Power Generation from Low Enthalpy Geothermal Fields by Design and Selection of Efficient Working Fluids for Organic Rankine Cycles

Athanasios I. Papadopoulos^{1*}, Mirko Stijepovic², Patrick Linke², Panos Seferlis^{1,3}, Spyros Voutetakis¹

¹Chemical Process Engineering Research Institute (C.P.E.R.I.), Centre for Research and Technology Hellas (CE.R.T.H.), PO Box 60361, 57001 Thessaloniki, Greece ²Chemical Engineering Department, Texas A&M University at Qatar, Qatar ³Department of Mechanical Engineering, Aristotle University of Thessaloniki, Greece

spapadopoulos@cperi.certh.gr

The presented work addresses the efficient power generation from low enthalpy geothermal fields through design and selection of working fluids for organic Rankine cycle (ORC) processes. 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 process performance of the obtained working fluids is evaluated using ORC process simulations, while other environmental (ODP, GWP) and safety (toxicity, flammability) characteristics are also considered. A suitable performance index is developed to enable consideration of variable heat source conditions for the ORC process. The proposed approach is illustrated through a case study that involves low-enthalpy geothermal fields with a broad range of representative temperature and flowrate characteristics. 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 °C, are frequently encountered in nature. However their use is largely restricted to heating purposes, despite their potential for utilization in power generation applications through the use of the ORC process. This 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. The process economic, operating and environmental performance depends on the properties of the selected working fluids and the ORC process features. Additionally, 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, the ORC process performance also depends on the characteristics of the employed field. Clearly, the consideration of ORC processes for power

Please cite this article as: Papadopoulos A. J., Seferlis P., Voutetakis S. and Linke P., (2010), Power generation from low enthalpy geothermal fields by design and selection of efficient working fluids for organic rankine cycles, Chemical Engineering Transactions, 21, 61-66 DOI: 10.3303/CET1021011

generation from low-enthalpy geothermal fields involves a significant number od decisions. Available research efforts (Tchanche et al., 2009; Maizza and Maizza, 2001) propose the utilization of organic fluids such as hydrocarbons and refrigerants, as their favorable thermal properties enable a significant increase in ORC power generation efficiency compared to conventional working fluids, such as water. However, in such cases the working fluids are selected from arbitrarily compiled databases that enable very limited screening of ORC working fluid candidates, while their suitability is not addressed based on ORC process features or geothermal field characteristics.

2. Proposed method and implementation

2.1 Design and selection methodology

The presented work employs a method that combines CAMD technology with the use of ORC process models to enable the rapid identification of optimum working fluid options and their corresponding ORC process performance features for low-enthalpy geothermal fields with a wide range of temperature and flowrate characteristics. This goal is approached through the adaptation of a generic methodology for integrated working fluid and ORC process design developed by Papadopoulos et al. (2010) on the basis of the methodology proposed by Papadopoulos and Linke (2005, 2006) for integrated CAMD and process design. The ozone depletion (ODP) and global warming potential (GWP) of the working fluids are additional important environmental properties that need to be considered. Properties such as toxicity and flammability are also important in ORC applications in order to ensure the safety of machinery and personnel. To address the complex decision making involved, the following design stages are proposed:

1) Identify molecular and process-related properties that can be used as performance measures.

2) Use multi-objective CAMD to design working fluids for optimum performance in a number of molecular properties selected as performance measures in stage (1).

3) Develop groups of reduced size out of the original set of optimum working fluids, with similar chemical, physical, environmental and/or safety characteristics.

4) Include the molecules contained in groups developed in stage (3) in ORC process simulations for a desired range of heat source conditions to enable assessment of their performance in important process-related properties.

5) Select the highest performing working fluids out of the groups developed in (4) based on assessment of the employed performance measures.

2.2 Employed 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_{ν}) 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 that 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 *ODP* and *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_i) must be low to maintain reduced operating costs.

2.3 Criteria for CAMD design and generation of groups

The use of multi-objective CAMD optimization technology aims to maximize fluid properties such as density (ρ) , enthalpy of vaporization (H_{ν}) and thermal conductivity (λ) and 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 to a set of molecules with optimum physical properties. The toxicity (C) and flammability (F) property values are calculated after the optimization stage for the obtained molecules, to determine their safety characteristics. However, they can also be utilized as optimization objectives. This leaves the environmental properties ODP and GWP to be determined. While all other considered properties can be calculated through group contribution (GC) methods (in the absence of experimental data), the calculation of ODP and GWP is not possible for all molecules, due to the availability of limited GC data. As a result, the ODP and GWP is assessed for each molecule based on generic guidelines derived from the known impact of particular chemical groups and atoms in ODP and GWP (Calm and Didion, 1998). In this respect, subgroups of molecules with similar structural-chemical characteristics are developed out of the obtained group of optimum molecules. Hence, the requirement to assess the ODP and GWP performance of the molecules also enables the implementation of stage (3) of the proposed method.

