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# CO2-BASED POWER CYCLES: WHAT EFFECT DOES ADDITIVE MOLECULAR COMPLEXITY HAVE ON THE CYCLE LAYOUT?

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#### ABSTRACT

Since their inception,  $CO_2$  power cycles have gained prominence for their superior performance and compactness. However, the efficiency of the simple supercritical  $CO_2$  cycle is hindered by relatively large temperature differences in the recuperator, leading to increased exergy destruction. Although complex cycles like the recompression or precompression cycles can reduce recuperator irreversibility, their higher complexity and additional equipment requirements raise the cost of the power plant.

This paper aims to demonstrate that recuperator irreversibility in a simple recuperated transcritical cycle can be alleviated using CO<sub>2</sub>-based mixtures, without resorting to complex cycles. This is achieved by comparing the efficiencies of simple and recompression cycles using CO<sub>2</sub>-based mixtures with nine additives of various molecular complexities:  $H_2S$ ,  $SO_2$ ,  $C_3H_8$ ,  $C_4H_{10}$ ,  $C_5H_{12}$ ,  $C_6H_6$ ,  $C_4H_4S$ , TiCl<sub>4</sub>, and  $C_6F_6$ . The effect of additive molar fraction (ranging from 0.05 to 0.5) on the efficiency of both cycles is examined.

Thermal efficiency optimisation reveals a correlation between the efficiency difference of the simple and recompression cycles and the molecular complexity of the working fluid. The reduction in recuperator irreversibility is attributed to the decrease in the difference in the isobaric specific heat capacities between the streams in the recuperator with the use of complex additives. Consequently, the advantage of a recompression cycle diminishes as the aggregate molecular complexity of the working fluid increases. Simple additives like  $H_2S$ ,  $SO_2$ , and  $C_3H_8$  result in recompression cycles outperforming simple recuperated cycles by 4% to 8% in terms of absolute thermal efficiency, depending on the additive and its molar fraction. Conversely, more complex additives like  $C_4H_4S$ , TiCl<sub>4</sub>, and  $C_6F_6$ , exhibit thermal efficiencies in simple recuperated cycles comparable to those of recompression cycles. The additive molar fraction at which both cycles achieve similar performances depends on the molecular complexity of the additive; the more complex the additive, the lower the additive molar fraction required to create a complex working fluid. Moreover, the split fraction in recompression cycles exhibits a similar correlation with molecular complexity as observed in the efficiency difference, suggesting that recompression cycles will morph into simple recuperated cycles as molecular complexity increases.

In conclusion, the use of additives provides an additional dimension through which the efficiency of  $CO_2$  cycles can be optimised, enabling improved performance without the need for complex cycles.

# Keywords: sCO<sub>2</sub> power cycle, sCO<sub>2</sub> mixtures, molecular complexity, cycle layout

#### NOMENCLATURE

Roman letters

- *p* Pressure [Pa]
- T Temperature [K or  $^{\circ}$ C]
- *h* Specific enthalpy  $[J kg^{-1}]$
- q Specific heat  $[J kg^{-1}]$
- *R* Gas constant  $[J kg^{-1}K^{-1}]$
- $\dot{m}$  Mass flow rate [kgs<sup>-1</sup>]

#### Greek letters

- $\eta$  Efficiency
- $\sigma$  Molecular complexity
- $\omega$  Acentric factor

#### Superscripts and subscripts

- p Pump
- rc Recompressor
- t Turbine
- s Simple cycle

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# 1. INTRODUCTION

Supercritical carbon dioxide (sCO<sub>2</sub>) Brayton cycles use CO<sub>2</sub> as working fluid for power generation. They have the advantage of high cycle efficiency with simple cycle layouts and adaptability to a wide range of heat source temperatures such as fossil fuel, solar, nuclear, and waste heat. Transcritical CO<sub>2</sub> (tCO<sub>2</sub>) Brayton cycles may also be used for power generation and are advantaged by a lower compression work because compression occurs in the liquid phase of CO<sub>2</sub>. There is a growing body of literature investigating CO<sub>2</sub>-mixtures as working fluids to adapt CO<sub>2</sub> power cycles for different applications. Several thermophysical properties of CO<sub>2</sub> can be modified using additives, such as the critical temperature and the specific heat capacity. A myriad of organic and inorganic additives have been studied for different applications.

