INFLUENCE OF THE USE OF AN INNOVATIVE NANOFLUID ON NET POWER PRODUCTION IN ORCS FOR LOW-GRADE WASTE HEAT RECOVERY APPLICATIONS

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ABSTRACT

In the industrial sector, medium, low and ultra-low temperature waste heat represents a significant source of energy loss as well as constitutes a harmful environmental effect, which must be avoided. Nonetheless, waste heat could represent a free and vast potential when a technology to recover effectively energy at low temperatures is utilized. In this context, the Organic Rankine Cycle (ORC) technology is a proven solution because, being the working fluid an organic substance with low boiling temperature, it is more suitable than water when low grade heat needs to be recovered.

The identification of a working fluid, performing significantly better than the others, is still far from being achieved, due to difficulty in the maximization of the heat transfer from low grade heat sources. To achieve higher heat transfer efficiencies, unconventional working fluids with enhanced thermal properties should also be investigated. Regarding this topic, nanofluids, suspensions of nanoparticles in a base fluid, synthesized intentionally to have enhanced thermal properties, might have the potential to increase ORCs efficiency.

This paper presents an in-depth investigation of the applications of an innovative nanofluid, based on a new class of nanoparticles – termed Metal-Organic Heat Carriers (MOHCs) - in the ORC field, developing a numerical model for assessing the nanofluid gain in terms of net power production. In particular, the possible combination of the base fluid R245fa with the nanoparticle MIL101, a robust Metal Organic Heat Carrier, is considered.

To properly model the reversible adsorption/desorption process, typical of the MOHC nanoparticles, experimental analyses were carried out for studying the uptake of the R245fa in MIL101 at different operating conditions and, starting from the experimental results, proper semi-empirical correlations were defined and adopted within the numerical model.

The resulting performance of the MIL101/R245fa were compared with those of the pure R245fa, whose cycle was optimized in order to maximize the net power output. Promising results were achieved in terms of system efficiency increase and heat exchanger area reduction.

1. INTRODUCTION

The main consumptions in all the industrialized countries is certainly represented by industrial processes, counting for about a third of the total energy demand (IEA 2015; Brückner et al. 2015) with 25% up to 55% of energy losses in the form of medium and low temperature Waste Heat (WH) due to the absence of internal heat demand.

Low efficiency values in power recovery from low and ultralow-grade heat sources are actually present in state-of-the-art systems. In particular, as regards Organic Rankine Cycles (ORC), the few available market solutions focused their attention on the maximization of nominal efficiency values, pushing costs into the background with efficiencies still stacked between 5% and 9%, but with accompanying prohibitive costs (5'000 to 8'000 ϵ/kW). Nevertheless, one of the most promising options for recovering

energy from low and ultralow-grade heat sources (<150 °C) is undoubtedly still the use of Organic Rankine Cycles (ORCs) (Huang et al. 2017).

To exploit the demonstrated large potential by ORC modules, the main issue that need solving is the lack of an organic working fluid that performs efficiently for low and ultralow-grade heat sources, namely, lower than 150°C and especially around 100°C. At these low-grade heat source temperatures, organic working fluids showed similar decaying performance (Lakew and Bolland 2010), mainly because of the difficulties in maximising the heat transfer from low grade heat sources.

To achieve higher heat transfer efficiencies, unconventional working fluids with enhanced thermal properties should be investigated. In this case, nanofluids, suspensions of nanoparticles in a base fluid that are synthesized intentionally to have enhanced thermal properties might have the potential to increase ORC efficiency. Although research on nanofluids is still debating on the achievable benefits (Chys et al. 2012; Buongiorno et al. 2009), nanofluids are still seen as the heat transfer media of the future (Michaelides 2014) and several research efforts have been made to investigate their potential in several application fields ranging from electronics to biomedical applications (Martinez et al. 2012). As regards the energy literature, all the studies dealing with nanofluids have focused on their application in solar-driven systems, such as the parabolic trough solar collector (Kumaresan et al. 2017; Mahian et al. 2017). Some of them have also considered the possible combination of these parabolic trough solar collectors with generation systems, driven by standard working fluids (Habibi et al. 2019; Loni et al. 2019; Bellos and Tzivanidis 2018). What emerges from these analyses is that nanoparticle suspensions can provide a moderate enhancement of the system thermal efficiency at low heat source temperatures.

