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# Thermodynamic analysis of carbon dioxide blends with low GWP (global warming potential) working fluids-based transcritical Rankine cycles for low-grade heat energy recovery

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# ABSTRACT

Carbon dioxide is a promising natural working fluid that can be used in transcritical Rankine cycles due to environmental and safety concerns. However, the high operation pressure has to be reduced and the relatively low efficiency of the system has to be increased. Traditional working fluids have been widely investigated to reclaim low-grade heat energy, and most of them have high GWPs (global warming potentials) or are flammable or even toxic. Consequently, to mitigate the above disadvantages, we studied zeotropic mixtures of carbon dioxide blends with 7 low GWP working fluids for use in a TRC (transcritical Rankine cycle) for low-grade heat conversion. The results revealed that these zeotropic mixtures can help improve the thermal efficiency of the TRC and decrease the operation pressure compared to that of pure CO<sub>2</sub>. Owing to the perfect thermal match in the heat transfer process, higher exergy efficiencies were achieved for the entire system when zeotropic mixtures were used than pure CO<sub>2</sub>. Maximum exergy efficiencies exist for the TRC at the corresponding optimal pressures for each mixture. Finally, the mixture CO<sub>2</sub>/R161 is recommended for small capacity instruments for its high efficiency, in spite of its high flammability; the mixtures CO<sub>2</sub>/R1234yf and CO<sub>2</sub>/R1234ze can be used in TRCs with larger capacities due to their lower flammability.

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# 1. Introduction

In recent years, the growing consumption of fossil fuels has caused several serious environmental issues such as climate change, acid rain, and air pollution. In addition, the energy shortage problem is growing more serious with the increasing demand for energy in the world. In this situation, the development and utilization of renewable energy sources are effective ways to solve energy and environmental problems. Renewable energy resources like solar energy and geothermal energy, as well as industrial waste heat, can partially alleviate the requirement for fossil fuels. Lowand medium- temperature heat sources with temperatures typically ranging from 100 to 200 °C are the most commonly available resources at present [1]. The temperature of the fluid in a solar collector can reach up to about 180  $^\circ C$  on summer days and 140  $^\circ C$ on winter days [2]. Furthermore, the temperature range of industrial waste heat is typically between ambient temperature and 250 °C [3]. However, these low- and moderate-temperature heat

0360-5442/\$ – see front matter © 2013 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.energy.2013.11.019 sources can hardly be used to generate electricity through the conventional power generation method.

To efficiently utilize these energy sources, many thermodynamic cycles such as the ORC (organic Rankine cycle), TRC (transcritical Rankine cycle), and Kalina cycle have been proposed to convert low-temperature thermal energy into power [4]. The ORC has been extensively investigated and is considered to be an excellent cycle for converting low-grade heat energy to electrical power. The Kalina cycle is more complex and needs more maintenance in its practical operation, though the efficiency of the Kalina cycle is 3% higher in comparison with those of the other two cycles [5]. Nevertheless, for pure working fluids, during the isothermal evaporation process, the constant evaporation temperature is mismatched with the temperature change of the heat source in the heat exchangers, and this causes a large number of irreversibilities. Partially, a traditional ORC is not suitable for sensible heat sources [6]. Compared with a conventional ORC, the working fluid in a TRC can be heated directly from liquid to the supercritical state, which results in a better thermal match in the gas heater/evaporator and reduces the exergy destruction in the heating process [7].

TRCs have been investigated widely as an effective method to recover the low-grade heat energy. Zhang et al. [2,8-14]





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Nomenclature		total	total
Cn	specific heat capacity (kJ/kg °C)	Greek symbols	
É	exergy (kW)	$\eta_{I}$	thermal efficiency (–)
h	specific enthalpy (kJ/kg)	$\eta_{\rm H}$	exergy efficiency $(-)$
Ι	irreversibility (kW)		
т	mass flow rate (kg/s)	Acronyms	
S	specific entropy (kJ/kg °C)	C	condenser
Т	temperature (°C)	CW	cooling water
р	pressure (MPa)	DME	dimethyl ether
Q	heat exchange capacity (kW)	GH	gas heater
W	work output (kW)	GWP	global warming potential
$X_{CO_2}$	mass fraction of $CO_2(-)$	HC	hydrocarbon
-		HFC	hydrofluorocarbon
Subscripts		HS	heat source
0	dead state	IHX	internal heat exchanger
1, 2, 2', 3, 4, 4', 5, 6 state point		LEL	lower explosive limit
b	boiling	LOC	limiting oxygen concentration
С	critical	ODP	ozone depletion potential
cal	calculated	OEL	occupational exposure limit
in	inlet	ORC	organic Rankine cycle
net	net	Р	pump
out	outlet	R	regenerator
pinch	pinch point	Т	turbine
sat	saturated state	TRC	transcritical Rankine cycle
spe	specified		

