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Non-conventional working fluids for thermal power generation: A review

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Abstract

New technology requirements derived from the exploitation of novel energy resources, and the needs for improvement of the energy efficiency of current power generation systems are pushing the industry towards the search of alternative working fluids. The great challenge for these non-conventional fluids is to provide satisfactory performances and fill the existing lack of media for some innovative energy applications. In this review a number of emerging working fluids for thermal power generation are presented. Also, a special emphasis is devoted to the discussion about new promising fluids, such as nanofluids or ionic liquids, that could be an important breakdown for power generation in the near future.

Keywords: thermal power generation, organic compounds, absorption cycles, ionic liquids, nanofluids.

1. Introduction

According to the Global Status Report on Renewables of 2013 (Mcginn et al., 2013), about 78.3% of today's worldwide power generation capacity relies on the thermal power conversion from fossil and nuclear fuels. Of the remaining percentage, about 78% is represented by hydropower systems, 1.5% by geothermal energy and less than 1% by concentrating solar power (IEA, 2013). Although the fossil fuel reserves depletion and the global warming effect are proved facts, and governments are promoting policies and strategies for the use of alternative energy resources, the reality reflects inertia against the transition between energy resources. The main obstacles to the wide introduction of renewable and non-conventional energy systems into the current energy mix are the high electricity production costs and/or the lack of technology development.

The primary conversion technology for the production of electricity from different energy sources (i.e. fossil fuels, nuclear power, biomass, geothermal, concentrating solar energy and ocean thermal energy) consists in the use of a heat engine, also called *thermal power conversion*. Examples of heat engines are the steam Rankine cycle, the Brayton cycle (or gas turbine) and the Stirling cycle. While today's electricity production technologies are dominated by steam Rankine cycles and gas turbines, new advanced power cycles are emerging as efficiency boosters and conversion technologies for renewable energy sources. Although the performance of these thermal power conversion cycles is limited by the Carnot factor, the required technology is well-known and performances are still higher or comparable to those of other power generation technologies (e.g. solar photovoltaic).

The necessity of improving the efficiency of current thermal power technologies, exploiting new resources, and the increasing restrictions on currently used working fluids are pushing the market towards the search of new alternative media. Furthermore, latest research discoveries that reveal great thermophysical properties of new fluids, such as nanofluids or ionic liquids, open possibilities for their use as working media for energy purposes.

The scope of this review is to present the state-of-the-art fluids that are used as storage or working media in thermal power plants, and introduce those which promising thermal properties bring them out as potential fluids for these purposes. This review excludes therefore any reference to the use of fluids in energy applications that do not imply thermal-mechanical conversions, such as thermoelectric or photovoltaic systems.

The review begins by examining the current power cycles and working media in use. The following section sets out the desirable characteristics of working fluids for thermal power conversion systems. This is followed by a presentation of different state-of-the-art and potential working fluids, as well as research results regarding their adequacy for energy applications. In the last section a discussion about the potential of the presented fluids and their possible future use is provided.

2. Conventional thermal power generation

2.1. Traditional thermal power conversion technologies

As mentioned in the introduction, steam Rankine cycles and gas turbines dominate the market technologies of power generation, representing roughly 56% and 19%, respectively, of the total installed capacity in 2007 (Kehlhofer et al., 2009), as shown in Figure 1.Nowadays these two technologies are starting being used in renewable schemes. For instance, steam turbines are part of the conversion technologies from geothermal resources, concentrating solar power (CSP) and biomass plants, while gas turbines and Diesel engines are being used in biogas and landfill plants. Although today the contribution of these energy systems is almost negligible, it is estimated to grow considerably in the midterm, so that thermal power conversion technologies will account for about 80% of the total installed capacity (Comission of the European Communities, 2008). With respect to the fossil fuels utilized, the market shares of new installations are about 40% for steam power plants (coal-fired), and about 60% for plants with gas turbines (including gas turbines and combined cycle fired with natural gas) (Rukes, 2004).

2.2. Traditional heat transfer fluids for power generation

While the heat transfer fluid used in Rankine power cycles is water, mixtures of air and combustion products act as working fluids in gas turbines and diesel engines. The composition of these gases depends strongly on the type of fuel used, but it consists mainly of CO_2, N_2, H_2O, O_2 and non-combusted fuels.

