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Natural gas sweetening by additive-aided extractive distillation for CO_2 freezing point depression

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Outline

- Processing of CO_2-rich, sour gas containing 50% CO_2 and 1% H_2S
- Aspects on H_2S removal
- Low-temperature CO_2 removal of natural gas
  - CO_2 removal by extractive distillation
  - CO_2 fractionation columns operating at temperatures below that of the CO_2 freezing point
  - Recirculation of heavy hydrocarbons to the low-temperature columns depressing actual CO_2 freeze-out temperature

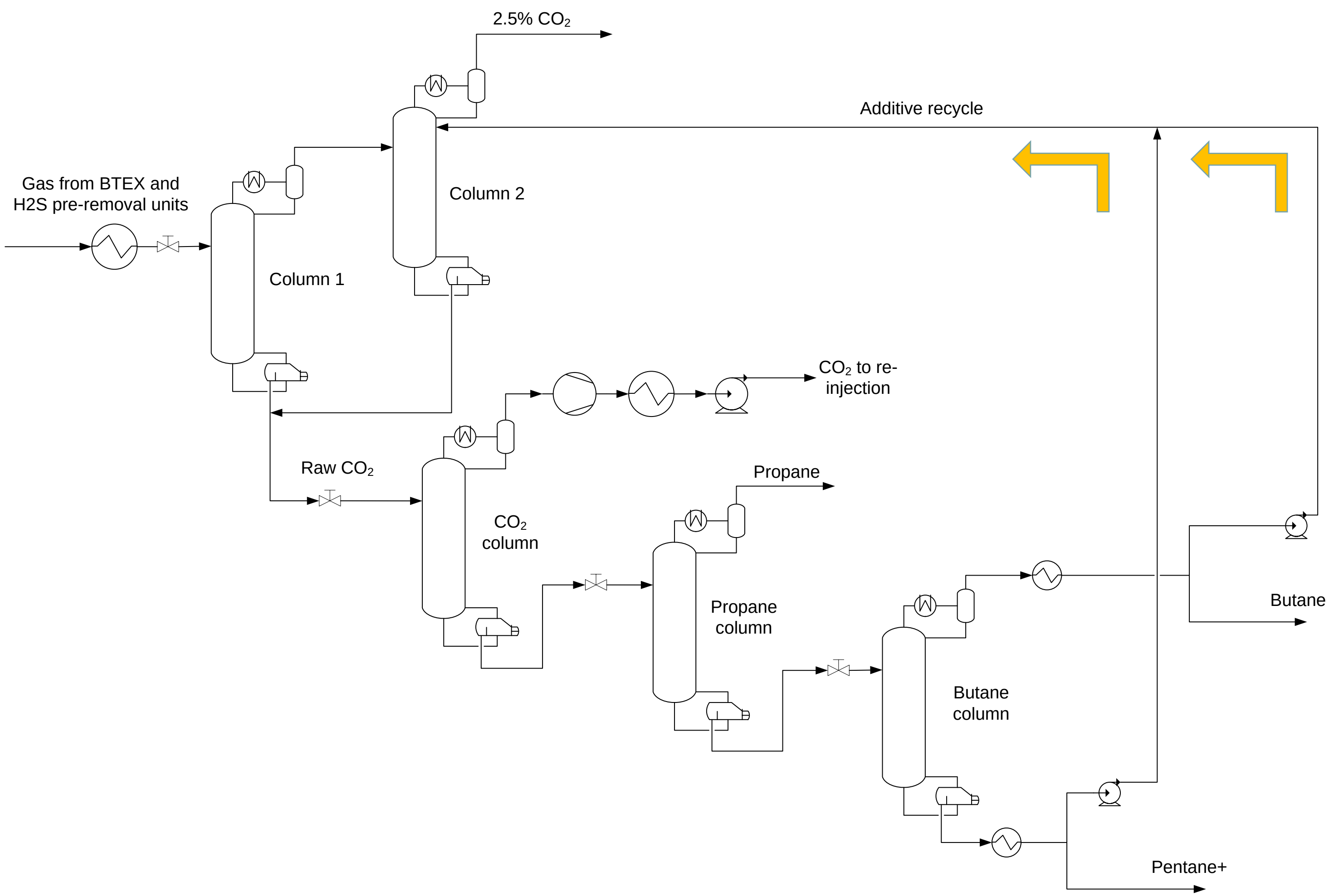
Natural gas composition and product specification

Sweetening CO_2/H_2S-rich raw gas to pipe gas specification

	Feed composition		Product specification	
Temperature	40	°C		
Pressure	70	bar		
Flowrate	590 000	Nm^3/hr		
	15	MSm^3/day		
Composition				
C_1	39.28	vol%		
C_2	3.5	vol%		
C_3	2.4	vol%		
C_4	1.8	vol%		
C_5	1.2	vol%		
C_{6+}	0.2	vol%		
CO_2	50	vol%	2.5	vol%
H_2S	1	vol%	21	ppm
Organic sulphides	0.02	vol%		
N_2	0.5	vol%	≈0.5	vol%
BTEX	0.1	vol%	0	vol%

