

Decomposition of NC under different conditions

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Outline

1. Motivation
2. Influence of oxygen
3. Influence of humidity
4. Decomposition at low temperature
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Motivation

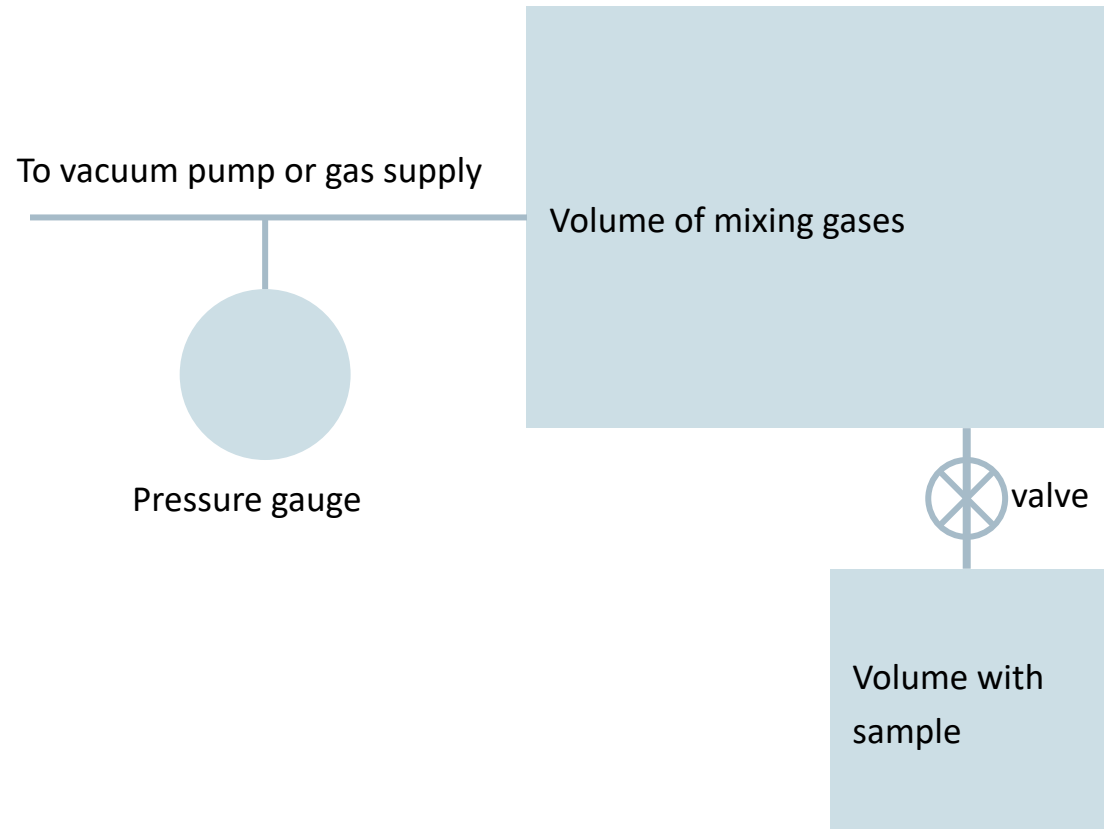
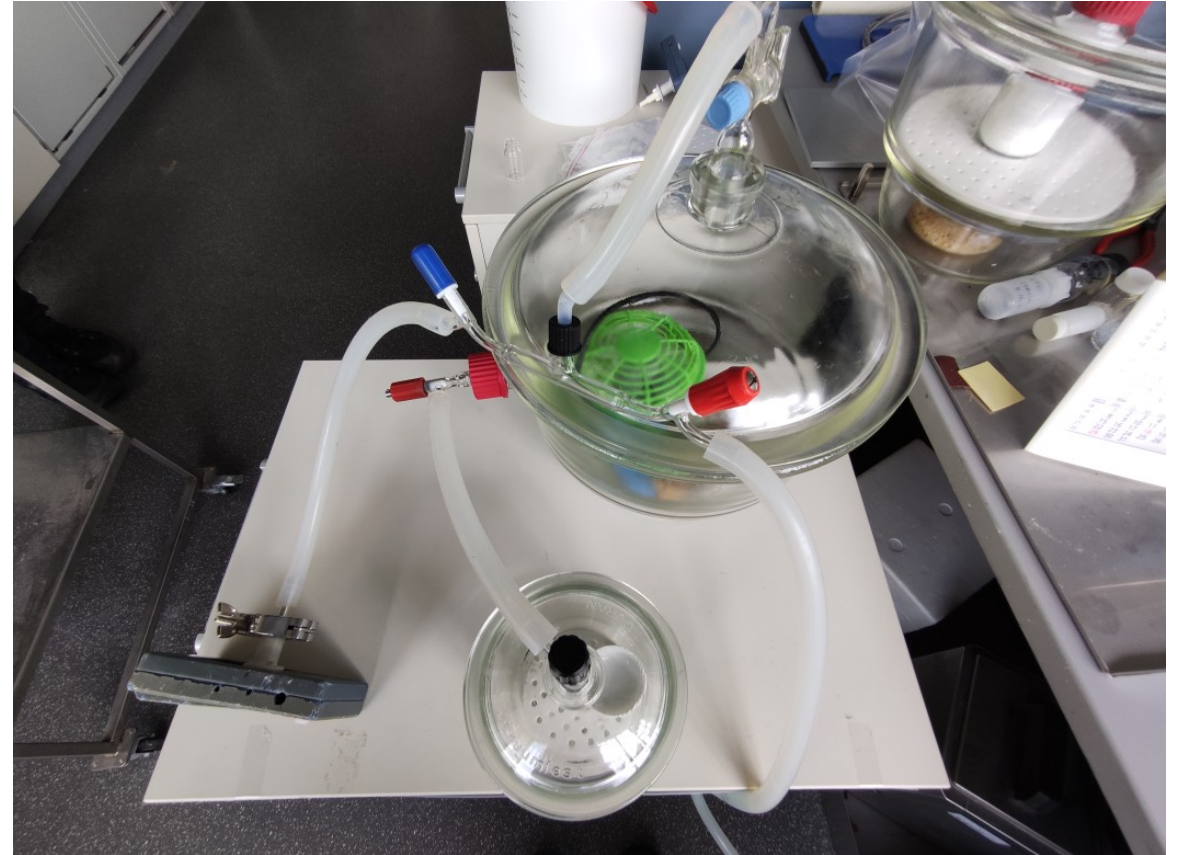
- Nitrocellulose is a well-known and extensively investigated starting point for propellants
- Some questions are still open to investigation and discussion
 - What is the influence of **oxygen** on decomposition of nitrocellulose?
 - What is the influence of **humidity** on decomposition of nitrocellulose?
 - Is the decomposition mechanism at higher temperatures different from the mechanism at lower temperature?
- Here, we investigated NC from MANUCO, France
 - Made from wood pulp
 - Nitrogen content 13.4 % (for ARC, oxygen) and 12.3 % (mass loss, humidity and low temperature)
- We thank MANUCO for providing the NC for our work!

