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The Effect of Impurities in Rich CO_2 Working Fluid on the Power Output of a 10 MW S-CO_2 Gas Turbine Power Plant

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ABSTRACT

The Carleton University Brayton Cycle Loop (CUBCL) is a project involving virtually all aspects of 10 MW supercritical carbon dioxide (S−CO_2) gas turbine design. Using CO_2 as the working fluid in such a supercritical power cycle has improved cycle performance with respect to the thermodynamic properties near the critical point. As working fluid density is a key factor, it is fully considered during the design.

The aim of this work is to investigate the effect of the non-condensable impurities such as Nitrogen (N_2), Oxygen (O_2), Carbon monoxide (CO) and Argon (Ar) which are common impurities in all CO_2 capture processes. The work is also extended to investigate the effect of condensable impurities such as Sulfur dioxide (SO_2) on the properties of rich CO_2. Different results have been gained to inform supercritical CO_2 gas turbine designers and operators on the effect of impurities of the working fluid not only on the power output but also on the degradation of the turbine component.

The analysis has shown that the pure CO_2 at main compressor inlet at T=308.15 K and P=8.55 MPa has a density of ρ =619.06 kg/ m^3, if the working fluid with rich 99% CO_2 contains the impure gases of Ar, O_2 and CO at 0.2%, and N_2 at 0.4% when compared to a pure CO_2 the density decreases to 500.45 kg/m^3 and the power output declines to 7.1%. Therefore, the 1.92 MW work requirement for the main compressor is increased up to 20%, and the overall cycle efficiency declines close to 7%. Further, when the N_2 concentration raises to 1% in rich 99% CO_2 the power output deceases to 8.5%. In this respect, levels of Nitrogen in particular should have very limited tolerance to keep the density at its max and thereby reduce the power loss. However, including

1% of impure condensable SO_2 in rich 99% CO_2 results in a higher density $\rho = 642.56$ kg/m^3 than pure CO_2, which increases the power output up to 1.4%. The presence of SO_2 in supercritical CO_2 environment provides the sulphite ions which is the most aggressive impure species causes passive metal surfaces. Therefore, if the efficiency increases beyond the design point the S-CO_2 gas turbine power plant could face degradation due to the presence of SO_2.

INTRODUCTION

There is high potential for S-CO_2 power cycles to enable alternative power generation systems that can increase plant efficiency, and one of the key considerations is the purity of the working fluid. Since much of the performance benefit of S-CO_2 cycles is derived from the physical properties of supercritical CO_2, the cycle efficiency will decrease as the concentration of CO_2 decreases.

Focusing on carbon dioxide CO_2 is critical, due to its interchangeable properties at different temperatures and pressures. It was selected because of these adaptable properties, as well as effective thermal stability, low corrosion levels with appropriate materials, availability and low cost; plus, the physical and thermodynamic properties are well researched. In addition, the cycle must be operated beyond the critical pressure of CO_2 [1]. Moisseytsev [2] demonstrates that for a 400 MW power plant an increase of 1% in cycle efficiency can raise the electricity product to 86.4 MWh per day, which leads to savings of approximately $0.79 million per year, or $31.54 million over a plant lifetime of 40 years. The working fluid must be pure to achieve highly efficient Brayton cycles [3].

The carbon dioxide captured from a power platform always contains impurities, including Argon (Ar), Oxygen (O_2), Carbon monoxide (CO), Nitrogen (N_2) and Sulfur dioxide (SO_2). CO_2 impurities at the main compressor inlet can potentially change the physical and chemical effects of S-CO_2 gas turbine performance [4].

Impurities in the CO_2 stream influence several important parameters of phase behavior, including density, viscosity and compressibility. Thus, it is important to understand the effects of different impurities on CO_2 properties and, ultimately, on the design of the turbine component.

The conditions of CO_2 at the compressor inlet are critical in the design of such cycles. Also, the impurity species diluted within the S-CO_2 will cause deviation from an ideal S-CO_2 cycle as these impurities will change the thermodynamic properties of the working fluid.

