

REVERSE ENGINEERING OF FLUID SELECTION FOR ORCS USING CUBIC EQUATIONS OF STATE

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ABSTRACT

Fluid selection for thermodynamic cycles like organic Rankine cycles remains an actual topic. Generally the search for a working fluid is based on experimental approaches or on a not very systematic trial and error approach. An alternative theory based reverse engineering approach is proposed and investigated here: The process should start with a model process, designed with respect to the boundary conditions and with (abstract) properties of the fluid needed to fit into this process, best described by some general equation of state and the corresponding fluid-describing parameters. These should be analyzed and optimized with respect to the defined model process, which also has to be optimized simultaneously. The degrees of freedom of the process are restricted to some crucial state variables with variation regimes defined with respect to the boundary conditions like the heat source, heat sink, technical restrictions etc.

Knowing the optimal fluid parameters, real fluids can be selected or even synthesized which have fluid defining properties in the optimum regime like critical temperature T_c or ideal gas capacities of heat c_p , also allowing to find new working fluids, not considered so far. The number and kind of the fluid-defining parameters is mainly based on the choice of the used equation of state (EOS). In the present work the cubic Peng-Robinson equation was chosen due to its moderate numerical expense, sufficient accuracy and a general availability of the fluid-defining parameters for many compounds.

The considered model-process is designed for a typical geothermal heat source with a temperature level of 423.15 K. The objective function is the thermal efficiency as a function of critical pressure p_c , T_c , acentric factor and c_p . Also, some crucial process variables have to be regarded as a problem variable. The results give clear hints regarding optimal fluid parameters of the analyzed process and deepen the thermodynamic understanding of the process. Finally, a strategy for screening large databases is explained. Several fluids from different substance groups were found to have high thermal efficiencies. These fluids will also have to fulfill further criteria, prior to their usage, but the method appears to be a good base for fluid selection.

1. INTRODUCTION

In the context of the expanded use of renewable energies and the increased use of low-temperature heat sources (geothermal, solar thermal, waste heat etc.) for electric power generation, ORCs find wider application. A crucial step in the development process of an ORC is the fluid selection according to different, criteria. Quoilin et al. have listed in their review [1] the most important criteria of fluid selection. Here the focus will be on thermodynamic criteria only, like a high thermal efficiency η and net power output P_{net} as well as acceptable pressures (evaporator and condenser).

Today, the basic thermodynamic approach of fluid selection starts with a model process, designed to defined boundary conditions like heat source and heat sink temperatures. Several preselected fluids, for which thermodynamic data are available, are tested with respect to a specific process parameter like thermal efficiency, exergy loss etc. and finally, the fluid which performs best is selected. For this approach, ample literature is available e.g.: [2,3]. An advanced approach is to combine the fluid selection step with the process optimization (e.g.: [4–6]); fitting the process to the respective working fluid improves the results considerably. Most of these studies are theoretical and use thermodynamic databases or EOS (equation of state) to calculate properties like enthalpy, entropy etc. Due to the ample scientific literature regarding fluid selection, a broader range of compounds were discussed as potential candidates, however, only a few are actually used in commercial ORC power plants [1]. The number of chemical compounds, which are in principle suitable as working fluids, will surely be larger. One problem of the basic approach is the high experimental or computational cost for every fluid to be tested, limiting the number of tested fluids and thus, there is the risk of neglecting potentially good fluids in the preselection step. Furthermore, the fluid rating is not objective; it is only based on the investigated fluid group or on results of other studies. An objective reference point, like the performance of an optimal fluid is missed.