Part 01

Influence of oxygen

Influence of oxygen

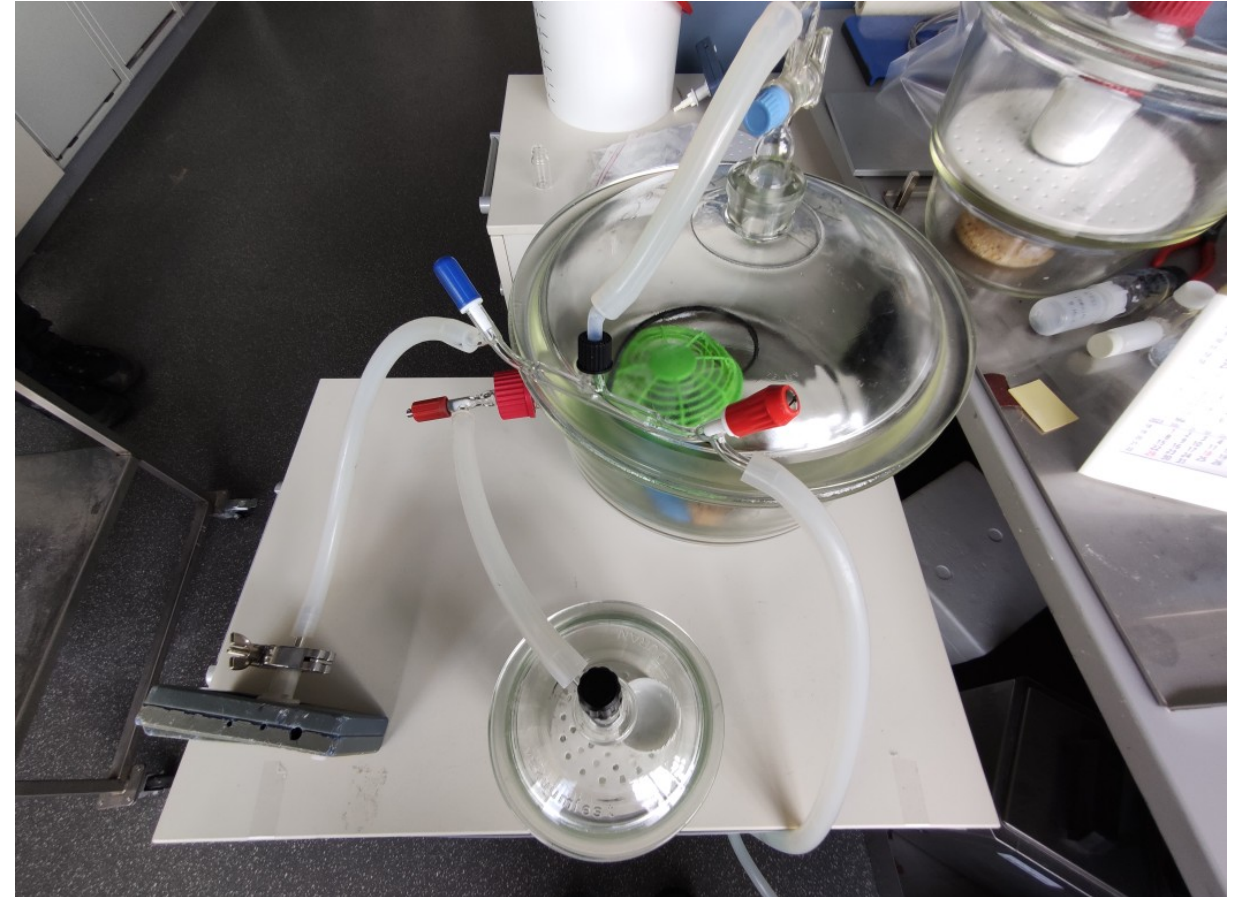
Preparing defined gas mixtures



Influence of oxygen

Preparing defined gas mixtures

- Mixtures of any number of inert gases possible
- Pressure gauge allows control of actual fractions of various gases
- Remote-controlled fan ensures homogenous mixture of gases with different

