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Innovative Approaches for Improving ORC Performance: A Review of Pure Fluids, Zeotropic Mixtures, and Nanoparticles

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ABSTRACT

Although the organic Rankine Cycle (ORC) is said to effectively capture low-grade heat, its commercialization has been limited because of working fluid constraints and inefficiencies resulting from operating at low temperatures. This study reviews the working fluids used in organic Rankine cycles and examines how nanoparticles could enhance the efficiency of the ORC, by enhancing the thermophysical properties of the working fluids. Results from this review showed that zeotropic mixtures of pure fluids, provide a viable approach to improving the thermophysical characteristics of organic working fluids and have the potential to achieve thermo-economic performance superior to that of individual pure fluids. Research results on the relative effectiveness of zeotropic mixtures and pure fluids, however, are conflicting and call for further study. Although nanofluids have shown potential as heat transfer fluids, there has not been much research done on them as organic Rankine cycle working fluids. In comparison to typical nanoparticles, metal-organic heat carriers have been recognized as having substantial potential to improve organic Rankine cycle thermodynamic efficiency. Future study on nanofluids, particularly in zeotropic mixtures, is crucial for the creation of new working fluids for developing ORCs that could achieve a balance between thermodynamic, economic, and environmental performance required to recover low-grade heat and the generation of electricity.

Keywords: *Nanofluids, nanoparticles, organic Rankine cycle, pure fluids, zeotropic mixtures*

I. Introduction

Organic Rankine cycle (ORC), among other technologies including the Kalina, liquid desiccant, absorption, and adsorption cycles, is increasingly recognised as an emerging technology with the potential for harnessing low-grade heat in a variety of applications, including electricity generation. Low-grade heat may be derived from several sources, including such as solar, biomass, industrial waste, and geothermal energy. This kind of heat has low temperatures, which limits its use for commercial applications [1]. The organic Rankine cycle closely resembles the Clausius Rankine Cycle, which is a steam power cycle. The fundamental distinction between the two is that the Clausius Rankine Cycle uses water and operates at temperatures above 300 °C, whereas the ORC operates at much lower temperatures thereby requiring the use of organic fluids with low critical temperatures such as refrigerants and other hydrocarbons [2], [3]. Despite the potential shown by Organic Rankine cycles (ORCs), a major hindrance to the commercialization of this technology is the suboptimal efficiency caused by the low operating temperatures and other physicochemical limitations of the organic working fluids. The operational efficiency of the

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ORC is mainly dictated by the heat source, choice of working fluids, selection of expander, and the heat exchanger size.

Studies have shown that raising the heat source temperature could also enhance the performance of ORC; the results imply that greater temperatures lead to greater performance. Liu *et al.* [4] assessed the theoretical performance of an ORC and found that the system achieved its maximum efficiency of 6.37 % when the temperature of the waste heat source was 200 °C. In the comparative study by Wang *et al.* [5], the performance of an ORC, which was fitted with a thermally powered pump, exhibited an improvement in efficiency from 11.3 % to 12.6 %. Additionally, the exergy efficiency of the system rose from 45.8 % to 51.3 % when the heat source temperature was elevated from 75 °C to 100 °C. Ismail *et al.* [6] undertook a study on the efficiency of a biomass-operated ORC unit which achieved temperatures as high as 300 °C and recorded a high thermal efficiency of 23.76 %. The use of parabolic troughs in ORC with temperatures not exceeding 227 °C, resulted in overall efficiencies of 7.5 % and 12.1 %, which was much higher compared to the efficiencies of 4.2 % attained with evacuated tubes and 3.2 % with flat-plate collectors [7].

Selecting the right working fluid is also vital for maximizing the efficiency of the ORC. Selecting the right working fluid is also vital for maximizing the efficiency of the ORC. In their study, Tocci *et al.* [8] emphasized the importance of correctly designing the expander and selecting a favourable working fluid in attaining optimal performance of the ORC for electricity generation. The study by Babatunde *et al.* [9] underlined the need to select the working fluid that is most appropriate to achieve the highest level of performance of the ORC. Working fluids used in ORCs may be classified as either pure substances or zeotropic mixtures depending on the composition. They could also be categorized as wet, dry, or isentropic according to their molecular mass. ORC operations prioritize the utilization of dry and isentropic fluids because of their superior thermophysical characteristics [10]. Organic working fluids could be either chlorine-based or fluorine-based; chlorine-based refrigerants, such as chlorofluorocarbons (CFC), and hydrochlorofluorocarbons (HCFC), possess a significant global warming potential (GWP), which contributes to the loss of the ozone layer [11]. Following the signing of the Kigali accord, these ozone-depleting substances (ODS) with high global warming potential (GWP) are being gradually eliminated, thereby necessitating the development of more environmentally friendly alternatives to be used in ORCs [12]. Fluorine-based refrigerants, such as hydrofluorocarbons (HFC), hydrocarbons (HC), and fluorocarbons also referred to as perfluorocarbons (PFC), are more environmentally friendly. These refrigerants have very low critical temperatures, resulting in reduced cycle efficiency. An appropriate organic working fluid should not only possess favourable thermophysical properties, but also be safe, non-hazardous, and environmentally friendly [13].