An alternative for fluid selection is a reverse engineering approach with simultaneous process optimization, proposed and investigated here for ORCs. Very recently, we have applied this approach to heat pump cycles [7]; the main procedure has already been described in detail there, thus, here only a brief overview of the method is given. The main idea is to find the optimal properties a fluid should have for the considered process with the defined boundary conditions. Therefore, fluid-descriptive parameters are regarded as continuous variables which are simultaneously optimized with chosen process parameters and with respect to an objective function like thermal efficiency or net power output. Every variable is restricted to physically reasonable values; furthermore, the optimization of process and fluid parameters is constrained by boundary conditions like temperature levels of heat source and heat sink, temperature differences at the pinch point, pressure limits, steam quality at the turbine outlet etc. The type of fluid-descriptive parameters depends on the chosen EOS (equation of state). It can either be defined on the macroscopic scale like critical point values combined with capacities of heat, as used e.g. in cubic EOS or based on a molecular description, as used by the PC-SAFT EOS [8]. After optimizing both, these abstract parameters and the process, the found optimal parameter combination, generally will not fit to real fluids. Thus, the approach continues with the search of real fluids with parameters near to the optimal values. One of the advantages is that also fluids would be considered which would not be investigated in the standard approach.

Comparable approaches for pure fluid selection for ORCs with various heat source temperatures, using some kind of reverse-engineering approach, are found in: [9–11]. Furthermore, a reverse-engineering approach was also used to find optimal fluid mixtures for ORCs [12,13]. All of these investigations are based on a Computer-Aided Molecular Design (CAMD) method; thus, the molecular structure is the optimized parameter. The calculation of the fluid properties is usually done via a group contribution method. A common intermediate step in all is the calculation of critical properties and of heat capacities. In the present work, those fluid parameters are directly optimized. The fluid property model is based on the less complex cubic Peng-Robinson EOS [14], also because the needed fluid parameters (see section 2.1) are known for many fluids. Often it was assumed that the cubic EOS are not accurate enough to describe the performance of fluids as working fluids. Analysis of our own and of others [15,16] for several refrigerants using a typical refrigeration cycle have shown that a fluid property model based on the Peng-Robinson EOS combined with the heat capacity of the ideal gas is accurate enough for the first step of fluid selection (see section 2.1). The reverse engineering approach for ORC-processes shall be investigated in the present paper for a simple ORC with a geothermal heat source at 423.15 K. The fluid and process optimizations are carried out regarding the thermal efficiency.

2. METHODS

The optimization is based on a simple Rankine cycle (see Figure 1) as found in any standard thermodynamic textbook (e.g.: [17]). It consists of a pump, an evaporator, a turbine and a condenser.

The process works between two fluid and temperature dependent pressure levels, with the high pressure in the evaporator and the low in the condenser. The condensation temperature is chosen to be 303.15 K and a mass flow of $\dot{m}_{gw} = 100$ kg/s of geothermal water with a constant heat capacity of 75 J/(mol·K) enters the evaporator at 423.15 K. According to a scenario that can be used for combined heat and power generation, the outlet temperature is 403.15 K, constantly. Condenser and evaporator are isobaric and the isentropic efficiencies of pump and turbine are chosen to be $\eta_p^s = 0.6$ and $\eta_t^s = 0.8$.

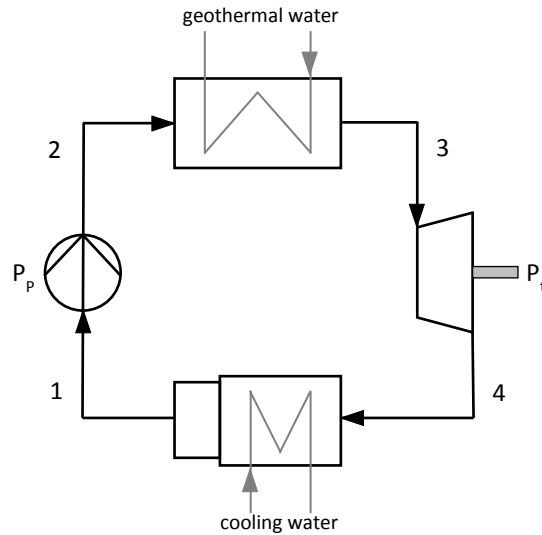


Figure 1: Working principle of the model process

The working fluid leaves the condenser at the condensation temperature and the fluid-dependent pressure as saturated liquid ($x_1 = 0$). From state 1 to 2 the fluid is pumped to the evaporator pressure which depends on the evaporation temperature, which is also a problem variable, constrained by the temperature profile of the geothermal water and a minimum pinch-temperature of 10 K. After heat is supplied (st2 – st3), the fluid is expanded in the turbine and finally, condensed from st4 to st1. Based on the inlet states of pump and turbine (st1, st3), the isentropic efficiencies and by means of the isentropic outlet states (st2^s, st4^s) the real outlet states can be calculated. The procedure as well as the respective equations can be found in any thermodynamic textbook (e.g.: [17]). Finally, the enthalpies at the outlet states apply to:

$$h_2 = \frac{h_2^s - h_1}{\eta_p^s} + h_1 \quad (1)$$

$$h_4 = h_3 + \eta_t^s(h_4^s - h_3) \quad (2)$$

State 3 can be saturated or superheated steam; it is defined by the temperature in state 3 which is also a degree of freedom for process optimization. It is constrained by the evaporation temperature and the geothermal water inlet temperature, taking into account the minimum pinch-temperature. The lower limit of the steam quality at state 4 is restricted to 0.9. From the energy balances for the various components the net power output and the input heat flow are calculated by:

$$|P_{net}| = |P_t| - P_p = \dot{n}_f[(h_3 - h_4) - (h_2 - h_1)] \quad (3)$$

$$\dot{Q}_{in} = \dot{n}_f(h_3 - h_2) \quad (4)$$

The molar flow rate of the working fluid is calculated from the energy balance of the geothermal water and equation (4):

$$\dot{n}_f = \frac{\dot{n}_{gw} \cdot c_{p,gw}(T_{gw,in} - T_{gw,out})}{h_3 - h_2} \quad (5)$$

Equations (3) and (4) lead to the well known expression of the thermal efficiency η :

$$\eta = \frac{|P_{net}|}{\dot{Q}_{in}} \quad (6)$$

By means of the energy balance $|P_{net}| = \dot{Q}_{in} - \dot{Q}_{out}$, the Gibbs equation $Tds = dh - vdp$ and the thermodynamic mean temperatures it can also be written as:

$$\eta = 1 - \frac{T_{m,low}(s_4 - s_1)}{T_{m,high}(s_3 - s_2)} \quad (7)$$

2.1. The fluid property model

The calculations of the objective function η requires the determination of the different thermodynamic properties temperature T , pressure p , specific volume v , enthalpy h , entropy s and the steam quality x for the different states.

The property model used here is based on the Peng-Robinson EOS and the T dependent ideal gas heat capacity. Within the simulations only a linear temperature dependence of the heat capacity was used, since it turned out that this is accurate enough for the small considered temperature ranges (T_3 - T_4). In order to find real fluids based on the optimal values the heat capacity were taken at 350 K together with the linear gradient at this temperature. Overall, the fluid descriptive parameters within the optimizations are T_c , p_c , ω , together with A and B for the temperature dependent ideal gas heat capacity $c_p(T) = A + B \cdot T$. All equations used in our property model can be found in Sandler's book [17]. The vapor liquid equilibrium calculation is done by means of the Ambrose-Walton method [18]; it is an empirical method and also based on T_c , p_c and ω . The Peng-Robinson EOS based property model is a good basis for fluid optimizing and screening, since it is easily and quickly solved, numerically and is sufficiently accurate, as shown earlier [7] the accuracy of our model appears to be reasonably good to be used in fluid screening purposes.

Table 1: Variable range for optimization, process parameters and constraints

parameter	value / range
critical temperature	$430 \leq T_c \leq 700$ K
acentric factor	$0.05 \leq \omega \leq 0.8$
heat capacity (ideal gas) at 350 K	$35 \leq c_p \leq 150$ J/(mol·K)
slope of heat capacity at 350 K	$0.01 \leq B \leq 0.6$ J/(mol·K ²)
evaporation temperature	T_{evap}^a
temperature in state 3	T_3^a
critical pressure	$3.0 \leq p_c \leq 12.0$ MPa
system pressure limits	$0.01 \leq p_{sys} \leq 2$ MPa
minimum steam quality in St 4	$x_{4,min} = 0.9$

^a Depending on the actual fluid parameter and a minimum pinch of 10 K

2.2. The optimization routine

The computer programs for optimizing and calculating the fluid properties are written in the programming language Python [19]. The optimization routine was the NLP-algorithm (Non-Linear-Problem) combined with the solver "ralg" taken from the OpenOpt package [20] which can handle both non-linear and non-smooth functions; furthermore, every optimizing parameter can be box-bounded and the optimization might be generally constrained.

