David Tomás Sánchez Martínez
Lourdes García Rodríguez
(coordinadores)

Proceedings of the 7th International Seminar on ORC Power Systems

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ORC

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SELECTION OF SUITABLE WORKING FLUID AND STORAGE MATERIAL FOR ORC COUPLED WITH THERMAL ENERGY STORAGE

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ABSTRACT

Some low-temperature energy sources (e.g., waste or solar heat) tend to be intermittent, and the heat supply from such sources may fluctuate over time. This kind of heat could be utilized using organic Rankine cycle (ORC) to generate electricity. Moreover, the increase in their reliability may be possible thanks to the application of thermal energy storage (TES), in which surplus thermal energy may be accumulated in the storage material. This energy can then be used in these periods of time when the heat source is not available or its output is limited. In this way, energy generation may be levelled. In some cases, a wide range of operating conditions and a variety of working fluids that are used in ORC systems mean that the choice of TES material may be difficult, since there are several types of TES materials, and each analysed case can give different material selections. Because of that, optimizing TES that is connected to the ORC system can be an interesting scientific challenge. Therefore, the aim of this study is to present the selection of proper working fluid-TES material pairs for different working conditions applied to a model of the ORC system coupled with TES. Various configurations of the ORC-TES system were investigated, taking into account differences between latent and sensible TES, and both for simple and recuperated cycles. The results obtained show that the combination of ORC with TES is promising for application in intermittent and fluctuating heat sources.

1. INTRODUCTION

Some of the energy sources that are in use have intermittent characteristics. This means that their parameters, like temperature and flow rate, are not constant and fluctuate over time. These energy sources include renewable energy sources, such as solar energy, as well as recovered waste heat from industrial processes or vehicles. The amplitude and duration of these changes vary, from relatively slow changes in the day-night cycle related to solar radiation to very fast changes in the internal combustion engines applied in vehicles, which may be caused by road conditions. To utilize this kind of intermittent and fluctuating heat source, an organic Rankine cycle (ORC) might be one of the promising technologies since it offers a wider range of operating temperatures. Moreover, the ORC system would typically have a certain point of maximum efficiency (Ahmed *et al*., 2021; Ahmed and Imre, 2023; Daniarta *et al*., 2021) for which it was designed. As the conditions shift away from the design point, the efficiency deteriorates. That means that if it harvests energy from fluctuating energy sources, it may operate in unfavourable operating conditions for a significant period of time.

In designing and operating the ORC, efficiency is not the only concern. If the operating conditions move sufficiently from the allowed operating range, it may be necessary to turn off the system from operation to prevent damage. This may be caused by the too high temperature of the heat source, which in turn could cause excess pressure of the working fluid, or its thermal decomposition. Having a relatively low temperature of the heat source might potentially lead to partial evaporation of the working fluid and then it might lead to increase droplets in the expander. In particular, for a turbine, operating in two-phase conditions is often avoided as it might result in expander damage. As an alternative, a promising way of levelling intermittent energy sources is by storing their thermal energy in the storage material. Thermal energy storages (TES), also called heat storages, vary in size, thermal power, operating temperature and type of storage material used. Different modes of operation are possible for TES. A smaller thermal energy storage would be sufficient to provide buffering of fluctuations, reducing peaks and valleys, while a larger thermal energy storage could be used to shift energy production to the time periods characterized by the highest energy demand (Daniarta and Kolasiński, 2021). With fluctuations reduced, the system can work near the design point for longer time periods, and in some cases, the size of the expander can be reduced, since it does not have to handle periodically increased input (Li et al., 2021).

Depending on the type of material used for thermal energy storage, thermal energy storage can be classified into:

- Sensible thermal energy storage (STES)—in which thermal energy is stored by changing the temperature of the storage material, such as hot water, sand, or rocks. As more energy is stored in the STES, the temperature of the material increases.
- Latent heat thermal energy storage (LTES)—in which thermal energy is absorbed and released by using phase change of the material (called phase change material - PCM), such as kinds of paraffin. The storage density of LTES is higher than the STES.
- Thermochemical energy storage (TCES)—in which reversible chemical reactions are used to provide even higher storage density than LTES. One of the reactions used is water adsorption in zeolites.

