POWER GENERATION FROM LOW ENTHALPY GEOTHERMAL FIELDS BY DESIGN AND SELECTION OF EFFICIENT WORKING FLUIDS FOR ORGANIC RANKINE CYCLES

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ABSTRACT
This work addresses the efficient power generation from low enthalpy geothermal fields through the use of a systematic method for the design and selection of heat exchange working fluids tailored for Organic Rankine Cycle (ORC) systems. A systematic methodology is employed that is based on the design of optimum working fluid candidates using a Computer Aided Molecular Design (CAMD) method. The performance of the designed fluids is evaluated using a model of the ORC system that enables simulation and economic design optimization. The performed evaluation also considers additional working fluid characteristics such as safety (toxicity and flammability) and environmental properties (ozone depletion potential and global warming potential) that are equally important to economic efficiency. An overall performance index is developed that facilitates the systematic evaluation of the working fluids for geothermal fields with a broad range of temperature and flowrate characteristics. ORC design and operating constraints are considered representing requirements in cases of power and heat co-generation. The proposed approach is illustrated through a case study involving different types of geothermal fields encountered in Greece. The obtained results reveal useful performance trade-offs among the considered working fluids under various geothermal field conditions.

1. INTRODUCTION
Geothermal fields are important renewable energy sources as they involve underground fluids of high thermal capacity. Low enthalpy geothermal fields, where heat is available at temperatures lower than 100^{o}C, are frequently encountered in nature. Greece represents a typical case of a country with numerous such fields incorporating identified overall thermal capacity of 300MW$_{th}$, which can be used to replace roughly 200.000 tons/yr of oil. However, less than 10% of this capacity is currently exploited, while its use is largely restricted to heating purposes using conventional, low-performance systems. Organic Rankine cycles represent an ideal technology for the efficient utilization of low enthalpy geothermal fields in

power and/or heat co-generation applications. The process involves the evaporation of a working fluid which draws heat from the low-grade heat source and then expands into a turbine that transforms energy into mechanical work. Subsequently, the vapour is condensed into a liquid with simultaneous heat rejection, while the liquid is pumped back to the heat exchanger to repeat the cycle. Clearly, the employed working fluid and ORC process features are expected to affect the system economic, operating, environmental and safety performance. Furthermore, the physical characteristics of the heat sources, namely the employed geothermal fields, are also expected to be of equal significance to the ORC system performance. This is because geothermal fields involve the flow of underground fluids with temperatures and flowrates that vary among different fields as they are scattered in different geographical areas. In this respect, there is a significant number of decisions that need to be addressed prior to the development of efficient and integrated working fluid-ORC systems for power and/or heat cogeneration from low-enthalpy geothermal fields. Previously reported research efforts focus on ORC-based power generation [1,2] using organic fluids such as hydrocarbons and refrigerants, as their favorable thermal properties enable a significant increase in ORC efficiency compared to conventional working fluids, such as water. In such approaches, working fluids are selected from arbitrarily compiled databases that enable very limited screening of ORC working fluid candidates. Their suitability is not addressed based on optimum working fluid and ORC process features or heat source characteristics, while the case of heat co-generation has yet to be addressed.

2. DESIGN APPROACH

2.1 Proposed decision-making methodology

The presented work targets the design and selection of ORC working fluids with optimum performance in numerous economic, operating, environmental and safety indices, to enable efficient power and/or heat co-generation from low enthalpy geothermal fields. The working fluids are designed for optimality in a number of molecular properties incorporating thermodynamic, environmental and safety fluid characteristics such as density, heat capacity, latent heat of vaporization, flammability, toxicity, ozone depletion and global warming potentials, to name a few. The obtained fluids are introduced into ORC process simulations considering a wide range of geothermal fields with different temperature and flowrate characteristics, to identify their effects on the operating performance of the employed ORC system. Working fluids presenting optimum performance in both operating and molecular properties are systematically selected and included in ORC process optimization, considering constraints that enable maximum power and/or heat co-generation. The complex decision making is approached through the adaptation of a generic methodology for integrated working fluid and ORC process design developed in [3] on the basis the methodology proposed in [4, 5] for integrated process amd Computer Aided Molecular Design (CAMD). This methodology is systematically realized within the following stages:

1) Identify molecular and ORC-related properties that can be used as performance measures.
2) Use multi-objective CAMD to develop working fluids for optimum performance in a number of molecular properties selected as performance measures in stage (1).
3) Include the molecules designed in stage (2) in ORC process simulations for a desired range of heat source conditions to enable assessment of their performance in important ORC-related properties identified in stage (1).
4) Develop groups of reduced size out of the available set of optimum working fluids, with similar chemical, physical, operating, environmental and/or safety characteristics identified in

the previous stages.
5) Select the highest performing working fluids out of each group developed in (4) based on assessment of the employed molecular and process-related performance measures.
6) Introduce the working fluids selected in stage (5) into ORC process optimization to identify working fluid-ORC process features of optimum economic performance.

