

Article

Thermal Stability and Thermodynamic Performances of Pure Siloxanes and Their Mixtures in Organic Rankine Cycles

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Abstract: Organic Rankine cycles are often the best solution for the conversion of thermal energy. The many working fluids include silicon oils. One crucial issue that determines the choice of a working fluid is its thermochemical stability, as this sets a limit to the maximum temperature at which the fluid can be used in a power plant. A second subject, much debated today, is the use of mixtures in ORCs. In the first part of this study, an investigation into the thermal stability of siloxanes using two different approaches was carried out. The results confirmed a limit working temperature for the considered siloxanes of about 300 °C, with a degradation that advanced significantly over time at 350 °C. In the second part of the study, an analysis of the thermodynamic performances of some siloxane mixtures was carried out. It was found that the efficiencies of the corresponding thermodynamic cycles were substantially the same as for the pure fluids used today. By changing the composition of the mixture, it was also possible to vary, within reasonable limits, the values of the condensation pressure, adapting the thermodynamic cycle to the different situations that can be encountered in current practice.

Keywords: organic Rankine cycles (ORC); thermal stability; siloxanes; mixture of fluids



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1. Introduction

Rankine cycles with organic working fluids are widely used in numerous industrial sectors (see, for example, [1–3]). Siloxanes are among the numerous working fluids proposed and used. Silicon oils are widely used as heat transfer fluids for high temperature applications [4–6]. They are considered nontoxic fluids and are available in many configurations, such as linear, cyclic, or with methyl and phenyl groups, which are characterised by different and specific properties. For example, the introduction of phenyl groups in the molecule can increase the thermal stability [7]. Fluorosilicones combine some of the advantages of fluorocarbons and of silicones and are proposed as lubricants for extreme pressure applications [7].

The viscosity of commercial silicones varies across a wide spectrum, ranging from 0.65 cSt to tens of millions of cSt, Anonymous₁. They are mainly adopted as heat transfer fluids, but they are also proposed as dielectric, hydraulic fluids, for power transmission and as damping fluids [7].

Regarding their use as heat transfer fluids, some of them are recommended for wide temperature ranges. For example, Syltherm HF is recommended for temperatures from −73 °C, Anonymous₂ to 260 °C, Anonymous₂; Syltherm 800 is provided for uses up to 400 °C, Anonymous₃.

Due to their good thermal stability, commercial silicones are also considered as heat transfer fluids in modern concentrating solar power systems using parabolic trough [8–10]. Helisol has been effectively employed in a solar test facility up to 425 °C for 480 h at 27 bar,

without any serious problems, except for the formation of some gases, but, according to the authors, without any serious consequences [6].

Silicon heat transfer fluids are mostly multi-component mixtures of dimethyl polysiloxanes with different molecular weights, which implies high boiling points, and, consequently, rather low vapour pressures at moderate temperatures. For example, at 100 °C, Syltherm HF and Syltherm 800 have a vapour pressure of about 0.03 bar and 0.05 bar, respectively, [4,5].

In spite of their rather low vapour pressures at temperatures close to environmental ones, some oligomer siloxanes are used today as working fluids in Rankine cycles, particularly, hexamethylsiloxane (MM) and octamethyltrisiloxane (MDM).

The use of cyclic siloxanes in organic fluid Rankine cycles (ORC) was first proposed in [11].

Nowadays, at least 320 biomass plants are operating across the world (about 60 in Italy) with sizes from 0.2 MWe to 8 MWe. The majority of them are cogenerative and use siloxanes as the working fluid. Biomass could still be considered a valid option to reduce the carbon emission footprint, as foreseen, for example, by the recent ambitious European decarbonisation plans [12].

Moreover, siloxanes, due to their good thermal stability, have recently been proposed for use in specific plant configurations at high-temperature [13].

Much valuable operational experience has been accumulated over past years and extensive practical information is available, as documented, for example, in [14,15].

Due to their wide use in organic Rankine cycles, in recent years many authors have published studies concerning the thermodynamic properties of certain oligomers, with the aim of improving their thermodynamic modeling by use of equations of state. In [16], for example, the authors optimised the parameters of a specific equation of state after a critical evaluation of the experimental thermodynamic properties available at that time for two linear and two cyclic methyl-siloxanes. In [17], measurements of density and of sound velocity in the liquid phase were presented for three methyl-siloxanes and the obtained data, integrating the many results accumulated over the last few years in the literature, and were used to calibrate a specific volumetric equation of state.

In [18], bubble pressures for three mixtures of linear siloxanes with different compositions over a temperature range of 270 K to 380 K, were reported.

Some transport property measurements are also available in the literature. For example, ref. [19] reported the values of the thermal conductivities for some pure linear and cyclic oligomers and for a mixture of 50% mass of two linear siloxanes in the temperature range from 290 K to 520 K and pressures from 1 bar to 100 bar. The same paper also presented some data on the dynamic viscosity at atmospheric pressure. Different and additional values for transport properties are also available in the technical literature of the fluid suppliers.

Some papers have presented and discussed measurements of heat transfer coefficients for pure siloxanes and for some mixtures. For example, in [20], for pure hexamethylsiloxane and octamethyltrisiloxane, and for some of their mixtures, the values of heat transfer coefficients in evaporation in a horizontal tube are presented, while in [21], some measurements of the Nusselt Number, in a vertical heated upward tube, are discussed regarding supercritical pressures for hexamethyldisiloxane.

In conclusion, silicones, as well as their wide use in industrial applications, have also been effectively adopted as working fluids in organic Rankine cycles and much information on the thermo-physical properties of the simpler siloxanes is now available. Moreover, in recent years the use of non-azeotropic mixtures, instead of pure fluids, in organic fluid Rankine cycles has been proposed; some of the previously cited publications specifically consider mixtures of siloxanes.

A crucial but still controversial problem in the use of unconventional working fluids in Rankine cycles is their thermal stability. In this study, we compared the results obtained from two different thermochemical stability approaches for some siloxanes. The

presented and discussed experimental procedure can also be applied to all pure candidate working fluids.

In the second part of the paper, we develop some thermodynamic evaluations of the performance of mixtures of siloxanes in the case of heat recovery. Currently, there are numerous proposals to use mixtures as working fluids in Rankine cycles, with contradictory results [22–24].

2. Thermal Stability of Siloxanes

In addition to the typical characteristics that a working fluid for organic Rankine cycle must have (e.g., favourable thermodynamic properties, low viscosity, good heat transfer characteristics, low or no toxicity, low or non-flammability, no negative effects on the environment and a reasonable cost), its thermal stability is crucial to define the maximum operating temperatures of the engine.

As the heat resistance of a molecule basically depends on its bond energies, BE provides a first rough indicator of thermal stability; however, it does not take into account possible chemical interactions with the environment where the fluid is used. It is calculated as the value of the standard enthalpy of formation $\Delta_f H_{gas}^0$ (at 25 °C) divided by the number n_B of the bonds in the molecule. More negative is the ratio $\Delta_f H_{gas}^0 / n_B \propto BE$ and reasonably higher is the mean value of the bond energy BE of the atoms in the molecule.

In Table 1, for example, we report the values of $\Delta_f H_{gas}^0$ for hexamethyldisiloxane, carbon tetrafluoride, sulphur hexafluoride and two hydrocarbons (n-pentane and iso-pentane).

Perfluorocarbons are considered to be among the most thermally stable fluids. In [25], carbon tetrafluoride in an Inconel bomb, after conditioning of the bomb surface, showed clear signs of decomposition starting from about 940 °C. Sulphur hexafluoride was used primarily as an electrical insulator and is considered to be inert. According to [26], it can be heated to 500 °C in quartz containers without any decomposition effects. The two hydrocarbons n-pentane and iso-pentane are representative working fluids for organic Rankine cycles operating at relatively low temperatures, and typically used for geothermal applications [27]. In [28], a solar power plant is described with an organic Rankine cycle using n-pentane with an inlet turbine temperature of 240 °C.

Table 1. Standard formation enthalpies $\Delta_f H_{gas}^0$ at 25 °C and the estimated mean energy bond EB for the atoms in the molecule for some compounds. The values of $\Delta_f H_{gas}^0$ are from [29].

Compound	$\Delta_f H_{gas}^0$ (kJ mol ^{−1})	EB (zJ/Bond)
MM (Hexamethyldisiloxane)	778	50
Carbon tetrafluoride	925	380
Sulphur hexafluoride	1209	330
n-Pentane	146	15
iso-Pentane	154	16

From the data in Table 1, hexamethyldisiloxane (and, by extension, the other siloxanes, linear and cyclic) should have a thermal stability significantly higher than that of hydrocarbons, without, however, reaching the typical levels of stability of the simpler perfluoro-carbons.