experimentally and theoretically studied the performance of a solar Rankine system using CO<sub>2</sub> as a working fluid. Experimental results showed that the power generation efficiency ranged from 8.78 to 9.45% [12] and that the COPs (coefficients of performance) of the cycle were 0.548 and 0.406 on typical summer and winter days in Japan, respectively [2]. Chen et al. [15–17] compared a carbon dioxide-based transcritical power cycle with a traditional ORC using R123 as a working fluid to recover the energy from industrial waste heat. The results indicated that a CO<sub>2</sub> transcritical power cycle showed a higher power output than that of the ORC, considering the thermal match of the heat transfer in the evaporator. Cayer et al. [18,19] introduced an IHX (internal heat exchanger) to a CO<sub>2</sub> transcritical power cycle system and found that the maximum energy efficiency increased and that the corresponding optimum pressure decreased by using the pinch analysis methodology. Vélez et al. [6,20] carried out an exhaustive simulation of a carbon dioxide-based transcritical power cycle. The results revealed that there exists a maximum value for the cycle energy efficiency as well as the net specific work at various turbine inlet temperatures and that a TRC was a reliable way to convert lowgrade heat energy. Guo et al. [21] compared the performances of CO<sub>2</sub> and 12 pure conventional working fluids used in a transcritical Rankine power cycle. They concluded that temperature glide of fluids that were well-matched in the evaporator can improve the power output. Chen et al. [22] also compared CO<sub>2</sub> with R32 as working fluids in a TRC. They concluded that the thermal efficiency of an R32-based cycle was 12.6%-18.7% higher than that of CO<sub>2</sub> at much lower pressures. Gu et al. [23] studied transcritical cycles with propane, R125, and R134a as working fluids by using geothermal sources (>190 °C) as heat sources, and propane and R134a were recommended for use in this cycle due to their high efficiencies. Saleh et al. [24] carried out a theoretical study on a TRC operating between 30 and 100 °C using R143a, R290 and R41 as working fluids, and the thermal efficiency, expansion ratio, and volume flow rate at the inlet of the turbine were discussed. Karellas et al. [7] investigated the performance of transcritical and subcritical Rankine cycles by using the working fluids R227ea and R134a at turbine inlet temperatures ranging from 105 to 135 °C. Schuster et al. [25] studied the performance of 12 pure working fluids, including water, R236fa, R245fa, and isobutene, used in transcritical and subcritical Rankine cycles with a heat source at 210 °C. Performance characteristics such as the work output, thermal efficiency, and heat transfer capacity were discussed.

From the above mentioned researches, CO<sub>2</sub> is considered to be a promising fluid for TRCs. It is an environmentally-friendly natural working fluid with zero ODP (ozone depletion potential) and a negligible GWP (global warming potential), and it is nonflammable and non-toxic [18]. In addition, it has favorable thermodynamics and transport properties. A disadvantage of CO<sub>2</sub> is its critical point, which is as low as 31.1 °C and its potential effect on the condensation process due to the temperature limitations of available cooling sources [4]. Another disadvantage of CO<sub>2</sub> is its high critical pressure, which is as high as 7.38 MPa. The normal operating pressure of a CO<sub>2</sub> system is usually above 10 MPa, which leads to safety concerns in a real operation. Besides CO<sub>2</sub>, some working fluids like HFCs (hydrofluorocarbons) and HC (hydrocarbons) have been selected and also used with TRCs [7,23-25]. These fluids have relatively high critical temperatures and low pressures and are well suited for TRCs in comparison with CO<sub>2</sub>. However, some of these conventional working fluids are either flammable or toxic and some of them have excessively high GWP values. These disadvantages impede the actual application of these working fluids in TRCs.

To solve the problem of high operational pressure in a  $CO_2$  transcritical refrigeration cycle,  $CO_2$  is blended with other pure working fluids such as R290 [26,27], R600, R600a [28], and DME (dimethyl ether) [29,30] and the operation pressure of the system is reduced efficiently. Furthermore, some researches [31–33] have shown that the addition of carbon dioxide or nitrogen added to a combustible gas can effectively reduce the combustion possibility

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