Water is the most used working fluid today thanks to a series of favorable thermophysical properties, thermal stability, excellent heat transfer properties, low price, extensive availability, and non-flammability or toxic character (Crook, 1994). However, the use of water in power cycles implies, also, a number of risks that must be considered. For instance, water has a relatively high freezing point, which makes it unsuitable for applications where the sink temperature is low, thus setting a limit for the condenser temperature. Also, the vapor

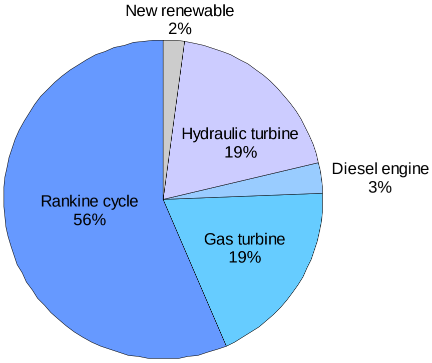

Figure 1. Worldwide installed capacity of different technologies for power generation in 2007. New renewables comprise wind turbines, biomass plants, geothermal and solar systems.

pressure change with temperature is high, if compared to other fluids, making it necessary to deal with very high pressures that require costly equipment for the installation. In addition, for the same temperature range of operation, water will present a wider pressure operation range, thus requiring complex multistage turbines. Moreover, condenser pressures are below the atmospheric pressure, with the consequent risk of air ingress in the cycle.

In the case of gas turbines and Diesel engines, the working fluid consists of a mixture of air and combustion exhaust gases and particles. Lately, the increasing restrictions on greenhouse gases emissions and the progress on carbon capture and storage processes (CCS) are introducing the use of pure oxygen as a comburent for combustion processes for gas turbines. Other configuration of the Brayton cycle consists in the addition of steam to the compressed air or the combustion gases, the so called evaporative gas turbine and steam injected gas turbine (Thern, 2005), to improve the efficiency of the conversion.

2.3. Emerging heat transfer fluids for power generation

The search for alternative working fluids for power generation processes is not new. Over the time a great number of scientists have questioned the utilization of the conventional working media, and investigated about alternative solutions, some of them successful and some not. As an example, among the most rare proposed power cycle media, we can cite the use of H_2 and O_2 for their combustion and use of steam in an open Rankine cycle (Roese, 1972).

In the last decades, the growing interest for producing power from renewable and non-conventional resources, which are usually available at low or medium temperatures, has boosted the search of new power conversion technologies and heat transfer fluids. As a case in point, the use of organic compounds in a Rankine cycle configuration, the so-called organic Rankine cycles (ORC), has experienced a huge development due to their suitability for different applications with reasonable efficiencies (Bao and Zhao, 2013; Hung et al., 1997). The large variety of organic fluids allows for the optimization of the cycle under specific conditions, according to thermodynamic criteria, but also to safety, environmental and economic requirements.

However, most of today's organic working fluids contain fluorine or chlorine, involving the risk of high global warming potential (GWP) and ozone depletion potential (ODP), respectively. The upcoming restrictions on greenhouse gases emissions (i.e. upcoming F-gas regulation) and ozone depleting substances (i.e. Montreal Protocol (Ozone Secretariat UNEP, 1987)) are causing the phase-out of a great part of the organic compounds being used today (e.g. HCFC). As a consequence the industry is moving towards the use of more environmentally friendly refrigerants.

Didion and Bivens (1990) already warned that the number of new potential refrigerants that met the same or better thermodynamic requirements as the replaced substances was limited. As a solution, in the early 90s Didion and Bivens proposed the use of refrigerant mixtures as alternative working fluids. The advantages offered by mixtures are their tunable thermophysical properties, that can be customized easily by changing their components and composition. However, despite the evidences of the better performance of refrigerant blends (Angelino et al., 1998) their presence in today's power generation systems is reduced, and still, they are subjected to the mentioned environmental restrictions.

Table 1. Main thermal power conversion technologies and working fluids used in them.

Thermal power cycle	Working fluid requirements	Examples of working fluids
Rankine cycle	Critical temperature of the fluid higher than the maximum temperature of the cycle	Water (high temperature applications) Organic refrigerants (low temperature applications) Fluids mixtures
Open-Brayton cycle	Combustion gases and air with low content of solid particles.	Air+Natural gas, O_2+Natural gas, Air+water+Natural gas
Stirling cycle	Gas with low heat capacity and high thermal conductivity	Air, Helium, H_2, nitrogen
Absorption cycle	The absorbent should have a high capability of absorbing the refrigerant, and the change in the boiling point should be important	LiBr+H_2O, NH_3+H_2O+LiBr
Supercritical Rankine cycles (closed Brayton cycle)	Critical temperature of the fluid lower than the minimum temperature of the cycle	CO_2, organic substances, air

For these reasons, it seems reasonable to investigate new working fluids and technologies that can be used for the conversion of thermal energy into mechanical power. Table 1 presents the main technologies for thermal power conversion along with the most used working fluids for each of them. In the next sections, different innovative fluid alternatives are commented, analyzing their suitability as heat transfer fluids and the current status of their application, if existing.

