

Pinch point analysis of heat exchangers for supercritical carbon dioxide with gaseous admixtures in CCS systems

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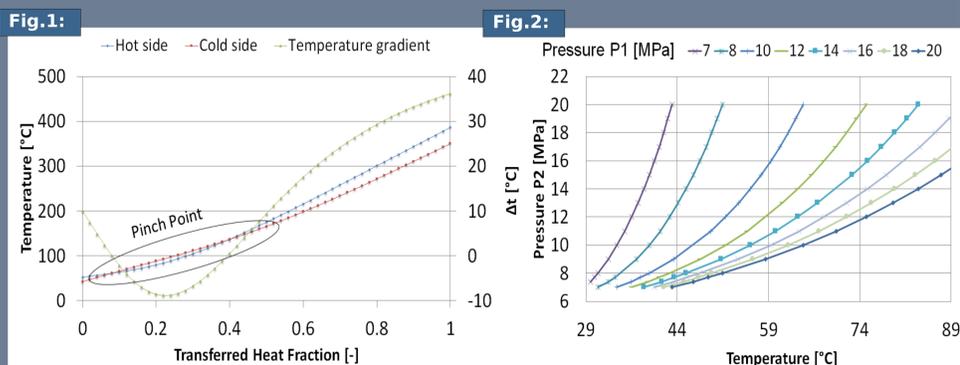
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Introduction

Supercritical carbon dioxide (S-CO₂) is in researchers' scope of interest for some time as an interesting and perspective working fluid for various applications in power cycles. Except for close loop operation, with recent emergence of urgency for CCS (Carbon dioxide Capture and Storage) systems, there is a need for new technologies employing CO₂. Supercritical state is the form into which captured CO₂ has to be compressed and cooled down for transport and storage. Transported and storage medium from CCS systems is not pure CO₂ but mixture with other components from combustion processes. Mostly it is a mixture with a high percentage of CO₂ (> 95.5%) and other ballast gases (nitrogen, water, carbon oxide, oxygen, hydrogen, argon). Amount of these gases is limited. On the other hand, they may have also a beneficial effect. This brings up necessity for reliable and economical design of the components working with this fluid (as heat exchanger, compressors, expanders, valves). Unlike in regular heat exchanger design, in heat exchangers with CO₂ on both hot and cold side, there is often present Pinch point so that terminal temperature difference approach doesn't provide reliable mean of heat exchanger calculation anymore.

Description of Pinch point and methodology

- Pinch point occurs in a place where heat capacity of both hot and cold fluid are equal.
- Particularly issue for CO₂-CO₂ recuperative heat exchangers operating over large temperature range and at different fluid pressure levels.
- Standard terminal temperature difference approach may give flawed result, shown on figure 1.
- For regenerative heat exchangers (same medium and mass flow on both hot and cold sides) has been in previous research derived dependency of Pinch Point fluid temperature on pressure levels. This Dependence of Pinch point is shown on figure 2.



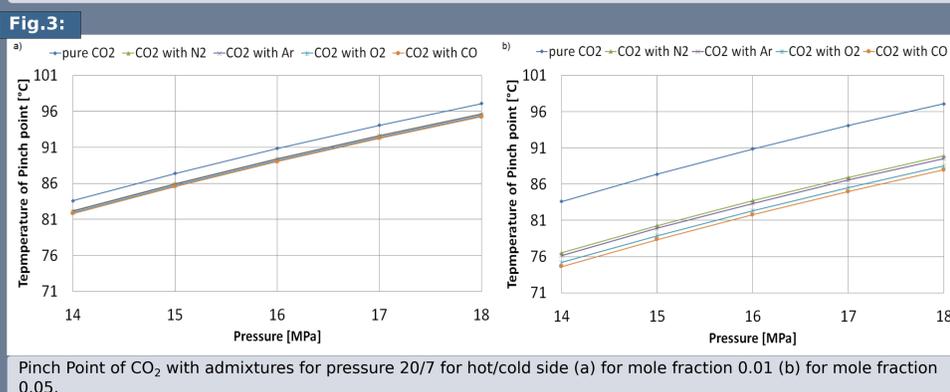
Theoretical Q-T diagram of CO₂ regenerative heat exchanger based only on terminal temperature difference.

Derived dependence of pinch point temperature of CO₂ as a function of pressure levels

Gaseous admixtures

- Admixtures alter mixture properties and pinch point temperature, Pinch point is shifted to lower temperatures and can be even eliminated from heat exchanger.
- This study focused only on binary mixtures, specifically on gases with higher critical point and present in CCS systems - Ar, N₂, O₂, CO. Additionally effect compared to Helium considered in supercritical CO₂.
- Effect of admixtures in detail investigated for 0.01 and 0.05 mol of admixtures and pressure levels of 7-20 MPa.
- Example of 20/7 MPa for hot/cold side shown on figure 3.

