The 21st International Conference on Thermal Science and Engineering of Serbia
SimTerm 2024
Niš, Serbia, Oct 22-25 2024
doi: 10.5937/SimTerm24159Z

Effect of Properties of Working Fluids on the Efficiency of a Low-Temperature Organic Rankine Cycle

Marija Živković[a] , Aleksandar Mijatović[b], Dejan Ivezić[c], Boban Pavlović[d]

[a]*University of Belgrade, Faculty of Mining and Geology, Belgrade, RS, marija.zivkovic@rgf.bg.ac.rs*
[b]*University of Belgrade, Faculty of Mining and Geology, Belgrade, 688, aleksandar.mijatovic@rgf.bg.ac.rs*
[c]*University of Belgrade, Faculty of Mining and Geology, Belgrade, RS, dejan.ivezic@rgf.bg.ac.rs*
[d] *University of Belgrade, Faculty of Mining and Geology, Belgrade, RS, boban.pavlovic@rgf.bg.ac.rs*

Abstract: Decarbonization of all segments of energy systems, both on the supply and demand side, is one of the main goals of the energy transition. Electricity supply in the future will largely rely on generation from intermittent energy sources: wind and solar. Locally available, non-utilized alternative low-temperature energy sources as hydro-geothermal wells, and abounded oil and gas wells, have the potential to provide continual energy production over the year. Electricity generation from these energy sources is carried out with working fluids with low evaporation temperatures. Commonly used fluids are categorized into several groups based on their chemical composition, which determines their thermophysical properties. In this paper the effect of chemical composition of six fluids from three groups on thermophysical properties was analyzed. The effect of fluids' properties on the efficiency of ORC is analyzed for the case of a typical range of temperatures of hydro-geothermal and abounded oil and gas wells in Serbia, which may be used as heat sources for electricity generation.

Keywords: Properties, Working fluids, Efficiency, ORC, Low temperature

1. Introduction

The transition to low or carbon-neutral energy systems implies the utilization of renewable and alternative energy sources across all segments of energy systems, both on the supply and demand sides [1]. Electricity generation is identified as a critical factor and a major contributor to the reduction of GHG emissions [2]. In addition, green electricity is a prerequisite for the decarbonization of final energy consumption [3] through the use of heat pumps, the introduction of electric vehicles, and the production of green hydrogen.

It is known that electricity can be generated from any renewable energy source. Scenarios describing future energy systems indicate high utilization and significant contributions from intermittent energy sources such as wind and solar [4]. However, the contribution of all renewable and alternative energy sources is expected, including low-temperature energy sources.

Low temperature heat sources can be utilized by Organic Rankine Cycle (ORC), which operates at lower pressures and temperatures [5]. Working fluids that can be used in performing ORC firstly need to have ability to evaporate at low temperatures and additionally to meet other requirements: an appropriate slope of the vapor saturation line in the T–s diagram, critical temperature and pressure, normal boiling temperature, global worming potential, and safety level [6].

Substances that may be used as working fluids are commonly categorized into several groups based on their chemical compositions. The main groups of fluids are hydrocarbons, halogenated hydrocarbons, and siloxanes.

This paper aims to examine the effect of working fluid properties on efficiency of ORC that utilize low-temperature heat sources, such as geothermal sources, heat from abandoned oil and gas wells, or waste heat from industry.

2. Working fluids for Organic Rankine Cycle

Technologies for electricity generation for utilizing low or medium-grade heat energy are based on the Kalina cycle, Organic Rankine cycle (ORC), and supercritical Brayton cycle with carbon dioxide. ORC is preferred due to its simplicity, low maintenance, and component availability [7]. The basic Organic Rankine Cycle is similar to the conventional steam Rankine cycle, and it is usually performed with organic fluid derived from carbon chemistry.

Working fluids used in ORCs are classified into three main categories based on the slope of the vapor saturation line in the T-S diagram, which is determined by the saturated properties of the fluids. Fluids are categorized as wet, isentropic, or dry (Figure 1) [8], based on the process of the isentropic expansion of the dry steam. If the process of expansion ends at two phase zone, the fluid is classified as wet. If the isentropic expansion closely follows the saturation curve, the fluid is classified as isentropic. If the expansion ends in the superheated vapor zone, the fluid is classified as dry.