3. Desired characteristics of heat transfer fluids

Summarizing the desirable characteristics of working fluids for thermal power cycles is not simple, since, although some properties are required in all the applications, most of them depend on the specific conversion technology used. As an example, Figure 2 shows how the thermodynamic properties of two different fluids affect the performance of an ORC. Table 2 enumerates the most important criteria to consider when selecting or searching for a heat transfer fluid for thermal power conversion. The partial or total agreement of each of the advanced fluids described in this work to each criterion is also indicated, although it will be explained in detail in each subsection.

According to MacFarlane, the specific heat capacity c_p of the fluid is one of the key properties in heat transfer applications (MacFarlane et al., 2014). Heat capacity is directly related to the heat admitted or rejected by a fluid for a specific change of temperature. This means that it is a measure of the capacity of the fluid to transfer heat, being high values recommendable. More in detail, Hillems (1999) stated that the volumetric heat capacity ($c_p \cdot \rho$) gives a better measure of the transferable heat quantity, and therefore accounts for the plant components size needed. Nevertheless, in the exceptional case of Stirling cycles, working fluids with lower heat capacities produce larger changes in pressure for a same amount of heat and are, therefore, preferred.

The thermal conductivity of heat transfer fluids is also an essential characteristic (Das et al., 2008) since it affects directly the size of heat exchangers. For this reason, high thermal conductivities are desirable.

In the case of high temperature applications, substances with low vapor pressures are preferred in order to avoid costly high pressure equipment, and to head off safety risks.

Viscosity is important for several aspects. Apart from the direct influence of the viscosity in the pressure drops in heat exchanger, it must also be considered that too high viscosities can increase the pumping work in the cycle.

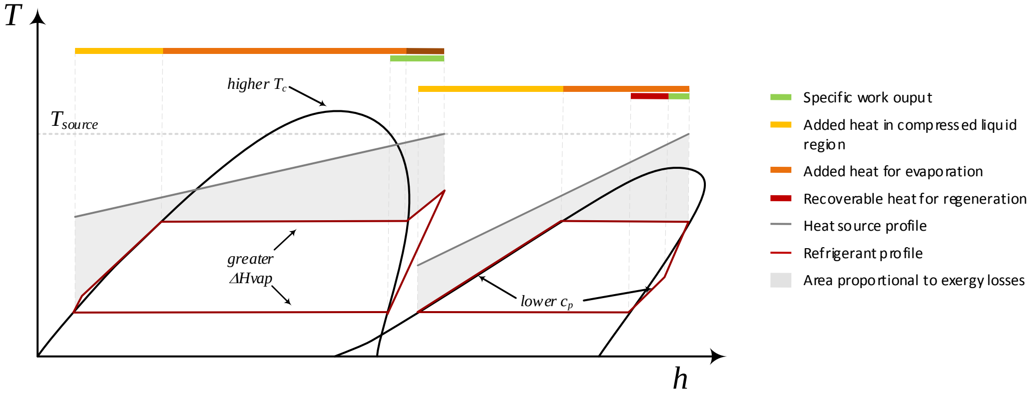

Figure 2. Influence of the fluid thermodynamic properties on an ORC performance. T-h diagram of two ORC running with two different fluids, wet (left) and dry (right). It can be observed how the critical temperature T_c, enthalpies of vaporization ΔH_{vap}, and heat capacities c_p, influence in the shape of the saturation curve, and thus, in the work output of the cycle, and heat addition conditions.

Low freezing points are desired, both for working fluids or thermal storage fluids. In the first case, it is necessary to work at low condensation temperatures without the risk of solidification of the working fluid. In the second case, the lower the freezing point is, the more moderate temperatures will be required to keep the fluid in the liquid state.

