Exergetic performance and comparative assessment of bottoming power cycles operating with carbon dioxide based binary mixture as working fluid

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Abstract

This paper evaluates the exergetic performance of gas turbine-bottoming power cycles operating with CO_2-Toluene (CO_2-C_7H_8) binary mixture as working fluid. A generic criterion for selection of CO_2-based binary mixture is delineated and composition of CO_2-C_7H_8 binary mixture is decided based on the required minimum cycle temperature compatible with ambient conditions. For the purpose of comparison and analysis, two bottoming cycle configurations are selected, and their realistic operating conditions are determined based on ambient conditions through sensitivity analysis. The performance of bottoming cycles using CO_2-C_7H_8 binary mixture are compared with bottoming cycles using pure CO_2 as working fluid at different ambient temperatures to highlight the benefits of exploiting CO_2-C_7H_8 binary mixture as working fluid in arid and harsh desert climates. Comparative analysis keeping maximum cycle temperature (TIT) fixed at 673 K because of thermal stability constraint reveals that the CO_2-C_7H_8 bottoming simple regenerative cycle (BSRC) configuration gives better exergetic performance compared to bottoming preheating cycle (BPHC) configuration using same working mixture at different ambient temperature conditions. As cycles operating with pure CO_2 can only perform better at lower ambient temperature conditions. With the increase in ambient temperatures, bottoming cycles with CO_2-C_7H_8 binary mixture outperform and produce significant gains in exergetic and energetic performance compared to pure CO_2 bottoming cycles. The maximum gain in exergetic efficiency in case of BSRC and BPHC are 26.83% and 18.71% respectively at operating ambient temperature of 313 K. Also, the overall gains in energetic efficiencies in case of BSRC and BPHC are 28.92% and 10.12% respectively. However, on the basis of smaller overall heat exchanger sizes (UA), BPHC configuration is predicted as better option for bottoming cycles operating in higher ambient temperature zones performing with higher exergetic efficiency.

Keywords

CO_2-Toluene binary mixture; Bottoming Brayton power cycles; CO_2-based mixtures; Exergy analysis; Preheating cycle; Comparative analysis

Introduction

Demand for distributed and efficient generation has led to various studies on micro-generators using waste and/or renewable energy resources. Sustainable development requires energy conversion systems which are both economically as well as environmentally sustainable. The conventional power systems, mostly using fossil fuels, although plays vital role in economic growth but so far but they pose risk to the environment in the form of global warming, depletion of ozone layer and reduction in fossil fuels. To meet the increasing energy demand while keeping checks over its harmful impacts on the environment is the main challenge for power industry in this era.

At present, several alternates for energy conversion are proposed and widely studied like Organic Rankine Cycles (ORCs) and Air Brayton cycles [1–4]. In recent years, supercritical carbon dioxide (sCO_2) power cycles are explored in numerous applications owing to favorable thermodynamic properties of CO_2[5]. CO_2 offers many benefits: such as zero ozone depletion potential, nontoxic, inexpensive and abundant in nature. Importantly, the critical point of CO_2 is at 31℃ when pressurized to 7.4MPa. The high density of CO_2 (or low compressibility factor) near critical point manifests in the form of lower compression work, higher cycle efficiency and compact cycle components. Owing to the less corrosive nature of CO_2, it has been used in high temperature applications like solar power tower powered sCO_2 Brayton cycles[6,7] and nuclear heat source powered sCO_2 Brayton cycles[8–10]. Numerous studies are also carried out on potential of sCO_2 Brayton cycles in high and low-grade waste heat recovery applications [11–13].

It is observed that the performance of sCO_2 power cycles is sensitive to variation in environmental temperature. The cycle efficiency drops considerably when operated at higher ambient temperatures since the heat rejection is at a higher temperature compared to the critical point of CO_2; therefore, the real gas benefits of using sCO_2 cannot be realized. Operating in arid and high temperature climatic conditions is important. For instance, the typical densely populated areas of the earth which have low precipitation and high mean annual temperatures are classified as BWh areas according to Köppen Climate Classification[14]. In such climatic conditions many densely populated regions and city exist such as Karachi, Riyadh, Dubai & most parts of MENA where the peak temperatures are in the range of 40℃ - 50℃ and constitute 12% of earth's land part.

The performance of sCO_2 power cycles at higher environmental temperature can be managed by shifting the critical point of CO_2 to higher temperature by addition of second compound in CO_2; this has been done by designing CO_2-based binary mixture[15]. The underlying idea is to design binary mixture of CO_2 with other organic or inorganic compound in order to shift the critical point of the mixture to higher temperatures[16] so that lowest operating temperature of the sCO_2 Brayton cycle is matched with high environmental temperatures typically of BWh areas.

Invernizzi *et* al[17,18] investigated various CO_2-based binary mixtures as working fluids in Brayton power cycles. He found significant improvement in efficiency of the Brayton power cycles operating with binary mixtures compared to sCO_2 power cycles. Seungjoon *et* al[19] studied the performance of Brayton cycles with CO_2-based binary mixtures in warm environments and found CO_2/R32 and CO_2/Toluene binary mixtures possessing better efficiency compared to sCO_2 power cycles. In solar power tower application, Manzolini *et* al[15] found that Brayton power cycles operating with CO_2/N_2O_4 and $CO_2/TiCl_4$ as working fluids perform better than conventional steam Rankine cycles in desert climates.

Carlos *et* al[20] analyzed eight CO_2/refrigerants binary mixtures in recuperative and non-recuperative transcritical Rankine cycles (TRC) and suggests pure CO_2 TRC as favorable option owing to compactness and better environmental value compared to TRC with CO_2/refrigerants. Similarly, Baomin *et* al [21] investigated CO_2 based low Global Warming Potential (GWP) zeotropic mixtures working fluids in TRC powered by low grade heat source. The authors recommended CO_2/R161 for small scale systems, while CO_2/R1234yf and CO_2/R1234ze for large scale systems.

In essence, the research on CO_2-based binary mixtures as working fluids in power cycles has been increasing in terms of working fluids selection and optimization of power cycles both for high temperature and low temperature heat sources [22,23]. Nonetheless, the main challenges are achievement of reasonable thermodynamic efficiencies, selection and characterization of additives for CO_2-based binary mixtures compatible with wide range of heat sources. Moreover, much of the work is carried out on thermodynamic properties and thermal stability of pure and mixture working fluids.

In heat recovery application, there are many studies on use of pure and mixtures of organic compounds in ORCs[24,25]. Iglesias *et* al[26] presented a review of most relevant architectures of ORCs and compared the performance with Trilateral cycles (TCs) for low-medium grade heat recovery. They found lower first law efficiencies (between 5% to 10%) in ORCs as compared to TCs which showed efficiencies between 36% and 51%. In addition, there are other safety and environmental issues associated with organic fluids which are high flammability of hydrocarbons, toxicity, high ozone depletion potential and high global warming potential of compounds which contain chloro-fluoro carbons. Low thermal stability of organic compounds also limits ORCs to low grade heat sources of maximum temperature not greater than 350℃-400℃. Due to such constraints, proper screening of compounds is required to use in any particular heat source application. Astolfi *et* al[27] compared the thermodynamic performance of ORCs and CO_2 power cycles in order to decide the optimum operating range. They found ORCs a suitable choice for maximum heat source temperature less than 350℃ and CO_2 cycles for higher maximum temperatures.

The exploitation of carbondioxide based binary mixture as working fluid in heat recovery bottoming cycles is a possible option owing to stable characteristics of carbondioxide and higher efficiency of carbondioxide cycles as discussed earlier. Notably, the binary mixture of carbondioxide with suitable organic compound in proper composition can potentially provide advantage in designing a mixture with desired properties[17].