In real-world conditions, as a result of the presence of different materials and substances (e.g., different metals and different types of gaskets, lubricants, air, water) the thermal stability of the fluid can be drastically reduced. Therefore, in general, it is better to refer to its thermochemical stability [30]. Nevertheless, for sufficiently high temperatures thermal decomposition is always present, with a rate increasing exponentially with the temperature; the problem is to identify the degradation rate and to estimate a reasonable and safe duration of the working fluid.

The degradation usually occurs with breakdown of the molecules into long- and short-chain compounds. The analysis of the degradation can be evaluated according to different methods (in static or dynamic tests) and by examination of the different chemical and

physical properties of the tested fluid (for example, analysing any carbonaceous residues, the flash point variation, the total acid number, the viscosity variations of the residual liquid, the variation in sub-atmospheric vapour pressure) or the composition of the residual liquid and gas phases by gas-chromatography or by use of mass-spectrometers [30,31].

A recent approach to the analysis of thermal stability involves a molecular dynamics simulation [32].

For the oligomer siloxanes, some thermal stability results are already provided in the literature. In [10], results for samples of MD₂M (decamethyltetrasiloxane, with a boiling temperature of 194 °C), and MD₃M (dodecamethylpentasiloxanes, with a boiling temperature of 230 °C), in glass and steel ampoules at 400 °C, after 48 h decomposed by twenty and forty percent, respectively, are presented.

In [33], MM (hexamethyldisiloxane) at 420 °C in a stainless steel tube, appeared to reach equilibrium after 72 h, but with a significant reduction in MM in the final mixture (about 50%, on a mass basis) and a large presence of methane (15–20% in the gas phase). From an analysis of the influence of the temperature (with a fixed time of 72 h), it appears that a safe temperature for MM would be 300 °C, with an estimated annual degradation mass rate of about 3.5%.

In [14], the authors examined fluid samples taken from eight different organic Rankine plants operating with MDM as the working fluid. The plants operated with a source maximum temperature equal to about 300 °C accumulated over a total of 460,000 working hours. The degradation of the working fluid (across a very wide range, from 5 to 34%) resulted in significant contamination of the used lubricants which increased with the operating time.

Variation in the sub-atmospheric vapour pressure of samples of hexamethyldisiloxane (MM) and octamethyltrisiloxane (MDM) after 80 h at different test temperatures are discussed in [34], according to a procedure previously presented in [35]. In stainless steel cylinders, the sample of MM after 80 h at 340 °C decomposed, according to chemical analysis of the liquid phase, by less than one percent, and the sample of MDM appeared un-decomposed after eighty hours at 350 °C. In spite of this, the sub-atmospheric vapour pressures, for both the samples, showed significant deviation from the reference curves, due to the important contribution of the non-condensable gases (mainly methane and carbon dioxide) produced, albeit in minimal quantities. Therefore, the sub-atmospheric vapour pressure variations are highly sensitive and could be too restrictive for the evaluation of the maximum operating temperatures of assumed working fluids.

Finally, according to [36], a sample of MM at 360 °C, in stainless steel, at 25 bar, in 72 h decomposed by approximately 4.6% (on a molar basis), at 300 °C. At a pressure of 17 bar, in the same time, the molar decomposition was 3.97%, with a mean degradation rate of approximately 38×10^{-3} mol/h—a result that does not seem to be consistent with that reported in [33].

To conclude, for siloxanes, some results relating to their thermal stability are available in the literature, but some of these seem inconsistent with each other due to the different approaches used. A chemical analysis of the products is always useful, but there are too many variables that affect thermochemical stability. A general approach to the problem, that could at minimum be used for a first selection among different fluids would, in our opinion, be useful, both for siloxane and all other fluids potentially usable in Rankine engines.

In the following, we describe two different experimental approaches and we present some results related to some simple siloxanes.

2.1. The Differential Scanning Calorimeter

The general objective of thermal screening of chemicals and mixtures is to identify whether the sample can undergo an exothermic process and the temperature range of its occurrence, which provides a preliminary indication of potential chemical reaction hazards. Calorimeters for thermal screening are available from various producers in different specifications and with different sensitivity. The same exothermic effect can be detected at different temperatures depending on the sensibility of the calorimeter used.

DSC directly measures the heat flow and the resulting thermal effect (endo- or exo-thermic) can be integrated to obtain the enthalpy of the transition. In a typical experiment, a small amount of a sample (2 mg to 5 mg) is placed in a pressure resistant metal container and is heated at a constant rate (5 K min^{-1}) in the temperature range of 30°C to 280°C (for a stainless steel container, with a viton sealing o-ring) or of 30°C to 500°C (for a gold-plated stainless steel container without an o-ring). The closed high-pressure containers are used to suppress/limit vaporisation and keep volatile decomposition products contained, which may contribute to further decomposition.

When the analysed material is closed in the container, the thermal behaviour strongly depends on the atmosphere present inside the pan; it is not important which gas type flows in the furnace but the atmosphere inside the crucible is important. Generally samples are enclosed in the pan, including the air present in the laboratory, inside the crucible. Exothermic effects in this situation can be generated by oxidation of the sample and not by thermal decomposition. In these sets of experiments, crucibles (made of stainless steel and gold-plated stainless steel) were closed and sealed in both air and in an inert (N_2) atmosphere, using a special apparatus to distinguish the effects due to the reaction of the sample with the gas (such as oxidation) and decomposition effects due to the thermal instability of the sample [37].

In Figure 1, as an example, the resulting diagram for MM samples in a gold-plated stainless steel container in an atmosphere of nitrogen is reported.

The samples were found to be substantially stable in stainless steel (both in air and in nitrogen) at least up to 280°C and in gold up to 500°C (in nitrogen). Similar results were obtained for MDM and D4.

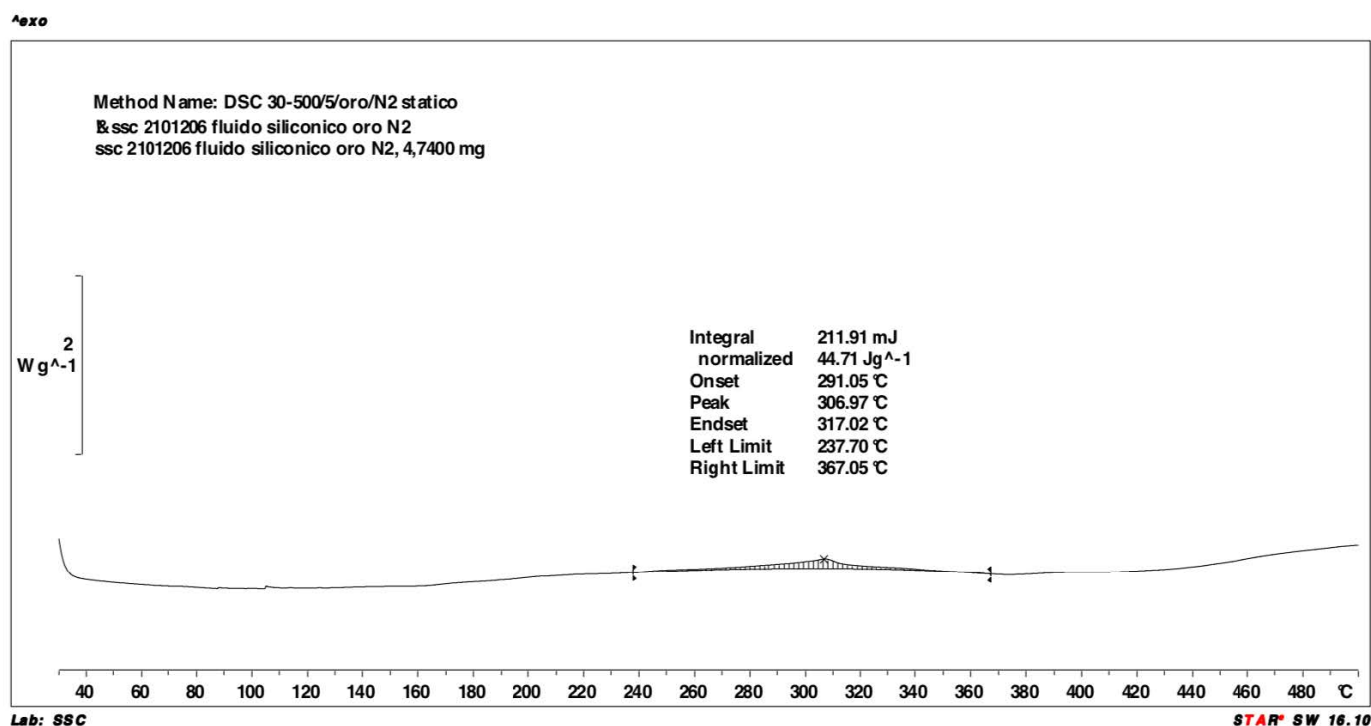


Figure 1. Results of DSC for MM samples in a gold-plated stainless steel container, in a nitrogen atmosphere.