In the specific case in which the working fluid is going to be used in a power cycle where absorption processes take place, Sun et al. (Sun et al., 2012) point out two exclusive characteristics of the fluid. Firstly, the authors recommend a large difference in boiling point between the mixture of absorbent and refrigerant, and the pure refrigerant, to facilitate the generation of refrigerant vapor. Secondly, the refrigerant should be in a high concentration in the absorbent to keep a low flow rate of the strong solution. In addition, it is recommended that the heat of vaporization should be high, which has been also claimed by other authors concerning working fluids for ORC (Bao and Zhao, 2013). This statement is, however, not homogeneous in different publications. In this sense, higher enthalpies of vaporization allow most of the heat to be added to the fluid in the two-phase region, which increases the average heat addition temperature. On the other hand, fluids with low vaporization enthalpies could be more convenient for heat sources which suffer from a strong cooling, therefore minimizing the mean temperature difference between the source stream and the refrigerant (Larjola, 1995). For these reasons, it cannot be concluded a specific requirement of the enthalpy of vaporization, and each case should be studied separately.

Finally, other obvious and desirable characteristics of any heat transfer fluid are enumerated as follows:
- Non-flammability, high or no flash point, no autoignition temperature: in order to avoid safety risks as well as not requiring especial equipment (e.g. pumps for flammable substances).
- Chemical and physical stability: to be compatible with the materials of the components of the plant (e.g. seals, lubricants, tubing materials), non-corrosive, high durability.
- Non-toxicity, low costs, non-ozone-depleter, non-green-house-gas.

4. Gaseous working fluids

Apart from the conventional gas turbines, gaseous working fluids are used in both supercritical Rankine cycles (or closed Brayton cycles) and Stirling engines. These two technologies, although not very extensively developed, are growing in interest as potential conversion methods for renewable resources.

Table 2. Desirable properties of working fluids for thermal power cycles. ✓: fluids in this group generally accomplish this property; ×: fluids in this group do not follow, in general, this property; ~: there are no conclusive trends for this property in this fluid group.

Property of interest	**Motivation**	**Organic refrigerants**	**Siloxanes**	**Ionic liquids**	**Nanofluids**
High specific heat capacity	High heat capacities are associated to higher capability of the fluid to absorb/reject heat	×	×	✓	✓
Low viscosity	High viscosity fluids increase pressure drops in tubing and heat exchangers, and work needed for pumping	~	×	×	×
High heat conductivity	High heat conductivity fluids require smaller heat exchangers	×	×	✓	✓
Low vapor pressure	High vapor pressures need from costly equipment and imply a risk.	×	✓	✓	✓
High thermal decomposition temperature (thermal stability)	Degradation of the fluid at high temperatures leads to significant changes in the performance of the conversion, or even corrosion or fouling problems.	×	✓	✓	✓
Low freezing point	In order to avoid partial or total solidification of the fluid in the system.	✓	✓	×	×
Low corrosivity	Corrosive substances can reduce the lifetime of installations and increase maintenance costs.	~	✓	×	~
Low GWP and ODP	Upcoming regulations will phase-out substances that do not accomplish with increasingly restrictive limits.	~	✓	✓	~
Low costs	For economic reasons	~	~	×	×
Low reactivity (chemically stable)	For safety and performance reasons	×	✓	✓	~
Low toxicity	For safety reasons	~	✓	~	~
Low flammability	For safety reasons	~	✓	✓	✓

In the first case, a great number of researchers are dealing with the design and analysis of these power cycles for their use in geothermal and solar systems (Vidhi et al., 2013; Zhang and Yamaguchi, 2011). Although most of the work is focused on the study of CO_2 supercritical cycles, vapors of organic fluids such as R134a or R143a are also under study. In general, organic vapors present lower pressures ratios, which involve simpler turbines. Nevertheless, the use of most of these gases can be restricted by environmental reasons and therefore inert fluids are still preferred.

Supercritical CO_2 cycles have been proved successfully to have performances up to 30% higher compared to those of subcritical Rankine cycles (Hough, 2009). However, their use today is exclusive to high temperature applications (such as fossil fuel plants) because the high pressure equipment needed for the installation makes them unsuitable for small scale power production.

In the case of Stirling cycles, working fluids such as air, nitrogen, hydrogen or helium provide significant cyclic volume changes for moderate temperature differences, and are thus the most commonly used. As alternatives, several authors have analyzed the use of mixtures of gases, or even two-phase fluids for Stirling engines. Organic substances, like ethane or R23, have also been studied as working fluids. The benefit of these last compounds, pointed out by

Invernizzi (2010), comes from their wide-ranging critical temperatures. In this sense, Invernizzi found that selecting the fluid, so that at the low temperature of the cycle it was in the dense gas region, could increase significantly the efficiency of the engine.

