THERMAL STABILITY OF HEXAMETHYLDISILOXANE (MM) FOR HIGH TEMPERATURE APPLICATIONS

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ABSTRACT

The design of efficient ORC units for the usage of industrial waste heat at high temperatures requires direct evaporating systems without an intermediate thermal oil circuit. Therefore, the thermal stability of high temperature working fluids gains importance. In this study, the thermal degradation of hexamethyldisiloxane (MM) is investigated in an electrically heated tube. The results include qualitative remarks on degradation products as well as the annual degradation rate as quantitative parameter. It is shown that MM is stable up to a temperature of 300 °C with annual degradation rates of less than 3.5 %. Furthermore, the break of a silicon-carbon bond can be a main chemical reaction that influences the thermal degradation. Finally, the impact of the results on the future design of ORC units is discussed.

1. INTRODUCTION

Linear siloxanes like hexamethyldisiloxane (MM) are promising working fluids for high temperature applications like biomass fired power plants (Obernberger, 1998; Obernberger et al., 2002). In such systems, a thermal oil circuit based on synthetic oils with degradation temperatures of more than 300 °C (Mang and Dresel, 2007) is used to avoid thermal stress of the ORC working fluid. However, for industrial waste heat recovery a trend is noticed to direct evaporating systems without thermal oil circuit. The advantages are higher efficiencies, lower investment costs and a much simpler system design. Although evaporation temperatures of MM are limited to a value below 240 °C for typical working pressures of about 17 bar, the film temperature at the heat exchanger surface, hot-spots within the heat exchanger and the failure mode (e.g. standstill of the ORC pump but no shutdown of the heat source) have to be kept in mind.

Therefore, if we want to use MM in a wide range of heat source temperatures, reliable data for its thermal stability are essential. Colonna et al. (2006) report a limit of 400 °C, however, the duration of the experiments, the heating rate and the pressure remain unclear. For cyclic siloxanes, Angelino (1993) gives a similar value of 400 °C. Dvornic (2000, 2008) investigates extensively thermal properties of polysiloxanes, however, without giving quantitative results for the degradation temperature of MM.

To attain such results, different methodologies concerning design of the test rig and evaluation method are found in literature. Ginosar et al. (2011) report a method to separate catalytic from thermal effects within a glass tube. The standard test procedure for the thermal stability of refrigerants is carried out almost similar (ANSI/ASHRAE, 2007). For the same chemical class, the method of adiabatic compression is used to avoid the thermal degradation at hot surfaces (Buravtsev et al., 1994). Thermogravimetric analyses within vacuum (Grassie and Macfarlane, 1978; Grassie et al., 1979; Deshpande and Rezac, 2002) as well as the analysis of different catalysts (Kuramochi et al.,

1993) are also widespread. A test rig designed especially for measurements of ORC working fluids, and in particular of methylbenzenes, is reported by Angelino et al. (1991). Calderazzi and Colonna (1997) use a similar test rig for different refrigerants. In both cases, the sample is located in a metallic cylinder and heated in an oven. Based on isothermal long-time experiments, the degradation rate is calculated.

In the present study, we redesign the test rig by using an electrical heated tube which allows for high heating rates which can be accurately controlled. The main objective is to gain more knowledge on the influence of the working fluid temperature as well as the duration of the experiment. Furthermore, knowledge about the chemical composition of the degradation products is of main interest for a secure operation of direct evaporating ORC systems.