2.3. Boundary conditions

It turned out, that the critical pressure has only an indirect impact on the thermal efficiency; the critical pressure influences the suitability range of the critical temperature with respect to the system pressure limits, and thus, it has a mediate impact on the thermal efficiency. As a result, p_c cannot be optimized with the chosen solver, and the optimizations are repeated for 10 values of p_c between 3.0

and 12.0 MPa with 1.0 MPa steps. Thus, the optimization parameters are T_c , ω , the evaporation temperature, the temperature at state 3 and the coefficients A and B of the linear temperature dependent function of the ideal gas heat capacity. Only subcritical processes are considered, therefore, the difference between T_c and the evaporation temperature must always be larger than 20 K. Besides this restriction, the evaporation temperature and the temperature in state 3 are limited by the temperature profile of the geothermal water and a minimum pinch of 10 K. Furthermore, T_3 has to be larger than T_{evap} . The parameter ranges of the ideal gas heat capacity at 350 K as well as the gradient were chosen so that values of most real fluids are within the limits. Here, the variable A is calculated from the slope of the linear equation and the value of c_p at 350 K. Table 1 gives an overview of the defined parameter limits and also over the remaining process variables, now.

As in the literature [9], the system pressures (p_{evap} , p_{cond}) are constrained between 0.01 and 2.0 MPa; they depend on the corresponding temperature levels, on the critical point and the acentric factor. Furthermore, for protection of the turbine the minimum steam quality ($x = m_v/m_{\text{total}}$) at the turbine outlet has to be larger than 0.9.

3. RESULTS AND DISCUSSION

Fluid and simultaneous process optimizations with the discussed parameters and constraints were carried out with the thermal efficiency η as objective function.

Table 2 shows the results of the η optimizations with respect to each critical pressure. It gets clear, that the optimal values of the thermal efficiency are always larger than 0.17 and increase with the critical pressure, marginally. The same is true for the associated critical temperatures, which increase from 602.75 K to 646.07 K. The optimal values of T_c correspond in combination with the optimal acentric factors to the respective maximum of T_c , which fulfills the pressure limits. However, investigations showed that p_c has no direct impact on η ; in fact, it influences only the suitability limit of the critical temperature with respect to the lower pressure limit. Higher critical pressures allow higher values of T_c , which lead to higher thermal efficiencies. The optimal acentric factor also increases with the critical pressure from 0.07 to 0.13; the values are near the lower boundary of ω ($\omega_{\text{min}} = 0.05$). This investigation showed that the direct impact of ω on the thermal efficiency is marginal; however, ω influences the suitability range of T_c with respect to the pressure limits. Lower values of the acentric factor lead to a shift of the T_c suitability limit to higher critical temperatures, which results in increased thermal efficiencies. Regarding the optimizations, a further reduction of ω is in conflict with the pinch condition at the starting point of evaporation; thus, smaller values of ω