Studies by the SCARABEUS project [1] concluded that mixtures of  $CO_2/TiCl_4$ ,  $CO_2/SO_2$ , and  $CO_2/C_6F_6$  can achieve cycle efficiencies above 50% depending on the cycle layout, turbine inlet temperature, and minimum cycle temperature [2–5]. It was found that mixtures outperform pure s $CO_2$  in both energy and exergy efficiencies, a difference which increases at higher ambient temperatures [6].

Studies by Valencia-Chapi and co-authors on 16 mixtures for CSP power blocks show the increase in cycle efficiency compared to pure sCO<sub>2</sub>. The gains in efficiency depend on the choices of additive, cycle layout, heat sink temperature, and mode of cooling [7–10]. The split fraction in a recompression cycles depends on the relative flow heat capacities of the hot and cold side of the recuperator; the greater the difference the more of the flow must be diverted and the lower the thermal efficiency [10]. Reportedly, efficiencies up to 60% were possible for specific mixture and cycle combinations [9].

Several studies of  $CO_2$ -mixture power blocks highlight he potential benefits of the technology for plants with elevated cooling temperatures [11–17]. For example, a comparison of pure  $CO_2$  with  $CO_2$ -Butane,  $CO_2$ -H<sub>2</sub>S, and  $CO_2$ -Propane recompression cycles for SPT plants showed that all mixtures achieve greater thermal efficiencies than pure  $CO_2$ , with  $CO_2$ -Propane the favoured choice [14].

A well-documented limitation of simple recuperated sCO<sub>2</sub> cycles is the internal pinch point in the recuperator which limits heat recuperation and the cycle efficiency. An internal pinch point is a consequence of the difference in the flow heat capacities  $(mC_p)$  of the two streams in the recuperator. The recompression cycle, shown in Fig. 2, avoids the pinch-point problem by dividing the recuperator into two; the high-temperature recuperator (HTR) and the low-temperature recuperator (LTR), while adding a recompressor (RC) after the low-temperature recuperator. The difference in heat-capacity rates is reduced by decreasing the mass flow rate of the high-pressure stream and allowing a smaller flow into the low temperature recuperator. The two high-pressure streams are then mixed before the high temperature recuperator where their combined heat-capacity rate is not too different from the low-pressure stream. This is by far the most widely studied cycle layout due to its high performance, especially in high-temperature applications.

The findings of previous studies indicate that the benefit of using a recompression cycle with  $CO_2$ -mixture depends on the additive. For example, the difference in the efficiency of a simple recuperated cycle and a recompression cycle is lesser with mixtures of  $CO_2$ /He and  $CO_2$ /Kr than with pure  $CO_2$  because the re-compressor operates away from the critical point, thus benefits less from real gas effects [18]. Moreover, a previous study has shown that recuperator irreversibility is influenced by the choice of the additive;  $CO_2$ /TiCl<sub>4</sub> and  $CO_2/C_6F_6$  reduced irreversibility, whilst  $CO_2/SO_2$  did not reduce it significantly [19].

Within the context of simple recuperative supercritical Brayton cycle, it was noted early on that a fluid with a high molar heat capacity would be preferable to minimize the difference of heat capacities between the cold and hot streams in the recuperator [20]. Fluids having a large ideal molar heat capacity exhibit a small difference in liquid and vapor state heat capacities. As the heat capacity rates of the two streams grow closer, internal irreversibilities in the recuperation process of the cycle decrease.

The molar heat capacity of a fluid is strongly dependent on its molecular complexity. Therefore, it may be hypothesised that additives that increase the molecular complexity of the  $CO_2$  mixture will lead to lower recuperator irreversibility, thus reducing the thermal efficiency advantage of a recompression cycle over a simple recuperated cycle. There has yet to be work dedicated to investigating this hypothesis. In this paper, the effect of additive molecular complexity on the thermal efficiency of simple and recompression cycles is compared by modelling and optimizing simple and recompression cycles of several  $CO_2$ -mixtures with different additives.

## 2. METHODOLOGY

Mathematical models were developed for both simple and recuperated cycles. A complete description of the thermodynamic models and optimisation process for the simple recuperated cycle were presented in a previous publication [19]. Therefore, what follows is a broad description of these models.

