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Chapter

Utilizing Computational Methods to Identify Low GWP Working Fluids for ORC Systems

*Zhiqiang Yang, Christophe Coquelet, Jiangtao Wu,
Nian Tang and Jian Lu*

Abstract

The Organic Rankine Cycle (ORC) power cycle is a well-established solution for harnessing heat sources to generate energy. Presently, ORC systems predominantly employ hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) as working fluids. However, these substances possess significant greenhouse gas effects and are slated for future bans. To address this, it is imperative to establish rational selection criteria and corresponding techniques for evaluating working fluids suitable for industrial ORC applications. This chapter presents the working fluid selection criteria and screening methods for environmentally friendly working fluids. The chapter is organized as follows: (1) The fundamentals of working fluids section provide a broad introduction to the core principles of working fluids; (2) the working fluid section outlines reasonable selection criteria for identifying potential alternatives; (3) the screening of ORC working fluids section discusses possible working fluid candidates, simulation approach, and thermodynamic models in detail, which is very important to access the thermodynamic performance of ORC cycle; and (4) an example of the simulation of an ORC for working fluid selection section demonstrates the strategy for the selection of a working fluid considering a defined ORC architecture.

Keywords: organic Rankine cycle, working fluid selection, process simulation, thermodynamic models, waste heat recovery

1. Introduction

According to data analysis, the energy utilization rate of developing countries is only 33%, which is 10–20% lower than that of developed countries [1]; and 60–65% of industrial energy consumption [2] is finally converted into low-grade waste heat with temperatures in the range 50–280°C, which has great potential for energy recovery. Utilizing the considerable number of undeveloped renewable waste heat is an effective means to alleviate energy shortages and achieve carbon neutrality.

The supercritical Rankine cycle, Kalina cycle, and trilateral flash cycle, and Organic Rankine Cycles (ORCs) are used for low-and medium-temperature waste heat recovery. Among them, ORCs are one of the most promising technologies for utilizing low-

grade waste heat. The working fluid is the carrier for energy transfer and conversion in the ORC system. Under the same working conditions, the performance of ORC systems with different working fluids varies widely, thus, working fluid screening has always been an important direction and hotspot in ORC research. There is also the possibility, if the level of heat is low, to combine the production of electricity and heat (cogeneration); depending on the request, we can produce high quality heat using a heat exchanger (coupled with heat pump alimented by ORC for example).

In recent years, an increased scrutiny has been placed on the environmental aspect of working fluids, and regulatory pressures are driving global awareness of their impact on the environment. In 2016, the Kigali Amendment to the Montreal Protocol was adopted [3], whereby committed states must reduce the production of hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) according to a set schedule. The ozone depletion potential (ODP) and low global warming potential (GWP) are of particular interest, and emphasis has been placed on choosing a working fluid that demonstrates an ability to meet these climate protection initiatives. The currently used working fluids HFCs, HCFCs, and PFCs will not be evaluated because of their ODP and high GWP concerns, respectively [4]. The HVAC&R (heating, ventilation, air conditioning, and refrigeration) industry has to focus on the search for working fluids with zero (or extremely low) ODP and low GWP [5].

To find suitable low-GWP working fluids, reasonable selection criteria and corresponding knowledge for screening working fluids of ORC system should be provided for industrial applications. This chapter will introduce the working fluids selection criterion and screening methods for eco-friendly working fluids.

2. Fundamentals of the organic rankine cycle

The organic Rankine cycle is a cycle of thermodynamic processes, carried out by thermal machines with the objective to convert heat into mechanical work. It is based on four processes, and the mechanical work is extracted from the temperature difference between a heat source and a cooler, which is often water flow or ambient air.

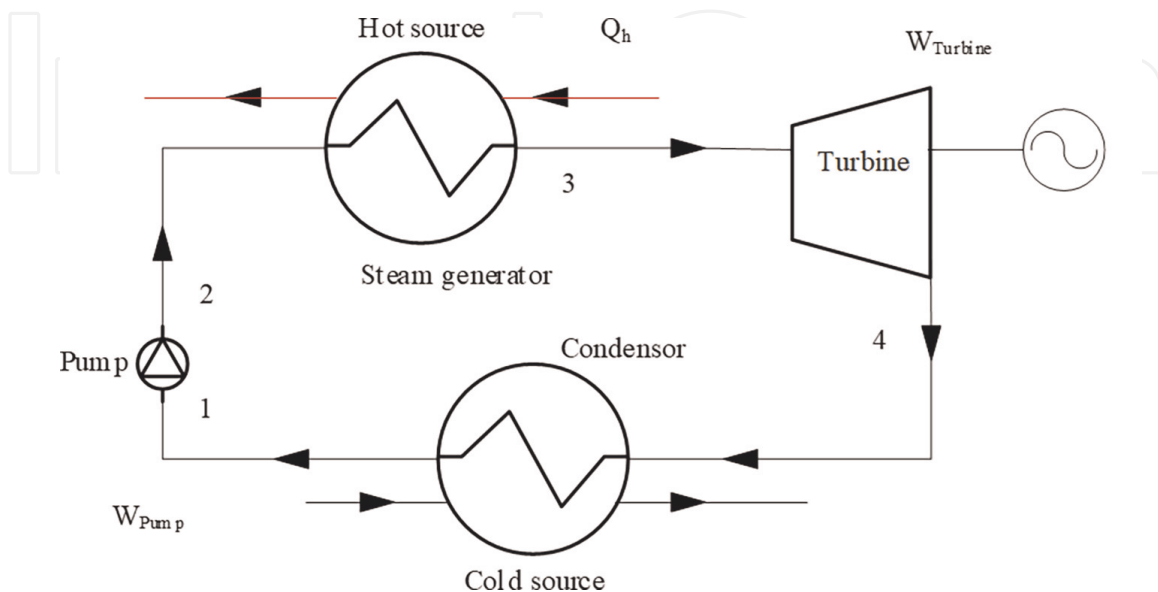


Figure 1.
Schematic of the Rankine cycle.

This type of cycle consists of a boiler/an evaporator, a condenser, a pump, and a turbine. **Figure 1** presents the cycle's elements as well as each numbered step. Then, **Figure 2** symbolizes the cycle (fluid) in a thermodynamic diagram of temperature-entropy (T-s diagram).

- Process 1–2: Adiabatic (or isentropic) pumping. The fluid has its pressure increased by the pump that, in an ideal case, should not allow any heat exchange with the environment. Therefore, the fluid has its temperature (and, consequently, its internal energy) increased.
- Process 2–3: Isobaric heat addition. The hot source transfers heat to the fluid, which in turn is vaporized, and reaches its maximum energy state in the cycle in 3. In the case of waste heat utilization, this corresponds to the energy needed to vaporize the pressurized fluid.
- Process 3–4: Isentropic expansion in a turbine. At this stage, the steam expands, and its temperature drops. Moreover, this is where the work is produced.
- Process 4–1: Isobaric heat rejection. Finally, the steam is cooled and condensed at constant pressure to the state of saturated liquid inside the condenser. The liquid then returns to the pump and the cycle starts again.

