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

\[ T_{\text{max}} \uparrow \rightarrow \eta \uparrow \rightarrow \text{thermal stability} \]

Octamethyltrisiloxane (MDM)

Water
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
$\Delta p$ deviation during iso-$T$ stress:

fluid: perfluoro-n-hexane  $T = 350 \, ^{\circ}\text{C}$

Simplicity

Low sensitivity

Arbitrariness:

which $\Delta p = \text{decomposition?}$
deviation of vapor pressure

Great sensitivity

Complexity

$\Delta p$-decomposition amount relation?

Arbitrariness:

$T$ range of $p_{sat}$ meas.?

$\Delta p$ → Change of composition
method

$p$ deviation during iso-$T$ stress

+ deviation of vapor pressure

+ chemical analysis after the **highest** stress temperature

result

no decomposition

decomposition at 240 °C (MM)
260 °C (MDM)

negligible decomposition at 340 °C (MM)
350 °C (MDM)
Thermal stability: critique to the method

Result affected by:

• vapor pressure value \( p_{vap} = f(\text{fluid}, T) \)

• 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
\( p_{\text{vap}} \) curve comparison

All fluid is stressed

Improved system: Greater deviation of \( p_{\text{sat}} \) curve

First system (Keulen et al.)

Improved system:
Improved procedure - chemical analysis:

**Liquid phase**

**Vapor phase**

Hexamethyldisiloxane (MM)
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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