Carbon dioxide mixtures for organic power cycles using waste heat sources

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Abstract. The theoretical study proposed here is based on the energy recovery of sensible heat sources of medium and low temperature levels from Rankine power cycles in which binary mixtures of carbon dioxide and organic fluids are the working fluids. In this sense, the impact of these blends on performance parameters in the basic Rankine cycle configuration is addressed, as well as, optimization analyses of global conductance to ensure the highest production of net power cycle. The results allowed identifying what mixtures stand out in each performance indicator, particularly at net power and first law efficiency.

1. Introduction
Currently, the population and world energy consumption are in constant grow [1]. Meanwhile, the energy production from fossil fuel that are the principal used to human activities produces many environmental problems as global warming, air pollution and acid rain [2]. In this scenario, the use of waste heat to energy production appears as an important alternative. In addition, waste heat has temperature levels suitable for electricity generation in many sectors (e.g. industrial), which will increase plant efficiency and simultaneously reduce thermal pollution caused for the direct release of that heat in the environment [3].

Organic rankine cycle (ORC) technologies are often used to convert waste heat into electricity [4,5]. ORC uses as working fluid an organic fluid (e.g. hydrocarbons, refrigerants, etc.). These fluids are known for having a low boiling temperature, and as result, have the potential to recover heat at temperature levels below those found in steam Rankine cycles [6]. This feature makes it the most suitable power cycle to recover heat from low (< 230 °C) and medium (< 370 °C) temperature heat sources, commonly found in solar, geothermal, biomass, industrial waste fields, among others [7].

The working fluid is one of the most important variables when designing ORC systems. This variable is crucial for these cycles use properly the thermal source, operate with high efficiency and enable the economic viability of the installation [8,9]. Screening studies indicate more than 50 organic and inorganic pure fluids as recommended working fluids for Rankine cycles with waste heat as heat source. However, some of them have been rejected due to environmental aspects, as required by the protocols, as well as security aspects (e.g. flammability and toxicity issues) or be thermodynamically undesirable [10]. These issues have been outlined in several works of carbon dioxide (CO₂) mixtures [11]. CO₂ has...
many advantages over safety and environmental aspects as well as differentiated thermophysical properties. Nonetheless, its low critical temperature (30.98 °C) imposes constraints for the condensation process when it used in Rankine cycles especially in tropical regions since it requires cooling fluids (e.g. air or water) with low temperature (< 25 °C).

The few studies related with Rankine cycles with CO₂ mixtures as working fluid are limited to give a description of this kind of cycle regarding to first and second thermodynamic laws. However, the main objective of this paper is highlight the virtues of CO₂ mixtures from traditional performance parameters, but this time being normalized by global conductance as size indicative of heat exchange devices and global warming potential (GWP) as environmental parameters. The use of normalized merit figures due to the fact that these, unlike individually considered, are highly dependent on the evaluated operating parameters regarding the occurrence of optimal values, allowing then to explore more easily the benefits of these working fluids in the cycle configuration considered.

2. Methodology

2.1. Cycle configuration
In general, the ORC inclined to be simpler, in particular because of low enthalpy changes during the expansion process which involves the use of only single-stage expander [12]. Thus, the configuration of frequent use for this system have been considered in the study; the basic Rankine cycle (BRC). The BRC schematic diagram with its T-s diagram are presented in the Figure 1. The BRC in the Figure 1 consists of the following process: 1-2 not isentropic compression, 2-3 mixture heat adding in to isobaric process, 3-4 not isentropic expansion in the turbine and 4-1 mixture heat rejection to cooling fluid in to isobaric process.

![Figure 1. BRC and T-s diagram to a mixture of CO₂ and R152a with mass fraction of CO₂ of 0.4.](image)

2.2. Working fluid selection
As previously mentioned, zeotropic mixtures of CO₂ and organic fluids will be considered as working fluids of the cycle. Unlike of pure fluids, zeotropic mixtures exhibit a glide temperature during phase change (e.g. condensation and evaporation). This particularity can be availed to produce a better matching between temperature profiles of mixture and heat and sink sources in the heat exchangers [4]. Therefore, the following criteria were considered when choosing the second component of the mixture:

- Organic fluids of kind hydrocarbon and refrigerants considered in the literature as appropriate working fluids for middle and low temperature heat sources.
• Zero ODP and GWP below of 1500. Although, the GWP value is notably higher than those commonly required in different settings, e.g. European regulations for mobile air conditioning [13], it is intended with this value does not exclude frequent use fluids such as R134a.
• Miscibility of components.

Therefore, organic fluids that attain of above requirements are presented in Table 1.

