AQUEOUS MIXTURE OF PYRIDINE AS WORKING FLUID IN STEAM TURBINE POWER PLANTS FOR HEAT RECOVERY OF WHRS ORC TECHNOLOGIES

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Abstract. This paper presents the results of a comprehensive numerical analysis focused on the thermodynamic behaviour and performance of simple and combined cycle power plants operating within the temperature range of 673–723 K, with particular attention to their integration into waste heat recovery systems (WHRS). A combined thermal circuit is considered, consisting of a once-through waste heat recovery boiler, a high-pressure water steam turbine, and a secondary turbine operating on an organic working fluid within the framework of an organic Rankine cycle (ORC). As a central innovation, the study explores the use of a water–pyridine mixture as the working fluid, which allows for extension of operating limits beyond those constrained by the thermal stability of conventional organic fluids. The high mutual solubility and chemical compatibility of pyridine with water permit the formation of a stable, single-phase high-temperature heat carrier. This feature enables the working fluid to withstand temperatures of 573-623 K at turbine inlet conditions, which is critical for maintaining performance where standard ORC fluids degrade. The thermodynamic properties of the pyridine–water mixture, including its specific enthalpy, entropy, and vapor pressure behaviour across relevant temperature and pressure ranges, have been rigorously determined through equation-of-state modelling. Simulation results indicate that the integration of the binary fluid into combined ORC or Flash/ORC cycles significantly increases overall system efficiency. The power plant configuration under consideration demonstrates a high level of conversion efficiency with a specific electrical output of 99.8 $kW \cdot kg^{-1}$ of working fluid, emphasizing the promising potential of the pyridine–water mixture in advanced WHRS technologies aimed at maximizing low-grade heat utilization.

Keywords: pyridine, aqueous mixtures, steam turbines, heat recovery, ORC cycle, working fluids.

Introduction

Working fluids are the most important component of a power plant and they determine technical and economic characteristics. The thermodynamic parameters of the power plant increase when using a working fluid with a low heat capacity of liquid and a high heat capacity of steam. An increase in the efficiency of the installation is ensured by increasing the Clausius number ($Cl = r/C_{ж}T_{н}$). In monographs [1-4], and numerous contemporary publications [5-11] the results of thermodynamic analysis of various technological schemes of power plants, selection of working fluids, and the results of tests of commercial installations are presented.

The global transition toward low-carbon energy systems has intensified the search for advanced technologies capable of recovering waste heat from industrial processes and improving the overall efficiency of power generation. In this context, Waste Heat Recovery Systems (WHRS) have emerged as a cornerstone in enhancing energy utilization, particularly within sectors where high-temperature exhaust gases are abundant yet underutilized. One of the most effective frameworks for harnessing such thermal energy is the Organic Rankine Cycle (ORC), which operates at lower temperatures than traditional Rankine cycles and is compatible with a broad range of low-boiling-point organic fluids. However, despite its widespread implementation, ORC is constrained by the thermal stability limits of conventional working fluids, which typically restrict its operation to temperatures below 573 K [12-15].

To address these limitations, recent research has focused on expanding the usable temperature range of ORC systems by exploring novel working fluids and mixtures with superior thermal stability, heat transfer characteristics, and compatibility with turbine materials. Among various candidates, pyridine and its aqueous mixtures have drawn growing attention due to their favorable thermodynamic properties and chemical robustness at elevated temperatures. Pyridine is known for its high boiling point, substantial vapor pressure gradient, and remarkable solubility in water, forming a stable binary system suitable for operation in mid-to high-temperature ranges. These properties make it a promising candidate for hybrid WHRS configurations that integrate both water-steam and organic fluid circuits [16; 17].

Despite the theoretical groundwork, practical implementations of binary mixtures like pyridine–water in WHRS remain underexplored. The thermodynamic characterization of such mixtures, particularly under turbine inlet conditions ranging from 573 to 623 K, is scarcely addressed in existing literature. Furthermore, the integration of these fluids into hybrid cycle architectures involving both water–steam and organic components requires detailed analysis of phase stability, energy conversion efficiency, and system compatibility [18].

The disadvantage of organic working fluids is their limited (low) thermal stability at high temperatures. When exposed to heat at temperatures of about 623-673 K, organic substances do not retain their physical properties (density, viscosity, heat capacity) and composition (decompose), which limits their use.

The temperature of thermal decomposition of organic matter depends on many parameters (temperature and heating conditions of the material with which the organic working fluid is in contact, the presence of oxygen, interaction with lubricants). Thus, the viscosity of a lubricant solution with an organic working fluid decreases compared to the viscosity of a pure lubricant. The thermal stability temperature of organic working fluids varies from 473 K (freon R22) to 753 K (toluene C_7H_8). An analysis of the parameters of combined power plants is given in [19].