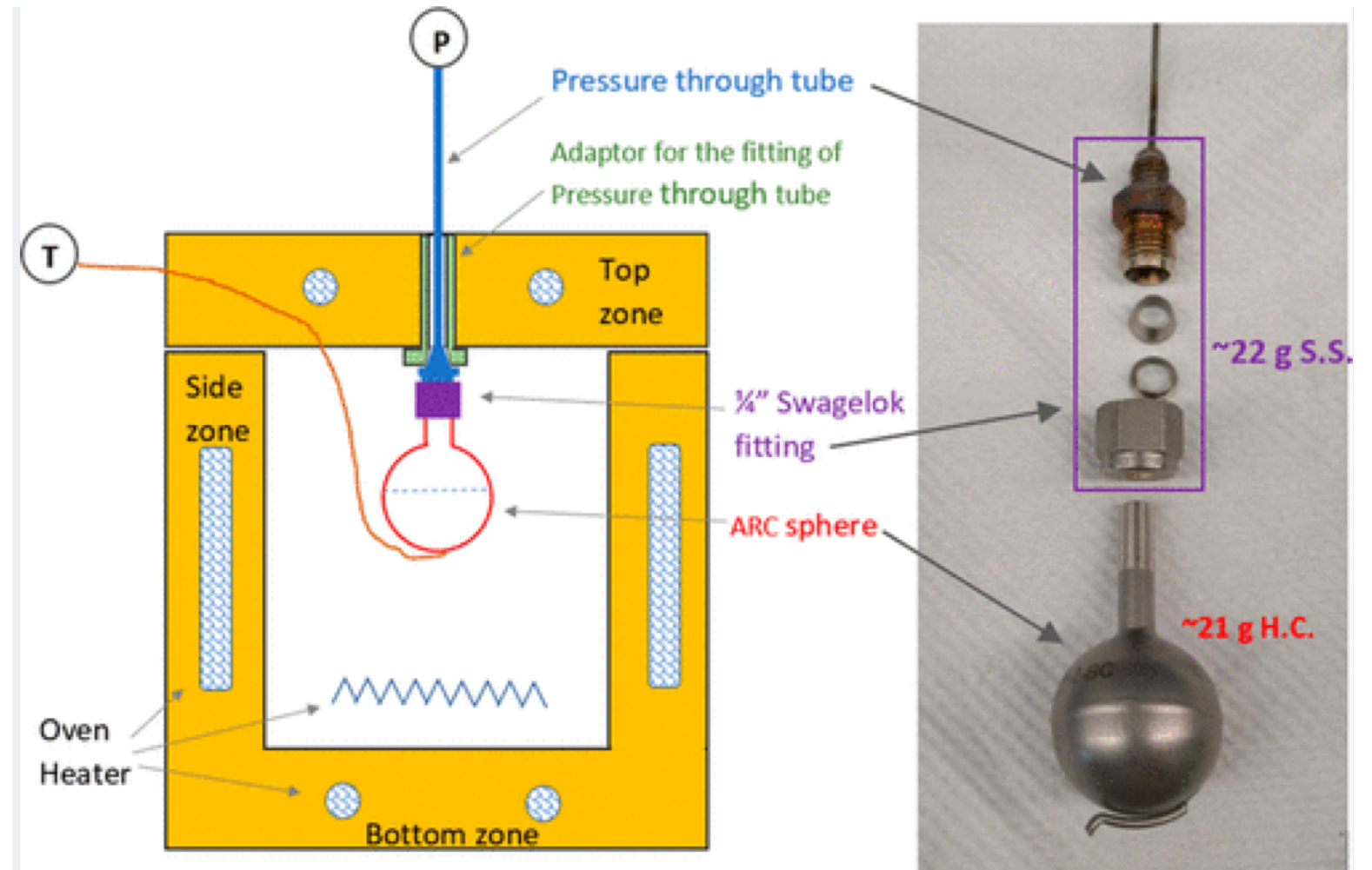


Influence of oxygen

Experimental

Characterization by using Accelerated Rate Calorimetry (ARC)

- 1 inch Ti bomb as sample vessel
- 300 mg sample mass
- Measurement of self heating