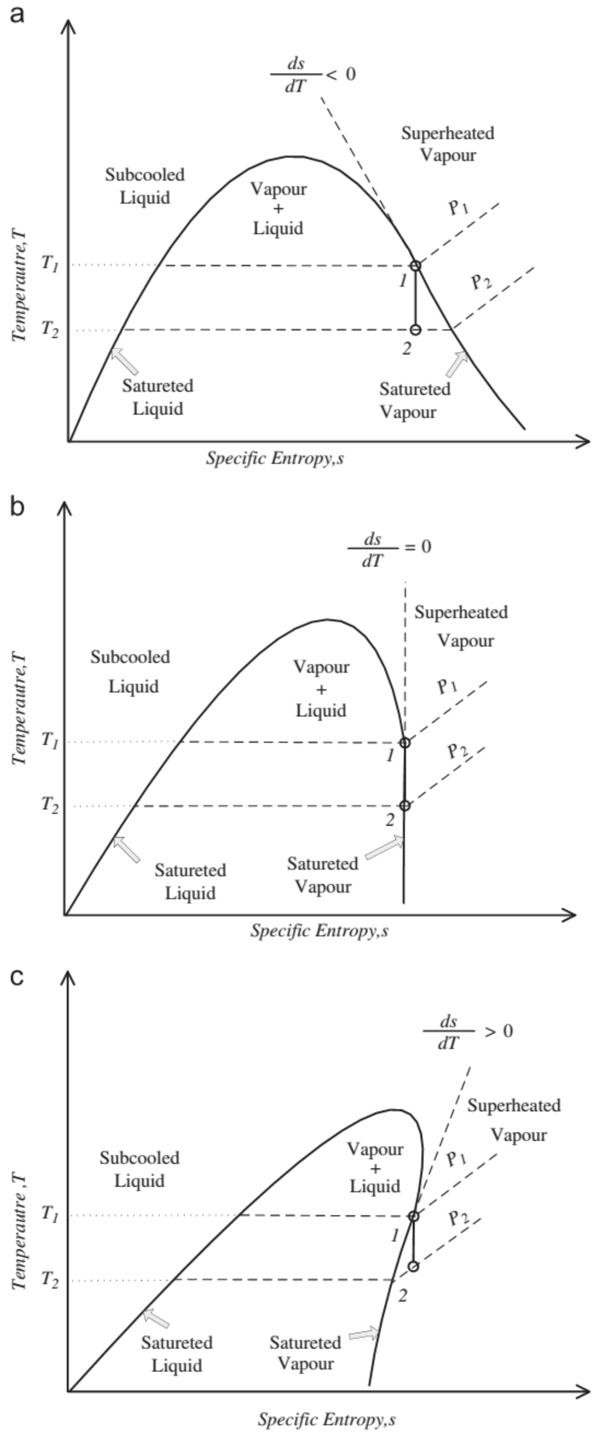


Figure 1. Classification of working fluids: a) wet, b) isentropic, c) dry [8]

The behavior of fluids during phase change has been the subject of many studies. It has been shown that the complexity of the molecular structure influences fluid behavior. Fluids with simple molecular structures are commonly wet fluids, while fluids with higher complexity tend to act as dry fluids. Intermediate fluids behave as isentropic fluids [9].

Additionally, dry fluids are high molecular mass organic fluids, wet fluids are low molecular mass organic fluids, and isentropic fluids have medium molecular mass [10].

Liu et al. [11], concluded that the presence of hydrogen bond in the molecules of some organic working fluids is a probable cause of some fluids behaving as wet fluids. This is due to their larger vaporizing enthalpies, which are inappropriate for application in ORC systems [10].

The performance, i.e. the efficiency of the ORC, is dependent on the thermo-physical characteristics of the working fluids, which are also influenced by chemical composition and the structure of the molecule.

