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## Design and commissioning of a thermal stability test-rig for mixtures as working fluids for ORC applications

L.Keulen<sup>a</sup>, C.Landolina<sup>b</sup>, A.Spinelli<sup>c</sup>, P.Iora<sup>d</sup>, C.Invernizzi<sup>d</sup>, L.Lietti<sup>c</sup>, A.Guardone<sup>a,\*</sup>

<sup>a</sup>Department of Aerospace Science & Technology, Politecnico di Milano, Via La Masa 35, 20156 Milano, Italy

<sup>b</sup>Department of Mechanical Engineering, Politecnico di Milano, Via La Masa 1, 20156 Milano, Italy

<sup>c</sup>Energy Department, Politecnico di Milano, Via Lambruschini 4, 20156 Milano, Italy

<sup>d</sup>Department of Mechanical and Industrial Engineering, University of Brescia, Via Branze 38, 25121 Brescia, Italy

### Abstract

A novel test-rig for studying the thermal stability of mixtures as working fluids for ORC applications was designed and commissioned at the Laboratory of Compressible-fluid dynamics for Renewable Energy Applications (CREA) of Politecnico di Milano, in collaboration with the University of Brescia. The set-up is a standard one, in which a vessel containing the fluid under scrutiny is placed in a vertical oven for  $\sim 100$  hours at a constant temperature  $T = T_{\text{stress}}$ . During the test, the pressure  $P$  is monitored to detect thermal decomposition of the fluid. After the test, the vessel is placed in a controlled thermal bath, where the pressure is measured at different value of the temperature  $T$ , with  $T < T_{\text{stress}}$  and  $T < T_c$  ( $T_c$  critical temperature). The resulting isochoric pressure-temperature dependence is compared to that obtained before the fluid underwent thermal stress. If departure from the initial fluid behavior is observed, significant thermal decomposition occurred and a chemical analysis of the decomposition products is carried out using gas chromatography and mass spectroscopy. The novelty of the set-up is the possibility of taking samples of both liquid and vapor phases of the fluid, a capability that was introduced to study thermal decomposition of mixtures, whose composition depends on the pressure and temperature, as well as to capture the more volatile products of thermal decomposition of pure fluids and mixtures. Preliminary experimental results are reported for the pure siloxane fluid MDM (Octamethyltrisiloxane,  $\text{C}_8\text{H}_{24}\text{O}_2\text{Si}_3$ ).

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**Keywords:** Thermal stability, Working fluids for ORC applications, Binary mixtures of siloxane fluids, MM (Hexamethyldisiloxane,  $\text{C}_6\text{H}_{18}\text{OSi}_2$ ), MDM (Octamethyltrisiloxane,  $\text{C}_8\text{H}_{24}\text{O}_2\text{Si}_3$ ), ORC applications

### 1. Introduction

Power cycles based on Rankine Cycle using water as working fluid are traditionally used in large power plants [1]. Due to the growing attention to energy efficiency and environmental issues, the use of Organic Rankine Cycles (ORCs) is now a widely used technology for small to medium scale power generation. They are used for many dif-

\* Corresponding author.

E-mail address: [alberto.guardone@polimi.it](mailto:alberto.guardone@polimi.it)

ferent applications, from industrial waste heat recovery to renewable energy applications, such as solar, biomass and geothermal energy [2,3]. In general whenever relatively low temperature energy sources are available [4]. Traditionally the working fluid in steam powered Rankine Cycles is water, the key-difference of ORCs is the use of organic compounds as working fluids. ORCs are applied to convert low/medium temperature heat sources (less than 500°C) and small/medium power plants (up to 3MW) [5]. For these applications the use of fluids with high molecular mass can be a better option with respect to water. The advantage of using organic compounds lies in the design and construction of the power plants, which are simpler and cheaper than steam Rankine Cycle plants for the small to medium power range [6].

A key aspect of the design of an ORC power plant is the selection of the working fluid. This selection depends on the source temperature and the size of the power plant. These properties are of great influence on the components within the power plant: heat exchanger, turbine, condenser and pump. The use of mixtures as working fluid can significantly increase the performance of the cycle because the mixture can be optimized so the temperature glide of the mixture matches, to some extent, the glide of the heat source fluid [7]. The use of a working fluid is limited by its thermal stability, outside which the fluid undertakes a structural decomposition. This can have a large impact on the system and cause loss of power or serious malfunctions of fundamental components [6,5]. Moderate decomposition give rise to mixtures which might modify the physical and thermodynamic properties of the working fluid and influence cycle performance, but by knowing the mixture properties the system can be adapted without loss of power or replacing the working fluid [8].

