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# DECISION-MAKING MATRIX FOR THE SELECTION OF MIXTURE IN ORC APPLICATION

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## ABSTRACT

ORC is an established and affordable technology to convert efficiently low/medium grade thermal energy to power. The choice of the working fluid is critical to the performance of the ORC. The use of zeotropic mixtures as a cycle working fluid could lead to an efficiency enhancement, thanks to the non-isothermal phase change occurring at both the condenser and the evaporator. Therefore, there has been a growing interest for mixtures, which are often studied by the means of optimization algorithms or thermodynamic calculations that lead to interesting results (Bederna *et al.*, 2021, Lecompte *et al.*, 2014). This work proposes an alternative approach. A selection methodology is used to conduct a preliminary screening to optimize the mixture choice in accordance with the targeted objectives. This methodology is applied to study cyclopentane-based mixtures. For this purpose, a large list of criteria is considered to achieve improved safety, maximized performances, ORC using more environmentally friendly fluids and respecting heat exchangers sizing while following specific technical constraints. Among these criteria, the temperature glide should be carefully taken into account: indeed, it is directly linked to the fractionating risk, which must be prevented for the good functioning of the cycle. Performing this study prior to the classical energetic analysis reduces the risk of exploring mixtures of incompatible or irrelevant fluids. This whole analysis yields a decision-making matrix, gathering selection criteria, relevant properties, and cycle performances. By adapting the different threshold of these criteria, this methodology is adaptable to large-scale ORC applications.

## 1 INTRODUCTION

Nowadays, energy is a major concern. Industry sector is one of the most energy consuming. The various crises currently experienced are raising prices to new heights and pushing the industry to re-evaluate their relationship to energy. In this context, the reduction of energy consumption and industrial waste heat recovery have become critical. The Organic Rankine Cycle (ORC) is a mature technology that allows harvesting industrial waste heat by converting thermal energy to electrical power. In order to optimize its efficiency according to the application, the components need to be properly sized and the working fluid must be well selected. Since ORC is a well-known classic thermodynamic cycle, a large range of fluids have already been tested and validated. However, there is still a great interest in the use of different pure fluids and zeotropic mixtures. For the latter, considering that the two fluids of such mixture have different condensation and boiling temperatures, the phase changes occurring within the cycle are not isothermal. Using an adapted mixture, the working fluid temperature can better follow the hot and cold source profile along the heat exchangers, thus improve the cycle performances. Moreover, mixtures are considered to potentially improve the cleanliness and safety of working fluids.

In the framework of the DECAGONE project (Horizon Europe), cyclopentane is chosen as the main component of the working fluid mixtures (Vescovo, 2019). A bibliographical study on mixtures commercially available and/or those studied in scientific literature is first conducted. Most cyclopentane-based mixtures commercially available consist of other similar alkanes (pentane, isopentane), or fluorinated gases (CFC, HFC). In the scientific literature, articles are mostly analyses and numerical studies. Most papers elaborate mixtures discussing thermodynamic performances

calculated using simulations (Wang *et al.*, 2022). In chemical engineering, computer-aided molecular design (CAMD) is used to design molecules and select optimum pure working fluid and mixtures (Papadopoulos *et al.*, 2013). Even if thermodynamic properties are considered in these studies, they are mainly used as performances indicators. It is rarely verified that the proposed mixtures are actually relevant with fluid compatibility studies or even experimental results. In this work, a different methodology is proposed. This methodology is based on the prior selection of one fluid of interest that is planned to be mixed with another specie. In order to ensure technical relevance of suggested mixtures, criteria selection are firstly defined to ensure their compatibility, before considering other thermodynamic properties of interest, energetic results and experimental data as tools of the mixture selection choice.

## 2 LIST OF CRITERIA

The NIST (National Institute of Standards and Technology) database is used to provide thermodynamic data for around 150 fluids, as a basis for a first fluid screening. In the database, four different data cases can be encountered concerning the mixtures properties calculations. In the best case, the exact mixture is present in the database. Then, a mixture with one actual fluid of the couple and one similar to the second fluid can be present, or a mixture with two similar fluids. Finally, in the worst case an estimation of the mixture properties is used. The values calculated later with a software using Refprop database should be used with caution, as their accuracy is uncertain.

