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Fluid selection and thermodynamic optimization of organic Rankine cycles for waste heat recovery applications

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Abstract

Organic Rankine cycles are effective to convert waste heat to power. One of the advantages and challenges of these cycles is that the most suitable working fluid and cycle configuration have to be selected for every application. Numerous fluids can be used in organic Rankine cycles, including hydrocarbons, HCFCs, HFCs, siloxanes, alcohols, or even mixtures of fluids. The selection of the working fluid can be based on many different criteria including the thermodynamic match with the heat source and sink, chemical stability, environmental concerns, safety, or cost and it is not possible to find a single best fluid for a given application. For this reason, the fluid selection and cycle optimization is usually a compromise between different factors. In this work, an organic Rankine cycle is proposed for a waste heat recovery application where the heat source is a 10 kg/s mass flow rate of air at 250 °C (with a low temperature limit of 100 °C) and the heat sink is liquid water at 10 °C. 80 pure working fluids from the REFPROP library were considered and several screening criteria were used to preselect 27 of these fluids. A robust, steady-state solver for cycles with and without recuperation was developed in MATLAB. The REFPROP libraries were linked to the solver to compute the thermodynamic properties of the working fluids. In order to select the most suitable fluids, a single objective, thermodynamic optimization was performed using a genetic algorithm with the second law efficiency as objective function and the expander performance of the optimal solutions was analyzed. The second law efficiency of the recuperated cycles was higher than that of simple cycles for most cases. In addition, the results show that the second law efficiency of simple cycles has a strong dependence with the choice of working fluid while it is relatively independent for recuperated cycles. The results of the optimization were presented in terms of a reduced temperature parameter to define some criteria for the selection of the optimal working fluids and cycle configurations. It was found that the transcritical-recuperated cycle configuration using *dry* or *isentropic* substances was optimal when the critical temperature of the working fluid is slightly lower than the temperature of the heat source. Conversely, no general trend was discovered for the optimal cycle configuration when critical temperature of the working fluid is higher than the temperature of the heat source.

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Keywords: heat-to-power; ORC; fluid screening; process modeling and simulation; genetic algorithm; transcritical; exergy;

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1. Introduction

A solid scientific consensus indicates that global warming is unequivocal and that it is caused by the increased concentration of greenhouse gases in the atmosphere. In addition, there is an agreement that the increased concentration of these gases is caused mainly by human activities and natural causes only represent a minor effect [1]. The recovery of waste heat from industrial processes is an effective manner to increase energy efficiency and reduce CO_2 emissions. Thermal energy from an industrial process can be regarded as waste heat when it cannot be used in direct applications, such as district heating. In this case, the heat can be potentially converted into power. The works by Quoilin et al. [2] and Colonna et. al [3] review applications where waste heat recovery is possible.

The conventional gas Brayton cycle and steam Rankine cycle are not well suited for heat sources of low to medium temperatures[1] because of thermodynamic and technical reasons, respectively [5]. The adoption of Rankine cycles using *dry* organic fluids with high molecular mass rules out many of the problems of using water as working fluid. These cycles are usually know as organic Rankine cycles (ORC) and the selection of the optimal working fluid and cycle configuration is one of the main challenges. This is usually investigated using an enumerative approach, in which every fluid candidate is simulated and optimized to find the best choice of working fluid and cycle layout.

