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Zeotropic Mixture Selection for an Organic Rankine Cycle Using a Single Screw Expander

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Abstract: The organic Rankine cycle (ORC) is a popular and promising technology that has been widely studied and adopted in renewable and sustainable energy utilization and low-grade waste heat recovery. The use of zeotropic mixtures in ORC has been attracting more and more attention because of the possibility to match the temperature profile of the heat source by non-isothermal phase change, which reduces the irreversibility in the evaporator and the condenser. The selection of working fluid and expander is strongly interconnected. As a novel expander, a single screw expander was selected and used in this paper for efficient utilization of the wet zeotropic mixtures listed in REFPROP 9.1 in a low-temperature subcritical ORC system. Five indicators, namely net work, thermal efficiency, heat exchange load of condenser, temperature glide in evaporator, and temperature glide in condenser, were used to analyze the performance of an ORC system with wet and isentropic zeotropic mixtures as working fluids. The calculation and analysis results indicate that R441A with an expander outlet temperature of 320 K may be the suitable zeotropic mixture used for both open and close type heat source. R436B may be selected with an expander outlet temperature of 315 K. R432A may be selected with an expander outlet temperature from 295 K to 310 K.

Keywords: wet zeotropic mixture; single screw expander; organic Rankine cycle; R441A; R436B; R432A

1. Introduction

The characteristics of the world energy structure, which is dominated by fossil energy, have caused two long-term problems, namely, the depletion of fossil energy and the environmental pollution caused by the utilization of fossil energy. In order to solve these two problems, we have to take all measures that are technically feasible, economically reasonable, environmentally and socially acceptable to improve the utilization efficiency of energy resources. Among these measures, the organic Rankine cycle (ORC) is a popular and promising technology that has been widely studied and adopted in renewable and sustainable energy utilization and low-grade waste heat recovery. Working fluid and expander are two research hotpots of ORC. The selection of working fluid and expander is strongly interconnected. Water is used as the working fluid of steam Rankine cycle which is usually used to exploit and utilize a heat source higher than 450 °C. Turbine that has a high efficiency is used as the expander in steam Rankine cycle. Organic substance is used as the working fluid of the organic Rankine cycle which is usually used for the exploitation and utilization of medium-low grade heat source whose temperature is lower than 250 °C. Unlike lower molecular weight fluids like water, turbine design considerations in less than 100 kW output capacities results in lower efficiencies compared to heavier molecular weight organic fluids. The thermodynamic performance, working condition, impact on the environment, and economic feasibility of an ORC system are greatly determined by the characteristics of working fluid [1,2]. CFCs that were invented in 1930s and have a high ozone depletion potential (ODP) and a highest Global Warming Potential (GWP), HCFCs that were invented in 1950s and have a lower ODP and a high GWP, and HFCs that were invented in 1990s and have no ODP but a high GWP, were dominant organic working fluids before the ratification of the Montreal Protocol in 1987 and the ratification of the Kyoto Protocol in 1997. Changes are driven by regulations. Only those working fluids with zero ODP and a very low GWP can be used at present and in the future. Mixtures (blends) can meet this requirement. Basically, mixtures can be classified into two categories: azeotropes that have a constant boiling point and composition throughout distillation and zoetropes that boil across a range of temperatures at any given pressure. 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 [3]. The earliest research on zeotropic refrigerants can be traced back to the late 1980s [4] and early 1990s [5,6]. Radermacher proposed several solution circuits used to eliminate the inherent requirement of complete phase changes in the heat exchangers [4,5]. Weng experimentally examined the heat transfer performance of the zeotropic refrigerant blends of carbon tetrafluoride (R14) and dichlorotetrafluoroethane (R114) during evaporative flow under various conditions [6]. Nowadays, the use of zeotropic mixtures in power cycles has been attracting more and more attention because of the possibility to match the temperature profile of the heat source by non-isothermal phase change, which reduces the irreversibility in the evaporator and the condenser. If the irreversibility of the heat transfer process is reduced and given the low-grade heat source, the potential of harnessing useful work from the heat source is increased [7]. This advantage is very important and useful to ORC system. Therefore, a lot of research work has been conducted. Lecompte et al. examined the thermodynamic performance of a non-superheated subcritical ORC with seven zeotropic mixture pairs as working fluid. They found the evaporator accounts for the highest exergy loss and the matching with the condenser heat profiles results the best performance [8]. Zhao and Bao proposed a thermodynamic model which mainly includes Jacob number. They used the ratio of evaporation temperature to the condensation temperature to study the thermal efficiency, output work, and exergy efficiency of ORC system with ten zeotropic mixture pairs as working fluid. The significant influence of heat source inlet temperature on the best composition of zeotropic mixtures was found. Compared with pure fluids, the zeotropic mixture performance can be improved by greater temperature glide of the mixture [9]. Habka and Ajib conduct a performance analysis of zeotropic mixtures used in ORC systems for geothermal water utilization. They found R438A, R422A, and R22M are more efficient than the pure fluids and can enhance the power productivity and geothermal water utilization at the source's temperatures of 80, 100, and 120 °C, respectively [10]. Deethayat et al. proposed a dimensionless term named "Figure of Merit" (FOM) and studied the thermal performance of six zeotropic mixtures used in a low-temperature ORC system. They also developed an empirical correlation which fits very well with literature to estimate the cycle efficiency from the FOM for all working fluids at condensing temperatures of 25–40 °C and evaporating temperatures of 80–130 °C [11]. Miao et al. proposed a thermodynamic selection criterion of zeotropic mixtures based on the exergy analysis of the subcritical ORC. They found the match condition with the heat source should be firstly satisfied when selecting working fluids. The proper temperature glide in the condenser can further improve the cycle performance [12]. Battista et al. developed a comprehensive thermodynamic model of the ORC plant, considering both hot and cold source available on board vehicle. They evaluated the best candidates based on: thermodynamic performance, pressure levels, fluid hazard levels and GWP, critical temperature, and the temperature glide. They found R245fa is a fluid that obtains a large net power increase when used in mixtures with hydrocarbons, compared to pure fluid an optimized R245fa/benzene mixture, for instance, attains an 11% net power increase [13]. Cipollone et al. presented a thermodynamic analysis of a trilateral flash cycle (TFC) system using recent pure fluids and mixtures for low grade heat to power conversion applications. They found mixtures appear more suitable for rotary volumetric machines having lower built in volume ratios [14].

The results given in different research work indicate that zeotropic mixtures show a better thermodynamic performance at low heat source temperatures than high heat source temperatures [3]. According to thermodynamic knowledge, not much exergy is available in low-temperature heat source compared with high-temperature heat source. Therefore, in order to make full use of the exergy in low-temperature heat source, selection of proper zeotropic mixture as working fluid is very important. Same as pure working fluids, mixtures can be classified by three types of saturated vapor curve as shown on *T-s* diagram, namely dry, with a positive slope, wet, with a negative slope and isentropic, with a vertical slope. [15]. Miao et al. claimed that the 'wet' mixtures have relatively lower cycle performance compare to 'dry' and 'isentropic' ones [12]. However, their conclusion is based on using a turbine as an expander. In order to avoid the damage on turbine blades caused by liquid droplets, a vapor quality that is high enough must be ensured. Therefore, superheating apparatus is needed for wet fluids when turbo-type expander/turbine is used in ORC system. However, second law analysis showed that superheating organic fluids increases the irreversibility and decreases the second law efficiency [16]. Moreover, since the objective of the ORC focuses on the use of heat at low and medium temperatures, the overheating of the vapor, as in the traditional steam Rankine cycle, is not appropriate and is a waste of exergy in low-and-medium heat sources [17–19].

Zeotropic mixtures can be artificially defined and mixed into dry or isentropic working fluids that are suitable for ORC. However, if we screen predefined mixtures listed in REFPROP 9.1 [20], it can be seen that most zeotropic mixtures are wet ones. They are applicable in ORC and they do not need to be superheated in ORC if an expander which can tolerate wet expansion of wet zeotropic mixtures can be found. This indicates that the selection of working fluid and expander is strongly interconnected.