Table 2: Results from η optimization

p_c [MPa]	T_c [K]	ω []	A [J/(mol·K)]	B [J/(mol·K ²)]	$c_p(350\text{K})$ [J/(mol·K)]	T_{evap} [K]	T_3 [K]	x_4 []	η []
3.0	602.75	0.07	0.01	0.10	35.01	396.62	413.15	0.92	0.175
4.0	607.75	0.09	0.00	0.10	35.00	396.57	413.15	0.92	0.175
5.0	619.91	0.09	0.00	0.10	35.00	396.47	413.15	0.92	0.176
6.0	625.36	0.10	0.03	0.10	35.03	396.43	413.15	0.92	0.176
7.0	626.54	0.12	0.01	0.10	35.01	396.42	413.15	0.91	0.176
8.0	638.33	0.10	0.00	0.10	35.00	396.33	413.15	0.91	0.176
9.0	647.55	0.09	0.04	0.10	35.04	396.27	413.15	0.91	0.176
10.0	645.16	0.11	0.00	0.10	35.00	396.28	413.15	0.91	0.177
11.0	647.56	0.12	0.02	0.10	35.02	396.26	413.15	0.91	0.177
12.0	646.07	0.13	0.00	0.10	35.00	396.27	413.15	0.91	0.177

lead to the need of decreasing the evaporation temperature, which results in a significant decrease of η , again. Therefore, the optimal acentric factors are slightly shifted to higher values. Regarding the molar heat capacity at the reference temperature ($T = 350$ K), the optimal value of $c_p(350\text{K}) = 35$ J/(mol·K) is independent of p_c , which correspond to the lower boundary of the $c_p(350\text{K})$ -domain. This

is also true for the parameter A which is always at the lower boundary. The optimal value of the parameter B (c_p gradient) is constantly 0.1, corresponding to the lowest value fulfilling the $c_p(350\text{K})$ restriction with respect to $A = 0$. The optimizations lead to evaporation temperatures slightly higher than 396 K; which is the respective maximum with regards to the minimum pinch point-temperature difference at the inception of evaporation. The temperature in state 3 is 413.15 K which is the maximum temperature which fulfills the pinch point requirement. All steam qualities at the turbine outlet (state 4) are larger than 0.91 and thus, above the boundary ($x_{4,\min} = 0.9$). The results of former fluid optimizations by Lampe et al. [9], Palma Flores et al. [11] and Papadopoulos et al. [10] show a different picture with respect to the optimal fluid properties. Although similar temperature domains were regarded here, fluids with lower critical temperatures and higher heat capacities reach the highest thermal efficiencies. As main difference to our scenario the authors did not specify the outlet temperature of the heat carrier; their objective was generating the highest possible net power output with respect to a defined heat carrier mass flow with fixed inlet temperature. Regarding such a scenario, our approach also leads to fluids with lower values of T_c and higher heat capacities. Thus, the exact design of the process influences the optimal fluid, essentially and a fluid recommendation based only on the heat source temperature seems to be not reasonable.

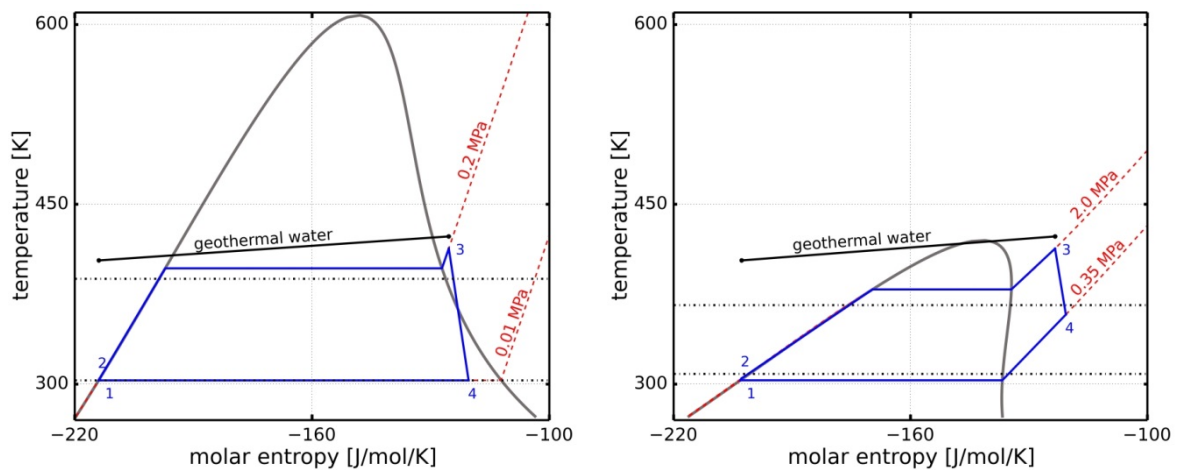


Figure 2: T-s plots of the η optimized fluid for $p_c = 4.0$ MPa (left) and of butene (right)

