

Optimal design of organic mixtures for low temperature energy recovery

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What is low-grade heat?

- Low-grade heat is a low-temperature ($<370^{\circ}\text{C}$) heat source that is expensive to recover (Quolin et al.,2013).
- Over 50% of the total heat generated in industry is in the form of low-grade heat (Wang Z.Q.et al.,2012).

- In the cement industry, for instance, 40% of the heat available for recovery is lost to the environment via flue gases. These flue gases have temperatures in the range of 215-315°C (Ayu T.T. et al.,2015).
- According to the US Department of Energy (DOE), 33% of the energy used in the manufacturing sector is waste heat. Approximately 60% of this waste heat is at temperatures below 230° (Jung H.C. et al.,2014).



Examples of low-grade heat sources:

- **Geothermal energy:** Range of temperatures 60°C - 200°C , (Yamamoto et al., 2001).
- **Solar energy:** Parabolic troughs work at temperatures $<300^{\circ}\text{C}$ (Quoilin S. et al., 2013).
- **Waste heat:** Liquid streams (50 – 300°C), stack losses (150 – 180°C), steam (100 – 250°C) and processing gases and vapours (80 – 300°C)(Galanis et al., 2019).
- **Biomass:** Range of temperatures of CHP output streams of 150°C - 320°C (Quolin et al., 2013).



Conventional Rankine Cycle

The **conventional Rankine cycle** (steam power cycle) has long been used for electricity generation. These systems **use water as working fluid** which makes the recovering of low-grade waste heat inefficient and expensive.

Recovering low-grade waste heat becomes economically feasible when using an **Organic Rankine Cycle**.

ORC

The **Organic Rankine cycle (ORC)** converts low-grade waste heat to electricity. The ORC uses an *organic working fluid instead of water*. Organic working fluids have lower boiling points than water and thus can be used to recover heat at lower temperatures.

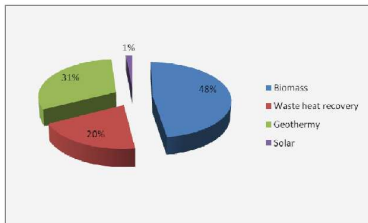


Figure 1: Applications of ORC in Industry.

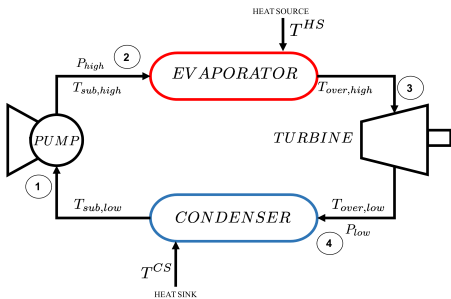


Figure 2: Rankine cycle flowsheet.

- The cycle consists of a pump, an evaporator, a turbine, and a condenser.
- The cycle performance depends on the thermodynamic properties of the working fluid. A working fluid can be a *mixture of components*.

Thermodynamic diagrams

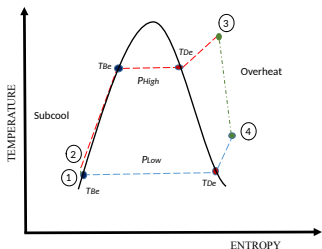


Figure 3: $T - S$ diagram for pure component

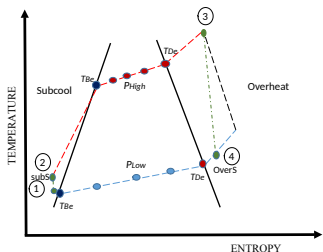


Figure 4: $T - S$ diagram for component mixture

Pure Component

- Under a constant-pressure phase change, the **temperature remains constant**.
- For a pure component, we have that $T_{Be} = T_{De}$.
- In the two-phase region, the process starts and ends at the saturation temperature.

Component Mixture

- Phase change occurs at a **range of temperatures** and compositions.
- For a mixture, we have that $T_{Be} \neq T_{De}$.
- This nonisothermal phase change of the mixture allows a better match between the temperature profiles of the working fluid and the heat source.