This paper is aimed at studying more in depth the benefits deriving from the application of an innovative nanofluid directly in a generation system, namely an ORC. To the authors' knowledge, no one has ever considered the possible use of a nanofluid as working fluid in an ORC system and, even more important, no one has ever investigated the use of a new class of nanoparticles - termed metal-organic heat carriers (MOHCs) - molecularly engineered to reversibly uptake and release the working fluid molecules in which they are suspended. Unlike standard nanoparticles (i.e. Al₂O₃, Al, SiO₂, CuO, Au, Fe₂O₃, ...), considered in the above mentioned studies, these MOHCs make it possible to extract additional heat from the endothermic enthalpy of desorption which can be as much as twice the level of the latent heat of vaporization of the pure fluid phase alone, showing a theoretically high potential for boosting heat transfer capacity (McGrail et al. 2013). Their possible use in energy systems in general and in ORCs in particular could allow to significantly increase system efficiencies but requires the development of adhoc numerical models, properly considering the adsorption/desorption process of the base working fluid in the MOHC nanoparticle structure. This process, allowing to exchange additional heat in comparison with standard nanoparticles, depends on several parameters (nanoparticle/base fluid pair, nanoparticle volume fraction, pressure and temperature above all) and it is not considered in literature models developed for standard nanofluids.

This paper focused on the pair between the base fluid R245fa and the nanoparticle MIL101 (Férey et al. 2005), a robust MOHC with high surface area, high porosity and high percentage by weight of fluid uptake, and frequently adopted for catalysis and adsorption (Chen et al. 2012). A numerical model was developed to analyse the performance of MIL101/R245fa in an ORC, by properly considering the reversible adsorption/desorption process through semi-empirical correlations.

2. THE ORC MODEL

A simple sub-critical ORC cycle to recover energy from a low temperature heat source, consisting of pump, evaporator, expander and condenser, is shown in Figure 1.

A fixed mass flow rate $\dot{m_s}$ of water equal to 5 kg/s was considered by entering the evaporator at inlet temperature $T_{s,in}$ of 100°C. The cooling fluid entering the condenser was assumed to be water at inlet temperature $T_{c,in}$ of 10 °C, in agreement with literature values (Lakew and Bolland 2010).

The model has been developed by means of the Matlab software whereas the thermodynamic data of the working fluids were provided by the software CoolProp (Bell et al. 2014).

Each component of the ORC cycle was modelled in steady-state conditions, neglecting pressure drops and heat losses. More details about the starting numerical model developed for analyzing ORC



performance using standard fluids can be found in (Cavazzini et al. 2017).

Figure 1: Scheme of the simple ORC (a) and its representation in a T-s diagram (b)

3. NANOFLUID IN ORC

3.1 Metal-Organic Heat Carrier behavior in a heat exchanger

The presence of metal-organic heat carriers (MOHCs) nanoparticles in the working fluid of an ORC changes the basic relevant equations of the ORC model, since it is necessary to take into account not only the dispersion of the nanoparticles in the pure working fluid but also the reversible adsorption/desorption of the working fluid in the nanoparticle structure. For example, in the evaporation process, the enthalpy difference between state point 2 and state point 3 $\Delta h_{2,3}$ of the cycle with standard organic fluid (Figure 1) is modified as follows (McGrail et al. 2013):

$$\Delta h_{2,3^{nf}} = \left[1 + \varphi \left(\frac{\Delta m_{f ads}}{m_{MOHC}} - 1\right)\right] \Delta h_{2,3} + \varphi \left[\overline{c_{p,MOHC}} \left(T_{3^{nf}} - T_{2}\right) + \frac{\Delta m_{f ads}}{m_{MOHC}} \overline{\Delta h}_{a}\right]$$
(2)

where:

- $\Delta h_{2,3^{nf}}$ is the enthalpy gain due to the adoption of the nanofluid in the heat exchanger;
- $\varphi = \frac{m_{MOHC}}{m_{wf}}$ is the nanoparticle mass fraction loading in the nanofluid;
- $\frac{\Delta m_{f \, ads}}{m_{MOHC}}$ is the working fluid mass per unit of MOHC mass desorbed between the inlet and the outlet of the heat exchanger, evaluated as the difference in working fluid mass uptake per unit of MOHC mass between the inlet of the heat exchanger (${}^{m_{f} \, ads,in}/m_{MOHC}$) and the outlet of the heat exchanger (${}^{m_{f} \, ads,in}/m_{MOHC}$) and the outlet of the heat exchanger (${}^{m_{f} \, ads,in}/m_{MOHC}$)
- T_2 the initial nanofluid temperature at the heat exchanger inlet;
- $T_{3^{nf}}$ is the temperature of the vaporized nanofluid at the heat exchanger outlet;
- $\overline{c_{p,MOHC}}$ is the average specific heat capacity of the MOHC between temperature T₂ and T_{3nf}, assumed equal to 1.1 J/(g K) according to the literature (McGrail et al. 2013).
- $\overline{\Delta h}_a$ is the average enthalpy of adsorption/desorption. This enthalpy depends on the distribution of binding energies among the adsorption sites in the nanoparticles and hence on the mass fraction loading in the nanofluid.

