# Sustainable working media selection for renewable energy technologies

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Abstract: The sustainable working media selection is one of the most important stages in renewable energy technologies. The compromise among such properties as contribution to greenhouse effect, flammability, toxicity, thermodynamic behaviour, performance specifications, and the others defines a sustainable decision. The aim of present work is to apply a fuzzy set methodology providing sustainability among thermodynamic, economic, and environmental requirements. The organic Rankine cycle (ORC) for the class of working fluids based on the hydrofluoroethers (HFE) is considered to demonstrate a proposed approach. To select new working fluids, which have no information on thermodynamic behavior, artificial neural networks (ANN) approach is offered to forecast the ORC energy efficiency. The ANN correlations for coefficient of performance (COP) and pressure ratio (output) as functions of critical temperature, critical pressure and normal boiling temperature (input) are built via REFPROP database. The validation set has been used to estimate the ORC energy efficiency without of thermodynamic property calculations. The accuracy of ANN prediction for the cycle performances does not exceed 4% relative to the training set values. The Bellman – Zadeh model as the intersection of membership functions (fuzzy criteria mappings) is applied to sustainable selection of working media.

Keywords: Working Fluids, Organic Rankine Cycle, Coefficient of Performance, Artificial Neural Networks

### **Nomenclature**

COP  K  K <sub>i</sub> M  n <sub>i</sub> p  RD  T	coefficient of performancegeneralized criterionmolar massgenole-1 number of atomic species (i) pressureMPa relative deviation% temperatureK	μ ρ Ψ C B opt	compressibility factor membership function density kg·m <sup>-3-3</sup> flammability index Subscripts critical boiling optimum thermodynamic
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The paradigm of sustainable development considers an integrated solution of the ecological, economic, social and cultural problems arising from the design of technical systems. The transformation of renewable energy sources into mechanical work mainly is based on the application of the Rankine cycle. The Rankine cycle working on organic substances, the Organic Rankine Cycle, has found wide application as renewable energy technologies (RET). There are many criteria of efficiency of RET and the extreme values are desirable to reach for each ones taken separately. Usually, three main goals are involved in the design process: thermodynamic, economic and environmental. The problem of prospective working media selection is closely connected with modern technologies based on the concept of sustainable development. To utilize low potential heat source, the ORC working fluids should possess normal boiling temperature below 350 K, practically vertical right boundary curve in the temperature - entropy diagram, high heat of evaporation, high density and comprehensible operational qualities. The selection of working fluids with desirable combination of such properties as contribution to greenhouse effect, flammability, toxicity, thermodynamic behavior, performance specifications, and the others is one of the most important stages in RET simulation and design. Working fluid selection problem has been tackled using achievements of molecular theory, engineering experience and experimental studies [1] - [4]. Clearly, a working fluid that combines all the desirable properties and has no undesirable properties does not exist.

## 1. Sustainable ORC working fluids selection

The aim of present work is to include a fuzzy set methodology in order to meet thermodynamic, economic, and environmental goals for working fluid selection in the ORC. To solve this problem, achievements of information technologies and the molecular theory, technical experience and experimental data are used. There is a multitude of efficiency criteria and the attainment of the extreme for each of them is the ultimate goal of the design. Usually a compromise among three basic criteria – energy, economic and ecological is considered. The generalized criterion of efficiency for all system as a whole is represented by a vector K, which includes local criteria  $K_i$  that reflect the set of requirements to ORC working fluids by the consumer.

### 1.1. Tailored working fluid concept

We consider here only such criteria, which are linked by certain relations R to the properties of working fluids P, i.e. the system defined by a three-tuple { K, R, P }. The relation R is a kind of technological operator and its structure can be determined via the equations of mass, momentum and energy balance, supplemented with the characteristic equation of state. It is usually impossible to estimate the performance attributes of refrigeration system from target properties (physical, chemical, ecological, and etc) correlated with molecular structure following to fundamental principles only. So, we need to enlist restricted experimental information to define real properties P via their model properties M (X). The set of model parameters X, as a mapping of the experimental data containing the observed properties P, gains in importance as information characteristics of substance by which its property behavior can be restored. A physical meaning is no less important for the vector X and should map the working fluid characteristics on the molecular level to select a proper molecular configuration. This is very convenient when one needs to be able to predict the properties of any molecular structure. The working fluid selection problem can be mathematically formulated as the multi-criteria optimization problem: to find

