

A Review of Efficient Working Fluid Selection for Solar Organic Rankine Cycle

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ABSTRACT

Nowadays our world faces many environmental problems and challenges. One of the most vital environmental challenges is high efficient power generation. Since two decades ago, organic Rankine cycles have been considered the most common and competitive power generation cycle to produce electricity from solar thermal energy.

In this paper, it reviews the selection of working fluids for solar organic Rankine cycle, including an analysis of the influence of working fluids' category and their thermo-physical properties on the organic Rankine cycle's performance, a summary of pure and mixture working fluids researches for organic Rankine cycle, a comparison of pure and mixture working fluids' applications.

Keywords: Organic Rankine cycle, Solar heat source, working fluid, selection

1. INTRODUCTION

Nowadays Electric power is one of the biggest needs of human's life. Largest proportion of power is still produced by steam Rankine cycle driven by fossil fuels. As is known to all, Fossil fuels consumption has so many environmental consequences such as air pollution, global warming, ozone layer depletion and acid rain [1]. However, using water as working fluid for steam Rankine cycle causes some problems, including need of superheating to prevent condensation during expansion, risk of erosion of turbine blades, excess pressure in the evaporator, complex and expensive turbines [2].

A Rankine cycle which uses organic materials with low boiling points as working fluid is called organic Rankine cycle. ORCs have simple structure, are highly reliable and could be

easily maintained. Industrial waste heat, solar energy, geothermal energy, biomass energy and ocean energy etc. could be used as heat source of an ORC. Meanwhile, in order to improve energy utilization, it can be easily combined with other thermodynamic cycles, such as the thermoelectric generator, fuel cell, internal combustion engine, micro turbine, seawater desalination system, Brayton cycle and gas turbine-modular helium reactor (GT-MHR). Furthermore, it also can be used as prime movers of combined cooling and power system, CHP, and CCHP systems [3].

Some researches had been done on working fluids of ORCs. Chen et al. [4] reviewed suitable pure working fluids for organic Rankine cycles, but not mixed working fluids, and furthermore, the comprehensive pure working fluid candidates and the optimal ones are not reviewed; Tchanche et al. [2] and Fredy et al. [5] made comprehensive reviews of organic Rankine cycle for all kinds of applications; Rayegan et al. [6] analyzed a comprehensive list of working fluids to find the most suitable fluids for a solar ORC. Also they proposed a procedure to compare working fluids when they are employed in the solar Rankine cycles with similar working conditions.

In this Paper, the influences of the working fluids' types and thermo-physical properties on organic Rankine cycle performance are discussed; then, the researches of pure and mixed working fluids are summarized, including the discussion of the working fluids screening results, the comparison of the pure and mixed working fluids and the clarification of mixture ORC advantages and disadvantages

The selection of a suitable working fluid for the Rankine cycle is complicated because of the variation of the cycle working conditions for each fluid according to the type of solar collector used (from low-temperature heat source of 80 °C to high-temperature of 500 °C heat source) and due to the availability of a great number of potentially suitable substances for each range of temperatures, including hydrocarbons, aromatic hydrocarbons, ethers, perfluorocarbons, CFCs, alcohols, siloxanes etc. [3].

2. WORKING FLUIDS' CLASSIFICATION

The slope of the saturation vapor curve in the temperature-entropy diagram affects the fluid applicability, cycle efficiency, and arrangement of associated equipment [7]. As shown in Fig. 1 [3], depending on the slope of the temperature-entropy curve to be infinity, positive, or negative, working fluids can be classified into isentropic, dry, or wet respectively [6].

It is observed from the T-s diagram that the saturated vapor phase of a dry fluid becomes superheated after isentropic expansion. While saturated vapor of an isentropic fluid remains at saturated phase through the turbine. That shows the fact that installing a regenerator is not necessary and it makes isentropic fluids become ideal working fluids for ORCs [7,8].

The negative slope of the T-s diagram for a wet fluid causes lots of saturated liquid in outlet stream of the turbine. Liquid formation causes severe problems for the turbine blades and it also reduces the isentropic efficiency of the turbine. Typically, the minimum dryness proportion at the outlet of a turbine is kept above 85%. To tackle this problem, wet fluids need to be superheated before entering the turbine [9].

