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# Comparative Thermodynamic Assessment of Various Super- and Trans-Critical Working Fluids for Low Temperature Power Generation Applications

*Araştırma Makalesi / Research Article*

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## ABSTRACT

Recently, energy need is exponentially increasing in the world while energy sources are decreasing rapidly. Therefore, this issue requires energy sources to be used more efficiently and urges professionals to utilize energy from low temperature energy sources such as waste heat and low temperature renewable sources. In this study, energy and exergy analyses of several clean working fluids are comparatively studied in several organic Rankine cycle configurations. CO<sub>2</sub>, N<sub>2</sub>O, and SF<sub>6</sub> fluids are compared with the conventional R23 in three ORC configurations, namely the basic ORC cycle, regenerative ORC cycle, and reheat and regenerative ORC cycle, respectively. Effects of various selected system and environmental parameters on the system performances are comprehensively investigated. Even though R23 shows the best energy and exergy performances than those of other investigated working fluids at low-temperature applications, N<sub>2</sub>O and CO<sub>2</sub> provide a clean solution to high GWP (global warming potential) R23 with similar performance characteristics at low and high temperature power generation applications.

**Keywords:** Organic rankine cycle, energy, exergy, R23, CO<sub>2</sub>, N<sub>2</sub>O, SF<sub>6</sub>.

## ÖZ

Son zamanlarda, enerji ihtiyacı dünyada katlanarak artarken enerji kaynakları hızla azalmaktadır. Bu yüzden, bu konu enerji kaynaklarının daha verimli kullanılması ve uzmanları atık ısı ve düşük sıcaklık yenilenebilir enerji kaynakları gibi düşük sıcaklık kaynaklarının kullanmalarını gerektirir. Bu çalışmada, birbirinden farklı temiz akışkanların enerji ve ekserji analizleri farklı organik Rankine çevrim konfigürasyonlarında karşılaştırmalı olarak incelenmiştir. CO<sub>2</sub>, N<sub>2</sub>O ve SF<sub>6</sub> akışkanları geleneksel R23 akışkanı ile sırasıyla temel organik Rankine çevrimi, ara buhar almalı organik Rankine çevrimi ve ara ısıtmalı- ara buhar almalı organik Rankine çevrimlerinde karşılaştırılmıştır. Çeşitli seçilmiş sistemlerin ve çevresel parametrelerin sistem performanslarına etkileri kapsamlı olarak incelenmiştir.

**Anahtar Kelimeler:** Organik rankine çevrimi, enerji, ekserji, R23, CO<sub>2</sub>, N<sub>2</sub>O, SF<sub>6</sub>.

## 1. INTRODUCTION

Nowadays, need of energy is increasing, however energy sources are decreasing rapidly. This situation requires energy sources used more efficiently. Most of the power producing plants works according to the Rankine cycle. Obtaining power from the sources at low temperature is getting important lately, and hence, instead of steam, fluids that supply high steam pressure at the same heating rate can be used. Organic Rankine cycle (ORC) compared to traditional power systems have the potential to work at lower temperature related to the working fluid used. Here, heat is generally supplied from outside such as industrial waste heat [1-3], solar energy [4-6] and geothermal and SOFC exhaust energy [7-11].

ORC has four main components [12]; these are pump, evaporator, turbine and condenser. Various fluids are used depending on the working conditions and different source temperatures in the ORC. Regeneration can be used to increase the efficiency of ORC, where ORC has an additional heat exchanger to provide heat transfer before the evaporator. This heat exchanger is used

between the hot fluid from turbine and the cold fluid from the pump. Thanks to heat exchanger, cold fluid enters the pump warmer. As a consequence, less energy is needed and system efficiency is increased. In ORC, as another method for increasing efficiency, fluid works on critical point. During the cycle before pressured again it expand in turbine, cools and condense and then reach low pressure zone. The fluid comes to low pressure zone, here its pressure increases and reach supercritical point. There is not a constant temperature in supercritical ORC systems since there is a not a constant pressure during the heating of the working fluid [13].

