

Research on the Effect of the Pinch Point Shift in Cycles with Supercritical Carbon Dioxide

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ABSTRACT

Supercritical carbon dioxide (S-CO₂) cycles are recently very perspective and are researched all around the world. Research of the S-CO₂ cycles is ongoing at the Czech Technical University (CTU) as well. Research on CTU is focused on the pinch point analysis. This point affects the entire loop and causes problems during the design of individual components. Therefore it is necessary to find the location of this point during the cycle design, for specific conditions (temperature, pressure). For known pressures and temperatures the pinch point can be found in several ways by using heat capacity profiles. If this point occurs in the heat exchanger, it causes complications in designs. Due to the pinch point, heat exchangers have a large size and a low efficiency. The pinch point can be removed with the addition of small amounts of another gas. The critical point of this other gas is at a different temperature and pressure. For the mixture of CO₂ and another gas the pinch point location will be altered, thereby allowing the removal of this point from the heat exchangers. However, adding other gases has affects the behavior of other components in the loop and the subsequent change in the cycle efficiency of the loop. This paper is focused on the research of the pinch point shifts in such a way that the loop is affected as little as possible and therefore the pinch point shift does not cause problems to the loop design. The first part of the paper is concerned with finding the optimal gas for the pinch point shift. It compares how a gas with the critical point lower than CO₂ and a gas with the critical point higher than CO₂ affects the pinch point location. Simultaneously, it focuses on finding the optimal level of concentration enabling the sufficient pinch point shift and how this concentration affects the entire loop. After this part the paper deals with the calculation of the basic thermal cycles with CO₂, which are compared with the thermal cycles with mixtures of CO₂ and other gases. Primarily, it is focused on the recompression cycle. These cycles are calculated for different pressure ratios and temperatures. Subsequently, their efficiencies are compared. Accordingly, it is possible to determine how and which gas has affected the entire loop at various concentrations as well as how this gas will cause the pinch point shift. It is necessary to determine the optimal mixture, which affects the loop, and thereby its efficiency, the least. At the same time however, it must move the pinch point in a way which affects the design and loop calculation and its components, especially heat exchangers, only minimally. The result of this paper will be the determination of an optimal mixture of CO₂ and other gases for various parameters cycles.

INTRODUCTION

Supercritical carbon dioxide (S-CO₂) cycles are recently very prospective and are researched all around the world. Research of the S-CO₂ cycles is necessary because there are several issues in the use of these cycles. These problems have an effect on the design of each component and thus have an effect on the whole cycle. One of the major problems is the pinch point. This is a point, in which the heat capacity of CO₂, are equal for two different pressure levels. If the pinch point it occurs in the heat exchanger it causes major problems in the design of heat exchangers for CO₂ cycle. Due to the pinch point, the heat exchangers have a large size and a low efficiency. The pinch point can be removed with the addition of small amounts of another gas. This paper focuses on the research of the pinch point shift in a manner that the loop is affected as little as possible. The first part of the paper aims finding the optimal gas for the pinch point shift. It compares how a gas with the critical point lower than CO₂ and a

gas with the critical point higher than CO₂ affects the pinch point location subsequently. The paper deals with the calculation of the basic thermal cycles with CO₂, which are compared with the thermal cycles of mixtures of CO₂ and other gases. Main focus is on the recompression cycle. The result of this paper will be the determination of an optimal mixture of CO₂ and other gases for various parameters cycles.

GASEOUS ADMIXTURES

The first part of this paper focuses on finding the optimal gas for the pinch point shift. Helium [3], Argon, Nitrogen and Oxygen were selected as the pure gases having the critical point lower than CO₂. The suitable gas with the critical point higher than CO₂ was not found. For the paper also Air was used [3], which is the mixture of Argon, Nitrogen and Oxygen. Air is modelled as 78% N₂, 21% O₂ and 1% Ar. The critical point for pure CO₂ and for another pure gases used are shown in table 1.

Table 1. The critical point of pure gases

Substance	Critical Pressure [MPa]	Critical Temperature [K]
CO ₂	7.37	304.13
Argon	4.86	150.69
Helium	0.23	5.19
Nitrogen	3.39	126.19
Air	3.85	132.84

Each gas, from table 1, has a different effect on the critical point shift. The shift of the critical point depends on the amount of gas added. The amount of added gas is indicated in Mole Fraction.