The practice shows that the commonly used working fluids are halogenated hydrocarbons, pentane, cyclopentane, n-heptane, hexane, hexamethyldisloxane (MM), octomethyisloxone (MDM) [12]. The performance of pentane, n-heptane, and hexane suggests that these fuels may contribute to greater efficiencies due to the high latent heat of vaporization. Working fluids with excellent thermal stability and low vapor pressure, such as hexamethyldisiloxane (MM) and octamethylisodimethylsiloxane (MDM), have been shown to increase Rankine cycle efficiency [12].

3. Methods and materials

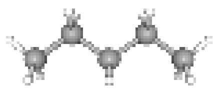
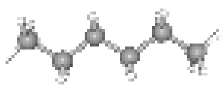
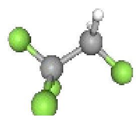
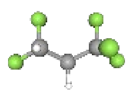
Given that the slope of vapor saturation curve and thermophysical properties of working fluids depend on the chemical composition, for the evaluation and analyses of working fluids properties on efficiency of ORC, six working fluids were selected, two from each group:

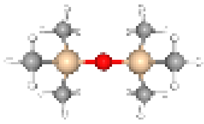
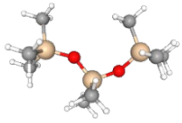
1. Hydrocarbons: n-pentane and n-hexane,
2. Halogenated hydrocarbons: R134a and R245fa,
3. Siloxanes: MM and MDM.

The first group of fluids includes more inert straight chain hydrocarbons (n-pentane and n-hexane), which lack the possibility of additional interactions between molecules. The second group includes hydrocarbons in which terminal H atoms are substituted by F atoms, so their polarity is significantly increased, as well as the possibility of additional dipole-dipole interactions. The third group of selected fluids consists of inactive siloxanes containing the main Si-O chain of different lengths of an inorganic chain with side hydrocarbon groups. These siloxanes are characterized by their bulkier molecules, which also influence their thermophysical properties.

Main data about the selected fluids are provided in Table 1.

Table 1. Basic data of selected working fluids [13, 14]

Working fluid	Name	Formula	Structural formula	Mollar mass kg/kmol	Acentric factor	Critical point temperature K
n-pentane	n-pentane	C_5H_{12}		72.148	0.25103	469.7
n-hexane	n-hexane	C_6H_{14}		86.175	0.3003	507.82
R134a	1,1,1,2-Tetrafluoro ethane	$C_2F_4H_2$		102.032	0.32684	374.21
R245 fa	1,1,1,3,3-Pentafluoro propane	$C_3F_5H_3$		134.047	0.3776	427.01

MM	Hexamethyldi siloxane	$C_6H_{18}OSi_2$		162.377	0.418	518.75
MDM	Octamethyltri siloxane	$C_8H_{24}O_2Si_3$		236.532	0.52806	564.09

Within the specified group, the increase of molar mass is followed with the increase of critical temperature and acentric factor [15]. The acentric factor describes deviations in thermodynamic properties of fluids containing non spherical molecules from their spherical counterparts. It is also a measure of the non-sphericity of molecules. Among examined fluids the highest value of acentric factor is MDM whose molecule has the most complex structure, while the lowest value has n-pentane.

Figure 2 presents T-s diagrams for each working fluid. Based on the slope of vapor saturation curve it can be concluded that each of them is suitable to operate in the ORC with the dry steam. Fluids with the highest molar mass and acentric factor (MM and MDM) act as exceptionally dry fluids.