Table 1. Organic Fluids chosen from REFPROP 9.1 database with GWP below 1500 [14].

| Fluid   | Chemical equation | ODP | GWP     | Safety Group | \( P_{\text{critical}} \) (MPa) | \( T_{\text{critical}} \) (°C) |
|---------|-------------------|-----|---------|--------------|---------------------------------|-------------------------------|
| R236ea  | \( C_3H_2F_6 \)   | 0   | 1410    | A1           | 3.50                            | 139.3                         |
| R134a   | \( C_2H_2F_4 \)   | 0   | 1110    | A1           | 4.06                            | 101.1                         |
| R245fa  | \( C_3H_3F_5 \)   | 0   | 1050    | B1           | 3.65                            | 154.0                         |
| R245ca  | \( C_3H_3F_5 \)   | 0   | 726     | -            | 3.93                            | 174.4                         |
| R32     | \( CHF_2 \)       | 0   | 716     | A2L          | 5.78                            | 78.10                         |
| R143a   | \( C_2H_2F_3 \)   | 0   | 352     | A2           | 5.24                            | 156.7                         |
| R152a   | \( C_2H_4F_2 \)   | 0   | 133     | A2           | 4.52                            | 113.3                         |
| R41     | \( CH_3F \)       | 0   | 107     | -            | 5.90                            | 44.10                         |
| R161    | \( C_2H_2F \)     | 0   | 12      | A3           | 5.09                            | 102.2                         |
| R1234ze | \( C_3H_2F_6 \)   | 0   | 6       | -            | 3.64                            | 109.4                         |

A: lower toxicity; B: higher toxicity; 1: no flame propagation; 2: lower flammability; 3: higher flammability; A2L: lower flammability with a maximum burning velocity of \( \leq 10 \text{ cm/s} \). Suffixes to safety classification indicate recommended changes that are not final yet (“r” for revision or addition).

2.3. Thermodynamic model

The thermodynamics analysis of the power cycle is outline from exergy and energy balances at the different system components. In order to simplify the analysis, some assumptions are made as follows:

• Kinetic and potential energy variations were disregarded in the system.
• Bubble temperature mixture (point 1 in Figure 1 and Figure 2) was considered as 30 °C in the simulations.
• The working fluids of heat and sink sources are air and water, respectively.
• Flow directions of working fluids in the internal heat exchanger (IHE) are countercurrent, and heat losses in IHE and condenser are ignored.
• The mixture quality at the turbine outlet must be greater or equal that 0.9.
• The environment temperature was set at 24 °C.
• The isentropic efficiency of turbine and pump were 0.65 and 0.85, respectively.
• The temperature difference between air hot and the mixture in the turbine inlet was fixed at 10 °C.
• The mixture mass flow in the cycle was fixed at 1 kg s\(^{-1}\).
• Pinch point values in the heat exchangers were fixed at 5 °C.
• The pressure of air hot and water at the inlet of heat exchangers was fixed at 100 kPa.
• The compositions of the zeotropic mixtures do not change in every process of the cycle.

Based on these assumptions and referring to the BRC presented in Figure 1, the mathematical model is given from Equation (1) to Equation (7). Pumping process:

\[
\eta_p = \frac{h_2 - h_1}{h_2'} - h_1' \quad \text{and} \quad \dot{W}_p = \dot{m}_{\text{mix}} (h_2 - h_1),
\]  

(1)

where \( h_2' \) and \( \dot{m}_{\text{mix}} \) in the Equation (1) are the isentropic enthalpy at the pump outlet and mixture mass flow, respectively. Expansion process:
\[ \eta_T = \frac{h_3 - h_{s}}{h_3 - h_{4s}} \quad \text{and} \quad \dot{W}_T = m_{\text{mix}}(h_3 - h_4), \] (2)

where \( h_{s} \) in the Equation (2) is the isentropic enthalpy at the turbine outlet. High-temperature heat transfer process:

\[ \dot{Q}_{\text{hphe}} = m_{\text{mix}}(h_3 - h_2) = m_{\text{air}}(h_{\text{air, in}} - h_{\text{air, out}}), \] (3)

where \( h_{4s}, h_{\text{air, in}} \) and \( h_{\text{air, out}} \) in the Equation (3) are the isentropic enthalpy at the turbine outlet and air enthalpy in the inlet and outlet of the high pressure heat exchanger, respectively. Condensation process:

\[ \dot{Q}_{\text{con}} = m_{\text{mix}}(h_4 - h_1) = m_{\text{water}}(h_{\text{water, out}} - h_{\text{water, in}}), \] (4)

where \( h_{\text{water, out}} \) and \( h_{\text{water, in}} \) in the Equation (4) are the outlet and inlet water enthalpy in the condenser, respectively. Net mechanical power output:

\[ \dot{W}_{\text{liq}} = (\dot{W}_T - \dot{W}_B) \] (5)

First-law efficiency:

\[ \eta_I = \frac{\dot{W}_{\text{liq}}}{\dot{Q}_{\text{hphe}}} \] (6)

Second-law efficiency:

\[ \eta_{II} = \frac{\dot{W}_{\text{liq}}}{m_{\text{air}}(h_{\text{air, in}} - h_0) - T_0(s_{\text{air, in}} - s_0)} \] (7)

Subscripts 1-4 between Equations (1) to Equation (7) refer to cycle state points of Figure 1, \( P \) to the pump and \( T \) to the turbine. The subscript \( \text{hphe} \) in the Equation (3) refers to high pressure heat exchanger, \( \text{con} \) to the condenser in the Equation (4) and \( \text{liq} \) to net power between Equations (5) to Equation (7). Finally, the “0” subscript in the Equation (7) refers to dead-state, i.e., \( T_0 = 24 \) °C and \( P_0 = 100 \) kPa. A computer program in Matlab® (R2014b) was developed to simulate the thermodynamic performance of the \( \text{CO}_2 \) mixtures under various operating conditions. However, the thermodynamic properties of the working fluids are calculated using REFPROP 9.1 [14].