The addition of helium into pure CO₂ resulted in the pressure increase from 7.37 to 10.59 MPa for mole fraction 0.05. For other gases the additions also lead to the increase of the critical pressure, but this increase is not as high as for helium with same mole fraction. It is interesting, that the addition of small amounts of Argon, Nitrogen or Oxygen, lead to the reduction of the critical pressure to 6.5 MPa. This is achieved for Oxygen and Nitrogen by adding mole fraction 0.001. The move of the critical pressure in dependent on the mole fraction as shown at Figure 1.

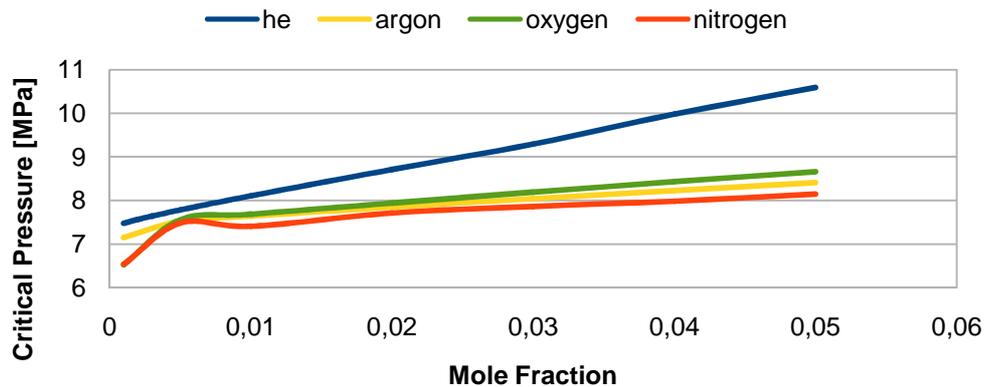


Figure 1. The shift of the Critical pressure for gaseous admixtures

The temperature of the critical point moves upwards for Helium and reaches 309.76 K for mole fraction 0.05. The temperature increases with addition of small amounts of gases but from mole fraction 0.005 the temperature starts to decrease. Nevertheless until the mole fraction of 0.005 the critical temperature does not exceed the critical temperature of pure CO₂. This applies for Argon, Nitrogen and Oxygen. The shift of the critical temperature in dependence on mole fraction is shown in Figure 2.

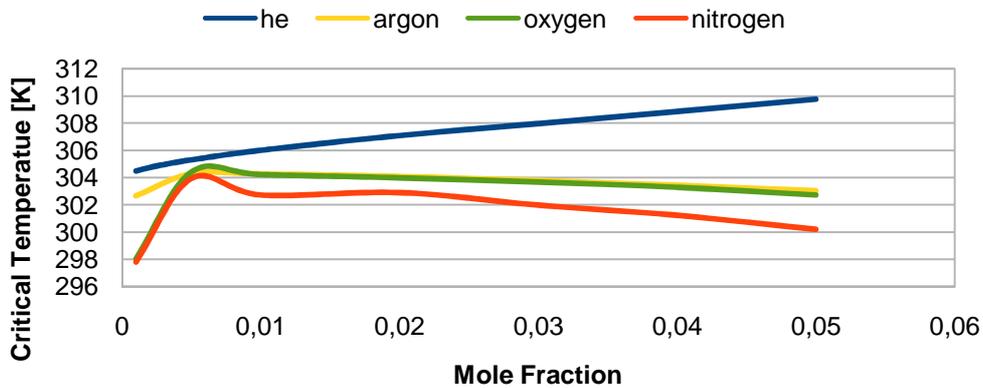


Figure 2. The shift of the Critical pressure for gaseous admixtures

EFFECT OF ADMIXTURES ON THE PINCH POINT

Pinch point occurs in a heat exchange at a point at which heat capacities are equal for two different pressure levels of the same medium if the flow is equal on both sides. Localizing the pinch point is very simple if one knows the heat capacity of CO₂ for different pressures and temperatures. This dependency is shown in Figure 3., where the curves describe the intersections of the heat capacities.