2.2. Variation in the Normal Boiling Temperature

Following the procedure described in [34,35], a sample of hexamethyldisiloxane was loaded, after a first conditioning of its internal surface, in a stainless steel cylinder, and, after an acceptable degassing, varying the thermal bath temperature, a reference vapour curve was obtained. In Figure 2, the reference vapour pressure for a sample of 29 g of hexamethyldisiloxane is shown. The estimated uncertainties of the measured pressures

and temperatures were about 2 mbar and 1 °C, respectively. In Figure 2, for comparison, the values of vapour pressures calculated by Aspen Plus[®] v9.0 are reported.

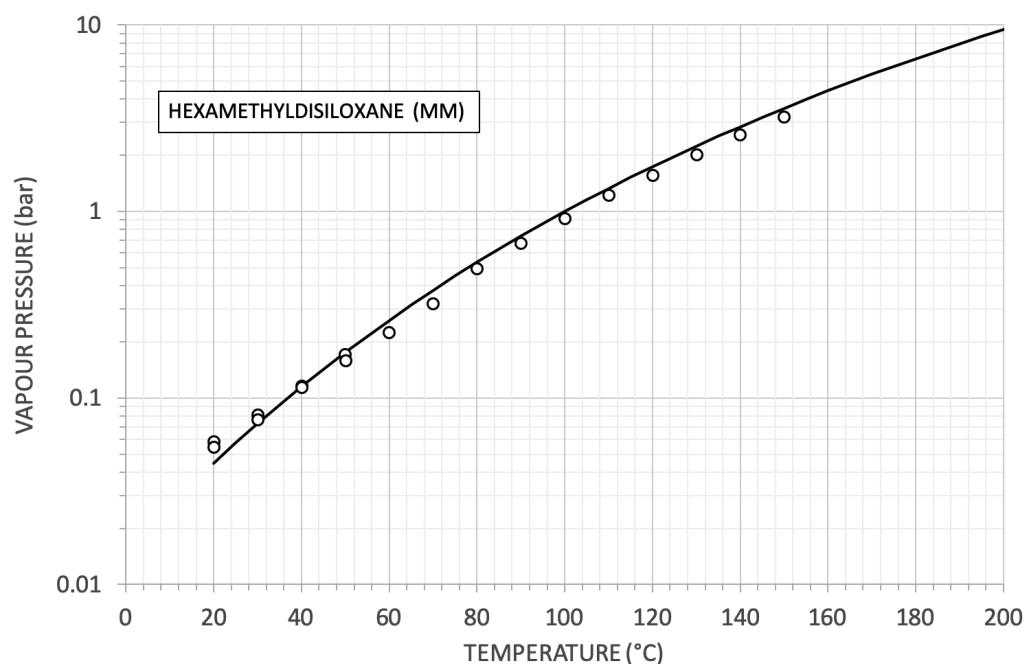


Figure 2. Vapour pressure of hexamethyldisiloxane (MM) as a function of temperature. The continuous line is from Aspen Plus[®] v9.0; the open circles are from our measured values.

The sample was placed repeatedly, for one hundred hours each time, in a muffle furnace at increasing test temperatures. Between each successive test the vapour pressure of the sample was measured.

In [35], the values of the sub-atmospheric vapour pressure, after each test, were compared with reference values (at the same temperatures) and the differences, correlated to the fraction of decomposed fluid, were assumed to represent an index of decomposition [30].

However, the methods followed in [30,35], appeared to overestimate the actual decomposition, as minimal degradation of the fluid produced non-condensable gases with significant over-pressure effects [34].

Therefore, we decided, after every temperature test, to consider only the variations in the vapour pressure near the atmospheric value, to estimate the variation of the normal boiling temperature and assume it represented an index of decomposition of the fluid. In this way, the misleading effects of the non-condensable gases were reduced. Only three values of vapour pressure were selected to estimate the normal boiling temperature (see Figure 3), and this, together with a relatively high temperature uncertainty (about one Celsius degree), unfortunately, introduced high uncertainties $u(T_B)$ in its calculated values (see Figure 4 and Table 2), due to the high $u(B)$ and $u(A)$ on the coefficients B and A of the used equation

$$\ln P = A + \frac{B}{T} \quad (1)$$

From Equation (1), the normal boiling temperature can be estimated by

$$T_B = \frac{B}{\ln P - A} \quad (2)$$

with a general uncertainty $u(T_B)$ equal to

$$u(T_B) = \sqrt{(dT_B/dB \times u(B))^2 + (dT_B/dA \times u(A))^2 + (dT_B/dP \times u(P))^2} \quad (3)$$

in which, $u(B)$ and $u(A)$ are the uncertainties of the coefficients B and A , respectively, and $u(P)$ is the uncertainty of the measured value of the pressure

Table 2 reports the values of the coefficients A and B after each test temperature, while Figure 3 and 4 show the resulting vapour pressure trends, and the corresponding values of T_B , respectively.

In Figure 3, the variation in the slope of the vapour pressure lines is evident, and, despite the high uncertainties, in Figure 4, a significant variation in the temperature T_B , can be seen at 450 °C. Figure 5 shows the confidence index of the variations of the coefficient B in the Equation (1); for the test temperature of 450 °C, the variation $\Delta B = |B - B_{ref}|$ results were significantly high, indicating a clear alteration in the fluid sample analysed. The parameter B has a direct physical meaning because it is also closely related to the heat of evaporation according to the Clausius–Clapeyron rule.

Table 2. Coefficients A and B of Equation (1) after the keeping of the sample of MM at different test temperatures, each time for one hundred hours.

Test Temperature (°C)	A	$u(A)$	B	$u(B)$
Reference	10.9653	0.78659	−4125.8982	293.2008
250	10.8103	0.7591	−4053.0637	285.3927
300	11.3394	0.75912	−4253.3055	284.539
350	10.1633	0.69293	−3825.6393	254.3471
400	10.0917	0.71663	−3776.8606	269.722
450	8.2482	0.57604	−3016.8684	215.1247

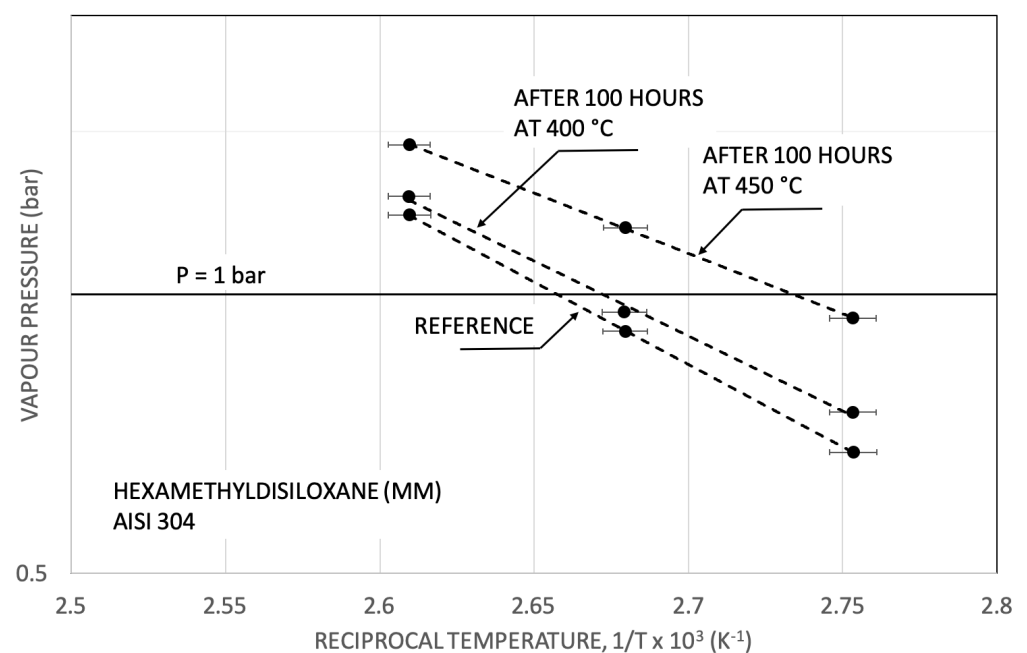


Figure 3. Vapour pressure for hexamethyldisiloxane (MM) near the ambient pressure after the fluid sample remained at three different temperatures for one hundred hours each time.