The continued search for suitable working fluids for ORCs resulted in the incorporation of nanoparticles into already existing organic working fluids as a way of enhancing the thermophysical properties. Nanofluids are created by dispersing particles or fibres that are less than 50 nm in length into base fluids such as refrigerants, water, oil, or other hydrocarbons to improve the physical and chemical properties (including heat capacity and thermal conductivity) of the fluids [14], [15]. A study undertaken by Saadatfar *et al.* [16] focused on simulating an organic Rankine cycle utilizing pentane that was infused with nanoparticles as the working fluid. The findings indicated a substantial improvement in cycle efficiency in comparison to when pure pentane was used. The method, although showcasing exceptional cycle efficiency, required reduced expander and heat exchanger sizes. In another study by Mondejar *et al.* [17], the working fluid had nanoparticles at a concentration of 1 % in it. The modelling results indicated a 4 % decrease in the heat exchanger size and an 18 % increase in the pressure drop of the boiler. These modifications, however, did not affect the energy utilized by the pump. This study reviews working fluids used in ORCs and examines how nanoparticles could improve the operation of ORCs by enhancing the working fluid's thermophysical properties.

II. Fundamentals of Organic Rankine Cycles

The operation of a simple ORC requires that the working fluid, which is usually a 2-phase organic fluid, enters the expander in the superheated vapour state and produces work while flowing through to the exit of the expander. It is then condensed to a saturated liquid in the condenser, before it is pumped back to the evaporator for heat addition, particularly from a low-grade heat source. The fluid exits the evaporator as a superheated vapour for the cycle to repeat. Organic working fluids have large molecular weights and are characterized by low critical pressures as well as temperatures [18].

The simple organic Rankine cycle set-up comprises the evaporator, turbine/expander, condenser, and pump. However, the introduction of devices such as recuperators, regenerators, and ejectors in the basic design could enhance the performance of the ORC. There are various ORC configurations found in literature, which are determined by the specific components' presence or absence in the ORC. These configurations were grouped into 5 categories by Li *et al.* [19], detailed in Fig. 1. These include basic ORC, ORC with recuperator, regenerative ORC, ORC with reheater, and ejector ORC. Other more complex configurations include cascade ORC and dual-loop vaporization ORC.

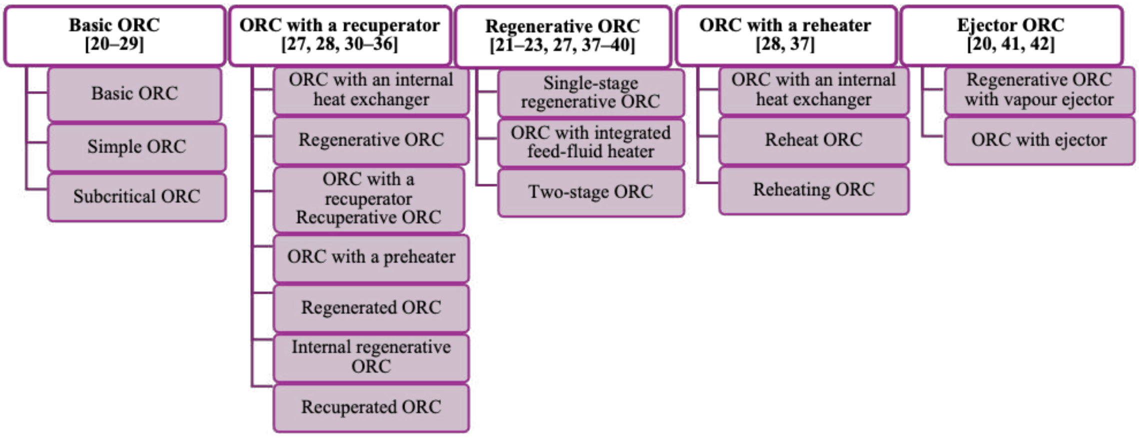

Fig. 1. Configurations of ORCs

The basic ORC consists of the most basic arrangement, which includes the evaporator, turbine, condenser, and pump. These components are essential to transform heat into work. The inherent simplicity of the fundamental ORC system makes it economically viable and straightforward to install and upkeep. The basic ORC is designed to efficiently convert waste heat generated from various sources including industrial activities into usable mechanical work, making it well-suited for applications that have relatively low power demands. Nevertheless, the lack of complementary elements in the fundamental ORC system restricts its capacity to enhance heat recovery and system efficiency. Consequently, this leads to reduced thermodynamic efficiency and greater irreversibilities, along with larger exergy losses as compared to the more complex arrangements.

The ORC, when equipped with a recuperator, often demonstrates improved overall performance since it can efficiently increase the working fluid's temperature by harnessing heat energy from the turbine output. The recuperator is positioned between the exit of the turbine and the intake of the evaporator to reclaim heat from the exhaust of the turbine and transfer it to the working fluid. This aids in minimizing the difference in temperature between the heat source and the working fluid. This arrangement guarantees that a greater amount of electricity is generated from the existing heat source.

The regenerative ORC is a modified version of the basic ORC that includes a regenerator, which functions as a heat exchanger. This regenerator enhances the utilisation of heat energy of the system by facilitating the movement of heat between the working fluid during the different phases of the cycle. The regenerator, which may be either closed feed or open feed, functions as a thermal storage device, moving heat energy from the hot working fluid and transferring it to the working fluid as it enters the evaporator. This process preheats the fluid before it experiences further expansion in the turbine.