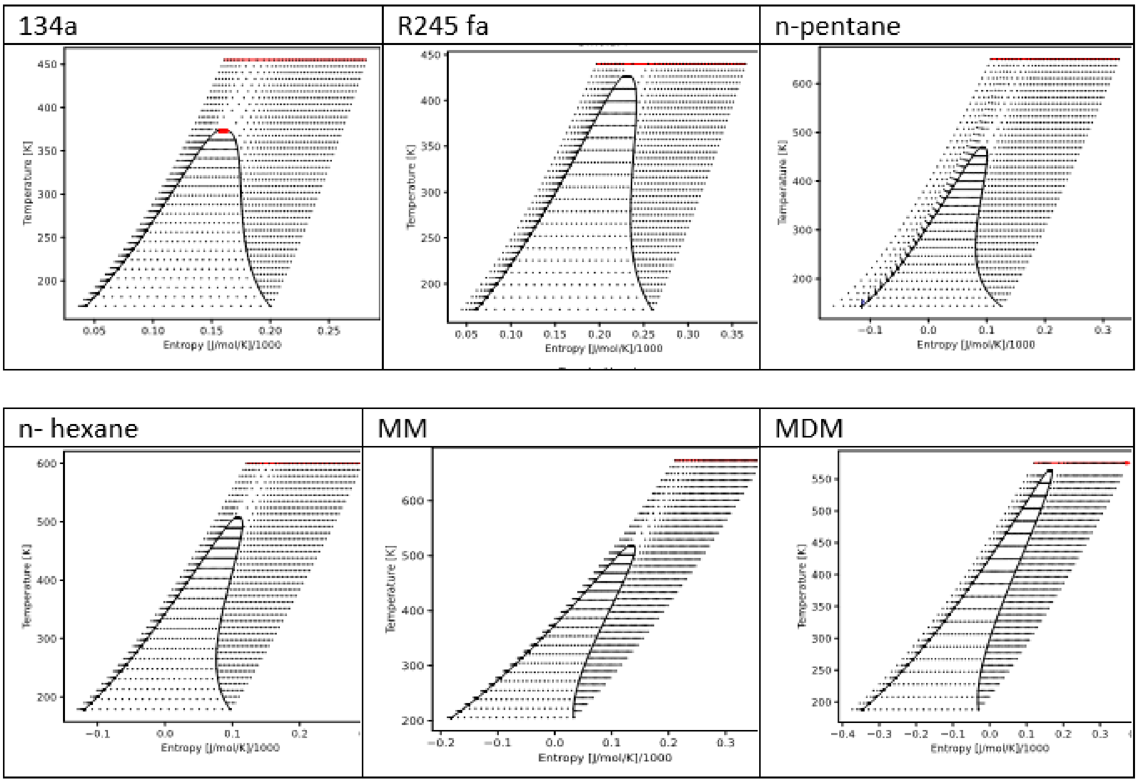


Figure 2. T-s diagrams for the selected fluids [13]

The effect of working fluids properties on the efficiency of ORC was analyzed for the case of dry steam cycle (Figure 3). This cycle is preferred over the superheated steam cycle due to the absence of superheating and required heat exchangers [13]. The highest temperature in the cycle was set to 70°C - temperature of evaporation, while the lowest temperature was 15°C - temperature of condensation. These temperatures were selected based on data from available low temperature heat sources in Serbia [16, 17]. The shapes of T-s diagrams presented at Figure 2 indicate that all selected fluids are suitable for the dry steam ORC in the given range of temperature.

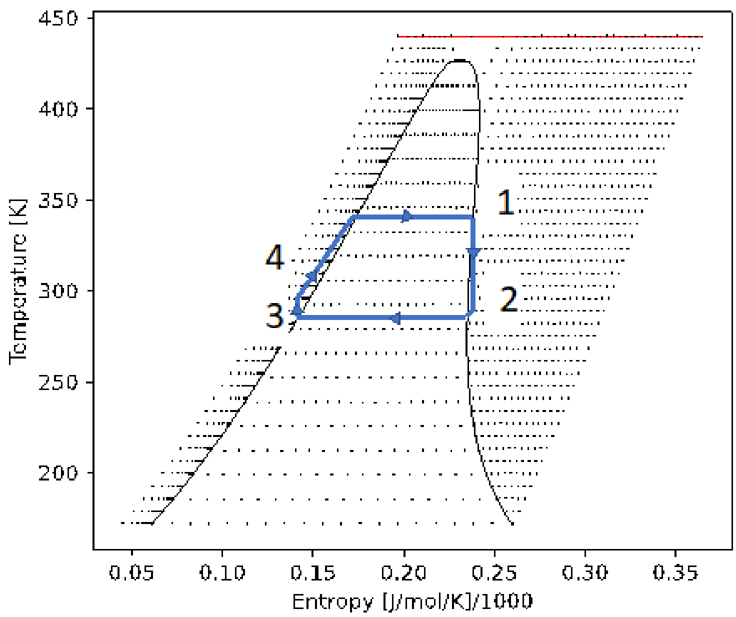


Figure 3. Rankine Cycle with dry steam

Efficiency of the ORC is determined by:

$$\eta = 1 - \frac{|h_3 - h_2|}{h_1 - h_4} \tag{1}$$

To calculate the thermodynamic properties for each state of the cycle, CoolProp software [13] was used to obtain values of properties for the selected fluids from, all from the same source.

