TECHNISCHE UNIVERSITÄT DRESDEN

DRESDEN concept

Sebastian Rath, Erik Mickoleit, Cornelia Breitkopf, Uwe Gampe, Andreas Jäger

Study of the Influence of Additives to CO_2 on Performance Parameters of a sCO_2-Cycle

4th European sCO_2-Conference
23.-24.04.21 – Prague, Czech Republic

tu-dresden.de/mw/iet/

Motivation

- The efficiency of sCO_2-cycles is essentially connected with the closeness to the critical point
- High fluctuations of fluid properties result in high sensitivity to the lower temperature level of the cycle
- Sufficient cooling is essential but usually a tradeoff between component size and recooling conditions → e.g. arid regions / air cooling

Idea behind using mixtures:

- Adaption of the fluid to better fit the individual process conditions
- Modification of the fluid instead of the system

→ **Extensive screening needed to identify feasible fluid combinations**

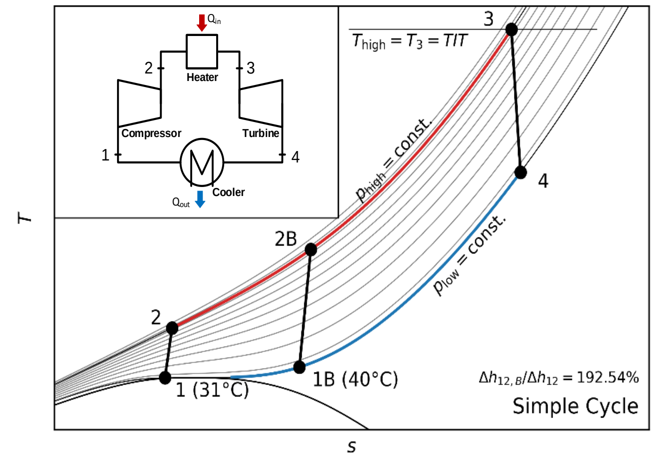


Fig. a): Influence of inlet temperature on the enthalpy difference of the compressor for near-critical compression of sCO_2

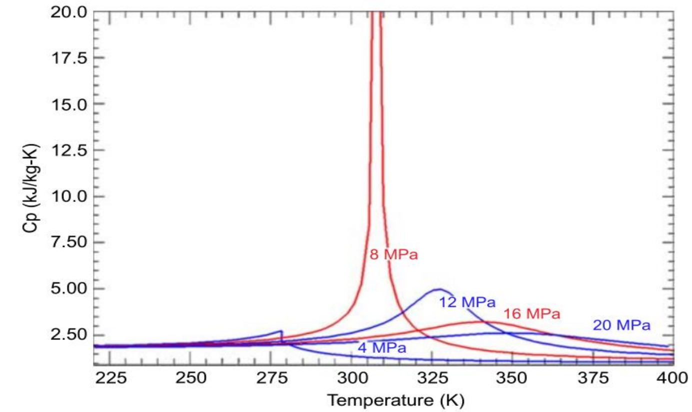


Fig. b): Variations in the heat capacity of CO_2 near the critical point

Source: Brun et. al. Fundamentals and Applications of Supercritical Carbon Dioxide (sCO2) Based Power Cycles

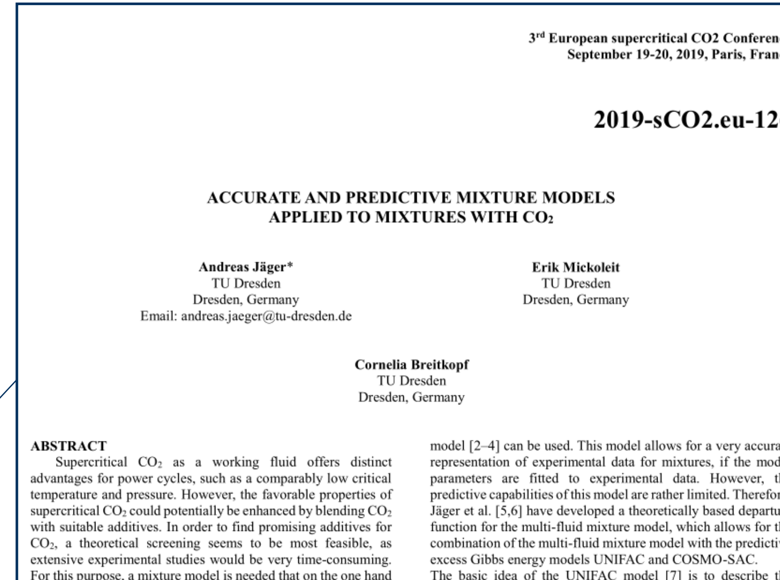
Mixture Models

Fluid modeling was done by using adapted mixture parameters as well as predictive methods