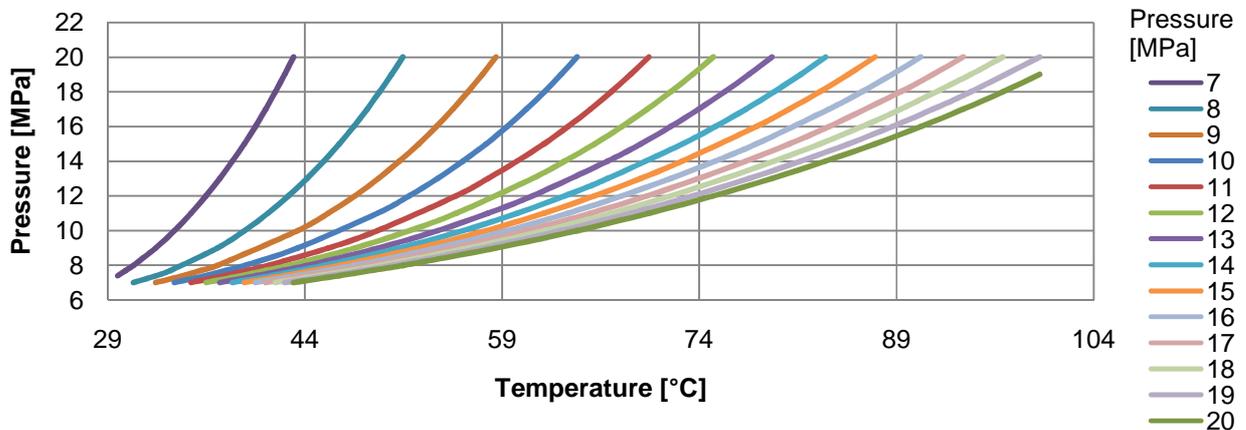


Figure 3. Dependence of pinch point location on the temperature and pressure

This same dependence was determined for all the used mixtures with mole fractions ranging from 0 to 0.02 for each of the gases. The minimum pressure is 7 MPa and maximum pressure is 20 MPa for used mixtures in this paper. The second pressure is 8 MPa for the calculation which are in this paper.

Pinch point is shifted by adding a small amount gas into pure CO₂. This shift is different for different pressure levels and the amount of gas added. However, addition of any small amount of gas will always cause a reduction of the pinch point temperature by a few degrees. Decrease of temperature increases with addition of more gas. In this paper we consider the addition of gas to maximum mole fraction 0.05.

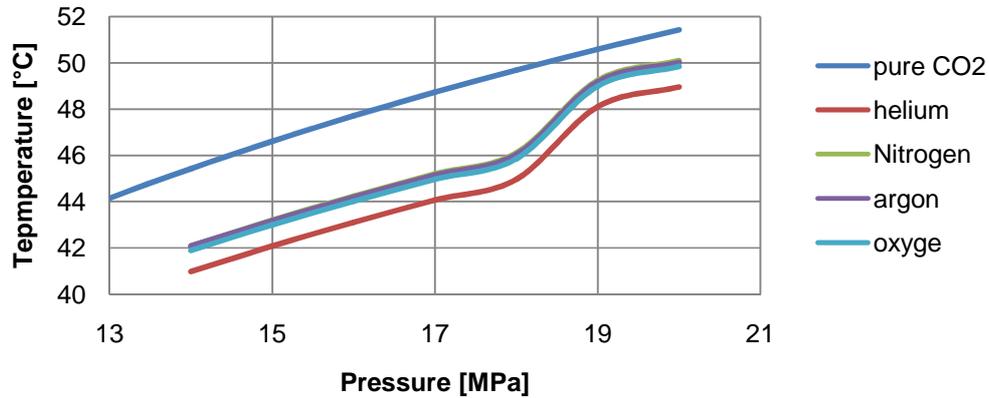


Figure 4. Dependence of pinch point temperature on pressure for mole fraction 0.01 and second pressure 8 MPa

Pinch point temperature dependence on pressure and the amount of gas for mole fraction 0.01 is shown in Figure 4. It is evident, that the largest decrease in temperature is after the addition of helium, for mole fraction 0.01. Nitrogen, Argon and Oxygen have approximately the same decrease in temperature. For example, pressure levels 8 and 18 MPa have the temperature of pinch point of 49.68 °C, for Helium the temperature is 44.97 °C and for Nitrogen the temperature is 46.1 °C.