#### 2.1 Simple Cycle

A schematic of a simple recuperative  $tCO_2$  cycle and its Temperature – Entropy (T-s) diagram are shown in Fig. 1.



FIGURE 1: T-s diagram and schematic of a simple recuperated tCO<sub>2</sub> cycle

The cycle is modelled by applying the first law of thermodynamics across each component. Throughout Equations 1 to 3 the terms w, q, and h refer to specific power, specific heat, specific enthalpy, respectively. Subscripts are used to denote the cycle components: P for pump; T for turbine; R for recuperator; H for primary heat exchanger; and L for condenser. Numerical subscripts are also used to denote points along the cycle.

By applying the conservation of mass and energy principle, the above energy terms can be expressed as:

$$w_p = h_2 - h_1 \tag{1}$$

$$w_t = h_4 - h_5 \tag{2}$$

$$q_h = h_3 - h_4 \tag{3}$$

The recuperator effectiveness is defined as the ratio of the actual heat load to the maximum attainable heat load from the stream with the lowest heat-capacity rate. The equation for effectiveness depends on the heat exchanger flow arrangement (counter or parallel). Because it allows for higher heat recuperation, a counterflow heat exchanger is better suited for this application than a parallel flow heat exchanger. The effectiveness of a counterflow recuperator is described by:

$$\epsilon = \frac{h_5 - h_6}{\min[(h_{@T_5, P_3} - h_{@T_2, P_2}), (h_{@T_5, P_5} - h_{@T_2, P_6})]}$$
(4)

where,  $\epsilon$  is the recuperator effectiveness and  $h_{(@T,P)}$  is the specific enthalpy evaluated at a certain temperature and pressure. Therefore, effectiveness depends on the maximum heat lost or gained by the stream with the lowest heat-capacity rate.

The thermal efficiency of a simple recuperated cycle ( $\eta_s$ ), which is often the main thermodynamic performance indicator, can be expressed as the ratio of the useful work produced to the heat consumed by the cycle:

$$\eta_s = \frac{w_t - w_p}{q_h} \tag{5}$$

#### 2.2 Recompression Cycle

In the recompression cycle, the flow is split into two streams after the low temperature recuperator and before the condenser. One of these two streams flows into the pump whilst the other flows to the recompression compressor. A schematic of the cycle layout is shown in Fig. 2. The cycle modelling assumptions made here are identical to those made for the simple recuperated cycle.

The split ratio  $(x_s)$  is the fraction of the mass flow that flows into the recompressor:

$$x_s = \frac{\dot{m}_{3b}}{\dot{m}_{3a} + \dot{m}_{3b}} \tag{6}$$

where the subscripts 3a and 3b denote the flow through the pump and re-compressor, respectively. Therefore, the specific work of the pump and re-compressor are defined as:

$$w_p = (1 - x_s)(h_2 - h_1) \tag{7}$$

$$w_{rc} = x_s (h_{3a} - h_8) \tag{8}$$



FIGURE 2: Recompression cycle. Red lines indicate high-pressure flows; blue low-pressure; dashed lines indicate split flow. Legend: low-temperature recuperator (LTR), high-temperature recuperator (HTR), primary heat exchanger (PHE), and recompressor (recomp).



FIGURE 3: T-s diagram and schematic of a recompression  $tCO_2$  cycle.

The specific enthalpy at the HTR high-pressure inlet (3) is calculated by applying the conservation of energy equation at the point where the two streams 3a and 3b converge:

$$h_3 = x_s h_{3b} + (1 - x_s) h_{3a} \tag{9}$$

Similarly, the energy conservation equation is applied at the LTR and HTR to produce Equations 10 and 11, respectively:

$$h_7 - h_8 = (1 - x_s)(h_{3a} - h_2) \tag{10}$$

$$h_6 - h_7 = h_4 - h_3 \tag{11}$$

The effectiveness of both LTR and HTR, shown in Equations 12 and 13, depend on the maximum attainable heat transfer by the flow of the lowest capacity rate; as was the case with recuperator of the simple cycle.

$$\epsilon_{LTR} = \frac{h_7 - h_8}{\min[((1 - x_s)(h_@T_7, P_{3a} - h_@T_2, P_2)), (h_@T_7, P_7 - h_@T_2, P_8)]} (12)$$

$$\epsilon_{HTR} = \frac{h_4 - h_3}{min[(h_{@T_4, P_8} - h_{@T_7, P_7}), (h_{@T_6, P_6} - h_{@T_3, P_7})]}$$
(13)

The system of equations for a recompression cycle is underdetermined, thus requires an initial assumption of  $T_3$  and iteration of Equations 8, 12, and 13.