→ Allows the consideration of a wide range of substances, including these where no adapted mixture parameters are available

Predictive mixture-model:
Combination of multi-fluid mixture models and excess Gibbs energy models:

- Combination of the best available equation of state with the best available mixing model (e.g. COSMO-SAC, Lorentz-Berthelot, ..)
- Recently developed by our group and already presented by A. Jäger at the 3rd sCO_2-Conference in Paris for application with CO_2
- Implemented and applied within the thermo-physical property software **TREND 4.0**



3rd European supercritical CO2 Conference
September 19-20, 2019, Paris, France

2019-sCO2.eu-126

ACCURATE AND PREDICTIVE MIXTURE MODELS APPLIED TO MIXTURES WITH CO_2

Andreas Jäger*
TU Dresden
Dresden, Germany
Email: andreas.jaeger@tu-dresden.de

Erik Mickoleit
TU Dresden
Dresden, Germany

Cornelia Breitkopf
TU Dresden
Dresden, Germany

ABSTRACT
Supercritical CO_2 as a working fluid offers distinct advantages for power cycles, such as a comparably low critical temperature and pressure. However, the favorable properties of supercritical CO_2 could potentially be enhanced by blending CO_2 with suitable additives. In order to find promising additives for CO_2, a theoretical screening seems to be most feasible, as extensive experimental studies would be very time-consuming. For this purpose, a mixture model is needed that on the one hand

model [2–4] can be used. This model allows for a very accurate representation of experimental data for mixtures, if the model parameters are fitted to experimental data. However, the predictive capabilities of this model are rather limited. Therefore, Jäger et al. [5,6] have developed a theoretically based departure function for the multi-fluid mixture model, which allows for the combination of the multi-fluid mixture model with the predictive excess Gibbs energy models UNIFAC and COSMO-SAC.
The basic idea of the UNIFAC model [7] is to describe the

Cycle Modeling

- Consideration of two rather simple cycle architectures as a basic model for screening
- Parameter range according to recooling conditions at elevated ambient temperatures, typical for e.g. CSP applications or hot summer days

Boundary condition	Symbol	Value
Min. temperature	$\vartheta_{low} \equiv$ CIT	31 .. 40 °C
Max. temperature	$\vartheta_{high} \equiv$ TIT	500 °C
Lower pressure level	p_{low}	7.4 MPa
Upper pressure level	p_{high}	20 MPa
Compressor efficiency	η_C	0.8
Turbine efficiency	η_T	0.9
Min. pinch point difference recuperator	ΔT_R	10 K