Opt 
$$K[K_1(X), K_2(X), ..., Kn(X)], X \in X_P$$
 (1)

We assume that  $K_j(X) = ||P_j, M_j(X)||$  is a "distance" between the desired (ideal) efficiency of system  $P_j$  and its real model  $M_j$ . For thermodynamic criterion,  $K_{th}$  the value  $P_j$  corresponds to the theoretical maximum of the efficiency objective function, e.g. efficiency of the Carnot cycle. Solution of multi-criteria problem is a finding of compromise among all criteria and constraints and can be formulated as follows: to construct the function

$$\mathbf{K} = K_1 \cap K_2 \cap \ldots \cap K_n. \tag{2}$$

The formal solution of problem is added up to determination of the optimum vector  $X_{opt}$  of such kind that  $|K(X_{opt})| > |K(X)|$  for any  $X \neq X_{opt}$  where > is preference sign. The model parameters  $X_{opt}$  identify a trade-off decision possessing to desired efficiency criteria. In our case the model parameters  $X_{opt}$  identify an optimum working medium having the desired complex of properties ("tailored" working fluid). Critical or/and fixed parameters of working fluids are typical examples of the information characteristics of substance linked with its molecular structure.

Attainment of the optimum decision corresponds to the compromise among various criteria and displays the quality of engineering decisions. Criteria of sustainable development cannot be formulated on a strict mathematical basis and always have subjective character. The several approaches for finding the compromise between local criteria and constructions of generalized criterion function were offered. For example, in traditional thermodynamics

analysis, the concept exergy or exergy-ecological costs is introduced for monetary and power values. Additive convolution of power (*COP*) and ecological (Global Warming Potential – *GWP*) parameters of efficiency has been offered for the analysis of refrigerating systems in TEWI criterion [4]. A weak point of such approaches is the implicit assumption about conformity of the economic (ecological) and energy efficiency objectives that contradicts a real situation. Finding the compromise actually is a non-trivial decision-making problem and cannot be formalized. There are some ways of transformation of vector criterion in scalar which were discussed earlier [5], [6].

## 1.2. Multicriteria making decision

Design objectives usually contradict with each other, so that is difficult to provide sustainable solution, which simultaneously satisfies both of them. Meaningful analysis of this ill-structured situation should include uncertainty conception. For the multicriteria problems the local criteria usually have a different physical meaning, and consequently, incomparable dimensions. It complicates the solution of a multicriteria problem and makes it necessary to introduce the procedure of normalizing criteria or making these criteria dimensionless. There is no unique method for the criteria normalizing and a choice of method depends on statement of problem having subjective nature. In the present study, a next sequence of decision-making steps is applied [6].

- Determination of the Pareto optimum (or compromise, or trade off) set  $X_P$  as the formal solution of multicriteria problem to minimize uncertainty sources;
- Fuzzification of goals as well as constraints to represent an ill-structured situation;
- Informal selection of convolution scheme to transform a vector criterion into scalar combination of vector components.

Sustainable decision is defined by the Bellman and Zadeh model [7] as the intersection of all local fuzzy criteria and is represented by its membership function  $\mu$ i(X) as follows:

$$\mu_C(X) = \mu_1(X) \cap \mu_2(X) \dots \cap \mu_n(X)$$
,  $i = 1, 2, \dots, n$ ;  $X \in X_P$  (3)

The membership function of the objectives and constraints can be chosen linear or nonlinear depending on the context of problem. One of possible fuzzy convolution schemes is presented below.