The first term of the right-hand side of eq. (2) accounts for the enthalpy gain of the organic working fluid, whereas the second term of the right-hand side of eq. (2) takes into account the further enthalpy represented by the sensible heat of the nanoparticles and the endothermic heat of desorption/absorption process of the working fluid molecules. The desorption process, requiring heat, is due to the unfavourable increase of the Gibbs free energy interaction potentials of the molecule load of the working fluid with the temperature (Sun et al. 2011).

Similar equations have been adopted to model the nanofluid behavior in the other ORC components.

3.2 Average enthalpy of desorption and mass uptake of the working fluid

The enthalpy of absorption/desorption $\overline{\Delta h}_a$ and the mass uptake of the working fluid are strictly related to the operating conditions (pressure and temperature) and to the considered pair of MOHC nanoparticle

and working fluid. So, to properly model the behavior of the MIL101/R245fa nanofluid in the ORC, it was necessary to carry out experimental analyses aimed at defining ad-hoc semi-empirical correlations. To do this, MIL101 was synthetized in the Pacific Northwest National Laboratory according to the procedure described by Annapureddy et al (Annapureddy et al. 2015) and gas adsorption experiments were carried out at four different temperatures (10, 25, 40, 60°C) using an Intelligent Gravimetric Analyzer (IGA, Hiden Instruments) and a water bath to maintain the temperature constant throughout the measurements. The resulting experimental values (coloured circles) for the four investigated temperatures are reported in Figure 2 where R245fa uptake V and p/p_0 are the R245fa absorbed per unit of MIL101 dry mass and the relative pressure, respectively. Similar results were also obtained for the desorption process.

By comparing the experimental values with the literature models, it is clear that the R245fa in MIL101 exhibits, at all temperatures, a type I behavior that is typical of monolayer adsorption (Gregg, Sing, and Salzberg 1967) and is well approximated by the Langmuir model (Langmuir 1918), represented by the following equation



Figure 2: Adsorption isotherms for R245fa in MIL101: R245fa mass uptake by weight of MIL101 [%] as a function of pressure. Experimental data (coloured circles) and fitting Langmuir model equations (coloured lines)



Figure 3: Enthalpy of absorption/desorption [kcal/mol] of R245fa in MIL101 as a function of the molar mass uptake per unit of dry mass [mmol/g]

where p and p_0 are the equilibrium and the saturation pressure of the adsorbate at the adsorption temperature respectively, *a* is the mass adsorbed per adsorbent mass unit at pressure p, C is a constant and a_m is the maximum monolayer mass capacity per adsorbent mass unit, which is also constant. Experimental data were hence used to determine the constants of the Langmuir equation (*C* and a_m).

By exploiting the extrapolated Langmuir equation (eq. 3), it was possible first to determine the enthalpy of desorption Δh_a (Figure 3) at different temperatures by means of the Clausius–Clapeyron equation:

$$\left(\frac{\partial(\ln p)}{\partial\left(\frac{1}{T}\right)}\right)_{w} = \frac{\Delta h_{a}}{R} \quad (4)$$

where *p* is the pressure, *T* is the temperature, *w* [mmol/g] is the absorbate molar uptake per unit of absorbent dry mass and *R* is the molar gas constant. The average value of Δh_a , $\overline{\Delta h}_a$ was about 8.7 kcal/mol.

Experimental data from the isotherms of R245fa in MIL101, reported in Figure 2, were also used as inputs in the Aspen Adsorption software (Aspen Tech) to determine the working fluid mass uptake by weight of MIL101 dry mass:

$$\frac{m_{R245fa}}{m_{MIL101}} = \frac{2.645 \cdot 10^{-7} \cdot e^{3973.66/T_i} \cdot p_i}{1 + 4.586 \cdot 10^{-5} \cdot e^{3758.81/T_i} \cdot p_i} \cdot MM_{f R245fa}$$
(5)

The obtained fits were compared with the experimental results of R245fa uptake, showing a very good agreement over the entire range of pressures and temperatures, with an average error of 3.12% (Figure 2).

