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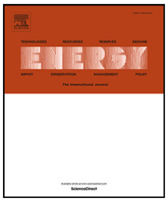

# Thermal stability of linear siloxanes and their mixtures

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## ABSTRACT

The working fluid thermal stability is one of the crucial features of an effective organic Rankine cycle. Hexamethyldisiloxane (MM - $C_6H_{18}OSi_2$) and octamethyltrisiloxane (MDM - $C_8H_{24}O_2Si_3$) are siloxane fluids currently exploited in high temperature organic Rankine cycles. However, data about their thermal stability are scarce or absent in literature. This manuscript presents a study of their behavior and decomposition at operating temperatures in the range 270 – 420 °C.

The assessment of thermal stability can be performed with several methods, which are either based on pressure anomalous variation in isothermal stresses or on the deviation of the saturation curves experimentally obtained before and after the fluid is thermally stressed. An enhanced method is proposed here, based on chemical analysis of both vapor and liquid phases of the sample before and after it is subjected to thermal stress. A comparison of the pre- and post-stress vapor–liquid equilibrium curve complements the analysis.

Results proved a higher stability for MM than for MDM. Moreover, due to the current interest in applying mixtures in organic Rankine cycles, an equimolar mixture of MM and MDM was also tested, which exhibit a behavior that appears to be different from the simple superimposition of pure fluid ones.

## 1. Introduction

In last decades, organic Rankine cycles (ORCs) gained a relevant role for power production from medium and low temperature energy sources, especially in the context of medium/low power range (few kW to hundreds MW) [1,2]. As working fluids, pure substances are the standard, but recent studies discuss the possible improvement of efficiency achievable by employing mixtures, see for instance [3]. Organic compounds exhibit a thermal stability limit which is not far from typical ORC maximum operating temperature. The thermal stability is a feature of the fluid itself and is influenced by temperature, exposure time to temperature and, mildly, by pressure [2]. The presence of contaminants within the fluid such as air, humidity, metals, and lubricants dramatically influences degradation. If the thermal behavior of the fluid is considered in relation to the presence of such substances the term thermochemical stability is used [2]. Decomposition products are detrimental for two reasons. On the one hand, they can compromise plant integrity, functionality or safety, since decomposition compounds are possibly corrosive, toxic, flammable or form solid particles which deposit on component surfaces. Essential parts can thus be damaged. On the other hand, significant decomposition and the consequent change of the fluid (mixture) thermodynamic properties and thus of the thermodynamic cycle, can deteriorate system performance. A typical example is the efficiency reduction entailed by the increased condenser pressure reached as volatile compounds form. Fluid degradation is unavoidable to some extent, except for very low working temperature, thus plant design guidelines have to consider the need of avoiding extensive decomposition and operating conditions should limit the penalization arising from the presence of degradation products. Chemically compatible materials must be employed, air and humidity leakages from external environment must be avoided, and actions should be taken to avoid the negative effect of decomposition products on the performance of the plant. Therefore, the assessment of the fluid thermal stability is crucial for a good system design. For example, Erhart et al. [4] analyzed working fluids from operating ORCs after several tens of thousand working hours, finding up to 34% of decomposition, thus leading to major performance losses.

Siloxanes are a class of organosilicon polymers and are working fluids largely employed in high temperature ORCs. Few thermal stability studies are available on pure siloxanes. A limit of 400 °C is reported by Colonna et al. [5] for siloxanes in general. A similar temperature range was provided by Angelino and Invernizzi [6] in case of cyclic siloxanes. Dvornic [7] studied extensively polysiloxanes but degradation temperatures are not mentioned. Preißinger [8] reports that siloxane MM can be safely used up to maximum temperature of 300 °C. Dai, Shi, and Qian [9] studied the thermal stability of MM assessing the influence of

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temperature, time and pressure, finding appreciable decomposition at a temperature level of about 240 °C. Chen et al. [10] recently simulated the pyrolysis of siloxane MM and proposed a series of reaction paths with the consequent indication of main decomposition products. The authors studied the thermal stability of both MM and MDM and results are reported in Keulen et al. [11]. Contrarily, no studies were found in literature about the thermal stability of linear siloxane mixtures.

The experience acquired during the campaign documented in [11] evidenced a limited capability of both the test method and the criterion selected to assess fluid stability in capturing the real entity of decomposition. Thus, an improved method, reported in this paper, was developed to investigate the thermal stability of hexamethyldisiloxane (siloxane MM), octamethyltrisiloxane (siloxane MDM), and of their equimolar mixture. Chemical analysis of the two phases (liquid and vapor) of a fluid sample before and after it undergoes thermal stress are compared, while the measured vapor–liquid equilibrium curve is used to complement the information derived from chemical analysis.

The paper structure is summarized in the following. Methods to assess the thermal stability available in literature are described in Section 2 along with their strengths and weak points. A new procedure capable of preventing ambiguity in the evaluation of thermal stability limits is described in Section 3. The facility employed for the documented research is described in Section 4, while the procedure for data analysis is presented in Section 5. Results are discussed in Section 6 and Section 7 reports the work essential conclusions.

## 2. Methods for determination of thermal stability

A first method for assessing the thermal stability of a fluid is to stress a sample at constant temperature $T$ while monitoring pressure $p$ over time (Blake et al. [12]). At constant temperature, if the nature of the sample of fluid changes due to thermal stress, pressure also changes, with respect to the initial value. Twelve chemical families of organic fluids (more than one hundred compounds) where tested using this method. This method was later used by Fisch and Verderame [13], Johns et al. [14,15], and Fabuss et al. [16]. Only massive decomposition can be detected using this principle, being the sensitivity to changes in sample composition quite low. However, its application is very simple. The thermal stability limit is determined by the stress temperature at which a predetermined limiting value of pressure rise per unit of time is passed.

A second method is based on the comparison of the vapor–liquid equilibrium pressure–temperature curve of a fluid sample before and after it underwent thermal stress. Limited quantities of decomposition products lead to a non-negligible deviation of the saturated vapor pressure curve, which leads the higher sensitivity of this method with respect to the previous one by Blake et al. [12]. The thermal decomposition of refrigerants was studied by Calderazzi and Colonna di Paliano [17] using this method in conjunction with chemical composition analysis of the liquid phase of the sample. The same method was used by Angelino and Invernizzi [18] to assess the thermal stability properties of refrigerant fluids having an ozone depletion potential equal to zero. Pasetti et al. [19] used statistical hypothesis tests to determine whether the deviation between the measured vapor–liquid equilibrium pressure–tmperature curves was due to decomposition instead of measurement uncertainties. They evaluated the thermal stability of hydrocarbons relevant for organic Rankine cycles applications.

In order to perform chemical analysis on both vapor and liquid fractions, the authors [11] modified the apparatus shown by Calderazzi and Colonna di Paliano [17] and Pasetti et al. [19], and applied the pressure–temperature vapor–liquid equilibrium curve comparison method to samples of siloxane fluids hexamethyldisiloxane (MM) and octamethyltrisiloxane (MDM) to study their thermal stability and decomposition products. The study envisaged the repeated stress of the same fluid sample at discrete temperature steps from 200 °C to 350 °C. Siloxane MM resulted to be stable up to 240 °C, while siloxane MDM to 260 °C (Keulen et al. [11]). The thermal stability limit is defined as the stress temperature corresponding to a deviation in the measured vapor pressure curves greater than the uncertainty related to the difference in vapor pressures themselves. Both the vapor and liquid fractions of the sample that underwent stress at the highest temperature depending on the fluid ($T = 340 - 350$ °C), were analyzed to determine their chemical composition. Negligible amounts of products formed upon decomposition were detected. The result of the chemical analysis and the vapor–liquid equilibrium curve deviation method are thus inconsistent. For the considered class of fluids, the ability of the employed method to provide reliable results seems questionable. The saturated vapor pressure of siloxanes is very low. Indeed, siloxane MM has a saturation pressure of about 43 mbar at an ambient temperature of $T = 20$ °C. Siloxane MDM is even less volatile, having a saturated vapor pressure of approximately 3.6 mbar at the same temperature. This means that very small amounts of products due to decomposition (methane as an example) can cause non negligible vapor pressure deviations. Thus, the thermal stability limit obtained comparing pressure–temperature vapor–liquid equilibrium curves can correspond to very negligible concentrations of products of decomposition, if applied to fluids that feature very low vapor pressures. Furthermore, the results of this method are related to how the tests are conducted. Indeed, the ability to appreciate the deviation between two vapor pressure curves depends on the temperature range at which the measurement is carried out. Low temperature means low vapor pressure, and large deviations in vapor pressure caused by small amounts of products of decomposition can be appreciated, while at high temperature the deviation is much more limited. Thus, the resulting thermal stability limit depends on the choice of the temperature interval of vapor pressure comparison. Furthermore, the portion of deviation between pressure–temperature curves that can be related to decomposition and thus the ability to detect a change in composition is directly related to the measurement uncertainty of pressure and temperature.