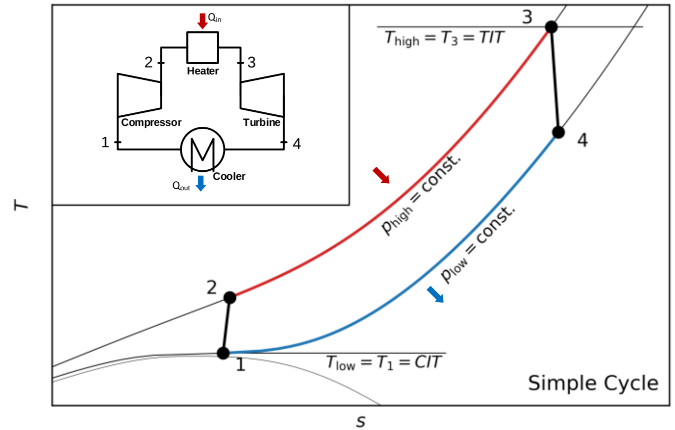


Fig. a): Block diagram and *T-s* diagram representation of the Simple Cycle

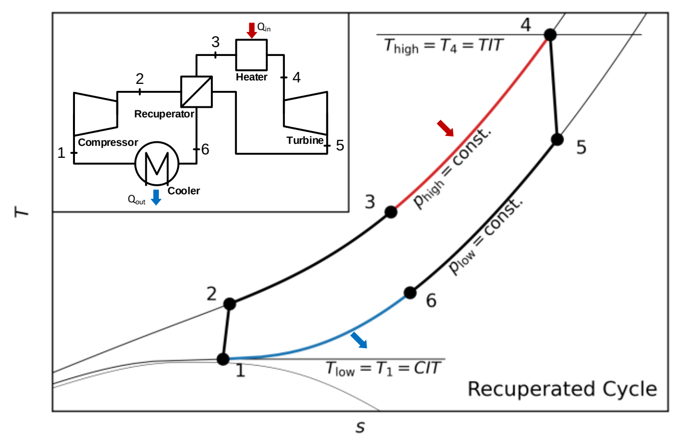


Fig. b): Block diagram and *T-s* diagram representation of the Recuperated Cycle

Overall screening

- Screening of a set of a total of 135 fluids in 11 concentrations up to 40 mol% each
- Fixed inlet temperature of ϑ_{low}= 40°C → “worst case” of the previously defined base scenario
- Comparison of the relative efficiency change with respect to pure CO_2

Criteria for valid results:

- Single-phase mixture at each process point
- No pinch point violation in the recuperator

After excluding invalid results, a total of 111 fluids remained for evaluation

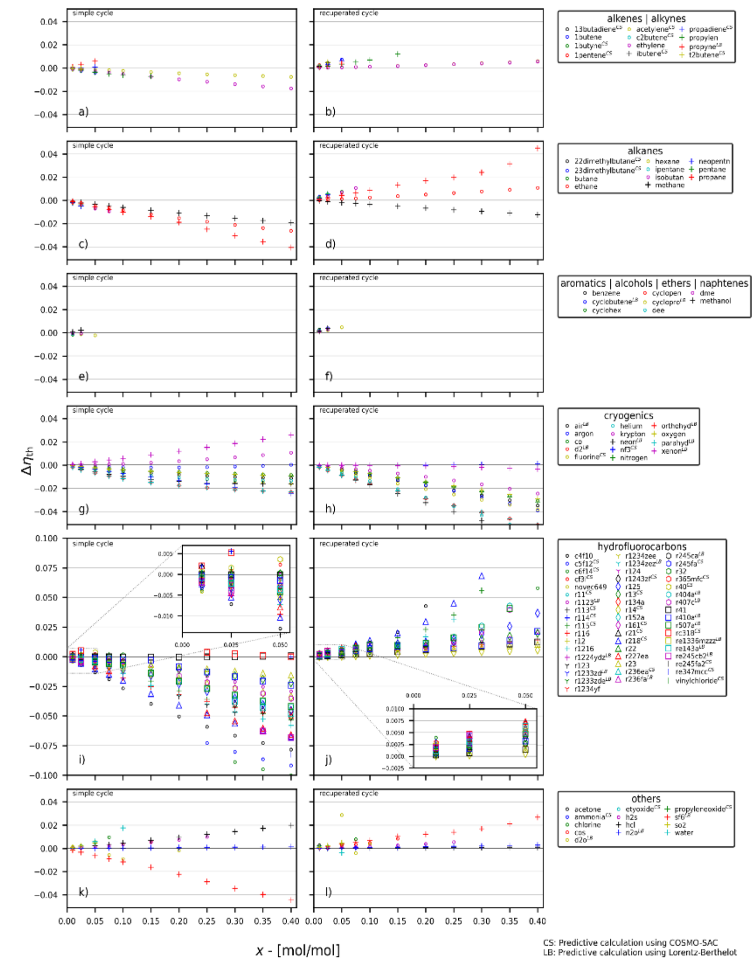
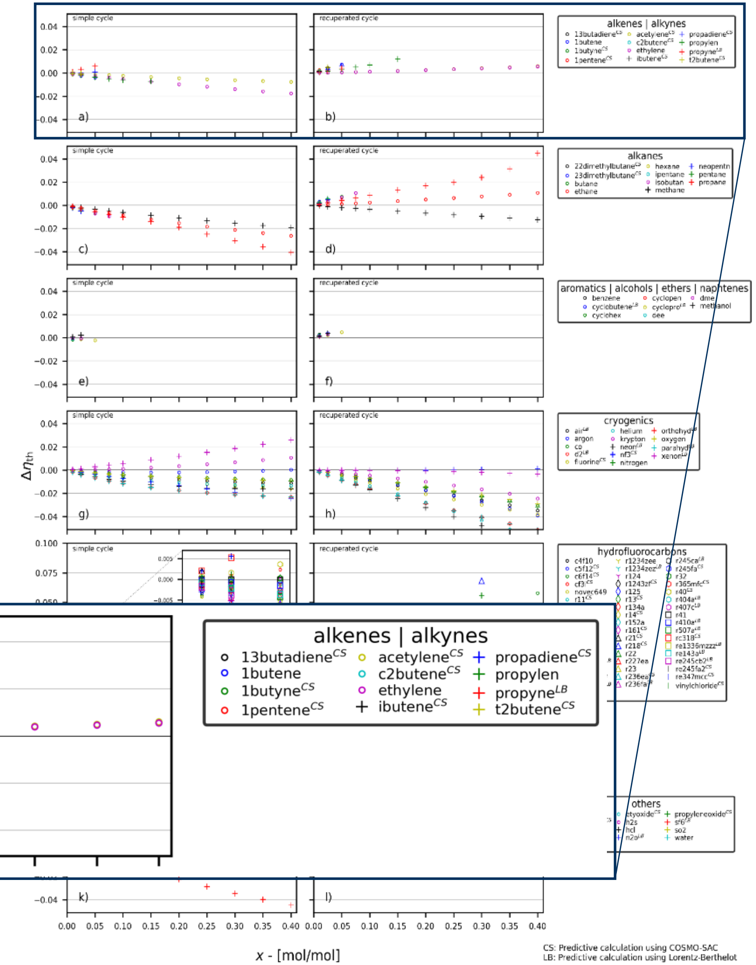