Expander is the critical device in an ORC system because it significantly affects thermodynamic performance of an ORC system and its cost ranks second in total system investment [21]. It includes turbo type and positive-displacement type. It has been mentioned that turbo type expander that are normally suitable for large scale ORC systems [19,22] but might not be favorable for small scale ORC units [23] and cannot be used as an expander for wet zeotropic mixture applications. If we screen positive-displacement expanders, such as rolling piston expander, scroll expander, and single screw expander, it can be found that the single screw expander is most suitable for wet zeotropic mixture application. It has the common advantages of positive-displacement expander, such as relatively high efficiency, high pressure ratio, low rotational speed, and tolerance of two-phase fluids [22]. Compared with rolling piston expander and scroll expander, single screw expander has many other advantages, such as balanced load of the screw, long service life, high volumetric efficiency, good performances in partial load, low leakage, low noise, low vibration, and simple configuration [23]. All these advantages have been attracting many researchers to carry out relevant study on design and application of single screw expander. The authors' research group has conducted a series of research works in the field of single screw expanders [23–31]. Normal and novel prototypes of single screw expanders have been experimentally studied [24,26,29]. The factors influencing the performance of a single screw expander have also been studied [26–28,30]. The applications of single screw expanders in ORC and refrigeration systems have also been introduced [23,25,31]. Brief descriptions and analyses of these research works can be found in our previous paper [32]. In a single screw structure, one screw can mesh with two or more starwheels. According to the shape, screw and starwheel can be divided into cylindrical (type C) and flat (type P). Therefore, these two types can be combined into four forms of single screw structure, namely PC type, PP type, CC type and CP type. These four forms are depicted in Figure 1. Because the first three forms are more difficult to process, the most commonly used single screw structure is the CP type. Figure 2 depicts the configuration of CP type single screw expander. Its working processes are depicted by Figure 3.

A demonstration project of ORC system using single screw expander with R123 as working fluid was established in Liulin (Shanxi Province, China). This project is used for waste heat recovery of the flue gas from a gas-fired internal combustion engine generator unit. The working condition parameters of the demonstration ORC system are listed in Table 1. The thermal efficiency of the ORC system is 8.81%. The output power of the demonstration project is 11 kW. Considering that R123 will be eliminated in the near future due to environmental factors, a selection of a pure working fluid for ORC using a single screw expander was conducted in our previous paper [21]. It is found that *cis*-butene may be the best candidate for working in a subcritical cycle. HFO working fluids are more suitable for working in near-critical cycles and HFO-1234ze(E) may be the best. In this paper, in order to efficiently use the wet zeotropic mixture in low-temperature subcritical ORC system, a single screw expander is selected and used in the system for analysis. Among all the predefined mixtures listed in REFPROP 9.1, four wet zeotropic mixtures and two isentropic zeotropic mixtures are selected to be the candidates for further calculation and analysis. On this basis, zeotropic mixture selection for ORC using single screw expander is conducted based on five indicators, namely net work, thermal efficiency, heat exchange load of condenser, temperature glide in evaporator, and temperature glide in condenser.

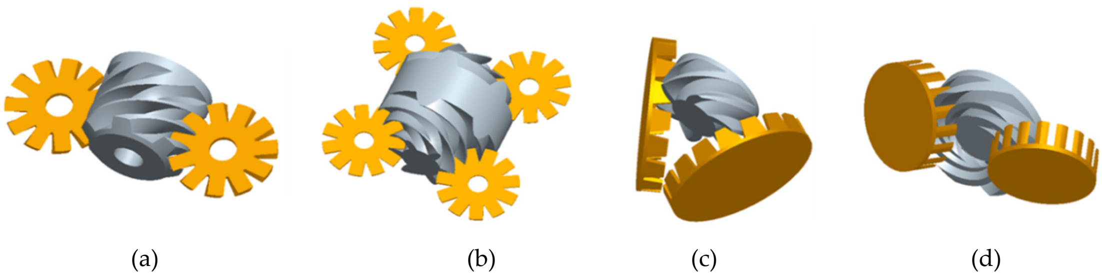


Figure 1. Four forms of single screw structure: (**a**) CP type; (**b**) CC type; (**c**) PP type; (**d**) PC type.

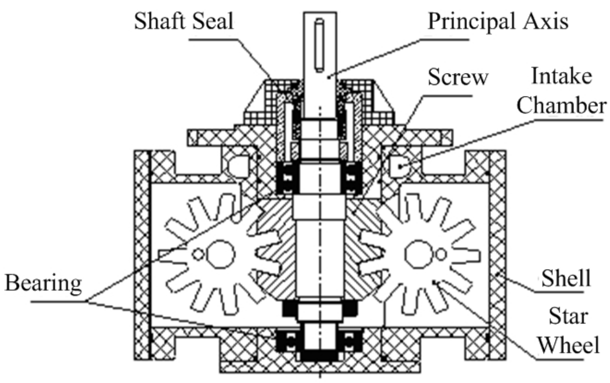


Figure 2. Configuration of CP type single screw expander.

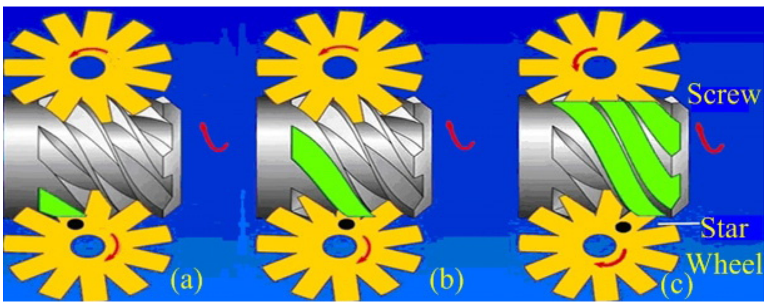


Figure 3. Working processes of CP type single screw expander (**a**) suction, (**b**) expansion, and (**c**) discharge.

Table 1. Working condition parameters of the demonstration ORC system

Working Condition Parameter.	Value
Heat source temperature (°C)	330–450
Mass flow rate of flue gas (heat source)	1700
Inlet pressure of expander (MPa)	1.6
Inlet temperature of expander (°C)	135
Working fluid flow(kg/h)	3100
Type of evaporator	shell-and-tube heat exchanger
Evaporation temperature (°C)	108–118
Type of condenser	tube-in-tube heat exchanger
Condensation temperature (°C)	30
Cooling water temperature (°C)	20

2. Basic Constraints and Preliminary Screening

Low-temperature heat sources can be divided into two categories: open type and closed type [33,34]. The inlet temperature and mass flow rate of an open-type heat source is known. The working mass of the heat source is directly discharged after being used. For closed type, the heat release is specific and the working mass of heat source is usually recycled after releasing heat. Therefore, different standards are used to measure these two types of heat source [34]. The maximum net work and the maximum thermal efficiency are used as the criteria for open type and closed type, respectively. Therefore, net work and thermal efficiency are adopted as the first two indicators for evaluating the performance of ORC using single screw expander with zeotropic mixture as working fluid. The third evaluation indicator is heat exchange load of condenser because it is the critical for calculating the cost of condenser that greatly influences the cost and economic performance of entire ORC system [21].

Zeotropic mixture performance can be improved by a greater temperature glide of the mixture [9]. In particular the temperature glide in the condenser can further improve the cycle performance [12]. Therefore, the fourth and fifth evaluation indicators are taken as temperature glide in evaporator and temperature glide in condenser.

Seventy nine (79) kinds of mixtures can be found in the REFPROP 9.1 software developed by the National Institute of Standards and Technology Laboratories (NIST, Gaithersburg, MD, USA) [20]. Among all these mixtures, 72 kinds of mixtures have identifying numbers given by American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE). According to the latest ASHRAE standard [35], zeotropic blends shall be assigned an identifying number in the 400 series and azeotropes shall be assigned an identifying number in the 500 series. Therefore, 61 kinds of zeotropic mixtures with identifying numbers in the 400 series can be selected. Their basic properties are listed in Table 2.

