10.18462/iir.gl.2018.1401

NATURAL REFRIGERANTS FOR LOW TEMPERATURE POWER CYCLES

Mina Shahrooz[(a)], Per Lundqvist[(a)], Petter Nekså[(b)]

[(a)] KTH Royal Institute of Technology

Stockholm, 100 44, Sweden, minash@kth.se

[(b)] SINTEF Energy Research and Norwegian University of Science and Technology

Trondheim, 7034, Norway, Petter.Neksa@sintef.no

ABSTRACT

Working fluid selection determines various characteristics of low temperature Rankine cycles. Among other factors, the selected working fluid affects thermal performance, apparatus size and economic feasibility of the cycle. Beyond only affecting characteristics of the system, unrealistic preconditions for the working fluid of the system may force the designers in using environmentally harmful mixtures and force the outcome beyond boundaries of environmental regulations. There has been numerous research and scrutiny on various working fluids, but due to the unstructured and unorganized orientation of previous studies, there is no comprehensive insight on relationship of different characteristics of the working fluid and overall performance of the system. This work intends to develop a numerical evaluation approach, using a modified stochastic optimization algorithm as a search engine. The paper further explores and questions the existing criteria for optimization of working fluids in Rankine cycle. Rather than just finding the optimum fluids for different cases, this study aims to investigate the behavior of different fluids around optimum points and see the bigger picture to find trends in different fluid behaviors. Analysis of results show two main behaviors among the fluids in subcritical cycles. In the first type behavior, the optimum points for output work, thermal efficiency and exergy efficiency lie very close to each other, while in second type, these optimum points are not close. There is a transition from first type behavior to second type for a ratio of critical temperature around 0.9 of heat source inlet temperature. These results also show the importance of key performance parameter determination.

Keywords: Rankine Cycle, Low Temperature, Cycle Analysis, Power Cycle, Waste Heat Recovery

1. INTRODUCTION

Today, energy production hangs on a cliff. On one side, ever-increasing demands for more and easily accessed energy drives the race to use more efficient materials and methods in design and operation of energy production systems. On the other hand, real and immediate impacts of hazardous methods of power production on our habitual environment severely limits the prospect of simplistic, cheap but dirty energy. To rescue, comes novel and much more complicated methods such as waste heat utilization, which could provide solutions to both power demands and environmental concerns. Low temperature Rankine cycle is a prominent example of such solutions providing a reliable and easy accessed power from low temperature heat sources. This cycle is commonly known as Organic Rankine Cycle (ORC) in the literature. Although baring the name organic in its title, ORCs have been utilized with inorganic fluids such as CO_2 and NH_3 as the working fluid of the system (Tchanche et al. 2011). Therefore, to avoid miswording, RC (Rankine Cycle) term will be used in this paper. Different configurations of the cycle featuring internal heat exchanger also have been introduced in different studies. Complex modularity of the RC combined with current low efficiency of these systems form a complex optimization problem, which affects the commercial stand and viability of use of RCs in general. The combination of modularity and performance considerations could limit the scope of optimization studies in the field. Majority of the previous studies in the field have focused on examining one type or one or multiple specific working fluids and finding optimum regimes for each one. Kang et al. (Kang et al. 2015) and Muhsen Hebka et al. (Habka and Ajib 2015) are examples of valuable efforts that compared a series of working fluids of the same kind. The first example examined mixtures of hydrocarbons with artificial refrigerants the latter investigated zeotropic mixtures with specific source of geothermal waters. Both mentioned studies focused on thermal efficiency of using a working fluid and utilizing exergy analysis to obtain the working fluid with the highest efficiency among the sample space. Yet it didn't mention the full spectrum of parameters affecting the cycle and most importantly considerations regarding environmental impacts of the fluid. In this paper, we seek to examine fluids and predefined mixtures in the REFPROP 9.1 database for mapping their performance in RC with specific conditions and limitations. These constraints try to be as broad as possible to cover the general cycles. In designing the optimum RC for a special application, many parameters affect the final solution. Some parameters are related to the designer's objective, including thermal and second law efficiency, output work and economic costs. Not all these parameters could be optimized at the same time. Therefore, there is always a trade-off between the parameters. Recent introduction of stochastic methods for optimization of RCs has made it possible to apply multiple objectives and case-specific constraints to the optimization case (Sadeghi et al. 2016). One prominent example of such studies in the field is on multi objective optimization of RCs using zeotropic mixtures. The mentioned study, also focused on thermal efficiency of working fluid in the cycle rather than the broad picture of the cycle, such the maximum pressure ratio, minimum pinch point, type of expander, maximum ambient temperature.