To increase the sensitivity of the method, the uncertainty associated with employed measurement devices and the temperature interval considered for the comparison of vapor–liquid equilibrium curves should be reduced. An increased sensitivity corresponds to detecting smaller and smaller amounts of products of decomposition whose engineering impact may depend on the peculiarities of each industrial application and on the properties of the products that are formed. It follows that, if the thermal stability limit is evaluated in terms of temperature, also the related entity of decomposition should be stated. Consequently, it is apparent the importance of obtaining an estimation of the concentrations of decomposition products as a function of stress temperature. In this way, the temperature range employed for the vapor–liquid equilibrium curve comparison and the value of pressure and temperature measurement uncertainty do not affect the result.

Also the pressure deviation during isothermal stress test method that was proposed by Blake et al. [12] needs to choose a limiting value for the pressure rise over time. Also in this case, the outcome of the test is affected by the chosen threshold.

## 3. Improved test procedure

By employing the methodologies proposed by Pasetti et al. [19], Calderazzi and Colonna di Paliano [17], and Blake et al. [12], the relation between the variation of vapor–liquid equilibrium pressure (or the deviation of pressure during the thermal stress) and the entity of decomposition is not readily obtainable (Section 2). Therefore, the authors developed an improved method for thermal stability determination, particularly suitable for organic fluids. It can be subdivided in the following 6 steps:

1. the chemical composition of the sample of fluid chosen for testing is analyzed using gas chromatography and mass spectrometry (GC–MS);

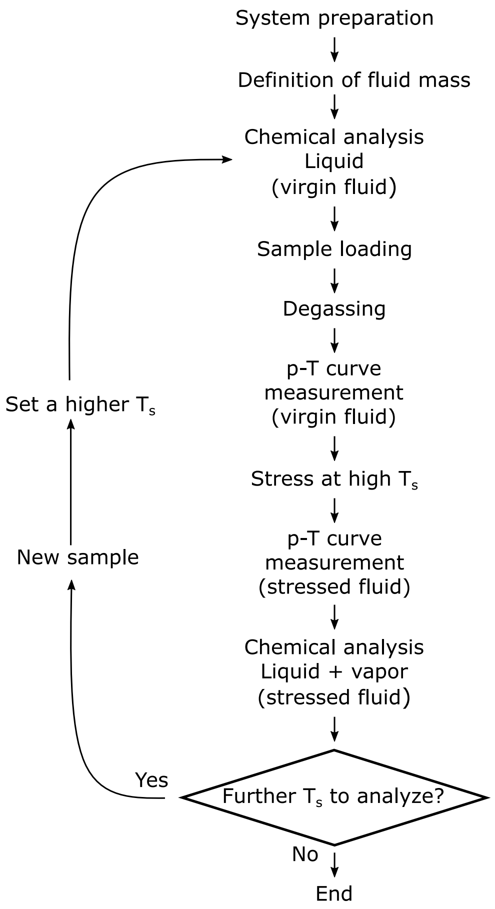

**Fig. 1.** Flow chart of the improved experimental procedure.

2. a small pressure vessel of 150 ml volume is filled with a predetermined amount of sample fluid and it is degassed to remove incondensable gases. The charged mass is 25 g for all cases of pure MM, pure MDM, and for their equimolar mixture. The design of the vessel allow for pressure and temperature measurements to be taken;
3. a thermal bath is used to control the temperature of the vessel to measure the pressure–temperature vapor–liquid equilibrium curve of the fluid under scrutiny;
4. the vessel is subjected at constant high temperature for at least 80 h (excluding the required ramp time) using an oven, to stress the sample fluid;
5. the same procedure of point 3. is applied to the stressed fluid to measure its vapor–liquid equilibrium curve which is then compared to the one obtained for the unstressed fluid. This information is complementary to the sample chemical composition data (see the next point 6.);
6. GC and MS are employed to analyze separately the liquid and vapor phase of the stressed fluid sample.

Fig. 1 reports a flowchart of the improved experimental procedure.

To obtain a full picture of the amounts of compounds formed upon decomposition as a function of stress temperature, the procedure being illustrated here is repeated varying the temperature of the stress phase. Each time, a completely new and virgin fluid sample is used. For varying temperature, Pasetti, Invernizzi, and Iora [19], Calderazzi and Colonna di Paliano [17], and Keulen et al. [11], stressed the same sample multiple times. The chemical composition of the sample, after being stressed at the highest temperature, was analyzed by both Keulen et al. [11](both liquid and vapor fractions) and Calderazzi and Colonna di Paliano [17] (liquid fraction only).

**Table 1**
Pressure transducer specifications. $u_{ins,95}(p)$ is the 95% confidence level uncertainty.

| Technology | Capacitance sensor |
|---|---|
| Measured quantity | Absolute pressure |
| Full scale | 1, 10, 35 bar |
| Expanded uncertainty $u_{ins,95}(p)$ | 0.6, 6, 21 mbar |

The procedure shown here gives an indication of the composition of decomposition products and their amounts in the vapor as well as the liquid fraction for varying temperature at which the fluid is stressed. Thus, the entity of decomposition as a function of stress temperatures is readily available. The result of this methodology is not dependent on assumptions on thresholds used to define the decomposition limit.

In industrial applications, knowing a maximum temperature limit that the process must not exceed to avoid decomposition of the working fluid is of paramount importance. As previously mentioned, this maximum temperature should be accompanied by an indication of the extent of decomposition, to be relevant. Indeed, the entity of decomposition increases with temperature and is present in a large range of temperatures. For this reason, from a physical point of view, taking a temperature level alone as thermal stability limit is not fully correct.

## 4. Experimental apparatus

The experimental apparatus is derived from the THErmal STAbility (THESTA) test rig presented in [11]. Fig. 2 reports a schematic of the improved design, called THESTA 2.0. The system is composed by:

- a test section (depicted in pink in Fig. 2), employed for vapor pressure measurements, thermal stress tests and loading of the selected sample;
- a connection section (depicted in green in Fig. 2), used to connect the vacuum pump and the helium tank used for leakage tests to the system;
- a loading section employed to load the fluid in the vessel.

All components are made of 316L stainless steel to prevent damages possibly caused by acid decomposition products, to assure a proper mechanical resistance and to limit the chemical interaction between inner surfaces and the fluid. The set-up is designed to carry out measurements on siloxane fluids and to permit the sampling of both liquid and vapor phases for chemical analysis. These kind of fluids feature a very low saturated vapor pressure, therefore the designed of the apparatus was carried out in order to measure pressures as low as 2 mbar. In order to cover the wide range of pressures corresponding to the temperature interval (−10, 350 °C) required to perform both saturation curve measurements and thermal stresses while preserving a good accuracy, the system is equipped with three pressure transducers of different full scale, 1, 10, and 35 bar, with a maximum operating temperature of 85 °C. All transducers are of capacitive type, with a nominal accuracy of 0.05% of the full scale, that combined with the measurement chain uncertainties yields a 95% confidence level expanded uncertainty of respectively 0.6, 6, and 21 mbar. In Table 1 the main pressure transducer data are reported.

Thermocouples, one of type $T$ and one of type K, are employed, respectively, for acquiring temperature along the saturation pressure measurement and the stress phase. Their 95% confidence level expanded uncertainty is 1 °C for $T$ the thermocouple and 2.5 °C for the K one. Thermocouples specifications are reported in Table 2.