Pure siloxane working fluids are prominent, successful working fluids for ORCs and mixtures of siloxanes are promising working fluids for ORCs. Thanks to their high-temperature thermal stability range, siloxanes are of interest for higher temperature applications of ORCs [9]. Siloxane fluids can be separated into two groups, linear and cyclic polymers and composed of alternating silicon oxygen atoms with methyl groups attached to the silicon atoms [10]. In principle, these siloxanes and mixtures of siloxanes can all be used as working fluids in ORCs depending on the power level and heat source temperature [11]. For the use of siloxanes and mixtures of siloxanes, reliable data about thermal stability is necessary as highlighted by Colonna et al.[1]. Several effects can influence the thermal stability of the working fluid besides temperature: the presence of impurities, especially water and oxygen which are almost always present in an actual plant; the time span a fluid is stressed, stressing the fluid at low temperature for an extensive period of time can also cause degradation; the pressure.

Some literature data about thermal stability limits of pure siloxanes are available. Colonna et al.[12] report limits of 400°C for siloxanes, Angelino and Invernizzi[13] provide similar results for cyclic siloxanes. An extensive research on polysiloxanes have been conducted by Dvornic[14] but without mentioning degradation temperatures. A recent study by Preißinger and Brüggemann[9] shows a thermal stability temperature of 300°C for hexamethyldisiloxane (MM) and annual degradation rate of less than 3.5%. No literature can be found about the influence of siloxane mixtures on the thermal stability.

The method used in this research was introduced by Blake et al.[15], who applied it to more than 100 organic fluids from 12 different chemical families, and is the first methodology that is based on the analysis of isothermal pressure deviations of fluids subjected to different thermal stress temperatures. This method was later used by Fisch and Verderame[16], Johns et al.[17][18], and Fabuss et al.[19]. Invernizzi developed the first method specifically for the evaluation of working fluids for ORCs based on the methodology from Blake et al.[15] and Calderazzi and di Paliano[20]. Invernizzi introduced the comparison of the vapor pressure before and after the thermal stress to determine decomposition of the fluid. This method has proven to be more effective to determine decomposition than only analyzing the pressure during the stress test. Due to the fact that pressure fluctuation indicating decomposition are not observed during the stress test, decomposition could still have occurred during the thermal stress test.

This research focuses on the design and commissioning of an experimental test-rig to determine thermal stability of pure fluids and mixtures for ORC applications. The method and experimental apparatus in this research is based on the methodology of Calderazzi and di Paliano[20] and Pasetti et al.[21] and uses statistical analysis to determine decomposition based on the deviation in vapor pressure introduced by Pasetti et al.[21]. The apparatus is improved so chemical analysis can be conducted on the decomposition products in the vapor and liquid phase.

The goal of this work is the commissioning of the test-rig and the determination of the thermal stability temperature and decomposition products of pure MDM. In future work other pure siloxanes and mixtures of siloxanes will be investigated as well as other effects which can influence the thermal stability.

## 2. Experimental apparatus

The experimental apparatus is based on the design of Pasetti et al.[21] and Calderazzi and di Paliano[20]. The set-up is improved for measurements of siloxane fluids and chemical analysis of the liquid and vapor phase. Due to the low vapor pressures of siloxane fluids [11] at temperatures close to ambient temperature, the apparatus is designed to measure low pressures down to 2 mbar. But to have the ability to measure a large range of stress temperatures and good accuracy an intermediate pressure of up to 10 bar can be measured and an upper pressure limit of 35 bar can be reached. Two thermocouples with different tolerance intervals are used to obtain the highest accuracy at each temperature level. Because of the goal to perform chemical analysis on the liquid and vapor phase a section is added for the extraction of the vapor phase. This is done to capture the more volatile products of thermal decomposition of pure fluid and mixtures, because the vapor and liquid phase composition can be different. As well as the study of thermal decomposition of mixtures whose composition depends on the pressure and temperature.

The schematic design of the apparatus used for the thermal stability measurement is shown in Fig. 1. The apparatus is divided into two sections, the test section which is used for the vapor pressure measurement and thermal stress test and the analysis section which is used to collect the gas sample for chemical analysis. The vacuum pump (E-3) is used to evacuate the test and analysis section. The fluid is loaded through a syringe (Syr) connected to the test section.

The thermal bath (B) is used for the measurement of the vapor pressure. The heat transfer liquid has a temperature range of  $-80^{\circ}\text{C}$  to  $55^{\circ}\text{C}$ . The temperature of the bath is controlled by a PID controller with a resolution of  $0.1^{\circ}\text{C}$  and a stability of  $\pm 0.02^{\circ}\text{C}$ . The furnace (F) is used for the thermal stress test, and the temperature can be varied from  $25^{\circ}\text{C}$  to  $1200^{\circ}\text{C}$  with a resolution of  $1^{\circ}\text{C}$  and stability of  $\pm 2^{\circ}\text{C}$  controlled by a PID controller.