In this article we first would explore potential of genetic Algorithm as a stochastic method to provide the global optimized points and then broadly quantify the existing criteria for optimization of working fluids in RCs to investigate viability of stochastic methods for optimum design. Further, rather than just finding the optimum fluids for different heat source temperatures and limitations, the idea is to see the bigger picture and analyze the behavior of different fluids, rather than just seeing a single optimum point. It is also an aim to, instead of introducing one fluid with one optimum point, study their behavior around the optimum points and the behavior of other performance parameters as well.

2. MODELLING AND METHODOLOGY

2.1 Mathematical Model

A basic Rankine cycle includes: pump, evaporator, expander and condenser. In a recuperative cycle, a recuperator option is also included in the cycle which is an internal heat exchanger to take advantage of superheated vapor at expander outlet and use it to preheat the fluid before entering the evaporator. Both subcritical and transcritical cycles are studied in this project. In the transcritical cycle, the evaporator is becoming a gas heater. Fig. 1 shows the layout for both basic and recuperative cycle as well as T-s diagram for subcritical and transcritical cycles for the basic layout configuration.

Energy and exergy balance equations in steady state conditions were used for cycle analysis (Lecompte et al. 2014). The important thermal parameters studied in this paper were: output work, thermal efficiency, exergy efficiency and internal exergy efficiency.

Thermal efficiency, also known as first law efficiency is defined as:

$$\eta_{\mathrm{I}} = \frac{\dot{W}_{\mathrm{net}}}{\dot{Q}_{\mathrm{evap.}}} \tag{1}$$

Where $\dot{W}_{\mathrm{net}}$ is output power and $\dot{Q}_{\mathrm{evap.}}$ is heat rate into evaporator both in kW.

However, for exergy efficiency two different definitions are found in the literature. One definition is based on exergy input to the system, while the other definition is based on the extracted exergy from the heat source. Lecompte et al. defines exergy efficiency (second law efficiency) as output work over exergy inlet to the system (Lecompte et al. 2014), (Fallah et al. 2016):

$$\eta_{\mathrm{II}} = \frac{\dot{W}_{\mathrm{net}}}{\dot{E}_{\mathrm{h,in}}} \tag{2}$$

Where, $\dot{E}_{\mathrm{h,in}}$ is the inlet exergy of heat source (hot side) in kW. Then, second law efficiency is further decomposed into a second law external efficiency ($\eta_{\mathrm{II,ext}}$) and a second law internal efficiency ($\eta_{\mathrm{II,int}}$).

$$\eta_{\mathrm{II}} = \eta_{\mathrm{II,ext}} \times \eta_{\mathrm{II,int}} \tag{3}$$

Where second law external efficiency is related to the exergy input to the cycle:

$$\eta_{\mathrm{II,ext}} = \frac{\Delta\dot{E}_{\mathrm{h}}}{\dot{E}_{\mathrm{h,in}}} \tag{4}$$

And second law internal efficiency is related to irreversibilities in the RC:

