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A review of recent research on the use of zeotropic mixtures in power generation systems

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Abstract

The use of zeotropic fluid mixtures in refrigeration cycles and heat pumps has been widely studied in the last three decades or so. However it is only in the past few years that the use of zeotropic mixtures in power generation applications has been analysed in a large number of studies, mostly with low grade heat as the energy source. This paper presents a review of the recent research on power cycles with zeotropic mixtures as the working fluid. The available literature primarily discusses the thermodynamic performance of the mixture power cycles through energy and exergy analyses but there are some studies which also consider the economic aspects through the investigation of capital investment costs or through a thermoeconomic analysis. The reviewed literature in this paper is divided based on the various applications such as solar energy based power systems, geothermal heat based power systems, waste heat recovery power systems, or generic studies. The fluid mixtures used in the various studies are listed along with the key operation parameters and the scale of the power plant. In order to limit the scope of the review, only the studies with system level analysis of various power cycles are considered. An overview of the key trends and general conclusions from the various studies and some possible directions for future research are also presented.

Keywords: Zeotropic mixture, Temperature glide, Power generation, Organic Rankine cycle, Ammonia-water mixture, Kalina cycle

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1. Introduction

Fluid mixtures have been widely studied for their use in refrigeration systems and heat pumps in the past few decades [1]. These include mixtures of natural as well as artificial refrigerants and could either be azeotropic or zeotropic. For an azeotropic mixture, the compositions of the liquid and the vapour phases are the same for a certain combination of temperature and pressure [1]. The state where this happens is called the *azeotropic point*. This point is highlighted in Fig. 1 for a binary azeotropic mixture with the azeotropic point boiling temperature lower than the boiling temperatures of both the pure fluid constituents of the mixture.

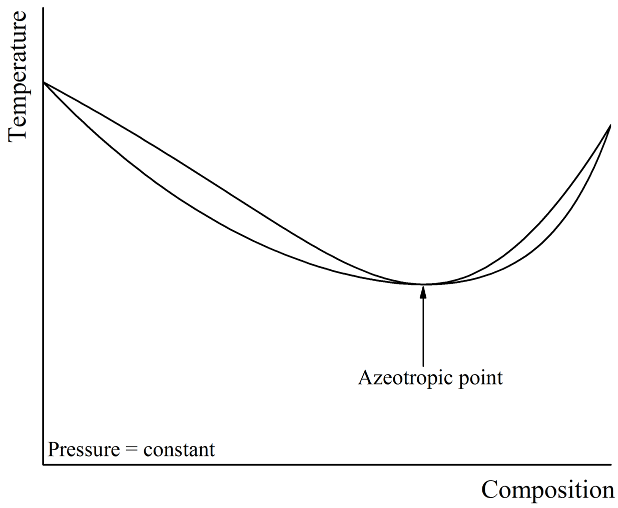

Figure 1: Schematic temperature-composition diagram for a binary azeotropic mixture at a constant pressure.

For a zeotropic mixture, on the other hand, the compositions of the liquid and the vapour phases are always different in the two-phase region. These mixtures have sometimes also been referred to as *non-azeotropic mixtures*. The temperature-composition diagram for a binary zeotropic mixture is shown in Fig. 2. In the figure, for any bulk fluid composition x at a state k in the two-phase region, the points 'A' and 'B' represent respectively the dew

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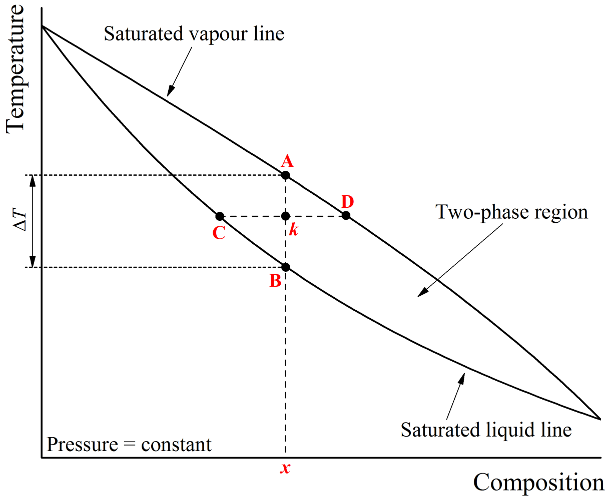


Figure 2: Schematic temperature-composition diagram for a binary zeotropic mixture at a constant pressure.

point and the bubble point temperatures for the mixture. The points 'C' and 'D' represent the liquid and the vapour saturation points for the equilibrium liquid and vapour phase compositions at that state, respectively. The temperature difference ΔT on the vertical axis of the figure represents the *temperature glide* for the mixture, i.e. the difference between the bubble and dew points for a particular mixture composition at a specified evaporation pressure. The composition here could either be the mole or the mass fraction with respect to one of the components. This temperature glide occurs during evaporation because of the evaporation of the more volatile component of the mixture first, thereby resulting in different compositions in the liquid and the vapour phases, and thus the continuously changing evaporation temperature at the same pressure until the entire mixture is evaporated. The same phenomenon is observed during condensation because of the condensation of the less volatile component of the mixture first.

In recent years, the use of fluid mixtures in power cycles has attracted increased interest because of the possibility to reduce the irreversibility during a two-phase heat transfer process, enabling to increase the average temperature of heat supply and/or decrease the average temperature of heat rejection, thereby resulting in better thermodynamic performance in terms of improved cycle efficiency. This reduction comes through the matching of the temperature profiles of the fluid mixture with those of the heat source and sink during evaporation and condensation, respectively, because of the occurrence of non-isothermal phase change.

This paper presents a review of the recent literature on the use of zeotropic mixture in power generation applications. The key conclusions drawn from the state-of-the-art along with guidelines for future research are also presented. The reviewed literature is divided based on the various applications such as solar energy based power systems, geothermal heat based power systems, waste/exhaust heat recovery (WHR) power systems, or generic studies. The fluid mixtures used in the various studies are listed along with the key operation parameters and the scale of the power plant. In order to limit the scope of the review, only the studies with system level analysis of the various power cycles are considered. Since the studies related to the estimation of the heat transfer coefficients and transport properties using fluid mixtures have been summarized previously [1–4], they are not included in this paper. The rest of the paper is structured as follows. Section 2 presents the summary of the literature on the use of zeotropic mixtures in organic Rankine cycle (ORC) power systems. Section 3 is dedicated to the studies investigating the use of ammonia-water mixtures for power generation applications. Section 4 presents an overview of the trends and general conclusions from the various studies. Section 5 suggests some possible directions for future research. Section 6 concludes the paper.

2. Organic Rankine cycle power systems

The use of ORC power systems has been investigated for many applications, operation conditions, and capacities [5–8]. Working fluid selection has been one of the key areas of research [9, 10] and a list of the various investigated fluids along with their alternative names is available in Ref. [11]. In this regard, the following subsections present an overview of the mixture ORCs based on the respective applications. A list of the recommended fluid mixtures from the studies comparing various mixtures for different applications is presented in Section 4.

2.1. Solar energy based ORC power systems

The various studies on solar energy based ORC power systems have typically been limited to heat source temperatures between around 80 °C and 150 °C and for plant capacities in the kW range. All the studies have evaluated the solar energy based ORC power systems through energy and exergy analyses while a few also conducting sensitivity analysis. In these studies, mostly hydrocarbon mixtures have been evaluated for the assumed operation conditions and generation capacities. Table 1 shows an overview of these studies with their details presented in the following text. In the studies where comparisons were made between the use of pure fluids and fluid mixtures, Table 1 presents the details corresponding to the mixture analysis.

Table 1: Studies with solar energy based ORC power systems. T_{hs} is the heat source temperature and T_{cs} is the cooling medium temperature. A '-' instead of the value indicates unavailable data.

Ref.	T_{hs} (°C)	T_{cs} (°C)	Capacity (kW)	Considered mixtures	Remarks
Prasad et al. [12]	100	35	-	R236ea/R600a/R601a/cyclohexane, R290/R600/R600a, R290/R600/R600a/R601/R601a/cyclohexane, R600/R600a/R601/R601a, R600a/R601/R601a/cyclohexane, R600a/R601a/cyclobutane/cyclohexane, R601a/cyclopentane/cyclohexane	Analysis based on exergy efficiency and volumetric expander work output
Baldasso et al. [13]	150	20	100	Various binary mixture combinations using R1234yf, R1234ze, R600, R600a, R601, R601a, cyclopentane, hexane, cyclohexane, and isohexane	Analysis based on overall plant efficiency
Bao et al. [14]	95-155†	-	-	R245fa/R601a	Novel auto-cascade power cycle configuration
Wang and Zhao [15]	85†	25‡	21.3-25.3	R152a/R245fa	Numerical and experimental analysis with different working fluid compositions

Garg et al. [16]	127-300	35‡	-	CO_2/R290 and CO_2/R601a	Energy and exergy analyses
Garg et al. [17]	107-152	35‡	100	R245fa/R601a	Energy and exergy analyses
Mavrou et al. [18]	80-95	30‡	1	R600/R601, R600a/R601, R600a/R601a, R601/hexane, R601a/hexane, R601a/isohexane, 1,1,1,3,3,3-hexafluoropropane/1-fluoromethoxy-2,2,2-trifluoromethylethane, neopentane/1,1,1-trifluoro-2-trifluoromethylbutane, neopentane/1,1,1-trifluoropentane, 1,1,1-trifluoro-2-trifluoromethylpropane/2,2-difluorohexane	Energy, exergy, and sensitivity analyses
Mavrou et al. [19]	80-95	-	1	R600a/R601, 1,1,1-trifluoropropane/2-fluoromethoxypropane, 1,1,1-trifluoropropane/1-fluoromethoxypropane, neopentane/1,1,1-trifluoro-2-trifluoromethylbutane, neopentane/2-fluoromethoxy-2-methylpropane	Energy, exergy, and sensitivity analyses
Mavrou et al. [20]	80-95	30‡	1	Various binary mixture combinations using hydrocarbons and hydrofluorocarbons	Energy, exergy, and sensitivity analyses

† Expander inlet temperature.

‡ Working fluid condenser outlet temperature.

Prasad et al. [12] analysed the performance of an ORC unit for power generation using solar thermal energy. The investigated layout consisted of an internal recuperator. The objective of the analysis was to maximize the exergy efficiency or the volumetric expander work output (i.e. the ratio of the expander power output to the volume flow rate of the working fluid at the expander outlet). The cycle performance was compared when using pure fluids and mixtures as the cycle working fluid. The main contribution of the paper was an approach to design suitable mixtures that can work with off-the-shelf expanders already available in the market, instead of having to come up with novel expander designs to suit the optimal working fluid. Baldasso et al. [13] presented a comparison between pure and mixed working fluids for an ORC unit operating with a parabolic trough solar field. The results indicated that the mixture of cyclopentane/cyclohexane performed better than its pure components in terms of the overall plant efficiency. Bao et al. [14] proposed a novel auto-cascade power cycle using mixtures as shown in Fig. 3. The results indicated that the optimal working fluid composition was different for the cycle configurations with and without the regenerator, and the solar collector I outlet temperature affected the cycle thermal efficiency most significantly.

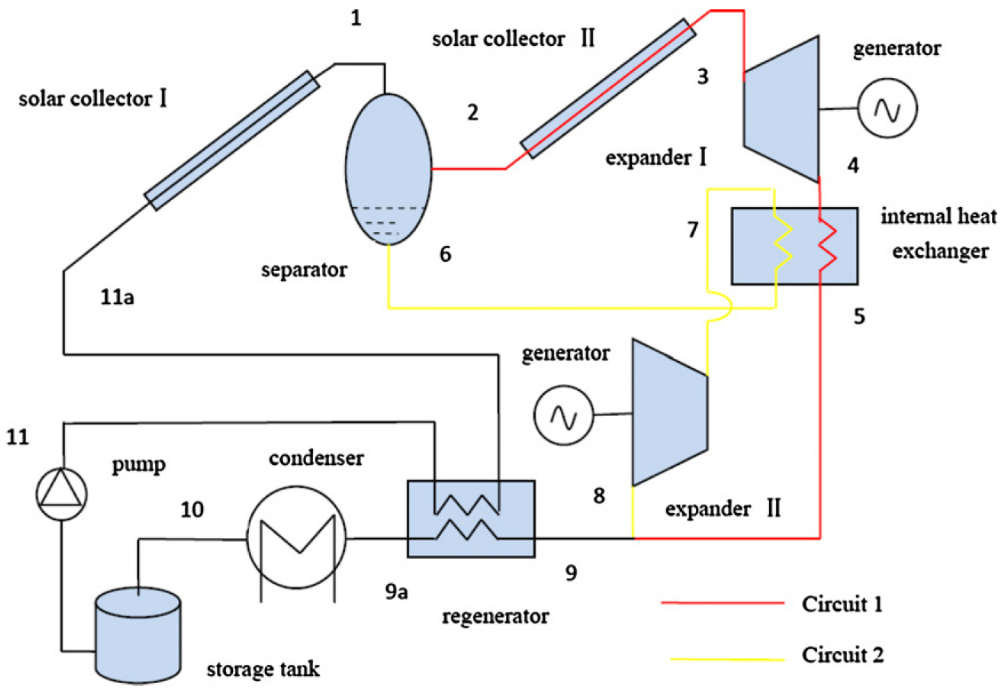


Figure 3: Auto-cascade low temperature solar power cycle [14].

Wang et al. [15, 21] presented the numerical and experimental analyses of low-temperature solar power cycles. A comparison was made between using different compositions of the working fluid mixture. Pure R245fa was found to result in the highest cycle efficiency among the compared alternatives. However, this came at the cost of requiring larger expander dimensions. Garg et al. [16, 17] evaluated the use of various mixture blends for use in solar ORC plants through energy and exergy analyses. For the blends with CO_2, the CO_2/R290 mixture performed similarly as pure propane, but with higher operating pressures. For the R245fa/R601a mixture, a 0.3/0.7 mole fraction mixture was found to be optimal because of reduced respective disadvantages of the pure components, i.e. the flammability and the high global warming potential. Mavrou et al. [18–20] analysed various conventional and novel working fluid mixtures for solar energy based ORC power systems. Energy and exergy analyses were performed along with a detailed sensitivity analysis and comparisons of the cycle performance were made on the basis of net power output and cycle thermal efficiency.

2.2. Geothermal heat based ORC power systems

The studies on geothermal heat based ORC power systems have typically been limited to heat source temperatures between around 70 °C and 150 °C and for plant capacities ranging between few kW to few MW. A couple of studies also considered higher heat source temperatures up to around 200 °C. The mixtures of hydrocarbons have been evaluated the most through thermodynamic (energy and exergy), thermoeconomic, and experimental analyses. Multi-objective optimizations including both thermodynamic and economic parameters have also been performed by some researchers. Table 2 shows an overview of these studies with their details presented in the following text. In the studies where comparisons were made between the use of pure fluids and fluid mixtures, Table 2 presents the details corresponding to the mixture analysis.