In the present study, the application of CO_2-based binary mixture in bottoming cycles is assessed for two different configurations. Detailed literature suggests that the application of using CO_2-based binary mixtures as heat-recovery units is not previously explored extensively especially when operated in hot/arid climates. Bottoming cycles have two challenges namely, maximizing efficiency and secondly conversion to useful work. For the purpose of analysis in this work, the heat source of bottoming cycles is exhaust heat of GE-LM2500 medium scale gas turbine. Primarily, appropriate organic compound for the binary mixture is selected on the basis of thermodynamic properties, heat source compatibility, health and safety characteristics. Secondly, the thermodynamic properties of the binary mixture are calculated, and accuracy of the thermodynamic method is ensured. Then, parametric evaluation using energy and exergy analysis is conducted to choose practical conditions for cycle performance. Eventually, the comparative analysis is carried out among pure CO_2 and CO_2-based binary mixture in bottoming cycles at different ambient/environmental temperatures. Based on comparison of energetic efficiency, exergetic efficiency, overall size of the heat exchangers (UA) and heat recovery, optimum configuration of bottoming cycle is recommended.

Selection and Properties of CO_2-Toluene binary mixture

Selection of organic additive

The selection of appropriate organic fluid as an additive for CO_2 based binary mixture is challenging. In reality, there are several measures which should be visited during selection [28]. The additive should be:

- Environmentally benign i.e. the GWP and ODP values lie within the safe limits proposed by the standards.
- Thermally stable at high temperatures.
- Auto ignition temperature should be far greater than higher cycle temperature i.e. 673 K (400℃).
- Critical point temperature should be higher than the CO_2 since, the objective here is to elevate the heat sink temperature to facilitate cycle cooling process in warm environments.
- Reasonable critical point pressure.
- Non-flammable, non-toxic and good material compatibility
- Accurate thermodynamic property data should be available.

In particular, it becomes difficult to find an additive which fulfills all the aspects mentioned above for a particular application as it requires both experimental and numerical studies. Therefore, here the selection of the additive is done on the basis of one important aspect compromising the other characteristic of little relevance. The candidate working fluids for additive selection are straight chain alkanes, siloxanes and aromatic hydrocarbons [18]. The straight chain alkanes have low thermal stability and most of them are flammable [18]. Various studies show that the aromatic hydrocarbons like benzene and toluene are comparatively more stable [29,30]. The critical point temperatures of aromatic hydrocarbons are also greater as compared to CO_2 which is beneficial to design a binary mixture with higher critical temperatures. Benzene cannot be a good choice owing to its hazardous effects on human health.

In recent years, Toluene has been investigated as a working fluid in ORCs for biomass, gas turbine and IC engine waste heat recovery applications [31–35]. It is moderately toxic, yet the harmful effects on human life can potentially be minimized using effective filtration techniques like activated carbon adsorption methods [36]. It is highly flammable (flash point temperature = 3°C). However, the flammability can be curbed by keeping the content (mole fraction) of Toluene lower in the binary mixture. Thanks to its higher thermal stability; it is found to be thermochemically stable till 400°C in static tests performed in a stainless steel circuit [30]. At low temperatures, Toluene shows excellent material compatibility with stainless steel and Aluminum [37], however, more studies are needed to determine the material compatibility at higher temperatures.

In view of the thermal stability, higher critical point temperature and reasonable critical pressure, Toluene can be selected as a favorable additive for CO_2 based binary mixture as working fluid in bottoming power cycles. **Table I** summarized the thermodynamic, safety and health characteristics of Toluene and CO_2.

Table I: Thermodynamic, safety and health characteristics of Toluene and CO_2.

Fluid	**Molar Mass (kg/kmol)**	**P_{cr} (bars)**	**T_{cr} (°C)**	**Thermal Stability limit (°C)**	**ODP**	**GWP**	**Autoignition Temperature (°C)**	**Flammability**
Toluene	92.14	41.08	318.6	400	0	low	480	Yes
CO_2	44.01	73.8	31.06	800	0	Very low	*Not flammable*	

Properties of the binary mixture

After the selection of a reasonably appropriate additive for the binary mixture, the next key objective is to study the thermodynamic properties including the calculation of dew and bubble lines, critical points and vapor-liquid equilibrium (VLE) of the CO_2-Toluene binary mixture at various compositions. This requires choosing an adequate equation of state (EoS) which can calculate thermodynamic and transport properties accurately. Cubic EoS like Peng-Robinson (PR) and Soave-Redlich-Kwong (SRK) EoS have been used widely to study the real gas properties of both pure substances and mixtures [38,39]. These EoS though are not proven to be very precise but they are capable of describing the thermodynamic behavior of many types of fluids and mixtures. In fact, for processes at higher pressure and temperatures, it is recommended to use cubic EoS [40].

Since its first publication in 1976, PR EoS has been used extensively to study the VLE and thermodynamic properties of pure fluids and their mixtures owing to its better predictive capability compared to other two constant EoS like SRK and van der Waals EoS. Various modifications are developed in recent past to enhance the accuracy as well as to improve the predictive capability of PR EoS [39].

Therefore, this study selected PR EoS and employed its original version in conjunction with van der Waals mixing rules to determine the properties of CO_2-Toluene binary mixture. The original PR EoS can be expressed as,

$$P = \frac{RT}{v-b} - \frac{\alpha a}{v(v+b)+b(v-b)} \qquad \text{Eq. 1}$$

$$\alpha = \left[1+k(1-\sqrt{T_r})\right]^2 \qquad \text{Eq. 2}$$

$$k = 0.37464 + 1.54226\omega - 0.26992\omega^2 \qquad \text{Eq. 3}$$

$$a = 0.45724\frac{R^2T_c^2}{P_c} \qquad \text{Eq. 4}$$

$$b = 0.0778\frac{RT_c}{P_c} \qquad \text{Eq. 5}$$

Then, van der Waals mixing rules for binary mixture can be expressed as,

$$a_m = \sum_j \sum_j z_i z_j a_{i,j} \qquad \text{Eq. 6}$$

$$b_m = \sum_j \sum_j z_i z_j b_{i,j} \qquad \text{Eq. 7}$$

$$a_{i,j} = \sqrt{a_i a_j}\left(1-k_{ij}\right) \qquad \text{Eq. 8}$$

$$b_{i,j} = \frac{b_i + b_j}{2} \qquad \text{Eq. 9}$$

Where, 'ω' is acentric factor of pure fluid. The value of binary interaction parameter 'k_{ij}' can be computed using experimental VLE data. Fortunately, the experimental VLE and critical points data for CO_2-Toluene binary mixture is available in literature. In addition, the value if k_{ij} calculated using the experimental data is also available in ASPEN plus databank i.e. k_{ij} = 0.1056.

So, the pure fluid properties given in **Table I** and value of k_{ij} are used in PR EoS to compute the VLE, P-T envelop and T-s diagrams of CO_2-Toluene binary mixture. All the calculations using PR EoS are carried out in ASPEN plus. The calculated isothermal VLE is compared with experimental data to ensure the accuracy of PR EoS as shown in **Figure 1**. As evident, the computed VLE is in close agreement with experimental VLE data.