The thermal bath (B) is used to set a stable temperature during vapor pressure measurements. The heat transfer oil can be employed

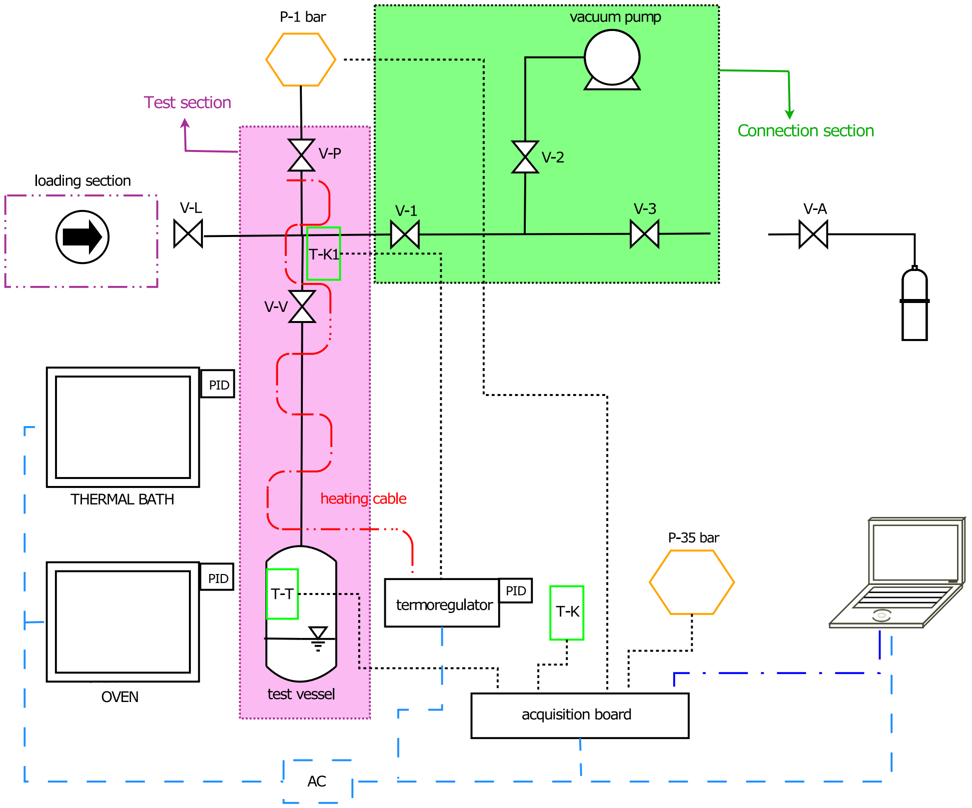

**Fig. 2.** Schematic of the improved version, the THESTA 2.0: vertical oven, thermal bath, (AC) AC power supply, (PID) control panel for temperature, (PC) personal computer for system control and data acquisition, (V-1...V-V) high pressure valves, (T-K and T-T) thermocouples for temperature measurement, (P-1, P-35) pressure transducers, (T-K1) thermocouple for temperature control of the heating cable.

**Table 2**
Thermocouples specifications. $u_{ins,95}(T)$ is the 95% confidence level uncertainty.

| Thermocouple type | T | K |
|---|---|---|
| Measurement interval | −133 – 400 °C | −270 – 1370 °C |
| $u_{ins,95}(T)$ | 1 °C for $-133 \le T \le 133$ °C<br>$0.0075T$ for $T > 133$ °C | 2.5 °C for $-270 \le T \le 333$ °C<br>$0.0075T$ for $T > 333$ °C |

from −20 °C to 200 °C. A PID controller regulates the temperature with a stability of ±0.02 °C.

The thermal stress is carried out by the furnace (F), where temperature can be controlled from 25 to 1200 °C and kept within ±2 °C of the setpoint value. The controller can be programmed to attain a predetermined increasing or decreasing ramp and to maintain a constant temperature for a predetermined time. The non-condensable gas removal is achieved by means of a vacuum pump.

To perform chemical analysis, the test vessel is isolated and detached from the system, after having minimized the vapor quality by cooling the vessel to −20 °C. In such a way the mass of fluid trapped outside the vessel between valve V-V and the pressure transducer P-1 is also minimized. The vessel is then pressurized up to 5 bar with a mixture of known composition of helium, nitrogen, and argon to dilute vapor components and to provide a carrier gas for the analysis. Indeed, the vessel is in two-phase conditions and the pressure is well below ambient one. Pressurization of the vessel is therefore needed to inject the sample in the GC. Finally, the vessel is connected to the gas chromatograph for the vapor phase analysis. The liquid phase sample is on the other hand collected at ambient pressure by opening the vessel and analyzed resorting to a gas chromatograph whose capillary column is connected to a FID (flame ionization detector) and to a (MS) mass spectrometer.

The overall design of the improved system results from the need of reducing as much as possible the portion of the setup containing the fluid and not subjected to high temperature during the stress phase. Indeed, in the works by Calderazzi and Colonna di Paliano [17], Pasetti, Invernizzi, and Iora [19] and Keulen et al. [11] the pressure was monitored along the thermal stress. Measuring pressure at the required high temperature entail non-negligible issues of sensor drift which would be for instance managed by building pressure–temperature calibration surfaces. To prevent such complexity, the mentioned researches were performed keeping pressure transducers at room temperature through an increase of the length of the pneumatic line connecting the sensor to the vessel. Such solution determines vapor condensation within the line and the condensate is not subjected to the thermal stress. At test conclusion the stressed sample is diluted by this unstressed liquid fraction. As a consequence, the relative fraction of decomposition products results lower as well as the deviation to the saturation curve.

In the improved system, the volume subjected to thermal stress is composed by the test vessel and the pipe connected to valve V-V. This volume is entirely contained in the oven during the stress phase, hence all the fluid under scrutiny is stressed. This requires to accept the impossibility of simply monitoring the pressure during the stress phase. However, due to its low sensitivity, the pressure deviation method during isothermal stress tests was abandoned as criterion for thermal stability analysis.

The maximization of the volume of fluid under stress entails one more positive consequence in case mixtures are tested. Portions of the test section at very different temperatures, may contain vapor or liquid with different compound concentration, depending on their density and volatility. This would lead to a mixture composition in the test vessel different from the expected one. The total volume of the system was reduced from 230 ml to about 170 ml.

When saturation pressure is measured, only the vessel is contained in the bath. Stratification between the pressure transducer P-1 and the vessel should be avoided. If a temperature gradient is present in the system, it can affect the temperature measurement itself and also the vapor pressure measurement, since a variation in temperature corresponds to a variation of density. To avoid stratification, a heating cable is placed along the pipe connecting the test vessel to the pressure transducer P-1. This system is effective for temperature higher than the ambient one, while for temperature below ambient an error is still present, though limited.

## 5. Data analysis

Vapor–liquid equilibrium (VLE) measurements are used to complement chemical analysis. The procedure employed to analyze the experimental data is reported in detail in [11] and is briefly recalled here.

### 5.1. VLE measurements

The $[p, T]$ values for each set point temperature of the thermal bath are obtained by averaging the pressure $p_{i,k}$ and temperature $T_{i,k}$ data recorded over 10 min of acquisition at time interval 5 s:

$$T_i = \frac{1}{n}\sum_{k=1}^{n} T_{i,k}, \tag{1a}$$

$$p_i = \frac{1}{n}\sum_{k=1}^{n} p_{i,k}, \tag{1b}$$

where the subscript $k = 1, 2, \ldots, n$ denotes the acquired samples for each of the $i = 1, 2, \ldots, m$ measurements at different set point temperature of the thermal bath. The variability of acquired data around the mean value can be expressed by evaluating the sample variances $s^2_{T_i}$ and $s^2_{p_i}$ of mean temperature $T_i$ and mean pressure $p_i$ respectively:

$$s^2_{T_i} = \frac{1}{n-1}\sum_{k=1}^{n} \left(T_{i,k} - T_i\right)^2, \tag{2a}$$

$$s^2_{p_i} = \frac{1}{n-1}\sum_{k=1}^{n} \left(p_{i,k} - p_i\right)^2, \tag{2b}$$

Uncertainties related to $T_i$ and $p_i$ are calculated taking into account the uncertainty coming from instrument calibration ($u_{ins}(T)$ and $u_{ins}(p)$) and the dispersion (namely the variances $s^2_{T_i}$ and $s^2_{p_i}$) of acquired samples:

$$u^2\left(T_i\right) = u^2_{ins}(T) + s^2_{T_i}, \tag{3a}$$

$$u^2\left(p_i\right) = u^2_{ins}(p) + s^2_{p_i}. \tag{3b}$$

This procedure holds for each measured $p - T$ curve.

