

Research Paper

Silicon Tetrachloride as innovative working fluid for high temperature Rankine cycles: Thermal Stability, material compatibility, and energy analysis

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ABSTRACT

Silicon Tetrachloride (SiCl_4) is proposed as a new potential working fluid for high-temperature Rankine Cycles. The capability to overcome the actual thermal stability limit of fluids commercially employed in the state-of-the-art Organic Rankine Cycles (ORC) is demonstrated by static thermal stability and material compatibility tests. Experimental static test proves its thermo-chemical stability with a conventional stainless-steel alloy (AISI 316L) up to 650 °C. A preliminary material compatibility analysis performed with optical microscope on the AISI 316L cylinder, after exposure of 300 h to SiCl_4 at temperature higher than 550 °C, confirms the potentiality of this fluid when coupled with high-grade heat sources. A thermodynamic analysis has been carried out accounting for the effect of operating conditions on the axial turbine efficiency. A comparison with fluids adopted in medium-high temperature ORCs is performed, evidencing that the proposed fluid could achieve more than + 10 % points as thermal efficiency gain compared to any commercial solutions when coupled with high-temperature sources such as solar, biomass, waste heat from industrial processes and prime movers. A 2 MW SiCl_4 cycle operating full-electric at 550 °C reaches a thermal efficiency of 38 %, exceeding values attainable by any other working fluid under similar conditions and power size.

Nomenclature.

Acronyms	
AAD	Average Absolute Deviation
CHP	Combined Heat and Power
CS	Corresponding States
CSP	Concentrated Solar Power
EoS	Equation of State
EU	European Union
GWP	Global Warming Potential
HAZ	Heat Affected Zone
HT	High Temperature
HTF	Heat Transfer Fluid
NBP	Normal Boiling Point
NFPA	National Fire Protection Association
ODP	Ozone Depletion Potential
ORC	Organic Rankine Cycle
PHE	Primary Heat Exchanger
PR	Peng Robinson
REF	Reference Curve

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Acronyms	
AAD	Average Absolute Deviation
Refprop	Reference Fluid Thermodynamic and Transport Properties
SP	Size Parameter, m
TIT	Turbine Inlet Temperature, °C
TRAPP	TRANsport Property Prediction
WHR	Waste Heat Recovery
Symbols	
$\Delta\pi$	Residual property π
Δh	Enthalpy Difference, kJ/kg
ΔT	Temperature Difference, °C
\dot{m}	Mass flow rate, kg s ⁻¹
P	Pressure, bar
Q	Thermal duty, MW
R	Universal Gas Constant
s	Entropy, kJ kg ⁻¹ K ⁻¹
T	Temperature
W	Mechanical work, MW

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Acronyms	
AAD	Average Absolute Deviation
x	Fraction
Z	Compressibility factor, –
Greek symbols	
η_{th}	Cycle Thermal Efficiency, –
$\eta_{Turbine}$	Turbine isentropic efficiency, –
η_{Pump}	Pump isentropic efficiency, –
ω	Pitzer acentric factor, –
σ	Molecular Complexity Parameter, –
Subscripts	
cr	Critical
ch	Channel
f	Friction term
in	Inlet
is	Isentropic
min	Minimum
max	Maximum
o	Zero-density
r	Ratio
red	Reduced
sat	Saturation
SV	Saturated Vapour
vap	Vapour
Superscripts	
r	Residual
ref	Reference fluid

1. Introduction

The EU net-zero emissions objective [1] requires an important expansion of the technologies adopted to exploit the available waste heat of industrial processes to reduce the primary energy consumption and the carbon footprint. Organic Rankine Cycle (ORC) is the leading technology in the field of waste heat recovery (WHR) from low-medium high temperature heat sources, typically from 120 °C to 450 °C [2]. The selection of the working fluid is a key task for the ORC design, making it flexible to each specific application with different heat source and heat sink. One of the main concern about the working fluid selection, especially when dealing with high temperature sources, is the thermal stability of organic fluids, which sets a constraint on the maximum operating temperature of the power cycle, strictly related to its thermodynamic efficiency. Thermal stability can be considered as the capability to preserve unchanged the physical properties of a fluid despite of heating. When a fluid is employed above its thermal stability limit, the activation energy required to break the weakest bond in the molecule is overcome and secondary products are formed. The chemical decomposition can cause engine malfunctions: (i) reaction products, that are typically light and incondensable compounds, can accumulate in the recuperator and the condenser, then reducing the available pressure ratio across the turbine; (ii) the heat transfer behaviour of the working fluid is negatively affected; (iii) the working fluid needs to be refilled and the products removed, increasing the operative costs; (iv) solid particles can be also produced causing fouling of the heat exchangers and erosion of the turbine blades.

To date, organic fluids employed in commercial ORC systems are limited to a maximum operating temperature of around 300 °C which is representative of the practical limits of the hydrocarbon family [3] and siloxanes [4]. At such temperature level, thermal decomposition reaction is usually active for the two fluid families above mentioned but, in case the kinetic of the reaction is within acceptable values, a fluid refill every few years compensates for its degradation. In the next section, thermal stability studies on working fluids for ORC systems will be summarized to better address the significant issue of thermal stability.

However, according to Papapetrou et al. [5], the EU's total waste heat potential is 300 TWh/year, with over 40 % available at temperatures exceeding 500 °C (mainly cement, iron and steel sectors). This highlights the necessity to enhance the thermal capability of fluids

adopted by the ORC technology, particularly in harnessing high-grade waste heat, to improve the thermal-to-electric conversion efficiency. The interest in a high conversion efficiency power block could arise in many different industrial sectors that normally produce high-temperature waste heat, in order to reduce the carbon footprint of industrial processes. An example could be the steel production by Electric Arc Furnaces, accounting for 28 % of the worldwide steel production [6], where the off-gas (that is produced as a by-product of the process) is characterised by an average temperature of about 750 °C. Industrial waste heat, known for its high-grade heat content, is not the sole source; exhaust gases from gas turbines also commonly reach temperatures in the range of 550–600 °C. Efficient heat recovery in these scenarios could be enhanced by employing a thermally stable working fluid. As stated by Colonna et al. [7], an ideal working fluid should remain thermally stable, when in contact with stainless steel, even at temperatures between 500 and 600 °C. Furthermore, this consideration extends to various applications including concentrated solar power, pyrolysis processes, and biomass boilers.

Thermally stable fluids capable to overcome the thermal stability threshold (300–350 °C) of state-of-the-art organic fluids could exploit more efficiently high-temperature heat sources that are characterized by a thermal power ranging from tens of kW to few MW, where conventional steam Rankine cycles are not the best techno-economical solution: they suffer from high capital costs, need for qualified personal to supervise the operations, low heat-recovery efficiency, as well as lower performance at part-load conditions [8]. Despite the mentioned drawbacks, they are largely considered for electrical power output above 2–5 MW_{el} when there is high-grade heat available, as in medium-large biomass-fired plants [9]. Macchi and Astolfi referred to the 5–20 MW output range as the “steam vs. ORC grey zone” [2]. In this output range, there is no clear winner between the state-of-the-art ORC and steam technologies, although ORC is gaining market positions due to its simple layout and good performance at part-load, thus lowering maintenance cost as well as almost zero supervision personal costs.

In this “grey zone”, also supercritical CO₂ (sCO₂) could play a role as potential working fluid, but it is not considered in this article for the following reasons: (i) sCO₂ Brayton cycles achieves good exploitation (cooling grade) of a sensible heat source only when a complex layout such as cascaded recuperative cycle (two turbines, two primary heat exchangers, two recuperators) is adopted [10]; (ii) the need of operating at near-critical conditions at the compressor intake to exploit the beneficial real gas effect with the associated risk of crossing the two-phase region [11]; (iii) the extremely high maximum cycle pressure (over 200 bar) compared to ORC (15–60 bar) and small-scale steam Rankine plants (60–90 bar); (iv) the design of the control system is particularly challenging especially in small scale power units (<0.5–5 MW_{el}) [12]. Echogen [13] manufactured the commercial EPS100 (8 MW nominal power output) heat recovery unit adopting sCO₂ with two turbines: one single-stage radial turbine drives the pump/compressor (2.7 MW shaft power) and one power turbine. However, when approaching lower power output, as in the EPS30 Echogen module (1.35 MW nominal output), such a complex architecture seems improbable to be adopted, and its declared thermal efficiency by catalogue is 18.8 % when coupled with a heat source at 500 °C, which is a value that can be overcome by commercial ORC systems at the same power output.

Given this premises, the aim of this work is to introduce a working fluid that is capable to fill this gap in the ORC technology and extend its market share.

Silicon Tetrachloride (SiCl₄), or Tetra-chlorosilane, is proposed here for the first time as innovative working fluid for power production in a high-temperature Rankine cycles. SiCl₄ is an inorganic compound industrially involved in the production of solar grade silicon. Remarkable thermal stability was expected from this metal halide, as it is involved in high temperature processes. The pure SiCl₄ is reported to be stable even at 1200 °C in the literature [14]. In the past, it was the

product of the reaction of SiO_2 and chlorine at a temperature of $1300\text{ }^\circ\text{C}$ [15]. SiCl_4 is the main by-product of polycrystalline silicon production by the Siemens process adopted to obtain solar-grade silicon. It is estimated that around 18–20 tons of SiCl_4 are produced as by-product for each ton of poly-silicon [16]. Considering that the annual production of polysilicon is estimated to be around 1.65–1.7 million tons to date, it means that the annual yield of SiCl_4 as undesired by-product is more than 30 million tons per year. The great abundance of SiCl_4 reflects its availability in the market at a low cost. In the Siemens process, Silicon Tetrachloride is obtained as by-product of the SiHCl_3 pyrolysis, and it is necessary to reduce the SiCl_4 near $900\text{ }^\circ\text{C}$ with hydrogen or H_2 -radicals to convert/recycle it into SiHCl_3 and increase the Si production [17]. Another pathway is the reutilization of the SiCl_4 by-product for the manufacturing of silica-based materials, for example fumed silica, optical fiber, ethyl silicate [18]; however, optical fiber level SiCl_4 requires extreme purity and must be further purified [19]. One of the key aspects of the production of solar-grade silicon is the effective recycle of SiCl_4 , and this work opens the path to another way to reutilize and make profit from by the polysilicon industry, in the circular economy point of view.