In the analysis, it is considered that the cycle operates in a steady-state, which means that all the state variables as well as the fluid flow do not change in time. Furthermore, the variation of the kinetic and the potential energy of the fluid are neglected. Thus, it is possible to calculate the efficiency linked to the ideal Rankine cycle by knowing the properties of the working fluid at different states/conditions. The ideal case occurs when the pump and turbine can guarantee isentropic conditions.

$$\eta = \frac{W_{turbine} - W_{pump}}{Q_h} \quad (1)$$

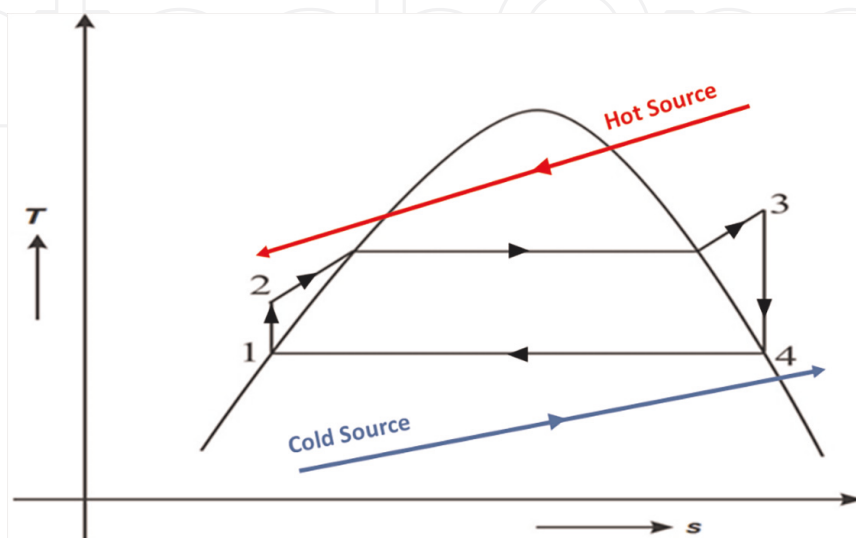


Figure 2.
Rankine cycle represented in the T-S diagram.

Eq. (1) states that the efficiency is equivalent to the difference between the work generated in the turbine and that needed to pressurize the fluid in the liquid state divided by the heat provided by the boiler. To find the value of these energies, it is necessary to apply the first law of thermodynamics in each cycle component (control volumes). In this case, the efficiency can be written in terms of enthalpy in each cycle point, as described in Eq. (2) below.

$$\eta = \frac{(h_3 - h_2) - (h_4 - h_1)}{h_3 - h_2} = 1 - \frac{h_4 - h_1}{h_3 - h_2} \quad (2)$$

There are some aspects that directly influence the efficiency of Rankine cycles. A detailed study of these aspects is carried out by McLinden et al. [6]. Basically, they are related to the increase of the temperature difference between the heat supplied and the heat rejected. For this purpose, some modifications in the cycle architecture are proposed and developed with the objective of taking advantage of the increase in performance that occurs at higher pressures but avoiding high steam humidity levels at the end of the expansion. These solutions include the use of intermediate heat exchangers and/or modifications of the flow rate of the hot source, the system's energy source.

3. Working fluid

After establishing the parameters of the Rankine cycle, the next step is the careful study of the working fluid. The working fluid plays an essential role in the system of the organic Rankine cycle. Its properties are important to the system's efficiency, and they determine the operation conditions such as operating temperature and pressure. Moreover, given the deterioration of the environment, shortage of energy resources, and extreme climate change, its environmental impact and economic viability should be considered as well.

3.1 Working fluid classification

Above all, depending on the slope dT/ds in a T-s diagram of each fluid in the state of saturation vapor, as shown in **Figure 3** [7], the working fluids can be divided into three categories:

- Dry fluids with $\frac{dT}{ds} > 0$ (e.g., pentane)
- Isentropic fluids with $\frac{dT}{ds} = 0$ (e.g., R11)
- Wet fluids with $\frac{dT}{ds} < 0$ (e.g., water)

It is investigated that the dry and isentropic fluids are more appropriate in the application of ORCs because there would be much less formation of liquid droplets compared to the wet fluids in the two-phase region, which could reduce the equipment damage such as erosion in the turbine. Apart from this, to delete the risk of liquid droplets, a superheating process is widely recommended for the wet working

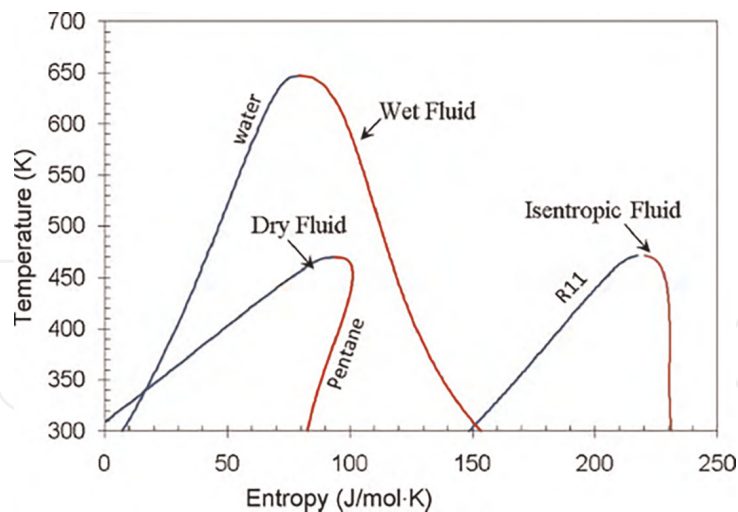


Figure 3.
Types of working fluids: Dry, isentropic, and wet.

fluids, at the expense of reduced efficiency and increased installation cost; whereas for dry fluids, superheat is unnecessary and can have an inverse impact on the ORC efficiency. In short, dry and isentropic fluids are always preferable candidates regarding operating and economic viability.

3.2 Criteria for fluid selection

When we chose the appropriate fluid candidates for the ORC application, the working fluids should be equipped with suitable chemical, thermodynamic, and transport properties and satisfy the requirements of environmental protection standards, cost, and safety.

3.2.1 Chemical property

Compared with the traditional steam Rankine cycle, organic fluids used in ORCs with high critical temperature, low triple point temperature, and low condensation temperature contribute notably to the recovery of heat from low temperature sources in terms of system performance [8].

3.2.1.1 Critical temperature

Critical temperature is considered as the primary criteria to select the working fluids by most studies. Liu et al. [8] indicated that the critical temperature should be as high as possible compared with the evaporation temperature in the application of a two-stage Rankine cycle in terms of ORC efficiency.

Some researchers [9] explored that for the pure working fluids, the hot source temperature should be 30–50°C higher than the critical temperature to gain the optimal thermodynamic performance, as for the fluids with similar critical temperature, a positive slope dT/ds of the saturation vapor line in T - s diagram is served as the second criteria.

3.2.1.2 Boiling temperature

Working fluids can be easy to handle in an ambient environment, thus, the boiling temperature is expected to be 02013–100°C.

3.2.1.3 Freezing point

The freezing point of the fluid must be lower than the lowest temperature of the cycle.

3.2.1.4 Triple point temperature

The triple point temperature should be as low as possible [7], and the condensation temperature should be below the lowest temperature of the ORC system, in case that the working fluids might freeze at any operating temperature in the cycle. Then, a condensation pressure slightly greater than the ambient pressure is preferred to prohibit air entering the ORC system [8]. In addition, the properties of organic fluids vary with operating conditions, and the thermal stability of working fluids need to be guaranteed at the range of working pressure and temperature for fear of chemical deterioration and decomposition at high temperature [10].

