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Thermodynamic Comparison of Organic Rankine Cycles Employing Liquid-Flooded Expansion or a Solution Circuit

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1 Introduction

The competing drivers of energy security and climate change mitigation have spurred the development of Organic Rankine Cycle (ORC) technology to harness low-grade heat (80°C -200°C) as a viable energy source [1]. Organic Rankine Cycles differ from traditional steam Rankine Cycles in their use of an organic liquid as opposed to steam as the working fluid. The term ORC is also applied generally to any Rankine cycle with a low-grade heat source. A theoretical investigation was conducted in the 1970s by Davidson [2] for integration with solar collectors; the analysis was further extended by Probert et al. [3]. These investigations revealed low cycle thermal efficiencies due to the low theoretical (Carnot) efficiency limit for the source and sink temperatures involved in the applications. Therefore, achieving efficiencies close to the Carnot limit is important for ensuring the economic feasibility of this technology. To this end, there have been numerous studies that have investigated different working fluids for an ORC [4,5,6,7]. It is clear that the choice of working fluid has a substantial impact on cycle efficiency as well as on system and component design [8]. Selection of a working fluid requires the evaluation of tradeoffs involving efficiency, flammability, turbine volumetric flow ratios, vapor pressures in the condenser, toxicity, cost, and more recently, Global Warming Potential (GWP) and Ozone Depletion Potential (ODP). The choice of a working fluid, therefore, depends fundamentally on the context of the application and the available machinery.

Once a working fluid for an application has been chosen, however, it is still possible to improve potential cycle efficiencies by modifying the cycle configuration [9]. Changing the cycle configuration preserves the fundamental thermodynamic properties of the chosen working fluid, and does not usually require the redesign or reselection of rotating component machinery. There is a large volume of literature that considers different working fluids in a single cycle configuration. There are far fewer studies examining novel cycle configurations. Furthermore, a comparative analysis between cycle configurations and working fluids is relatively scarce in the literature.

In the present work, the thermodynamic performance of two novel modifications to a traditional Organic Rankine Cycle is investigated: Organic Rankine Cycle with Liquid-Flooded Expansion (ORCLFE) and Organic Rankine Cycle with Solution Circuit (ORCSC). The working fluids considered for the ORC and ORCLFE are ammonia, water, CO₂, acetone, pentane, R134a and R245fa. The working fluid pairs considered for the ORCSC are ammonia-water and CO₂-acetone. The primary focus of this work is a comparative analysis of the different cycles, rather than the strengths and weaknesses of the individual working fluids. It should be noted that thermodynamic considerations alone are insufficient to declare an optimum cycle for an application. However, they represent an important first step in identifying an optimum cycle and working fluid for a given application with a roughly constant-temperature heat source.

2 Description of Cycles

2.1 Organic Rankine Cycle with Liquid-Flooded Expansion

The Organic Rankine Cycle with Liquid-Flooded Expansion (ORCLFE) [10] involves "flooding" the expansion device with a subcooled liquid that is in thermal equilibrium with the primary working fluid, while simultaneously expanding the primary working fluid through the same device. An appropriate flooding liquid will not flash into vapor during this process. Without liquid flooding, the primary working fluid undergoes a significant temperature drop

during expansion. For an appropriate choice of flow rates, the flooding liquid acts as a heat source for the vapor and maintains higher temperatures in the vapor throughout the expansion process. Since flooding liquids typically have a high volumetric heat capacity compared to the primary working fluid vapor, relatively low volumetric flow rates of liquid are needed to realize a process with relatively small temperature changes. Liquid-flooded expansion is readily accommodated using a positive displacement expander such as a scroll or screw machine [11]. Figure 1 shows a schematic diagram of the ORCLFE.

In the cycle, both the primary working fluid (1) and the flooding medium (2) are pumped to the high system pressure. The working fluid is then preheated by an internal regenerator (3). At this point, the working fluid (4) and flooding medium (5) are heated to the same temperature using the heat source. The fluids are then mixed (6) and expanded together through the expander (7). After the expansion process, the working fluid is separated from the flooding medium (8). The flooded expansion guarantees that the working fluid is still significantly superheated at the expander outlet. This allows the working fluid to pass through an internal regenerator to preheat the fluid entering the condenser (9). The remaining heat in the working fluid is then rejected to the environment by means of a condenser (10). At the other side of the separator (11), the flooding medium is simply pumped back to the high-side pressure, and enough heat is added to restore it to the high-side temperature to complete the cycle.