2.2 Computer aided molecular design (CAMD)

The design of working fluids using CAMD is based on the systematic combination of molecular (functional) groups with the aim to synthesize a molecule of particular chemical structure and physicochemical properties. Such properties are calculated using group contribution methods, which are based on databases containing a pre-registered contribution of each molecular group in the molecular structure containing this group. The desired properties take the form of design targets in the context of an optimization problem formulation, allowing the systematic consideration and combination of the available molecular groups for the design of an optimum molecular structure.

The CAMD methodology employed for the design of ORC working fluids in this work follows the optimization-based approach proposed in [6] and extended to multi-objective design optimization in [4]. Molecules are described as a set of functional groups allowed to link together, while groups are characterised by their free bonds and functionality and classified as either aromatic or non-aromatic depending on the availability of free bonds. Valence of the group is the overall amount of non-aromatic free bonds and functionality relates to the atoms within the group, and the way in which they are bonded. This establishes the contribution of each of the $\boldsymbol{k}$ available groups to the overall behaviour of the molecule. Molecules are represented by a molecular vector $\boldsymbol{M}_k$, composed by the group vector $\boldsymbol{m}_k$ and the composition matrix $\boldsymbol{A}_k$. The molecular vector $\boldsymbol{M}_k$ is therefore defined as follows:

$$M_k = m_k \cdot A_k \tag{1}$$

where the group vector m_k details the groups included in the molecule, and the composition vector A_k contains information on the number of occurrences of each group. Group vectors are generated based on a set of connectivity constraints ensuring feasible molecules.

The molecules represented through the M_k vector are optimized against a desired performance measure using an optimization algorithm, such as Simulated Annealing (SA). In the context of multi-objective optimization, the employed performance measure involves a set of indices representing design targets (i.e. objective functions) which are aggregated into a single index to perform the necessary algorithmic operations In mathematical terms, the multi-objective optimization CAMD problem can be written as follows:

$$\underset{d}{optimize}\ F_1(x,d),\ldots,F_n(x,d) \tag{2}$$

Subject to

$$h(x,d) = 0 \tag{3}$$

$$g(x,d) \le 0 \tag{4}$$

$$x^L \le x \le x^U \tag{5}$$

$$d^L \le d \le d^U \tag{6}$$

$$\forall x \in X, d \in D \rightarrow R$$

where x and d are the vectors of the state and the design variables, respectively. Vector d may contain vectors $\boldsymbol{m_k}$, $\boldsymbol{A_k}$ in addition to other design options. Vector F_i (x,d) (i=1,n) represents the

considered set of n objective functions, while h (x,d) and g (x,d) are vectors of equality and inequality constraints representing the employed models and the operating or design constraints. The indices L and U represent upper and lower bounds utilized for all the variables. X and D are the domains determined by the upper and lower bounds corresponding to the state and design variables. To enable the simultaneous assessment of the desired set of objective functions through the algorithmic operations of SA, the objective function that is actually optimized takes the form of an aggregate objective function as follows:

$$f(x,d) = \sum_{i=1}^{n} w_i F_i(x,d) + \sum_{j=1}^{m} Pen_j g_j(x,d) + \sum_{e=1}^{l} Pen_e h_e(x,d) \quad (7)$$

where w_i is a set of weights imposed in each objective function F_i, either based on its considered significance or randomly to enable a search of all the potential combinations [4]. Pen_j and Pen_e represent penalty weights that might be imposed to inequality or equality constraints, while m and l represent the total considered inequality and equality constraints, respectively. The continuous assessment of equation (7) through the SA algorithmic operations results to the iterative generation of new solutions. Since usually there is no single solution that optimizes (i.e. minimizes or maximizes) all the objective functions simultaneously, a set of solutions is required to be identified where at least one of the objectives is better than the others. This set is called the nondominated (Pareto or efficient) set. As a result, the generated designs are ranked in terms of optimality based on comparison of the objective function values representing one solution in the nondominated set with the objective function values of the other solutions contained in the set.

