Titanium tetrachloride as novel working fluid for high temperature Rankine Cycles: Thermodynamic analysis and experimental assessment of the thermal stability

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In this paper, Titanium tetrachloride ($TiCl_4$) is analyzed/assessed and proposed as a new potential work-ing fluid in Rankine Cycles. Besides its good thermodynamic properties, $TiCl_4$ is in fact a fairly low cost, non-carcinogenic fluid, with zero Global Warming Potential (GWP) and Ozone Depleting Potential (ODP) and it is currently employed in high temperature industrial processes. It is however very reactive with humid air and water. A preliminary thermodynamic analysis confirms its possible application in power plants with maximum temperature up to 500 °C, considerably higher than the ORC state-of-the-art technology, performing electrical efficiencies as high as 35–40%. This suggests the potential use of $TiCl_4$ as an alternative fluid in ORCs allowing the exploitation of high temperature sources (up to 500 °C), typically used in steam cycles. To assess the possibility of operating the cycle in such high temperature conditions, we carried out an experimental thermal stress analysis, showing that the fluid is remarkably stable at temperatures up to 500 °C, even in presence of P91 and Cupronickel, two materials typically employed in the high temperature section of power cycles.

Keywords: Titanium tetrachloride, Organic, Rankine, Cycles, Thermal stability, Thermodynamic analysis

HIGHLIGHTS

- Titanium tetrachloride is proposed as new fluid in high temperature Rankine cycles.
- We show experimentally that it is remarkably stable at temperatures up to 500 °C.
- Resulting plant efficiencies of 35–40% are higher than state-of-the-art ORCs.
- Its high reactivity with water poses some concerns in the design of a power plant.

1. Introduction

Organic Rankine Cycles represent a well-established technology for the conversion of heat into electricity, especially for small-medium power size where a traditional steam plant poses technological challenges. Several applications can be found in the fields of geothermal power, solar power, biomass exploitation and low grade heat recovery [1–8].

To date, the suitability of many categories of working fluids has been evaluated in terms of their thermodynamic properties as well as other more practical aspects such as availability, costs, toxicity and flammability. A comprehensive review of the potential candidate fluids for ORCs can be found in [9].

Nonetheless, working fluids used in ORC plants are typically affected by chemical decomposition phenomena, whenever the operating temperature exceeds a certain threshold [10–12]. This fact sets the temperature limits of the power cycle to values that are currently below 400 °C, thus limiting the potential plant conversion efficiency in case of higher temperature heat sources .

Data available in the literature on the thermal stability of working fluid in the temperature range of interest for ORC applications, are scarce and somewhat contradictory [13–15]. Studies of the thermal stability of organic fluids dates back to the early 60s. In 1961, Blake et al. [16] introduced for the first time a test methodology based on the analysis of isothermal pressure deviations of fluids that undergo to different thermal stress temperatures. In

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Nomenclature

CHP	combined heat and power	s	entropy (J mol^{-1} K^{-1})
LP	low pressure	s_{SV}	entropy of the saturated vapor
P	pressure (bar)	T	temperature (K)
R	ideal gas constant (kJ mol^{-1} K^{-1})	T_{cr}	critical temperature
h	enthalpy (kJ mol^{-1})	σ	molecular complexity parameter
HP	high pressure	ω	acentric factor

fact, the most frequently detected variation in the physical properties of a compound during its decomposition is the increase of vapor pressure due to the formation of volatile compounds. This method was later used by other authors, who investigated the thermal stability of several organic fluids in the temperature range typical of aviation and aerospace applications [17–19].

An improvement of this approach can be obtained through the comparison between the vapor pressure of the fluid before and after the thermal stress test, especially in conditions of fairly low pressure, where the effects of the formation of volatile compounds are more evident. This method has proved more effective than the analysis of the pressure changes during the thermal stress tests, especially in the case of weak but important decomposition phenomena [20].

Based on this method three papers was recently published by two of the authors, focusing on thermal stability of perfluorohexane [11] three hydrocarbons [12] and HFO-123yf [21].

Aiming at addressing the need of highly stable fluids, in this work the possibility to employ Titanium tetrachloride ($TiCl_4$) as a novel working fluid in high temperature Rankine Cycles is investigated. In fact the use of $TiCl_4$ is well-known in high temperature industrial processes, such as the Kroll process carried out at 700–1000 °C [22,23], exploited for the production of metallic Titanium. Moreover, $TiCl_4$ has also been proposed for newer high temperature applications such as the thermochemical production of Titanium dioxide (TiO_2) at 1500–2000 K [24] and for chemical vapor deposition applications at 1000–2000 K di [25]. The study of $TiCl_4$ as a heat pipe fluid is proposed by Davarakonda and Olminsky [26] and the thermo-physical properties of $TiCl_4$ as a heat pipe fluid are evaluated by NASA [27]. These considerations and studies support the idea of adopting $TiCl_4$ in high temperature RCs (see also Ref. [28]).

The paper is organized as follows. In Section 2 some properties of $TiCl_4$ relevant to its application as working fluid in RCs are provided. In Section 3 a preliminary thermodynamic analysis aiming at the assessment of the potentiality of its use for power generation, particularly in comparison with low size steam plants, is performed. In Section 4 the results of the experimental study of its thermal stability are reported. In Section 5 the conclusions are deduced.

2. Properties of $TiCl_4$

Titanium tetrachloride belongs to the family of the Halides. At room temperature it appears as a transparent and colorless liquid. It reacts violently with water, even with the small amounts contained in humid air, to generate heat and corrosive gases containing hydrogen chloride. In presence of water it is also corrosive for many metals.