- Initial approximation *X*-vector is chosen. Maximum (minimum) values for each criterion  $K_i$  are established via scalar maximization (minimization). Results are denoted as "ideal" points  $\{X_i^0, j = 1...m\}$ .
- Maximum and minimum boundaries for criteria are defined:

$$K_{i}^{min} = \min_{j} K_{j}(X_{j}^{0}) = K_{i}(X_{i}^{0}), \ i = 1...n; \ K_{i}^{max} = \max_{j} K_{j}(X_{j}^{0}), \ i = 1...n. \tag{4}$$

The membership functions are assumed for all fuzzy goals as follows

$$\mu_{Ki}(X) = \begin{cases} 0, & \text{if } K_i(X) > K_i^{max} \\ \frac{K_i^{max} - K_i}{K_i^{max} - K_i^{min}} & \text{if } K_i^{min} < K_i \le K_i^{max}, \\ 1, & \text{if } K_i(X) \le K_i^{min} \end{cases}$$

$$(5)$$

A final decision is determined as the intersection of all fuzzy criteria represented by its membership functions. This problem is reduced to the standard nonlinear programming problem.

# 1.3. Cycle configurations

Three main configurations of ORC are considered (Fig. 1) for typical working fluids R717, R123, and cyclohexane. The modeling of characteristics of the ORC is based on the First and Second Laws of thermodynamics and described elsewhere [8].

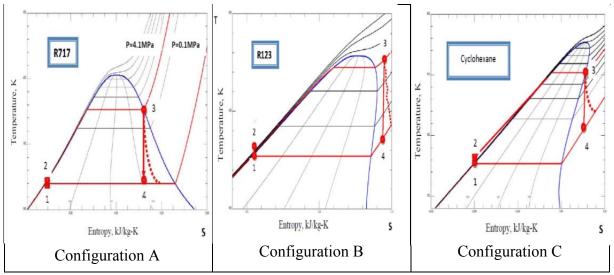


Fig. 1. ORC cycle configurations for different working fluids

### 2. ORC energy efficiency appraisal via artificial neural networks

Thermodynamic behavior of one-component substances in gas and liquid phases has identical topological structure similar to the cubic equations of state. The reliable quantitative description of a thermodynamic surface can be achieved via similarity theory. From this point of view, critical temperature  $-T_C$  and pressure  $-P_C$  together with normal boiling temperature  $-T_B$  are the most rational parameters which provide correct description of thermodynamic surfaces near the saturation curve.

### 2.1. Construction of ANN correlations. Results and discussion

To select the ORC working fluid with better properties we need preliminary estimating thermodynamic properties and assessment of different efficiency criteria. To evaluate the cycle performance data the artificial neural networks capable to recognize complex input – output relationships is applied. At first step the training set was used to calculate the main cycle characteristics. In Table 1 temperature boundaries  $(T_3, T_4)$  and a range of admissible pressures (Pmin, Pmax) which characterize the operating conditions for ORC configurations are given.

ANN represents the mathematical tool which during training allows establishing dependences between input data and target characteristics of any complexity. The purpose of training is to find factors of communications between neurons, which define abilities of a neural network to allocation of the latent relationships between input and output values. After training, the network becomes capable to forecast new data on the basis of the limited sample of known interrelations between input and output values. In this case, we aspire on the basis of the known information on the input  $T_C$ ,  $P_C$  and  $T_B$  for restricted set of known substances which are connected by complex relationships with output value -COP, to predict energy efficiency

of the Rankine cycle for little-studied working fluids only from critical parameters and normal boiling temperature. The ANN correlations for COP (output) as function of critical temperature, critical pressure and normal boiling temperature (input) are built on the REFPROP 8.0 database [9]. The training set consists of 15 components (R134a, R123, R1270, R717, R600a, R290, R245fa, R245ca, R236fa, R227ea, R142b, R125, R113, R22, R32).