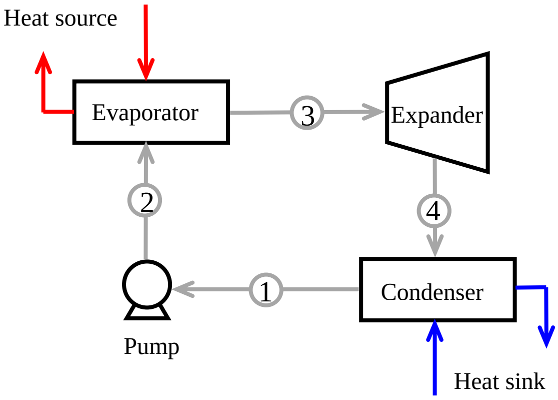

Fig. 1a: cycle layout for basic configuration

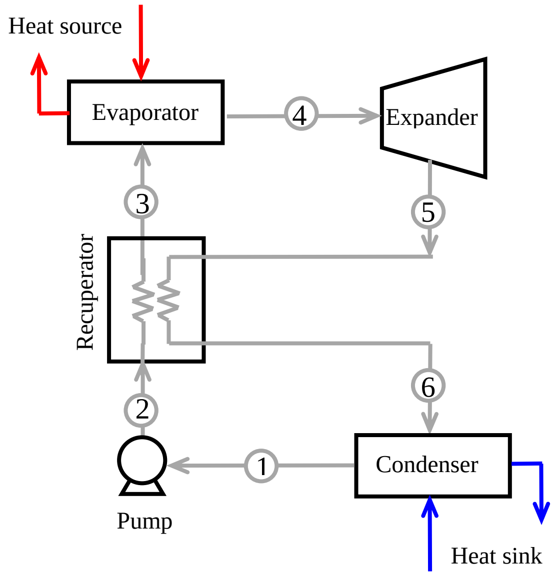

Fig. 1b: cycle layout for recuperative configuration

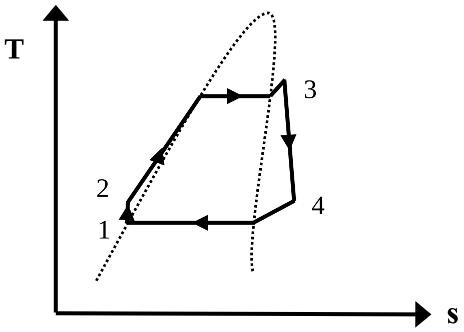

Fig. 1c: T-s diagram for subcritical cycle (basic config.)

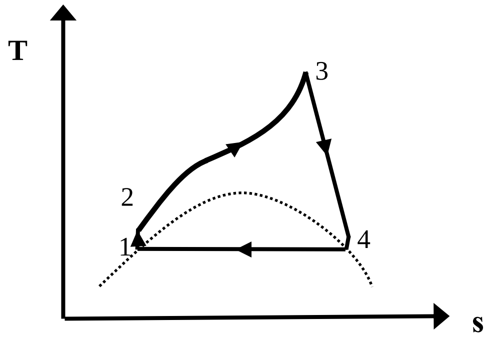

Fig. 1d: T-s diagram for transcritical cycle (basic config.)

Figure 1 Rankine Cycle layout and T-s diagram

$$\eta_{II,int} = \frac{\dot{W}_{net}}{\Delta\dot{E}_h} \tag{5}$$

Where $\Delta\dot{E}_h$ is the extracted exergy from heat source in kW. Galindo et al define exergy efficiency as Eq. 5, taking extracted exergy into account (Galindo et al. 2016). In cases where the fuel is burnt to provide the heat input to the system, assuming there is no heat loss to the ambient, these two terms would be the same. However, in cases with heat extraction as in waste heat recovery and bottoming cycles, these two different definitions imply different meanings. Many publications refer to exergy efficiency as the objective function of their optimization which makes this definition very important. Therefore, in this paper both terms were studied to observe and analyze their behaviors and differences and check the consequences of optimization based on different definitions.

It should be noted that in Eq. 2, with the same heat source inlet temperature, the behavior of exergy efficiency for different fluids would be the same as the behavior of output work.

2.2 Fluid Screening

As a first step, pure fluids in the REFPROP 9.1 database were screened for optimization. Preliminary criteria were applied on the list of fluids to choose the suitable fluids for optimization and testing. These criteria include:

- Natural fluids: Only natural fluids were considered in this investigation since synthetic fluids were not within the interest of the project due to environmental concerns. Consequently, zero ODP (Ozone Depletion Potential) and low GWP (Global Warming Potential) were preselected for optimization.
- Critical temperature: Fluids with critical temperature higher than ambient temperature were selected to make condensation possible. Therefore, methane and ethylene were omitted from the list of fluids.