Fig. a): Synoptical plot of the screening results

Overall screening

- Each group contains mixtures that lead to an increase in efficiency in one of the two processes
- Distinct “trend reversal” of some fluids when comparing both cycle architectures
- Noticeable mixing gaps for several fluids
- Absence of solutions due to pinch point violations in the recuperator



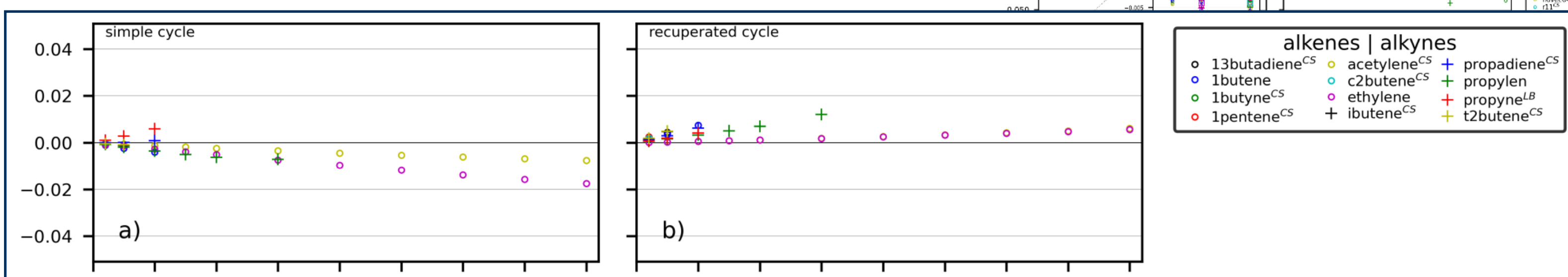


Fig. a): Synoptical plot of the screening results

Selection of promising mixture candidates

Selection of 5 mixture candidates of which each:

- Showed a significant increase in efficiency in one of the two process architectures
- General suitability for use in technical systems (e.g. exclusion of HCl despite good performance)
- Comparatively low environmental impact

Name	Chem. Symbol	Mixing Model	$\Delta\eta_{\mathrm{th,max}}$ Simple cycle	$\Delta\eta_{\mathrm{th,max}}$ Recuperated cycle
Carbonyl sulfide	COS	Adjusted	$\approx +1.0\%$	$\approx +0.5\%$
Krypton	Kr	Adjusted	$\approx +1.2\%$	$\approx -2.2\%$
Propane	C_3H_8	Adjusted	$\approx -4.2\%$	$\approx +4.2\%$
Sulfur hexafluoride	SF_6	LB	$\approx -4.2\%$	$\approx +2.3\%$
Xenon	Xe	LB	$\approx +2.2\%$	$\approx -0.25\%$