Table 1. COP comparison for the organic Rankine cycle with ANN calculations

Working	Cycle	$T_C$ ,	$P_{C_i}$	$T_{B_{i}}$	$\frac{T_3}{T_3}$	$T_4$ ,	$P_{min,}$	$P_{max,}$	COP,	COP,	RD,
fluid	Type	${}^{0}C$	MPa	${}^{0}\overset{D}{C}$	${}^{0}C$	${}^{\scriptscriptstyle 0}\!\overset{\scriptscriptstyle \circ}{C}$	<i>МРа</i>	MPa	%,[8]	%, ANN	%
R32	A	78.11	57.8	-51.7	31.3	30.0	19.3	20.0	0.36	0.38	-4.5
R32	В	78.11	57.8	-51.7	100.0	97.7	19.3	20.0	0.42	0.44	-4.3
R125	A	66.18	36.3	-48.1	40.1	30.0	15.6	20.0	2.32	2.38	-2.3
R125	В	66.18	36.3	-48.1	100.0	91.9	15.6	20.0	2.36		0.1
RE125	A	81.34	33.5	-35	100.0	79.0	10.1	20.0	5.77		-4.3
R134a	A	101.0	40.6	-26.1	67.7	30.0	7.7	20.0	7.74		0.1
RE134	C	147.1	42.3	5.5	100.0	41.0	2.5	16.6	12.56		0.7
R143a	A	72.73	37.6	-47.2	43.6	30.0	14.4	20.0	3.14		1.9
R143a	В	72.73	37.6	-47.2	100.0	87.3	14.4	20.0	3.31	2.98	10.0
R152a	A	113.5	44.9	-24	72.6	30.0	6.8	20.0	8.82	8.78	0.4
R152a	В	113.5	44.9	-24	100.0	53.8	6.9	20.0	9.22	9.27	-0.5
RE170	A	126.8	52.4	-24.8	75.1	30.0	6.7	20.0	9.38	9.29	0.9
RE170	В	126.8	52.4	-24.8	100.0	53.0	6.7	20.0	9.68	9.84	-1.6
R218	C	71.89	26.8	-36.8	58.9	33.6	10.0	20.0	5.22		0.0
R227ea	C	101.7	29.3	-16.4	83.8	44.2	5.3	20.0	9.20	9.22	-0.2
R236ea	C	139.2	34.1	6.19	100.0	53.9	2.4	15.7	12.02	12.16	-1.1
R245ca	C	174.4	39.2	25.1	100.0	53.7	1.2	9.3	12.79		-1.3
R236fa	C	125.5	32.0	-1.4	100.0	48.6	3.2	19.3	11.63	11.55	0.6
R245fa	C	154.0	36.4	15.1	100.0	50.7	1.8	12.7	12.52	12.51	0.1
RE245mc	C	133.6	28.9	5.59	100.0	54.5	2.4	14.9	11.84		0.2
RC270	A	124.6	54.9	-31.5	100.0	41.6	8.2	20.0	8.86	8.62	2.7
R290	A	96.65	42.5	-42.1	57.1	30.0	10.7	20.0	5.91	5.91	-0.1
R290	В	96.65	42.5	-42.1	100.0	76.0	10.7	20.0	6.11	6.18	-1.2
RC318	C	115.2	27.8	-6	98.9	54.7	3.6	20.0	10.97	10.69	2.6
RE347mc	C	164.5	24.8	34.23	100.0	56.4	3.6	20.0	11.72	11.22	4.3
R600	C	152.0	38.0	-0.5	100.0	48.4	2.8	15.3	12.58	12.53	0.4
R600a	C	135.0	36.5	-11.7	100.0	45.3	4.0	20.0	12.12	12.11	0.1
R601	C	196.5	33.7	27.8	100.0	57.7	0.8	5.9	12.91	12.87	0.3
R601a	C	187.7	33.9	36.1	100.0	58.4	1.1	7.2	12.75	12.75	-0.0
R1270	Α	92.42	46.7	-47.7	48.5	30.0	13.1	20.0	4.28	4.28	-0.1
R1270	В	92.42	46.7	-47.7	100.0	81.2	13.1	20.0	4.53	4.16	8.2
C5F12	C	148.8	20.4	29	100.0	72.7	1.04	7.6	10.49		0.0
CF3I	A	123.3	39.5	-21.9	85.2	30.0	5.6	20.0	10.63	10.68	-0.5
CF3I	В	123.3	39.5	-21.9	100.0	39.6	5.6	20.0	10.93	10.93	-0.0
n-hexane	С	234.7	30.1	341.8	100.0	61.9	0.2	2.5	13.00	13.00	0.0

The construction of ANN includes the following sequence of actions: a choice of initial data for training; a choice of architecture of a network; dialogue selection of ANN parameters; process of training; check of adequacy of training (validation); and forecasting. Calculations were performed in Matlab Neural Network Toolbox environment (<a href="http://www.mathworks.com">http://www.mathworks.com</a>). The back propagation algorithm has been used for ANN training. Output values in the initial

sample were calculated for various configurations of cycles based on thermodynamic properties as reported in [8]. As input values the given  $T_C$ ,  $P_C$  and  $T_B$  are used. The various architectures of neural networks with different neuron numbers and activation functions in the first and second layers were considered. The third layer of a network always contains one neuron with linear active function.