The identification of a new working fluid, starting from its interesting characteristics available in literature, has to be followed by a rigorous procedure that includes experimental test and modelling to confirm its good potentialities and expand the known database. Thus, the main goal of this work is to experimentally demonstrate the thermo-chemical capability of SiCl_4 and its material compatibility, and to provide preliminary indications about the performance gain achievable when using this working fluid compared to state-of-the-art ORC working fluids. Starting from a literature review on the maximum operating temperature of the conventional ORC working fluids, thermal stability, and material compatibility test with AISI 316L stainless steel have been performed to assess the SiCl_4 temperature threshold in realistic conditions. Furthermore, a comprehensive fluid characterisation has been carried out tuning the selected thermodynamic model and transport properties model with the available experimental data. The knowledge on the proper thermophysical properties models aims at providing all the necessary information to design the power cycles components adopting SiCl_4 working fluid. Eventually this work presents a preliminary estimate of the power cycle performance using the investigated fluid under various operating conditions and power outputs to highlight the benefits of its adoption in ORC cycle with respect to other conventional organic fluids.

2. Literature review on ORC working fluids thermal stability

The working fluid thermal stability poses a significant challenge for the lifetime and operability of the ORCs as well as for the power cycle performance. Over the last years, this temperature threshold has been investigated by different research groups for several fluid chemical classes such as hydrocarbons, refrigerants, and siloxanes. One of the main goals is to find out a specific working fluid that can withstand at temperature higher than $350\text{--}400\text{ }^\circ\text{C}$.

Pereira et al. [20] explored different methods for assessing the thermal stability of organic fluids, distinguishing between static and dynamic tests. The static isochoric method developed in our Fluid Test Laboratory of the University of Brescia by Invernizzi [2122] is based on the concept that even a small breakdown of the fluid can cause an appreciable variation in vapor pressure determined by the partial pressure of decomposition products. This method involves measuring vapor pressure both before and after subjecting the fluid to thermal stress within a closed volume manufactured from carefully chosen

material. This technique allows for the identification of degradation products, particularly when focusing on sub-atmospheric vapour pressures. Notably, in comparison to alternative methods, this approach offers the unique benefit of quantifying the actual impact of degradation products on vapor pressure. Consequently, it facilitates a comprehensive assessment of the influence of degradation products on important parameters, such as the pressure ratio across the turbine and subsequent effects on power output. During the past years, the static survey method has been applied to several working fluids in our laboratory such as hydrocarbons [223], zero-ODP refrigerants [23], fluorinated alcohols [24], perfluorocarbons [25].

Table 1 summarises the thermal stability of different fluids potentially applicable for ORC applications, along with their critical parameters and normal boiling point (NBP).

Hydrocarbons (HC) exhibit variable levels of thermo-chemical stability based on their molecular structure. In general, cyclic hydrocarbons have a higher activation energy compared to linear ones. In fact, as a result of a previous study conducted in our laboratory, cyclopentane had a decomposition rate 20 times lower than n-pentane at $350\text{ }^\circ\text{C}$ [3]. While toluene and cyclopentane were found to have similar decomposition rates at $350\text{ }^\circ\text{C}$, the decomposition rate of cyclopentane increases rapidly above $350\text{ }^\circ\text{C}$, whereas toluene maintains an acceptable decomposition rate even up to $400\text{ }^\circ\text{C}$. Despite that, cyclopentane is commonly used in commercial “high-temperature” ORC units below $300\text{ }^\circ\text{C}$ as bulk-temperature [26]. This standard approach provides a safety margin to significant molecular cleavage, also because most of the thermal degradation of the working fluid occurs within the thermal boundary layer that is at a temperature higher than the bulk. Toluene is acknowledged as one of the most thermally stable HC, with literature works supporting its low degradation rate up to $400\text{ }^\circ\text{C}$ [2728]. However, in practice, toluene is applied in biomass-fired ORC units up to a maximum cycle temperature of $320\text{ }^\circ\text{C}$ (Triogen company [29]), in direct heat transfer mode.

Dai et al. [30] experimentally explored the thermal stability of n-pentane above $330\text{ }^\circ\text{C}$ proving that the pressure has no significant influence on the unimolecular decomposition reaction, where the rate of decomposition is mainly dependent on the temperature of the system.

Ginosar et al. [31] conducted tests on the thermal stability of cyclopentane at 240 , 300 , and $350\text{ }^\circ\text{C}$ at 4.3 MPa in a glass-lined heated tube. Their findings suggest safe application in an ORC if the cycle maximum temperature is maintained below $300\text{ }^\circ\text{C}$ and air is excluded from the system. However, it is crucial to assess the thermal stability of a working fluid in contact with materials commonly employed in the high-temperature sections of a power plant, such as stainless steel or Inconel alloys. This evaluation is essential as the material can act as a catalyst for the unimolecular decomposition reaction.

Organic fluids containing the hydroxyl group ($-\text{OH}$) are characterized by even lower thermal stability compared to hydrocarbons as attested by previous experimental campaigns on 2,2,2-trifluoroethanol ($\text{C}_2\text{H}_3\text{F}_3\text{O}$) and n-butanol ($\text{C}_4\text{H}_{10}\text{O}$). Appreciable decomposition was observed on the n-butanol sample following the initial thermal stress at $220\text{ }^\circ\text{C}$. On the other hand, the rate of decomposition of trifluoroethanol at $300\text{ }^\circ\text{C}$ was found to be ten times lower than that of n-butanol, due to fluorine content stabilizing the molecule.

Hydrofluorocarbons (HFC) possess superior thermal stability compared to the HC counterpart due to high C-F bond energy. As a rule of thumb, the more the C-F bond compared to the C-H bonds present in the molecule the higher the thermal stability of the fluid, due to minor probability of collisions on the weakest bond. In fact, past investigation with the static survey method in our Fluid Test Lab proved that zero-

Table 1
Thermal stability threshold of different potential fluids for ORC applications.

Fluid	Chemical Formula	Thermal Stability Threshold [°C]	Reference	Critical Temperature [°C]	Critical Pressure [bar]	NBP [°C]
R-1311	CF ₃ I	102	[33]	122	40.4	-22.5
R-7146	SF ₆	204	[33]	45.5	37.6	-63.9
R-141b	C ₂ H ₃ Cl ₂ F	90	[33]	204.3	42.1	-32
HFC-245fa	C ₃ F ₅ H ₃	300–320	[2332]	154	36.5	15.3
HFC-143a	C ₂ H ₃ F ₃	350	[23]	72.7	37.6	-47.6
HFC-236fa	C ₃ H ₂ F ₆	400	[23]	124.9	32	-1.4
HFC-23	CHF ₃	400	[23]	25.9	48.4	-82
HFC-227ea	C ₃ HF ₇	425	[23]	103.5	29.5	-17
HFC-134a	C ₂ H ₂ F ₄	368	[33]	101.1	40.7	-26.3
HFO-1336mzz(Z)	C ₄ H ₂ F ₆	250–270	[4748]	171.3	29	33.4
HFO-1336mzz(E)	C ₄ H ₂ F ₆	230–250	[49]	137.7	31.5	7.5
HFO-1234ze(E)	C ₃ H ₂ F ₄	180	[50]	109.4	36.4	-19
HFO-1234yf	C ₃ F ₄ H ₂	170–200	[3537]	95	33.8	-29
HFC-32	CH ₂ F ₂	250–270	[49]	78.1	58	-51.7
HFC-125	CH ₂ F ₅	396	[33]	66	35.9	-48.5
TFE	C ₂ H ₃ F ₃ O	250	[24]	227	48.3	74
n-butanol	C ₄ H ₁₀ O	220	[24]	289.8	43.7	118
n-butane	C ₄ H ₁₀	290	[22]	190	38	-0.5
Isopentane	C ₅ H ₁₂	290	[22]	187.2	33.8	27.8
Cyclopentane	C ₅ H ₁₀	350	[2231]	238.6	44.4	49.3
n-pentane	C ₅ H ₁₂	280–320	[33032]	196.6	33.7	36.1
Toluene	C ₇ H ₈	400	[3272851]	320	41.1	110.6
n-hexane	C ₆ H ₁₄	260–280	[52]	234.7	30.3	68.7
Perfluorohexane	C ₆ F ₁₄	350–400	[25]	179.6	18.1	57.2
Novec 649	C ₆ F ₁₂ O	300	[53]	169	18.8	49
Novec 4710	C ₄ F ₇ N	300	[54]	112.9	25	-4.7
MM	C ₆ H ₁₈ OSi ₂	300–320	[4140]	246.7	19.4	100.5
MDM	C ₈ H ₂₄ O ₂ Si ₃	300–320	[40]	290.2	14.1	153
Titanium Tetrachloride	TiCl ₄	500	[45]	364.9	46.6	136.4
Silicon Tetrachloride	SiCl ₄	> 650	This work	234.9	35.9	57

ODP HFC refrigerants possess exceptionally high thermal stability limit [23]: 425 °C for HFC-227ea, 400 °C for HFC-23 and HFC-236fa, 350 °C for HFC-143a and 300 °C for HFC-245fa. Dai et al. [32] obtained similar results by measuring the fluoride ion concentration as a product of the decomposition reaction: 400 °C for HFC-236fa, 320 °C for HFC-245fa. The thermal stability threshold of several refrigerants was also experimentally evaluated by Calderazzi and Colonna di Paliano [33] in a static isochoric setup, confirming the good thermo-chemical stability of fluorinated compounds: 368 °C for HFC-134a (C₂H₂F₄) and 396 °C for HFC-125 (C₂HF₅). On the other hand, they found poor results on chemical species containing C-I and S-F bonds: 102 °C for R-1311 (CF₃I) and 204 °C for R-7146 (SF₆). However, refrigerants possess relatively low critical temperature (below 150 °C in most of the cases except for few compounds such as R133mzz(Z) with 171.3 °C), then they are not suitable as working fluids in ORC systems coupled with very-high temperature heat sources, that is the main topic of this article. In fact, it is well known that the optimal working fluid to couple with a sensible heat source is one whose critical temperature is directly proportional to the temperature level of the source. For instance, Scaccabarozzi et al. [34] demonstrated that the optimal fluids for heat recovery from internal combustion engines have critical temperature in the range 65–85 % of the heat source temperature. For this reason refrigerants are applied mostly in ORC systems driven by geothermal energy [35] and low-grade waste heat [36]. An important issue deriving from the thermal cracking of hydrofluorocarbons is that hydrofluoric acid (HF) is produced as degradation product [37].