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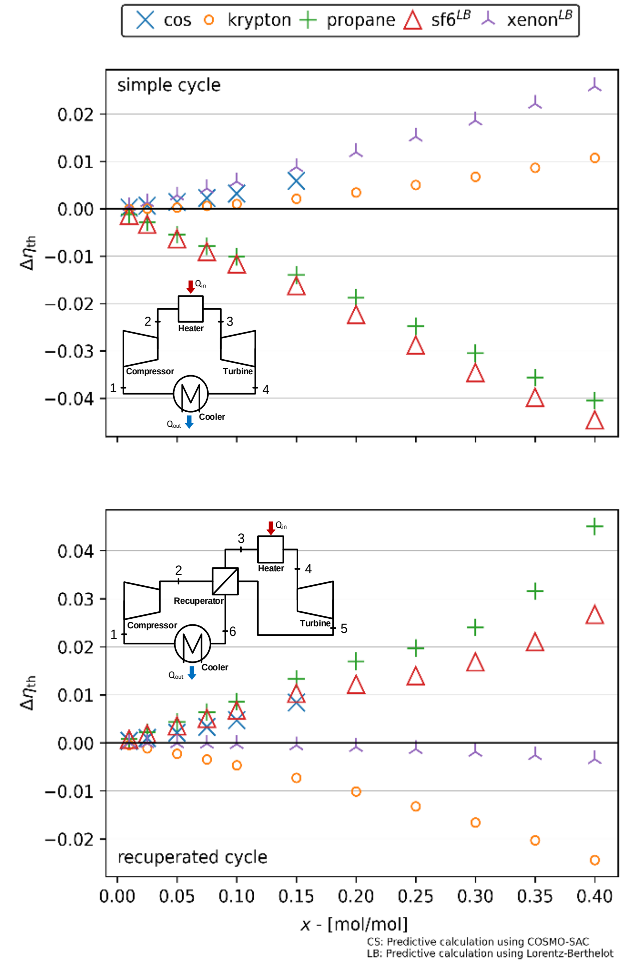

Fig. a): Comparative plot of the mixture candidates

Previously described effects are also apparent in the selection:

- Trend reversal in most of the candidates in varying strength
- Limited solubility for higher concentrations of **COS** in **CO_2**
- Similar behavior of **C_3H_8** and **SF_6** as well as the noble gases **Kr** and **Xe**
- **COS** is exceptional as it leads to higher efficiencies in both cycles

Change of the process in the h-s diagram

Kr and **Xe** | Simple Cycle ↑ Recuperated Cycle ↓

- Reduction in the total amount of added heat $\Delta h_{Q,\mathrm{tot}}$ and recuperated heat Δh_{R} with higher concentrations
- Isobar slope / turbine enthalpy difference Δh_{T} remains almost unaffected
- Higher compression work Δh_{C} for higher concentrations **(Kr)**

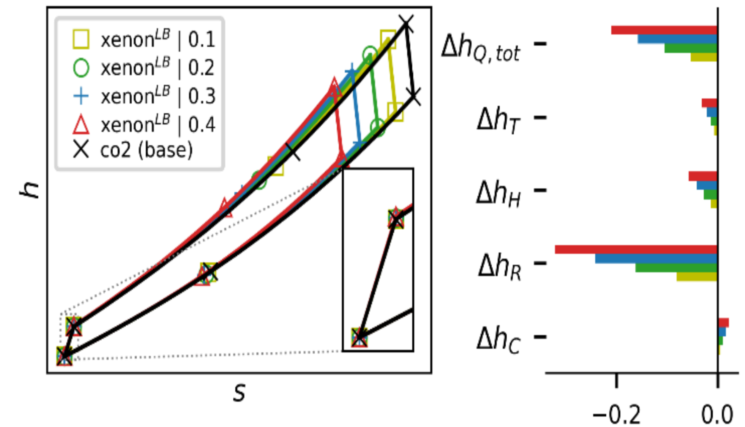

Fig. a): *H-s* diagram and enthalpy differences for different concentrations of CO_2 and Xe