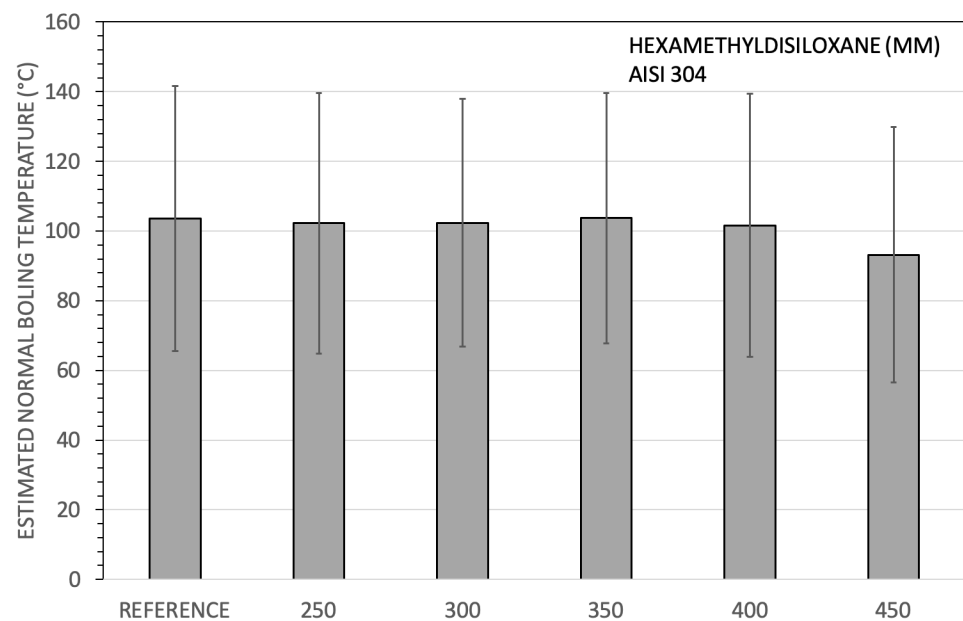


Figure 4. Normal boiling temperatures of a sample of hexamethyldisiloxane (MM) after it remained at different temperatures for one hundred hours each time.

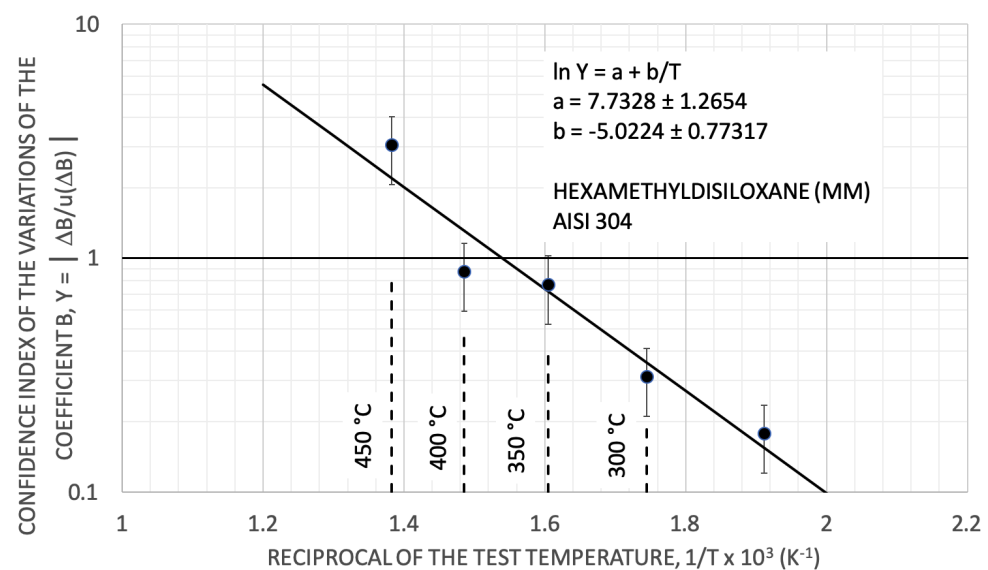


Figure 5. Relative variations in the B coefficient in Equation (1) for a sample of hexamethyldisiloxane (MM) after its keeping at different temperatures for one hundred hours each time.

In the case considered here, a temperature in the range 350 °C to 400 °C can be considered to be a limit working temperature value for hexamethyldisiloxane (without significant contamination, in AISI 304), a result which is in accordance with the conclusion in [34]. Some other papers and publications suggest maximum working temperatures for siloxanes of 400 °C to 425 °C. On the other hand, according to [38], samples of hexamethyldisiloxane in low carbon steel with air and probable humidity traces, decomposed substantially after about 312 h.

It is well known that the presence of contaminants greatly reduces the thermal resistance of working fluids. Clearly, only a chemical analysis can quantify the real degree of decomposition. However, the approach described here could be useful for a relative comparison among different pure fluids, and, after appropriate calibration, it could also provide an indication of the rate of decomposition, which probably is always present, even at relatively low temperatures.

For a fixed temperature, the decomposition could also increase with time in accordance with the kinetics governing the complex chemical reactions involved in the process. So, for a rough analysis of the possible effect of time on the decomposition, we considered a sample of MM at 350 °C for time intervals of 100 h each.

After each time interval, we measured the vapour pressure near the ambient pressure. In Figure 6, values of the resulting ratio $Y = |\Delta B/u(\Delta B)|$ as a function of time are shown. Despite the high uncertainty in the calculated values, an increase in Y with time is evident, suggesting an increase in decomposition, occurring significantly after about 300 h, when Y results were greater than unity. The corresponding variation in the normal boiling temperature was 1–2 °C, as can be seen in Figure 7.

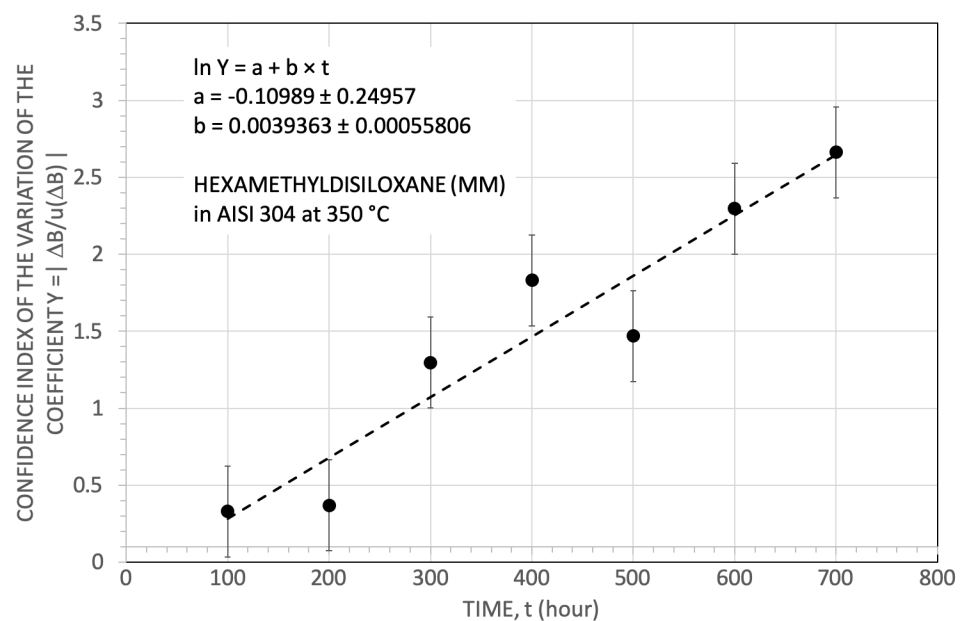


Figure 6. Relative variations (the confidence index) in the B coefficient in Equation (1) for a sample of hexamethyldisiloxane (MM) at 350 °C for time intervals of 100 h each.

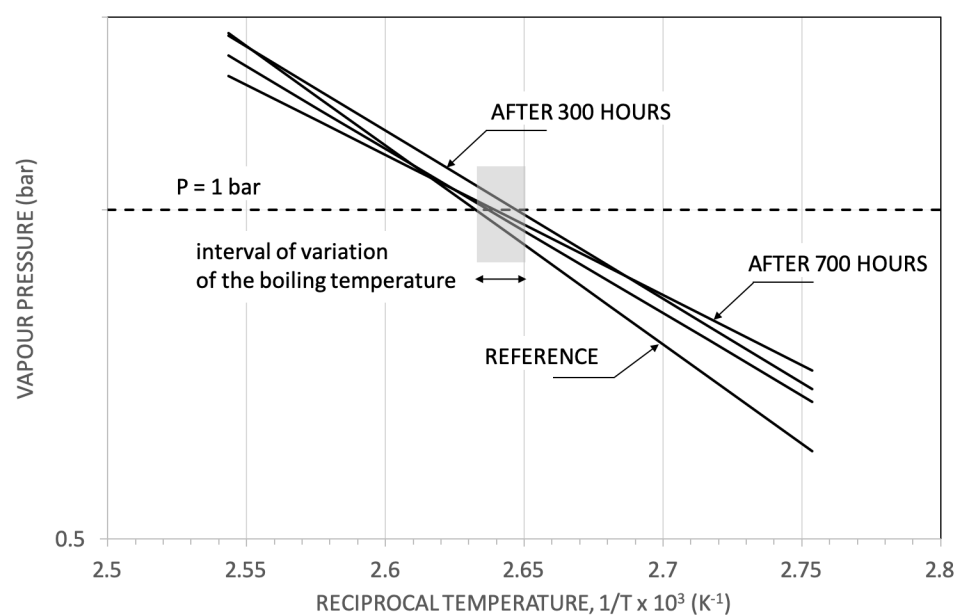


Figure 7. Vapour pressure for a sample of hexamethyldisiloxane (MM) at 350 °C after time intervals of 100 h each.