### 5.2. Chemical analysis

Regarding chemical analysis, the adopted procedure is slightly different for liquid and vapor. For the vapor phase, the association between chromatogram peaks and compounds is based on the comparison with a reference chromatogram obtained with a mixture of known species. Indeed, the time at which a compound is eluted (called retention time, $RT$) depends on the compound only, if all other instrument parameters are kept constant. Thus, by comparing the retention time of each peak with the one on the reference chromatogram it is possible to identify the species present in the sample. On the quantitative side, the concentration of each compound is obtained through the application of a response factor, that relates the actual response of the detector (in terms of chromatogram peak area) to the concentration.

The test vessel is pressurized with inert gas before the analysis and, accordingly, this needs to be considered as data are processed. In fact, the analysis is performed at ambient temperature $T_{amb}$, corresponding to a pressure in the vessel, prior to dilution, $p\left(T_{amb}\right)$. The vessel is then pressurized and the overall pressure can be expressed, with the hypothesis of ideal mixture, as

$$p = p_{DG} + p_{ND} = p x_{DG} + p_{ND}, \tag{4}$$

where $p$ is the overall pressure in the vessel after dilution, $p_{DG}$ is the partial pressure of dilution gases, $p_{ND}$ is the pressure in the vessel before the dilution, and $x_{DG}$ is the molar fraction of dilution gases. By obtaining $x_{DG}$ from Eq. (4), it is possible to calculate the molar fraction of each compound $x_i$ in the vessel before dilution as

$$x_i = \frac{x_{i,dil}}{1 - x_{DG}} = \frac{x_{i,dil} \cdot p}{p_{ND}}, \tag{5}$$

where $x_{i,dil}$ is the molar fraction of each compound after dilution (i.e. the concentration measured by the instrument).

Regarding the liquid fraction, the mass spectrometer detector provides a chromatogram with a mass spectrum (in terms of abundance as a function of mass-to-charge $m/z$ ratio) for each detected peak. The identification of the various peaks is obtained by comparison of each mass spectrum with a reference standard. This permits the identification of the species present in the liquid sample. A quasi-quantitative information on the relative amounts of each compound is provided by the chromatogram obtained with the FID (flame ionization detector), being this type of detector preferable with respect to the spectrometer for quantitative analysis. Each peak of the FID chromatogram is associated to a compound by comparison with the mass chromatogram provided by the MS, since compounds are eluted in the same order from the two columns and the shape of peaks is similar. The FID gives a response that is proportional to the mass fraction of each compound. The molar fraction is then easily obtained knowing the molar mass of each species.

## 6. Results

The thermal stability of siloxane MM and MDM was tested using the methodology described in Section 3. The fluids were supplied by Clearco Products Co. and were used without further purification. The supplier states that the sample of siloxane MM contains <0.1% of pentamethyldisiloxane ($C_5H_{15}OSi_2$) and <0.5% of trimethylsilanol (MOH, $C_3H_{10}OSi$). Regarding siloxane MDM, the sample is declared to contain <0.1% of dodecamethylcyclohexasiloxane ($D_6$, $C_{12}H_{36}O_6Si_6$), <0.1% of decamethylcyclopentasiloxane ($D_5$, $C_{10}H_{30}O_5Si_5$) and <0.1% of octamethylcyclotetrasiloxane ($D_4$, $C_8H_{24}O_4Si_4$). Since the result of chemical analysis of the experimental campaign reported by the authors in [11] was a negligible decomposition after stress at temperature $T_s = 340 - 350$ °C, the experiments presented here were carried out mainly at higher temperatures, namely at 270 °C, 350 °C, 390 °C, and 420 °C for both MM and MDM. For MDM only a test at 310 °C was added, to verify the peculiar non-monotone pattern of VLE curves for increasing stress temperature. VLE measurements are used as complementary data to chemical analysis.

### 6.1. Siloxane MM

Siloxane MM was tested at stress temperature $T_s$ of 270 °C, 350 °C, 390 °C, and 420 °C. In the following, results of VLE measurements, and chemical analysis are reported.

#### 6.1.1. Pressure deviation in VLE measurements

Fig. 3 reports the VLE curve measured for virgin fluid samples used for the stress test at 270 °C, 350 °C, 390 °C, and 420 °C, compared with values predicted by RefProp and with data reported by Stull [20] and Abbas et al. [21]. A different sample was used for each stress temperature, thus the virgin fluid VLE curve was measured each time and four different sets of data are shown. The accordance between experimental points of this work and those predicted by RefProp and

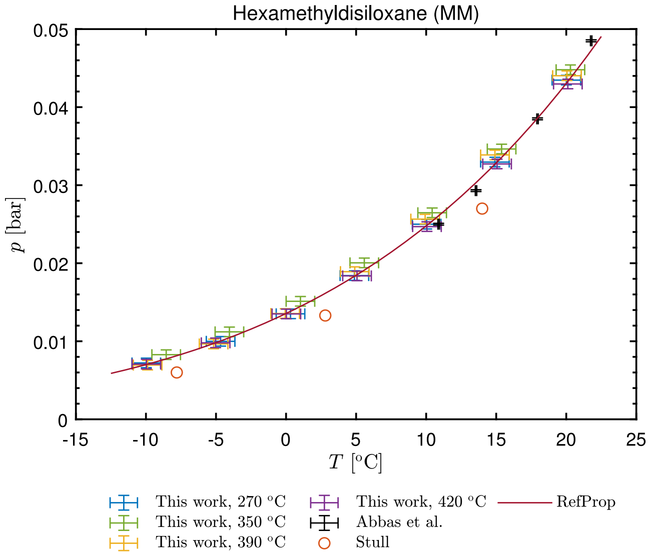

**Fig. 3.** Experimental saturation curve of virgin MM employed for test at $T_s \in [270\,^{\circ}\mathrm{C}, 420\,^{\circ}\mathrm{C}]$, in the range $[-10\,^{\circ}\mathrm{C}, 20\,^{\circ}\mathrm{C}]$, compared with the curve predicted by RefProp® and with data published by Stull [20] and Abbas et al. [21].

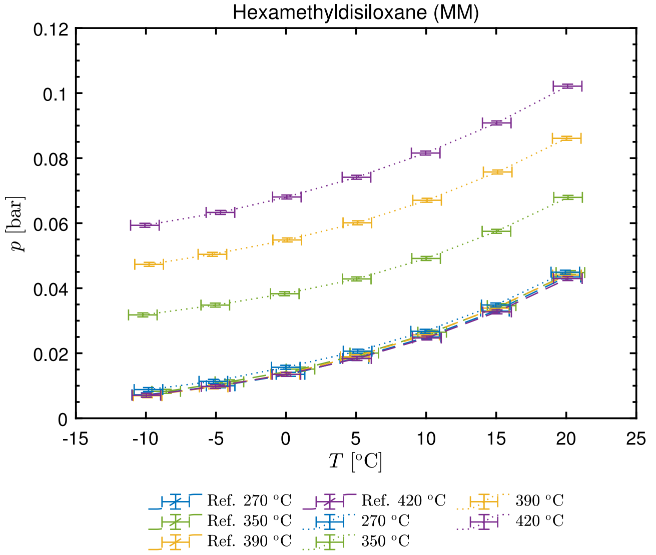

**Fig. 4.** Comparison of VLE curves of MM samples stressed at $T_s \in [270\,^{\circ}\mathrm{C}, 420\,^{\circ}\mathrm{C}]$. Measurements of the reference (virgin) fluid (dashed lines) along with those performed after the fluid underwent thermal stress (dotted lines), with 95% confidence level uncertainties.

reported by Abbas et al. [21] is very good. Data reported by Stull [20] seem detached from the others. However, experimental uncertainty related to these measurements is not reported, thus a proper comparison cannot be carried out.

