Evaluation of carbon dioxide blends with isopentane and propane as working fluids for organic Rankine cycles

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HIGHLIGHTS

► Non-water based working fluids and their mixtures for power generation.
► Results for carbon dioxide blends with isopentane and propane.
► Appropriation of irreversibilities in cycle components.
► Entropy generation based on pinch point of regenerator and heat source temperature.

ARTICLE INFO

ABSTRACT

The main theme of this paper is to study the flammability suppression of hydrocarbons by blending with carbon dioxide, and to evaluate these mixtures as possible working fluids in organic Rankine cycle for medium temperature concentrated solar power applications. The analysis takes into account inevitable irreversibilities in the turbine, the pump, and heat exchangers. While the isopentane + CO_2 mixture suffers from high irreversibility mainly in the regenerator owing to a large temperature glide, the propane + CO_2 mixture performs more or less the same as pure propane *albeit* with high cycle pressures. In general, large temperature glides at condensing pressures extend the heat recovery into the two-phase dome, which is an advantage. However, at the same time, the shift of the pinch point towards the warm end of the regenerator is found to be a major cause of irreversibility. In fact, as the number of carbon atoms in alkanes decreases, their blend with CO_2 moves the pinch point to the colder end of the regenerator. This results in lower entropy generation in the regenerator and improved cycle efficiency of propane + CO_2 mixtures. With this mixture, real cycle efficiencies of 15–18% are achievable at a moderate source temperature of 573 K. Applicability for a wide range of source temperatures is found to be an added advantage of this mixture.

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1. Introduction

Abatement of anthropogenic greenhouse gas emissions revolves around generation of more electrical energy from a given fossil fuel based heat source or utilizing a renewable heat source. The present situation is that the quantum of thermal energy dispensed through the chimney in a steam based thermal power plant is nearly the same as the amount of electrical energy fed to the grid. Electrical energy and economic prosperity are intricately inter-related. At the same time, there are innumerable rural/remote human settlements across the globe having virtually no grid connected electricity. Any efforts to supplement the conventional electrical energy generation with carbon neutral methodologies or installing distributed power plants powered by non-fossil fuels or renewable thermal energy sources should be construed as contributions towards meeting international obligations on combating global warming. As a corollary, such developments can also be adopted to harness the low grade process waste heat in several industries.

Since it is appreciated that steam based Rankine cycles will be unviable for sub-MW level power generation [1], engineering community has relentlessly explored other fluids, notably organic compounds [2]. The refrigeration industry has striven to move away from high global warming potential (GWP) working fluids (such as hydrofluorocarbons) for commercial and industrial refrigeration, and this has led to adoption of natural working fluids such as ammonia, carbon dioxide, and hydrocarbons [3]. There is no

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Nomenclature

c_p	specific heat at constant pressure, kJ/kg K
h	specific enthalpy, kJ/kg
$\dot{I}$	irreversibility rate, kW
K	proportionality constant of turbine leakage
L	leakage loss
$\dot{m}$	mass flow rate, kg/s
p	pressure, bar
P	power, kW
$\dot{Q}$	flow rate, m³/s
Q	heat transfer, kJ
S	entropy, kJ/K
s	specific entropy, kJ/kg K
T	temperature, K

Greek letters

η	efficiency
ρ	density, kg/m³

Subscripts

amb	ambient
b	boiler
c	critical
cond	condenser
f	liquid
g	gas
gen	generation
HTF	heat transfer fluid
i	inlet
o	outlet
p	pump
pp	pinch point
reg	regenerator
sat	saturation
t	turbine
th	thermal
wf	working fluid
1, to 6	states on ideal thermodynamic cycle

Superscript

|	
'	states on real thermodynamic cycle

reason why this logic cannot be extended for working fluids in organic Rankine cycles (ORC). This paper is motivated by such a philosophy. Hydrocarbons as working fluids for ORC is fairly well explored [2,4–6]. However, we realize that there are operational safety issues of hydrocarbons because of their flammability. Consequently, we explore a mixture of a hydrocarbon which is adequately blended with an inert component such that the resulting working fluid is not flammable. This approach, again, is tempered by the work of Oellrich et al. [7] who investigated flammability suppression of mixtures of propane and perfluoropropane as possible refrigerants. Our school of thought is also supported by the data of Zabetakis [8] which led to the inference that adding an inert component up to 30% mole fraction is often adequate to take most hydrocarbons outside the flammability envelope. Invernizzi et al. [9] also analyzed supercritical Brayton cycle with the mixtures of hydrocarbons and CO_2 at a temperature of 673 K. For refrigeration cycles also blends of CO_2 and hydrocarbons have been studied to suppress the flammability of the latter [10]. In an earlier article [11], we have dealt with blending isopentane with a high molecular weight inert component R-245fa. Although the results were encouraging, the mixture had sufficiently high GWP. In this paper, our approach is to blend the hydrocarbon with another natural working fluid so that the resulting mixture retains predominantly the good features of hydrocarbons and yet has virtually no GWP. It is not difficult to visualize that carbon dioxide would be the most natural choice. However, such a mixture should be amenable for reasonable operating pressures in the ORC. It is also imminent that the mixture would have non-isothermal condensation and evaporation. Indeed, this feature endows an additional benefit in the proposed analysis. Preferably, the entire cycle should operate above atmospheric pressure so that ingress of ambient air is avoided. In the light of the above criteria, the chosen ORC working fluids are blends of carbon dioxide with isopentane and propane. Among them, the former is a dry fluid, implying that $(\partial T/\partial s)_{\text{saturated vapor}} > 0$ [12]. Despite the fact that the latter is a wet fluid, the operating conditions are such that no wet expansion occurs. The operational limits imposed for the analysis are upper cycle pressures not exceeding 100 bar, heat source temperatures up to 573 K which are attainable from parabolic concentrators in the case of solar thermal energy, or industrial waste heat from boilers used for process steam, or even exhaust of diesel generator sets.

2. Choice of working fluids

Alkanes amenable to the philosophy of this paper are those with C_3–C_5. Ethane + CO_2 mixtures have very low critical temperatures such that condensation is seldom possible at typical ambient conditions in tropical regions. CO_2 mixtures with isobutane and isopentane are conducive to conventional Rankine cycle operation (with condensation and boiling) because of their high critical temperatures. In the case of propane, the high pressure segment is entirely in the supercritical region. Since this adds novelty to the Rankine cycle, we choose propane and isopentane as two base alkanes in this work.