2.2 Organic Rankine Cycle with Solution Circuit

The Organic Rankine Cycle with Solution Circuit (ORCSC), first proposed by Maloney and Robertson [12], employs a zeotropic mixture of the primary working fluid and an absorbent characterized by a large boiling point difference. This enables the separation of the more volatile component (the primary working fluid) in the vapor phase from the solution in the liquid phase for a range of source temperatures. The use of a zeotropic fluid results in a temperature glide during the phase change process. As the mixture is heated or cooled at constant pressure, the saturation temperatures are not constant, and instead vary with the composition changes of the liquid and vapor phases. In general, working pairs used in absorption cycles, such as ammoniawater, are good candidates for use in the ORCSC. Groll and Radermacher [13] outlined the advantages of using novel working pairs such as carbon dioxide-acetone in such a cycle, represented in Figure 2.

State (1) represents the outlet of the desorber (note that a separator may be used to separate the vapor and liquid streams at the desorber outlet). At this state, the waste heat stream has heated the mixture, and the absorbate is desorbed from the solution. The absorbate vapor stream (which may contain a portion of absorbent vapor) then enters the expander, where it is expanded to its low-pressure state (2). State (3) represents the outlet of the absorber, where the absorbate has been resorbed into the solution to form a rich solution. Since absorption is an exothermic process, the absorber rejects heat to the environment during this process. Following this, the rich solution is pumped to the high-pressure state (4) and is subsequently preheated by an internal heat exchanger (5) before entering the desorber. State (6) represents the liquid-phase weak solution at the desorber outlet. The weak solution stream is then subcooled (7) through the internal heat exchanger, and expanded to the low-pressure state (8) by an expansion valve.

3 Thermodynamic Modeling

Thermodynamic models were developed for each cycle, ORC, ORCLFE and ORCSC using Engineering Equation Solver (EES) [14]. All fluid properties were obtained from REFPROP 9.0

[15], which was linked to EES, with the exception of the ammonia-water mixture, for which properties were obtained from the built-in external procedure in EES. The models are based on the assumptions listed in Table 1. For these assumptions and a specified source temperature, each cycle has one or two free variables remaining, as shown in Table 2.

The cycle Second Law efficiency is then maximized with respect to the free variable(s) over a range of source temperatures so that the maximum efficiency of each cycle can be compared to the others. In this work, the Second Law efficiency is defined as the thermal (First Law) efficiency divided by the theoretical maximum (Carnot) efficiency:

$$\eta_{II} = \frac{\frac{W_{net}}{Q_{in}}}{1 - \frac{T_L}{T_H}} = \frac{\eta_{thermal}}{\eta_{Carnot}}$$
(1)

Embedded in this performance metric is the assumption that the heat source and sink are constant-temperature reservoirs.

Transcritical cycles were included in the design space of the ORC and ORCLFE. For the ORCLFE, the flooding medium is assumed to be an incompressible liquid that is immiscible and chemically non-reactive with the working fluid. The density and specific heat of the flooding medium are assumed to be similar to those of lubricating oil. Equations for the thermodynamic properties were obtained from Hugenroth [16].

For the ORCSC the rich solution concentration was constrained to be greater than 50% by mass with one exception for CO_2 -acetone, described in the results. The high-side pressure was set by assuming the weak solution at the outlet of the desorber to be a saturated liquid at the maximum cycle temperature. The absorbate vapor concentration is set by assuming a saturated vapor in equilibrium with the saturated-liquid weak solution at the outlet of the desorber. A detailed description of the thermodynamic analysis for the ORCSC is presented in Krishna *et al.* [17] and Krishna [18]; a similar analysis for the ORCLFE is presented in Woodland *et al.* [10] with additional details pertaining to liquid-flooded expansion presented in Hugenroth [16].