Material compatibility should be considered as well. Noncorrosive and non-eroding fluids are preferred for the ORC installation.

3.2.2 Thermodynamic property

The thermodynamic performance and economy of the ORC system are closely related to the physical properties of the working fluid, which will affect the efficiency, operating conditions, and equipment size of the ORC system. The thermophysical properties of working fluid mainly include the following:

3.2.2.1 Vaporization latent heat

In terms of installation size and therefore the ORC cost, fluids with high latent heat and high density are proposed to be the preferable candidates [11] because the higher the latent heat, the greater heat is absorbed in the evaporation step; but at the same time, the higher the density, the lower are the specific volume and volume flow rate. Both could mean that the system can provide more power outputs with the same equipment size. However, some researchers [12] have an inverse opinion on the latent heat of vaporization, given that better operating condition is provided at the turbine inlet for fluids with low latent heat in the saturated vapor state for the application of low-grade waste heat recovery.

3.2.2.2 Density

High vapor density is important, especially for fluids showing a very low condensing pressure (e.g., silicon oils). A low density leads to a higher volume flow rate: the pressure drops in the heat exchangers are increased, and the size of the expander must be increased. This has a non-negligible impact on the cost of the system.

3.2.2.3 *Specific heat*

Liquid's specific heat should be low so that it could decrease the work consumed by the pump and increase the work output indirectly. The working fluids with high liquid specific heats can absorb more heat from the hot source, which increases the output power of the ORC system.

3.2.2.4 *Speed of sound*

Moreover, organic fluids usually have a low speed of sound because of their large molecular weight, thus, the flowing rate is limited in the expander that largely influences the size of ORC turbines [13]; besides, it causes additional shock wave loss on account of the supersonic phenomenon appeared at the nozzle outlet of the expander.

3.2.2.5 *Phase diagram*

The thermodynamic property such as the phase diagram is also significant in the analysis and application of ORC.

3.2.3 *Transport property*

To decrease the installation cost and increase the space utilization, fluids with low dynamic viscosity and high thermal conductivity contribute to an enhancement of heat transfer and, in consequence, a reduction of heat exchanger size [13].

3.2.4 *Environmental criteria*

In general, there are three parameters that we need to consider in the aspect of environmental criteria: ozone depletion potential (ODP), global warming potential (GWP), and atmospheric lifetime (ALT).

ODP represents the degradation effect on the ozone layer in the atmosphere of each fluid, then GWP is a measure of the total energy that fluid gases can trap in the atmosphere relative to the heat absorbed by the same amount of carbon dioxide emission during a given time, whereas ALT represents the potential for the atmospheric accumulation of each chemical. The Montreal Protocol in 1987 proposed the phase out of ozone-depleting substances such as CFCs and HCFC, and the Kyoto Protocol proposed the reduction of greenhouse gases emissions, such as carbon dioxide, methane, nitrous oxide, hydrofluorocarbons (HFCs), perfluorocarbons (PFCs) and sulfur hexafluoride (SF₆). Generally, working fluids with zero ODP values, minimal GWP values, and low ALT values are recommended during the selection of working fluids [14].

3.2.5 *Safety criteria*

In choosing suitable working fluids, the potential operating dangerousness needs to be considered. According to the ASHRAE 34 safety classification standard, the fluids are classified into two toxicity groups A and B and into three flammability groups 1, 2, and 3, as shown in **Table 1** [14]. In general, fluids with nontoxic, nonflammable, and noncorrosive characteristics are preferable; however, in practice, it is hard to meet all the criteria so a relatively satisfactory fluid is sufficient during the selection.

	Class A	Class B	
Toxicity	No evidence	Evidence	
Concentration	< 400 ppm	< concentration limit	
	Class 1	Class 2	Class 3
Flammability	No flame propagation	Possible flame propagation	High flammability
Condition	In open air under normal condition	In open air under normal condition	Under any condition

Table 1.
Classification of fluids according to toxicity and flammability.

All in all, working fluids with high critical temperature, high density, high latent heat, low triple point temperature, low condensation temperature, condensation pressure slightly higher than the atmospheric pressure, zero ODP, low GWP, low ATL, and low risk of toxicity and flammability are expected in terms of system efficiency, economy, environmental protection, and safety.

4. Selection of ORC working fluids

4.1 Working fluid candidates for ORC

Several studies have been performed to find candidate molecules as alternative working fluids for refrigeration [15], heat pumping, and ORC applications [16]. Considering various criteria (particularly low toxicity, low flammability, low GWP, and high energy efficiency), only a few single-component compounds are suitable for many of the relevant applications. According to the research of McLinden [6, 15], only a small part of elements in the periodic table would form compounds volatile enough to serve as working fluids. Molecules meeting the screening criteria for working fluids should be limited to small molecules less than or equal to 18 atoms, and the molecules comprise only the elements C, H, F, Cl, Br, O, N, or S. Hundreds of substances can be considered as working fluid candidates for ORC application, including hydrofluoroethers (HFEs), hydrofluorocarbons (HFCs), ethers (HEs), unsaturated hydrofluoroolefins (HFO), hydrofluoroiodocarbons (HFIC), fluoroiodocarbons (FIC), fluorinated alcohols, and fluorinated ketones. **Table 2** exhibits pure working fluid candidates for the ORC system.

Category/Name	Product Name	ODP ^{c,d}	GWP ^{b,c}	P _c / MPa ^e	T _c / °C ^e	T _b / °C ^e	Safety classification ^a
Fluorinated ethers							
Pentafluorodimethylether	RE125	0	14,900	3.326	80.7	-34.55	—
Methyl-trifluoromethyl-ether	RE143a	0	756	3.635	104.77	-23.58	—
2-Difluoromethoxy-1,1,1-trifluoroethane	RE245fa2	0	659	3.433	171.73	29.25	—
Heptafluoropropyl-methyl-ether	RE347mcc	0	575	2.478	164.55	34.18	—