Zabetakis [8] has shown that addition of 0.3 mol fraction of carbon dioxide takes propane and n-pentane outside the flammability envelope. Although, no corresponding data are available for isopentane, we assume that the flammability behavior of the two isomers will be similar. Hence, our further analysis is based on two mixtures, namely isopentane (0.7 mol fraction) + carbon dioxide (0.3 mol fraction) and propane (0.7 mol fraction) + carbon dioxide (0.3 mol fraction). Temperature glide (defined as the difference between the dew point and the bubble point along an isobar) for these mixtures is shown in Fig. 1. In the rest of this paper, reference to mixture implies 0.7 mol fraction of flammable hydrocarbon and 0.3 mol fraction of CO_2. Table 1 lists relevant thermodynamic data for the chosen working fluids. The existence of $s_{g\text{max}}$ determines whether the working fluid is a dry or wet fluid. The temperature glides on the other hand are substantially large (of the order of 40–100 °C) in the case of isopentane mixture and no more than 40 °C in the case of propane mixture. These data are judiciously used to enhance the zone of heat recovery.
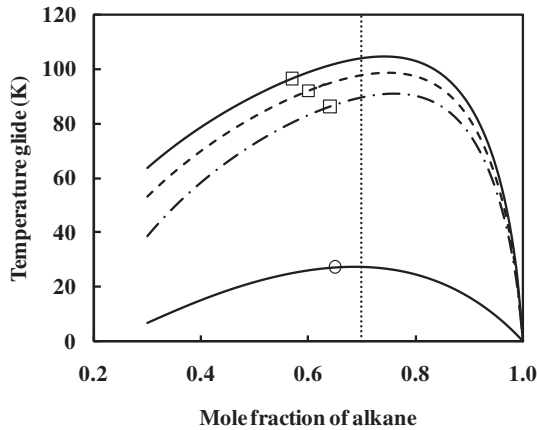
Fig. 1. Temperature glide variation against mole fraction of isopentane and propane. Legend: □ isopentane + CO_2, ○ propane + CO_2, ——— $p_{sat,308}$, – – – – 1.25 $p_{sat,308}$, — — — 1.5 $p_{sat,308}$, ········· line of mole fraction = 0.7.

3. Thermodynamic analysis

The thermodynamic analysis is carried out for a minimum cycle temperature of 308 K, which is slightly above the ambient temperature in tropical developing countries where medium temperature concentrated solar power is highly relevant. Thus the bubble point of the mixture/working fluid is set to be 308 K. Consequently, the minimum operating pressure is the bubble point pressure at this temperature. We also set a condition of this pressure to be greater than atmospheric such that no air infiltration is possible. As seen from Table 1, this condition is satisfied for the chosen mixtures. Indeed, the penalty of non-flammable hydrocarbon mixture is operation under pressures fairly higher than in other ORC options. The case of pure isopentane as the ORC working fluid has already been dealt with in our earlier paper [11]. Mixture of isopentane and CO_2 and pure propane in addition to its mixture with carbon dioxide. Fig. 2 shows the schematic diagram of the ORC. Among the chosen mixtures, isopentane + CO_2 system will operate in the sub-critical region whereas propane + CO_2 will do so in the transcritical region. Typical processes are depicted on the $T–s$ plane in Figs. 3 and 4. Heat transfer fluid (HTF) absorbs thermal energy from a source such as a solar collector, waste heat or a biomass boiler, and transfers it to the working fluid. The regenerator improves cycle efficiency by recovering the enthalpy of the turbine discharge stream to heat the high pressure liquid stream emerging from the pump. Following assumptions are made to analyze the cycle:

i. turbine inlet temperature (T_3 or $T_{3'}$) is limited to 573 K which is the upper limit of REFPROP [13] for isopentane and CO_2 mixture.

Table 1
Thermodynamic data for the selected working fluids [13].

	CO_2	Isopentane	Propane	Mixture[a] of CO_2 with	
				Isopentane	Propane
T_c (K)	304.13	460.35	369.89	447	354.48
p_c (bar)	73.77	33.78	42.51	64.88	61.42
p_{sat} at 308 K (bar)	–	1.28	12.13	24.65	35.52
s_{gmax} occurs at (bar, K)	——[b]	26.4, 444	——[b]	29.96, 421	——[b]

[a] Mole fraction of CO_2 = 0.3.
[b] Wet fluid.
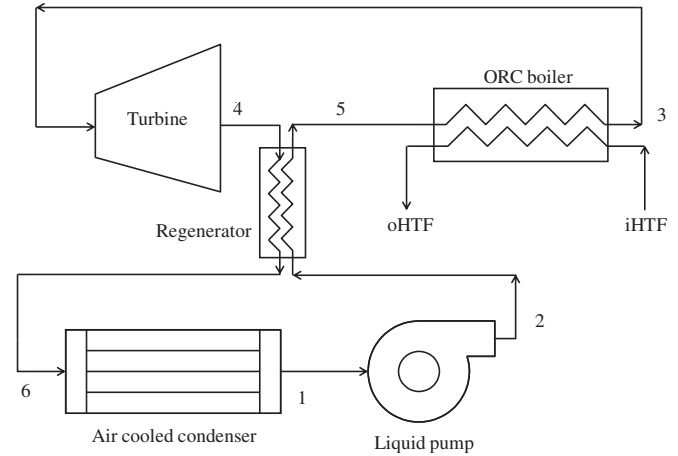
Fig. 2. Schematic of an ORC.

ii. isentropic efficiencies of the turbine and the pump are assumed to be 65% and 85%, respectively. The efficiencies are expressed as

$$\eta_T = \frac{(h_{3'} - h_{4'})}{(h_{3'} - h_4)} = 0.65 \tag{1}$$

$$\eta_p = \frac{(h_2 - h_1)}{(h_{2'} - h_1)} = 0.85 \tag{2}$$

Turbine efficiencies reported in the literature range from 40 to 75% for a small capacity of ∼1.73 kW [14] R-245fa system. Although, higher efficiencies of 75–85% have been assumed [15,16], we wish to use a conservative value of 65%.

iii. minimum temperature difference across streams is restricted to 5 K in the case of regenerator and 10 K in the case of the boiler in order to avoid pinch point.