From Table 2, it can be seen that HCFCs, such as R22, R124, and R142b, and HFCs, such as R32, R134a, R143a, R152a, and R125, are the components of zeotropic mixtures. HCFCs and HFCs have been banned due to their high GWP. Therefore, the zeotropic mixtures containing HCFCs and HFCs are screened out for further analysis. The remaining six zeotropic mixtures for further analysis, including four wet ones and two isentropic ones, and their critical temperatures are listed in Table 3. The components of the remaining zeotropic mixtures are propylene, dimethyl ether, propylene, propane, isobutane, ethane, and butane. They all have very low GWP [36] but belongs to A3 of safety group that means a higher flammability but a lower toxicity [35].

Table 2. Basic properties of the 61 zeotropic mixtures.

Identifying Number	Components	Composition/Mass %	Safety Group [35]	Type
R401A	R22/R152a/R124	53/13/34	A1	wet
R401B	R22/R152a/R124	61/11/28	A1	wet
R401C	R22/R152a/R124	33/15/52	A1	wet
R402A	R125/propane/R22	60/2/38	A1	wet
R402B	R125/propane/R22	38/2/60	A1	wet
R403A	propane/R22/R218	5/75/20	A2	wet
R430B	propane/R22/R218	5/56/39	A1	wet
R404A	R125/R134a/R143a	44/4/52	A1	wet
R405A	R22/R152a/R142b/RC318	45/7/5.5/42.5	A1	wet
R406A	R22/isobutane/R142b	55/4/41	A2	wet
R407A	R32/R125/R134a	20/40/40	A1	wet
R407B	R32/R125/R134a	10/70/20	A1	wet
R407C	R32/R125/R134a	23/25/52	A1	wet
R407D	R32/R125/R134a	15/15/70	A1	wet
R407E	R32/R125/R134a	25/15/60	A1	wet
R407F	R32/R125/R134a	30/30/40	A1	wet
R408A	R125/R143a/R22	7/46/47	A1	wet
R409A	R22/R124/R142b	60/25/15	A1	wet
R409B	R22/R124/R142b	65/25/10	A1	wet
R410A	R32/R125	50/50	A1	wet
R410B	R32/R125	45/55	A1	wet
R411A	propylene/R22/R152a	1.5/87.5/11	A2	wet
R411B	propylene/R22/R152a	3/94/3	A2	wet
R412A	R22/R218/R142b	70/5/25	A2	wet
R413A	R218/R134a/isobutane	9/88/3	A2	wet
R414A	R22/R124/isobutane/R142b	51/28.5/4/16.5	A1	wet
R414B	R22/R124/isobutane/R142b	50/39/1.5/9.5	A1	wet
R415A	R22/R152a	82/18	A2	wet
R415B	R22/R152a	25/75	A2	wet
R416A	R134a/R124/butane	59/39.5/1.5	A1	wet
R417A	R125/R134a/butane	46.6/50/3.4	A1	wet
R418A	propane/R22/R152a	1.5/96/2.5	A2	wet
R419A	R125/R134a/dimethylether	77/19/4	A2	wet
R420A	R134a/R142b	88/12	A1	wet
R421A	R125/R134a	58/42	A1	wet
R421B	R125/R134a	85/15	A1	wet
R422A	R125/R134a/isobutane	85.1/11.5/3.4	A1	wet
R422B	R125/R134a/isobutane	55/42/3	A1	wet
R422C	R125/R134a/isobutane	82/15/3	A1	wet
R422D	R125/R134a/isobutane	65.1/31.5/3.4	A1	wet
R423A	R134a/R227ea	52.5/47.5	A1	isentropic
R424A	R125/R134a/isobutane/butane/ isopentane	50.5/47/0.9/1/0.6	A1	wet
R425A	R32/R134a/R227ea	18.5/69.5/12	A1	wet
R426A	R125/R134a/butane/isopentane	5.1/93/1.3/0.6	A1	wet
R427A	R32/R125/R143a/R134a	15/25/10/50	A1	wet
R428A	R125/R143a/propane/isobutane	77.5/20/0.6/1.9	A1	wet
R429A	dimethylether/R152a/isobutane	60/10/30	A3	wet
R430A	R152a/isobutane	76/24	A3	wet
R431A	propane/R152a	71/29	A3	wet
R432A	propylene/dimethylether	80/20	A3	wet
R433A	propylene/propane	30/70	A3	wet
R434A	R125/R143a/R134a/isobutane	63.2/18/16/2.8	A1	wet
R435A	dimethylether/R152a	80/20	A3	wet
R436A	propane/isobutane	56/44	A3	isentropic
R436B	propane/isobutane	52/48	A3	isentropic
R437A	R125/R134a/butane/pentane	19.5/78.5/1.4/0.6	A1	wet
R438A	R32/R125/R134a/butane/ isopentane	8.5/45/44.2/1.7/0.6	A1	wet
R441A	ethane/propane/isobutane/butane	3.1/54.8/6/36.1	A3	wet
R442A	R32/R125/R134a/R152a/R227ea	31/31/30/3/5	A1	wet
R443A	propylene/propane/isobutane	55/40/5	A3	wet
R444A	R32/R152a/R1234ze(E)	12/5/83	A2L [1]	wet

[1] A2L is lower flammability refrigerants with a maximum burning velocity of ≤ 10 cm/s.

Table 3. Main thermodynamic and safety properties of six zeotropic mixtures.

Identifying Number	Critical Temperature (T_c)/K	The Extreme Temperature of Subcritical Region ($0.9T_C$)/K	Components	Composition /Mass %	Safety Group	Type
R432A	370.41	333.37	propylene/ dimethylether	80/20	A3	wet
R433A	367.57	330.81	propylene/ propane	30/70	A3	wet
R436A	389.04	350.14	propane/ isobutane	56/44	A3	isentropic
R436B	390.58	351.52	propane/ isobutane	52/48	A3	isentropic
R441A	391.62	352.46	ethane/propane/ isobutane/butane	3.1/54.8/6/36.1	A3	wet
R443A	369.16	332.24	propylene/propane /isobutane	55/40/5	A3	wet

3. Subcritical Cycle Analysis without Considering Isentropic Efficiency of Expander

First of all, it should be mentioned that the maximum operating temperature of single screw expander should not exceed 130 °C (400 K) due to the restriction of sealing material, lubricating oil, and starwheel material. The critical temperatures of all the zeotropic mixtures listed in Table 3 are lower than 400 K. Therefore, they are suitable candidates for zeotropic selection for ORC using single screw expander.

3.1. Thermodynamic Setting and Description

Generally speaking, an ORC usually runs in a subcritical rather than a transcritical or supercritical state due to the considerations of chemical stability and thermal stability of organic working fluid. Considering that four zeotropic mixtures are wet ones, $0.9T_c$ (critical temperature) is used to be the extreme temperature of subcritical region. That is to say, $0.9T_c$ (critical temperature) is also taken as the inlet temperature of the expander. On this basis, a subcritical ORC using single screw expander with wet zeotropic mixture as working fluid can be established and depicted by Figure 4.

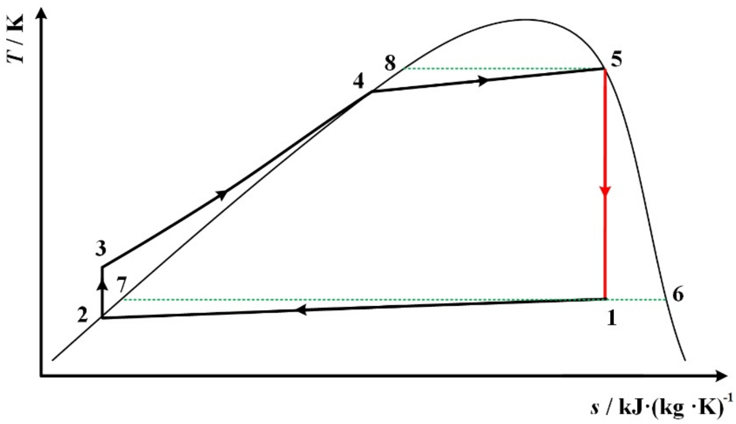


Figure 4. Subcritical ORC using single screw expander with wet zeotropic mixture as working fluid.