Many studies have been performed for ORC systems with trans-critical and supercritical fluids. Hung [14] examined the effect of wasted heat of ORC. In this study, he used benzene, toluene, p-Xylene, R 113 and R123. As a result, he has shown that irreversibility depends on heat sources. R113 and R123 have high performance in low temperature while p-Xylene has low irreversibility in high temperature. Chen et al. [15] have compared the CO<sub>2</sub> trans-critical power cycle with ORC system using R123. As a result, a trans-critical CO<sub>2</sub> power system supply higher power output than the ORC using R123.

Mago et al. [16] have contrasted a regenerative ORC with

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the basic ORC. They have used the dry organic working fluids such as R 113, R 245 ca, R123 and isobutene in their study. As a result, they have showed regenerative ORCs have a higher thermal efficiency than the basic ORC. Gang et al. [17] have analyzed low temperature solar thermal electric generation using regenerative organic Rankine cycle. The results show that the maximum regenerative ORC efficiency is higher than that without the regenerative cycle.

Xu and Liu [18] proposed a new design method for supercritical ORCs. They used R218, R134a and R236fa as fluids for utilization of flue gases available at 150°C. As a result, the maximum cycle efficiencies of R236fa and R134a are higher than that of R218, having the lowest critical temperature. Yin et al. [19] investigated super-critical/trans-critical thermodynamic cycles using mixtures of SF<sub>6</sub>-CO<sub>2</sub> as fluids. As a result, if the inlet pressure of pump higher than critical, the cycle efficiency decreases with increases SF<sub>6</sub> fraction.

Meinel et al. [20] considered a two stage ORC with domestic heat recovery. They are compared to the regenerative pre-heating design with state of the art cycles. Astolfi et al. [21] investigated thermodynamic analysis and optimization of different ORC cycle types such as subcritical and trans-critical. Maraver et al. [22] evaluated the thermodynamic optimization of organic Rankine cycle for power generation. Their study is supply the optimization of operating conditions for different type cycles such as subcritical and trans-critical. They used R134a, R245fa, Solkatherm, n-Pentane, Octamethyltrisiloxane and Toluene as fluids in their study. The results show that the critical temperature of working fluids is much higher than the temperature of the heat source cause low vapor densities while the critical temperature of working fluids is lower than the heat source temperature cause low thermodynamic performance. Braimakis et al. [23] investigated subcritical ORC system and supercritical ORC system using five natural refrigerants for a waste heat recovery organic Rankine cycle. They have calculated the several technical parameters such as the turbine size and rotational speed. As a result, they have shown that maximum exergy efficiency ranges from 15 to 40% for temperatures between 150°C and 300°C, respectively.

Toffolo et al. [24] evaluated the design parameters of organic Rankine cycle and search of the sub-supercritical with or without superheating and regeneration cycle configuration. They used two working fluids such as isobutane and R134a while the source temperature is between 130 and 180°C in their study. Andreasen et al. [25] analysed and optimized the organic Rankine cycle using pure fluids, predefined mixtures and binary optimized working fluids. As a result, the mixed working fluids increased the net power output of the cycle while decreased pressure levels.

In this study, thermodynamic analysis has been made by means of the program developed using Engineering Equation Solver (EES) for conventional, regenerative,