Though intensive research of mixtures has been conducted recently, the issues are complex and need further study. This requires identification and explanations of the effect of every substance in the mixture, as different diluents and S-CO_2 will influence the power cycle and all components in the cycle [5].

The goal of analyzing the purity of the working fluid is to minimize equipment damage and loss of efficiency, while maximizing reliability.

REFPROP Version 10 software was used to calculate the physical properties of the CO_2 gas mixtures. This program, developed by the National Institute of Standards and Technology (NIST), calculates the thermodynamic and transport properties of important industrial fluids and their mixtures to an accuracy within 0.03% of the density near critical point, with a maximum error of 0.2% for the working region of the cycle [2].

10 MW CUBCL Supercritical CO$_2$ Brayton Cycle Layout

The 10 MW re-compression cycle from the 2015 US Department of Energy, provided the data for this paper [6]. The design of the compression cycle Figure 1 is very precise, with two compressors functioning identically but with different thermodynamic properties and flow rates. Here, the main compressor mass flow is $\dot{m} = 70.3$ kg/s and the bypass compressor mass flow is $\dot{m} = 34.2$ kg/s. The 10 MW S-CO$_2$ CUBCL T − S diagram in Figure 2 shows that once the fluid passes through the primary heater and expands through the turbine inlet it will produce energy, as shown in steps 6 and 7. The heat contained in the hot fluid will be absorbed by the high temperature (HTR) and low temperature recuperators (LTR), as shown in steps 7 and 8, and after passing through the LTR and is split into two different streams, as shown in steps 1 and 10. One stream goes through the cooler for heat rejection, then on to the main compressor as shown in steps 1 and 2, while the other stream passes through the bypass compressor where it is compressed to $P = 23.99$ MPa, as shown in steps 11 − 12.

The fluid pressure is increased by the main compressor to preheat the fluid in the LTR as shown in steps 2 and 3, and the fluid streams at steps 3 and 12 are merged at step 4 before entering the HTR 4 − 5. The energy from the primary heat source is transferred at a temperature of 1089.15 K to the S-CO$_2$ working fluid, as shown in steps 5 and 6. There is more analysis of the main compressor than the re-compressor (bypass compressor) as the re-compressor operates at a temperature and pressure beyond the critical point ($T_{recomp} = 361.15$ K $P_{recomp} = 8.69$ MPa), and is easier to design and monitor. The main compressor recycle line can be tied upstream of the cooler to avoid re-compressor overheating and allow the gas to recycle continuously. The temperature of the main compressor inlet should be as close to the critical point as possible for optimal efficiency. As well, the pressure of the entire cycle can be measured at the main compressor outlet, since it has the highest pressure in the cycle ($P = 24.13$ MPa) and the lowest temperature $T = 308.15$ K [6] [7]. The preliminary compressor geometry must be calculated in the design mode to identify the best starting point for further evaluation in the analysis model and implementing a smart condition monitoring system is very important during transient and steady state operation.

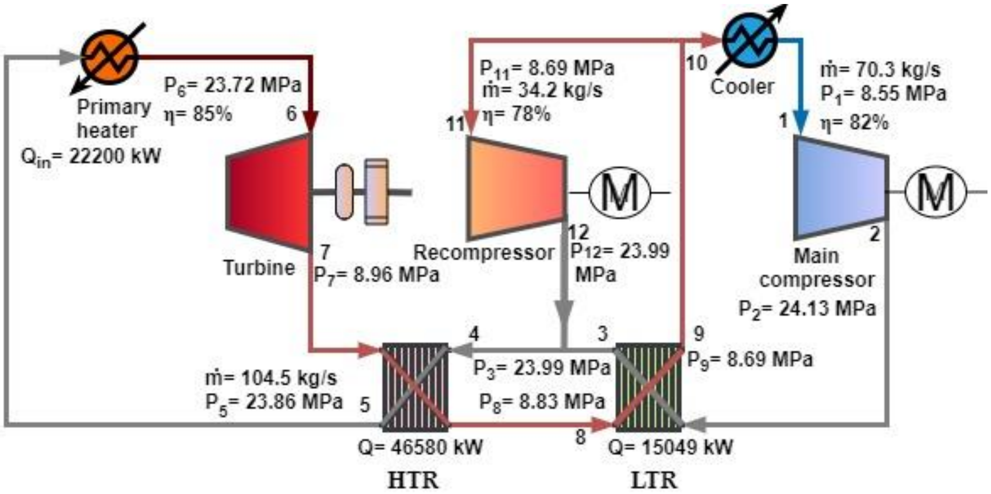

Figure 1. 10 MW S-CO$_2$ Carleton University Brayton Cycle Loop (CUBCL) layout.