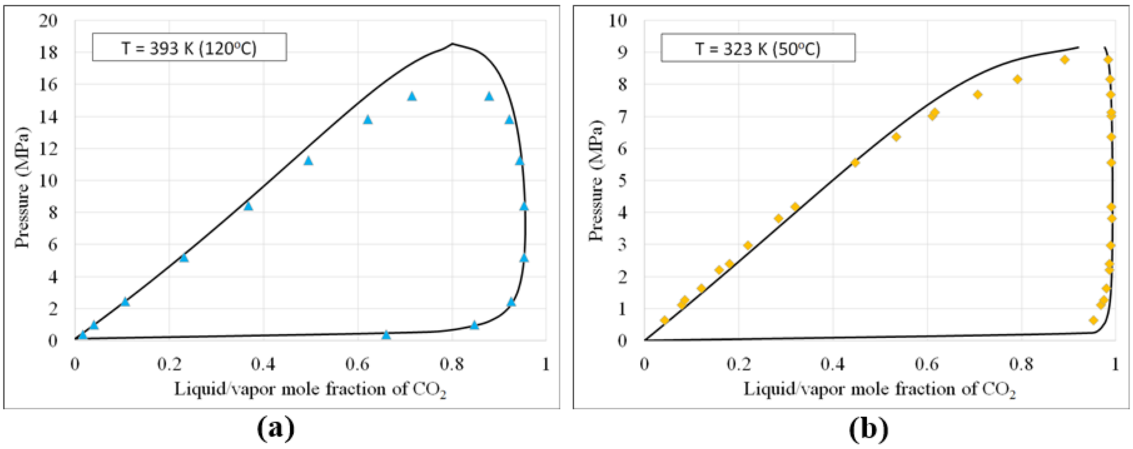

Figure 1: VLE of CO_2-Toluene binary mixture at (a) T=393 K and (b) T=323 K computed using PR EoS in Aspen Plus. The experimental data taken from [41,42].

Critical points are also recorded from P-T envelop at different composition and compared with available experimental data. **Figure 2** shows the critical locus computed using ASPEN plus and compared with REFPROP and available experimental data [41,43]. The difference of critical loci is due to the different methods followed by ASPEN plus and REFPROP; ASPEN plus uses PR EoS while REFPROP uses Kunz and Wagner model. Nevertheless, the model is reasonably accurate and matches well with experimental data.

Composition of the binary mixture

The bubble and dew lines for CO_2 and Toluene and their binary mixture at two compositions are also plotted in T-s plane to identify the cycle conditions. **Figure 3** shows T-s plot along with isobars at different pressures for pure CO_2, pure Toluene and 0.95 CO_2/0.05 Toluene and 0.9 CO_2/0.1 Toluene composition binary mixtures. The increase in critical temperature by adoption of CO_2-based binary mixture is evident.

For adequate heat rejection of bottoming power cycle at warm ambient conditions, the design minimum cycle temperature (or condensation temperature) is chosen to be T_{min} = 50°C. For 0.95 CO_2/0.05 Toluene composition, the design T_{min} lies inside the critical region where the PR EoS fails to compute properties as evident from **Figure 3**. Whereas, for 0.9 CO_2/0.1 Toluene composition, the design T_{min} occur on the bubble line at bubble pressure of 9.14 MPa which is a suitable condensation condition. The cycle T_{min} on the bubble line is beneficial in terms of smaller compression/pump work and the resulting power cycle is to be a condensing cycle as proposed earlier by Angelino [44]. Thus, 0.9 CO_2/0.1 Toluene composition is decided as working fluid to study the thermodynamic performance of bottoming power cycles and comparison with pure CO_2 bottoming power cycles.

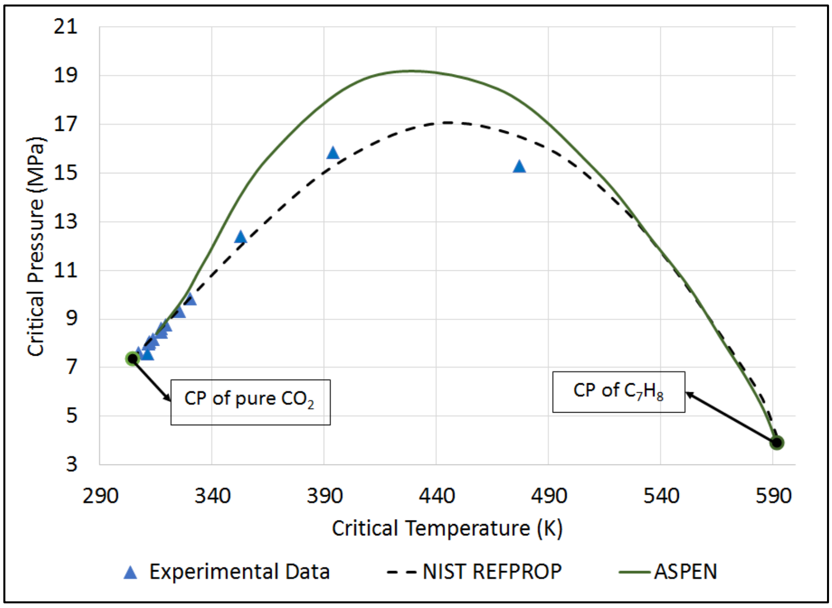

Figure 2: Critical loci of CO_2-Toluene binary mixture in P-T plane. The experimental data is taken from [41,43].

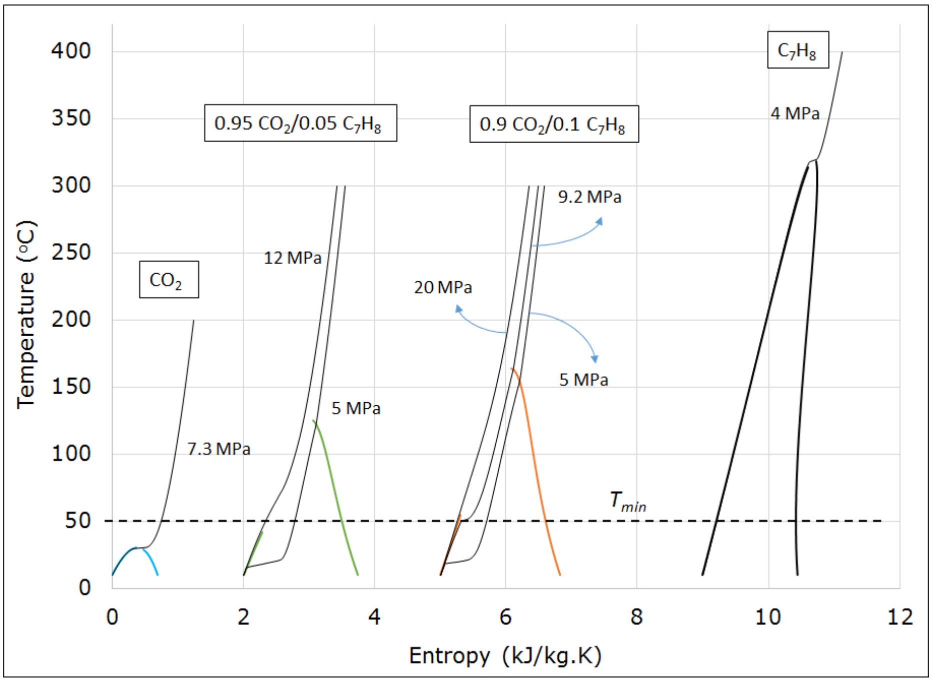

Figure 3: T-s diagram of CO_2, Toluene and their binary mixtures at two compositions. This figure is adapted from [17].

Thermodynamic Method

General electric (GE) LM2500 gas turbine[45] is selected as the reference topping gas turbine for bottoming power cycles. The specifications of the topping cycle and exhaust gas composition are illustrated in **Table II**. Because of the thermal stability limit (i.e. 400 °C) imposed by Toluene, a medium scale gas turbine system is chosen here.