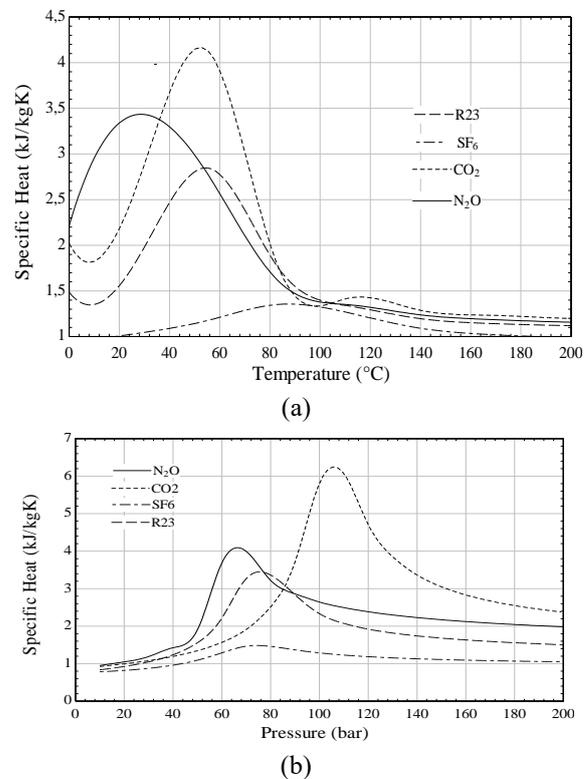
and reheat & regenerative ORC with working fluids R23, CO<sub>2</sub>, N<sub>2</sub>O and SF<sub>6</sub>. Related to various source temperature and pressure ratio, the systems are investigated through thermodynamic performances. Some properties of studied working fluids are provided in Table 1. Since Rankine cycles working with supercritical fluids have more pump power consumption than those of trans-critical working fluids, the pump pressure ratio as well as the source temperature are taken to be main input parameters to thermodynamically optimize the system.

**Table 1.** Some properties of considered working fluids.

Fluid	Critical Temperature (°C)	Critical Pressure (kPa)	GWP (100 years)
R23	25.9	4836	9800
CO <sub>2</sub>	31.0	7380	1
N <sub>2</sub> O	36.4	7240	170
SF <sub>6</sub>	45.55	3758	23900

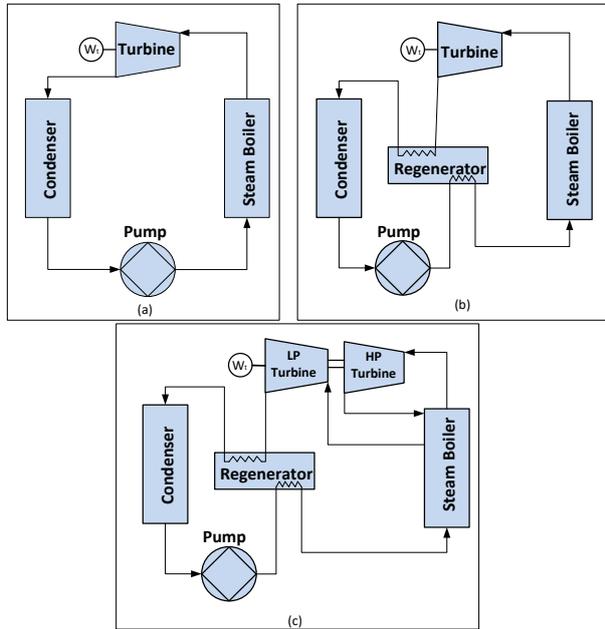
**2. SYSTEMS DESCRIPTION**

Motivation behind the selection of aforementioned working fluids as alternatives is that their critical properties are comparatively lower. Figure 1 visualizes a comparison of specific heat variation of these fluids. While CO<sub>2</sub> shows superiority to other fluids, N<sub>2</sub>O shows the highest potential at low temperature and pressure levels, which is worthwhile to investigate.



**Figure 1.** Variation of specific heats of selected working fluids at different (a) temperatures, and (b) pressures.

Three basic configurations of the ORC unit are considered for the analysis. The first system is the conventional four-component ORC cycle, while the second and third systems are the reheat and regenerative versions as visualized in Figure 2. Input parameters and their range of variation for optimization are provided in Table 2.



**Figure 2.** ORC configurations; (a) Conventional, (b) Regenerative, and (c) Reheat and regenerative.

**Table 2.** Input data and range of variation

Input parameter	Unit	Range
Reference Temperature	°C	0-40
Reference Pressure	kPa	1
Pressure Ratio	-	1.1-3
Source Temperature	°C	100-450
Turbine& Pump isentropic efficiency	%	90%
Turbine & Pump mechanical efficiency	%	85%

### 3. ANALYSES AND ASSESSMENT

Since the main target of the study is to perform a generic comparison between aforementioned working fluids, many assumptions are made in order to keep the ORC configurations as simple as possible resulting in a decreased error through comparison. Below assumptions are made for the analysis:

- All system components are assumed to be ideal, and all corresponding components are studied without any type of specific losses.
- Pressure losses through all installments are neglected.
- All working fluids are taken to be real gases.
- The main optimization parameters are selected as the

source temperature and pump pressure ratio for parametric optimization.