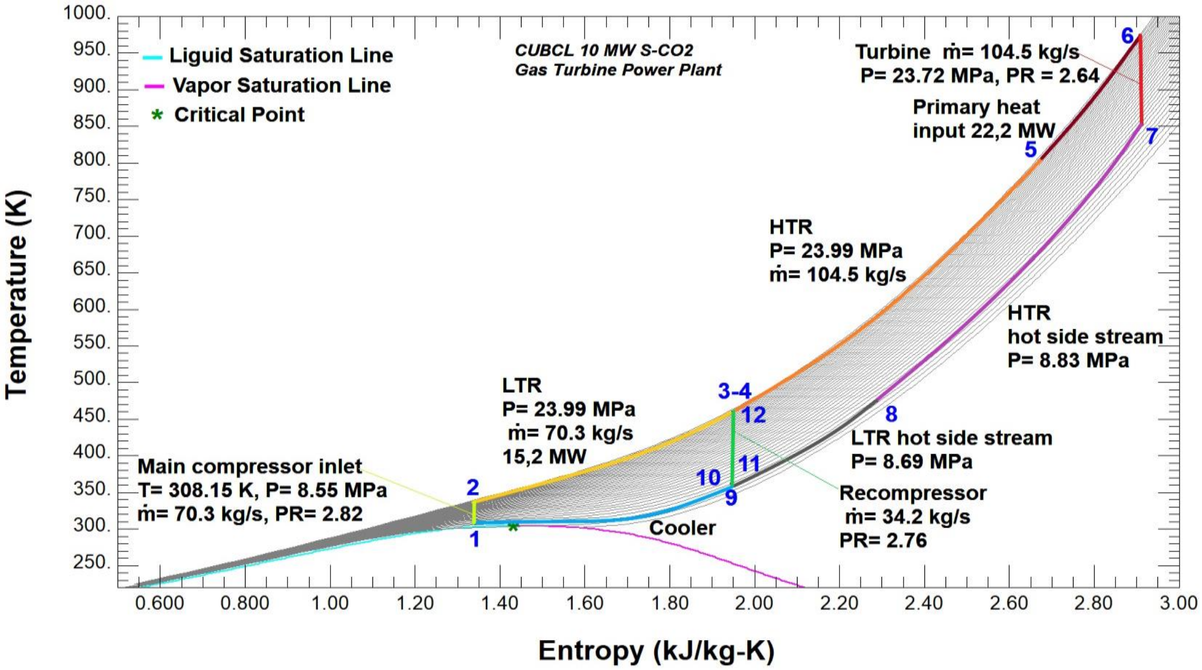

Figure 2. T-s diagram for the 10 MW S-CO$_2$ gas turbine Brayton cycle.

Numerical analysis

Theoretical analysis was conducted to identify effects on the working fluid gas properties and the performance characteristics of a 10 MW S-CO$_2$ gas turbine from impurities in the CO$_2$ working fluid, which ideally should be pure.

The specific enthalpy (h_1) and entropy (S_1) of the fluid entering the turbomachine can be determined, since the main compressor isentropic efficiency, inlet pressure and temperature are known, as shown in Table 1:

Table 1. CUBCL 10 MW S-CO$_2$ gas turbine turbomachinery inlet condition.

