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EVALUATION OF POTENTIAL FLUIDS FOR LOW TEMPERATURE ORGANIC RANKINE CYCLE

Juliana Silva Brasil
Richardson Leandro Nunes
Thalles Coimbra Borba Roldão
Luben Cabezas Gómez
Cristiano Bigonha Tibiriçá

University of São Paulo, EESC, Heat Transfer Research Group; São Carlos, SP, Brazil, 13566-590.

juliana.brasil@usp.br, eng_richard.nunes@gmail.com, thallescbr@usp.br, lubencg@sc.usp.br, bigonha@sc.usp.br

Abstract. Organic Rankine cycle (ORC) is a potentially viable technology to recover energy of low-grade heat sources, which implies greater energy efficiency as well as a reduction in the use of fossil fuels, which are harmful to the environment. Reused heat can come either from traditional sources, such as industrial waste heat or from alternative sources (solar, geothermal). Understanding the operation of this cycle for different fluids, under given conditions, is useful to assess its suitability and indicate the most favorable operating conditions. This research evaluates the thermal efficiency of the saturated organic Rankine cycle (ORC), for different fluids, comparing a numerically solved equation model with an analytical model. Considering evaporation temperatures varying between 80°C and 100°C, the relative error of the cycle efficiency obtained in each of the two approaches was calculated. The dry hydrofluoroethers fluids HFE7000, HFE 7100, HFE7200 and HFE7500 showed the greatest discrepancies in efficiency between the two models, greater than 10%. For the other fluids considered, the analytical modeling proved to be satisfactory, with zero error for wet fluids such as ammonia and methanol. Hydrofluorolefin fluids stood out for their high thermal efficiency and favorable environmental characteristics, as well as toluene and R601a hydrocarbons.

Keywords: Organic Rankine Cycle, working fluids, Low-grade thermal waste recovery.

1. INTRODUCTION

The growing concern with environmental issues has mobilized the industry in order to carry out increasingly efficient processes that cause less environmental impact. In this sense, the adaptation of the Rankine cycle to the organic Rankine cycle can be an alternative, since the cycle uses low temperature heat sources, reusing thermal energy from other processes (internal combustion engines, WHR from industrial processes) or using renewable energy sources (biomass, solar, geothermal).

According to Kumar and Rakshit (2021), the main applications for WHR, waste heat recovery, with heat sources up to 100°C, are: water heating, dehumidification and the organic Rankine cycle.

Previous works carried out comparative analysis between selected fluids in an organic Rankine cycle with different heat sources. Rayegan and Tao (2011) suggest for solar ORCs that fluids containing chlorine atoms and wet fluids should be discarded and that thermal and exergetic efficiencies are determining characteristics for selection. Bahrami et al. (2022) evaluates the application of low GWP fluids reviewing different methodologies for the selection of working fluids and suggests the HFOs R1366mzz(Z) and R1234ze(Z) as potential fluids.

Wang et al. (2013) indicates that the selection of the working fluid is mainly determined by the temperature of the hot source and suggests that for heat sources at 365K and 395K the optimal fluids among those evaluated would be R22, R290, R134a and R227a for the first temperature and R152a, R124 and R235fa for the second temperature.

Bao and Zhao (2013) reviews studies indicating which fluids are recommended for each one of them considering the temperature of the hot source and the evaporation temperature and highlighting the performance indicators evaluated. First law efficiency stands out as the most recurrent performance indicator and WHR as the most used heat source.

Likewise, Quoilin et al. (2011) reviews studies indicating recommended fluids and, additionally, suggests that for each fluid under study the optimal evaporation temperature is obtained, for which the greatest possible efficiency is obtained, considering the other limiting conditions.

Gupta et al. (2022) evaluates Solar ORCs and proposes the following criteria for selection of the working fluid: environmental sustainability (GWP and ODP assessment), critical temperature, thermal stability and safety aspects (flammability, toxicity and corrosion).

The present work evaluates the efficiency of a saturated Rankine cycle for different fluids, also analyzing environmental, safety and operational viability aspects of each one of them. To calculate the efficiency, an analytical model is proposed, whose result will be compared for validation with a numerical model.