In a *T-s* diagram, a significant difference between dry (or isentropic) fluid and wet fluid is the existence of a point on which the entropy value reaches the maximum on saturated vapor curve ranging from normal boiling point to critical point. This point is located near the critical point and defined as the turning point. Its more detailed discussion can be found in paper [37]; other details about the role of this point can be seen elsewhere [38]. The turning point temperature is the limit of subcritical ORC which adopts turbo-type expander [37]. As for the two isentropic zeotropic mixtures, R436A and R436B, which are listed in Table 3, their turning point temperatures are 334.5 K and 342.5 K, respectively.

Because single screw expander that can tolerate vapor-liquid two-phase expansion is adopted in this study, $0.9T_c$ (critical temperature), which is a litter higher than turning point temperature, is still taken as the inlet temperature of the expander when wet zeotropic mixture is used as working fluid.

According to [18], 320 K and 290 K are the recommended condensation temperatures for the working fluids with high and low critical temperatures, respectively. These two condensation temperatures can be achieved by air cooling and water cooling. Accordingly, in order to make a detailed analysis, the thermodynamic performance of the above six zeotropic mixtures, including four wet ones and two isentropic ones, are calculated when the temperature of expander outlet varies from 290 K to 320 K.

The expander outlet states of four wet zeotropic mixtures are at vapor-liquid two-phase region. However, the expander outlet states of two isentropic zeotropic mixtures, R436A and R436B, are different. R436A's expander outlet is at vapor-liquid two-phase region, while R436B at superheated region. On this basis, a subcritical ORC using single screw expander with isentropic zeotropic mixture as working fluid can be established and depicted by Figure 5.

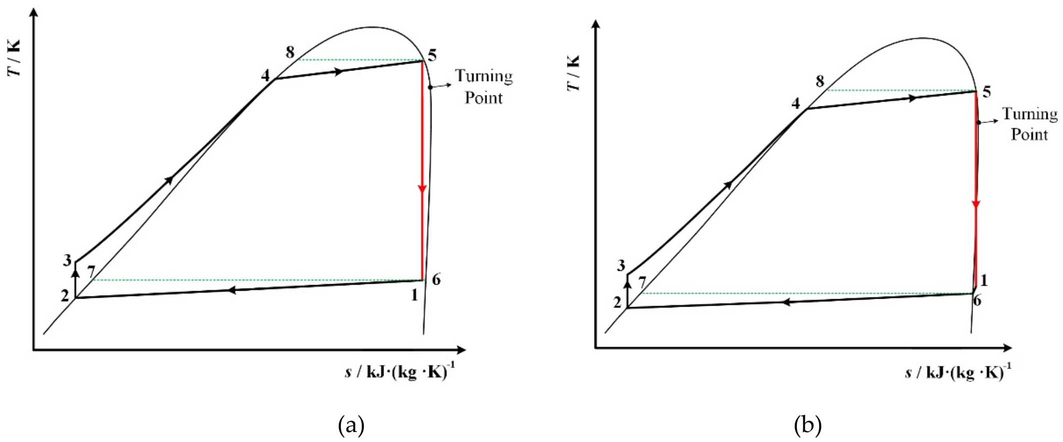


Figure 5. Subcritical ORC using single screw expander with isentropic zeotropic mixture as working fluid: (**a**)expander outlet at vapor-liquid two-phase region for R436A; (**b**)expander outlet at superheated region. for R436B.

All the state points in Figures 4 and 5 are described in Table 4.

Table 4. Description and determination of state points in Figures 4 and 5.

State Point	Description	Determination
1	expander outlet	$s_1 = s_5$
2	condenser outlet, at saturated liquid state	$p_2 = p_1$
3	pump outlet	$s_3 = s_2, p_3 = p_4$
4	at saturated liquid state	$p_4 = p_5$
5	expander inlet	$s_5 = s_1, T_5 = 0.9T_c$
6	at saturated vapor state	$T_6 = T_1$ for Figures 1 and 5a, $p_6 = p_1$ for Figure 5b
7	at saturated liquid state	$T_7 = T_6$
8	at saturated liquid state	$T_8 = T_5$

In Figures 4 and 5, net work is calculated by:

$$w_{net} = (h_5 - h_1) - (h_3 - h_2) \tag{1}$$

thermal efficiency is calculated by:

$$\eta = \frac{w_{net}}{q_e} = \frac{(h_5 - h_1) - (h_3 - h_2)}{h_5 - h_3} \tag{2}$$

heat exchange load of condenser is calculated by:

$$q_c = h_1 - h_2 \tag{3}$$

temperature glide in evaporator is calculated by:

$$\Delta T_e = T_5 - T_4 \tag{4}$$

temperature glide in condenser is calculated by:

$$\Delta T_c = T_6 - T_2 \tag{5}$$

and vapor quality for four wet zeotropic mixtures and one isentropic mixture(R436A) is calculated by:

$$x = \frac{s_1 - s_7}{s_6 - s_7} \tag{6}$$

In the above equations, h is enthalpy, s is entropy, T is temperature, w is work, q is heat exchange, η is thermal efficiency, c stands for condenser and condensation, e stands for evaporator and evaporation, and the numbers are the state points in the figure. In the following equations, h, s, T, w, q, η, and the numbers have the same meanings.

3.2. Results and Discussion

Table 5 lists the net work, thermal efficiency, heat exchange load of condenser, temperature glide in evaporator, temperature glide in condenser, and vapor quality of four wet zeotropic mixtures and two isentropic zeotropic mixtures when expander outlet temperature is known.

From the data listed in Table 5, it can be seen that among the six zeotropic mixtures, R441A has the best performance in net work, thermal efficiency, temperature glide in evaporator, and temperature glide in condenser, while R433A has the best performance in heat exchange load of condenser.

The vapor quality of four wet zeotropic mixtures increases with the increase of expander outlet temperature. As for two isentropic zeotropic mixtures, the vapor quality of R436A increases at first and then decreases. R436B does not have a vapor quality because its expander outlet is in the superheated region. The vapor quality of these five zeotropic mixtures is very high. In other words, they are very close to saturated vapor state.

For all six zeotropic mixtures, their four indexes, including net work, thermal efficiency, heat exchange load of condenser, and temperature glide in condenser, decrease with the increase of expander outlet temperature. The variation trends of these four indexes with the increase of expander outlet temperature are depicted in Figure 6.

Table 5. Thermodynamic performance of six zeotropic mixtures when expander outlet temperature is known.

