AN IMPROVED METHOD FOR THE INVESTIGATION OF THERMAL STABILITY OF ORGANIC FLUIDS

Simone Gallarini[1*], Andrea Spinelli[1], Luca Lietti[1], Alberto Guardone[2]

[1] Politecnico di Milano, Energy Department,
Via Lambruschini 4/a, 20156 Milano, Italy

[2] Politecnico di Milano, Department of Aerospace Science and Technology,
Via La Masa 34, 20156 Milano, Italy

* simone.gallarini@polimi.it

ABSTRACT

The thermal stability of the working fluid is a key aspect for the design of an efficient organic Rankine cycle. Different methods for assessing thermal stability are available in literature, based either on pressure deviation during an isothermal stress test or on the comparison of the vapor pressure curve measured before and after the fluid underwent thermal stress. Both these methods present strong and weak points. On this basis, an improved methodology for thermal stability analysis is proposed here. During a single test, a sample of the fluid under scrutiny is placed in a closed vessel and stressed at constant temperature for 80 hours. The vapor pressure curve of virgin and stressed fluids are measured and compared. If present, the deviation between the curves provides an indication of the decomposition extent. Further, the virgin and stressed fluid composition, measured, for both liquid and vapor phase, by means of gas chromatography and mass spectrometry are compared. This permits to obtain a trend of the sample composition for varying stress temperature, whereas by using the vapor pressure method the quantitative relation between deviation and decomposition amount cannot be easily retrieved.

An experimental campaign is being carried out at CREA Laboratory of Politecnico di Milano (Italy) on linear siloxanes MM and MDM and on equimolar mixtures of MM/MDM. Linear siloxanes were chosen due to their wide employment as pure working fluids in high temperature organic Rankine cycles. Early results obtained employing the improved methodology are reported here and compared to those obtained using the comparison of vapor pressure only.

1. INTRODUCTION

Steam Rankine cycles are traditionally used to exploit energy sources in large power plants (see Colonna et al. (2015)). The use of organic compounds as working fluids in organic Rankine cycles (ORC) is now a widely used technology for small to medium scale power generation. ORCs are coupled to low/medium temperature heat sources (less than 500 °C) in small/medium power plants (up to 100 MW) (see Colonna et al. (2015); Macchi and Astolfi (2017)). The selection of the working fluid depends on the source temperature and has a major influence on the design and performances of plant components. The use and operating range of a working fluid is restricted by its thermal stability limit, namely the temperature beyond which the fluid undertakes a significant structural decomposition. This can have a large impact on the system and cause loss of power or serious malfunctions of fundamental components (see Badr et al. (1985); Ginosar et al. (2011)). Furthermore, thermal decomposition may lead to formation of toxic or highly flammable fluids, that can cause relevant safety problems during the operation of the plant.

Siloxanes are widely used working fluids for high temperature ORCs, due to their high thermal stability range. However, reliable data about their thermal stability are still scarce, but they are necessary as highlighted by Colonna et al. (2015). For this reason an experimental campaign was recently carried out on MM and MDM at the Laboratory of Compressible-fluid dynamics for Renewable Energy Applica-

tions (CREA Lab) of Politecnico di Milano. Early results were published in Keulen et al. (2018). The experience gained during this first campaign showed that the experimental procedure and the adopted criterion for determining the thermal stability of the fluid had some limits in capturing the real entity of decomposition. The objective of the present paper is to provide a critical reflection on available methods for determining thermal stability, while offering a solution that can possibly remove the limits of previously considered methods. Moreover, some technical aspects related to the implementation of such type of measurements on fluids featuring low saturation pressure at ambient temperature, as it is the case of siloxanes, are addressed.

The paper is structured as follows: Section 2 deals with methods for determining thermal stability described in literature and highlights their strength and weaknesses. Section 3 presents a novel procedure that can avoid the pitfalls of methods previously discussed. Remarks on the experimental apparatus to be used and details on the experimental procedure are given in Subsection 3.1. Section 4 provides an early comparison between measurements performed using different methods. Section 5 reports the conclusions of the work.