2. WORKING FLUIDS

The organic Rankine cycle considered in this work is characterized by the use of low temperature heat sources (up to 100°C) and fluids with less environmental impact, such as natural fluids. When using low-temperature heat sources, it is necessary to use fluids with a lower boiling temperature and higher vapor pressure than water, which is the fluid used in the conventional Rankine cycle.

There are different types of working fluids on the market, which may or may not meet national environmental impact requirements as well as operate more efficiently under specific conditions.

Thirty-three fluids were considered in this work, which are listed in Tab.1 with their respective properties, according to Calm and Hourahan (2001), Zinsalo et al. (2022) and Qyyum et al. (2022). In Tab.1, the characteristics to be considered in the discussion of this work are presented, namely: performance (cycle efficiency), operating limits (critical temperature and pressure), environmental impact (GWP and ODP values) and safety (limit of exposure and flammability).

The GWP (Global Warming Potential) is a numerical indicator, in relation to CO₂, of how much a certain substance supports global warming. The ODP (Ozone Depletion Potential), also a numerical indicator, related to CFCs, indicates how harmful a certain substance is to the ozone layer. These indicators help to identify which fluids are most harmful to the environment. As established in the Montreal Protocol, to which Brazil is a signatory, fluids with a high ODP value, that is, which have a greater impact on the destruction of the ozone layer, should be avoided and, subsequently, banned. In 1999, fluids classified as CFCs (chlorofluorocarbons) were banned from production in Brazil. By 2040, according to the Kigali Amendment, HCFCs (hydrochlorofluorocarbons) must also be banned. These two indicators do not end the environmental impacts caused by fluids, however they are the main environmental aspects evaluated.

In order to meet the aforementioned charges related to environmental impacts, new fluids were developed, among which we can highlight: HFCs (hydrofluorocarbons), which have low ODP but high GWP; HFOs (hydrofluorolefins) which, despite low or null values of ODP and GWP, cause another type of environmental impact by breaking down into perfluoroalkylcarboxylic acids, which are deposited in rivers and lakes, offering a risk of contamination to organisms in that environment and HFEs (hydrofluorethers).

The critical pressure and temperature (P_{cr.} and T_{cr.} respectively) indicate the extreme operating conditions for a given fluid, so that the cycle cannot operate at a temperature or pressure higher than the critical one. It will be necessary to choose a fluid with a greater operating range.

As for safety, the limit in ppm of the fluid in the air was evaluated, for a human exposure of 8 hours a day and the percentage in the air for which the refrigerant becomes flammable. Another relevant aspect considered in the work is the safety classification proposed by ASHRAE Standard 34 (American Society of Heating, Refrigerating and Air-Conditioning Engineers).

Table 1. characteristics, environmental effects and safety aspects of fluids.

Fluids		Characteristics			Environmental Effects		Safety		
		Type	T _{cr.} (°C)	P _{cr.} (MPa)	GWP	ODP	Group (ASHRAE Standard 34)	Exposure limit (ppm)	Flammability (% v/v no ar)
Methanol	alcohol	wet	240.2	8.1					
Ethanol	alcohol	wet	240.8	6.15					
Toluene	hydrocarbon	dry	318.6	4.13	3.3	0			
Acetone	organic	wet	234.9	4.7			A4	1000	2.5
Cyclohexane	hydrocarbon	dry	280.4	04.08		0			
R11	CFC	isentropic	198	4.4	4600	1000	A1	1000	none
R141b	HCFC	isentropic	204.2	4.25	700	0.1	none	500	5.8