Dry and isentropic fluids are preferable than wet fluids under the same working conditions as there is no need to overheat the vapor and employing such fluids cause no problem for the turbine [10]. Hung et al. [8,11] thought that isentropic fluids are most suitable for recovering low-temperature waste heat. Their researches revealed that wet fluids with very steep saturated vapor curves in T-s diagram have a better overall performance in energy conversion efficiencies than dry fluids and isentropic fluids. They are not always suitable for ORC systems when other thermo physical properties are taken into consideration.

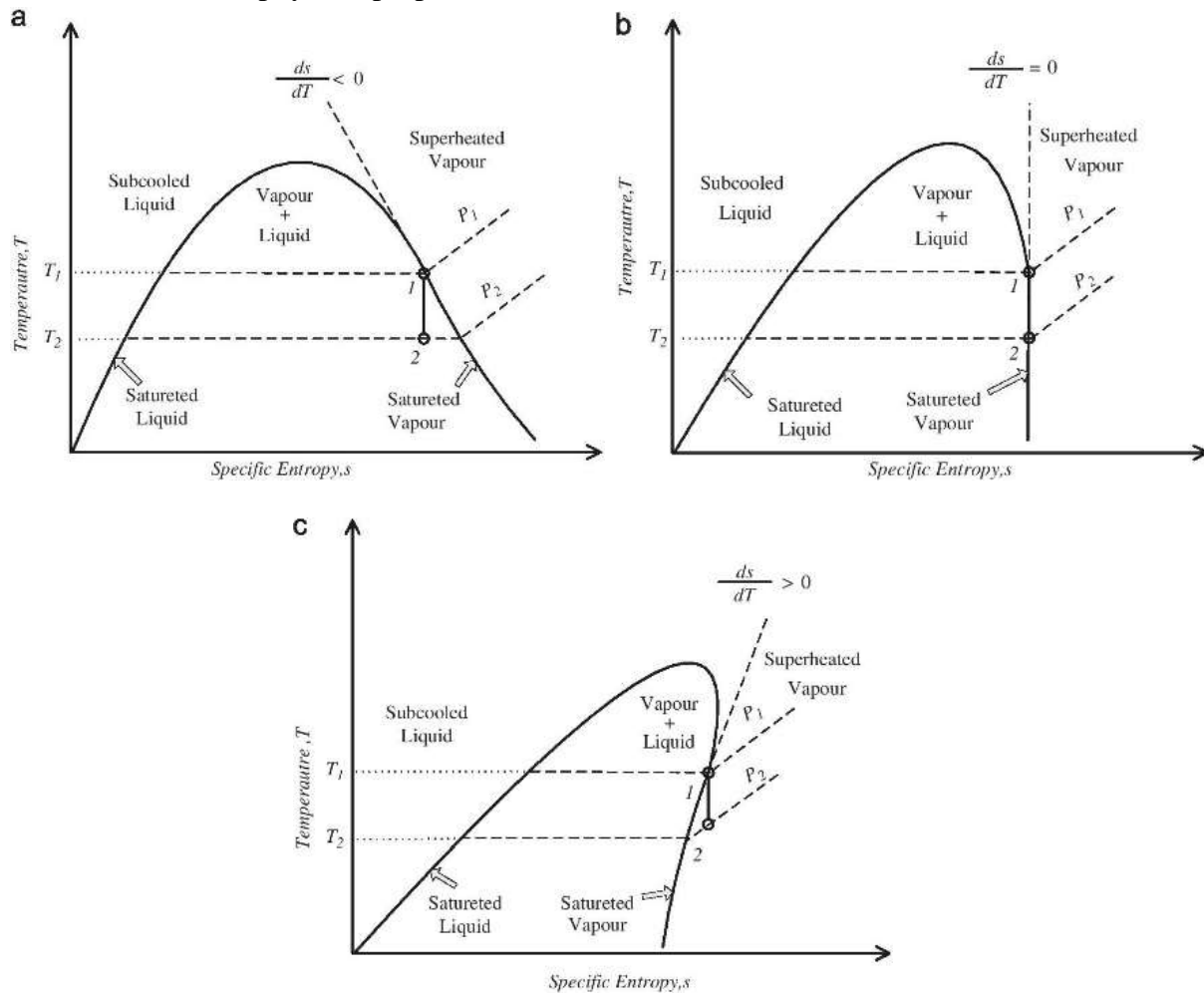


Fig. 1. Diagram T-s for fluids (a) wet, (b) isentropic and (c) dry.

