COMPARATIVE ANALYSIS OF FLUIDS USED IN ORGANIC RANKINE CYCLES

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ABSTRACT: Organic Rankine Cycles (ORCs) offer a viable path to converting low-grade heat sources—such as waste heat from industrial processes, vehicle exhaust, solar irradiation, and geothermal energy—into electrical power. The choice of working fluid critically influences performance, safety, environmental impact, and economic viability. This study provides a comparative analysis of ORC fluids, focusing on classifications (dry, wet, isentropic), their thermodynamic behavior on T-s diagrams, and how these properties interact with evaporation and condensation processes to determine system efficiency and reliability
Performance metrics—thermal efficiency, exergy efficiency, net work output, and irreversibility—are evaluated across representative fluids (e.g., R123, R134a, R11, R141B, R227ea/R245fa) and operating conditions.

KEY WORDS: dry, wet, isentropic fluids; performance metrics

1. INTRODUCTION

Organic Rankine Cycles (ORCs) have emerged as a promising technology for the conversion of low-grade heat-from sources such as waste heat from industrial processes, vehicle engine exhaust, solar irradiation, or geothermal reservoirs-into useful electrical power.
Unlike conventional steam cycles that use water as the working fluid, ORCs employ organic fluids such as refrigerants, hydrocarbons, and specially formulated mixtures, which offer lower boiling points and reduced operating pressures. Not only does this enable improved efficiency in energy recovery from low- to medium-temperature sources, but it also provides significant advantages in terms of system compactness and adaptability to different scales of power generation [1].
The selection of an appropriate working fluid is critical to the overall performance, safety, and environmental impact of the ORC system. Several factors govern this decision, including thermodynamic characteristics (e.g., critical temperature and pressure, latent heat, specific heat, and density), environmental aspects such as Global Warming Potential (GWP) and Ozone Depletion Potential (ODP), and practical considerations like material compatibility and economic viability. This article offers a comparative analysis of various fluids used in ORC applications, with detailed discussions on their classifications, performance metrics, and suitability for different heat recovery applications. By integrating visual representations such as detailed tables and flow diagrams, this study provides an in-depth evaluation intended to guide researchers and engineers in selecting the optimal working fluid for specific ORC implementations [2].

2. CLASSIFICATION AND PROPERTIES OF WORKING FLUIDS

The thermodynamic behavior of working fluids in ORCs is generally categorized into three types based on the shape of their saturation vapor curve plotted on a temperature-entropy (T-s) diagram: dry, wet, and isentropic. The classification is based on the gradient of the saturated-vapor curve, where a positive slope indicates a dry fluid, an infinite slope denotes an isentropic fluid, and a negative slope corresponds to a wet fluid –

figure 1. This classification plays a crucial role in understanding the performance characteristics of fluids when expanding in turbines, especially under saturated or superheated conditions.

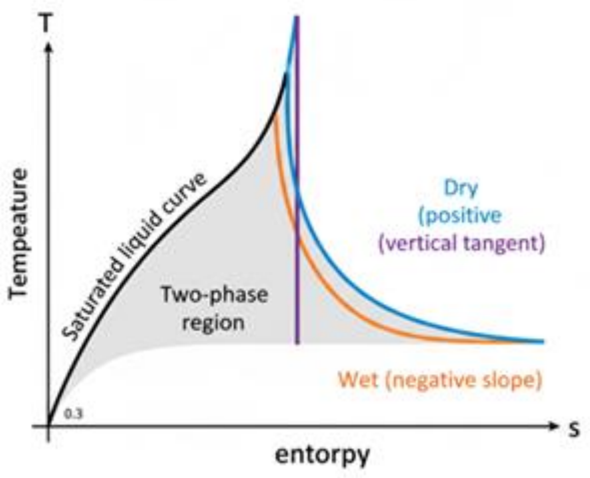

Fig. 1. Schematic T-s diagrams illustrating the slopes of ORC working fluids.