2. METHODS FOR DETERMINATION OF THERMAL STABILITY

Blake et al. (1961) introduced a method for determining the thermal stability in which the fluid is stressed at constant temperature T, while pressure p is monitored. If a deviation of pressure at constant temperature is observed, this is attributable to the change in composition of the sample. This method was applied to more than one hundred organic fluids from twelve different chemical families. Later, Fisch and Verderame (1961), Johns et al. (1962a,b), and Fabuss et al. (1963) also used this method, whose indubitable strength is the simplicity. On the other hand it has a limited sensitivity and permits the detection of massive decomposition only. To establish a thermal stability limit is necessary to set a threshold on the pressure rise in time. When this threshold is passed, the temperature at which the stress is being carried out represents the thermal stability limit.

Calderazzi and Colonna di Paliano (1997) determined the decomposition of refrigerants by comparing the saturated vapor pressure curve of the fluid measured before and after the thermal stress and the chemical analysis of the liquid fraction. This method is more sensitive than the one by Blake et al. (1961) in detecting limited decomposition effects. Indeed, if the vapor pressure is measured at low temperature, even low amounts of decomposition products have a major impact on the measured saturated vapor pressure. Later, Angelino and Invernizzi (2003) applied this methodology to zero ODP refrigerants. Pasetti et al. (2014) improved the data analysis method introducing a procedure based on statistical hypothesis test to assess if the deviation in measured vapor pressure could be attributed to measurement uncertainties or not (hence to decomposition). This method was applied by Pasetti et al. (2014) to several hydrocarbons employed in organic Rankine cycle systems.

Keulen et al. (2018) used the methodology and experimental apparatus introduced by Calderazzi and Colonna di Paliano (1997) and Pasetti et al. (2014), improved to perform chemical analysis on the decomposition products on both vapor and liquid phase. The research was focused on the determination of the thermal stability limit and decomposition products of siloxane fluids hexamethyldisiloxane (MM) and octamethyltrisiloxane (MDM). The research carried out by Keulen et al. (2018) showed that the method by Pasetti et al. (2014) evidenced a thermal stability limit of 240 °C for siloxane MM and of 260 °C for siloxane MDM. The same fluid sample was stressed consecutively from 200 °C to 340 ÷ 350°C. The reported thermal stability limit corresponds to the stress temperature at which the difference in measured vapor pressure curves before and after the stress is higher than the one corresponding to 99% confidence level expanded uncertainty of the difference of vapor pressure curves, thus it cannot be explained by measurement uncertainty only. Chemical analysis on both the vapor and liquid phase were carried out on the sample after the stress at the highest temperature (T = 340 ÷ 350°C). Analysis showed negligible amounts of decomposition products. This inconsistent result pones a question on the capability of the applied method to provide reliable results, at least for siloxanes. Indeed, this class of fluids shows a very

low saturated vapor pressure (e.g. $p \approx 43$ mbar at $T = 20\,°C$ for MM and $p \approx 3.6$ mbar at $T = 20\,°C$ for MDM) and a very low concentration of decomposition products (like methane, for example) has a major impact on the value of measured vapor pressure, leading to a pressure deviation that is certainly not attributable to measurement uncertainties. The comparison of vapor pressure curves alone can result in a thermal stability limit corresponding to negligible amounts of decomposition products, for fluids that have such low vapor pressures. Further, this method is not only based on physical considerations and the result depends on two different aspects:

- The temperature range at which the vapor pressure curve is measured impacts on the value of vapor pressure, thus, for low temperatures, small amounts of decomposition products lead to large variations in vapor pressure, whereas at high temperatures the impact is much more limited. If the vapor pressure is measured in a high temperature range, this behavior can lead to the conclusion that the thermal stability is higher than it would have been possible to conclude if the vapor pressure was measured in a low temperature range.

- The value of measurement uncertainty on both pressure and temperature impacts on the value of deviation between vapor pressure curves that can be attributed to measurement uncertainty and not to decomposition of the fluid sample, thus affecting directly the test result.