3. THE THERMO-PHYSICAL PROPERTIES

System efficiency, operating conditions, environmental impact and economic viability are strongly affected by working fluids' properties.

3.1 Vaporization latent heat

High vaporization latent heat causes most of the heat to be added during the phase change process, so there is no need for expansion and superheating to achieve higher efficiency [12]. From the point of view of output work, fluids with higher latent heat produce larger unit work output in the same working conditions [4]. Working fluids with lower vaporization latent

heat are more suitable for low or medium temperature heat sources, e.g. solar heat, waste heat, etc. Lower vaporization latent heat causes the heat transfer process in the evaporator to occur at variable temperature. Reduction in the temperature difference between the fluids in the heat exchanger decreases the irreversibility of the heat transfer process [13].

The enthalpy ratio of vaporization (the ratio of the latent heat of vaporization to the sensible heat) should be of high value to increase the cycle's thermal efficiency, as high values of the vaporization enthalpy ratio reduce the amount of heat required for preheating the working fluid [14]. However, the smaller enthalpy ratio of vaporization means the larger exergy efficiency.

3.2 Density

High vapor density is a key factor. The higher vapor density causes the lower volume flow rate. Therefore, the result is smaller expander. This property has a non-negligible impact on the cost of the system [4].

Isentropic efficiency is affected by size parameter and volume flow ratio (the ratio of turbine outlet volume flow rate to inlet volume flow rate) [15]. According to Macchi and Perdichizzi [15], a higher value of SP results in larger turbine size. Also the lower values of VFR lead to higher turbine efficiency.

3.3 Specific heat

Low specific heat could decrease the work consumed by pump and increase the work output [4]. However, the liquid specific heat does not directly affect either the pump work or the total work [16].

3.4 Critical temperature

Turbine pressure expansion ratio depends on two factors: critical temperature and acentric factor. If the condensation temperature and the ratio of evaporation temperature and condensation temperature are kept constant, the turbine pressure expansion ratio increases with the acentric factor and the critical temperature.

According to Rayegan et al. [6], the maximum practical thermal efficiency and corresponding performance factors for preselected working fluids confirm that fluids with higher critical temperatures have better performance in the ORC. Their research shows that the higher critical temperature allows setting the evaporation temperature at a higher level that leads to the higher thermal efficiency of the cycle. Also the exergy efficiency has almost the same trend of thermal efficiency with respect to the critical temperature of the fluid.

3.5 Boiling temperature

Mago et al. [17] conducted a research on R113, R123, R245ca and Isobutane as working fluids for both basic and regenerative ORCs. By comparing simulation results, it became clear that the fluid which shows the best thermal efficiency is the one that has the highest boiling point among the selected fluids. According to Joback [18], higher critical temperature means higher boiling point for a fluid in the same fluid family. But it's not true when fluids are not in the same fluid family.

3.6 Molecular weight

The molecular weight of the selected fluid is related to the used turbine; fluids with molecular weight lower than 90 kg/mol are suitable for use in multistage turbine as they require multistage turbines to overcome the difficulty of high efflux velocities [19]. On the other hand, fluids with molecular weight higher than 90 kg/mol are suitable for use in single stage turbine [20] due to their low peripheral speed [21].

3.7 Molecular complexity

Molecular complexity is defined as [22]:

$$\sigma = \frac{T_{CR}}{R} \left(\frac{\partial S}{\partial T} \right)_{SV, T_r=0.7} \quad (1)$$

where P_r and T_r are reduced pressure and temperature respectively, R is gas constant and SV stands for saturation vapor.

The higher slope of the entropy-temperature diagram results in higher molecular complexity [6]. If the molecular complexity increases, the heat capacity ratio γ decreases, and the slope of the saturated vapor line becomes positive: the more positive, the more complex is the molecular structure [23].