Overview of extractive distillation process

Recirculation of heavy hydrocarbons for CO_2 freezing point depression



H_2S removal

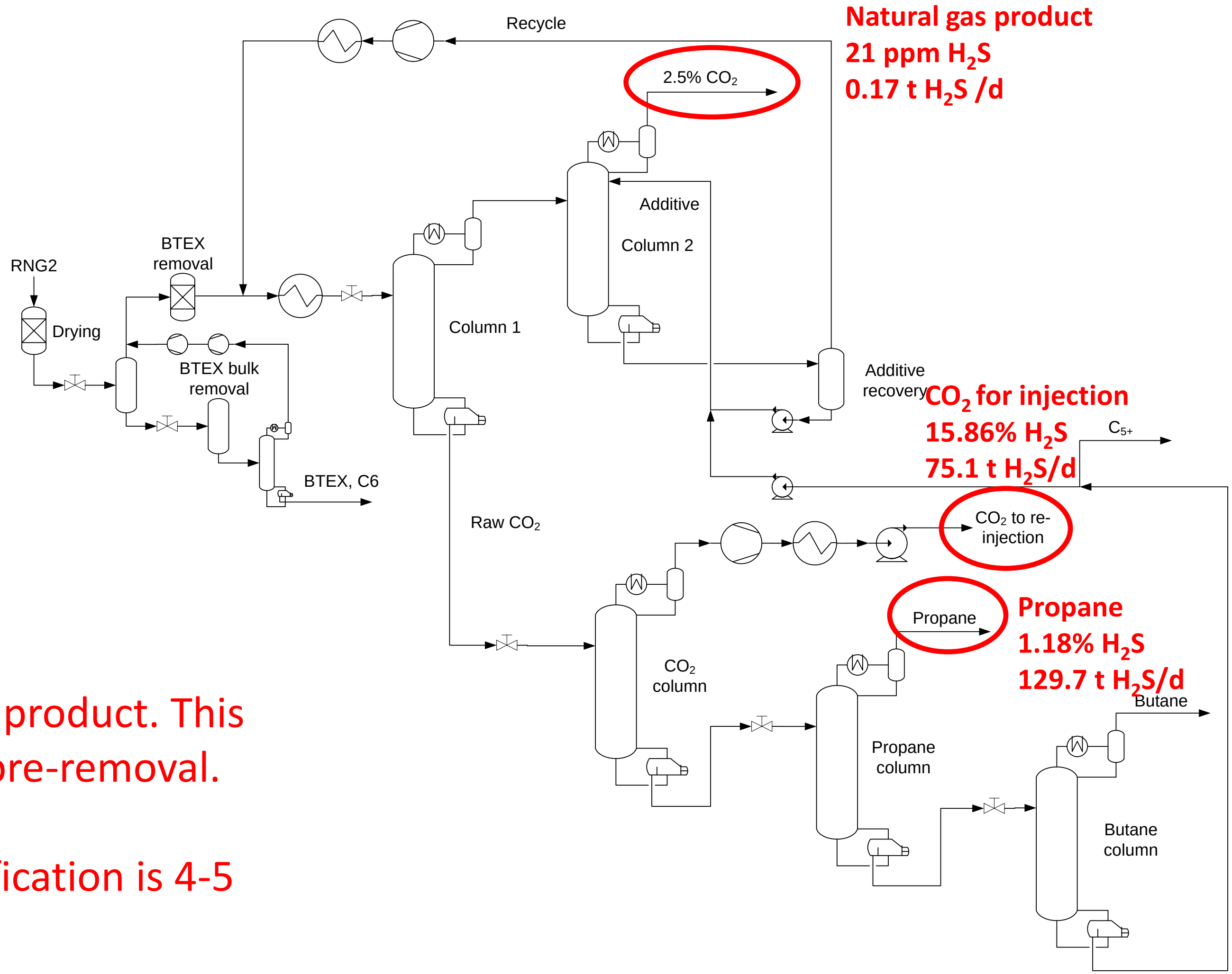
- H_2S can in principle be removed prior to CO_2 bulk removal ('pre-removal') or from separation products ('post-removal')

- Arguments for pre-removal
  - Pre-removal is standard
  - No infiltration of H_2S into fractionation train, minimises corrosion risk
  - Safety measure in case of failure in dehydration unit

- Arguments for post-removal
  - Fractionation system needs to be dry in any case, due to low-temperature operation
  - Molsieve dehydration to ≈0.1 ppm; Dew point < 100°C; No free water present
  - H_2S ends up mainly in CO_2 to be re-injected and propane product
  - Propane sweetening can be carried out with significantly smaller absorption column

H_2S product concentrations – post-removal

Natural gas feed composition (vol%)	
C1	39.28
C2	3.5
C3	2.4
C4	1.8
C5	1.2
C6+	0.2
CO_2	50
H_2S	1
Organic sulphides	0.02
N_2	0.5
BTEX	0.1



21 ppm H_2S in natural gas product. This can be obtained without pre-removal.

A normal sweet-gas specification is 4-5 ppm H_2S.

General recommendations for H_2S disposal

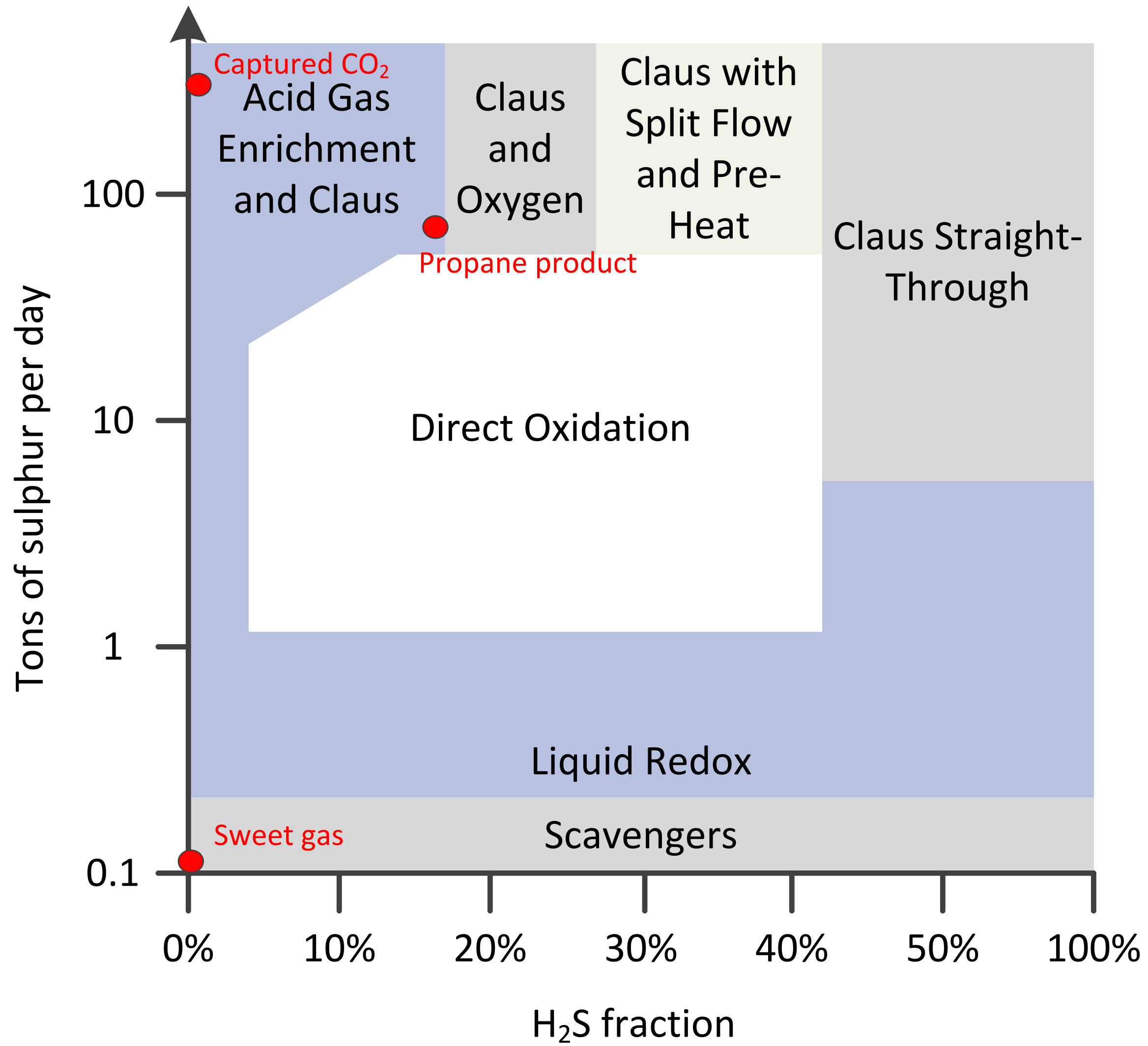
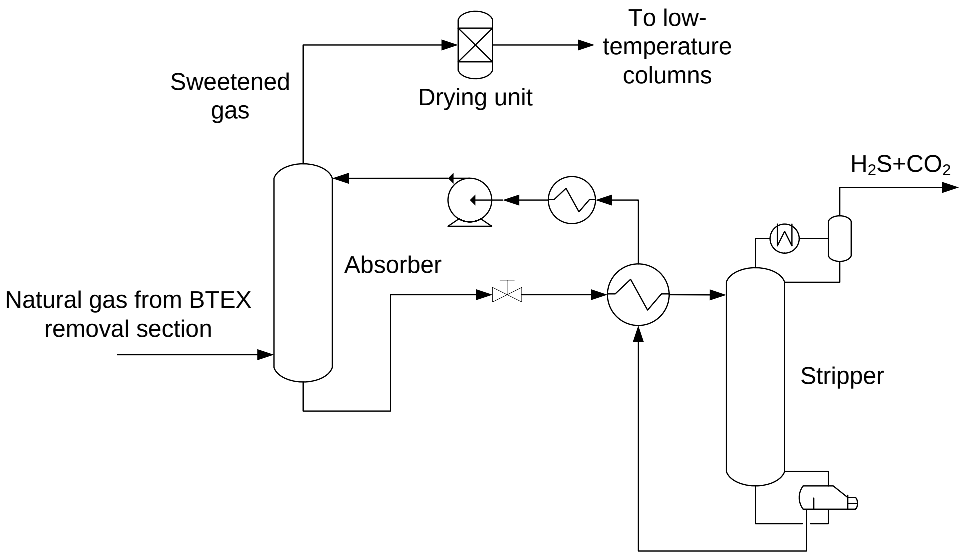


