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Abstract

The Organic Rankine Cycle (ORC) offers a promising solution for converting low-grade heat into electricity by utilizing organic fluids with favorable thermodynamic properties. This study explores the impact of different working fluids on ORC efficiency across various configurations. Through experimental and simulation analyses, the study identifies R142b, FC-72 and dichloromethane as top performers under different conditions. Results demonstrate that fluid selection critically influences ORC performance. This research underscores the ORC's versatility in enhancing energy efficiency and reducing waste across industrial applications.

*Keywords:* Rankine Cycle, GAMS, Fluid selection;

## Introduction

The Organic Rankine Cycle (ORC) represents a significant advancement in power generation technology, leveraging low-grade heat sources for the production of electricity. Named after its working principle derived from the conventional Rankine cycle, the ORC differentiates itself by employing organic fluids with favorable thermodynamic properties instead of water. This adaptation allows the ORC to efficiently exploit heat from diverse and typically low-temperature sources, such as geothermal reservoirs, solar thermal energy, industrial waste heat, and biomass combustion.

The selection of an appropriate working fluid is a critical aspect of optimizing ORC performance. The ideal fluid must possess several key characteristics to ensure efficiency and safety. These include

suitable boiling and condensation points relative to the heat source and sink, high thermal stability, low viscosity, and minimal environmental impact. Additionally, the fluid should exhibit a high molecular weight and density, which contribute to higher cycle efficiency and lower volumetric flow rates.

Evaluating potential working fluids involves a comprehensive analysis of their thermophysical properties and compatibility with system components. Fluids such as refrigerants, hydrocarbons, and siloxanes are commonly considered due to their varied boiling points and thermal properties. Moreover, the environmental and safety considerations, such as global warming potential (GWP) and flammability, are integral to the selection process.

In summary, the ORC's adaptability to low-temperature heat sources and the judicious choice of working fluid renders it a versatile and sustainable option for enhancing energy efficiency and mitigating waste. Continued research and development in this field aim to refine fluid selection criteria and expand the applicability of ORC technology across various industrial sectors.

Abbas et al. [1] experimentally examined a cascaded two-Organic Rankine Cycle (ORC) system across various temperatures and pressures to optimize performance. Cyclopentane was used in the high-temperature (HT) cycle, while pentane, butane, and propane were tested in the low-temperature (LT) cycle. Results highlighted that pentane maximized heat transfer, absorbing 23 kW, but most heat from the HT cycle was not transferred to the LT cycle.

Yu et al. [2] focuses on optimizing the design and operation of a solar energy-driven ORC system utilizing a parabolic trough collector and a two-tank sensible thermal energy storage system. Results showed that a recuperative ORC significantly outperforms a basic ORC, with toluene emerging as the best working fluid despite vacuum condensation issues.

Abbas et al. [3] explored the thermal efficiency of a Cascaded Dual-Organic Rankine Cycle (CD-ORC) system using alkanes and low-GWP refrigerants through simulations with EBSILON@Professional. The analysis revealed that thermal efficiency in the HT-ORC is influenced by the critical temperature, molecular mass, and critical pressure of the working fluids, with cyclic alkanes like cyclohexane showing superior performance. In the LT-ORC, refrigerants with high critical temperatures, such as R1366mzz(Z) and R1233zd(E), achieved the highest efficiency. The CD-ORC system demonstrated a potential 25% efficiency improvement over regular ORC systems.

Figure 1. Rankine cycle for Config. A [4]

In the following, the thermodynamic modeling of the ORC (Organic Rankine Cycle) is examined. To model this cycle using various assumptions, three different approaches for the thermodynamic simulation of the cycle shown in Figure 1.