In the ORC with a reheater, the working fluid undergoes reheating, which involves utilizing an external source of heat. This reheating process occurs after the fluid expands in the first stage of the turbine before it enters the second stage of the turbine. Following the expansion of the working fluid in the turbine, there is a substantial decrease in its temperature before it is subsequently reheated to a higher degree. Incorporating a reheating procedure elevates both the temperature and enthalpy of the working fluid before it enters the turbine's second stage. This modification enhances the energy conversion of the cycle.

III. Organic Working Fluids

To enhance the efficiency of ORCs, it is essential to consider the thermophysical characteristics of the working fluids. These parameters are specific heat capacity, thermal conductivity, latent heat of vaporization, specific volume, molecular weight, critical temperature, and critical pressure. Selecting an appropriate working fluid for a certain application is not limited to a single best option. It depends on several factors such as chemical stability, environmental effect, safety, cost, and thermodynamic compatibility with the heat source. Consequently, fluid selection and cycle optimisation frequently necessitate a compromise among various factors. Other important issues which need to be examined in addition to the thermophysical qualities are safety, cost, availability, toxicity, chemical stability at extreme temperatures, and environmental factors [43].

Working fluids used in ORCs could be classified as either pure fluids or zeotropic mixtures of pure fluids. While pure fluids have the same chemical composition throughout the fluid resulting in the same boiling point, Zeotropic mixtures are made up of two or more pure fluids that have differing boiling points, resulting in a gradual shift in temperature throughout the phase transition process. Badr *et al.* [44] used the slope of the saturation vapour curve of the T-s diagram to classify pure working fluids as wet, isentropic, and dry fluids as shown in Figure 2 and was further confirmed in Kruzel *et al.* [45] and Vicencio *et al.* [46]. Wet fluids have a negative slope, isentropic fluids have a medium slope and appear vertical while dry fluids have a positive slope on the T-s diagram.

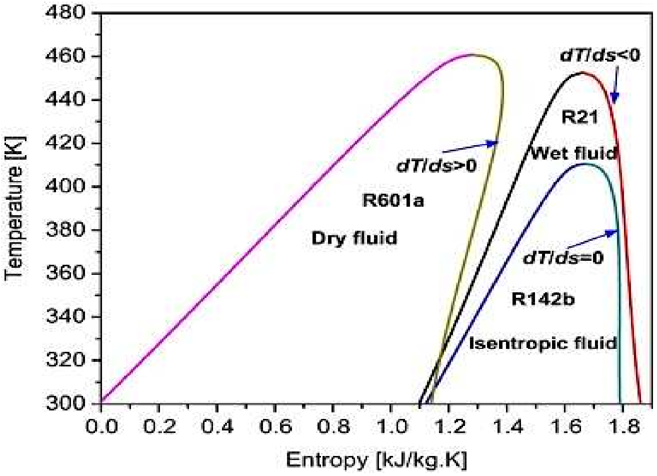

Fig. 2. Classification of organic working fluids using T-s diagram [28], [44]–[46]

Györke *et al.* [47] reclassified pure organic working fluids into eight new categories as a way of addressing the limitations of the traditional classification in Badr *et al.* [44]. Györke *et al.* [47] considered the traditional classification as insufficient in reliably predicting or preventing the production of liquid droplets in the low-pressure region of an ORC expander. The new technique made use of the relative placement of several distinguishing markers including the equilibrium states at low temperatures, the critical point, and the entropy extremes of the saturated vapour curve on the T-s diagram to categorise the working fluids. In this categorisation, the sequence in which the characteristic points or markers, mentioned above, appear was arranged in the order of increasing entropy.

1. Pure Fluids

Many research efforts have focused on exploring Pure Fluids within ORC operations with the singular goal of enhancing performance under different working conditions. Vidhi *et al.* [48] examined the efficiency of a supercritical ORC using various working fluids, fuelled by a geothermal heat source. The study made use of different pure fluids including R23, R32, R125, R143a, R134a, R218, and R170, to determine the best fluids for under operating conditions. The temperature of the heat source was varied within the range of 125 °C to 200 °C to examine its impact on the efficiency of the cycle under both steady and changing pressure ratios. The energy and exergy efficiencies were calculated for each working fluid, and the most optimal fluid was chosen. The research reveals that thermal efficiency of up to 21 % could be achieved by using a source temperature of 200 °C and a cooling water temperature of 10 °C. Thermal efficiencies of over 12 % were achieved for sources with medium temperatures between 125 °C to 150 °C.

The potential of using a regenerative ORC to harness heat from low-grade sources that were 200 °C in temperature was investigated by Siddiqui *et al.* [49]. The performance of twenty-one binary zeotropic mixtures and seven different pure fluids as possible working fluids was evaluated in this research. The results indicated that the pure organic fluids exhibited superior exergy efficiency, better specific net power output, and reduced heat exchange area needed in comparison to the binary zeotropic mixtures. RE347mcc had the highest exergy efficiency among the pure fluids, with neopentane, isopentane, and pentane following in descending order. Cyclopentane has the greatest potential for power generation per mass flow rate of the working fluid while being the least efficient with regard to energy.

While the source of heat remains constant, a working fluid with a lower critical temperature exhibits better performance because the choice of working fluid is mostly influenced by the temperature of the heat source, particularly when the temperature is very low. The commonly utilized working fluids in ORCs, excluding R21, are classified into six categories based on the heat source temperature shown in Figure 3 [50–53].