4 Modeling Results

Figure 3 presents the Second Law efficiency of a conventional ORC with no regeneration for various working fluids as a function of the source temperature. Depending on the working fluid and source temperature, Second Law efficiencies exceeding 50% are possible. Apart from carbon dioxide and water, the other working fluids have a maximum Second Law efficiency in the source temperature range considered here and show some degradation of performance at higher source temperatures. This is due to several factors: 1.) Higher source temperatures require higher evaporating pressures to maximize system thermal efficiency. The higher evaporating pressures result in a greater proportion of heat input in the subcooled liquid region of the working fluid, where heat transfer irreversibilities are higher against a constant-temperature source. 2.) For many fluids, the source temperature exceeds the critical temperature of the fluid, resulting in a transcritical cycle where the advantages of a constant-temperature heat input against a constant-temperature source are not realized. 3.) For dry working fluids (R245fa and pentane), the expander exhaust gases become more superheated with increasing source temperature, resulting in wasted availability against the heat sink. The cycle with water as the working fluid avoids

issue 2 because of its high critical temperature and issue 3 by expanding directly into the vapor dome. Acetone shows the same behavior except at the highest temperature studied (200°C) where it evaporates near the critical temperature.

Due to the high superheat in the expander exhaust gas for dry working fluids such as pentane and R245fa, it is common practice to use a regenerative heat exchanger between the expander exhaust gas and the liquid at the pump discharge as illustrated in Figure 1. The Second Law efficiency of such a cycle (without liquid-flooded expansion) as a function of source temperature is given in Figure 4.

For wet working fluids, such as ammonia, water, acetone, and R134a, regeneration was only applied when the expander exhaust stream was superheated. The optimization routine was allowed to increase the superheat at the expander inlet for these fluids (by decreasing the evaporating pressure) to allow for some superheat in the expander exhaust gases if this yielded a more efficient result. Figure 4 shows that the addition of a regenerator results in much better performance for dry working fluids at high temperatures because the availability in the expander exhaust stream is not wasted. However, very wet fluids, such as water and ammonia, show no improvement from this simple regenerative scheme because the expander exhaust temperature is not significantly higher than the pump discharge temperature. This point leads to one of the key advantages of liquid-flooded expansion in the ORCLFE. The more isothermal expansion process ensures that the expander exhaust gases are significantly superheated. Wet working fluids can then employ a regenerative heat exchanger to recover the availability.

The Second Law efficiency of the ORCLFE as a function of source temperature is given in Figure 5. To identify the relative improvement of the ORCLFE over the ORC with a regenerator, the efficiency improvement is listed as a percentage for four source temperatures in Table 3.

It can be seen from Table 3 that water and acetone show significant improvement as a result of liquid-flooded expansion. The improvement is only marginal for pentane and R245fa because regeneration with the expander exhaust gases is already possible for these fluids without liquid-flooded expansion.

Figure 6 presents the Second Law efficiencies of an ORCSC with working pair CO_2 -acetone, and of an ORC using CO_2 or acetone as the working fluid as a function of source temperature. Figure 7 shows the Second Law efficiencies of an ORCSC with working pair ammonia-water, and of an ORC using ammonia or water as the working fluid as a function of source temperature. For the working pairs studied, the ORCSC is always less efficient than an ORC using either the pure absorbate or the pure absorbent as the working fluid.

The reason for the low efficiencies of the ORCSC can be explained by examining a process diagram of the cycle presented on a temperature-entropy plot in Figure 8. The figure shows the three vapor domes corresponding to the three different absorbate concentrations present in the ORCSC – the weak solution, the rich solution and the vapor concentrations, respectively. It is noted that the critical point for a mixture does not lie at the top of the dome, as it would in the case of a pure fluid, but rather at the point of tangency between the critical pressure isobar and the vapor dome, as indicated for each concentration pair in Figure 8 (since mixture properties are difficult to determine near the critical point, a best estimate is given). Also, the lines of constant

quality for a mixture do not behave as they do for a pure fluid. A point inside the vapor dome may have considerably less quality for a mixture than a point at the same location in the vapor dome of a pure fluid (as an example, state point 2 in Figure 8 has a quality of 78%). The cycle process is given in the context of these three domes, where the state points correspond to those given in the cycle schematic in Figure 2. The heat source and sink temperatures used for this case are also given.