Thermodynamic analysis of all three configurations are based on simplified steady-state modeling of all components through mass, energy, entropy, and exergy balances as follows [26]:

$$\sum \dot{m}_i - \sum \dot{m}_o = \Delta m_{sys} \quad (1)$$

$$\dot{E}_{in} - \dot{E}_{out} = \Delta E_{sys} \quad (2)$$

$$\dot{E}x_{in} - \dot{E}x_{out} - \dot{E}x_{des} - \dot{E}x^Q = \Delta E x_{sys} \quad (3)$$

$$\dot{S}_{in} - \dot{S}_{out} + \sum (\dot{Q}_r/T_r) + \dot{S}_{gen} = \Delta S_{sys} \quad (4)$$

Here, the definition  $E x$  refers to exergy rate and calculated with its specific form as follows:

$$\dot{E}x = \dot{m} \cdot ex \quad (5)$$

And the specific exergy is the sum of chemical and physical exergy of a substance which are also defined in the flowing equations below, as follows:

$$ex = ex_{ph} + ex_{ch} \quad (6)$$

$$ex_{ph} = (h - h_o) - T_o \cdot (s - s_o) \quad (7)$$

$$ex_{ch} = \sum x_i \bar{e}x_{ch}^o - RT_o \cdot \sum x_i \ln(x_i) \quad (8)$$

The third and fourth components of Eq. (3) refer to thermal exergy and exergy destruction rates as follows:

$$\dot{E}x^Q = \dot{Q} \cdot (1 - \frac{T_L}{T_H}) \quad (9)$$

$$\dot{E}x_{des} = \dot{I} = T_o \cdot \dot{S}_{gen} \quad (10)$$

Since this study aims to compare the effects of various system parameters, system configurations and specifically working fluid selection, the best way to compile and compare all these data may be possible by considering the overall performance indicators of the relevant thermal system. Therefore, energy and exergy efficiencies are selected to be the main performance indicators. Energy and exergy efficiencies of conventional and regenerative ORC system are same and defined as follows:

$$\eta_{ORC} = \frac{\dot{W}_T - \dot{W}_P}{\dot{Q}_{heater}} \quad (11)$$

$$\psi_{ORC} = \frac{\dot{W}_T - \dot{W}_P}{\dot{Q}_{heater}(1 - \frac{T_{ref}}{T_{source}})} \quad (12)$$

The denominator of Eq. (12) also results in the thermal exergy input of the heater unit. For the reheat and regenerative cycle:

$$\eta_{ORC} = \frac{\dot{W}_{T1} + \dot{W}_{T2} - \dot{W}_P}{\dot{Q}_{heater}} \quad (13)$$

$$\psi_{ORC} = \frac{\dot{W}_{T1} + \dot{W}_{T2} - \dot{W}_P}{\dot{Q}_{heater}(1 - \frac{T_{ref}}{T_{source}})} \quad (14)$$

For all configurations, one can also define the exergy efficiency as the second law efficiency by considering its Carnot factor, which results the same as in the exergy efficiency definitions, as follows:

$$\eta_{II} = \frac{\eta_{ORC}}{\eta_{car}} \quad (15)$$

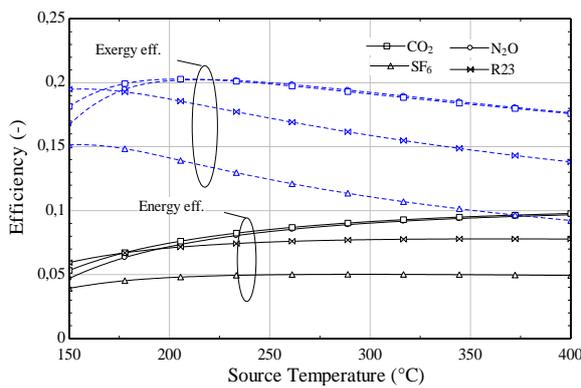
where

$$\eta_{car} = 1 - \frac{T_L}{T_H} \quad (16)$$

Even though results of the second law efficiency and the exergy efficiency show uniform changes and similar results for this present study, it would not be suitable to use second law efficiency definition when the investigated thermal system includes chemical reactions.