Angelino and Invernizzi [38] proposed the adoption of cyclic poly-methylsiloxanes in organic cycles proving that little degradation occurs even up to 400 °C, and siloxanes are, to date, a commercial solution adopted in high-temperature ORC units, especially hexamethyldisiloxane (MM, C₆H₁₈OSi) and octamethyltrisiloxane (MDM, C₈H₂₄O₂Si₃)

[39]. Keulen et al. [40], adopting the methodology proposed in our laboratory in conjunction with chemical analysis, determined that appreciable decomposition of MM and MDM was detectable at 240 °C and 260 °C respectively. However, from a practical perspective, what matters is not only that the degradation reaction is active at a certain temperature, but more importantly, the rate at which this reaction occurs. In fact, Preißinger et al. [41] demonstrated that MM has an annual degradation rate lower than 3.5 % at 300 °C. For this reason, in commercial units, MM is usually adopted up to a maximum cycle temperature around 300 °C [26]. Wang et al. [42] studied the influence of MM thermal decomposition on the ORC system, leading to a decrease in net power and thermal efficiency but also in incomplete evaporation and acid corrosion in the evaporator. Siloxanes are commonly used in biomass-driven ORC, with thermal oil loop as heat carrier, at turbine inlet temperatures lower than 300 °C [39].

The 400 °C barrier as maximum cycle temperature can be approached, and eventually overcome, if hydrofluorocarbons rich in fluorine or totally perfluorinated compounds are considered as working fluids. As a drawback, the more the fluorine atoms the higher the global warming potential and cost. Perfluorohexane (C₆F₁₄) has been tested by Lasala et al. [25] in our Fluid Test Laboratory, in a mixture with carbon dioxide, and early signs of decomposition occurred after thermal stress at 400 °C while at the previous thermal stress (350 °C) no decomposition phenomena was observed. However, perfluorohexane has a high GWP_{100-y} value equal to 9300, and there are some concerns about the material compatibility of perfluorinated compounds even with Inconel alloys [43].

One of the most significant results, in terms of thermal stability of working fluids for ORC, was obtained by Di Nanno et al. [44] from NASA, that patented the adoption of a mixture of fluorocarbons, pentafluorobenzene (C₆HF₅) and hexafluorobenzene (C₆F₆) [44], called RC-

1 mixture, for WHR application, as no thermal decomposition occurred up to 468 °C.

Recently, Titanium Tetrachloride (TiCl_4) was proposed by Invernizzi et al. [45] as working fluid for high-temperature Rankine cycles up to 500 °C [45] and in binary mixtures with CO_2 for CSP application [46]. The main drawback related to the applicability of metal halides is the extremely high reactivity with water and moisture present in the air (hydrolysis) due to vacant d-orbitals. According to a previous experimental campaign carried out in our Fluid Test Laboratory, TiCl_4 resulted to be stable up to 500 °C in stainless steel alloy, which is a significant improvement compared to other fluids. However, the extreme tendency of TiCl_4 to hydrolyse when in contact with humid air poses serious challenges for its application in power cycles as pure fluid: on one hand the high normal boiling point of TiCl_4 (136.4 °C) leads to work in sub-atmospheric conditions in the turbine, recuperator, and condenser in order to have good system performance; on the other hand, a low minimum pressure level implies that the infiltration of air (and the consequent reaction with the fluid) in the system is hard to avoid. Eventually, in this work, another metal halide, SiCl_4 , is investigated: the experimental procedure and results are reported in the next section.

From this overview, it becomes evident how challenging it is to enhance the thermal-to-electric efficiency of ORC systems when very-high temperature sources are available, given that the thermochemical stability of the working fluid remains the most limiting factor in the increment of the cycle maximum temperature.

3. Thermal stability of SiCl_4 and material compatibility test

The thermal stability of SiCl_4 is experimentally assessed using the static survey method implemented in the Fluids Test Laboratory of the University of Brescia, as mentioned earlier. This approach relies on measuring the change of vapour pressure after thermal stress at constant temperature compared to the same property of the fresh fluid (not thermally stressed). The experimental apparatus and procedure implemented are well described in [22]. Nonetheless, for a more visual representation, the key components are illustrated in Fig. 1 and summarized in Tables 2-3.

The core of the system is the sample cylinder manufactured by Swagelok is AISI 316L, which is a material commonly adopted in power plants. As illustrated in Fig. 1 (left), the cylinder features two welded connections: one for the loading tube, and the other one for the housing of the temperature probe (thermocouple), responsible for measuring the bulk fluid temperature. Two pressure transmitters have been used

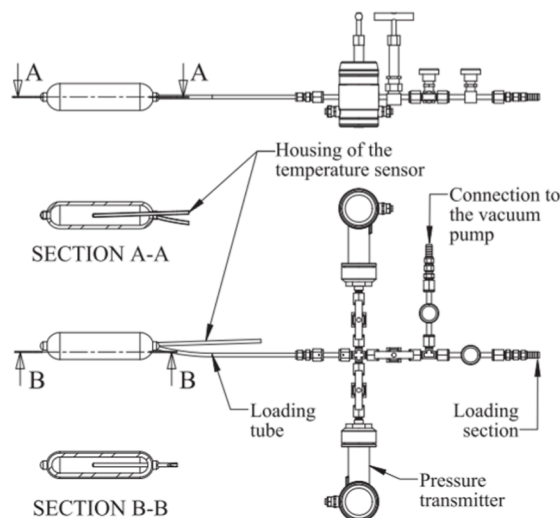


Table 2
Equipment for thermal stability testing.

Type	Manufacturer	Model	Characteristics
Sample cylinder	Swagelok	–	Internal Volume 150 cm ³ Material AISI 316L
Needle valves	Swagelok	SS-4H-V13	–
Vacuum pump	Dami Cosmos	MP90DEVV	P_{\min} 1 mbar
Scale	Mettler-Toledo	MS12002TS	FS: 12.2 kg – Accuracy 0.1 g
Thermostatic bath	Julabo	Julabo FP 40	–45/150 °C – Resolution 0.1 °C

Table 3
Instruments for thermal stability testing.

Type	Manufacturer	Model	Measurement range	Accuracy
Pressure transmitter 1	Keller	Klay 2000-SAN	0..10 bar*	0.1 % of full-scale
Pressure transmitter 2	Keller	Klay 2000-SAN	0..100 bar*	0.1 % of full-scale
Thermocouple	Tersid	Type K	–200–1270 °C	Tolerance class I

* Adjustable span (1–10 bar for transmitter 1, 20–100 bar for transmitter 2).

during the test: a low-pressure transmitter with adjustable full scale in the range 1–10 bar to measure the vapour pressure of the fluid with good accuracy, and one high-pressure transmitter (20–100 adjustable span) to monitor the pressure during the thermal stress in the muffle furnace. All the wetted parts of the system, including the pressure transmitters, are manufactured in AISI 316. When the fluid is subjected to thermal stress in the muffle furnace, the valve adjacent to the low-pressure transmitter is closed to protect it from overpressure, and the pressure is recorded only with the high-pressure transmitter.

The thermal stability test involves the following steps: (i) evacuation of the system using a vacuum pump; (ii) introduction of a pre-defined mass of fluid into the cylinder; (iii) placement of the cylinder vertically in a thermostatic bath for measuring the reference vapor pressure of the fresh fluid within a predetermined temperature range; (iv) horizontal placement of the system in a muffle furnace for a 100-hours thermal stress at a selected constant temperature; (v) after the thermal stress, returning the system to the thermostatic bath to measure vapor



Fig. 1. schematization of the main components for thermal stability test (left), and system under thermal stress in a muffle furnace (right).

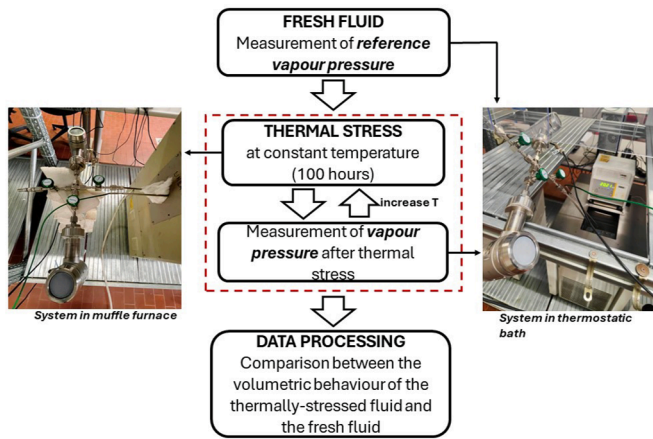


Fig. 2. Schematization of the methodology adopted for the thermal stability test.

pressure within the same temperature range as the reference test; (vi) repeating the process by placing the system in the muffle furnace for another thermal stress at a higher temperature; (vii) iteratively repeating steps (v) to (vi) until the desired temperature level in the muffle furnace is reached. The test concludes when either the target temperature is achieved during the thermal stress or when a significant divergence in volumetric behavior of the fluid is noticed compared to the reference behaviour. The most relevant steps of the methodology are also represented in Fig. 2.

The supplier of the fluid is Merck, and the declared purity is higher than 99 %. A sample of 22 g of liquid SiCl_4 has been charged in the cylinder with fixed volume of 150 cm^3 .

As already discussed in previous works [324], signs of degradation phenomena are more evident at sub-atmospheric vapour pressure condition, where the partial pressure of light and volatile decomposition products noticeably increases the pressure deviation with respect to the fresh fluid. Consequently, given SiCl_4 's normal boiling point around $57 \text{ }^\circ\text{C}$, the reference vapor pressure ("REF" in Fig. 3) was measured from $0\text{--}50 \text{ }^\circ\text{C}$ with $10 \text{ }^\circ\text{C}$ intervals.

The sample fluid experienced five consecutive stress tests in the

muffle furnace at temperature from $450 \text{ }^\circ\text{C}$ to $650 \text{ }^\circ\text{C}$, with steps of $50 \text{ }^\circ\text{C}$. The test concluded at $650 \text{ }^\circ\text{C}$ even if no thermal breakdown of the fluid was observed in order to avoid possible system overpressure occurring at higher temperatures. At the end of each 100-hours stress test, the saturation pressure curve was measured and compared with that of the fresh fluid (reference volumetric behaviour) in order to detect possible signs of decompositions. The vapour pressures measured after each 100-hours thermal stress and the one of the reference fresh fluid are reported in Fig. 3.

From Fig. 3, it is possible to conclude that the pure SiCl_4 in AISI 316L is stable up to $650 \text{ }^\circ\text{C}$ as no vapour pressure deviations are appreciable. Unlike previous tests on different fluids for ORC applications conducted in our laboratory, no post processing of the data, such as the calculation of the rate of unimolecular decomposition [3], was feasible since no pressure deviations higher than the instrumental uncertainty were measured. Looking at the application point of view, the outstanding result obtained up to $650 \text{ }^\circ\text{C}$ with a relatively low-cost material, compared to nickel-based alloys or other special metals, is very promising and proves the high potentialities of this fluid in high-temperature applications. Based on current investigation, SiCl_4 can be safely utilized up to a bulk temperature of $650 \text{ }^\circ\text{C}$ without experiencing degradation. This temperature threshold aligns well with the thermal requirements of next-generation CSP plants [55], for example.