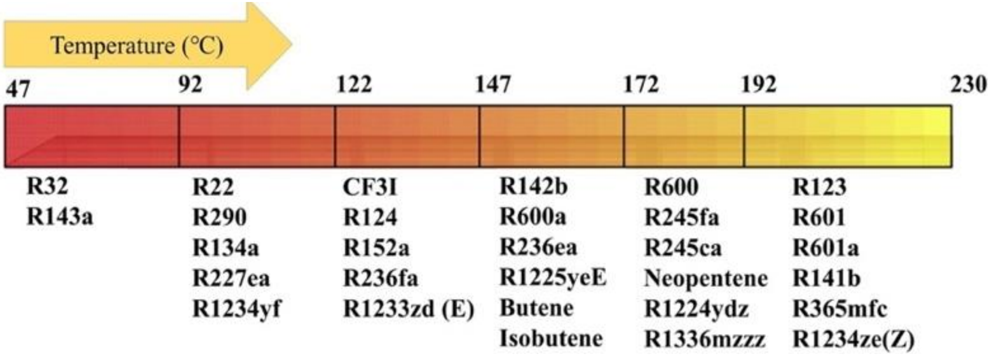

Fig. 3. Working fluid optimisation with heat source temperature [50–53]

Table 1 presents an extensive overview of the different working fluids frequently utilized in ORCs, along with their essential characteristics. These characteristics include molecular weight, critical temperature, critical pressure, global warming potential (GWP), ozone depletion potential (ODP), flammability, and toxicity. Most pure organic fluids have an ozone depletion potential (ODP) of 0, making them environmentally safe. Nevertheless, there are some cases, such as R123, R22, R113, and R12, whose ODP exceeds 0. In contrast, about 50 % of the fluids included in Table 1 possess a GWP that is 20 or less, and the other 50 % have a GWP that could potentially reach up to 8500. In terms of flammability and toxicity, only 30 % of the fluids considered were non-flammable whereas 8 % were toxic.

2. *Zeotropic Mixtures*

Zeotropic mixtures are increasingly being employed in ORC because of their ability to match the heat source's temperature profile through non-isothermal phase transition. This alignment helps to minimize irreversibilities in both the evaporator and the condenser [57, 58]. Zeotropic mixtures have been touted to have better heat transfer properties with smaller average temperature differences when compared to pure fluids, resulting in better thermodynamic performance but larger sizes of heat exchangers [59]. Li *et al.* [60] simulated the operation of a basic ORC and a regenerative ORC with both pure fluids and zeotropic mixtures and found that zeotropic mixtures produced better thermodynamic as well as economic performance in comparison to pure fluids. Wu *et al.* [61] in a performance assessment considered three zeotropic mixtures; R227ea/R245fa, Butane/R245fa, and RC318/R245fa, and concluded that the thermal efficiency of zeotropic mixtures could be enhanced. However, this improvement may not always result in better economic performance.

Table 1: Common pure organic fluids for ORC systems

Working Fluid	Molecular Weight (kg/mol)	Critical Temperature (°C)	Critical Pressure (Bar)	GWP	ODP	Flammable?	Toxic?
i-Butane	0.058	134.67	36.29	3	0	Yes	No
n-Pentane	0.072	196.55	33.68	3	0	Yes	No
n-Butane	0.058	151.98	37.96	4	0	Yes	No
i-Pentane	0.072	187.2	33.78	5	0	Yes	No
R290	0.044	96.74	42.51	11	0	Yes	No
i-Butene	0.056	144.94	40.1	20	0	Yes	No
R152a	0.066	113.26	45.17	120	0	Yes	No
R32	0.052	78.11	57.82	650	0	Yes	No
R245ca	0.134	174	39.3	693	0	Yes	No
R227ea	0.17	101.75	29.25	3220	0	Yes	No
R125	0.12	66.02	36.18	3500	0	Yes	No
R143a	0.084	72.7	37.61	4300	0	Yes	No
R1336mzz(Z)	0.164	171.3	26	2	0	No	No
R1234yf	0.114	95	33.81	4	0	No	No
R1234ze	0.114	109.4	36.4	6	0	No	No
R161	0.048	102.2	50.9	12	0	No	No
R245fa	0.134	154.01	36.51	1030	0	No	No
R236ea	0.152	139.29	34.2	1200	0	No	No
R134a	0.102	101.06	40	1300	0	No	No
R123	0.153	183.68	36.72	0	0.02	No	No
Toluene	0.092	318.1	41.26	0	0	Yes	Yes
R22	0.086	96.15	49.9	1700	0.06	Yes	Yes
R113	0.187	214.06	33.92	4800	0.8	Yes	Yes
R12	0.121	111.97	41.36	8500	0.9	Yes	Yes

(Source: [54]-[56])