Table 2: Studies with geothermal heat based ORC power systems. T_{hs} is the heat source temperature and T_{cs} is the cooling medium temperature. A '-' instead of the value indicates unavailable data.

Ref.	T_{hs} (°C)	T_{cs} (°C)	Capacity (kW)	Considered mixtures	Remarks
Heberle et al. [22]	80-180	15	1500-1700	R227ea/R245fa, R600a/R601a	Numerical simulation and second law analysis
Heberle and Brüggemann [23]	100-180	15	1500-1700	RC318/R134a, R134a/R236fa, R134a/R245fa, R152a/R245fa, R227ea/R236fa, R227ea/R245fa, R236fa/R365mfc, R236fa/R245fa, R245fa/R365mfc, R290/R600a, R600/R601, R600a/R601a, R601/hexane, R601/isohexane	Thermoeconomic optimization, calculation of specific investment costs
Basaran and Ozgener [24]	96	7	200-1600	R401a, R409a, R413a, R415a	Analysis based on net power output and exergy efficiency
Jialing et al. [25]	110	20	9-19	R245fa/R601a	Parametric optimization for maximum net power output
Liu et al. [26]	110-150	20	1200-3600	R600a/R601a	Analysis based on net power output, turbine size, and heat exchanger area requirement

Yue et al. [27]	90-140	10	7.5-13	R600a/R601a	Temperature profile matching in the evaporator and condenser
Li et al. [28]	70-120	-	0.5[◇]	R245fa/R601a	Experimental study with scroll expander
Yin et al. [29]	140-190	10	-	CO_2/SF_6	Analysis based on cycle efficiency
Kang et al. [30]	110	20	8-30	R1234yf/R600a, R1234yf/R601a, R1234ze/R600a, R1234ze/R601a, R134a/R600a, R134a/R601a, R227ea/R600a, R227ea/R601a, R245fa/R600a, R245fa/R601a	Parametric optimization for highest net power output
Oyewunmi and Markides [31]	98	20	160-215	R227ea/R245fa, R601/hexane	Multi-objective cost-power optimization
Sadeghi et al. [32]	100	25[‡]	640-975	R22m, R402a, R404a, R407a, R410a, R422a, R438a, R402b, R403b, R422d	Thermodynamic analysis and multi-objective optimization
Habka and Ajib [33]	80-120	15	7-35	R22m, R402a, R404a, R407a, R410a, R422a, R437a, R438a, R402b, R403b, R422d	Analysis with and without cogeneration
Lu et al. [34]	140	20	24-39	R245fa/R600a and R600/R601a	Parametric study
Baik et al. [35]	100	20	340	R125/R134a, R125/R227ea, R125/R236ea, R125/R245fa	Transcritical ORC power system

Radulovic and Castaneda [36]	87-207	15	-	RC318/R143a, R124/R143a	Parametric optimization of a transcritical ORC power system
Preißinger et al. [37]	100-190	15	2800-3650$^{\diamond}$	R227ea/R245fa	Economic comparison between subcritical and transcritical ORC power systems

$^{\diamond}$ Expander capacity.

‡ Working fluid condenser outlet temperature.

Heberle et al. [22, 23] presented detailed numerical simulations and thermoeconomic optimization of an ORC unit for low enthalpy geothermal sources. An ORC unit with a recuperator was optimized and analysed. From the thermodynamic perspective, the results indicated in a higher second law efficiency with fluid mixtures than with pure working fluids because of the non-isothermal phase change [22]. This was mainly because of a better matching of the hot and cold temperature profiles in the heat exchangers. In particular, the irreversibility in the condensers decreased significantly. The results also indicated that the operating configurations where the temperature profiles in the condenser matched better were the more efficient ones. From the thermoeconomic perspective, the specific investment costs for the cycle using mixtures was found to be higher than for the cycle using pure working fluids [23]. This was mainly because of lower values of two-phase heat transfer coefficients for the mixtures than those for the pure fluids resulting in larger heat exchanger area requirements for the mixture cycle. However, because of the higher power generation and higher annual electricity production as a result of lower irreversibility, the electricity generation costs were found to be lower when using mixtures by between 4 % and 10 % as compared with using pure fluids. In short, the higher investment costs were compensated by the higher amount of electricity generation from the plants using mixtures, thus resulting in better economic performance in terms of electricity generation costs when using mixtures as compared with using pure working fluids.

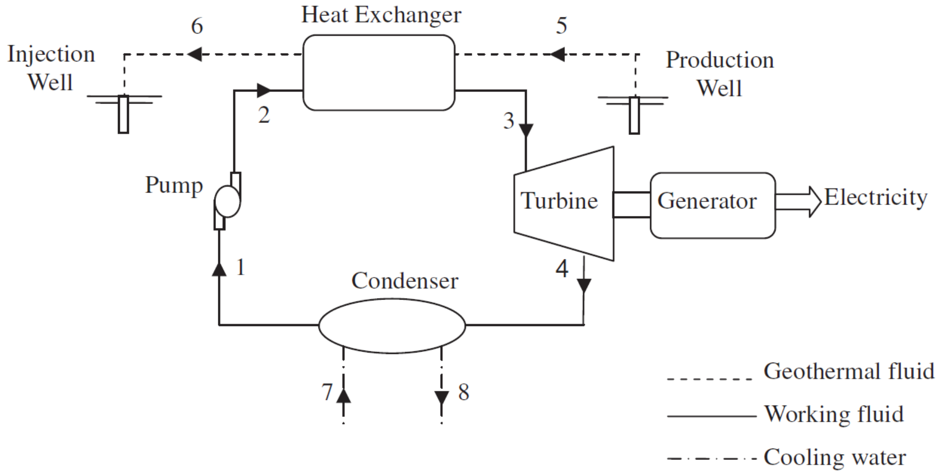


Figure 4: Basic geothermal heat based ORC power system [24].

Basaran and Ozgener [24] analysed a basic ORC unit for geothermal power production and compared the use of several pure and mixed working fluids. The cycle is shown in Fig. 4. The results indicated that for the analysed operating conditions, the considered mixtures were only better than two of the eight pure working fluids in terms of the net power output and the exergy efficiency of the plant. Jialing et al. [25] presented a parametric optimization of a geothermal ORC power system using a R245fa/R601a mixture as the working fluid. The optimal composition and operating conditions for the maximum net power output were determined. Liu et al. [26] presented the parametric optimization and performance analysis of a geothermal ORC power system with R600a/R601a as the working fluid. The performance of the plant was evaluated in terms of net power output, turbine size, and heat exchanger area requirements. Optimal fluid compositions were determined for the different performance indicators. The same mixture was also analysed by Yue et al. [27] with respect to the hot and cold side temperature profile matching in the evaporator and the condenser. Optimal temperature differences in the different heat exchangers were determined. Li et al. [28] experimentally compared the performances of ORCs using pure R245fa with that of ORCs using R245fa/R601a mixture with a scroll expander. The use of fluid mixture resulted in slightly higher cycle thermal efficiency (by about 0.07 percentage point). Yin et al. [29] evaluated the use of CO_2/SF_6 mixture in a geothermal Rankine cycle power system with a recuperator. Compositions resulting in the highest cycle efficiency were determined.

Kang et al. [30] performed the parametric optimization and performance analysis of a geothermal ORC power system with zeotropic mixtures. The results suggested the presence of an optimal mixture composition resulting in the maximum net power output for every mixture. This optimal composition was found to be the one that resulted in the maximum temperature glide in the evaporator. The presence of an optimal evaporating temperature was also noticed. Oyewunmi and Markides [31] presented a thermoeconomic and heat transfer optimization of fluid mixtures for geothermal ORC power systems. A multi-objective cost-power optimization was performed and optimal fluid mixtures and their compositions were identified for the highest thermodynamic efficiency and the lowest capital investment costs. The cycles with pure fluids were found to be generally cheaper than those with fluid mixtures. Sadeghi et al. [32] presented a thermodynamic analysis and multi-objective optimization of various ORC configurations (with one or two evaporators) using zeotropic mixtures as working fluid. The decision variables included the evaporation pressure, the minimum pinch point temperature difference, and the degree of superheat. The results indicated a 24 % to 28 % increase in power generation using mixtures than with pure working fluids. Habka and Ajib [33] evaluated the performance of geothermal ORC power systems with mixtures for plant configurations with and without cogeneration. The results showed that the power generation and heat source utilization may be improved by using mixtures. Lu et al. [34] presented the results from a parametric analysis of two ORC configurations, with one and two recuperators, respectively. The analysis was performed by varying the condenser bubble temperature and the condenser cooling water temperature rise and mass flow rate.

Some studies have also investigated the use of transcritical ORCs for geothermal power plants where the working fluid mixture is evaporated in a supercritical state, i.e. at pressures greater than the critical pressure, while the condensation takes place in the subcritical state. Baik et al. [35] presented an analysis of a mixture transcritical cycle in order to estimate the potential increase in the power output from the plant. The numerical analysis included the heat exchanger models and a comparison was made between the pure and mixture working fluids on the basis of the heat exchanger area requirement. The rates of exergy destruction in the various cycle components were also calculated. The mixture transcritical cycle resulted in about 11 % higher power generation than the pure fluid subcritical cycle under same simulation conditions, primarily because of lower irreversibility in the heating process. Radulovic and Castaneda [36] presented a parametric optimization of six zeotropic mixture compositions in a transcritical ORC. The results indicated that the cycles with the evaluated mixtures showed higher thermal efficiencies by up to 15 % than those with the respective pure components at the same operational conditions. Preißinger et al. [37] presented a comparison between using pure and mixed working fluids in subcritical and transcritical cycle configurations from an economic perspective. The results suggested that for a heat source temperature equal to 130 °C, the subcritical configurations generated higher gross power than the transcritical configurations. However, using transcritical ORCs with pure fluids or subcritical ORCs with fluid mixtures result in either similar or lower payback periods than the subcritical ORCs with pure fluids even with relatively higher specific investment costs. The analysis in this work assumed same total capital investment costs for the subcritical, the transcritical, and the fluid mixture power cycle systems.

2.3. Waste/Exhaust heat recovery ORC power systems

The studies on the use of ORC power systems for WHR applications have been conducted for a wide range of heat source temperatures (between around 50 °C and 560 °C) and plant capacities (between around 0.5 kW and 74 MW). The various mixtures have been evaluated based on first law, second law, and economic analyses. The studies have provided general guidelines on the selection of optimal fluids and mixture compositions for various operating conditions and types of heat sources. Table 3 shows an overview of these studies with their details presented in the following text. The applications include heat recovery from diesel engine exhaust, flue gas from gas turbines or coal-fired power plants, industrial waste heat, and other similar sources. In the studies where comparisons were made between the use of pure fluids and fluid mixtures, Table 3 presents the details corresponding to the mixture analysis.

Table 3: Studies with ORC units used for WHR applications. T_{hs} is the heat source temperature and T_{cs} is the cooling medium temperature. A '-' instead of the value indicates unavailable data.

Ref.	T_{hs} (°C)	T_{cs} (°C)	Capacity (kW)	Considered mixtures	Remarks
Hærvig et al. [38]	50-280	15	-	R170/R290, R290/R600, R290/R601	Guidelines for selection of optimal working fluids
Oyewunmi et al. [39]	330	20	500-30 000	R600/decane, perfluorobutane/perfluorodecane	Analysis based on net power output and specific costs
Li et al. [40]	150	20	20-100	Binary mixture combinations of various pure fluids from the REFPROP database	Analysis based on LCOE
Mondejar and Thern [41]	77-177	17	3-45.8	Binary mixture combinations of various pure fluids from the REFPROP database	Analysis using isentropic mixtures based on net power output
Xiao et al. [42]	150	20	2-90	R245fa/R600a, R245fa/R601, R245fa/R601a, R600a/R601a	Multi-objective optimization
Wu et al. [43]	120-170	15	-	R13I1/R601a, R245fa/R601a	Matching of pinch point temperature differences
Li and Dai [44]	250	17	180-310	R123/R245fa, R600a/R601a	Thermoeconomic analysis

Kolahi et al. [45]	425.7	20	40-80	R236ea/hexane, R236ea/cyclohexane, R236ea/isohexane, R245fa/hexane, R245fa/cyclohexane, R245fa/isohexane	Thermodynamic and economic analyses
Le et al. [46]	150	20	1040-1620	R245fa/R601	Thermodynamic and economic optimizations
Feng et al. [47]	150	20	1.4-2	R245fa/R601	Analysis based on exergy efficiency and LCOE
Feng et al. [48]	120	20	-	R227ea/R245fa Analysis with exergy efficiency and LCOE	
Weith et al. [49]	375	15	<30	MDM/MM	Analysis based on second law efficiency with and without cogeneration
Heberle and Brüggemann [50]	150	15	325	R600a/R601a	Thermoeconomic analysis
Guo et al. [51]	130	20	1450	R600a/R601	Analysis based on first law efficiency, heat exchanger area, volumetric flow rate, and other parameters
Song et al. [52]	485-560	35[‡]	2.6-62.8	R416a	CNG engine
Wang et al. [53]	170-545	30[‡]	0.6-22.9	R416a	Diesel engine

Zhang et al. [54]	150-550	35	4-30	R245fa/R601a (0.3/0.7 mole fraction)	Analysis based on net power output and cycle efficiency
Jung et al. [55]	158.7	15.3	1$^\diamond$	R365mfc/R245fa (0.515/0.485 mole fraction)	Experimental and numerical analyses
Yang et al. [56]	170-545	30	2-25	R401a, R402b, R407b, R407d, R409a, R409b, R411b, R415b	Diesel engine at various operating conditions
Yang et al. [57]	200-550	30	0.5-35	R152a/R245fa	Diesel engine at various operating conditions
Zhou et al. [58]	-	25	11-14	RC318/R1234yf, RC318/R245fa, R1234yf/R600	Dual-loop power cycle configuration
Shu et al. [59]	519	-	17-21	R11/benzene, R11/cyclopentane, R11/cyclohexane, R123/benzene, R123/cyclopentane, R123/cyclohexane	Analysis based on cycle efficiencies
Song and Gu [60]	300	25	80-90	R11/cyclohexane, R141b/cyclohexane	Analysis based on net power output
Braimakis et al. [61]	150-300	20	-	R290/cyclopentane, R290/hexane, R290/R600, R290/R601, R600/cyclopentane, R600/hexane, R600/R601, R601/cyclopentane, R601/hexane, cyclopentane/hexane	Analysis of subcritical and transcritical power cycle configurations based on exergy efficiency
Lee et al. [62]	87.7	–160*	74 100	R14/R23/R30, R14/R23/R236fa, R14/R23/R245fa, R14/R23/R601	Design and optimization

* LNG heat sink.

◇ Expander capacity.

‡ Working fluid condenser outlet temperature.