The decomposition of the working fluid with time has a generally negative effect on the thermodynamics of the cycles (see ([39], p. 148) and [40], for example), and, in the worst situation, it could damage the functioning of key engine components [15]. It is therefore important to have information on how decomposition proceeds over time.

3. Mixtures of Siloxanes as Working Fluids

In Table 3, there are some thermodynamic properties of the two first simpler methylsiloxanes, with a linear molecule (MM, MDM) and with a cyclic structure (D₃ and D₄). Hexamethylcyclotrisiloxane (D₃) has a freezing temperature of 64 °C at atmospheric pressure—as such, it is not really feasible as a working fluid in Rankine cycles using organic fluids. The linear methylsiloxanes with a molecular complexity greater than that of MDM have a boiling temperature which is excessively high, and, in our opinion, they are also not attractive as working fluids in Rankine cycles.

Table 3. Some thermodynamic properties of two linear and two cyclic siloxanes.

Compound	T_{cr}^a (°C)	P_{cr}^b (bar)	MW ^c	T_B^d (°C)	T_f^e (°C)	σ^f
MM (Hexamethyldisiloxane)	245.85	19.2	162.38	100.52	−68.22	29
MDM (Octamethyltrisiloxane)	291.25	14.6	236.53	152.55	−80	43.66
D ₃ (Hexamethylcyclotrisiloxane)	281.05	17.8	222.46	134	64	33.76
D ₄ (Octamethylcyclotetrasiloxane)	313.35	13.172	296.62	175	17.58	53.25

^a Critical temperature; ^b Critical pressure; ^c Molecular weight; ^d Normal boiling temperature; ^e Freezing temperature; ^f Parameter of molecular complexity: $\sigma = (dS/dT)_{0.7T_{cr}} \times T_{cr}/R$, with the derivative evaluated on the dew line, [39], p. 109.

Generally speaking, the molecular complexity of methylsiloxanes is very high and so is the parameter σ , as reported in Table 3. As a consequence, the slope of the saturated vapour line in a thermodynamic T-S diagram for these fluids is largely positive. On the other hand, the cooling during the expansion is relatively small, and, consequently, the thermal power recovered (in the recuperator) has to be high in comparison to the produced net power.

A second thermodynamic drawback is the typical high normal boiling temperature of methylsiloxanes, which implies high volumetric expansion ratios that, in turn, require two or three stage turbines, notwithstanding the low specific expansion work.

Nonetheless, as is well known, MM and MDM, owing to their low toxicity and low flammability, are frequently used as working fluids in Rankine cycles with an electric power size of about one MW.

Figure 8 shows the vapour pressure curves for MM, MDM and D₄. At a pressure of 0.05 bar, a practical reasonable minimum limiting value for the condensing pressure, the corresponding condensation temperatures are reported in Figure: 22 °C for MM; 65 °C and 84 °C for MDM and D₄, respectively. Thus, cycles with MDM or D₄ are normally adopted in cogenerative applications (or CHP plants).

Lately, many papers have investigated the use of non-azeotropic mixtures instead of pure fluids as working fluids in Rankine cycles. The potential advantages of the use of non-azeotropic mixtures are well known; the temperature “glides” (a continuous temperature variation) in evaporation (which is useful when the heat source is of variable temperature and when the required evaporation thermal power is a sensible fraction of the total input cycle thermal power) and in condensation.

The condensation “glide” could be useful when, in cogenerative systems, the maximum temperature of the cooling water and a minimum internal temperature approach are fixed.

Among the disadvantages of the use of mixtures are their heat transfer coefficients during evaporation and condensation that, generally, are lower than that of the pure fluids [41,42].

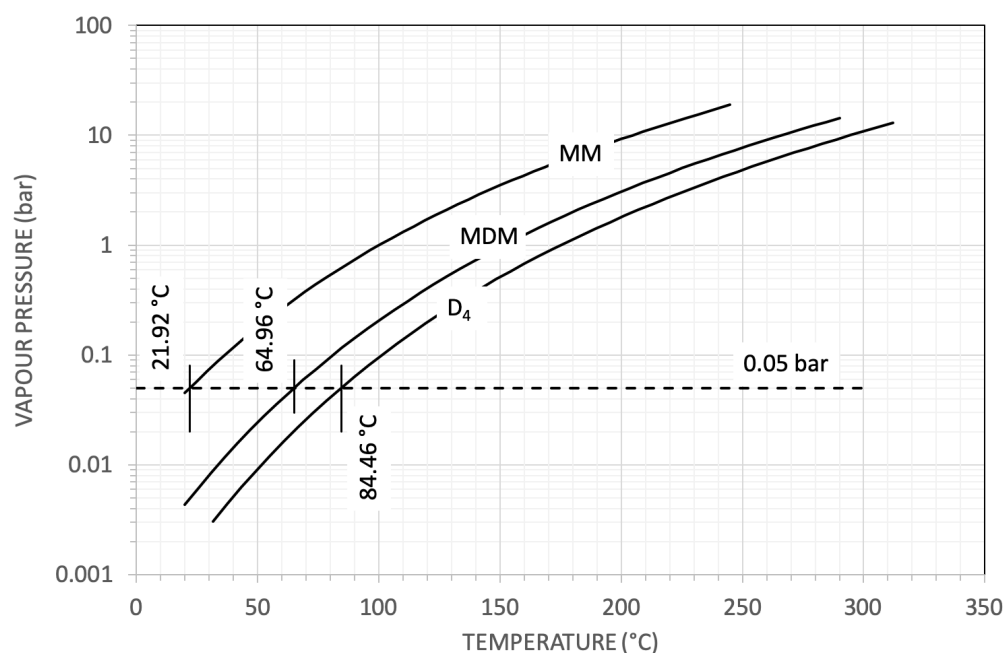


Figure 8. Vapour pressures curves for some siloxanes. From Aspen Plus[®] v.9.0.

For example, in [20], the authors analysed the performances of mixtures of MM and MDM in Rankine cycles and estimated increases of 1 to 14 percent in the required heat transfer areas of the evaporator, according to the mixture composition, against obtaining an increase of only 1 to 2 points in the exergetic efficiency in a CHP configuration.

In [43], the authors developed some performance evaluations for a hybrid solar-biomass plant in Ottana (Italy). Siloxane mixtures of MM and MDM were considered and compared with the use of pure MM. According to the authors, the net power and the annual net energy increased by about 1 to 2 percent and between 2 to 5 percent, respectively, but with an appreciable increase also in the required heat transfer surfaces (18 to 21 percent).

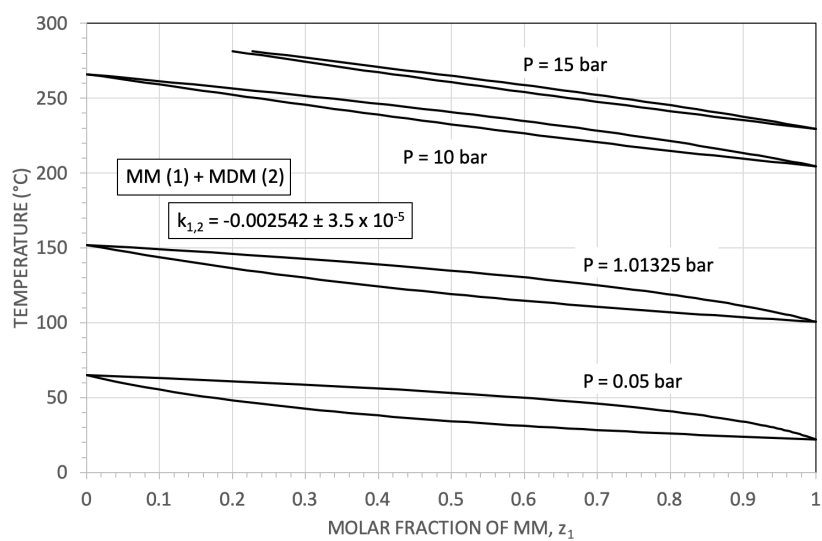
In [44], the authors, taking as a reference case a CHP plant using MDM as the working fluid, considered many binary (and some ternary) mixtures of linear (from MM to MD₆M) and cyclic (from D₃ to D₆) methylsiloxane, obtaining, in the best case, an increase in electrical efficiency from 18.7% to 20.6% (about two points).

From the literature data, in the case of siloxanes, the use of mixtures instead of pure fluids generally leads to a benefit in the conversion efficiencies, but with limited margins. On the other hand, the concrete possibility of a significant increase in the overall cost of the plant must be considered.