These technologies differ not only in operating principles but also in storage capacity, power, storage period, the time needed to charge and discharge them, efficiency and cost (Sarbu and Sebarchievici, 2018). 324

A recent review reported that TES could be connected with ORC systems for different purposes, either directly or indirectly (Daniarta et al., 2023). In a direct system, the working fluid flows through TES, whereas in an indirect, an additional medium is used to transfer the heat. Only a few modeling simulation and experimental investigation were found in the study of literature. A prior study (Kolasiński and Daniarta, 2021) reported simulation results of sizing TES for the ORC system. However, only simple ORC with selected TES material was examined. Therefore, to extend the study, in this paper, a modelling analysis was carried out for ORC systems powered by thermal energy storage considering recuperated systems, which can be the state of the art of this paper. A comparison between different working fluids and storage materials was described. Both sensible and latent heat storage materials were analysed. Their efficiency, and thermal energy storage size (i.e., the amount of the storage material required) were evaluated. For simplification, only direct systems, without intermediate working fluids, were considered.

2. MODEL OF THE SYSTEM

Two types of ORC systems, which are simple and recuperated ORCs, are considered in the present analysis. The design of both systems is presented in Figure 1. The simple system, which is composed of four main components: evaporator (which for the purpose of this analysis can be subdivided into preheater, evaporator and in some cases superheater), expander, condenser (which for the purpose of this analysis can be subdivided into precooler and condenser), and pump.

Furthermore, recuperated ORC as the second type of the considered system in this analysis, has an additional component (see Figure 1) in which an internal heat exchanger is used to recover heat from the working fluid flowing from the outlet of the expander and use it to heat up the liquid working fluid at the inlet to the evaporator. This configuration is more commonly applied for ORC systems using complex (dry) working fluids, because of the higher thermal power at the outlet of the expander (Astolfi, 2017).

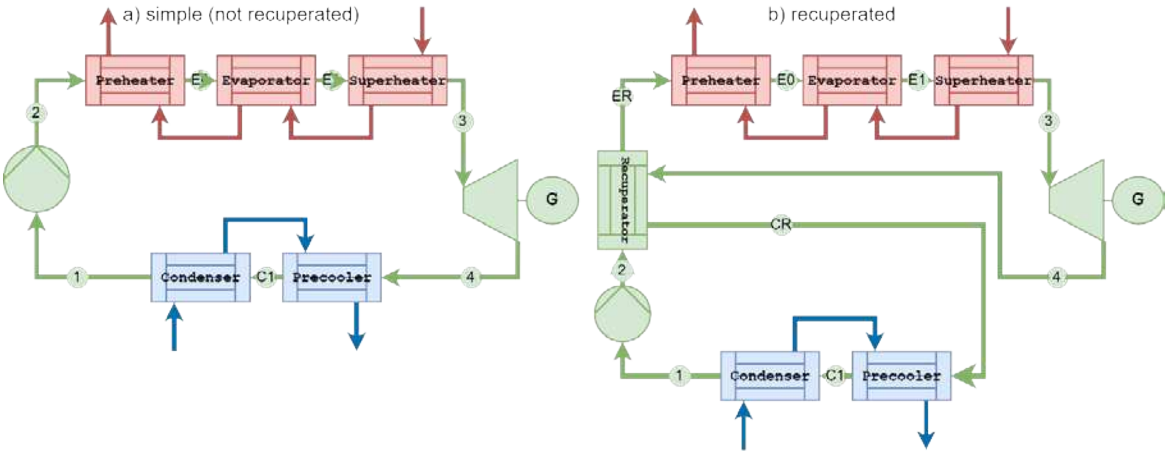

Figure 1: Design of a) simple and b) recuperated ORCs

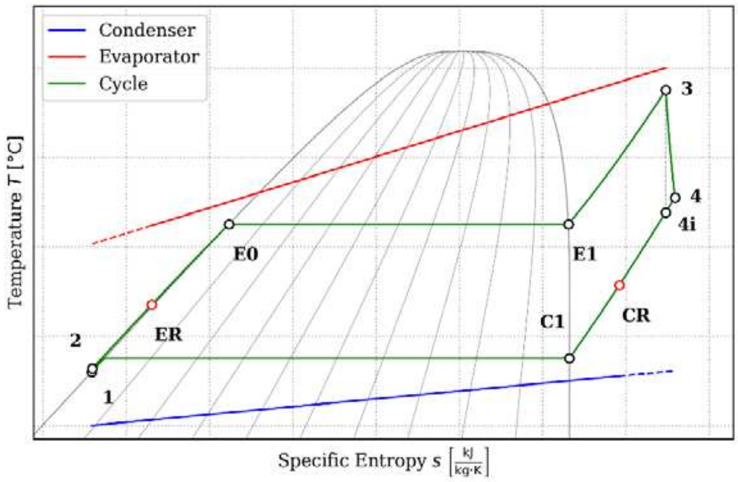

Figure 2: Simple and recuperated ORC on T-s diagram

Cycle diagrams for both of them are similar in the temperature-entropy diagram shown in Figure 2, with the exception of two additional characteristic state points for the recuperated system.