Hærvig et al. [38] proposed some general guidelines for selection of optimal working fluids for an ORC for WHR applications. The guidelines included the analysis of both pure and mixed working fluids for a wide range of operating conditions. With regards to mixtures, the guidelines suggested that the optimal compositions of the mixtures are those where the critical temperature of the mixture is approximately 30 °C to 50 °C lower than the heat source temperature, and the temperature glide during condensation is close to the temperature rise of the cooling source. Oyewunmi et al. [39] analysed the use of the SAFT-VR Mie equation of state for estimating the thermodynamic properties of pure and mixed working fluids. The results indicated that the use of pure fluids generally resulted in cycles with higher net power outputs and lower specific costs among the compared alternatives. The use of mixtures was however found to be beneficial in operating conditions with limited availability of the cooling medium or in cogeneration applications. Li et al. [40] evaluated the potential of using zeotropic mixtures as working fluids in ORC power systems for WHR applications. The results suggested that the ORCs with mixtures operated with higher levelized costs of electricity (LCOE) than the ORCs with pure fluids. Mondejar and Thern [41] analysed the use of isentropic mixtures in ORC power systems for the utilization of low to medium temperature industrial waste heat. The use of isentropic mixtures presents the possibility to minimize the need for recuperation and superheating, two issues common with using dry and wet working fluids, respectively. The results indicated 15 % to 35 % higher net power output with the ORC using isentropic mixtures as compared with the corresponding pure components.

Xiao et al. [42] presented a multi-objective optimization of evaporation and condensation temperatures for subcritical ORCs using pure or mixed working fluids. The optimization objectives were to simultaneously minimize the specific investment cost (i.e. the ratio of the total capital investment cost to the net power output from the plant) and the ratio of the total rate of exergy destruction to the exergy drop of the exhaust gas while supplying heat to the ORC working fluid. The results indicated that the performance of the mixed working fluids was not always better than that of the pure fluids, and that there are optimal values of evaporation and condensation temperatures for different working fluids. The effect of the different values of minimum pinch point temperature differences on the optimization function was also analysed. A similar analysis on the determination and matching of the pinch point temperature differences was also presented by Wu et al. [43]. Li and Dai [44] presented a thermoeconomic analysis of a mixture ORC for WHR applications. The performance indicators were net power output, the first and second law efficiencies, specific investment cost, the area of heat exchangers per unit of net power output, and the energy saving and emission reduction potentials. In general, the mixed working fluids were found to perform better than the pure working fluids from the economic perspective in both the basic ORC and the ORC with a recuperator. Kolahi et al. [45] presented the thermodynamic and economic analyses of an ORC unit for WHR from the exhaust gases of large diesel engines on an offshore platform. The mixture ORC was found to be thermodynamically superior to the pure fluid ORCs in terms of cycle efficiency. The recuperative ORC resulted in higher payback periods than the basic ORC because of higher specific investment cost due to the presence of an additional heat exchanger.

Le et al. [46] presented the thermodynamic and economic optimizations of subcritical ORCs for WHR applications. The study compared the performance of the ORC unit when using pure or mixture working fluids. The optimization objectives were to maximize the exergy efficiency and minimize the LCOE. The results suggested that the highest exergy efficiency and the minimum LCOE were shown by the configuration using pure R601. Feng et al. [47, 48] compared the performances of using pure or mixed working fluids in a WHR ORC power system. The comparisons were made on the basis of exergy efficiency and LCOE. The results indicated worse economic performance for the mixtures than the pure fluids. Weith et al. [49] analysed the performance of using siloxane mixtures for recovering heat from a high temperature exhaust gas. Since the temperature for the available exhaust gas was higher than the stable operating temperature of the siloxane mixtures, an intermediate thermal oil loop was used to transfer the heat from the exhaust gas to the ORC working fluid as shown in Fig. 5. The results suggested higher second law efficiency when using mixtures in both power-only and cogeneration modes, but with different compositions. However, the required heat exchanger areas were also larger for the mixtures than for the pure fluids.

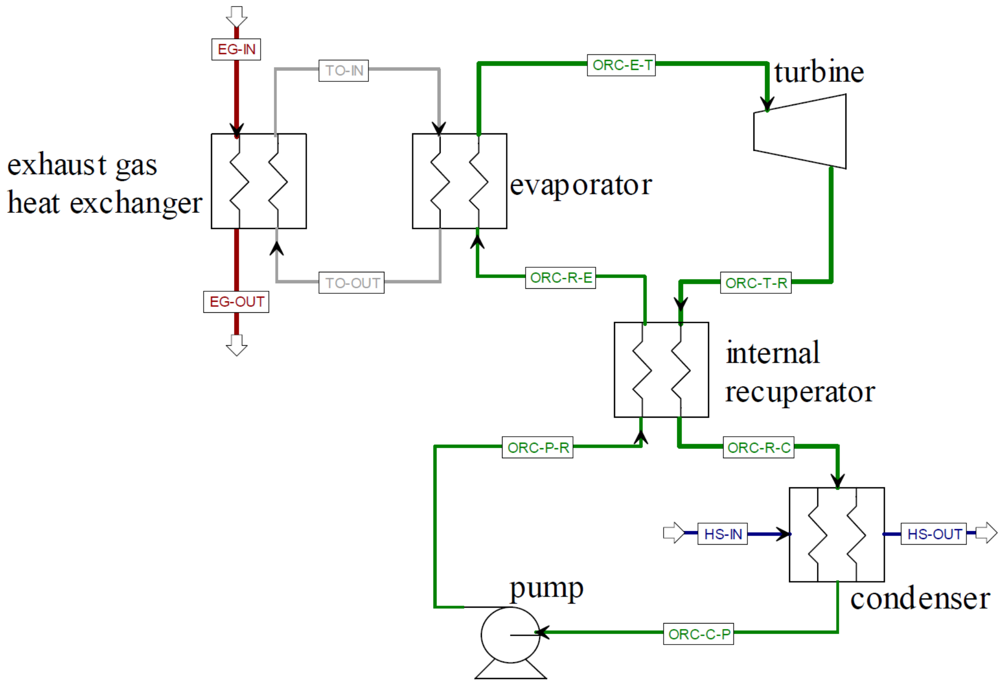


Figure 5: WHR ORC power system with an intermediate thermal oil loop [49]. In the layout, 'EG' is exhaust gas, 'TO' is thermal oil, 'HS' is the heat sink or cooling medium, and the ORC working fluid streams 'ORC-E-T', 'ORC-T-R', 'ORC-R-C', 'ORC-C-P', 'ORC-P-R', and 'ORC-R-E' respectively represent the streams between the evaporator and the turbine, the turbine and the recuperator, the recuperator and the condenser, the condenser and the pump, the pump and the recuperator, and the recuperator and the evaporator.

Heberle and Brüggemann [50] presented a thermoeconomic analysis of using pure fluids and zeotropic mixtures in an ORC power system for WHR. The results suggested that lower values for minimum pinch point temperature differences in the evaporator and higher values in condenser are better for more cost-effective designs. Among the compared fluids, pure R600a resulted in the configuration with the lowest specific investment costs, but the configuration with R600a/R601a resulted in the lowest LCOE.

Guo et al. [51] analysed the performance of an ORC power system for WHR from the flue gas from a pulverized coal-fired power plant. The results suggested that there is no optimal composition that could simultaneously result in the best for all the performance indicators (i.e. first law efficiency, heat exchanger area, mass flow rate, volumetric flow rate, etc.) The results also indicated that the mixture composition which best matched the heat

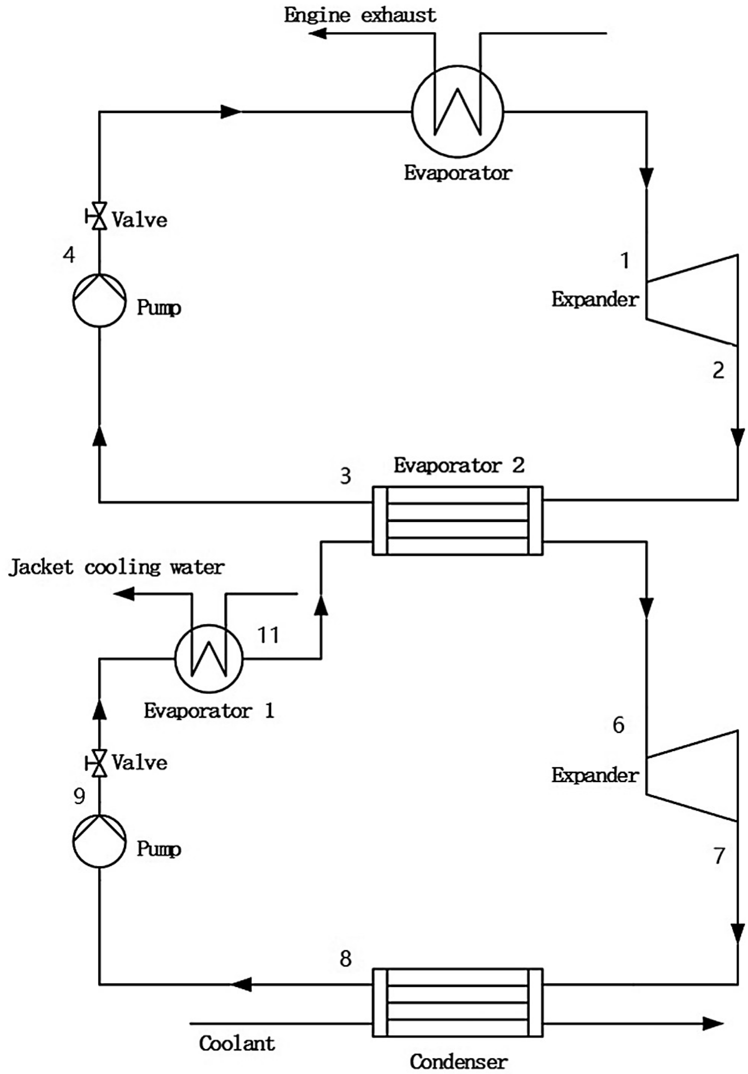


Figure 6: Dual-loop WHR plant with two bottoming cycles [58].

sink temperature profile resulted in the highest efficiency, while the composition that best matched the heat source temperature profile resulted in the lowest degree of superheat. The performance of an ORC unit using the mixture R416a was analysed for WHR from the exhaust gases from a compressed natural gas (CNG) engine [52] and a diesel engine [53]. A comparison was also made with the performance using some pure fluids [53]. Among the compared fluids for the diesel engine exhaust WHR, pure R600 resulted in the best WHR efficiency. Zhang et al. [54] analysed the performance of using pure and zeotropic mixture working fluids in an ORC power system with a recuperator for WHR from a diesel engine.

The mixture R245fa/R601a resulted in higher net power output and cycle efficiency than pure R245fa. Jung et al. [55] presented the results from an experimental and numerical analyses of a mixture ORC. The heat source was the exhaust gas from a 30 kW gas turbine.

Yang et al. [56, 57] analysed the use of zeotropic mixtures for WHR from the exhaust of a diesel engine. The heat source (i.e. the diesel engine exhaust) parameters at various engine operating conditions were measured experimentally. These parameters were then used to numerically evaluate the ORC performance. Zhou et al. [58] analysed the performance of using zeotropic mixtures for WHR from the exhaust of an internal combustion engine using a dual-loop system with two bottoming cycles as shown in Fig. 6. The top loop uses water as the working fluid while the bottom loop uses a zeotropic mixture. Shu et al. [59] investigated the use of hydrocarbon mixtures for WHR from the exhaust of an engine. Since hydrocarbons are flammable, retardants were added to form a hydrocarbon-retardant mixture as the working fluid. The results indicated at the presence of different optimal mixture compositions for highest cycle efficiencies at different evaporation temperatures. A similar study with two hydrocarbon-retardant mixtures was also carried out by Song and Gu [60]. The results indicated higher net power output by up to 13.3 % when using mixtures as compared with pure cyclohexane.

Braimakis et al. [61] compared several natural refrigerants and their mixtures for use in an ORC power system with heat source temperatures between 150 °C and 300 °C. The comparison included both subcritical and transcritical operation of the power cycle. The results suggested that it is possible to obtain different pure fluids, zeotropic mixtures, or different compositions of zeotropic mixtures resulting in the maximum exergy efficiency for the power cycle for different types and temperatures of the heat source. At the same time, the results indicated that the overall cycle exergy efficiency is also dependent on how well the cooling source in the condenser matches with the working fluid condensation temperature glide. The transcritical ORC configuration was found to be justifiable only when the critical temperature of the working fluid was significantly lower than the heat source temperature. Lee et al. [62] presented the design and optimization of a mixture ORC with a liquefied natural gas (LNG) heat sink. The performance of ternary fluid mixtures was analysed in this study.

2.4. Other studies

The studies presented in this section have been conducted assuming a generic heat source for a wide range of heat source temperatures (between around 25 °C and 300 °C) and plant capacities (between around 1 kW and 7.5 MW). The various mixtures have been evaluated based on energy, exergy, and economic analyses. Various atypical plant configurations such as the split-cycle, cascade power cycle, power cycle with pool boiling, and power cycle with partial evaporation have also been investigated. The simultaneous optimization of the power cycle with the working fluid composition has also been proposed. Table 4 shows an overview of these generic studies with their details presented in the following text. In the studies where comparisons were made between the use of pure fluids and fluid mixtures, Table 4 presents the details corresponding to the mixture analysis.

Table 4: Studies with generic ORC power systems. T_{hs} is the heat source temperature and T_{cs} is the cooling medium temperature. A '-' instead of the value indicates unavailable data.