The comparison of VLE measurements performed on the reference fluid relative to each stress temperature $T_s$ and on the stressed samples is reported in Fig. 4. The reference fluid data are, of course, the same of those presented in Fig. 3 and are reported connected by a dashed line, as opposed to the stressed fluid VLE data, which are distinguishable by the dotted line. The deviation is limited for $T_s = 270\,^{\circ}\mathrm{C}$, where uncertainty bars are partially overlapped to the virgin fluid ones. For increasing stress temperature, however, the deviation becomes clear. For temperature of stress from 270 °C to 420 °C, a monotone trend of increasing mean level of VLE pressure is observed, clearly pointing out the decomposition of the fluid.

#### 6.1.2. *Chemical analysis*

For the stressed sample liquid and vapor fraction were chemically analyzed, while only on the liquid phase was analyzed for the virgin fluid. Results in terms of percentage molar fractions of both vapor liquid are shown in Fig. 5. Regarding the liquid phase (Fig. 5(a)), virgin and stressed fluid composition are compared. The reference fluid contains unidentified hydrocarbons $C_6H_{12}$ and $C_6H_{14}$, and trimethylsilanol (MOH) as impurities. For increasing stress temperature very small quantities of both cyclic ($D_3$,[1] $D_4$[2]) and linear ($MD_2M$[3], $MD_3M$[4]) siloxanes appear in traces. The notation $M^{C2H5}M$ means that an ethyl $C_2H_5-$ radical substituted a methyl $CH_3-$ one, thus giving ethylpentamethyldisiloxane ($C_7H_{20}OSi_2$). The main decomposition product is MDM, that was not detected in the reference fluid. The impurity MOH seems to undergo decomposition. A detailed view of MM is reported, in linear scale: the quantity of components formed upon decomposition is negligible, since they cause a small variation of the molar fraction of the main component, always above 99.4%.

Fig. 5(b) depicts the analysis results for the vapor phase. Main decomposition products are light hydrocarbons ($CH_4$, $C_2H_4$, and $C_2H_6$) and results of the oxidation of carbon ($CO_2$ and CO). Methane is the most abundant species and the amount dependence on stress temperature is clear; from about 1% at 270 °C to about 56% at 420 °C. Increasing quantities of both ethane and ethylene are found, with the former reaching about 15% after the highest stress temperature. The presence of carbon monoxide and carbon dioxide is an indicator of imperfect degassing, which, however, is really difficult to achieve for fluids featuring such low vapor pressures. The decrease of both $CO_2$ and CO at 420 °C may be explained by the finite amount of oxygen in the sample, which limits the formation of carbon oxides, with respect to the huge amount of organic fluid available for decomposition reactions, which makes hydrocarbon fractions increase. Last, but not least, it must be recalled that the presented molar fractions are referred to the whole vapor phase, thus accounting for the presence of high boiling compounds such as MM, that cannot be detected by the employed GC column.

It is worth noticing that the dominant presence of light hydrocarbons as decomposition products in the vapor phase as well as of MDM in liquid phase was expected and it is also in accordance with the pyrolysis reaction paths predicted by simulations in [10]. Similarly, the presence of $CO_2$ and CO, ascribed to imperfect degassing, is compatible with simulation results presented in [22] where decomposition reaction paths in presence of oxygen were proposed.

### 6.2. *Siloxane MDM*

Siloxane MDM was tested at stress temperature $T_s$ of 270 °C, 310 °C 350 °C, 390 °C, and 420 °C. VLE measurement results, confidence index analysis and chemical analysis are reported in the following.

#### 6.2.1. *Pressure deviation in VLE measurements*

As for all other tests, the VLE curve of the reference virgin fluid was measured. Fig. 6 reports the VLE curve of the virgin fluid sample used for the stress test at 270 °C, 350 °C, 390 °C, and 420 °C, compared with values predicted by RefProp and with data reported by Stull [20]. In this case also, a different sample is prepared for each stress test. The accordance between experimental data and those predicted by RefProp is fairly good. For low temperatures, the presence of residual air impurity is noticeable as an increase of measured pressure. The degassing was performed through repeated heating, cooling (to condense as much as possible the organic fluid) and degassing cycles. It is has to be noticed

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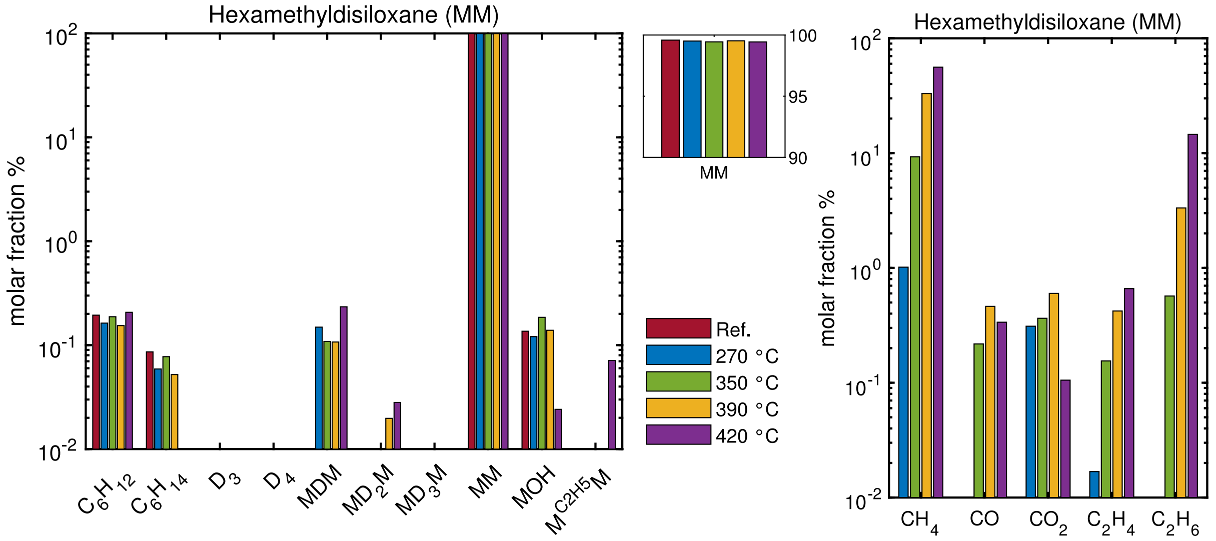
[1] Hexamethylciclotrisiloxane – $C_6H_{18}O_3Si_3$.
[2] Octamethylciclotetrasiloxane – $C_8H_{24}O_4Si_4$.
[3] Decamethyltetrasiloxane – $C_{10}H_{30}O_3Si_4$.
[4] Dodecamethylpentasiloxane – $C_{12}H_{36}O_4Si_5$.



(a) *Liquid phase.* (b) *Vapor phase.*

**Fig. 5.** Chemical analysis of MM samples.

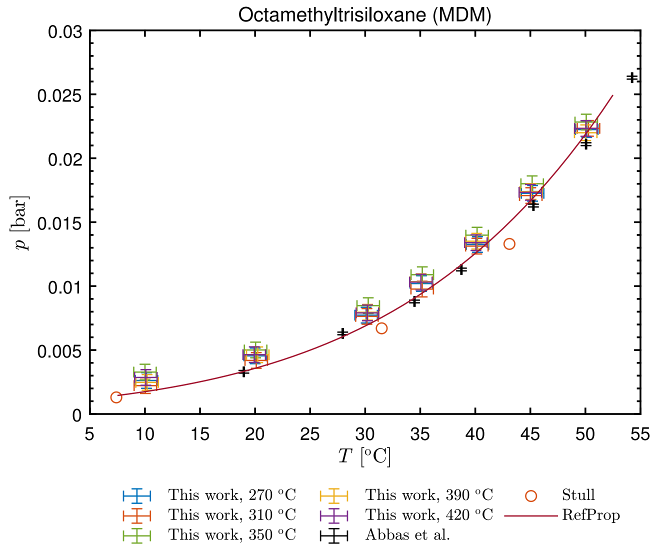


**Fig. 6.** Experimental saturation curve of MDM, in the range [5 °C, 55 °C], compared with the curve predicted by the thermodynamic library RefProp® and with data published by Stull [20] and Abbas et al. [21].