Therefore, the thermal stability of organic substances limits the upper temperature in the steam turbine cycle. The works [20] present the results of the study of aqueous mixtures as working fluids in ORC installations. Zeotropic mixtures of hydrocarbons, refrigerants and siloxanes are studied. Three mixtures are studied, namely water-2.2.2-trifluoroethanol, water-acetonitrile, water-methylpyrazine. It is shown that mixtures of organic liquids with water are safer, and their flammability and toxicity are reduced as well. Therefore, research into mixtures of water with organic liquids is going on [21-23].

This study aims to fill that gap by presenting a comprehensive thermodynamic analysis of a combined WHRS configuration utilizing a pyridine–water mixture as the working fluid in the organic branch of the system. The research focuses on quantifying thermal efficiency, evaluating mixture properties across relevant temperature-pressure regimes, and demonstrating the viability of using the fluid in conditions where other organic compounds would fail. The objective is to extend the operational boundaries of ORC-based WHRS by introducing and validating a novel working fluid system that maintains both stability and efficiency under demanding thermal conditions.

Research methodology

The general methodology is outlined in [1; 2]. The calculations for the parameters of the simple ORC scheme (Figure 1) were carried out according to [3].

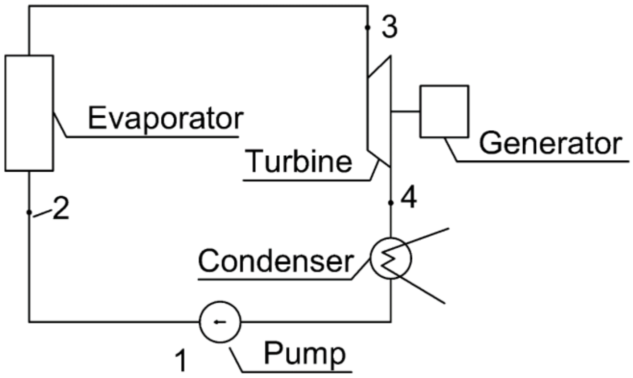

Fig. 1. **Scheme of a simple ORC power plant:** 1, 2, 3, 4 – cycle points

Results and Discussion

Pyridine is the simplest six-numbered aromatic heterocycle (C_5H_5N – azacyclohexatriene), it has a general toxic effect and is highly soluble in water.

Physical properties of pyridine:

- thermal stability temperature T = 673 K;
- critical temperature T_{cr} = 621 K;
- critical pressure P_{cr} = 5633 kPa;
- molecular weight μ = 79.1 kg·kmol^{-1};
- heat of vaporization ΔH = 441.5 kJ·kg^{-1};

- derivative value ξ = -1.32;
- density ρ = 0.9819 g·cm^{-3};
- melting temperature t = 231.4 K;
- heat capacity of liquid Cl = 135.6 J· (mol·K)$^{-1}$;
- boiling point under normal conditions T = 388.6 K.

The high solubility of pyridine in water allows the mixtures to be used as working fluids. The pyridine-water mixture improves the safety and thermal stability of working fluids.

Physical and thermophysical properties are given in Table. 1.

Table 1

Thermodynamic and physical properties of working fluids

Property	**Working fluid**		
	Benzene	Toluene	Pyridine
Mg, m·s^{-1}	78.1	92.1	79.1
P_{cr}, kPa	5180	4219	5630
T_{cr}, K	288.9	318.6	346.8
$T_{нк}$, K	353.1	383.6	388
T_{ign}, K	560	530	482
ΔH, kJ·kg^{-1}	394.4	363	444
Cpl, kJ· (kg·K)$^{-1}$	2.02	2.1	1.93
μ, 10^{-6} Pa·s^{-1}	320	244	310
λ, 10^{3} W·(m·K)$^{-1}$	130	117	135
Cl, J·(mol·K)$^{-1}$	0.58	0.47	0.59
Ja	2.26	2.3	2.1
$dS{\cdot}dT^{-1}$	+	+	+
Cp_0/R	136	156	135

The values of ΔH, C_p, μ, $dS{\cdot}dT^{-1}$ are taken at $T_{нк}$; values of Ja ($T1$, $T2$) are taken at $T1$ = 423 K, $T2$ = 323 K.

To compare the properties of pyridine, the well-studied properties of benzene and toluene are given. Analysis of the properties of pyridine shows its advantages: low molecular weight (79.1 g·mol^{-1}), high critical temperature (621 K), high heat of vaporization at normal temperature, higher value of the Clausius criterion. The sign of the $dS{\cdot}dT^{-1}$ derivative and the value of the molecular characteristics of Cp_0/R = 16 indicate that pyridine belongs to dry fluids. Transport characteristics (coefficients of dynamic viscosity and thermal conductivity) are also not inferior to benzene and toluene [16].