2.4. Validation

Once the model and the thermodynamic states of the cycle were defined, the first results obtained were used for validation purposes in relation to studies published in the literature. In order to exemplify the validation process, Figure 2 shows concordance between the data and those presented by Dai, Li and Ma [15]. As can be observed, the agreement between the data was very good for both first law efficiency (\( \eta_I \)) and net power (\( \dot{W}_{\text{liq}} \)), with the highest deviations in relation to the data of [15] less than 0.9% for \( \eta_I \) and 1.8% for \( \dot{W}_{\text{liq}} \).
3. Results

3.1. Parametric evaluation of carbon dioxide mixtures on first law efficiency and liquid power

The Figure 3a and Figure 3b show the impact of turbine inlet pressure on $\dot{W}_{\text{liq}}$ and $\eta_I$ for different CO$_2$ mixtures, respectively. The mixtures with CO$_2$ mass fraction lower than 50% (R-1234ze, R-152a, R-161, R-32 and R-41), stand out for presenting higher net power with lower pressure level when compared to pure CO$_2$. The low or moderate presence of CO$_2$ in these mixtures ends up exerting a slight influence on the properties of these refrigerants and, therefore, these mixtures end up producing higher $\dot{W}_{\text{liq}}$. Among this group, the CO$_2$/R-161 mixture stands out, which, in addition to producing the highest power among the mixtures analyzed, has an enough CO$_2$ fraction to suppress its flammability. On the other hand, mixtures with a CO$_2$ mass fraction higher than 50% (R-134a, R-236ea, R-245fa and R-245ca) have lower $\dot{W}_{\text{liq}}$, i.e., the increase in CO$_2$ reduces the $\dot{W}_{\text{liq}}$ produced by these mixtures. The thermal efficiency is low for these systems, which demonstrates that a small portion of the heat received by the system is converted into $\dot{W}_{\text{liq}}$. Comparing the results obtained for the mixtures with those for pure CO$_2$, it can be observed that the mixtures present relatively the same performance under simulated conditions, however, pure CO$_2$ has several restrictions, such as the need for high operating pressures to achieve higher efficiency and low condensation temperature ($<25$ °C), which implies that the cooling fluid should have even lower temperatures.
The second law efficiency results for this group of mixtures are shown in Figure 4. The results showed that among the evaluated working fluids, the CO$_2$/R-32 mixture stands out for achieving remarkably higher second law efficiency ($\eta_{II}$) than the others. This is mainly due to the fact that this mixture requires a lower flow rate to ensure the pinch point value of 5°C in the high pressure heat exchanger. The mass flow of the exhaust gases from the heat source operating with the CO$_2$/R-152 and CO$_2$/R-161 mixtures is considerably high and, as a result, these have lower $\eta_{II}$ in the system. The exhaust gas flow for pure CO$_2$ is low and, therefore, its second law performance is evidently superior.

3.2. Global conductance of organic Rankine cycle with dioxide carbon mixtures

The Figure 5 presents values for global conductance ($UA_{Total}$) defined by the sum of the global conductance of the condenser and the high pressure heat exchanger. ($UA$) includes thermal characteristics of the working fluids and materials used in each one of these exchangers as well as their heat transfer areas. The value of ($UA$) provides an estimate of the system size, so the smaller the value, more compact the system will be. The results show that the mixtures that have a low CO$_2$ fraction present high values of ($UA$), with the exception of the CO$_2$ mixture with R-1234ze. The remaining mixtures, on the other hand, those with high CO$_2$ fraction present the characteristic trend of pure CO$_2$, that is, low total conductance.

4. Conclusions

Preliminary analyses indicate that, as with pure fluids, it is not possible to define a blend that exhibits optimal behavior in relation to all performance indicators evaluated. However, the results allowed identifying which mixtures stand out in each indicator, particularly at net power ($W_{liq}$) and first law efficiency ($\eta_{I}$). Thus, blends providing $W_{liq}$ are considered to be the most relevant in these analyses, as they allow extracting the greatest potential from a frequently rejected heat sources. Also, preliminarily,
it was found that several binary mixtures have little information in the literature regarding phase equilibrium data, at least in specific pressure and temperature ranges of Rankine cycles, especially the blend of CO$_2$ with R-161.

CO$_2$ mixtures with HCs were not directly addressed. However, there are a large number of possible pairs for this class of fluids since they present low GWP values (usually < 20). Preliminarily, it was found that several of these mixtures have a high glide which would determine their exclusion from the analysis. An excessive glide temperature value can result in the fractionation of the mixture during the phase change process that would result in a rapid change in the mixture composition in the system if a leak occurs, which would negatively impact the cycle operation, therefore, more careful studies will be carried out in relation to this class of fluids.

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