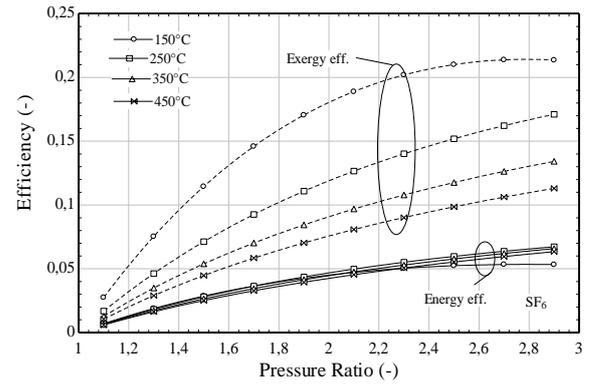
#### 4. RESULTS AND DISCUSSION

Even though the higher source temperature thermodynamically results in a higher specific work production from any thermal power production plants, it generally brings higher irreversibilities due to high temperature difference between low and high temperature limits. Fig. 3 represents this change; R23 shows the highest energy and exergy efficiencies at lower source temperature values while it drastically decreases at higher temperatures making the CO<sub>2</sub> and N<sub>2</sub>O superior than its performance values. 175°C is breakthrough point for the superiority of the supercritical fluids. After 200°C, all working fluids present a similar decreasing trend.

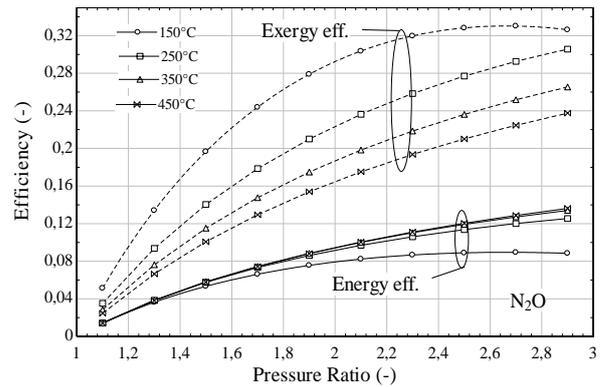


**Figure 3.** Effect of source temperature on the conventional ORC.

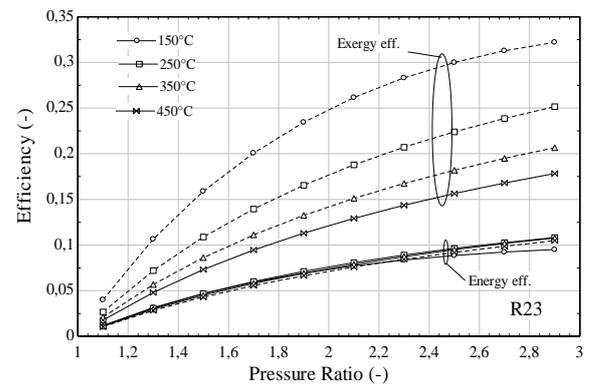
Higher pressure ratios, in general, affect the thermodynamic performances for all considered fluids in a favorable way, however, there are two exceptions CO<sub>2</sub> and N<sub>2</sub>O fluids. Fig. 4 visualizes effects of source temperature and pressure ratios for the conventional ORC, where at pressure ratios higher than 2.6, and at lowest source temperature, exergy efficiency of CO<sub>2</sub> and N<sub>2</sub>O working fluids shows a decreasing trend as shown in Fig 4b and 4d. This outcome is possibly due to very high pressure requirement for both working fluids and further increased high pressure side brings a very high amount of pump work requirement. It is also useful to note that energy efficiencies of all considered fluids also increase at higher pressure ratios and decrease at higher source temperature values. At lower source temperatures all super-critical working fluids starts showing a decreasing energy efficiency trend while R23 is stable at this degree.



