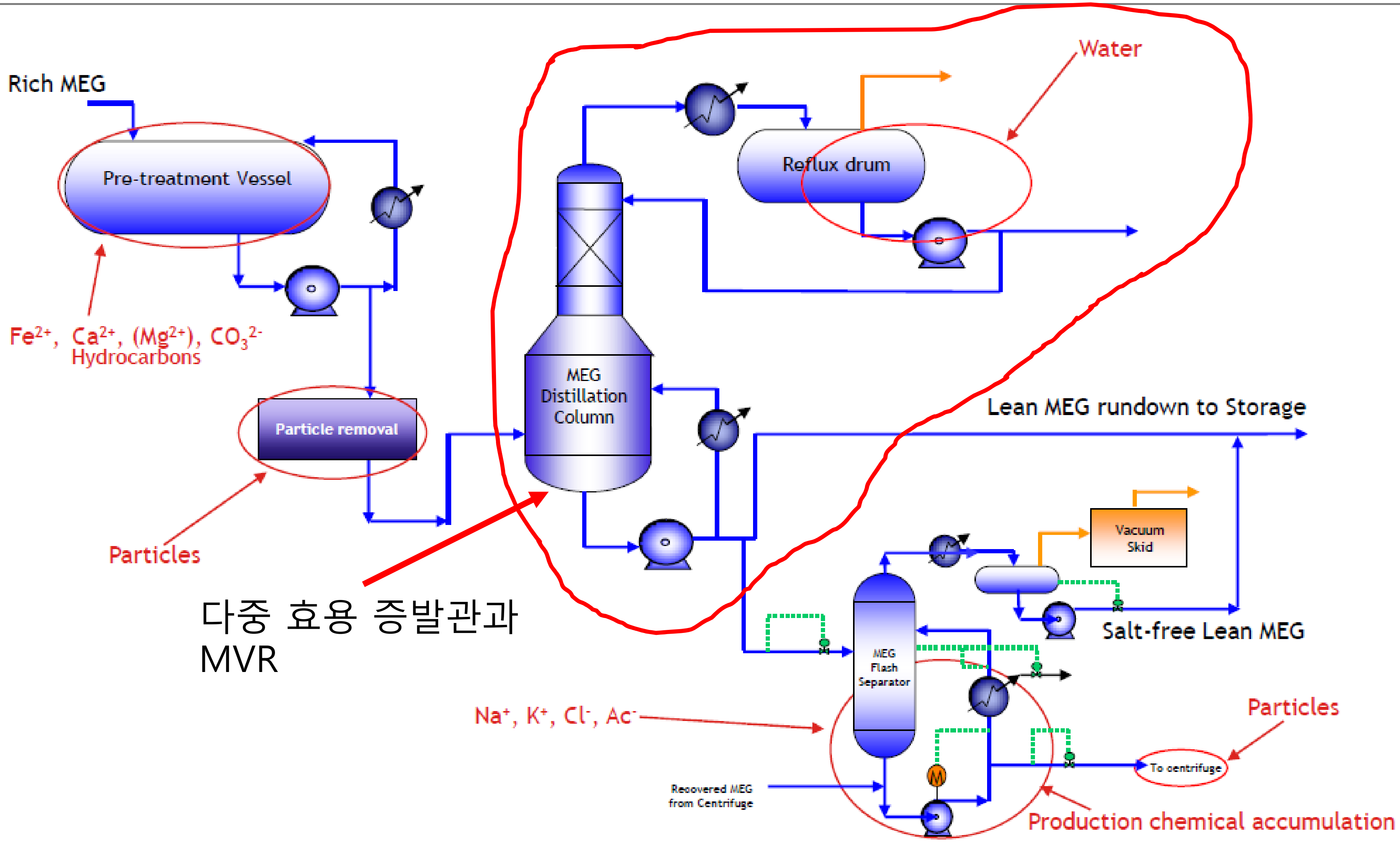
The Closed-Loop MEG Recovery System:



MEG Regeneration System Design:



MEG Regeneration System Design:



다중 효용 증발관과
MVR

The Closed-Loop MEG Recovery System:

- Impurities will accumulate and/or precipitate in a closed loop system if not taken care of:
- Main concerns:
  - Formation water
    - Sodium (Na^+) and other monovalent cations (K^+)
    - Calcium (Ca^{2+}) and other divalent cations (Mg^{2+}, Ba^{2+}, Sr^{2+},….)
    - Organic acids
  - Pipeline corrosion: (CO_2, H_2S)
    - Iron (Fe^{2+})
  - Completion fluids
    - Highly soluble salts (high density)
    - For example, $CaCl_2$, $CaBr_2$, $Ca(HCOO)_2$

The Closed-Loop MEG Recovery System:

- Formation water salt load:

Species	ppm	mM
Na^{+}	26,557	1,154.7
K^{+}	257	6.67
Ca^{2+}	1,306	32.57
Mg^{2+}	282	11.6
Ba^{2+}	5	0.04
Sr^{2+}	51	0.58
Fe^{2+}	1	0.02
Cl^{-}	42,208	1,189.0
Br^{-}	89	1.11
$SO4^{2-}$	3,629	37.76
HCO^{3-}	607	9.95

Chemistry of MEG Systems:

- Various types of salts have different properties:
- Low soluble salts (Ca^{2+}, Mg^{2+}, $CO3^{2+}$, CHO^{3-})
  - Divalent cations will easily precipitate and for scale on undesired locations at low concentration.
- High soluble salts (Na^{+}, K^{+}, Cl^{-})
  - Monovalent cations may accumulate up to > 75,000 mg/L without precipitation.
  - Precipitation by super saturation