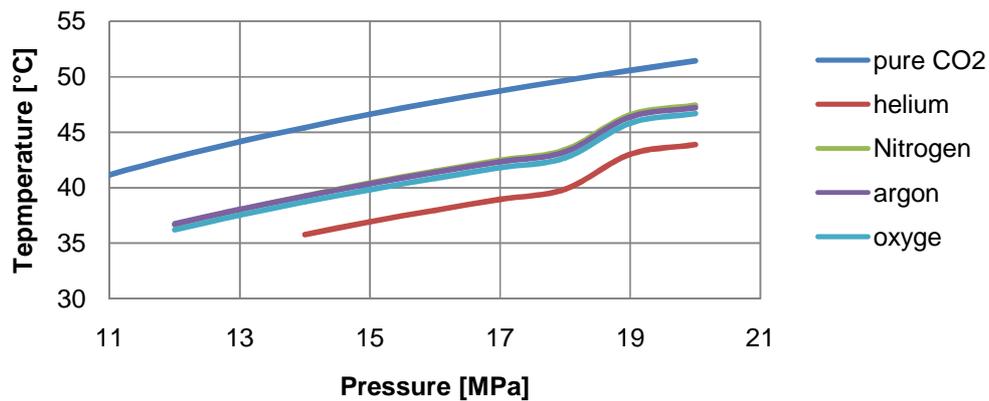


Figure 5. Dependence of pinch point temperature on pressure for mole fraction 0.03 and second pressure 8 MPa

A similar behaviour of the decrease of the pinch point temperature can be seen for mole fraction 0.03 as shown in Figure 5. The decreases of temperature is greater than for the mole fraction 0.01. For example, the pressure level 8 and 14 MPa have temperature of pinch point about 10 °C less than for pure CO₂.

In Figure 6 the decrease for mole fraction 0.05 is shown. The largest decrease of the temperature is achieved again with Helium.

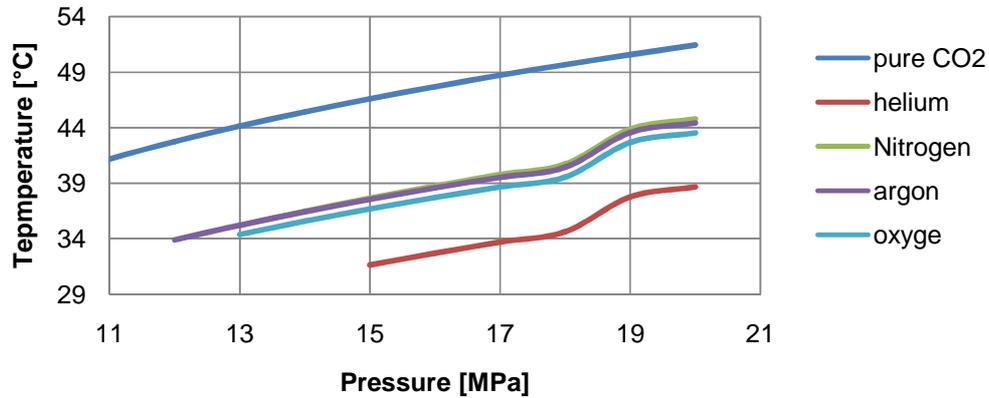


Figure 6. Dependence of pinch point temperature on pressure for mole fraction 0.05 and second pressure 8 MPa

It can be concluded that the shift of pinch point is possible even with small amounts of gases additions. This procedure can be applied to quickly find the pinch point and to eliminate the problems with pinch point for the calculation of the heat exchanger. Time needed for calculation is reduced as well as the size and associated costs of the heat exchanger. However, adding gas to pure CO₂ can lead to a decrease in the efficiency for the other components of the loop. This could cause a drop of the overall cycle efficiency. Therefore, selecting the correct ratio of gaseous admixture for minimal decrease of the cycle efficiency is essential.

THE CALCULATION OF BASIC CYCLES EFFICIENCIES

In this part of the paper the calculation of basic thermal cycles with CO₂ are performed. The obtained efficiencies are compared with efficiencies of the thermal cycles with mixtures of CO₂ and Nitrogen, Oxygen or Argon or mixture of CO₂ and Air. Primarily, it is focused on the recompression cycle, but for comparison the results of the simple Brayton cycles will be shown. These cycles are calculated for different pressure ratios and different temperatures. The basic cycles parameters for the calculation are shown in Table 2.