Due to the use of a zeotropic mixture in the ORCSC, there is a significant temperature glide during the heat addition process in the desorber (given from points 5 to 5*, where 5* represents the state just before adiabatic separation into states 1 and 6). This results in significant irreversibility when the heat source is modeled as a constant-temperature heat input. The same is true for the heat rejection process (given from points 3* to 3, where 3* represents the state just after adiabatic mixing of states 2 and 8). The area between the temperature profiles of the working fluid and the heat source/sink is representative of the irreversibility in the heat addition (5 to 5*) and heat rejection (3* to 3) processes. The general shape of the process diagram remains the same regardless of the source temperature. Therefore, the higher availability for a higher source temperature is balanced by a roughly proportional amount of heat input in the "glide region" of the process diagram. This results in roughly flat second law efficiencies versus source temperature as can be seen in Figure 6 and Figure 7.

The abrupt increase in efficiency at the 200°C source temperature for the CO₂-acetone working pair can be explained by the shrinking vapor bubbles seen in a temperature-concentration plot as pressure is increased. This phenomenon is shown in Figure 9. As an example, a rich solution

concentration of 0.5 and a desorber pressure of 3000 kPa do not admit a two-phase state for a source temperature of 200°C. Increasing the pressure to 6000 kPa raises the dew temperature from 143.5°C to 163.8°C. However, a further increase in pressure to 9000 kPa reduces the dew temperature back to 149.9°C. Higher concentrations exhibit the same phenomenon at increasingly lower dew temperatures. Further increases in pressure continue to shrink the vapor bubble until the pressure exceeds the critical pressure of the mixture for any concentration. Therefore, in order to maintain a solution circuit (i.e., a separation of the liquid and vapor phases after the desorption process), very low absorbate concentrations are required for high source temperatures. For a 200°C source temperature, a CO₂ concentration below the constraint of 50% was required. As the absorbate concentration is decreased, the temperature glide in the desorption and absorption processes is reduced. Since the heat source and sink are at constant temperature, this results in a more efficient cycle. For very low concentrations (less than 1% by mass), efficiency was shown to increase for both CO₂-acetone and ammonia-water working pairs at all source temperatures. However, this results in a cycle that has high concentrations of acetone or water even in the vapor phase, as opposed to CO₂ or ammonia. This leads to a departure from the traditional view of an ORCSC, in which the absorbate concentration in the rich solution is a significant portion of the total mass. Therefore, the results for low absorbate concentrations are omitted in the present work, and the concentration of CO2 for the 200°C source temperature was limited to a minimum of 10% by mass. Additionally, there are significant practical challenges in operating an ORCSC with high concentrations of wet working fluids such as water or acetone, as discussed below.

5 Thermodynamic Versus Practical Considerations

5.1 Organic Rankine Cycle

At first glance, a conventional ORC with the best performing working fluid (Figure 3) would appear to be the ideal thermodynamics-based choice due to its combination of simplicity and performance. For example, the optimum efficiency for a basic ORC with water as the working fluid is higher than the efficiency of the ORCLFE and the ORCSC for the majority of working fluids. However, it is important to note that several practical considerations should be weighed together with the thermodynamic results presented in this work. The use of water requires a low vapor quality and low density at the expander exhaust, a high expander pressure ratio, and vacuum pressure condensation. Restricting the exhaust quality at the expander outlet has a significant impact on cycle efficiency as seen when comparing Figure 10 and Figure 11. In the case where the exhaust quality is restricted to be a minimum value, the evaporation temperature is substantially reduced whereas the superheated region is enlarged, resulting in significant irreversibilities compared to the case with no quality restrictions.

The issue of low vapor quality at the expander exhaust is eliminated in the ORCLFE with a resulting boost in efficiency. However, the issues of pressure ratio, low density vapor, and vacuum pressures remain. High pressure ratios require multiple expansion stages. The sub-atmospheric pressure makes air leakage into the system a challenge. The low working fluid density is a capacity concern, requiring large-diameter piping and a large expander to achieve a capacity comparable to that of denser working fluids. Therefore, despite the promising efficiency of water as a working fluid for the source temperatures considered, the practical concerns associated with its use may be prohibitive.