The thermal efficiency of a recompression cycle  $(\eta_r)$  can be expressed as the ratio of the useful work produced to the heat consumed by the cycle:

$$\eta_r = \frac{w_t - (w_p + w_{rc})}{q_h} \tag{14}$$

Finally, the difference in efficiency between the recompression and simple cycle for the same mixture and additive molar fraction is defined as:

$$\eta_{r-s} = \eta_r - \eta_s \tag{15}$$

#### 2.3 Optimisation Conditions

Both simple and recompression cycles are optimised for a range of additive molar fractions and their efficiencies are compared. A summary of the simple and recompression cycles design and optimisation assumptions is provided in Table 1.

A parametric study was conducted by changing the additive molar fraction and optimizing cycle conditions for the resulting mixture compositions each time. To find the optimal cycle conditions that achieve the highest overall cycle efficiency, the cycle efficiency defined by Equations 5 and 14 were set as the objective function, while the maximum turbine inlet pressure and minimum internal temperature approach (MITA) in the recuperators were set as constraints.

Within the optimisation problem, all cycle conditions were held constant, except for recuperator effectiveness ( $\epsilon$ ) and turbine pressure ratio (r), which were used as optimisation design variables. Recuperator effectiveness was allowed to vary to ensure a MITA of 5°C at the recuperator pinch point in line with previous work on CO<sub>2</sub>-based cycles [3–6].

Cycle analysis was based on a unit mass flow rate through all components. Heat exchange processes with heat source and heat sink were not considered. However, heat exchange within the recuperator was probed to ensure that the heat profiles of the two streams do not overlap and create a negative pinch point temperature. The recuperators were discretised into cells in search of the internal pinch point.

The pump inlet temperature  $(T_1)$  is set to  $15^{\circ}$ C. This temperature was chosen so that compression occurs below or near the critical temperature for all the mixtures considered here. Therefore, all cycles are transcritical and the difference between the sub-critical and super-critical specific heat capacity at constant pressure will persist. The pump inlet was assumed to be subcooled by  $2^{\circ}$ C below the saturation pressure. Consequently, the pump inlet pressure ( $P_1$ ) is equal to the saturation pressure of the fluid at  $17^{\circ}$ C. The turbine inlet temperature ( $T_4$ ) was set to  $700^{\circ}$ C, which is expected from an advanced CSP receiver employing liquid sodium or solid particles as its Heat Transfer Medium. Additionally, the turbine inlet pressure ( $P_4$ ) was restricted to 25 MPa [21]. The range of molar fractions of the additives was set to 0.05-0.50 to prevent the additive from becoming the dominant compound in the mixture.

TABLE 1: Inputs required for cycle solution

| <b>Controlled Parameters</b>                             |                          |      |  |  |  |  |  |
|--|--------------------------|------|--|--|--|--|--|
| Parameter  | Range                    | Unit |  |  |  |  |  |
| Additive molar fraction                                  | 0.05-0.5                 | -    |  |  |  |  |  |
| Turbine inlet temperature $(T_4)$                        | 700                      | °C   |  |  |  |  |  |
| Pump inlet temperature $(T_1)$                           | 15                       | °C   |  |  |  |  |  |
| Pump isentropic efficiency( $\eta_p$ )                   | 85                       | o%   |  |  |  |  |  |
| Turbine isentropic efficiency( $\eta_t$ )                | 90                       | %    |  |  |  |  |  |
| Recompressor isentropic efficiency( $\eta_{rc}$ )        | 85                       | %    |  |  |  |  |  |
| Minimum internal temperature approach (MITA)             | 5                        | °C   |  |  |  |  |  |
| $\Delta p/p$ of Primary heat exchanger                   | 0.015                    | -    |  |  |  |  |  |
| $\Delta p/p$ of Recuperator high- and low-pressure sides | 0.01 and 0.015           | -    |  |  |  |  |  |
| $\Delta p/p$ of condenser                                | 0.02                     | -    |  |  |  |  |  |
| Dependant Parameters                                     |                          |      |  |  |  |  |  |
| Pump inlet $pressure(P_1)$                               | $P_{\text{sat}@(T_1+2)}$ | MPa  |  |  |  |  |  |
| Turbine inlet $pressure(P_4)$                            | Max (25)                 | MPa  |  |  |  |  |  |
| Optimised Parameters                                     |                          |      |  |  |  |  |  |
| Pressure ratio $(r)$                                     | 2 to Max $(P_4)/P_1$     | -    |  |  |  |  |  |
| Recuperator effectiveness( $\epsilon$ )                  | 80 to 98                 | %    |  |  |  |  |  |
| Split fraction( $x_{e}$ )                                | 0 to 1                   | -    |  |  |  |  |  |