In this study, the modeling simulation was developed using several assumptions, as follows:

- Isentropic efficiencies of the expander and pump (η_{exp} and η_P) are constant and equal to 0.8 and 0.7 respectively,
- There is no superheating (i.e., thermodynamic properties of working fluid in point E1 and 3 are the same),
- Subcooling temperature (ΔT_{sub}) is constant, and equal to 3,
- Temperature differences between mediums (pinch point temperature) (ΔT) are constant and equal to 5,
- Condensation temperature (T_C) is constant and equal to 30 °C,
- Heat losses to the environment, as well as pressure drops in heat exchangers and pipelines, are assumed to be negligible,
- Heat is supplied to the cycle directly from the TES,

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- In recuperated cycle, the ΔT_{low} (temperature difference between point 2 and CR, as described in Equation (4)) is set for half of the temperature difference between C1 and 4.

Several different working fluids with low global warming potential (GWP) and low ozone depletion potential (ODP) were selected in this study due to limited negative environmental effects. For instance, some HFOs and hydrocarbons are chosen including Novec649, R1233zd, R1234yf, R1234ze(E), R1234ze(Z), R1243zf, Neopentane, Isobutane, Isobutene, Isopentane, n-Pentane and n-Propane. The thermal properties of the working fluids were taken from the CoolProp library (Bell et al., 2014). Moreover, various TES materials and their properties were taken from the articles (Daniarta et al., 2022; Kolasiński and Daniarta, 2021) such as Monel, stainless steel 446, sandstone, granite, chrome brick, concrete, chamotte brick, silicon carbide, magnesite brick and rapeseed, soybean, sunflower, cotton, and jatropha oils. Variations of specific heat capacity of the selected sensible TES materials vs. temperature based on that data are depicted in Figure 3.

In calculations, for latent TES, it is assumed that the discharge process happens entirely in isothermal conditions during the phase change. Moreover, for sensible TES, the discharge is proceeded in non-isothermal conditions. In further analysis, it was assumed that the starting temperature is 20 °C lower than the critical temperature of the working fluid, or equal to the maximum temperature of the TES material (as presented in Figure 3), or 180 °C, whichever is smaller. Under these conditions, the highest calculated pressure was 27 bars (n-Propane), which can be handled using commercially available heat exchangers. Discharge is assumed to continue as long as the expansion ratio (i.e., pressure ratio between expanders inlet and outlet) is equal at least to 2 and the temperature of storage material is at least 50 °C.

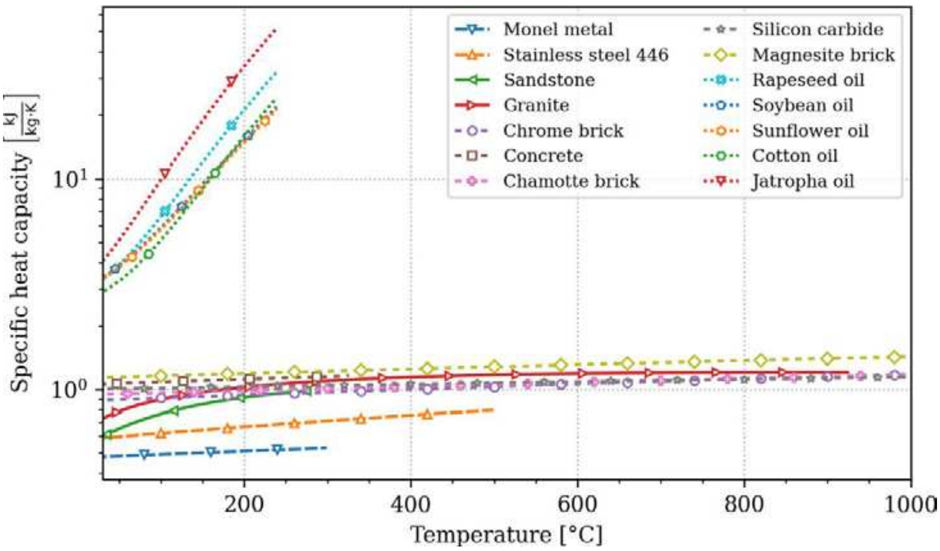

Figure 3: Variation of specific heat capacity vs. temperature of different sensible TES materials, where the data is taken from (Kolasiński and Daniarta, 2021)

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3. MATHEMATICAL MODEL AND RESULTS

Based on the above-mentioned assumptions, the thermal properties of the working fluid in characteristic points of the system can be calculated. Using them it is possible to determine other assessment parameters, such as heat input, the net output power and the net efficiency of the ORC system expressed in Equations (1) – (3).