R123	HCFC	isentropic	183.7	3.6	120	0.02	B1	50	none
R717 (ammonia)	inorganic	wet	132.3	11.33	<1	0	B2	25	15.1
R1234ze(Z)	HFO	isentropic	150.1	3.53	20	0	A3		
R601a (isopentane)	hydrocarbon	dry	187.4	3.37	0	0	none	600	1
R245fa	HFC	isentropic	154.1	3.64	820	0	A1	500	none
Butene	hydrocarbon		146.1	4.00					
R1224yd(Z)	HFO		155.5	3.33	0.88	0	A1	1000	
R1336mzz(Z)	HFO	dry	171.3	2.9	2	0	A1	500	
R600a (isobutane)	hydrocarbon	isentropic	134.7	3.64	20	0	A3	1000	1.7
HFE7200	HFE	dry	209.8		55	0			
R152a	HFC	wet	113.2	4.51	190	0	A2	1000	3.9
HFE7000	HFE	dry	165	2.48	530	0			
HFE7100	HFE	dry	195.3		320	0			none
R236fa	HFC	dry	124.9	3.2	9400	0	A1	1000	none
HFE7500	HFE	dry	261	1.55	90	0			none
R1234ze(E)	HFO	isentropic	109.4	3.6	7	0	A3		
R161	HFC	wet	102.2	4.7	10	0	none		3.8
R1243zf	HFC	isentropic	103.8	3,51	<150	0			
R134a	HFC	wet	101.1	04.06	1600	0.0005	A1	1000	none
RC318	FC	dry	115.2	2.78	11200	0	A1	1000	none
R22	HCFC	wet	96.2	4.99	1900	0.05	A1	1000	none
R1225ye(Z)	HFO		106.9	3.53	<1	0	A3	no toxic	
R290 (propane)	hydrocarbon	isentropic	96.7	4.24	20	0	A3	1000	2.1
R1234yf	HFO	isentropic	94.7	3.82	<1	0	A3	500	

The classification of the fluid between dry, wet and isentropic is useful to assess the eventual need for superheating before the expander, since wet fluids, if not superheated, become a two-phase liquid-vapor mixture during expansion which can degrade the expander. The behavior of the three types of fluids is determined by the derivative of the saturated vapor line of the T - s diagram of the fluid, it will be dry if $dt/ds > 0$, isentropic if $dt/ds = 0$ or wet if $dt/ds < 0$.

3. METHODOLOGY

Two approaches to the analysis of the organic rankine cycle were considered in this work, an analytical model, with the development of expressions for the calculation of efficiency, and a numerical model, both in the EES. The equation used to calculate the thermal efficiency of the cycle in the numerical model, $\eta_{th,num.}$, is indicated in Eq. (1) and for the analytical model in Eq. (2) (Eq.(3), Eq.(4) and Eq.(5) are auxiliaries), $\eta_{th(p,t)}$, as proposed by Scagnolatto et al. (2021).

$$\eta_{th,num.} = \frac{W_t - W_b}{Q_e} = \frac{(i_3 - i_4) - (i_2 - i_1)}{i_3 - i_{2r}} \quad (1)$$

Where i indicates the enthalpy and the numerical indices of the points of the ORC.

$$\eta_{th(p,t)} = \eta_t \cdot \eta_{th,ana.} - (\eta_p^{-1} - \eta_t) \cdot PWHR \quad (2)$$

$$\eta_{th,ana.} = 1 - \frac{\theta_r \cdot (1 + j_{a_{pre}})}{1 + \frac{1}{2} \cdot (1 + \theta_r) \cdot j_{a_{pre}}} \quad (3)$$

Where $\eta_{th, ana}$ corresponds to the efficiency of the analytical model if the pump efficiencies, η_p , and the expander, η_t , were considered 1, θ_T corresponds to the ratio between the condensing temperature, T_{cond} , and the evaporating temperature, T_{evap} e Ja_{pre} corresponds to the preheat Jacob number, which is the ratio of sensible heat to latent heat in a process and is calculated by Eq.(4), where q_{2-3} is the heat transferred from the hot source and $\overline{c}_{p,l}$ is the specific heat.

$$Ja_{pre} = \frac{\overline{c}_{p,l} \cdot (T_{evap} - T_{cond})}{q_{2-3}} \quad (4)$$

$$PWHR = \frac{v_i \cdot (P_{evap} - P_{cond})}{\overline{c}_{p,l} \cdot (T_{evap} - T_{cond}) + q_{2-3}} \quad (5)$$

The data indicated in Tab.2 were considered in the analysis. The effect of the exchanger effectiveness was neglected. The superheat varied in the values of 0°C, 5°C, 10°C, 15°C and 20°C, varying the evaporation temperature so that the sum of the superheat with the evaporation temperature did not exceed 100°C.

Table 2. Data used for analysis.