Halides have been considered as suitable working fluids in heat pipes, in the temperature range from 200 to 400 °C [26–30], as well as in Rankine Cycles [28]. Indeed, Titanium tetrachloride would be particularly desirable in the latter application, thanks to its high molar weight and low molecular complexity.

Table 1
Thermodynamic properties of $TiCl_4$.

Melting point (°C)	−24.1
Boiling point (°C)	135.9
Critical temperature (°C)	364.9
Critical pressure (bar)	46.6
Molecular complexity parameter σ[a]	1.991
Evaporation temperature at 5 kPa (°C)	53
Acentric factor ω	0.284
Molar mass (g/mole)	189.7

[a] Calculated according to Eq. (1).

Some of the physical properties of $TiCl_4$ relevant to its application as working fluid in Rankine Cycle are listed in Table 1.

The parameter of molecular complexity (σ) is primarily a function of the heat capacity of the vapor and, as a consequence, it is directly related to the molecular structure of the fluid. It can be defined as [10]

$$\sigma = \frac{T_{cr}}{R}\left[\frac{dS_{SV}}{dT}\right]_{T_r=0.7} \tag{1}$$

where S_{SV} is the entropy of the saturated vapor, T_{cr} the critical temperature, T_r the reduced temperature and R the ideal gas constant.

An increase of σ implies: (i) an increase in the superheating of the vapor after an isentropic turbine expansion, (ii) a lower temperature drop through the expansion for a given pressure ratio and (iii) an increase of the slope of the saturated vapor line [3]. All these aspects are generally disadvantageous in ORCs as they require the use of a recuperator. In terms of molar mass, high values are beneficial for the design of the turbine since they imply low enthalpy variation during the expansion for a fixed pressure ratio, resulting in a reduction of the number of stages and of the costs.

Summing up, the thermodynamic properties of $TiCl_4$ suggest its potential use as working fluid in power cycles. It has features in many respects similar to those of steam, with the advantage of a considerably higher molar weight.

3. Thermodynamic analysis

In this section, the use $TiCl_4$ as working fluid in a recuperative power plant operating with maximum temperature up to 500 °C is analyzed. This limit is chosen as upper bound since, as notable in Fig. 8, at this temperature the working fluid appears stable. Over this limit the thermal stability is not so undoubted. However, this temperature is considerably higher than the typical values in state-of-the-art technology of ORC plants, where maximum temperatures are limited by the thermal stability of the working fluid. Thanks to its thermodynamic and chemical characteristics, $TiCl_4$ can allow to reach higher maximum temperatures, as it will be proved from the experimental analysis carried out in Section 4.

In this section a parametric analysis is presented. It is varied the maximum temperature and the maximum pressure in order to define the trend of the efficiency of the thermodynamic cycles.

The plant scheme and the calculation assumptions are summarized in Fig. 1 and Table 2 respectively. Clearly, the plant configuration is that of a recuperative cycle, with the recuperator positioned between the pump and the boiler aiming at recovering part of the energy available from the turbine exhaust stream. As discussed in Section 2, this component becomes necessary, given the thermodynamic properties of $TiCl_4$, in order to enhance the plant conversion efficiency. The range of the variables and the value of fixed parameters are common for the investigated plant. Calculations are carried with software Aspen Plus V7.3 adopting the Peng-Robinson equation of state. The parameters of the $TiCl_4$ are available within Aspen Plus. The thermodynamic model is validated with respect to the experimental data of the vapor pressure available in the literature as it will be discusses in Section 4 (see Fig. 7a). Fig. 2 reports the cycle efficiency curve plotted as function of the evaporating pressure, for three different turbine inlet temperatures, in the range 400–500 °C. The highest efficiency of 36.2% is obtained in case of maximum temperature of 500 °C at the pressure of 40 bar. From the trend of the curves it is notable that, increasing the temperature, the cycle efficiency increases and that the maximum of each curve is at higher evaporation pressure. The values of pressure that maximize the efficiency of the cycle are comprised in the range 25–45 bar for the investigated temperatures. These pressure and temperature are common for small-scale steam power plants. It is worth noting that the resulting optimized pressure interval refers to the range of subcritical cycles. Fig. 3 shows the power cycle in the Temperature-entropy diagram in the aforementioned optimized conditions, while Table 3 reports the values of the relevant thermodynamic variables in each point of the cycle. From the figure is possible to see that the expansion occurs in the dry region since both the inlet and the outlet of the turbine involve superheated vapor. From the point of view of the possible heat sources that can be effectively exploited by this power cycle, it can be seen from Fig. 4 that the heat introduced in the cycle provides an almost linear increase of the temperature of the working fluid, from point 2 to point 4 (with exception of the temperature plateau occurring during evaporation). Thus, heat sources suitable to match the variable temperature profile of the

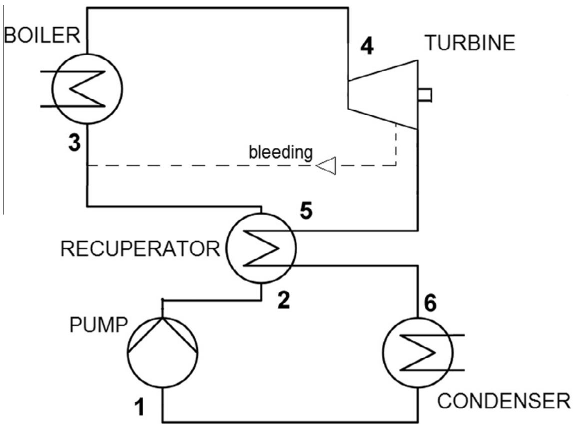

Fig. 1. Plant layout assumed for the thermodynamic analysis.

Table 2
Calculation assumptions.