Dry Fluids

Dry fluids exhibit a positively sloping saturated-vapor line, which ensures that during expansion the vapor remains superheated relative to the saturation condition. These fluids usually otter a high thermal efficiency under proper operating conditions and are particularly suitable tor systems requiring a high-quality vapor inlet to turbines [1].

Common examples include R11, R123, and R141B that belong to Group 1 of working fluids with lower condensation pressures (around 100 kPa) and consequently higher thermal efficiencies (typically around 23-25%) [1,2].

Wet Fluids

Wet fluids are characterized by a negatively sloping saturated vapor curve. They tend to condense during expansion it not properly superheated, which might require additional system modifications such as the use of a superheater to prevent turbine blade erosion. Fluids such as R134a and R404a tall into this category. Wet fluids often present more dispersed performance data as their thermodynamic properties vary significantly with operating conditions [3].

lsentropic Fluids

lsentropic fluids exhibit an almost vertical or infinite slope in the T-s diagram. These fluids maintain nearly constant entropy during the phase change process and can provide stable and predictable performance under various operating conditions. Their unique behavior mitigates the risk of droplet formation during expansion and ensures improved turbine efficiency [4].

Beyond thermodynamic properties, working fluid selection must factor in environmental impacts and safety. Parameters such as GWP and ODP are critical in today's regulatory climate. Fluids with high ODP or GWP, for example, R11 and certain chlorofluorocarbons, have been phased out or are scheduled for removal from industrial use to reduce adverse environmental impacts [5]. Moreover, the safety classification-assessed via standards like the ASHRAE safety categorization-and material compatibility with system components exert significant influence on the selection process [6].

Economics aspects, including fluids availability and operational cost, also weigh heavily in the selection process. In some studies, fluids such as R236fa and R124 were compared not only by thermal efficiency but also by assessing fluid consumption and overall economic impact – leading to decision on optimal selection for particular applications (e.g. ship engine waste heat recovery or waste heat from internal combustion engine).

Figure 2 point out the differences between dry, wet and isentropic fluids.

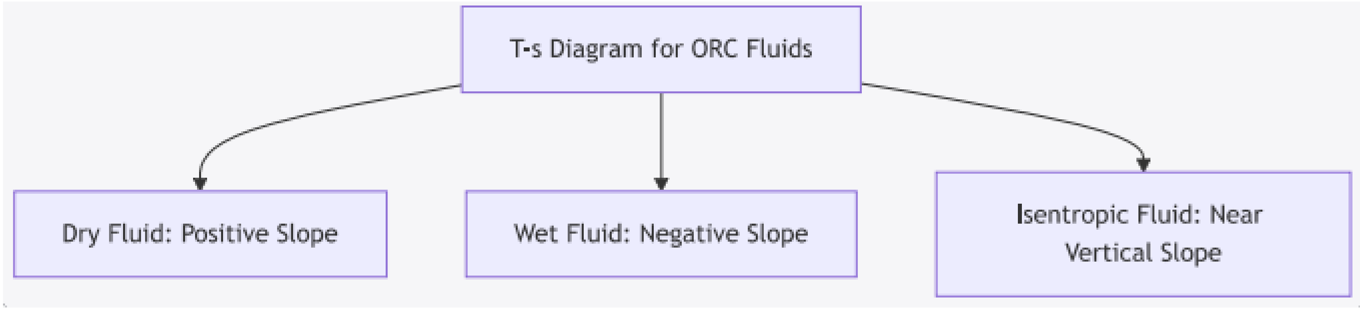

Fig 2. Classification of ORC working fluids

3. PERFORMANCE ANALYSIS OF ORC SYSTEMS

The performance of an ORC system is significantly influenced by the choice of working fluid. Performance metrics such as thermal efficiency, exergy efficiency, net work output, and cycle irreversibility are used to evaluate the effectiveness of different fluids.