For configuration A two hidden layers were used. The first contained two neurons and the second – one. As activation function the hyperbolic tangent was used. The training sample data for working fluids R125, R143a, R32 and R1270 were chosen. Testing was done for R152a, CF3I, and RE170. Check of adequacy was done for R290 and R134a. Results are listed in Table 1.

For configuration B two hidden layers were used. The first contained five neurons and the second – one. As activation function the hyperbolic tangent was used. As training sample data for working fluids R125, R143a, R152a, and RC270 were used. Testing was performed for RE125, R1270 CF3I and RE170. Check for adequacy was considered for R32 and R290. Results are listed in Table 1.

Construction of an artificial neural network for a configuration  $\,C$  coincides with architecture of a network for a configuration  $\,B$ . Training sample included the following working fluids: R218, R236fa, RE245mc,  $C_5F_{12}$ , R600, R601a, and n-hexane. Testing was done on the set of substances: R227ea, R236ea, RE134, R245fa RE347mcc, R601, and final verification accordingly for RC318, R600a, and R245ca.

Results of COP calculation for different ORC configurations are given in Table 1. Deviations of "experimental" values of COP [8] from calculated by means of the trained artificial neural network are within the error of calculations via the multi-constant equations of state [10] – [12]. Appreciable deviations of a relative error (more than 5 %) are observed for low COP values that have no principal meaning because we are interested by the working fluids with the maximal power efficiency.

The organic Rankine cycle for the class of working fluids based on the hydrofluoroethers (HFE) is considered to demonstrate a proposed approach. Critical properties of HFEs were taken from Ambrose *et al* [13]. Flammability indices correlated to atomic species by simple ratio of fluoride  $(n_F)$  and hydrogen  $(n_H)$  atoms  $\Psi = n_F/(n_F + n_H)$  are given in Table 2. The normal boiling points for HFEs were restored from Murata *et al.* correlations [14]. Temperature boundaries were taken for configuration A in range 300...315K.

To select the trade-off working fluid the membership functions (5) for energy efficiency  $(\mu_{COP})$  and ecological safety  $(\mu_{GWP})$  as function of critical parameters were calculated at following assumptions:  $COP^{max} = COP^{Carnot}$ ;  $COP^{min} = 3.64$  and  $GWP^{max} = 500$ ;  $GWP^{min} = 0$ . Flammability index  $(\Psi > 0.7)$  was considered as constraint. Intersection of membership functions defines the compromise solution for each HFEs under consideration. Final decision is chosen after comparison of compromise solutions with flammability index.

449mccc) ( $C_4F_9OCH_3$ ), and HFE-7200 (HFE-569mccc) ( $C_4F_9OC_2H_5$ ). The  $C_5H_2F_6O_2$  flammability index is also appropriate ( $\Psi = 0.75$ ) but near limiting value 0.7.