5.2 Organic Rankine Cycle with Solution Circuit

It may be tempting to dismiss the ORCSC as unfavorable due to the low efficiencies estimated for this cycle. However, it should be noted that the reported Second Law efficiencies assume that the heat source is a constant-temperature reservoir. A real heat source fluid would begin to cool as it heats the cycle working fluid. This could severely limit the maximum evaporating temperature of a traditional ORC as the heat source stream reaches a pinch point against the liquid to two-phase transition of the working fluid. This also limits the capacity of an ORC since less exergy can be extracted from a finite-capacity heat source. In contrast, the ORCSC may be able to reach higher capacities and average working fluid temperatures by being better able to match the temperature profile of the heat source stream with its two-phase temperature glide. A similar argument can be made between the working fluid and the heat sink fluid. Therefore, the ORCSC should not be rejected entirely until more application-specific studies, which consider the temperature profiles and capacities of the source, sink, and working fluid streams, are conducted. Other practical advantages of the ORCSC include the potential for lower system pressures as compared to a cycle with the pure absorbate as the working fluid, and the potential for capacity control by changing the concentration of the working fluid mixture [17]. Moreover, only two working fluid pairs were studied out of a broad range of possible binary mixtures. More binary mixture data are needed to study the wide range of working fluid combinations that may be possible with the ORCSC. It should be noted that for certain working pairs such as those analyzed here, the expansion process results in some vapor quality at the expander outlet (for example, a quality of 78% for the cycle shown in Figure 8). This may be eliminated by modifying the cycle configuration and using a superheater following the desorber, resulting in a configuration similar to the Kalina cycle [19]. Using high concentrations of a wet absorbent (such as water or acetone) in the working pair exacerbates the problem, and is therefore likely to outweigh any efficiency benefit.

5.3 Organic Rankine Cycle with Liquid-Flooded Expansion

The ORCLFE may emerge as the best cycle configuration. It improves the efficiency of all working fluids when an optimal amount of flooding liquid is used. However, the ORCLFE is not without its practical challenges. For example, it requires the selection of a flooding medium that is not miscible or reactive with the primary working fluid. It also requires the use of a positive-displacement expander since liquid flooding would be detrimental to a dynamic machine. In addition, the ORCLFE requires the waste heat source to separately heat the working fluid and the flooding medium, which impacts the exergetic conversion efficiency of the cycle.

It is evident that the optimal choice for an ORC and working fluid may be highly applicationspecific. It depends primarily on the capacity of the heat source stream and the desired exergetic conversion efficiency of the ORC relative to other variables. Appropriate selection thus requires a more thorough investigation of the tradeoffs between efficiency, ability to match the heat source temperature profile, variability in the heat source and sink streams, cost of implementation, and size constraints. Investigating these tradeoffs, however, requires experimental study. Ongoing work is targeted at more detailed comparative analysis and practical feasibility using three experimental test stands, one for each of these cycles.

6 Conclusions

A levelized thermodynamic comparison of a conventional ORC system with two novel ORC concepts employing a variety of working fluids is presented. This is an important step towards

determination of an optimal ORC for a given application. A simple ORC with water as the working fluid yielded almost 65% of the Carnot efficiency for a constant heat source temperature, and was found to be more efficient than many of the enhanced cycles. However, a range of practical considerations must be taken into account and weighed together with the thermodynamic optima presented here. For example, when using water in an ORC as modeled here, the water expands into the vapor dome and generates a low vapor quality and low density at the expander exhaust. In addition, the ORC has a high expander pressure ratio, and vacuum pressure condensation. These issues may make water unattractive as the working fluid. The ORCSC appears to be the poorest performer, but it provides the ability to use a temperature glide to match the temperature profiles of real source and sink fluids and facilitates intrinsic capacity control. This may lead to higher overall system efficiencies when coupled with sources that have varying heat input temperatures or loads. More application-specific studies that address the nature and capacity of the source and sink streams are required to identify where this ability may be most advantageous. The ORCLFE always improves system efficiency and mitigates expander exhaust quality concerns for wet working fluids. However, it limits the choice of expander to positive displacement designs and requires the selection of a flooding medium that does not mix or react with the primary working fluid. Three test systems will be investigated in ongoing work to identify the thermodynamic and the practical advantages and tradeoffs of the ORC, ORCSC, and ORCLFE systems.