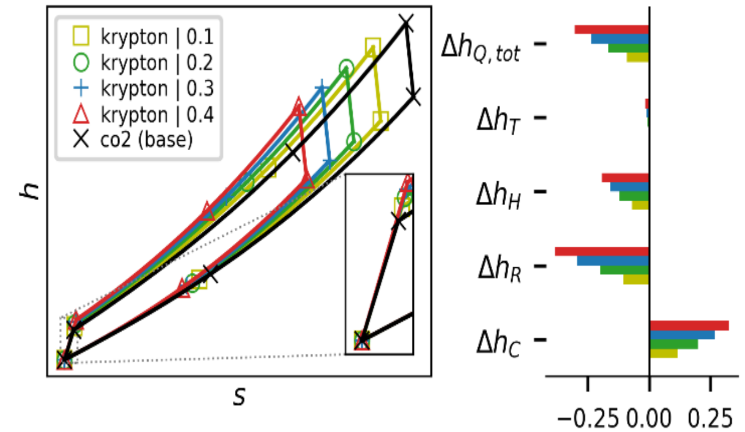

Fig. b): *H-s* diagram and enthalpy differences for different concentrations of CO_2 and Kr

Change of the process in the h-s diagram

Kr and **Xe** | Simple Cycle ↑ Recuperated Cycle ↓

– Reduction in the total amount of added heat $\Delta h_{\mathrm{Q,tot}}$ and recuperated heat Δh_{R} with higher concentrations

– Isobar slope / turbine enthalpy difference Δh_{T} remains almost unaffected

– Higher compression work Δh_{C} for higher concentrations (Kr)

C_3H_8 and **SF_6** | Simple Cycle ↓ Recuperated Cycle ↑

– Notable increase in $\Delta h_{\mathrm{Q,tot}}$ and Δh_{R} with higher concentrations, greater increase in Δh_{R} than $\Delta h_{\mathrm{Q,tot}}$

→ Potential increase in recuperator costs!

– Reduction in Δh_{C}, almost no change in Δh_{T}

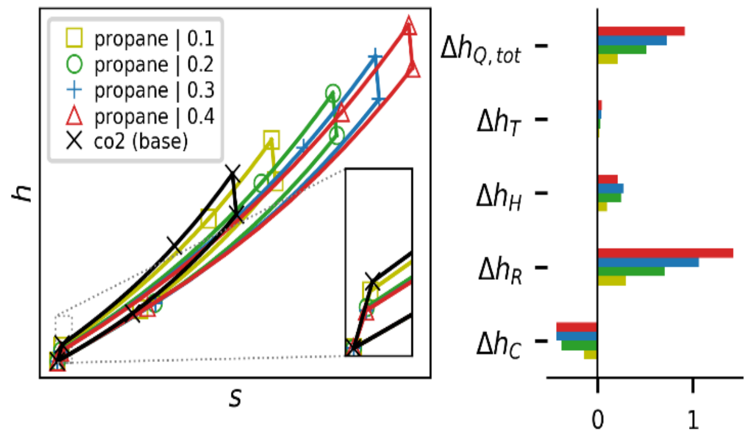

Fig. a): *H-s* diagram and enthalpy differences for different concentrations of CO_2 and propane

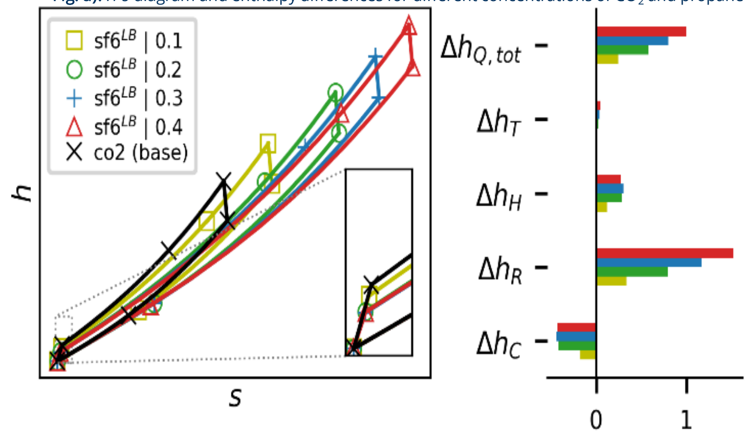

Fig. b): *H-s* diagram and enthalpy differences for different concentrations of CO_2 and SF_6

Change of the process in the h-s diagram

Kr and **Xe** | Simple Cycle ↑ Recuperated Cycle ↓

- Reduction in the total amount of added heat $\Delta h_{\mathrm{Q,tot}}$ and recuperated heat Δh_{R} with higher concentrations
- Isobar slope / turbine enthalpy difference Δh_{T} remains almost unaffected
- Higher compression work Δh_{C} for higher concentrations (Kr)

C_3H_8 and SF_6 | Simple Cycle ↓ Recuperated Cycle ↑

- Notable increase in $\Delta h_{\mathrm{Q,tot}}$ and Δh_{R} with higher concentrations, greater increase in Δh_{R} than $\Delta h_{\mathrm{Q,tot}}$

→ But: potential increase in Recuperator costs!