Condensing pressure (bar)	0.05
Turbine isentropic efficiency (%)	80
Pump isentropic efficiency (%)	70
Minimum ΔT in the recuperator (°C)	15

No pressure losses in the heat exchangers.

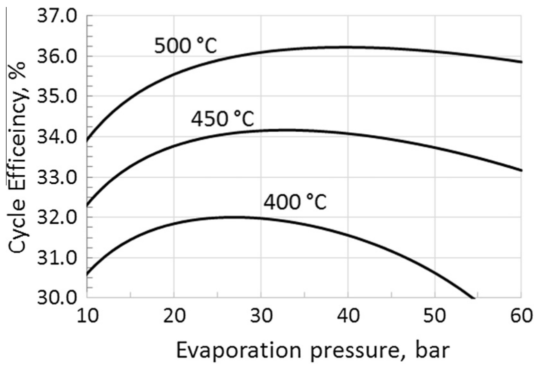

Fig. 2. No-bleeding cycle efficiency as function of the evaporation pressure of $TiCl_4$ for three values of turbine inlet temperatures. Calculation assumptions as by Table 2.

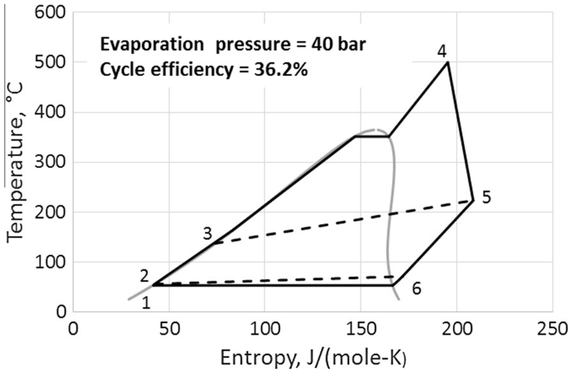

Fig. 3. Optimized thermodynamic cycle with $TiCl_4$ in the Temperature-entropy plane in case of turbine inlet temperature of 500 °C. Dashed lines refers to temperature profiles within the recuperator.

Table 3
Thermodynamic properties in each point of the optimized thermodynamic cycle with $TiCl_4$ shown in Fig. 3.

Point	T (°C)	P (bar)	h (kJ/mole)	s (J/(mole K))
1	53	0.05	−799.73	41.8
2	56	40	−799.08	42.6
3	163	40	−783.72	82.8
4	500	40	−717.17	195.3
5	223	0.05	−741.89	208.5
6	71	0.05	−757.25	171.7

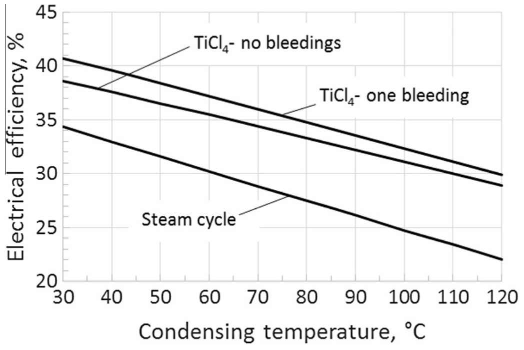

Fig. 4. Electrical efficiency as function of the condensing temperature for CHP units based on the three plant solutions considered in Table 4.

working fluid can be the exhausts of industrial processes (i.e. steel or glass industry), as well as the exhaust gases of a fairly small size gas turbine.

The remarkably high cycle efficiencies suggest the potential use of $TiCl_4$ in Rankine cycles currently available in the range from few tens of kW to a few MW with high-temperature sources. As well, this solution may become advantageous if compared to low size steam cycles in the range of 5–10 MW, resulting in a more straightforward design of the turbomachinery, with no impairment in terms of overall plant efficiency. To better justify this conclusion, the thermodynamic results obtained for the recuperative cycle with $TiCl_4$ are compared to with those of a steam cycle with the design data reported in Table 2, the only difference being that the recuperator is replaced by a regenerative deareator, fed by a single bleeding at 5 bar extracted from the steam turbine. The evaporation pressure is limited in this case to 40 bar - although its optimization would result in a supercritical cycle - given the fairly small size of the reference steam plant, and to limit the excess of wet steam at the steam turbine outlet.

To complete the analysis, a recuperative $TiCl_4$ cycle, with a single bleeding extracted from the turbine at the optimized pressure, is also considered. In fact, it can be observed that, while the heat recovery profile of the recuperative cycle with no bleedings shown in Fig. 3 is well suited in case of a variable temperature heat source, the presence of bleedings would improve the cycle performances whenever a constant or nearly constant temperature source is exploited. This can be the case of heat obtained from a fuel combustion, concentrated solar power plants, fluidized beds or more complex cycle arrangements such as binary plants [15,28,31].

Thermodynamic results of this comparison are listed in Table 4, showing a net advantage in terms of conversion efficiency of the two considered $TiCl_4$ solutions (36.2% and 38.0%) with respect to the steam plant (33.6%). Moreover, these figures may turn out to be even more favorable to $TiCl_4$ considering that, in comparison with steam, a reasonably higher turbine isentropic efficiency should be expected.

For example, with reference to the cycle in Fig. 3, it can be observed that the relatively low isentropic enthalpy drop of the $TiCl_4$ cycle in comparison with that of the steam cycle (about one tenth) should permit in principle a single stage turbine. On the other hand, its higher volume flow ratio compel the use of a multistage turbine. These differences between the two fluids are due to the gap of the molar masses. Higher molar mass corresponds to lower turbine enthalpy drops with positive effect on the number of stages. In spite of this, for a power of about 1000 kW, a three stages turbine, the first with an admission degree of 25% (an action stage), at 10,000 rpm, seems feasible. The difference of the outlet turbine temperature is due to the complexity between the two molecules. Even if the $TiCl_4$ is not a complex molecule, the higher number of atoms brings to a lower difference in the expansion temperature. This different behavior allows expanding $TiCl_4$ in the dry region.