Rather obviously, by reducing both measurement uncertainty and the temperature range at which vapor pressure curves are compared, it is possible to detect smaller and smaller quantities of decomposition products. The impact of such limited fluid decomposition on industrial applications cannot be assessed and may depend on the particular application and on the nature of degradation products. For this reason, rather than looking for a thermal stability limit in terms of temperature, where the entity of decomposition is not fully meaningful, it appears more significant to look for a trend of decomposition products concentrations for varying temperature. This method removes the ambiguity introduced by the value of measurement uncertainty and by the range of saturation temperature investigated.

It is worth noting that also the method proposed by Blake et al. (1961) suffers from this kind of ambiguity, since the thermal stability limit depends on the limiting value chosen for the time rate of pressure rise during an isothermal stress test.

3. AN IMPROVED METHOD FOR THERMAL STABILITY ASSESSMENT

As discussed in Section 2, using the methods by Blake et al. (1961) and Calderazzi and Colonna di Paliano (1997) and Pasetti et al. (2014) the interpretation of results is not straightforward. Thus, a novel method for determining thermal stability of organic fluids was developed.

The procedure is the following:

1. a sample of the fluid to be tested is analyzed by means of gas chromatography - mass spectrometry (GC-MS), to obtain a reference composition of the liquid phase of the fluid under scrutiny;

2. the fluid sample is loaded in a pressure vessel, where pressure and temperature can be measured, and it is then degassed;

3. the vapor-liquid equilibrium curve of the sample is measured by imposing constant temperature through vessel immersion in a thermal bath;

4. the fluid is stressed in an oven at constant temperature for 80 h;

5. the vapor-liquid equilibrium curve of the stressed sample is measured. This measurements are performed, compared to the virgin fluid ones and used to complement chemical analysis results (see the next point 6.);

6. samples of the liquid and vapor phase are collected and analyzed separately by means of GC-MS.

This procedure is entirely repeated for different stress temperatures, thus a different fluid sample is stressed and analyzed each time. This is in contrast to the procedure adopted by Calderazzi and Colonna di Paliano (1997), Pasetti et al. (2014) and Keulen et al. (2018), that stressed the same fluid sample repeatedly at different temperature. Calderazzi and Colonna di Paliano (1997) and Keulen et al. (2018) performed chemical analysis (the former on liquid phase only, the latter on both liquid and vapor phases) after the stress at the highest temperature.

The presented method permits to obtain a trend of the concentrations of decomposition products in both vapor and liquid phases for different stress temperature. Therefore, this procedure allows to have a clear indication of the entity of decomposition at different temperatures; moreover, it provides results that are free from arbitrary assumptions on the criteria applied to define the decomposition temperature. This consideration is of fundamental importance.

The definition of a temperature limit not to be exceeded in the operation of plants may be useful in practical applications and in a design context. However, if this temperature is not clearly related to a definition of the extent of decomposition, it is of little engineering relevance. The reason for this statement comes from the physics of decomposition which is not an on/off process that activates once a certain temperature is reached. Decomposition occurs in a wide range of temperatures at a rate increasing with temperature; thus a single temperature as a marker of thermal stability limit is physically meaningless.

### 3.1 PECULIARITIES OF EXPERIMENTAL APPARATUS AND PROCEDURE

From the experimental apparatus point of view, attention must be paid to some details. Calderazzi and Colonna di Paliano (1997), Pasetti et al. (2014) and Keulen et al. (2018) monitored the pressure during the stress phase. Pressure measurements at high temperature pose the problem of sensor calibration curve drift due to thermal effects. To avoid such complication, all three studies opted for maintaining pressure transducers at ambient temperature by increasing the distance between the sensor and the test vessel. Of course, this causes vapor condensation in the pressure line. Liquid within the pressure line at ambient temperature is not stressed, thus, once the test is concluded, it dilutes the stressed sample. This results in lower relative percentage of decomposition products detected by chemical analysis and in lower vapor pressure curve deviation. The experimental method presented in this work does not require pressure monitoring during the stress phase, thus the test vessel can be isolated from the rest of the system permitting to stress the fluid sample in its entirety. During vapor pressure measurements it is still possible to accurately measure pressure using a pressure transducer operating in the limited range of temperature where the saturation curve is measured. This range is typically close enough to ambient temperature to avoid significant drift phenomena.