iv. pressure drop of 3.5% is assumed to take place in the heat addition and rejection processes. Mathematically
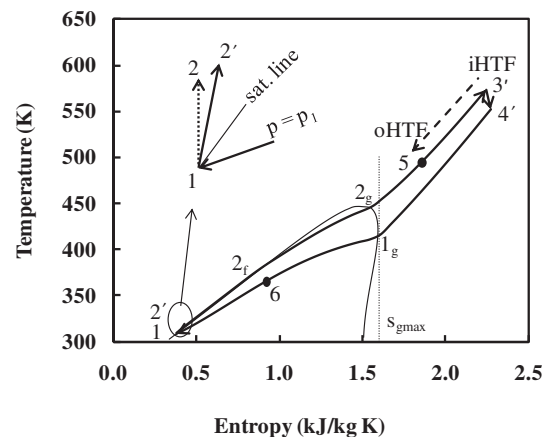
Fig. 3. $T–s$ chart of ORC for isopentane + CO_2 mixture at a pressure ratio of 2.0 and source temperature 573 K. 1 to 2′ – pumping; 2′to 2f – sensible heating in the regenerator; 2f to 2g – evaporation in the regenerator; 2g to 5 – superheating in the regenerator; 5 to 3′ – heat addition in boiler; 3′ to 4′ – expansion in turbine; 4′ to 1g – desuperheating in the regenerator; 1g to 6 – condensation in the regenerator; 6 to 1: heat rejection in air cooled condenser. 2′-2f-2g-5-3′ – processes at high pressure; 4′-1g-6-1 – processes at low pressure heat transfer to working fluid by HTF.
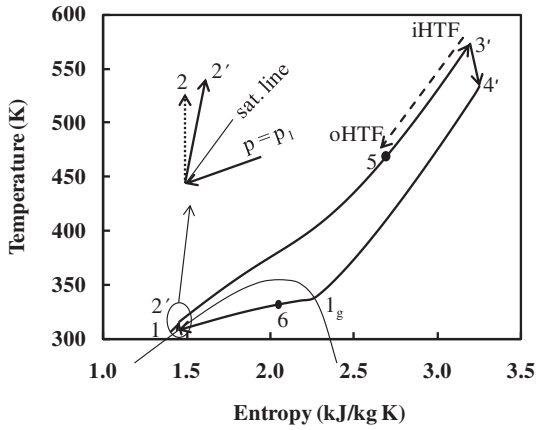
Fig. 4. T–s chart of ORC for propane + CO_2 mixture at the pump outlet pressure of 100 bar (expansion ratio ∼ 2.6) and source temperature 573 K. 1 to 2′ − pumping; 2′ to 5 − heat addition in the regenerator; 5 to 3′ − heat addition in boiler; 3′ to 4′ − expansion in turbine, 4′ to 1g − desuperheating in the regenerator, 1g to 6 − condensation in the regenerator, 6 to 1: heat rejection in air cooled condenser. 2′-5-3′ − processes at high pressure; 4′-1g-6-1 − processes at low pressure heat transfer to working fluid by HTF.

$$p_{2'} - p_{3'} = 0.035 p_{3'} \tag{3}$$

$$p_{4'} - p_1 = 0.035 p_1 \tag{4}$$

v. pressure drops in the regenerator and the boiler for the high pressure stream, and those in the regenerator and the condenser for the low pressure stream are apportioned in the same ratio as the enthalpy change in the respective streams. Mathematically,

$$p_5 = p_{2'} - (p_{2'} - p_{3'}) \frac{h_5 - h_{2'}}{h_{3'} - h_{2'}} \tag{5}$$

$$p_6 = p_{4'} - (p_{4'} - p_1) \frac{h_{4'} - h_6}{h_{4'} - h_1} \tag{6}$$

vi. There is a leakage loss, L, defined as ratio of mass flow rate throttled through turbine to total mass flow rate. Mathematically,

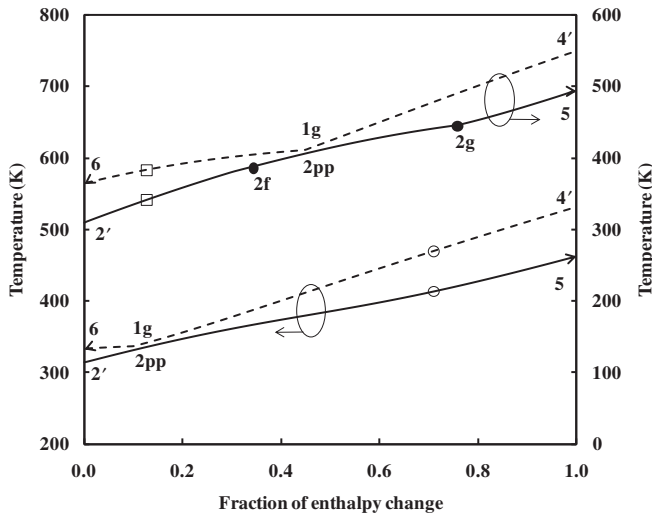$$L = \frac{\dot{m}_{\text{leakage}}}{\dot{m}_{\text{total}}} \tag{7}$$

This loss is included to account for a small fraction of fluid that evades expansion through the rotor but bypasses it at the blade tip. If pressure differential is the major driving force for the leakage, we can write

$$L = K \sqrt{p_{3'} - p_{4'}} \tag{8}$$

The leakage loss is assumed to be 2% for a specific case of isopentane mixture as working fluid and a turbine expansion pressure ratio of 2 for the following operating conditions:

$T_1 = 308$ K, $p_{4'} = 25.5$ bar, $p_{3'} = 51.07$ bar and $L = 0.02$, we get $K = (0.0039 \text{ bar})^{-0.5}$. For other expansion ratios and differentials $(p_{3'} - p_{4'})$, the leakage loss is re-appropriated as per the above equation.

The real cycle analysis embedding the above sources of irreversibilities is benchmarked against an ideal cycle. Further,
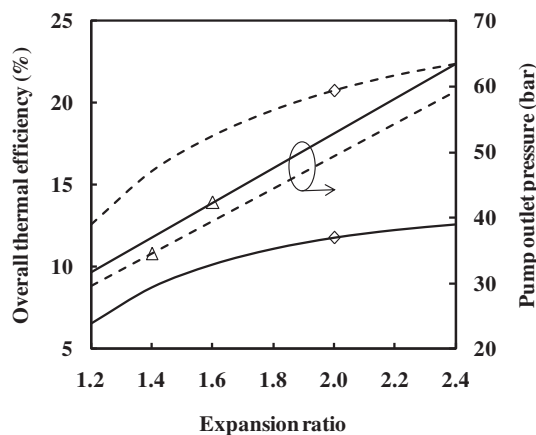
partitioning of irreversibilities in the turbine, the pump and heat exchangers (i.e. regenerator and boiler) are also reported.

Working fluids discussed in detail are i) isopentane + CO_2, ii) propane + CO_2 and iii) pure propane. Parametric analysis covers a) turbine inlet to outlet pressure ratio (henceforth referred to as expansion ratio) from 1.2 to 2.4 for isopentane and CO_2 mixture, 1.8 to 4 for propane and CO_2 mixture and 3.8 to 8 for pure propane case, b) the heat source temperature variation from 400 to 573 K, which is commensurate with medium temperature ORC operating range.