Turbomachinery	Temperature (K)		Pressure (MPa)		η %
	in	out	in	out	
Main compressor	308.15	351.15	8.55	24.13	82%
Re-compressor	361.15	467.15	8.69	23.99	78%
Turbine	973.15	854.15	23.72	8.96	85%

Specific enthalpy (h_{s2}) can be calculated at the turbomachine outlet if it is entropically processed, which depends on the specific entropy and outlet pressure at the inlet. The isentropic specific work (wi) can be calculated according to:

$$w_{isent} = (h_1 - h_{s2}) \tag{1}$$

$$W = \dot{m} * w_{isent} \tag{2}$$

and the definition of the isentropic efficiency, (i.e. the actual specific work (w) of the compressor) can be calculated as:

$$w_{comp} = \frac{w_{isent}}{\eta_{isent}} \tag{3}$$

$$w_{\ main-comp} = \dot{m}(h_2 - h_1) \tag{4}$$

$$w_{re-comp} = \dot{m}(h_{12} - h_{11}) \tag{5}$$

and the turbine as:

$$w_{turbine} = w_{isent} * \eta_{isent} \tag{6}$$

$$w_{turbine} = \dot{m}(h_6 - h_7) \tag{7}$$

$$w_{net} = w_{turbine} - w_{main-comp} - w_{re-comp} \tag{8}$$

The specific enthalpy (h_{s2}) of the fluid located at the outlet of the adiabatic turbomachine is calculated according to the following energy balance equation:

$$h_{s2} \ = \ h_1 - w \tag{9}$$

The thermodynamic state at the outlet of the turbomachine can be determined using the calculated outlet enthalpy and known outlet pressure [8]. The integration process is calculated as the final outlet enthalpy h_2, and used to calculate the equivalent isentropic efficiency as shown below:

$$\eta_{main-comp} = \frac{(h_{2s} - h_1)}{(h_2 - h_1)} \tag{10}$$

$$\eta_{re-comp} = \frac{(h_{12s} - h_{11})}{(h_{12} - h_{11})} \tag{11}$$

$$LTR = \dot{m}_2(h_3 - h_2) = \dot{m}_8(h_8 - h_9) \tag{12}$$

$$HTR = \dot{m}_5(h_5 - h_4) = \dot{m}_7(h_7 - h_8) \tag{13}$$

$$Q_{core} = \dot{m}_5(h_6 - h_5) \tag{14}$$

$$\eta_{turbine} = \frac{(h_6 - h_7)}{(h_6 - h_{7s})} \tag{15}$$

$$Q_{pre-cooler} = \dot{m}_1(h_9 - h_1) \tag{16}$$

$$\eta_{total} = \frac{w_{net}}{Q_{in}} \tag{17}$$

RESULTS AND DISCUSSION

Achieving high power S-CO_2 gas turbine power plant output is highly dependent on the purity of the working fluid. Impurities in CO_2 can have significant impact on the density near the critical point. High density CO_2 fluid will reduce the turbine footprint and running cost. However, this is not the case if the fluid has impurities.

The density as a function of the total impurity concentration is shown in Figure 3. Applying equations 18 and 19 to calculate the power output shows that an impurity of 0.4% SO_2 reduces the overall cycle efficiency by 2.4%, which has relatively little influence on the density. However, with the same impure concentration of 0.4 % N_2 the density and overall cycle efficiency reduced by 7.1%.

$$\dot{m}_{main-comp} = \rho * A * c \tag{18}$$

where mass flow ($\dot{m}$) through a fixed geometry is a function of the axial cross section area (A) and the speed of sound (c), and ρ is the density.

$$P_{el} = \dot{m}(h_6 - h_7)_{turbine} - \dot{m}(h_2 - h_1)_{main\_comp} - \dot{m}(h_{12} - h_{11})_{re\_comp} \tag{19}$$

where P_{el} is electrical power and h is the enthalpy.

This is clear by the fact that non-condensable impurities are less dense than CO_2, and thus have greater volume and decreased density. There would be no volume increase if they had the same molar volume as CO_2, provided the interactions between unlike molecules are negligible [6] [9] [10].