2.4 Process performance criteria

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). In this respect, their combined assessment is

facilitated by utilization of the index defined as: $I_{i,j,l} = \sum_{k=1}^{N_p} a_{i,j,k,l} \cdot x_{i,j,k,l}^*$, 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 the flowrate and temperature of the field, respectively. Scaling gives equal importance to each property employed in equation (1). In this work

it is realized through the standardization method: $x_{i,j,k,l}^* = \frac{x_{i,j,k,l} - \mu_{i,j,k}^{N_{wf}}}{\sigma_{i,j,k}^{N_{wf}}}$, where $x_{i,j,k,l}$

represents the original value of the property, $\mu_{i,j,k}^{N_{wf}}$ and $\sigma_{i,j,k}^{N_{wf}}$ 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.

3. Case study

The proposed developments are illustrated through a case study that considers the development of optimum ORC working fluid options based on 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 Figure 1, b) the maximum temperature of the working fluid is always considered to be 10°C lower than the considered T_{fl} , c) the minimum temperature of the working fluid is 35 °C and d) the maximum acceptable liquid fraction in the turbine outlet is 8%, in order to avoid malfunction or destruction of the turbine. The AspenPlus software is utilized for the simulation of the ORC process.

The working fluids obtained at the CAMD stage are reported in Table 1, with results regarding process related and safety characteristics and the process performance index for T_{fl} =90 °C and F_{fl} =20 m³/h. They are all available in the AspenPlus databases, while several of them (dimethyl ether, methyl formate etc.) have been previously considered as refrigerants (Calm and Didion, 1998). Based on their chemical structure, smaller sized groups (Table 1) 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 (Tsai, 2009). Ethers, methyl formate and acetaldehyde present zero ODP and negligible GWP (Dawson and Spannagle, 2008), while no data are available for methanol (Tchanche et al., 2009). 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 (Ravishankara et al., 2009).

| Molecule type and name | η | $P_{\rm max}$ | \mathbf{P}_{\min} | m_{f} | I _{20,90,1} | F | С |
|----------------------------|------|---------------|---------------------|---------|----------------------|------|------|
| | (%) | (atm) | (atm) | (kg/h) | | | |
| 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 |

Table 1: Process related and safety performance of designed working fluids

The environmental characteristics allow the exclusion of fluids (6) and (12) 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. 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. The assessment of all the considered criteria result to selection of the working fluids reported in Figure 1. Such fluids are evaluated for temperature and flowrate combinations that are commonly observed in geothermal fields. It appears that methyl formate enables the highest process 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. 2-methyl-1,3-butadiene and 2-methyl-1butene are close to 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.

4. Conclusions

This work presents a systematic approach to 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 within 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 performance related trade-offs.

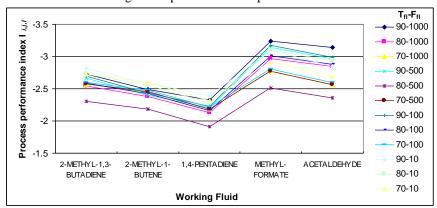


Figure 1: Process related performance of selected working fluids for a broad range of geothermal field temperatures (T_{fl}) and flowrates (F_{fl})

Acknowledgements

Funding from the John S. Latsis Public Benefit Foundation is gratefully acknowledged by Dr Papadopoulos and Dr. Voutetakis.

References

- Calm J.M. and Didion D.A., 1998, Trade-offs in refrigerant selections: Past, present, and future, Int. J. Refrig., 21(4), 308.
- Dawson B. and Spannagle M., 2008, The complete guide to climate change, Taylor & Francis.
- Maizza, V. and Maizza, A., 2001, Unconventional working fluids in organic Rankinecycles for waste energy recovery systems, App. Therm. Eng., 21(3), 381.
- Papadopoulos A.I., Stijepovic M., and Linke P., 2010, On the systematic design and selection of optimal working fluids for Organic Rankine Cycles, Applied Thermal Engineering., 30, 760.
- Papadopoulos A.I. and P. Linke., 2006, Multiobjective molecular design for integrated process-solvent systems synthesis, AIChE J., 52(3), 1057.
- Papadopoulos A.I. and P. Linke., 2006, Efficient integration of optimal solvent and process design using molecular clustering, Chem. Eng. Sci., 61, 6316.
- Ravishankara A.R., Daniel J.S., Portmann R.W., 2009, Nitrous oxide (N2O): The dominant ozone-depleting substance emitted in the 21st century, Science, 326, 123.
- Tchanche B.F., Papadakis G., Lambrinos G., Frangoudakis A., 2009, Fluid selection for a low-temperature solar organic Rankine cycle, Appied Thermal Eng., 29, 2468.
- Tsai W. T., Environmental risk assessment of hydrofluoroethers (HFEs), 2005, J. Hazard. Materials, 119, 69.