Comparing the characteristics that determine the safety group of working fluids, one can see that pyridine belongs to B2L group, benzene belongs to B2, and toluene belongs to A3 [21; 22].

The ORC power plant scheme includes an evaporator, a turbine, a condenser, a pump and an electric generator. The temperature of under recovery in the heat exchange equipment is assumed to be 3 K. Below are the results of a numerical calculation of the thermodynamic parameters of technological installations with the working fluid pyridine and a pyridine-water mixture.

These results clearly demonstrate the superior thermodynamic behavior of pyridine in comparison with classical aromatic hydrocarbons often used in ORC applications. The inclusion of a pyridine–water mixture further enhances the flexibility of the cycle, enabling stable operation at lower steam temperatures while maintaining high thermal efficiency. This hybrid approach ensures broader applicability of the system to heat recovery from medium-grade industrial waste heat sources. Additionally, the close thermophysical match between pyridine and conventional fluids like benzene and toluene allows for practical integration into existing ORC infrastructure without significant redesign of the flow or heat exchange equipment.

Fig. 2 shows the change in the Clausius criterion for various substances depending on temperature and shows the influence of the Clausius criterion on the thermal efficiency of a cycle with various working fluids.

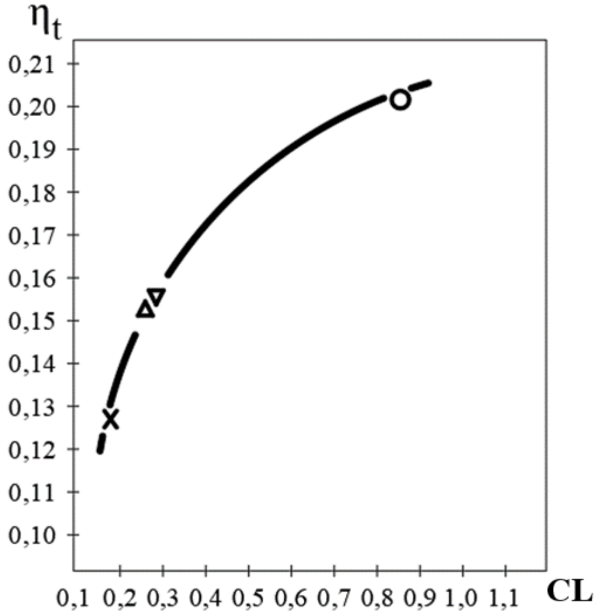

Fig. 2. **Cycle efficiency in the function of *Cl* criterion for various working fluids:**
x - acetone, ○ – methanol, △ – benzene, ▽- toluene

Case 1 (1-4). The source of heat is a geothermal fluid with a temperature of 200 °C.

Calculation results:

- consumption of geothermal fluid is 1 $kg \cdot s^{-1}$;
- geothermal fluid temperature (inlet) is 473 K;
- geothermal fluid temperature (outlet) is 380.6 K;
- working fluid flow rate is 0.2587 $kg \cdot s^{-1}$;
- steam pressure after turbines is 30 kPa;
- total generated electrical power is 44.8 $kW \cdot kg^{-1}$;
- pump drive power is 0.102 kW;
- cycle efficiency is 11.2%.

Case 2 (5-8). The heat source is a geothermal fluid with a temperature of 200 °C.

Calculation results:

- geothermal fluid rate is 1 $kg \cdot s^{-1}$;
- geothermal fluid temperature (inlet) is 473 K;
- geothermal fluid temperature (outlet) is 398 K;
- working fluid flow rate is 0.2120 $kg \cdot s^{-1}$;
- steam pressure after turbines is 100 kPa;
- total generated electrical power is 26.40 $kW \cdot kg^{-1}$;
- pump drive power is 0.118 kW;
- cycle efficiency is 8.1%.

Case 3 (9-12). The heat source is fuel gases with a temperature of 350 °C.

Calculation results:

- consumption of combustion products is 1 $kg \cdot s^{-1}$;
- flow rate of working fluid C_5H_5N/H_20 (25/75) is 0.1263 $kg \cdot s^{-1}$;
- temperature of combustion products is 623 K;
- temperature of under-recovery in heat exchangers and temperature difference at the pinch point, ΔT is 3 K;

- total generated power is 58.87 kW·kg^{-1};
- pump drive power is 0.67 kW·kg^{-1};
- temperature of fuel gases at the outlet is 429 K;
- cycle efficiency is 26.38%.

Case 4. (13-16) The heat source is fuel gases with a temperature of 350 °C.

Calculation results:

- fuel gas consumption is 1 kg·s^{-1};
- flow rate of working fluid C_5H_5N/H_20 (75/25) is 0.4203 kg·s^{-1};
- total generated electrical power is 99.86 kW·kg^{-1};
- pump drive power is 4.76 kW·kg^{-1};
- flue gas temperature is 335 K;
- cycle efficiency is 26.15%.