3.1. Performance indicators

The parameters of interest are

(i) the overall thermal efficiency of cycle defined as

$$\eta_{\text{Thermal}} = \frac{(h_{3'} - h_{4'}) - (h_{2'} - h_1)}{h_{3'} - h_5} \tag{9}$$

(ii) mass flow rate for a net output power (P) calculated as

$$\dot{m}_{\text{wf}} = \frac{P}{(h_{3'} - h_{4'}) - (h_{2'} - h_1)} \tag{10}$$

(iii) corresponding volumetric flow rate at the inlet conditions of the turbine

$$\dot{Q}_{3'} = \frac{\dot{m}_{\text{wf}}}{\rho_{3'}} \tag{11}$$

(iv) irreversibilities in the cycle, which will be discussed in detail in Section 5.

All calculations were carried out on Matlab 7.10.0 (R-2010) platform, which was programmed to invoke REFPROP for all thermodynamic property calculations.

4. Results and discussion

4.1. Justification of mixture options

In the case of propane + CO_2 mixture, practical upper pressures will be supercritical, whereby states 2f and 2g (Fig. 5) will be absent. The upper cycle pressures are analyzed up to 150 bar although practical limits are set to be around 100 bar. For optimizing the cycle performance, temperature glide should be used in a judicious way such that the heat recovery zone is extended and the consequences of pinch point are overcome. The regenerator temperature profiles are shown in Fig. 5. Since temperature at state 1g is higher than temperature at state 2′, heat recovery process can be extended to the two-phase region of the low pressure stream. The most probable thermodynamic state of occurrence of pinch point is the point of intersection of the turbine exhaust pressure isobar with the saturated vapour curve, which will happen in the regenerator. We identify this point as 1g (on the low pressure stream) and 2pp on the high pressure stream. Minimum $(T_{1g} - T_{2pp})$ is set to 5 K. Appendix A describes the method adopted to estimate h_5 when pressure drops in the boiler and regenerator are accounted for.

Fig. 5. Temperature profiles in the regenerator. Legend: —— cold high pressure fluid, ———— warm low pressure fluid, ○ propane + CO_2 mixture for expansion ratio of 2.6 (left ordinate), □ isopentane + CO_2 mixture for expansion ratio of 2.4 (right ordinate).
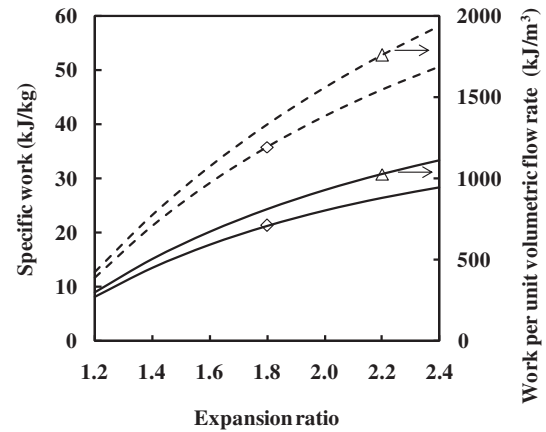
4.2. Results for isopentane + CO_2 mixtures

Expansion ratios are limited to 2.4 lest the boiler pressure exceed the critical pressure of the mixture (64.88 bar), such that the entire Rankine cycle remains sub-critical. Fig. 6 shows efficiency variation for different pressure ratios at a source temperature of 573 K. Thermal efficiency of only 12.6% is possible at the maximum expansion ratio of 2.4. If we set a threshold real cycle efficiency of 10%, the range of expansion ratios is too narrow for this mixture (1.6–2.4). Large difference between real and ideal cycle efficiencies is due to irreversibilities introduced by non-idealities which will be discussed in detail in Section 5.

Fig. 7 shows specific work output and work output per unit volumetric flow rate at turbine outlet conditions for ideal and real cycles. Both replicate the pattern of efficiency. Availability of large amount of specific work per unit volumetric flow rate at turbine outlet will result in small turbine housing sizes. Small temperature drop during expansion in turbine (Fig. 3) augments the relevance of the regenerator in the heat addition process, the consequence of which is that the ratio of work output to heat recovered in the regenerator will be very small (as seen in Fig. 8). Even at the
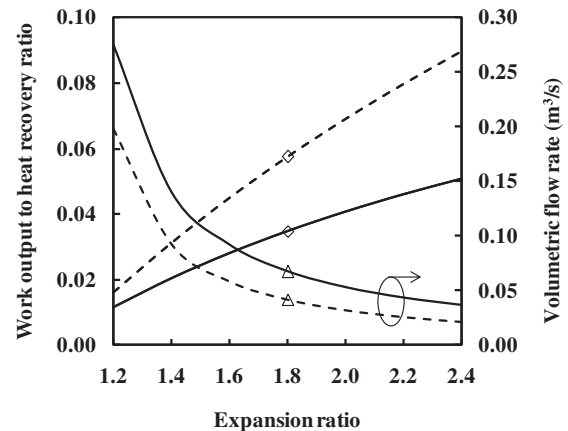

Fig. 7. Specific work and work per unit volumetric flow rate at turbine outlet for isopentane + CO_2 mixture at various expansion ratios. Legend: ———— ideal cycle, —— real cycle, ◇ specific work (left ordinate), △ work per unit volumetric flow rate (right ordinate).

maximum expansion ratio, it is no more than 5%. This is a result of large irreversible heat transfer in the regenerator for isopentane + CO_2 mixtures, which will be discussed in greater detail in Section 5. Volumetric flow rate at turbine inlet conditions decreases by a large factor with expansion ratio (Fig. 8). Volumetric flow rates at turbine outlet for the chosen mixture in this paper are quite good in comparison to pure R-245fa, mixture of R-245fa and isopentane proposed for the fixed power generation of 100 kW [11]. While it is preferable to have a low volumetric flow rate at turbine outlet from turbine casing size point of view, fairly large volumetric flow rates will be desirable at turbine inlet to avoid partial admission losses.

Temperature sensitivity analysis is performed for pressure ratios of 1.6, 1.8, and 2.0. At each expansion ratio there is a minimum temperature of the source that will prevent any part of expansion proceeding through the two-phase region. In an ideal cycle, this is the temperature at the point of intersection of the chosen high pressure isobar and the isentropes through s_{gmax}. For the pressure ratios possible, this temperature range is 450–573 K, which can be classified as medium temperature ORC obtainable from parabolic concentrating collectors with two-axis tracking. In the case of a real cycle, the process 3′–4′ in Fig. 3 can be, at best, tangent to the

Fig. 6. Overall thermal efficiency and pump discharge pressures for isopentane + CO_2 mixture at various expansion ratios. Legend: ———— ideal cycle, —— real cycle, ◇ overall thermal efficiency (left ordinate), △ pump discharge pressures (right ordinate).