Table 2. The basic cycles parameters

Constans parameters		
Main Compressor inlet temperature	32	°C
Compressor efficiency	81	%
Turbine efficiency	90	%
Recuperator efficiency	95	%
Main compressor outlet pressure	20	MPa
Various parameters		
Turbine inlet temperature	550 to 600	°C
Pressure ratio	2.7 to 3.1	

The calculations were done for turbine inlet temperature 550 and 600 °C, and the five pressure ratios 2.75, 2.8, 2.9, 3 and 3.1 for each turbine inlet temperature.

Recompression cycle

Recompression cycle is one of the most commonly used thermal cycles for CO₂. Cycle efficiency was calculated for the parameters specified in table 2. The heat and pressure losses were not considered in the calculation. Dependence of cycle efficiency for pure CO₂ and for the pressure ratio from 2.3 to 4 is shown in Figure 7.

Cycle efficiency slowly decreases after adding the small amounts of gases. This decrease is on the order of 0.1 % per 0.008 mole fraction. This is shown in Figure 8 and Figure 9. Cycle efficiency subsequently decreases for large amounts of gases. This decrease is shown in Figure 10. Dependence of the cycle efficiency on the mole fraction in Figure 10 is for Helium.

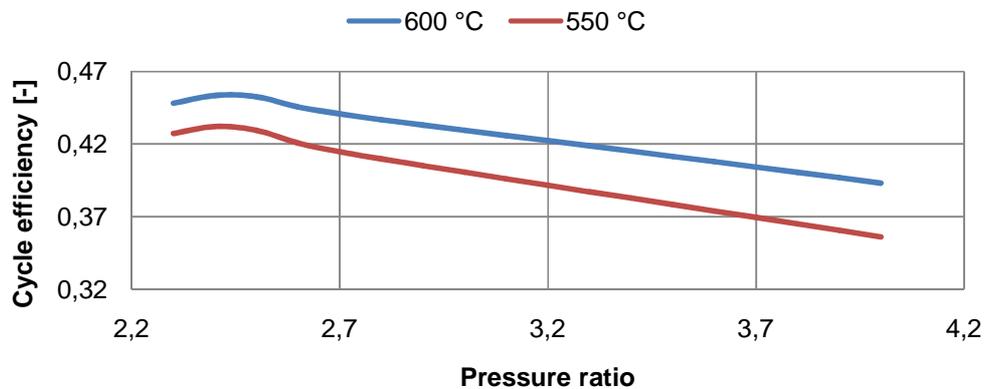


Figure 7. Dependence of the cycle efficiency on the pressure ratio for pure CO₂ and for turbine inlet temperature 550 °C and 600 °C

The dependence of the cycle efficiency on the mole fraction in Figure 8 and in Figure 9 is for Helium. The pressure ratios were chosen as the most probable pressure ratios used for thermal cycles with CO₂. Dependence for turbine inlet temperature 600 °C is shown in Figure 8.

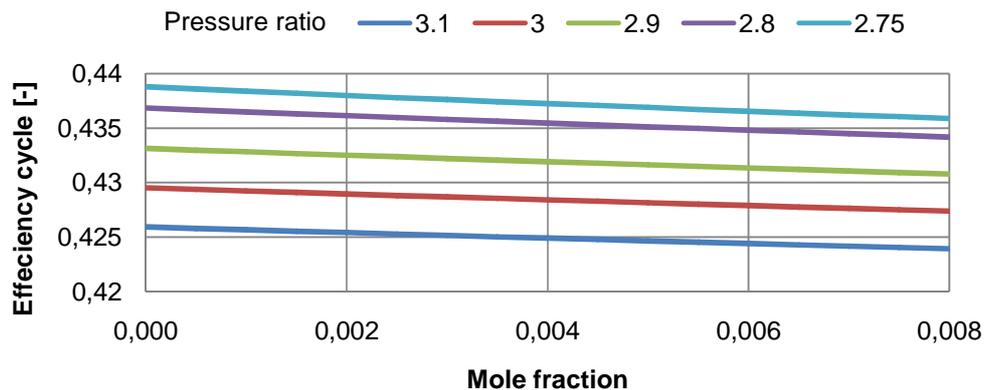


Figure 8. Dependence of the cycle efficiency on the mole fraction for Helium and for turbine inlet temperature 600 °C