3.3 Numerical model of the ORC, using nanofluid as working fluid

The development of a numerical model for simulating the nanofluid performance in an ORC system presents some issues, mainly related to the fact that it is not possible to acquire the nanofluid properties by means of standard software (i.e. CoolProp) as is the case for pure fluids and mixtures. To overcome this setback, eq. 2 have been adopted to determine the enthalpy at the outlet of the different ORC components.

As regards the nanofluid specific heat, it can be determined by assuming thermal equilibrium between the nanoparticles and the base fluid phase, adopting the simplified equation (Lee and Mudawar 2007):



Figure 4: Iterative procedure for determining the temperature $T_{3^{nf}}$ and enthalpy $h_{3^{nf}}$ of the nanofluid at the outlet of the evaporator in the numerical model

 $c_{p,nf} = (1 - \varphi)c_{p,wf} + \varphi c_{p,MOHC}$ (6) Because of the low nanoparticle mass load fraction ($\varphi < 2\%$) and because of the specific heat of the nanoparticle $(\overline{c_{p,MOHC}} = 1.1 \frac{kJ}{kgK})$, the nanofluid specific heat differs less than 1% from the base fluid specific heat. For this reason, it was assumed to be equal to the base fluid one: $c_{p,nf} \cong c_{p,wf}$.

As regards the enthalpy at the outlet of the ORC components (eq. 2), it depends on the pressure and the temperature of the nanofluid, which is unknown. To determine this, an iterative procedure was applied (Figure 4).

4. OPTIMIZATION PROCEDURE

To maximize the net power output Pnet of the ORC, the numerical model was combined with the optimization algorithm ASD-PSO (Ardizzon, Cavazzini, and Pavesi 2015), a recent evolution of the standard PSO already successfully adopted in ORC optimization problems (Cavazzini et al. 2017).

The algorithm optimized the evaporating pressure, the temperature difference at the pinch point in both the heat exchangers and the approach point temperature difference at the evaporator. The condenser approach point was considered to be constant to ensure a feasible heat exchange for a wide range of pinch point values.

As regards the search bounds, the temperature differences at the pinch points were fixed to vary between 5° and 25°C, whereas those at the approach point were between 10°C and 25°C.

The evaporating pressure limits were fixed as follows:

Since the working fluid at the evaporator outlet could be superheated vapour and the ORC cycle was subcritical, the maximum evaporating pressure was fixed to the minimum between the pressure at a saturation temperature equal to $T_{3,min} = T_{s,in} - (\Delta T_{ap})_{u,evap}$ and the pressure 1 bar below the

Table 1: Comparison between the pure R245fa and the MIL101/R245fa nanofluid at a heat source temperature of 100°C. Operating conditions optimized for the pure R245fa fluid

	R245fa	R245fa/MIL101
p _{evap} (bar)	5.51	5.51
T ₃ (°C)	75.0	74.5
T ₄ (°C)	53.3	52.7
m_{MOHC} (g)	-	24.31
$\Delta m_{abs,2-3}$ (g)	-	0.194
$\Delta m_{abs,3-4}$ (g)	-	-0.029
P _{net} [kW]	49.1	49.1
A _{tot} [m ²]	76.0	66.3

critical pressure, as suggested by (Drescher and Brüggemann 2007)

Since the evaporating pressure cannot be lower than the condensing pressure, the minimum evaporating pressure was assumed to be equal to the maximum condensing pressure, that is the pressure at a saturation temperature equal to $T_{1,max} = T_{c,in} + \left(\Delta T_{ap}\right)_{u.cond}$

5. RESULTS

To better appreciate the contribution of the MOHC suspension in the working fluid, two different comparisons between the performance of the MIL101/R245fa

nanofluid and those of the pure R245fa were carried out.

In the first comparison, the pure R245fa fluid was compared with a fixed value of nanoparticle volume fraction suspended in the R245fa fluid ($\varphi = 0.7\%$), selected according to the literature (McGrail et al. 2013). Moreover, the cycle parameters of the R245fa fluid were optimized to maximize the net power output whereas, for the nanofluid, the cycle parameters were not optimized and the nanofluid operated in the ORC operating conditions of the R245fa.