Rayegan et al. [6] shows that at both low and medium temperature levels and based on all performance factors higher molecular complexity results in a more effective regenerative cycle. In their research the only exceptions to this rule were Benzene and Cyclohexane [6]. However, for waste heat or geothermal binary plants, the greater molecular complexity, the less system efficiency and work output [24]. In brief, select working fluids according to molecular complexity should be based on the type of heat source.

3.8 Viscosity

The fluid viscosity should be low in both vapor and liquid phases to increase the heat transfer coefficient and to reduce the friction losses in the heat exchangers [25].

3.9 Conductivity

High thermal conductivities lead to high heat transfer coefficients in the heat exchangers.

3.10 Freezing point

The fluid freezing point must be lower than the cycle lowest temperature [25].

4. PURE WORKING FLUIDS

Because of strong effect of suitable working fluids' selection on ORCs performance, many researchers have carried on working fluid screening. As a screening method, they mostly build steady-state simulation model of the ORC cycle and run it with different working fluids [3].

Due to so diverse working fluids, different types of heat source and working conditions, and different performance indicators, no single fluid has been identified as optimal for the ORC [3].

Different types of pure fluids have been reported in the literature for solar Rankine cycles. Table 1 [26] shows the pure working fluid candidates used in solar ORCs. As shown, the most of researches have been conducted on Hydrocarbons, refrigerants (including natural refrigerants), siloxanes and alcohols. Generally, high thermal efficiency ORCs are achievable by using hydrocarbons rather than refrigerants. This means hydrocarbons have a higher potential to produce power in a Rankine cycle than refrigerants because of their relatively high critical temperature. On the other hand, hydrocarbons are more flammable in comparison to refrigerants. In general, the same as thermal efficiency, the exergy efficiency of refrigerants are lower than hydrocarbons [26].

Some refrigerants, such as the chlorofluorocarbons (CFCs) and the hydrochlorofluorocarbons (HCFC) fluids are not ozone safe. Hence there is restrictions on the use of many refrigerants of high ozone depleting potential (ODP) [27].

Different refrigerants, of a wide range of critical pressures and temperatures, have been screened in the literature. R245fa is the most used working fluid in investigations. It has lower pressure levels as compared to the natural refrigerant CO₂ (R744), which means that cheaper equipment and solar collectors could be used [28].

For very low temperature sources, R134a can be a suitable candidate as it is nontoxic and nonflammable, it has zero ODP and its GWP (global warming potential) is 1300 [29]. and it was chosen to be the most suitable working fluid for temperatures lower than 90 °C based on the second law efficiency and total irreversibility [30]. Rayegan et al. [6] selected R245fa and R245ca as the most suitable refrigerants for a solar ORC at low and medium temperature.

On the other hand, natural refrigerants, such as hydrocarbons, ammonia or CO₂, have zero ODP and zero or low GWP and can be suitable candidates rather than synthetic refrigerants. Pentane (R601) is considered to be the second commonly used working fluid in solar Rankine cycles [31].

Butane (R600) and isobutane (R600a) were recommended for the range of temperatures between 70 °C and 120 °C [32]. However, those hydrocarbons are highly flammable.

Carbon dioxide is inexpensive, non-toxic, non-explosive, non-flammable and abundant in nature. Also it has low ODP and GWP [33]. The low critical temperature and pressure of CO₂ (31.1 °C and 7.38 MPa) facilitates the operation within the supercritical region of the fluid using sources of heat at low temperature range (30–200 °C) [34].

For hydrocarbon working fluids, toluene is more suitable to be employed at high temperatures. It was early used in the Kuwaiti-German project in the 1980s and resulted in high efficiency [35]. Benzene and Cyclohexane were also considered in the investigations and recommended in some works. Rayegan et al. [6] selected Benzen and Cyclohexane as the most suitable hydrocarbon for a solar ORC at the low temperature level. While their investigations reveal that Acetone and Benzene are the best for a solar ORC at the medium temperature.