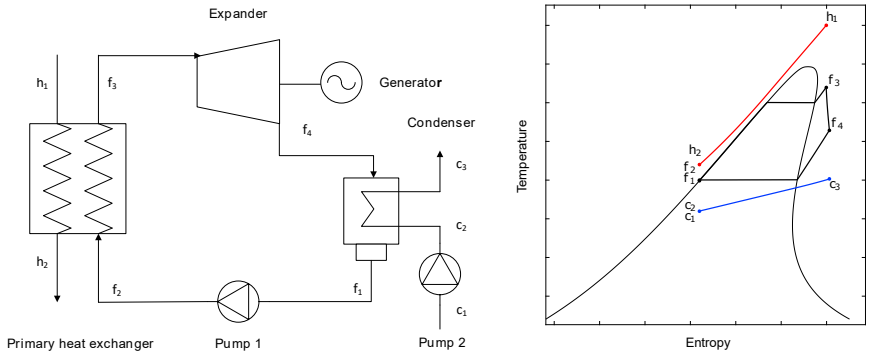
In the last years, there have been several works on the fluid selection and *thermodynamic optimization* of Rankine cycles for waste heat recovery applications. Dai et al. [6] analyzed waste heat recovery from a source of 16 kg/s at 145 °C. They used a *genetic algorithm* to optimize the second law efficiency of Rankine cycles for 10 different working fluids. Wang et al. [7] presented a working fluid selection and multiobjective optimization using a *simulated annealing* algorithm. In that work, they analyzed 13 working fluids for heat sources from 100 to 220 °C. Larsen et al. [8] studied Rankine cycles for waste heat recovery in marine applications (180–360 °C). They considered 109 working fluids and used a *genetic algorithm* with the first law efficiency as objective function for the optimization. These works found the optima solutions for different case studies and provided qualitative guidelines for the selection of working fluid and cycle configuration. However, they did not provide any quantitative criterion.

Astolfi et al. [9,10] analyzed ORC for the exploitation of geothermal brines from 120 °C to 180 °C in a two-part paper where they perform both a thermodynamic optimization [9] and a techno-economic optimization [10]. They used an *active set* algorithm with the second law efficiency as the objective function for the thermodynamic optimization. 54 working fluid were studied considering both simple and recuperated cycles in subcritical and transcritical configurations. These works are highlighted because it was the first time (to the authors' knowledge) when a simple quantitative criterion was presented to select the optimum working fluid and cycle configuration for a given heat source. They found that the optimal plant efficiencies are obtained for transcritical, recuperated configurations when ratio of the critical temperature of the working fluid to the inlet temperature of the heat source is between 0.88–0.92.

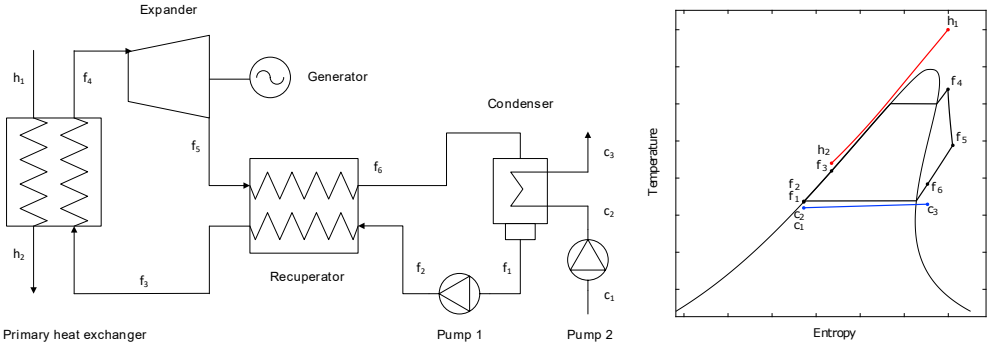
Other authors have also proposed quantitative criteria relating the critical temperature of the working fluid and the inlet temperature of the hot source. Zhai et al. [11] analyzed heat sources in the 150–350 °C range and proposed an indicator to select the optimum working fluid as a function of the critical and boiling temperatures. Yang et al. [12] analyzed heat sources in the 150–300 °C range and proposed a correlation for the critical temperature of the working fluid as a function of the heat source inlet temperature. Despite both works cover a wide range of temperature and give a quantitative criterion for the selection of the optimum working fluid, they are limited to simple, subcritical cycles.

The aim of the present study is to: 1) find the optimal working fluid and cycle configuration for a waste heat source of hot air at 250 °C in order to extend the results from [9] to other temperature ranges, 2) discuss if superheating should always be as low as possible, and 3) analyze the expander performance of the optima solutions. Different cycle configurations (subcritical-transcritical, saturated-superheated, simple-recuperated) and 80 pure working fluids were considered in this work. The fluid screening methodology used to reduce the number of fluid candidates, the details of the cycle simulation and optimization, and the expander analysis are described in Section 2. After this, the results of the fluid screening, thermodynamic optimization, and expander performance are presented and discussed in Section 3. Finally, Section 4 contains the main conclusions drawn from the results obtained in this work.