Input parameters	Symbol	Values
heat entrance	q_{2-3}	1kW
high temperature	$T_{evap} + \Delta T_{sup}$	90°C+0°C, 95°C+0°C, 100°C+0°C, 90°C+10°C, 85°C+15°C, 80°C+20°C
low temperature	T_{cond}	30°C
turbine efficiency	η_t	0.7
pump efficiency	η_p	0.7

4. RESULTS AND DISCUSSION

Tab.3 presents, in descending order, the efficiency results obtained for all conditions of temperature and degree of superheat considered, for the two models evaluated.

Table 3. Efficiencies obtained by numerical (NS) and analytical models (AM).

Fluids	Efficiency, 90°C		Efficiency, 95°C		Efficiency, 100°C		Efficiency, 90°C, 10°C/sup.		Efficiency, 85°C, 15°C/sup.		Efficiency, 80°C, 20°C/sup.	
	AM	NS	AM	NS	AM	NS	AM	NS	AM	NS	AM	NS
Methanol	0.1088	0.1084	0.1157	0.1152	0.1223	0.1218	0.1089	0.1089	0.1016	0.102	0.0941	0.0948
Ethanol	0.1074	0.1064	0.1141	0.113	0.1206	0.1193	0.1075	0.1067	0.1005	0.0999	0.0931	0.0930
Toluene	0.1045	0.1037	0.1109	0.1099	0.1171	0.1159	0.1047	0.104	0.0980	0.0976	0.0909	0.0908
Acetone	0.1042	0.1028	0.1105	0.1089	0.1166	0.1149	0.1044	0.1034	0.0977	0.0972	0.0908	0.0908
Cyclohexane	0.1027	0.1014	0.1089	0.1073	0.1148	0.113	0.103	0.1012	0.0965	0.0948	0.0897	0.0882
R11	0.1016	0.1002	0.1076	0.106	0.1134	0.1114	0.102	0.1009	0.0956	0.0950	0.0889	0.0887
R141b	0.1007	0.0995	0.1066	0.1051	0.1121	0.1104	0.1011	0.0998	0.0949	0.0939	0.0883	0.0876
R123	0.0986	0.0978	0.1043	0.1033	0.1096	0.1084	0.0991	0.0978	0.0933	0.0920	0.087	0.0858

R717 (ammonia)	0.0975	0.0973	0.1025	0.1023	0.107	0.1068	0.0982	0.0985	0.0927	0.0935	0.0866	0.0880
R1234ze(Z)	0.0961	0.0953	0.1013	0.1004	0.1061	0.105	0.0969	0.0959	0.0914	0.0906	0.0855	0.0848
R601a (isopentane)	0.0974	0.0949	0.1029	0.0999	0.1081	0.1047	0.0981	0.0941	0.0924	0.0883	0.0862	0.0822
R245fa	0.0952	0.0940	0.1003	0.0989	0.1051	0.1035	0.0961	0.0940	0.0907	0.0886	0.0848	0.0828
Butene	0.0944	0.0937	0.0994	0.0986	0.104	0.1031	0.0953	0.0943	0.0901	0.0891	0.0843	0.0834
R1224yd(Z)	0.0952	0.0937	0.1004	0.0985	0.1052	0.1031	0.0961	0.0936	0.0907	0.0882	0.0848	0.0823
R1336mzz(z)	0.0966	0.0931	0.1021	0.0979	0.1073	0.1024	0.0974	0.0922	0.0918	0.0867	0.0856	0.0808
R600a (isobutane)	0.0910	0.0900	0.0955	0.0944	0.0995	0.0984	0.0923	0.0902	0.0876	0.0853	0.0822	0.0798
HFE7200	0.0969	0.0887	0.1025	0.0931	0.1079	0.0971	0.0978	0.0864	0.0921	0.0807	0.0859	0.0748
R152a	0.0881	0.0884	0.0913	0.0919	0.0936	0.0947	0.0899	0.0910	0.0859	0.0876	0.0810	0.0831
HFE7000	0.0933	0.0878	0.0984	0.0920	0.1032	0.096	0.0944	0.0864	0.0892	0.0811	0.0835	0.0755
HFE7100	0.0950	0.0877	0.1004	0.0919	0.1055	0.0958	0.0959	0.0858	0.0904	0.0805	0.0845	0.0748
R236fa	0.0890	0.0876	0.0931	0.0916	0.0967	0.0952	0.0906	0.0878	0.0862	0.0830	0.0811	0.0778
HFE7500	0.0963	0.0868	0.1018	0.0909	0.107	0.0946	0.0973	0.0842	0.0917	0.0786	0.0856	0.0728
R1234ze(E)	0.0839	0.0844	0.0865	0.0874	0.0880	0.0897	0.086	0.0865	0.0829	0.0826	0.0785	0.0779
R161	0.0815	0.0832	0.0819	0.0849	0.0772	0.0842	0.0848	0.0876	0.0821	0.0851	0.0780	0.0815
R1243zf	0.0813	0.0824	0.0829	0.0847	0.0816	0.0854	0.0844	0.0858	0.0815	0.0824	0.0774	0.0779
R134a	0.0800	0.0813	0.0804	0.0829	0.0745	0.0814	0.0834	0.0857	0.0809	0.0830	0.0770	0.0789
RC318	0.0839	0.0806	0.0872	0.0839	0.0899	0.0867	0.0861	0.0800	0.0825	0.0757	0.0780	0.0709
R22	0.0749	0.0782	0.0682	0.0766	-	-	0.0796	0.0841	0.0784	0.0824	0.0753	0.0795
R1225ye(Z)	0.0825	0.0774	0.0848	0.0786	0.0858	0.0779	0.0850	0.0799	0.0819	0.0775	0.0777	0.0740
R290 (propane)	0.0734	0.0766	0.0689	0.0759	-	-	0.0783	0.0826	0.0771	0.0804	0.0741	0.0768
R1234yf	0.0719	0.0749	-	-	-	-	0.0774	0.0808	0.0766	0.0781	0.0737	0.0743