Concerning the degassing procedure, it is normally carried out by repeating cycles of heating, cooling (or freezing) and degassing. It is worth noting that with fluids exhibiting a low saturation pressure such as siloxane MDM ($p \approx 0.1$ mbar at $T = -20\,°C$, as predicted by RefProp) degassing at low temperature requires high performance vacuum pumps. Indeed, if the saturated vapor pressure of the fluid at the considered temperature is lower than the minimum achievable pressure by the pump, non-condensable gases remain in the vessel.

4. COMPARISON OF EARLY RESULTS

In this section some early results obtained with the method presented in this work are shown and compared to the results obtained by Keulen et al. (2018).

Regarding the pressure deviations during isothermal stress tests the quantity to be monitored can be reduced to the ratio of pressure to temperature $p/T = nR/V$, where p is the pressure, T is the temperature, n is the amount of constituents, R is the universal gas constant and V is the system volume. Indeed, if no changes in composition of the sample are present, n remains constant and the ratio p/T does not change. Figure 1 reports the relative percentage change of p/T defined as $\frac{(p/T - p_0/T_0)}{p_0/T_0}$ as a function of test time during a stress test performed on siloxane MM at $340\,°C$ by Keulen et al. (2018). No significant change
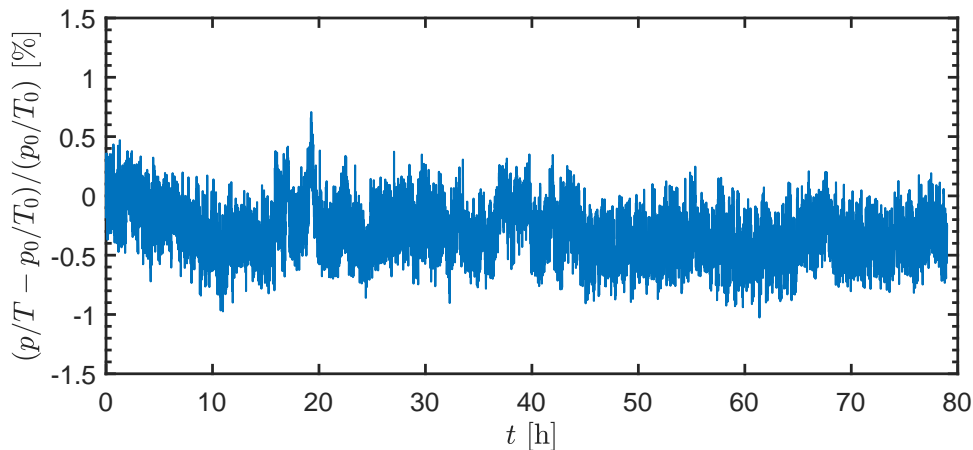
Figure 1: Percentage deviation of the p/T ratio during a stress test carried out at $340\,°C$ **on siloxane MM by Keulen et al. (2018), calculated as** $\frac{(p/T - p_0/T_0)}{p_0/T_0}$. **Reference pressure** p_0 **and temperature** T_0 **are calculated as the mean acquired pressure and temperature over the first hour of test time. These data were not published in the cited paper.**

in p/T is noticeable. However, the analysis of vapor pressure measurements showed that decomposition occurred. Figure 2 reports vapor pressure measurements along with the saturated vapor pressure curve predicted by RefProp for MM. The difference between measurements on the reference virgin fluid and the one carried out by Keulen et al. (2018) (yellow, with dotted line) is evident, thus indicating decomposition. This confirms the lower sensitivity of the method of the evaluation of isothermal pressure deviations with respect to the vapor pressure comparison one.

Some tests carried out with the improved procedure presented in this work are now discussed and compared to those reported by Keulen et al. (2018). Figure 2 reports measurements of vapor pressure of unstressed siloxane MM along with measurements of vapor pressure of the sample after being stressed. Points on the dotted line represent measurements reported by Keulen et al. (2018), while points on the dashed line represent measurements performed with the proposed procedure, described in Section 3 of this work. The trend of increasing mean level of the vapor pressure curve for increasing stress temperature is confirmed by both groups of measurements. However, the curve measured after the stress at $340\,°C$ in this work lies at much higher pressure with respect to measurements reported by Keulen et al. (2018). As described in Section 3.1, the current method does not require the monitoring of pressure during the stress test, thus it is possible to avoid cold parts where unstressed fluid accumulates. Thus the whole fluid sample is stressed, resulting in a more noticeable effect of decomposition on the value of vapor pressure.