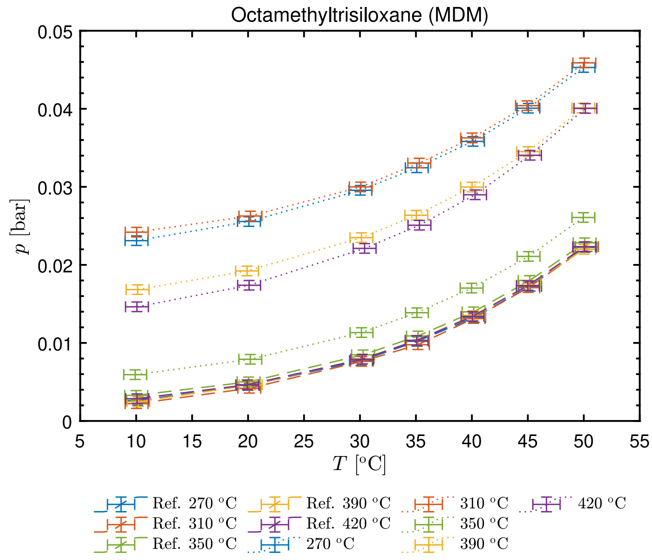


**Fig. 7.** Comparison of VLE curves of MDM samples stressed at $T_s \in [270\,°C, 420\,°C]$. Measurements of the reference (virgin) fluid (dashed lines) along with those performed after the fluid underwent thermal stress (dotted lines), with 95% confidence level uncertainties.

that low-volatility compounds as siloxanes (saturation pressure as low as 0.1 mbar at $T = -20\,°C$ for MDM) require a high performance vacuum pump for degassing, since vapors exhibiting saturation pressure below the minimum value attainable with the pump cannot be extracted by the vessel, acting as non-condensable gases. Thus, to improve the degassing, the removal of non-condensable gases was carried out at 20 °C (corresponding to a saturation pressure of MDM slightly higher than the minimum one achievable by the vacuum pump) instead of −20 °C (as for MM).

A comparison of VLE measurements carried out before and after siloxane MDM underwent thermal stress is reported in Fig. 7. Reference fluid data (virgin) are reported with dashed line, while data pertaining to the stressed fluid are connected by dotted lines. Appreciable deviations are observed. The variation of the mean level of the VLE curve is non-monotone for increasing stress temperature, being pressure relative to $T_s = 270\,°C$, $310\,°C$ the highest, and the one relative to $T_s = 350\,°C$ the lowest. However, the deviation is clear at any temperature.

### 6.2.2. *Chemical analysis*

The results of the chemical analysis that were performed on samples of virgin and stressed MDM are shown in Fig. 8. The liquid fraction (Fig. 8(a)) of the reference fluid contained impurities of siloxanes, namely $D_4$, MM, $MD_2M$, and MOH, probably coming from the production process. $D_3$, $D_5$,[5] $MD_3M$, $MD_4M$,[6] and $MD_5M$,[7] which were not present in the reference fluid, formed as a result of decomposition. Traces of $M^HM$ are detected after $T_s = 420\,°C$, where this notation means that an hydrogen atom substituted a methyl group, thus forming pentamethyldisiloxane. For increasing stress temperature, molar fractions of all decomposition products increase. Relative quantities

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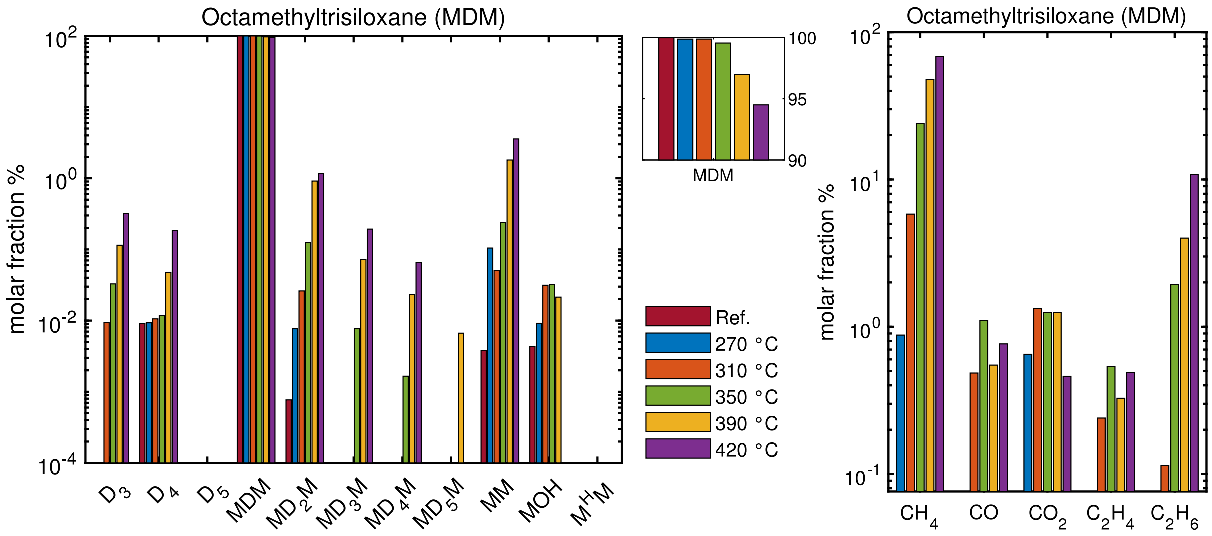
[5] Decamethylcyclopentasiloxane – $C_{10}H_{30}O_5Si_5$.

[6] Tetradecamethylhexasiloxane – $C_{14}H_{42}O_5Si_6$.

[7] Hexadecamethylheptasiloxane – $C_{16}H_{48}O_6Si_7$.



(a) *Liquid phase.*

(b) *Vapor phase.*

**Fig. 8.** Chemical analysis of MDM samples.

of siloxane products decreases for increasing number of silicon atoms constituting the molecule. The fraction of MDM varies slightly up to $T_s = 310\,^{\circ}\mathrm{C}$, as visible in the top-detailed view of MDM bars in Fig. 8(a). For increasing stress temperature up to 420 °C, the fraction of MDM undergoes a significant reduction to 94.5%.

Outcomes from the chemical analysis of the vapor fraction are reported in Fig. 8(b). Detected decomposition products are methane, ethane, ethylene. Both carbon dioxide and carbon monoxide are detected and indicate the presence of a small amount of air in the sample, which is even more difficult to avoid than for the case of MM, due to the lower vapor pressure of MDM, as discussed in Section 6.2.1. The molar fractions of $CH_4$ and $C_2H_6$ increase by almost two orders of magnitude, as a result of the increase of stress temperature. Methane is the most abundant product, reaching a molar fraction of about 70%.

### 6.3. *Equimolar MM/MDM mixture*

After the thermal stability characterization of pure MM and MDM fluids, an equimolar mixture of MM and MDM was investigated. The interest in mixtures of organic fluids derives from a possible increase of system efficiency (Angelino and Colonna [23], Macchi and Astolfi [2]) due to a better matching between the cooling of the hot source and the heating and evaporation line of the working fluid. Indeed, in a zeotropic mixture, the phase change is not isothermal, resulting in a temperature profile that reduces the mean temperature difference on the hot heat exchanger, thus reducing entropy production. The use of mixtures in ORCs is still very limited, mainly due to the increase of heat exchanger surface required by both the reduction of mean temperature differences and of phase transition heat transfer coefficients, which are lower for a mixture than for the pure fluid. Furthermore, possible plant leakages may change the mixture composition to undesired values, thus causing malfunctions or requiring complex chemical analysis to set up replenishment.

Regarding the thermal stability, if main components of the mixture are molecularly similar, they may decompose to form the other component, hindering the effects of degradation. No literature about the thermal stability of mixtures of siloxanes is currently available, therefore the study here reported was carried out.