Evaporation temperatures above 94.7°C (95°C and 100°C, considered in this work) are unfeasible for R1234yf, R290 and R22, as they are higher than their critical temperatures. The increase in superheat to levels of 10°C, 15°C and 20°C and the consequent decrease in the evaporation temperature reduce the cycle efficiency, especially for wet fluids, which are those that require the most superheat.

In Tab.3, in gray, the efficiencies and the respective conditions (evaporation temperature and degree of superheat) are highlighted for which each of the fluids can be applied in a Rankine cycle with a maximum high temperature of 100°C, without that there is a two-phase condition during expansion. It is observed that wet fluids have the highest degrees of superheating and, even so, ammonia still has a two-phase condition at the end of expansion, as shown in Fig.1, in which the orange line indicates the cycle without superheating and with temperature of evaporation of 90°C and the purple line indicates the cycle with superheat of 20°C and evaporation temperature of 80°C. Ammonia also has the drawback of high toxicity.

Ethanol and methanol, even requiring a superheat of 20°C, still have high efficiency, however, as they are flammable fluids, they require careful handling. Ethanol, Cyclohexane, Benzene and Toluene operate at pressures below atmospheric.

Fluids with efficiency greater than 0.1 are cyclohexane, toluene, acetone, R11 and R141B. The last two are high GWP and ODP fluids, with the production and importation of R11 being prohibited in the country and those of R141B should be extinguished by 2040 in the country, since Brazil is a signatory to the Montreal Protocol. Cyclohexane and toluene, even with GWP values less than 3.3, are toxic fluids. Fluids R123 and R22 are also in the process of being replaced, which should take place by 2040. Despite the low ODP value, they still have a high GWP.

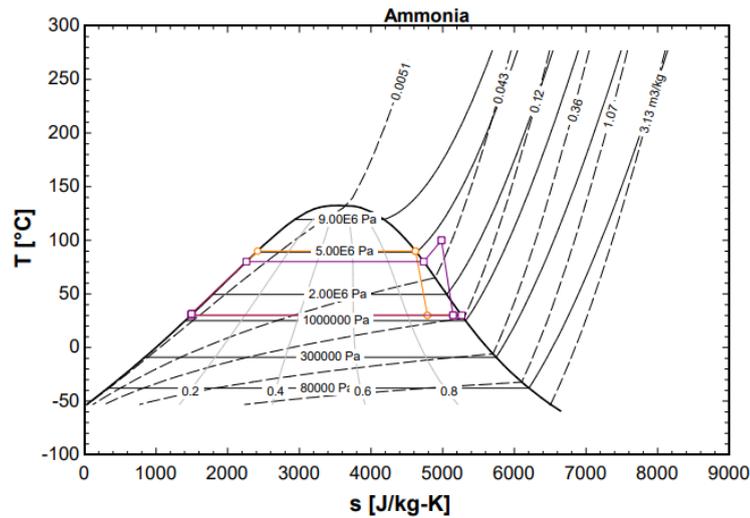


Figure 1. T-s diagram of Ammonia for two operating conditions.