The selection of relevant discriminating criteria is crucial, as they are the backbone of the methodology. They need to ensure that the fluids validating the thresholds required enable the good functioning of the process and the safety of the installation. These criteria are split into two classes depending on their criticality: some of them are strict criteria, which means that no variation of the values set are accepted; the other ones are adjustable, so the initial thresholds are open to discussion. This flexibility allows obtaining a greater number of candidates if needed after the screening. Hereafter are listed the criteria with their class and for some of them thresholds.

### 2.1 Auto-ignition Temperature

This first parameter is of great importance as it is a safety guarantor. The minimum required value is strict and depends on the highest temperature possibly reached by the working fluid in the cycle. It is relevant to allow for a safety margin by using a threshold greater than this temperature. Cyclopentane auto-ignition temperature is obtained from a safety data sheet (Carl Roth, 2022).

### 2.2 Mixing

The fluids studied must be miscible with the preselected working fluid. Only two fluids were identified as non-miscible until then. The miscibility is a criterion that will be checked experimentally for the reduced list of fluids remaining after the selection.

### 2.3 GWP, ODP, Toxicity

This criterion includes three indicators concerning environment and safety. First, the GWP (Global Warming Potential) value is limited to ensure that the selected fluids have a reduced carbon footprint. Then, the ODP (Ozone Depletion Potential) is considered in order to discard the targeted fluids by Montreal protocol from the considered fluids (CFC, HCFC). More generally, these environment criteria also eliminate HFC and PFC of the list of fluids. Finally, a toxicity criterion is considered. In this application, the American NFPA (National Fire Protection Association) standard 704 is used, as it can be found in safety data sheet of a wide range of fluids. Four indicators are taken into account: health hazard, fire hazard, reactivity, specific hazard. The limits to set for these toxicity indicators should be chosen accordingly to the considered standards and regulations. For this application, the focus is put on health hazard indicator that should not be above two (chosen as limit value). As other standards and regulations exist such as CLP (Classification, Labelling, Packaging) and HAP (Hazardous Air Pollutants) for example, it is relevant to search for more information concerning the fluids after the first selection process.

## 2.4 Fractionating risk

This criterion is essential. The fractionating phenomenon can occur during a phase change, when the vapour phase consists of one of the components, and the liquid phase consists of the other one. This separation of the mixture could lead to important issues in the cycle. It was observed that a limitation to a 15 K temperature glide (temperature difference of the mixture components during a phase change) should help avoiding this risk (Heberle *et al.*, 2012). In order to keep fluids for which a significant quantity can be mixed with the first fluid, the temperature glide of the mixtures is limited to a maximum of 15 K for a given minimum mass fraction of additive.

## 2.5 Flammability

Two values characterize the flammability range of a fluid: its lower flammability limit (Lfl) and its upper flammability limit (Ufl). In some cases, mixtures are studied to improve the safety of the cycle, so increasing the Lfl can be of great importance. Many pure fluids flammability limits and a quantitative model used to estimate mixtures lower flammability limits are provided in ISO (International Organization for Standardization) standard (ISO 10156, 2017). With a view to improving safety, the minimum value accepted during the selection process should be the lower flammability limit of the first fluid composing the mixture.

## 2.6 Liquid phase

The selected fluids must have a melting point lower than the cold source minimum temperature. Actually, the melting point must also be lower than the potential colder temperatures occurring in the geographical area of the ORC installation to prevent any risk of solidification of the working fluids. Moreover, they need to be able to condense at room temperature and low pressure, and have a reasonable vapour pressure.

## 2.7 Properties definition

Finally, the definition of the properties concerns the NIST Refprop database (Lemmon *et al.*, 2022). In fact, after the first screening, energetic calculations provide performance element to refine the selection; thus, the thermodynamic properties need to be defined at least up to the highest temperatures reached by the cycle for the calculation. As it does not involve safety issue this is an adjustable criterion.