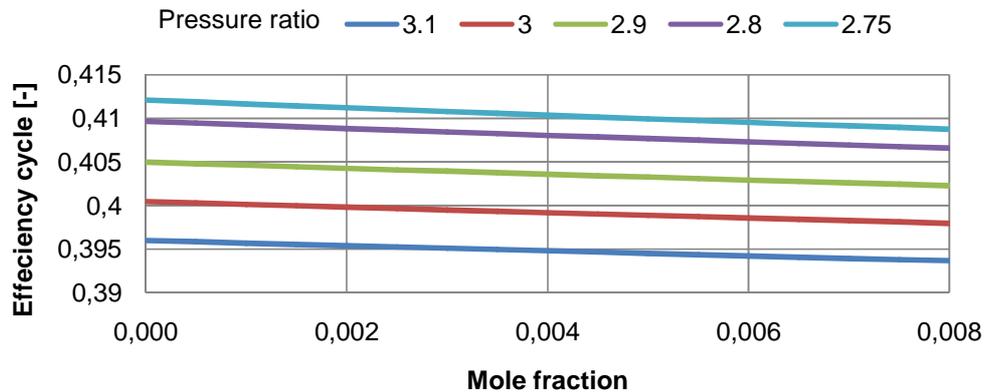


Figure 9. Dependence of the cycle efficiency on the mole fraction for Helium and for turbine inlet temperature 550 °C

The dependence for turbine inlet temperature 550 °C is shown in Figure 9. Decrease in efficiency has approximately the same course for all pressure ratios as shown in Figure 8 and 9. Therefore, it is further calculated only with the pressure ratio 3.1. For other pressure ratios a similar pattern to that of helium is expected.

The dependence of the cycle efficiency on the mole fraction for Helium, Argon, Oxygen Nitrogen and Air is shown in Figure 10. This dependence is for pressure ratio 3.1.

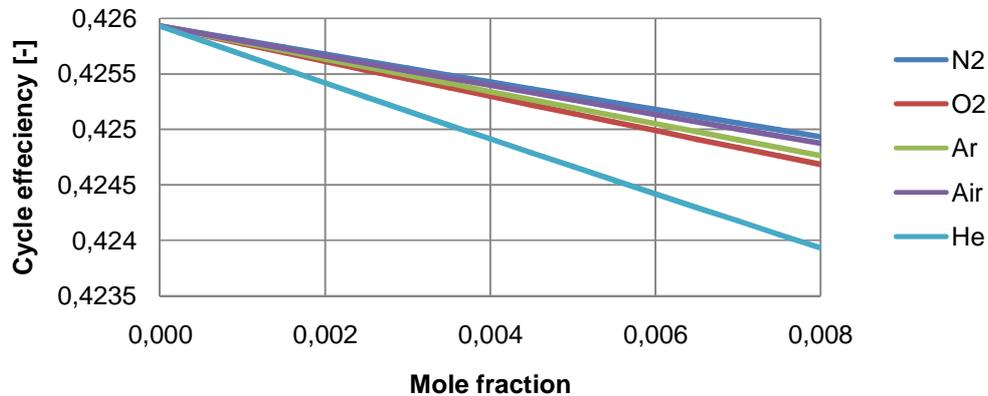


Figure 10. Dependence of the cycle efficiency on the mole fraction for pressure ratio 3.1

The largest decrease of the efficiency has Helium, will Nitrogen has the smallest decrease. However, this decrease is very small for the mole fraction into 0.01. Efficiency decrease for the mole fraction into 0.05 is acceptable. The optimum mole fraction is from 0.01 to 0.02. In this range there is no large influence on efficiency, but it is sufficient to cause the pinch point shift by a few degrees.

Simple Brayton cycle

The same procedure was applied to the Simple Brayton cycle. Dependence of the cycle efficiency for pure CO₂ and for the pressure ratio from 2.3 to 4 is shown in Figure 11.

The calculation was performed for a pressure ratio 3.1 and the turbine inlet temperature of 600 °C. The calculations were performed similarly for other cycle temperature and pressure values as in the case of the recompression cycle. The dependence of the cycle efficiency on the mole fraction is shown in Figure 12.