← All salts must be removed

← Accumulation can be tolerated

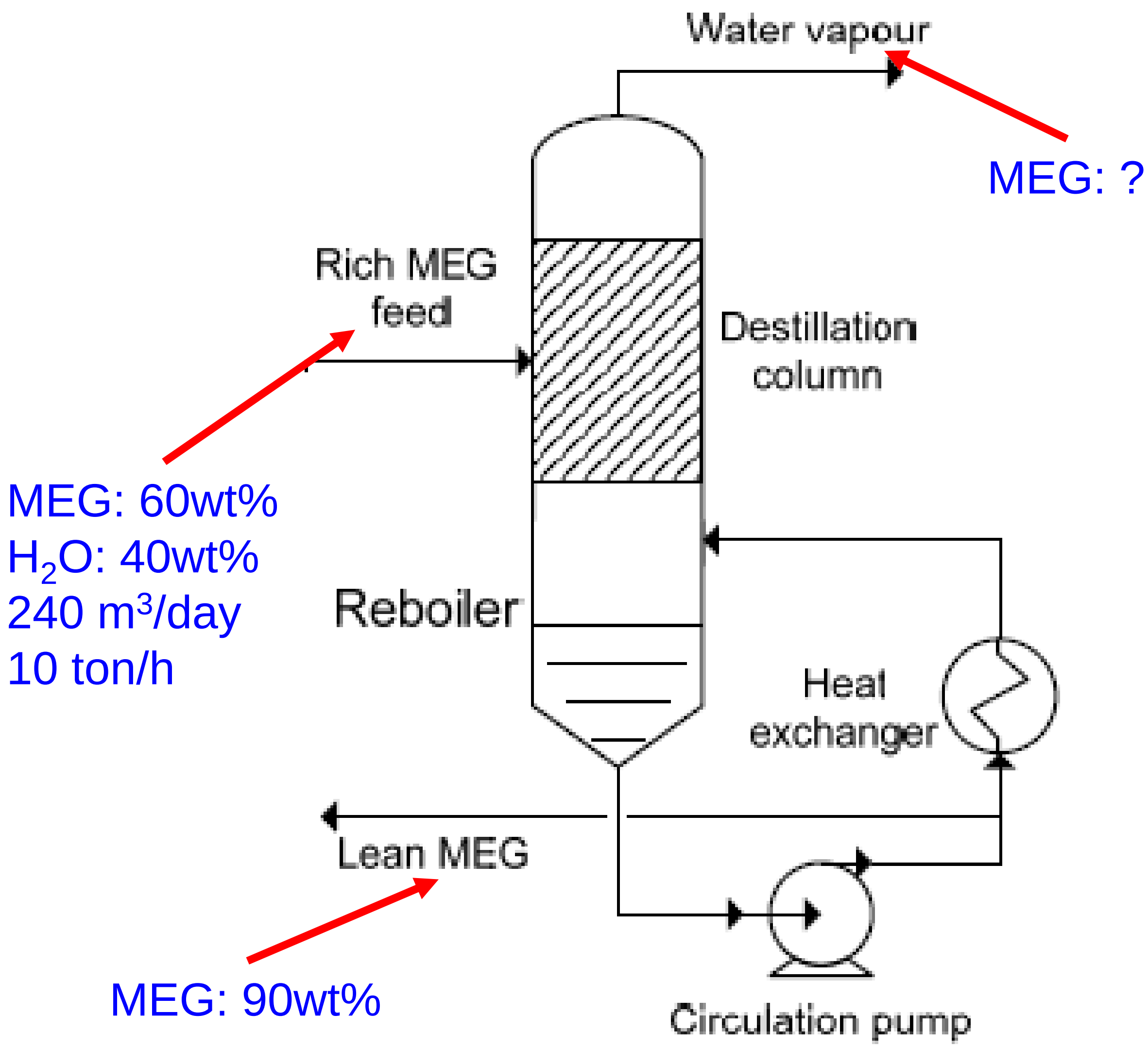
2 MEG Regeneration Unit 관련 특허조사

MEG Regeneration Unit 관련 특허조사

Patent Number	**Title**
EP 2 860 168 A1	System and process for removal of organic carboxylates from mono ethylene glycol (MEG) water streams by acidification and vaporization under vacuum.
US 20130118989A1	Process scheme to improve divalent metal salts removal from mono ethylene glycol (MEG)