Finally, it can be observed that at the assumed condensing pressure of 5 kPa, the corresponding condensing temperature of $TiCl_4$ is appreciably higher than that of H_2O (53 versus 33 °C). The assumed value for the condensing pressure is typical of a steam power plant, in consideration of the environment temperature. This would yield significant benefits in condenser design, especially for air-cooled condensers and suggests the possibility of employing $TiCl_4$ in Combined Heat and Power (CHP) units. In Fig. 4, the electrical efficiency of the resulting CHP units based on the three plant solutions considered in Table 4 is plotted as function of the condensing temperature. Notably, the CHP units with $TiCl_4$ again show better performances than the classical steam CHP, with an increase of the electrical efficiency ranging from about 4–8 percentage points. At low condensing temperature, the $TiCl_4$ cycle with one bleeding exhibits efficiencies over 40%. At condensing temperatures useful for many cogeneration applications (say, 60–80 °C), the $TiCl_4$ cycle maintains efficiency levels above 35%, still better than the one of a steam cycle condensing at 30 °C.

4. Experimental analysis of the thermal stability of $TiCl_4$

The method adopted to assess the thermal stability of $TiCl_4$ is based on the analysis of the deviations in saturation pressure curves that may occur after subjecting the fluid to thermal stress tests at increasing temperature. The set of activities that define a thermal stability test can be grouped into four steps, namely (a) set up of the test circuit filled with the sample fluid, (b) evaluation of the reference vapor pressure of the virgin fluid, (c) thermal stress test in a furnace, (d) measurement of the vapor pressure curve and comparison to the reference value. A detailed description of this procedure is reported in [12]. In the present analysis, a sample of 46.1 g of $TiCl_4$ is used in the test circuit shown in Fig. 5. The amount of fluid is determined in order to obtain two-phase conditions in the temperature range 0–350 °C, defined for the evaluation of the reference vapor pressure curve, given the fixed volume of 164 cm^3 of the test circuit. The test circuit is made of AISI 316, thanks to its proven compatibility with $TiCl_4$ [32,33].

The values of the vapor pressure of the virgin fluid obtained from the experimental tests, from 0 °C to 350 °C, are reported in Fig. 6a showing a good agreement with the literature values. The vapor pressure curve assumed as reference in the experimental analysis is shown in Fig. 6b.

The sample fluid experienced three consecutive stress tests at temperature of 400 °C, 500 °C and 550 °C by introducing the test circuit into a muffle furnace. At the end of each 80 h stress test, the saturation pressure curve was measured again, and compared with that of the virgin fluid in order to detect possible sign of decompositions. Fig. 7 shows the comparison of the saturation

Table 4
Thermodynamic comparison between cycles with $TiCl_4$ and steam as working fluid. Calculation assumptions as by Table 2.

Plant solution	$TiCl_4$ no bleedings	$TiCl_4$ one bleeding	H_2O one bleeding
Turbine inlet temperature (°C)	500	500	500
Evaporation pressure (bar)	40	40	40
Number of bleedings	–	1	1
Optimized bleeding pressure (bar)	–	9	5
Cycle efficiency (%)	36.2	38.0	33.6
Condensing temperature (°C)	53	53	33
Isentropic enthalpy change through the HP expansion (kJ/kg)	163	42	574
Isentropic enthalpy change through the LP expansion (kJ/kg)	–	121	707
Isentropic volume flow ratio through the HP expansion	543	4.3	5.0
Isentropic volume flow ratio through the LP expansion	–	125.0	54.5
Vapor fraction at turbine outlet (%)	100	100	0.93
Turbine outlet temperature (°C)	223	219	33

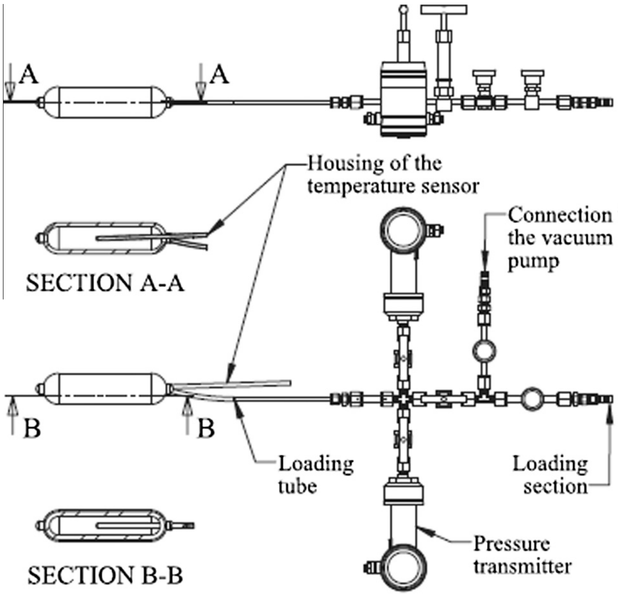

Fig. 5. Test circuit utilized for the thermal stability analysis [12].

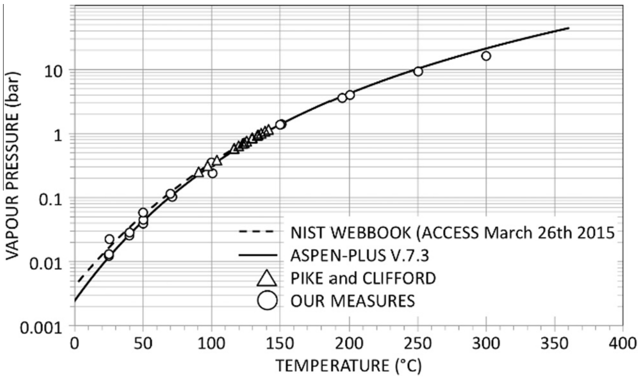

Fig. 6a. Comparison among the measured vapor pressure curve with values obtained from literature and calculated with Aspen Plus using Peng-Robinson equation of state.