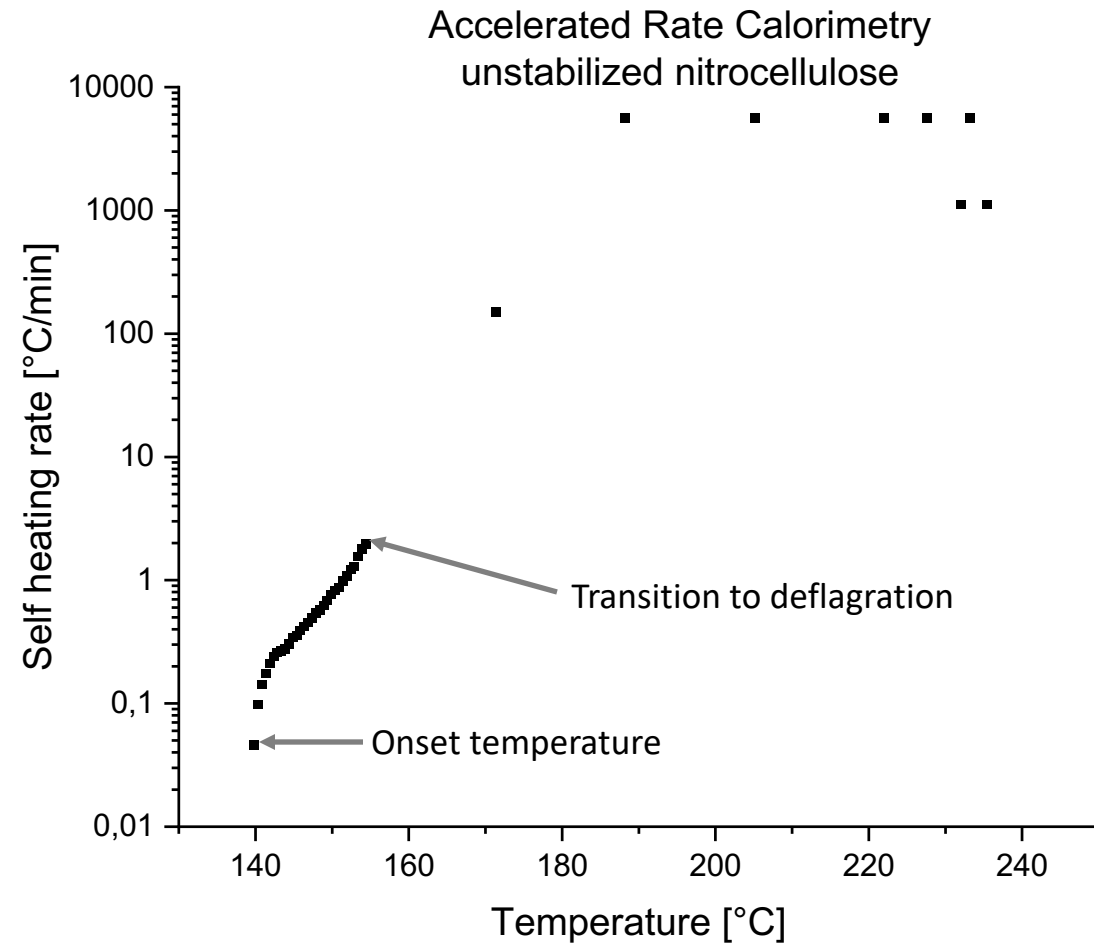


From Min Sheng, Daniel Valco, Craig Tucker: **Heat Loss in Accelerating Rate Calorimetry Analysis and Thermal Lag for High Self-Heat Rates**, *Org. Process Res. Dev.* 2021, 25, 1, 108–119