In this work, 25 g of equimolar mixture of MM and MDM were tested at 270 °C, 350 °C, 390 °C, and 420 °C.

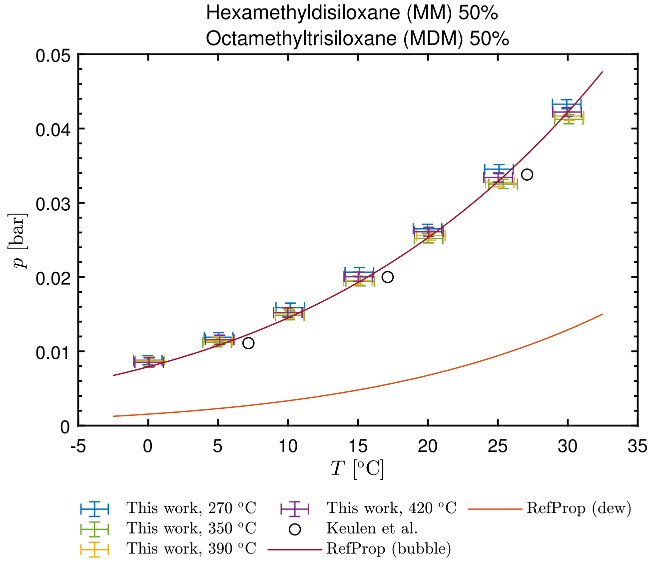


**Fig. 9.** Experimental VLE curve of equimolar mixture of MM and MDM, in the range [0 °C, 30 °C], compared with the bubble and dew curve predicted by the thermodynamic library RefProp and with data published by Keulen et al. [24].

#### 6.3.1. *Pressure deviation in VLE measurements*

For the mixture also, the VLE curve of the virgin fluid was measured. Fig. 9 reports the VLE curve of the mixture, compared to data measured by Keulen et al. [24] and the dew and bubble curve calculated with RefProp. Due to the loaded mass and the temperature range, the VLE curve is practically indistinguishable from the bubble curve. The experimental VLE curve measured in this work is compatible with the bubble curve obtained from the model implemented RefProp, while it is slightly higher than data from Keulen et al. [24]. However, Keulen et al. [24] used an apparatus specifically conceived for the accurate measurements of bubble curves, which is not the case of this system. They report that extreme care must be taken in fluid degassing of this class of fluids. Thus the higher value of pressure obtained here may be ascribed to residual amounts of non-condensable gases, which are difficult to remove, as already discussed in previous sections. Nevertheless, the aim of this work is not the accurate measurement of the bubble line of the mixture, but to have a reference curve representing

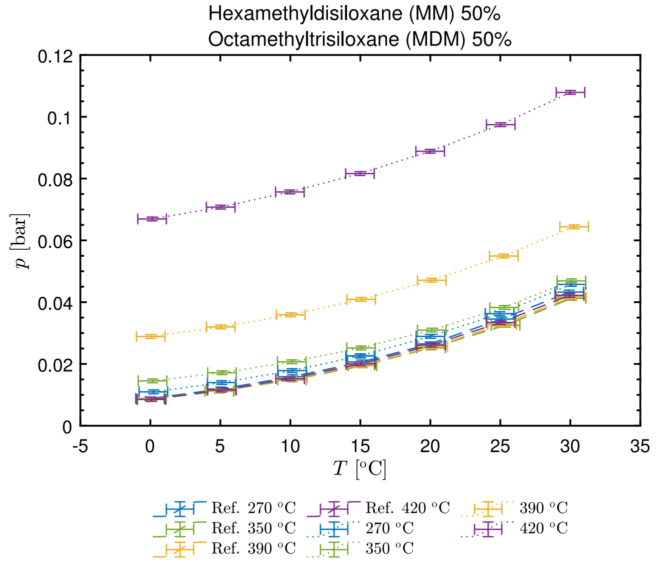


**Fig. 10.** Comparison of VLE curves of equimolar MM/MDM mixture samples stressed at $T_s \in [270\,°C, 420\,°C]$. Measurements of the reference (virgin) fluid (dashed lines) along with those performed after the fluid underwent thermal stress (dotted lines), with 95% confidence level uncertainties.

the virgin fluid, thus the accordance of presented data is considered more than satisfactory.

Fig. 10 reports the VLE curve measured on the virgin and on the stressed fluid, in terms of pressure $p$ as a function of temperature $T$. Data relative to the virgin fluid are represented with the dashed line, while those pertaining to the stressed fluid are plotted with the dotted line. After $T_s = 270\,°C$, the deviation is very small. Increasing deviation is appreciable for increasing stress temperature $T_s$, which becomes relevant starting from $T_s = 350\,°C$.

### 6.3.2. Chemical analysis

Chemical analyses were carried out on mixture samples as it was done for the pure fluids. Results of the liquid phase analysis are shown in Fig. 11(a). The untreated sample contains the $C_6$ hydrocarbons coming from MM, $D_4$ coming from MDM, and MOH which was contained in both original samples. From the chemical analysis it results that the composition of the mixture is slightly shifted towards siloxane MM, being 51.6% and 48.3% the molar fraction of MM and MDM respectively.

Components not present in the virgin fluid and formed due to decomposition are $D_3$, $MD_2M$, $MD_3M$, $MD_4M$ and $M^HM$, even if the amounts of some of them are very limited. In the sample stressed at 420 °C, $MD^HM$ was detected, where the notation indicates (as in previous sections) that hydrogen substituted a methyl group in MDM, thus forming heptamethyltrisiloxane ($C_7H_{22}O_2Si_3$). Traces of $MD_5M$ and $M^{C2H5}M$ are also found. Molar fractions of siloxanes other than the two main components increase for increasing stress temperature, as a result of decomposition. Also in this case, for increasing molecular weight, relative amounts of siloxane products reduces.

Regarding the main components, the fraction of MDM slightly increases at the expense of MM from 270 °C to 350 °C, while considerably decreases between 350 °C and 390 °C with a corresponding increase in the MM fraction. At 420 °C the fraction of MDM has a further slight decrease, while MM remains stable.

Results of the analysis of the vapor phase are plotted in 11(b). As for the previously analyzed cases, detected products are methane, ethane, ethylene, carbon dioxide, and carbon monoxide. The presence of air is confirmed in this case also by the presence of $CO_2$ and CO. The fraction of carbon monoxide remains almost unvaried for increasing $T_s$, while $CO_2$ consistently decreases. As already seen for the pure compounds, the molar fractions of methane and ethane show a sharp increase for increasing temperature, and are confirmed as the main decomposition products found in the vapor phase, reaching about 70% and 10% respectively.

### 6.4. Results discussion

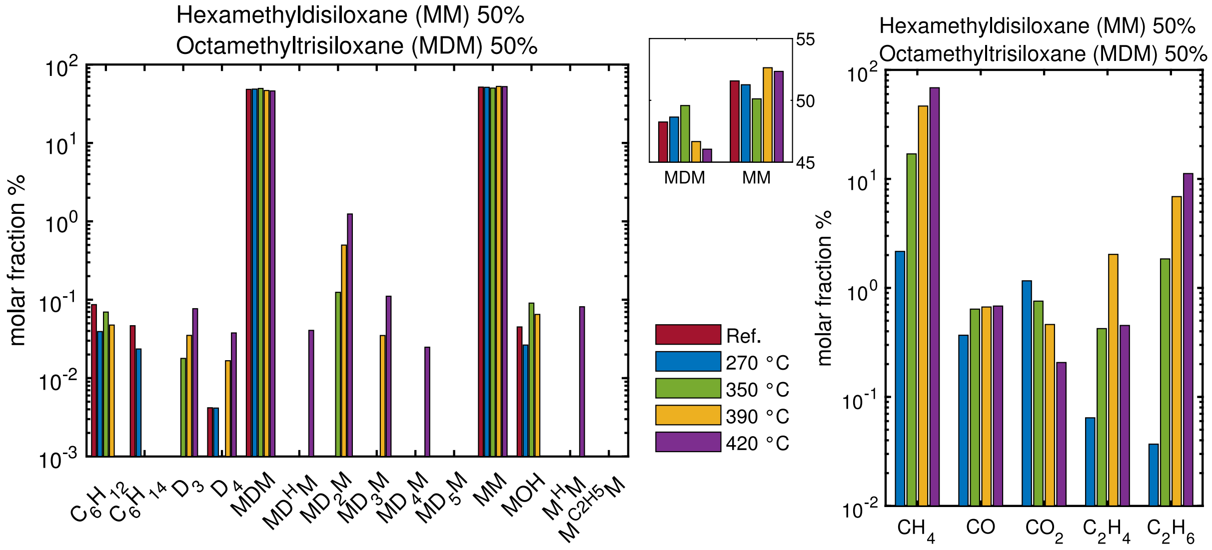
The description of results of tests carried out on the three fluids given in the previous sections, is now followed by a comparative discussion on the results and adopted methods.