## Configuration A – Approach 1

To model the thermodynamics of Figure 1 using Approach 1, which is based on obtaining the enthalpy of different streams, assumptions include: the turbine outlet pressure is 1 bar, zero pressure drop for equipment, a minimum temperature approach of 5°C for cycle heat exchangers, an evaporator outlet temperature of 165°C, purity of each stream, condenser outlet temperature slightly less than the boiling point of the substance, a 1°C temperature increase across the pump, 75% pump efficiency, 80% turbine isentropic efficiency, 95% electric motor efficiency, and operational constraints such as the turbine inlet being fully vapor and the turbine outlet having a steam quality that can decrease to 90%

as mentioned in [2]. The specifications of the hot water flow rate are given in Table 1.

Table 1. Waste Water property

Parameter	Value
Pressure	10 bara
Temperature	170 °C
Flowrate	100 kg/s
Composition	Pure Water

To determine the enthalpy of each stream, Equation 1 is used. The actual enthalpy of each stream includes three to four parameters: the ideal gas enthalpy, the residual enthalpy indicating the deviation from the ideal state, the formation enthalpy which is a constant value for the substance, and if the substance is in the liquid phase, the enthalpy of vaporization should be added to the actual enthalpy.

$$H^{real} = H^{ig} + H^{res} + H^{form} + H^{vap} \quad eq.1$$

If the stream is two-phase, Equation 2 must be used, which calculates the enthalpy for saturated vapor and liquid, and then the vapor fraction of the stream is inserted into the equation to obtain the actual enthalpy.

$$H = vap. \text{ frac} * H^{Sat.vap} + (1 - vap. \text{ frac}) * H^{Sat.liq} \quad eq.2$$

To calculate the ideal gas enthalpy of a stream, Equation 3 is used. Coefficients a to f are read from the Aspen HYSYS software, and by inputting the temperature in Kelvin into Equation 3, the ideal gas enthalpy (Kj / Kg) is obtained.

$$H^{ig} = a + bT + cT^2 + dT^3 + eT^4 + fT^5 \quad eq.3$$

To calculate the second parameter in Equation 1, the residual enthalpy, existing EOS<sup>1</sup> are used. Considering the problem's requirements, the PR<sup>2</sup> equation of state is chosen. Using the relations provided in [5], presented as Equations 4 to 12, the desired parameter is calculated. To solve the cubic equation in Equation 5, the Kamath method is used.

$$H^{Res} = RT \left( Z - 1 - \frac{A}{B\sqrt{8}} \left( 1 + \frac{m\sqrt{T_r}}{\sqrt{\alpha}} \right) \ln \left[ \frac{Z + \frac{(1+\sqrt{2})B}{Z + (1-\sqrt{2})B}}{Z + (1-\sqrt{2})B} \right] \right) \quad eq.4$$

$$Z^3 - (1 - B)Z^2 + (A - 2B - 3B^2)Z - (AB - B^2 - B^3) \quad eq.5$$

$$T_r = \frac{T}{T_c} \quad eq.6$$

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<sup>1</sup>Equations of State

<sup>2</sup>Peng Robinson

$$\alpha = \left[ 1 + m \left( 1 - T_r^{0.5} \right) \right]^2 \text{ eq.7}$$

$$m = 0.375 + 1.54\omega - 0.27\omega^2 \text{ eq.8}$$

$$a = 0.457235 \frac{R^2 T_c^2}{P_c} * \alpha \text{ eq.9}$$

$$b = 0.077796 \frac{RT_c}{P_c} \text{ eq.10}$$

$$A = \frac{aP}{(RT)^2} \text{ eq.11}$$

$$B = \frac{bP}{RT} \text{ eq.12}$$

Assuming the purity of each stream, by substituting either the temperature or pressure of a stream, other parameters of that stream, such as the fugacity coefficient (Equations 13 & 14) or the compressibility factor, can be calculated.

$$\text{for pure system} \rightarrow \varphi^v = \varphi^l \text{ eq.13}$$

$$\ln(\varphi) = (z - 1) - \ln(z - B) + \frac{A}{2B\sqrt{2}} \ln \left( \frac{z + (1 - \sqrt{2})B}{z + (1 + \sqrt{2})B} \right) \text{ eq.14}$$

