EXPERIMENTAL INVESTIGATIONS OF HEAT TRANSFER CHARACTERISTICS AND THERMAL STABILITY OF SILOXANES

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Introduction
Siloxanes as working fluids in ORC Power Systems

- Siloxanes are potential working fluids for ORC power systems.
- Advantages: long-term experiences, low toxicity and GWP = 0.
- Mainly used as ORC working fluids for high-temperature heat sources like biomass-fired power plants or waste heat recovery units.

Experimental investigation

Heat transfer coefficient
- Comparison to correlations
- Economic evaluation (pure fluids and mixtures)

Thermal stability
- Maximum process temperatures
- Decomposition products
Introduction
Investigated working fluids

- Hexamethyldisiloxane (MM); n = 0
- Octamethyltrisiloxane (MDM); n = 1
- Decamethyltetrasiloxane (MD$_2$M); n = 2

Fluid properties:

<table>
<thead>
<tr>
<th>Structural formula</th>
<th>$T_{\text{crit}}$ (°C)</th>
<th>$p_{\text{crit}}$ (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MM $\text{C}<em>6\text{H}</em>{18}\text{OSi}_2$</td>
<td>245.6</td>
<td>19.4</td>
</tr>
<tr>
<td>MDM $\text{C}<em>8\text{H}</em>{24}\text{O}_2\text{Si}_3$</td>
<td>290.4</td>
<td>14.2</td>
</tr>
<tr>
<td>MD$<em>2$M $\text{C}</em>{10}\text{H}_{30}\text{O}_3\text{Si}_4$</td>
<td>326.3</td>
<td>12.3</td>
</tr>
</tbody>
</table>
Heat transfer characteristics
Experimental setup

- $p_{max} = 25$ bar
- $T_{max} = 260$ °C

Test conditions:
- $\dot{q} = 8 - 18$ kW/m$^2$
- $G = 50 - 400$ kg/(m$^2$s)
- Electrical heated steel pipe (DC power)
- Length: 5 m
Heat transfer characteristics
Evaporation – Test section

Data reduction:

\[ h_j = \frac{\dot{q}}{T_{W,i} - T_{\text{sat}}(p)} \]

\[ T_{W,i} = \bar{T}_{W,o} + \frac{\dot{q}_i}{4\lambda} \cdot (r_o^2 - r_i^2) + \frac{\dot{q}_i}{2\lambda} \cdot \ln \left( \frac{r_i}{r_o} \right) \cdot r_o^2 \]

\[ \bar{T}_{W,o} = \frac{T_{TC,\text{top}} + 2 \cdot T_{TC,\text{middle}} + T_{TC,\text{bottom}}}{4} \]
**Results**

**Variation of mass flux density – MM**

- $h$ increases with increasing mass flux density.
- $h$ decreases with increasing vapour quality.

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**Graph:**
- Heat transfer coefficient (kW/m$^2$K) vs. vapour quality (-)
- Vapour quality $G$ (kg/(m$^2$s))
- Heat transfer coefficient $h$ increases with increasing mass flux density.
- Heat transfer coefficient $h$ decreases with increasing vapour quality.

**Legend:**
- G (kg/(m$^2$s))
  - 50
  - 100
  - 200
  - 300
  - 400

**Additional Information:**
- MM
- $p = 9$ bar;
- $q = 8$ kW/m$^2$
Results
Variation of heat flux density – MM

- No significant influence of heat flux density
- $h$ decreases with increasing vapour quality

Heat transfer coefficient (kW/m$^2$K) vs. vapour quality (-)

$G = 200 \text{ kg/(m}^2\text{s)}$; $T_{sat} = 220 ^\circ \text{C}$
Results
Variation of examined working fluid – statistical and systematic uncertainties

- Different behaviour of MM and MDM depending on vapour quality
- Statistical uncertainties (5 repetitions)
- Systematic uncertainties ($\Delta A/A; \Delta P/P$, $\Delta T_{W,o}/T_{W,o}$, $\Delta p_{sat}/p_{sat}$)

$T_{sat} = 198 \, ^\circ C; \, G = 200 \, \text{kg/(m}^2\text{s}); \, q = 15.9 \, \text{kW/m}^2$
Results
Comparison to correlations

Experimental Data
Kandlikar (1998)
Saitoh et al. (2007)

**MM; G = 200 kg/(m²s); T\text{\textit{sat}} = 198 °C; q = 15.8 kW/m²**
Results
Comparison to correlations

Experimental Data
Kandlikar (1998)
Saitoh et al. (2007)