#### 2.4 Choice of additives

Nine additives were considered in the study of simple and recompression transcritical cycles. These additives were chosen so that they produce mixtures with critical temperatures above the preset pump inlet temperature of  $15^{\circ}$ C. The additives are listed in Table 2, along with select properties of interest. Moreover, the aim of this study is not to find the optimal mixture, rather is to study the effect of the molecular complexity of the additives on cycle performance; therefore, the selection of the additives at elevated temperatures nor their environmental impacts.

To estimate the thermophysical properties of the working fluids, the Peng-Robinson (PR) Equation of State (EoS) was chosen in addition to van der Waals mixing rules to model binary mixtures. A binary interaction parameter  $(k_{ij})$  must be defined when using the van der Waals mixing rules. Apart from CO<sub>2</sub>/TiCl<sub>4</sub>, the values of  $k_{ij}$  in Table 3 were obtained by fitting PR EoS to experimental data from the sources listed in the same table.

The critical properties of the mixture will depend on the additive molar fraction. As such, the loci of critical temperature and pressure for all the mixtures considered are shown in Fig. 4 and Fig. 5.

### 3. RESULTS AND DISCUSSION

Generally, recompression cycles have thermal efficiencies that are equal to or greater than that of the simple recuperated cycle, as shown in Fig. 6. The recompression cycle is more efficient at the lowest additive fraction (0.05) for all mixtures.

TABLE 2: Physical and thermodynamic properties of pure compounds (collected from DIPPR database and from [22])

| Name                   | Chemical          | Molar mass | Acentric factor | Critical temperature | Critical pressure |
|------------------------|-------------------|------------|-----------------|----------------------|-------------------|
|                        | formula           | (g/mol)    | $(\omega)$      | (K)                  | (MPa)             |
| Hydrogen sulphide      | $H_2S$            | 34.01      | 0.081           | 373.2                | 8.94              |
| Sulfur dioxide         | $SO_2$            | 64.06      | 0.245           | 430.8                | 7.88              |
| Propane                | $C_3H_8$          | 36.46      | 0.133           | 324.7                | 8.31              |
| n-Butane               | $C_4H_{10}$       | 58.12      | 0.199           | 425.2                | 3.80              |
| n-Pentane              | $C_5H_{12}$       | 72.15      | 0.251           | 469.2                | 3.37              |
| Benzene                | $C_6H_6$          | 78.11      | 0.212           | 562.1                | 4.89              |
| Thiophene              | $C_4H_4S$         | 84.14      | 0.197           | 579.4                | 5.69              |
| Titanium tetrachloride | TiCl <sub>4</sub> | 189.7      | 0.284           | 639.1                | 4.66              |
| Hexafluorobenzene      | $C_6F_6$          | 186.1      | 0.395           | 516.7                | 3.27              |

TABLE 3: Values of  $k_{ij}$  that minimise the error between PR EoS and experimental data

| Mixture                                     | k <sub>ij</sub> | $\Delta k_{ij}$ | Source of data |
|---|-----------------|-----------------|----------------|
| CO <sub>2</sub> /H <sub>2</sub> S           | 0.0871          | 0.0035          | [23]           |
| $CO_2/SO_2$                                 | 0.0243          | 0.0031          | [24]           |
| $CO_2/C_3H_8$                               | 0.0954          | 0.0637          | [25]           |
| $\mathrm{CO}_2/\mathrm{C}_4\mathrm{H}_{10}$ | 0.1228          | 0.0449          | [26]           |
| $\mathrm{CO}_2/\mathrm{C}_5\mathrm{H}_{12}$ | 0.1350          | 0.0414          | [27]           |
| $CO_2/C_6H_6$                               | 0.0874          | 0.0341          | [28]           |
| $CO_2/C_4H_4S$                              | 0.0639          | 0.0329          | [29]           |
| CO <sub>2</sub> /TiCl <sub>4</sub>          | 0.0745          | 0.0456          | [30]           |
| $CO_2/C_6F_6$                               | 0.0312          | 0.0104          | [31]           |

