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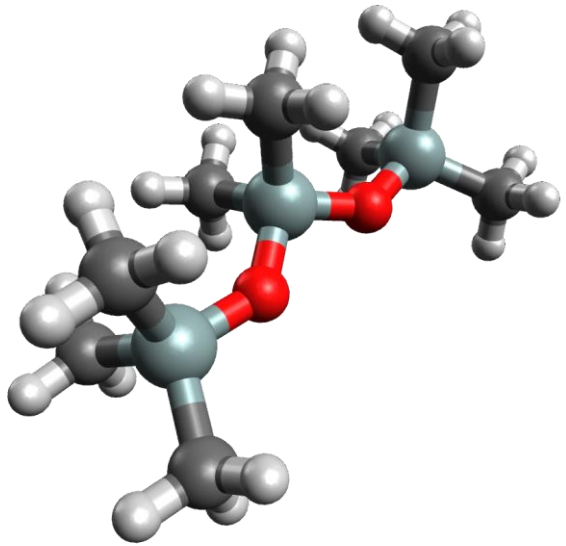
An improved method for the investigation of thermal stability of organic fluids



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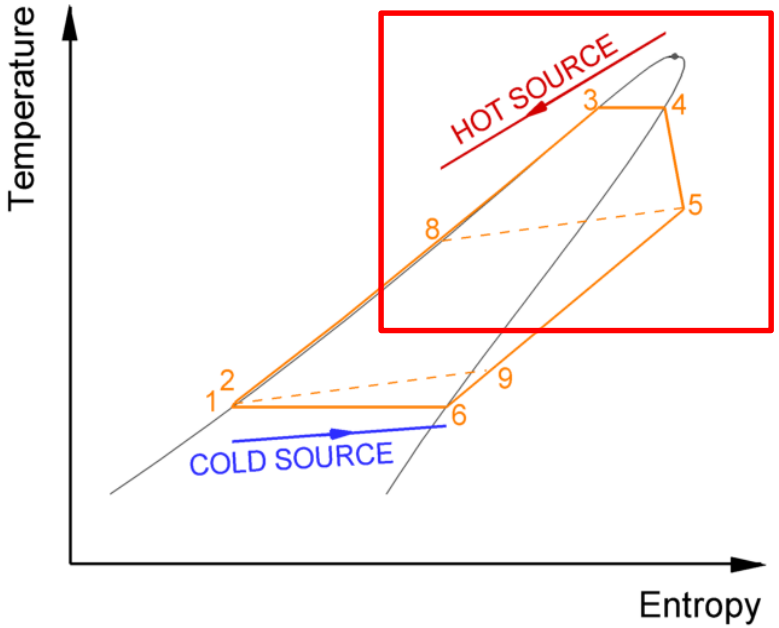
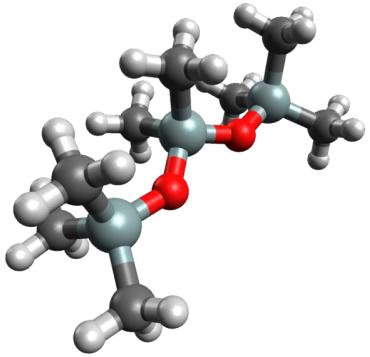
summary

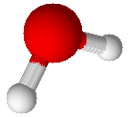
- Introduction
- Methods for the determination of thermal stability
- An improved method for thermal stability assessment
- Comparison of early results
- Conclusion

organic Rankine cycles





Octamethyltrisiloxane
MDM



Water

$T_{max} \uparrow \rightarrow \eta \uparrow$

thermal stability

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Thermal stability of hexamethyldisiloxane and octamethyltrisiloxane