To find the molar flow rate of the pure component in the cycle, Equation 15 is used, which determines the molar flow rate of the component by balancing the energy in the cycle's evaporator.

$$\dot{n} (H_1 - H_4) = \dot{m}_w C_{p,w} (T - 5) \quad \text{eq.15}$$

Subsequently, the thermodynamic parameters of the mentioned cycle are calculated, and the pump's required work is determined using Equation 16 & 17. Finally, the turbine's generated work is calculated using Equation 18.

$$H_{pump} = \frac{(P_4 - P_3) * \dot{n} * MW}{density} \quad \text{eq.16}$$

$$W_{pump} = \frac{H_{pump}}{\eta_{pump}} \quad \text{eq.17}$$

$$W_{turbine} = \dot{n} (H_1 - H_2) \quad \text{eq.18}$$

To select among the 74 components listed in the provided Excel file, two constraints are applied: the condenser outlet temperature must be at least 30°C, and the selected component must have a boiling point lower than water. By applying these constraints, 15 components listed in Table 2 are identified as candidates for the best substance for this cycle.

Table 2. Candidates for best component

Working Fluid		
2,2-dimethylbutane	FC72	R113
4-methyl-2-pentene	Isohexane	Benzene
Acetone	Methanol	Ethanol
Cyclopentane	n-hexane	n-heptane
Dichloromethane	n-pentane	R141b

In this approach, five components - dichloromethane, FC-72, methanol, n-heptane, and R-113 - are selected.

## Configuration A – Approach 2

In Approach 2, similar to the previous case, the mentioned relations and assumptions are used, with the difference that the turbine outlet is assumed to be saturated vapor at 1 bar pressure, ensuring no liquid forms inside the turbine. Therefore, only the vapor enthalpy is used, resulting in reduced generated work. The same components as in Approach 1 are used in Approach 2.

## Configuration A – Approach 3

In Approach 3, the general relations of the previous two approaches are used, with the difference that since only dichloromethane converts to approximately 94% liquid, and the other components remain in their gaseous state, the vapor fraction of this component is included in the equations. Additionally, using Equation 19 [6], the turbine outlet temperature is calculated considering the pressure drop and the K value, which equals  $C_p/C_v$  of the component in the ideal state, and the turbine's isentropic efficiency equal to 80%. The components used in the Approach 3 are the same as those in the previous two approaches.

$$\eta_{turbine} = \frac{1 - \frac{T_2}{T_1}}{1 - \pi_i^{\frac{1-k}{k}}} \quad eq.19$$

## Configuration B

In the Bonus section of this project, the performance comparison among five components - isohexane, FC-72, R-113, dichloromethane, and R-141b - is conducted. This section follows the structure shown in Figure 2.

Figure 2. Configuration B[4]

The assumptions used in this section are similar to those of Approach 3 in Configuration 1, with the difference that the pump outlet temperature is considered to be 304.15 K to maintain the 5°C approach temperature for the middle heat

exchanger in Figure 2. With this assumption, the minimum approach temperature for all candidate components is met. Also, the UA values are derived from [7] considering the water-organic fluid type, and the required area for the cycle’s evaporator is determined and substituted into the equations. In this section, similar to the previous sections, the primary task is to calculate the actual enthalpy of the cycle streams, assuming the turbine inlet stream is at 165°C and in the saturated vapor state. By calculating the enthalpy of streams 1, 6, 2, 5, and 4 and using two additional relations compared to the previous approaches, 20, 21 and 22, the turbine work, cycle work, and all required parameters are determined and calculated.

$$H_6 - H_5 = H_3 - H_2 \quad eq.20$$

$$U * A * f * LMTD = \dot{m}_w C_{p,w} (T) \quad eq.21$$

$$LMTD = \frac{(T_{in,waste}-T_1)-(T_{out,waste}-T_6)}{\ln \frac{(T_{in,waste}-T_1)}{(T_{out,waste}-T_6)}} \quad eq.22$$

## Results & discussion

This section consolidates and interprets the model results for Configuration A (Approaches 1–3) and Configuration B, and cross-checks them against Aspen HYSYS. All thermodynamic properties were calculated with the Peng–Robinson EOS and Kamath’s cubic handling; agreement with HYSYS is reported via the per-row error columns in Tables 3–6.