2. METHODOLOGY

2.1 Test rig and procedure

A stainless steel tube with a length of 220 mm and an outer diameter of 18 mm is electrically heated according to Figure 1. The volume of the reactor accounts for 70.2 ml. The power of the heating wire is 850 W on a length of 5 m allowing a continuous and uniform heating of up to 450 °C. Compared to the heating in an oven, faster heating rates are achieved and the heating rate can be chosen constant for all tests. Within a second tube with an outer diameter of 3 mm the temperature within the reactor is measured with a thermocouple and used as pre-set temperature for the isothermal test procedure. To ensure constant test conditions, the reactor volume is flushed with nitrogen and evacuated two times before each test. The vacuum pump has a pressure limit of 1.0E-6 bar. Therefore, the remaining mass of nitrogen in the reactor is negligible. A sample mass of about 7 g is fed into the reactor through the filling valve at the bottom of the tube. Afterwards the reactor is sealed through blind plugs, heated until the preset temperature with a constant heating rate of 0.3 K/s and the time measurement starts. After the test period, the electrical heating is switched off and the reactor is cooled down to ambient temperature through natural convection. Subsequently, the analysis of the time-dependent temperature and pressure curve as well as the analysis of vapour and liquid phase by means of gas chromatography, mass spectroscopy and Karl-Fischer-titration is carried out. The raw material is MM with a purity of 97 % from the company Wacker Chemie in Burghausen, Germany (Wacker® AK 0.65).
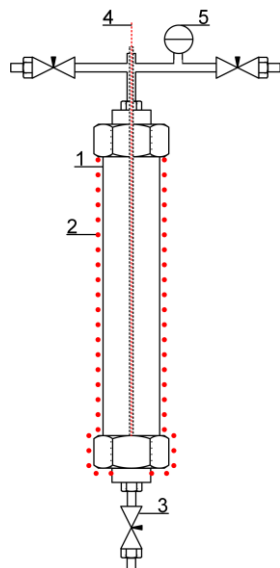

Figure 1: Stainless steel tube (1), electrical heating wire (2), needle valve (3), thermocouple (4) and pressure sensor (5)

Figure 2: Reactor in the lab

2.2 Evaluation method

To describe the evaluation method, an experiment with a temperature of 420 °C and duration of 72 h is selected exemplarily.

First of all, the heating period is analysed. Figure 3 shows the pressure within the tube depending on temperature. The characteristic progression of the bubble line is obtained until a pressure of about 10 bar. However, due to the fact that the heating is much faster than the mixing of the fluid within the reactor, the vapour pressure at a specific temperature is lower than it is expected. Afterwards the slope of the curve drops as the specific volume of MM within the reactor is higher than the critical specific volume (Stephan et al., 2009). Due to the subsequent full mixing within the reactor, the pressure increases marginally at a constant temperature of 420 °C. The slightly right bended part between 120 °C and 160 °C is caused by contaminants within the raw material.

Secondly, the pressure profile during the isothermal test period in Figure 4 shows a value of 15.2 bar with a fluctuation range of 0.05 bar. The pressure changes indicate the formation of molecules with lower or higher molecular mass. The noise signal of the pressure sensor (±5 mbar) does not affect the result. As the pressure changes are not clearly pronounced, further evaluation methods are needed.
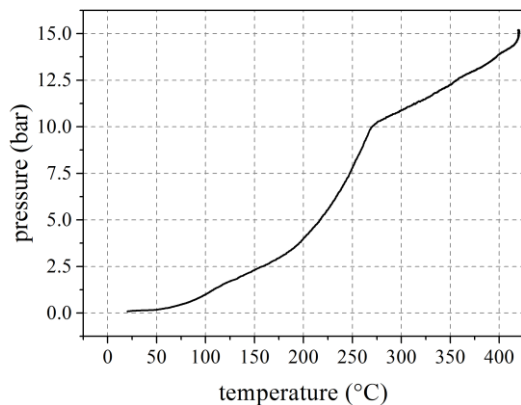
Figure 3: Pressure depending on temperature during heating period ($T = 420$ °C, $t = 72$ h)
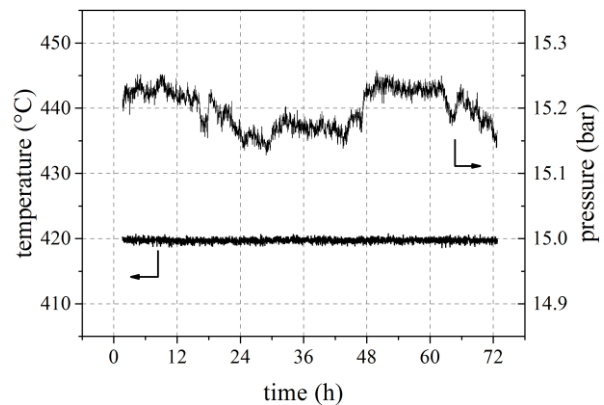
Figure 4: Temperature and pressure depending on time ($T = 420$ °C, $t = 72$ h)