- Reduction in Δh_{C}, almost no change in Δh_{T}

COS | Simple Cycle ↑ | Recuperated Cycle ↑

- Distinct reduction in Δh_{C}
- Only moderate changes in the added amount of heat as well as the isobar slope

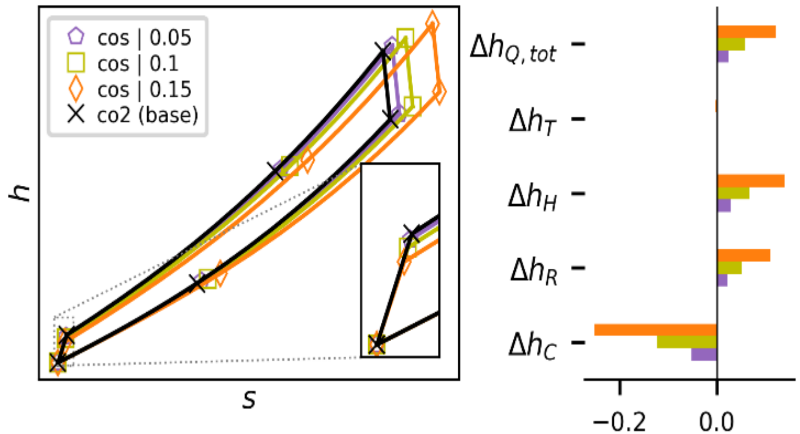

Fig. a): H-s diagram and enthalpy differences for different concentrations of CO_2 and COS

Change of effects with varying CIT

Kr and **Xe**
- Efficiency increase almost independent from CIT for the simple cycle
- Slight reduction in the efficiency for the recuperated case with higher temperatures

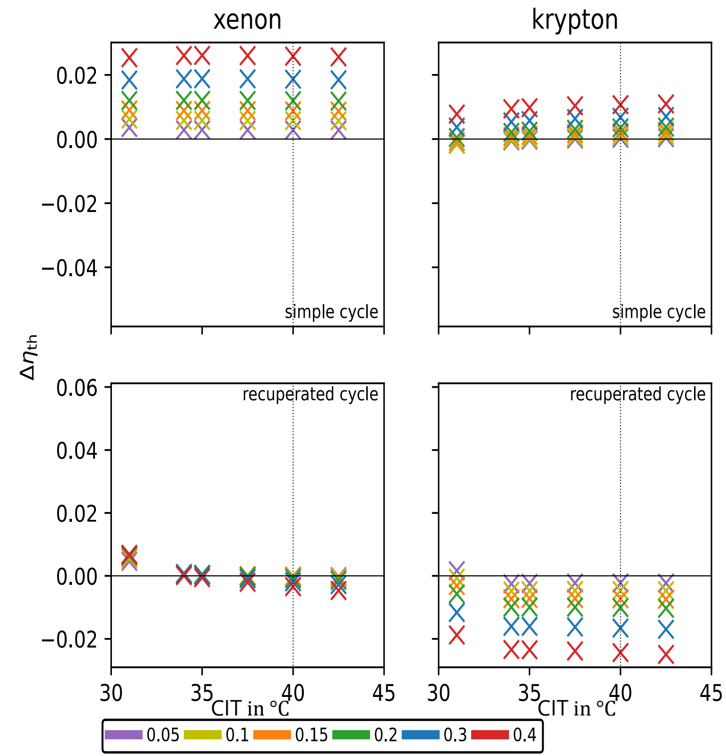

Fig. a): Efficiency change by addition of Kr or Xe for varying CIT

Change of effects with varying CIT

Kr and **Xe**
- Efficiency increase almost independent from CIT for the simple cycle
- Slight reduction in the efficiency for the recuperated case with higher temperatures

C_3H_8 and **SF_6**
- Almost same behavior despite pinch point violation for propane in the recuperator
- Significant decrease in efficiency for all concentrations in the simple cycle
- Effects in the recuperated case differ with the concentration of the additive