$$\dot{Q}_{in} = \dot{m}_f \cdot \Delta h_{in} = \dot{m}_f \cdot (h_3 - h_2) \tag{1}$$

$$W_{net} = W_{exp} - W_{pump} = \dot{m}_f \cdot \left(\Delta h_{exp} - \Delta h_{pump}\right) = \dot{m}_f \cdot [(h_3 - h_4) - (h_2 - h_1)] \tag{2}$$

$$\eta_{net} = \frac{W_{net}}{\dot{Q}_{in}} \tag{3}$$

Recuperated ORC can be described in a way similar to the simple ORC, while two additional points can be determined if a parameter ΔT_{low} is introduced by Equation (4). This parameter describes the low-end temperature difference, that is, between the points CR (gas flowing out from the recuperator into the condenser) and 2 (liquid flowing out from the pump into the recuperator).

$$T_{CR} = T_2 + \Delta T_{low} \tag{4}$$

The specific enthalpy of the working fluid for the second of the added points can be calculated from the energy balance of the heat exchanger that is described in Equation (5).

$$\dot{m}_F \cdot (h_4 - h_{CR}) = \dot{m}_f (h_{ER} - h_2) \tag{5}$$

Furthermore, the net power of the ORC system and efficiency can be calculated in the same way as the simple ORC using Equations (2) and (3), however, because of the introduction of the recuperator, $\dot{Q}_{in}$ is smaller, and efficiency is higher (see, Equation (6)).

$$\dot{Q}_{in} = \dot{m}_f \cdot (h_3 - h_{ER}) \tag{6}$$

The amount of heat that can be stored in TES depends on the mass of the TES material, the temperature difference between charged and discharged conditions, and the specific heat capacity of the TES material, as given in Equation (7).

$$Q_{TES} = c_p(T_{sm})|_{T_{charged}}^{T_{discharged}} \cdot \left(T_{charged} - T_{discharged}\right) \cdot m_{sm} \tag{7}$$

As the temperature of the thermal energy storage material changes, so does its specific heat capacity. Based on the experimental data, the function $c_p(T_{sm})$ can be approximated by a polynomial equation, which in general form is given by Equation (8).

$$c_p(T_{sm}) = c_0 + c_1 \cdot T + c_2 \cdot T^2 + \cdots + c_n T^n \tag{8}$$

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For the PCMs used in the latent TES, assuming that the TES is fully charged when the material is completely melted, and fully discharged, when the material is completely solidified, the whole process is isothermal. Two parameters such as melting temperature and melting enthalpy are sufficient to determine stored heat. In this case, melting temperature describes the temperature at which the process takes place. In addition, melting enthalpy describes specific heat stored by the phase change. Therefore, for LTES, Equation (7) can be expressed as a function of melting enthalpy that is described in Equation (9).

$$Q_{LTES} = m_{sm} \cdot \Delta h_{melting} \tag{9}$$

One of the aims in the selection of the TES material is to minimize the required mass to store the heat so that the space requirements and cost of TES could be minimized. In the previous work (Kolasiński and Daniarta, 2021), a dimensionless parameter ζ_{sm} for sizing of the heat storage was introduced, which is defined as a ratio of the mass of the thermal energy storage material needed to store heat, to the mass of the working fluid, as given by Equation (10).

$$\zeta_{sm} = \frac{m_{sm}}{m_f} = \frac{\Delta h_{HE}}{c_p(T_{sm})|_{T_{charged}}^{T_{discharged}} \cdot \left(T_{charged} - T_{discharged}\right)} \tag{10}$$

For latent TES, it can be simplified to the form given by Equation (11).

$$\zeta_{sm} = \frac{m_{sm}}{m_f} = \frac{\Delta h_{HE}}{\Delta h_{melting}} \tag{11}$$

This parameter can be calculated separately for the precooler ($\zeta_{precooler}$) and evaporator ($\zeta_{evaporator}$), or as the total for both of them (ζ_{total}).