The comparison of the pressure in the reactor before and after the experiment (Figure 5 and Figure 6) confirms the formation of molecules with lower molecular mass than MM. At a constant temperature and a fixed volume of the reactor, the pressure after the experiment is much higher as before which is caused by high vapour pressure of the degradation products.
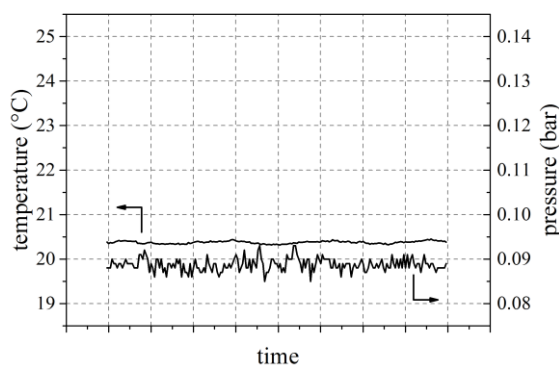
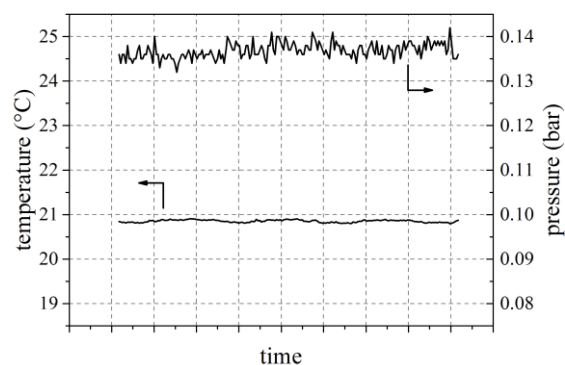Figure 5: Temperature and pressure before experiment ($T = 420$ °C, $t = 72$ h)

Figure 6: Temperature and pressure after experiment ($T = 420$ °C, $t = 72$ h)

The chemical analysis of the products and the raw material by means of gas chromatography proves the assumption of low molecular substances. The mean relative error caused by the gas chromatograph is lower that 2 %. All components with a mass fraction higher than 0.4 % in the vapour phase are displayed in Figure 7. The mass fraction of MM drops to 58 %. The main

degradation products are low molecular hydrocarbons. This confirms the results from laser impulse experiments of Manders and Bellama (Manders and Bellama, 1985). Within the liquid phase traces of high molecular siloxanes are measured which fits the theory of Dvornic (Dvornic, 2000, 2008). However, the mass fraction of MM within the liquid phase still exceeds 99 % and indicates that the degradation products are mainly found in the vapour phase. As water catalyses the thermal degradation of many organic compounds, the water content of the raw material is measured by means of Karl-Fischer titration which gives a marginal value of 140 ppm. Furthermore, the nitrogen-flushing of the reactor and the subsequent evacuation ensures that no free water or contaminants remain within the tube which would influence the experiments.
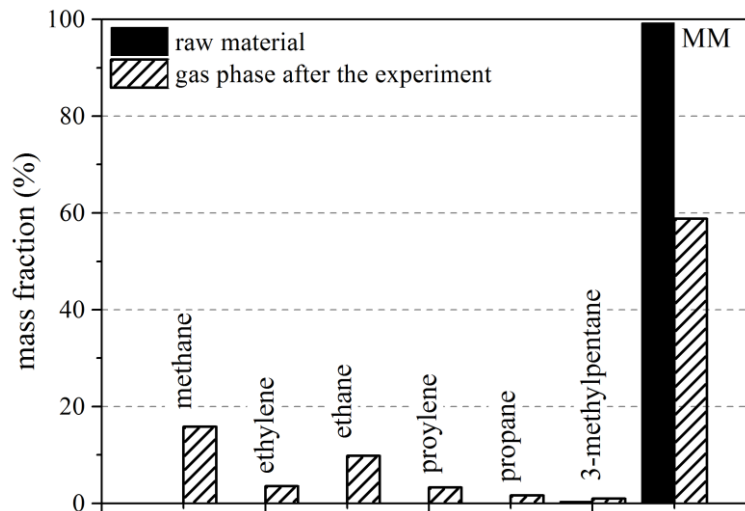