**Table 1:** Criteria values for DECAGONE project

Criterion	Class	Threshold in DECAGONE project
Auto-ignition temperature	Strict	$\geq 550$ K
Mixing	Strict	Miscible with cyclopentane
GWP, ODP & toxicity	Strict	Low GWP ( $< 100$ ), ODP $\sim 0$ NFPA health rating $\leq 2$
Solidification temperature	Strict	$\leq 250$ K
Fractionating risk	Adjustable	Volume fraction minimum of 5 %, 10 % is preferred, of 2 <sup>nd</sup> fluid can be added without exceeding the temperature glide limit of 15 K
Flammability	Adjustable	LFL $\geq 0.5$ %, 1.1 % is preferred
Liquid phase	Adjustable	Can condense at room temperature & low pressure, vapour pressure not too low
Properties definition	Adjustable	Thermodynamic properties defined at least up to 525 K, 550 K is preferred

The fractionating risk criterion was the last one applied. Thus, it has been possible to observe how the list of selected fluids would change if the threshold was modified. In this case, all the preferred criteria are kept. As an example, lowering the value to 10 K or increasing the value to 20 K would not change the list of selected fluids. The impact would be observed on the mass fraction allowed that would either decrease or increase.

It highlights that the selection with the criterion chosen is relevant, and that the exact temperature glide value is not critical for the fluids selection: more than 80 % of the fluids of the initial database are discarded by the other criteria.

## 2.8 First screening

Applying these criteria, a reduced number of candidates are highlighted. This list can be increased with the adjustable parameters. To be more specific, fluids with the least amount of unmet criteria are preferred. Logically, isomers and fluids of the same specie as the first one are represented. However, it is noted that some fluids may have grey areas. Various references found may sometimes give contradictory values concerning certain points, and some values may not be available. Moreover, information that could have a different impact on the fluid selection are provided by other means, such as different standards concerning toxicity for example.

**Table 2:** Selected fluids

Main Fluid	Cyclopentane
Fluid n°1	Acetone
Fluid n°2	Butane
Fluid n°3	Isobutene
Fluid n°4	Isopentane
Fluid n°5	Isobutane
Fluid n°6	2,2-Dimethylbutane
Fluid n°7	2,3-Dimethylbutane
Fluid n°8	Isooctane
Fluid n°9	Hexamethyldisiloxane
Fluid n°10	Butene
Fluid n°11	Cis-butene
Fluid n°12	Trans-Butene

Once candidates fulfilling the requirements are identified, the screening progresses in two directions. Based on this short-list, different analyses are performed. On the one hand, there is a great interest in performing experimental tests. Material compatibility tests between the working fluid candidates and the ORC components are important to prove their suitability; also, thermodynamic properties oriented tests (checking database values, confirming that the estimation of mixtures flammability is correct, etc...) aim to confirm that the selection is relevant. On the other hand, energetic calculations add a performance aspect to the selection that helps classifying the previously selected fluids.

## 3 ADVANCED SELECTION

Once the first selection based on criteria is done, other parameters are used in order to refine the candidates list. Reviewing performances of a certain number of mixtures helps identifying thermodynamic properties of interest.

Whether zeotropic mixtures being studied with a performance or a safety objective, energy results are taken into account in the final choice of working fluid. For this reason, calculations are relevant, even with a simplified model. In fact, if the Refprop database is used, results are only estimations, so the point is to have qualitative results, overall behaviours. In order to do that, a large range of parameters of interest should be monitored as a function of the fluids mixed and their respective mass fractions.

### 3.1 Cycle operability

First, the temperature glides must be checked because in such calculations the consideration of the thermodynamic cycle and the changes that can occur, such as pressure drops in various components for example, can influence it. As it is one of the most important selection criteria, a second verification of the glide is relevant. Mixing a pure fluid with one of the additive from the fluid short list can induce a modification of the ORC cycle.

Then, temperature pinch points at the various heat exchangers (minimum temperature difference between the cold fluid and the hot fluid at the condenser, evaporator, and recuperator if used) need to be verified to ensure that the phase changes and heat exchanges are consistent. Temperatures and pressures in the whole cycle are also looked at with the same objective of good operability.

### 3.2 Cycle performances

Classic results are compared to the ones obtained with a pure fluid. The turbine power and cycle efficiency are calculated for the mixtures with varying mass fraction of the additive. Due to the use of zeotropic mixtures, the turbine work and the cycle efficiency can reach a maximum for a specific mass fraction of a mixture. They behave independently; these two maximum are generally reached for different mass fractions. When such behaviour was observed, it is interesting to note that these performance peaks do not necessarily correspond to the highest temperature glide. Moreover, as the fluids considered have been selected in the basis of their compatibility and not their potential performance enhancement, the performances maximum can correspond in some cases to the initial pure fluid instead of a mixture.