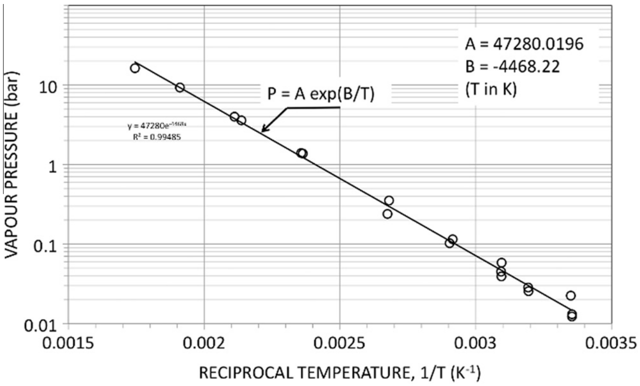

Fig. 6b. Vapor pressure curve assumed as reference.

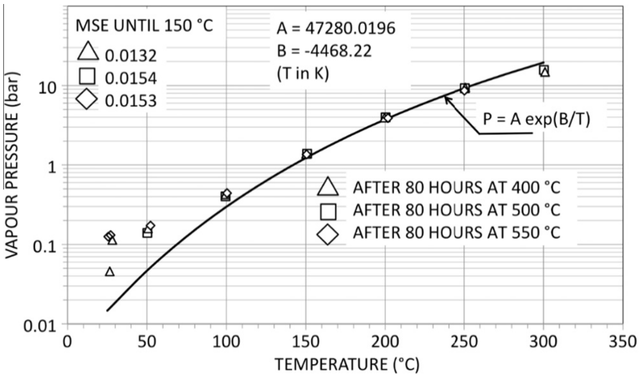

Fig. 7. Saturation pressure curves after the stress tests at 400, 500 and 550 °C compared with the reference values. MSE is the Mean Squared Error defined as $MSE = \frac{1}{N}\sum_{i=1}^{N}(P_{exp,i} - P_{ref,i})^2$ where P_{exp} is the measured pressure, P_{ref} reference pressure and N the number of points.

curves, while Figs. 8–10 report the values of temperature and pressure recorded during the three thermal stress tests. It can be noticed a substantial deviation in the vapor pressure curves up to 100 °C, while the values measured at higher temperature show only slight variations from the curve of the virgin fluid (Fig. 7), implying that only a limited decomposition, if any, could have been occurred. Moreover, the data recorded during the three stress tests (Figs. 8–10) show a pressure reduction of a few percentage points, not supported by a corresponding change in temperature. Since no evident leakages were detected in the test circuit,[1] the hypothesis of a slight decomposition of the sample fluid with either a reduction of the moles in the gas phase or the formation of solid deposits seems reasonable. It is worth noting that, according to Fig. 7, these possible signs of initial decomposition appeared after the stress test at 400 °C and were not amplified by the following stress tests at 500 and 550 °C.

A further experimental campaign was carried out in order to ascertain whether the presence of metals, other than the AISI 316 used for the test circuit, could influence the thermal stability of $TiCl_4$. To this purpose, two samples of metals, namely P91 and Cupronickel, were introduced in the test circuit to be in contact with the $TiCl_4$ during a thermal stability stress carried out at 500 °C. P91 is an alloy used in steam generators and heat recovery steam generators, that can operate with steam at temperature and pressure up to 600 °C and 200 bar respectively. Cupronickel is a Copper-Nickel alloy (88% Cu and 10% Ni in the sample used in this experiment) showing good resistance to corrosion, widely utilized in heat exchangers and condensers.

By following the same procedure described before, a single thermal stress test at 500 °C was carried out. Temperature and pressure data recorded during the thermal stress test are shown in Fig. 11, while Fig. 12 presents the vapor pressure curve measured after the stress, compared with the curves obtained in all the previous cases.

It can be observed that the presence of the two metals has only a minor impact on the thermal stability of $TiCl_4$. In fact, by comparing Fig. 11 with Figs. 8–10, a similar pressure reduction profile can be evidenced during the stress test, although the case with metals results in a higher percentage decrease: at the same stress temperature of 500 °C the pressure reduction of the test circuit filled with only $TiCl_4$ is about 2.5%, (Fig. 9) while it reaches about 8% in case of metals (Fig. 11). Nonetheless, the comparison of the saturation curves (Fig. 12) proves a good stability of $TiCl_4$ in presence of the two metals. Indeed, for $1/T < 0.0027\ K^{-1}$ (corresponding to temperatures higher than 100 °C), the measured pressure values are in good agreement with those of the previous cases; similarly, the overpressure observed at lower temperature has the same order

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[1] The weight of the test circuit remained unchanged during the tests. Eventually, the circuit was filled with Helium and kept at 30 bar for 30 h. During this time span, no appreciable pressure losses was observed.