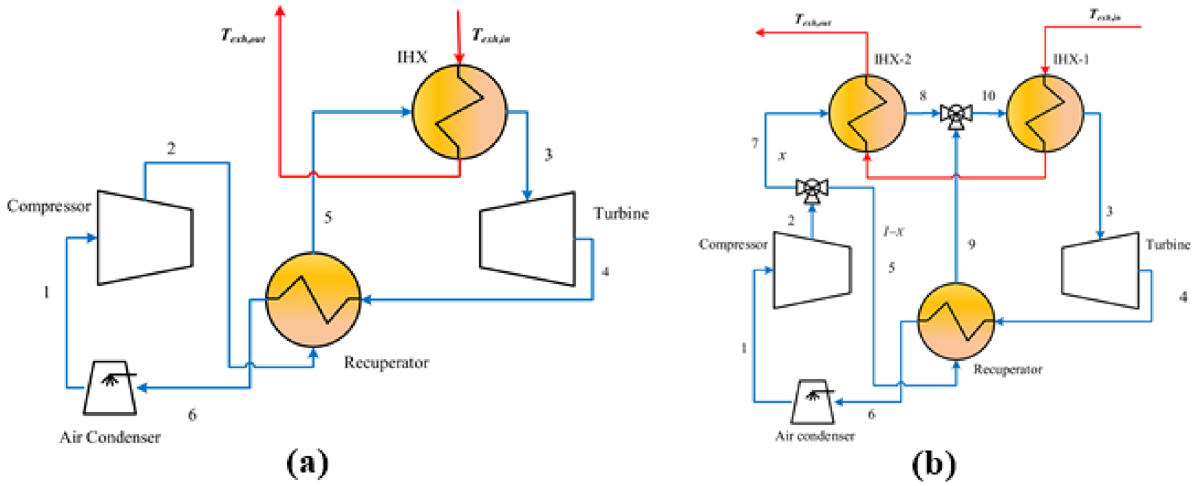

Figure 4: Bottoming cycle configurations, (a) Bottoming simple regenerative cycle (BSRC), (b) Bottoming preheating cycle (BPHC)

The analysis on topping cycle is not included since this study focuses on the performance of bottoming cycles operating with CO_2-Toluene (from now onwards refer to as CO_2-C_7H_8) binary mixture. Two plant configurations are analyzed for topping cycle exhaust heat recovery, these are: Bottoming Simple Regenerative Cycle (BSRC) and Bottoming Partial Heating Cycle (BPHC) also refer to as preheating cycle in literature. Both configurations are shown in **Figure 4**. BSRC is the simpler configuration with one recuperator and one integrated heat exchanger (IHX) for heat recovery; this configuration is often employed in literature for WHR applications to compare the performance with other complex cycle configurations. BPHC is a slightly complex configuration with mass split after compression in order to recover more heat from exhaust gases and to achieve better thermal match in the recuperator. This cycle proved to be high performance cycle in WHR supercritical CO_2 power cycles [11,46,47] that's why this configuration is selected here in the case of CO_2-C_7H_8 binary mixture condensation power cycles.

Table II: GE LM2500 topping gas turbine specification and exhaust gas composition.

Parameter	Value	Exhaust gas composition	
Power Output	24.8 MW	**Component**	**Mole Fractions**
Efficiency	35.1 %	**CO_2**	0.03
Pressure Ratio (P.R)	19	**Nitrogen**	0.76
Mass Flow Rate of exhaust gases (MFR)	71 Kg/Sec	**Oxygen**	0.14
Exhaust gases Temperature ($T_{exh,in}$)	798 K (525°C)	**Water**	0.07

The cycle model and specifications are developed in ASPEN plus calculation environment. IHX and recuperator are modeled using minimum temperature difference approach known as MITA approach. This approach divides a heat exchanger into internal zones and computes temperatures and temperature differences in each zone employing energy balance and converges the final solution according to given value of MITA. This approach seems more reliable as compared to conventional methods which assume the effectiveness value for a heat exchanger and computes the outlet temperatures considering the entire heat exchanger as a black box. Moreover, MITA approach also provides the conditions at which pinch occurs inside a heat exchanger so that to avoid those conditions during cycle calculations.

Air Condenser Modeling

To model air condenser in the bottoming cycles, a designed value of temperature difference at the outlet of condenser is considered i.e. 10℃ and the cycle minimum temperature (T_{min}) or compressor inlet temperature are calculated using,

$$T_{\min} = T_{amb} + 10°\mathrm{C} \qquad \text{Eq. 10}$$

This approach is beneficial to avoid pinch in air condensers during changes in ambient temperatures (T_{amb}) [3].

Performance Indicators

The energy balance calculations are carried out using ASPEN plus followed by computation of first law efficiency using following equation:

$$\eta_I = \frac{\dot{W}_{net}}{\dot{Q}_{in}} \qquad \text{Eq. 11}$$

For second law or exergetic analysis, the exergy of each stream is calculated, and exergy destroyed in each component of the power cycle is determined using exergy balance[48–50]. The exergy balance for each component of the cycle are given in **Table III**.

Table III: Exergy balance equations for components of the bottoming power cycles.

Component	Exergy balance	Eq. No
Compressor	$E_{d,C} = W_C + E_x - E_{x,2}$	Eq. 12
Turbine	$E_{d,T} = -W_T + E_{x,3} - E_{x,4}$	Eq. 13
Recuperator	$E_{d,rec} = E_{x,5} - E_{x,9} + E_{x,4} - E_{x,6}$	Eq. 14
Condenser	$E_{d,cond} = E_{x,6} - E_{x,1} + E_{x,Air\ in} - E_{x,Air\ out}$	Eq. 15
IHX-1	$E_{d,IHX1} = E_{x,exhin} - E_{x,exhout,i} + E_{x,10} - E_{x,3}$	Eq. 16
IHX-2	$E_{d,IHX2} = E_{x,exhin,i} - E_{x,exhout} + E_{x,7} - E_{x,8}$	Eq. 17

Total exergy destroyed, exergy input, exergetic efficiency and exergy destruction ratio are computed using Eqs 9, 10, 11 and 12 respectively, as follows:

$$\dot{E}_d = \dot{E}_{d,C} + \dot{E}_{d,T} + \dot{E}_{d,rec} + \dot{E}_{d,cond} + \dot{E}_{d,IHX1} + \dot{E}_{d,IHX2} \qquad \text{Eq. 18}$$

$$\dot{E}_{\mathrm{input}} = \dot{E}_{x,exhin} - \dot{E}_{x,exhout} + \dot{E}_{x,Air\ in} - \dot{E}_{x,Air\ out} \qquad \text{Eq. 19}$$

$$\eta_{II} = 1 - \frac{\dot{E}_d}{\dot{E}_{\mathrm{input}}} \qquad \text{Eq. 20}$$

$$\dot{E}_{d,ratio} = \frac{\dot{E}_d}{\dot{E}_{\mathrm{input}}} \qquad \text{Eq. 21}$$

Validation

The accuracy of the thermodynamic method of this study is ensured by validation with the analysis done in previous studies. The validation is performed for SRC configuration since the PHC configuration is not studied yet in case of CO_2-based binary mixture as working fluid.

The validation is carried out at following conditions taken from the literature reference: *Composition*: 0.95 CO_2/0.05 CO_2-C_7H_8, T_{min} = 326 K, P_{min} = 12 MPa, T_{max} = 623 K, P_{max} = 30 MPa and turbomachinery efficiencies = 85%. The results are extracted from the plot available in Figure 15 of the reference. **Table IV** shows the comparison of temperatures and η_I with the reference. The matching of results shows the accuracy of the method followed in this study.