- Melting point: The selected fluids should have lower melting point compared to the coldest ambient temperature during the year to avoid liquid freezing (Papadopoulos et al. 2010).
- Condensing pressure: Sub atmospheric condensation pressure has been avoided due to the possibility of air suction to the system.

2.3 Optimization Algorithm

Stochastic optimization methods provide a unique possibility to search a vast area of possibilities before converging on a specific operation point with a global optimum value. This enables the designer to optimally choose a point compromise between multiple, often counter-acting, criteria. Genetic Algorithm (GA) has two characteristics that broaden the mentioned scope. In each iteration, the genetic algorithm would provide multiple random sets of target parameters which are both results of selective survival of optimum values of previous iterations and random mutations. By choosing high rate of mutations and dense populations in each iteration, the designer can reach broader scope of search. In this study, in addition to choosing high number of population members (100) and high mutation rate (0.06), the default genetic algorithm was also modified to act as a search tool and provide a terrain of optimum choices to evaluate against other criteria. In addition to using GA to find the optimum points, the effect of changing variables within a range was also studied to see the behavior around the optimum points

In this section, various hypotheses and assumptions in the optimization are presented: All the analyses are done in steady state and per 1 (kg/s) heat source air flow. Potential, kinetic energy and friction losses are neglected. MATLAB genetic algorithm is used together with REFPROP 9.1 database. The option of using recuperator is also considered. Expander inlet is considered saturated to superheated vapor. To avoid air suction to the system, the minimum condensing pressure has been set to atmospheric pressure. In case of working fluid leakage to the atmosphere, it is possible to recharge the system. However, in case of air suction, it will not be possible to take out the air from the system. To avoid liquid droplets, wet expansion has been avoided and the expander outlet point has been set in superheated region. Pump and expander were modelled with fixed isentropic efficiency and pinch point analysis was employed for heat exchanger analysis. The optimizations are based on simulations both without constraint on heat source outlet temperature and by setting a minimum of 100 °C. The results will be presented for both cases.

Based on the cycle layout and heat source outlet temperature limitation, different cases are defined. Table 1 shows case definition for tests.

Table 1- Case definition

Case #	Cycle configuration	Limitation on heat source outlet temperature
Case (1)	Basic	No
Case (2)	Basic	Yes (100 °C)
Case (3)	Recuperative	No
Case (4)	Recuperative	Yes (100 °C)

One important issue in the RC optimization, is the objective function. We want to know what output parameter to maximize or minimize. This is a very complicated question and not easy to answer. Other than thermodynamic parameters, cost related parameters are also very important and should be considered. However, in this phase of the project, our focus is on thermodynamic optimization. Different papers use different parameters for optimization. Possible parameters could be thermal efficiency, output work, exergy efficiency and destructed exergy. Some other parameters could refer to the size of the system like heat exchanger area and turbine size parameters. Regarding exergy efficiency, the wording could be confusing as explained in section 2.1. In this project, output work was used as the main objective function, while the behavior of other thermal parameters was also studied.

Variables in this optimization were evaporating pressure and expander inlet temperature. Condensing pressure and temperature were set to have a minimum of 101.3 kPa and 25 °C respectively. Expander inlet temperature was set to vary in saturated vapor and superheated region. Table 2 shows the fixed parameters for optimization.

Table 2- Hypotheses for modelling

Parameter	Value
Heat source	Air with inlet temperature 150, 200, 250 °C
Heat sink	River water with inlet temperature 10 °C
Ambient temperature and pressure	10 °C, 101.325 kPa
Pump isentropic efficiency	0.9

Expander isentropic efficiency	0.8
Minimum condensing temperature and pressure	25 °C, 101.325 kPa
Pinch point in evaporator and condenser	10 °C
Pinch point in recuperator (if included)	10 °C

3. RESULTS

3.1 Fluid behavior in subcritical cycle

Analysis of results in the subcritical region shows two main behaviors, shown in Fig. 2. In type A behavior (Fig. 2a), the optimum point is close to the end of pressure range i.e. critical pressure while in type B (Fig. 2b), the optimum point lies in the middle of the pressure range. This behavior analysis is based on the evaporator pressure location. These contours do not necessarily mean that the optimum expander inlet temperature is saturated vapor. These are just examples, and the optimum temperature could be anywhere in the saturated to superheated region based on the case and heat source temperature.