The dependence of the cycle efficiency on the mole fraction for Helium, Argon, Oxygen Nitrogen and Air is shown in Figure 13. This dependence of the cycle efficiency is for pressure ratio 3.1.

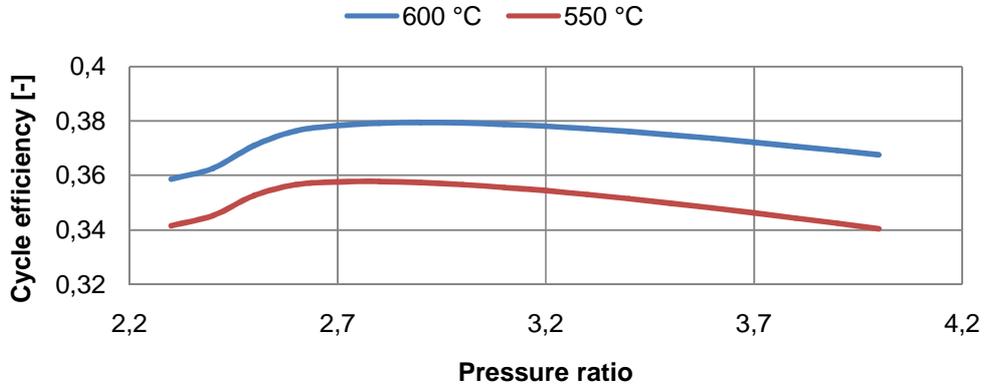


Figure 11. Dependence of the cycle efficiency on the pressure ratio for pure CO₂

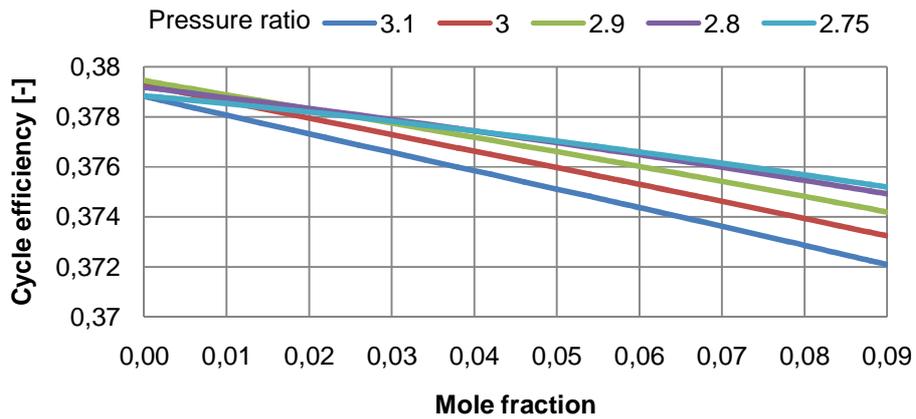


Figure 12. Dependence of the cycle efficiency on the mole fraction for Helium and for turbine inlet temperature 600 °C

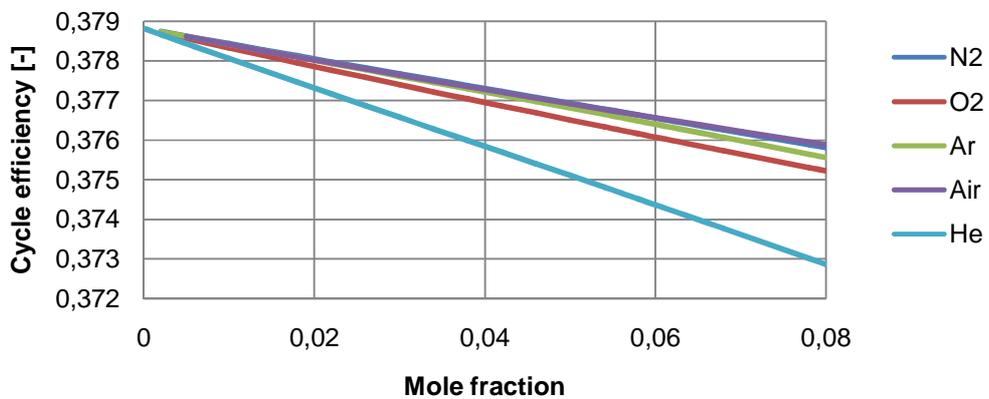


Figure 13. Dependence of the cycle efficiency on the mole fraction for pressure ratio 3.1

It is obvious that the largest decrease of the efficiency has Helium, while Nitrogen has the smallest decrease as in the case of the recompression cycle. The optimum fraction is the same as for the recompression cycle.