Category/Name	Product Name	ODP ^{c,d}	GWP ^{b,c}	P _c / MPa ^e	T _c / °C ^e	T _b / °C ^e	Safety classification ^a
Hydrocarbons							
Propane	R290	0	—	4.251	96.74	-42.11	A3
Isobutane	R600a	0	—	3.629	134.66	-11.74	A3
Butane	R600	0	—	3.796	151.98	-0.49	A3
pentane	R601	0	—	3.367	196.55	36.05	A3
Propene	R1270	0	—	4.555	91.06	-47.61	A3
Aromatics							
Toluene	C ₇ H ₈	0	—	4.1263	318.6	110.6	—
Hydrofluorocarbons (HFCs)							
Fluoroethane	R161	0	12	5.027	102.16	-37.7	—
Difluoromethane	R32	0	675	5.782	78.10	-51.65	A2
1,1-Difluoroethane	R152a	0	124	4.516	113.26	-24.02	A1
1,1,1,2-Tetrafluoroethane	R134a	0	1430	4.059	101.06	-26.07	A1
1,1,2,2-Tetrafluoroethane	R134	0	1100		118.59	-23	—
1,1,1,2,3,3,3-Heptafluoropropane	R227ea	0	3220	2.925	101.75	-16.34	A1
1,1,1,2,3,3,3-Heptafluoropropane	R263fa	0	9810	3.420	139.29	6.17	A1
1,1,1,3,3-Pentafluoropropane	R245fa	0	1030	3.651	153.86	15.04	B1
1,1,2,2,3-Pentafluoropropane	R245cb	0	—	3.940	174.42	25.26	—
1,1,1,3,3-Pentafluorobutane	R365mfc	0	794	3.266	186.85	40.19	—
Perfluorocarbons (PCFs)							
Hexafluoroethane	R116	0	12,200	19.88	3.048	-78.09	A1
Octafluoropropane	R218	0	8830	71.87	2.640	-36.79	A1
Octafluorocyclobutane	RC318	0	10,300	115.2	2.777	5.96	A1
Chlorofluorocarbons (CFCs)							
Trichlorofluoromethane	R11	1	4660	4.407	197.96	23.70	A1
Dichlorodifluoromethane	R12	0.82	10,200	4.136	111.97	-29.75	A1
Hydrochlorofluorocarbons (HCFCs)							
Chlorodifluoromethane	R22	0.44	1760	4.990	96.14	-40.81	A1
1,1-Dichloro-1-fluoroethane	R141B	0.12	782	4.21	204	32.05	—
1-Chloro-1,1-difluoroethane	R142B	0.06	1980	4.06	137	-9.12	A2
Hydrofluoroolefins (HFOs)							
2,3,3,3-Tetrafluoropropene	R1234yf	0	4	3.382	94.7	-29.48	A2
<i>E</i> -1,3,3,3-tetrafluoropropene	R1234ze (E)	0	7	3.634	109.36	-18.97	A2L
<i>Z</i> -1,3,3,3-tetrafluoropropene	R1234ze (Z)	0	4	3.531	150.12	9.73	A2
3,3,3-trifluoropropene	R1243zf	0	1	3.518	103.78	-25.42	A2L

Category/Name	Product Name	ODP ^{c,d}	GWP ^{b,c}	P _c / MPa ^e	T _c / °C ^e	T _b / °C ^e	Safety classification ^a
E-1,2-dichloroethene	R1130(E)	0.00024	5	—	234.1	321	B2
Z-1,1,1,4,4,4-hexafluorobutene	R1336mzz (Z)	0	2.05	2.903	171.4	33.45	A1
E-1,1,1,4,4,4-hexafluorobutene	R1336mzz (E)	0	9	2.063	137.7	7.43	A1
E-1-chloro-3,3,3-trifluoropropene	R1233zd (E)	0.00034	4.5	3.624	166.45	18.26	A1
Trifluoroemthane	R1311	0.01	1	—	123.3	7.4	A1
1,1-difluoroethene	R1132a	0	0.05	—	30.1	-20	A2
Z – 1-chloro-2,3,3,3-tetrafluoropropene	R1224yd (Z)	0.00023	0.88	—	155.5	14	A1
Alcohols							
Methanol	—	0	—	8.103	239.45	64.48	—
Ethanol	—	0	—	6.268	241.56	78.42	—
Ethers							
Dimethyl-ether	RE170	0	—	5.336	127.23	-24.78	—
Diethyl-ether	R610	0	—	3.64	193	34.55	—
Inorganics							
Ammonia	R717	0	—	1.133	132.41	-33.31	B2
Water	R718	0	—	2.206	373.95	100.00	—
Carbon dioxide	R744	0	—	7.377	3096	-78.46	A1

^aReference [17]. ^bReference [18]. ^cReference [19]. ^dReference [20]. ^eReference [21].

Table 2.
Basic properties of alternative working fluids.

What needs to be emphasized here is that the molecular screening of working fluids requires a trade-off between GWP, toxicity, flammability, and normal boiling point. Taking halogen compounds as an example (**Figure 4**), we can observe rules as follows:

- Increasing the number of Cl atoms in the molecule increases the boiling point of the molecule and increases the toxicity of the molecule.
- Increasing the number of H atoms in the molecule decreases the toxicity of the molecule, but the flammability also increases.
- Increasing the number of F atoms in the molecule increases the stability of the molecule, but the GWP value also increases.

More than 60 million single-component fluids have been screened in a comprehensive project to develop new low-GWP working fluids [22]. Many molecules meet

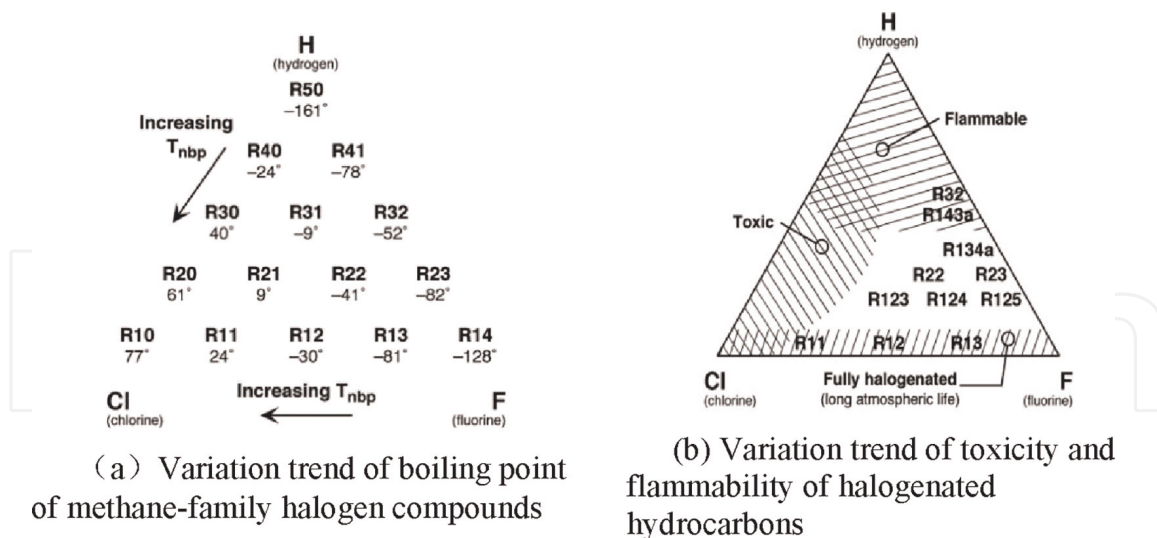


Figure 4. Variation trend of boiling point, toxicity, flammability, and atmospheric lifetime for halogen compounds as a function of element [19]. (a) Variation trend of boiling point of methane-family halogen compounds. (b) Variation trend of toxicity and flammability of halogenated hydrocarbons.

the requirement of a suitable critical temperature, but the number of molecules decreases dramatically while satisfying both the requirement of low GWP. For each additional screening requirement, the number of optional molecules decreases dramatically. Only 138 molecules with an estimated critical temperature between 47 and 147°C and GWP below 1000 have been identified by McLinden and co-workers [19]. Because the GWP became an important sector for screening suitable working fluids, some of HFOs and HCFOs have been considered as the optional fourth-generation eco-friendly working fluids for heat pumps and ORC systems [20, 23].