Zeotropic Mixture	Expander Outlet Temperature T_1/K	Net Work/kJ·kg^{-1}	Thermal Efficiency/%	Heat Exchange Load of Condenser/kJ·kg^{-1}	Temperature Glide in Evaporator/K	Temperature Glide in Condenser/K	Vapor Quality
R432A	290	43.84	11.28	344.67	0.899	1.43	0.9450
	295	37.94	10.10	337.84		1.37	0.9491
	300	32.24	8.89	330.58		1.3	0.9534
	305	26.82	7.67	322.86		1.24	0.9579
	310	21.54	6.41	314.75		1.18	0.9628
	315	16.54	5.13	306.15		1.12	0.9685
	320	11.69	3.79	297.08		1.06	0.9749
R433A	290	40.11	10.66	336.24	0.263	0.32	0.9633
	295	34.37	9.46	328.91		0.32	0.9661
	300	28.89	8.25	321.13		0.31	0.9689
	305	23.61	7.02	312.89		0.31	0.9720
	310	18.55	5.75	304.16		0.3	0.9755
	315	13.74	4.45	294.92		0.29	0.9794
	320	9.13	3.10	285.13		0.28	0.9844
R436A	290	60.66	14.25	365.12	5.236	7.29	0.9973
	295	54.40	13.17	358.79		7.17	0.9980
	300	48.40	12.09	352.04		7.05	0.9985
	305	42.59	10.99	344.87		6.92	0.9987
	310	36.99	9.88	337.27		6.78	0.9987
	315	31.60	8.76	329.23		6.62	0.9983
	320	26.42	7.61	320.72		6.46	0.9979
R436B	290	62.39	14.58	365.65	5.342	7.48	N/A
	295	56.15	13.51	359.37		7.37	
	300	50.17	12.45	352.72		7.28	
	305	44.34	11.37	345.61		7.14	
	310	38.70	10.27	338.02		6.96	
	315	33.35	9.18	330.01		6.8	
	320	28.17	8.05	321.58		6.64	
R441A	290	69.38	14.68	403.38	12.958	18.54	0.9880
	295	62.56	13.60	397.28		18.20	0.9895
	300	55.94	12.52	390.79		17.85	0.9907
	305	49.56	11.44	383.83		17.48	0.9916
	310	43.40	10.34	376.44		17.09	0.9922
	315	37.47	9.23	368.59		16.68	0.9928
	320	31.75	8.10	360.25		16.26	0.9930
R443A	290	42.35	11.02	341.82	1.904	2.33	0.9580
	295	36.50	9.83	334.78		2.3	0.9611
	300	30.86	8.62	327.30		2.26	0.9644
	305	25.47	7.39	319.35		2.21	0.9678
	310	20.29	6.13	310.94		2.17	0.9717
	315	15.35	4.84	302.01		2.11	0.9760
	320	10.59	3.49	292.55		2.05	0.9812

From Figure 6a, it can be seen that R441A has the highest net work while R433A has the lowest. When the expander outlet temperature varies from 290 K to 320 K, R433A has the highest reduction, which is from 40.11 kJ/kg to 9.13 kJ/kg, a 77.24% decrease in net work. R441A has the lowest reduction, which is from 69.38 kJ/kg to 31.75 kJ/kg, a 54.24% decrease. From Figure 6b, it can be seen that R441A has the highest thermal efficiency and R433A has the lowest. When expander outlet temperature varies from 290 K to 320 K, R433A has the highest reduction, which is from 10.66% to 3.10%, a 70.89% decrease in thermal efficiency. R436B has the lowest reduction, which is from 14.58% to 8.05%, a 44.74% decrease. From Figure 6c, it can be seen that R441A has the highest heat exchange load of condenser and R433A has the lowest.

When the expander outlet temperature varies from 290 K to 320 K, R433A has the highest reduction, which is from 336.24 kJ/kg to 285.13 kJ/kg, a 15.20% decrease in heat exchange load of condenser. R441A has the lowest reduction, which is from 403.38 kJ/kg to 360.25 kJ/kg, a 10.69% decrease. From Figure 6d, it can be seen that R441A has the highest temperature glide in condenser while R433A has the lowest. When expander outlet temperature varies from 290 K to 320 K, R432A has the highest reduction, which is from 1.43 K to 1.06 K, a 25.87% decrease in temperature glide in condenser. R436B has the lowest reduction, which is from 7.48 K to 6.64 K, a 11.23% decrease.

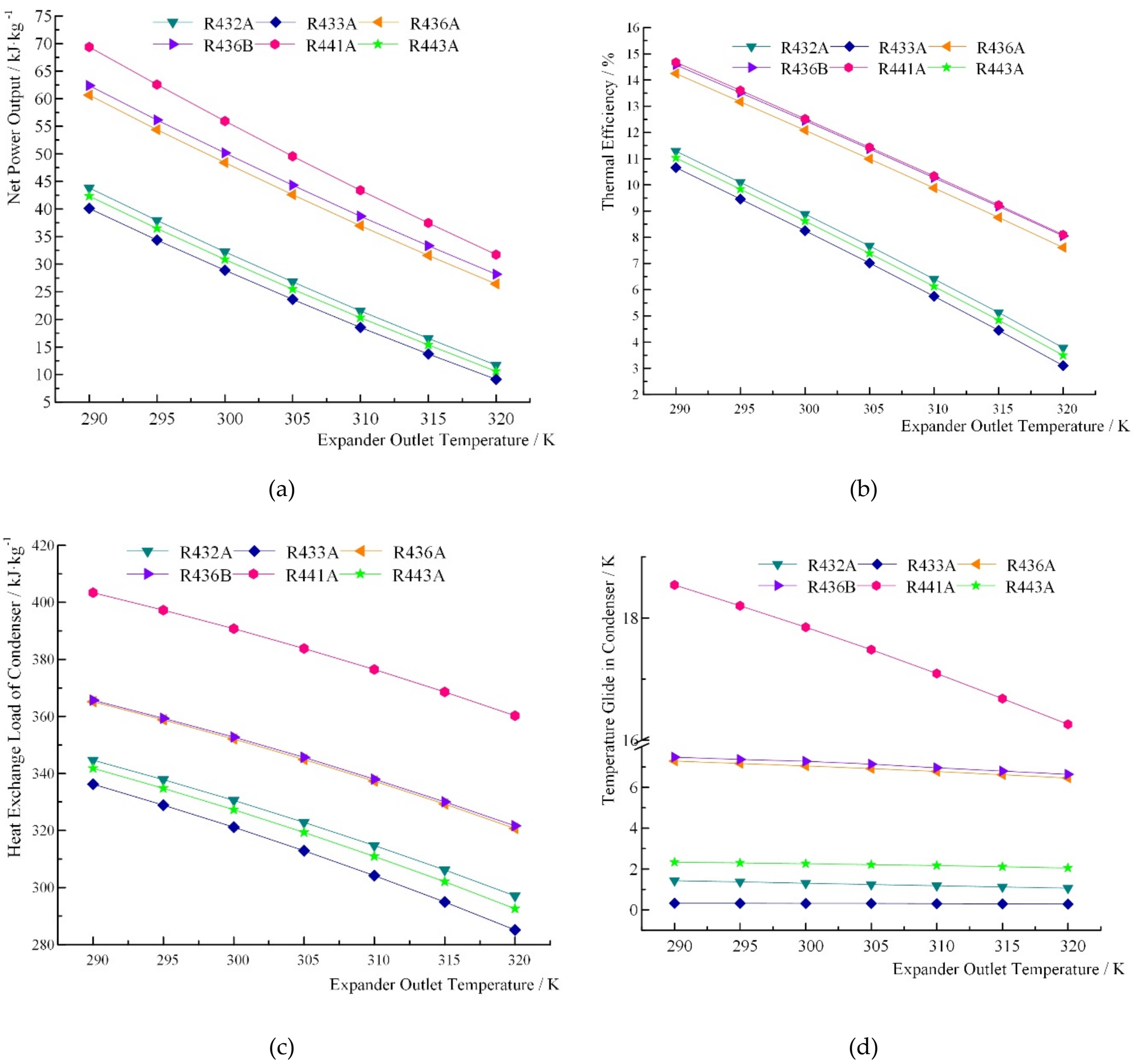


Figure 6. Variation trend of four indexes with the increase of expander outlet temperature: (**a**) net work; (**b**) thermal efficiency; (**c**) heat exchange load of condenser; (**d**) temperature glide in condenser.