Figure 3 reports the same kind of measurements as Figure 2 performed on siloxane MDM. Also here, the mean level of vapor pressure trend is confirmed by both groups of measurements, being the vapor pressure curve measured after the stress at $270\,°C$ higher that the one performed after $350\,°C$. The same consideration about the avoidance of condensed fluid holds also here. However, measurements performed on the fluid sample stressed at $350\,°C$ are at lower pressure for tests performed within this work than those reported in Keulen et al. (2018). The reason for this may lie on the different experimental method. The decreasing trend of saturation pressure curves from $270\,°C$ to $350\,°C$, seems to point out that in this temperature range decomposition leads to the formation of heavy compounds. Since the new procedure does not suffer from the dilution by condensed fluid in pressure lines, the influence of these high boiling compounds on the vapor pressure curve of the tests performed in this work may be more pronounced. Further tests are being carried out and chemical analysis will clarify this aspect. Chart in Figure 3 reports two different set of values for the reference curve of the unstressed fluid. Measurements by Keulen et al. (2018) were obtained by degassing at $-20\,°C$, while measurements in this work were
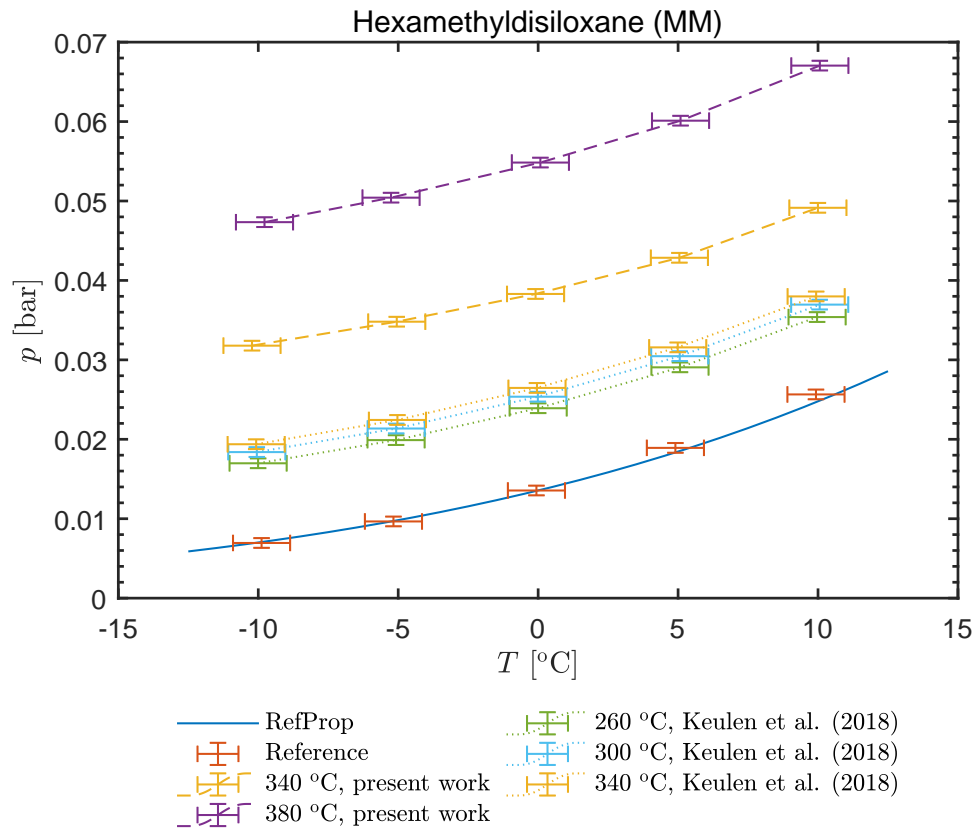
Figure 2: Comparison of saturation pressure of siloxane MM from Keulen et al. (2018) (error bars connected with dotted lines) with the one obtained with the improved experimental method presented in this work (error bars connected with dashed lines). The vapor pressure given by RefProp is also reported (solid line) as a reference.

obtained by degassing at 20 °C. It appears obvious that the greater pressure corresponding to the higher degassing temperature permits a better degassing, being the saturation pressure of the fluid very close to the lowest pressure achievable by the vacuum pump.