Figure reproduced from: Linde. Sulphur Process Technology (2012).

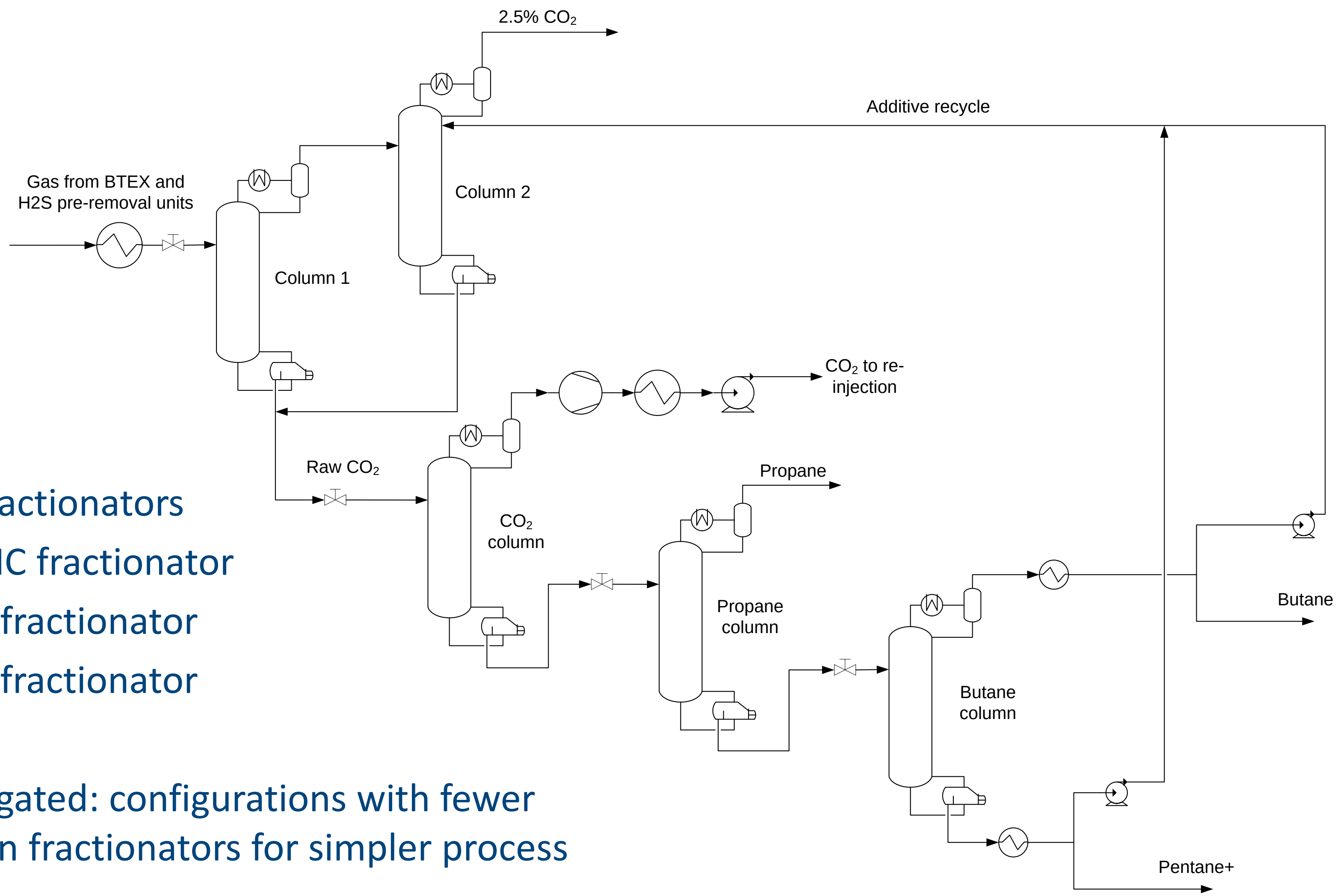
H_2S pre-removal

Selective MDEA absorption



	Feed		Sweet gas	Propane product		CO_2 product
	CO_2 [mol%]	H_2S [ppmv]	H_2S [ppmv]	H_2S [ppmv]	H_2S [kg/hr]	H_2S [ppmv]
No removal	50	10 000	21	158 000	3130	11 800
MDEA	43	100	0.29	1600	30	130
MDEA + scavenger	43	10	0.26	200	3.7	16
MDEA + scavenger	43	1	0.25	65	1.2	5
MDEA + scavenger	43	0.1	0.25	51	0.93	4