Table IV: Validation of results for SRC configuration operating with CO_2-C_7H_8 binary mixture

Parameter	**Literature**[17]	**Present Work**	**Percentage Difference %**
T_2	361	358	-0.83
T_6	498	486.6	-2.29
T_4	538	540.5	0.46
T_5	373	378	1.34
η_I	22.40%	23%	2.68

Results and Discussion

Exergetic Performance

In this section, the performance of bottoming cycles operating with CO_2-C_7H_8 binary mixture are delineated. The thermodynamic performance indicators considered for the analysis are energetic efficiency, power output, exergetic efficiency and overall UA value of heat exchangers. In addition, the mass flow rates of working fluids and mass split in BPHC configuration are also studied.

Table V: Operating conditions for exergetic analysis of the bottoming power cycles.

Parameter	***Value***
Cycle minimum temperature T_{min} (K)	323 K
Cycle minimum pressure P_{min} (MPa)	P_{sat} @ T_{min} = 9.14 MPa
Cycle maximum temperature, TIT (K)	673 K
Turbomachinery isentropic efficiency (%)	80%
Pinch point in heat recovery units(s)	10 K

The internal heat exchanger (recuperator) is a very sensitive component of any recuperative cycle because of its location in the cycle; the amount of heat recuperation in the recuperator decides the heat load of components which are located ahead of the recuperator. In power cycles considered in this study, the components which are connected at outlet streams of the recuperator are cooler/condenser and heat recovery unit (IHX-I). Therefore, the influence of minimum internal temperature difference in the recuperator ($MITA_R$) on cycle performance parameters is investigated.

The input operating conditions for cycle calculations are given in **Table V.** The simultaneous effect of $MITA_R$ and cycle maximum pressure (P_{max}) on energetic and exergetic performance of the cycles are studied. **Figure 5** illustrates the exergetic efficiency and exergy destruction rate ratio of both BSRC and BPHC operating with CO_2-C_7H_8 binary mixture. In both cycle configurations, the exergetic performance increases with increase in cycle maximum pressure. The effect of $MITA_R$ shows that the maximum performance occurs at small value of $MITA_R$ for both cycle configurations. It is evident that the performance of BPHC is lower than the BSRC mainly due to larger exergy destruction ratio of the cycle components. This result here in case of the binary mixture is a converse of the performance in case pure CO_2 bottoming power cycles in which BPHC performed better than BSRC as found by various studies in literature[46,47]. **Figure 5** also demonstrate that the influence of $MITA_R$ on the exergetic performance in BSRC is comparatively more as compared to BPHC in which the exergetic performance is not very sensitive to change in $MITA_R$ since the three performance lines are closer to each other.

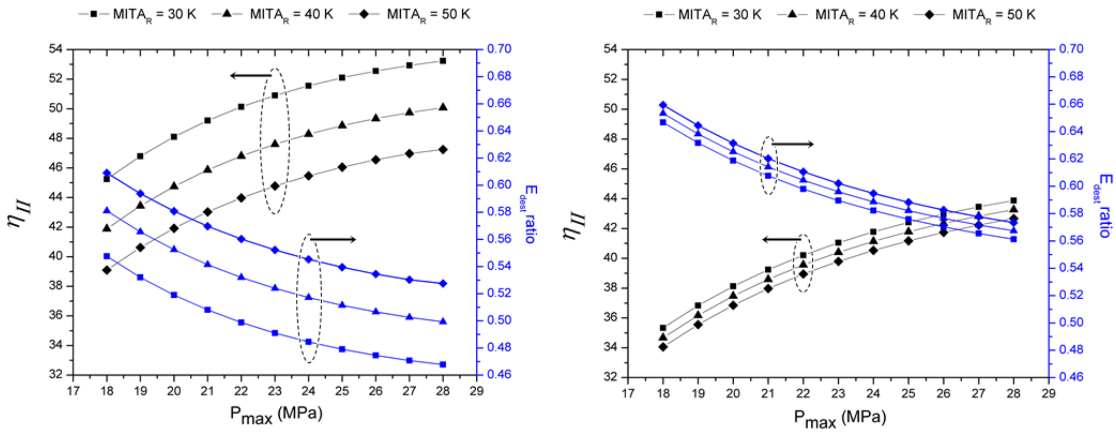

Figure 5: Exergetic efficiency and exergy destruction ratio of (a) BSRC and (b) BPHC with respect to cycle maximum pressure and minimum temperature difference inside the recuperator ($MITA_R$).

Figure 6 displays the overall UA of heat exchangers and mass flow rate of working fluid mixture for both cycle configurations. The overall UA of heat exchangers provides the indication of overall size footprint of the power cycle. The increase in P_{max} results in decrease in overall UA for both cycle configurations. However, the BPHC shows lower overall UA values as compared to BSRC even though the number of components in the BPHC is large. A very large value of overall UA for BSRC at $MITA_R$ = 30 K is also evident which is the indication of very low minimum temperature in any of the heat exchanger in the cycle (i.e. occurrence of pinch), which is physically impossible. Therefore, low values of P_{max} are evidenced to be not suitable for operation of the bottoming cycles. Furthermore, mass flow rate of binary mixture working fluid is also lower at larger values of P_{max} which seems to be a good point in terms of cycle size and maintenance cost. The net power produced by both cycle configurations are shown in **Figure 7**. The BPHC produced more power compared to BSRC and the difference is more prominent at larger values of $MITA_R$.

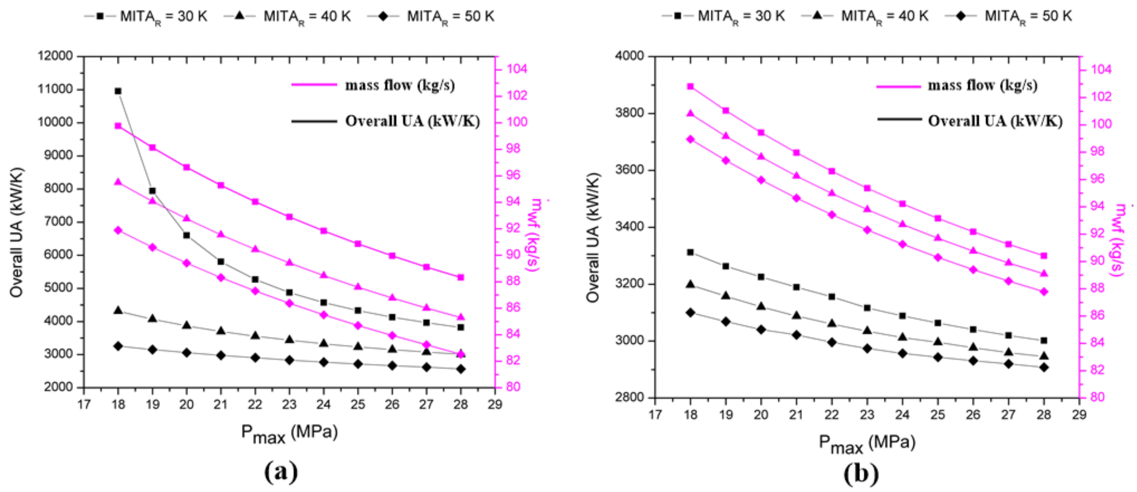

Figure 6: Overall UA of heat exchangers (black color) and working fluid mass flowrate (violet color) of (a) BSRC and (b) BPHC with variation in cycle maximum pressure and minimum internal temperature difference inside the recuperator ($MITA_R$).

As a result of sensitivity analysis, practical performance conditions for both cycle configurations are decided keeping in view that the smaller values of $MITA_R$ leads to larger overall UA (i.e. larger size of power cycle), on the other hand, very high values of P_{max} can cause difficulty in component design. Thus, $MITA_R$ = 40 K and P_{max} = 25 MPa are decided as a reasonable performance condition. The T-Q curve of recuperator of both cycles at the decided condition are shown in **Figure 8**. As shown, the minimum internal temperature difference i.e. pinch point in case of BSRC occur at hot stream outlet and cold stream inlet while in case of BPHC the pinch point occurs at hot stream inlet and cold stream outlet. This difference arises due to the difference of specific heats and mass flow rates in the recuperator of the two cycle configurations.