Butene is one of the recommended fluids for a heat source temperature between 420 and 445 K [21] and has a critical pressure of 4.04 MPa and thus, it is interesting to compare it with the optimal fluid at 4 MPa. Further fluid properties of butene can be found in Table 3. Figure 2 shows the Ts-diagram of the η optimized fluid for $p_c = 4.0$ MPa (left) and for the optimized process using butene as working fluid (right). Isobars (dashed lines), lines for the resultant thermodynamic mean temperatures (dash-dotted lines) and the temperature regime of the geothermal water are included. With respect to the discussed boundary conditions and based on the optimized process with butene a thermal efficiency of $\eta = 0.1245$ is reached, while the optimal fluid has a thermal efficiency of $\eta = 0.175$. First of all, a direct comparison of the two fluids shows a significantly elongated saturation regime for the optimal fluid, which results mainly from the higher critical temperature. The lower value of T_c (for butene) leads also to increased vapor pressures (η -opt: $p_{\text{cond}} = 0.01$ MPa, butene: $p_{\text{cond}} = 0.35$ MPa) and a significantly increased pressure difference (η -opt: $\Delta p_{12} = 0.19$ MPa, butene: $\Delta p = 1.65$ MPa), although the temperature difference ($T_{\text{evap}} - T_{\text{cond}}$) is smaller. Furthermore, smaller evaporation entropies at constant temperature levels are constituted by lower values of T_c . The flatter slope of the saturated liquid line and the partially negative gradient of the saturated steam line for butene result mainly from the higher value of the heat capacity (η -opt: $c_p(350\text{K}) = 35$ J/(mol·K), butene: $c_p(350\text{K}) = 103.86$ J/(mol·K)). The small slope of the isobaric line at evaporation pressure in the domain of the subcooled liquid, the smaller evaporation entropy and the decreased evaporation temperature lead to a significantly reduced thermodynamic mean temperature at the higher pressure level. Based on the superheating in st3 and the regime of the saturated steam line, butene leaves the turbine as superheated steam resulting in a higher value of the thermodynamic mean temperature at

condensation pressure. The spreading of either thermodynamic mean temperature is directly related to the thermal efficiency of the process (eq. (7)); therefore, a higher spreading results in larger values of η , in general. Due to it, the smaller spreading for butene, compared to the optimal fluid, leads to a strongly reduced thermal efficiency.

Finally, the optimizations of the thermal efficiency lead to fluids with small values of $c_p(350\text{K})$, highest possible critical temperatures and small acentric factors. Such fluids are wet fluids with an elongated saturation regime, typically.

3.1. (Real) fluid selection

After having found optimal fluid parameters, real fluids with similar parameters must be found or could even be synthesized. A detailed description of the fluid selection process was discussed for heat pumps and is found in [7]. Here, we give only a brief description of the selection process. A small fluid database with 284 records taken from different sources [22–24] was used here. It contains values of T_c , p_c , ω and 4 or 5 coefficients for an equation for the isobaric ideal gas heat capacity for every record. In order to compare with optimization results, the value of $c_p(350)$ as well as the gradient at this temperature were calculated. The fluid selection process is ordered in three steps and can also be efficiently applied to large databases:

Step I – Preselection with respect to the pressure limits

Using the Ambrose-Walton equation [18], vapor pressures at given temperatures can be calculated, analytically. The aim of step I is the exclusion of fluids, which do not fulfill the pressure restrictions at the given temperature levels. While, the condensation temperature is clearly defined as 303.15 K and the vapor pressure can directly be calculated; the evaporation temperature is a problem variable and is not defined, explicitly. However, it is assumed that fluids not fulfilling the higher pressure limit at the poor condensation temperature of 340 K will not reach good thermal efficiencies and are omitted. Additionally, it was found that fluids with good thermal efficiencies have vapor pressures significantly below the limit. In the present work with the used database, the above-mentioned temperature levels and the boundary conditions ($0.01 \leq p_{\text{sys}} \leq 2 \text{ MPa}$), from this step the number of potential fluids was reduced from 284 to 106.