Oyewunmi *et al.* [62] examined the performance of an ORC with n-pentane/n-hexane working fluid in a 50/50 ratio as well as R245fa/R227ea working fluid in a 60/40 ratio. The findings revealed that, while the mixtures produced superior thermodynamic performance indexes, they needed bigger heat exchangers, leading to a 14 % increase in the unit cost of electricity production in comparison to the individual pure fluids utilized in the study. Heberle *et al.* [63] studied i-butane, i-pentane, and R245fa as pure fluids and i-butane/i-pentane mixture in an ORC and discovered that the i-butane/i-pentane mixture in the ratio 90/10 had the lowest specific costs/exergy in comparison to the individual pure fluids. When Andreasen *et al.* [64] studied the operation of R32 and R134a pure working fluids with the mixture R32/R134a (in a 65/35 mole ratio), the mixture produced 3.4 % greater net power production compared to R32 at an equivalent system cost. Yang *et al.* [65] studied the performance of R32 and R1234yf as pure working fluids with the mixture R1234yf/R32 and discovered that, when the mass fraction was optimized, the mixture R1234yf/R32 produced 1.46 % and 4.88 % higher thermo-economic performance than the pure working fluids R1234yf and R32 respectively. When R236ea, R245fa, hexane, c-hexane, i-hexane, and their mixtures were studied by Kolahi *et al.* [66], the mixture R236ea/c-hexane produced the highest efficiency of 14.57 % when used in a simple ORC and 16.81 % when used in an ORC with an internal heat exchanger (IHE). In this same study, the mixture R245fa/c-hexane yielded the minimum specific investment cost as well as the least payback period. Andreasen *et al.* [59] used the pure working fluids R1234yf, i-butane, propane, i-pentane, and their mixtures in an ORC investigation. The mixture R1234yf/i-butane (53.3/46.7) produced the most favourable net present value (NPV) compared to the pure fluid R1234yf, which happened to be the most economical pure working fluid in the investigation. Comparing the individual performance of R245fa and i-pentane pure fluids with R245fa/i-pentane mixtures for fixed power output and condensation pressure, Imran *et al.* [67] recorded a 13 % lower heat transfer area per output power in the case of the mixtures than the pure fluids. Xi *et al.* [68] concluded that the mixture of working fluids obtained lower electricity production cost (EPC) when compared to the pure working fluids in the study on the optimisation of four (4) mixtures and five (5) individual pure fluids to decrease the cost of electricity generation. At the end of the study, R245fa/i-pentane and R245fa/pentane emerged as the best-working fluid pairs that could produce the lowest EPC. Yang *et al.* [69] examined the economic results of R236fa, R245fa and R1336mzz(Z) and their various mixtures in an ORC and concluded that the two-fluid mixtures produced better economic performance when compared to the individual fluids. However, the three-fluid mixtures resulted in the best economic performance, outperforming the best two-fluid mixture by about 1.7 %. Yang [70], in a study to determine the thermodynamic and economic performance of R245fa, R1234ze, R236fa, R600 and their mixtures, concluded that the mixture R1234ze/R600 resulted in a payback period lower than the individual pure fluids and the other mixtures investigated.

While several research works have shown that zeotropic mixtures exhibit superior thermodynamic as well as economic performance compared to their individual pure fluids, other studies have reached contrasting conclusions, finding that some pure fluids have higher thermo-economic performance than their zeotropic mixtures. Pentane and R245fa pure fluids and mixtures of the same were used in an ORC by Le *et al.* [71], in a study that sought to optimise the exergy efficiency and minimize the levelized cost of electricity (LCOE) concluded that n-pentane produced the best results, even though, the zeotropic mixture produced favourable results too. In an economic optimisation of an ORC using pure working fluids R134a, R152a, R161, and R245fa as well as their mixtures, Garg *et al.* [72] recorded lower performance indexes for the mixtures when compared to the pure fluids, a situation attributed to their slightly lower cycle efficiencies. In a study where the extractable turbine power and economic performance were determined for i-butane, butane, i-pentane, pentane, and their mixtures, it emerged that i-butane resulted in the highest extractable turbine power and also had the shortest payback period compared to the various mixtures employed in the study [73]. Li *et al.* [74] proposed that zeotropic mixtures may not always outperform pure fluids since they noticed that larger heat exchangers are needed in some circumstances where zeotropic mixtures were utilized, a situation they attributed to the low-temperature gradient in the heat exchanger. Zhang *et al.* [58] studied the choice of zeotropic mixtures for ORC (out of a collection of 61 zeotropic mixtures) using a single screw expander and identified R441A, R436B, and R432A as viable alternatives for ORC operations in place of pure fluids.

Other investigations demonstrated comparable thermo-economic performance between pure working fluids and their zeotropic mixtures, with the feasibility of zeotropic mixtures contingent upon either the total capital cost or the modelling parameters for the condenser. In a study by Fang *et al.* [75], in which pure working fluids (decane and toluene which have high critical temperatures and R245fa and R123 with low critical temperatures) and their zeotropic mixtures were analysed, concluded that although the working fluids that have high critical temperatures demonstrated superior thermos-economic performance, the zeotropic mixtures did not improve thermos-economic performance significantly. The use of zeotropic mixtures, however, led to a significant reduction in the heat transfer area of the heat exchangers when the evaporation temperature was high. Pure perfluorobutane, when used in a study, where the cooling water quantities were unlimited, showed increased thermal and power output efficiencies compared to perfluorodecane mixtures [76]. However, in situations where the quantity of cooling water is restricted, zeotropic mixtures demonstrate superior efficacy compared to pure working fluids.

III. Nanoparticles in ORC Operations

The use of nanoparticles is being continually investigated for their ability to enhance the performance of ORCs via the improvement of thermophysical properties of the working fluids. Nanofluids, consisting of nanoparticles dispersed in a base fluid, exhibit enhanced thermophysical characteristics in comparison to conventional fluids. Nanoparticles have been mostly used in ORCs to augment the thermophysical characteristics of heat transfer fluids in heat exchangers, namely condensers and evaporators. Prajapati *et al.* [77] used CuO as the heat transfer fluid and R245fa as the working fluid in the ORC system due to its easy accessibility and lower cost in comparison to Al_2O_3 (which has superior thermophysical characteristics). Loni *et al.* [78] employed nanofluid (Al_2O_3/oil) in a solar dish concentrator and R601 as the working fluid in the ORC system. The findings showed that raising the concentration of nanofluid improved the thermal performance of the solar system as well as the production of power. The study found that a quantity of 1.1 % nanoparticles led to a 19.3 % increase in performance. When CuO/oil, SiO_2/oil and Al_2O_3/oil were used as heat transfer fluid in a solar ORC system by Loni *et al.* [79], the findings showed a 2 % - 3 % increase in the thermal efficiency of CuO/oil and Al_2O_3/oil with SiO_2/oil having the least influence on improving the efficiency of the ORC system.