As can be seen in Table 1, a significant gain in total heat exchanger area is achieved but no significant increase in the net power output is obtained. The main reason of this result is related to the high value of evaporating pressure, limiting the endothermic desorption process and hence the contribution of the MOHCs in terms of net power output. This is also evident in Figure 5, reporting the cycles of the pure fluid R245fa (blue line) and that of the nanofluid (pink line) in the T-s diagram. The enthalpy gain due to the nanofluid is limited, allowing to achieve similar values of maximum cycle temperature T_3 (75.0 vs 74.5). However, another contribution should be also ascribed to the nanofluid. Indeed, while desorption generates entropy, adsorption processes reduce the total entropy of a system. As the nanofluid

mass volume machon of 0.9% and 1%.				
	$\phi^{=0.9\%}$	$\phi^{=1.0\%}$		
T ₃ (°C)	74.3	74.2		
T ₄ (°C)	52.6	52.5		
m_{MOHC} (g)	24.35	24.36		
$\Delta m_{abs,2-3}$ (g)	0.193	0.192		
$\Delta m_{abs,3-4}$ (g)	-0.029	-0.029		
P _{net} [kW]	49.21	49.22		
A _{tot} [m ²]	65.9	65.8		

Table 2: Operating points of the MIL101/R245fa nanofluid at the heat source temperature of 100° C with the mass volume fraction of 0.9% and 1%.

cools in the turbine, it becomes thermodynamically favorable for readsorption of working fluid molecules (Table 1) and the corresponding adsorption process produces a slightly more isentropic expansion in the turbine, improving its overall efficiency. However, since the operating conditions and in particular operating pressures of the nanofluid cycle were not optimized to favour the adsorption process, the increase in turbine efficiency was significant only at higher heat source

temperature temperature (for 150°C the turbine efficiency increases from 80.0% to 81.2%).

To increase the contribution of the nanofluid, the mass volume fraction of the nanoparticles was increased, from 0.7% up to 1%.

As it can be seen in Table 2, reporting the results for 0.9% and 1%, the increase of the mass fraction allowed to gain a little bit in terms of net power output and further confirmed the positive contribution in terms of total heat exchanger area, reduced by 14.5% in comparison with the pure fluid. However, the high value of the evaporation pressure confirmed its negative influence on the desorption process, limiting the positive contribution of the first term of eq. 2 in the achievement of a significant enthalpy gain at the outlet of the evaporator.

However, the results obtained by these preliminary analyses clearly highlights the promising potential of the MOHC nanoparticles, whose contribution can be maximized by properly tuning and optimizing the operating conditions and the nanoparticle mass fraction.

6. CONCLUSIONS

This paper presents a numerical analysis aimed at preliminary assessing the potential benefits of the adoption of an innovative nanofluid in waste heat recovery applications. The nanofluid was characterized by the suspension of the metal-organic heat carriers (MOHC) nanoparticles in the working fluid, enabling additional heat to be potentially extracted (in comparison with standard nanofluids) from the endothermic enthalpy of desorption. More specifically, the possible combination of the base fluid R245fa with the MOHC nanoparticle MIL101 was considered.

To properly model the reversible adsorption/desorption process, experimental analyses were carried out for studying the uptake of the R245fa in MIL101 at different operating conditions and, starting from the experimental results, proper semi-empirical correlations were defined and implemented in the numerical



Figure 5: Cycles of the pure fluid R245fa (blue line) and of the R245fa/MIL101 nanofluid (pink line) in the T-s diagram

model specifically developed for assessing the nanofluid gain in terms of net power output.

The comparison between the pure R245fa and the R245fa/MIL101 nanofluid highlighted a significant contribution of the nanofluid in the heat exchanger with a reduction of more than 14% of the total heat exchanger areas. On the other side, the operating pressure in the evaporator resulted to limit the endothermic desorption

process of the working fluid absorbed in the nanoparticles with a consequent limitation of the expected enthalpy gain in comparison with standard fluids.

Benefits were also obtained by increasing the mass volume fraction of the nanoparticles suspended in the working fluid. Further potential benefits are expected by optimizing even this value together with the operating pressures and temperatures.

NOMENCI ATUDE

	NOMENCLATURE	
c _p	heat capacity at constant pressure	(kJ/kg K)
h	enthalpy	(kJ/kg)
m	mass	(g)
m	mass flow rate	(kg/s)
MM	molar mass	(kg/kmol)
р	pressure	(bar)
Р	power	(kW)
S	entropy	(kJ/°C mol)
Т	temperature	(°C)
Wi	Absorbate molar uptake per unit of absorbent mass	(kmol/kg)
Δh_a	enthalpy of adsorption/desorption	(kJ/kg)
φ	nanoparticle mass fraction	(-)

Subscript

ads	adsorbate
ap	approach point
net	net
nf	nanofluid
wf	working fluid

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