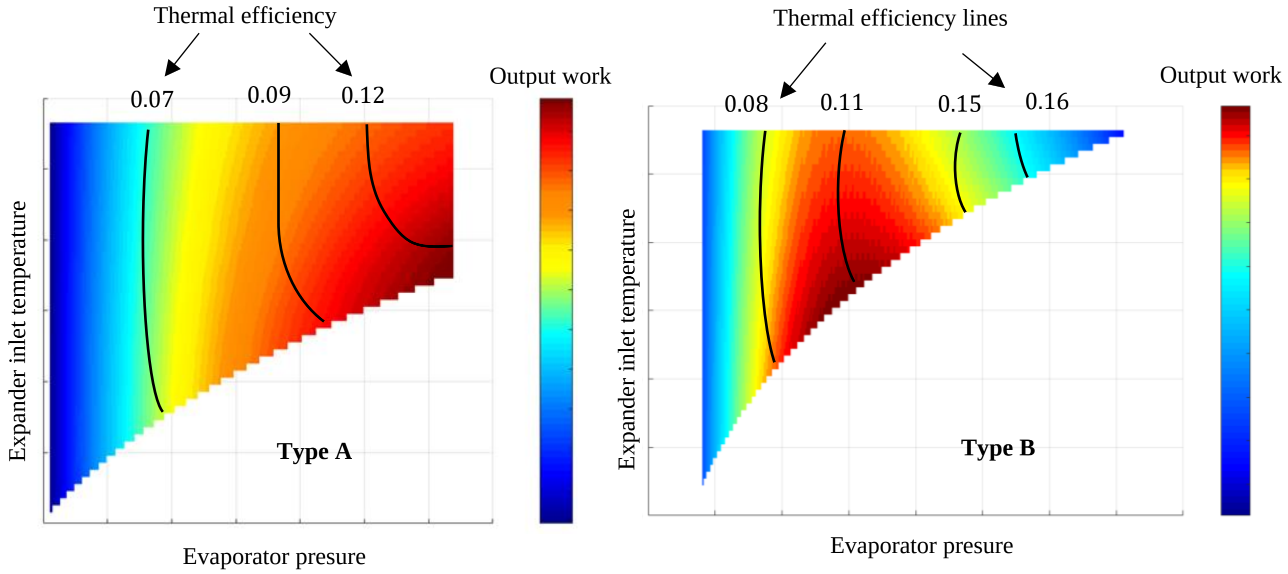

Figure 2 Output work and thermal efficiency contours, left: (2a) type A behavior, right: (2b) type B behavior

The importance of this behavior distinction is not just the location of optimum points, but also the behavior of thermal efficiency and internal exergy efficiency. In both type A and B, both thermal efficiency and internal exergy efficiency have increasing trends with increasing evaporator pressure. Therefore, in type B, the optimum work point is far from the optimum thermal efficiency and internal exergy efficiency point. However, in type B fluids, these three optimum points lie close to each other and in case the designer wants to move away from critical point, it is possible to have three optimum points close to each other. A trend was observed for transition from type A to B with regards to critical temperature. It was observed that, this type of transition depends on critical temperature of the fluid (T_c) and heat source inlet temperature ($T_{h,in}$). Table 3 shows the transition point for different heat source temperatures. Fluids having lower critical temperature, behave as type A and fluids with higher critical temperature behave as type B. It could be concluded that the transition point occurs for a ratio around 0.9 of heat source temperature (temperatures in degree Kelvin).