MM; $G = 200 \text{ kg/(m}^2\text{s)}$; $T_{\text{sat}} = 198 \degree \text{C}$; $q = 15.8 \text{ kW/m}^2$
Results
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**MDM;** $G = 200 \text{ kg/(m}^2\text{s)}; \ T_{\text{sat}} = 198 ^\circ \text{C}; \ q = 15.8 \text{ kW/m}^2$
Comparison to correlations

Experimental Data
Kandlikar (1998)
Saitoh et al. (2007)

MDM; \( G = 200 \text{ kg/(m}^2\text{s)} \); \( T_{\text{sat}} = 198^\circ\text{C} \); \( q = 15.8 \text{ kW/m}^2 \)
Results
Comparison to correlations – working fluid: MM

- All measured local $h$
- Mean relative deviation (Kandlikar) 25.1%
- Saitoh et al. 49.0%
- Mean relative deviation (MDM – Kandlikar) 40.9%
Heat transfer measurements
Main results

- Heat transfer coefficients are measured for process temperatures up to 250 °C.
- Empirical model of Kandlikar shows a good agreement to the experimental data.
Thermal stability
Experimental setup

Test conditions:
- $p_{\text{max}} = 30 \text{ bar}$
- $T_{\text{max}} = 500 \, ^\circ C$

- $t = 72 \, \text{h}$
- $T = 240 - 420 \, ^\circ C$
- Electrical heated by heating wire
- Analysed by gas chromatography/mass spectroscopy
Results
Liquid phase, 360 °C, 144 h

- Fluid: Wacker® AK 0.65
- Purity: > 97 mass-%
- Formation of higher chained siloxanes in accordance to Dvornic, Gelest, Inc.

![Graph showing counter vs. time](image)
Results
Gas phase, 72 h

- Averaged molar concentration before tests: 99.4 mol-%
- Formation of methane and ethane in accordance to Manders and Bellama, Journal of Polymer Science, 1985
Conclusions and Future work

- Heat transfer and thermal stability measurements were carried out for selected siloxanes.
- The correlation of Kandlikar shows the best agreement to experimental data.
- No significant amount of decomposition products for heat transfer test conditions.
- Heat transfer characteristics of the mixture MM/MDM and MM/MDM/MD$_2$M.
- Investigation of enhanced tubes and alternative working fluids.
- Long-term and dynamic tests concerning thermal stability.
Acknowledgements

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TAO

Partial financing of the thermal stability test rig

WACKER

Free provision of Wacker® AK 0.65
Thank you
www.zet.uni-bayreuth.de

Florian Heberle, Markus Preißinger, Theresa Weith and Dieter Brüggemann
Heat transfer characteristics
Evaporation – Test section

Data reduction:

\[ x_i = \frac{h_i - h'}{h'' - h'} \quad i = 1 - 10 \]

\[ h_i = h_{i-1} + \Delta h = h_{i-1} + \frac{P_i}{m_{TF}} \]

\[ h_0 = h(T_{sat} - 0.5K) \quad \rightarrow \text{subcooled} \]
Results
Variation of saturation pressure - MM

MM

\[ G = 200 \text{ kg/(m}^2\text{)}; \]
\[ q = 15.8 \text{ kW/m}^2 \]

\begin{align*}
\text{heat transfer coefficient (W/m}^2\text{K)} \\
\text{vapour quality (-)} \\
\text{p}_{\text{sat}} \text{ (bar)} \\
\end{align*}

0.0 0.2 0.4 0.6 0.8 1.0
0 1000 2000 3000 4000 5000 6000 7000

heat transfer coefficient (W/m$^2$K)
vapour quality (-)
\( p_{\text{sat}} \) (bar)

- 5.8
- 7.75
- 9
- 13

\( G = 200 \text{ kg/(m}^2\text{)}; \)
\( q = 15.8 \text{ kW/m}^2 \)
Results
Variation of examined working fluid

$T_{sat} = 220 \, ^\circ C$;
$G = 200 \, kg/(m^2 \cdot s)$;
$q = 15.9 \, kW/m^2$
Results
Comparison to correlations – Model of Kandlikar

\[
htc_{tp} = \begin{cases} 
htc_{tp,\text{nbd}} \\
htc_{tp,\text{cbd}} 
\end{cases}
\]

\[
htc_{tp,\text{nbd}} = 0.6683 \cdot Co^{-0.2} \cdot (1 - x)^{0.8} \cdot htc_{LO} + 1058 \cdot Bo^{0.7} \cdot (1 - x)^{0.8} \cdot F_{fl}
\cdot htc_{LO}
\]