The efficiencies obtained by the analytical method present a maximum error of 17.55% in relation to the efficiencies obtained by the numerical model for the HFE7500 fluid and a minimum error of 0% for methanol and acetone. It is observed that the fluids HFE7000, HFE7100, HFE7200 and HFE7500 are the ones with the greatest discrepancy in efficiency between the two models, with relative errors between 10 and 18%, as indicated in Fig.3. The fluids R1225ye(Z) (isentropic), RC318 (dry) and R22 (wet) also showed considerable discrepancies, with relative errors between 10 and 12%.

In Fig.2 it is evident that the HFE fluids are all dry and R1225ye(Z) is isentropic.

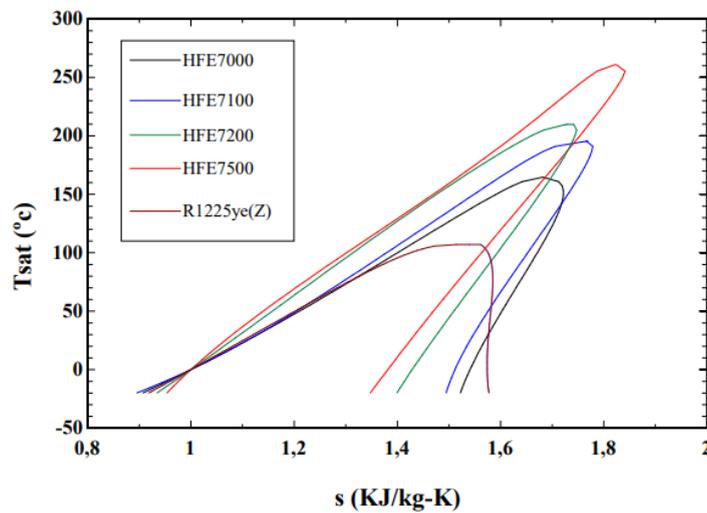


Figure 2. Comparison of T-s diagrams of the fluids with the highest error between models.

It can also be seen from Fig.3 that the fluids with the smallest discrepancy between the two methods are methanol and ammonia, both wet fluids. R1234ze(E) fluid (isentropic) also has a low discrepancy.