Table 1. Pure working fluids used in investigations of the solar Rankine cycle

Working Fluid	Collector Type	Maximum and Minimum Turbine Inlet Temperature Values (°C)
Inorganics		
Water (R718)	FPC	
	PTC	312–390
	LFR	250
	Parabolic Dish	340
CO ₂ (R744)	N.A	75
	ETC	125–200
Ammonia (R717)	PTC	130
	ETC	70–120
	FPC	85
	CPC	
Hydrocarbons (HCs)	PTC	150
	N.A	75
	PTC	
	N.A	
Ethane (R170)	PTC	70–150
Propylene (R1270)	ETC	86.4
	PTC	150
Propane (R290)	ETC	85
	FPC	68.2–120
	CPC	
	PTC	
butane (R600)	N.A	75
	ETC	70–120
	FPC	
	CPC	
Butene	PTC	137–170
	N.A	75–150
	N.A	125
	N.A	
Isobutane (R600a)	ETC	120–145
	FPC	80–100
	CPC	95–124
	PTC	140–150
Isobutene	N.A	75–150
	N.A	100–150
	N.A	100–150
	N.A	100–150
Cis-butene	N.A	100–150
	N.A	100–150
	N.A	100–150
	N.A	100–150
Trans-butene	N.A	100–150
	N.A	100–150
	N.A	100–150
	N.A	100–150
Pentane (R601)	ETC	
	FPC	70–75
	CPC	
	PTC	70–213.7
LFR	LFR	
	Parabolic Dish	
	N.A	75–186
	ETC	145
Isopentane (R601a)	FPC	95–118
	CPC	95
	PTC	119–289
	N.A	80–177
Cyclopentane	PTC	140
	ETC, FPC, CPC	
NeoPentane	N.A	152
	N.A	
Hexane	ETC, FPC	
	CPC	130–150
	PTC	140–236
	LFR	216
Isohexane	N.A	226
	PTC	140–246
	LFR	206
	N.A	216
cyclohexane	ETC	
	FPC	
	CPC	
	PTC	140–302
Methyl Cyclohexane	LFR	262
	N.A	75–272
	PTC	
	PTC	
Propyl Cyclohexane	ETC, FPC	
	PTC	263.7–288
	LFR	248
	N.A	258
n-Heptane	N.A	

Table 1. Pure working fluids used in investigations of the solar Rankine cycle (continued)

Working Fluid	Collector Type	Maximum and Minimum Turbine Inlet Temperature Values (°C)
Benzene	CPC	
	PTC	287–294
	LFR	264
n-Octane	N.A	100–274
	ETC, FPC	
	PTC	291.9
n-Nonane	N.A	
	PTC	
Decane	N.A	
Dodecane	PTC	
Toluene	N.A	
	ETC, FPC	
	PTC	280–380
	LFR	297
	Parabolic Dish	320
O-Xylene	N.A	307
	PTC	306.6
Ethylbenzene	ETC, FPC	
	PTC	341.9
N-propylbenzene	PTC	360–377.34
N-butylbenzene	ETC, FPC, PTC	PTC: 388.2
Alcohols		
Methanol	ETC	120
	Parabolic Dish	
	N.A	75
Ethanol	ETC	100–150
	CPC	
	Parabolic Dish	
	N.A	75–140
n-Butanol	PTC	150.3
Ketones		
Acetone	PTC	250–400
	N.A	100–213
Hydrofluorocarbons (HFCs)		
R32	N.A	75
R161 (Fluoroethane)	PTC	150
R134a	ETC	70–120
	FPC	70–85
	CPC	
	PTC	70–200
	N.A	50–75
	N.A	
R143a	N.A	
R152a	ETC	70–120
	FPC	
	CPC	
R227ea	PTC	
	N.A	75
	ETC	120
	FPC	70–88.4
R236fa	CPC	
	N.A	77.5–150
	ETC	
	FPC	101.5
R236ea	N.A	70.7–150
	ETC	
	FPC	111.65
R245fa	PTC	179.1
	N.A	74–150
	ETC	75–150
	FPC	70–125
	CPC	95–100
	PTC	75–250
R245ca	LFR	125–170.15
	N.A	77.2–150
	ETC	145
	FPC	70–119
	CPC	95
RC318	PTC	110
	N.A	100–158
	ETC	120
	FPC	85–98.75
	PTC	146.3
	N.A	75–106