Fig. 8. Work output to heat recovery ratio and turbine inlet volumetric flow rate for isopentane + CO_2 mixture at various expansion ratios. Legend: - - - - ideal cycle, —— real cycle, ◇ work output to heat recovery ratio (left ordinate), △ volumetric flow rate (right ordinate).

saturation curve on the T–s plane which could marginally reduce the lower threshold.

In Fig. 9 we show the temperature sensitivity of efficiencies wherein the lower thresholds are marked. If a minimum efficiency requirement of 10% is set (shown by a dotted line), at an expansion ratio of 1.6 there is no flexibility in the temperature range of operation. If the expansion ratio is enhanced to 1.8 or 2, the lower threshold of operating temperature range can be down to ~540 and ~530 K, respectively.

From the above analysis, it can be deduced that though isopentane + CO_2 mixture has all the desirable environmental merits, it suffers from large temperature glides, low efficiencies and limited domain of expansion ratios and temperature range of operation. The disadvantage of large glide can be overcome by replacing isopentane with propane. The next sub-section deals with this mixture.

4.3. Characteristics of propane + CO_2 mixture

The minimum pressure for 308 K saturated liquid state will now be 35.52 bar, which is higher than in the previous case. Fig. 1 also shows the temperature glides for this mixture at this pressure. The concept of s_{gmax} will not be relevant because the mixture is also a wet fluid like its components. The minimum high side pressure is chosen to be the critical pressure (61.42 bar) such that heat addition isobar does not have the temperature glide problem. This will result in a minimum expansion ratio of 1.8. The case of pure propane as an ORC fluid is also discussed to bring out the effect of mixing with CO_2. In this case the minimum pressure is 12.13 bar which is the saturation pressure of propane at 308 K. Expansion ratios up to 8 are considered.

Fig. 10 shows plots of efficiency and pump discharge pressures for various expansion ratios at a source temperature of 573 K. While pure propane has relatively flat real cycle efficiency, the expansion ratio has a pronounced effect in the case of the mixture. At an expansion ratio of 4, the mixture has a slightly better efficiency even after accounting for various non-idealities. However, it must be pointed out that the high side pressures are substantially larger in the case of the mixture than in pure propane. Fig. 11 shows specific work and work output per unit volume flow rate at the exit conditions of the turbine. Qualitatively they are similar to those in the case of isopentane + CO_2 mixture (Fig. 7). But quantitatively, the work output is significantly larger in the case of propane + CO_2

Fig. 10. Overall thermal efficiency (left ordinate) and pump outlet pressures (right ordinate) *vs* expansion ratio for propane and propane + CO_2 mixture at turbine inlet temperature of 573 K. Legend: —— real cycle, ———— ideal cycle, ○ mixture, □ propane.

mixture. This implies that the fluid circulation rates in propane + CO_2 mixture power plant will be quite small compared to those in isopentane + CO_2 mixture. High densities associated with the propane + CO_2 mixture result in higher work output per unit volumetric flow rate at exit than in the case of pure propane. This effect is also evident in Fig. 12, analogous to Fig. 8, which shows the required volumetric flow rates at turbine inlet conditions and ratio of work output to heat recovery. At the maximum efficiency of respective fluids, this ratio is nearly three times for propane + CO_2 mixture, indicating that heat transfer in the regenerator will be smaller than in the case of isopentane + CO_2 mixture.

Fig. 13 shows temperature sensitivity of the two fluids for an expansion ratio of 2.6 for propane + CO_2 mixture and 7 for pure propane. In the case of propane + CO_2 mixture, this expansion ratio results in upper cycle pressure of ~100 bar, which is taken as the limit from the point of view of safety. In the case of propane at an expansion ratio of 7, the efficiency plateau is reached. The merit of propane + CO_2 mixture over isopentane + CO_2 mixture is again evident from the range of temperature of operation. The lower threshold for the former can be reduced down to 460 K, which was 530 K even at the highest expansion ratio for the latter.
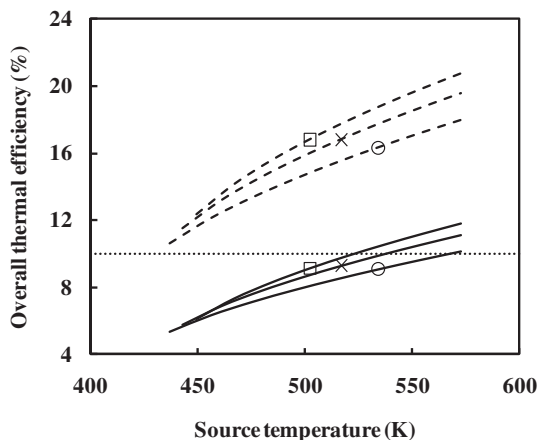

Fig. 9. Ideal and real cycle efficiency for isopentane + CO_2 mixture at various source temperatures. Legend: ———— ideal cycle, —— real cycle, ○ expansion ratio of 1.6, × expansion ratio of 1.8, □ expansion ratio of 2.0.
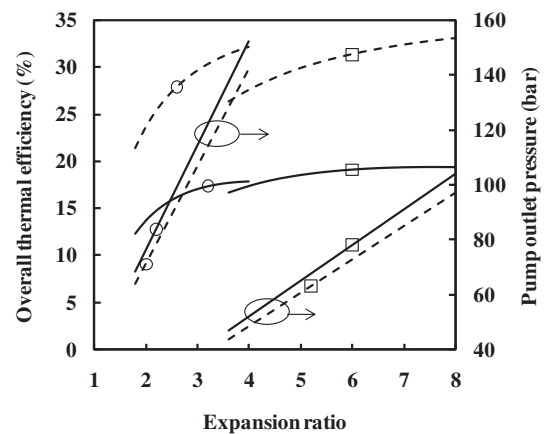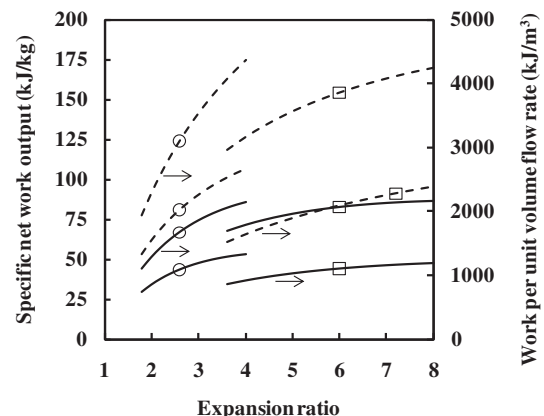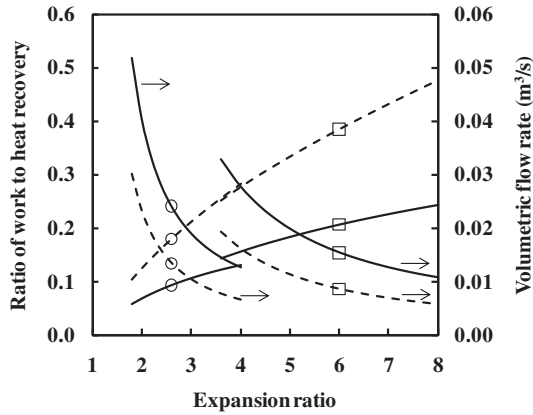