[1] Several authors, including [3] and [4] classify waste heat sources according to their temperature level as: low-temperature ($T < 230$ °C), medium-temperature (230 °C $< T <$ 650 °C), and high-temperature ($T > 650$ °C).



(a) Simple cycle.



(b) Recuperated cycle

Fig. 1: Process flow diagram and $T - s$ diagram of simple and recuperated the cycles.

2. Methodology

2.1. Case study description

The case study analyzed in this work is a waste heat recovery application where the heat source is a 10 kg/s stream of air at 250 °C and the heat sink is liquid water at 10 °C . An hypothetical downstream gas cleaning facility limits the minimum temperature of the heat source to 100 °C. Both the simple and recuperated cycle layouts and the saturated, superheated, and transcritical configurations were considered. The process flow diagrams and the $T - s$ diagrams of the simple and recuperated cycles are shown in Fig. 1.

In this case study, the use of a recuperator can be beneficial from a thermodynamic point of view because there exists a limitation for the lower temperature of the heat source and, therefore, the superheated vapor leaving the expander can be used to preheat the liquid entering the primary heat exchanger without limiting the exploitation of the heat source. If the temperature of the heat source could be reduced to the ambient temperature (no limitation for the lower temperature of the heat source), the use of the recuperator would indeed *increase* the efficiency of the Rankine cycle, but it would also *decrease* utilization of the heat source and the overall thermal efficiency of the plant would not be improved. This was recognized by some authors including Astolfi et al. [9].

The parameters of the Rankine cycles can be categorized into two groups, fixed parameters and degrees of freedom. The values of the fixed parameters used for the simulation of the simple and recuperated cycles are summarized in Table 1. The expander inlet pressure, the superheating temperature approach, and the cold temperature of the cold source were used as independent variables (the superheating temperature approach and the expander inlet temperature are equivalent because the temperature of the hot source is fixed). Only two optimization constraints were used during the optimization, the minimum superheating approach at the inlet of the expander (10 °C) and the minimum hot source outlet temperature (100 °C).

Table 1: Fixed parameters used for the optimization.

Characteristics of the heat source and sink		
Ambient pressure	p_o	101.325 kPa
Ambient temperature	T_o	10 ^{o}C
Heat sink inlet temperature	T_{c1}	10 ^{o}C
Heat source inlet temperature	T_{h1}	250 ^{o}C
Heat source mass flow rate	$\dot{m}_h$	10 kg/s
Heat sink fluid		Water
Heat source fluid		Air
Minimum temperature differences		
Primary heat exchanger	ΔT_{PrHE}	10 ^{o}C
Condenser	ΔT_{cond}	10 ^{o}C
Recuperator	ΔT_{recup}	10 ^{o}C
Pressure drops		
Primary heat exchanger (heat source)	$\Delta p_{h,PrHE}$	1%
Primary heat exchanger (working fluid)	$\Delta p_{f,PrHE}$	1%
Condenser (working fluid)	$\Delta p_{f,cond}$	1%
Condenser (heat sink)	$\Delta p_{c,cond}$	1%
Recuperator (hot side)	$\Delta p_{f,recup}$	1%
Recuperator (cold side)	$\Delta p_{f,recup}$	1%
Other assumptions		
Pump polytropic efficiency	η_{pump}	85%
Expander polytropic efficiency	$\eta_{expander}$	85%
Subcooling after the condenser	$\Delta T_{subcool}$	1 ^{o}C

Table 2: List of fluids considered in this work.