Step II – Fit of a function for η estimation

From the presented optimizations it was found that small values of $c_p(350\text{K})$ and ω as well as critical temperatures between 600 and 650 K (depending on p_c) lead to high values of η . Further investigations pointed out that T_c and $c_p(350\text{K})$ are the critical and most sensitive variables for the thermal efficiency. The critical pressure has no direct impact and the effect of ω is marginal and can be neglected. Basically, with respect to this knowledge, fluids with properties near the optimum can be chosen for further investigation. However, finding a fluid with properties very close to the optimum is not probable, thus, fluid selection represents usually a compromise. Because of the unknown sensitivity of η with respect to the individual parameters, the fluid selection along this path is always in danger of missing attractive combinations of the parameters. Thus, by means of the optimization algorithm a function for η estimation as a function of T_c , $c_p(350\text{K})$ and the optimized process parameters (T_{evap} , T_3) was fitted to 100 combinations of T_c and $c_p(350\text{K})$. Ten critical temperatures between 360 and 600 K as well as 10 values of $c_p(350\text{K})$ between 35 and 150 J/(mol·K) were selected. The critical pressure was fixed at 4.0 MPa and the acentric factor was set to 0.10, which is the mean value resulting from the optimizations. Here, pressure restrictions were not considered, since in step I all fluids not fulfilling the restrictions were excluded. Four polynomials, each of degree 3, with overall 12 coefficients were fitted to the optimization results. A comparison between the values of η estimated by the polynomials and calculated by our fluid property model results in an absolute mean percentage error of 7.6 %, from the 106 fluids remaining from step I. However, the largest errors are found for fluids with poor η ; comparing only fluids with $\eta > 0.16$ (35 records) the absolute mean percentage error is decreased to 1.96 %. Finally, by means of the fit also large databases can be screened efficiently for good fluids.

The 2nd step requires the greatest computational effort of the 3 matching steps. The 100 optimizations for the fit can be done by a common computer (CPU: i5-3750, RAM: 8 GB) in about 30 minutes.

Step III - Final fluid selection for further investigation

With the results of step II, fluids with probably high thermal efficiencies can be chosen for further investigations, regarding other fluid criteria. Besides the estimation by the polynomials, the process optimization should be repeated once again for this limited number of fluids, to obtain the correct values. In step II 35 fluids with $\eta > 0.16$ were found; Table 3 shows 10 of them, exemplarily. Furthermore, the 5 fluids recommended by Wang et al. [21] for heat source temperatures between 420 and 445 K are also listed (No. 11 – 15). Those fluids all have thermal efficiencies smaller than 0.1245 and are with respect to the process regarded in this work much less efficient than the fluids resulting from our selection. Using our approach for a similar process as regarded in this work, but without fixing the heat source outlet temperature (regarding only power generation) leads also to the fluids 11-15 as top ranked. It follows, that besides the heat source temperature, further process parameters influence the choice of optimal fluids. Among the top-ranked fluids are conventional refrigerants like R150, R20 or R30 as well as fluids like bromine or acetonitrile, which are extremely toxic and/or corrosive compounds. However, this investigation is only meant as an example and perhaps some of the fluids like methanol, ethanol or acetone appear to be worth further investigations regarding other suitability criteria.