CO_2 separation by low-temperature extractive distillation

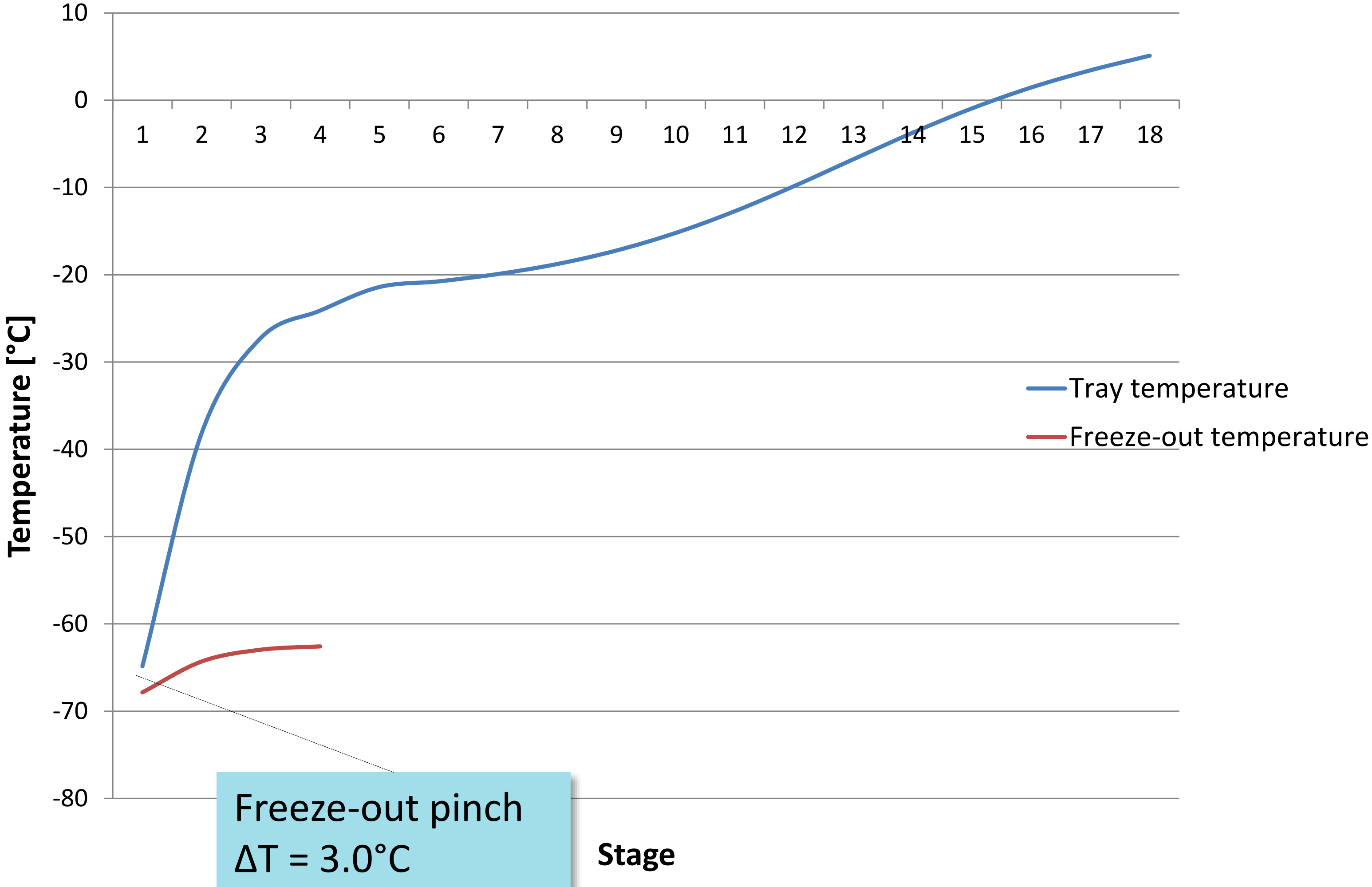


Base layout

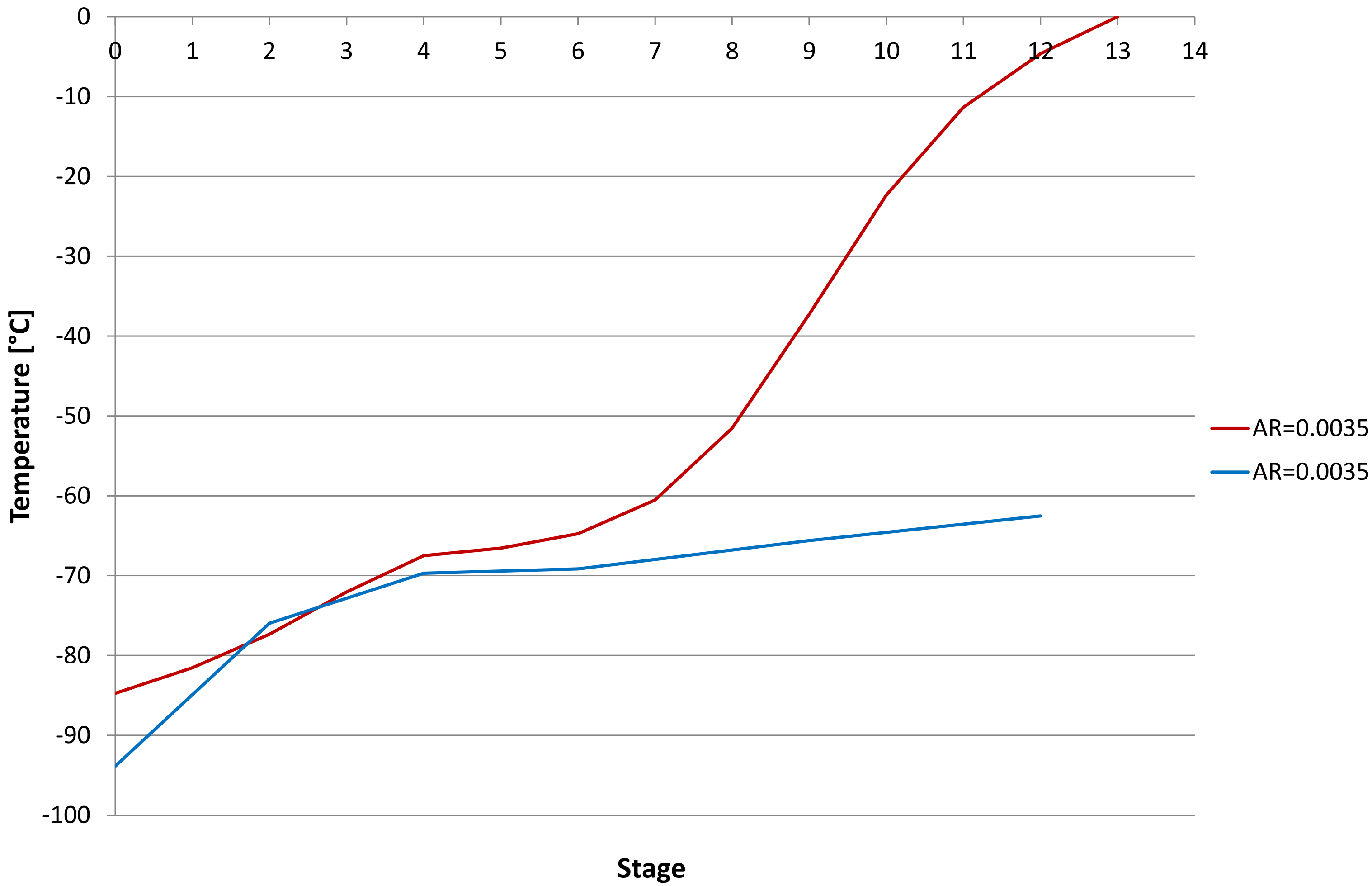
- 2 CO_2 fractionators
- CO_2 /HHC fractionator
- C3/C4+ fractionator
- C4/C5+ fractionator