Thermodynamic parameters for all cases of the cycle are given in Table. 2

Table 2

Thermodynamic parameters of the cycle

Cycle points	*P*, kPa	*T*, K	*ρ*, kg·m^{-3}	*h*, kJ·kg^{-1}	*S*, kJ·(kg·K)$^{-1}$
1	30	291.0	997.253	-5687.5552	0.6354
2	325	291.1	997.358	-5687.1608	0.6356
3	325	470.0	2.828	-4137.2338	4.6329
4	30	357.9	0.337	-4310.4323	4.8018
5	100	291.0	997.289	-5687.4984	0.6353
6	515	291.1	997.438	-5686.9435	0.6357
7	513	470.0	4.541	-4141.5217	4.5412
8	100	388.5	1.042	-4265.9270	4.6224
9	6	291.0	997.241	-5687.5591	0.6355
10	4000	291.7	998.658	-5682.2190	0.6389
11	4000	620.0	0.881	-3915.3737	4.4540
12	6	304.0	0.079	-4386.8050	4.9719
13	4	291.0	488.799	66.713	-0.6886
14	8400	293.4	991.859	78.0349	-0.6796
15	8400	620.0	342.743	943.3538	1.2149
16	4	302.3	0.1017	705.7786	1.4795

To perform the thermodynamic analysis of the proposed cycles, calculations were carried out using the Engineering Equation Solver (EES), which allows for robust modeling of non-ideal fluids and complex thermodynamic processes with high precision. The core of the simulation was based on the application of the first and second laws of thermodynamics to steady-flow processes, considering real fluid properties obtained from built-in REFPROP-compatible databases. Each component of the cycle, the evaporator, turbine, condenser, and pump, was modeled using energy balance equations, entropy change analysis, and isentropic efficiency corrections where applicable. The working fluid properties of pyridine and the pyridine–water mixture were defined using temperature-dependent correlations for enthalpy, entropy, specific heat, and phase behaviour, with transport properties incorporated into the energy transfer calculations in heat exchangers.

Three configurations were considered: a conventional ORC using pure pyridine, a Flash/ORC hybrid using pyridine–water mixture, and a reference case using a standard fluid such as toluene. For each case, identical boundary conditions were applied to enable direct comparison. The inlet temperature of the heat source (interpreted as geothermal or waste heat fluid) was fixed at 693 K for high-temperature scenarios and 593 K for medium-temperature applications, with a minimum temperature difference (pinch point) of 3 K in the evaporator and condenser. The mass flow rate of the working fluid was determined iteratively to optimize net output while maintaining thermal and hydraulic feasibility. The back pressure was adjusted to remain above the saturation pressure to avoid condensation within the turbine stage.

Comparative results show that the pyridine-based cycles outperform conventional organic fluids in terms of thermal efficiency and specific network output, especially under mid-range temperature constraints where classical fluids show degradation or limited thermodynamic performance. The Flash/ORC configuration with the pyridine–water mixture demonstrated an improved match to the temperature profile of the heat source, reducing exergy destruction in the evaporator and leading to a better utilization factor. Although no direct experimental data for the pyridine–water mixture under these specific conditions were available, the numerical results were cross-validated against known performance data for benzene and toluene-based cycles from existing literature, showing consistent thermodynamic trends and deviations within an acceptable margin of ± 5%. This confirms the reliability of the models used and indicates the practical viability of using pyridine-based mixtures in next-generation WHRS systems.

Conclusions

The results of calculating the parameters of cycles using pyridine as a working fluid show the following technological advantages:

1. Pyridine has a high temperature of thermal stability (T = 643-673 K), a high critical temperature (T_{cr} = 620 K), (toluene, T_{cr} = 592 K) and not high critical pressure P_{cr} = 5633 kPa, not high molecular weight μ = 79.1 kg·kmol^{-1}, (toluene, μ = 92 kg·kmol^{-1}). Normal boiling point (T_{nb} = 366 K).
2. Clausius criterion Cl = 1.43 (toluene, Cl = 0.66), high heat of vaporization ΔH = 441.5 kJ·kg^{-1}, (toluene ΔH = 399.5 kJ·kg^{-1}), low pump power consumptions that indicates the debatable possibility and prospects of using pyridine as a working fluid in steam turbine units of heat recovery systems in the temperature range up to 573-723 K and the steam temperature in front of the turbine up to 623 K.
3. The high specific production of total electrical power when using an aqueous mixture of C_5H_5N/H_2O (75/25) is 99.8 kW·k g^{-1}.

Author contributions

All authors contributed equally. All authors have read and agreed to the published version of the manuscript.

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