Influence of oxygen

Example of ARC results

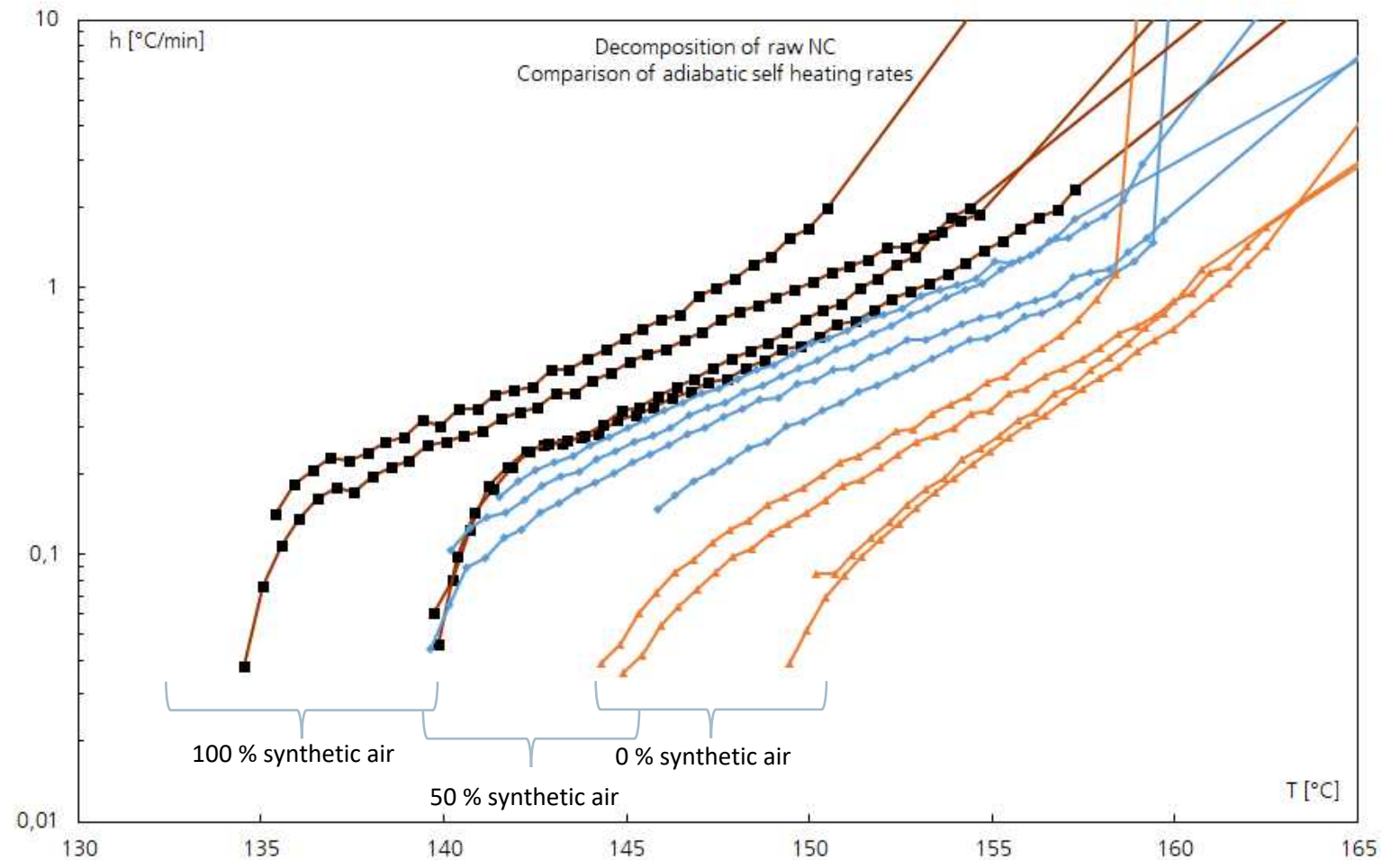
- ARC shows the self heating of the sample due to reaction heat
- As no heat flow into the environment occurs, the sample heats up and the reaction accelerates
- Faster reaction results in higher heat generation and accelerates reaction further



Influence of oxygen

Overview ARC results

- Onset temperature seems to shift to lower temperature as oxygen concentration increases
- Deflagration temperature shifts accordingly
- Slope of self heating process seems to remain constant