2.3 Considered performance measures

There are numerous molecular or process-related properties that can be considered as performance measures in the design and selection of ORC working fluids. Several of them are employed in the presented work as they represent important performance measures, as follows:

1) The fluid density (ρ) must be high either in liquid or vapor phase, as it enables increase of the mass flowrate and reduction of the equipment size.

2) The fluid enthalpy of vaporization (H_v) must be high to enable the entire available heat to be added during phase change, and to achieve an almost vertical saturation vapor line that leads to reduced moisture formation during expansion in the turbine.

3) The fluid liquid heat capacity (Cp_l) must be low as it has a similar effect to the design of the working fluid as that of the enthalpy of vaporization.

4) The fluid viscosity (μ) must be low both in liquid and vapor phase to enable increased heat transfer and reduced energy consumption.

5) The fluid thermal conductivity (λ) must be high to enable increased heat transfer coefficients in both the vaporizer and condenser of the ORC process.

6) The fluid melting point (T_m) must be lower than the minimum ORC process temperature to avoid solidification of the fluid.

7) The fluid critical temperature and pressure (T_c, P_c) must be higher than the maximum ORC process temperature and pressure, respectively

8) The fluid ozone depletion potential (ODP) and global warming potential (GWP) must be kept at minimum levels to enable an environmentally friendly behaviour.

9) The fluid toxicity (C) and flammability (F) must be kept at minimum levels in order to ensure a safe ORC process system.

10) The ORC process efficiency (η) must be high as it enables increased power production and decreased power consumption.
11) The maximum and minimum process pressures (P_{max}, P_{min}) must be maintained at low levels, yet over atmospheric pressure, as high or vacuum pressures involve the use of expensive equipment.
12) The fluid mass flowrate (m_f) must be low to maintain reduced operating costs.

2.4 Selection procedure

The use of multi-objective CAMD optimization technology aims to maximize fluid properties such as density (ρ), enthalpy of vaporization (H_v) and thermal conductivity (λ) and to minimize the fluid liquid heat capacity (C_{pl}) and viscosity (μ), subject to melting point (T_m) and critical temperature (T_c) constraints. The optimization performed using the above objective functions results in a set of molecules with optimum physical properties. The safety properties, namely toxicity (C) and flammability (F), are calculated immediately after CAMD optimization for the obtained molecules, as shown in Figure 1. Although this is done because the employed thermodynamic properties are already sufficient to enable the identification of working fluids with optimum characteristics, safety properties can also be utilized as optimization objectives if desired. This leaves the environmental properties ODP and GWP to be determined, prior to proceeding to stage (3) of the employed design methodology. While all other considered properties can be calculated through group contribution (GC) methods (if experimental data are unavailable), the calculation of ODP and GWP is not possible for all molecules, due to limitations involved in available GC methods (data is available only for few groups). As a result, the ODP and GWP is assessed for each molecule based on generic guidelines that are derived from the known impact of particular chemical groups and atoms in ozone depletion and global warming [7]. In this respect, all molecules are first introduced into ORC process simulations in order to obtain their operating performance characteristics using indices such as process efficiency (η), maximum and minimum process pressures (P_{max}, P_{min}) and fluid mass flowrate (m_f). Subsequently, the molecules are classified into groups of reduced size based on their ODP and GWP characteristics in stage (4). This enables an efficient assessment of their environmental performance characteristics with respect to their operating and safety properties.