Table 2. Critical parameters, COP, and flammability index for hydrofluoroethers

Working fluids	M, gmole <sup>-1</sup>	$T_c$ , $K$		$\rho_c$ , $g cm^{-3}$		Ψ	COP,%
C <sub>2</sub> HF <sub>5</sub> O	136.021	354.49	3.35	0.579	0.267	0.83	3.64
$C_2H_2F_4O$	118.030	420.25	4.23	0.529	0.270	0.67	3.94
$C_2H_3F_3O$	100.040	498.50	4.82	0.485	0.240	0.50	3.94
$C_3F_6O$	166.022	361.90	3.06	0.610	0.277	1.00	3.64
$C_3F_8O_2$	220.018	372.40	2.33	0.610	0.271	1.00	3.65
$C_3HF_7O$	186.028	387.80	2.62	0.550	0.275	0.88	3.75
$C_3H_2F_6O$	168.038	428.90	3.04	0.553	0.269	0.75	3.94
$C_3H_3F_5O$	150.047	462.03	3.54	0.553	0.259	0.63	3.94
$C_3H_3F_5O$	150.047	406.82	2.89	0.500	0.256	0.63	3.92
$C_3H_5F_3O$	114.066	449.05	3.51	0.412	0.260	0.38	3.94
$C_4F_8O$	216.029	400.00	2.69	0.680	0.257	1.00	3.89
$C_4F_{10}O$	254.026	391.70	1.87	0.630	0.232	1.00	3.75
$C_4HF_7O_2$	214.038	452.88	2.87	0.597	0.273	0.88	3.94
$C_4HF_7O_2$	214.038	435.06	2.65	0.569	0.275	0.88	3.94
C <sub>4</sub> HF <sub>9</sub> O	236.036	412.63	2.26	0.499	0.311	0.90	3.93
$C_4H_2F_8O$	218.045	421.60	2.33	0.533	0.272	0.80	3.94
$C_4H_2F_8O$	218.045	444.63	2.57	0.581	0.261	0.80	3.94
$C_4H_2F_8O_2$	234.045	449.81	2.41	0.571	0.265	0.80	3.94
$C_4H_3F_5O$	162.058	455.03	2.91	0.486	0.258	0.63	3.94
$C_4H_3F_7O$	200.055	455.10	2.77	0.576	0.255	0.70	3.94
$C_4H_3F_7O$	200.055	437.60	2.48	0.530	0.257	0.70	3.94
$C_4H_3F_7O$	200.055	433.21	2.55	0.542	0.261	0.70	3.94
$C_4H_3F_7O$	200.055	463.89	2.71	0.541	0.260	0.70	3.96
$C_4H_4F_6O$	182.064	459.60	2.70	0.481	0.267	0.60	3.95
$C_4H_4F_6O$	182.064	476.31	2.78	0.500	0.256	0.60	4.03
$C_4H_5F_5O$	164.074	431.13	2.53	0.448	0.258	0.50	3.94
$C_5F_{10}O$	266.037	427.00	1.90	0.600	0.237	1.00	3.82
$C_5H_2F_6O_2$	208.059	485.10	2.77	0.720	0.198	0.75	4.11
$C_5H_2F_{10}O$	268.053	447.40	2.14	0.582	0.265	0.83	3.84
$C_5H_3F_7O$	212.066	476.55	2.58	0.538	0.256	0.70	4.03
$C_5H_3F_7O$	212.066	467.64	2.52	0.518	0.266	0.70	4.00
$C_5H_3F_9O$	250.062	475.74	2.23	0.563	0.251	0.75	3.90
$C_5H_3F_9O$	250.062	462.72	2.37	0.558	0.276	0.75	3.93
$C_5H_3F_9O$	250.062	473.01	2.24	0.550	0.259	0.75	3.90
$C_5H_5F_5O$	176.085	475.54	2.64	0.494	0.238	0.50	4.05
$C_5H_5F_7O$	214.081	481.54	2.38	0.497	0.256	0.58	3.92
$C_6H_3F_9O$	262.073	498.97	2.20	0.520	0.267	0.75	3.82
$C_6H_3F_{11}O$	300.070	486.48	1.95	0.567	0.255	0.79	3.89
$C_6H_5F_9O$	264.089	482.02	1.98	0.518	0.251	0.64	3.90

### 2.1. Conclusions

Fuzzy set approach is powerful tool to finding of compromise among energy efficiency, environmental constraints and economic indices of working media in conceptual RET design. In this work, criteria of sustainable development for renewable energy technologies of transformation low potential sources of heat into work on the basis of the ORC were

developed. For search of new working fluids, which have no information on thermodynamic behavior, ANN approach is proposed to forecast energy efficiency of the Rankine cycle. On the basis of the limited data about critical parameters and normal boiling temperature of substances for various configurations of cycles, the values of COP are determined without the calculation of thermodynamic properties.

This study is one of first attempts to apply methodology of tailored substances to selecting optimum working fluid for ORC. Construction of ANN correlations between information characteristics of working fluids and criteria of efficiency of Rankine cycle narrows the area of compromise search in the space of competitive economic, environmental and technological criteria.

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