Reference	T_{hs} (°C)	T_{cs} (°C)	Capacity (kW)	Considered mixtures	Remarks
Chys et al. [63]	150-250	25-35	109.5-293.1	Various mixture combinations of R245fa, R364mfc, R600a, R601, R601a, hexane, cyclohexane, and isohexane, and of MM and MDM	Comparison of mixtures between low and high heat supply temperatures
Aghahosseini and Dincer [64]	150-200	25[‡]	100	R404a, R407c	Energy and exergy analyses
Lecompte et al. [65]	120-160	20	1570-1980	R245fa/R365mfc, R245fa/R601, R600a/R601a, R601/hexane, R601a/hexane, R601a/cyclohexane, R601a/isohexane	Exergy analysis
Zhao and Bao [66]	125-185	20	85-360	R227ea/R236ea, R227ea/R236fa, R227ea/R245ca, R227ea/R245fa, R236ea/R236fa, R236ea/R245ca, R236ea/R245fa, R236fa/R245ca, R236fa/R245fa, R245ca/R245fa	Analysis based on net power output
Luo et al. [67]	120-280	15	18-153	Binary mixture combinations of various pure fluids from the REFPROP database	Low global warming potential fluids
Wu et al. [68]	120	25	4100-5100	RC318/R245fa, R227ea/R245fa, R245fa/R600	Thermal and economic analysis

Xi et al. [69]	100-180	35‡	30-250	R245fa/R601, R245fa/R601a, R245fa/butene, R245fa/cisbutene	Economic evaluation and optimization
Andreasen et al. [70]	90-120	15	400-1500	Binary mixture combinations of various pure fluids from the REFPROP database	Generic methodology with working fluid as optimization parameter
Andreasen et al. [71]	90	15	50-600	R134a/R32 (0.35/0.65 mole fraction)	Multi-objective optimization
Deethayat et al. [72]	115	27	46-50	R152a/R245fa	Analysis based on first and second law efficiencies
Deethayat et al. [73]	80-130†	25-40‡	16	R152a/R245ca, R152a/R245fa, R227ea/R245ca, R227ea/R245fa, R236ea/R245ca, R236ea/R245fa	Analysis based on figure of merit
Dong et al. [74]	250-300	30-80	4.8-15.2	MDM/MM	Analysis based on first law efficiency
Guo et al. [75]	95-200	20-32	-	Binary mixture combinations using R134a, R227ea, R236ea, R245fa, R290, R600, R600a, R601, and R601a	Comparison of pure and mixture working fluids
Collings et al. [76]	100	-	1000	R134a/R245fa	Dynamic analysis with air-cooled condenser
Yoon et al. [77]	26	5	20	R152a/R32	Power cycle configuration with vapour-liquid ejector

Kim et al. [78]	25-85	-161^{*}	-	R14/R170, R14/R290, R14/R600, R14/R600a, R170/R600, R170/R600a, R170/R601, R290/R601, R50/R600, R50/R600a, R50/R601	Cascade power cycle configuration
Andreasen et al. [79]	90-120	15	400-1250	Binary mixture combinations using R290, R600, R600a, R601, and R601a	Orgaic split-cycle
Chen et al. [80]	120-200	20-30	-	Binary mixture combinations of several refrigerants	Transcritical ORC power system
Dai et al. [81]	120-240†	10-60‡	10-50	CO_2/R1234yf, CO_2/R1234ze, CO_2/R1270, CO_2/R134a, CO_2/R152a, CO_2/R161, CO_2/R32	Transcritical ORC power system
Pan et al. [82]	200	40‡	100-360	CO_2/R290	Transcritical ORC power system
Rajabloo et al. [83]	167/300	47/90‡	1300-3100	Various binary mixture combinations using either hydrocarbons or siloxanes	Pool boiling feasibility analysis
Liu et al. [84]	140-300	20-70	29-36	R600/R601, R600/R601a, R600a/R601, R600a/R601a, octane/decane, nonane/decane, MDM/MD_2M	Effect of condensation temperature glide
Zhou et al. [85]	120	25	3.5-6.5	R227ea/R245fa	Partial evaporation
Abadi et al. [86]	80-120	12-26	1$^{\diamond}$	R134a/R245fa (0.4/0.6 mole fraction)	Experimental analysis
Wang et al. [87]	90-135	-	1	R600a/R601a	Experimental analysis

Molina-Thierry and Flores-Tlacuahuac [88]	90-150	30	400-7500	Study on identification of mixture components and composition	Simultaneous mixture composition and power cycle design

* LNG heat sink.

◇ Expander capacity.

† Expander inlet temperature.

‡ Working fluid condenser outlet temperature.

Chys et al. [63] assessed the potential of using zeotropic mixtures in ORC power systems. The results indicated that the advantage of using zeotropic mixtures as working fluids is more prominent with low temperature heat sources than with high temperature ones. Aghahosseini and Dincer [64] presented the results from a comparative analysis between using pure and mixed working fluids in an ORC power system through energy and exergy analyses. Lecompte et al. [65] also presented the exergy analysis of using zeotropic mixtures as working fluids in subcritical ORCs. The optimization objective was to maximize the second law efficiency of the power cycle. The results suggested an improvement in the second law efficiency with mixed working fluids as compared with the pure fluids. Zhao and Bao [66] presented a thermodynamic analysis of a mixture ORC. The results indicated at the presence of an optimal evaporating temperature resulting in the highest net power output. Luo et al. [67] evaluated the use of low global warming potential fluids in ORC power systems. The performance of both pure fluids and their mixtures was investigated. Wu et al. [68] performed thermal and economic analyses of mixture ORCs. The results suggested that the use of mixtures results in higher first and second law efficiencies and net power output from the plant than the use of pure working fluids, but at the same time the mixtures have a lower economic performance because of larger heat exchanger area requirements. The optimal mixture compositions were those where the temperature glide of the mixture was the closest to the temperature rise of the cooling water in the condenser. Xi et al. [69] presented an economic evaluation and optimization of an ORC power system with several mixtures using R245fa as a flame retardant. The mixtures were found to result in lower electricity production costs than their corresponding pure fluid components, mainly because of the lower capital investment cost for the evaporator.

Andreasen et al. [70, 71] optimized the ORC power systems using pure and mixed working fluids for the utilization of low grade heat. A generic methodology was proposed where the working fluid was included as an optimization parameter in the numerical model. The optimization results indicated that the use of mixtures could increase the net power output from the plant [70]. In the multi-objective optimization with the simultaneous maximization of net power output and the minimization of ORC unit investment cost, the mixture ORC faired better than the ORCs with the constituent pure fluids as the cycle working fluid with 3.4 % higher net power output at the same total investment cost [71]. Deethayat et al. [72, 73] presented the results from a performance analysis of mixture ORCs with and without a recuperator based on first and second law efficiencies [72] and figure of merit [73]. Dong et al. [74] analysed the use of zeotropic mixtures in a high temperature ORC power system with a recuperator. The results demonstrated that the use of zeotropic mixtures resulted in higher first law efficiency than the constituent pure fluids. Guo et al. [75] presented the comparison of various pure and mixed working fluids for the utilization of low temperature heat sources. The results indicated that the mixed working fluids performed better with lower heat source temperature and higher temperature gradients for both the heat source and the heat sink. Pure fluids performed better when the conditions were reversed.

Collings et al. [76] dynamically analysed a mixture ORC power system with an air-cooled condenser. The ORC unit included an additional composition control system which allowed it to operate with varying working fluid composition to suit the ambient conditions. Yoon et al. [77] presented the performance analysis of a mixture power cycle using a vapour-liquid ejector and two expanders for ocean thermal energy conversion (OTEC) applications. The optimal fluid composition for maximum cycle efficiency was determined. For a similar application, Kim et al. [78] presented the design and optimization of a cascade ORC power system with sea water as the heat source and LNG as the heat sink. Andreasen et al. [79] presented the design and optimization of an organic split-cycle as shown in Fig. 7 with an improved boiling process. The results suggested that the use of the organic split-cycle resulted in a higher net power output for lower values of heat source temperature, but this performance improvement came at the cost of significant increase in the cycle complexity. Chen et al. [80] analysed a transcritical mixture ORC for the conversion of low grade heat into power. The transcritical ORC with mixtures resulted in 10 % to 30 % higher cycle efficiency values than the subcritical ORC. Dai et al. [81] analysed transcritical power cycles with mixtures including CO_2 as one of the components. A similar cycle was also studied by Pan et al. [82] where the optimal values of net power output and cycle efficiency at various supercritical heating pressures were presented.

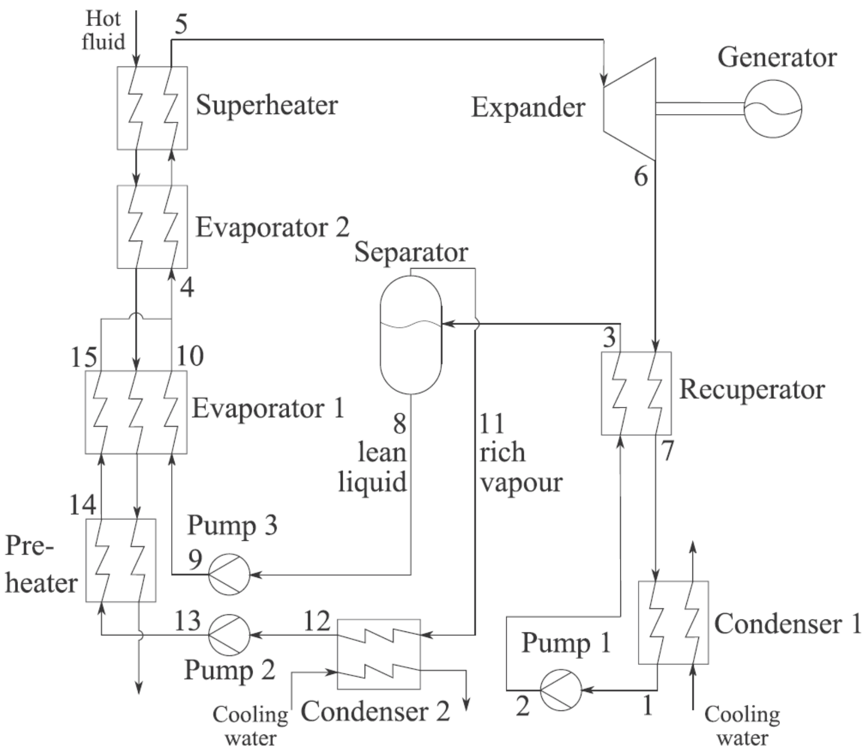


Figure 7: Organic split-cycle for mixtures [79].

Among other studies, Rajabloo et al. [83] assessed the feasibility of using pool boiling with mixture ORCs for geothermal power generation ($T_{\mathrm{hs}} = 167$ °C) and biomass combustion based power generation ($T_{\mathrm{hs}} = 300$ °C). The results suggested that the plant configuration with pool boiling showed lower, but comparable thermodynamic performance as the plant configuration with a once-through evaporator. However, since the plant performance did not significantly deteriorate with pool boiling, it could be considered as a feasible alternative because of easier control. Liu et al. [84] analysed the effect of condensation temperature glide on the performance of mixture ORCs with geothermal water or biomass as the heat source. A method to determine the optimal condensation pressure was presented. Zhou et al. [85] analysed an ORC with partial evaporation, i.e. the expander received a stream in two-phase flow. The results indicated that the optimized partial evaporation ORC configuration produced 24.7 % more power than the subcritical ORC configuration. Abadi et al. [86] presented the experimental study of a mixture ORC. The results suggested that a higher net power output by about 50 % to 75 % was achievable using the mixture as compared with the pure working fluid for heat source temperatures between 80 °C and 100 °C. In another experimental analysis [89], the influence of the various operation parameters on the mixture composition shift, i.e. the difference between the charge composition and the circulating composition of the working fluid, was presented. The results indicated at an increase in the circulating composition as compared with the charge composition with increasing mass flow rate of the heat source, feed pump frequency, and length of the evaporator, and with decreasing cooling medium temperature. Wang et al. [87] presented the results from an experimental study quantifying the effect of varying the heat source temperature on the cycle output. Studies with simultaneous design of optimal mixtures and the power cycle have also been carried out [88, 90]. These studies focused primarily on the molecular design of the various compounds to be used in the power cycle as working fluids.

3. Ammonia-water power systems

Among the various investigated mixtures, the ammonia-water mixture has been studied more than any other mixture and for a wide range of operating conditions. The ammonia-water mixture has been studied particularly for two different power cycle configurations. These are the ammonia-water Rankine cycle and the Kalina cycle. The key difference between these two cycles is that in the Kalina cycle, it is possible to have different fluid compositions for different streams within the cycle by employing vapour-liquid separators. In contrast, the ammonia-water Rankine cycle has a similar layout as the ORC but with ammonia-water mixture as the cycle working fluid. In this case, the composition of the working fluid remains the same everywhere in the cycle. As the research on the Kalina cycle was reviewed some years ago by Zhang et al. [91], only the publications since then are discussed in this paper.

3.1. Ammonia-water Rankine cycle power systems

The studies with the ammonia-water Rankine cycle power systems have been conducted typically for moderate values of heat source temperature (between around 120 °C and 330 °C) and a wide range of plant capacities (between around 30 kW and 1.3 MW). In addition to the usual energy and exergy analyses, the publications also included parametric studies, exergoeconomic analysis, and thermodynamic optimizations. Table 5 shows an overview of these studies while their details are presented in the following text. An ammonia-water Rankine cycle with and without a recuperator is shown in Fig. 8. In the studies where comparisons were made between the ammonia-water Rankine cycle and other power cycles, Table 5 presents the details corresponding to the ammonia-water Rankine cycle.

Table 5: Studies with ammonia-water Rankine cycle power systems. T_{hs} is the heat source temperature and T_{cs} is the cooling medium temperature. A '-' instead of the value indicates unavailable data.

Reference	Application	T_{hs} (°C)	T_{cs} (°C)	Capacity (kW)	Remarks
Mohammadkhani et al. [92]	Generic	180	15	-	Exergoeconomic analysis
Koroneos and Rovas [93]	Geothermal	120	20	$737.5^{\diamond}$	Exergy analysis
Kim et al. [94, 95]	WHR	180	15	-	Energy and exergy analyses, variation in working fluid composition
Kim et al. [96, 97]	WHR	200	$-20\text{-}40^{*,\ddagger}$	32	Energy and exergy analyses
Wang et al. [98]	WHR	200	-159.35^{*}	389.4	Parametric study and thermodynamic optimization
Pierobon and Rokni [99]	WHR	$250^{\dagger}$	$25^{\ddagger}$	1130-1290	Thermodynamic analysis
Khankari and Karmakar [100]	WHR	$121\text{-}198^{\dagger}$	25	412-832	Parametric study and thermodynamic analysis

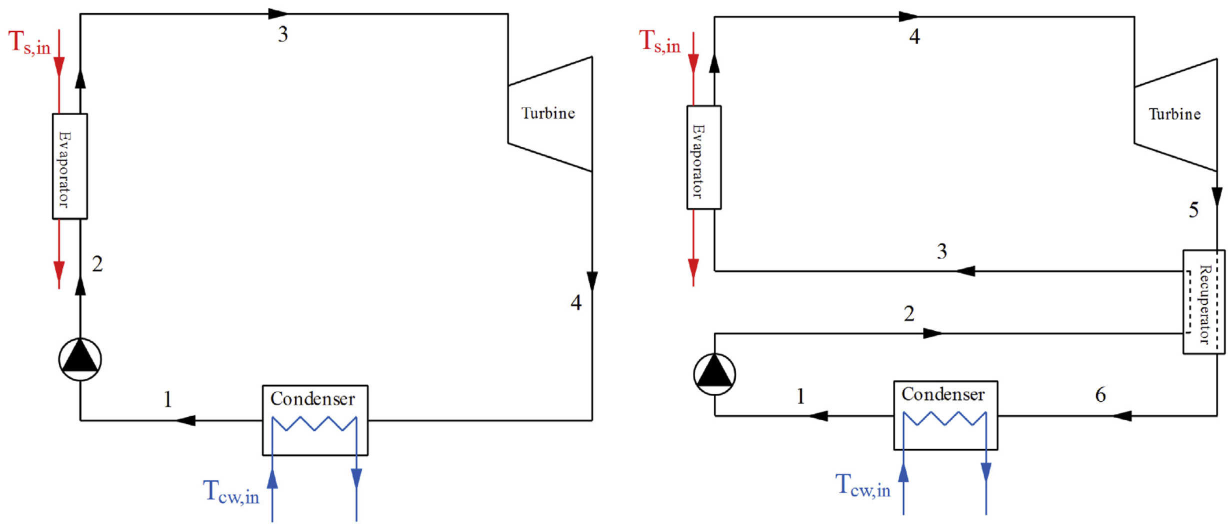
Wang et al. [101]	WHR	327	5-55‡	-	Feasibility study of using ammonia-water power cycles
Mohtaram et al. [102]	WHR	304	25	-	Parametric study

* LNG heat sink.