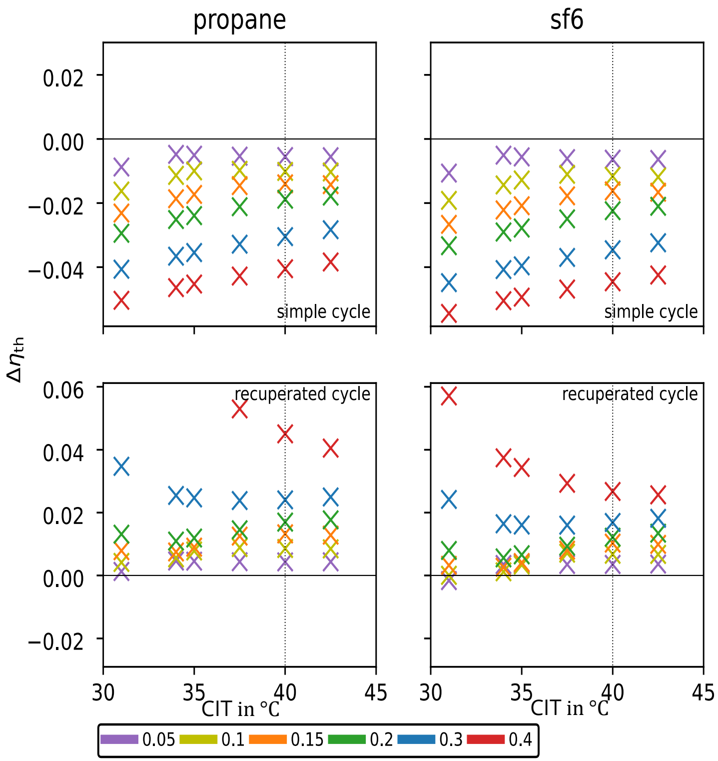

Fig. a): Efficiency change by addition of C_3H_8 (propane) or SF_6 for varying CIT

Change of effects with varying CIT

Kr and **Xe**
- Efficiency increase almost independent from CIT for the simple cycle
- Slight reduction in the efficiency for the recuperated case with higher temperatures

C_3H_8 and SF_6
- Almost same behavior despite pinch point violation for propane in the recuperator
- Significant decrease in efficiency for all concentrations in the simple cycle
- Effects in the recuperated case differ with the concentration of the additive

COS
- Absence of results shows the limited solubility → violation of the criteria of a single phase at every process point
- Same behavior for both cycles with a slight decrease in efficiency for higher CIT

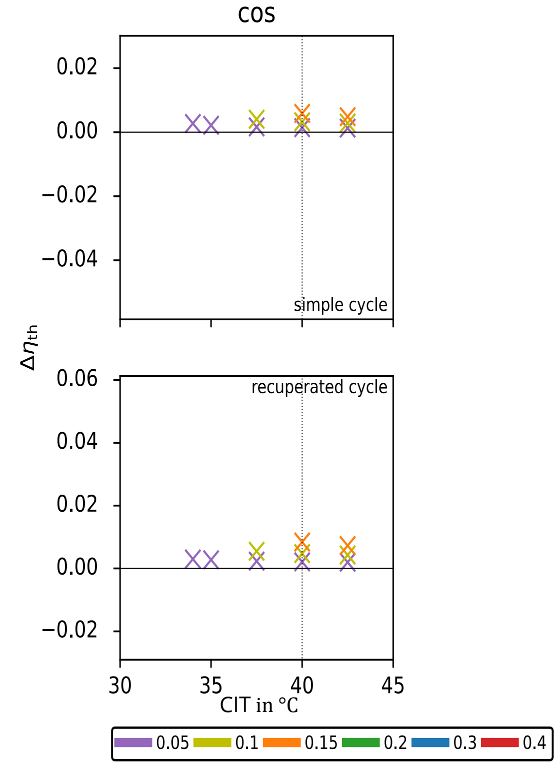

Fig. a): Efficiency change by addition of COS for varying CIT

Conclusion

Study of the Influence of Additives to CO_2 on Performance Parameters of a sCO_2-Cycle

- Analysis of a total of 135 fluids by using adapted mixture parameters as well as predictive methods
- Application to a base scenario with two different cycle architectures operated at elevated CIT
- Detailed evaluation of 5 promising mixing partners

With the use of additives, sCO_2-cycles can be optimized for changing operating conditions

- Efficiency increases up to 4% compared to pure CO_2 could be predicted
- Different effects of the individual mixing partners require targeted adaptation to the individual case
- Efficiency increase and suitability must be tested independently → Further evaluation needed

»Wissen schafft Brücken.«

Thank you for listening.