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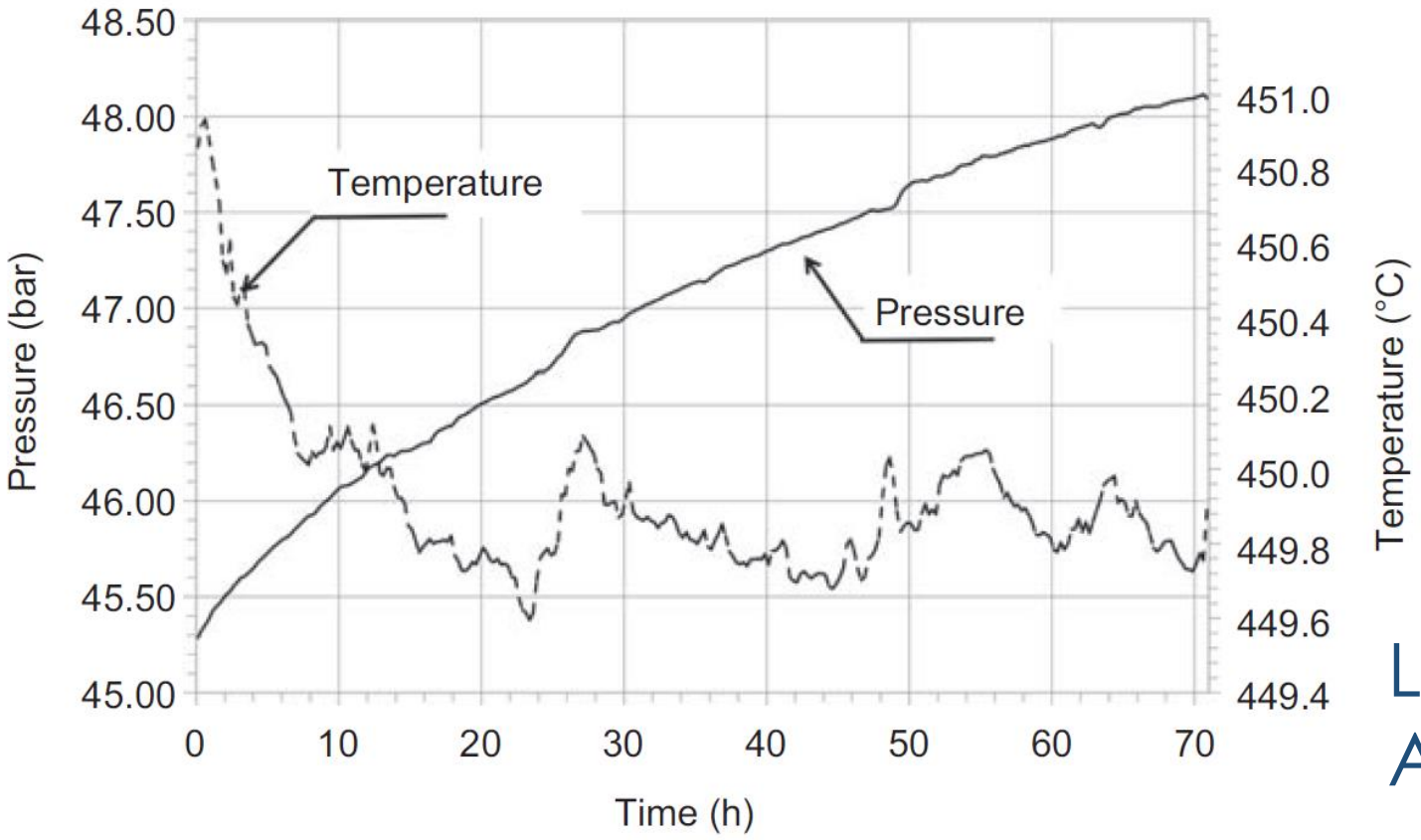
OUTCOME: limits of the experimental method in capturing the real entity of decomposition.

GOAL:

critical reflection on methods for thermal stability study

overcome the limits of discussed methods

p deviation during iso-T stress:



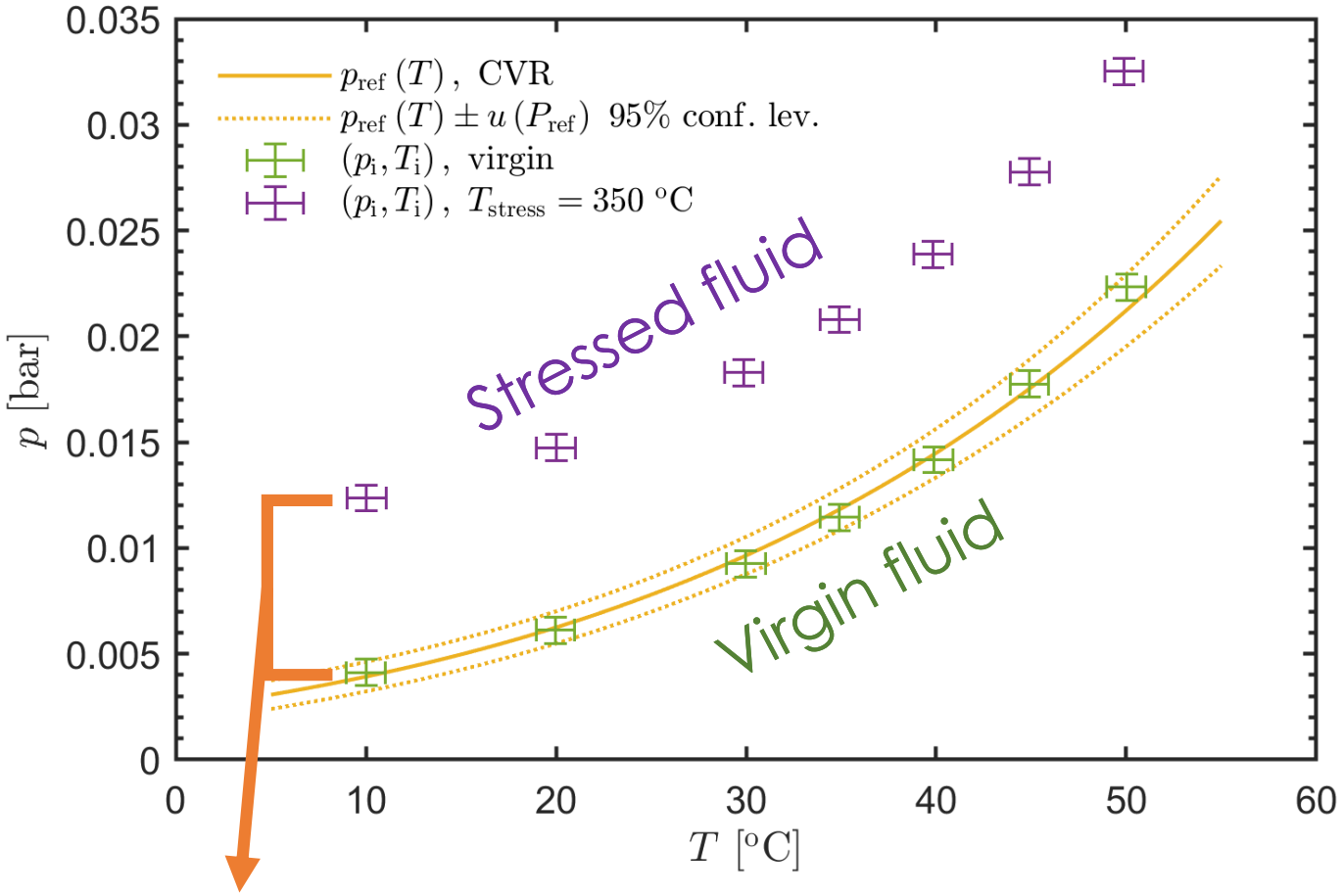
Simplicity

Low sensitivity
Arbitrariness:
which Δp = decomposition?

fluid: perfluoro-n-hexane $T = 350\,°\mathrm{C}$

Figure from Organic Rankine Cycle (ORC) Power Systems, Macchi, Astolfi

deviation of vapor pressure



Δp → Change of composition

Great sensitivity

Complexity

Δp-decomposition amount relation?

Arbitrariness:

T range of p_{sat} meas.?

method		result
p deviation during iso-T stress	→	no decomposition
+		
deviation of vapor pressure	→	decomposition at 240 °C (MM) 260 °C (MDM)
+		
chemical analysis after the **highest** stress temperature	→	negligible decomposition at 340 °C (MM) 350 °C (MDM)

Thermal stability: critique to the method

Result affected by:

- vapor pressure value $p_{vap} = f(fluid, T)$
- measurement uncertainty

ambiguous relation between p_{vap} deviation and decomposition

improved experimental procedure

stress for 80 h
in closed volume

+

vapor pressure
comparison

+

chemical analysis
before and after
each stress temperature

Trend of chemical composition for increasing stress temperature

Clear indication of entity of decomposition

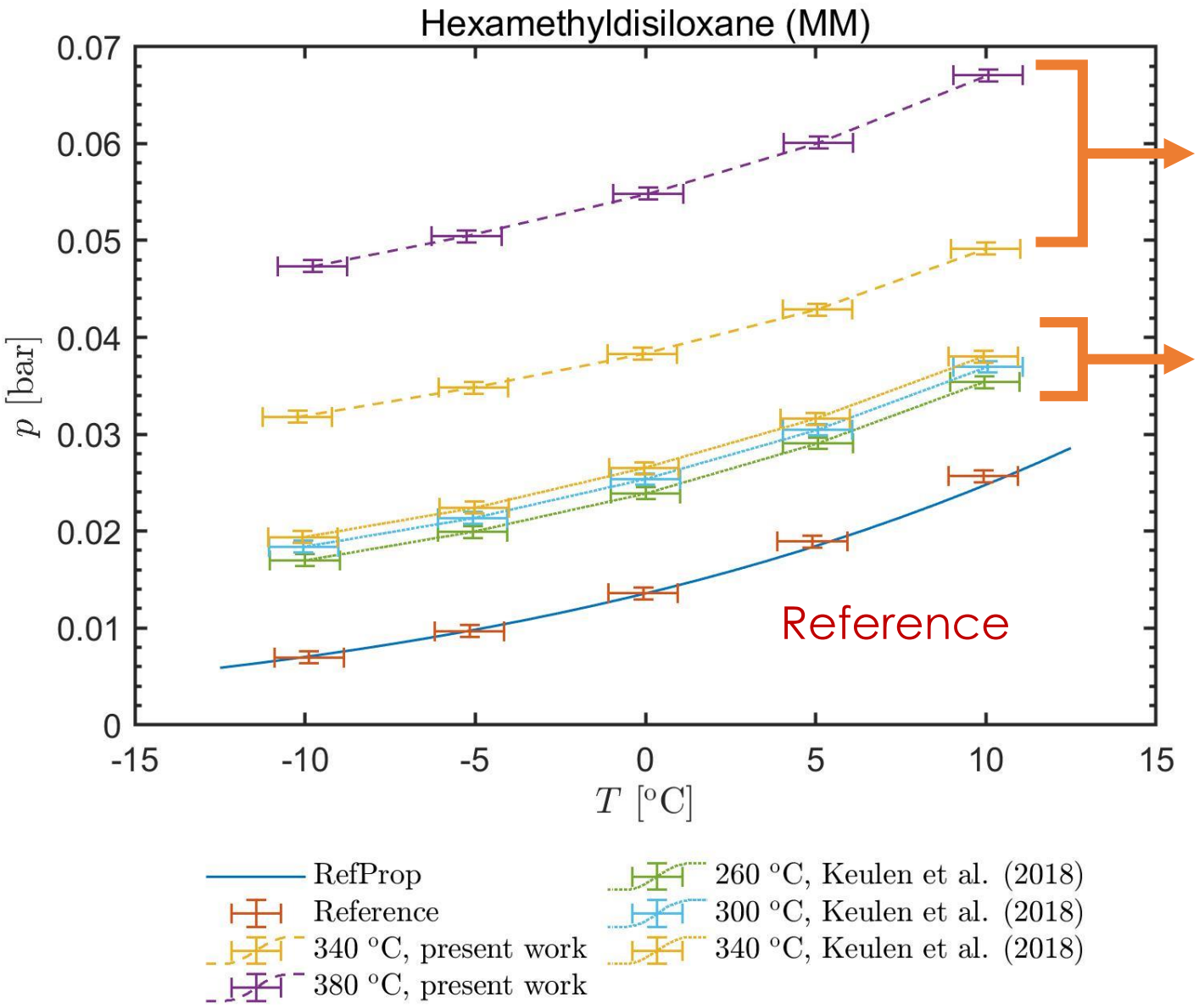
No arbitrary assumptions required

Great complexity

Cost

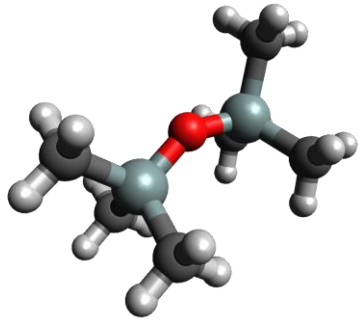
Time of test

p_{vap} curve comparison



Improved system

First system (Keulen et al.)