Carbon nanotubes (CNTs) are a kind of nanoparticle that has garnered a lot of interest because of its exceptional heat capacity and thermal conductivity. However, CNTs have found common usage in heat transfer fluids carbon nanotubes (CNT), which may be multi-walled (MWCNT) or single-walled (SWCNT), have been reported to have better thermal conductivity as well as heat capacity compared to other nanoparticles, that have relatively similar thermophysical properties, especially Al_2O_3 and CuO. The study showed similar trends for all the nanoparticles in the areas studied including reduction in boiler area, increase in boiler pressure drop as well as pump power consumption. In the end, the study revealed that employing nano-organic working fluids culminated in a 4 % reduction in the heat exchanger for a 1 % concentration of nanoparticles. Although the pressure drop increased to about 18 % for the case of nanoparticles, this did not result in any significant increase in the pump's power consumption [80]. Using multi-walled carbon nanotubes in oil as heat transfer fluid for the solar collector and R113 as working fluid for the ORC system yielded better system efficiencies and lower levelized cost of electricity compared to using just the base fluids [81].

The use of nanofluids in ORC systems for purposes other than usage as heat transfer fluid in solar collectors has not been studied extensively. So far, an extensive literature search points to two (2) publications utilizing standard nanoparticles as working fluids in ORC systems; "*Conceptual Modelling of Nanofluid ORC for Solar Thermal Polygeneration*" by Saadatfar *et al.* [16] and "*Prospects of the Use of Nanofluids as Working Fluids for ORC Power Systems*" by Mondejar *et al.* [17]. The study in which the prospects of nano organic working fluids were examined for ORC power systems, revealed Al_2O_3 (45 % occurrences), CuO (35 % occurrences), and ZnO (15 % occurrences) are the commonest nanoparticles employed in ORC studies [17]. Other particles with less than 5 % occurrences in the study were Ag, SiO_2, TiO_2, Sb_2O_5:SnO_2 and carbon nanotubes. According to Saadatfar *et al.*, utilizing nanofluids greatly increases the cycle efficiency when compared to pure n-pentane [16]. The model used silver (Ag) nanoparticles dissolved in n-pentane (0.5 % W/v concentration). Additionally, the study supported previous research's findings about the condenser and evaporator size reductions. Table 2 displays the thermophysical characteristics of some of the most prevalent nanoparticles.

The search for better thermophysical characteristics in organic working fluids led to the creation of metal-organic heat carriers, innovative nanofluids consisting of metal-organic framework (MOF) nanoparticles dispersed in different base fluids, including refrigerants. According to McGrail *et al.* [82], MOHCs are a unique class of nanoparticles that have been specifically designed to both absorb and discharge substances from the fluids they are placed in. MOHCs allow for the extraction of extra heat from the endothermic enthalpy of desorption, which can be up to double the level of the pure fluid phase's latent heat of vaporization. Calculations by McGrail *et al.* for MOHC/R123 nanofluid showed a potential of up to 15 % increment in the ORCs power output. Experiments in capillary tubes conducted in this study demonstrated that there was no deposition of nanoparticles on the tube walls during the liquid-vapour transition when the entrance Reynolds number (RE) did not exceed 100 [82]. A combination of R245fa with MIL101 (a MOHC nanoparticle) was studied by Cavazzini *et al.* [83], who determined that the resultant nanofluid not only boosted system efficiency but also reduced the heat exchanger size, hence affecting the economic feasibility of the ORC system.

Table 2. Thermophysical properties of some common (standard) nanoparticles

Nanoparticle	Heat Capacity, c_p (kJ/kg K)	Thermal Conductivity, k (W/m.K)	Density,ρ (kg/m^3)
CuO	0.55	33	6320
Al_2O_3	0.85	25	3960
TiO_2	0.68	8.4	4230
SiO_2	0.93	1.4	2650
ZnO	0.43	13	5610
Ag	0.24	407	10490
SWCNT	2.10	3000	2170
MWCNT	0.733	2586	2100

(Source: [17], [80])

Nanofluids involving single base fluids, as of the time of this study, have not been studied extensively with only three (3) combinations mentioned in the literature relating to ORC applications. These combinations which showed enhanced performance when compared to the base fluids include R601/Ag, R245fa/MIL101 and R123/MOHC. Although nanofluids involving zeotropic mixtures of organic working fluids have not been studied for ORC applications, studies involving their applications in refrigeration have been reported to optimise the performance of the refrigeration systems due to the enhanced thermophysical properties of the resulting fluids [84].