Table 1 reports the results of the chemical analysis performed on the reference unstressed fluid and on the stressed samples of MM tests. Regarding the stressed fluid, chemical analysis are performed on both the liquid and vapor phases, while for the reference fluid, analysis are performed on the liquid phase only. For the liquid phase, the GC-MS analysis yields a quasi-quantitative result in terms of molar percentage between detected components. Regarding the vapor phase, reported data are estimated molar fractions relative to the whole vapor phase. In the reference fluid, MM is the main component, with small amounts of Trimethylsilanol and C_6 hydrocarbons. After the stress at 340 °C and 380 °C, MM remains the main component in the liquid phase. As a result of decomposition, cyclic siloxanes and heavier linear siloxanes are formed. In the vapor phase, Methane, Carbon Dioxide, Carbon Monoxide, Ethane and Ethylene are detected as decomposition products. The main decomposition product is Methane. The amount of decomposition products in the vapor phase increases for increasing stress temperature, in accordance with the increase in measured vapor pressure (see figure 2). Table 2 reports the same kind of results for the tests performed with siloxane MDM. In the reference fluid, MDM is the main component, with small amounts of Trimethylsilanol, MM, MD_2M and D_4. After the stress at 270 °C, 350 °C and 390 °C, MDM remains the main component in the liquid phase. As a result of decomposition, cyclic siloxanes, MM and heavier linear siloxanes are formed. Also here, detected decomposition products in the vapor phase are Methane, Carbon Dioxide, Carbon Monoxide, Ethane and Ethylene, with CH_4 being the main component. It is worth nothing that despite the increase of the Methane fraction in the vapor phase (from about 1% at 270 °C to about 48% at 390 °C) the vapor pressure curve level decreases after 270 °C (see
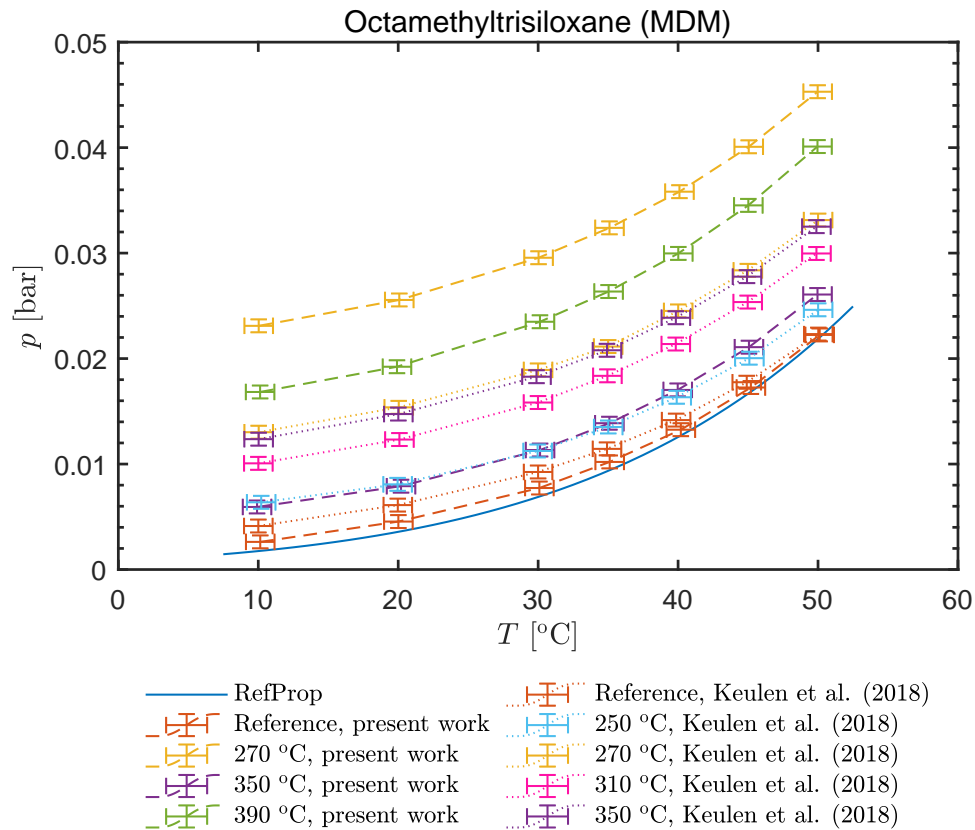
Figure 3: Comparison of saturation pressure of siloxane MDM from Keulen et al. (2018) (error bars connected with dotted lines) with the one obtained with the improved experimental method presented in this work (error bars connected with dashed lines). The vapor pressure given by RefProp is also reported (solid line) as a reference.