Another important aspect, for the commercialization of an ORC cycle with a new working fluid, is the material compatibility (especially at the maximum operating temperature). For this reason, a preliminary medium term thermal stability and material compatibility test of 300 h in AISI 316L was carried out at $550 \text{ }^\circ\text{C}$, a temperature level compatible with several high-temperature applications (e.g. solar, biomass, waste heat, etc.). After the thermal stress, the thermal stability has been verified in comparison with the reference vapour pressure line: no signs of degradation of the fluid have been detected, and the vessel has been cut and analysed in cross-section by means of an optical microscope to assess the interactions between the metal and the fluid.

The microstructural analysis to evaluate the interaction produced by the prolonged contact with the high-temperature atmosphere of SiCl_4 has been performed by means of a Reichert-Jung MeF3 optical microscope equipped with Leica qWin software for image analysis at Metal Labs of the University of Brescia [56]. The optical microscope analysis (Fig. 4) shows that the interaction between the AISI 316L cylinder walls

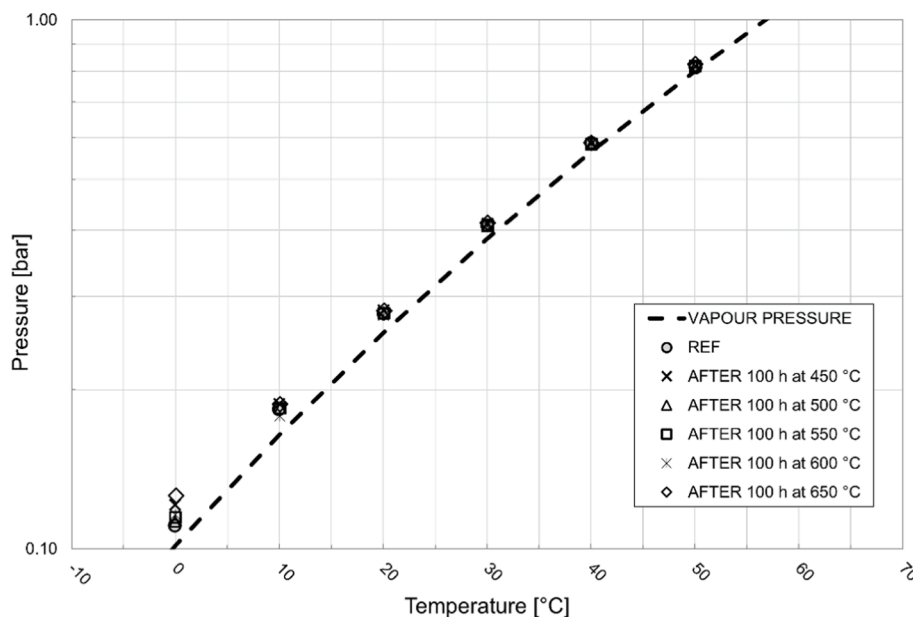


Fig. 3. Saturation pressures of SiCl_4 after different 100-hours thermal stress test from $450 \text{ }^\circ\text{C}$ to $650 \text{ }^\circ\text{C}$ ($50 \text{ }^\circ\text{C}$ step) compared with the reference values ("REF") and the simulated vapour pressure (dashed line) with Peng Robinson EoS (logarithmic scale).

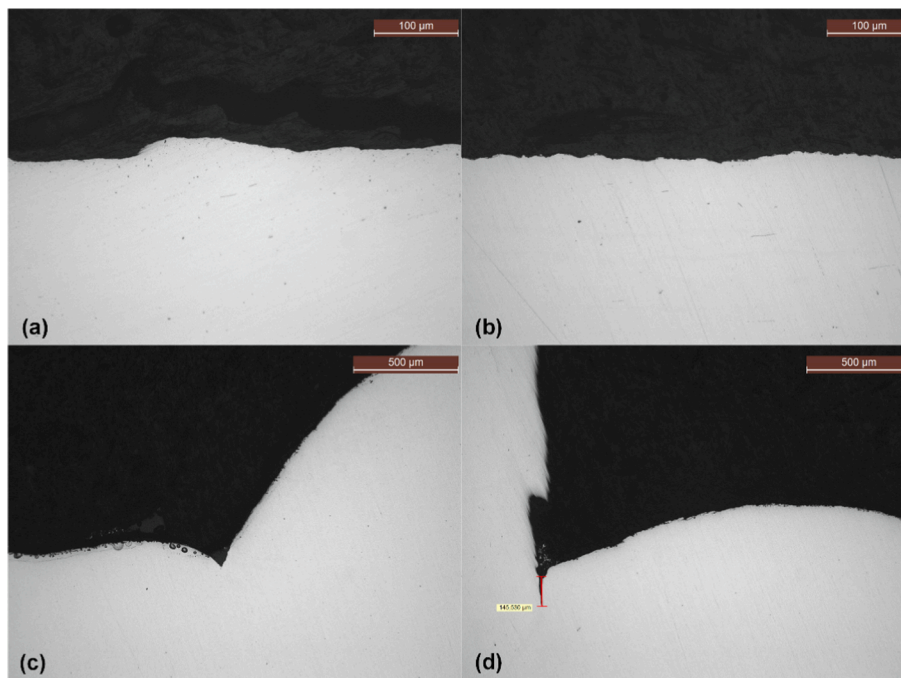


Fig. 4. Optical analysis results on the base-metal (a,b) and HAZ (c,d) after exposition for 300 h at 550 °C in SiCl₄ atmosphere.

and SiCl₄ is weak both in the base-metal and in the heat-affected zone (HAZ) of the welding. Only in one welding sample a crack was detected (Fig. 4-d), but it should be a pre-existing defect as already noticed in other non-stressed cylinders. The wall surface appears slightly jagged because of the coarse internal finishing. Eventually, this analysis gives encouraging results for the applicability of the fluid at 550 °C in AISI 316L.

4. Silicon Tetrachloride: Characteristics and thermophysical properties

Silicon Tetrachloride (SiCl₄) is a non-flammable metal halide that, at ambient conditions, is a colourless liquid. SiCl₄ possesses zero Ozone Depletion Potential (ODP) and Global Warming Potential (GWP), it is non-carcinogenic and non-flammable, and it is relatively low cost since it is widely produced as by-product in the silicon industry.

The normal boiling point of SiCl₄ (around 57 °C) allows to operate the system above ambient pressure at reasonably low condensing temperatures, avoiding air in-leakage phenomena. For instance, achieving sub-atmospheric condensation (and air infiltration) is practically not feasible for Titanium Tetrachloride since its normal boiling point is 136.4 °C. Thus, cogeneration solutions where the fluid is condensed at 100 °C are particularly attractive for SiCl₄, with minimum cycle pressure

of 3.34 bar which eliminate the risks of air infiltrations and the need of a vacuum pump followed by a fluid recovery unit, while condensing TiCl₄ at 100 °C in combined heat and power (CHP) applications requires 0.32 bar as minimum cycle pressure. Moreover, SiCl₄ is much less water-reactive than TiCl₄, as reported in the literature [57] and qualitatively confirmed by our laboratory experience. It is possible to conclude that SiCl₄ appears to be less problematic: it is necessary to guarantee a good degree of vacuum, paying attention during the phase when the circuit is being charged, to avoid contact with moisture in the air, then during the entire plant lifetime the reactivity with water becomes a marginal problem operating above ambient pressure.

The main thermodynamic properties of SiCl₄ are listed in Table 4.

SiCl₄ is a non-polar molecule, thus only London dispersion forces dominates the intermolecular interactions. The apparently anomalous low normal boiling point of SiCl₄ (around 57 °C), compared to other tetrahalides such as CCl₄ (121 °C), CBr₄ (189.5 °C), and TiCl₄ (136.4 °C), is due to its large molar volume [63]. The large molar volume entails a high molecular radius between molecules and then weak intermolecular forces.

The low critical pressure (35.9 bar) allows for the application of the fluid in transcritical conditions, that could be advantageous for the coupling with a high-temperature sensible heat source. In fact, the critical pressure of the fluids adopted in the existing supercritical ORCs, reported in the public literature, exceeds the one of SiCl₄. As an example, in 2012, Turboden realized a 500 kW_{el} prototype with supercritical R134a as working fluid ($P_c = 40.06$ bar) [2] to improve the conversion efficiency in geothermal applications. In the same year, the Houston-based company TAS Energy delivered a 22 MW_{el} supercritical power cycle using the same fluid for the Neal Hot Springs geothermal plant [64]. In 2012, a 7.5 MW_{el} waste heat recovery ORC was installed at a natural gas pumping station working with supercritical butane ($P_c = 38$ bar).

The high molecular weight entails low enthalpy drop in the turbine, with the benefit of requiring few turbine stages but the penalty of needing large internal heat recovery exchanger (recuperator). From the molecular complexity parameter, calculated accordingly to Eq. (1), it is possible to conclude that SiCl₄ is not a complex fluid, however it is an isentropic fluid, i.e. the slope of the saturation curve is nearly vertical in

Table 4

Thermodynamic properties of Silicon Tetrachloride.

Parameter	Units	Value
Critical Temperature [58]	°C	234.9
Critical Pressure [58]	bar	35.9
Normal Boiling Point [5960]	°C	56.63/57.6
Melting Point ^b	°C	-68
Saturated Liquid Density (20 °C) [61]	kg/m ³	1480
Pitzer Acentric Factor ^b	-	0.224
Critical Compressibility Factor Z_c^b	-	0.271
Molar Mass	g/mol	169.9
Pitzer Acentric Factor ω^b	-	0.224
Molecular Complexity parameter σ^a	-	1.37

^a Calculated according to Equation (1).

^b According to NIST Database in Aspen Plus V12[62].