◇ Expander capacity.

† Expander inlet temperature.

‡ Working fluid condenser outlet temperature.



(a) Without recuperator. (b) With recuperator.

Figure 8: Ammonia-water Rankine cycle [92]. $T_{\mathrm{s,in}}$ is the heat source inlet temperature and $T_{\mathrm{cw,in}}$ is the cooling medium inlet temperature.

Mohammadkhani et al. [92] presented an exergoeconomic comparison between ammonia-water Rankine cycle power systems with and without a recuperator. The results indicated that unlike the results from the energy and exergy analyses, the ammonia-water Rankine cycle power system without the recuperator performs better in an exergoeconomic analysis than the ammonia-water Rankine cycle power system with a recuperator. Among various cycle parameters, the working fluid composition was found to affect the exergoeconomic performance of the power cycles most significantly. The results also indicated that with increasing ammonia mass fraction in the working fluid, the rates of exergy destruction in the heat exchangers increased because of the larger mean temperature difference. Koroneos and Rovas [93] presented an exergy analysis of a geothermal power plant where the fluid at the geothermal turbine outlet is used as the heat source to the ammonia-water mixture in an ammonia-water Rankine cycle unit. Kim et al. [94, 95] presented a comparison between the ammonia-water Rankine cycles with and without a recuperator through energy and exergy analyses. The effect of varying the working fluid composition on the thermodynamic performance of the cycles was also examined. The results indicated that the ammonia-water Rankine cycle with a recuperator resulted in better thermal and exergy efficiencies than the ammonia-water Rankine cycle without the recuperator.

A few studies have also investigated the performance of an ammonia-water Rankine cycle power system with heat rejection to a heat sink using LNG as the cooling medium. Kim et al. [96, 97] presented the energy and exergy analyses of a combined ammonia-water Rankine and LNG bottoming cycle power plant as shown in Fig. 9. In this plant, the heat source for the ammonia-water Rankine cycle is waste heat, while the heat rejection takes place in a condenser with LNG as the cooling medium. The results indicated that the cycle performance is most significantly influenced by the working fluid composition. Wang et al. [98] presented the effects of varying the turbine inlet pressure, temperature, and ammonia mass fraction, and the minimum pinch point and the approach temperature differences in the heat recovery vapour generator on the cycle performance. A thermodynamic optimization for the ammonia-water Rankine cycle unit with LNG heat sink was performed with three objective functions: maximize exergy efficiency and minimize the total heat transfer capability and the turbine size parameter. Pierobon and Rokni [99] presented an analysis of a hybrid plant with a gasification system, solid oxide fuel cell, and an ammonia-water Rankine cycle unit with a recuperator. The gasifier converts wood chips to syngas which is then used to operate the fuel cell. The excess heat from the fuel cell serves as the heat source for the ammonia-water Rankine cycle unit.

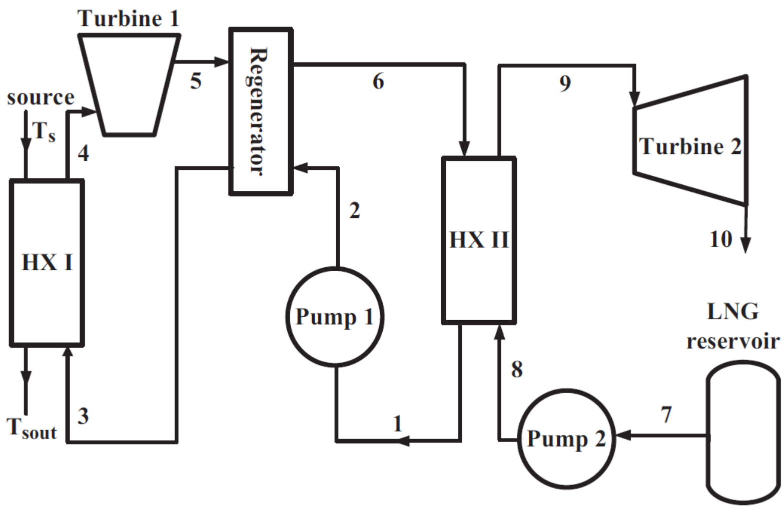


Figure 9: Ammonia-water Rankine cycle unit with a bottoming LNG power cycle [96]. T_s is the heat source inlet temperature and T_{sout} is the heat source outlet temperature from the heat exchanger HX I.

Khankari and Karmakar [100] presented an analysis of possible power generation from coal mill rejection. Various turbine inlet conditions were examined in the study. The results suggested that the payback period for installing such a power generation system would be about 5.5 years with 80 % plant availability factor and 100 % plant load factor. Wang et al. [101] developed a code for the estimation of the thermodynamic properties of the ammonia-water mixture and used this code to assess the possibility of using an ammonia-water Rankine cycle in a pressurized water reactor nuclear power plant. A comparison was made between the performances of the ammonia-water Rankine cycles with and without a recuperator and a flash Kalina cycle. The results suggested that the flash Kalina cycle could attain a thermal efficiency of 34.8 % but with a more complex cycle layout, whereas a slightly lower cycle efficiency of 31.2 % may be attained with a much simpler ammonia-water Rankine cycle with recuperator. Momeni et al. [103] presented the results from the thermoeconomic optimization of a three stage combined cycle power plant with a gas turbine on top, a steam Rankine cycle in the middle, and an ammonia-water Rankine cycle at the bottom. The simultaneous maximization of the exergy efficiency and minimization of the total cost rate was the optimization objective. Mohtaram et al. [102] presented the results from the evaluation of the effect of varying the compressor pressure ratio in a combined cycle power plant with an ammonia-water Rankine cycle or a simple steam Rankine cycle as the bottoming cycle.

3.2. Solar energy based Kalina cycle power systems

The studies on solar energy based Kalina cycle power systems have been conducted with both low and high temperature Kalina cycle configurations, depending on the type of solar collectors. The plants have been investigated using energy and exergy analyses, parametric studies, and thermoeconomic optimizations. Table 6 shows an overview of these studies with their details presented in the following text. These include the use of a Kalina cycle unit with both non-concentrating and concentrating solar collectors. In the studies where comparisons were made between the Kalina cycle and other power cycles, Table 6 presents the details corresponding to the Kalina cycle.

Table 6: Studies with solar energy based Kalina cycle power systems. T_{hs} is the heat source temperature and T_{cs} is the cooling medium temperature. A '-' instead of the value indicates unavailable data.

Reference	T_{hs} (°C)	T_{cs} (°C)	Capacity (kW)	Remarks
Sun et al. [104, 105]	60-76	4-4.5	-	Energy and exergy analyses and optimization
Shankar Ganesh and Srinivas [106]	130-150	30	-	Parametric and cycle configuration studies
Shankar Ganesh and Srinivas [107]	190-225	25	-	Parametric study and exergy analysis
Shankar Ganesh and Srinivas [108]	500	$35^{\ddagger}$	-	Parametric study and exergy analysis
Ashouri et al. [109]	$90\text{-}108^{\dagger}$	-	-	Techno-economic analysis, estimation of annual solar fraction and LCOE
Boyaghchi and Sabaghian [110]	120	5	1800-2300	Multi-objective optimization
Knudsen et al. [111]	$550^{\dagger}$	30	-	Energy and exergy analyses

Modi et al. [112, 113]	450[†]	20	25 000[§]	Feasibility study through energy and exergy analyses
Modi et al. [114–116]	500[†]	20	20 000	Part-load performance analysis, thermoeconomic optimization

[†] Expander inlet temperature.

[‡] Working fluid condenser outlet temperature.

[§] Heat input to the power cycle.

Sun et al. [104, 105] presented the energy and exergy analyses and optimization of a solar-boosted Kalina cycle power system (KCS-11 layout). The use of compound parabolic collectors and an auxiliary superheater in order to increase the turbine inlet temperature was analysed for the climatic conditions of Japan. The use of compound parabolic collectors with a Kalina cycle power system was also studied by Wang et al. [117]. In their layout, they also had a thermal storage tank and an auxiliary heater as shown in Fig. 10. The Kalina cycle unit had two separators and the analysis was conducted for the climatic conditions of China. The results indicated that the net power output and the cycle efficiency were less sensitive to the turbine inlet temperature and an optimal turbine inlet pressure and basic solution ammonia mass fraction may be obtained depending on whether the net power output or the maximum cycle efficiency is the optimization objective. The presence of the thermal storage system enabled the plant to operate in a continuous and stable manner. Astaraei et al. [118] presented an analysis of a solar-driven Kalina cycle power system with an auxiliary heater for satisfying the electricity demands of high-rise buildings in Iran. Flat plat solar collectors were used in the investigated plant. The results suggested that in five provinces of Iran, the solar Kalina plant could generate more electricity than the potential demand.

Shankar Ganesh and Srinivas [106–108] presented an analysis of Kalina cycles with a parabolic trough solar field with different operating temperatures. For a low temperature operation, different positioning of the recuperators within the Kalina cycle was in-

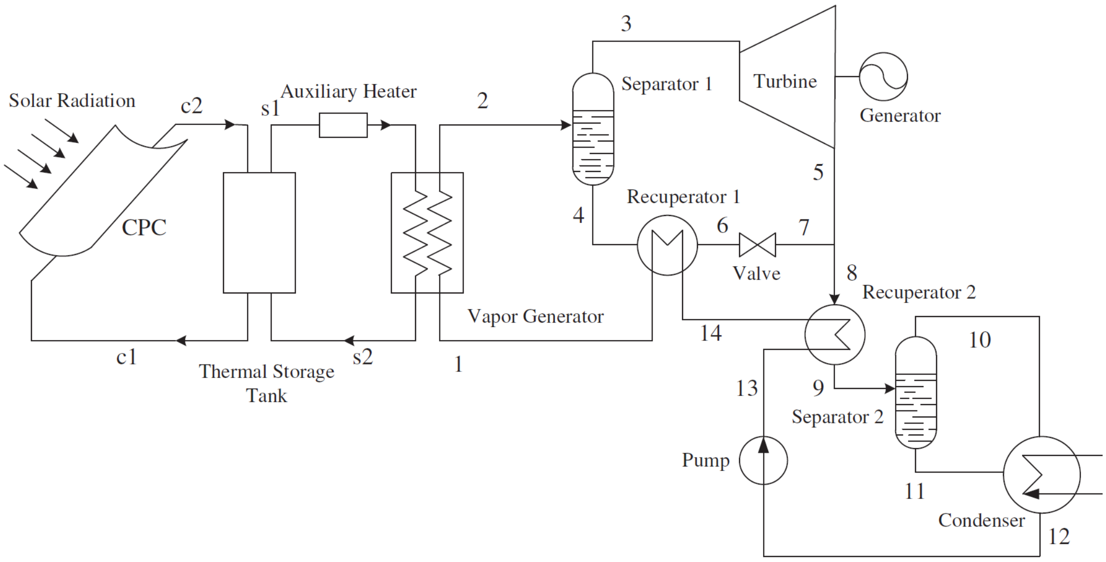


Figure 10: Low temperature solar energy based Kalina cycle power system [117]. ‘CPC’ implies compound parabolic collectors.

vestigated [106]. Exergy analysis was also conducted for the analysed Kalina cycle layouts [107, 108]. Among the Kalina cycle components, the highest rates of exergy destruction were for the turbine and the heat recovery vapour generator. Ashouri et al. [109] presented a techno-economic assessment of a Kalina cycle unit operating with a parabolic trough solar field for the climatic conditions of Iran. The annual solar fraction and LCOE for the power plant were estimated along with the potential savings in the use of fossil fuel. The results suggested that the presence of thermal storage and an auxiliary heater reduced the temperature fluctuations in the Kalina cycle operation, and that the highest rates of exergy destruction occurred in the solar field and the vapour generator. Boyaghchi and Sabaghian [110] presented a multi-objective optimization of a Kalina cycle unit with parabolic trough solar field using the genetic algorithm. The three objectives for the optimization were the maximization of the energy efficiency and the exergy efficiency, and the minimization of the total capital investment cost. Among the considered decision variables, the evaporator outlet temperature influenced the results most significantly.

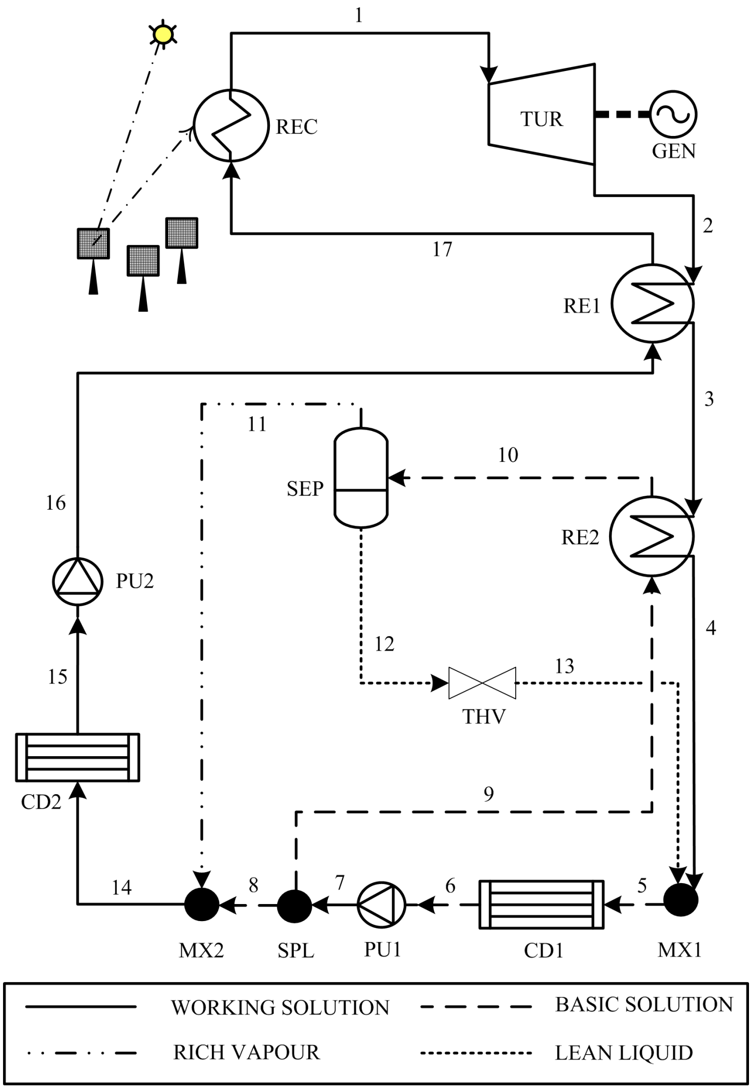


Figure 11: High temperature Kalina cycle KC12 for a central receiver concentrating solar power plant with direct steam generation [114]. In the layout, REC is the receiver/boiler, TUR is the turbine, GEN is the generator, SEP is the vapour-liquid separator, RE$*$ is the recuperator, PU$*$ is the pump, CD$*$ is the condenser, MX$*$ is the mixer (where '$*$' denotes the respective component number), SPL is the splitter, and THV is the throttling valve.