The presence of Stirling engines nowadays is predominated by their use for decentralized small scale electricity production, or in solar powered dish Stirling systems. In these later ones, normally helium or hydrogen are used as working fluids.

5. New working fluids for ORC

Because of the mentioned restrictions on environmental parameters, that affect principally the existing organic compounds, new organic substances are under research for their use in thermal power cycles. In the case of high-temperature applications, siloxanes are successfully already being used as an alternative to heavy hydrocarbons, with negligible GWP and ODP values. The only requisite of siloxanes is the regeneration of the gases at the outlet of the turbine in the power cycle, necessary to have good conversion efficiencies. Also recently, several authors have pointed out at the use of phenylnaphtalenes as working fluids for high temperatures (Bell et al., 2012; McFarlane et al., 2010).

For the low and medium temperature range, hydrofluoroolefins arise as replacement working fluids, with exceptional low global warming potential and atmospheric lifetime. Among the so called fourth generation refrigerants, we can mention R1233zd(E), R1234yf or R1234zeE. According to Liu et al. (Liu et al., 2014), who analyzed the performance of several hydrofluoroolefins in ORC, these working fluids appear as promising substitutes, not only because of their environmental parameters but also because they can offer higher performances.

6. Working fluids for absorption cycles

Absorption cycles are power cycles where the working fluid has two components: the absorbent and the refrigerant. The composition of the mixture varies along the cycle so that only a mixture with high content of the refrigerant (strong solution) runs through the turbine. At the outlet of the expander, the strong solution is mixed with the weak solution coming from the mixture separator and the refrigerant is reabsorbed in the absorbent at low pressure. Examples of power cycles based on this principle are the Kalina cycle, used in geothermal plants and waste heat recovery, or the Maloney-Robertson cycle. In general, absorption cycles are reported to yield better performances than Rankine cycle, but as a drawback, associated capital costs are higher due to the extra components. The most used refrigerants are water, ammonia, alcohol, and halogenated hydrocarbons (Sun et al., 2012). Common absorbents can be LiBr, $LiNO_3$, trifluoroethanol or hexafluoroisopropanol.

Khamooshi et al. (Khamooshi et al., 2013) remarked the significant impact of the working fluid in the performance of absorption cycles, therefore becoming the search of new fluid pairs of great importance. Many different combinations of fluids have been studied (Privat et al., 2013; Yin et al., 2000). However, still water seems to be the most utilized refrigerant. In general, the blend H_2O+LiBr performs better at lower resource temperatures (Yin et al., 2000). Nevertheless, working fluids based on organic refrigerants appear more promising for specific cases such as solar energy systems, waste heat or geothermal heat sources (Sun et al., 2012).

7. New potential working fluids

7.1. Nanofluids

7.1.1. Definition

Nanofluids are defined as dilute liquid suspensions of metallic or nonmetallic nanoparticles in traditional heat transfer fluids (Das et al., 2008), where nanoparticles are particle which size is below 100 nm (Schmid, 2011). This concept was firstly conceived by S.U.S. Choi as a breakdown of most of the current technical barriers for heat transfer fluids. The main novelty of nanofluids resides in the fact that very small quantities of nanoparticles can change dramatically the thermal properties of the base fluid. As base fluids can be water, oil, ethylene glycol or refrigerants (Annapureddy et al., 2014; Das et al., 2008). Particles used in nanofluids can consist of oxide ceramics (e.g. Al_2O_3), nitride ceramics (e.g. AlN), carbide ceramics (e.g. SiC), metals (e.g. Cu), semiconductors (e.g. TiO_2), carbon nanotubes and composite materials.

For more than 100 years it has been a common practice to enhance the thermal conductivity of heat transfer fluids by adding solid particles to them (Das et al., 2008). However, according to Das et al. (2008) the conventional solid fluid suspensions are not beneficial since they need from a high content of particles (usually more than 10% in volume) to be effective, which results in more pressure drops and pumping power. In addition, these particles settle rapidly. As a solution, nanofluids promise to overcome these difficulties.