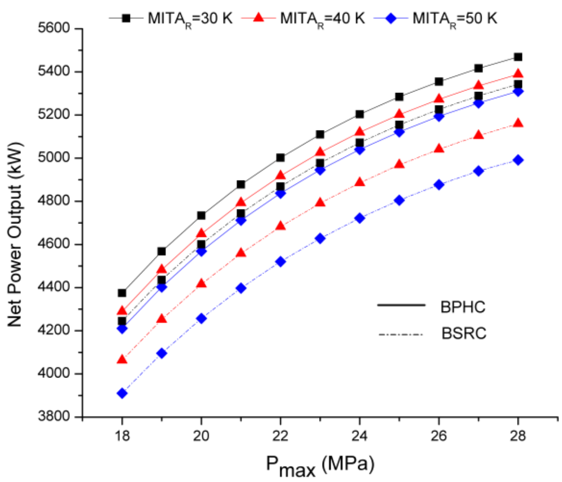

Figure 7: Net power produced by BSRC (dotted lines) and BPHC (solid lines) with variation in cycle maximum pressure and minimum internal temperature difference inside the recuperator ($MITA_R$).

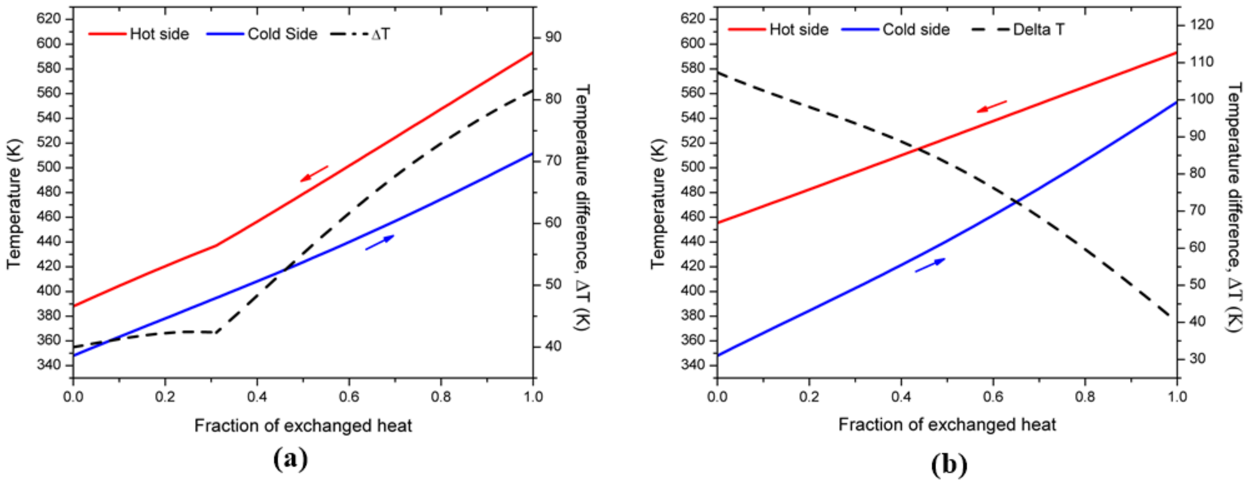

Figure 8: Temperature-heat exchange (T-Q) curves of recuperator in (a) BSRC and (b) BPHC. Hot stream corresponds to stream coming from turbine side while cold stream corresponds to stream coming from compressor side. Dotted lines show temperature difference between the two streams.

The distribution of input exergy into net power output and exergy destruction rates for the components of two cycle configurations at decided conditions are shown in **Figure 9**. In BSRC, comparatively larger portion of exergy input is converted to net power output that is why it has larger exergetic efficiency as discussed above. Also, maximum exergy is destroyed in the recuperator owing to large temperature differences. The second component with large exergy destruction rate is IHX and then condenser at third level. In case of BPHC, the condenser showed largest exergy destruction rate because it also deals with large temperature differences. Due to the mass split in BPHC, the recuperator doesn't cool the hot side from turbine to significantly lower temperature as in the case of BSRC. As a result, the heat load of condenser increases which also enhances the exergy destruction rate in it. Hence, recuperator and condenser are the critical components both in BSRC and BPHC in terms of component design. The results of both bottoming power cycles at decided practical conditions are summarized in **Table VI**.

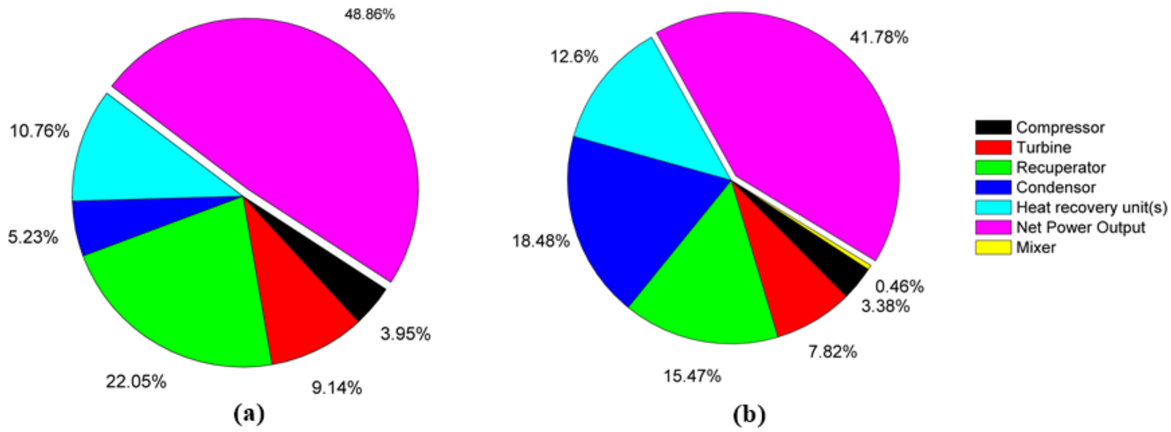

Figure 9: Distribution of input exergy from topping gas turbine exhaust into net power output and exergy destruction rates in components of (a) BSRC and (b)BPHC at decided conditions.

Table VI: Summary of results at P_{max} = 25 MPa, $MITA_R$ = 40 K.

Performance Parameter	CO_2-C_7H_8 BSRC	CO_2-C_7H_8 BPHC
η_I (%)	22.58	15.10
η_{II} (%)	48.86	41.78
$\dot{W}_{net}$ (kW)	4968.86	5201.93
$\dot{Q}_{recv}$ (kW)	22001.35	34440.83
UA (kW/K)	3232.28	2995.71
$\dot{m}_{CO2}$ (kg/s)	87.59	91.70
x	*No split*	0.50

Thermodynamic Comparison

Table VI have demonstrated important results on the performance of two configurations of bottoming cycles operating with CO_2-C_7H_8 binary mixture as working fluid. However, it is interesting to compare the performance with the bottoming cycles operating with pure CO_2 to observe the influence of P_{max} and T_{amb} on the performance and to determine the optimal operating range for different working fluids. Comparative assessment is also essential to ascertain the benefits and drawbacks of use of CO_2-C_7H_8 binary mixture in bottoming power cycles.