Number	Chemical name	Alternative name	Class[a]	Met screening criteria	Simulation results
1	Ethane	R170	Alkane	yes	no
2	Propane	R290	Alkane	yes	no
3	n-Butane	R600	Alkane	yes	yes
4	2-Methylpropane	Isobutane - R600a	Alkane	yes	no
5	Pentane	R601	Alkane	yes	yes
6	2,2-Dimethylpropane	Neopentane	Alkane	yes	no
7	Hexane	-	Alkane	yes	yes
8	2-Methylpentane	Isohexane	Alkane	yes	no
9	Heptane	-	Alkane	yes	no
10	Propene	Propylene - R1270	Alkene	yes	no
11	1-Butene	Butene	Alkene	yes	yes
12	Cis-2-butene	Cis-butene	Alkene	yes	no
13	Trans-2-butene	Trans-butene	Alkene	yes	no
14	2-Methyl-1-propene	Isobutene	Alkene	yes	no
15	Cyclopentane	-	Cycloalkane	yes	yes
16	Cyclohexane	-	Cycloalkane	yes	yes
17	Methylcyclohexane	-	Cycloalkane	yes	no
18	Benzene	-	Aromatic	yes	yes
19	Methylbenzene	Toluene	Aromatic	yes	yes
20	1,1-Difluoroethane	R152a	Hydrofluorocarbon	no	yes
21	Hexamethyldisiloxane	MM	Linear Siloxane	yes	yes
22	Octamethyltrisiloxane	MDM	Linear Siloxane	no	yes
23	Propanone	Acetone	Ketone	yes	no
24	Ethyl alcohol	Ethanol	Alcohol	yes	yes
25	Methanol	Methanol	Alcohol	yes	no
26	Methoxymethane	Dimethylether	Ether	yes	yes
27	Ammonia	R717	Inorganic	yes	yes
28	Carbon dioxide	R744	Inorganic	yes	yes
29	Water	R718	Inorganic	yes	yes

2.2. Fluid screening methodology

The choice of working fluid is usually investigated using an enumerative approach, in which every fluid candidate is simulated and optimized with respect to some objective function. This type of analysis can be very time consuming and a preliminary filtering can be useful to reduce the domain of possible solutions. This analysis is known as fluid screening and consists of the elimination of possible candidates if they are not appropriate for the application. There are many possible screening criteria, including thermodynamic match with the heat source and sink, environmental concerns (*ozone depletion potential* - ODP and *global warming potential* - GWP), the cost and availability of the fluid, chemical stability, corrosivity, and safety considerations, such as toxicity or flammability. The screening criteria used in this work were the following:

- The critical temperature has to be higher than the ambient temperature to make condensation possible.
- The melting temperature has to be lower than the ambient temperature to avoid freezing during shutdown time.
- The saturation pressure at ambient temperature has to be higher than 1 kPa to limit the vacuum in the condenser.
- The ODP of the working fluid has to be zero (ODP with respect to R11, as defined in the Montreal Protocol).
- The GWP of the working fluid has to be lower than 200 (GWP over 100 years with respect to CO_2).
- The minimum and maximum temperature limits of the equation of state have to be wider than temperature span of the thermodynamic cycle (ambient temperature 10 °C and heat source temperature of 250 °C). This ensures chemical stability because the upper temperature limit of the equations of state of REFPROP is near the point of decomposition of the working fluid.

2.3. Simulation and optimization methodology

Every optimization problem comprises three essential steps, the definition of an objective function of interest, the development of a mathematical model to compute the objective function, and the application of an optimization algorithm to find a set of independent variables that yield an optimum value of the objective function. In this work, a thermodynamic objective function was used to optimize organic Rankine cycles. There are several thermodynamic objective functions that lead to the same optimal solution, such as the net power output and the first law efficiency. However, the second law efficiency (η_{II}) was preferred because it gives information about the potential for improvement of the cycle. The second law efficiency is defined by Eq. 1, where $\dot{W}_{net}$ is the net power output and $\dot{E}_{in,max}$ is the maximum amount of exergy that can be recovered due to the limitation of the lowest temperature of the heat source.

$$\text{Objective Function} \implies \eta_{II} = \frac{\dot{W}_{net}}{\dot{E}_{in,max}} \tag{1}$$