Table 3: Top-ranked fluids resulting from the fluid selection (No. 1-10), as well as fluids recommended by [21]

No.	Fluid	η []	T_c [K]	p_c [MPa]	ω []	$c_p(350K)$ [J/(mol·K)]
1	Bromine	0.1737	584.1	10.30	0.129	36.47
2	Acetonitrile	0.1711	545.5	4.83	0.334	59.46
3	Methanol	0.1700	512.5	8.08	0.565	50.35
4	1,2-Dichloroethane (R150)	0.1693	566.0	5.36	0.250	88.77
5	Chloroform (R20)	0.1685	536.5	5.55	0.229	71.49
6	Ethanol	0.1685	514.0	6.15	0.645	77.86
7	Dichloromethane (R30)	0.1676	510.1	6.08	0.198	57.49
8	Benzene	0.1673	562.0	4.90	0.210	106.00
9	Fluorobenzene	0.1655	560.0	4.55	0.248	118.38
10	Acetone	0.1654	508.3	4.70	0.306	88.62
11	Butene	0.1245	419.9	4.04	0.189	103.86
12	Isobutene	0.1237	417.9	4.00	0.199	100.44
13	1,1,1,2,3,3-Hexafluoropropane (R236ea)	0.1218	412.4	3.50	0.379	140.81
14	1-Chloro-1,1-difluoroethane (R142b)	0.1145	409.6	4.33	0.251	94.73
15	Isobutane (R600a)	0.1122	407.8	3.64	0.184	118.52

4. CONCLUSIONS

In this work the reverse engineering approach for fluid selection, recently introduced for heat pump cycles, is now applied to ORCs. It appears to be a more promising approach to first start thinking about an optimal process with optimal fluid parameters, instead of screening well investigated fluids. Furthermore, based on the reverse engineering approach, fluids that were not well investigated so far, can be found, and also more is learned about the fluid properties which are important for the cycle. This also leads to an objective value which represents the performance of a hypothetical best fluid.

The presented approach consists of the simultaneous numerical optimization of fluid-descriptive parameters and some process parameters, the latter could easily be extended. Here, the fluid property model is the cubic Peng-Robinson equation of state and a linear equation for the temperature dependent isobaric ideal gas heat capacity. Thus, the needed fluid-descriptive parameters are the

critical temperature, the critical pressure, the acentric factor and two coefficients for the heat capacity. These values are not too numerous and available for many compounds and could in future also be extended to apply group additivity methods to search for further fluids or for calculations of other fluid properties like thermal conductivity and viscosity, without increasing the number of parameters to be optimized.

First of all, it was shown, that the reverse engineering approach also can be applied to ORCs, efficiently. It was pointed out, that the results of the optimization are thermodynamically reasonable and lead to a deeper understanding of the interrelation of fluid and process parameters. Based on the optimized fluid parameters a procedure was presented to find real fluids near the optimum. Therefore, an equation for the prediction of η based on the most important variables was fitted.

Several fluids with higher values of η than the usually recommended ones for the here defined heat source temperature were found. Some of them, like bromine or acetonitrile will probably never be used as working fluids, but other like acetone or methanol may be worth further investigation. Comparing the optimal fluid parameters found in this work to the results of fluid optimizations by other authors allow the conclusion, that, besides the heat source temperature, also other criteria and parameters influence the optimal fluid choice, clearly. Further investigations regarding the influence of the process design or boundaries on the optimal fluid parameters are needed for a deeper insight.

NOMENCLATURE

A	coefficient of the molar isobaric heat capacity (intercept)	(J/mol/K)
B	coefficient of the molar isobaric heat capacity (gradient)	(J/mol/K ²)
c_p	molar isobaric heat capacity	(J/mol/K)
h	molar enthalpy	(J/mol)
\dot{m}	mass flow rate	(kg/s)
\dot{n}	molar flow rate	(mol/s)
P	power	(MW)
P	pressure	(MPa)
\dot{Q}	heat flow	(MW)
s	molar entropy	(J/mol/K)
st	state	(-)
T	temperature	(K)
\dot{V}	volume flow rate	(m ³ /s)
v	molar volume	(m ³ /mol)
w	molar work	(MJ/mol)
x	steam quality	(-)
η	thermal efficiency	(-)
ω	acentric factor	(-)

Subscripts

c	critical
cond	condensation
evap	evaporation
gw	geothermal water
f	working fluid
p	pump
s	isentropic
sys	system
t	turbine

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