The tubing, connectors, valves, and vessels in the test section are made from 316L stainless-steel to withstand a pressure up to 64 bar at  $426^{\circ}\text{C}$ . The vessels (E-1,2) have a volume of  $150\text{ cm}^3$ . The vessels are sealed on one end with a clean TIG weld process. The sample vessel is connected by a TIG weld to three tubes for the housing of the thermocouple, loading tube and the tube connected to the measuring section. The total volume of the circuit is determined at  $230\text{ cm}^3$ .

The measurement instrumentation is made up of three absolute capacitive pressure transducers (P-1,2,3) and two thermocouples (T-1,2). The pressure transducers have full scales of 1 bar, 10 bar and 35 bar and expanded uncertainty of 0.05% of FS and exhibiting a linear calibration curve. Possible zero offset of the pressure readings are compensated at atmospheric conditions through a comparison with pressure measured by a high accuracy barometer of 0.15 mbar accuracy. The uncertainty is computed taking into account the contribution of the transducer and the acquisition system [22]. The transducer technical data is shown in Table 1. The thermocouples are a T-type for temperatures below  $400^{\circ}\text{C}$  and K-type for temperature up to  $1370^{\circ}\text{C}$ . The expanded uncertainty of the thermocouple is taken as 95% confidence interval of the thermocouples tolerance. The thermocouples technical data is shown in Table 1.

The digital samples are monitored by the national instruments acquisition system. The acquired data is processed by a model programmed in the LabVIEW® environment.

## 3. Measurement procedure

*Preparation of experimental apparatus:* To remove all impurities, the entire test section is disassembled and all the components are immersed in acetone for 30 minutes. Subsequently all the components are baked at  $80^{\circ}\text{C}$ , cooled down and cleaned with Nitrogen. The first leakage test is performed to check if the circuit is leak proof under vacuum conditions. At ambient conditions the circuit is evacuated to 3.5 mbar, the lowest obtainable pressure with the vacuum pump. After this the pressure and temperature are registered for  $\sim 48$  hours. The registered pressure is compared to the reference pressure calculated from the ideal gas law to take into account temperature fluctuations during the measurement. The vacuum leakage test is passed if the registered pressure does not deviate more than 0.5 mbar from the reference pressure, the uncertainty of the 1 bar pressure transducers used during the measurement. Second the pressure leakage test is performed by pressurizing the system with helium at 10 bar. The temperature and pressure are registered for  $\sim 48$  hours and the registered pressure is again compared to the reference pressure calculated from the ideal gas law. The pressure leakage test is passed if the registered pressure does not deviate more than 17.5 mbar, the uncertainty of the 35 bar pressure transducer, from the reference pressure. After the cleaning and leakage tests the circuit is set under 3.5 mbar vacuum.

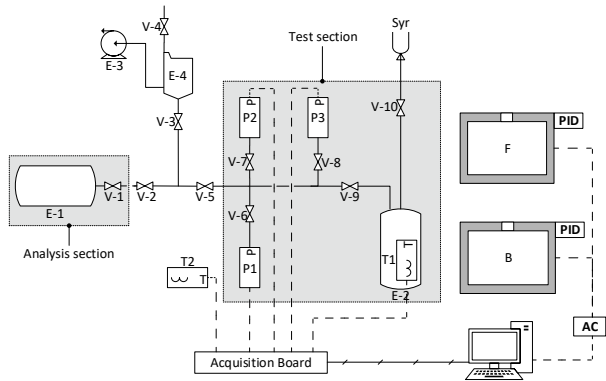


Fig. 1: Schematic diagram of the experimental apparatus: Temperature controlled oven (F), thermal bath (B), 150 cm<sup>3</sup> vessels (E-1,2), pressure transducers (P-1,2,3), thermocouples (T-1,2), valves (V), vacuum pump (E-3), vacuum trap (E-4), loading syringe (Syr).

Table 1: Measurement instrumentation specification.