A comparative analysis of several nanoparticles utilised in ORC systems, emphasising their benefits and limitations is presented in Table 3. Nanoparticles such as CuO and Al_2O_3

Table 3. Comparative analysis of nanoparticles used in ORC systems [14 - 16], [77], [81]

Nanoparticle	Advantages	Drawbacks
CuO	- High thermal conductivity which improves the heat transfer properties in ORC systems - Cost-effective compared to other metallic nanoparticles - Enhances both heat absorption and dissipation, boosting system efficiency	- Prone to agglomeration, which can reduce long-term effectiveness - Long-term stability is a concern, especially in extended operations
Al_2O_3	- Good thermal stability and chemical resistance - Chemically inert, reducing the risk of reactions with the working fluid - Improves thermal conductivity and reduces thermal resistance in heat exchangers	- Lower thermal conductivity compared to metallic nanoparticles like CuO - Tends to sediment over time, leading to potential fouling and reduced performance
ZnO	- High thermal conductivity with strong photothermal properties - Antibacterial and environmentally friendly - Shows promise for improving heat transfer and enhancing ORC efficiency	- Prone to agglomeration, leading to reduced long-term stability - Expensive compared to CuO and Al_2O_3
TiO_2	- High chemical stability, making it suitable for long-term use - Environmentally friendly and non-toxic compared to some other nanoparticles - Moderate thermal conductivity with potential for improved heat transfer	- Lower thermal conductivity compared to metals like CuO and Ag. - Tendency to form aggregates, reducing stability in the long run
Ag	- Among the highest thermal conductivity of nanoparticles - Exceptional enhancement in heat transfer properties - Reduced heat exchanger size due to its superior conductivity	- Very high cost, limiting widespread commercial use - Prone to oxidation, which can reduce long-term performance - Toxicity concerns in large quantities
SiO_2	- High thermal stability and very low toxicity - Excellent dispersion in organic fluids, reducing sedimentation risks - Enhances heat transfer with moderate thermal conductivity improvement	- Lower thermal conductivity compared to metallic nanoparticles - Ineffective at significantly enhancing heat transfer in high-temperature ORC systems
CNT	- Extremely high thermal conductivity, superior for heat transfer - Lightweight, contributing to reduced energy consumption for fluid circulation - Flexible for applications, with the ability to modify properties to suit needs	- High cost, limiting widespread adoption - Challenges in ensuring dispersion stability (CNTs tend to cluster if not properly dispersed) - Environmental concerns due to non-biodegradability and potential health risks

are frequently utilised for their capacity to enhance thermal conductivity and heat transmission. CuO provides high conductivity at a reduced cost; yet it is plagued by agglomeration and long-term stability challenges. Al_2O_3 exhibits chemical stability; nonetheless, it is prone to sedimentation over time, thereby diminishing system efficiency. ZnO, TiO_2, and SiO_2 have favourable thermal and environmental characteristics; nonetheless, they encounter drawbacks like elevated prices, diminished conductivity, and difficulties with agglomeration. Ag possesses superior thermal conductivity, greatly enhancing heat transmission; nevertheless, its elevated cost and susceptibility to oxidation impede its widespread application. Carbon Nanotubes (CNTs) provide superior conductivity and flexibility; nonetheless, they are costly and pose challenges with dispersion stability and environmental impact. The selection of nanoparticles necessitates a balance between improved ORC performance, long-term stability, and economic factors.

V. Critical Evaluation of Existing Research

Recent research has been dedicated to optimizing the performance of ORCs. This involves selecting appropriate working fluids, ensuring dependable heat sources, and configuring the ORC in the most efficient way to obtain the best possible performance. The following critical assessments are derived from the literature review:

i. The heat sources usually generate temperatures within the range of 80 °C to 200 °C and could be higher, depending on the specific source of heat. Table 4, which shows the typical operating temperatures of various heat sources for ORC operations, reveals that industrial waste heat, exhaust gases and concentrating solar thermal can achieve the highest temperatures [85], [86].

Table 4. Typical operating temperatures of various heat sources for ORC operations

Heat source	Temperature range
Waste heat from industrial processes	100 °C – 500 °C
Exhaust gases from internal combustion (IC) engines	100 °C – 500 °C
Geothermal energy	80 °C – 350 °C
Solar energy	80 °C – 500 °C
Biomass combustion	200 °C – 450 °C

(Source: [85], [86])

ii. Working fluid selection for the ORC operation is substantially influenced by the temperature of the heat source. As seen in Figure 3, the various working fluids have specific critical temperatures which essentially influence their performance under different temperature conditions. While the heat source remains constant, a working fluid with a lower critical temperature exhibits better performance because the choice of working fluid is mostly influenced by the heat source temperature, particularly at low temperatures. On the other hand, fluids with elevated critical temperatures are appropriate for heat sources operating at greater temperatures.

iii. The efficiency of the ORC is directly influenced by the configuration of the cycle, making it a crucial element in the design of ORC systems. The fundamental setup of the ORC comprises a turbine, a condenser, a pump, and a heat source. Enhancing the performance of the ORC may be achieved by integrating supplementary components like a recuperator, a regenerator, and an ejector into the fundamental setup. Data from Chowdhury *et al.* [87] was modified in Figure 4, showing that ORCs with regeneration have higher efficiencies at lower operating temperatures compared to simple organic Rankine cycles.