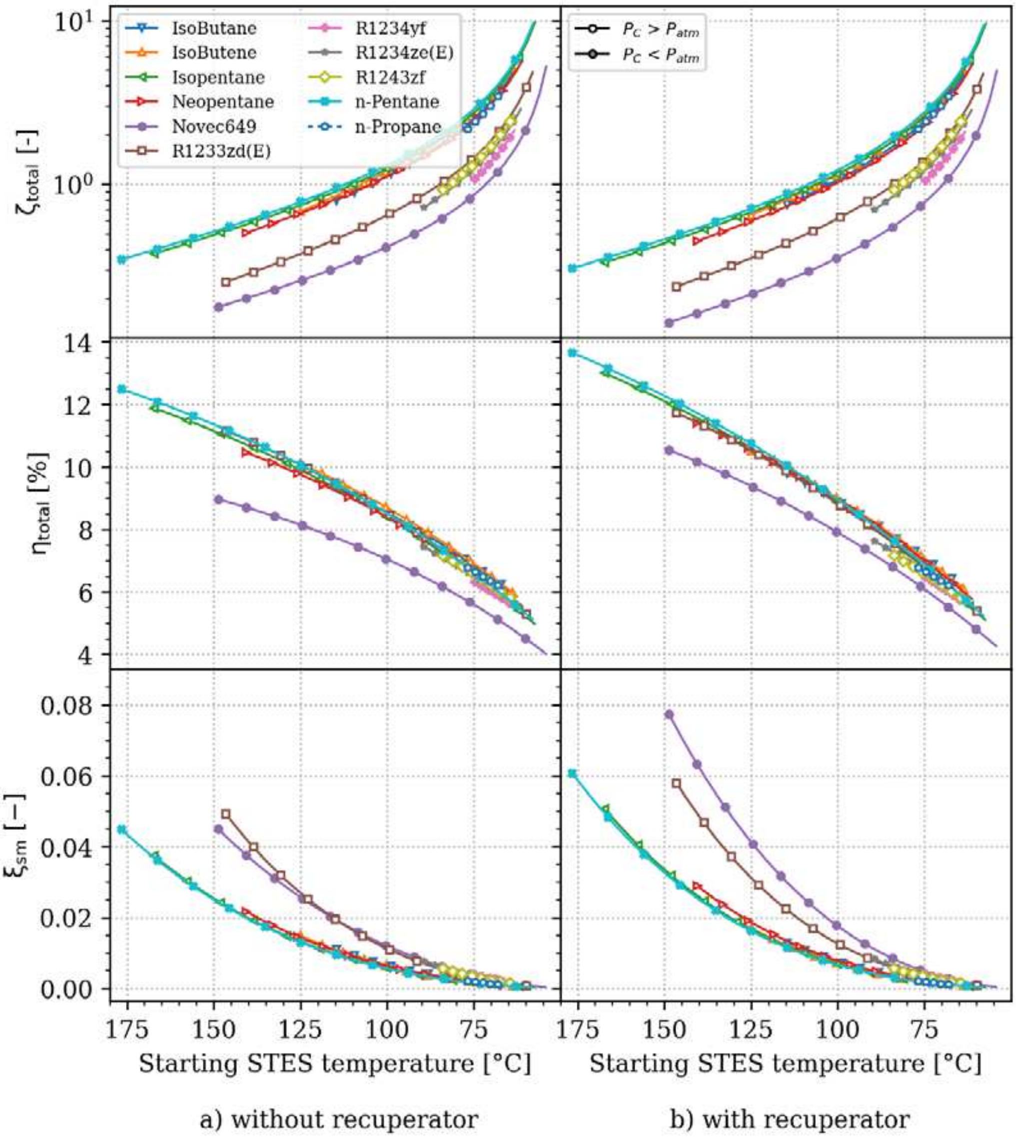

Figure 4: Variation of assessment parameters of ORC with TES vs starting STES temperature, for jatropha oil and working fluids with low GWP and no ODP.

The mass of the storage material, that is needed to implement TES, is not the only parameter that should be evaluated. The efficiency of different ORCs with different working fluids also needs to be evaluated. The total efficiency of the discharge could be defined as a ratio of work generated by the ORC during the discharge, to the heat input during that time, as shown in Equation (12).

$$\eta_{total} = \frac{\int_{t,charged}^{t,discharged} W_{net} \cdot dt}{Q_{TES}} \tag{12}$$

For LTES, since the temperature of the thermal energy storage material is constant, the ORC system can work in steady-state conditions, and net power output during the discharge would remain constant. In this case, η_{total} would be equal to η_{net}.

For sensible heat, as the STES is discharging, the temperature decreases, which lowers the pressure ratio in the cycle, and by extension the power output and efficiency. The discharging process is limited by the minimum pressure difference for which the expander can operate properly. For that type of TES material, the transient discharge process can be approximated by a series of quasi-steady-state processes as follows:

1. The discharge process is divided into n steps so that during each, the same amount of heat accumulated in TES is used,
2. For each step, the temperature of the LTES is found based on Equation (7),
3. For that temperature, working fluid parameters for characteristic state points are determined, and
4. For these points, the assessment parameters of the cycle are calculated.