- The results for mole fraction 0.01: The highest the Pinch point shift is for CO, shift is about 1.75 °C ± 0.1 °C
- The results for mole fraction 0.05: The largest shift of Pinch point is for CO, shift is 8.72 °C ± 0.5 °C
- The shift of pinch point has a linear dependence. Increase of admixture mole fraction by 0.01 moves Pinch point downwards about same temperature.



Pinch Point of CO₂ with admixtures for pressure 20/7 for hot/cold side (a) for mole fraction 0.01 (b) for mole fraction 0.05.

Heat exchangers examples

The heat exchanger considered as counter flow shell & tube (37 tubes 10x1,5mm in 120x10 mm tube).

Two types of the heat exchangers:

Regenerative CO₂-CO₂ heat exchanger

Mass flow	2.5	[kg/s]
Inlet temperature of hot side	42	[°C]
Outlet temperature of hot side	160	[°C]
Pressure of hot side	20	[MPa]
Pressure of cold side	8	[MPa]

CO₂ cooler with water on cold side

Mass flow of side with CO ₂	2.5	[kg/s]
Mass flow of side with H ₂ O	2	[kg/s]
Inlet temperature of side with CO ₂	42	[°C]
Outlet temperature of side with CO ₂	32	[°C]
Inlet temperature of side with H ₂ O	25	[°C]
Pressure of side with CO ₂	12	[MPa]
Pressure of side with H ₂ O	0.5	[MPa]

The calculation is divided.

- The first step: find occurrence and temperature of the Pinch point
- The second step: choose a minimal temperature gradient in the Pinch point
- The three step: calculate step-by-step the development of hot and cold stream temperature from Pinch point towards the cold end and subsequently towards the hot end.

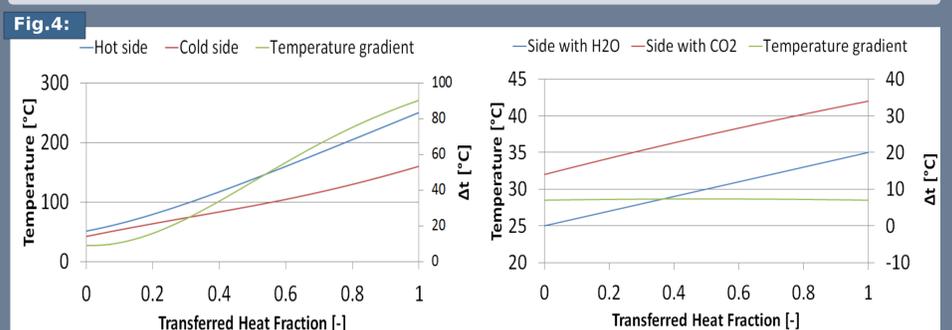
For mole fraction of 0.01: The best admixture to CO₂ is Ar.

For mole fraction of 0.05: Similar results can be observed. Admixtures with Argon for reducing the size of the heat exchanger are suitable.

Mole fraction	0.01	0.05	[-]
Pure CO ₂	22.96		
CO ₂ with Ar	21.90	19.49	[m]
CO ₂ with CO	22.23	19.72	
CO ₂ with O ₂	22.28	19.64	
CO ₂ with N ₂	22.36	19.81	

In case cooler: Different results compared with regenerative heat exchanger can be observed. Size of the cooler increases by presence of admixtures. Reason are worse heat transfer properties of the mixture

Mole fraction	0.01	0.05	[-]
Pure CO ₂	2.33		
CO ₂ with Ar	2.44	3.17	[m]
CO ₂ with CO	2.52	3.65	
CO ₂ with O ₂	2.49	3.49	
CO ₂ with N ₂	2.51	3.45	



The result of heat exchanger with pure CO₂, hot and cold side pressures 20 and 8 MPa.

The result of cooler with binary mixture CO₂ and CO.

Conclusion

- Gaseous admixtures have a positive effect on the shift of Pinch point down to lower temperatures.
- It can be observed, that interesting gas for adjusting the Pinch point is CO.
- Overall positive effect is up to approximately 0.01 mol admixture content. Effect on the heat exchangers size is positive for regenerative heat exchanger.
- Effect is negative for coolers, possibly more than doubling their size. The gaseous admixtures adversely affect heat transfer and thus is increased the required heat transfer area.
- Further research about use others binary mixtures or mixtures with more additives is necessary. Multicomponent mixtures are a further step for a study.