Additionally, some input parameters, such as turbine inlet temperature or pump pressure, can be modified to observe if the cycle behaves as expected.

Finally, mixing a pure fluid with an additive can require modifying the size of the ORC components, for a given performance. Two sizing parameters provide a better comprehension of how using a mixture instead of a pure fluid influences the ORC components. On the one hand, the heat exchangers are characterized with the Logarithmic Mean Temperature Difference (LMTD) as listed in equation (1):

$$\Phi = U * A * F * \text{LMTD} \quad (1)$$

With  $\Phi$  the thermal power (W), U the heat transfer coefficient ( $\text{W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$ ), A the surface exchange area ( $\text{m}^2$ ) and F a corrective factor (–).

The pure fluid coefficient (product of heat transfer coefficient by the surface area of the heat exchanger) and the mixture ones are compared and a rough model is used to approximate the ratios of heat transfer coefficients, as observed by Zühlsdorf *et al.* (2019). A similar result has recently been measured by Blondel (2021). In the end, the ratio of the heat exchangers sizing for the various mixtures by the heat exchanger sizing of the pure cyclopentane cycle is obtained.

On the other hand, the turbine size is also a valuable parameter. It is related to the coefficient SP (Invernizzi and Ahmed Sheikh, 2018), for Size Parameter, listed in (2):

$$\text{SP} = \frac{\sqrt{\dot{V}}}{(h_{\text{in}} - h_{\text{out}})^{0.25}} \quad (2)$$

With SP the size parameter (m),  $\dot{V}$  the isentropic volume flow ( $\text{m}^3 \cdot \text{s}^{-1}$ ) and h the specific enthalpy (J/kg) at turbine inlet and outlet.

In terms of both footprint and cost, the size of ORC components is an important parameter to consider.

**Table 3:** Energetic results obtained for the fluid selected

Property / Fluid	Mass fraction considered for mixtures	Mixtures energetic results			
		Wt variation (%)	Efficiency variation	A <sub>mix</sub> /A <sub>cyclo</sub>	SP <sub>mix</sub> /SP <sub>cyclo</sub>
Main Fluid	100%	0	(20,54) +0%	1,000	1,000
Fluid n°1	50%	0,41	-2,29%	1,31	0,950
Fluid n°2	20%	0,87	-0,87%	1,25	0,950
Fluid n°3	10%	1,32	-0,51%	1,30	0,976
Fluid n°4	50%	-4,51	-1,32%	1,20	0,933
Fluid n°5	10%	1,23	-0,48%	1,29	0,977
Fluid n°6	50%	-7,29	-0,31%	1,20	1,022
Fluid n°7	50%	-6,33	0,12%	1,24	1,064
Fluid n°8	15%	4,01	1,81%	1,43	1,169
Fluid n°9	20%	2,96	1,44%	1,41	1,181
Fluid n°10	10%	1,82	-0,51%	1,30	0,977
Fluid n°11	20%	1,50	-0,96%	1,27	0,950
Fluid n°12	20%	1,41	-0,97%	1,27	0,950

### 3.3 Parameters of interest

In fact, some of them could directly affect the results: condensation and evaporation pressures, critical temperature and pressure (Wang *et al.*, 2022). Even though they are not selection criteria, these parameters are to be considered as they could affect the fluid choice for performance and operability. Moreover, in order to ensure the operability of the ORC loop, additional thermodynamic parameters are evaluated: vapour pressure, viscosity, and fluid behaviour. Vapour pressure is an important parameter regarding the mixture crossing the heat exchangers. Viscosity is linked to the good pumpability of the fluid mixture throughout the hydraulic circuit, and affects heat exchange. Critical temperature and pressure are directly related to the state of the mixture and must be chosen to avoid supercritical state during the cycle. Finally, the behaviour (wet, isentropic or dry) has influence on the thermodynamic cycle. Dry fluids are usually preferred over wet fluids as overheating the fluid is not necessary before the expansion.