Fig. 11. Specific work output (left ordinate) and work per unit volumetric flow rate (right ordinate) *vs* expansion ratio for propane and propane + CO_2 mixture at turbine inlet temperature of 573 K. Legend: —— real cycle, ———— ideal cycle, ○ mixture, □ propane.

Fig. 12. Work output to heat recovery ratio (left ordinate) and volumetric flow rates at turbine inlet (right ordinate) vs expansion ratio for propane and propane + CO_2 mixture at source temperature of 573 K. Legend: —— real cycle, –––– ideal cycle, ○ mixture, □ propane.

While there is no doubt that propane is a good ORC fluid for the chosen temperature range, its flammability inhibits adoption. If we were to utilize this fluid retaining its good thermal characteristics, by and large, the alternative will be to suppress the disadvantage by blending with an inert component such as CO_2. But, addition of this low boiling point inert component raises the equilibrium saturation pressure. If we are willing to compromise with this operating pressure liability in return to flammability, propane + CO_2 mixture can be a good alternative that has all environmental and thermal issues answered. Efficiencies of about 15% are attainable, which is competitive given its environmental disposition. Indeed, the pressures associated ($\sim$100 bar) are not unreasonably high because there are several systems of transcritical CO_2 refrigeration cycles operating under this order of pressures [3]. However, the additional engineering problem to be tackled is this high pressure level in conjunction with temperatures in 600 K range, which could introduce numerous design and safety related complexities. However, material problems for turbines at high pressures and operating temperatures are well surmounted in steam and natural gas based power plants.

5. Irreversibility analysis

Through the above analyses, it is seen that overall efficiencies are quite low (15%) even for heat source temperatures of 573 K at
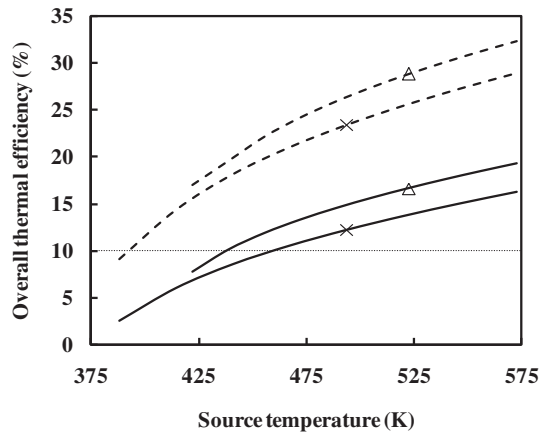
Fig. 13. Ideal and real cycle efficiency vs source temperature at different expansion ratios for propane and propane + CO_2 mixture. Legend: –––– ideal cycle, —— real cycle, ○ mixture (expansion ratio 2.6), □ propane (expansion ratio 7).

which Carnot efficiency would be $\sim$46%. It is worthwhile auditing irreversibilities and exploring what engineering developments should occur before these cycles can be made commercially viable. In this section this exercise is undertaken. *Prima facie*, the regenerator appeared to be the largest source of irreversibility because a substantial amount of enthalpy in the working fluid is actually utilized for heating rather than being expended in the turbine to generate work. While the regenerator is a clear source of irreversibility, there are several other components, namely the turbine, the boiler, the condenser and the liquid pump, each of which would make their own contributions. In this section, an attempt is made to partition these contributions towards irreversibility.

Irreversibilities in boiler are calculated on the basis of the minimum entropy generation technique developed in Ref. [11], assuming that a HTF is required and it has constant heat transfer properties in the zone of interest. Following are other assumptions to complete the analysis:

i. reference temperature (T_{amb}) is 298 K
ii. a minimum of 10 K temperature difference is required at state 5 in the counter flow heat exchanger (Figs. 3 and 4), i.e.

$$T_{oHTF} - T_5 = 10 \text{ K} \tag{12}$$

To simulate the temperature profile of HTF in boiler, we arrive at the required heat source temperature (T_{iHTF}), assuming that the entropy generation at the two ends of the boiler remains the same. Consequently,

$$(dS_{gen})_{iHTF-3'} = (dS_{gen})_{oHTF-5} \tag{13}$$

Entropy generation due to heat transfer of dQ in a small element of the regenerator at state 5 of high pressure fluid and at state 3′ (Figs. 3 and 4) can be expressed as

$$(dS_{gen})_{oHTF-5} = \frac{dQ}{T_5} - \frac{dQ}{T_{oHTF}} = \left(\frac{T_{oHTF} - T_5}{T_{oHTF}T_5}\right)dQ \tag{14}$$

$$(dS_{gen})_{iHTF-3'} = \frac{dQ}{T_{3'}} - \frac{dQ}{T_{iHTF}} = \left(\frac{T_{iHTF} - T_{3'}}{T_{iHTF} - T_{3'}}\right)dQ \tag{15}$$

Inserting Eqs. (14) and (15) in Eq. (13), we get

$$\left(\frac{T_{iHTF} - T_{3'}}{T_{iHTF}T_{3'}}\right) = \left(\frac{T_{oHTF} - T_5}{T_{oHTF}T_5}\right) \tag{16}$$

which can be solved for T_{iHTF} as given below

$$T_{iHTF} = \frac{T_{oHTF}T_5T_{3'}}{T_{oHTF}T_5 - T_{3'}(T_{oHTF} - T_5)} \tag{17}$$

For a given $T_{3'}$, the required HTF inlet temperature to boiler (T_{iHTF}) can be calculated from the above equation. Details of irreversibility calculations for the boiler are elaborated in Appendix B. Irreversibilities in the other components are calculated from the equations given below:

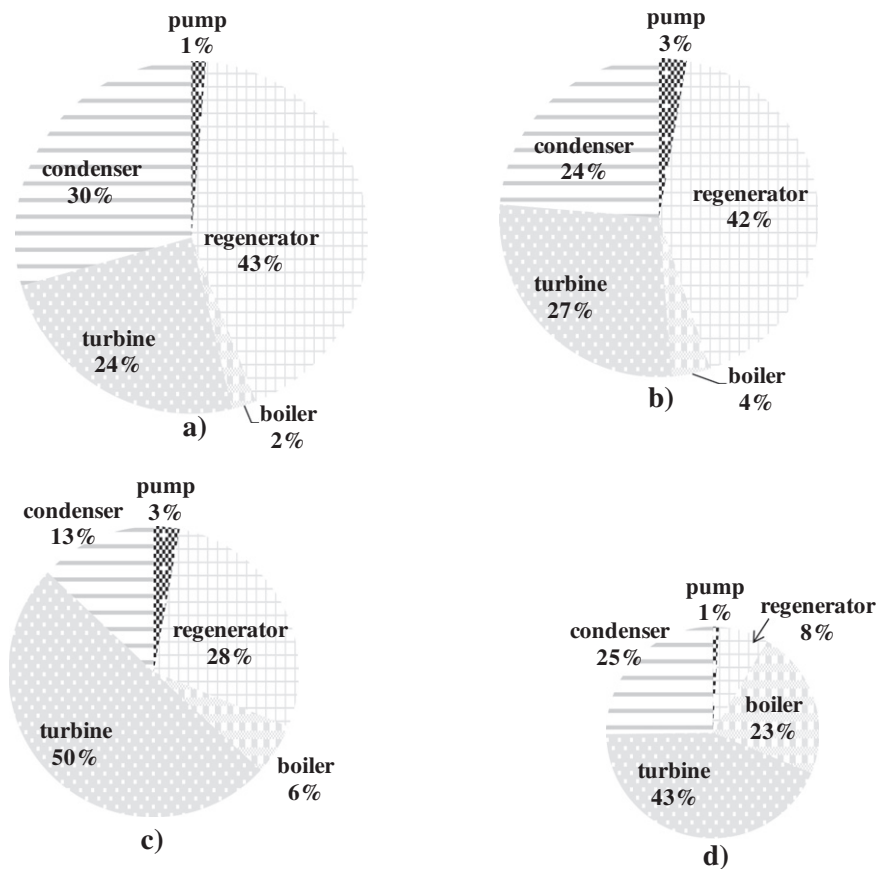$$\dot{I}_{pump} = \dot{m}_{wf}T_{amb}(s_{2'} - s_1) \tag{18}$$

$$\dot{I}_{regenerator} = \dot{m}_{wf}T_{amb}(s_5 + s_6 - s_{2'} - s_{4'}) \tag{19}$$

$$\dot{I}_{turbine} = \dot{m}_{wf}T_{amb}(s_{4'} - s_{3'}) \tag{20}$$

$$\dot{I}_{condenser} = \dot{m}_{wf}T_{amb}\left(s_1 - s_6 + \frac{h_1 - h_6}{T_{amb}}\right) \tag{21}$$
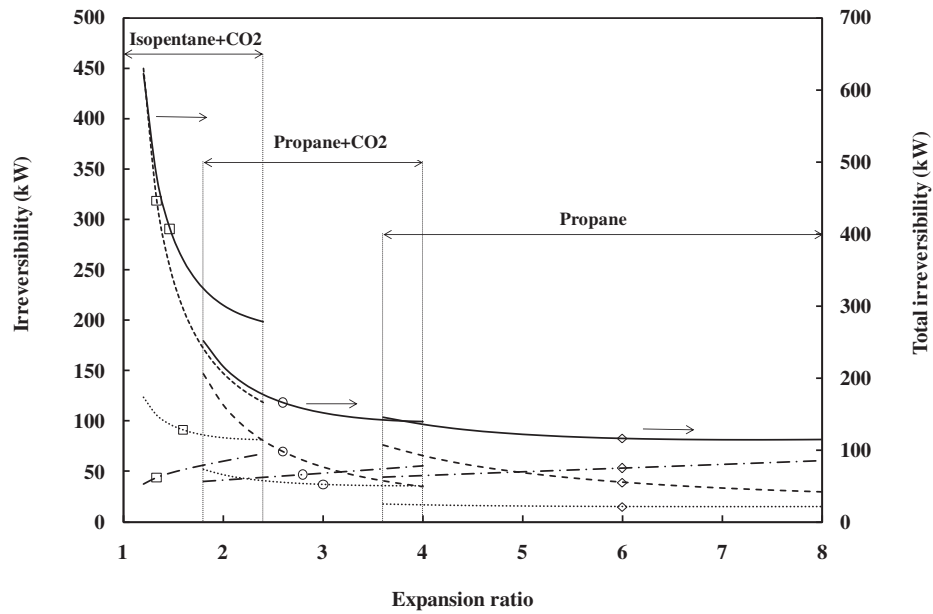
Fig. 14. Component wise (left ordinate) and total irreversibility (right ordinate) for various expansion ratios. Legend: - - - - regenerator, − − − turbine, ·········· condenser; ——— total, □ isopentane + CO_2 mixture, ○ propane + CO_2 mixture, ◇ propane.

Fig. 15. Fraction of irreversibility generation. a) isopentane + CO_2 mixture (expansion ratio of 2.4), b) propane + CO_2 mixture (expansion ratio of ∼2.6), c) propane (expansion ratio of 7.2), d) isopentane + R-245fa mixture (expansion ratio of 10) [11].

In Eq. (21) it is assumed that the heat rejection in the condenser occurs to an infinite reservoir at the ambient temperature.

Fig. 14 summarizes major sources of irreversibility and the sum of all sources. Boiler and pump contributions are not shown as their contribution is very small, as evidenced in Fig. 15. If we segregate sources of irreversibilities into power and non-power blocks, the irreversibility in the latter, in general, will be equal to or larger than in the former. As pointed out earlier that if the temperature glide is too large, as in the case of isopentane + CO_2 mixture, firstly, the total irreversibility itself is quite large and secondly, the irreversibility in the regenerator surpasses that in every other component. Its decreasing trend is due to two reasons: a) decrease in mass flow rate, and b) reduction in $T_{4'}$ resulting in lower heat recovery potential.