In order to compute the objective function, a one-through, causal, steady state model was implemented in MATLAB [13] for the simulation of the Rankine cycle. Both simple and recuperated cycles and saturated, superheated, and transcritical configurations were considered. REFPROP [14] was used for the computation of the thermodynamic properties. In order to find the pinch points in the heat exchangers, they were discretized and the temperature differences were computed in each node. For subcritical configurations, the MATLAB model is able to identify a phase change and add one extra node to compute the pinch point exactly. The expander and pump were modeled using fixed values of polytropic efficiency. Instead of dividing the processes into several small stages, the states at the outlet of the expander and pump were computed solving the ordinary differential equations expressed by Eq. 2 and Eq. 3.

$$\left(\frac{\mathrm{d}h}{\mathrm{d}p}\right)_{exp} = \frac{1}{\rho} \cdot \eta_{exp} \tag{2}$$

$$\left(\frac{\mathrm{d}h}{\mathrm{d}p}\right)_{pump} = \frac{1}{\rho} \cdot \frac{1}{\eta_{pump}} \tag{3}$$

The last step of the optimization process is the selection of the optimization algorithm to find the optimum value for the objective function. In this work, the genetic algorithm implemented in MATLAB [15] was used for the optimization. Genetic algorithms are direct search methods that mimic the biological processes or chromosomal crossover and mutation to explore the space of independent variables in order to find the global optimum solution of the problem. Genetic algorithms do not rely on the gradient of the objective function and they are parallelizable.

2.4. Expander performance methodology

The optimization carried out in this work is purely thermodynamic and it may lead to solutions that are unfeasible in practice. In particular, the optimal solution may lead to complex and expensive expander technology. For the sake of illustration, the technical feasibility of an axial turbine with two stages was assessed using the correlation proposed by Astolfi and Macchi, [16]. This correlation predicts the efficiency of the turbine as a function function of the size parameter and the volume ratio, $\eta_{exp} = \eta_{exp}(\mathrm{SP}, V_r)$. These two parameters are defined by Eq. 4 and Eq. 5.

$$\mathrm{SP} = \frac{\dot{V}_{out,s}{}^{1/2}}{\Delta h_s^{1/4}} = \frac{(\dot{m}_{out}/\rho_{out,s})^{1/2}}{(h_{in} - h_{out,s})^{1/4}} \tag{4}$$

$$V_r = \frac{\dot{V}_{out,s}}{\dot{V}_{in}} = \frac{\rho_{in}}{\rho_{out,s}} \tag{5}$$

The contour lines of efficiency are shown in Fig. 3. The range of validity of this correlation is $0.02\,\mathrm{m} \leq \mathrm{SP} \leq 1.00\,\mathrm{m}$ and $1 \leq V_r \leq 200$ and the turbine efficiency will deteriorate when $\mathrm{SP} \leq 0.02\,\mathrm{m}$ or when $V_r \geq 200$. As discussed in the original paper, this correlation was developed assuming a complex ideal gas with a heat capacity ratio, $\gamma = 1.05$ representative of a generic organic fluid and its scope is to obtain a preliminary prediction of the turbine efficiency for organic Rankine cycles. It is uncertain if the correlation is accurate for turbines using simpler, inorganic molecules such as water, ammonia, or carbon dioxide.

The size parameter and the volume ratio were computed using the variables from the thermodynamic optimization based on a constant value of expander polytropic efficiency, $\eta_{exp} = 0.85$. The purpose of this analysis is to assess if the turbine design would be feasible in practice and study if the results might be different if the turbine performance is taken into account during the optimization instead of assuming a constant value for the efficiency.

3. Results and discussion

3.1. Results of the fluid screening

The list of the working fluids studied in this work is reported in Table 2. From the 80 fluids originally considered, only 27 met the screening criteria described in Sec. 2.2. In order to save computational time and to avoid the simulation of substances with similar properties, only 15 of these fluids were simulated and optimized. This is because fluids like butane, butene, cis-butene, trans-butene, and isobutene, or acetone, methanol, and ethanol have similar properties and the results from the optimization are expected to be comparable. Only one representative fluid was considered in these cases. R152a and MDM were simulated despite they did not meet the screening criteria to include a hydrofluorocarbon and a second siloxane in the analysis. R152a did not pass the screening criteria because the suggested maximum temperature for the equation of state included in REFPROP was slightly lower than the heat source temperature and MDM because its saturation pressure at 10 °C was slightly lower than 1 kPa.