Comparison at varying P_{max}

Figure 10(a) shows the influence of P_{max} on the exergetic efficiency of all cases of bottoming power cycles investigated in this study at $MITA_R$ = 40 K. As noted earlier, the exergetic efficiency of all cycles is increasing with increase in P_{max}. The BSRC configuration in case of pure CO_2 and CO_2-C_7H_8 working fluids demonstrate higher exergetic performance as compared to BPHC configuration. Figure 10(b) illustrates net power produced with variation in P_{max}. The overall trend demonstrates that the power cycle configurations operating with CO_2-C_7H_8 working fluid produced more power compared to configurations with pure CO_2 working fluid. The behavior of overall UA for all investigated cycles is shown in Figure 10(c). The overall UA of cycles operating CO_2-C_7H_8 working fluid are higher compared to cycles with pure CO_2.

Inclusively, the higher exergetic performance and power output in power cycles operating with CO_2-C_7H_8 working fluid comes with higher overall UA i.e. larger power plant size footprint.

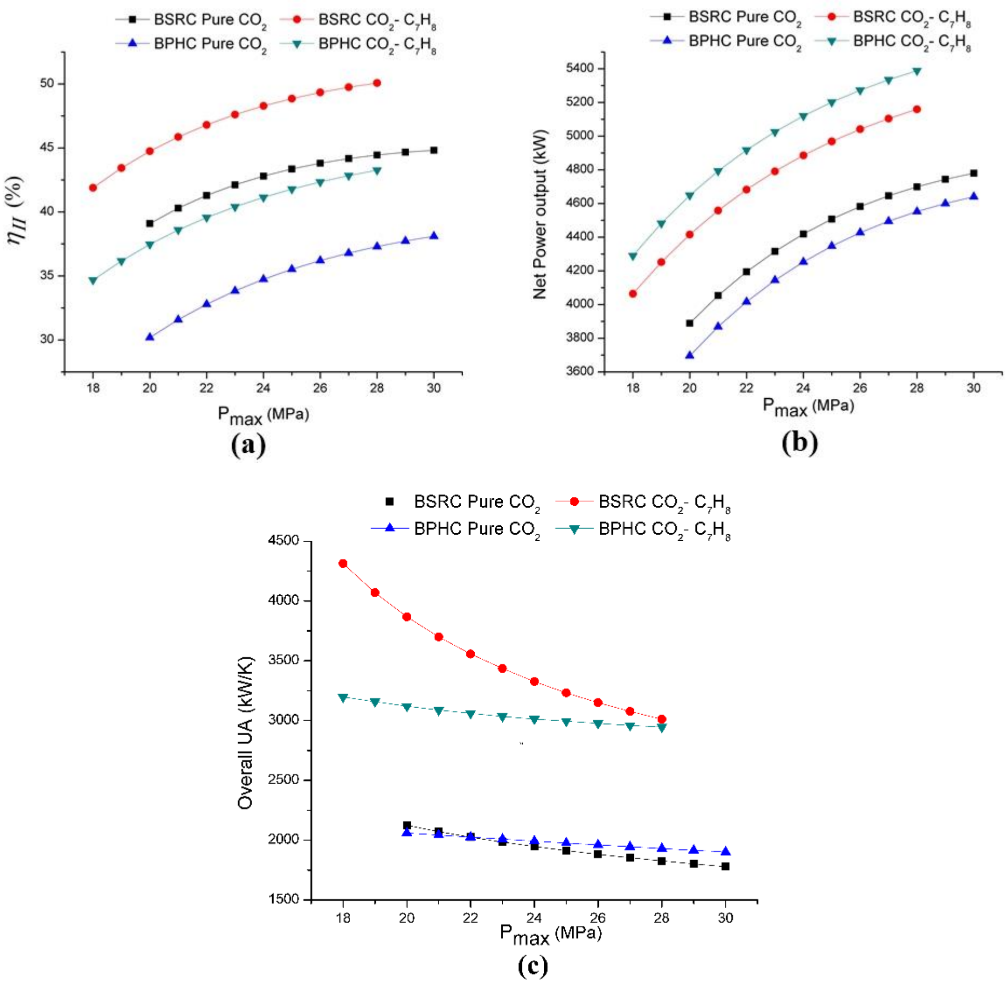

Figure 10: Comparison of exergetic efficiency (a), power output (b) and overall UA (c) of two bottoming cycles configurations operating with pure CO_2 and CO_2-C_7H_8 binary mixture at varying P_{max}.

Comparison at varying T_{amb}

The influence of variation in ambient temperature on the performance of BSRC and BPHC in case of CO_2-C_7H_8 and pure CO_2 working fluids is also investigated. The purpose is to study the cycle performance when cycle is operating in off design conditions; the variation in T_{amb} changes the cycle condensing temperature T_{min} , which significantly influences the cycle performance. In case of binary mixture of CO_2-C_7H_8, the critical temperature is shifted to higher critical temperature (as shown in Figure 3 in properties section) to match with hot ambient conditions. So, here a comparative analysis is performed to highlight the benefit of CO_2-C_7H_8 binary mixture for power cycle subject to varying condensation temperatures.

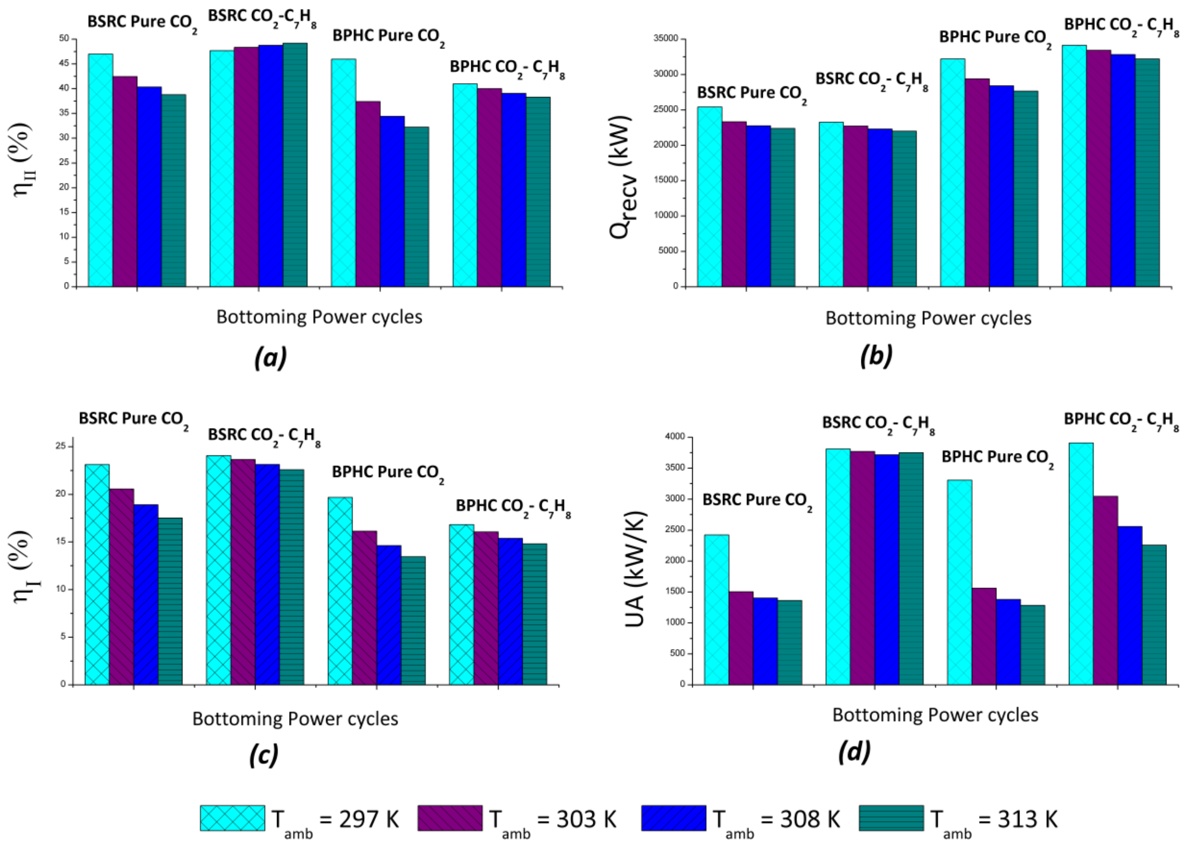

Figure 11: Thermodynamic comparison of bottoming power cycles operating with CO_2-C_7H_8 and pure CO_2 as working fluids at four ambient temperature conditions.
(a) Exergetic efficiency (b) Heat recovery (c) Energetic efficiency and (d) overall UA of heat exchangers.
Table VII: Conditions for comparative analysis among CO_2-C_7H_8 and pure CO_2 bottoming power cycles