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Figure Captions

- Figure 1: Schematic representation of the ORCLFE.
- Figure 2: Schematic representation of the ORCSC.
- Figure 3: Second Law efficiency of conventional ORCs as a function of source temperature.
- Figure 4: Second Law efficiency of ORCs with regeneration as a function of source temperature.
- Figure 5: Second Law efficiency of ORCLFE as a function of source temperature.
- Figure 6: Second Law efficiency of an ORCSC with CO_2 -acetone, an ORC with pure CO_2 , and one with pure acetone as a function of source temperature.
- Figure 7: Second Law efficiency of an ORCSC with ammonia-water, an ORC with pure ammonia, and one with pure water as a function of source temperature.
- Figure 8: Representative T-s process diagram for an ORCSC using CO_2 -acetone with a source temperature of 160°C and sink temperature of 20°C.
- Figure 9: Temperature-concentration diagram for CO₂-acetone showing shrinking vapor bubbles at higher pressures.
- Figure 10: Representative T-s process diagram for an ORC using water as the working fluid with no constraint on quality at the expander outlet. A source temperature of 200°C and a sink temperature of 20°C were used. Lines of constant quality are shown inside the vapor dome.
- Figure 11: Representative T-s process diagram for an ORC using water as the working fluid with a quality constraint of 1 at the expander outlet. A source temperature of 200°C and a sink temperature of 20°C were used.



Figure 1: Schematic representation of the ORCLFE.



Figure 2: Schematic representation of the ORCSC.



Figure 3: Second Law efficiency of conventional ORCs as a function of source temperature.



Figure 4: Second Law efficiency of ORCs with regeneration as a function of source

temperature.



Figure 5: Second Law efficiency of ORCLFE as a function of source temperature.



Figure 6: Second Law efficiency of an ORCSC with CO_2 -acetone, an ORC with pure CO_2 , and one with pure acetone as a function of source temperature.



Figure 7: Second Law efficiency of an ORCSC with ammonia-water, an ORC with pure ammonia, and one with pure water as a function of source temperature.



Figure 8: Representative T-s process diagram for an ORCSC using CO₂-acetone with a source temperature of 160°C and sink temperature of 20°C.



Figure 9: Temperature-concentration diagram for CO₂-acetone showing shrinking vapor bubbles at higher pressures.



Figure 10: Representative T-s process diagram for an ORC using water as the working fluid with no constraint on quality at the expander outlet. A source temperature of 200°C and a sink temperature of 20°C were used. Lines of constant quality are shown inside the vapor dome.



Figure 11: Representative T-s process diagram for an ORC using water as the working fluid with a quality constraint of 1 at the expander outlet. A source temperature of 200°C and a sink temperature of 20°C were used.

Table Captions

- Table 1:Assumptions made in the thermodynamic models.
- Table 2:Constrained design variables in the thermodynamic models.
- Table 3:Efficiency improvement of ORCLFE relative to ORC with regenerator [%].

Description	Value			
Condenser, absorber outlet subcooling				
Temperature difference between heat sink and condenser/absorber outlet	5 °C			
Heat sink temperature	20 °C			
Temperature difference between heat source and evaporator/desorber outlet	10 °C			
Regenerator/internal heat exchanger effectiveness	0.95			
Pump isentropic efficiency	0.6			
Expander isentropic efficiency	0.8			
Negligible pressure drop in lines, separators, and heat exchangers	_			
Negligible heat loss in lines, mixer, separator, pumps, and expander	_			
Complete separation of liquid and gas phases	_			

Table 1: Assumptions made in the thermodynamic models.

Cycle	Constrained Design Variables								
ORC	High-side (evaporating) pressure								
ORCLFE	High-side (evaporating) pressure, mass flow ratio of flooding liquid to working fluid								
ORCSC	Rich solution concentration (absorber outlet), weak solution concentration								

Table 2: Constrained design variables in the thermodynamic models.

	Ammonia	Water	CO ₂	Acetone	Pentane	R134a	R245fa
80°C	0.0	3.2	2.6	5.5	2.7	3.2	2.9
120°C	0.0	6.1	6.4	11.0	4.9	6.8	6.3
160°C	6.8	8.5	0.0	15.2	7.0	6.6	7.7
200°C	14.2	10.5	0.7	17.7	7.8	2.7	7.2

Table 3: Efficiency improvement of ORCLFE relative to ORC with regenerator [%].