4. Results and discussion

Results for efficiencies of the dry steam ORC for each of examined fluids are presented in Table 2.

Table 2. Basic data of selected working fluids

Fluid	Efficiency	Heat of evaporation at 70°C, kJ/kg
n-pentane	0.1381	328.0
n-hexane	0.1383	334.3
R134a	0.1320	124.6
R245fa	0.1346	161.9
MM	0.1291	208.1
MDM	0.1270	186.8

The results show that the efficiency of the cycle is dependent on the properties of the selected working fluid. The highest efficiency is achieved with n-hexane (0.1383), which is approximately 9% higher compared to the lowest efficiency, obtained with MDM (0.1270).

The highest efficiency is observed with hydrocarbons as working fluids and the lowest with siloxanes. Within the examined group the higher efficiency is attributed to fluids with a higher heat of phase change at the temperature of evaporation (Table 2).

Figure 4 illustrates the relationship between efficiency and the acentric factor. In most cases, a higher efficiency corresponds with a lower acentric factor.

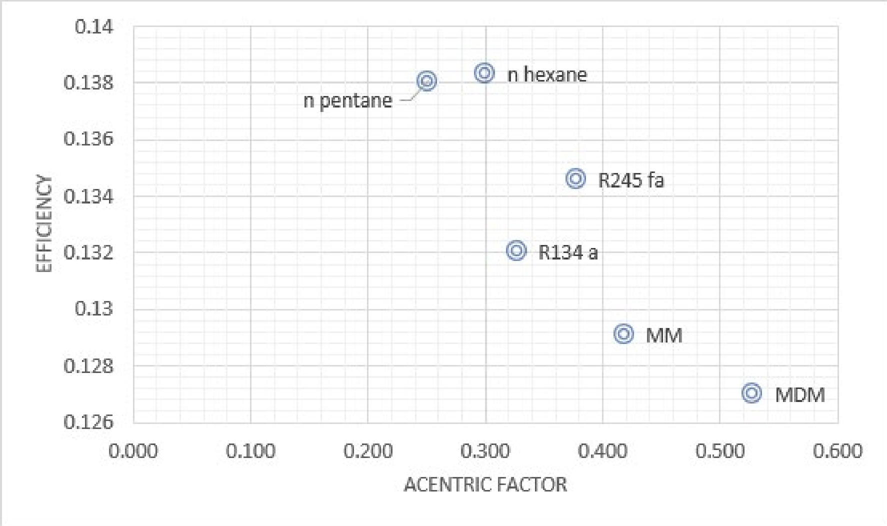


Figure 4. Relation between acentric factor and efficiency

Further analysis of the results shows that the highest temperature at the exit of the turbine was achieved for MDM as the working fluid, while the lowest was observed with R 134a. This was the only case when expansion in the turbine ended in the zone of the wet vapor. No significant relationships between efficiency and other fluid properties were observed.

The highest efficiencies are attributed to fluids with isentropic slope of the vapor saturation curve, such as n-pentane and n-hexane. In these cases, the expansion process in the turbine closely follows the vapor saturation curve.

5. Conclusion

Low temperature energy sources can be utilized for electricity generation by implementing Organic Rankine Cycle. However, the efficiency of such cycles is relatively low, since the difference between the temperature of the heat source and heat sink is small.

For the dry steam ORC effect of properties of six working fluids is analyzed. It is shown that chemical composition affects thermophysical properties of the fluid, including the shape of vapor saturation curve.

The efficiency of the cycle depends on the properties of the working fluid, such as its composition and structure. In the analyzed cases the highest efficiency was achieved with hydrocarbons which have near isentropic slope of the saturation curve in the observed temperature interval between the heat sink and the heat source.