By carrying out these calculations for all the working fluid and storage material pairs, the efficiencies of ORC systems and needed amounts of TES materials can be compared. As an example, the results obtained for the jatropha oil are presented in Figure 4. Jatropha oil was selected because of its high specific heat capacity, as seen in Figure 3. As can be seen, the obtained results indicate that Novec649 seems to be a good choice for the working fluid in the analysed case, if minimizing the amount of the storage material in relation to the amount of the working fluid (ζ_{total}) is the only objective. For Jatropha oil-based STES, which operates between 100 °C and 50 °C, it has a 36% lower value than the next best fluid (R1233zd(E)). However, the total efficiency for Novec649 (η_{total} - also presented in Figure 4) is very low. On the other hand, n-pentane which shows very high η_{total}, got very high value of (ζ_{total}). This is true for both non-recuperated and recuperated cycles.

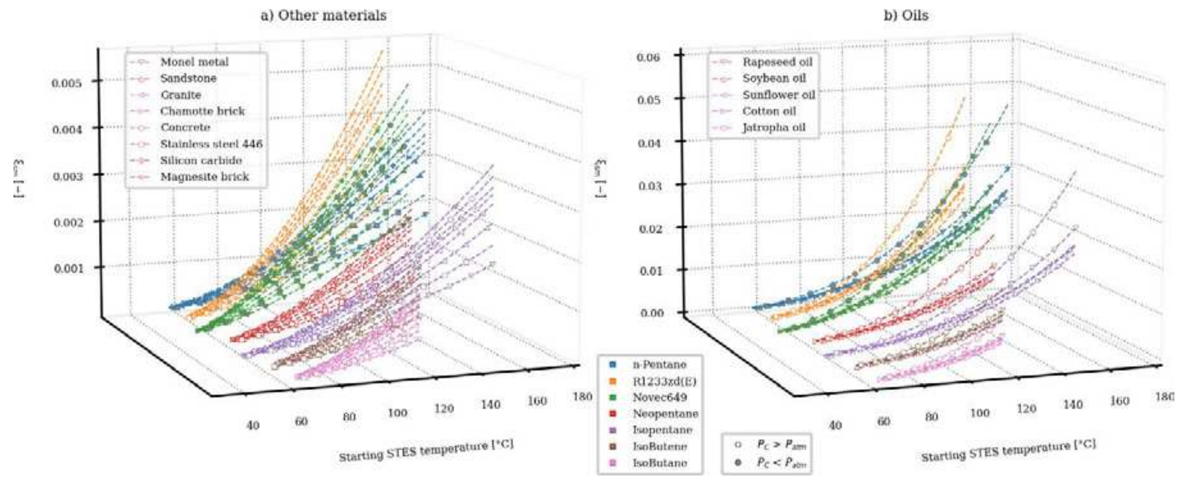

Figure 5: ξ_{sm} of ORC with TES vs starting STES temperature, for different sensible storage materials and working fluids with low GWP and no ODP.

In order to combine ζ_{total} and η_{total}, a new parameter ξ_{sm} can be introduced, which can be defined as a ratio of total efficiency to the nth power, to the parameter ζ_{total} as given by Equation (13). The purpose of exponent n is to give more weight to the efficiency of the cycle, and in this case, a value of 2 was assumed. The relative importance of efficiency and the amount of storage material depends on the specific case. For volume-constrained applications, the weight of ζ_{total} is higher.

$$\xi_{sm} = \frac{(\eta_{total})^n}{\zeta_{total}} = \frac{(\eta_{total})^2}{\zeta_{total}} \tag{13}$$

For the non-recuperated cycle obtained ξ_{sm} values show best results from around 105 °C for R1233zd(E). R1233zd(E) requires significantly less storage material than n-pentane and gives very similar efficiency. R1234ze(Z) and Novec649 both give similar values, like R1233zd(E) for lower temperatures. The worst value of ξ_{sm} was obtained for n-pentane.

The subplots on the right side of Figure 4 show the same values calculated for the recuperated cycle. Unsurprisingly, recuperation largely improves both ξ_{sm} and η_{total} for Novec649, and other dry working fluids. It has very little influence on ζ_{total}, so, the difference in ξ_{sm} between non-recuperated and recuperated cycles, are almost entirely results of changed η_{total}. Because of that, if recuperation is used, Novec649 obtains much better values.