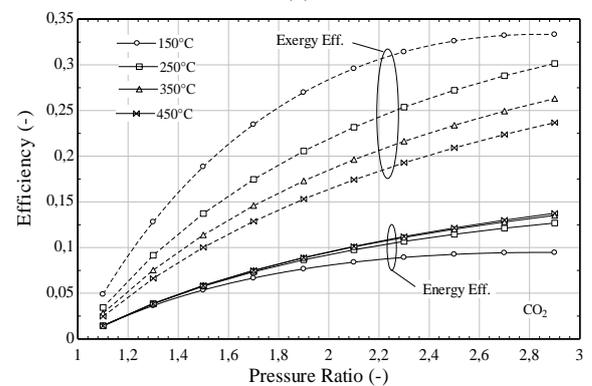
(a)



(b)



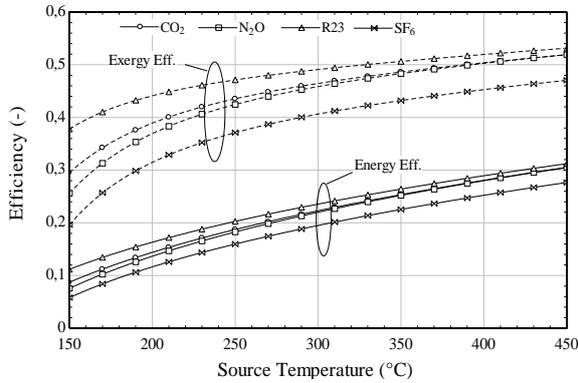
(c)



(d)

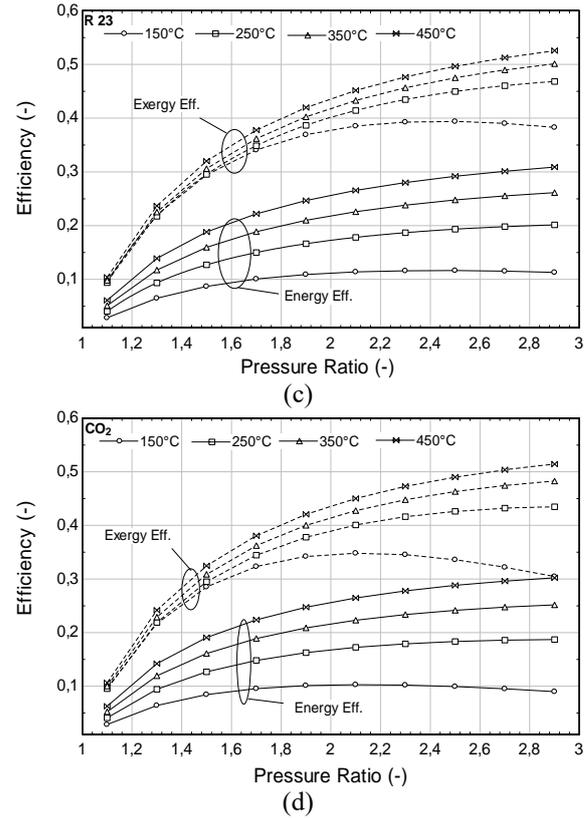
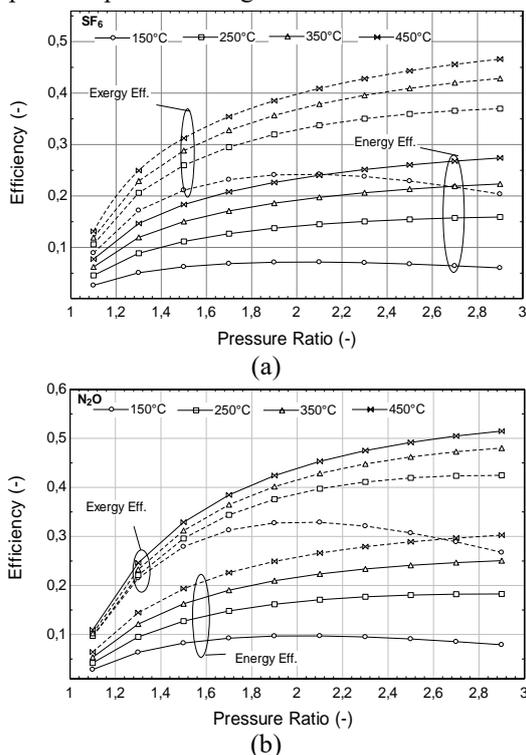
**Figure 4.** Effect of pressure ratio on the conventional ORC at various source temperatures; (a) SF<sub>6</sub> (b) N<sub>2</sub>O (c) R23, (d) CO<sub>2</sub>.