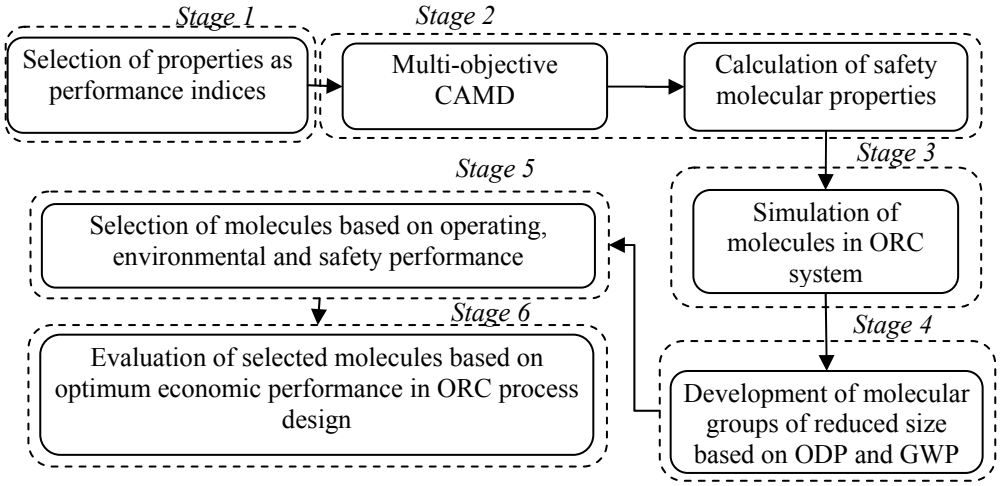

Figure 1: Implementation of proposed method

2.5 Unified selection index under variable heat source conditions

The determination of the working fluid process performance requires their simulation using an ORC process model. The simulations determine the values of the considered process-related properties. Such properties often represent variable performance drives (i.e. in the presented work high n, low m_f and low P_{max}, P_{min} but not lower than atmospheric pressure, are required), while they also need to be considered for different heat source conditions (i.e. temperature, flowrate etc.) In this respect, their combined assessment is facilitated by utilization of the following index:

$$I_{i,j,l}=\sum_{k=1}^{N_p} a_{i,j,k,l} \cdot x^*_{i,j,k,l} \tag{8}$$

where $x^*_{i,j,k,l}$ represents the considered scaled property for each working fluid l out of a total of N_p properties and $a_{i,j,k,l}$ represents a coefficient that takes the value of (+1) for properties that need to be minimized and (-1) for properties that need to be maximized. To enable calculation of the index for geothermal fields with different characteristics, the subscripts i and j represent different fields determined by their flowrate and temperature, respectively. Scaling gives equal importance to each property employed in equation (8). In this work it is realized through the standardization method, as follows:

$$x^*_{i,j,k,l}=\frac{x_{i,j,k,l}-\mu^{N_{wf}}_{i,j,k}}{\sigma^{N_{wf}}_{i,j,k}} \tag{9}$$

where $x_{i,j,k,l}$ represents the original value of the property, $\mu^{N_{wf}}_{i,j,k}$ and $\sigma^{N_{wf}}_{i,j,k}$ represent the mean and standard deviation of the considered property, calculated over the entire set of working fluids (l=1, …,N_{wf}) for a particular set of field flowrate and temperature. Based on the above equations, the selection of working fluids with increased performance in process related properties translates to minimization of the employed index, at each field temperature and flowrate level, as follows:

$$\min I_{i,j,l}= I^*_{i,j,l} + Pen_{i,j,l} \tag{10}$$

3. CASE STUDY DATA

The proposed developments are illustrated through a case study on power and heat co-generation from low enthalpy geothermal fields. In the case of Greece, such fields involve underground fluids with flowrates (F_{fl}) and temperatures (T_{fl}) in the range of 15-1000m^3/hr and 25-99^{o}C, respectively [8]. The realization of the proposed methodology up to stage 5 of Figure 1 involves the following assumptions: a) the system heat is supplied by geothermal fields that present the fluid temperatures (T_{fl}) and flowrates (F_{fl}) shown in Table 1, b) the maximum temperature of the working fluid is always considered to be 10^{o}C lower than the considered T_{fl}, c) the minimum temperature of the working fluid is 35^{o}C and d) the maximum acceptable liquid fraction in the turbine outlet is 8%, in order to avoid malfunction or destruction of the turbine, e) the critical pressure of each working fluid is higher than the maximum operating pressure of the ORC process. The AspenPlus software is utilized for the simulation of the ORC process.

Table 1: Considered geothermal field characteristics

Field type	T_{fl} (°C)	F_{fl} (m^3/hr)	Field type	T_{fl} (°C)	F_{fl} (m^3/hr)
1	90	1000	11	70	200
2	80	1000	12	90	100
3	70	1000	13	80	100
4	60	1000	14	70	100
5	90	500	15	90	20
6	80	500	16	80	20
7	70	500	17	70	20
8	60	500	18	90	10
9	90	200	19	80	10
10	80	200	20	70	10

The CAMD stage considers 32 functional groups, based on the availability of the corresponding group contribution data. Aromatics are not considered due to their high toxicity, compared to non-aromatic groups. Furthermore, halogens such as chlorine, bromine and iodine are also excluded due to their significant contribution to high ODP and GWP.