US 6444095 B1	System for recovering glycol from glycol/brine streams
US 8329963 B2	Removing solids in mono-ethylene glycol reclamation
US 2016/0101403 A1	System and method for pH control of lean meg product from MEG regeneration and reclamation packages
OTC 18010	Advances in Glycol Reclamation Technology
WO 2010080038 A1	Method for regeneration and reclamation of mono ethylene glycol using a vacuum slip stream

3 Process Simulation

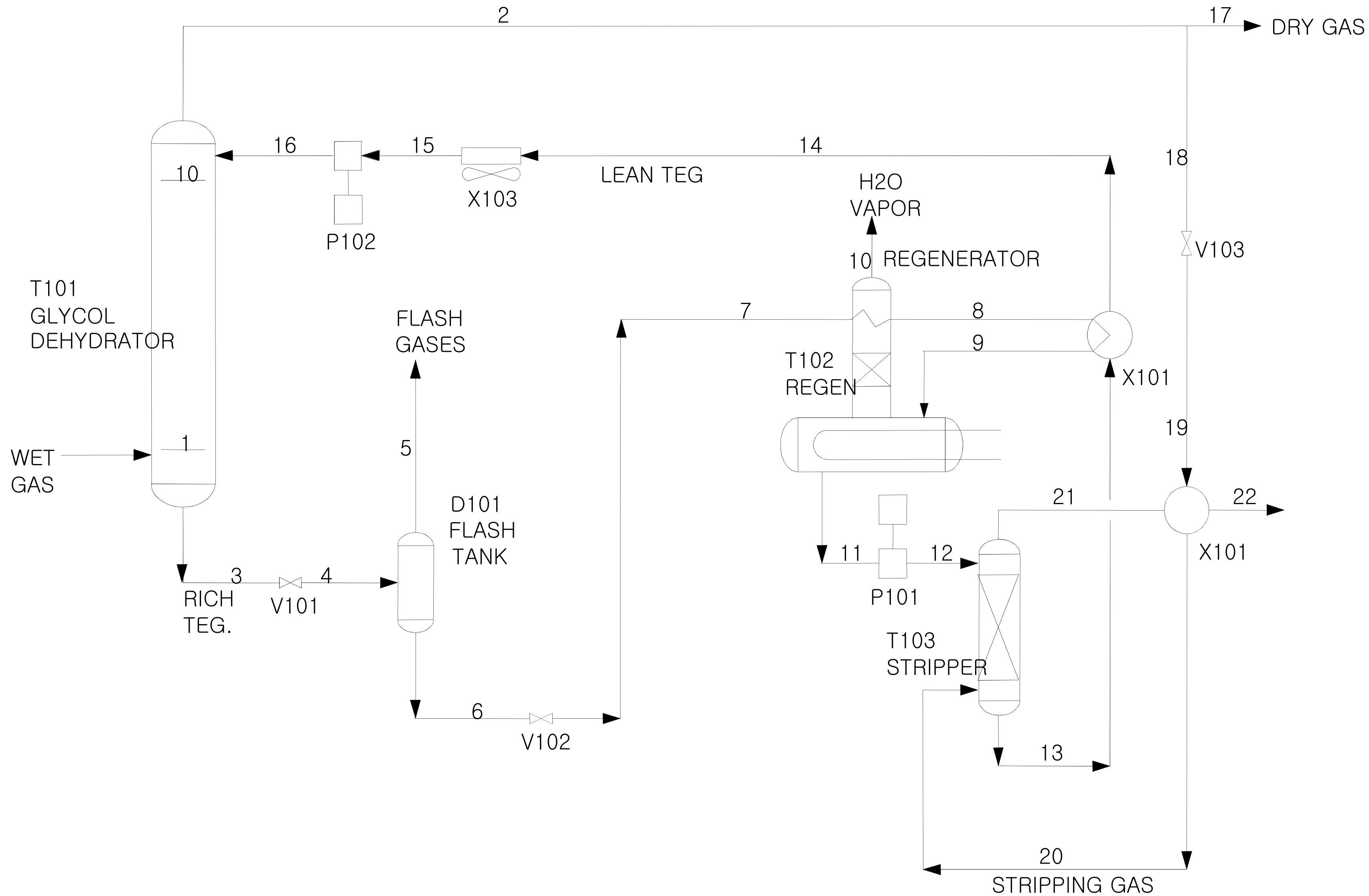
MEG Regeneration Unit Simulation:



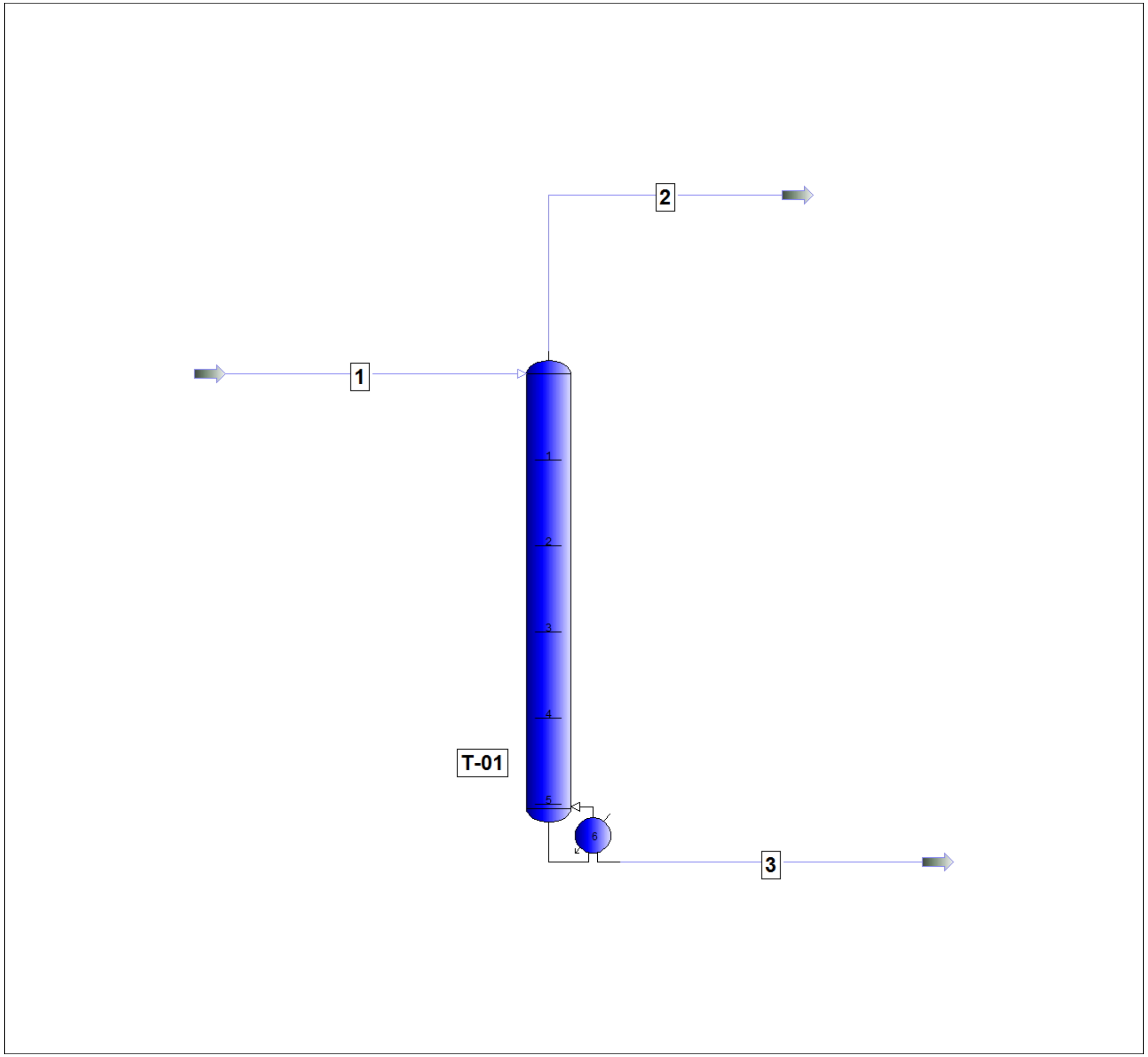
Glycol Dehydration (Glycol Package):