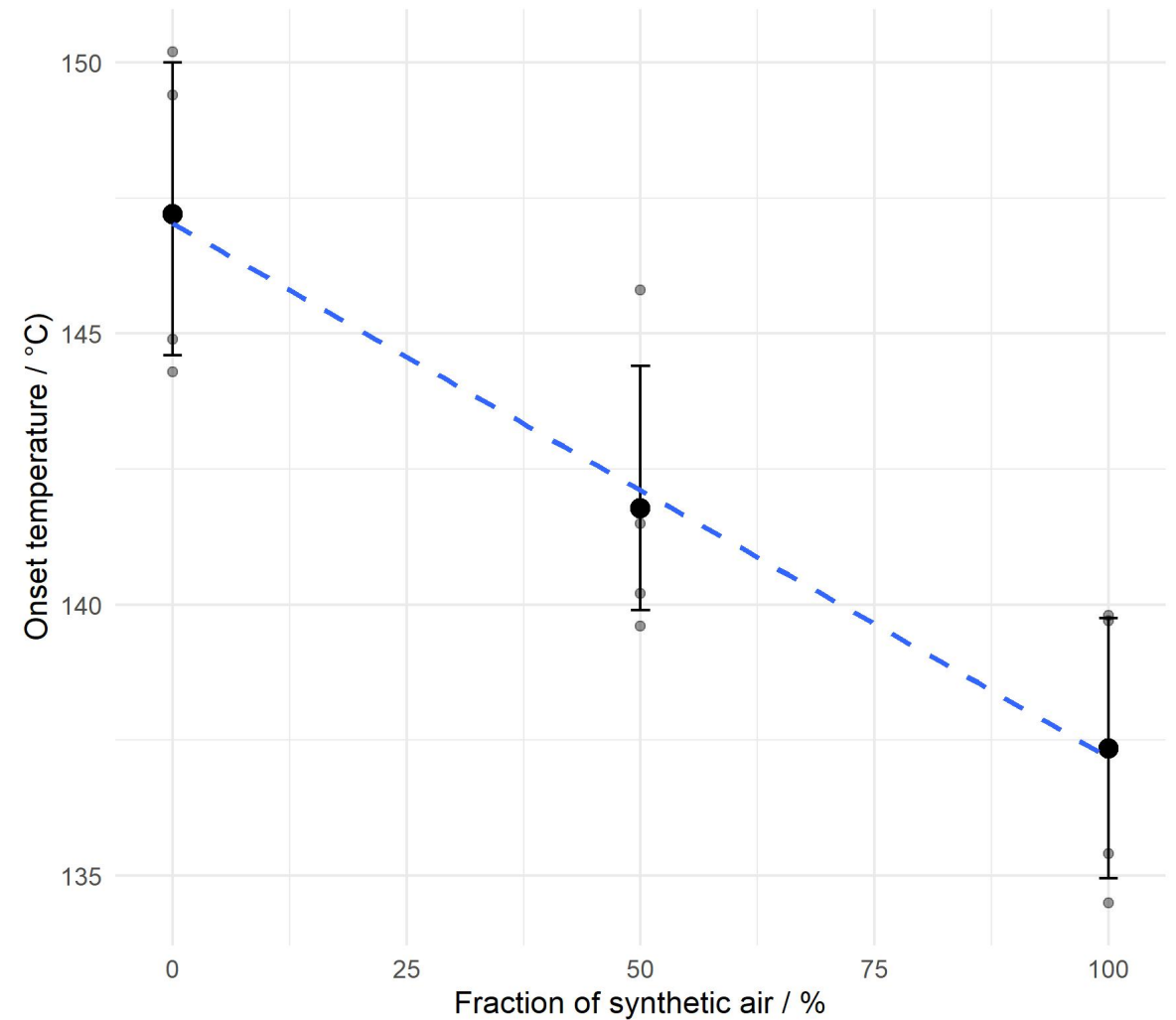
Influence of oxygen

Onset temperature

- Five-fold measurement to make observation representable
- Constant decrease of onset temperature by 0.1 °C per 1 % of synthetic air
- Onset temperatures scatter but influence of oxygen concentration is statically significant