Increased source temperature for the regenerative ORC approximates both efficiencies with a similar increasing trend while R23 is superior to all other super-critical fluids at lower source temperatures, as shown in Fig. 5.



**Figure 5.** Effect of source temperature on the regenerative ORC.

As in the conventional cycle, the pressure ratio-source temperature couple's effect on the system performances are also represented in Fig. 6. As an expected outcome from the learning at the conventional cycle, here exergy efficiency values again show a decreasing trend at higher efficiencies for all super-critical fluids due to increased pump work load. However, the performance characteristics of the SF<sub>6</sub> fluid is drastically lower than those of other three working fluids, and hence, evaluation of this fluid has not been performed for the reheat & regenerative cycle configuration. One should note that at low source temperature values, performances of CO<sub>2</sub> and N<sub>2</sub>O are lower than their values represented for the conventional cycle. This outcome is due to higher pump inlet temperature, which is not favorable for fluids being pumped at supercritical region.



**Figure 6.** Effect of pressure ratio on the regenerative ORC at various source temperatures; (a) SF<sub>6</sub> (b) N<sub>2</sub>O (c) R23, (d) CO<sub>2</sub>.

As for the reheat & regenerative ORC, performance results are presented for the remaining working fluids, showing comparable performance characteristics using the results from the prior two configurations. Here, a different parametric study (Fig. 7a) is undertaken to observe the change in the regenerator outlet temperature which has a direct effect on pump work requirement of specifically CO<sub>2</sub> and N<sub>2</sub>O. Even though outlet temperature of R23 is significantly higher than those of CO<sub>2</sub> and N<sub>2</sub>O at higher source temperature values, it is obvious from Fig. 7b that performance characteristics of all three fluids does not significantly show different results at higher source temperature applications. However, both the energy and exergy efficiency results for the R23 still shows higher results at lower source temperature values, which makes this working fluid more suitable for low-temperature power generation applications. Considering, a very high GWP value for the R23 as mentioned in Table 1, use of CO<sub>2</sub> would lead to a clean and economic power generation option.

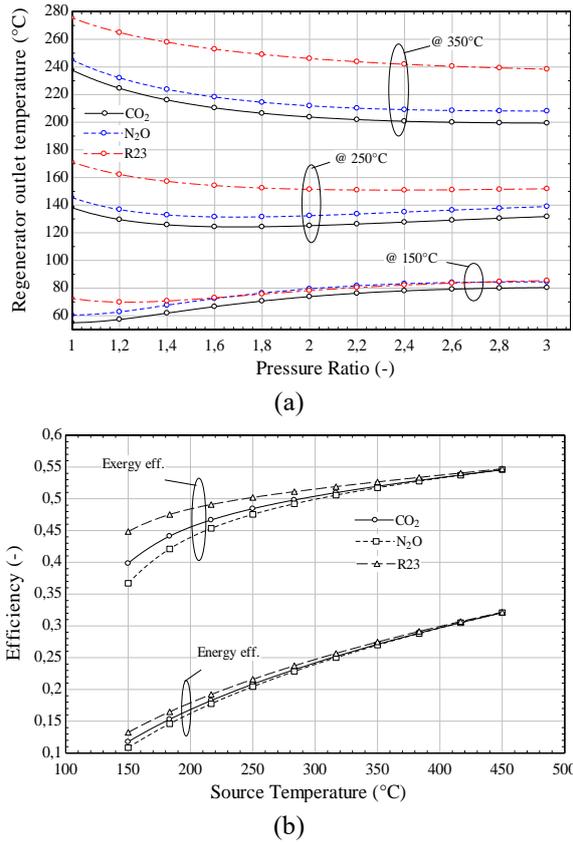


Figure 7. Effects of pressure ratio and source temperature on down selected ORC working fluid on the reheat and regenerative ORC.