#### Pressure Transducer:

Manufacturer	Setra-ASM1
Technology	Capacitance sensor
Measured quantity	Absolute Pressure
Full scale	1 bar, 10 bar, 35 bar
Expanded uncertainty	±0.05% FS

#### Thermocouple:

Manufacturer	Tersid-MTS 15000
Technology	Mineral Oxide
Type T (Cu/Cu-Ni)	-133°C to 400°C
Type K (Ni-Cr/Ni-Al)	-270°C to 1370°C
Expanded uncertainty	0.0038T

**Preparation, loading and degasification of the fluid sample:** The fluid quantity to be loaded into the circuit is determined taking into consideration that (i) the pressure must not exceed the full scale of the highest pressure transducer ( $P_{FS} = 35$  bar), (ii) during the vapor pressure measurement the fluid remains in two-phase conditions and (iii) ensure the fluid is in the vapor phase during the thermal stress tests. The fluid is loaded into the circuit by connecting the syringe to the test section shown in Fig. 1. After the loading procedure the fluid is degassed to remove air and other non-condensable gases. For degasification the circuit is put in the thermal bath at 50°C for one hour to facilitate the gas expulsion. Subsequently the fluid is maintained at -40°C and degassed using the vacuum pump. This procedure is repeated until the pressure after two consecutive steps returns to the same value to ensure all non-condensable gases are extracted from the system.

**Vapor pressure measurement of the reference fluid:** The vapor pressure of the non-stressed fluid, also called reference fluid, is measured as reference to determine decomposition by comparison with the stressed fluids vapor pressures. The vapor pressure is measured in the range between 10°C and 50°C, with increments of  $\Delta T = 10^\circ\text{C}$  [10°C, 30°C] and  $\Delta T = 5^\circ\text{C}$  [30°C, 50°C]. The temperature range is chosen taking into account the range of the thermal bath and the accuracy of the lowest full scale pressure transducer as stated in Section 2 so the pressure remains above the transducers uncertainty during the vapor pressure measurement. Each pair of  $P - T$  values is recorded for 10 minutes corresponding to 120 acquisition samples.

**Thermal stress test:** The sample vessel containing the fluid under scrutiny is placed in a vertical oven for ~ 80 hours at a constant temperature ( $T_{\text{stress}}$ ). During the test, pressure and temperature are monitored by the acquisition system. The fluid is in the vapor phase during all the thermal stress tests and therefore the composition is homogeneous in the system. It is possible that condensation occurs in the lines outside of the furnace, but due to the continuous flowing of gases through the system it is assumed that all the fluid is stressed equally during the 80 hours.

**Vapor pressure measurement of the stressed fluid:** After the thermal stress test, the vapor pressure of the stressed fluid is measured using the same experimental procedure and temperature range as for the reference fluid.

**Extraction of fluid samples and chemical analysis:** Chemical analysis is performed when decomposition is detected during the comparison of the reference and stressed fluid vapor pressure, see Section 4 for decomposition criteria. Both liquid and vapor phase of the stressed fluid are evaluated. If decomposition is detected, the system is pressurized (ca. 2 bar) with a He/N<sub>2</sub> mixture (N<sub>2</sub> 1% v/v as internal standard) to dilute the gases formed upon decomposition of the fluid, if any. Then the valve connecting the analysis vessel (E-1) shown in Fig. 1, previously evacuated and set under vacuum, is opened and accordingly part of the gaseous mixture flows spontaneously into the vessel to balance the pressure in the system. Therefore this procedure allows the extraction of the gases formed within the sample vessel (E-2). The analysis vessel (E-1) is eventually detached from the apparatus and the gaseous mixture analyzed by Gas Chromatographic (GC) analysis by using a micro-GC equipped with 2 capillary columns (molecular sieve and

poraplot Q) in a parallel arrangement, connected to thermal conductivity detectors (TCDs). This method allows the quali-quantitative analysis of the gaseous species formed into the sample vessel upon the thermal treatment of the fluid. The composition of the liquid of the stressed fluid is also determined; for this purpose samples were taken and analyzed by High Resolution GC (HRGC) by using a gas chromatograph equipped with capillary columns attached to a Flame Ionization Detector (FID) and to mass spectrometer (MS), respectively. This allowed the quali-quantitative analysis of the liquid products as well.

#### 4. Data analysis

To evaluate the thermal stability and decomposition of the stressed fluid three analysis are conducted. Those consist in measuring (i) deviations of pressure during each thermal stress test, (ii) deviations of fluid vapor pressures after it has undergone each thermal stress test, from reference fluid vapor pressures, and (iii) compositions of the finally decomposed fluid.

The analysis of the pressure deviation during the thermal stress tests is an adequate method to detect large decomposition phenomena, but often it is inadequate to identify weaker decomposition phenomena. Vapor pressure deviations are thus evaluated at low temperature because those are easier and more accurate to measure. This method allows a more sensitive evaluation of decomposition phenomena. Chemical analysis of the liquid and gas phase are finally performed to identify the decomposition products. Both phases are analyzed to take into account the different composition between the liquid and gas phase in mixtures.