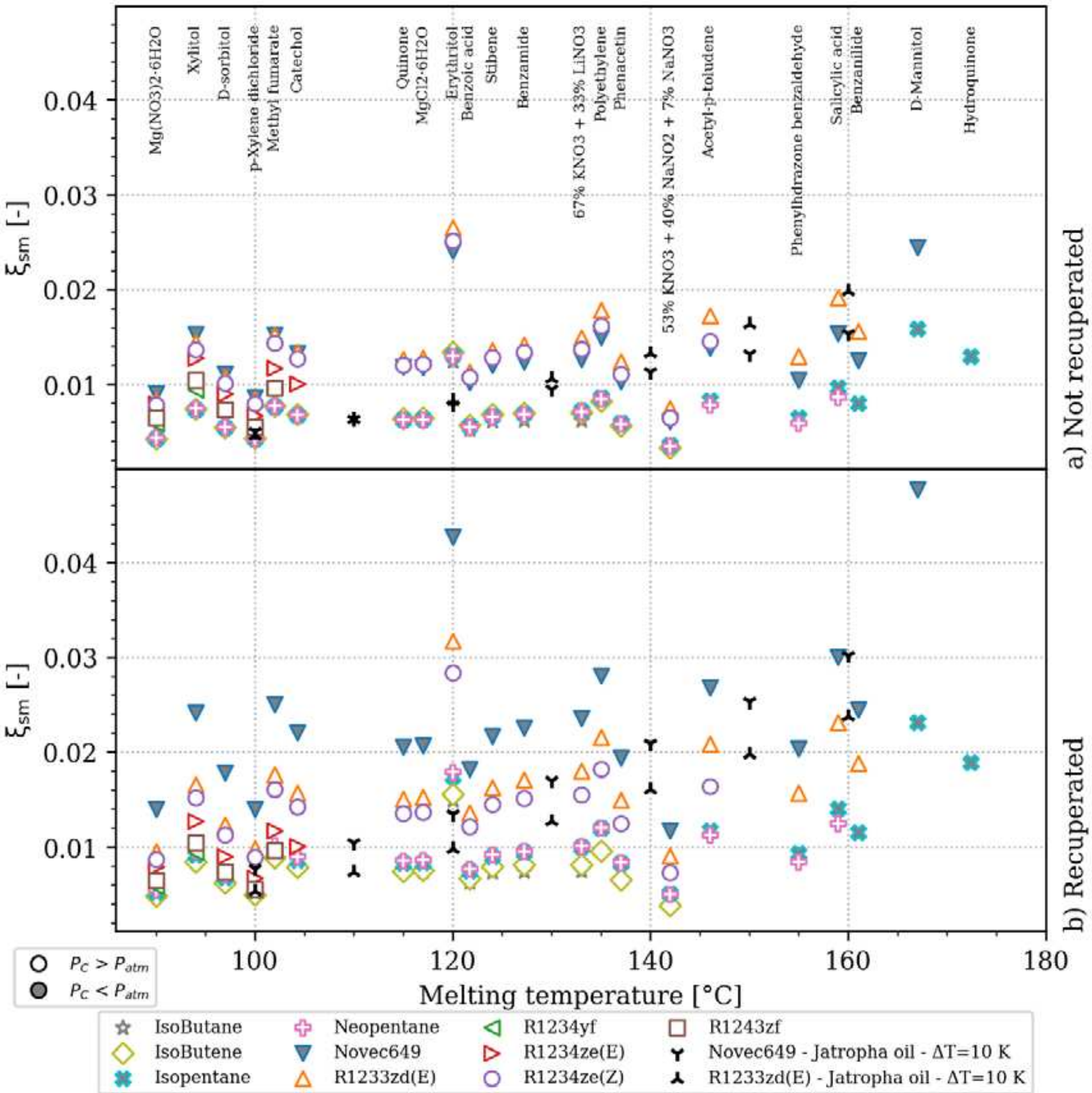

Figure 6: Variation of assessment parameter ξ_{sm} of ORC with TES vs. starting melting temperature of PCM for different materials and working fluids with low GWP and no ODP. PCM parameters are taken from (Daniarta et al., 2022). For comparison, also presented are values for two working fluids (Novec649 and R1233zd(E)) with sensible storage material (Jatropha oil) with the temperature difference between during the discharge 10 K.

In Figure 5, values calculated for the rest of the storage materials, with non-recuperated ORC, were presented. They were separated between oils and other materials since oil has an order of magnitude higher specific heat capacity. As can be seen, the results are similar to those shown in Figure 4. R1233zd(E), R1234ze(Z), and Novec 649 give very good results.

In Figure 6, ξ_{sm} values calculated for latent storage materials are presented, as a function of their melting temperature. By comparing the results, with Figure 5, it can be noticed, that while PCMs perform significantly better than solid sensible storage materials, vegetable oils can reach the same order of magnitude as PCMs. Unlike PCMs, however, they do not give the advantage of stable temperature output, and by extension, stable operating conditions. As can be seen, however, even with temperature difference limited to 10 K, they perform comparable to PCMs. Additionally, oils give the possibility of using them at the same time as heat transfer fluids in CSP (concentrated solar power) and other applications (Nitedem et al., 2017), simplifying the construction of the heat exchanger.