Table 3- Transient analysis from type A to type B behavior

Heat source (°C)	**Fluid**	**Type**	T_c **(°C)**	$\frac{T_c}{T_{h,in}}$ **(K/K)**
150	carbonyl sulfide	A	105	0.89
	cyclopropane	B	125	0.94
200	cis-butene	A	162	0.94
	isopentane	B	187	0.97
250	pentane	A	196	0.89
	isohexane	B	224	0.95

10.18462/iir.gl.2018.1401

There are two types of constraints that could be applied on the model: one; the types of constraints which may disqualify some data point on the behavior graph of the fluid. These constraints include: no wet expansion, limitation on heat source or heat sink outlet temperature. One the other hand, some practical constraints may change overall behavior of the graph. This behavior trend could be maintained for first type constraints. In type A behavior, the total increasing trend could be maintained. However, in type B, it depends which part of the graph is disqualified. Disqualified points below the optimum pressure have different effects on the shape, compared to disqualified points above optimum pressure. This conclusion was derived comparing cases 1 and 3, and 2 and 4.

3.2 Effect of condensing temperature

Condensing temperature is a very important parameter that affects output work. In this project, fluids were set to have minimum condensing temperature of 25 °C and a minimum pressure of 101.3 kPa. Fluids having higher critical temperature than 200 °C, results in having higher condensing temperatures due to the pressure limit. Therefore, by increasing this temperature, the output work decreases. The span between condensing temperature and critical temperature is also important in subcritical cycles. Lower condensing temperatures while having very low critical temperature also results in low output work in subcritical cycles.

3.3 Case discussion

Analysis of results show that adding a recuperator does not increase work output where there is no limitation for heat source outlet temperature (comparing case 1 and 3). It only increases thermal efficiency due to increased heat source outlet temperature. This could, however, be beneficial for the cases with limitation on heat source outlet temperature. In that case, both output work and consequently, thermal efficiency are increased by adding a recuperator to the cycle (comparing case 2 and 4).
Therefore, the two main cases become case 1 and case 4: case 1 for cases without limitation and case 4 for cases with limitation and recuperator option.
Fig. 3a shows the results of output work optimization for different heat source temperatures in subcritical case 1 optimization. As a result of sharper increase of output work for higher input temperatures, the optimum range of the graphs decreased significantly. This notes the importance of precise optimization in higher input temperatures and more constraints on the type of the working fluid in high input temperature designs. Furthermore, optimum critical temperature decreases as the input temperature increases forcing the system to operate in type A region. For lower heat source temperatures, the optimum points lie both in type A and type B region. As the heat source temperature increases, these optimum points move towards region A.