figure 3). This behavior may be due to the formation of heavy compounds (not detectable by the GC column adopted for the vapor phase analysis and detected in small amounts in the liquid phase) or solid particles. This aspect needs further investigation and further tests are currently underway. Quantitatively, concentrations of compounds found in the vapor phase during this work are 5 to 10 times higher than the one presented by Keulen et al. (2018).

Further tests at higher and lower stress temperatures than those presented here on MM, MDM and their mixtures are currently being performed and will be available in the near future.

5. CONCLUSIONS

In this paper, different methods for testing and analyzing the thermal stability of an organic fluid were shown, discussing their strength and weaknesses. The method based on the analysis of pressure deviation at constant temperature is straightforward to apply, but its sensitivity to decomposition phenomena is extremely limited. The method based on the comparison of vapor pressure curves measured on the unstressed and stressed fluid is very sensitive in detecting even small decomposition effects, if the vapor pressure curve is measured at low temperature and a measurement chain with low uncertainty is adopted. Both these methods lack in a clear connection between the result of the test in term of decomposition temperature and entity of decomposition: the thermal stability temperature is defined as the one at which a threshold set not only based on physical considerations is passed. For this reasons, an improved method based on performing chemical analysis on both stressed and unstressed fluid was presented. If this procedure is repeated for different stress temperatures, it is possible to obtain a picture of decomposition products and their amount for different stress temperature. Thus, the definition of an arbitrary criterion

Table 1: Chemical analysis results of liquid and vapor phase of stressed MM fluid after stress at 340 °C and 380 °C. Results of the chemical analysis of the liquid phase of the unstressed reference fluid are also reported. For the liquid phase, the results are given in relative molar percentage between detected components. For the vapor phase results are given in molar percentage relative to the whole vapor phase.

	Component	Reference [%]	T_{stress} = 340 °C [%]	T_{stress} = 380 °C [%]
Liquid phase	Trimethylsilanol	< 0.2	0.2	0.1
	MM	> 99.5	99.4	99.5
	MDM	-	0.1	0.1
	MD$_2$M	-	Traces	< 0.02
	MD$_3$M	-	Traces	Traces
	Disiloxane, Ethylpentamethyl-	-	-	Traces
	D$_3$	-	Traces	Traces
	D$_4$	-	Traces	Traces
	C$_6$H$_{14}$	0.1	0.1	0.1
	C$_6$H$_{12}$	0.2	0.2	0.2
Vapor phase	Carbon monoxide		0.2	0.5
	Carbon dioxide		0.4	0.6
	Methane		9.3	33.0
	Ethane		0.6	3.3
	Ethylene		0.2	0.4

Table 2: Chemical analysis results of liquid and vapor phase of stressed MDM fluid after stress at 270 °C, 350 °C, and 390 °C. Results of the chemical analysis of the liquid phase of the unstressed reference fluid are also reported. For the liquid phase, the results are given in relative molar percentage between detected components. For the vapor phase results are given in molar percentage relative to the whole vapor phase.