Decomposition of NC under different oxygen contents

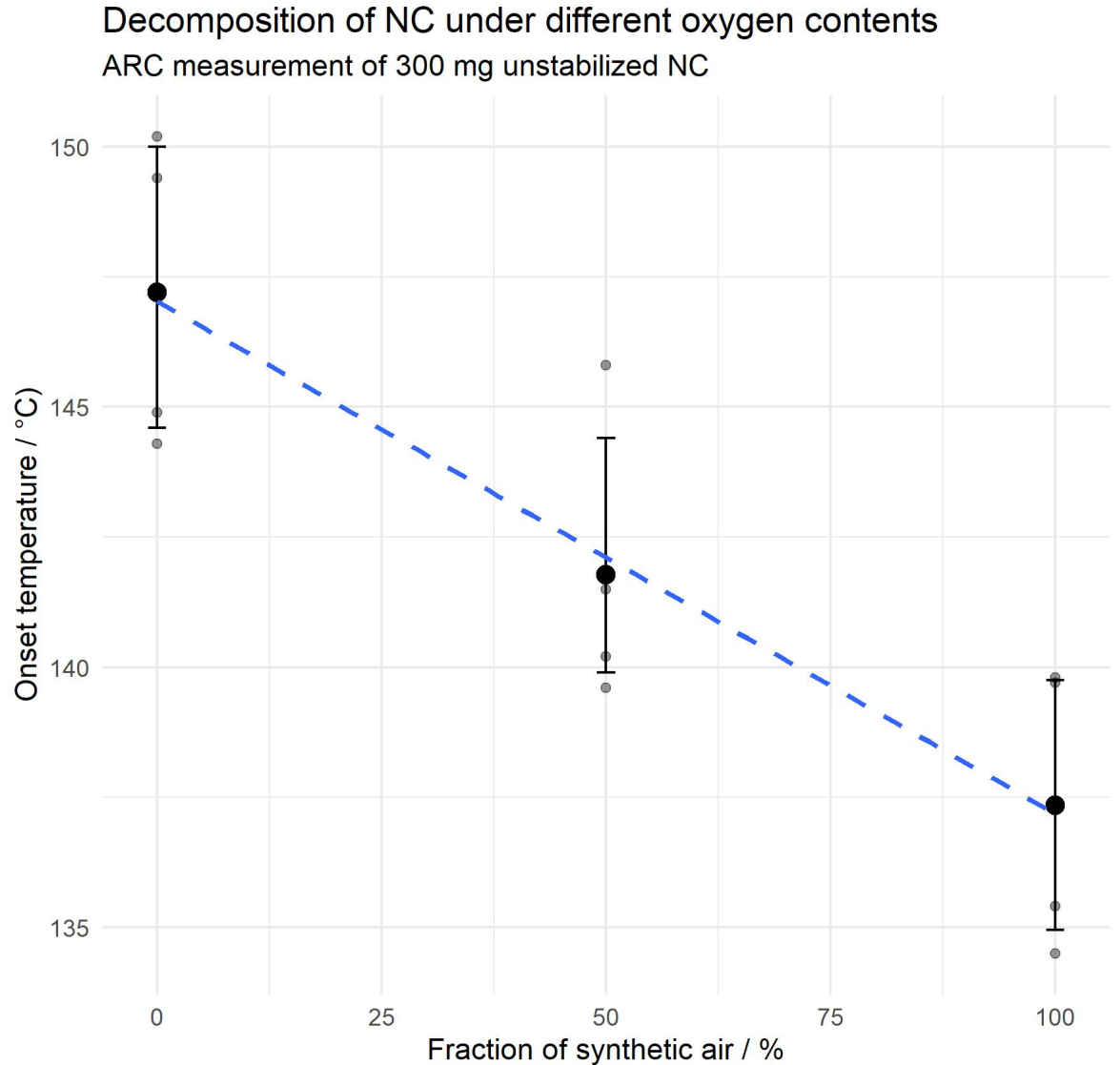
ARC measurement of 300 mg unstabilized NC



Influence of oxygen

Interpretation

- Oxygen has significant influence on onset temperature but not on self heating rate
- Linear dependency suggests that oxygen is partaking in a chemical reaction and does not serve as a catalyst
- One possibility is that oxygen oxidizes NO to NO₂, NO is formed during NC decomposition
- NO₂ is catalyzing NC decomposition
- From linear dependency, one can assume that oxygen is the limiting factor