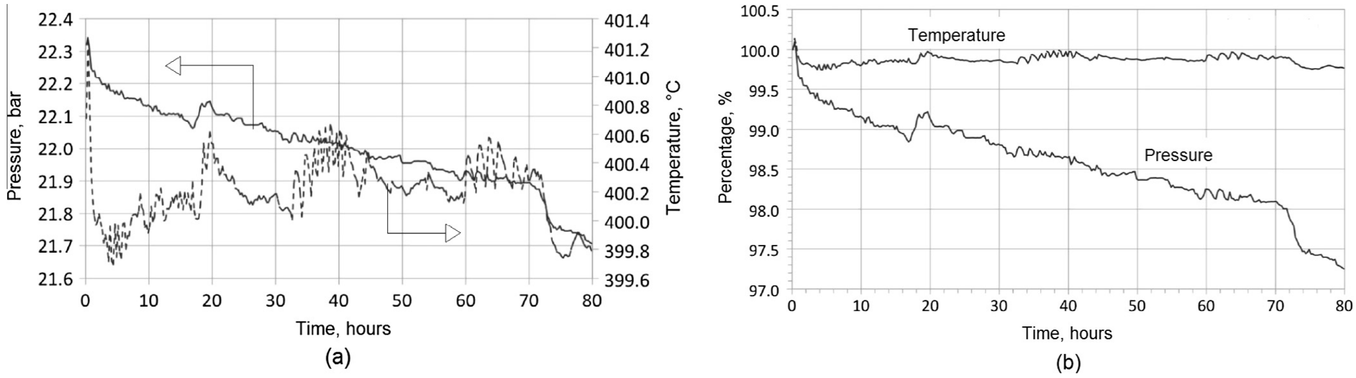

Fig. 8. Values of temperature and pressure recorded during the thermal stress test carried out at 400 °C: absolute values (a) and percentage variation from the initial values (b).

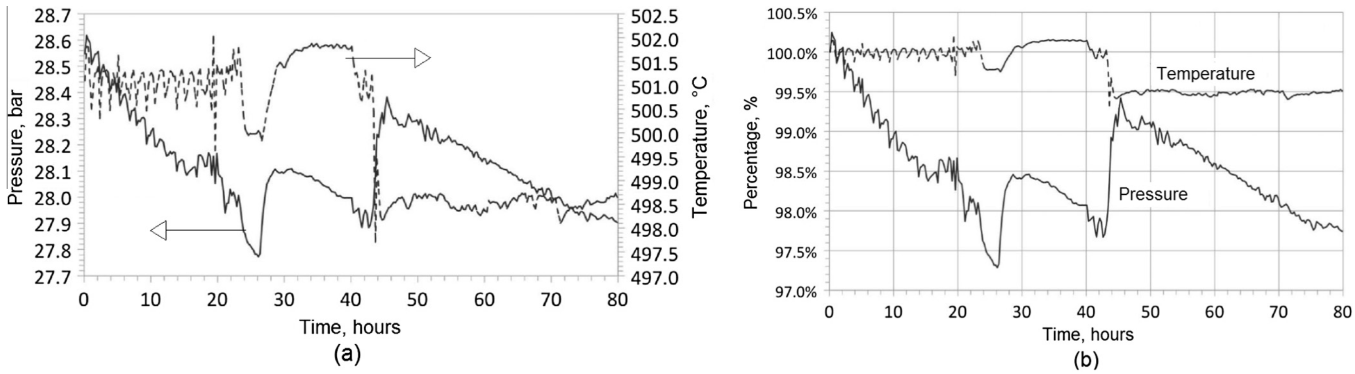

Fig. 9. Values of temperature and pressure recorded during the thermal stress test carried out at 500 °C: absolute values (a) and percentage variation from the initial values (b).

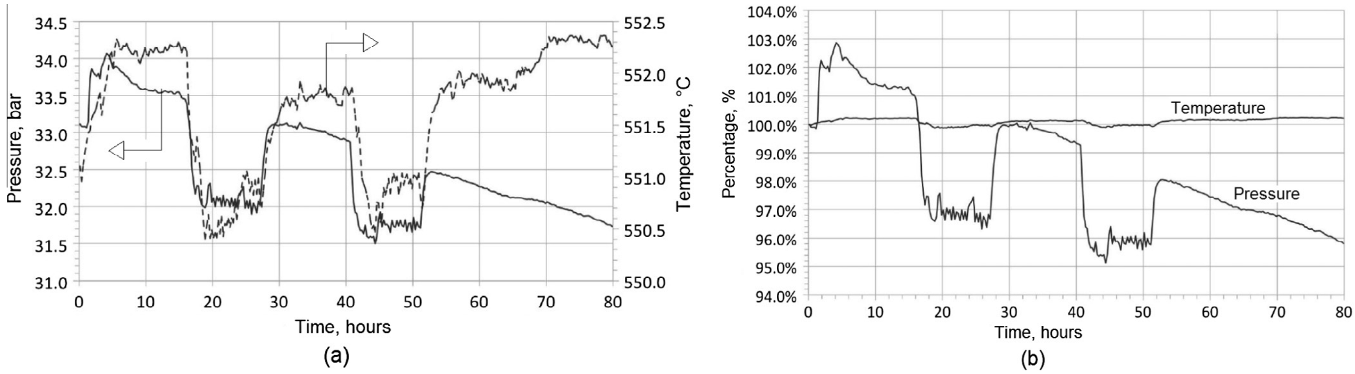

Fig. 10. Values of temperature and pressure recorded during the thermal stress test carried out at 550 °C: absolute values (a) and percentage variation from the initial values (b).