The layout for a high temperature Kalina cycle differs significantly from that of a low temperature Kalina cycle. An example of a Kalina cycle for a high temperature central receiver concentrating solar power plant with direct steam generation is shown in Fig. 11. Knudsen et al. [111] presented the energy and exergy analyses of a Kalina cycle unit with direct steam generation that could be operated with either a parabolic trough or a central receiver solar field. Modi et al. [112, 113] assessed the possibility of using a Kalina cycle unit in a central receiver concentrating solar power plant through energy and exergy analyses. The results indicated that the highest rate of exergy destruction in the power cycle occurs in the receiver/boiler. The study was continued with a full thermoeconomic optimization [114, 119] with the minimization of LCOE as the objective function by combining the detailed thermodynamic design [115] and the part-load models [116] in order to evaluate the cycle performance over a year. The results suggested that a Kalina cycle power system without storage cannot compete with the state-of-the-art steam Rankine cycle power system for high temperature solar power applications when considering both the thermodynamic and the economic aspects.

3.3. Geothermal heat based Kalina cycle power systems

The studies on geothermal heat based Kalina cycle power systems have been conducted with heat source temperatures between around 100 °C and 180 °C and for plant capacities between around 6 kW and 6.3 MW. The plants have been analysed based on their energy and exergy efficiencies, part-load performances, and economic feasibility. The performance of the Kalina cycle power systems have also been compared to that of the ORC power systems. Table 7 shows an overview of these studies with their details presented in the following text. In the studies where comparisons were made between the Kalina cycle and other power cycles, Table 7 presents the details corresponding to the Kalina cycle.

Table 7: Studies with geothermal heat based Kalina cycle power systems. T_{hs} is the heat source temperature and T_{cs} is the cooling medium temperature. A '-' instead of the value indicates unavailable data.

Reference	T_{hs} (°C)	T_{cs} (°C)	Capacity (kW)	Remarks
Campos Rodríguez et al. [120]	100	25	1444-1756	Exergy and economic analyses, comparison with ORC power system
Walraven et al. [121]	100-150	15-30	-	Exergy analysis

Li and Dai [122]	120-132	17	139-200	Thermoeconomic performance analysis
Coskun et al. [123, 124]	140-180	18	5900-6300	Analysis based on net power output and first and second law efficiencies
Shokati et al. [125]	175	30[‡]	1600-4600	Exergoeconomic analysis and optimization
Mergner and Weimer [126]	120	13	6-8.5	Analysis with different cycle configurations
Arslan [127]	130[†]	22[‡]	-	Optimization and life cycle cost analysis
Saffari et al. [128]	124	5	1962-2216	Thermodynamic analysis and optimization with energy and exergy efficiencies
Wang et al. [129]	151.8	30[‡]	263.6	Thermodynamic analysis and optimization with cycle efficiency
Fallah et al. [130]	100	25	1672	Advanced exergy analysis
Li et al. [131]	116-128	0-35	1100-2700	Off-design performance analysis
Wang and Yu [132]	120	-	500-2000	Working fluid composition variation following the ambient conditions

† Expander inlet temperature.

‡ Working fluid condenser outlet temperature.

Campos Rodríguez et al. [120] presented a comparison of a Kalina cycle and an ORC with 15 pure fluids for a geothermal plant in Brazil based on exergy and economic parameters. The optimal Kalina cycle configuration resulted in 17.8 % lower LCOE value than the optimal ORC configuration. A comparison between the Kalina cycle and various ORC configurations was also presented by Walraven et al. [121]. Both subcritical and transcritical ORC configurations using about 80 pure working fluids were compared with the Kalina cycle on the basis of cycle exergy efficiency. The results indicated that for geothermal fluid temperatures around 70 °C, the Kalina cycle and the various ORCs perform similarly, but for all other considered heat source temperatures, the ORCs performed better. Li and Dai [122] compared the thermoeconomic performances of a Kalina cycle and a transcritical CO_2 power cycle for operation in China. The results indicated that the Kalina cycle performed better than the transcritical CO_2 power cycle from both the thermodynamic (net power output and thermal efficiency) and the economic (specific investment cost) aspects.

Coskun et al. [123, 124] presented a comparison of double flash, binary, combined flash/binary, and Kalina cycle power systems for medium temperature geothermal plants in Turkey. The results suggested that the Kalina cycle resulted in the maximum power output and the highest first law and second law efficiencies among the compared cycles. When comparing the capital investment costs for producing a unit amount of electricity, the Kalina and the double flash cycle power systems had similar costs which were the lowest among the compared alternatives. Shokati et al. [125] presented the exergoeconomic analysis and optimization based comparison of a Kalina cycle power system and basic, dual-fluid, and dual-pressure ORC power systems. The various power cycle systems were optimized for maximizing the produced electrical power while simultaneously minimizing the unit cost of the produced power. Among the considered alternatives, the dual-pressure ORC power system resulted in the maximum electrical power produced while the Kalina cycle power system resulted in the minimum cost of the produced power in their respective optimum operating states. From the exergoeconomic perspective, the turbines in the various power cycle systems resulted in the maximum cost rates, therefore these need to be paid more attention to while designing the plants. Mergner and Weimer [126] presented a comparison between the performances of two layouts for a geothermal Kalina cycle power system. The first one is the KCS-34 layout and the second one is a layout based on a Siemens patent (termed as 'KC SG1' in the paper). The main difference between the two layouts is the positioning of the internal heat recovery recuperator. The results indicated that the KC SG1

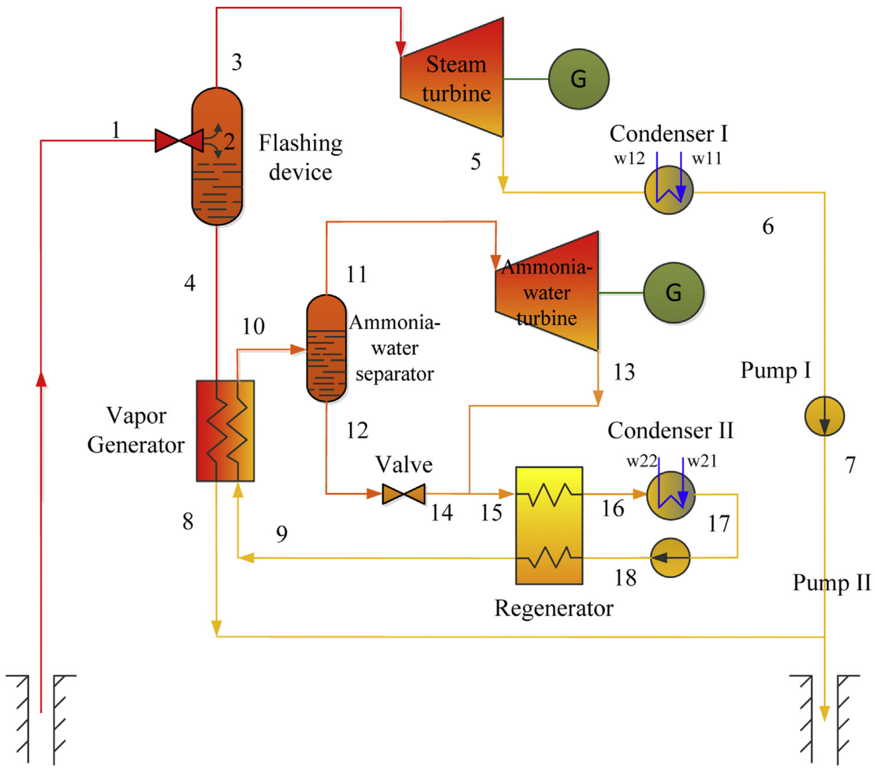


Figure 12: Flash-binary geothermal power plant with a Kalina cycle unit [129].

layout performed slightly better than the KCS-34 layout in terms of cycle efficiency.

Among other studies, Arslan [127] optimized a Kalina cycle power system (KCS-34) for use with medium temperature geothermal sources in Turkey using artificial neural networks. A life cycle cost analysis was also presented. Similarly, Saffari et al. [128] presented the thermodynamic analysis and optimization of a geothermal Kalina cycle power system located in Iceland using an artificial bee colony algorithm. The optimization objectives were to maximize the cycle thermal and exergy efficiencies. A parametric study indicated that the thermal and the exergy efficiencies for the cycle first increased and then decreased with increasing separator inlet temperature and pressure, basic ammonia mass fraction, and the mass flow rate of the working fluid. Wang et al. [129] presented the thermodynamic analysis and optimization of a flash-binary geothermal power plant where the liquid stream from the geothermal flash separator was used as a heat source to the Kalina cycle working fluid. The plant layout is shown in Fig. 12. The results indicated at the presence of an optimal flash pressure and optimal ammonia-water turbine inlet pressure and temperature in order to obtain the highest overall plant efficiency. Fallah et al. [130] investigated a geothermal Kalina cycle power system using advanced exergy analysis. The results suggested to focus on the performance of the condenser, the turbine, and the evaporator from the advanced exergy perspective. The off-design performance analysis of a low temperature geothermal Kalina cycle power system was presented by Li et al. [131]. A sliding pressure strategy was used in order to operate the cycle with varying geothermal source mass flow rate and temperature and the cooling medium inlet temperature. The results indicated that the speed adjustment of the working fluid pump for the sliding pressure operation is more sensitive to the heat source temperature than to the heat sink temperature. However, the heat sink temperature affects the net power output and thermal efficiency of the plant more than the heat source temperature. Wang and Yu [132] analysed a Kalina cycle layout with the possibility to adjust the working fluid composition to suit the ambient (i.e. cooling medium) conditions.

3.4. Waste/Exhaust heat recovery Kalina cycle power systems

The studies analysing Kalina cycle power systems for WHR applications have been conducted for a wide range of heat source temperatures (between around 35 °C and 440 °C) and plant capacities (between around 2 kW and 25 MW). Heat recovery possibility from a variety of heat sources has been investigated. The publications include energy, exergy, and exergoeconomic analyses, parametric studies, thermoeconomic analysis and optimizations, and comparison with ORC power systems. Some atypical configurations such as the Kalina split-cycle and dual pressure cycle have also been investigated. Table 8 shows an overview of these studies with their details presented in the following text. In the studies where comparisons were made between the Kalina cycle and other power cycles, Table 8 presents the details corresponding to the Kalina cycle.

Table 8: Studies with Kalina cycle power systems used for WHR applications. T_{hs} is the heat source temperature and T_{cs} is the cooling medium temperature. A '-' instead of the value indicates unavailable data.

Reference	T_{hs} (°C)	T_{cs} (°C)	Capacity (kW)	Remarks

Matsuda [133]	120	25	3300	Thermal performance analysis
Yue et al. [134]	439	20	10-217	Net power output at various engine loads
Rezaee and Houshmand [135]	-	-	46.9	Energy and exergy analyses
Gholamian and Zare [136]	246	28‡	11.8	Analysis based on net power output
Chew et al. [137]	36-176	30-45	1310	Thermodynamic comparison with ORCs and heat pumps
Nemati et al. [138]	156	25	600-1000	Analysis based on exergy efficiency
Singh and Kaushik [139, 140]	134.3	32.5	600	Energy and exergy analyses, exergoeconomic optimization
Singh and Kaushik [141, 142]	119-124	38‡	4300	Thermoeconomic analysis
Momeni and Shokouhmand [143]	120-389	27	2700-8600	Analysis based on net power output and first law efficiency
Mahmoudi et al. [144]	136	25	18 500-24 900	Thermoeconomic analysis
Peng et al. [145, 146]	156†	24‡	-	Energy and exergy analyses
Zhao et al. [147]	345.7	30‡	25 401	Analysis based on second law efficiency
Li et al. [148]	105-150	35‡	2-40	Thermoeconomic analysis
Zare et al. [149, 150]	199.6	25	27 330-38 140	Thermodynamic and exergoeconomic analyses
Mahmoudi et al. [151]	214	25	32 300-53 250	Exergoeconomic analysis

Larsen et al. [152], Nguyen et al. [153]	346	25-40	1700-1900	Energy, exergy, and cost analyses for a Kalina split-cycle
Junye et al. [154], Hua et al. [155, 156]	225-350	25	-	Thermal performance analysis and optimization
Zhang et al. [157], Chen et al. [158]	250-340	15-25	470-500	Analysis with power generation and heating modes
Guo et al. [159]	350-400	25	900-1100	Analysis with a dual-pressure evaporation cycle configuration
Zhu et al. [160]	400	25	-	Analysis with a dual-pressure evaporation cycle configuration

† Expander inlet temperature.

‡ Working fluid condenser outlet temperature.

Matsuda [133] presented the thermal performance of a Kalina cycle unit for utilizing low grade heat from a refinery in Japan. Yue et al. [134] presented a comparison of a Kalina cycle and a transcritical ORC with pure fluids for exhaust heat recovery from an internal combustion engine. The net power output from the WHR cycles was calculated for different engine loads (20 % to 100 %). The results suggested that the transcritical ORC is advantageous because of a better overall WHR efficiency, low operation pressure, and simpler cycle configuration. Rezaee and Houshmand [135] presented the energy and exergy analyses of the KCS-11 Kalina cycle power system for WHR from a proton exchange membrane fuel cell. Gholamian and Zare [136] presented a comparison of the Kalina cycle and an ORC for WHR from a solid oxide fuel cell and gas turbine hybrid power plant. The heat input to the WHR power cycles came from the gas turbine exhaust. The results suggested that for this case, the ORC performed better than the Kalina cycle in terms of net power output using the given waste heat stream. Chew et al. [137] presented a comparison between using a Kalina cycle, an ORC, and heat pumps in order to improve the energy efficiency of dividing-wall distillation columns through WHR. The results indicated that for a waste heat temperature over 150 °C, the Kalina cycle and the ORC with cooling water as the heat sink are favoured over the heat pump based configurations. Nemati et al. [138] compared the thermodynamic performance of an ORC and a Kalina cycle for WHR from a cogeneration system. The results indicated that from an exergy efficiency perspective, the ORC performs about 0.2 percentage point better with much lower operating pressures (about 10 bar as compared with about 38 bar for the Kalina cycle).