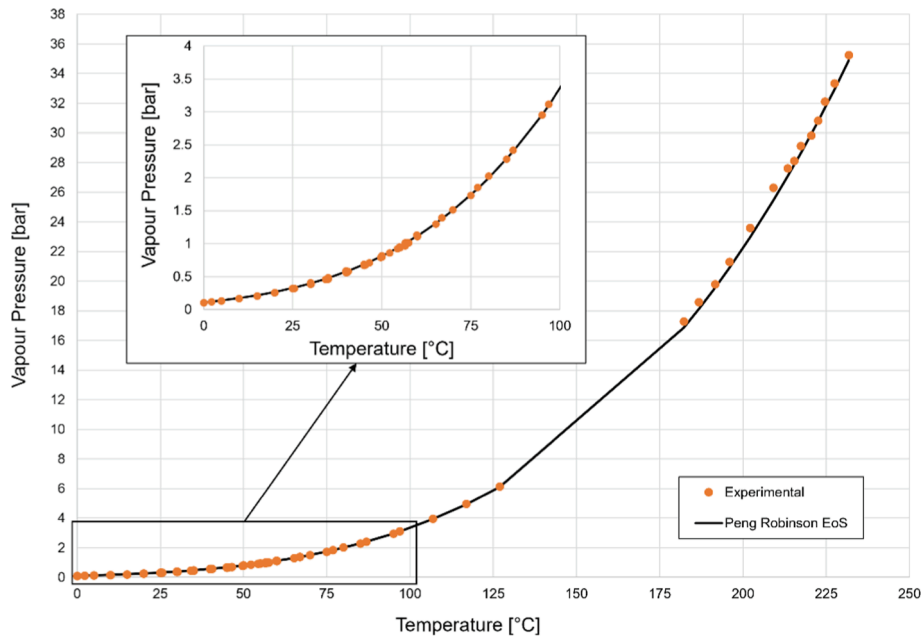


Fig. 5. Experimental vapour pressure (dots) vs simulated with PR EoS (solid line), with a focus on low temperatures.

a temperature-specific entropy (T-s) diagram.

$$\sigma = \frac{T_{cr}}{R} \left[\frac{dS_{SV}}{dT} \right]_{T_{red}=0.7} \quad (1)$$

A reliable thermodynamic model is necessary to calculate the thermodynamic properties of the working fluid during the transformations in the closed power cycle. It is well recognized that the most important property for the thermodynamic assessment of a cycle that works at saturation conditions is the vapour pressure. Experimental vapour pressures of SiCl_4 are available in the NIST Database of Aspen Plus V12 from slightly above the melting point to the critical point. The Peng Robinson (PR) equation of state (EoS) in its original formulation [65], with parameters reported in Table 4, has been used for the thermodynamic cycle evaluation since it has an average absolute deviation (AAD) on the experimental vapour pressure data equal to 1.22 %, in the temperature range from 40 °C to the critical temperature. Fig. 5 represents the experimental vapour pressure available in NIST Database and the simulated vapour-pressure curve with the PR EoS.

The work of Prat et al. [66] includes many correlations that fits experimental data for SiCl_4 ; in particular, their correlation for liquid density was found to fit very well the few available data in NIST database of Aspen Plus. In Aspen Plus environment, the Rackett equation has been used to determine the liquid density of the SiCl_4 since the AAD compared to the Prat correlation is 0.03 %. A reliable liquid density model is necessary to perform the pump selection and design.

An eventual leak can be easily identified through a hydrochloric acid (HCl) detector, as a product of hydrolysis with humid air. In addition, there is much experience in handling silanes in the solar-grade polysilicon manufacturing, which could be useful for the required safety measures. According to the NFPA 704 Hazard Identification System, SiCl_4 is hazardous in terms of toxicity; as every chlorine-based gas, it is classified as a material that on short exposure could cause serious temporary or residual injury (Health Hazard 3). So, the fluid must be safely applied in a closed system with precautions on avoiding leakage in closed ambient, as it is an ORC which is inspected and tested in pressure against leaks during assembly. The toxicity is associated to formation of HCl when it comes in contact with humid ambient air. However, eventual necessary venting of the fluid (due to overpressure, maintenance, or flange leaking, for instance) can be totally neutralized through sodium

hydroxide (NaOH) solution making this a secondary issue, as practiced in our laboratory experience. Caustic solution is the most common scrubbing liquid adopted for acid-gas control, such as HCl and SO_x , then probably already available at the power plant facility especially if furnaces are installed. In case of working fluid leakage, it is easy to detect by controlling the values of HCl.

Even if Silicon Tetrachloride is a hazardous compound, it is largely employed in the industrial field (especially in polysilicon, silica-based materials, and optical fiber productions) so there are many proven safety procedures and expertise. Silicon tetrachloride is not classified for environmental effects under the EU Globally Harmonized System (GHS).

4.1. Fine tuning of transport properties of SiCl_4

Considering using SiCl_4 as working fluid, it is important to assess not only thermodynamic but also transport properties. For heat exchangers design and rating, it is essential to possess reliable transport properties models for a wide range of operating conditions. This is particularly important when dealing with supercritical/transcritical cycles, where the fluid experience large variation in thermophysical properties. Moreover, in transcritical cycles, there is the need for models capable of describing transport properties along the high-pressure isobar, during the “transition” from liquid to supercritical gas, with continuity. A generic transport property is calculated as a sum of a “zero-density” property π_0 and a “residual property” $\Delta\pi$:

$$\pi(T, p) = \pi_0(T) + \Delta\pi(T, p) \quad (2)$$

The zero-density term π_0 can be calculated with methods that are derived from the rigorous kinetic theory of gases, whilst almost all the methods available to describe the residual property $\Delta\pi$ are empirical or semi-theoretical [67], with the corresponding-state (CS) based methods being the most applied. In an ORC, the turbine exhaust as well as the hot stream in the recuperator is constituted by a low-density superheated vapour whose transport properties are dominated by the “zero-density” term. In this fluid region, the associate error of the models, deriving from rigorous theory methods, is usually low (below 5 % for most cases [67]).

On the other hand, in the dense regions as in high-pressure isobar, the residual term becomes predominant, and the property prediction is strongly influenced by the selected property model. For this reason, in this work a proper tuning of the friction-theory (f-theory) models for the

Table 5
Fitted parameters of f-theory thermal conductivity model for SiCl₄.

Compound	a ₀	a ₁	a ₂	b ₀	b ₁	b ₂	A ₀	B ₀	Φ _c
SiCl ₄	-9.0261	0.1060	-0.4060	11.2441	0.3683	-0.4127	0.0012	0.2839	0

description of the residual viscosity and thermal conductivity has been carried out in MATLAB [68] environment. More information about the transport properties models can be found in the [Supplementary Material](#) section.

In particular, the residual viscosity has been modelled with the general one-parameter friction theory model of Quiñones-Cisneros et al. [69] in conjunction with the PR EoS (using the parameters presented in [Table 1](#)). Particular relevance, in the fitting procedure, was given to available liquid data (i.e. high-density field). The correlation for the liquid viscosity of SiCl₄ provided by Prat [66], tuned on experimental data from 20 °C to the normal boiling point, has been used, together with the experimental vapour viscosities from the NIST database in Aspen Plus® environment [62], for the optimisation of the f-theory general one-parameter viscosity model [69]. The critical characteristic viscosity of SiCl₄, which is a degree of freedom of the one-parameter f-

theory model, has been optimized here to the value $\eta_{c,\text{SiCl}_4} = 426.14 \mu\text{P}$ to fit the available experimental viscosities of the fluid.

In the same way, the recent friction-theory model for thermal conductivity [70] has been optimized for SiCl₄. Available liquid and vapour thermal conductivity data [7172] have been used to tune the coefficients needed for the property description. The coefficients retrieved using nonlinear data-fitting “lsqcurvefit” algorithm, in MATLAB’s Optimization Toolbox, are reported in [Table 5](#). The optimization procedure and the capability of the selected models to describe even complex systems are described in [73].

The two main transport properties models available in Aspen Plus environment, valid both for dense liquid and gas phases, are the TRAPP [74] and Chung-Lee-Starling [75] models: both the models make use of the CS approach for the calculation of the residual property. The comparison between the in-house optimized f-theory model and the above-

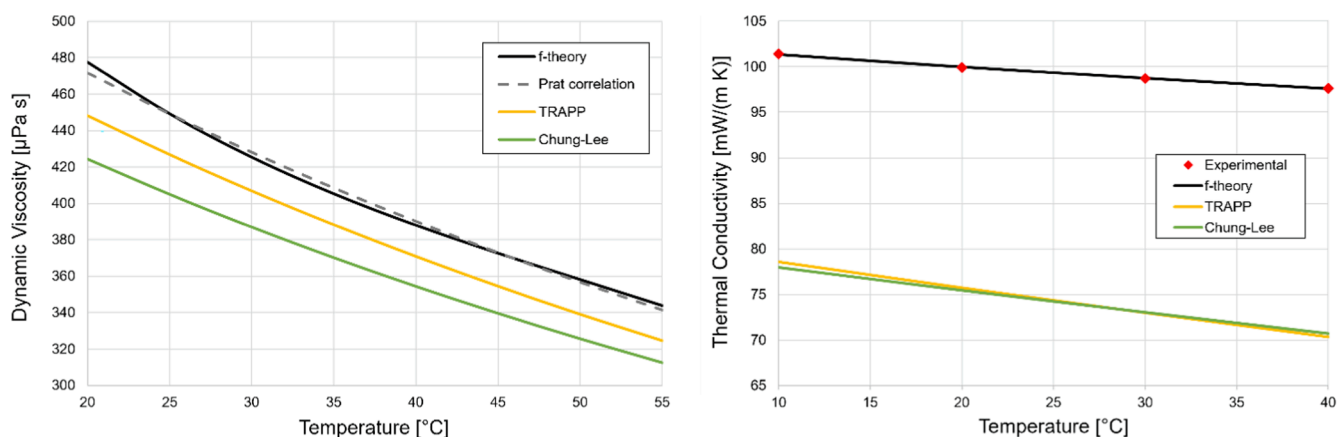


Fig. 6. Comparison between the optimized f-theory models for viscosity (left) and thermal conductivity (right), and other models available in commercial software for both liquid and vapour regions (TRAPP and Chung-Lee), with experimental saturated liquid thermal conductivities [71] (red dots) and Prat correlation [66] for viscosity which is tuned on experimental data.