	Component	Reference [%]	T_{stress} = 270 °C [%]	T_{stress} = 350 °C [%]	T_{stress} = 390 °C [%]
Liquid phase	Trimethylsilanol	< 0.1	< 0.01	< 0.04	< 0.03
	MM	< 0.1	0.1	0.2	1.8
	MDM	> 99.9	99.9	99.6	97.0
	MD$_2$M	Traces	< 0.01	0.1	0.9
	MD$_3$M	-	-	< 0.01	0.1
	MD$_4$M	-	-	Traces	< 0.03
	MD$_5$M	-	-	-	< 0.01
	D$_3$	-	-	< 0.04	0.1
	D$_4$	0.1	< 0.01	< 0.02	<0.1
Vapor phase	Carbon monoxide		-	1.1	0.5
	Carbon dioxide		0.7	1.3	1.3
	Methane		0.9	24.0	47.8
	Ethane		-	1.9	4.0
	Ethylene		0.1	0.5	0.3

for defining a thermal stability temperature is avoided. Practical issues in performing measurements involved in thermal stability experiments, such as the condensation of fluid vapor in pressure transducer lines and the degassing of fluids with low saturation pressure, were also discussed. Concluding, data from experiments carried out with the improved method were compared to data obtained with the method of vapor pressure comparison. Data of chemical analysis concerning the tests used for comparison were reported and discussed.

An extensive experimental campaign on siloxane MM, siloxane MDM, and their mixtures is currently being performed using the improved method and results will be available in the near future.

REFERENCES

Angelino, G. and Invernizzi, C. (2003). Experimental investigation on the thermal stability of some new zero odp refrigerants. *International Journal of Refrigeration*, 26(1):51 – 58.

Badr, O., Probert, S., and O'Callaghan, P. (1985). Selecting a working fluid for a Rankine-cycle engine. *Appl. Energy*, 21(1):1–42.

Blake, E., Hammann, W., Edwards, J. W., Reichard, T., and Ort, M. R. (1961). Thermal Stability as a Function of Chemical Structure. *J. Chem. Eng. Data*, 6(1):87–98.

Calderazzi, L. and Colonna di Paliano, P. (1997). Thermal stability of R-134a, R-141b, R-13I1, R-7146, R-125 associated with stainless steel as a containing material. *Int. J. Refrig*, 20(6):381 – 389.

Colonna, P., Casati, E., Trapp, C., Mathijssen, T., Larjola, J., Turunen-Saaresti, T., and Uusitalo, A. (2015). Organic Rankine Cycle Power Systems: From the Concept to Current Technology, Applications, and an Outlook to the Future. *J. Eng. Gas Turbines Power*, 137(10).

Fabuss, M. A., Borsanyi, A. S., Fabuss, B. M., and Smith, J. O. (1963). Thermal Stability Studies of Pure Hydrocarbons in a High Pressure Isoteniscope. *J. Chem. Eng. Data*, 8(1):64–69.

Fisch, K. R. and Verderame, F. D. (1961). Automatic Recording Apparatus for Thermal Stability Determinations. *J. Chem. Eng. Data*, 6(1):131–134.

Ginosar, D. M., Petkovic, L. M., and Guillen, D. P. (2011). Thermal Stability of Cyclopentane as an Organic Rankine Cycle Working Fluid. *Energy & Fuels*, 25(9):4138–4144.

Johns, I. B., McElhill, E. A., and Smith, J. O. (1962a). Thermal Stability of Organic Compounds. *I&EC Product Research and Development*, 1(1):2–6.

Johns, I. B., McElhill, E. A., and Smith, J. O. (1962b). Thermal Stability of Some Organic Compounds. *J. Chem. Eng. Data*, 7(2):277–281.

Keulen, L., Gallarini, S., Landolina, C., Spinelli, A., Iora, P., Invernizzi, C., Lietti, L., and Guardone, A. (2018). Thermal stability of hexamethyldisiloxane and octamethyltrisiloxane. *Energy*, 165:868 – 876.

Macchi, E. and Astolfi, M. (2017). *Organic Rankine Cycle (ORC) Power Systems. Technologies and applications*. Woodhead Publishing Series in Energy: Number 107, Elsevier, New York.

Pasetti, M., Invernizzi, C. M., and Iora, P. (2014). Thermal stability of working fluids for organic Rankine cycles: An improved survey method and experimental results for cyclopentane, isopentane and n-butane. *Appl. Therm. Eng.*, 73(1):764 – 774.

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