3.2. Results of the thermodynamic optimization

The thermodynamic optimization for both the simple and recuperated configurations was performed for the 15 fluids included in Table 2. For the case of water, the recuperated configuration did not converge and only the results for the simple configuration were found. The same is true for carbon dioxide and the simple configuration. The results of the optimization are shown in Fig. 2, where the second law efficiency is plotted as a function of the ratio of the critical temperature of the working fluid to the inlet temperature of the heat source (in Kelvin degrees). This temperature parameter was first adopted by Astolfi et al. [9,10] (to the best of the authors' knowledge) and it can be used to define general rules for the selection of working fluid and cycle configuration.

Each point of Fig. 2 gives the best cycle configuration and optimum second law efficiency for a given working fluid. The main trend observed is that the second law efficiency of recuperated cycles is higher than that of simple cycles. In addition, the second law efficiency of recuperated cycles is fairly high for every fluid (except for ammonia), in other words, the optimum second law efficiency of recuperated cycles is, to some extent, independent of the working fluid. Despite the thermal efficiency is high for almost every fluid, the maximum efficiencies were found for the transcritical-recuperated configuration with *dry* or *isentropic* fluids (butane, pentane, butene, dimethylether, and

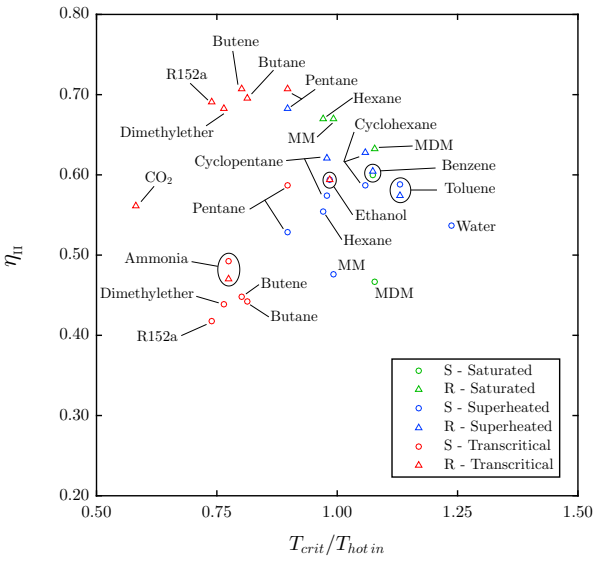


Fig. 2: Second law efficiency of the cycle as a function of the reduced temperature parameter.

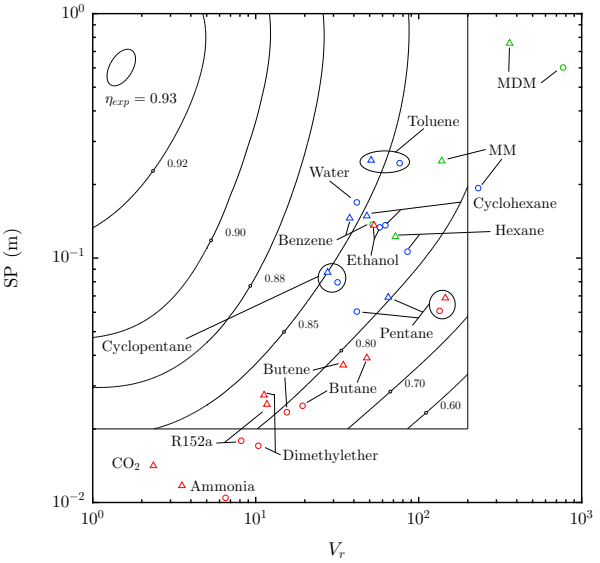


Fig. 3: Expected efficiency for a two-stage axial turbine as a function of the volume ratio and the size parameter.