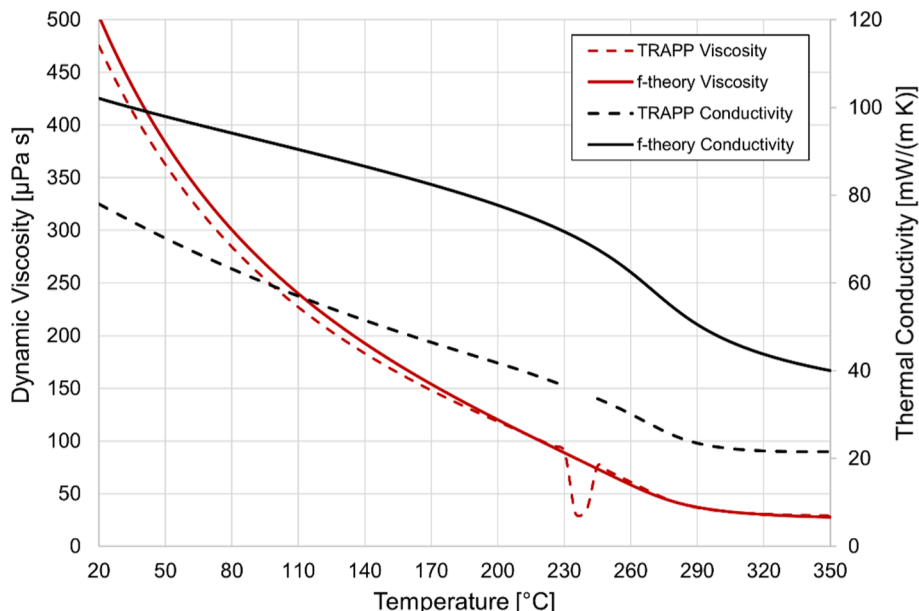


Fig. 7. Trend of transport properties along a supercritical isobar (60 bar) as predicted by the optimized f-theory model and by TRAPP model.

mentioned models for the viscosity and thermal conductivity is reported in Fig. 6 for the dense region (liquid phase).

As highlighted by Fig. 6, the optimized f-theory model for viscosity is the most appropriate for the transport property prediction in the dense phase. It was found an average absolute deviation (AAD) equal to 0.55 % compared to the correlation of Prat for viscosity, which is tuned on experimental data. Since the experimental data referenced by Prat were not found in the open literature, we considered the Prat relation as reference for the viscosity. The methods available in Aspen Plus noticeably underestimate the thermal conductivity of liquid SiCl_4 , which noticeably affect in a negative way the heat transfer coefficient calculation in the dense regions, i.e., the cold side of the recuperator and of the primary heat exchanger/evaporator as well as the liquid phase in the condenser. This is particularly evident if dealing with a supercritical fluid, whose behaviour is intermediate between a liquid and a gas.

Fig. 7 shows the trend of the transport properties of SiCl_4 at supercritical pressure (60 bar), representative of potential operating condition in ORC system application. Even in this case, the TRAPP model appears to underestimate the thermal conductivity of the fluid compared to the optimized f-theory model, while the simulated viscosity values are aligned: the discontinuity of the TRAPP method is due to computational error of Aspen Plus software near the critical temperature. It is worth noting that the Reynolds number prediction is not affected much by the model selection, since similar viscosity is found, but the Prandtl number and, therefore, the heat transfer coefficient would be drastically underestimated in high-pressure conditions if TRAPP or Chung-Lee models are selected during the heat exchanger design.

5. Thermodynamic analysis of SiCl_4 power cycle

In the previous sections, the working fluid thermophysical properties and its thermal stability limits have been investigated. Here, a preliminary overview on the power cycle efficiency attainable with SiCl_4 as working fluid is performed in Aspen Plus v12 [62] using the PR EoS.

A typical ORC recuperative cycle layout is investigated, according to Fig. 8. As regards the condensation pressure, a pressure slightly above the ambient pressure is adopted in this work to avoid air in-leakage phenomena. Moreover, a condensation above ambient pressure generally implies a reduction of volumetric flow rates, avoiding technical issues in the last turbine stage design. Although the fluid is not complex (see Table 2), the adoption of a recuperator to preheat the pumped liquid, by exploiting the thermal power available from the turbine exhaust, is essential to achieve good cycle efficiency due to a high turbine inlet temperature (TIT).

The main assumptions and parameters of the cycle are reported in Table 6. To have a realistic picture of the potentiality of the proposed

Table 6

SiCl_4 power cycle assumptions at design conditions.

Parameters	Values
Minimum Pressure	1.05 bar
Minimum Temperature	58 °C ^a
Turbine Inlet Temperature	450 – 650 °C
ΔT_{\min} Recuperator	15 °C
Pressure Drop Recuperator (Hot/Cold side)	1 %
Pressure Drop PHE and Condenser	2 %
Turbine Isentropic Efficiency	calculated ^b
Pump Isentropic Efficiency	65 %

^a No subcooling is considered.

^b from 3-stages correlation[76].

working fluid, the fluid machine efficiencies are set according to a conventional ORC size of 2 MW gross mechanical output (no electro-mechanical losses included).

The efficiency of the pump is set at 65 %, a reasonable value [77] considering that high-head multi-stage pumps are required for the explored transcritical conditions. The turbine isentropic efficiency (total-to-static) has been evaluated in each different design condition according to the correlation of Astolfi and Macchi [76], which has been tuned on several ORC turbines/working fluids designed with their own Axtur code. According to the correlation, the turbine efficiency depends on the isentropic volumetric ratio $V_r = V_{\text{out, is}}/V_{\text{in}}$ and the size parameter $SP = V_{\text{out, is}}^{0.5}/\Delta h_{\text{is}}^{0.25}$. The volume expansion ratio was assumed by Macchi and Perdichizzi [78] in 1981 as a similarity parameter to reduce the impact of the working fluid, treating it as an ideal gas. They also noted that when extending efficiency data to turbines of markedly different sizes, non-similarity effects arise because certain parameters cannot be proportionally scaled with the primary geometry. To counter the adverse impact on efficiency when reducing the size of the axial turbine beyond a specific threshold, they introduced the size parameter (SP): the efficiency experiences a drop of up to 9 % when reducing it from 0.20 m to 0.01 m. The correlation for three-stage turbines has been implemented in Aspen Plus environment to evaluate, in each design point, the impact of the operating conditions on the turbine efficiency. The adopted procedure provides more reliable results than the commonly used approach based on constant isentropic efficiency of the turbine, especially for ORCs.

The cycle thermal efficiency, calculated as in Equation (3), is reported in Fig. 9 at four different turbine inlet temperatures (in the 450–650 °C range coherently with thermal stability test) as function of the maximum pressure. Considering that the critical pressure is 35.9 bar, both subcritical and transcritical conditions have been explored in Fig. 9. The recuperator of the cycle is simulated by adopting 200 internal

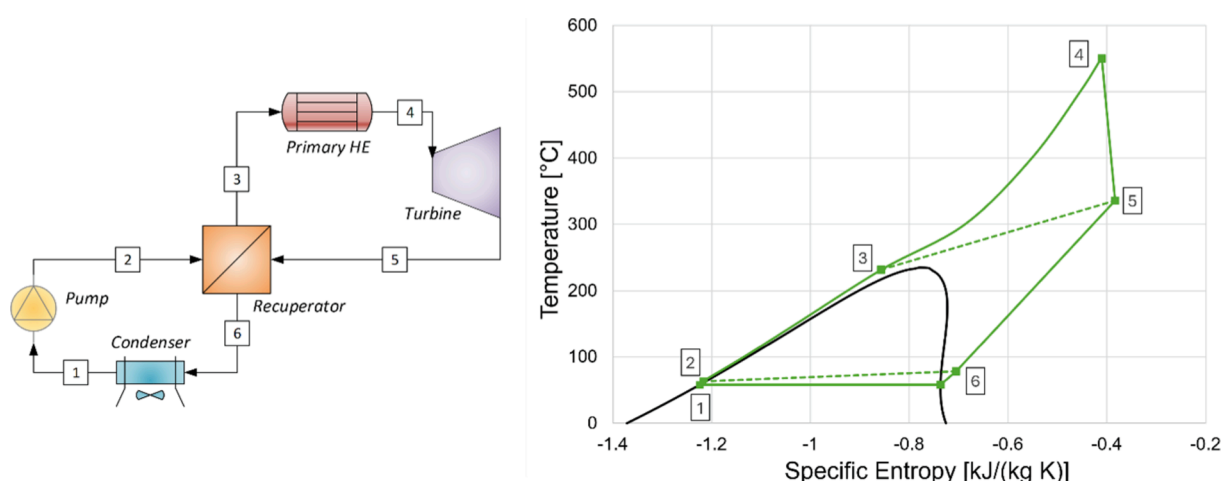


Fig. 8. Cycle layout (left) and temperature vs specific entropy diagram of SiCl_4 (right), considering TIT = 550 °C, T_{\min} = 58 °C, and P_{\max} = 60 bar.

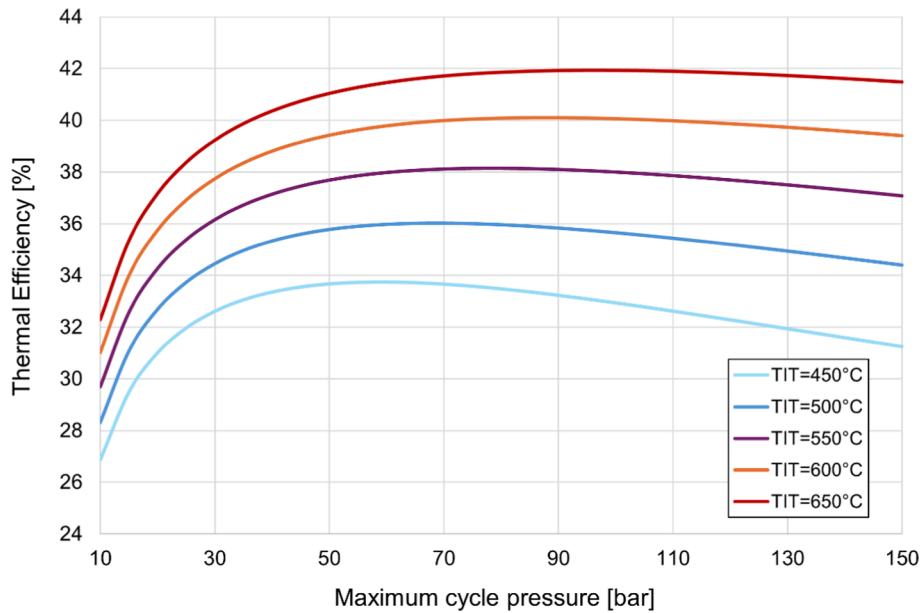


Fig. 9. Thermal efficiency of 2 MW_{gross} SiCl₄ cycle as function of the maximum pressure at different TIT, with the assumptions of Table 3 ($P_{\min} = 1.05$ bar, $T_{\min} = 58$ °C).

Table 7

Thermodynamic conditions of SiCl₄ cycle (Fig. 8).