Organics Fluids

The thermodynamic properties of working fluids will affect:

- System Efficiency
- Operational Conditions
- Environmental Impact

Requirements for working fluids:

- Should be a dry (no water) or isentropic fluid
- Should be chemically stable
- Should not induce fouling, corrosiveness, toxicity and flammability
- Should be of low cost

Organic Mixtures

It is possible to design a multicomponent mixture to improve efficiency. In particular, by altering its composition, we can manipulate:

- Temperature gradients at phase equilibria
- Pressure ratio
- Superheating degree

Recall that **nonisothermal phase changes** induced by mixtures can increase efficiency.

Problem definition

We can optimize the performance of an ORC by:

- Determination of the **type of components** in the mixture
- Determination of the **amount of each component** in the mixture
- Determination of the **operation conditions** of the Rankine cycle subunits

Set of organic working fluids (Palma-Flores O. et al.,2014):

	Component
R-21	Dichlorofluoromethane
R-22	Chlorodifluoromethane
R-23a	Trifluoromethane
R-32	Difluoromethane
R-41a	Fluoromethane
R-116a	Hexafluoroethane
R-125	Pentafluoroethane
R-134a	1,1,1,2-Tetrafluoroethane
R-141b	1,1-Dichloro-1-fluoroethane
R-142b	1-Chloro-1,1-difluoroethane
R-143a	1,1,1-Trifluoroethane
R-152a	1,1-Difluoroethane
R-170a	Ethane
R-218	Octafluoropropane

	Component
R-227ea	1,1,1,2,3,3,3-Heptafluoropropane
R-245ca	1,1,2,2,3-Pentafluoropropane
HC-270	Cyclopropane
R-290	Propane
R-C318	Octafluorocyclobutane
R-3-1-10	Decafluorobutane
FC-4-1-12	Dodecafluoropentane
R-600	Butane
R-600a	Isobutane
R-601	Pentane
R-1270	Propene
	Propyne
	Benzene
	Toluene

Optimization Model formulation

Objective function

Maximize Overall Cycle Efficiency (η)

Decision variables

- Composition z_i
- Temperatures of working fluid T_{fe}
- Pressures of working fluid P_e

Constraints

Subject to :

- Enthalpy
- Heat capacity
- Energy balances
- Entropy
- Compressed volume
- Saturation liquid volume
- Vapor pressure
- Fugacity coefficient
- Activity coefficient
- Equilibrium
- Mol fraction and compositions
- Temperature limits
- Pressure limits

Efficiency of the cycle

$$\eta = \frac{W_{net}}{q_{in}} \quad (1)$$

The maximization of this objective will generate the *best net output to input ratio of energy*:

$$\eta = \frac{(\hat{H}_{over,high} - \hat{H}_{over,low}) - (\hat{h}_{sub,high} - \hat{h}_{sub,low})}{(\hat{H}_{over,high} - \hat{h}_{sub,high})} \quad (2)$$

The net work and the heat inlet are defined in terms of the *enthalpy changes* subcooled and superheated points in the cycle.

Enthalpy calculations

Enthalpy of working fluid

The enthalpy of the saturated liquid mixture:

$$\hat{h}_e = h_0 + \sum_i^{N_C} z_i \left(\int_{T_0}^{T_{Be}} C_{pL,i}(T) dT + \int_{P_0}^{P_e} v_{L,Bei}(P) dP \right) + H_e^E, \forall e \quad (3)$$

The enthalpy of the saturated vapor mixture:

$$\hat{H}_e = \hat{h}_e - H_e^E + \sum_i^{N_C} z_i \left(\Delta h_{ie}^{LV} - H_{ie}^R + \int_{T_{Be}}^{T_{De}} C_{p,i}^{IG}(T) dT \right) + \hat{H}_e^R, \forall e \quad (4)$$

Enthalpy change of the heat source

$$\Delta H_{HS,f} = \int_{T_{HS,OUT}}^{T_f^{HS}} C_{pL,HS}(T) dT, \forall f \quad (5)$$

Enthalpy change of the heat sink

$$\Delta H_{CS,f} = \int_{T_{CS,INT}}^{T_f^{CS}} C_{pL,CS}(T) dT, \forall f \quad (6)$$