Comparative analysis has shown that fluids with lower condensation pressure (e.g. group 1 fluids) tend to achieve higher thermal efficiency, often within the rage of 23-25% [6]. Moreover, practical studies have identified optimal working fluids for various application scales, with water being favored for medium to small-scale power plants where the conventional steam Rankine cycle would be less effective.

Thermal efficiency in ORC systems is closely linked to the evaporation and condensation processes. Experiments have demonstrated that increasing the inlet turbine pressure, especially for systems employing saturated working fluids, generally leads to improvements in energy and exergy efficiencies [6]. Dry fluids, in particular, when operated in a saturated condition, exhibit higher thermal performance and lower cycle irreversibility due to minimized droplet formation during turbine expansion [7].

The exergy efficiency provides an indication of how much of the available energy is converted into useful work while accounting tor inherent losses. Studies have shown that fluids with moderate critical temperatures offer favorable exergy efficiencies under optimized conditions. For example, comparisons among fluids such as R123, R113, R141b, and R11 reveal that certain fluids can yield both high thermal and exergy efficiencies when tuned tor optimal operating conditions [7].

Table 1 summarizes the key performance parameters-physical properties, thermal efficiency, and exergy efficiency-tor selected working fluids.

Table 1: Comparative performance metrics for selected ORC working fluids.

Working Fluid	Critical Temperature (oC)	Condensation Pressure (kPa)	*Thermal* Efficiency (%)	Exergy Efficiency (%)
R123 (Group 1)	~83.7	~100	23-25	High
R1154a and R141B	Similar to R123	Moderate	22-24	High
R134a (Wet Fluid)	Lower than dry fluids	Higher than Group 1	18-20	Moderate
R600a (lsobutane)	Variable	Moderate	15-18	Moderate
R227ea/ R245fa Mixture	Optimized for geothermal	Variable	17-22	High

The data highlights the relationships between condensation pressures, critical temperatures, and efficiencies reported in various studies [6, 7, 8].

Another important aspect is the influence of evaporation temperature on performance parameters. Graphical analyses have revealed that, tor dry/isentropic fluids, parameters such as net work output and thermal efficiency decrease as the critical temperature increases, while parameters related to irreversibility and heat recovery efficiency show inverse relationships [5].

The inlet temperature of the hot fluid and the evaporation temperature in the ORC's evaporator play decisive roles in system performance. Research indicates that variations in these temperatures alter efficiency curves noticeably. For instance, increasing the turbine inlet pressure can improve the net work output; however, a high evaporation temperature using a wet fluid may lead to irregular performance trends compared to the more predictable behavior observed with dry/isentropic fluids [5]. These relationships are depicted in several performance trend figures from the literature that show nearly monotonic relationships for dry fluids and more dispersion for wet fluids.

Figure 2 outlines the key stages and decision points in evaluating the performance of working fluids within an ORC system.

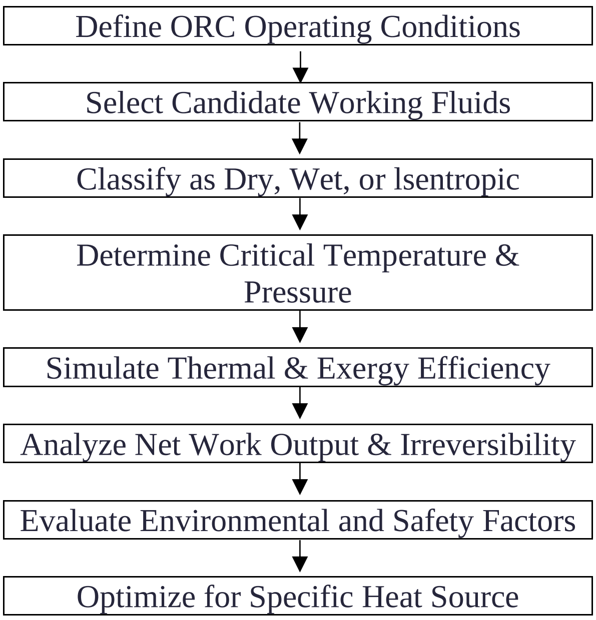

Figure 2: Flowchart summarizing the process for performance evaluation and optimization of ORC working fluids, integrating key thermodynamic and environmental evaluation steps [5].