Stage 6 of the proposed method is realized in order to identify working fluids that enable maximum power production and further efficient utilization of the heat rejected in the condenser. The rejected heat is used for district and greenhouse heating applications. The evaluation of the working fluids will take place for geothermal fields of type 12, 15, 16, 18, 19 as shown in Table 1. These fields present temperatures and flowrates in the ranges 90-80°C and 10-100m^3/hr, respectively. They are selected in order to investigate the option of co-generation when heat sources of low capacity are available. The thermal requirements of the considered applications involve specific limits in the temperature of the heat that is utilized in each case. For both district and greenhouse heating, it is considered that the heat content must be available at 55°C at least, hence assuming a realistic temperature drop of 20°C the cooling water is assumed to return in the condenser at 35°C. Accordingly, a similar allowed temperature drop of 20°C is assumed for the fluid (water) of the geothermal field. The aim of the performed optimization is to identify the optimum heat exchange areas in the vaporizer and condenser in order to enable maximum heat recovery with minimum capital cost. This goal is represented by the following objective function [3]:

$$f = \frac{10xR_{gross}}{C_{CAP}} \tag{11}$$

where R_{gross} represents the gross income for a 10yr lifetime and C_{CAP} the capital cost. It is further assumed that the capital cost of the ORC process can be estimated as a sum of capital costs of the vaporizer and the condenser. This is reasonable because more than 90% of the process capital cost is assigned on the heat exchangers. Further details for this objective function can be found in [3].

4. RESULTS AND DISCUSSION

The working fluids obtained at the CAMD stage are reported in Table 2, with results regarding process related and safety characteristics and the process performance index for T_{fl}=90°C and F_{fl}=20m^3/hr. They are all available in the AspenPlus databases, while several of them (dimethyl

ether, methyl formate etc.) have been previously considered as refrigerants [7]. Based on their chemical structure, smaller sized groups (Table 2) are developed from the optimum group of working fluids. With regards to their environmental performance (ODP, GWP), hydrocarbons present zero ODP and low GWP. Hydrofluorocarbons are considered as greenhouse gases due to increased GWP [9]. Ethers, methyl formate and acetaldehyde present zero ODP and negligible GWP [10], while no data are available for methanol [1]. Amines have yet to be studied thoroughly regarding GWP and ODP, however few amine containing compounds break down into the greenhouse and ozone depleting gas nitrous oxide [11].
The environmental characteristics allow the exclusion of fluid (6) from further consideration. The toxicity of all fluids is relatively low, compared to the much higher toxicity of molecules such as aromatics. Flammability values greater than 0.6 are generally not acceptable because such fluids are considered strongly flammable. However, in cases of fluids (4) and (14) there is a significant trade-off between high flammability and high process performance. The process performance index provides a transparent and unified reflection of the considered properties. Unfavorable process properties result to positive index values, while favorable process properties result to negative index values.

Table 2: Designed working fluids with operating and safety performance results

Molecule type and name	η (%)	P_{max} (atm)	P_{min} (atm)	m_f (kg/hr)	$I_{20,90,1}$	F	C
Hydrocarbons							
1) Butane	7.51	9.85	3.23	13069	-0.5	0.56	1.94
2) 2-Methyl-1,3-butadiene	8.02	3.77	1.08	12840	-2.77	0.59	2.49
3) 2-Methyl-1-butene	7.88	4.14	1.15	12869	-2.5	0.59	2.83
4) 1,4-Pentadiene	7.94	4.62	1.47	14230	-2.29	0.62	1.54
5) 1,3-Butadiene	7.64	11.29	3.72	12699	-0.34	0.59	1.25
Hydrofluorocarbons							
6) 3,3,3-Trifluoro-propene	6.82	21.22	7.54	27580	4.63	0.41	2.19
Ethers							
7) Methoxy-ethene	7.88	9.38	2.82	12469	-1.25	0.72	0.89
8) Methoxy-ethane	7.78	8.82	2.68	12620	-1.23	0.56	1.24
9) Dimethyl-ether	7.32	22.19	7.72	12828	2.95	0.57	0.95
10) Dimethoxy-methane	8.20	3.23	0.79	13030	1.98	0.60	0.83
11) Methyl-propyl-ether	8.02	3.44	0.87	12585	2.07	0.60	1.54
Amines							
12) N-Methyl-methanamine	7.94	9.98	2.82	9246	-1.51	0.56	1.24
Formates							
13) Methyl-formate	8.33	4.57	1.14	10806	-3.22	0.56	1.60
Aldehydes							
14) Acetaldehyde	8.28	5.96	1.54	8370	-3.02	0.67	2.01
Alcohols							
15) Methanol	8.60	1.84	0.27	4204	1.48	0.59	1.02