Parameter	***Value***	
	CO_2-C_7H_8 cycles	**Pure CO_2 cycles**
Cycle minimum temperature T_{min} (K)	Depends on Ambient Temperature	
Cycle minimum pressure P_{min} (MPa)	P_{sat} @T_{min}	1.1 P_{cr} [17]
Cycle maximum temperature, TIT (K)	673 K	
Pressure ratio	2.7	
Turbomachinery isentropic efficiency (%)	80%	
Pinch point in heat recovery units(s)	10 K in IHX-I 40 K in IHX-II	
Pinch point in recuperator	40 K	

The general conditions for comparison are given in **Table VII**. In case of CO_2-C_7H_8 bottoming cycles, the cycle minimum pressure at certain value of T_{min} is the saturation pressure i.e. P_{sat} @T_{min}, since the condition lie on bubble line of the binary mixture. However, cycle minimum pressure P_{min} in case of pure CO_2 bottoming power cycles is considered to be slightly larger than critical point pressure of pure CO_2 owing to two vital reasons:

- The selection of P_{min} larger than critical pressure enhances the thermodynamic efficiencies of pure CO_2 cycles at higher cycle minimum temperatures (T_{min}) [17].

- To avoid the risk of two-phase flow at the compressor inlet which is detrimental for the performance of compressor [51,52].

Figure 11 illustrates the energetic efficiency, exergetic efficiency, heat recovery and overall UA of BSRC and BPHC configurations in case of both CO_2-C_7H_8 and pure CO_2 as working fluids.

Following points can be extracted from this comparative analysis:

- Considering the energetic and exergetic performance of pure CO_2 bottoming cycles, the cycles shows greater efficiencies at T_{amb} = 297 K, but the performance is decreasing at higher values of T_{amb}. Also, the performance of BSRC is better than BPHC at higher T_{amb} conditions.
- Considering the energetic and exergetic performance of CO_2-C_7H_8 bottoming cycles, the BSRC performs better than BPHC at all T_{amb} conditions.

Table VIII: Percentage gain in energetic and exergetic performance in CO_2-C_7H_8 bottoming cycles with reference to pure CO_2 bottoming cycles.

T_{amb}	CO_2-C_7H_8 BSRC		CO_2-C_7H_8 BPHC	
	η_{II}	η_I	η_{II}	η_I
297	1.47	4.06	-10.91	-14.47
303	13.88	15.10	6.96	-0.47
308	20.84	22.38	13.50	5.22
313	26.83	28.92	18.71	10.12

- The bottoming cycles with CO_2-C_7H_8 shows better energetic and exergetic performance at higher T_{amb} conditions as compared to their pure CO_2 counterpart configurations. The percentage gain in performance of CO_2-C_7H_8 bottoming cycles with reference to pure CO_2 bottoming cycles is recorded in **Table VIII**. As evident, the gain in case of CO_2-C_7H_8 BSRC is more as compared to CO_2-C_7H_8 BPHC particularly at higher ambient temperatures.
- In terms of heat recovery, the BPHC reveals higher values in case of both CO_2-C_7H_8 and pure CO_2 cycles.
- The BSRC depicts highest overall UA among all the cases while bottoming cycles with pure CO_2 shows smaller UA values. However, BPHC with CO_2-C_7H_8 shows reasonable UA values at higher T_{amb} conditions.

Based on comparative analysis, it is evident that the bottoming cycles operating CO_2-C_7H_8 working fluid performs better than bottoming cycles with pure CO_2 at higher T_{amb} conditions. Besides, the BSRC with CO_2-C_7H_8 shows highest thermodynamic performance but at the cost of larger UA compared to other configurations. BPHC with CO_2-C_7H_8 can be selected as better choice for hot/arid climatic conditions because it shows not only better performance at higher T_{amb} conditions but also with smaller UA i.e. smaller plant size footprint. In addition, CO_2-C_7H_8 BPHC is more beneficial in terms of lowering the emissions owing to larger heat recovery from exhaust gases.

Conclusion

This paper analyzed the energetic and exergetic performance of Gas-Turbine bottoming cycles operating with CO_2-Toluene binary mixture as working fluid. Two bottoming cycles configurations are selected from the best practice in literature; BSRC and BPHC configurations. The practical operating conditions for both cycles are decided based on sensitivity analysis. Moreover, a thorough comparative analysis at identical operating conditions is carried out to draw the main benefits of using CO_2-C_7H_8 binary mixture in place of pure CO_2 as working fluid in bottoming cycles.

Following points can be concluded from this study:

- Sensitivity analysis of cycle maximum pressure (P_{max}) and minimum temperature difference inside the recuperator ($MITA_R$) suggests P_{max} = 25 MPa and $MITA_R$ = 40 K as practical performance conditions keeping in view the exergetic performance and size footprint of the power cycle.
- The main cause of exergy destruction in both power cycle configurations with CO_2-C_7H_8 binary mixture are heat exchangers (IHX(s), recuperator and condenser.
- Comparative analysis among bottoming cycles configurations reveals that bottoming cycles operating with CO_2-C_7H_8 binary mixture yield better energetic and exergetic performance as compared to bottoming cycles with pure CO_2.
- The gain in energetic and exergetic performance of CO_2-C_7H_8 bottoming cycles with reference to pure CO_2 bottoming cycles is assessed; the performance gain increases with increase in ambient temperature. At maximum condition of T_{amb} = 313 K, the gain in energetic and exergetic efficiency in case of BSRC are 28.92% and 26.83 % respectively. Whereas, the gain in case of BPHC are 10.12% and 18.71% respectively.
- Inclusively, the higher exergetic performance and power output in power cycles operating with CO_2-C_7H_8 working fluid comes with comparatively higher overall UA i.e. larger power plant size footprint.
- Taking into consideration both thermodynamic performance and overall UA, BPHC configuration is suggested as reasonable choice for higher ambient temperature conditions.

Nomenclature

Symbols and Abbreviations	
BSRC	Bottoming simple regenerative cycle
BPHC	Bottoming preheating cycle
CP	Critical point
EoS	Equation of state
GWP	Global warming potential
IHX	Integrated heat exchanger
MITA	Minimum internal temperature approach
ODP	Ozone depletion potential
PR	Peng Robinson
$\dot{Q}_{in}$	Heat input in integrated heat exchanger
R	Gas constant
T_r	Reduced temperature
UA	Heat transfer coefficient times area of heat exchanger
VLE	Vapor liquid equilibrium
x	Mass split

Greek letters	
η	Efficiency
ω	Acentric factor of a fluid
Subscripts	
amb	Ambient
cr	Critical point
exh	Exhaust gases
max	Maximum
m	Mixture
recv	Recovery
R	Recuperator
I	Energy efficiency
II	Exergy efficiency

Declaration of Interest

None.

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