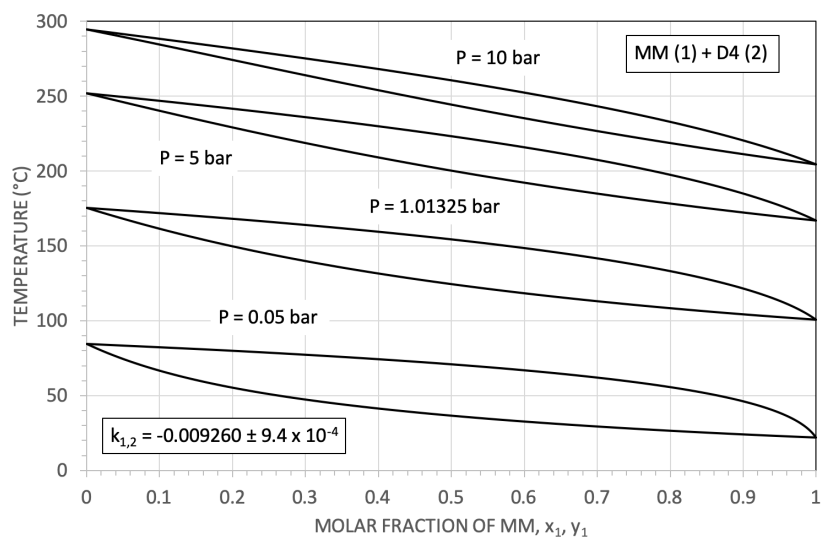
However, it is difficult to directly compare the results of the literature data with each other given the different assumptions for the design parameters and the calculation hypotheses. After a brief discussion of the approach followed here to evaluate the required thermodynamic properties, in the next sections, we will develop some further simple cycle thermodynamic analyses.

3.1. Evaluation of the Thermodynamic Properties of Some Siloxane Mixtures

From the data available in Aspen Plus[®] v.9.0 (from the NIST data bank), the binary interaction coefficients $k_{1,2}$ for the simple Peng–Robinson equation of state were evaluated for mixtures of MM and MDM, and for mixtures of MM and D₄. The regressed values and their standard deviation are shown in Figure 9, with some results of the calculated vapour-liquid equilibria at different pressures. The temperature “glides” were lower for mixtures of MM and MDM than the corresponding values for mixtures of MM and D₄, and, in both cases, the temperature differences significantly reduced with pressure.



(a)



(b)

Figure 9. Vapour-liquid equilibrium lines for mixtures of siloxanes. (a) T-xy diagram for MM/MDM at different pressures. (b) T-xy diagram for MM/D₄ mixtures.

In Figure 10, as an indicative example, some P-T envelopes and the critical locus for MM and D₄ mixtures are reported.

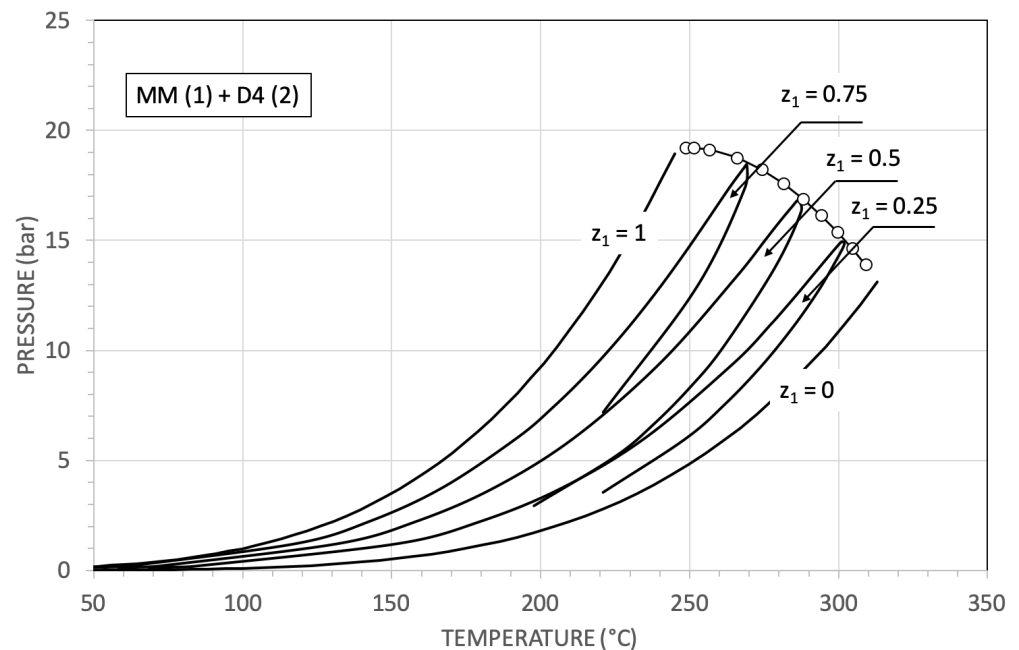


Figure 10. Pressure-temperature envelopes and critical locus for mixtures of MM/D₄ at different molar composition.

Both the mixtures seem rather “ideal”, with continuous and regular variations of the critical point with the composition. However, for any mixture, it is possible to obtain a continuous variation of the condensation pressure, for example, by varying the composition. This, generally, could itself provide a beneficial degree of freedom in the choice of the mixture.

In Figure 11, for example, for a dew temperature of 60 °C, the variations in the corresponding pressure and in the temperature “glide” with the composition are reported for the two mixtures considered. The maximum temperature difference between the dew and the bubble point at a molar composition of 0.5 for both the mixtures and the value for MM + D₄ was about double the corresponding value for the mixture MM + MDM.

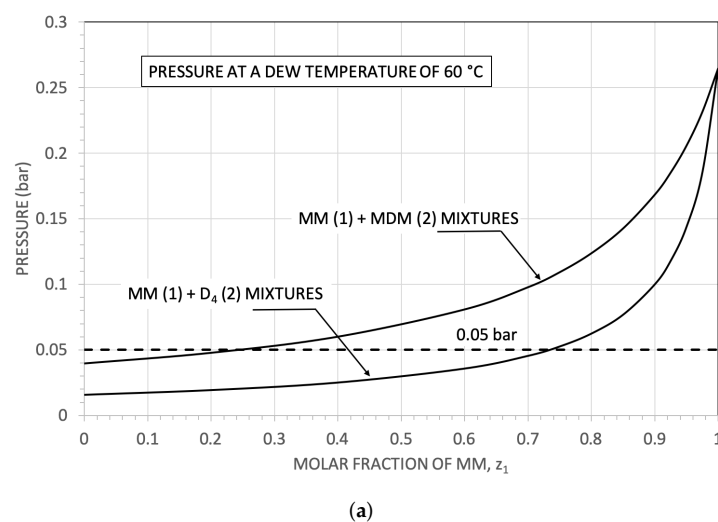


Figure 11. *Cont.*

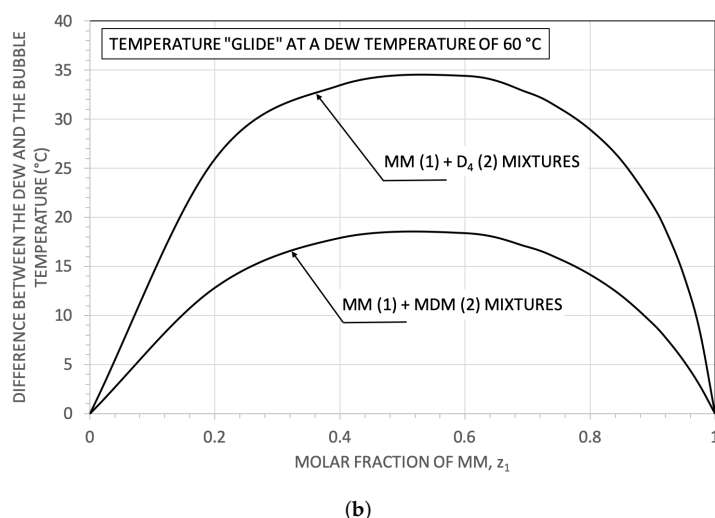


Figure 11. (a) Variation in the dew pressure and (b) variation in the temperature “glide” for two mixtures of siloxanes as a function of their molar composition. The dew temperature is fixed at 60 °C.

Fixing, for example, a functional pressure of 0.05 bar, at a dew temperature of 60 °C, this may be obtained with a molar composition of about $z_1 = 0.25$ and of about $z_1 = 0.75$ for mixtures of MM(1) + MDM(2) and MM(1) + D₄(2), respectively.

A comparison among bubble points, evaluated with the assumed thermodynamic model and the experimental values reported in [18], was carried out. Unfortunately, in the cited reference, the experimental results were reported only in a graphical form and the comparison can only be qualitative. Nonetheless, the results were completely acceptable.