4. APPLICATIONS OF ORC FLUID SELECTION

The application of ORC technologies varies widely depending on the thermal source and operational scale. The selection of the working fluid must be tailored to the specific application to maximize efficiency and economic feasibility.

One of the most promising applications of ORC technology is waste heat recovery (WHR) from internal combustion engines. Studies have shown that when recovering waste heat from a ship's main engine or automobile engine exhaust, the safety of the working fluid is paramount due to the challenging environment in the engine room. An analysis of several candidate fluids concluded that R365mfc, due to its superior work capacity in the defined evaporation pressure range, was optimal for such applications. The inherent low boiling point and moderate pressure conditions of these fluids are well suited for capturing the relatively low-grade heat present in engine exhaust systems [6].

Solar-driven ORC systems utilize working fluids that can operate efficiently with the moderate temperatures provided by flat plate collectors or parabolic trough collectors. For instance, in solar-ORC applications, fluids such as R365mfc have been identified as promising due to their compatibility with the thermal input and improved performance through internal heat exchanger optimization [2, 7].

Geothermal applications, on the other hand, benefit from working fluids that can handle variations in low enthalpy inputs. Mixtures like R227ea/R245fa have been reported to achieve high efficiencies in low-enthalpy geothermal ORC systems by optimizing the thermodynamic cycle [7].

Beyond engine exhaust and renewable energy sources, numerous industrial processes produce significant quantities of otherwise wasted heat. In these cases, ORC systems are designed to interface with heat recovery components, including superheaters and regenerative circuits, to maximize the conversion of low-grade heat into electrical power. Comparative studies using fluids such as R123, R113, and toluene have demonstrated that even small improvements in thermal and exergy efficiencies can yield considerable economic benefits, especially when integrated into complex industrial cogeneration systems [8]. The trade-offs between efficiency, fluid consumption, and environmental viability must be rigorously balanced in the design phase.

Table 2 summarizes various ORC application scenarios along with the corresponding recommended working fluids along with key performance comments:

Table 2: Overview of ORC applications and selected working fluids based on performance and environmental criteria.

Application Area	**Thermal Source**	**Recommended Working Fluid(s)**	**Key Performance Notes**
Waste Heat Recovery (Engine WHR)	Exhaust gas/cooling systems	R365mtc, R123	High work output and safety considerations [6,11]
Solar ORC (Low-Temperature)	Solar irradiation/flat plate	R365mtc, Neopentane mixtures	Improved efficiency via integrated exchangers [10,12]
Geothermal ORC	Low-enthalpy geothermal fluid	R227ea/ R245ta, R123	Optimized tor energy conversion from low-grade heat [11,13]
Industrial & Combined Cycle Systems	Waste heat from industrial processes	R113, R141B, Toluene	Balances thermal efficiency and environmental impact [14,15]

5. CONCLUSIONS

This comparative analysis consolidates evidence that the selection of working fluids for Organic Rankine Cycles (ORCs) is a multidimensional optimization problem, where thermodynamic performance, safety, environmental impact, and economic viability must be balanced for each specific heat source and operating regime. The fluids studied—ranging across dry, wet, and isentropic classifications—demonstrate clear trends that can guide design choices and system-level integration.

Application context governs fluid selection. For waste heat recovery from internal combustion engines, fluids with favorable work capacity and safe operating ranges (e.g., certain hydrofluorocarbons and hydrocarbon blends) emerge as practical choices. Solar-ORC and geothermal-ORC applications benefit from mixtures or specific hydrocarbons that balance moderate evaporation temperatures with robust efficiency. Industrial cogeneration contexts require fluids that harmonize performance with environmental constraints and supply stability.

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