Also investigated: configurations with fewer hydrocarbon fractionators for simpler process

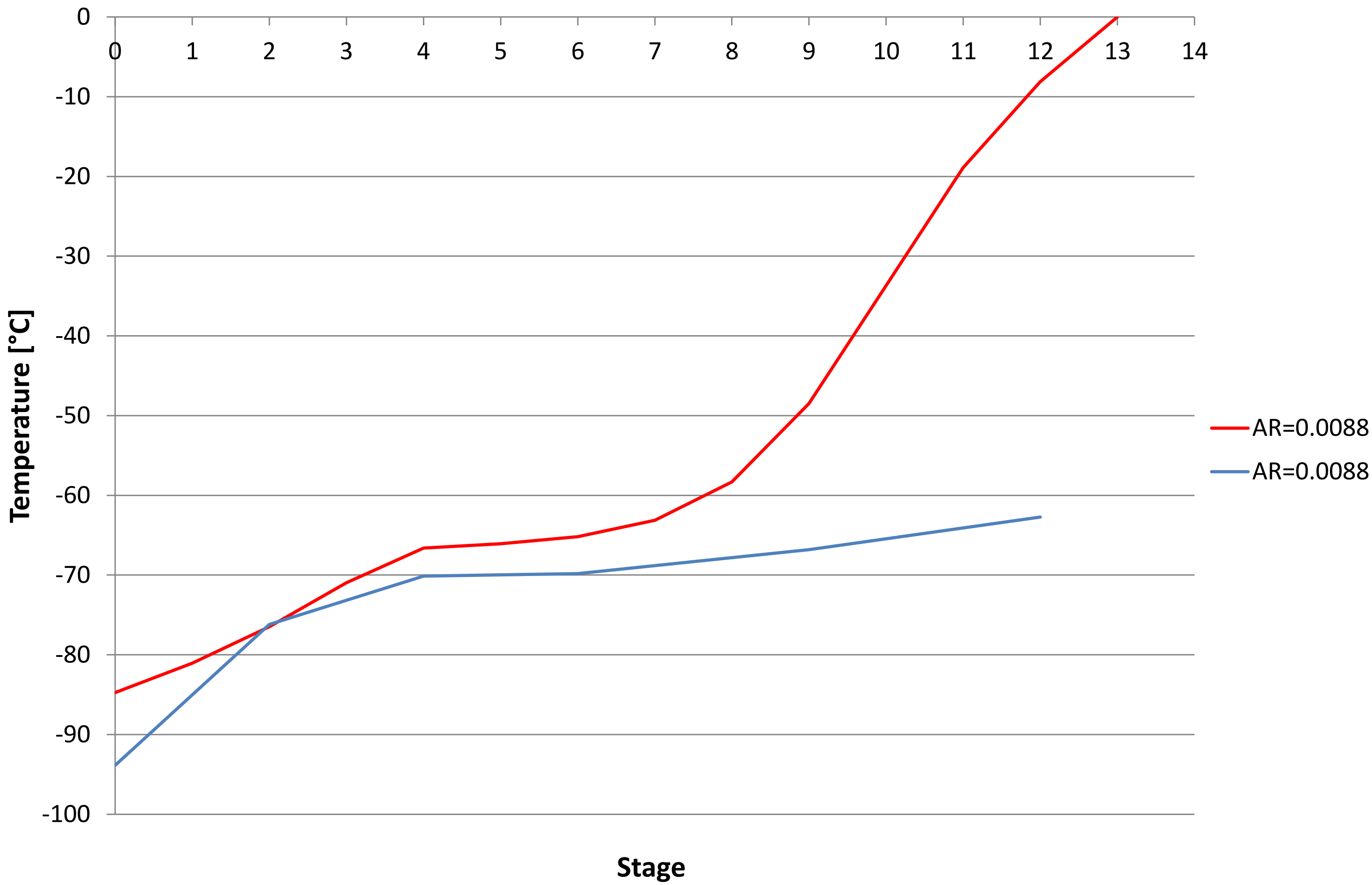
Temperature profile of column 1 – no additive recirculation



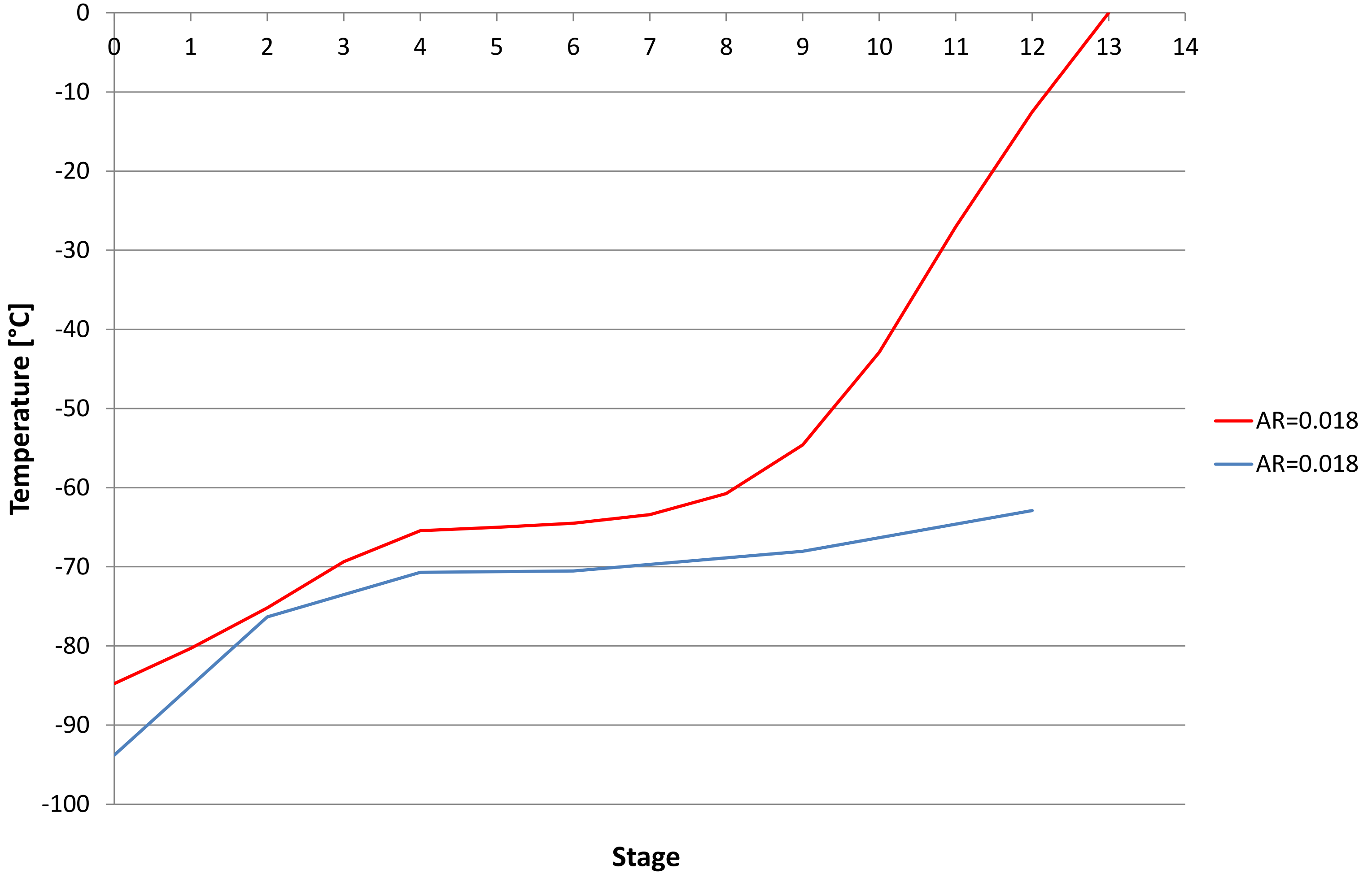
Temperature profile of column 2 – additive ratio = 0.35% (mol additive / mol feed)