Because metals in solid form have thermal conductivities that are several orders of magnitudes higher than those of fluids, it is expected that nanofluids will have an enhanced thermal conductivity. Moreover, the higher heat transfer surface of particles enhances heat conduction (Das et al., 2008). Also, due to the small size of the particles, the suspension stability is higher and setting times are less than those observed for millimeter particle suspensions. Nanofluids have also been claimed to increase the critical heat flux (CHF), which is beneficial for any process involving the boiling of the fluid (Canter, 2009). Another benefit of nanofluids is that, according to Das el al. (Das et al., 2008), their use can decrease the pumping demand, reduce the inventory of heat transfer fluid and provide energy savings.

In general nanofluids are reported by a great number of researchers to have enhanced thermophysical properties such as thermal conductivity, thermal diffusivity, viscosity and convective heat transfer coefficients compared to those of the host fluids (Canter, 2009; Wong and De Leon, 2010). Less optimistic, however, are McGrail et al. (McGrail et al., 2013), who remarked that the reported benefits of nanofluids for heat transfer purposes were sometimes inconsistent and overestimated. In the same sense, it is stated in (Canter, 2009) that although experimental data showed a general improvement of the thermal conductivity of the base fluids, the enhancement is not as high as initially reported in the first studies. The authors enumerated, as disadvantages of the use of nanofluids for thermal power generation, a large mismatch between the particle and working fluid molecules density, the need for surfactants, and the reduction of the bulk fluid density that does the work. For these reasons the authors commented that the gains in efficiency assumed to nanofluids could be overlapped.

7.1.2. Potential of nanofluids for energy conversion

The potential of nanofluids for their use in energy applications is being investigated in different contexts, such as carbon capture (CCS) (Lee et al., 2012), automotive coolants or fuel additives (Wong and De Leon, 2010). Regarding the use of nanofluids for thermal purposes, it has been found, as an example, that nanofluids based on copper and carbon nanotubes (CNT) exhibit very high thermal conductivities compare to those of the host liquids. Also it has been pointed out that there is no linear relationship for this property with the concentration of nanoparticles. However, it has been proved that in some nanofluids there is a strong dependence between the thermal conductivity and the temperature and size of the particles (Das et al., 2008).

In the field of energy generation, Wong and De Leon (2010) suggested the use of nanofluids as working fluids to extract geothermal energy. Because of the improved heat-transfer characteristics for low temperatures and temperatures on the supercritical water region, there can be a gain in the heat-to-power conversion efficiency by using nanofluids.

Also, it is stated in (Canter, 2009) that the use of nanoparticles has been found to improve the boiling heat transfer of refrigerants, which can be an important finding for the power industry.

7.1.3. Metal organic heat carriers (MOHC)

The term metal organic heat carriers (MOHC) denotes a special group of nanofluids consisting of a heat transfer fluid that incorporates nanoparticles of metal organic frameworks (MOF). MOF are porous materials that consist of metal ions allocated into organic molecules (MacGillivray, 2010), and are currently under study for their interesting properties for applications like CO_2 capture, hydrogen storage and gas separation. In general, a number of ideal properties are attributed to MOHC such as high enhanced thermophysical properties and high thermal stabilities (McGrail et al., 2013). In fact, McGrail et al. (2013) presented MOHC as new nanofluids capable of overcoming most of the drawbacks previously mentioned for nanofluids (need for surfactants, mismatch between particle and fluid densities, and working fluid displacement).

Several authors (Annapureddy et al., 2014; McGrail et al., 2013) have suggested the use of MOHC as promising working fluids for organic Rankine cycles. Their results claim that by using MOHC more heat can be extracted from the heat sources, thus having higher enthalpy at the turbine inlet and higher power output. On another note, the authors also claim that desorption enthalpies for MOHC are greater than those of pure fluids.

However, the main challenge for MOHC, as for nanofluids, is to keep the stability of the nanoparticle dispersion. In this regard, Annapureddy et al. (2014) refuse the use of surfactants in the working fluids to increase the stability due to the potential problems that they can generate, such as changes in boiling point, zeotropic behavior, increased viscosity, and reduced heat transfer capabilities.

7.1.4. Examples of current use

As an example, Infinite Turbine is an ORC manufacturer that currently markets a modular ORC using radial turbines and a heat transfer fluid containing nanoparticle additives. According to the manufacturers these nanoparticles enhance the heat transfer capabilities of the fluid in both the evaporator and condenser, thus increasing the efficiency of the system (Cycle and Turbine, 2012). Except for this particular case, the application of nanofluids as working fluids for power generation is still rare.