Streams	T [°C]	P [bar]	x_{vap} [-]
1	58	1.05	0
2	63.7	60	0
3	232.3	59.4	1
4	550	58.2	1
5	336.8	1.08	1
6	78.7	1.07	1

Table 8

Summary of 2 MW_{gross} SiCl₄ cycle design conditions (Table 7).

Parameters	units	Values
\dot{m}	kg/s	18.9
W_{pump}	kW	122.2
W_{turbine}	kW	2122.2
$Q_{\text{in,PHE}}$	kW	5266.7
$Q_{\text{recuperator}}$	kW	2868.2
$Q_{\text{condenser}}$	kW	3266.8
$UA_{\text{recuperator}}$	kW/K	66.3
η_{pump}	%	65
η_{turbine}	%	86.6
η_{th}	%	38

zones to account for large heat capacity variation along the supercritical isobar.

$$\eta_{\text{th}} = \frac{W_{\text{Turbine}} - W_{\text{Pump}}}{Q_{\text{in}}} = \frac{\dot{m}(h_4 - h_5) - \dot{m}(h_2 - h_1)}{\dot{m}(h_4 - h_3)} \quad (3)$$

The optimum maximum cycle pressure lies between 50 and 90 bar depending on the TIT. Considering the 550 °C thermal level, which is compatible with several high temperature sources and indirect coupling with molten salts as heat transfer fluid (HTF), the optimal maximum pressure results to be 80 bar with an associated efficiency of 38.14 %. However, there is a plateau of the thermal efficiency above a certain pressure level (around 50–60 bar). For this reason, in the following considerations we will consider 60 bar(a) as the design conditions, where the design efficiency is 38 %. The selected operating conditions of the power block, according to Fig. 8, are reported in detail in Tables 7–8.

At the abovementioned design conditions, the expansion volumetric

ratio results 40.8, while the SP parameter is 0.12 m. A three stages expander is so a reasonable solution to distribute the volume flow variation along multiple stages. Following the correlation of Astolfi and Macchi, a turbine efficiency of 86.6 % (as in Table 5) is found.

Furthermore, to broaden the overview regarding the performance of the thermodynamic cycle operating with SiCl₄, a sensitivity analysis on minimum temperature and plant size will be presented herein. In particular, condensation temperature is ranged from 30 °C to 100 °C to cover design conditions from water-cooling to cogeneration. In Fig. 10, the resulting three-stages turbine and cycle efficiency are showed fixing the 2 MW gross mechanical output.

The design turbine efficiency increases with the increase of minimum cycle temperature due to the reduction of the volumetric ratio across the machine, given by the increase of saturation pressure in the condenser. On the other hand, at fixed output, by increasing the saturation pressure the turbine experiences a reduction of the size of the turbine (SP parameter in Fig. 10-right) that enhances secondary losses, but this effect is not predominant compared to the beneficial reduction of the volumetric flow ratio. This analysis suggests the great potentiality of SiCl₄ in CHP mode, especially when the ORC is driven by high-grade heat. A thermal efficiency above 32.5 % can be achieved by SiCl₄ when condensing at 100 °C. This result is considerably higher than any value achieved by state-of-the-art ORCs in CHP application, where typical efficiency is in the range 16–19 % [3929].

In Fig. 11, the effect of mass flow rate, thus power output, on the turbine efficiency is explored, at fixed pressure ratio (volumetric ratio). It can be noted, from Fig. 11, that there is a threshold value (around 2 MW) below which the three-stage turbine efficiency drastically reduces. Fig. 11 provides a good picture of the attainable efficiency in CHP applications, assuming a condensation temperature of 100 °C: the gross cycle efficiency exceeds 33 % for mechanical output above 4 MW adopting a three-stages turbine solution, which is a noticeable result. From this analysis, it is clear that the proposed fluid could potentially compete with steam Rankine cycles in CHP applications where high-grade heat is available.

To highlight the benefits of adopting SiCl₄ as working fluid, a comparison between the investigated solution and other fluids for high-temperature (HT) ORC is performed. Steam Rankine cycles and sCO₂, as well as CO₂-based mixtures [7980], are excluded from the analysis because the interest is here focused on the medium–low power size

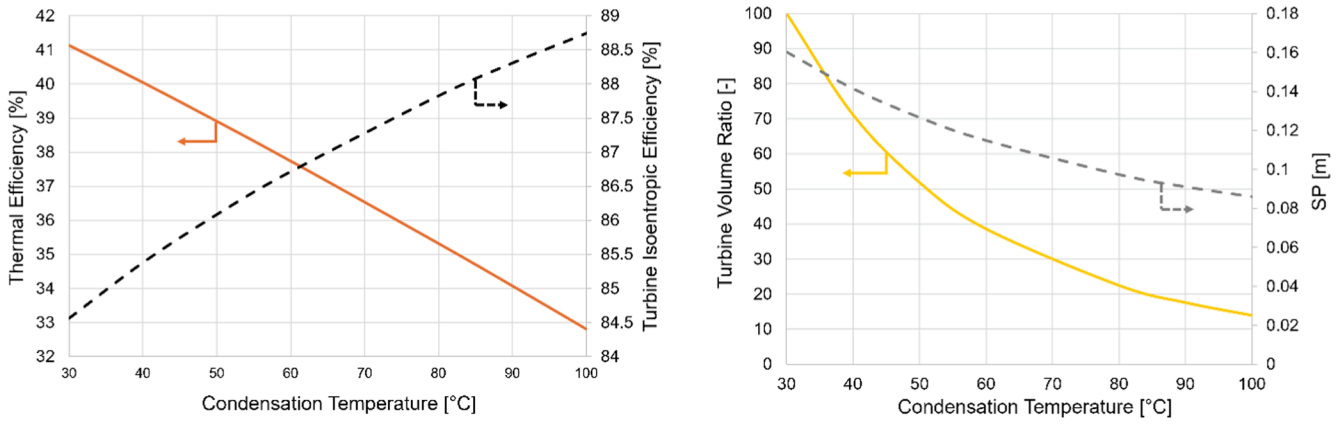


Fig. 10. Sensitivity on the cycle minimum temperature and its impact on the 2 MW_{gross} SiCl₄ cycle and three-stages turbine efficiency (left) and three-stages turbine parameters (right), considering TIT = 550 °C and P_{max} = 60 bar.

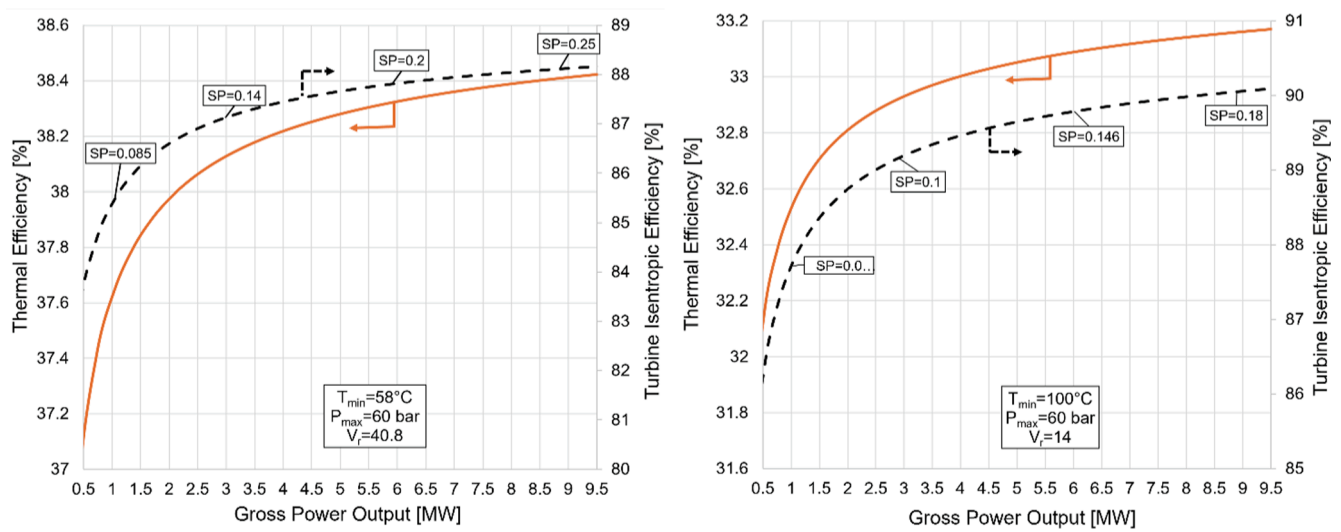


Fig. 11. impact of power size on the three-stage turbine efficiency and on the SiCl₄ cycle thermal efficiency, in scenarios of full-electric (left) and CHP (right).

Table 9

List of high-temperature working fluids for ORC with their applicable bulk temperature limit and main characteristics.

Working Fluid	T _{max} [°C]	Source	T _{cr} [°C]	P _{cr} [bar]	P _{sat} @ 80 °C [bar]	GWP	ODP	NFPA Health	NFPA Flammability
SiCl ₄	650*	This work	234.9	35.9	2	~0	0	3	0
TiCl ₄	500	[45]	364.9	46.6	0.15	~0	0	3	0
Perfluorohexane	400	[25]	179.6	18.1	2.07	9300	0	1	0
Toluene	320	[823]	320	41.1	0.37	3	0	2	3
MM	300	[41]	246.7	19.4	0.54	~0	0	2	4
Cyclopentane	275	[22]	239	45.1	2.5	5	0	1	3

*The investigation in this work proves 650 °C, but further analysis could overcome this limit.

(from tens of kW to few MW power output).

A survey of working fluid commercially adopted for HT heat sources in ORC application and additional fluids proposed in literature, at research stage, is presented in Table 9 together with the maximum temperature at which the fluids can be applied without presence of degradation reaction or with acceptable decomposition rate. A review of commercially available ORC solutions for medium–high temperature applications can be found in the work of Vescovo [26] from Turboden company.

The maximum operating temperatures of the considered fluids serve as a practical threshold, as indicated in Table 9. This table reflects their thermal stability limit, incorporating a safety margin to account for

potential hot spots and the thermal boundary layer. Epping et al. [29] reported the operating conditions of the toluene cycle as adopted by Tri-O-gen company, with minimum cycle temperature of 55 °C and a TIT equal to 320 °C. In fact, as result of a previous work [3] in our Fluid Test Lab, no significant degradation of toluene was found after 80-hours thermal stress at 325 °C. It is worth to mention that the configuration adopted by Tri-O-gen consists into the combination of turbine, generator and pump running at high speed (25,000 rpm) without the need for a gearbox and shaft seals. A similar solution could be investigated also for SiCl₄ to guarantee a completely hermetic design due to its reactive nature.