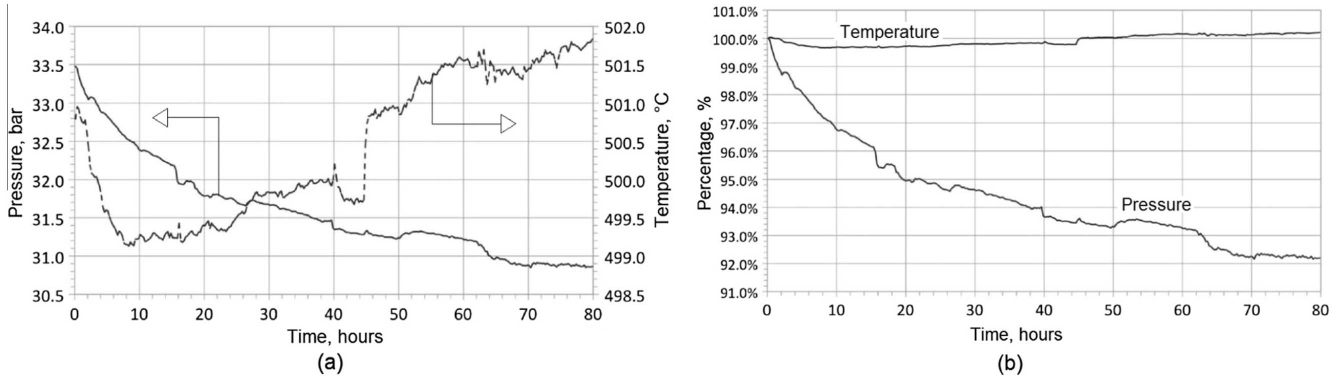

Fig. 11. Values of temperature and pressure recorded during the thermal stress test carried out at 500 °C with samples of P91 and Cupronickel inserted in the test circuit: absolute values (a) and percentage variation from the initial values (b).

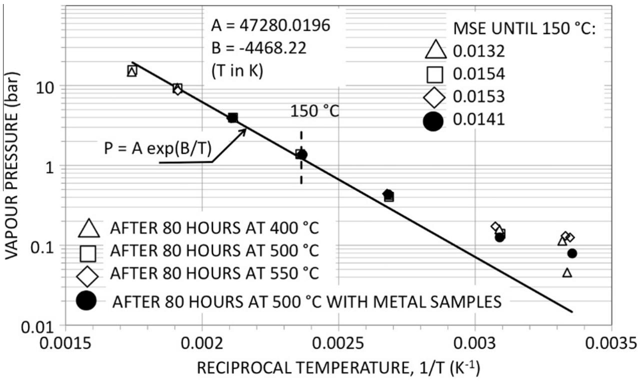

Fig. 12. Summary of the vapor pressure curves obtained after each stress test carried out in the experimental analysis. MSE is the Mean Squared Error defined as $MSE = \frac{1}{N}\sum_{i=1}^{N}(P_{exp,i} - P_{ref,i})^2$ where P_{exp} is the measured pressure, P_{ref} reference pressure and N the number of points.

of magnitude, indicating that under the conditions of this experimental study, no further significant degradation of the fluid can be envisaged after the initial signs appeared at 400 °C. Therefore we can conclude that $TiCl_4$ proves to be remarkably stable at temperatures up to 500 °C.

5. Conclusions

The preliminary studies performed on the use of $TiCl_4$ as a potential innovative working fluid in high temperature Rankine Cycle show interesting results. $TiCl_4$ is a fairly low cost, non-carcinogenic fluid, with zero global warming and ozone depleting potential and it is already employed in high temperature industrial processes.

Thermodynamics properties of $TiCl_4$ are in principle suitable for applications in ORC plants: to many respects it is similar to steam, with the advantage of a considerably higher molar weight.

From a preliminary thermodynamic analysis, it is shown that Rankine cycles that employ $TiCl_4$ have considerably higher efficiencies than the up-to-date ORC technology. As well, this solution becomes advantageous if compared to low size steam cycles in the range of 5–10 MW, resulting in a more straightforward design of the turbines, with no impairment in terms of overall plant performance. This is primarily a consequence of the remarkably high thermal stability of $TiCl_4$. In fact, according to the results of the experimental campaign conducted and here described, the fluid can be employed in power cycle with maximum temperature up to 500 °C. Notably, this value was confirmed also by the analysis carried out in presence of two metals, namely P91 and Cupronickel, typically employed in high temperature section of power cycles.

On the debit side, the use of $TiCl_4$ poses some important concerns in view of the construction of real power plant. One major drawback is certainly represented by its high and violent reactivity with water, even with the small amounts contained in humid air, generating heat and corrosive gases containing hydrogen chloride. This clearly requires a specific design of the plant layout to avoid any contact with the external atmosphere. Moreover, the results of the thermal stability, although very promising so far, need further confirms in long lasting tests (here limited to 80 h) as well in presence of other classes of materials employed in the plant components, with whom $TiCl_4$ may result in contact.

In a forthcoming paper the potential feasibility Rankine cycles using $TiCl_4$ will be discussed through a preliminary design and techno-economic analysis of a 1 MW Rankine cycle.

References

[1] M. Astolfi, M.C. Romano, P. Bombarda, E. Macchi, Binary ORC (organic Rankine cycles) power plants for the exploitation of medium-low temperature geothermal sources - Part A: thermodynamic optimization, Energy 66 (2014) 423–434.

[2] C. Invernizzi, P. Iora, Heat recovery from a gas microturbine by vapour jet refrigeration systems, Appl. Therm. Eng. 25 (2005) 1233–1246.

[3] C. Invernizzi, P. Iora, P. Silva, Bottoming micro-Rankine cycles for micro-gas turbines, Appl. Therm. Eng. 27 (2007) 100–110.

[4] S. Lecompte, H. Huisseune, M. van den Broek, B. Vanslambrouck, M. De Paepe, Review of organic Rankine cycle (ORC) architectures for waste heat recovery, Renew. Sustain. Energy Rev. 47 (2015) 448–461.

[5] A. Giuffrida, Modelling the performance of a scroll expander for small organic Rankine cycles when changing the working fluid, Appl. Therm. Eng. 70 (5) (2014) 1040–1049.