Energy Balances

Energy balances in two-phase region (condenser and evaporator):

$$n_{HS}\Delta H_{HS,f} + \hat{h}_{sub,high} = \Psi_f(\hat{H}_{high} - \hat{h}_{high}) + \hat{h}_{high}, \forall f \quad (7)$$

$$n_{HS}\Delta H_{HS,f} = q_{IN} \quad (8a)$$

$$q_{IN} = \hat{H}_{over,high} - \hat{h}_{sub,high} \quad (8b)$$

$$n_{CS}\Delta H_{CS,f} + \hat{h}_{sub,low} = \Psi_f(\hat{H}_{over,low} - \hat{h}_{sub,low}) + \hat{h}_{sub,low}, \forall f \quad (9)$$

$$n_{CS}\Delta H_{CS,f} = q_{OUT} \quad (10a)$$

$$q_{OUT} = \hat{H}_{over,low} - \hat{h}_{sub,low} \quad (10b)$$

Here, n_{HS} is the molar ratio between the heat source and the working fluid and n_{CS} is the molar ratio between the sink source and the working fluid.

Entropy Calculations

The entropy of the saturated liquid mixture:

$$\hat{s}_e = s_0 + \sum_i^{N_C} z_i \left(\int_{T_0}^{T_{Be}} \frac{C_{pL,i}(T)}{T} dT \right) + S_e^E, \forall e \quad (11)$$

The entropy of the saturated vapor mixture:

$$\hat{S}_e = \hat{s}_e - \hat{S}_e^E + \sum_i^{N_C} z_i \left(\frac{\Delta h_{ie}^{LV}}{T_{Be}} - S_{ie}^R + \int_{T_{Be}}^{T_{De}} \frac{C_{p,i}^{IG}(T)}{T} dT \right) + \hat{S}_e^R, \forall e \quad (12)$$

Fugacity and Activity Coefficient Calculations

The **fugacity coefficient** is calculated using a the group contribution equation of state PSRK (Predictive Soave-Redlich-Kwong):

$$\ln \hat{\phi}_{ife} = \frac{\beta_{ife}}{\hat{\beta}_{fe}} (\hat{Z}_{fe} - \beta_{fe}) + \bar{\alpha}_{ife} \ln \frac{\hat{Z}_{fe} + \hat{\beta}_{fe}}{\hat{Z}_{fe}}, \forall i, f, e \quad (13)$$

The **activity coefficient** is calculated using UNIFAC:

$$\ln \gamma_{ifpe} = \ln \gamma_{ifpe}^C + \ln \gamma_{ifpe}^R, \forall i, f, p, e \quad (14)$$

Equilibrium Calculations

The **vapor-liquid** equilibrium conditions are calculated through the Rachford Rice equation:

$$\sum_i^{N_C} \frac{z_i(1 - K_{ife})}{1 + \Psi_f(K_{ife} - 1)} = 0, \forall f, e \quad (15)$$

where K_{ife} is the phase equilibrium ratio:

$$K_{ife} = \frac{\gamma_{ifL_e} P_{ife}^{sat} \phi_{ife}^{sat} \exp \int_{P_{ife}^{sat}}^{P_e} \frac{\nu_{L,ife}(P)}{R_g T_{fe}} dP}{\hat{\phi}_{ife} P_e}, \forall i, f, e \quad (16)$$

Mol fraction and composition of phases:

The mol fractions and composition of the phases satisfy:

$$\sum_i^{N_C} z_i = 1 \quad (17)$$

$$\sum_i^{N_C} x_{ifpe} = 1 \quad (18)$$

where the subscript p indicates liquid/Vapor (L,V) phases. The compositions of the vapor and liquid phases (L/V):

$$x_{ifLe} = \frac{z_i}{1 + \Psi_f(K_{ife} - 1)}, \forall i, f, e \quad (19a)$$

$$x_{ifVe} = \frac{z_i K_{ife}}{1 + \Psi_f(K_{ife} - 1)}, \forall i, f, e \quad (19b)$$

Temperature and Pressure constraints

Temperature constraints are used to achieve heat exchange between the working fluid and heat source. In two-phase region, the equations are given by:

$$T_{f,high} + \Delta T_{min}^S \leq T_f^{HS}, \forall f \quad (20a)$$

$$T_{f,low} + \Delta T_{min}^S \geq T_f^{CS}, \forall f \quad (20b)$$

In the single-phase regions, the temperature constraints are:

$$\hat{T}_{sub,high} + \Delta T_{min}^S \leq T^{HS,OUT} \quad (21a)$$

$$\hat{T}_{over,high} + \Delta T_{min}^S \leq T^{HS,IN} \quad (21b)$$

$$\hat{T}_{sub,low} - \Delta T_{min}^S \geq T^{CS,IN} \quad (21c)$$

$$\hat{T}_{over,low} - \Delta T_{min}^S \geq T^{CS,OUT} \quad (21d)$$

$$P_{high} \geq P_{low} + \Delta P_{min} \quad (22)$$

Study case

Molina et.al., 2015 previously studied the design of working fluids for ORCs using a low temperature source ($< 200^{\circ}\text{C}$). The authors used the following system parameters:

Parameters for the model

Parameter	value	units
$T^{HS,IN}$	423.15(150)	$K(^{\circ}\text{C})$
$T^{CS,IN}$	293.15(20)	$K(^{\circ}\text{C})$
η_{SP}	0.9	-
η_{ST}	0.9	-
ΔT^{CS}	10	$K(^{\circ}\text{C})$
ΔT^{HS}	20	$K(^{\circ}\text{C})$
ΔP_{min}	1	bar
ΔT_{min}	5	K
R_g	8.314	$\text{kJkmol}^{-1}\text{K}^{-1}$
N_{ψ}	3	$\text{kJkmol}^{-1}\text{K}^{-1}$

Comparison of Single- and Multi-Component Mixtures

$T^{HS,IN} (^{\circ}C)$	150		
	ORC		Conventional RC
	Mix	Pure Organic fluid	Water
Z_{n-C_4}	0.3499	-	-
Z_{n-C_5}	0.6551	1.000	-
Z_{R-718}	-	-	1.000
$F_{obj}(\eta)$	0.182	0.1677	0.0260
W_{net}	7442.2307	6345.2856	1168.4839
q_{IN}	38357.9482	37841.8716	44964.4060
# variables	3283		

We implemented the model in GAMS and solved it with CONOPT.

Dealing with Uncertainty

We are interested in designing a working fluid capable of **withstanding uncertainty** in variables affecting the operation of the ORC.

Stochastic Formulation

We formulate a stochastic nonlinear programming problem of the form:

$$\begin{aligned} & \underset{x,y}{\text{minimize}} && f(x) + \mathbb{E}[g(x, y(\Xi), \Xi)] \\ & \text{subject to} && h(x) \geq 0, \\ & && m(x, y(\xi), \xi) \geq 0, \end{aligned} \tag{23}$$

where \mathbb{E} denotes mathematical expectation with respect to the random variable Ξ , x are design variables, and $y(\Xi)$ are operational variables.

Uncertainty in Temperature of Heat Source

Want to find an optimal mixture for the ORC that is optimal for a range of heat source temperatures. We use a range of (150 – 130°C) with 5 scenarios:

Scenario set Ξ	ξ_1	ξ_2	ξ_3	ξ_4	ξ_5
$T^{HS} (^{\circ}C)$	150	145	140	135	130

Perfect Information Design (optimal mixture for each temperature):

	Scenario set Ξ				
Composition	ξ_1	ξ_2	ξ_3	ξ_4	ξ_5
$Z_{R-245ca}$	-	0.0280	0.2977	0.2795	0.1941
$Z_{FC-4-1-12}$	-	-	-	0.0435	0.0990
Z_{C_4}	0.3499	0.1605	-	-	-
Z_{C_5}	0.6551	0.8115	0.7023	0.6770	0.7069
Cycle Efficiency η	0.1823	0.1789	0.1752	0.1691	0.1625
Expected Value $\mathbb{E}[\eta]$	0.174				

Stochastic Design (optimal mixture to handle all temperatures):

	Scenario set Ξ				
Composition of Mixture	ξ_1	ξ_2	ξ_3	ξ_4	ξ_5
$ZR-245ca$	-				
$ZFC-4-1-12$	-				
ZC_4	0.2109				
ZC_5	0.7891				
Efficiency of cycle η	0.1714	0.1714	0.1714	0.1683	0.1622
Expected Value \mathbb{E}	0.169				

Conclusions

- The use of **multicomponent mixtures** as working fluids can significantly increase the efficiency of Organic Rankine Cycles (ORC). Such cycles are used to recover waste heat at low temperatures (<370 °C).
- **Uncertainty** impacts the performance of the cycle and the amount of energy that can be recovered. We proposed a stochastic programming formulation to mitigate uncertainty effects.
- In future work, we will consider uncertainty in other **system parameters** (e.g., equipment efficiencies) and we will use **risk measures** to mitigate extreme events.

THANKS