In practice, performing experimental tests on various points regarding mixture properties as well as obtaining data from fluid suppliers would bring significant information on fluids and compatibility. Indeed, mixtures properties such as thermal stability, auto-ignition temperature, flammability, but also classic thermodynamic properties, are estimated or based on rough model. Compatibility tests are finally conducted to verify the compatibility of studied mixtures with ORC components materials.

Finally, another parameter must be considered in the very last steps of the selection process. When selecting a pure fluid and especially the supplier, the impurities rate is critical. In fact, depending on the impurities nature and level, the impact on performances could be significant. A few percent of another specie could affect thermodynamic parameters such as condensation and evaporation pressures, resulting in a reduction of the performances. At the very end, the price may also affect the choice between the remaining promising fluids.

#### 4 DECISION-MAKING MATRIX

The working fluid selection process is based on all the elements previously presented: the first selection criteria, the typical thermodynamic properties, the energetic results and the experimental tests. As they all are important to a certain degree, creating a table resuming all of these properties and performances gives a global overview of each fluid potential. Thus, this decision-making matrix enables optimizing the choice of the fluid mixture.

As presented above, seven main criteria are used to select the most compatible fluids: auto-ignition temperature, GWP and ODP, thermal range for properties, lower flammability limit, maximum mass fraction of fluid respecting the temperature glide criterion, solidification temperature, and NFPA rating. However, if they are essential to the screening, some of them will not be taken into account in the final decision. In fact, the auto-ignition temperature, for example, has no further impact: fluids must meet the criterion ( $T > 550$  K), but it is not of high importance if their auto-ignition temperature is of 600 or 700 K. Only four of the seven parameters are actually kept in the matrix: lower flammability limit (for the mixtures), thermal range for properties, NFPA rating and environment.

Then, several pure fluids thermodynamic properties are involved in the selection as explained earlier: vapour pressure, viscosity, critical pressure, critical temperature and fluid behaviour (dry, isentropic or wet).

Afterwards, ORC simulation results give performance-oriented results. This information is estimated and needs to be considered as qualitative result to compare to pure fluid cycle. Many values must be monitored with different mass fractions of the fluids: turbine power, efficiency, ratio of SP coefficient of a mixture cycle and of a pure cyclopentane cycle, ratio of evaporator surface of a mixture cycle and of a pure cyclopentane cycle. In addition to that, some thermodynamic properties mentioned are calculated: working fluid viscosity at the pump outlet, and critical pressure and temperature of the mixtures.

Finally, an evaluation of the level of uncertainties is added. It considers the estimations of mixtures properties calculations (flammability, performances), contradictory references found (NFPA rating, GWP and ODP values, flammability limits) and any unknown or not found values. Thus, the complete decision-making matrix is formed so the second fluid composing the mixture can be selected in accordance with the objectives. The next table is an example of matrix, filled with signs (+, o or -), indicating if the parameter is interesting compared to pure cyclopentane. The concentrations indicated for the mass fractions considered for mixtures were estimated using Refprop, being the maximum allowable fraction so that mixtures respect the maximum 15 K glide criterion. A 50% mass fraction means (for the fluid considered here) that the threshold is not reached for any concentration.

Fluids can be classified regarding their relevancy from the matrix, by weighting the various criteria based on their importance for the considered application: for example, with a safety-driven approach flammability and NFPA rating could be prioritized. Thus, doing this for all matrix criteria the best candidates can be identified. The results may differ from CAMD and thermo-economic methods. Indeed, the NIST database was used for this study, so it does not take into account all existing fluids and molecules; moreover, economic impact specific to each fluid is not studied.

The matrix allows a global theoretical global view of the most critical properties of the fluids identified ; however as explained before this is a tool dedicated to pre-selection, and experimental work is necessary to confirm the good behaviour of the mixtures and to reduce the uncertainties due to the estimations made with the various models used.