From Table 5, it can be seen that the temperature glide in condenser of R441A ranges from 16 K to 18 K. If we assume a coolant with a temperature of 15 °C and a condenser pinch point temperature difference of 5 °C, all being realistic average values, then the minimum attainable working fluid expander exit temperature must be between 36 °C (15 °C + 5 °C + 16 °C = 36 °C =309 K) and 38 °C (15 °C + 5 °C + 18 °C = 38 °C = 311 K). Take the average value of these two temperatures, i.e., 310 K. Moreover, if we assume the expander exit temperature is 290 K, which is lower than the above average temperature, then in the case of R441a, would require the coolant temperature to be 290 K–17 K–5 K = 268 K(−5 °C), a temperature only attainable in arctic conditions. Therefore, 290 K is not a reasonable and feasible expander exit temperature for R441A. Based on the same principle, the other three exit temperatures, which are 295 K, 300 K, and 305 K, are not reasonable and feasible for R441A. Taken together, 310 K, 315 K, and 320 K are three reasonable and feasible expander exit temperatures for R441A.Because the expander inlet temperature is fixed at 0.9T_c for each zeotropic mixture, the temperature glide in evaporator keeps constant. The relation between the temperature glide in evaporator and the extreme temperature of subcritical region, which is 0.9T_c (critical temperature), is depicted in Figure 7. From Figure 7, it can be seen that R441A that has the highest critical temperature among all six zeotropic mixtures has the highest temperature glide in evaporator.

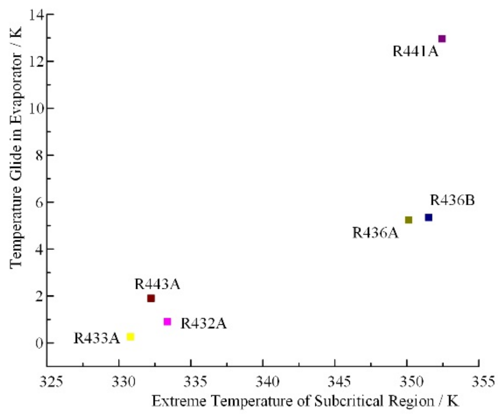


Figure 7. Relation between the temperature glide in condenser and the extreme temperature of subcritical region.

Table 6 lists the rank of six zeotropic mixtures. In Table 6, the heat exchange load of condenser is sorted from small to large, and the remaining items are sorted from large to small.

Table 6. The rank of 6 zeotropic mixtures.

Rank	Net Work	Thermal Efficiency	Heat Exchange Load of Condenser	Temperature Glide in Evaporator	Temperature Glide in Condenser
R441A	R441A	R433A	R441A	R441A	R441A
R436B	R436B	R443A	R436B	R436B	R436B
R436A	R436A	R432A	R436A	R436A	R436A
R432A	R432A	R436A	R443A	R443A	R432A
R443A	R443A	R436B	R432A	R432A	R443A
R433A	R433A	R441A	R433A	R433A	R433A

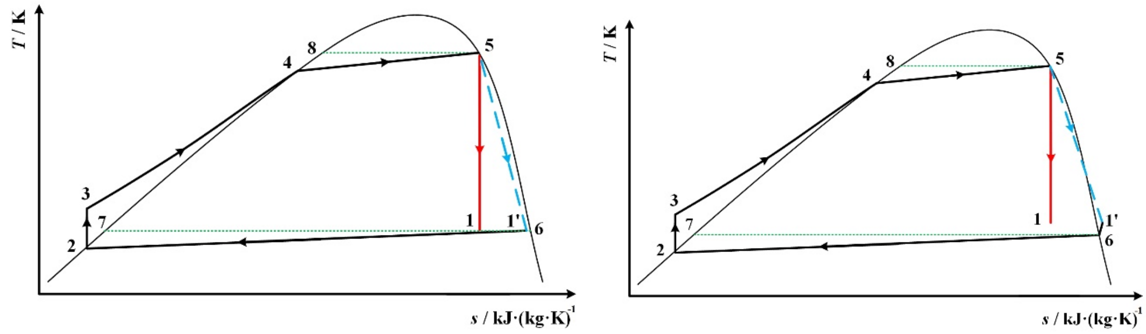
From the above analysis, it can be seen that R441A, which is a wet zeotropic mixture, can be selected as a suitable working fluid in subcritical ORC using single screw expander without considering isentropic efficiency of expander. It is suitable for both open and closed type heat source with a higher cost in heat exchanger. Its reasonable and feasible expander exit temperatures range from 310 K to 320 K.

4. Subcritical Cycle Analysis Considering Isentropic Efficiency of Expander

The above section has analyzed ideal subcritical ORC using single screw expander with zeotropic mixture as working fluid. It is based on isentropic efficiency of single screw expander is 100%. However, in practical application, its isentropic efficiency should be considered. Nowadays screw expanders show a much larger technical maturity than scroll and piston expanders [39]. The internal efficiency of single screw expander has exceeded 50% and the maximum is about 65% [25,40]. Therefore, 65% is used for analysis of single screw expander in this section.

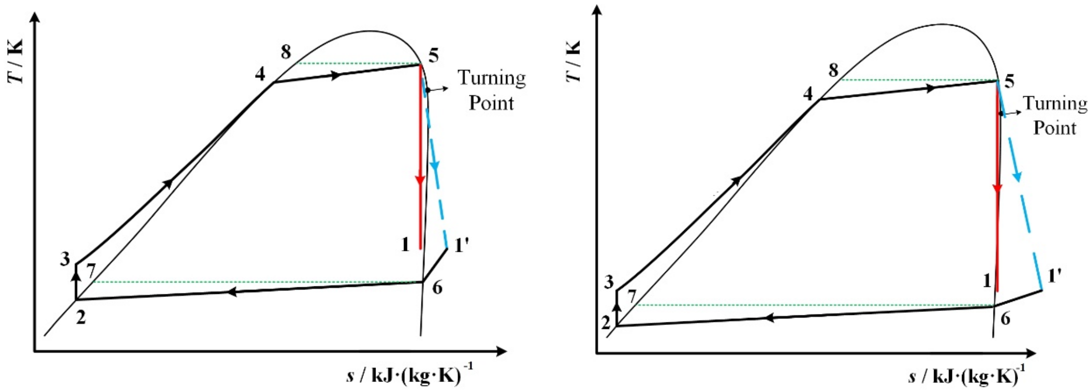
4.1. Thermodynamic Setting and Description

Figure 8 depicts a subcritical ORC using a single screw expander with a wet zeotropic mixture as working fluid when considering the isentropic efficiency of the expander. Figure 9 depicts a subcritical ORC using a single screw expander with an isentropic zeotropic mixture as working fluid when considering the isentropic efficiency of the expander. In these figures, the blue dotted lines represent the expansion processes which has considered isentropic efficiency of expander. Here it should be noted that whether the isentropic efficiency is considered or not, the outlet temperature of the single screw expander remains the same. That is to say, $T_{1'} = T_1$ in Figures 8 and 9.



(a) (b)

Figure 8. Subcritical ORC using single screw expander with wet zeotropic mixture as working fluid when considering isentropic efficiency of expander: (**a**) expander outlet at vapor-liquid two-phase region; (**b**) expander outlet at superheated region.



(a) (b)

Figure 9. Subcritical ORC using single screw expander with isentropic zeotropic mixture as working fluid when considering isentropic efficiency of expander: (**a**) expander outlet at superheated region for R436A; (**b**) expander outlet at superheated region for R436B.

All the state points in Figures 8 and 9 are described in Table 7.

Table 7. Description and determination of state points in Figures 8 and 9.