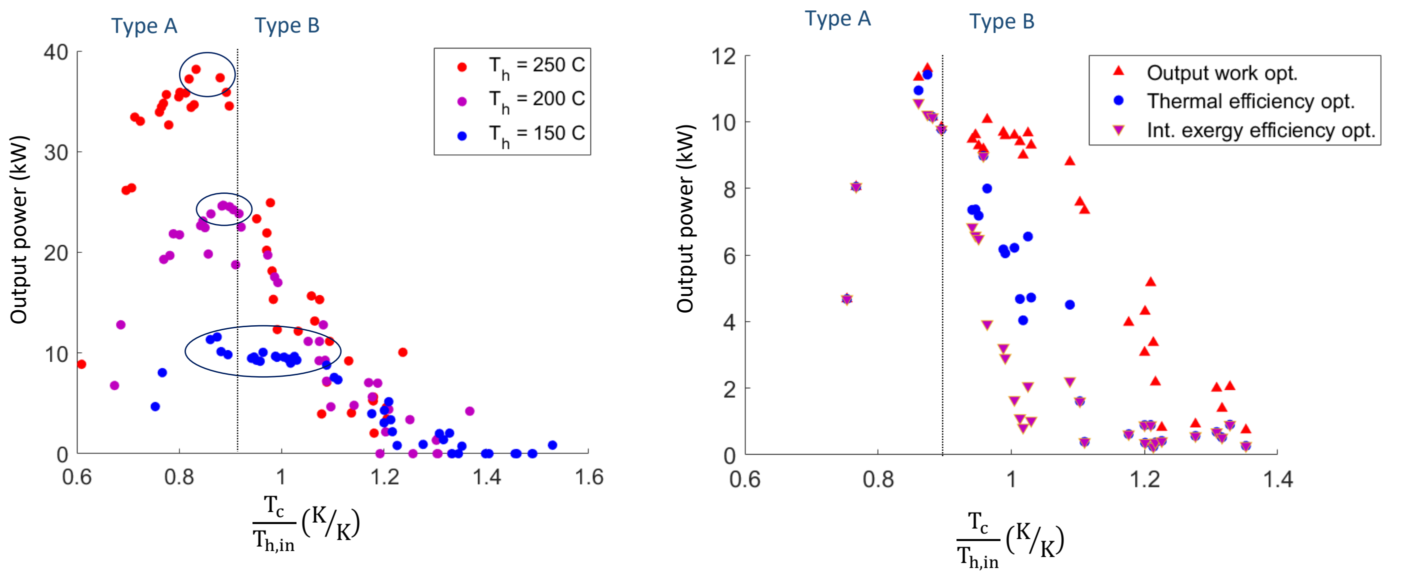

Figure 3 left: (3a) Output power for different heat source temperature in subcritical case 1, right: (3b) Effect of different optimization objectives on output work in subcritical case 1 with heat source of 150 °C

Comparing the results of subcritical case 1 and case 4 shows that applying recuperator with constraint on minimum heat source outlet temperature, does not change the optimum point trends in Fig. 3a.

Clearly, the optimum points in transcritical cycles are higher compared to the same condition optimum subcritical cycle. This boost is more in very low critical temperature fluids where they do not have opportunity to generate more power in subcritical cycle. One important inorganic fluid in transcritical cycle is CO_2. For lower heat source temperatures, the output work difference between optimum point for CO_2 and other organic fluids is low (CO_2 producing less power). As the heat source temperature is increased, this difference becomes higher.

3.4 Effect of objective function

Fig. 3b shows the effect of different optimization objectives for subcritical case 1, with heat source temperature of 150 °C. In this graph, output work is plotted for three different optimization objectives: maximum output power, maximum thermal efficiency and maximum internal exergy efficiency. The results indicate that in type A behavior ($T_c/\mathrm{T_{h,in}} < 0.9$), the optimum points of the three mentioned optimizations lie very close to each other. However, in type B region, by increasing critical temperature, the graphs separate from each other. Internal exergy efficiency optimization is closer to output work optimization compared to thermal efficiency optimization. This issue highlights the importance of proper optimization model in region B behavior which are specially in the optimum point list of lower temperature heat sources.
Using efficiency as objective function could be very tricky. High efficiency point could be very far from high output power point, unless using exergy efficiency defined as Eq. 2. It is probable that very little amount of heat is extracted, but high percentage of it, is converted to power which results in high efficiency but very low and unfeasible output power.

3.5 List of working fluids

In this section, a list of natural working fluids for both subcritical and transcritical cycles for case 1 is presented in Table 4 to have more insight to the trends and differences between different fluids, as discussed in above sections.
It should be noted that this list is just to show the trend of optimization results for different fluids and as an example, sulfur dioxide is not considered a safe refrigerant for working fluid suggestion.

Table 4- Working fluid list for both subcritical and transcritical cycles, case 1 with heat source temperature of 250 °C

$\mathbf{T_{h,in} = 250\ °C}$			**Subcritical cycle**			**Transcritical cycle**		
Fluid	$\mathbf{T_c}$ **(°C)**	$\mathbf{T_c/T_{h,in}\ \left(\frac{K}{K}\right)}$	$\mathbf{W_{net}}$ **(kW)**	$\mathbf{\eta_I}$	$\mathbf{\eta_{II,int}}$	$\mathbf{W_{net}}$ **(kW)**	$\mathbf{\eta_I}$	$\mathbf{\eta_{II,int}}$
carbon dioxide	31.0	0.581	-	-	-	30.1	0.165	0.489
ethane	32.2	0.583	-	-	-	27.8	0.153	0.451
propylene	91.1	0.696	26.2	0.121	0.395	36.7	0.181	0.566
propane	96.7	0.707	26.4	0.122	0.398	35.9	0.174	0.551
carbonyl sulfide	105.6	0.724	33.0	0.164	0.489	38.7	0.198	0.607
cyclopropane	125.1	0.761	33.9	0.161	0.502	38.4	0.193	0.597
dimethyl ether	127.2	0.765	34.4	0.162	0.510	39.2	0.190	0.601
propyne	129.2	0.769	34.8	0.169	0.515	38.8	0.198	0.607
isobutane	134.6	0.780	32.7	0.151	0.484	37.1	0.177	0.565
isobutene	144.9	0.799	35.4	0.164	0.525	38.8	0.185	0.591
butene	146.1	0.801	35.9	0.167	0.532	39.0	0.187	0.596
butane	151.9	0.813	35.8	0.166	0.530	38.5	0.182	0.585
trans-butene	155.4	0.819	37.2	0.174	0.551	39.6	0.189	0.604
sulfur dioxide	157.4	0.823	34.4	0.206	0.509	-	-	-
neopentane	160.5	0.829	34.7	0.160	0.513	36.7	0.172	0.555
cis-butene	162.6	0.833	38.2	0.181	0.565	39.9	0.192	0.610
isopentane	187.2	0.880	37.3	0.177	0.553	38.0	0.181	0.579
diethyl ether	193.5	0.892	35.9	0.176	0.532	-	-	-
pentane	196.5	0.898	34.5	0.174	0.511	35.4	0.176	0.548