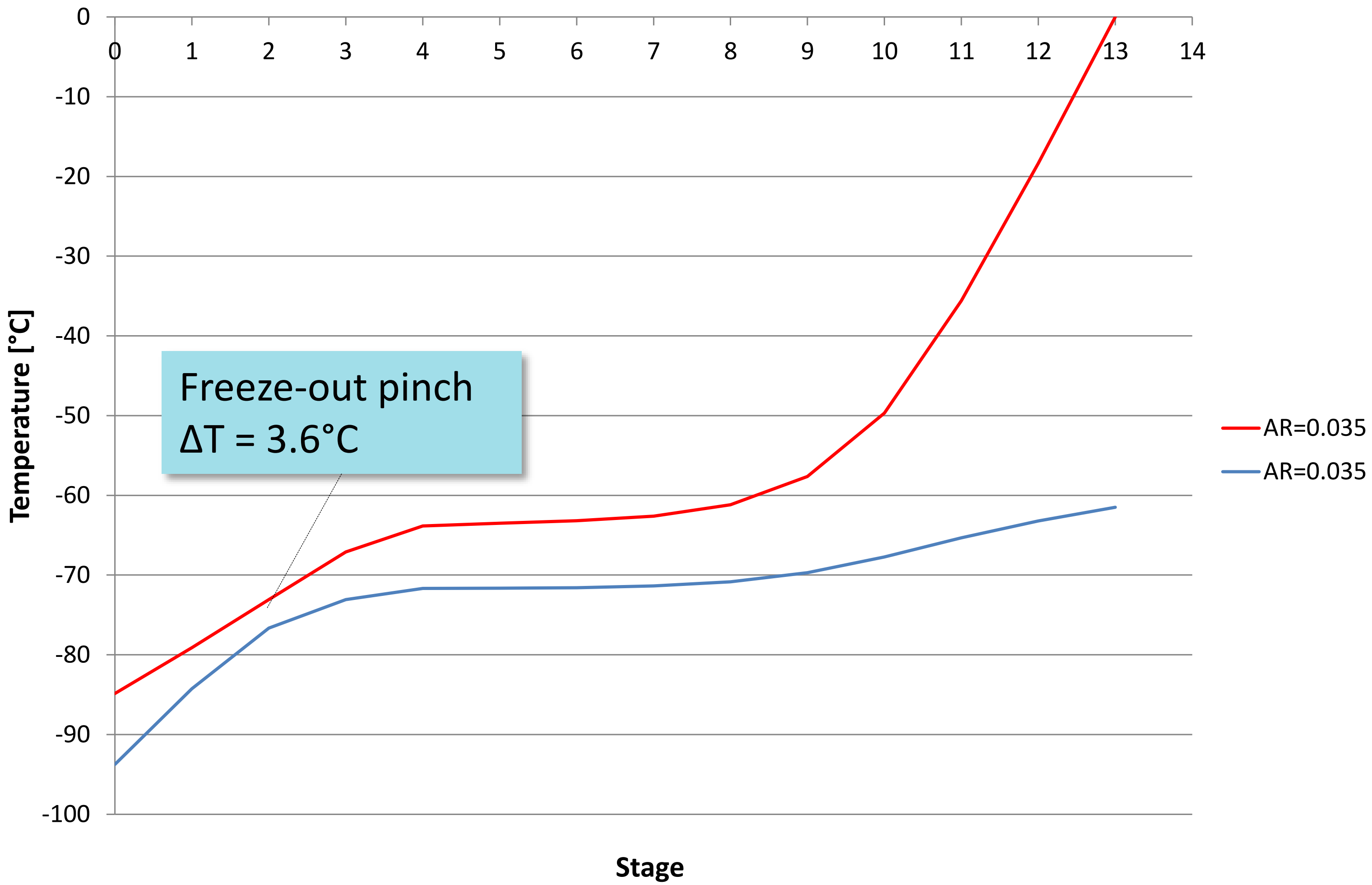
Temperature profile of column 2 – additive ratio = 0.88% (mol additive / mol feed)