Figure 7: Mass fraction of vapour phase after the experiment and of raw material
($T = 420$ °C, $t = 72$ h, relative error caused by gas chromatograph < 2 %)

3. RESULTS

3.1 Influence of temperature on thermal degradation

The influence of temperature on the thermal degradation is evaluated in Figure 8. The mass fraction of MM drops with increasing temperature. Below a temperature of 300 °C, methane is the dominant degradation product and higher molecular hydrocarbons are hardly detected. At 360 °C, higher amounts of ethane and ethylene are detected for the first time. The mass fraction of propane and propylene remains below 1.5 %. This value increases up to 7.3 % at 420 °C. In general, the variation margin of the mass fraction increases with increasing temperature.

3.2 Influence of time on thermal degradation

In general, the retention time within an ORC evaporator is far less than 72 h. However, due to impropriate mixing and dead volume, high residence times may occur in reality as well. Furthermore, short retention times could give knowledge about the chemical reactions involved in the degradation process. Therefore, the influence of time on the degradation is evaluated. A temperature of 420 °C is chosen to attain high degradation rates which are essential for meaningful results on the influence of time. The mass fraction of MM in Figure 9 drops and the ones of the degradation products increase with increasing time. The slope is almost linear within the first 24 h, for longer times the curves flatten.
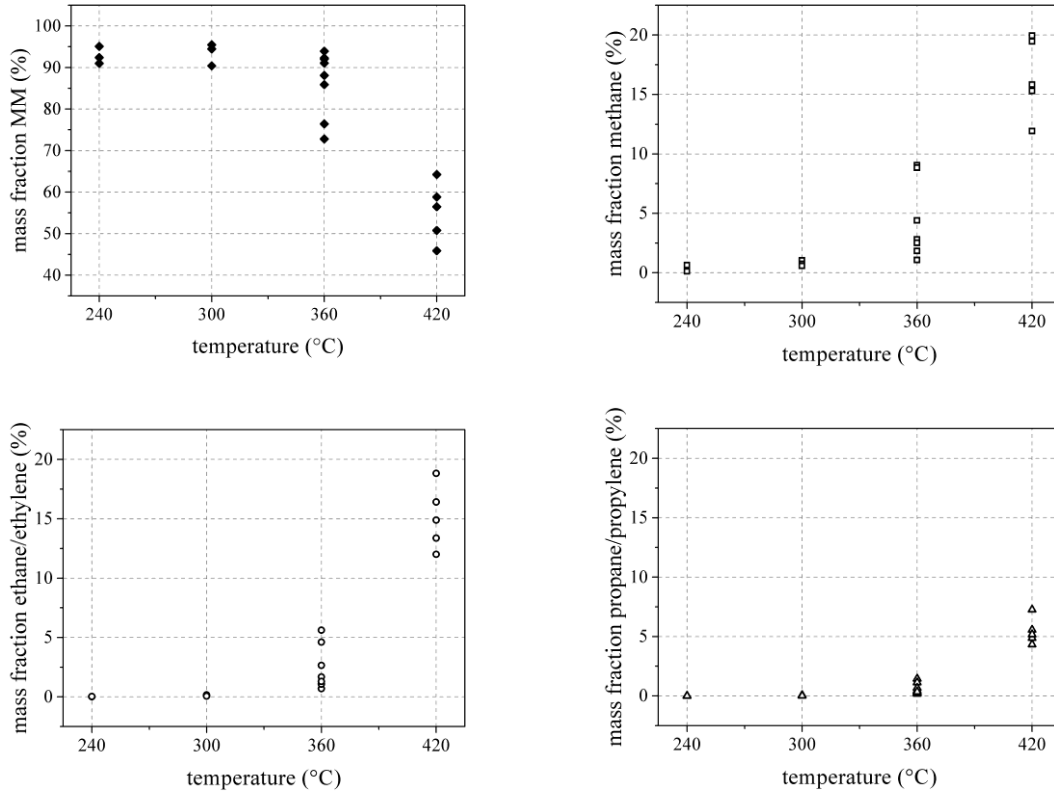
Figure 8: Mass fraction of MM, methane, ethane/ethylene and propane/propylene in the vapour phase after the experiment depending on temperature (t = 72 h)
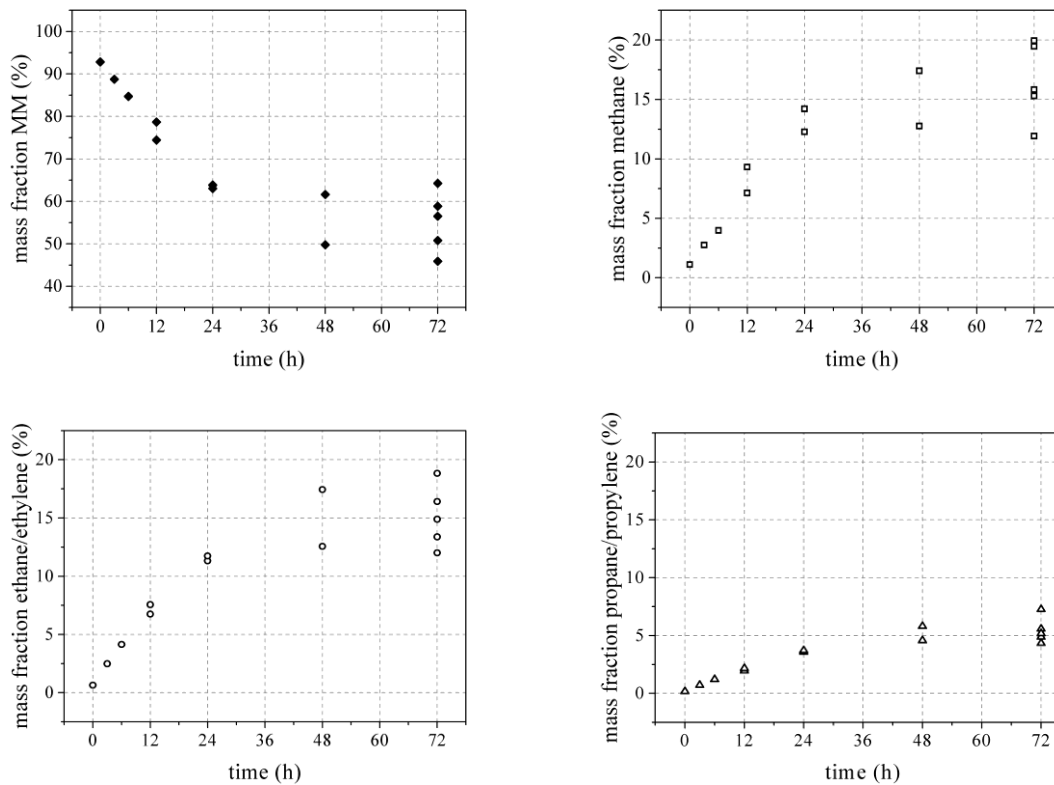

Figure 9: Mass fraction of MM, methane, ethane/ethylene and propane/propylene in the vapour phase after the experiment depending on time (T = 420 °C)