The first evaluation is the analysis of the pressure deviation during the thermal stress tests. Because of the difficulty in reproducing and maintaining exact isothermal conditions during the thermal stress, the analysis is performed by comparing the percentage deviation of pressure and temperature over time. Any deviation in pressure that is not supported by a comparable deviation in temperature indicates possible thermal decomposition. Variation in the percentage deviation indicates fluid decomposition, but it is insufficient to exclude decomposition if no variation is observed.

The second evaluation is based on the deviation of the stressed fluids vapor pressure from the reference fluid vapor pressure as described by Pasetti et al.[21]. The purpose of the vapor pressure analysis is the identification of deviations that can not be justified by measurement uncertainties. The composition of the loaded non-stressed fluid is known for pure fluids and for the mixtures. First the vapor pressure of the non-stressed fluid is measured and the stressed fluid after every stressed test as described in Section 3. Every stressed fluid vapor pressure is compared to the non-stressed fluid vapor pressure. Because the stressed fluid is directly compared to the non-stressed fluid, and the same experimental measurement procedure is performed, any deviation in vapor pressure indicates a change in the composition of the pure fluid or mixture and so thermal decomposition. This method only uses the difference in vapor pressure between non-stressed and stressed fluid as indication for thermal decomposition and can not be used for Vapor-Liquid Equilibrium measurements.

First the vapor pressure of the non-stressed fluid, also called reference fluid, is evaluated. The vapor pressure data of the reference fluid is interpolated by means of the Clausius-Clapeyron equation [23] to obtain a reference equation  $P_{ref}(T)$  in bar, and the uncertainty of the reference equation is determined [24,25]. Subsequently the deviation is determined at temperature  $T$  given in degrees Celsius, between the vapor pressure of the fluid after the thermal stress test,  $P_{T_{stress}}(T)$  and the reference fluid,  $P_{ref}(T)$ . Which is defined as  $\Delta P_{T_{stress}}^{ref}(T) = P_{T_{stress}}(T) - P_{ref}(T)$  given in bar, and the uncertainty of the deviation,  $u[\Delta P_{T_{stress}}^{ref}(T)]$  in bar, is expressed as suggested by Hugh W. and W. Glenn[26]. Here the subscript  $T_{stress}$  indicates the temperature at which the fluid is stressed and  $T$  the temperature at which the vapor pressure is measured. The confidence index,  $i_C[\Delta P_{T_{stress}}^{ref}(T)] = \Delta P_{T_{stress}}^{ref}(T)/u[\Delta P_{T_{stress}}^{ref}(T)]$ , of the vapor pressure deviation is defined and evaluated as suggested by Pasetti et al.[21]. The coverage factor  $k_p$  is applied in order to explain deviation of the measurement procedure. The confidence index is equal to the coverage factor, from this it follows that the larger the confidence index, the lower is the probability that the deviation from the reference value can be justified by the measurement uncertainty. The following assumptions are made with given confidence levels of  $p_1 = 90\%$  and  $p_2 = 99\%$  with respectively coverage factors of  $k_{p_1} = 1.645$  and  $k_{p_2} = 2.576$ :

- $|i_C(\Delta P)| \leq k_{p_1}$ , the pressure deviation can be reasonably explained by the measurement uncertainty.
- $k_{p_1} < |i_C(\Delta P)| \leq k_{p_2}$ , the pressure deviation can be explained by the measurement uncertainty only by extending it to high confidence levels. This means that the measured pressure change can be attributed, with high probability, to decomposition of the fluid.

- $|i_C(\Delta P)| > k_{p_2}$ : the pressure deviation can be explained by extending the measurement uncertainty over the 99% confidence levels. This means that the pressure deviation certainly represents the effect of decomposition of the fluid.

## 5. Results and discussion

The primary goal of this research was the design and commissioning of a thermal stability test-rig. The test-rig is build to determine the thermal stability and decomposition products for pure fluids and mixtures as working fluids for ORC applications.

The linear siloxane fluid MDM is thermally stressed. The fluid purity of MDM as stated by the supplier is larger than 99.7%, which is confirmed by chemical analysis conducted on the fluid listed in Table 2.

Two samples of MDM were tested for several temperatures following the procedure in Section 3. The first sample 18 grams was stressed at 200°C and 250°C. Because the first sample evaporated at higher temperatures and the fluid temperature was not properly controlled, a new sample was loaded for further tests. The second sample of 9.5 grams was stressed from 260°C to 350°C.

The measured vapor pressure data with uncertainties ( $P_{\text{vap}}$ ) of the reference fluid along with the calculated reference curve ( $P_{\text{ref}}$ ) is shown in Fig. 2. As seen in the picture the vapor pressure measurements stay within the limits of the reference curve uncertainties which indicate a good estimation of the reference curve.