Current barriers to the introduction of nanofluids focus on the minimization of the particle aggregation, and the study of fouling, clogging, corrosion, abrasion, and long-term stability of the fluid (Wong and De Leon, 2010). This is of especial importance for power generation systems since nanofluids can raise erosion and fouling problems when going through turbines and condensers (Wong and De Leon, 2010).

Also, another problem pointed out by Wong and De Leon (Wong and De Leon, 2010), is the unpredictable content of nanoparticles in the vapor phase, which can hinder the study of their performance in new power cycles.

7.2. Ionic liquids

7.2.1. Definition

In its most general sense, the term *ionic liquids* (ILs) refer to a wide variety of salts that are liquid at ambient conditions (Kirchner and Clare,

2009) and consist of an organic cation and an inorganic anion (Khamooshi et al., 2013). ILs can be grouped into three categories: molten salts, ionic solutions and liquid metals (Hansen and McDonald, 2006; MacFarlane et al., 2014). The term molten salts is usually employed to refer to IL with high melting point temperature (Kirchner and Clare, 2009). Ionic solutions consist of a neutral or polar liquid base with a solute, which can be atomic ions or macroions, that dissociates into positive and negative ions. Liquid metals are molten salts in which free electrons provide very high electrical conductivities.

The thermophysical behavior of ILs cannot be easily ranged due to the huge variety of ILs, since it depends strongly on their molecular structure. For example, although ILs are considered as non-volatile substances (Khamooshi et al., 2013), the existence of volatile ILs has been reported. In the same way, some ILs can be combustible while most of them are claimed to be non-flammable, or even flame retardants. Only their ion conductivity is a common property (Kirchner and Clare, 2009). In this sense, according to MacFarlane et al. (2014) ILs are dominated by strong electrostatic forces between their molecular ions, which induces, generally, low volatility and flammability, as well as high chemical and electrochemical stability. Most of ionic liquids present also high thermal stabilities, which makes them suitable for their use as heat transfer fluids (MacFarlane et al., 2014). Also, ILs have generally melting points lower than inorganic salts.

Regarding the thermal conductivity of ionic liquids, it appears to be slightly higher than that of the organic molecular liquids (Ribeiro et al., 2009) and almost independent of temperature. It is remarked, however, that the knowledge about the relation between the thermal conductivity and the molecular structure is still very limited (MacFarlane et al., 2014).

Very recently the novel concept of 'ionanofluids' has been employed to denote the use of nanoparticles in ionic liquids. Ribeiro et al. (2009) stated that nanoparticles can even enhance the conductivity and heat capacity of the base ionic fluids, and therefore ionanofluids could be potential heat transfer fluids. This new conception, along with the possible use of ILs mixtures, give a view of the wide variety of potential working fluids, and show therefore that further research in the field is still needed.

7.2.2. Potential of ILs for energy conversion

Several authors have already noticed the use of ionic liquids for their use in energy applications such as thermoelectrochemical cells, fuel cells, dye-sensitized solar cells, CO_2 and SO_2 capture and separation, and production of H_2 by water splitting (MacFarlane et al., 2014; Smiglak et al., 2014). Although most immediate and attractive applications are those involving the electrochemical behavior of ILs, there is an ongoing and emerging research for the use of ILs as fluids for thermal energy storage applications. Currently, the number of available fluids with low or medium melting points (i.e. below 100°C, between 100-200°C) is scarce. Therefore ILs with melting temperatures in these ranges are of special interest. For these cases, a high enthalpy of fusion is required if ILs are intended to be used in storage applications (Smiglak et al., 2014).

A much less investigated application of ILs is their use as working fluids in thermal power cycles such as organic Rankine cycles. Smiglack et al (2014) suggest that organic salts offer a great potential for this technology. In this sense, ILs of the tetra-arylphosphonium cation family are pointed out by the authors to exhibit an exceptional thermal stability, that could be of interest for its use at high temperatures. Moreover, according to Khamooshi et al. (2013) ILs can be a potential non-toxic alternative to most of the working fluids currently in use in absorption cycles. Additionally, regarding the use of ILs in thermal storage systems for power generation (e.g. thermal storage in concentrating solar plants), ILs present the great advantage of being able to be stored in open systems due to the very low vapor pressure.

7.2.3. Examples of current use

The use of ILs as heat transfer fluids in thermal storage systems for concentrating solar systems is already a fact, being several commercial ILs considered for this purpose (McFarlane et al., 2010). However their presence in storage thermal systems is limited.