The trends in Fig. 6 may be put into three categories based on the efficiency difference  $(\eta_{r-s})$  between the two cycles: constant, gradually diminishing, and abruptly diminishing.

The subplots are arranged in order of decreasing  $\eta_{r-s}$ ; left to right and top to bottom. For the first mixture of CO<sub>2</sub>/H<sub>2</sub>S,  $\eta_{r-s}$  remains relatively constant and H<sub>2</sub>S is not expected to alleviate the irreversibility in the recuperator of a simple recuperated cycle; therefore, the recompression cycle will be more efficient than the simple recuperated cycle for the entire range of additive molar fractions under the same operating temperatures. The addition of SO<sub>2</sub> slightly alleviates the recuperator irreversibility, thus the modest change in  $\eta_{r-s}$ . With CO<sub>2</sub>/propane, an increase in the molar fraction of propane brings the efficiency of the recompression cycle closer to that of the simple recuperated cycle, yet the former will clearly be more advantageous than latter. The decrease in  $\eta_{r-s}$  becomes greater as more complex additives are used where the efficiencies of the two cycles converge. With mixtures of butane, pentane, and benzene, this convergence occurs



FIGURE 4: Critical temperature of the mixtures across additive molar fractions.

at lower amounts of additive fraction as more complex additives are used, indicating a correlation between the molecular complexity of the additive and the rate at which  $\eta_{r-s}$  diminishes with the additive molar fraction; the more complex the additive, the lesser fraction of it is needed to overcome recuperator irreversibility. Mixtures containing the most complex additives, CO<sub>2</sub>/TiCl<sub>4</sub>, CO<sub>2</sub>/thiophene, CO<sub>2</sub>/C<sub>6</sub>F<sub>6</sub>, and CO<sub>2</sub>/C<sub>6</sub>H<sub>6</sub>, overcome recuperator irreversibility at relatively low additive molar fractions below 0.2.

As suggested by a previous study, the recompression cycle may be thought of as two cycles operating in conjunction with each other [8]: one that is driven by the pump which cycles through points 1 to 8, as in a simple recuperated cycle, and another that is driven by the recompressor which cycles through 3a, 4, 5, 6, 7, and 8. A schematic of this theoretical partition of the recompression cycle is shown in Fig. 7. The amount of







FIGURE 6: Thermal efficiency of simple recuperated (solid line) and recompression (dashed line) cycles across additive molar fractions.

mass flowing in the recompressor-driven cycle depends on the irreversibility of the heat exchange in the LTR. Therefore, the split fraction  $(x_s)$  can be thought of as a measure of the need for recuperator irreversibility alleviation; the higher the split fraction, the greater is the amount of flow diverted to the recompressor, the closer are the heat flow capacities of the low- and high-pressure streams.

The trend in the recompression cycle efficiency may be better understood by examining the trend in the flow split fraction, which is shown in Fig. 8. For additive fractions that achieve comparable efficiencies in both the recompression and simple cycles, the split fraction is zero; flow is not diverted to the recompressor. Therefore, the recompression cycle in those cases is in effect a









FIGURE 7: Theoretical partition of the recompression cycle into two cycles

simple recuperated cycle.



FIGURE 8: Split fraction in recompression cycles for the range of additive molar fractions studied.