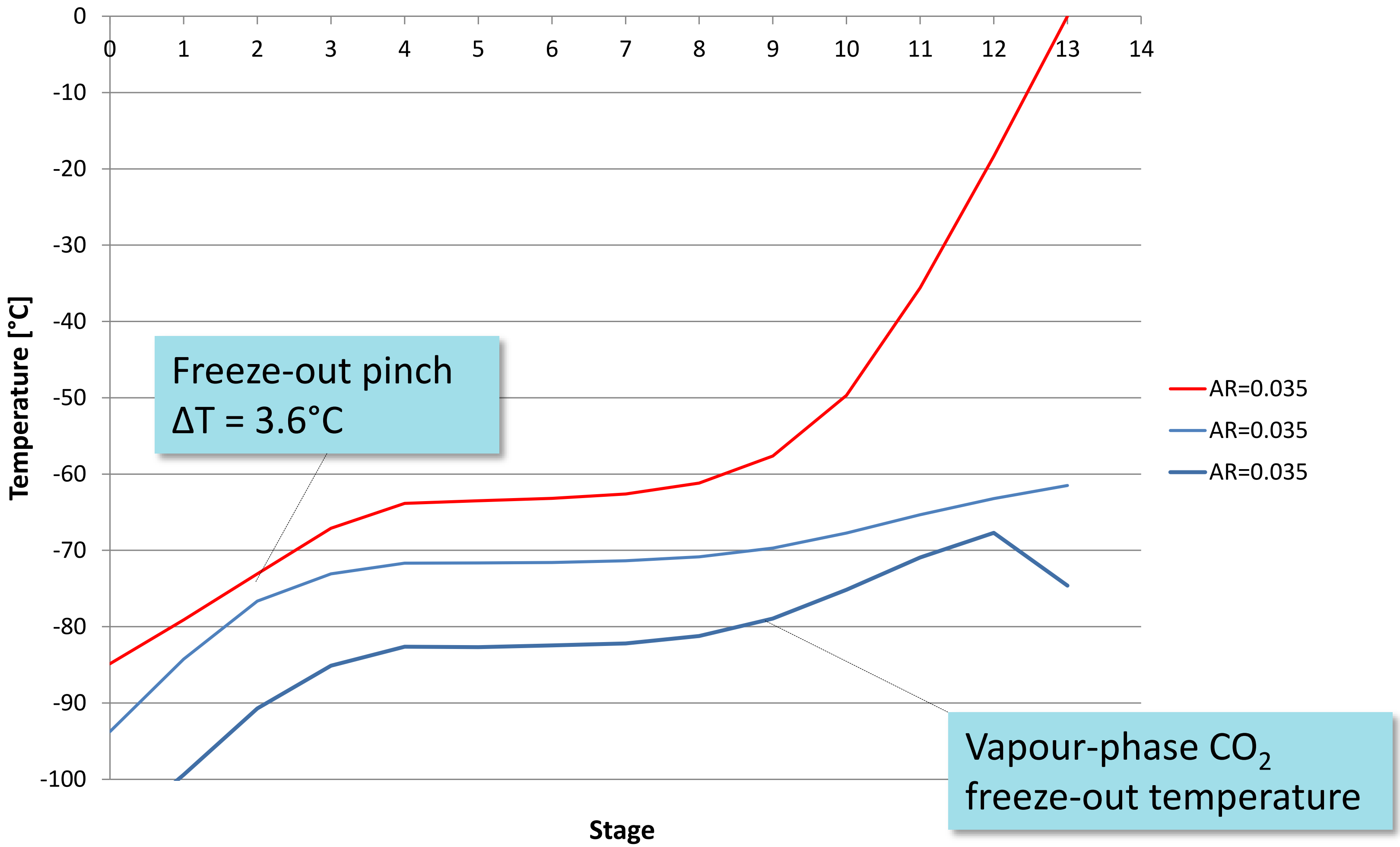
Temperature profile of column 2 – additive ratio = 1.8% (mol additive / mol feed)



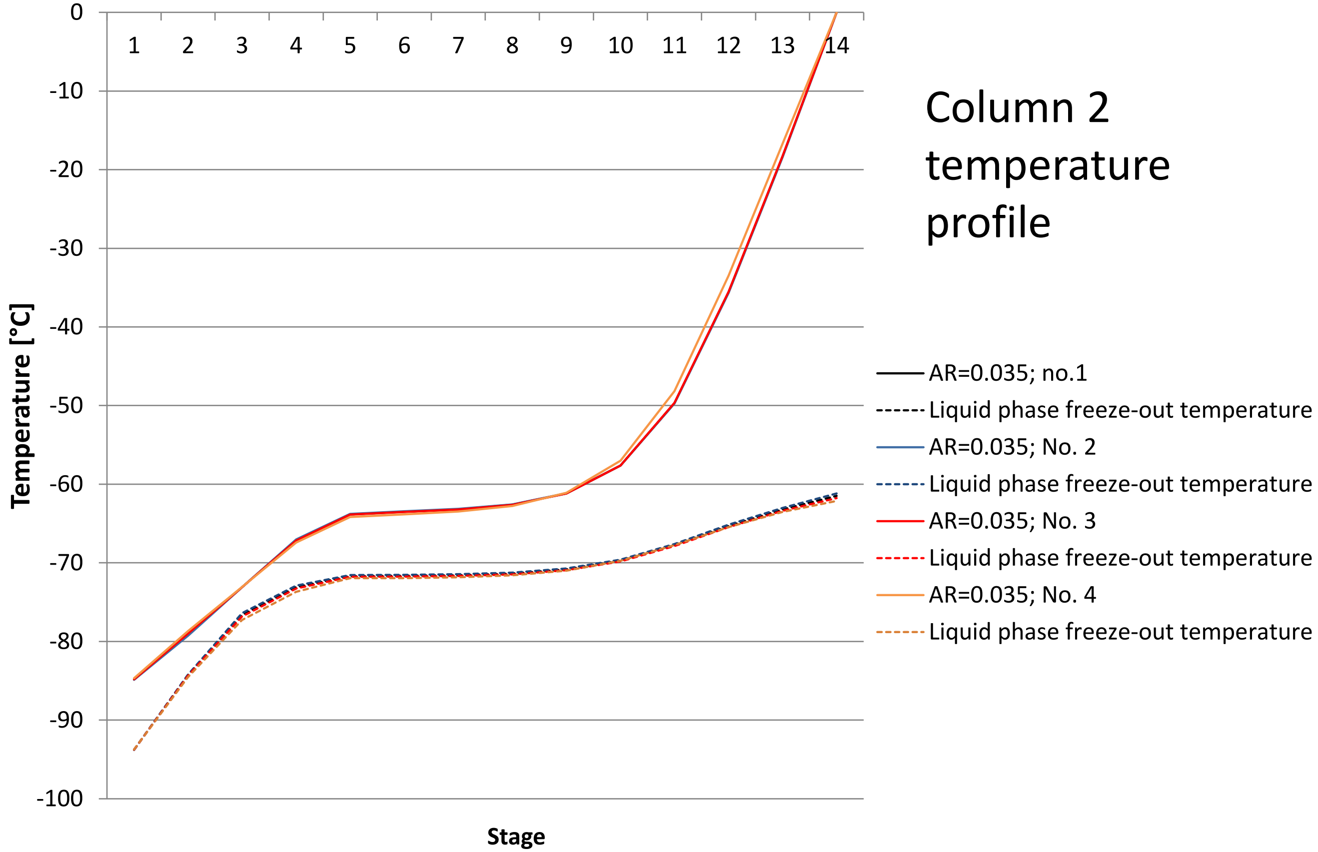
Temperature profile of column 2 – additive ratio = 3.5% (mol additive / mol feed)



Temperature profile of column 2 – additive ratio = 3.5% (mol additive / mol feed)