As a matter of facts, 320 °C stands as the highest temperature

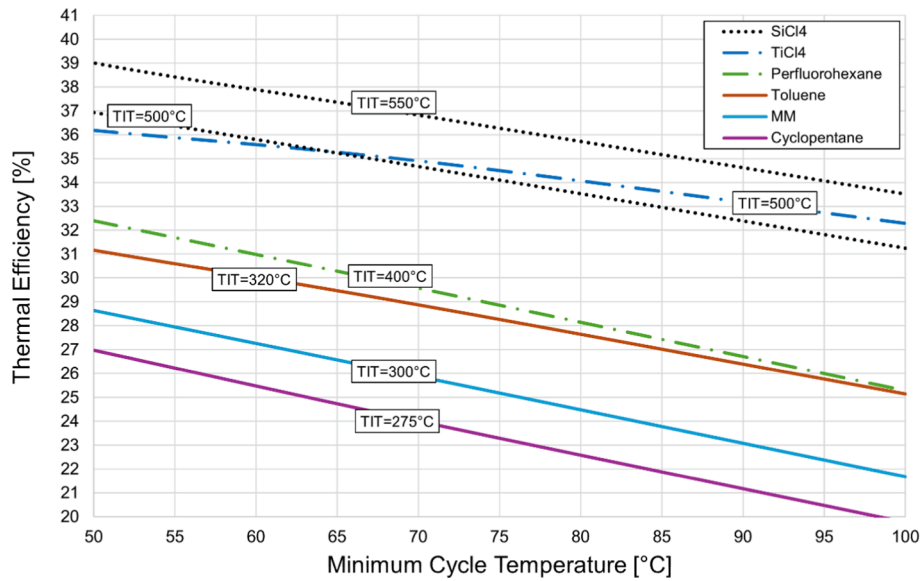


Fig. 12. Thermal efficiency of 2 MW_{gross} HT-ORCs as function of the minimum cycle temperature in optimized conditions, when coupled with sources above 550 °C. The dotted line represents the SiCl₄ cycle proposed, dashed lines represent fluids that have been proposed only at research stage, solid lines represent commercially adopted fluids. The fluids are simulated with TIT lower than 550 °C and constrained by their thermal stability limit (Table 3).

Table 10
characteristics of 2 MW_{gross} HT-ORCs at 100 °C minimum cycle temperature.

Working Fluid	Optimal Cycle Maximum Pressure [bar]	\dot{m} [kg/s]	$\Delta h_{is,turbine}$ [kJ/kg]	$V_{r,turbine}$ [-]	SP [m]	$\eta_{turbine}$	η_{th}
SiCl ₄	95*	24.4	106.1	21.4	0.08	87.4	33.5
TiCl ₄	40	19.6	123.8	92.8	0.19	85.4	32.3
Perfluorohexane	75	64	44.1	19.2	0.11	88.6	25.3
Toluene	28	15.2	157.6	43.1	0.15	87.1	25.1
MM	24	32.5	75.8	31.3	0.17	88.2	21.7
Cyclopentane	40	21.5	113.2	10.6	0.09	89.4	19.7

*95 bar is the best efficiency point when condensing at 100 °C, even if there is a plateau ($\eta_{th} = 33\%$ is reached at 65 bar).

recorded in commercial ORC units, although Turboden [81] reports a newly developed unit operating up to approximately 400 °C as its latest advancement.

The thermal efficiency have been assessed as a function of the minimum cycle temperature in the range 50–100 °C, keeping the same assumptions on the turbomachines and heat exchangers, already defined in Table 3. A recuperated ORC layout with a fixed gross mechanical output of 2 MW have been considered. The fluids have been evaluated at maximum cycle temperatures considering the corresponding thermal stability limit, as reported in Table 9, and a maximum limit of 550 °C. The PR EoS has been used to perform the analysis in Aspen Plus environment.

In Fig. 12, the performance of HT ORCs with the different fluids have been compared in applications with available high-grade heat (above 550 °C), such as biomass, CSP, heat recovery from prime movers and from flue gases of industries and incinerators. For each condensation temperature, the maximum pressure which determine the best efficiency point has been considered. It is important to highlight that in the WHR sector thermal efficiency is not the only important parameter. The capability to efficiently cool the sensible heat source down to the minimum temperature limit (heat recovery factor) plays a significant role in the overall plant efficiency (i.e. the net power output divided by the maximum thermal power available from the sensible heat source). However, the heat recovery factor of an ORC plant can be significantly enhanced by adopting a split configuration [39], a practice commonly employed in CHP and WHR plants. Notably, the use of a split architecture can enhance the heat recovery efficiency of the Organic Rankine Cycle (ORC) without adversely affecting its thermal efficiency, within

certain limits.

The sensitivity on the condensation temperature reflects different design conditions, from full electric to CHP mode. The comparison allows the reader to have a panoramic on the potential efficiency gain achievable with the proposed SiCl₄ in comparison with the commercially available solutions (solid lines) as well as with thermally stable fluids proposed at a research stage (dashed lines) in the past years. The performance of SiCl₄ cycle is also presented at a TIT equal to 500 °C for comparison with TiCl₄, considering the latter fluid's maximum allowable temperature. As evident in Fig. 12, TiCl₄ surpasses SiCl₄ in cogeneration applications, but the opposite occurs at low condensation temperatures due to large volume ratios across the turbine of TiCl₄.

Considering the low efficiency reached by the state-of-the-art fluids (solid lines in Fig. 12), in correspondence of high-temperature sources ORCs are unlikely to be adopted, at least for power output above 2–5 MW_{el}, where the specific cost and efficiency of steam cycles justify their choice. Instead, the results provided by this preliminary analysis prove the potentiality of SiCl₄ to be competitive with steam Rankine cycles for both low and high-power output.

Going into details, the differences among the different fluids under the identified optimal conditions are presented in Table 10 considering the case of 100 °C condensation temperature, representative of a CHP plant.

Titanium Tetrachloride (TiCl₄) appears to be not suitable for a three-stage turbine solution since, condensing at 50 °C, the volumetric ratio across the turbine overcome the value of 500 by evaporating above 35 bar. In fact, at 50 °C condensing temperature, TiCl₄ has a saturation pressure equal to 0.043 bar, which poses challenges in the last turbine

stage and condenser design. As reported in Table 7, the volumetric ratio reduces in CHP application, condensing at 100 °C, but the minimum cycle pressure is still below the atmospheric one. As already mentioned, the extremely reactive nature of TiCl₄ with humid air, in conjunction with its high normal boiling point (136.4 °C), poses serious question on its applicability in a power plant. Moreover, no analysis on material compatibility have been performed.

As indicated by the results presented in Table 10, the volumetric ratio of SiCl₄ is lower than that of MM. However, the lower turbine efficiency can be attributed to the lower size parameter, which is associated with the lower volumetric flow rate at the outlet.

SiCl₄ demonstrates the potential for a thermal efficiency gain of more than 10 % compared to state-of-the-art fluids used in commercial high-temperature ORC (HT-ORC) units, surpassing a thermal efficiency of 38 % in full-electric mode. This preliminary analysis highlights the promising capabilities of the proposed fluid, particularly in the presence of high-temperature heat sources.

6. Conclusions

Silicon Tetrachloride (SiCl₄) emerges as an innovative working fluid designed for very-high-temperature Rankine cycles. Experimental tests conducted in our Fluid Test Laboratory at the University of Brescia reveal the exceptional thermal stability of SiCl₄, surpassing the thermal capabilities of current state-of-the-art fluids utilized in Organic Rankine Cycle (ORC) systems. Notably, SiCl₄ demonstrates resilience under extreme conditions, exhibiting no signs of thermal degradation even at the maximum tested temperature of 650 °C. State-of-the-art fluids used in ORC units are restricted to maximum operating temperatures below 300–350 °C due to thermal stability thresholds. In contrast, the superior thermal capability of SiCl₄ makes it a promising solution for advancing high-temperature energy conversion systems.

Furthermore, going beyond the thermal stability test, an additional 300-hour thermal stress at 550 °C, followed by detailed metallographic analysis, has uncovered promising results, suggesting mild interaction in terms of material compatibility between SiCl₄ and AISI 316L stainless steel. This underscores the practical viability of SiCl₄ in high-temperature applications.

In the context of employing SiCl₄ as the working fluid, an assessment of its thermophysical properties was conducted. While the PR EoS demonstrated adequacy from a thermodynamic standpoint, it was crucial to fine-tune transport property models within the MATLAB environment for an accurate representation of dynamic viscosity and thermal conductivity.

A preliminary thermodynamic analysis of the recuperated SiCl₄ cycle layout was conducted, considering the influence of operating conditions on turbine efficiency. The assessment of various design parameters affecting the thermal efficiency of the SiCl₄ cycle included condensation temperature, maximum pressure, and power output. Demonstrating feasibility, a 2 MW_{gross} SiCl₄ cycle, condensing at 100 °C in CHP application with a maximum temperature of 550 °C, could achieve a thermal efficiency surpassing 33 %. In full-electric application, the SiCl₄ cycle could reach a thermal efficiency of 38 %, exceeding values achievable by any other working fluid under similar conditions and power size.

The primary challenge linked to the use of this fluid is its reactivity with humid air, leading to the production of HCl, though in a milder way compared to TiCl₄. This presents operational difficulties, particularly in sustaining pressures above atmospheric levels to avoid air in-leakage. Nevertheless, the unusually low normal boiling point of SiCl₄ (57 °C), in comparison to other tetrachlorides, facilitates operation at pressures above atmospheric. Moreover, any potential leak of working fluid can be easily identified using an HCl detector and neutralized with a sodium hydroxide (NaOH) solution.

In conclusion, SiCl₄ exhibits a potential + 10 % points gain in thermal efficiency compared to other ORC fluids used in high-temperature units, particularly when coupled with high-temperature sources

(above 550 °C) such as biomass, solar, prime movers, incinerators, and industrial flue gases. The preliminary results obtained in this article proves SiCl₄ as an appealing working fluid for enhancing the efficiency of high-temperature energy conversion systems.

CRedit authorship contribution statement

M. Doninelli: Writing – original draft, Validation, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **G. Di Marcoberardino:** Writing – review & editing, Supervision, Methodology, Investigation. **P. Iora:** Writing – review & editing, Supervision, Project administration, Investigation. **M. Gelfi:** Writing – review & editing, Supervision, Software, Investigation. **C.M. Invernizzi:** Writing – review & editing, Visualization, Supervision, Methodology. **G. Manzolini:** Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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