Singh and Kaushik [139, 140] presented the energy analysis, exergy analysis, and exergoeconomic optimization of a Kalina cycle as a bottoming cycle to a coal-fired steam power plant. The KCS-11 layout was analysed in the study. The maximum rate of exergy destruction occurred in the Kalina cycle evaporator and an optimal ammonia mass fraction could be found for each turbine inlet pressure. The turbine had a low exergoeconomic factor, therefore the cycle performance may be improved by investing in a more efficient design. In a similar study, a Brayton-Rankine-Kalina combined triple power cycle using the KCS-34 layout for the Kalina cycle was evaluated from a thermoeconomic perspective [141, 142]. Momeni and Shokouhmand [143] presented a comparison between a Kalina cycle and an ammonia-water Rankine cycle as the bottoming cycle to a gas turbine and steam Rankine combined cycle power plant. The Brayton-Rankine-Kalina cycle power system resulted in lower first law efficiency and net power output than the combination with the ammonia-water Rankine cycle. Mahmoudi et al. [144] presented a thermoeconomic analysis of a combined supercritical CO_2 recompression Brayton-Kalina cycle power system. The proposed cycle resulted in up to 10 % higher exergy efficiency and up to 4.9 % lower product unit cost than the configuration without the Kalina cycle.

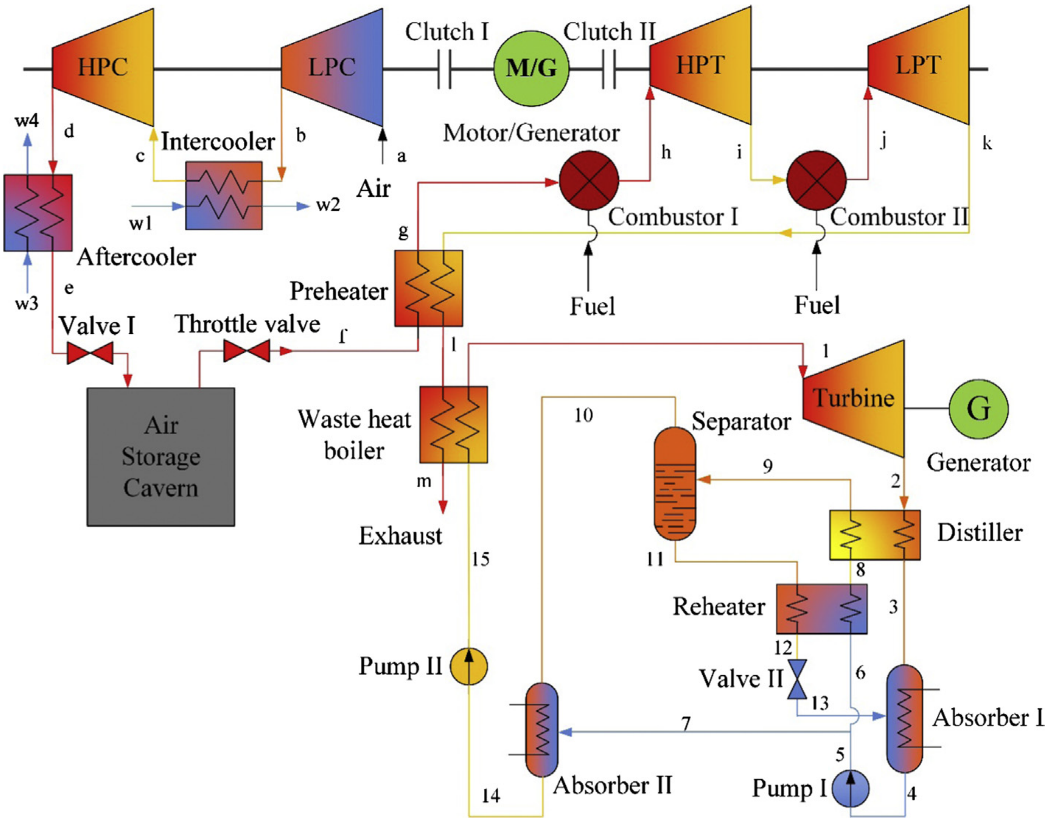


Figure 13: A gas turbine and Kalina cycle integrated power plant with a compressed air energy storage system [147]. 'HPC' is the high pressure compressor, 'LPC' is the low pressure compressor, 'HPT' is the high pressure turbine, and 'LPT' is the low pressure turbine.

Peng et al. [145, 146] presented the thermodynamic and exergy analyses of a solar gas turbine coupled with a Kalina bottoming cycle. The heat input to the Kalina cycle came from the compressor intercooling and the gas turbine exhaust air. One of the key advantages from this configuration as compared with a conventional solar tower power plant was that the proposed configuration had the potential to conserve about 69 % of the water consumption in the arid areas where such plants are most likely to be installed and operated. Zhao et al. [147] analysed a gas turbine and Kalina cycle integrated power plant with a compressed air energy storage system. The layout of this configuration is shown in Fig. 13 and includes the KCS-6 Kalina cycle configuration. The results indicated about a 4 percentage point increment in the second law efficiency for the proposed configuration as compared with a configuration without the Kalina cycle. Li et al. [148] presented the results from a thermoeconomic comparison between a Kalina cycle unit and an ORC unit operating with a compressed air energy storage system. The thermoeconomically optimal Kalina cycle unit resulted in a higher exergy efficiency than the corresponding ORC unit by about 6 percentage points. Zare et al. [149, 150] presented a thermodynamic comparison between a Kalina cycle unit and an ORC unit for WHR from a gas turbine modular helium reactor plant. They also presented the results from the exergoeconomic assessment of employing the Kalina cycle unit for this purpose. The results indicated that the configuration with the ORC unit had higher first and second law efficiencies than the configuration with the Kalina cycle unit. The ORC unit also required a lower operating pressure than the Kalina cycle unit. The results from the exergoeconomic analysis of a similar configuration were presented by Mahmoudi et al. [151].

The Kalina cycle power system has also been investigated in variations other than its standard layouts. Larsen et al. [152] presented the optimization and a simplified cost analysis of the Kalina split-cycle power system with primary focus on the boiler, the turbine, and the mixing system subsections of the cycle. They also compared the performance of a normal Kalina cycle power sytem to that of the Kalina split-cycle power system. Nguyen et al. [153] conducted an exergy analysis of the Kalina split-cycle power system. These studies [152, 153] concluded that the Kalina split-cycle power system with reheat was better than the normal Kalina cycle power system in terms of cycle efficiency but this improvement came at the price of increased capital investment cost and a more complex cycle design. Junye et al. [154] analysed the thermal performance of a modified Kalina cycle power system. The modification in the layout was the addition of a recuperative preheater and a water-cooled solution cooler in the cycle. The results indicated a higher power recovery through better recuperation within the cycle. In a continuation to this study, the cycle with the preheater, but without the solution cooler, was further optimized and analysed [155, 156]. The objectives were to maximize the power generation from the available waste heat and analyse the variable turbine inlet composition power regulation approach. Zhang et al. [157, 158] analysed a similar Kalina cycle layout but for possible operation either in power generation mode for non-heating season or in heating mode for heating season (as ammonia-water Rankine cycle). Guo et al. [159] also presented an analysis of a similar layout and compared its performance with that of a dual-pressure evaporation Kalina cycle power system. A similar comparative study was made by Zhu et al. [160] with a dual-pressure Kalina cycle layout with the second evaporator operating in parallel with the economizer.

3.5. Other studies

Table 9 shows an overview of some generic studies evaluating a Kalina cycle power system together with a study on a biomass-fired Kalina cycle power system. In the studies where comparisons were made between the Kalina cycle and other power cycles, Table 9 presents the details corresponding to the Kalina cycle. The generic studies have been conducted for a wide range of heat source temperatures (between around 60 °C and 400 °C) and plant capacities (between around 2 kW and 1.3 MW), while the biomass-fired Kalina cycle was evaluated for heat source temperatures between 300 °C and 525 °C and plant capacities between 450 kW and 610 kW. The details of these studies are presented in the following text.

Table 9: Other studies with power cycles using ammonia-water mixture as the working fluid. T_{hs} is the heat source temperature and T_{cs} is the cooling medium temperature. A '-' instead of the value indicates unavailable data.

Reference	T_{hs} (°C)	T_{cs} (°C)	Capacity (kW)	Remarks
Yari et al. [161]	120	$40^{\ddagger}$	600-1300	Exergoeconomic analysis
Victor et al. [162]	$100\text{-}250^{\dagger}$	$25\text{-}40^{\ddagger}$	-	Working fluid composition optimization
Elsayed et al. [163]	60-200	10	-	Feasibility study with alternative zeotropic mixtures in Kalina cycle
Eller et al. [164]	200-400	15		Second law analysis
Li et al. [165]	105-150	$35^{\dagger}$	8-26	Analysis based on net power output and cycle efficiency

He et al. [166]	127	5-30	2-5	Analysis based on net power output
Sadeghi et al. [167]	150-200†	-	220-478	Analysis based on cycle efficiency
Cao et al. [168]	300-525†	20‡	450-610	Analysis based on net power output and cycle efficiency

† Expander inlet temperature.

‡ Working fluid condenser outlet temperature.

Yari et al. [161] presented an exergoeconomic comparison between a Kalina cycle, a trilateral Rankine cycle, and an ORC with pure working fluids for low grade heat sources. The analysed Kalina cycle layout was KCS-11. The results indicated that using an ORC unit for power generation from low grade heat sources is the most advantageous among the compared alternatives from an economic perspective. Victor et al. [162] optimized the composition of the working fluids in a Kalina cycle unit and an ORC unit with mixtures as working fluid. For the comparison, binary combinations of several fluids were considered including hydrocarbons, hydrofluorocarbons, and alcohols. Alcohol-water mixtures were also considered. The results indicated that different working fluid compositions are optimal for different operating temperatures and pressures for the Kalina cycle unit, and the alcohol-water mixtures could increase the cycle efficiency for heat source temperatures between 220 °C to 250 °C. Elsayed et al. [163] evaluated the feasibility of using alternative zeotropic mixtures in the Kalina cycle KCS-11 power system. Among the 19 evaluated binary mixtures, the R1270/R290 mixture outperformed the ammonia-water mixture in terms of the cycle thermal efficiency, while the other mixtures exhibited similar performances as the ammonia-water mixture. In a similar kind of study, Eller et al. [164] analysed the use of several binary mixtures in a Kalina cycle with heat source temperatures between 200 °C and 400 °C. The performance results were compared with those of subcritical and supercritical ORCs. The results indicated that the ORC power system performed better than the Kalina cycle power system by up to 13 % in terms of the second law efficiency.

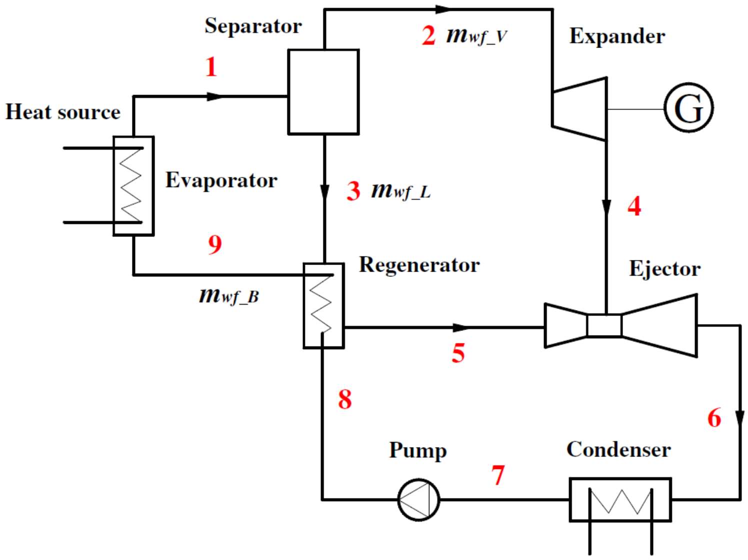


Figure 14: A Kalina cycle power system with ejector [165]. In the layout, the subscripts 'wf_B', 'wf_V', and 'wf_L' represent the basic working fluid, the ammonia-rich vapour, and the ammonia-lean liquid, respectively.

Li et al. [165] analysed a Kalina cycle power system with ejector as shown in Fig. 14. In the proposed configuration, the ejector replaced the combination of a throttle valve and a mixer typically used in a Kalina cycle unit. This was done so as to avoid the throttling losses in the cycle while reducing the pressure at the turbine outlet for better cycle efficiency. The results indicated that both the net power output and the cycle thermal efficiency are higher for the Kalina cycle power system with ejector than the Kalina cycle power system without one. He et al. [166] proposed two Kalina cycle (KCS-11) configurations by replacing the throttle valve with a two-phase expander in order to increase the utilization of low grade heat sources. One of the modified configurations resulted in 2 % to 9.4 % higher net work output than the standard Kalina cycle power system with a throttle valve. In a similar kind of study, Sadeghi et al. [167] proposed and optimized a double-turbine Kalina cycle power system with two separators using the artificial bee colony algorithm. Optimal values for the inlet temperature and pressure for one of the separators were reported for obtaining the highest thermal efficiency. Cao et al. [168] presented a thermodynamic analysis of a biomass-fired Kalina cycle power system in which the cycle working fluid is preheated in a regenerative heater just before entering the boiler using an extracted stream from the turbine.

The results suggested that an optimal combination of the turbine extraction pressure and the corresponding extraction flow fraction result in the maximum net power output and cycle efficiency.

4. Discussion

Most of the research on the use of zeotropic mixtures until now has focused primarily on the thermodynamic performance analysis of the power cycles. The power output from any power cycle is mainly governed by how much heat is extracted from the heat source and the thermal efficiency of the power cycle. Thus, for example, when optimizing an ORC power system, the maximum cycle pressure which maximizes the power output from the cycle is typically not the same as the one maximizing the thermal efficiency. Additionally, there may be a dependency on the minimum allowable exit temperature for the heat source. In this regard, the results have mostly indicated at better thermodynamic performances with mixtures than with pure fluids from the energy and exergy efficiency perspectives, especially for low temperature heat sources. In particular, the highest performance improvements as compared with using pure fluids have been observed when the temperature glide of the mixture matches the temperature profile of the cooling medium in the condenser. A possible explanation is that this is the most effective way of maximizing the average temperature difference between the average temperature of heat supply and the average temperature of heat rejection, in turn maximizing the thermal efficiency of the power cycle.