R152a) when $0.75 < T_{crit}/T_{h1} < 0.90$. The maximum efficiency[2] was attained for pentane ($T_{crit}/T_{h1} = 0.898$. Despite the dimensionless temperature parameter of ammonia is favorable (0.775), the second law efficiency is low because the slope of the vapor saturation curve of ammonia in the $T - s$ diagram is negative, *wet fluid*, and the recuperation potential is limited. The results from this work are in agreement with the work by Astolfi et al. [9], where they concluded that optimal plant efficiencies are obtained for fluids with transcritical, recuperated configurations when the reduced temperature parameter lies in the range 0.88–0.92. The findings of this work suggest that the narrow range of [9], $0.88 < T_{crit}/T_{h1} < 0.92$, can be extended to $0.75 < T_{crit}/T_{h1} < 0.90$ and that wet fluids should be avoided. This parameter can be a powerful design tool for the rapid selection of working fluid and cycle configuration.

Several studies [6,9,17] suggest that saturated cycles are the optimal solution from the thermodynamic point of view when the critical temperature of the working fluid is higher than the maximum temperature attainable by the cycle ($T_{crit}/T_{h1} > 1$). Not all of the results of this work met this criterion. For example, the optimal solution for toluene ($T_{crit}/T_{h1} = 1.131$) was the superheated configuration for both the simple and the recuperated cycles, while for MDM ($T_{crit}/T_{h1} = 1.078$) the saturated configuration was the optimal solution with and without recuperator. In addition, the optimal solutions for benzene ($T_{crit}/T_{h1} = 1.074$) were saturated for the simple cycle and superheated for the recuperated cycle. These counterexamples suggest that, despite the *accepted* guideline that minimizing superheating leads to highest thermodynamic performance, the optimal cycle configuration cannot be determined a priori for $T_{crit}/T_{h1} > 1$ and each working fluid should be optimized to find the best cycle configuration (saturated or superheated).

3.3. Expander performance results

The efficiency predicted using the correlation from [16] for a two-stage axial turbine is plotted in Fig. 2 for each working fluid. The the results of the thermodynamic optimization were based on the assumption of $\eta_{exp} = 0.85$. It can be observed that subcritical cycles have higher values of SP than transcritical cycles. This is because the density at the outlet of the expander is high for transcritical cycles. As a result, transcritical cycles lead to smaller and more compact turbines. However, SP ≤ 0.02 m for some transcritical cycles (carbon dioxide, ammonia, R152a, and dimethylether) and the efficiency is expected to deteriorate because the secondary and leakage losses increase as the turbine size decreases [16]. This could make these working fluids unfeasible in practice for this case study.

[2] Two optimal configurations of similar efficiency were found for pentane. The maximum efficiency was found for the transcritical configuration ($\eta_{II} = 70.76\%$), while the efficiency of the subcritical superheated configuration was lower ($\eta_{II} = 68.26\%$).

Despite the transcritical cycles were found to be optimum when a fixed value of $\eta_{exp} = 0.85$ was assumed, it can be observed that the predicted turbine efficiency for transcritical cycles is lower because the values of the size parameter are low for this cycle configuration. Conversely, the turbine efficiency of some subcritical cycles is close to or even higher than $\eta_{exp} = 0.85$. This analysis suggests that the thermodynamic optimization might lead to to different solutions if the turbine performance is accounted during the optimization. This highlights the importance of including technical considerations to find the optimum working fluid and cycle configuration for a given application.

4. Conclusions

The following conclusions were drawn from the results of this work:

- With few exceptions, the second law efficiency of recuperated cycles was higher than that of simple cycles. This is because the lowest temperature of the heat source was limited.
- The second law efficiency of simple cycles has a strong dependence with the choice of working fluid while it is relatively independent for recuperated cycles.
- Transcritical-recuperated cycles using dry or isentropic working fluid have the highest thermodynamic efficiencies when $0.75 < T_{crit}/T_{h1} < 0.90$. Wet fluids do not follow this trend.
- If $T_{crit}/T_{h1} > 1$ the optimum cycle configuration (saturated or superheated) can not be determined a priori and each working fluid should be optimized to find the best cycle configuration. This contrasts with the accepted guideline that minimizing superheating leads to higher thermodynamic performances.
- Transcritical cycles lead to more compact expander designs than subcritical cycles. In addition, the performance of axial turbines is expected to be lower for transcritical cycles than for subcritical cycles.

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