THE CALCULATION OF HEAT EXCHANGER

The last part of this paper is calculation of heat exchanger. This calculation is performed in order to understand the effect the gaseous admixtures have on the design of a heat exchanger. The major problem for the calculation is the pinch point. The first step is to find the pinch point in heat exchanger.

Following the determination of the pinch point, it is possible to proceed by changing the parameters of the cycle to provide a positive Δt in the heat exchanger

Due to the pinch point it is necessary to ensure positive temperature gradient Δt in heat exchanger. Therefore the calculation was divided into two calculations. The first calculation was carried out from the pinch point to the cold end and the second calculation was carried out from the pinch point to the hot end of the heat exchanger Δt equal to 10°C , was selected on the pinch point. If the pinch point is not in the heat exchanger, minimum temperature gradient on the cold end of the heat exchanger is used.

Table 3. The temperature of the pinch point for pressure 25 and 12.5 MPa

	Temperature[$^{\circ}\text{C}$]
Pure CO ₂	84.28
Helium	82.26
Oxygen	82.60
Nitrogen	82.90
Argon	83.23

The temperatures of the pinch point are shown in Table 3. These temperatures are for the mole fraction 0.01 and the calculation was performed with the same mole fraction too.

Table 4. Basic parameters for heat exchanger

Presssure primary side	25	MPa
Presssure secondary side	12.5	MPa
Mass flow	2.5	kg/s
Tempererature t_1	42	$^{\circ}\text{C}$
Tempererature t_2	160	$^{\circ}\text{C}$

For the calculation, counter current heat exchanger is selected. This is a tube heat exchanger. Both working substances are pure CO₂ or the same mixture. The heat exchanger is operating at pressures of 12.5 and 25 MPa. Basic parameters for heat exchanger are shown in Table 4. The results are shown in Table 5.

Table 5. The results for the heat exchanger

	Total Length [m]	Thermal Power [kW]
Pure CO₂	34.02	609.14
Helium	34.00	604.84
Oxygen	33.83	605.73
Nitrogen	33.95	605.75
Argon	32.91	605.00

The calculation shows a small reduction in thermal power and length of the heat exchanger. For all calculations NIST Standard Reference Database 23, Version 9.1 was used.

CONCLUSIONS

The gaseous admixtures have effect on pinch point, thermal cycle efficiency, heat exchanger and other components. This influence can be positive but also negative it depends on the required parameters for cycle.

Even for the small amounts of gases the shift of pinch point is possible. This is a positive effect but shifts the pinch point only a few degrees. The removal of the pinch point in heat exchanger is only possible for some pressure levels. However influence on the heat exchanger is positive. For this type of the heat exchanger the size is slightly smaller.

The procedure can be used to eliminate problems with the pinch point for the calculation of the heat exchanger.

In this paper Helium was considered because it is assumed that it will be the most likely candidate for a leak detection in gas cycles. Other gases are used because they are contained in air i.e. Argon, Nitrogen and Oxygen. It is very probable that air will occur as impurities in the cycle. The effect of these gases is similar as for Helium. It is possible to use others gases for example CO or another mixture as air. Further research is necessary.

Cycle efficiency decrease is very small for small amounts of gas additions. Therefore, it is possible to consider S-CO₂ cycle with these gaseous admixtures. Further research is necessary to determine the optimal amount of gases for different pressure levels and for different connections of cycle and possibly other gas additions.

Furthermore it is very important to consider the possible chemical reaction of these gases with each other and with the structural materials. In general all gases had a positive effect on the cycle but it is necessary to verify at reasonable amounts the influence on the other components.

NOMENCLATURE

CO ₂	=	Carbon dioxide
Ar	=	Argon
He	=	Helium
N ₂	=	Nitrogen
O ₂	=	Oxygen
Δt	=	Temperature gradient
CO	=	Carbon monoxide

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