In addition, a possible explanation for the largest improvement in terms of thermal efficiency for low temperature heat sources is that the relative increase in temperature difference between the average temperature of heat supply and the average temperature of heat rejection (due to the use of mixtures) is comparatively higher for low temperature heat sources than for high temperature heat sources where a significant portion of the heat supply might be used for superheating and/or preheating. For mixture power cycles in general, the optimal mixture compositions have been found to be dependent on the cycle layout (i.e. the presence and/or location of the recuperators) for both the ORC power systems and the ammonia-water power systems, the objective function (thermodynamic, economic, or thermoeconomic), the assumed pinch point conditions, and the relation between the heat source temperature and the working fluid evaporation pressure and critical temperature.

In many studies, the performance of mixture power cycles has been compared with that of the power cycles with the pure fluids that constitute the mixture. In such cases, it cannot always be concluded with certainty that the analysed mixtures are also more efficient than other pure working fluids that could have been considered for similar applications and operating conditions. Therefore, a recent trend has been to consider the various fluids (both pure fluids and mixtures) as an optimization decision variable. In this way, all the possible pure fluids and their suitable mixtures will be considered within the optimization resulting in the optimal solution with the best pure fluid or mixture. One bottleneck in this approach is the significantly increased computational time because of the huge number of combinations of fluids and the various compositions for each such combination. Another recent approach has been to include a computer aided molecular design process within the numerical procedure in order to design (rather than identify from the input alternatives) the optimal chemical composition of the working fluid for the best satisfaction of the objective function.

4.1. ORC power systems

Table 10 presents the recommended mixtures from the studies on ORC power systems where various mixtures were compared for different applications. The table presents the overview from only those studies where a particular mixture was specifically identified as optimal among the compared alternatives. As may be observed from Table 10, the literature consists of analyses based on several parameters such as net power output from the plant, the first and second law efficiencies, the volumetric expander work, the turbine size parameter, or a combination of multiple performance indicators. From the literature on mixture ORCs, it may be observed that hundreds of fluids have been considered in many combinations in various studies depending on the application and the operating conditions. The applications are primarily about utilizing renewable or waste heat energy sources. Most of the studies analysed the use of binary mixtures, but few studies also considered the use of mixtures with three or more components.

Table 10: Recommended mixtures for various applications and operating conditions for ORC power systems. T_{hs} is the heat source temperature. A '-' instead of the value indicates unavailable data.

Reference	Application	T_{hs} (°C)	Performance indicator	Recommended mixture(s)
Prasad et al. [12]	Solar	100	Second law efficiency, volumetric expander work	R290/R600/R600a
Baldasso et al. [13]	Solar	150	First law efficiency, annual electricity production	Cyclopentane/cyclohexane
Mavrou et al. [18]	Solar	80-95	First law efficiency, exergy efficiency	Neopentane/1,1,1-trifluoropentane
Mavrou et al. [19]	Solar	80-95	Net power output, first law efficiency	Neopentane/2-fluoromethoxy-2-methylpropane
Mavrou et al. [20]	Solar	80-95	Net power output, first law efficiency	1,1,1-trifluoropropane/1-fluoromethoxypropane
Heberle et al. [22]	Geothermal	80-180	Second law efficiency	R227ea/R245fa ($T_{\mathrm{hs}} < 180$ °C), R600a/R601a ($T_{\mathrm{hs}} = 180$ °C)
Heberle and Brüggemann [23]	Geothermal	100-180	Specific investment cost, electricity generation cost	R227ea/R245fa, R290/R600a, R600a/R601a (depending on T_{hs})
Kang et al. [30]	Geothermal	110	Net power output	R245fa/R600a
Sadeghi et al. [32]	Geothermal	100	Net power output, turbine size parameter	R407a

Habka and Ajib [33]	Geothermal	80-120	Net power output, first law efficiency, second law efficiency, turbine size parameter	R22m, R422a, R438a
Baik et al. [35]	Geothermal	100	Net power output	R125/R245fa
Radulovic and Castaneda [36]	Geothermal	87-207	First law efficiency, second law efficiency	R124/R143a
Xiao et al. [42]	WHR	150	Multi-objective function	R245fa/R601 ($T_{\mathrm{ev}} < 117$ °C and $T_{\mathrm{cd}} < 47$ °C)
Kolahi et al. [45]	WHR	425.7	Net power output, first law efficiency, second law efficiency	R236ea/cyclohexane
Yang et al. [56]	WHR	170-545	Net power output, first law efficiency, second law efficiency, WHR efficiency, power output increasing rate	R402b, R407b, R415b
Zhou et al. [58]	WHR	-	Net power output, first law efficiency	RC318/R1234yf
Shu et al. [59]	WHR	519	First law efficiency, exergy loss	R11/benzene
Song and Gu [60]	WHR	300	Net power output, second law efficiency	R141b/cyclohexane
Braimakis et al. [61]	WHR	150-300	Second law efficiency	R290/R600, R600/hexane, R600/cyclopentane (depending on T_{hs})
Lee et al. [62]	WHR	87.7	Net power output, first law efficiency	R14/R23/R601

Chys et al. [63]	Generic	150-250	Net power output	R245fa/R601a/isohexane ($T_{\mathrm{hs}} = 150$ °C), MM/MDM ($T_{\mathrm{hs}} = 250$ °C)
Lecompte et al. [65]	Generic	120-160	Second law efficiency	R601a/isohexane (120 °C $< T_{\mathrm{hs}} <$ 130 °C), R600a/R601a (130 °C $< T_{\mathrm{hs}} <$ 160 °C)
Xi et al. [69]	Generic	100-180	Electricity production cost	R245fa/R601 (110 °C $< T_{\mathrm{hs}} <$ 130 °C), R245fa/R601a (140 °C $< T_{\mathrm{hs}} <$ 180 °C)
Andreasen et al. [70]	Generic	90-120	Net power output	R170/R290 ($T_{\mathrm{hs}} = 90$ °C)
Kim et al. [78]	Generic	25-85	Net power output	R14/R290 (first stage), R170/R601 (second and third stages)
Andreasen et al. [79]	Generic	90-120	Net power output	R600a/R601 ($T_{\mathrm{hs}} = 90$ °C), R290/R600a ($T_{\mathrm{hs}} = 120$ °C)
Chen et al. [80]	Generic	120-200	First law efficiency	R134a/R32
Dai et al. [81]	Generic	120-240†	Net power output, first law efficiency, second law efficiency	CO_2/R1234yf, CO_2/R1234ze, CO_2/R161 (depending on plant capacity)

† Expander inlet temperature.

4.2. Ammonia-water power systems

The ammonia-water mixture based power cycles have been investigated in a significant number of publications, both independently and in comparison with other power cycles. This is because of the possibility to use ammonia-water mixture for a very wide range of heat source or operation temperatures (90 °C to 550 °C). Most of the commonly studied refrigerants and organic compounds would decompose at such high temperatures. The ammonia-water mixture has mostly been investigated for waste heat recovery applications. The general consensus has been that, in order to obtain higher cycle efficiencies, the Kalina cycle requires a much more complex layout than its competitors such as ORCs for low temperature applications and steam Rankine cycles for high temperature applications. In addition, it also requires higher operating pressures for achieving similar output from the power plant. There are some exceptions where the Kalina cycle resulted in better performance, from both thermodynamic and economic perspectives, but these are few and for specific applications. For the Kalina cycle, the most important parameters affecting the cycle performance are the heat source temperature, the expander inlet conditions, and the separator inlet conditions.

4.3. Economic aspects

Only a few publications have considered the economic aspects in their analysis, mostly through the calculation of the total or the specific capital investment costs. The general consensus among such publications is that even though the mixtures might perform better thermodynamically, their performance is worse than pure fluids in terms of the heat exchanger area requirement and the associated capital investment costs. This has been primarily attributed to the decrease in the heat transfer coefficients especially in the two-phase region because of the additional mass transfer resistance and changes in the transport properties as compared with the pure fluids. In this regard, however, some contradictory results are present, e.g. Heberle and Brüggemann [23] mentioned that the use of fluid mixtures in ORC power systems resulted in a higher specific investment cost as compared with using pure fluids for most of the considered cases, whereas Li and Dai [44] presented an opposite trend.

These contradictions are present because of one or more of the following reasons: (1) different types and temperatures of the heat source, (2) different ways to estimate the thermophysical properties of the fluids and the heat transfer coefficients in the single and the two-phase regions, (3) consideration of different and limited number of fluids in the various studies, (4) different capacity of the considered cases (few kW to MW), and (5) different cost estimation methods and the associated assumptions. The heat sources have a significant impact on the estimation of the heat exchanger areas for the boiler or the heat recovery vapour generator. If flue gases are considered as the heat source, then it is most likely that the overall heat transfer coefficient will be nearly equal to the heat transfer coefficient on the gas side of the boiler and the estimation of the heat transfer coefficient on the working fluid side becomes less relevant. Whereas if liquids such as hot water or thermal oil are considered as the heat sources, then the heat transfer coefficients on the working fluid side have a significant impact on the overall heat transfer coefficients and therefore only applicable correlations should be used in such cases, particularly for the two-phase region. Similarly, for the condensation process, suitable corrections such as the Silver-Bell-Ghaly method [169] should be used.

There are only a small number of studies which present a thermoeconomic analysis by estimating the cost of electricity generation or LCOE with the size estimation of the various power plant components (e.g. Refs. [23, 46, 47, 69] for small capacity ORC power systems and Refs. [109, 114, 120] for Kalina cycle power systems). Even in these studies, it is not always that detailed suitable heat transfer models are used or the part-load performance of the power plants is considered. For heat sources which are consistently available throughout the year such as geothermal hot water or an industrial waste heat stream, not considering the part-load performance does not affect the estimations significantly. But for sources such as solar energy, the variations in the available incident energy over the year must be taken into account in the LCOE estimations. Among the publications with the estimation of LCOE, there are again some contradictory results such as both pure fluids and mixtures resulting in lower LCOE depending on the heat source characteristics and the associated modelling assumptions. Furthermore, more recent publications have favoured mixtures in low temperature ORC power systems with regards to LCOE [23, 69], whereas for the high temperature systems, the Kalina cycle power system was found to result in worse performance than state-of-the-art steam Rankine cycle power system [114]. In conclusion, it is difficult to definitively conclude anything generic on the economic performance of the power systems with fluid mixtures and further research is required especially for low grade heat recovery ORC and ammonia-water power systems and the comparison of their LCOE with state-of-the-art solutions.

5. Research prospects

Since so many fluid mixture combinations have been considered for a wide range of operating conditions, it is difficult to recommend any particular optimal fluids for mixture ORC power systems. It is therefore recommended that the optimal fluids and their compositions should be identified on a case by case basis through a thorough thermoeconomic analysis. As a first stage in this process, the fluids to be considered must be shortlisted based on their global warming and ozone depletion potentials and on the local legislation which might recommend phasing out of certain groups of fluids in the next 5–10 years. These include, for example, the phasing out of hydrofluorocarbons as per the Montreal protocol and limitations on the use of fluorinated gases as per a European Parliament directive [170–172].

The future research should then focus on combining the thermodynamic design models with the part-load performance and economic models for forming a more conclusive outlook on the true thermoeconomic benefits of using mixtures for power generation applications. This requires developing robust methods for estimating the size/geometry of the various cycle components along with developing realistic cost functions for various operating conditions and plant capacities in order to assess the associated costs. One important aspect from the system level design perspective is the assumption regarding the location of the pinch points in the heat exchanger, especially during two-phase flow. In this regard, recent studies have clearly highlighted that the location of the occurrence of pinch point should not be assumed beforehand as it completely depends on the curvature of the two-phase temperature profile of the zeotropic mixture. Therefore, it is recommended that this aspect is directly incorporated in the thermodynamic design simulation through heat exchanger discretization in order to avoid designs with unusually low pinch point temperature differences or second law violations.

More research is also needed in identifying the underlying causes for the dependence of the cycle efficiency and net power output on the thermophysical properties of the fluid mixtures, e.g. how critical temperature and pressure, specific heat capacity, or similar properties of the working fluids affect the overall cycle performance for given operating conditions and optimization criteria, how these parameters affect the performance depending on the minimum allowable heat source exit temperature, and so on. As most of the research on the use of zeotropic mixtures comes from the analysis of refrigeration cycles and heat pumps, not much data is available on the heat transfer coefficients for these mixtures in the temperature ranges suitable for power cycles. This is one of areas where significant potential for future research is present from both experimental and numerical perspectives. Heat exchanger designs specifically suitable for mixture two-phase heat transfer need to be developed. Similarly, suitable designs for expanders for use with mixtures also need to be developed, analysed, and optimized for various operating conditions and scales.

6. Conclusion

The use of zeotropic fluid mixtures in energy conversion systems has been widely studied for refrigeration plants and heat pumps in the last few decades. However it is only recently that the use of these mixtures in power cycles has attracted increased interest because of the possibility to reduce the irreversibility during a two-phase heat transfer process, thereby resulting in better thermodynamic performance. Based on the review of the recent literature, the following overall conclusions may be drawn. Most of the studies considered the use of mixtures for the conversion of low grade heat to power. In general, the results indicate better thermodynamic performance when using the mixtures with low heat source temperatures than with high heat source temperatures. The majority of the studies primarily focused on the thermodynamic performance of the power cycles with zeotropic mixtures and assessing the potential to improve the thermodynamic performance as compared with using pure working fluids. The use of mixtures have mostly been found to result in improved thermodynamic performance of the power cycle with respect to the net power output and first and second law efficiencies.

Only a few studies also investigated the economic aspects of mixture power cycles, primarily through the estimation of the capital investment costs and sometimes through the estimation of LCOE or payback periods. The general consensus from the economic studies until now is that the mixture power cycles incur higher capital investment costs than pure fluid power cycles, mainly because of bigger heat exchanger area requirements. Recent studies however also indicate lower values of LCOE with mixture power cycles than the pure fluid power cycles, particularly for low temperature ORC power systems. This is because of compensating the higher capital investment costs by the higher revenue generation with mixture power cycles due to better cycle efficiencies and higher net power outputs.

The future research on the use of zeotropic mixtures may focus on more thorough thermoeconomic analyses including the thermodynamic design, the part-load performance, and the economic models in the numerical models. More research is also required towards developing more robust heat transfer and pressure drop correlations together with more reliable cost functions for better estimation of the thermoeconomic performance of the mixture power cycles. Lastly, research is also required on developing novel heat exchanger and expander designs suitable specifically for use with zeotropic mixtures.

Nomenclature

CNG	compressed natural gas
CO_2	carbon dioxide
LCOE	levelized cost of electricity
LNG	liquefied natural gas
MD_2M	decamethyltetrasiloxane
MDM	octamethyltrisiloxane

MM hexamethyldisiloxane

ORC organic Rankine cycle

OTEC ocean thermal energy conversion

SF_6 sulphur hexafluoride

T_{cd} condensation temperature, °C

T_{cs} cooling medium temperature, °C

T_{ev} evaporation temperature, °C

T_{hs} heat source temperature, °C

WHR waste/exhaust heat recovery

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