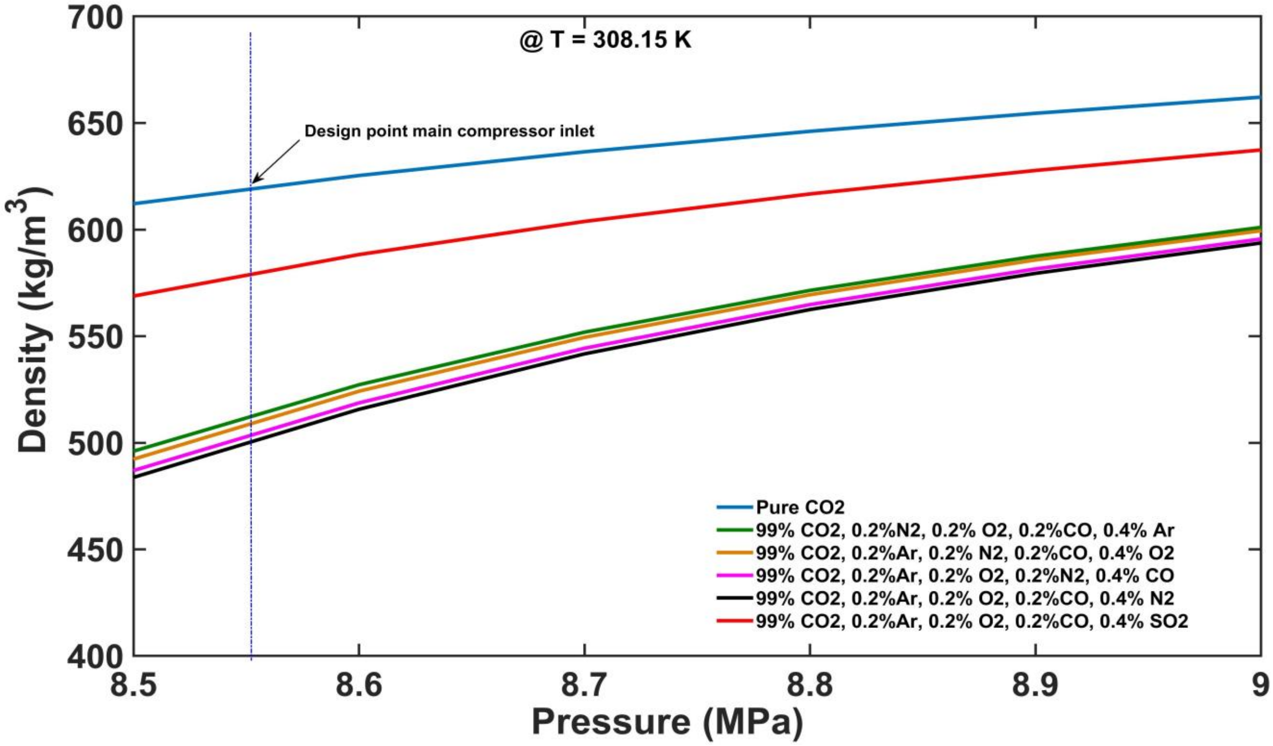

Figure 3. Density reduction due to impurities at the main compressor inlet of a 10 MW S-CO_2 gas turbine.

Lower gas turbine cycle efficiency is caused by decreased density due to impurities, and Table 2 shows the degree of power loss for expected and practical situations. It is very clear that the relationship between the purity of the working fluid and the turbine power output is inversely proportional, in that the power output declines as impurity concentration is increased.

The reduction is higher when Nitrogen is present, while there is lower effect with Argon, Since the molecular weight ratio of impurities in the mixture compared to that of pure CO_2 as (MW_{CO2}/ MW_{impure}) head for 1, where the density change becomes insignificant.

This change occurred in all non-condensable impurities except the condensable sulfur dioxide binary mixture, where the effect of smaller molecular weight is also significant. Density reduction is closely related to the increased volume of the mixture, as non-condensable impurities are less dense than CO_2 and thus have higher volume. As well, at fixed inlet temperature and pressure Table 2, if the working fluid with rich 99% CO_2 contains the impure gases of Ar, O_2 and CO at 0.2%, and N_2 at 0.4%, the density declines to 500.46 kg/m^3. The work of the main compressor at design point is 1.92 MW, however, due to the impurities the work raises up to 20%, the main compressor consumes more power and the power output declines to near 7%. This dramatic phenomenon occurs due to the compressibility declines as concentration of non-condensable impurities raises. Non-condensable gas impurities significantly reduce the density of the CO_2, since they are less dense than CO_2 and have greater volume [4] [11] [12].