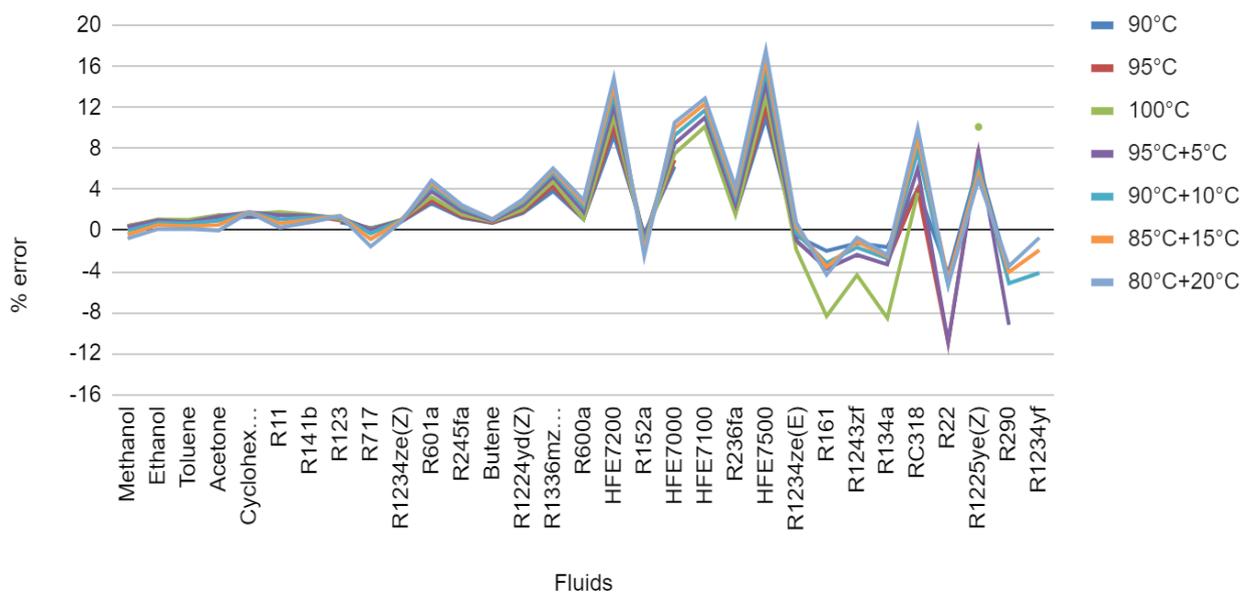


Figure 3. Comparison of percentage error efficiency between analytical model and numerical solution.

5. CONCLUSION

With the exception of hydrofluoroether fluids and R1225ye(Z), it was found that the proposed analytical model is suitable for calculating the thermal efficiency of the organic Rankine cycle, presenting relative errors of less than 5% for 22 of the 31 fluids analyzed.

For dry and isentropic fluids, it was observed that higher efficiency values are obtained when the evaporation temperature is high, without the occurrence of superheat, with higher efficiency being verified for the temperature of 100°C. For wet fluids, however, it is advantageous to reduce the evaporation temperature and increase the superheat, especially for the condition of evaporation temperature of 90°C and superheat of 10°C, as expansion outside the two-phase liquid-vapor region is guaranteed for the most of the considered wet fluids and additionally, for fluids such as R161, R134a and R1243zf, efficiencies are obtained superior to the condition of evaporation temperature of 100°C without superheating.

6. REFERENCES

- Bahrami, M., Pourfayaz, F., Kasaeian, A., 2022. "Low global warming potential (GWP) working fluids (WFs) for Organic Rankine Cycle (ORC) applications". *Energy Reports*, Vol. 8, pp. 2976-2988.
- Bao, J., Zhao, L., 2013. "A review of working fluid and expander selections for organic Rankine cycle". *Renewable and Sustainable Energy Reviews*, Vol. 24, pp. 325-342.
- Calm, J. M. and Hourahan, G. C., 2001. "Refrigerant Data Summary". *Engineered Systems*, Vol. 18, n.11, pp. 74-88.
- Gupta, P. R., Tiware, A. K., Said, Z., 2022. "Solar organic Rankine cycle and its poly-generation applications - A review". *Sustainable Energy Technologies and Assessments*, Vol. 49.
- Kumar, A. and Rakshit, D., 2021. "A critical review on waste heat recovery utilization with special focus on Organic Rankine Cycle applications". *Cleaner Engineering and Technology*, Vol. 5.
- Quoilin, S., Declaye, S., Tchanche, B. F., Lemort, V., 2011. "Thermo-economic optimization of waste heat recovery Organic Rankine Cycles". *Applied Thermal Engineering*, Vol. 31, pp. 2885-2893.
- Qyyun, M. A., Khan, A., Ali, S., Khurram, M. S., Mao, N., Naquash, A., Noon, A. A. and Lee, M., 2022. "Assessment of working fluids, thermal resources and cooling utilities for Organic Rankine Cycles: State-of-the-art comparison, challenges, commercial status, and future prospects". *Energy Conversion and Management*, Vol. 252.
- Rayegan, R. and Tao, Y. X., 2011. "A procedure to select working fluids for Solar Organic Rankine Cycles (ORCs)". *Renewable Energy*, Vol. 36, pp. 659-670.

- Wang, D., Ling, X., Peng, H., Liu, L., Tao, L., 2013. "Efficiency and optimal performance evaluation of organic Rankine cycle for low grade waste heat power generation". *Energy*, Vol. 50, pp. 343-352.
- Zinsalo, J. M., Lamarche, L., Raymond, J., 2022. "Performance analysis and working fluid selection of an Organic Rankine Cycle Power Plant coupled to an Enhanced Geothermal System". *Energy*, Vol. 245.

7. RESPONSIBILITY NOTICE

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