In pure fluid Rankine cycles, the entire contribution to heat recovery occurs in the desuperheating zone. In the case of mixtures, this can be extended into the two-phase zone. Thus, the regenerator can be divided into two parts in which the low pressure stream rejects heat, namely, 4' to 1g and 1g to 6 (as seen in Figs. 3–5). Referring to Fig. 5, in the case of propane + CO_2 mixture 91% the heat recovery occurs in the former, which is the desuperheating zone as against 56% in the case of isopentane + CO_2 mixture. It can be deduced that a smaller temperature glide in the two-phase dome of the propane + CO_2 mixture shifts the domain of two-phase heat recovery zone towards the colder end of the regenerator. This feature is responsible for a lower irreversibility in the regenerator of propane + CO_2 mixture. Further, it is not difficult to comprehend that reducing the number of carbon atoms in the alkane reduces the temperature glide. However, this argument cannot be stretched to ethane + CO_2 mixture because the cycle can no longer be operated as a Rankine cycle, as the critical point of that mixture is at ~296 K which is below the normally encountered ambient conditions. As far as the total irreversibility is concerned, the mixture of propane + CO_2 seems to be an extension of propane to lower expansion ratios. In all cases, the total irreversibility is larger than the work output of the cycle, which is a dominant reason for low efficiencies.

"Non-flammable" hydrocarbon mixtures with CO_2 that are suitable for ORCs will be only those with propane, butane and isopentane. However, large irreversibilities associated with isopentane (which were also comparable with those of isobutane) lead to the conclusion that propane + CO_2 mixture will be preferable despite transcritical operation and large operating pressures.

6. Conclusions

Utilizing the eco-friendly disposition of hydrocarbons and yet obviating their flammability led the choice of blending them with carbon dioxide such that a 70% mole fraction of the hydrocarbon and 30% mole fraction of carbon dioxide gives a conservative approach to suppression of flammability and yet limiting maximum operating pressures to 100 bar. Propane and isopentane are the two hydrocarbons adopted for a detailed investigation. Common features are high pressures, large temperature glides. The distinguishing features are summarized below:

1. The upper operating pressure needs to be below 60 bar for isopentane + CO_2 mixture to retain the basic Rankine cycle structure of heat addition to include the two-phase region. In the case of propane + CO_2 mixtures, it is in excess of 62 bar because the heat addition process is outside the two-phase dome.
2. The temperature glides encountered in the low pressure region of two-phase dome are about 100 K for isopentane + CO_2 mixtures which is only 30 K for propane + CO_2 mixture.

3. For a given source temperature of 573 K, isopentane + CO_2 mixture yield an efficiency of about 12% which is substantially lower than 17% in propane + CO_2 mixture.
4. Isopentane + CO_2 mixture has smaller tolerance to fluctuations in source temperature (530–573 K) than propane + CO_2 mixtures (465–573 K) for a lower threshold of 10% efficiency.
5. Appropriation of component irreversibilities indicates that the largest source is the regenerator.
6. Large temperature glides in the condensation regime lead to large entropy generation in the regenerator, from which it can be deduced that propane + CO_2 mixtures will have smaller irreversibilities.
7. Irreversibility in the regenerator is sensitive to location of the pinch point. A pinch point close to the cold end is preferable. This is inherently possible by mixing CO_2 with an alkane having fewer carbon atoms in its molecule. While propane satisfies this condition, mixture of CO_2 and ethane is not feasible as ORC fluid because of low critical temperature which makes the cycle non-condensing.

Acknowledgements

Appendix A

To arrive at temperature profiles in the regenerator, temperatures at states 2pp, 6, 5 are required which need to be derived from a knowledge of thermodynamic states at 4', 2' and 1g (Fig. 5). The pinch point temperature difference is set to 5 K, that is

$$T_{2pp} = T_{1g} - 5 \tag{A.1}$$

As a first approximation, pressure at 2pp is evaluated as,

$$p_{2pp} = \frac{p_{2'} + p_{3'}}{2} \tag{A.2}$$

h_{2pp} can now be calculated. Pressure at state 2pp can be updated by the assumption of linear behavior of pressure drop against the enthalpy changes (Eqs (5) and (6)). Applying 1st law of thermodynamics between 1g to 6 and 2' to 2pp, we get

$$h_{1g} - h_6 = h_{2pp} - h_{2'} \tag{A.3}$$

which can be used to determine p_6 as follows:

$$p_6 = p_{4'} - (p_{4'} - p_1) \frac{h_{4'} - h_6}{h_{4'} - h_1} \tag{A.4}$$

$T_6(p_6,h_6)$ can be determined. Applying the 1st law to the entire regenerator

$$h_{4'} - h_6 = h_5 - h_{2'} \tag{A.5}$$

h_5 can be evaluated and hence p_5 can be determined from the following equation:

$$p_5 = p_{2'} - (p_{2'} - p_{3'}) \frac{h_{2'} - h_5}{h_{2'} - h_3} \tag{A.6}$$

$T_5(p_5,h_5)$ can then be determined.

Appendix B

Irreversibility generation in boiler is given as

$$\dot{I}_{boiler} = T_{amb}\left(\Delta S_{HTF} + \Delta S_{wf}\right) \tag{B.1}$$

$$\Delta S_{HTF} = \dot{m}_{HTF}c_{p,HTF}\ln\left(\frac{T_{oHTF}}{T_{iHTF}}\right) \tag{B.2}$$

$$\Delta S_{wf} = \dot{m}_{wf}(s_{3'} - s_5) \tag{B.3}$$

Application of the 1st Law of Thermodynamics to the boiler assuming constant thermal properties of HTF gives

$$\dot{m}_{wf}(h_{3'} - h_5) = \dot{m}_{HTF}c_{p,HTF}(T_{iHTF} - T_{oHTF})$$

$$\frac{\dot{m}_{HTF}}{\dot{m}_{wf}}c_{p,HTF} = \frac{h_{3'} - h_5}{T_{iHTF} - T_{oHTF}} \tag{B.4}$$

Using Eqs. (B.1) to (B.4) we can eliminate the need for knowing the HTF characteristics

$$\dot{I}_{boiler} = \dot{m}_{HTF}T_{amb}c_{p,HTF}\ln\left(\frac{T_{oHTF}}{T_{iHTF}}\right) + \dot{m}_{wf}T_{amb}(s_{3'} - s_5) \tag{B.5}$$

$$\dot{I}_{boiler} = \dot{m}_{wf}T_{amb}\left[\frac{\dot{m}_{HTF}}{\dot{m}_{wf}}c_{p,HTF}\ln\left(\frac{T_{oHTF}}{T_{iHTF}}\right) + (s_{3'} - s_5)\right] \tag{B.6}$$

$$\dot{I}_{boiler} = \dot{m}_{wf}T_{amb}\left[\frac{h_{3'} - h_5}{T_{iHTF} - T_{oHTF}}\ln\left(\frac{T_{oHTF}}{T_{iHTF}}\right) + (s_{3'} - s_5)\right] \tag{B.7}$$

Through this analysis we show that above calculation scheme can be made applicable for any HTF.

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