Effect of varying the recirculated additive composition

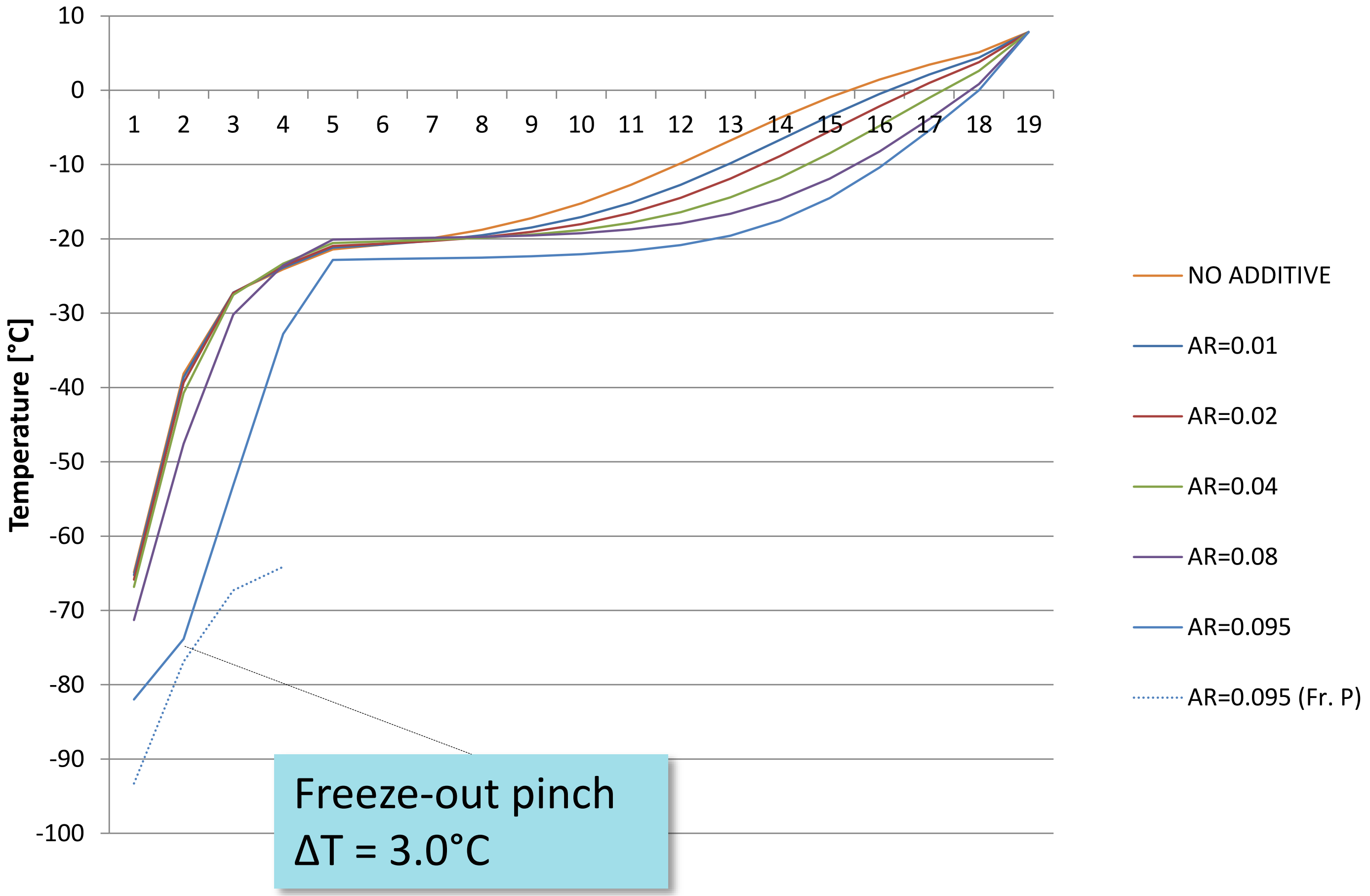


Column 2 temperature profile

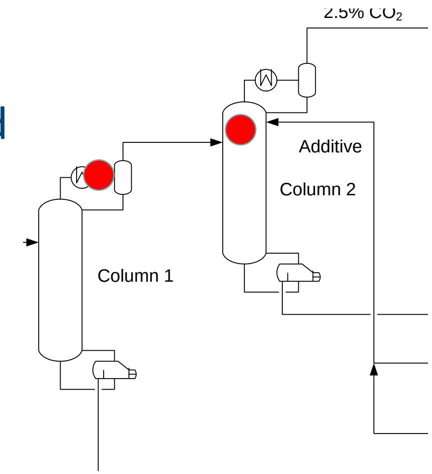
	Composition of recycled additive stream [mol%]						
No.	C_1	C_2	C_3	C_4 (n+i)	C_5 (n+i)	C_6	CO_2
1	0.0	0.0	0.6	49.4	47.5	2.5	0
2	0.0	0.0	2.3	21.4	72.1	4.1	0
3	0.0	0.0	0.0	72.5	26.2	1.3	0
4	0	0.1	36.1	36.7	24.7	1.3	1.0

Single-stage CO_2 separation column

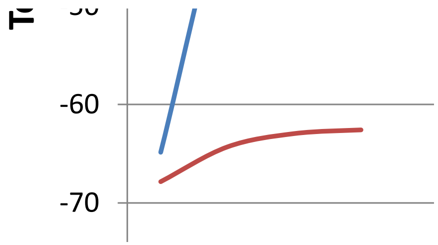
Possible to obtain pipe gas quality (2.5%) in a single-column configuration when the additive recirculation ratio is about 9.5%



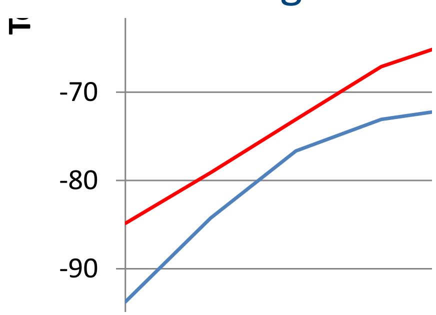
Freeze-out pinch considerations



- The minimum temperature difference between tray temperature and CO_2 freeze-out temperature occurs in different locations in the configuration with two CO_2 separator columns
- **Column 1:** Pinch in condenser → Risk of cold spot and freeze-out on exchanger surface



- **Column 2:** Pinch in tray. Required safety margin (ΔT_{min}) depending on axial heat and mass transfer and degree of equilibrium/non-equilibrium conditions



Conclusions and further work

- Pipeline quality natural gas can be produced from gas with high initial CO_2 concentration – 50% in the investigated case – by low-temperature distillation
- The pipeline quality can be obtained with one or two fractionation columns for CO_2 removal
- With two columns, no additive recirculation is in principle required for the first column if specified correctly
- The second column needs approximately 0.035 mol additive per mol feed recirculation to obtain > 3°C freeze-out pinch temperature margin
- A single-column configuration requires about 0.095 mol additive per mol feed recirculation in order to keep pinch temperature margin > 3°C
- The number of fractionators for C2, C3, C4 etc. depends on the overall product specifications targeted in the process

Conclusions and further work

- HHC fractionation columns are likely to be required. In this regard, the CO_2 removal process may be considered to be a sub-process within, and an added functionality to, the NGL extraction and fractionation plant
- H_2S removal can in principle and under certain conditions be carried out post CO_2 removal, as the low-temperature system must be operated in dry conditions with no free-water formation
- H_2S pre-removal, however, will reduce the risk of corrosion in case of dehydration malfunctioning, and is recommended
- The freeze-out estimations are based on tool embedded in Aspen HYSYS. Theoretical freeze-out calculations must therefore be verified by experimental measurements
- Detailed mass and heat transfer simulations are needed to determine required temperature margin for safe operation avoiding freeze-out in the low-temperature CO_2 separation columns

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