Table 2. Shows the degree of power loss due to 0.4% impurities in rich 99%CO_2 working fluid for the 10 MW S-CO_2 gas turbine power plant.

Component	T (K)	P (MPa)	ρ kg/m^3	$\dot{m}_{main\text{-}com}$ Kg/s	Cycle η%	Power loses %
Pure CO_2	308.15	8.55	619.06	70.3	47.9	0
99%CO_2, 0.2%Ar, 0.2% O_2, 0.2% CO, 0.4% N_2	308.15	8.55	500.46	56.8	40.7	7.1
99%CO_2, 0.2%Ar, 0.2% O_2, 0.2% N_2, 0.4% CO	308.15	8.55	503.59	57.1	40.9	6.9
99%CO_2, 0.2%Ar, 0.2% N_2, 0.2% CO, 0.4% O_2	308.15	8.55	509.10	57.8	41.3	6.6
99%CO_2, 0.2%N_2, 0.2% O_2, 0.2% CO, 0.4% Ar	308.15	8.55	512.49	58.1	41.5	6.4
99%CO_2, 0.2%Ar, 0.2% O_2, 0.2% CO, 0.4% SO_2	308.15	8.55	579.16	65.7	45.5	2.4

Figure 4. Increased concentration of SO_2 from 0.4% to 0.7% decreases the density by 7% and the power output declines 0.25%. This is due to the physical properties of condensable SO_2, which can be compressed more easily than CO_2.

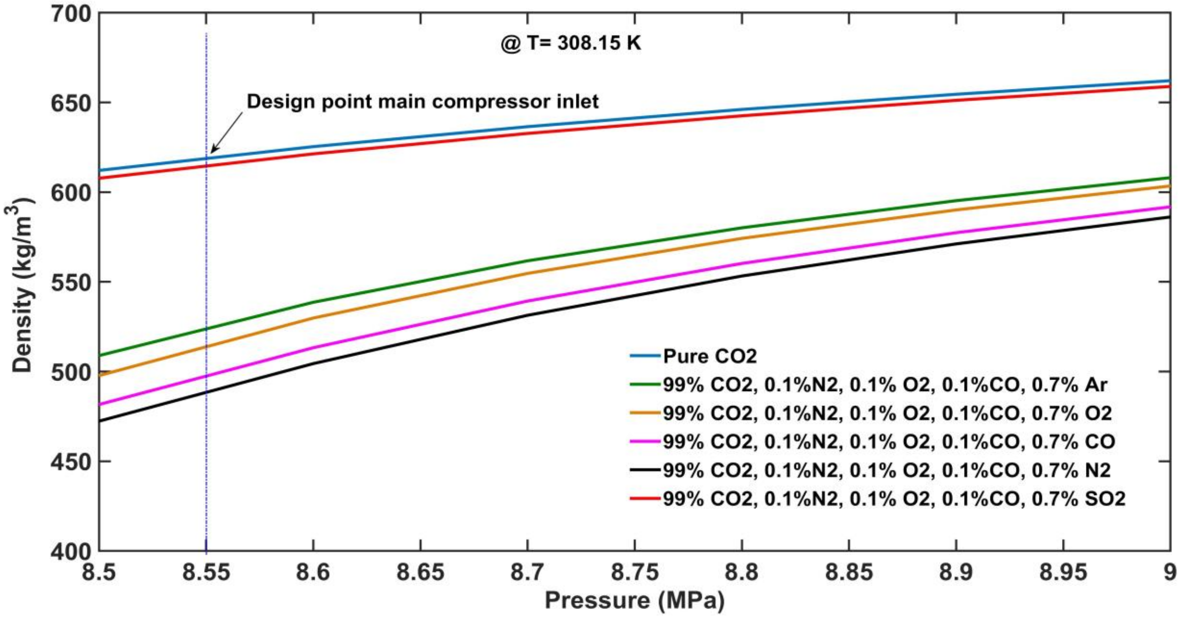

Figure 4. Density reduction at the main compressor inlet at a concentration of 0.7% for 10 MW S-CO_2 gas turbine.