The assessment of all the considered criteria result to selection of the working fluids reported in Figure 2. It appears that Methyl-formate (13) enables the highest operating performance for the entire range of considered conditions and also presents favorable values in all other properties. Acetaldehyde is also of high performance but highly flammable, similarly to 1,4-Pentadiene (4). 2-Methyl-1,3-butadiene (2) and 2-Methyl-1-butene (3) are close, but not over

the cut-off limit for flammability. However, they can be considered as useful alternatives to methyl formate, as hydrocarbons are generally utilized in several applications (e.g. refrigeration) due to favorable environmental properties. Working fluids (8) and (12) are also considered as representatives of the amines and ethers groups for the next stage, as they have similar or better values in safety properties than the other considered working fluids, while their mass flowrate and efficiency values are also close.

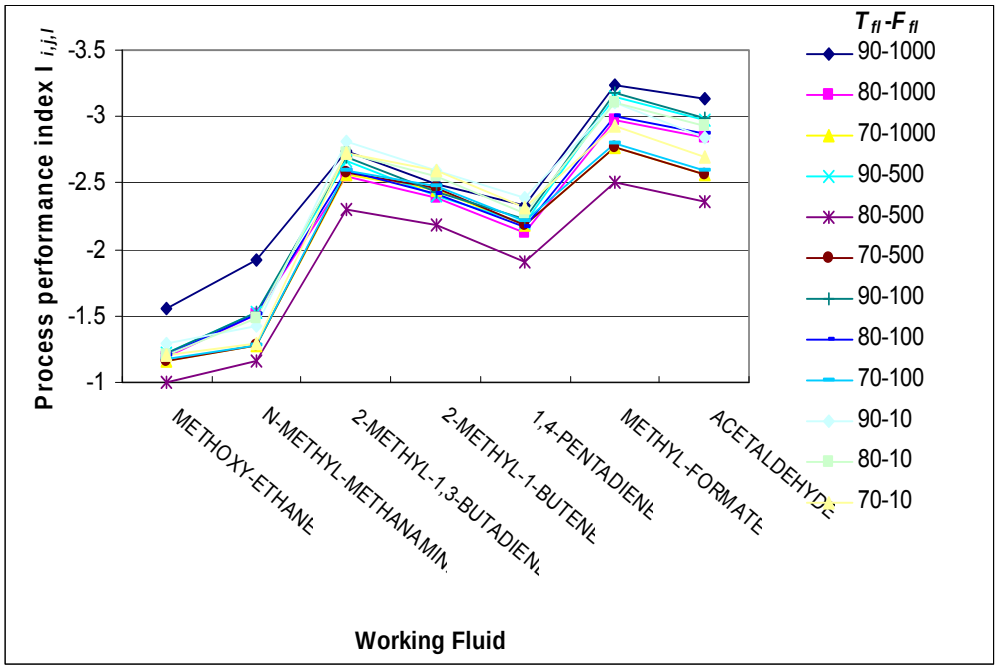

Figure 2: Operating performance of working fluids in ORC for a broad range of geothermal field characteristics

Following the identification of highly performing working fluids in terms of operating, environmental and safety performance, these fluids are selected in order to be evaluated in terms of their economic performance in the optimization of an ORC system, under the temperature constraints considered for power and heat co-generation. The obtained results are shown in Table 3, involving molecules M1-M4 which are quite common in existing commercial refrigeration or ORC applications. Molecule 2-methyl-1,3-butadiene is not considered due to the absence of the required property data from the ASPEN databases. It appears that Methyl-formate (13) enables the highest economic performance in the ORC system, while working fluids such as Methoxy-ethane (7) and N-Methyl-methanamine (12) also present high economic performance which ranks them higher than 1,4-Pentadiene. This is because the increasing operating pressures were considered to directly result in decreasing operating performance in Table and Figure 2, while in Table 3 it is assumed that working fluids with an operating pressure range close (higher or lower) to that of 1,4-Pentadiene will not have a significant economic impact on the process. Such an assumption is reasonable hence the effects of pressure in the equipment are not taken into account in the employed objective function. In any case, the economic performance of the working fluids with objective function

values close or higher than 1 is similar. On the other hand, it appears that molecules M1-M4 present a reduced economic performance compared to the molecules designed in this work.