[6] T. Rajabloo, P. Iora, C.M. Invernizzi, Mixture of working fluids in ORC plants with pool boiler evaporator, Appl. Therm. Eng. 98 (2015) 1–9. 5 April 2016.

[7] M. Yari, S.M. Mahmoudi, Utilization of waste heat from GT-MHR for power generation in organic Rankine cycles, Appl. Therm. Eng. 30 (2010) 366–375.

[8] S.L. Gomez Alaez, P. Bombarda, C.M. Invernizzi, P. Iora, P. Silva, Evaluation of ORC modules performance adopting commercial plastic heat exchangers, Appl. Energy 154 (2015) (2015) 882–890.

[9] J. Bao, L. Zhao, A review of working fluid and expander selections for organic Rankine cycle, Renew. Sustain. Energy Rev. 24 (2013) 325–342.

[10] C. Invernizzi, Closed Power Cycle, Thermodynamic Foundamentals and Applications, Springer-Verlag, London, 2013.

[11] S. Lasala, C.M. Invernizzi, P. Iora, P. Chiesa, E. Macchi, Thermal stability analysis of perfluorohexane, in: Proceedings of the 7th International Conference on Applied Energy – ICAE, March 28–31 2015, Abu Dhabi, United Arab Emirates.

[12] M. Pasetti, C.M. Invernizzi, P. Iora, Thermal stability of working fluids for organic Rankine cycles: an improved survey method and experimental results for cyclopentane, isopentane and n-butane, Appl. Therm. Eng. 73 (2014) 762–772.

[13] O. Badr, S.D. Probert, P.W. O'Callaghan, Selecting a working fluid for a Rankine-cycle engine, Appl. Energy 21 (1985) 1–42.

[14] G. Angelino, C. Invernizzi, Cyclic methylsiloxanes as working fluids for space power cycles, J. Sol. Energy Eng. Trans. ASME 115 (1993) 130–137.

[15] D.J. Schroeder, N. Leslie, Organic Rankine cycle working fluid considerations for waste heat to power applications, ASHRAE Trans. 116 (2010) 525–533.

[16] E.S. Blake, W.C. Hammann, J.W. Edwards, T.E. Reichard, M.R. Ort, Thermal stability as a function of chemical structure, J. Chem. Eng. Data 6 (1961) 87–98.

[17] K.R. Fisch, F.D. Verderame, Automatic recording apparatus for thermal stability determinations, J. Chem. Eng. Data 6 (1961) e131–e134.

[18] I.B. Johns, E.A. McElhill, J.O. Smith, Thermal stability of organic compounds, Ind. Eng. Chem. Prod. Res. Dev. 1 (1962) 2–6.

[19] M.A. Fabuss, A.S. Borsanyi, B.M. Fabuss, J.O. Smith, Thermal stability studies of pure hydrocarbons in a high pressure isoteniscope, J. Chem. Eng. Data 8 (1963) 64–69.

[20] C.M. Invernizzi, Thermal stability investigation of organic working fluids: an experimental apparatus and some calibration results, La Termotec XLIV (1990) 69–76 (in Italian).

[21] C.M. Invernizzi, P. Iora, M. Preißinger, G. Manzolini, HFOs as substitute for R-134a as working fluids in ORC power plants: a thermodynamic assessment and thermal stability analysis, Appl. Therm. Eng. 103 (2016) 790–797.

[22] W. Kroll, The production of ductile titanium, Trans. Electrochem. Soc. 78 (1) (1940) 35–47.

[23] R.B. Subramanyam, Some recent innovations in the Kroll process of titanium sponge production, Bull. Mater. Sci. 16 (6) (1993) 433–451.

[24] R.H. West, G.J.O. Beran, W.H. Green, e.M. Kraft, First-principles thermochemistry for the production of TiO_2 from $TiCl_4$, J. Phys. Chem. 111 (18) (2007) 3560–3565.

[25] F. Teyssandier, M.D. Allendorf, Thermodynamics and kinetics of gas-phase reactions in the Ti-Cl-H system, J. Electrochem. Soc. 145 (6) (1998) 2167–2178.

[26] A. Devarakonda, J.K. Olminsky, An evaluation of halides and other substances as potential heat pipe fluids, in: 2nd International Energy Conversion Engineering Conference, Rhode Island, 2004.

[27] A. Devarakonda, W.G. Anderson, Thermo-Physical Properties of Intermediate Temperature Heat Pipe Fluids 10, 2005.

[28] P. Bombarda, C. Invernizzi, Binary liquid metal-organic Rankine cycle for small power distributed high efficiency systems, J. Power Energy (2014).

[29] W.G. Anderson, J.H. Rosenfeld, D.e Ye M. Agirasa, Evaluation of heat pipe working fluids in the temperature range 450–700 K, in: In space Technology and Applications International Forum - STAIF 2004, 2004.

[30] W.G. Anderson, Intermediate Temperature Fluids for Heat Pipes and Loop Heat Pipes, in: 15th International Heat Pipe Conference, Clemson, USA, 2010.

[31] A. Giostri, M. Binotti, P. Silva, E. Macchi, G. Manzolini, Comparison of two linear collectors in solar thermal plants: parabolic trough versus Fresnel, J. Sol. Energy Eng., Trans. ASME 135 (1) (2013) 11001.

[32] J. Herzeler, P. Roth, High-temperature decomposition of TiCl4 based on Cl-concentration measurements, Proc. Combust. Inst. 29 (2002) 1353–1359.

[33] TiCl4 subcommittee of Titanium Dioxide Manufacturers Association, Safety advice for storage and handling of anhydrous titanium tetrachloride, Cefic, Brussels, 2012.