However, as shown in Table 3, increasing the concentration from 0.4% to 0.7% N_2 with impurities concentration of Ar, O_2 and CO at 0.1%, has a major impact on the density, decreases the mass flow rate by 21%, raises the main compressor work to 11% and decreases the power output by 7.8%.

The N_2 impurity in the CO_2 causes the greatest reduction in the main compressor discharge pressure. This can be attributed to the sever reduction in the overall fluid density because sharp contrast between molar mass of N_2 (28.01kg/ kmol) to CO_2 (44.01 kg/ kmol). As main compressor work is inversely proportional to the working fluid density, it is clear that diverse types of impurities have different effects on additional cycle efficiency reduction. Also, the non condensable impurities mixed with CO_2 working fluid flow out of the compressor's discharge port in gaseous phase because the outer pressures generated are below their critical pressures. For example, at pure components the N_2 critical pressure is 3.39 MPa whereas CO_2 is 7.39 MPa. Therefore, more work needed in order to increase shaft speed to maintain required power output [13].

Table 3. The effect of 0.7% impurities on the density and power output for 10 MW S-CO_2 gas turbine power plant.

Component	T (K)	P (MPa)	ρ kg/m^3	$\dot{m}_{main\text{-}comp}$ (kg/s)	Cycle η %	Power loses %
Pure CO_2	308.15	8.55	619.06	70.3	47.9	0.0
99%CO_2, 0.1%Ar, 0.1%O_2, 0.1%CO, 0.7% N_2	308.15	8.55	488.99	55.5	40.1	7.8
99%CO_2, 0.1%Ar, 0.1%O_2, 0.1%N_2, 0.7% CO	308.15	8.55	498.14	56.5	40.6	7.3
99%CO_2, 0.1%Ar, 0.1%N_2, 0.1%CO, 0.7% O_2	308.15	8.55	514.77	58.4	41.6	6.3
99%CO_2, 0.1%N_2, 0.1%O_2, 0.1%CO, 0.7% Ar	308.15	8.55	524.7	59.5	42.2	5.7
99%CO_2, 0.1%Ar, 0.1%O_2, 0.1%CO, 0.7% SO_2	308.15	8.55	614.87	69.8	47.7	0.2

In addition to non-condensable Ar, CO, O_2 and N_2, SO_2 is also a common condensable impurity in CO_2 streams. Figure 5 shows that due to the physical properties of SO_2, particularly the high critical temperature of T= 430.65 K, there are diverse effects on the density behavior of CO_2 mixtures. Since SO_2 can be compressed more easily than CO_2, mixing the two can increase the compressibility of CO_2, and thereby increase the overall density. As shown in Table 4, a rich 99% CO_2 mixture with 1% SO_2 increases the density close to 4% above pure CO_2, and the power output to 1.4%. The present of Sulfur dioxide in a supercritical CO2 region can corrode turbine blades and materials. Further in a subcritical region SO_2 products Iron sulphite hydrate ($FeSO_3 \cdot 3H_2O$) which is another significant effect that considered as one of the corrosion products [14] [15] [16]. Figure 5 also shows that with non-condensable impure 1% N_2 the density decreases significantly by up to 22.7%, while the 10 MW S-CO_2 gas turbine power output drops to 8.5%.