MM

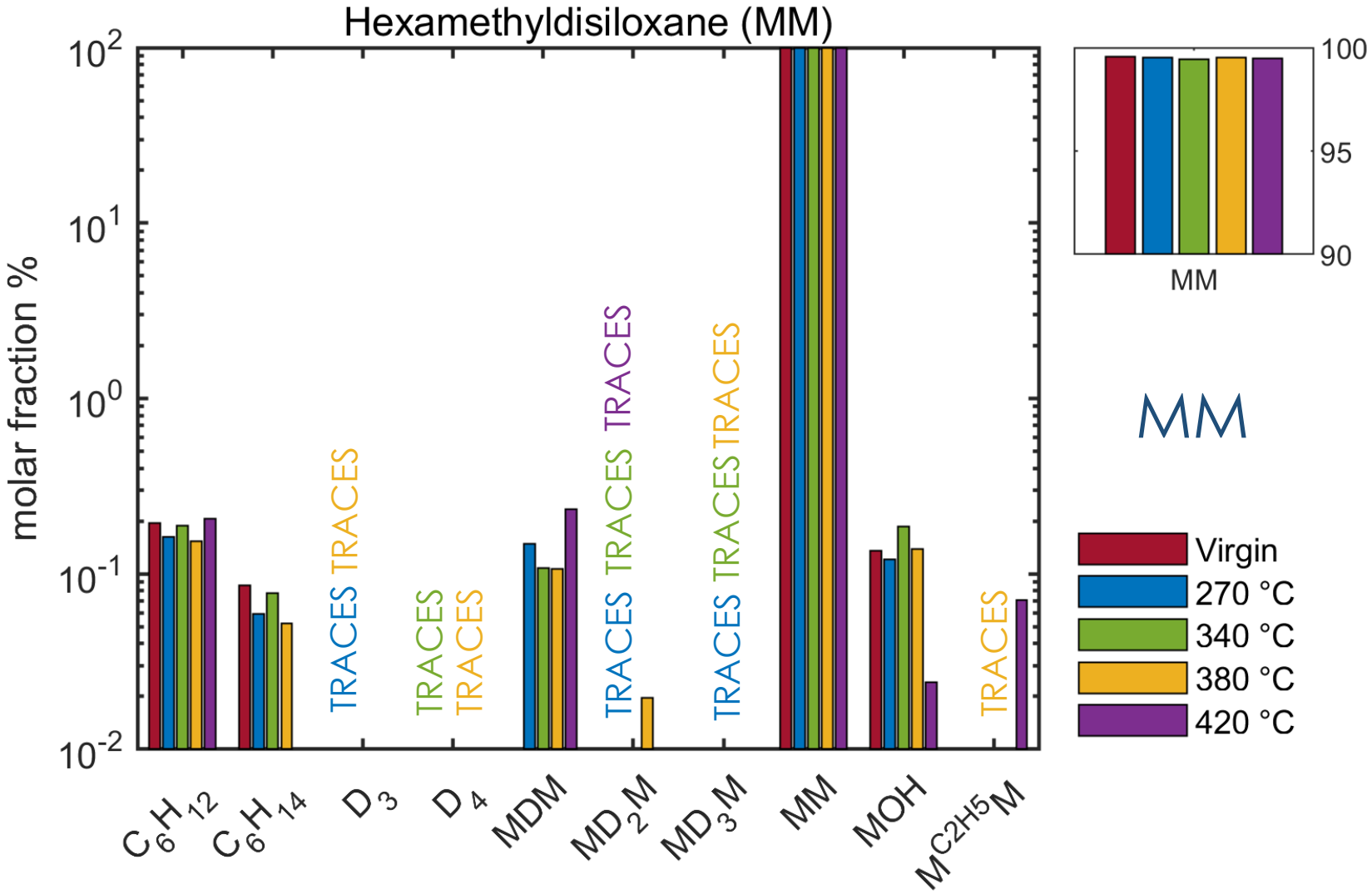
Improved system:

All fluid is stressed

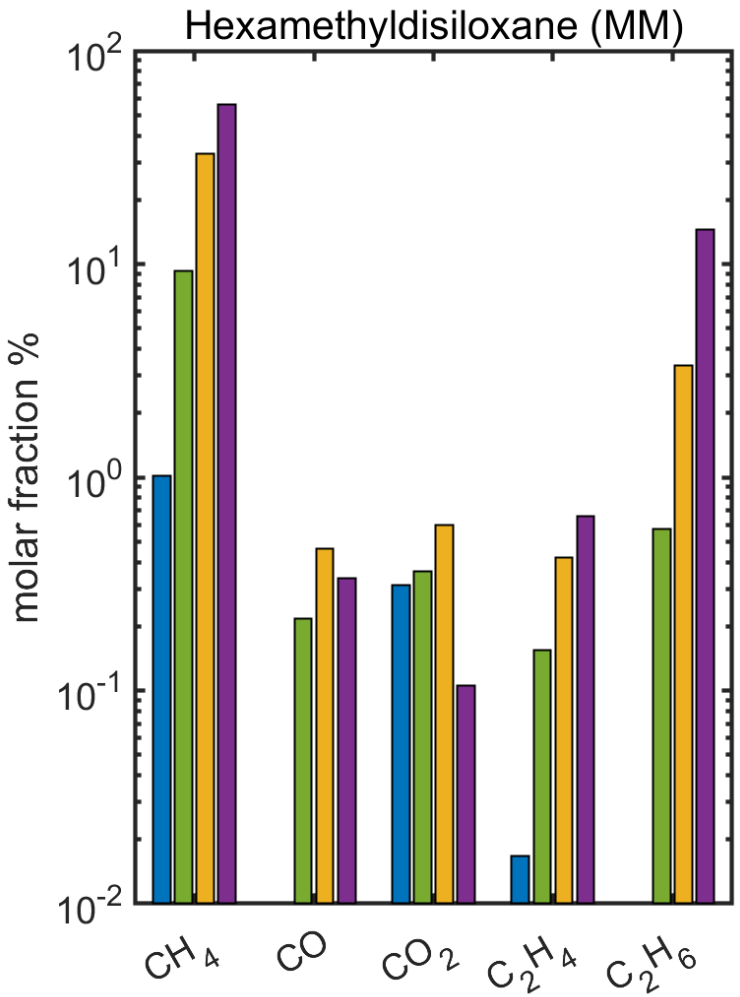
Greater deviation of p_{sat} curve

Improved procedure - chemical analysis:

liquid phase

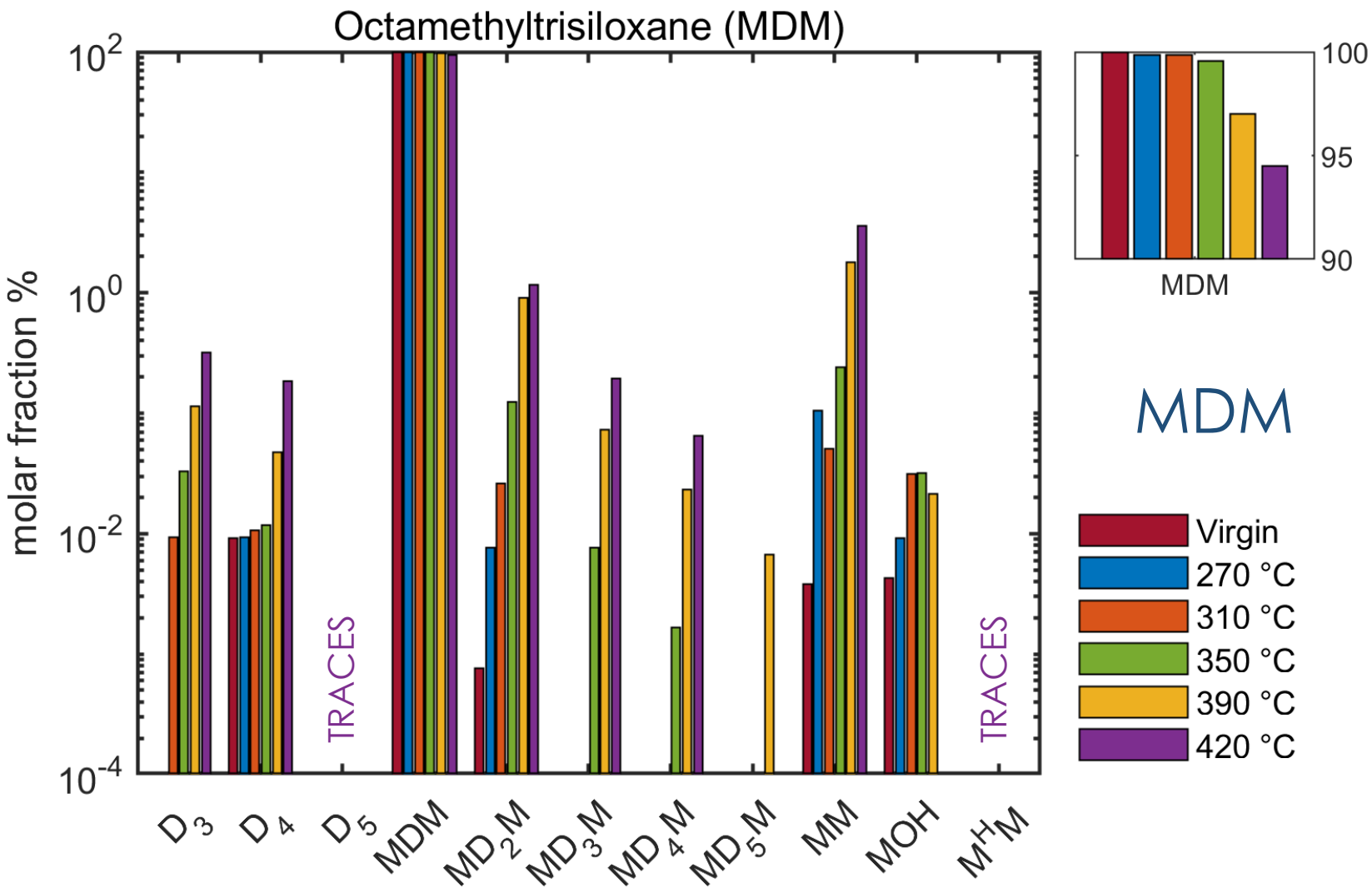


vapor phase

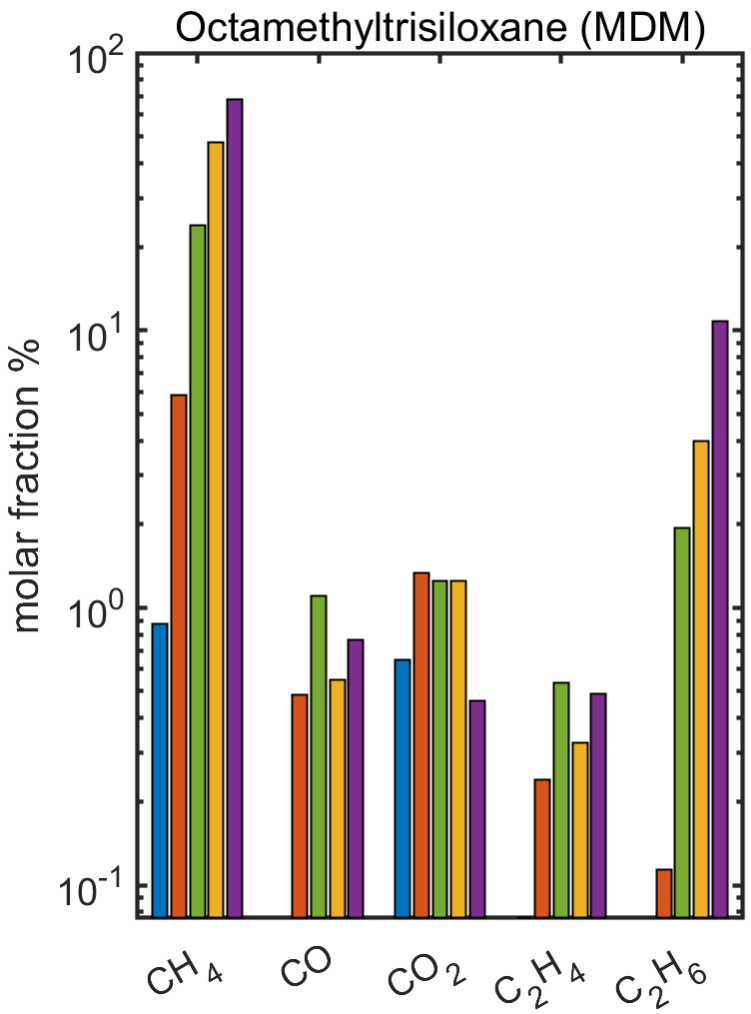


Improved procedure - chemical analysis:

liquid phase



vapor phase



conclusions

- Different methods for testing thermal stability were analyzed
- Methods based on p do not give a clear indication of the entity of decomposition
- Chemical analysis after stress at different T solve the problem
- The method was applied to MM and MDM
  - MM: negligible decomposition in liquid, significant amount of CH_4 in vapor
  - MDM: appreciable decomposition in liquid and significant amount of CH_4 at 350 °C

Current activities and future developments

- Tests on mixtures of MDM and MM

- Tests with contaminants
- Development of a non-static test loop
- Tests on refrigerants

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