- Natural gas dehydration with Triethylene Glycol (TEG).
- Uses the SRKM equation of state.
- Rigorously models either VLE or VLLE behavior.
- T range: 80 ^{o}F to 400 ^{o}F.
  P range: Up to 2,000 psia.
- Glycol (EG, DEG or TEG) and water must be present.

Gas Dehydration Using TEG:



MEG Regeneration Simulation Using PRO/II:



MEG Regeneration Simulation Using PRO/II:

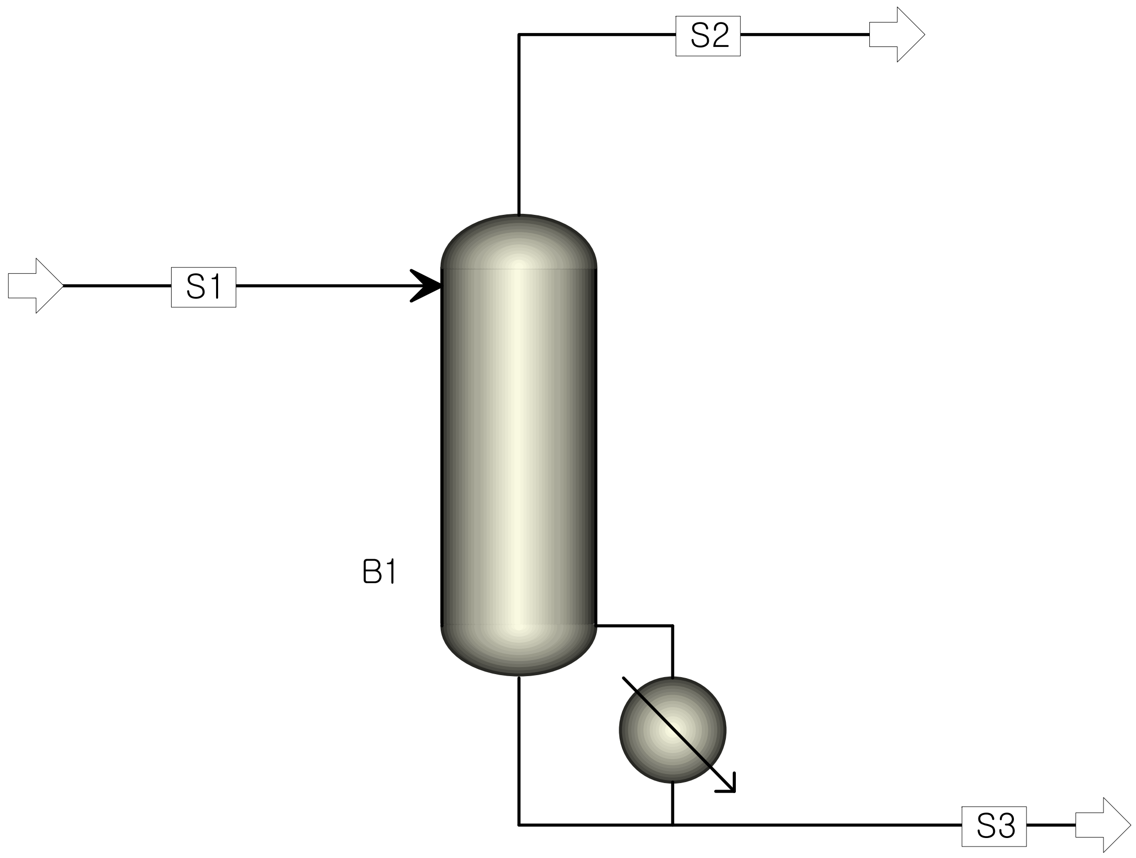
COLUMN SUMMARY

TRAY	TEMP DEG C	PRESSURE TORR	NET FLOW RATES KG/HR LIQUID	VAPOR	FEED	PRODUCT	HEATER DUTIES M*KCAL/HR
1	**110.3**	**760.00**	10927.3		10000.0L	3456.3V	
2	110.3	761.00	10927.9	4383.5			
3	110.4	762.00	10929.6	4384.1			
4	110.5	763.00	10954.9	4385.8			
5	113.2	764.00	11541.4	4411.1			
6R	**139.8**	**765.00**		4997.6		6543.8L	**2.4489**

MEG Regeneration Simulation Using PRO/II:

STREAM ID	1	2	3
NAME			
PHASE	LIQUID	VAPOR	LIQUID
THERMO ID	GLYC01	GLYC01	GLYC01
FLUID WEIGHT PERCENTS			
1 H2O	40.0000	96.7990	10.0000
2 EG	**60.0000**	**3.2010**	**90.0000**
TOTAL RATE, KG/HR	10000.0000	3456.2545	6543.7550
TEMPERATURE, C	50.0000	110.2673	139.7686
PRESSURE, TORR	1000.0000	760.0000	765.0000
ENTHALPY, M*KCAL/HR	0.3471	2.2036	0.5925
MOLECULAR WEIGHT	31.3773	18.4341	49.8729
WEIGHT FRAC VAPOR	0.0000	1.0000	0.0000
WEIGHT FRAC LIQUID	1.0000	0.0000	1.0000

MEG Regeneration Simulation Using Aspen:



MEG Regeneration Simulation Using Aspen:

Stage	Temperature	Pressure	Heat duty	Liquid from	Vapor from
	C	bar	Gcal/hr	kg/hr	kg/hr
1	108.7884	1.01325		10871.8827	3441.01615
2	108.8265	1.014583		10872.4696	4312.89895
3	108.8686	1.015916		10873.7566	4313.4859
4	109.0098	1.01725		10893.0919	4314.77307
5	111.4478	1.018583		11421.1131	4334.10842
6	138.1225	1.019916	**2.413523**	6558.98396	4862.12964

MEG Regeneration Simulation Using Aspen:

Heat and Material Balance Table				
Stream ID		S1	S2	S3
Temperature	C	50.0	108.8	138.1
Pressure	bar	1.333	1.013	1.020
Vapor Frac		0.000	1.000	0.000
Mole Flow	kmol/hr	318.701	187.187	131.514
Mass Flow	kg/hr	10000.000	3441.016	6558.984
Volume Flow	cum/hr	9.540	5866.514	6.557
Enthalpy	Gcal/hr	-25.577	-10.739	-12.425
Mass Flow	kg/hr			
WATER		4000.000	3344.100	655.900
EG		6000.000	96.916	5903.084
Mass Frac				
WATER		0.400	0.972	0.100
EG		0.600	0.028	0.900
Mole Flow	kmol/hr			
WATER		222.034	185.626	36.408
EG		96.667	1.561	95.106

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- Formation water salt load:

Species	ppm	mM
Na^{+}	26,557	1,154.7
K^{+}	257	6.67
Ca^{2+}	1,306	32.57
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Br^{-}	89	1.11
$SO4^{2-}$	3,629	37.76
HCO^{3-}	607	9.95

Feedstock Information: (Aspen Plus)

- Feed components:

Component ID	Type	Component name	Alias
NA+	Conventional	NA+	NA+
K+	Conventional	K+	K+
CA++	Conventional	CA++	CA+2
MG++	Conventional	MG++	MG+2
BA++	Conventional	BA++	BA+2
SR++	Conventional	SR++	SR+2
FE++	Conventional	FE++	FE+2
CL-	Conventional	CL-	CL-
BR-	Conventional	BR-	BR-
SO4--	Conventional	SO4--	SO4-2
HCO3-	Conventional	HCO3-	HCO3-
H2O	Conventional	WATER	H2O

THANK YOU