4.2 Assessment of cycle performance

For a given application (cold source temperature, hot source temperature, cycle structure, etc.), the screening of working fluids is basically such a process: first, build a steady-state simulation model of the ORC cycle under a given heat source and heat sink conditions, and then run this model with different working fluids.

4.2.1 Simulation approach

We propose an approach to the full modeling of an ORC system. We have only considered a system thermodynamic approach based on the thermodynamic properties of the working fluid. For doing this and as previously commented, some assumptions should be made to simplify the analysis, because geometric parameters of pump, turbine and heat exchangers are initially unknown and have to be designed. These assumptions are essential for different reasons: to ensure the functioning of the cycle according to the thermodynamics laws, avoiding, for example, at some point in the cycle, the fluid temperature exceeds the limits established by the external sources. Moreover, they can also allow a more precise selection of the best working fluid for each application, as it is possible to vary the used fluids and their evaporation and condensation pressures/temperatures. Finally, estimations such as pumping and expansion losses can be made to obtain results that are more similar to what is expected in real processes, in which the heat exchangers are not perfectly isolated

from the environment; therefore, the heat exchangers that occur in the system are not considered perfectly reversible. Moreover, assumptions concerning pinch temperature can also be made to create a more realistic simulation of the ORC and the best comparison of the performance for each working fluid tested.

The proposed architecture for the analyzed cycle in this paper is shown in **Figure 5**.

It is observed that in this architecture, pre- and superheating zones are separated as well as pre- and supercooling zones to simplify the analysis of heating and cooling processes in boilers and condensers. The hypotheses that guide this cycle and make possible calculations for each state are the following:

- Perfect heat exchange in evaporator (2–3) and condenser (4–1), that is, the losses are negligible, and all heat recovered is absorbed by the working fluid.
- All heat additions between States 2 and 3 as well as all heat rejections between States 4 and 1 are isobaric.
- An isothermal compression efficiency $\eta_{ip} = 90\%$ is assumed, and a mechanical efficiency $\eta_{mp} = 80\%$ for the pump. Values are not standardized but are in a range commonly considered in literature.
- The working fluid leaves the state of saturated liquid in 2 and reaches the saturated vapor state in 3.
- An isothermal expansion efficiency $\eta_{it} = 80\%$ is assumed, and a mechanical efficiency $\eta_{mt} = 80\%$ for the turbine. Values are not standardized but are in a range commonly considered in literature.
- The working fluid leaves the state of overheat vapor in 4 and reaches the saturated liquid state in 1.
- Pinch point temperature, which means the minimum difference between the working fluid temperature and the hot/cold source temperatures (that occurs when the fluid evaporates/condensates) $\Delta T_{evp}/\Delta T_{cnd}$ is 3 K. This value was based

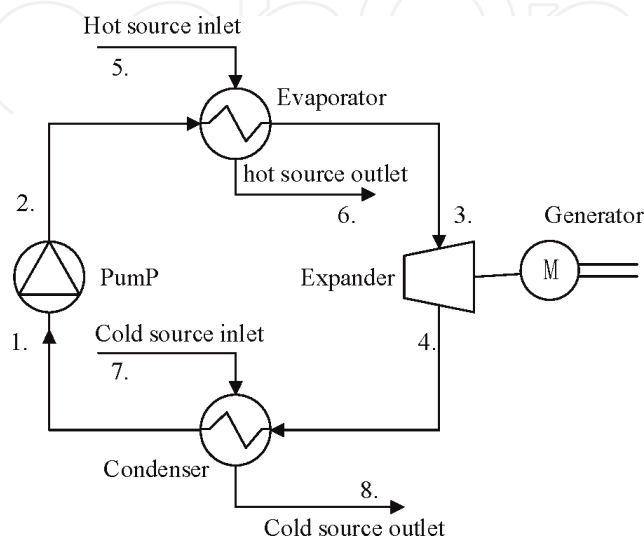


Figure 5.
Schema of the cycle used in the calculation.

on that described in [12], but the value equal to 5 K can also be considered because as the pinch point temperature decreases, the heat transfer effectiveness increases.

- The overheating temperature of the working fluid ΔT_{sup} is 3 K.
- The supercooling temperature of the working fluid ΔT_{sub} is 0.5 K [24].

In this example, we studied the application of waste heat from annealing furnaces, where the hot source is fixed as water at 363.15 K (90°C), within the temperature ranges mentioned in [25]. On the other side, the cold source is the cheapest and the most common substance: air, at 288.15 K (15°C) and 1 Atm (0.101 MPa). From this, the working fluid evaporation and condensation temperatures are adjusted to include this defined range. **Figure 6** shows a graph created to better illustrate all these cycle processes in the T - s diagram.

However, to calculate the power produced by the ORC and its efficiency, it is necessary to know the working fluid properties, such as enthalpy, entropy, and density in various states. These values are obtained from the NIST Reference Fluid Thermodynamic and Transport Properties Database (REFPROP) [26], a software whose library includes many substances (including organic compounds studied in this article) and which can be integrated with other calculation environments.

4.2.2 Thermodynamics models

Section 4.2.1 provides methods for calculating the heat and work quantities associated with various processes, but they are useless without knowledge of the thermodynamic and transport properties. Thermodynamic properties differ from one molecule to another, and the laws of thermodynamics themselves do not provide any description or model of material behavior.

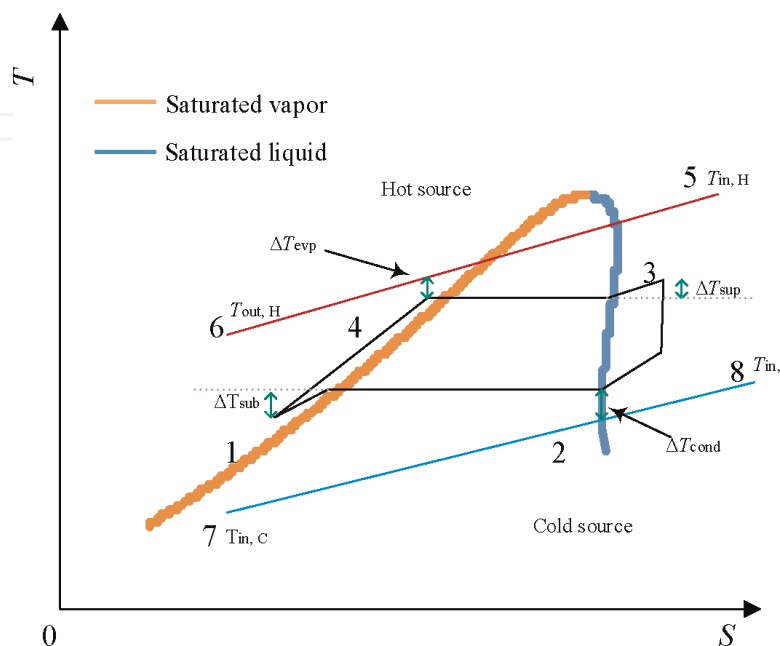


Figure 6.
 T - s diagram of the modeled cycle.

An equation of state (EOS) is used to describe the thermodynamic state and the thermodynamic properties of a substance, and the functional formula is used to describe the relationship among pressure, temperature, and volume (pvT) for pure substances and mixtures. Using thermodynamic differential derivation, the thermodynamic properties and phase equilibrium of substances can be calculated from the EOS.