Configuration A — Approach 1 (Table 3) - FC-72 emerges as the best candidate in this approach. - Turbine work and pump work from the model are 22,639.9 kW and 311.66 kW, respectively, yielding a net cycle work of approximately 22.33 MW. - State properties (Z factors and enthalpies) match HYSYS closely; average deviations are within about 0.3%, confirming the PR+Kamath implementation is consistent with the flowsheet simulator.

Configuration A — Approach 2 (Table 4) - Under the saturated-vapor constraint at the turbine outlet (1 bar), the model reports turbine and pump works of 20,290.6 kW and 311.54 kW, giving a net work of roughly 19.98 MW. - FC-72 remains the preferred fluid under these assumptions. The reduction in net work versus Approach 1 is expected because the outlet quality constraint limits the expansion end-point and effective pressure ratio. - Agreement with HYSYS remains strong (average errors ~0.35%).

Configuration A — Approach 3 (Table 5) - With the additional modeling assumptions in Approach 3, dichloromethane (DCM) becomes the selected fluid. - Turbine and pump works are 8,705.6 kW and 240.62 kW, respectively, implying

a net work of about 8.46 MW. - Despite the lower power, thermodynamic consistency is high (errors  $\sim 0.57\%$ ). The drop in net work aligns with the tighter end-state constraints and different fluid behavior near saturation.

Configuration B (Table 6) - For the recuperated cycle, R141b is identified as the top candidate among the tested set. - Turbine and pump works are 9,330.12 kW and 400.54 kW, respectively, giving a net work near 8.93 MW. - The inversion in ranking between DCM and R141b compared with Configuration A is physically plausible: in Config B, the turbine exhaust thermodynamic state and the recuperator thermal match can favor fluids that leave the turbine superheated, improving internal heat recovery.

Cross-comparison and trends - Among Configuration A approaches, Approach 1 delivers the highest net work (22.33 MW), followed by Approach 2 (19.98 MW), then Approach 3 (8.46 MW). The ordering follows directly from the outlet state constraints and effective expansion spans. - Configuration B in this dataset provides 8.93 MW with R141b. Whether Config B surpasses Config A depends on the working-fluid set and recuperator pinch/UA assumptions; with a broader fluid set and tuned heat-integration, recuperation often improves net work at otherwise fixed constraints. - Across all cases, Z-factor and enthalpy agreements with HYSYS (typically  $<1-3\%$ ) validate the PR EOS + Kamath property route used in the equation-oriented model.

Takeaways - FC-72 is consistently strong under Approaches 1–2 of Config A; DCM performs best under the stricter Approach-3 constraints; R141b leads in Config B with recuperation. - Differences in net work across approaches reflect constraint choices (outlet quality, saturation vs. superheat) rather than inconsistencies. When the outlet is forced to saturated vapor, the expansion end-point temperature rises, reducing specific work. - For design, selecting the approach should follow the intended turbine design window and heat-exchanger pinch/UA targets; if recuperation is pursued, fluids exiting superheated can improve internal heat recovery and overall performance. # Conclusion

The performance evaluation of different working fluids in ORC systems reveals significant insights into optimizing energy efficiency. The experimental studies and simulations demonstrate that the selection of appropriate working fluids, such as cyclopentane, FC-72, and dichloromethane, is crucial for maximizing the efficiency of ORC configurations. The findings show that FC-72 consistently achieved the highest net work output across different approaches, emphasizing the importance of molecular weight and density in fluid performance. The comparison between various configurations also highlights that fluids exiting the turbine in a saturated vapor state perform better than those in a superheated state, due to enhanced thermal exchange capabilities.

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