**Table 4a:** Example of qualitative decision-making matrix (restrictive criteria)

	<b>Property / Fluid</b>	Main fluid	Fluid n°1	Fluid n°2	Fluid n°3	Fluid n°4	Fluid n°5
	Mass fraction considered for mixtures	100%	50%	20%	10%	50%	10%
2 - Selection criteria	Thermal range for properties (pure fluid)	+	+	+	+	+	+
	NFPA (pure fluid)	o	o	o	-	o	+
	Environment (pure fluid)	o	+	o	o	o	o
	Lower Flammability Limit (mixture)	o	++	+	+	+	+
3.2 - Mixtures energetic results	Wt variation	o	+	+	+	-	+
	Efficiency variation	o	--	-	-	-	-
	Amix/Acyclo	o	-	-	-	-	-
	SPmix/SPcyclo	o	+	+	+	+	+
3.3 - Thermodynamic properties	Fluid behavior (pure fluid)	+	-	+	+	+	+
	Vapor pressure at 25°C (pure fluid)	o	o	o	o	o	o
	Viscosity pump outlet (mixture)	o	+	+	o	+	-
	Critical pressure (mixture)	o	o	o	o	-	o
	Critical temperature (mixture)	o	o	-	o	-	o
General	Thermodynamic model uncertainties	o	-	--	--	-	-
	All uncertainties	o	-	--	--	-	-

**Table 4b:** Example of qualitative decision-making matrix (adjustable criteria)

	<b>Property / Fluid</b>	Main fluid	Fluid n°6	Fluid n°7	Fluid n°8	Fluid n°9	Fluid n°10	Fluid n°11	Fluid n°12
	Mass fraction considered for mixtures	100%	50%	50%	15%	20%	10%	20%	20%
2 - Selection criteria	Thermal range for properties (pure fluid)	+	+	+	+	+	-	-	-
	NFPA (pure fluid)	o	-	o	?	?	o	o	o
	Environment (pure fluid)	o	?	?	?	?	?	-	?
	Lower Flammability Limit (mixture)	o	?	-	-	--	+	+	++
3.2 - Mixtures energetic results	Wt variation	o	-	-	+	+	+	+	+
	Efficiency variation	o	-	+	+	+	-	-	-
	Amix/Acyclo	o	-	-	-	-	-	-	-
	SPmix/SPcyclo	o	-	-	--	--	+	+	+
3.3 - Thermodynamic properties	Fluid behavior (pure fluid)	+	+	+	+	+	-	+	+
	Vapor pressure at 25°C (pure fluid)	o	o	o	-	-	o	o	o
	Viscosity pump outlet (mixture)	o	+	+	-	-	o	+	+
	Critical pressure (mixture)	o	-	o	o	o	o	o	o
	Critical temperature (mixture)	o	o	o	o	o	o	o	-
General	Thermodynamic model uncertainties	o	--	--	--	---	--	--	--
	All uncertainties	o	----	---	----	-----	---	--	---

**Table 5:** Example of values rating

	Criterion	Value	Sign
2 - Selection criteria	Thermal range for properties (K)	$\geq 550$	+
		$525 < x < 550$	-
	NFWA health rating	0	+
		1 2	o -
Environment	GWP < 1	+	
	$1 < \text{GWP} < 10$ $10 < \text{GWP} < 100$	o -	
LFL (Vol. %)	Lfl > 1.2	++	
	$1.2 > \text{Lfl} > 1.1$	+	
	Lfl = 1.1	o	
	$1 < \text{Lfl} < 1.1$	-	
	Lfl < 1	--	
3.2 - Mixtures energetic results	Wt variation	$0\% < x < 10\%$	+
		$-10\% < x < 0\%$	-
	Efficiency variation	$0\% < x < +2\%$	+
		$-2\% < x < 0\%$ < - 2 %	- --
Amix/Acylo	> 1	-	
SPmix/SPcylo	$-10\% < x < 0\%$	+	
	$0 < x < +10\%$	-	
	> + 10 %	--	
3.3 - Thermodynamic properties	Fluid behavior	Dry	+
		Wet	-
	Vapor pressure (Pa)	< 1E+04 or > 5E+05	-
	Viscosity pump outlet (Pa.s)	< 3.70E-04	+
		> 3.80E-04	-
Critical pressure (bar)	< 40	-	
Critical temperature (K)	< 493	-	
General	Thermodynamic uncertainties	1 similar fluid used	-
		2 similar fluids used Estimation	-- ---
	Other uncertainties	?	-