As already mentioned, the trends clearly suggest a relation between the molecular complexity of the additives and recuperator irreversibility. To quantify this relation, molecular complexity ( $\sigma$ ) will be defined in accordance with the definition used by Invernizzi [32]:

$$\sigma \approx \frac{C_p^o}{0.7R} - \frac{\ln 10}{0.49} \times \frac{7}{3}(\omega + 1)$$
(16)

Where  $C_p^o$  is the specific isobaric heat capacity at the dew point at a reduced temperature of 0.7, R is the specific gas constant, and  $\omega$  is the acentric factor which indicates the nonsphericity (centricity) of molecules as listed in Table 2. Although originally developed for pure fluids,  $\sigma$  is extended to calculate the complexity of mixtures here; therefore, each mixture and additive molar fraction combination will have a specified molecular complexity. Using this approach, the relation between  $\sigma$  and  $\eta_{r-s}$  is shown in Fig. 9. The trend observed between the two variables agrees with the trends observed in the cycle efficiencies in Fig. 6. Additives that have molecular structures similar to CO<sub>2</sub>, namely H<sub>2</sub>S and SO<sub>2</sub>, have an insignificant effect on the molecular complexity of the resulting mixture, thus an insignificant effect on the difference between the recompression and simple recuperated cycles. The effect of complexity is most evident with additives that are slightly more complex than CO<sub>2</sub>, namely propane, butane, and pentane, because the increase in complexity with additive molar fraction is gradual, and so is the reduction in  $\eta_{r-s}$ .



FIGURE 9: Correlation between molecular complexity and the difference between the recompression and simple recuperated cycles. The size of the points indicates the additive molar fraction; the larger the point the greater the additive molar fraction. A trend line has been added to show the asymptotic nature of the relation.

Ideally, the trend should be asymptotic to  $\eta_{r-s} = 0$ ; the recompression efficiency would not be lower than the simple recuperated cycle. However, even if the split fraction becomes zero, at which none of the flow is diverted to the recompressor, the recompression cycle has an additional pressure drop because of the additional recuperator. Therefore, the efficiency of the

recompression cycle may drop below that of the simple recuperated cycle; but in practice this would not be the case because a single recuperator would be used for a split fraction of zero. In other words, this is a modeling artifact that may be resolved by assuming a single recuperator if the split fraction is equal to zero.

A clear-cut complexity threshold above which the recompression and simple recuperated cycle have the same efficiency is not discernible. This could be due to other factors that affect cycle efficiency such as the pressure ratio, pressure drop in the heat exchanger, or the uncertainty in the calculation of fluid properties. The complexity of the additives relative to  $CO_2$  may also be observed by comparing the shape of their saturation domes in the reduced temperature-entropy plane, as shown in Fig. 10. The slope of the curve  $\frac{\partial T}{\partial s}$  indicates the complexity of the fluid, the lower the slope, the more complex the fluid.



FIGURE 10: Saturation domes of the pure additives compared to  $CO_2$  in the reduced temperature-entropy plane.

#### 4. CONCLUSION

This paper has explored the performance of recompression cycles in comparison to simple recuperated cycles with several CO<sub>2</sub>-based mixtures using different additives. A clear relationship between the molecular complexity of additives and the efficiency difference ( $\eta_{r-s}$ ) between the two cycle configurations has been demonstrated.

The recompression cycles outperform simple recuperated cycles when the additive molecular complexity and fraction are low, especially for mixtures of  $CO_2/H_2S$  and  $CO_2/SO_2$ . The addition of  $H_2S$  or  $SO_2$  has a minimal effect on alleviating recuperator irreversibility, making the recompression cycle the more efficient choice over a wide range of additive molar fractions. As the complexity of the additives increases, the efficiencies of the two cycles converge at lower additive fractions, indicating that more complex additives require less of their fraction to overcome recuperator irreversibility.

Moreover, the split fraction  $(x_s)$  indicates the need for recuperator irreversibility alleviation, with higher split fractions indicating greater diversion of flow to the recompressor. When both cycle configurations achieve comparable efficiencies, the split fraction is zero, effectively rendering the recompression cycle equivalent to a simple recuperated cycle.

In summary, this study provides insights into the performance of recompression cycles with different additive mixtures, highlighting the importance of molecular complexity as a key factor in determining their relative efficiencies. These findings contribute to a better understanding of the thermodynamic behavior of these cycles and have the potential to inform the design and optimization of power cycles operating with  $CO_2$  cycles.

As a next step, it is recommended that a wider selection of additives of varying molecular complexities are studied to discern a molecular complexity threshold for the choice between recompression and simple recuperated cycles. Also, the study may be expanded to other cycle layouts such as the precompression cycle. Moreover, the analysis of this paper is limited to transcritical cycles, therefore a broader analysis should also investigate supercritical cycles as well.

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