Equations of state can roughly be divided into four categories as follows:

1. Ideal-gas law

The ideal-gas law is the simplest EOS. It is based on two basic assumptions: (1) gas molecules do not occupy volume and are elastic molecules and (2) no interaction force between molecules. The ideal gas law can be written as Eq. (3), and the pvT relationship is obtained by molecular motion theory and statistical methods.

$$p = \frac{RT}{v} \quad (3)$$

where p, T, and v are pressure, temperature, and molar volume, respectively, and R is the gas constant.

In the low-density limit, all kinds of EOS reduce to the ideal gas law. Ideal gas law cannot be applied with liquid.

2. Virial equation of state

The virial equation of state (EOS) is a polynomial series in pressure or in inverse volume whose coefficients are functions only of T for a pure fluid.

$$Z = 1 + B\left(\frac{P}{RT}\right) + (C - B^2)\left(\frac{P}{RT}\right)^2 + \dots \quad (4)$$

where the coefficients B and C are the second and third virial coefficients, respectively.

The expressions for the second virial coefficient can be obtained from the Tsonopoulos model [27], which is only applied to the saturated vapor because it cannot be used for liquids or at high pressures.

The Benedict-Webb-Rubin (BWR) EOS is an empirical extension of the virial EOS. The BWR expressions are based on the pioneering work of Benedict, Webb, and Rubin (1940 and 1942) who combined polynomials in temperature with power series and exponentials of density into an eight-parameter form [28]. Additional terms and parameters were later introduced by others to formulate modified Benedict-Webb-Rubin (MBWR) EOS.

The general form of BWR/MBWR correlations is

$$Z = 1 + f_1(T)/v + f_2(T)/v^2 + f_3(T)/v^n + f_4(T)[(\alpha + \gamma/v^2)/V^m] \exp(-\gamma/v) \quad (5)$$

3. Cubic equation of state

The first practical cubic equation of state was proposed by van der Waals in 1873 [29]; the development of the modern cubic equation of state started from the Redlich Kwong (RK) equation published in 1949 [30], which is improvements to the van der

Waals equation. Based on the previous work, Peng and Robinson [31] proposed the Peng Robinson (PR) state equation in 1976, and its form is as follows:

$$p = \frac{RT}{v-b} - \frac{a(T)}{v(v+b) + b(v-b)} \quad (6)$$

The parameters a and b are related to the critical pressure, critical temperature, and acentric factor as shown in Eqs. (6) and (7).

$$a(T) = 0.457235 \frac{R^2 T_c^2 \alpha(T)}{p_c} \quad (7)$$

$$b = 0.077796 \frac{RT_c}{p_c} \quad (8)$$

$$\alpha(T) = [1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1 - T_r^{0.5})]^2 \quad (9)$$

where ω is the acentric factor, $T_r = T/T_c$, T and T_c represent reduced temperature and critical temperature.

In 1982, Patel and Teja [14] corrected the compressibility factor of the state equation to a parameter related to the substance and obtained the Patel Teja equation of state (PT EOS). The fluid properties of a certain component near the vapor-liquid critical point are difficult to obtain from cubic EOS. Modification of the Patel Teja EOS (mPT EOS) as proposed by Coquelet et al. [32] permits to better estimating the thermodynamic properties close to the critical point.

The RK, PR, PT, and mPT equations are representative of cubic EOS. This type of EOS is characterized by fewer parameters, simple form, and fast solution speed, and is widely used in industry. They differ in their accuracy to estimate the densities, particularly the liquid and supercritical fluid densities.

4. Fundamental equation of state based on Helmholtz energy

The Helmholtz energy-based equations are the most accurate EOS at a time when they were just coming into widespread use. The Helmholtz energy model was developed by NIST and included in the REFPROP software. Helmholtz-type equations of state (also called fundamental equations of state) are explained in terms of reduced molar Helmholtz free energy (see Eq. 10) wherein superscript ig concerns ideal gas contribution and superscript x concerns residual contribution. This equation contains several adjustable parameters α_i and α_k , t_k , d_k , and l_k . Experimental data are required to adjust these parameters. Therefore, numerous and accurate experimental data (phase equilibria and volumetric properties essentially) are required. In comparison to the previous cited equations, the fundamental equation of state guarantees a very accurate prediction of the thermodynamic properties at the condition of the availability and the quality of the experimental data.

$$\alpha(\delta, \tau) = \frac{A}{RT} = \alpha^{id} + \alpha^r + \sum N_k \delta^{d_k} \tau^{t_k} + \sum N_k \delta^{d_k} \tau^{t_k} \exp(-\delta^{l_k}) \quad (10)$$

Temperature and density are expressed in dimensionless variables $\delta = \frac{\rho}{\rho_c}$ and $\tau = \frac{T}{T_c}$. ρ_c and T_c are the critical density and temperature, respectively. This equation

of state is parametrized for numerous working fluids that can be potentially used for ORC systems. These fluids can be pure components or mixtures. NIST REFPROP software has established a very accurate thermodynamics database for all the most commonly used working fluids based on the Helmholtz EOS. In addition, this model can be applied for the mixture. Mixing rules based on multifluid approximation are considered for the computation of the new critical properties (ρ_C and T_C) corresponding to the mixture. Binary interaction parameters have to be determined on the experimental base (phase equilibria and volumetric properties).

5. What can be one strategy for working fluid selection?

In the process of working fluid selection (**Figure 7**), the knowledge of thermodynamic properties is essential, but the step consisting of the utilization of virtual machine or process simulator software is also essential to screen some working fluids and reduce the list of potential candidates. For this essential step, the question of the thermodynamic model, predictive or not, and its accuracy is also essential. Once a list of fluids has been selected, it will be necessary to refine the thermodynamic model through data acquisition and adjustment of the parameters of the selected thermodynamic models [13].

The working fluid can be a pure fluid or a mixture. The advantage of a zeotropic mixture is its possibility to adapt the temperature glide to the variation of temperature of the heat or cold sources. With the adapted zeotropic mixture, we have the possibility to the irreversible low in heat exchanger. Zhang et al. [34] have proposed a very interesting analysis of the performance of an ORC in the context of ocean thermal energy conversion in 2022. Similar utilization of zeotropic working fluid is realized with the utilization of geothermal water as a heat source (Liu et al. [35]). It was observed that the utilization of the adapted zeotropic working fluid will lead to better matches of the temperature profiles of the working fluid and the heat source [13].