State Point	Description	Determination
1	expander outlet without considering isentropic efficiency	$s_1 = s_5$
1′	expander outlet considering isentropic efficiency	$T_{1'} = T_1$, $p_{1'} = p_6$
2	condenser outlet, at saturated liquid state	$p_2 = p_6$
3	pump outlet	$s_3 = s_2$, $p_3 = p_4$
4	at saturated liquid state	$p_4 = p_5$
5	expander inlet	$s_5 = s_1$, $T_5 = 0.9T_c$
6	At saturated vapor state	$T_6 = T_{1'}$ for Figure 5a, $p_6 = p_{1'}$ for Figures 8b and 9a and Figure 9b
7	at saturated liquid state	$T_7 = T_6$
8	at saturated liquid state	$T_8 = T_5$

In Figures 8 and 9, isentropic efficiency is calculated by:

$$\eta_{ex} = \frac{h_5 - h_1}{h_5 - h_1} \tag{7}$$

net work is calculated by:

$$w_{net} = (h_5 - h_{1'}) - (h_3 - h_2) \tag{8}$$

thermal efficiency is calculated by:

$$\eta = \frac{w_{net}}{q_e} = \frac{(h_5 - h_{1'}) - (h_3 - h_2)}{h_5 - h_3} \tag{9}$$

heat exchange load of condenser is calculated by:

$$q_c = h_{1'} - h_2 \tag{10}$$

temperature glide in evaporator is calculated by:

$$\Delta T_e = T_5 - T_4 \tag{11}$$

temperature glide in condenser is calculated by:

$$\Delta T_c = T_6 - T_2 \tag{12}$$

and vapor quality for the wet zeotropic mixture depicted in Figure 8a is calculated by:

$$x = \frac{s_{1'} - s_7}{s_6 - s_7} \tag{13}$$

4.2. Results and Discussion

Table 8 lists the net work, thermal efficiency, heat exchange load of condenser, temperature glide in the evaporator, temperature glide in the condenser, and vapor quality of four wet zeotropic mixtures and two isentropic zeotropic mixtures when the expander outlet temperature is known and considering isentropic efficiency of expander.

From the data listed in Table 8, it can be seen that when considering the isentropic efficiency of s single screw expander, the expansion process for different zeotropic mixtures is different. For R433A, its expander outlet is in the superheated region, shown by Figure 8b, when the outlet temperature varies from 290 K to 300 K and in the vapor-liquid two-phase region, shown by Figure 8a, when the outlet temperature varies from 305 K to 320 K. Similarly, for R443A, its expander outlet is in the superheated region, shown by Figure 8b, when the outlet temperature varies from 290 K to 295 K and in the vapor-liquid two-phase region, shown by Figure 8a, when the outlet temperature varies from 300 K to 320 K.

For two isentropic zeotropic mixtures, R436A and R436B, their expander outlets are always the superheated region, shown by Figure 9a,b, respectively.

For R441A that is a wet zeotropic mixture, its expander outlet is in the superheated region which is shown by Figure 8b. For another wet zeotropic mixture, R432A, its expander outlet is always in the vapor-liquid two-phase region, which is shown by Figure 8a.

As mentioned above, for R436A, R436B, and R441A, their expander outlets are always in the superheated region. Therefore, these three zeotropic mixtures need to be condensed from a superheated state to a saturated vapor state and then to a saturated liquid state. There is a very high temperature glide in the condenser. This makes the condenser outlet temperature extremely low. For example, when the expander outlet temperature is 310 K, R436A's condenser outlet temperature is 280.81 K and R436B's is 276.96 K. When the expander outlet temperature is 315 K, the condenser outlet temperature of R441A is only 278.77 K. These three condenser outlet temperatures are only slightly above 0 °C (273.15 K). It is difficult and uneconomical to reach this condensation temperature by using an air cooling or water cooling system, therefore, in subcritical ORC systems for R436A and R436B, the expander outlet temperature should be above 310 K. It should be above 315 K for the R441A system. This consideration confirms the rationality of the condensation temperature proposed in [18].

Table 8. Thermodynamic performance of six zeotropic mixtures when expander outlet temperature is known and considering isentropic efficiency of expander.

Zeotropic Mixture	Expander Outlet Temperature $T_{1'}$/K	Net Work/kJ·kg^{-1}	Thermal Efficiency/%	Heat Exchange Load of Condenser/kJ·kg^{-1}	Temperature Glide in Evaporator/K	Temperature Glide in Condenser/K	Vapor Quality
R432A	290	27.56	7.09	361.21	0.899	1.53	0.9903
	295	23.77	6.32	352.21		1.45	0.9895
	300	20.13	5.55	342.87		1.37	0.9888
	305	16.68	4.77	333.12		1.29	0.9882
	310	13.38	3.98	323.04		1.22	0.9881
	315	10.20	3.16	312.55		1.15	0.9886
	320	7.18	2.32	301.65		1.08	0.9899
R433A	290	25.07	6.55	357.54	0.263	0.34	N/A
	295	21.46	5.85	345.36		0.33	
	300	18.00	5.12	333.46		0.32	
	305	14.65	4.35	321.85		0.31	0.9998
	310	11.49	3.56	311.25		0.30	0.9983
	315	8.45	2.74	300.21		0.29	0.9970
	320	5.61	1.91	288.68		0.29	0.9967
R436A	290	N/A	N/A	N/A	5.236	N/A	N/A
	295						
	300						
	305						
	310						
	315	19.31	4.81	382.36		7.07	
	320	16.09	4.27	360.47		6.81	
R436B	290	N/A	N/A	N/A	5.342	N/A	N/A
	295						
	300						
	305						
	310						
	315	20.37	4.97	389.67		7.31	
	320	17.17	4.48	366.15		7.03	
R441A	290	N/A	N/A	N/A	12.958	N/A	N/A
	295						
	300						
	305						
	310						
	315						
	320	19.52	4.57	407.94		17.42	
R443A	290	26.55	6.84	361.71	1.904	2.57	N/A
	295	22.85	6.12	350.27		2.50	
	300	19.28	5.38	339.33		2.42	0.9996
	305	15.86	4.59	329.33		2.34	0.99784
	310	12.58	3.79	318.93		2.27	0.9965
	315	9.45	2.98	308.10		2.19	0.9956
	320	6.51	2.15	296.79		2.11	0.9953

Among all five evaluation indicators, temperature glide in the evaporator remains unchanged whether the isentropic efficiency of the expander is considered or not. The other four evaluation indicators, including net work, thermal efficiency, heat exchange load of condenser, and temperature glide in the condenser, decrease with the increase of expander outlet temperature when considering the isentropic efficiency of the expander. The variation trends of these four indicators with the increase of expander outlet temperature are depicted in Figure 10.