Fig. 8 represents the optimum pressure ratio values considering the total irreversibilities occurring in the modified ORC. Lowest specific irreversibility is obtainable at pressure ratio ranges from 1.6 to 2, for both clean working fluids. This trend also shows an optimum point for both highest energy and exergy efficiency results.

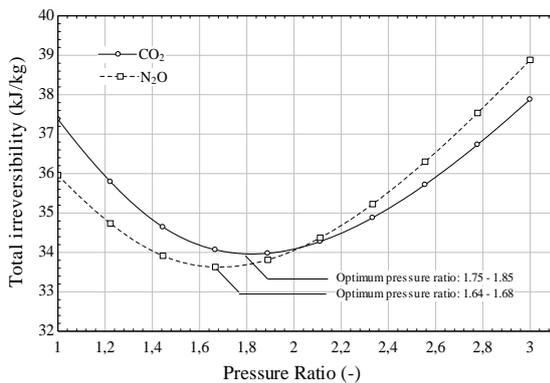


Figure 8. Optimum pressure ratio for the selected working fluids.

A final comparison of energy and exergy efficiencies of all working fluids investigated and all ORC configurations are compiled in Fig. 9. An unexpected trend is observed for CO<sub>2</sub> and N<sub>2</sub>O at the regenerative

ORC that thermodynamic performances of both working fluids are lower than those of at the conventional ORC. R23 shows significant results at lower source temperatures, while performance characteristics are similar at higher source temperatures.

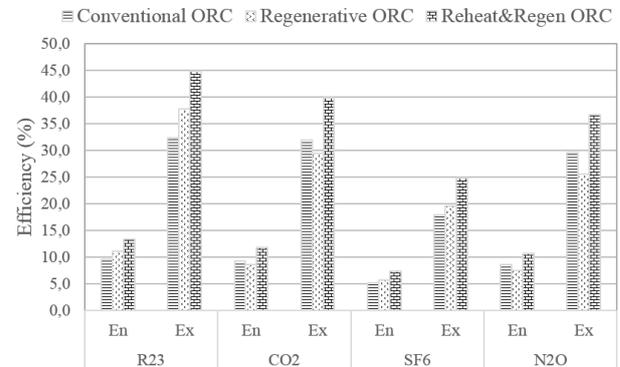


Figure 9. Performance comparison of working fluids and ORC configurations at 150°C source temperature.

## 5. CONCLUSION

A parametric optimization of three configurations of an RC is performed with various working fluids showing similarity with their critical properties. Following results are obtained from the undertaken study:

- SF<sub>6</sub> is not a good match to replace R23 with its low performance characteristics.
- At higher source temperatures, thermodynamic performances of CO<sub>2</sub> and N<sub>2</sub>O show approximate results as of R23, while low source temperature applications indicate the superiority of R23.
- The main drawback of CO<sub>2</sub> and N<sub>2</sub>O is that they cause higher work consumption of pumps at lower source temperature. Therefore, an optimal pressure ratio should be selected for these working fluids.

Overall, CO<sub>2</sub> and N<sub>2</sub>O working fluids can be good candidates to replace R23 with their low-very low GWP values and comparable thermodynamic performances.

## NOMENCLATURE

- ex* : specific exergy (kJ/kg)  
*Q* : Heat (kJ)  
*R* : Universal gas constant (kJ/kmolK)  
*s* : specific entropy (kJ/kgK)  
*W* : Work (kJ)

### Greek letters

- $\eta$  : Energy efficiency (%)  
 $\psi$  : Exergy efficiency (%)

### Superscripts

- 0 : reference

### Subscripts

*ch* : Chemical  
*des* : Destruction  
*gen* : Generation  
*p* : Pumps  
*ph* : Physical  
*ref* : Reference  
*sys* : System  
*t* : Turbine

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