The temperature and pressure are registered during the thermal stress test. During the tests no pressure deviations occur, which are not relatable to temperature fluctuations, thus showing no evidence of fluid decomposition. Though large temperature fluctuations are observed during the thermal stress test, up to 5%. This can be related to ambient temperature fluctuations in the room and cooled down fluid vapor returning from the measurement section outside of the oven into the sample vessel.

Although the analysis during the thermal stress test does not reveal thermal decomposition, the vapor pressure deviations in Fig. 3 show deviation from the reference fluid and thus indicating thermal decomposition. The confidence analysis in Fig. 4 reveals already decomposition at 250°C between 90% and 99% level of confidence. For higher temperatures the confidence index increases above the 99% level of confidence, which surely represents the effect of thermal decomposition. From 260°C and higher the confidence index stagnates, indicating no further decomposition after 260°C. Decomposition is also observed by chemical analysis, though the decomposition is very limited. Table 2 shows the decomposition of the reference MDM fluid, the reference fluid and the liquid phase are given in relative percentage between the detected components, this percentage does not correspond to the molar or mass fraction of each component. the MDM content in the liquid phase decreases from 99.972% to 99.917%. Some components could not be verified by the database [27] and are listed as undefined. The vapor phase analysis shows that volatile gases in the order of  $\mu\text{mol}$  are formed due to decomposition.

## 6. Conclusion

In this work the design and methodology of an experimental test-rig for the determination of thermal stability and decomposition products for ORC systems has been presented. The test-rig is designed to determine thermal stability temperatures based on methods already used in literature. Though the novelty of the set-up is the possibility to measure the thermal stability of mixtures as well as chemical analysis of the liquid and vapor phase. This is an important addition to determine the decomposition products. Because the composition between the vapor and liquid phase can vary due to a possibly larger concentration of volatile products in the vapor phase.

Together with the description of the apparatus and test methodology, the thermal stability temperature and decomposition products of MDM is determined in this research. MDM is stressed under various temperature between 200°C and 350°C and the fluid was analyzed by pressure deviation during the stress test as well as vapor pressure deviations from the reference fluid in Figs. 3 and 4. Finally chemical analysis, GC, MS and FID, are performed to determine the decomposition products.

Pressure deviations during the thermal stress test show no sign of thermal decomposition. But based on the results of the deviation of the vapor pressure from the reference fluid in Fig. 4 it can be seen that appreciable decomposition of MDM is occurring at 250°C and stabilizes at 260°C and higher. Indicating no further decomposition after 260°C.

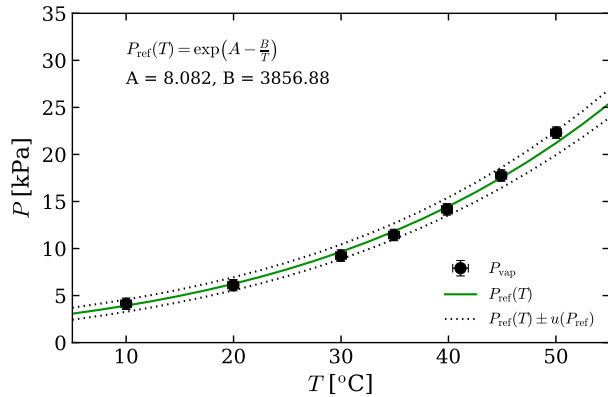


Fig. 2: Vapor pressure of reference MDM fluid. The figure shows the vapor pressure of the reference fluid (●) including uncertainties. The reference curve (—). The dotted lines (·) show the reference curve including uncertainty.

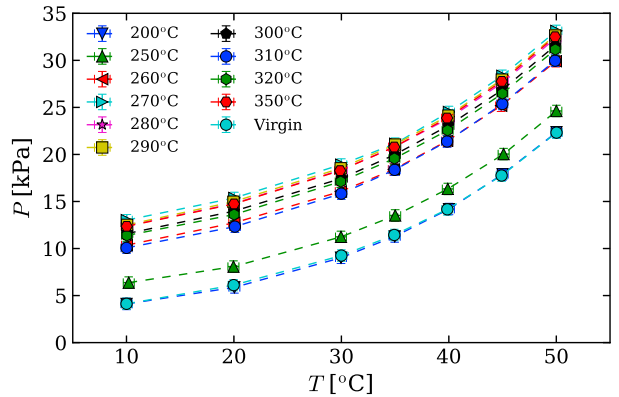


Fig. 3: Vapor pressure measurement including uncertainty of MDM after the various stress tests.