Siloxane MM shows an increasing VLE pressure for increasing stress temperature, with deviations that become significant above 270 °C. Qualitatively, this is in accordance with the results shown in [11]. On the other side, siloxane MDM does not show such monotone behavior, with deviations that are maximum at 270 °C. This behavior is also qualitatively similar to what was observed by Keulen et al. [11]. However, quantitative differences are present, both in MM and MDM cases between results shown in Keulen et al. [11] and this paper. The reason for that is to be attributed to the difference in both experimental procedure and apparatus employed. Indeed, in the former campaign, the same sample of fluid was stressed multiple times at increasing temperature $T_s$, while for tests presented here, the sample was stressed directly at the needed temperature $T_s$, employing the improved apparatus of Fig. 2, designed to minimize the volume outside the oven. Indeed, the condensed fluid present in the portion external to the oven undergoes no or only limited stress. Moreover, stressing the same sample at increasing temperatures may have an influence on the final result at the highest stress temperature, due to the repetitive stress. For these reasons, the improved procedure and apparatus (THESTA 2.0) are considered to provide more reliable results.

Chemical analysis were performed after each stress at different temperature $T_s$, thus making possible to obtain a trend and an order of magnitude of fractions of the components of the mixture. Decomposition products found in the liquid phase are siloxanes, both linear and cyclic, present in decreasing amounts as the molecular weight increases. MDM is the only relevant decomposition product of MM in liquid phase. Only traces of other substances were detected. This result is in accordance with data reported in [11]. MDM shows a relevant decomposition in liquid phase, with MM and $MD_2M$ as main products, followed by other heavier siloxanes in lower amounts. Such small quantities are comparable with the accuracy of the GC, thus featuring a high relative uncertainty; however their detection still contribute in yielding a picture of the trend of each component fraction. Furthermore, the overall quantity of degradation products is relevant and impacting on the fraction of MDM, which reduces by about 5%. In the vapor phase, detected components are light alkanes and alkenes, with a higher fraction of methane in case of MDM with respect to MM.

The measure of VLE curves together with liquid chemical analysis suggests that, in case of MDM, mainly high boiling compounds are formed. Indeed, the deviation of vapor pressure remains rather contained, while MDM in liquid phase decreases considerably. The high fraction of methane and ethane in vapor phase is compatible with the low volatility of MDM. The opposite is suggested for MM, where its molar fraction in liquid phase remains almost unchanged, while the deviation of VLE pressure is greater than for MDM. The presence of a lower percentage of $CH_4$ and $C_2H_6$ in the vapor phase of MM tests with respect to MDM ones is compatible with the higher volatility of MM.

Degradation products found in the vapor phase of siloxane MM tests are in accordance with those reported by Manders and Bellama [25] after laser induced degradation. Two papers by M. Preißinger [8] and Dai, Shi, and Qian [9] about the thermal stability of hexamethyldisiloxane for temperature intervals of interest for the ORC field were found in literature. The first one reported traces of high molecular weight siloxanes in liquid phase, with MM still exceeding 99%, after a test at $T_s = 420\,°C$ for 72 h. Vapor fraction degradation products are light hydrocarbons, like methane, ethane, ethylene, propane, propylene. Dai,



(a) *Liquid phase.* (b) *Vapor phase.*

**Fig. 11.** Chemical analysis of MM/MDM equimolar mixture samples.

Shi, and Qian [9] confirmed the presence of the same compounds in vapor phase after stress at 360 °C. Regarding the liquid phase, linear siloxanes MDM, $MD_2M$ and $MD_3M$ were found beside MM, in decreasing amounts. The authors claim that a negligible mass of vapor products was detected and they observed non negligible decomposition in liquid phase, even at moderate temperatures up to 320 °C.

Concerning the MM/MDM equimolar mixture, from VLE measurements the trend is of a monotone increase of vapor pressure with stress temperature. The low deviation of curves until $T_s = 350\,^{\circ}\mathrm{C}$ is compatible with liquid fraction chemical analysis, where a decrease in the fraction of MM and a corresponding increase of the fraction of MDM is observed, thus contributing to maintaining the measured vapor pressure low. The interaction between the two main components of the mixture seems to be complex and not a simple additive effect of the behavior of the two components. For low stress temperatures, the decomposition of siloxane MM appears to be predominant, while if temperature is increased to 390 °C and above, the decomposition of MDM seems to prevail. Based on the results of pure fluids, the non negligible degradation of MDM at high temperature was expected, while the considerable reduction of MM fraction at low temperature is somehow unexpected, since pure MM fluid showed limited decomposition.

## 7. Conclusions

The paper presented an improved method to asses organic fluid thermal stability and was applied to pure siloxane MM, MDM, and to a MM/MDM equimolar mixture. The experimental method revision was motivated by contradictory results yielded by the method adopted in [11]. After a careful analysis, the VLE pressure deviation method evidenced a lack in clearly relating decomposition extent to temperature; also, the temperature of thermal stability was specified according to a threshold defined not only on a physical basis. For fluids having a vapor pressure as low as a few millibars, the deviation results significant even for very limited degradation. For these reasons, a methodology prescribing chemical analysis of the fluid before and after its thermal stress was established. The procedure, replicated at all stress temperature, allows to obtain a qualitative and quantitative picture and the trend of decomposition product formation at different temperatures. Thus removing the need of setting an arbitrary criterion for defining a thermal stability temperature.

The thermal stability of siloxane MM, MDM and their equimolar mixture was analyzed adopting the improved methodology. Results show that in all cases decomposition products in liquid phase are siloxanes of increasing molecular complexity, while in the vapor phase light hydrocarbons are mainly detected. MM showed to form mainly decomposition products in the vapor phase, while the opposite holds for MDM.

In a plant (e.g. an ORC system), the elimination of non-condensable gases is rather simple, by means of a vacuum pump. In this respect the use of MM as working fluid it is more manageable than MDM. The relevant decomposition found at high temperature in the liquid phase of siloxane MDM samples suggests that attention needs to be paid to its thermal stability, since the removal of high boiling compounds is rather complex. These products may remain mixed in the working fluid, altering its properties and possibly causing performance degradation.

The 50%/50% mixture exhibit a complex behavior, with MM decomposition prevailing at low stress temperature and MDM degradation increasing at high temperature.

Finally, it is also worth to recall here that thermal stability of a compound is not sharply defined by a value of temperature, but rather by an indication of a temperature limit below which the concentration of decomposition products formed is acceptable for a specific application. In this respect thermal stability tests, as those presented here, are typically carried out in an almost inert environment and therefore provide indications on thermal stability which represent an upper limit. Extension of such indications to fluid employment in actual plants needs to be carefully considered, since in an actual system the fluid behavior is influenced by the presence of carbon steel instead of stainless steel and of pollutant as lubricants, air, and humidity, which may promote the decomposition reactions, thus reducing the maximum temperature compatible with a decomposition acceptable for the considered application.

## CRediT authorship contribution statement

**Simone Gallarini:** Conceptualization, Methodology, Investigation, Data curation, Software, Visualization, Writing – original draft, Writing – review & editing. **Andrea Spinelli:** Conceptualization, Methodology, Investigation, Project administration, Supervision, Writing – original draft, Writing – review & editing. **Luca Lietti:** Conceptualization, Methodology, Investigation, Supervision, Writing – review & editing. **Alberto Guardone:** Conceptualization, Project administration, Supervision, Funding acquisition, Writing – review & editing.

## 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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