3.2. The Performances of Siloxane Mixtures in Thermodynamic Cycles

With reference to the mixtures discussed in Section 3.1, we developed a thermodynamic analysis for Rankine cycles by recovering heat from a hot oil source (Therminol 66, [45]) at 300 °C considering a mass flow rate of one kilogram per second. The calculation assumptions are in Table 4. The typical cycle scheme assumed is provided in Figure 12.

At the condenser, we assumed cold water was available at 45 °C to be heated up to 55 °C, temperature levels which are compatible with the planned last generation district heating systems [46].

As constraints, we assumed a minimum condensation pressure of 0.05 bar, in accordance with the design indications of typical commercial available biomass boilers (see, for example, [15,44]) and a temperature of the thermal oil after cooling equal to 250 °C.

Table 4. Design parameters assumed for the thermodynamic cycle calculations.

Minimum internal temperature approach in the recuperator:	20 °C
Minimum internal temperature approach in the heater:	20 °C
Minimum internal temperature approach in the condenser:	5 °C
Temperature increase in the cooling water:	10 °C
Water inlet temperature:	45 °C
Oil hot temperature:	300 °C
Mass flow rate of the oil:	1 kg s ^{−1}
Superheating degree in the heater:	5 °C
Pressure drops:	none
(Isentropic) Turbine efficiency:	0.85
Pump efficiency:	0.8

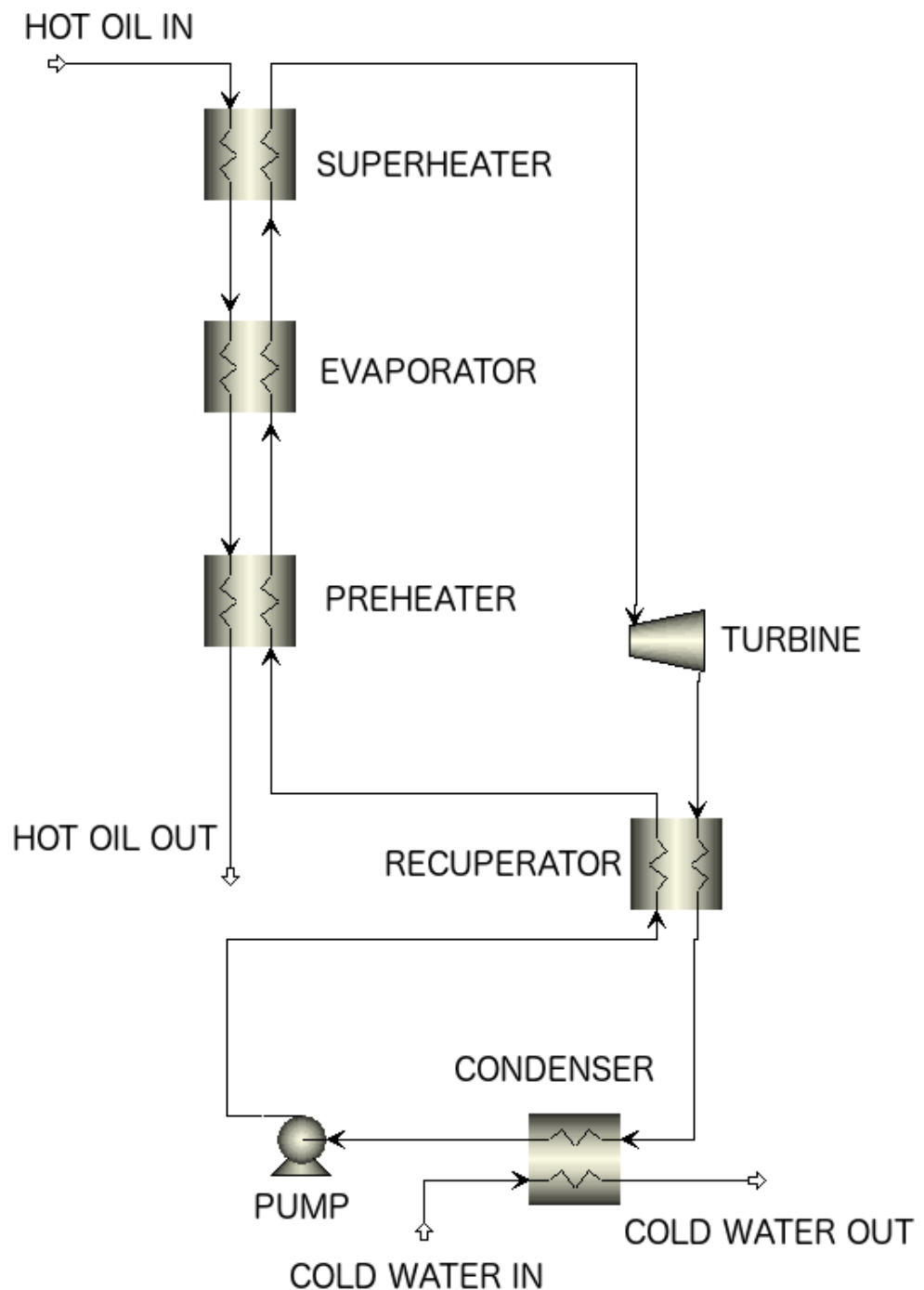


Figure 12. The considered thermodynamic cycle scheme. The corresponding $T - \dot{Q}$ diagrams for two cases are reported in Figure 14.

From Figure 13a, pure thermodynamic cycles using pure MM tended to excessively cool the hot source. Only cycles with pure D_4 , or with mixtures with a molar fraction of MM lower than 0.25, guaranteed a minimum oil temperature of 250 °C. On the other hand, according to Table 5, only a molar composition $z_1 = 0.25$ provided a condensation pressure equal to about 0.05 bar.

With respect to MM(1) + MDM(2), only a mixture with a molar composition $z_1 = 0.2$ provided the required minimum hot oil temperature and an adequate condensation pressure (see Figure 13b and Table 5).

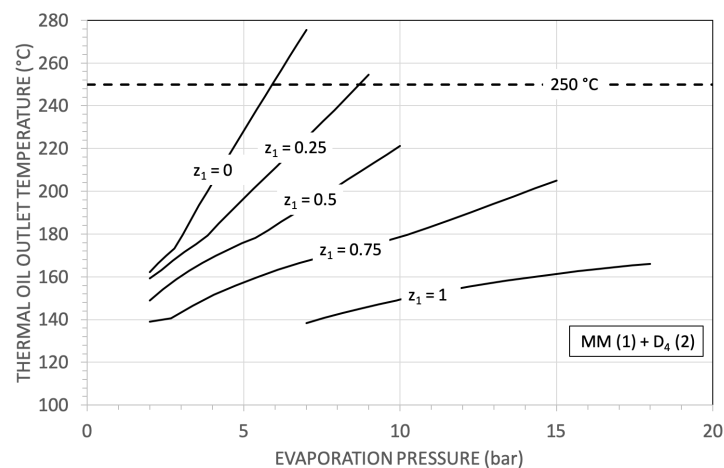
For the mixtures MM(1) + D_4 (2) ($z_1 = 0.25$) and for MM(1) + MDM(2) ($z_1 = 0.2$), the calculated efficiencies of the corresponding thermodynamic cycles were 0.253 and

0.264, respectively (Table 5). The two cycles, in a plane temperature–power, are shown in Figure 14.

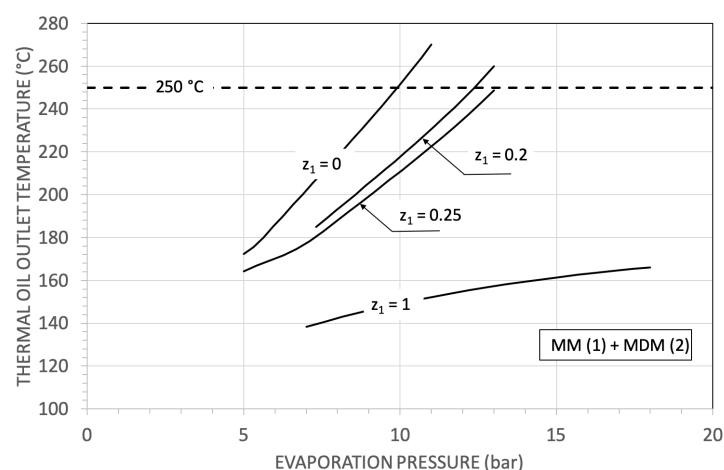
The better efficiency of the mixture MM(1) + MDM(2) ($z_1 = 0.2$) was substantially due to a lower *LMTD* at the condenser, about 9.5 °C, sixty percent of the corresponding value for the mixture MM(1) + D₄(2) ($z_1 = 0.25$) (Table 5). On the other hand, as a consequence, the corresponding condenser *UA* results were about 1.73 times greater.

Some results related to the turbine are shown in Table 6, for a reference isentropic power of one MW. The isentropic enthalpy drops were relatively low in both cases, but the volumetric expansion ratios results were high, 251 and 344 for the mixture MM(1) + D₄(2) and for MM(1) + MDM(2), respectively. The difference was substantially due to the higher evaporation pressure of MM(1) + MDM(2) (12.5 bar) with respect to that of MM(1) + D₄(2) (9 bar).