The challenge for future research to facilitate their introduction turns around the characterization of the corrosion behavior of ILs, since it has not been investigated in detail yet, and it can affect the plant integrity, efficiency and operation (Uerdingen et al., 2005). Also, although ILs are assumed to be non-toxic, Zhao et al. (2007) stated that they are, in nature, toxic, although their negligible vapor pressure prevents them from spreading in the environment. For this reason the authors claim that it is necessary to place in front the safety matters and prefer to design non-toxic ILs.

8. Conclusions and outlook

This paper reviews several groups of working fluids that are used nowadays in thermal power conversion systems, or show a great potential for their utilization in the near future. The most important parameters for the selection of working fluids are discussed, and the suitability of each of the fluid groups here presented according to them is commented. A summary of the advantages and disadvantages of each fluid group is given in Table 3.

Although still water and combustion gases are the most used heat transfer fluids in today's thermal power production cycles, new alternatives are making their way in efficiency configurations and renewable energy schemes. This is the case of most of organic compounds, previously used in refrigeration units, that provide satisfactory performances for the power production from low heat sources. More recently, siloxanes are successfully being used in high-temperature applications.

Table 3. Summary of the advantages and disadvantages of the presented working fluids.

Fluid group	Advantages	Disadvantages
Water	Thermally stable, non-toxic, non-flammable, high availability, low cost, known technology.	High freezing point, high vapor pressures, large enthalpy drops (complex turbine designs needed).
Air + Combustion gases	High availability, high temperature operation, high performance, known technology.	Fuel limitations to avoid presence of particles in the turbine, performance affection due to humidity and composition variations.
Organic compounds	Low boiling temperatures (suitable for low temperature applications), huge variety of compounds, relatively low vapor pressures.	A great number of them are ozone depleters or greenhouse gases, many of them are potentially toxic or flammable.
Siloxanes	High critical temperatures (suitable for high temperature applications), low-toxicity, non-corrosive, low vapor pressures.	Need of regenerative configurations to be viable, higher viscosity.
Inert gases	Non-toxic, non-flammable, capability of power generation even from low temperature lifts.	Leaks risk, high working pressures.
Nanofluids	Higher heat capacities, enhanced thermal conductivity, higher convective heat transfer coefficients, higher thermal diffusivity.	Particle settling, need of surfactants that modify the thermophysical properties, reduction of bulk fluid density, particle presence in the turbine.
Ionic Liquids	High flexibility and tunable properties, low volatility and flammability, high thermal stability, low and medium melting points.	Possible enhanced corrosion, high cost, possible toxicity.

Nevertheless state-of-the-art research findings are pointing out to the promising thermal properties of innovative fluids. This is the case of nanofluids and ionic fluids. In the first group, nanoparticles of highly thermally conductive materials in suspension of common heat transfer fluids enhance their thermal properties significantly. In the second group, their ionic nature is associated with strong intermolecular forces that provide them high thermal stability and low vapor pressure, and make them ideal for thermal power conversion processes.

While both organic substances and siloxanes are present in a great number of power cycles today, and their use is on the increase, mixtures of fluids and blends for absorption power cycles are still in a developing stage. In the case of more innovative fluids, such as nanofluids or ionic liquids, more research is needed to confirm their suitability for these systems, since still a number of questions need from further research (e.g. behavior of the fluids in their expansion in turbines, performance in heat exchangers). Nevertheless, the presence of some of these fluids in existing installations as heat storage fluids (e.g. ionic liquids in concentrating solar thermal plants) and the positive results in recent research studies about their properties are putting forward them as promising working fluids in thermal power cycles.

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Appendix: Glossary

Heat transfer fluid: liquid or gas used in industrial processes or power generation systems to transfer thermal energy between heat sources and sinks.

Working fluid: liquid or gas that performs the conversion between thermal and mechanical energy in a heat engine.

Organic Rankine cycle (ORC): thermal power cycle consisting of an evaporator and condenser in which heat is absorbed from a heat source and released to a sink at lower temperature, producing mechanical power through the expansion of an organic working fluid.

Absorption: physical or chemical process by which atoms, molecules or ions of a substance are taken up by the bulk phase (gas, liquid or solid) of another substance.

Absorption cycle: thermal power cycle which working fluid consists of an absorbent and a refrigerant. The mixture composition varies along the cycle, thanks to the addition of separators and absorbers.

Flash point: lowest temperature of a substance for which it vaporizes and creates ignitable mixtures with air.