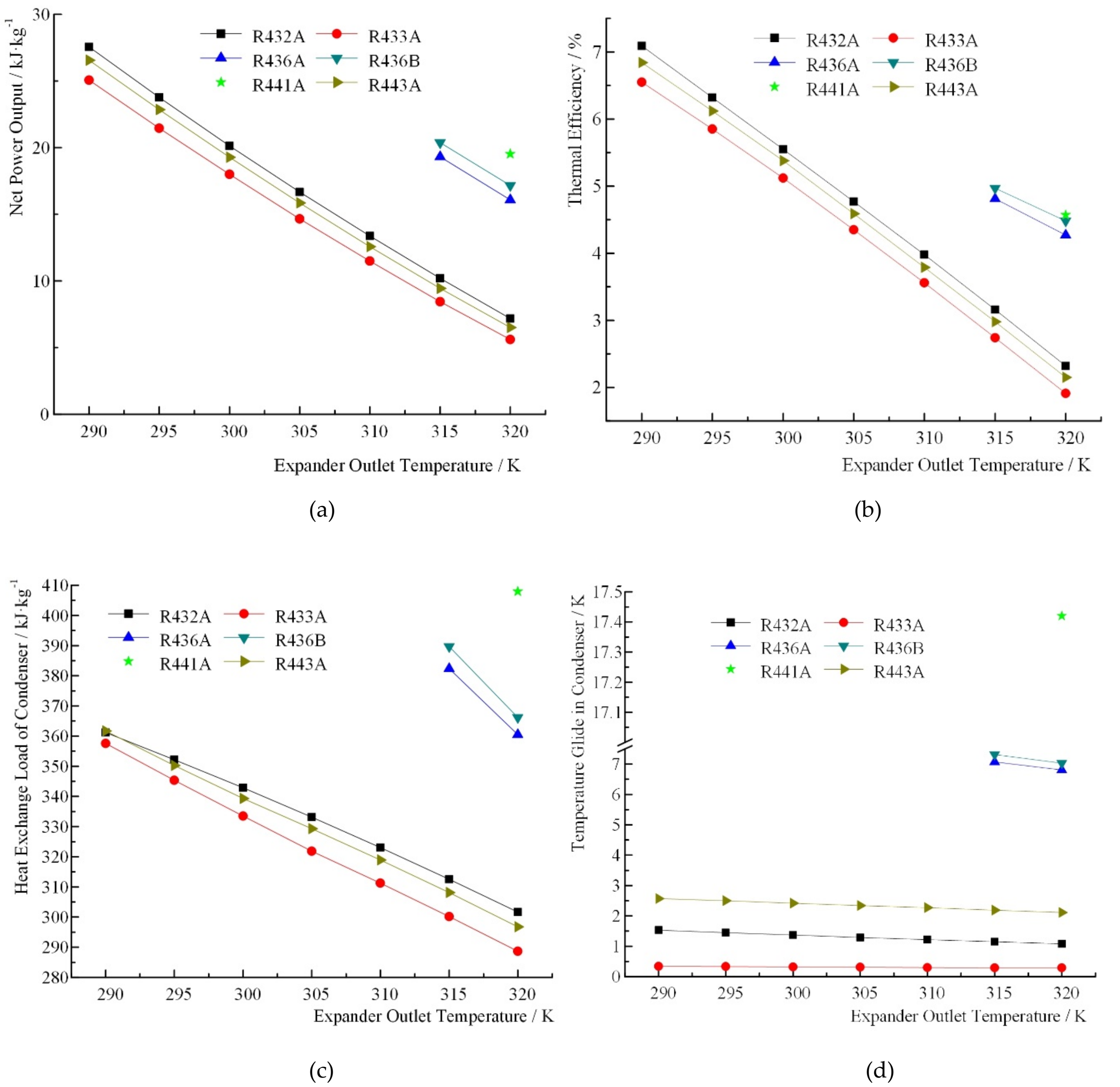


Figure 10. Variation trend of four indicators with the increase of expander outlet temperature when considering isentropic efficiency of expander: (**a**) net work; (**b**) thermal efficiency; (**c**) heat exchange load of condenser; (**d**) temperature glide in condenser.

From Figure 10a,b, it can be seen that R441A has the best performance when the expander outlet temperature is 320 K. R436B performs best at 315 K. R432A performs best from 290 K to 310 K. From Figure 10c, it can be seen that R433A has the lowest condenser heat exchange load from 290 K to 320 K. R441A has the highest at 320 K. R432A has a moderate value from 290 K to 320 K. From Figure 10d, it can be seen that R441A has the highest temperature glide in the condenser at 320 K. R432A has the moderate from 290 K to 320 K.

If we assume a coolant with a temperature of 15 °C and a condenser pinch point temperature difference of 5 °C, all being realistic average values, then the minimum attainable working fluid expander exit temperature must be 20 °C (15 °C + 5 °C, 293 K) plus the temperature glide in the condenser. Therefore, 290 K is not a reasonable and feasible expander outlet temperature for each working fluid.

The relation between vapor quality at expander outlet and expander outlet temperature is depicted by Figure 11. Without considering the isentropic efficiency of the expander, the vapor quality at the expander outlet increases with the increase of expander outlet temperature. When considering the isentropic efficiency of the expander, for R433A and R443A, their vapor quality at the expander outlet decreases with the increase of the expander outlet temperature. This is because the state of the expander outlet gradually changes from a superheated state to a two-phase state, whereas, R432A's expander outlet state is always in the two-phase region. There is a point with the longest distance from the outlet of the single screw expander to the saturated vapor curve. It is shown as "Point A" in Figure 12. With the increase of the expander outlet temperature, the vapor quality at the expander outlet decreases at first and then increases. This is because the distance from the outlet of the expander to the saturated vapor curve increases first and then decreases with the increase of the expander outlet temperature. Point A has the longest distance.

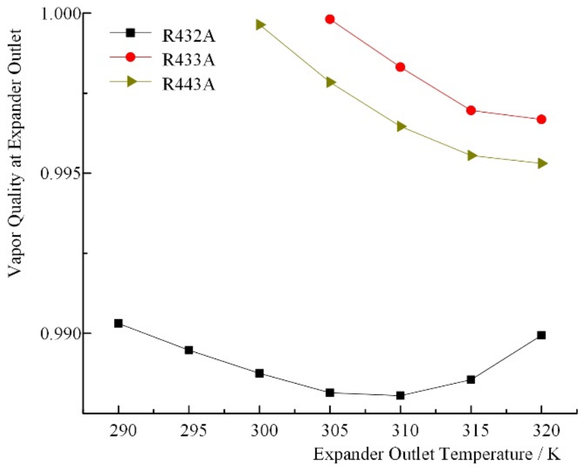


Figure 11. Relation between vapor quality at the expander outlet and the expander outlet temperature.

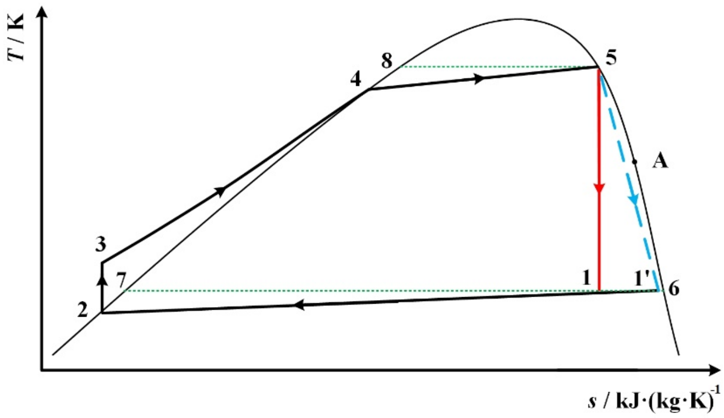


Figure 12. Point A with the longest distance between the outlet of the single screw expander and the saturated vapor curve.

Based on the above discussion and analysis, it can be seen that when considering the isentropic efficiency of a single screw expander, R441A with an expander outlet temperature of 320 K may be the suitable zeotropic mixture used for both open and close type heat sources. R436B may be selected for an expander outlet temperature of 315 K. R432A may be selected for an expander outlet temperature from 295 K to 310 K.

5. Conclusions

The organic Rankine cycle (ORC) is a popular and promising technology that has been widely studied and adopted in renewable and sustainable energy utilization and low-grade waste heat recovery. The use of zeotropic mixtures in ORC reduces the irreversibility in the evaporator and the condenser, thereby improving the thermodynamic performance. The selection of working fluid and expander are strongly interconnected. In order to make better use of the wet zeotropic mixture, a single screw expander, which is a novel expander with a tolerance of vapor-liquid two-phase expansion, was used in this paper for efficient utilization of the wet zeotropic mixtures listed in REFPROP 9.1 in a low-temperature subcritical ORC system.

Five indicators, namely net work, thermal efficiency, heat exchange load of condenser, temperature glide in evaporator, and temperature glide in the condenser, were used to analyze the performance of an ORC system with wet and isentropic zeotropic mixtures as working fluids.

Through calculation and analysis, it can be seen that R441A, which is a wet zeotropic mixture, can be selected as a suitable working fluid in subcritical ORC using a single screw expander without considering the isentropic efficiency of the expander. It is suitable for both open and closed type heat sources. Its reasonable and feasible expander exit temperatures range from 310 K to 320 K. When considering the isentropic efficiency of a single screw expander, R441A with an expander outlet temperature of 320 K may be the suitable zeotropic mixture for both open and close type heat sources. R436B may be selected for an expander outlet temperature of 315 K. R432A may be selected for an expander outlet temperature from 295 K to 310 K.

All three selected zeotropic mixtures belong to the A3 safety group classification which means a lower toxicity but a higher flammability. These three mixtures have very low GWP due to their components. In future practical applications, it is necessary to consider the ORC system complexity that may be caused by the use of the mixture.

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Conflicts of Interest: The authors declare no conflict of interest.

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