10.18462/iir.gl.2018.1401

4. CONCLUSIONS

An algorithm based on stochastic optimization method was established. A wide range of natural working fluids was investigated with this algorithm to find the optimum output work points for different heat source temperatures. This investigation revealed that optimization of the cycle in limited range of variables does not result in achieving globally optimum configuration with regards to all thermal performance parameters. We proposed certain measures to achieve the optimum system. However, the complexity of more advanced systems, for example systems working with zeotropic mixtures, requires more advanced and capable numerical methods to achieve the optimum design. As we present one such method, the mentioned limitations are a reminder that these methods such as deep learning and data analysis methods should have the broadest possible scope even amid existence of discontinuities and abnormalities in the variable selection.

ACKNOWLEGEMENT

This publication has been funded by HighEFF - Centre for an Energy Efficient and Competitive Industry for the Future, an 8-year Research Centre under the FME-scheme (Centre for Environment-friendly Energy Research, 257632/E20). The authors gratefully acknowledge the financial support from the Research Council of Norway and user partners of HighEFF.

REFERENCES

Fallah, M., S. Mohammad, S. Mahmoudi, M. Yari, and R.Akbarpour Ghiasi. 2016. "Advanced Exergy Analysis of the Kalina Cycle Applied for Low Temperature Enhanced Geothermal System." *ENERGY CONVERSION AND MANAGEMENT* 108:190–201.

Galindo, J., S. Ruiz, V. Dolz, and L. Royo-Pascual. 2016. "Advanced Exergy Analysis for a Bottoming Organic Rankine Cycle Coupled to an Internal Combustion Engine."

Habka, Muhsen and Salman Ajib. 2015. "Evaluation of Mixtures Performances in Organic Rankine Cycle When Utilizing the Geothermal Water with and without Cogeneration." *Applied Energy* 154:567–76.

Kang, Zhenhua, Jialing Zhu, Xinli Lu, Tailu Li, and Xiujie Wu. 2015. "Parametric Optimization and Performance Analysis of Zeotropic Mixtures for an Organic Rankine Cycle Driven by Low-Medium Temperature Geothermal Fluids." *Applied Thermal Engineering* 89:323–31.

Lecompte, S., B. Ameel, D. Ziviani, M. van den Broek, and M. De Paepe. 2014. "Exergy Analysis of Zeotropic Mixtures as Working Fluids in Organic Rankine Cycles." *Energy Conversion and Management* 85:727–39.

Sadeghi, Mohsen, Arash Nemati, Alireza ghavimi, and Mortaza Yari. 2016. "Thermodynamic Analysis and Multi-Objective Optimization of Various ORC (Organic Rankine Cycle) Configurations Using Zeotropic Mixtures." *Energy* 109:791–802.

Tchanche, Bertrand F., Gr. Lambrinos, A. Frangoudakis, and G. Papadakis. 2011. "Low-Grade Heat Conversion into Power Using Organic Rankine Cycles – A Review of Various Applications." *Renewable and Sustainable Energy Reviews* 15(8):3963–79.