Table 3: Economic performance of working fluids for power and heat co-generation

ID	Molecule name	Vaporizer		Condenser		*f*
		Area (m^2)	Cost ($)	Area (m^2)	Cost ($)	
13	Methyl formate	125.8	28640	45.5	18920	1.1
12	N-Methyl-methanamine	108.7	26020	45.5	19390	1.08
7	Methoxy-ethane	120.7	28370	40.9	18480	1.02
4	1,4-Pentadiene	147	31510	52	19140	0.96
3	2-Methyl-1-butene	163.5	33210	65.7	21220	0.90
1	Butane	146.8	32350	45.5	18320	0.89
M1	Propane	36.1	19060	47.7	21810	0.75
M2	1,1-Difluoro-ethane	146.1	35100	58.3	22370	0.70
M3	Tetrafluoroethane	196.2	40920	50.5	20990	0.64
M4	Water	78.3	21990	604.1	85990	0.49

From the working fluids available in Table 3, the ones with objective function values greater than 2-Methyl-1-butene are selected to be considered in the design of ORC systems for fields of type 12, 15, 16, 18, 19, with the aim to investigate their performance for different heat source conditions. The obtained results are shown in Figure 3. Obviously, the economic performances are different for each type of field due to the different capacities of the considered heat source. A uniform trend is observed in terms of the economic performance of the working fluids in all the considered types of geothermal fields. In some cases Methyl-formate (13) ranks clearly first, while in some other cases it has a very similar performance with N-Methyl-methanamine (12). On the other hand, working fluid 1, 4-Pentadiene ranks clearly last.

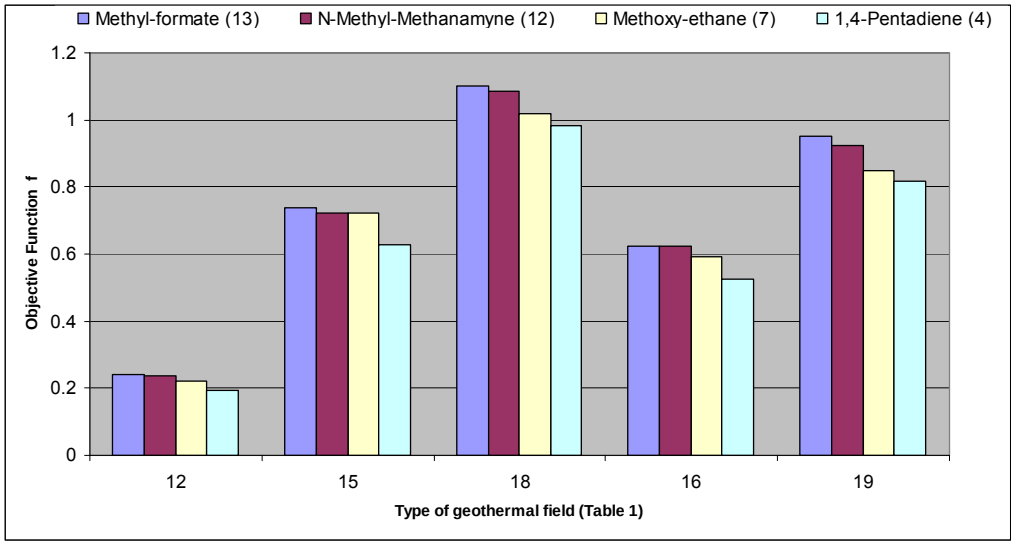

Figure 3: Comparative economic results for highly performing working fluids in different geothermal fields

5. CONSLUCIONS

This work presents a systematic approach for the design and selection of working fluids for ORC processes applied to low-enthalpy geothermal fields. The considered problem is decomposed to several design and selection stages, in the form of a generic methodology. Several criteria are considered at each stage that enable an objective assessment of all the emerging options based on numerous important working fluid and process related properties. The proposed method leads to identification of working fluids covering various performance characteristics under variable heat source conditions and enables the selection of working fluid options based on insights that reveal useful performance trade-offs.

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