Table 1. Pure working fluids used in investigations of the solar Rankine cycle (continued)

Working Fluid	Collector Type	Maximum and Minimum Turbine Inlet Temperature Values (°C)
R365mc	FPC N.A	> 70
Chlorofluorocarbons (CFCs)		
R11	ETC Parabolic Dish	120
R12	ETC FPC PTC N.A	70-120 70-85 70 75
R113	CPC PTC LFR Parabolic Dish N.A	136 200-242 202 75-150
R114	N.A	75
Hydrochlorofluorocarbons (HCFCs)		
R22	FPC PTC	70-85 70
R123	ETC PTC FPC CPC Two Stage: CPC, FPC N.A	100-150 180-200 99-124 120 75-155
R141b	ETC CPC Parabolic Dish N.A	100-150 75
Perfluorocarbons (PFCs)		
R218 (Octafluoropropane)	ETC FPC PTC N.A	113.7 59.1-87.34 75.7-150 57
Perfluorobutane (C4F10)	N.A	107
Perfluoropentane (C5F12)	N.A	141
Hydrofluoroolefins (HFOs)		
R1234yf	FPC PTC	70 115-140
R1234ze	FPC PTC	70 115-140
Siloxanes		
MM (hexamethyldisiloxane)	ETC, FPC PTC N.A	235-400
MDM (octamethyltrisiloxane)	ETC, FPC PTC N.A	307.3-312.7
MD2M (Decamethyltetrasiloxane)	ETC, FPC, PTC	PTC: 336.4
MD4M (Dodecamethylpentasiloxane)	PTC	
D4 (Octamethylecyclotetrasiloxane)	PTC N.A	280-365
D6 (Dodecamethylcyclohexasiloxane)	PTC	312.7
OMTS	PTC LFR	300 260
HMDS	PTC LFR	225 215
Ethers		
Diethylether (R610)	ETC, FPC, PTC	200
Fluorinated Ethers		
RE134	ETC, FPC PTC	143.7
RE245	ETC, FPC PTC	188.2

Siloxanes, such as MM and D4, and alcohols, such as ethanol and methanol, were also considered in published studies but not as much as hydrocarbons and refrigerants. As compared to other working fluids, siloxanes have better thermal stability, lower toxicity and can improve the flow through cycle efficiency due to the fluid behavior of siloxanes (Bethe-Zel'dovich-Thompson) which is reflected on the flow through the turbine [36].

Bao et al. [21] referred to three working fluids for solar Rankine cycle applications. Their recommended fluid was based on specific working conditions of turbine inlet temperatures and pressures and condensation temperatures. It can be seen that two fluids are both recommended in the same range of temperatures ($< 100\text{ }^{\circ}\text{C}$), R601 [37] and R134a [30].

5. Mixtures

Some heat sources have varying temperature such as waste heat and geothermal. Pure working fluids are not suitable for these heat sources. Pure fluids have the properties of boiling and condensing at constant temperature, which leads to large temperature differences in the vapor generator and condenser and in turn inevitably increases their irreversibility. In other side, when a mixture is used as working fluid, heat can be supplied or rejected at variable temperature but still at constant pressure. The variable-temperature heat transfer process alleviates the temperature mismatch between hot and cold streams in heat exchanging components of the system, which then increases the irreversibility and reduces the exergy destruction in the power cycles [38]. The researches about zeotropic mixture ORC are increasing, but it's still limited.

Wang and Zhao [43] used a mixture of R245fa/R152a at three different mass fractions as the working fluid in a low-temperature solar ORC. They put an internal heat exchanger after the turbine to reclaim more heat to improve the efficiency. However, the efficiency of the solar ORC using pure R245fa was higher than any of the zeotropic mixtures. Wang et al. [39] conducted another research on the same mixture. They performed an experimental study at constant volume flow rates to compare pure fluid R245fa with the mixture R245fa/R152a of two different compositions. This investigation revealed that there is a potential to improve the overall efficiency by recovering the heat of partial condensation using an external heat exchanger.