\[
htc_{tp,\text{cbd}} = 1.136 \cdot Co^{-0.9} \cdot (1 - x)^{0.8} \cdot htc_{LO} + 667.2 \cdot Bo^{0.7} \cdot (1 - x)^{0.8} \cdot F_{fl} \cdot htc_{LO}
\]

\[
htc_{LO} = \frac{(\zeta/2) (Re_{LO} - 1000) \cdot Pr_l}{1,0 + 12,7 \cdot \sqrt{\zeta/2 (Pr_{l}^{2/3} - 1)}} \cdot \left(\frac{\lambda_l}{d_i}\right)
\]

\[
Bo = \frac{\dot{q}}{G \cdot \Delta h} = \frac{A_{cs} \cdot \dot{q}}{\dot{m} \cdot (h'' - h')}
\]

\[
Co = \left(\frac{\rho_g}{\rho_l}\right)^{0.5} \left(\frac{1 - x}{x}\right)^{0.8}
\]
Results

Comparison to correlations – Model of Saitoh et al.

\[ htc_{tp} = F htc_l + S htc_{pool} \]

\[ F = 1 + \left( \frac{1}{x} \right)^{1.05} + (1 + We_g^{-0.4}) \]

\[ S = 1/1 + (Re_{tp} \cdot 10^{-4})^{1.405} \]

\[ htc_l = 0.223 \frac{\lambda_l}{D} \left( \frac{G(1-x)D}{\eta_l} \right)^{0.8} \cdot \left( \frac{c_p l \eta_l}{\lambda_l} \right)^{0.8} \]

\[ htc_{pool} = 207 \frac{\lambda_l}{d_b} \left( \frac{q d_b}{\lambda_l T_l} \right)^{0.745} \cdot \left( \frac{\rho g}{\rho_l} \right)^{0.581} \cdot Pr_l^{0.533} \]
Results
Comparison to correlations – working fluid: MM

- Measured local $htc$
- Mean relative deviation (Kandlikar) 25.1%
- Saitoh et al. 49.0%
Results
Homogenous temperature profile

![Graph showing homogenous temperature profile](image)

inner wall temperature (°C) vs. length of test section (m)

- $t_1$
- $t_2$
- $t_3$
- $t_4$
Results

![Graph showing inner wall temperature vs. length of test section for MM top and MM bottom.](image)

- **MM top**
- **MM bottom**

inner wall temperature (°C) vs. length of test section (m)
Results
Results
Flow regimes - MM

The graph illustrates the transition between different flow regimes based on the mass flux $G$ and the position $x$.

- **Annular** flow is characterized by a single continuous liquid film on the wall, with no gas phase visible.
- **Stratified** flow shows distinct layers of liquid and gas, with clear boundaries between them.
- **Stratified wavy** flow indicates a dynamic interface with waves, typical of unstable stratified flows.
- **Intermittent** flow represents periods of liquid and gas, often observed in two-phase flows.
- **Mist flow** occurs with small droplets dispersed in the gas phase, resembling a misty appearance.

The graph uses different markers and colors to distinguish between the various flow regimes, providing a clear visual representation of the transition conditions.
Results
Flow regimes – MDM

![Graph showing flow regimes](image-url)
Results
Fluid properties

<table>
<thead>
<tr>
<th></th>
<th>$p_{\text{sat}}$ (bar)</th>
<th>$p_{\text{red}}$</th>
<th>$\rho_v$ (kg/m$^3$)</th>
<th>$\rho_l / \rho_v$</th>
<th>$\sigma$ (N/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MM</td>
<td>9.03</td>
<td>0.47</td>
<td>53.54</td>
<td>10.05</td>
<td>0.0154</td>
</tr>
<tr>
<td>MDM</td>
<td>2.90</td>
<td>0.21</td>
<td>20.82</td>
<td>29.44</td>
<td>0.0166</td>
</tr>
</tbody>
</table>

- Higher vapour density for MM $\rightarrow$ lower vapour velocity at same mass flux.
- Nucleate dominates at low vapour qualities, caused by low surface tension and liquid-to-vapour density ratio.
- Lower surface tension increase the probability of liquid entrainment in the vapour core.
- Suppression of nucleate boiling is delayed by higher vapour density (lower velocity).
Thermal stability
Temperature distribution

![Diagram with graphs showing temperature distribution](image)

- **a)**
- **b)**
- **c)**
Outline

Test procedure

1. [Diagram with N2 and 15 min]

2. [Diagram with Tauchrohr]

3. [Diagram with Vakuumpumpe]

4. [Diagram with empty structure]

Test procedure
Outline
Dynamic test rig