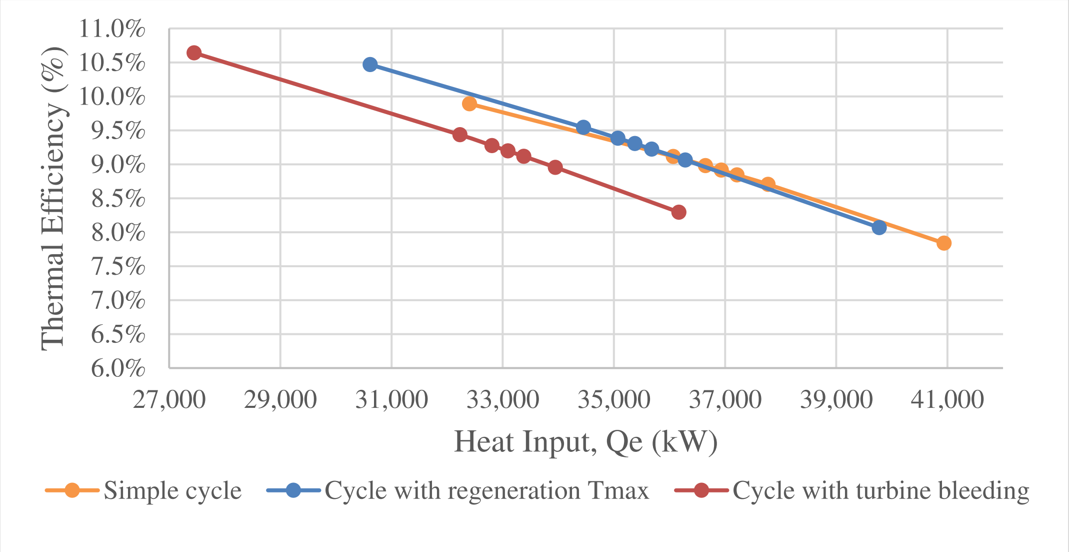

Fig. 4. Comparative analysis of thermal energy and efficiency for different ORC configurations modified from [87]

iv. The choice of working fluids is vital for achieving optimum performance in ORC operations. Working fluids for ORCs have, therefore, been extensively studied for this purpose. The performance of common working fluids used in ORCs, which include both pure fluids and zeotropic mixtures, has shown diverse outcomes. However, the bulk of studies indicate that using zeotropic mixtures generally leads to enhanced thermodynamic performance. Nevertheless, the correlation between this factor and improved economic performance remains inconclusive since available literature gives conflicting findings on this matter. This is because systems with zeotropic mixtures are known to produce lower temperature gradients in the heat exchangers and as such may need bigger heat exchangers in comparison to systems with pure fluids.

v. The study of nanoparticles in organic working fluids is relatively new to the field of ORCs seeing there are not many publications on the subject. This is although nanoparticles in ORC have mostly been found as an enhancement for heat transfer fluids, especially in solar organic Rankine cycles. The usage of nanoparticles in enhancing the properties of organic working fluids has focused on two (2) classes of nanoparticles; the traditional nanoparticles in Table 2 and the metal-organic heat carriers, both of which have been reported in literature to have improved the performance of the organic Rankine cycles although not much has been reported on their economic performance.

vi. The commercialization of the ORC technology has not been popular because of the relatively low efficiencies due to factors including low-grade heat source, organic working fluids and the selection of other components selection including expander/turbine. This low efficiency makes the technology not economically viable and that has been the focus of various research works; to improve the efficiency and by extension, how well the system performs economically. The analysis of organic working fluids for this purpose has yielded varying results across the working fluid ranges; pure fluids, zeotropic mixture and nanofluids (which are basically nanoparticles in organic working fluids, whether pure fluids or zeotropic mixtures). Pure fluids, which are the most common and have been studied extensively, in most literature fall short when compared to zeotropic mixtures in terms of thermodynamic performance in addition to economic performance. However, a few works of literature report no significant difference in both economic and thermodynamic performance when the two (2) fluids are compared while some other literature reports the pure fluids to have better performance than zeotropic mixture, although these are very few. Studies on the introduction of nanoparticles into organic working fluids have largely focused on thermodynamic performance and are silent on economic performance, leaving room for studies in the field.

VI. Conclusions

Organic Rankine cycles have been touted as the most effective low-grade heat recovery systems with many uses, particularly in electricity production. Yet, their effectiveness is hindered by the low operational temperatures and physicochemical constraints of the organic working fluids used. This review emphasized the significant impact of working fluids, which are classified as either pure fluids or zeotropic mixtures, on organic Rankine cycle performance.

i. Zeotropic mixtures generally offer enhanced thermal efficiency and economic performance in ORC systems by improving the thermophysical properties of working fluids. However, their benefits can vary significantly depending on specific application scenarios, highlighting the need for case-by-case evaluation to optimize performance.

ii. While zeotropic mixtures often outperform pure fluids in ORC systems, there are instances where pure fluids might be more effective. This suggests that the choice of working fluid should be tailored to the specific operational conditions and goals of the ORC system.

iii. Nanoparticles, particularly metal-organic heat carriers, demonstrate substantial potential in improving the thermodynamic efficiency of ORC systems. They enhance the heat transfer characteristics of working fluids, making them a promising avenue for further research and development in ORC technology.

iv. Achieving a balance between thermodynamic, economic, and environmental performance is crucial for the advancement of ORC systems. The integration of zeotropic mixtures and nanofluids presents a viable pathway to optimize these factors, leading to more efficient and sustainable low-grade heat recovery systems.

v. There is a critical need for more experimental research on the use of nanofluids, particularly in conjunction with zeotropic mixtures, to validate their potential benefits in ORC systems. Additionally, the development of new, environmentally friendly working fluids that meet the demands of ORC systems will be essential for advancing the technology and broadening its commercial application.

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