These high volumetric expansion ratios require at least two to three axial turbine stages to obtain high isentropic expansion efficiencies. The lower isentropic enthalpy drop for MM(1) + D₄(2) was a consequence of the greater molecular weight of D₄ compared to that of MDM (see Table 3).



(a)



(b)

Figure 13. Thermal oil outlet temperature from the heat recovery heat exchanger as a function of the evaporation temperature and for different mixture compositions, for (a) a mixture of MM and D₄ and (b) a binary mixture of MM and MDM.

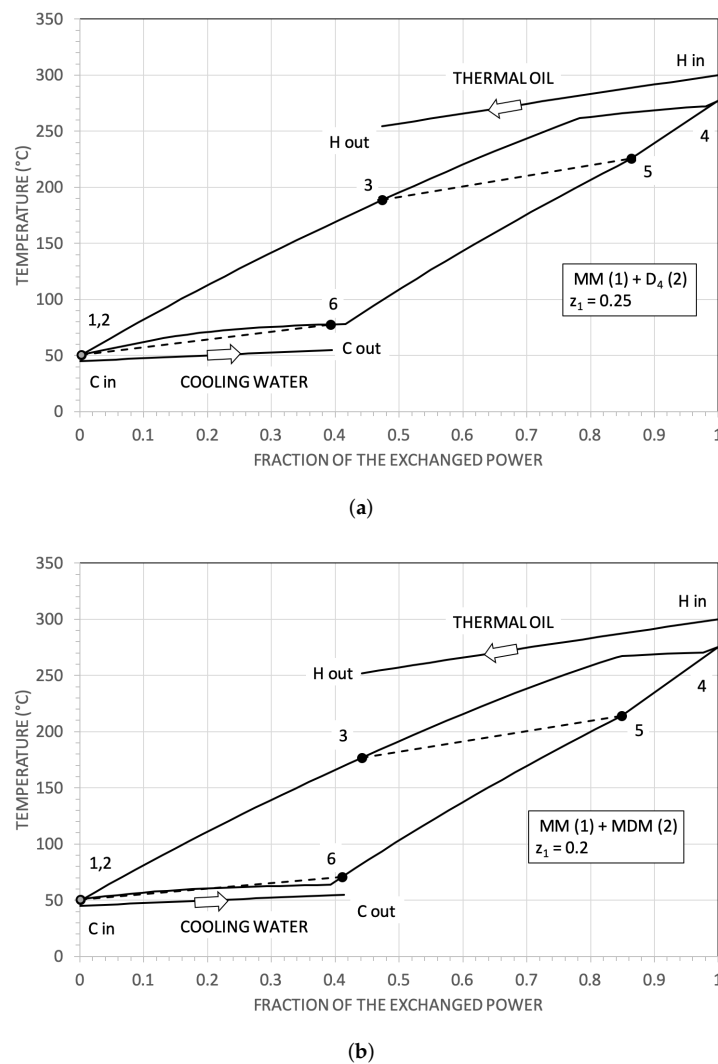


Figure 14. Two siloxane mixtures cycles, in the temperature - power exchanged plane, at optimal compositions and evaporation pressures. The design cycle parameters are shown in Table 4. In accordance with the simpler cycle configuration usually adopted, 1–2 represents the liquid compression, 2–3/5–6 the recuperator, 3–4 the pre-heating and the boiling, 4–5 the expansion in turbine, and 6–1 the condensation process. (a) for a mixture of MM(1) + D₄(2) at $z_1 = 0.25$; (b) for a mixture of MM(1) + MDM(2) at $z_1 = 0.2$.

Table 5. Some cycle results. Hot oil mass flow rate: one kilo per second.

Working Fluid	Cycle Efficiency (%)	Condensation Pressure (mbar)	Evaporation Pressure (bar)	$LMTD^a$ Condenser (°C)	$UA/\dot{W}^b$ Condenser (°C ⁻¹)
MM(1) + D ₄ (2) $z_1 = 0.25$ (molar fraction)	25.34	49.04	9.0	15.71	0.187
MM(1) + MDM(2) $z_1 = 0.2$ (molar fraction)	26.42	56.75	12.5	9.46	0.295

^a Average logarithmic mean temperature difference for the whole condenser; ^b Calculated total $U \times A$, the product of overall heat transfer coefficient U and heat transfer area A for the condenser per unit of useful power.

Table 6. Some turbine results. A comparison. Isentropic power one MW.

Working Fluid	Volumetric Isentropic Expansion Ratio ^a	Isentropic Enthalpy Drop (kJ kg ^{−1})	Size Parameter ^b (m)
MM(1) + D ₄ (2) z ₁ = 0.25 (molar fraction)	251.12	79.61	0.3752
MM(1) + MDM(2) z ₁ = 0.2 (molar fraction)	344.47	94.65	0.3294

$$^a VFR = \frac{\dot{V}_{out,S}}{\dot{V}_{in}}, [47]; ^b SP = \frac{\sqrt{\dot{V}_{out,S}}}{\Delta H_{25}^{0,25}}, [47].$$

4. Conclusions

From the previous discussion, regarding thermal stability, it follows that, in an inert environment, the thermochemical stability of the fluid samples analysed is naturally very high—at least up to 500 °C for MM in a gold-plated stainless steel container, with a nitrogen atmosphere. A method such as the differential scanning calorimeter could be a valid option for a first screening, as long as it is possible to use metal containers in steel even at high temperatures, with or without suitable sealing o-rings.

The measurement of the vapour pressure, for instance around the atmospheric value, for pure fluids, provided a good indication of the thermal stability of the working fluid candidate. However, in order to substantially improve the results, an accuracy in the measurement of temperatures at least one order of magnitude higher than that of our measuring system is required.

In any case, the vapour pressure measure was reconfirmed as a valid approach to analysing the thermo-chemical decomposition. For hexamethyldisiloxane (MM), a limit temperature of thermal stability of 300 °C to 350 °C was reconfirmed, in the absence of specific contaminants. However, at 350 °C the decomposition significantly progressed over time. A detailed analysis was conducted here only for MM, but the results are easily extendable to MDM as well, given its similar molecular structure.

The approach described here could be applied to any (pure) fluid. For mixtures of fluids, the measurement of vapour pressure could be replaced by isochore measurements.

With respect to the thermodynamics of the mixtures of polysiloxanes, in the cases considered, according to the assumptions made and to the selected thermodynamic models, the results suggest that:

- from a strictly thermodynamic point of view, for the considered mixtures, there was no significant improvement in the cycle efficiency compared to a pure fluid (for example, we obtained a value of about 25–26 per cent, the same as for pure MDM). On the other hand, the modest temperature “glides” obtained in condensation, closely follows the relatively low heating (10 °C) of the water used for the condensation.
- The isobaric temperature variations during a change of phase (with fixed composition of the mixture) generally decreased with increase in the bubble temperature. So, if the temperature “glide” in condensation is low, the corresponding lower “glide” in evaporation may result in a negligible contribution to the cooling of the heat source.

For the cases considered, good performances were obtained with a condensing pressure of about 50 mbar to 60 mbar. With pure MDM, for example, at the assumed condensation temperature, the minimum pressure would be only 37 mbar, which could be problematic for the design of the engine.

With mixtures, the design of the heat exchangers (in particular of the condenser) can be critical, both from the point of view of their geometrical configuration, and, in general, because of the limited knowledge of accurate values of the relevant necessary transport properties.

In the case of the mixture MM(1) + MDM(2), with z₁ = 0.2, for example, the values of the overall *UA* for the condenser per unit of useful power results were the same as that of pure MDM, i.e., about 0.3 °C^{−1}. Therefore, the correct value of *U* (the overall heat transfer coefficient) becomes crucial for the correct evaluation of the surface of the heat exchanger.

Finally, in the case of mixtures, it is possible by varying their composition to modify, to some extent, the design pressure, the critical point and the temperature “glide”, which, in principle, would enable adaptation of the engine to different power sizes.

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Abbreviations, Symbols and Subscripts

P	pressure (bar)
T	temperature ($^{\circ}\text{C}$ or K)
T_B	normal boiling temperature ($^{\circ}\text{C}$ or K)
UA	the product of overall heat transfer coefficient U and the heat transfer area A ($\text{W }^{\circ}\text{C}^{-1}$)
$u(X)$	measurement uncertainty for the physical quantity X (dimensions of X)
$\dot{V}_{in}$	inlet volumetric flow rate ($\text{m}^3 \text{s}^{-1}$)
$\dot{V}_{out, S}$	outlet isentropic volumetric flow rate ($\text{m}^3 \text{s}^{-1}$)
z	molar fraction
ΔH_S	specific isentropic enthalpy drop (J kg^{-1})

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