In regards to heat exchangers it is worth mentioning that not all types of heat exchangers are compatible or suitable for use with TES due to pressure, design, construction, and other parameters (Daniarta et al., 2023).

4. SUMMARY AND CONCLUSIONS

This paper presents the results of modeling analysis of ORC and TES power systems performed for different working fluid and TES material pairs. Both sensible and latent working fluids were considered, as well as the effects of recuperation. Some remarks can be concluded as follows:

- Working fluid and TES material pairs were evaluated based on the amount of storage material needed to accumulate heat for a given amount of the working fluid. Additionally, the total efficiency of the TES discharge process was calculated. To combine the two criteria, an additional parameter ξ_{sm} was introduced, defined as a ratio of square total efficiency, to the ζ_{sm} (ratio of the storage material mass to the working fluid mass).
- For analyzed working fluids, in the simple, non-recuperated configuration, the best value was obtained for R1233zd(E) above 105°C, while the worst was obtained for n-pentane. Presented results may be applied for working fluid and thermal energy storage material selection for ORC systems which are utilizing TES as heat sources. The recuperation has very little effect on ζ_{total}, it improves however the total efficiency, particularly of dry working fluids, like Novec 649, and, because of that improves their ξ_{sm}. For that reason, Novec 649 performed better than other fluids in this variant. It should be pointed out however, that recuperation requires an additional heat exchanger, which decreases benefits from the reduced amount of the storage material needed, both in terms of the volume and in terms of cost, which effects were not estimated in this study. Additionally, to obtain 30 °C condensation temperature Novec 649, would require vacuum in condenser, and would therefore be better suited for applications with higher heat sink temperature.
- Generally, R1233zd(E) can be regarded as a good choice for applications with TES, thanks to both high efficiency and low amount of storage material needed.
- It also was shown, that, thanks to their large specific heat capacity, vegetable oils and especially jatropha oil, can perform comparably to some PCM materials. They can even outperform them if a large temperature drop during discharge is allowed.
- The further works of the authors on the presented topic will be focused on experimental validation of the obtained results.

NOMENCLATURE

c_p	specific heat capacity	$(\frac{kJ}{kg \cdot K})$	$\dot{Q}$	heat flux	(kW)
h	specific enthalpy	$(\frac{kJ}{kg})$	T	temperature	(K)
			W	power	(kW)
$\dot{m}$	mass flow	$(\frac{kg}{s})$	η	efficiency	(−)
Q	heat	(kJ)	ζ_{sm}/ξ_{sm}	parameters for sizing TES	(−)

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Subscript

sub	subcooling
f	working fluid
sm	storage material
in	input
out	output
TES	thermal energy storage
exp	expander
pump	pump
net	netto
1	point after condenser
2	point after pump
3	point after evaporator
4	point after expander
CR	low-pressure side recuperator outlet
ER	high-pressure side recuperator outlet

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This book contains the compilation of works contributed to the *7th International Seminar on Organic Rankine Cycle Power Systems* (ORC 2023), held in Seville between the 4th and 6th of September 2023. The event was hosted by Universidad de Sevilla on behalf of the Knowledge Centre on Organic Rankine Cycle Technology (KCORC), incorporated in The Netherlands.

The ORC conference, organized biennially, stems as the only conference that is specific to ORC technology, therefore gathering a diverse community whose affiliation spans across all the interested stakeholders, not only in this particular technology but also and in a broader context, in the energy transition. Original equipment manufacturers, professional associations, end-users, investors, policy makers, academics, scientists feel at home at ORC 2023.

The almost 100 proceedings in this book cover a wide variety of topics, from fundamentals to system integration through component design, accounting for thermodynamic performance as well as component design. In addition to this, and as a new track in 2023, works on heat pump technology were also accepted in order to raise awareness of the strong ties between both technologies, specifically in energy storage applications.

This book provides an excellent overview of the current maturity of power systems based on Organic Rankine Cycle technology for applications as diverse as geothermal and waste heat recovery in industry or downstream of other prime movers (e.g., marine applications). It is also an excellent source of information to understand the current challenges faced by the technology, stemming from a very competitive market and increasingly stringent environmental regulations.

The organizers of ORC 2023 hope that the reader finds this work as exciting as the attendees to the conference and, maybe, make the decision to join the 8th edition to the conference in 2025.

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