4. DISCUSSION

4.1 Qualitative evaluation of degradation products

The formation of C1-/C2- and C3-hydrocarbons suggests that the break of a Si-C-bond and the subsequent formation of methyl radicals can be seen as the start reaction of thermal degradation. The increased variation margin above a temperature of 360 °C in Figure 8 suggests complex recombination effects which differ especially for longer times of the experiment and are strongly influenced by number and kind of available radicals. The theory of free radicals is also supported by the results in Figure 9. The lower the duration of the experiment, the fewer radicals are available and the straighter forward is their influence on the mass fraction especially of MM, methane and ethane/ethylene. This leads to the characteristic linear slope for times lower than 24 h. The number and types of radicals and, therefore, the variation margin increases for longer times of the experiments.

4.2 Quantitative evaluation of degradation

The mass of gaseous MM before and after the experiment is calculated from the composition of the vapour phase. In combination with the overall mass of MM in the reactor, the annual degradation rate is deduced (Figure 10).
The typical exponential progression according to Arrhenius' law is observed. The absolute value for temperatures below 300 °C is mainly lower than the typical leakage rates of 3 %/a (Heberle et al., 2012) that are assumed for geothermal applications. The degradation rate increases considerably for temperatures higher than 300 °C.
Figure 10 also gives the error-containing values for the degradation rate if we assume the following typical errors for the input data of the calculation:

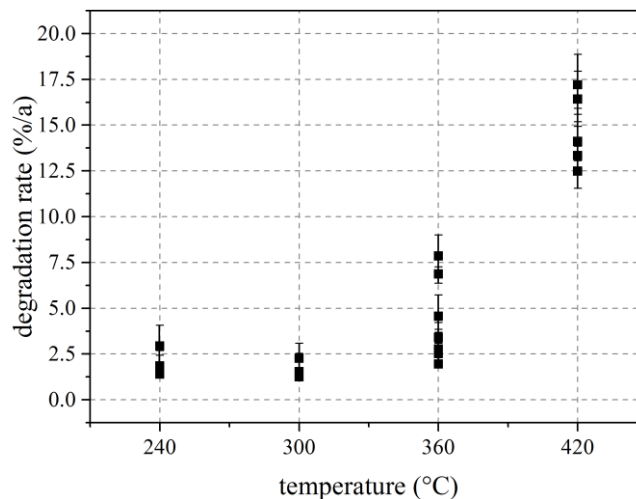|	
volume of the reactor and mass of MM in the reactor	± 2.0 %
mass fraction of MM in liquid and vapour phase	± 2.0 %
density of MM in liquid and vapour phase	± 1.0 %

Figure 10: Degradation rate depending on temperature (t = 72 h)

The dependency of the annual degradation rate on the duration of the experiments in Figure 11 shows a steep decrease for times lower than 12 h, subsequently the curve flattens. Note that error-containing minimum and maximum values are given again. It is obvious that the relative failure increases for lower durations of the experiment as the values are extrapolated to gain the annual degradation rate. Furthermore, according to Figure 11 the annual degradation rates which were calculated from the experiments for duration of 72 h (Figure 10) are probably higher in real ORC units, in which the retention time of the working fluid in the evaporator is far less. To account for this, a test series is carried out in which MM is just heated up to the pre-set temperature and instantly cooled down

afterwards. Therefore, it is possible to "simulate" the heating in the evaporator and instant cooling in the turbine and condenser in an ORC unit. It is shown that the amount of low molecular hydrocarbons is low until a temperature of 300 °C (Figure 12). At 360 °C, the mass fraction of methane increases. Subsequently, the mass fraction of ethane/ethylene and propane/propylene increases at 420 °C. This again proves the assumption that the break of a Si-C-bondage and the set free methyl radicals influence the thermal degradation of MM.
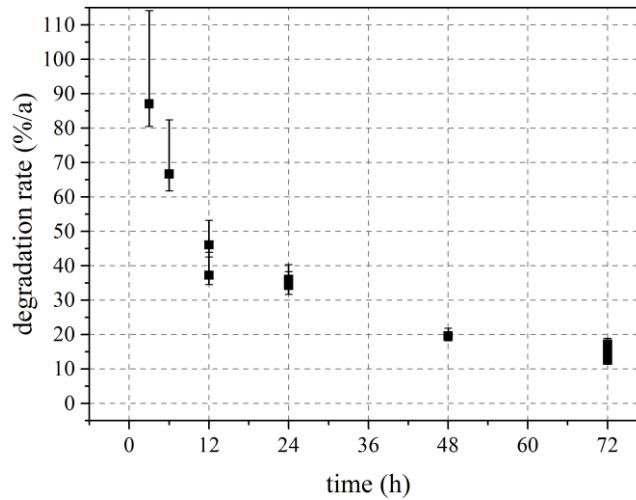