Bao et al. [40] used a zeotropic mixture of two dry fluids isopentane and R245fa in their auto cascade system with two stage turbines. The thermal efficiency of the system, with the concentration 32% of R245fa by mass, was found to be significantly higher as compared with the system that uses either pure R245fa or isopentane.

On the other hand, Mavrou et al. [41,42–44] used computer-aided methods and numerical simulation to investigate the performance of the solar ORCs using conventional and novel mixtures. Novel mixtures of alkanes, fluorinated alkanes or fluoromethoxy-alkanes were designed and have been assessed and compared with conventional mixtures [42]. Results showed that better efficiencies could be obtained with these novel mixtures. Further comparison between conventional and novel mixtures was introduced in [41], in which the

Table 2. Mixture working fluids used in investigations of the solar Rankine cycle

Collector Type	Working Fluids
N.A	R245fa/R152a
FPC	R245fa/R152a
N.A	Isopentane/R245fa
FPC	Isopentane/Isobutane Isopentane/Hexane Isopentane/Isohexane Pentane/Hexane Butane/Pentane Isobutane/Pentane 1,1,1,3,3,3-hexafluoro-propane/1-fluoromethoxy – 2,2,2-trifluoro-methyl-ethane Neopentane/1,1,1-trifluoro – 2-trifluoro-methyl-butane Neopentane/1,1,1-trifluoropentane 1,1,1-trifluoro – 2-trifluoromethylpropane/2,2-difluoro-hexane
FPC	1,1,1-Trifluoro-propane (C3H5F3)/2-Fluoromethoxy-propane 1,1,1-Trifluoro-propane/1-Fluoromethoxy-propane Neopentane/ 1,1,1-Trifluoro – 2-trifluoro-methyl-butane Neopentane/ 2-Fluoromethoxy – 2-methylpropane
PTC	Butane/Isopentane Cyclohexane/Cyclopentane Cyclohexane/Hexane Cyclohexane/Isohexane Cyclohexane/Isopentane Cyclohexane/Pentane Cyclopentane/Hexane Cyclopentane/Isopentane Cyclopentane/Pentane Hexane/Isohexane Hexane/Isopentane Hexane/Pentane Isohexane/Pentane Isohexane/Isopentane
FPC	Isopentane/Isobutane Butane/Pentane Butane/Isopentane Isobutane/Pentane Octane/Decane Nonane/Decane Propane/Hexane Propane/Isopentane Propane/Pentane 1,1,1-Trifluoro-propane/2-Fluoromethoxy-propane 1,1,1-trifluoro-propane/1-Fluoromethoxy-propane 1,1,1,3,3,3-Hexafluoro-propane/1,1,1-Trifluoro – 2-(fluoromethoxy)ethane Neopentane/1,1,1-Trifluoro – 2-trifluoro-methyl-butane Neopentane/ 2-Fluoromethoxy – 2-methylpropane Neopentane/ 1,1,1-Trifluoropentane 1,1,1-Trifluoro-butane/ 1,1,1-Trifluoropentane 1,1,1-Trifluoro-butane/ 1,1,1-Trifluoro – 3-(fluoromethoxy) – 2-methylpropane 1,1,1-Trifluoro – 2-trifluoromethylpropane/ 2,2-Difluoro-hexane Neopentane/ 1,1,1,3,3,5,5,5-Octafluoro-pentane

impact of heat source variability was considered. Table 2 [26] shows the mixture working fluids used in investigations of the solar Rankine cycle.

6. Conclusion

This paper provides a comprehensive overview of the working fluids effects on the solar organic Rankine cycle and the selection of the appropriate working fluid for the solar ORC. Working fluids were divided into three categories (wet, dry and isentropic). Dry and isentropic fluids are preferable than wet fluids under the same working conditions. The thermos-physical properties of working fluids can be used as a performance index for comparison between different fluids, and of which, the ratio of vaporization latent heat and sensible heat, critical parameters and molecular complexity are more important. The selection of working fluid is a function of heat source types, temperature level and the performance indices, which should be included in every design process of ORC plants. mixed working fluids have good temperature matching to improve the overall efficiency, but the screening of mixture compositions and fractions need further been researched. a list of pure and mixture working fluids in literature was provided. Finally, an overview of various researches on pure and mixture working fluids were presented.

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