## 5 CONCLUSIONS

This paper presents a methodology for the selection of fluids composing a zeotropic mixture for ORC applications. This method is aiming to prevent performing long and expensive mixtures experimental studies on a wide variety of potential fluids. By selecting promising candidates, time and resources may be saved. Starting with a predefined main fluid, a first list of discriminating criteria is used to filter a fluid database and obtain a reduced quantity of compatible fluids. Then, thermodynamic properties and energy results are reviewed and included in a decision-making matrix. Finally, other parameters, resulting of laboratory tests or given by suppliers, can complete the screening, confirming the choices and refining the list of promising fluids. These tests are the best mean to validate the assumptions and estimations that have been made. The remaining candidates can then be classified according not only to their compatibility but also to the performances of the mixtures they are a part. The filling of the decision-making matrix, adaptable to the specificities and the main objectives of the project, is the last step of the optimized selection process.

This detailed method is supposed to facilitate the selection and ensure that the mixtures formed demonstrate great compatibility. The selection criteria are adaptable to the ORC configurations, and the

discussion is open about their relevance and other usable parameters for the choice of the fluids. It would be interesting to apply this matrix to fluid selections performed in literature, and to observe if the identified fluids are similar or not to the ones selected with other methods.

Regarding the DECAGONE project, additional experimental work, focusing on mixture properties and material compatibility, follows this mixture study to lead to the final mixture choice.

## NOMENCLATURE

$\Phi$	thermal power	(W)
A	heat exchange surface	(m <sup>2</sup> )
F	corrective factor	(–)
SP	size parameter	(m)
U	heat transfer coefficient	(W. m <sup>-1</sup> . K <sup>-1</sup> )
$\dot{V}$	isentropic volume flow	(m <sup>3</sup> . s <sup>-1</sup> )
h	specific enthalpy	(J/kg)

### Subscript

in	turbine inlet
out	turbine outlet

## REFERENCES

- Bederna, B.G.; Barta, R.B.; Hesse, U. 2021, Composition optimization of zeotropic mixtures for ORC systems considering constraints, *6<sup>th</sup> International Seminar on ORC Power Systems*.
- Blondel, Q. 2021, Etude et optimisation énergétique des mélanges zéotropes pour les cycles thermodynamiques de Rankine. *PhD Thesis*. University of Grenoble Alpes.
- Heberle, F; Preißinger, M; Brüggemann, D. 2012, Zeotropic mixtures as working fluids in organic Rankine cycles for low-enthalpy geothermal resources. *Renew Energy*. 37(1), p. 364-370.
- Invernizzi, C.M.; Ahmed Sheikh, N. 2018, High-efficiency small-scale combined heat and power organic binary Rankine cycles. *Energies*, vol.11, 994.
- Lecompte, S.; Ameel, B.; Ziviani, D. ; van Den Broek, M. ; de Paepe, M. 2014, Exergy analysis of zeotropic mixtures as working fluids in Organic Rankine Cycles, *Energy Convers. Manag.*, vol. 85, p. 727-739.
- Lemmon, E. W.; Bell, I. H.; Huber, M. L.; McLinden, M. O. 2022, *NIST Standard Reference Database 23, NIST Reference Fluid Thermodynamic and Transport Properties, version 10.0*; Standard Reference Data Program, National Institute of Standards and Technology.
- Papadopoulos, A. I.; Stijepovic, M.; Linke, P.; Seferlis, P.; Voutetakis, S. 2013, Toward Optimum Working Fluid Mixtures for Organic Rankine Cycles using Molecular Design and Sensitivity Analysis, *Ind. Eng. Chem. Res.* 52(34), p. 12116-12133.
- Vescovo R. 2019, High temperature organic rankine cycle (HT-ORC) for cogeneration of steam and power, *AIP Conference Proceedings* 2191, 020153
- Wang, E.; Zhang, M.; Meng, F.; Zhang, H. 2022, Zeotropic working fluid selection for an organic Rankine cycle bottoming with a marine engine. *Energy*. vol. 243, article 123097.
- Zühlsdorf, B.; Jensen, J.; Elmegaard, B. Heat pump working fluid selection—economic and thermodynamic comparison of criteria and boundary conditions, *Int. J. Refrig.*, vol.98, p. 500-513.
- Cyclopentane*, Safety Data Sheet No. 2191, Carl Roth
- ISO 10156:2017, *Gas cylinders – Gases and gas mixtures – Determination of fire potential and oxidizing ability for the selection of cylinder valve outlets*.

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