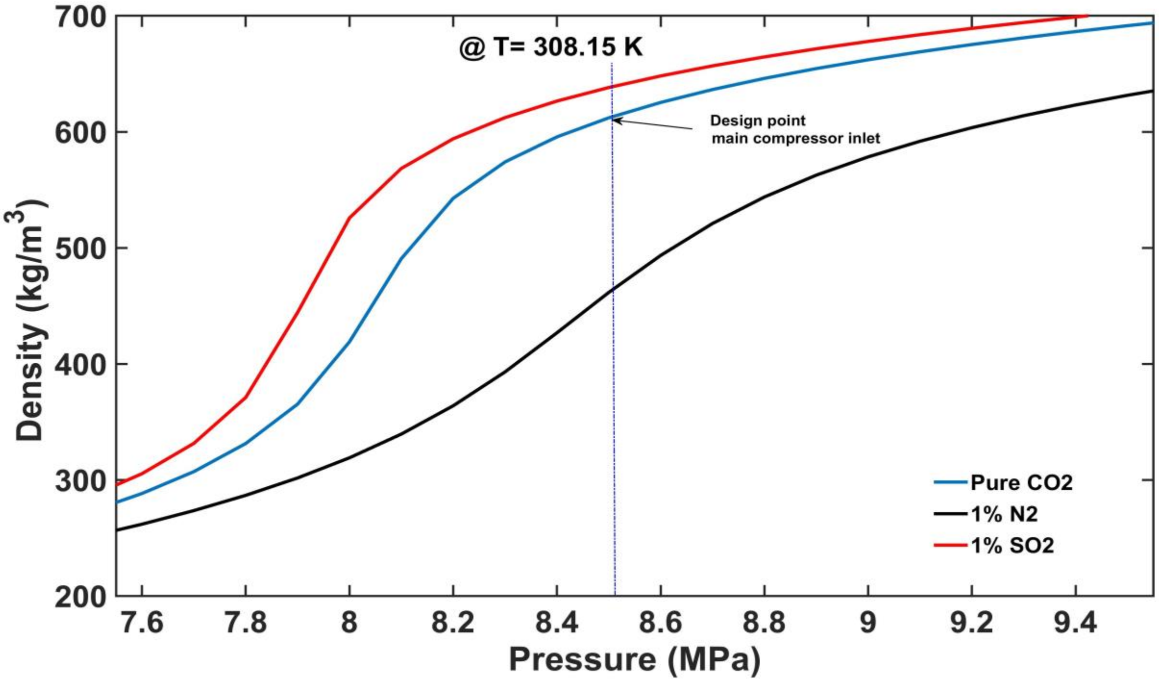

Figure 5. The effect of SO_2 and N_2 concentrations of 1% on the density of rich 99% CO_2.

Table 4. The effects of SO_2 and N_2 concentrations of 1% on the density and overall cycle efficiency of rich 99% CO_2 working fluid for the10 MW S-CO_2 gas turbine power plant.

Component	T (K)	P (MPa)	ρ kg/m³	$\dot{m}_{main\text{-}comp}$ kg/s	Cycle η %	Power Changes %
Pure CO_2	308.15	8.55	619.06	70.3	47.9	0.0
99%CO_2, 1% N_2	308.15	8.55	478.11	54.2	39.4	-8.5
99%CO_2, 1% SO_2	308.15	8.55	642.56	72.9	49.4	+1.4

Conclusions

The effects of impurities in CO_2 working fluid on CO_2 density were investigated, and it was determined that impurities can have significant impact on the thermodynamic properties of 10 MW S-CO_2 gas turbine working fluid, as well as affect the design, turbine cost and operation. Different key issues were addressed, and several significant findings were revealed, including:

Non-condensable impurities: N_2, O_2, CO and Ar reduced the working fluid density of a 10 MW S-CO_2 gas turbine at the main compressor inlet. For example, a mixture of 99% CO_2 and 1% N_2 caused maximum density reduction and reduced the power output to 8.5%. Therefore, impure N_2 should be closely monitored during turbine operation, and have very limited tolerance.

Condensable species SO_2 had different effects on CO_2 physical properties, including increasing both the density and the power output. Impure SO_2 is more condensable than CO_2, and concentration of 1% in reach 99% CO_2 at mentioned main compressor design point can increase the power output up to 1.4%. However, there should be no tolerance for SO_2 in the working fluid. An increase in SO_2 concentration in subcritical CO_2 region rapidly degrades turbomachinery's component by corrosion. Thus, understanding the concentration of impurities in the working fluid for promising S-CO_2 gas turbine is vital not only avoiding corrosion-related damage but also to choose proper component materials and improving the efficiency and capacity of supercritical S-CO_2 gas turbines.

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