The lowest efficiency was obtained with siloxanes as working fluids, which acts as exceptionally dry fluids and have the biggest values of acentric factors among examined fluids. It can be concluded that the problem is complex, with intervening influential parameters that are not easy to identify.

The potential application of ORC must be carefully evaluated, as changes in the working fluid can significantly affect efficiency, which certainly should not be neglected, particularly in low-efficiency cycles.

Acknowledgements

The research was supported by funds provided by the Ministry of Science, Technological Development, and Innovation under Contracts No. 451-03-65/2024-03/200126 and 451-03-66/2024-03/200126.

References

[1] Lamnatou, C., Cristofari, C., Chemisana, D., Renewable energy sources as a catalyst for energy transition: Technological innovations and an example of the energy transition in France, Renewable Energy 221 (2024), 119600
[2] Távora Maia, R.G., Garcia, K.C., What they say, what they do and how they do it: An evaluation of the energy transition and GHG emissions of electricity companies, Energy Policy 174 (2023), 113462

[3] Georg Thomaßen, G., Kavvadias, K., Jiménez Navarro, J.P., The decarbonisation of the EU heating sector through electrification: A parametric analysis, Energy Policy 148 (2021), Part A, 111929
[4] Lotfipour, A., Mohtavipour, S.S., A multi-criteria decision-making model to determine the optimal share of variable renewable energy sources in a wholesale electricity market, Sustainable Energy, Grids and Networks 39 (2024), 101408
[5] Karimi, S., Safavi, A., Bahram, S., Optimizing electricity generation through the utilization of wasted heat from process streams in a LURGI methanol plant, Heliyon 10 (2024), e30982
[6] Vivian, J., Manente, G., Lazzaretto, A., A general framework to select working fluid and configuration of ORCs for low-to-medium temperature heat sources, Applied Energy 156 (2015), pp. 727-746
[7] Chitgar, N., Hemmati, A., Sadrzadeh, M., A comparative performance analysis, working fluid selection, and machine learning optimization of ORC systems driven by geothermal energy, Energy Conversion and Management 286 (2023), 117072
[8] Bao, J., Zhao, L., A review of working fluid and expander selections for organic Rankine cycle, Renewable and Sustainable Energy Reviews 24 (2013), pp. 325-342
[9] Herath, H.M.D.P., Wijewardane, M.A., Ranasinghe, R.A.C.P., Jayasekera, J.G.A.S., Working fluid selection of Organic Rankine Cycles, Energy Reports 6 (2020), pp. 680-686
[10] Babatunde, A.F., Sunday, O.O., A Review of Working Fluids for Organic Rankine Cycle (ORC) Applications, IOP Conf. Series: Materials Science and Engineering 413 (2018), 012019
[11] Liu, B., Chien, K., Wang, C., Effect of working fluids on organic Rankine cycle for waste heat recovery, Energy 29 (2004), pp. 1207-1217
[12] Chowdhury, A.S., Ehsan, M.M., A Critical Overview of Working Fluids in Organic Rankine, Supercritical Rankine, and Supercritical Brayton Cycles Under Various Heat Grade Sources, International Journal of Thermofluids 20 (2023), 100426
[13] CoolProp Team, CoolProp Version 6.4.0. (2024), http://www.coolprop.org.
[14] PubChem., Compound ID, (2024), https://pubchem.ncbi.nlm.nih.gov/compound/24705#section=3D-Conformer
[15] Matuszewska, D., Kuta, M., Gorski, J., A thermodynamic assessment of working fluids in ORC systems, EPJ Web of Conferences 213 (2019), 02057
[16] Ilić, M., Živković, M., Danilović, D., Crnogorac, M., Karović Maričić, V., Tomić, L., Određivanje teorijskog termičkog potencijala napuštenih naftnih i gasnih bušotina, Tehnika – Rudarstvo, Geologija i Matalurgija 74 (2023), 6, pp. 667-672 (In Serbian)
[17] Soleša. M., Đajić, N., Parađanin, LJ., Proizvodnja i korišćenje geotermalne energije, Rudarsko-geološki fakultet, Beograd, 1995 (In Serbian)