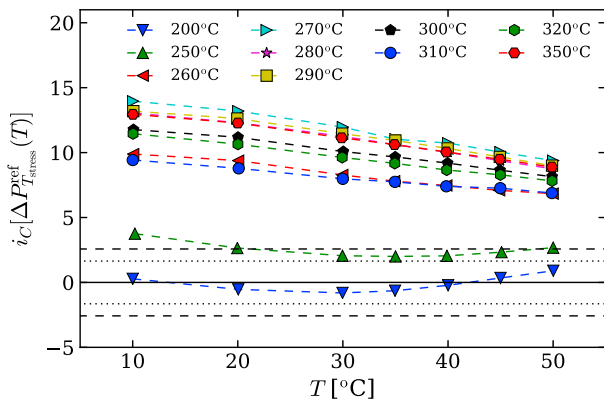


Fig. 4: Confidence index of the vapor pressure deviation between the reference fluid and stressed fluid. The dashed lines (---) represent the 99% confidence level and the dotted lines (·) the 90% confidence level.

Table 2: Chemical analysis results of liquid reference MDM fluid and liquid and gas phase of stressed MDM fluid. The results for the reference fluid and liquid phase are given in relative percentage between detected components and the vapor phase is given in  $\mu\text{mol}$ .

Component	Reference [%]	Liquid [%]
MOH	0.0028	0.0061
MM	0.0028	0.0182
MDM	99.972	99.917
D <sub>4</sub>	0.0117	0.0145
MD <sub>2</sub> M	0.0039	0.0113
Undefined	0.0065	0.0287

Component	Vapor [ $\mu\text{mol}$ ]
Methane	0.948
Ethylene	0.025
Ethane	0.05
CO <sub>2</sub>	0.524

Though rearranging of molecules could occur, creating equilibrium conditions with varying compositions. Decomposition is also verified by chemical analysis of the liquid and vapor phase of the stressed fluid, though the decomposition is very limited as seen in Table 2. Volatile gases are formed as decomposition products, these volatile gases can have a large influence on the fluid properties because of the low vapor pressure of MDM in comparison with the formed volatile gases. When the fluid is stressed for a longer period more volatile gases form and the effect of these gases can have a larger impact on the behavior of the fluid.

It can also be concluded that large temperature fluctuation occur during the thermal stress test, which makes it difficult to determine a precise thermal stability temperature. As mentioned in Section 5 the fluctuation in ambient temperature as well as cooled vapor returning into the sample vessel can have a large influence on the temperature. For future research the set-up, specifically the measuring section, has to be more thermally isolated and kept at a constant temperature.

Further research will entail the study of thermal stability and decomposition products of other siloxane fluids, siloxane mixtures and other effects which can influence the thermal stability: the time span a fluid is stressed; pressure; impurities and supercritical conditions.