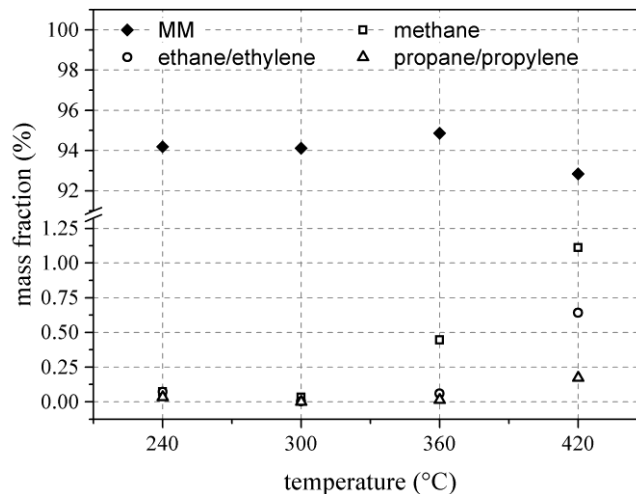Figure 11: Degradation rate depending on time ($T = 420$ °C)

Figure 12: Mass fraction of MM, methane, ethane/ethylene and propane/propylene in the vapour phase after the experiment depending on temperature (test series: heating and instant cooling)

4.3 Impact on the set-up of ORC power units

From the gained results, it can be concluded that the use of MM in ORC units without intermediate thermal oil circuit is possible as long as the fluid temperature does not exceed 300 °C. As the thermodynamic suitable evaporation temperatures are around 240 °C, these conditions can be achieved if special care on evaporator design, particularly concerning film temperature and hotspots, is taken. Furthermore, Figure 12 shows that the formation of methane is an indicator for the thermal degradation. Therefore, in future ORC units a methane sensor could be placed at the top of the evaporator to give evidence on the degradation of MM (for example in case of unforeseen hotspots or in failure mode). In combination with a bleeder valve, the degradation products could be released before influencing the whole ORC system.

5. CONCLUSIONS

The thermal degradation of MM depending on temperature and time was analysed qualitatively and quantitatively and the impact on the set-up of ORC power units was pointed out. The main results can be summarized as follows:

- The main degradation products of MM are low molecular hydrocarbons like methane, ethane/ethylene and propane/propylene.
- The degradation rate is strongly influenced not only by the temperature but also by the retention time.
- MM is stable up to a temperature of 300 °C with annual degradation rates of less than 3.5 %.
- Methane can be used as indicator for ongoing thermal degradation of MM.
- The design of direct evaporating systems based on MM requires special care concerning film temperature and avoiding hot spots in the evaporator.

Ongoing and future work will include the evaluation of free water on the thermal degradation of MM and the comparison with other linear siloxanes (MDM, MD$_2$M). Furthermore, a dynamic test rig including pump, preheater, evaporator, superheater, throttle valve and condenser is planned to account for mechanical stress of the working fluid due to the cycle as well.

NOMENCLATURE

C	carbon	
MDM	octamethyltrisiloxane	
MD$_2$M	decamethyltetrasiloxane	
MM	hexamethyldisiloxane	
ORC	Organic Rankine Cycle	
Si	silicon	
t	time	(h)
T	temperature	(°C)

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