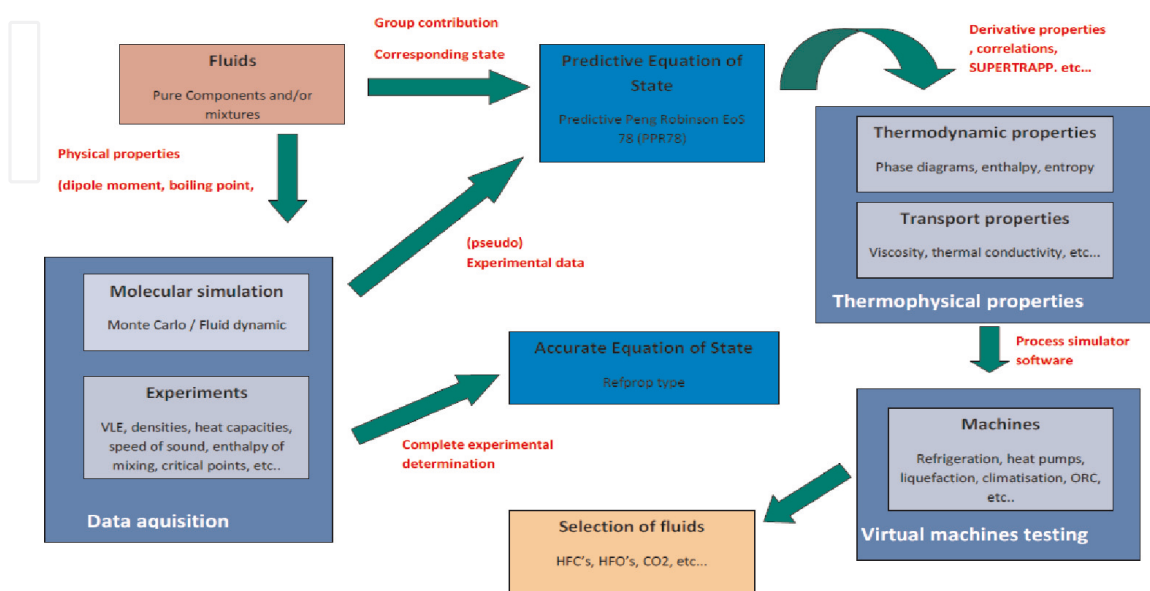


Figure 7.
A strategy for working fluid selection [33].

6. Example of simulation of an ORC for working fluid selection

This section illustrates the strategy presented on working fluid selection. We propose to discuss an example of selecting a fluid for utilizing available waste heat. In our case study, we have one heat source at the temperature of 120°C and one cold source at the temperature of 15°C.

We remind that the purpose of an ORC system is to generate power from low-temperature heat sources. Traditionally, water is used as the working fluid in Rankine cycle applications. However, because of its characteristics, water is not suitable for all applications, especially when the power of the heat source is low (unlike in coal, gas, or nuclear power stations). In a study by Dickes et al. [36] various case studies for ORC applications were presented, covering different power levels. The study discussed several working fluids, considering their impact on the environment (zero Ozone Depletion Potential [ODP] and lower Global Warming Potential [GWP]), as well as their inflammability and toxicity. To select the most suitable working fluid, a virtual machine can be used to simulate a simple ORC system. It is important to clearly define the main characteristics of the simple ORC system to conduct the simulation effectively.

1. Selection of a working fluid. In our case study, we have considered pure fluid. We will consider R1233zd(E) (*trans* 1-chloro 3,3,3-trifluoropropene), R600 (n-butane), R365mfc (1,1,1,3,3-pentafluorobutane) and the reference fluid R245fa (1,1,1,3,3-pentafluoropropane). The properties of the selected working fluid are presented in **Table 3**.
2. The level of temperature of the heat source for the vapor generator (120°C) with a difference of temperature with the working of 5°C (fix pinch temperature).
3. The level of temperature of the cold source (condenser) is 15°C with a difference of temperature with the working of 5°C (fix pinch temperature).
4. The pump and turbine with isentropic compression of the liquid and expansion of gas, respectively. Isentropic efficiencies are 0.7 and 0.8, respectively.

Fluid	Full name	Chemical Formula	Family	T_C /K	P_c /bar	Acentric factor	Molar mass /g.mol ⁻¹	GWP	Safety data
R245fa	1,1,1,3,3-pentafluoropropane	C ₃ H ₅ F ₃	HFC	427	36.51	0.3776	134	1030	B1
R1233zd (E)	<i>trans</i> 1-chloro 3,3,3-trifluoropropene	C ₃ F ₃ Cl	HFO	440	36.24	0.3025	130.5	1	A1
R600	n-butane	C ₄ H ₁₀	HC	425	37.96	0.2002	58.12	1	A3
R365mfc	1,1,1,3,3-pentafluorobutane	C ₃ H ₅ F ₅	HFC	460	32.66	0.3800	148.00	860	A2

Table 3. Properties of the selected working fluids from NIST data base [26] and safety data issued from ASHRAE 34, 20,010 [17].

5. The mole flow is the same (1 kmol.h^{-1}).
6. The heat exchangers work at constant pressure. At the outlet of the evaporator, the working fluid is at its dew point. At the outlet of the condenser, the working fluid is at its bubble point.
7. At the outlet of the pump, we have a pre-heater connected to the regenerator located at the outlet of the turbine.

The simulation is realized using the Aspen plus software [37]. The Peng Robinson equation of state is considered for all the calculation. Four heater modules have been selected with heat flux connection between REGEN and PRE-HEAT (recuperation of heat). It can also be called Internal Heat Exchanger. GENV is the generator of vapor, and COND is the condenser. Normally, this process contributes to increased work output and so obtains a better overall efficiency. One TURBINE and one PUMP have also been considered.

The thermodynamic performance can be evaluated by considering two coefficients:

1. the energy efficiency given by the work produce over the heat absorbed by the cycle (Eq. 3)

$$\eta = \frac{W_P + W_T}{Q_{GENV}} = \frac{(h_2 - h_1) + (h_4 - h_3)}{h_1 - h_{4bis}} \quad (11)$$

2. the volumetric capacity (VC), which corresponds to the work produce per unit of working fluid. If you need an important work, energy, and if the volumetric capacity is low, you need a large flow of working fluid. This means you need to pay attention to the design and sizing of the pipe.

$$Vc = \rho_1 W_P + \rho_3 W_T = \rho_1 (h_2 - h_1) + \rho_3 (h_4 - h_3) \quad (12)$$

The results of each simulation are presented in **Tables 4-8**. **Table 8** presents the comparison of the performances.

Exergy efficiency can also be considered to compare the performance of the fluid (**Table 8**). This analysis is very useful for ORC: exergy can be considered as the quality of energy because it represents the useful part of energy. The definition is given by Eq. 13. T_0 is the ambient temperature and T_h is the temperature of working fluid at the outlet of the generator of vapor. For pure working fluid and for our case study, this criterion is not a very different form of energy efficiency, but it can be very

States (Figure 8)	1	2	2BIS	3	4	4BIS
Temperature/°C	110.0	61.0	20.0	20.0	20.9	49.0
Pressure /bar	15.9	1.3	1.3	1.3	15.9	15.9

Table 4.
Values of temperature and pressure for R245fa of each point of the cycle.

States (Figure 8)	1	2	2BIS	3	4	4BIS
Temperature/°C	110.0	70.3	20.0	20.0	20.4	59.5
Pressure /bar	7.0	0.5	0.5	0.5	7.0	7.0

Table 5.
 Values of temperature and pressure for R365mfc of each point of the cycle.

States (Figure 8)	1	2	2BIS	3	4	4BIS
Temperature/°C	110.0	57.3	20.0	20.0	20.8	46.6
Pressure /bar	13.2	1.1	1.1	1.1	13.2	13.2

Table 6.
 Values of temperature and pressure for R1233zd of each point of the cycle.

States (Figure 8)	1	2	2BIS	3	4	4BIS
Temperature/°C	110.0	59.1	20.0	20.0	21.3	49.5
Pressure /bar	18.9	2.1	2.1	2.1	18.9	18.9

Table 7.
 Values of temperature and pressure for R600 of each point of the cycle.