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## References

- [1] Colonna, P., Casati, E., Trapp, C., Mathijssen, T., Larjola, J., Turunen-Saaresti, T., et al. Organic Rankine Cycle Power Systems: From the Concept to Current Technology, Applications, and an Outlook to the Future. *J Eng Gas Turbines Power* 2015;137(10). doi:10.1115/1.4029884.
- [2] Wang, M., Wang, J., Zhao, Y., Zhao, P., Dai, Y.. Thermodynamic analysis and optimization of a solar-driven regenerative organic Rankine cycle (ORC) based on flat-plate solar collectors. *Appl Therm Eng* 2013;50(1):816–825. doi:10.1016/j.applthermaleng.2012.08.013.
- [3] Minea, V.. Power generation with {ORC} machines using low-grade waste heat or renewable energy. *Appl Therm Eng* 2014;69(1-2):143–154. doi:10.1016/j.applthermaleng.2014.04.054.
- [4] Invernizzi, C., Iora, P., Silva, P.. Bottoming micro-Rankine cycles for micro-gas turbines. *Appl Therm Eng* 2007;27(1):100 – 110. doi:10.1016/j.applthermaleng.2006.05.003.
- [5] Ginosar, D.M., Petkovic, L.M., Guillen, D.P.. Thermal Stability of Cyclopentane as an Organic Rankine Cycle Working Fluid. *Energy & Fuels* 2011;25(9):4138–4144. doi:10.1021/ef200639r.
- [6] Badr, O., Probert, S., O’Callaghan, P.. Selecting a working fluid for a Rankine-cycle engine. *Appl Energy* 1985;21(1):1–42. doi:10.1016/0306-2619(85)90072-8.
- [7] Angelino, G., di Paliano, P.C.. Multicomponent Working Fluids For Organic Rankine Cycles (ORCs). *Energy* 1998;23(6):449–463. doi:10.1016/S0360-5442(98)00009-7.
- [8] Invernizzi, C., Bonalumi, D.. 5 - thermal stability of organic fluids for organic rankine cycle systems. In: Macchi, E., Astolfi, M., editors. *Organic Rankine Cycle (ORC) Power Systems*. Woodhead Publishing. ISBN 978-0-08-100510-1; 2017, p. 121 – 151. doi:10.1016/B978-0-08-100510-1.00005-3.
- [9] Preißinger, M., Brüggemann, D.. Thermal Stability of Hexamethyldisiloxane (MM) for High-Temperature Organic Rankine Cycle (ORC). *Energies* 2016;9(3). doi:10.3390/en9030183.
- [10] Fernández, F., Prieto, M., Surez, I.. Thermodynamic analysis of high-temperature regenerative organic Rankine cycles using siloxanes as working fluids. *Energy* 2011;36(8):5239 – 5249. doi:10.1016/j.energy.2011.06.028.
- [11] Colonna, P., Guardone, A., Nannan, N.R.. Siloxanes: A new class of candidate Bethe-Zeldovich-Thompson fluids. *Phys Fluids* 2007;19(8):086102. doi:10.1063/1.2759533.
- [12] Colonna, P., Nannan, N., Guardone, A., Lemmon, E.. Multiparameter equations of state for selected siloxanes. *Fluid Phase Equilib* 2006;244(2):193 – 211. doi:10.1016/j.fluid.2006.04.015.
- [13] Angelino, G., Invernizzi, C.. Cyclic Methylsiloxanes as Working Fluids for Space Power Cycles. *J Sol Energy Eng* 1993;115(3). doi:10.1115/1.2930039.
- [14] Dvornic, P.R.. *Thermal Properties of Polysiloxanes*. Dordrecht: Springer Netherlands; 2000. ISBN 978-94-011-3939-7. doi:10.1007/978-94-011-3939-7\_7.
- [15] Blake, E., Hammann, W., Edwards, J.W., Reichard, T., Ort, M.R.. Thermal Stability as a Function of Chemical Structure. *J Chem Eng Data* 1961;6(1):87–98. doi:10.1021/je60009a020.
- [16] Fisch, K.R., Verderame, F.D.. Automatic Recording Apparatus for Thermal Stability Determinations. *J Chem Eng Data* 1961;6(1):131–134. doi:10.1021/je60009a027.
- [17] Johns, I.B., McElhill, E.A., Smith, J.O.. Thermal Stability of Organic Compounds. *I&EC Product Research and Development* 1962;1(1):2–6. doi:10.1021/i360001a001.
- [18] Johns, I.B., McElhill, E.A., Smith, J.O.. Thermal Stability of Some Organic Compounds. *J Chem Eng Data* 1962;7(2):277–281. doi:10.1021/je60013a036.
- [19] Fabuss, M.A., Borsanyi, A.S., Fabuss, B.M., Smith, J.O.. Thermal Stability Studies of Pure Hydrocarbons in a High Pressure Isoteniscope. *J Chem Eng Data* 1963;8(1):64–69. doi:10.1021/je60016a018.
- [20] Calderazzi, L., di Paliano, P.C.. Thermal stability of R-134a, R-141b, R-131I, R-7146, R-125 associated with stainless steel as a containing material. *Int J Refrig* 1997;20(6):381 – 389. doi:10.1016/S0140-7007(97)00043-1.
- [21] Pasetti, M., Invernizzi, C.M., Iora, P.. 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* 2014;73(1):764 – 774. doi:10.1016/j.applthermaleng.2014.08.017.
- [22] Doebelin, E.O.. *Measurement Systems Application and Design*. 4 ed.; McGraw-Hill College; 1989.
- [23] Poling, B.E., Prausnitz, J.M., O’Connell, J.P.. *The properties of gases and liquids*. 5 ed.; New York: McGraw-Hill; 2000. ISBN 0070116822 9780070116825.
- [24] Leon, S.J., Björck, k., Gander, W.. Gram-Schmidt orthogonalization: 100 years and more. *Numerical Linear Algebra with Applications* 2013;20(3):492–532. doi:10.1002/nla.1839.
- [25] Montgomery, D.C., Runger, G.C.. *Applied Statistics and Probability for Engineers*. 6 ed.; Wiley; 2013.
- [26] Hugh W., C., W. Glenn, S.. *Experimentation, Validation, and Uncertainty Analysis for Engineers*. 3 ed.; Wiley; 2009.
- [27] Wiley Registry of Mass Spectral Data 7th Edition. 2000. URL: <https://www.wiley.com>.