Mass enthalpy /kJ.kg ⁻¹	States (Figure 8)						$\eta/\%$	VC/ m ⁻³	Mass flow/ kg.h ¹	$\eta_{EX}/\%$
	1	2	2BIS	3	4	4BIS				
R245fa	-8700.3	-8727.4	-8764.4	-8957.7	-8956.2	-8919.2	11.7	4557	134.05	49.7
R600	-2058.6	-2109.6	-2179.5	-2548.4	-2544.4	-2474.4	11.3	4902	58.12	48.0
R1233zd (E)	54.08	24.92	-5.94	-199.81	-198.48	-167.63	12.6	3754	130.50	53.4
R365mfc	-7722.39	-7755.78	-7805.78	-7989.19	-7988.47	-7938.48	15.1	2186	148.08	64.4

Table 8.
 Cycle comparison between the 4 working fluids selected.

useful if a heating power is given (and not a temperature) or a zeotropic mixture is used and if the temperature of the heat or cold sources vary.

$$\eta_{EX} = \frac{\text{Exergy recovered}}{\text{Exergy consumed}} = \frac{W}{Q_h \left(1 - \frac{T_0}{T_h}\right)} \quad (13)$$

$1 - \frac{T_0}{T_h}$ is also called the Carnot's factor. Eqs. 11 and 13 are considered in our example (**Table 8**), and we can observe that the most efficient fluid is R365mfc (it will be same if exergy efficiency is calculated but the half of the energy that can be used by the steam generator is transformed into work). R365mfc has the highest critical temperature value. However, its volumetric capacity (VC) is very low, requiring a larger quantity of fluid (due to its low density compared to other fluids). Additionally, it is worth noting that the condenser pressure is lower than the atmospheric pressure,

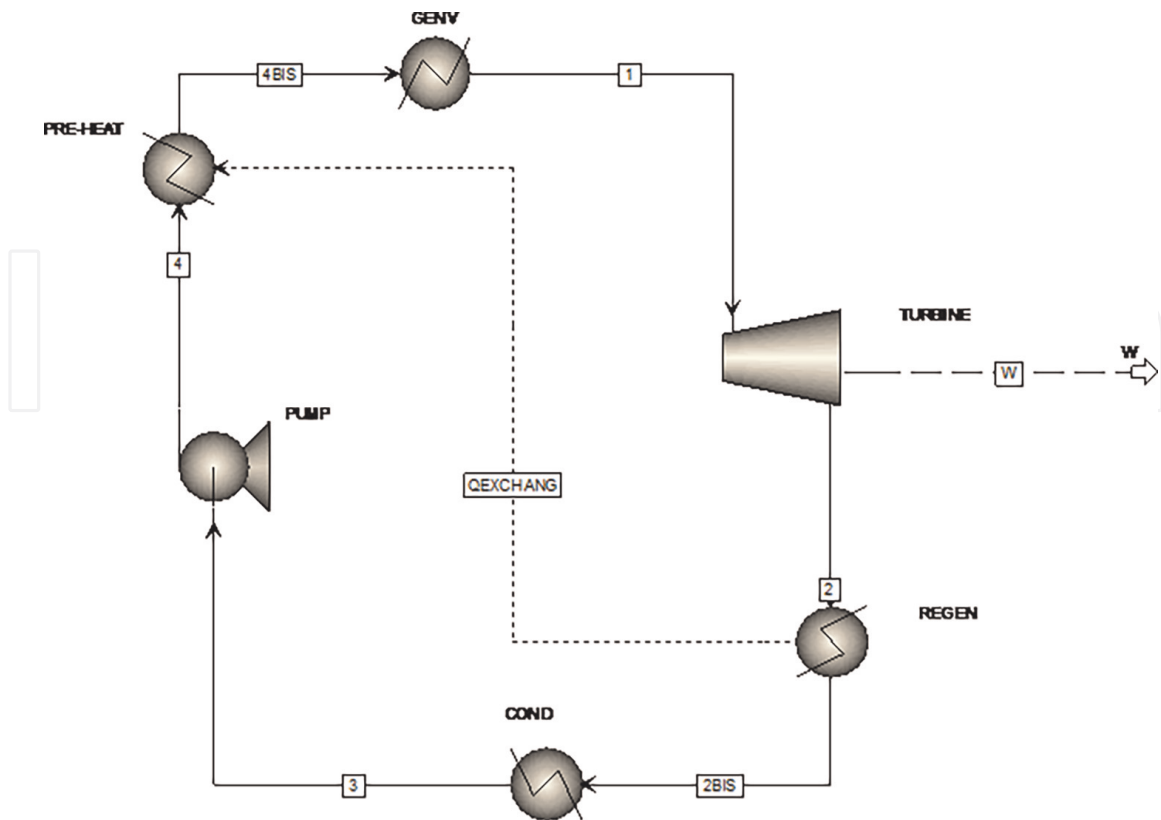


Figure 8. Structure of the organic Rankine cycle using Aspen plus with recuperator (internal heat exchanger).

which is not recommended. Based on the ORC performance as well as environmental, hygiene, and safety criteria (EHS), it appears that the most suitable fluid for this example is R1233zd(E). The criteria related to installation volume, environmental protection, and operator safety should play an important role in future studies. For a complete selection of the fluid, it will be interesting to size the different equipment of the ORC and to evaluate if the sizing is normal in terms of the surface of heat exchangers or the speed of fluid in the turbine (subsonic flow) for example.

7. Conclusion and outlook

This book chapter proposes a virtual technique for the selection of low-GWP working fluids for the ORC system. The criteria for working fluids selection and simulation approach for assessing the cycle performance were introduced to the reads in detail. The selection criteria mainly include the chemical property (critical, boiling, and triple temperatures), thermodynamic property (Vaporization latent heat, density, heat capacity, phase equilibrium, etc.), transport property (dynamic viscosity and thermal conductivity), environmental property (low GWP and zero ODP), and safety (non-toxic, non-flammable). Depending on the application and the level of temperature of the heat source, no perfect fluid exists. It is important to proceed to a selection by considering the different characteristics of the sources and the application. In general, the differences between the cycle efficiencies of the working fluids are not very significant if the selections based on critical and boiling temperatures are correctly realized. For further investigations, it will be of interest to size the different

components in the cycle. It concerns the design of heat exchangers or turbine or pump based on the estimation of transport properties of the working fluid. The thermodynamic performance of ORC systems can be improved by modifying its architecture using a regenerator as presented in our example or removing a part of the working fluid circulating in the turbine into the mixing heater. In consequence, the analysis of the performance of working fluid has to be remade. Moreover, the thermodynamic performance of ORC systems can be improved by using zeotropic mixtures as the working fluid. A zeotropic working fluid with a temperature glide of 5°C or greater can improve the efficiency and performance of the thermodynamic cycle by matching the temperature glide between the heat transfer fluid and the working fluid in a counterflow heat exchanger. This kind of matching, so-called temperature glide matching, can maintain the temperature difference between the heat exchange fluid and the working fluid in a constant, thereby reducing the irreversibility in the heat transfer process, improving performance and energy and exergy efficiency.

Conflict of interest

The authors declare no conflict of interest.

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