Part 02

Influence of humidity

Influence of humidity

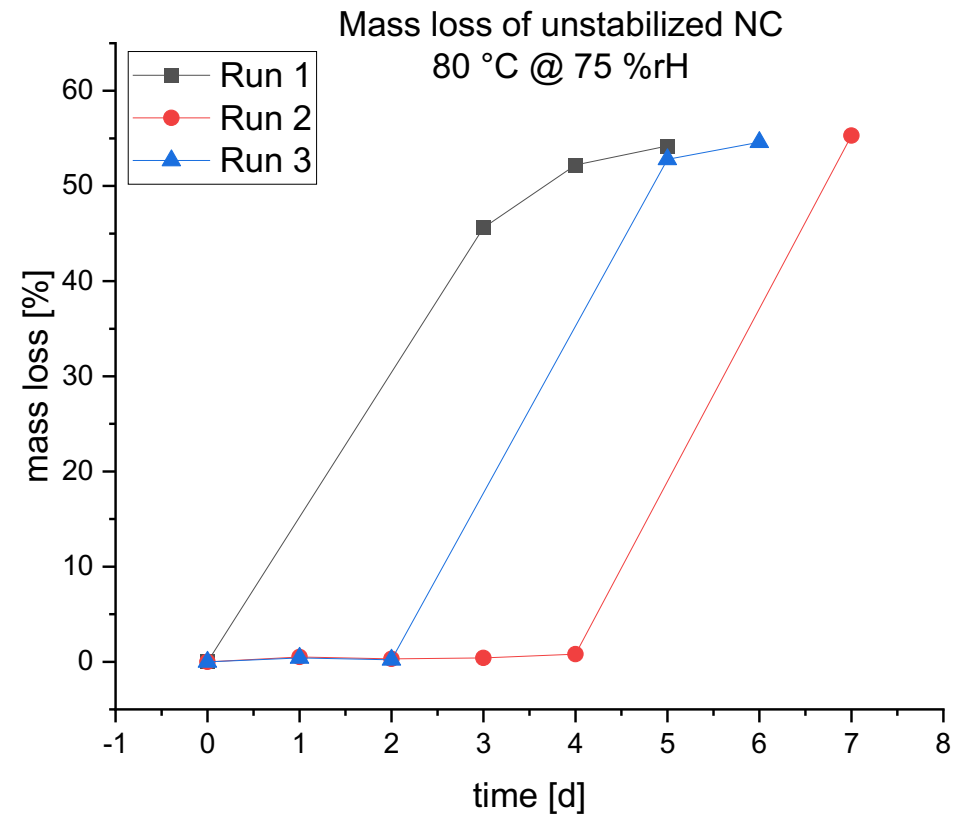
Experimental

- 1 g of sample placed in a glass vial
- All vials are placed in a climate-controlled chamber
- Two samples in parallel
- Vials are stored openly for 10 min climate-controlled chamber to allow equilibration of humidity
- After defined time, vials are retrieved and stored openly at 35 °C in an oven to remove humidity and prevent condensation
- Vials are closed and weighed after colling down to room temperature
- Temperature between 60 °C and 80 °C
- Humidity levels at 25 %, 50 % and 75 %
- Samples are weighed on a regular basis until decomposition occurs

Influence of humidity

Mass loss of climate-controlled unstabilized NC

Three different runs result in completely different decomposition behaviors



Influence of humidity

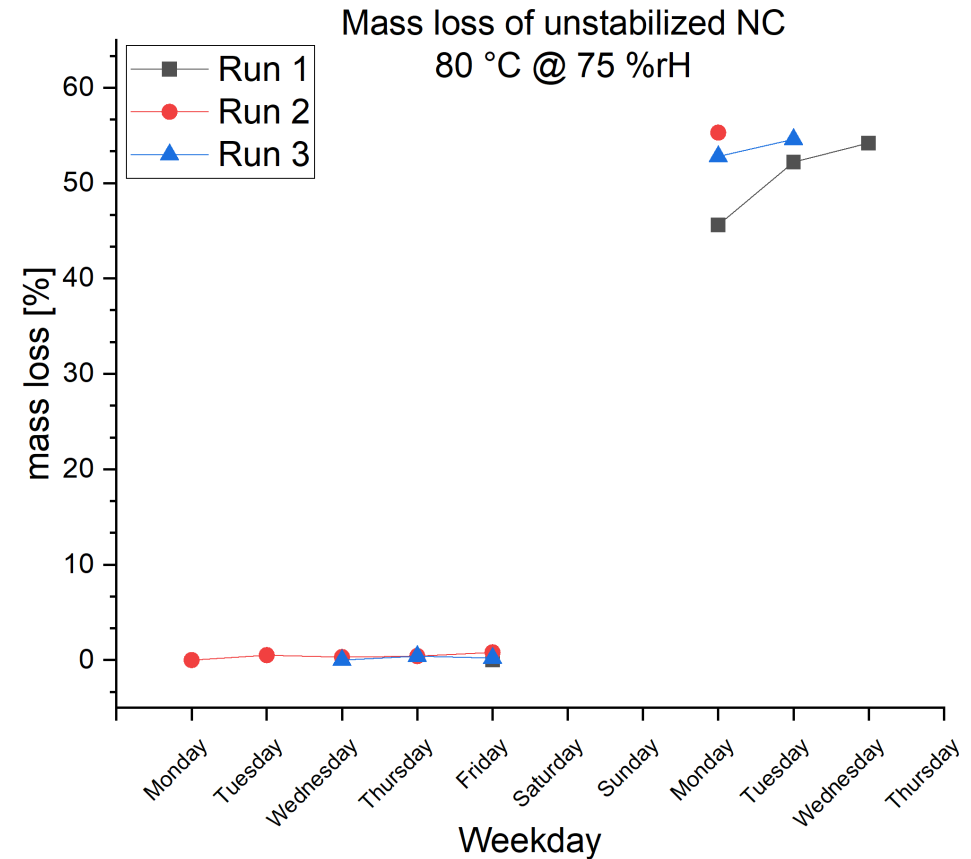
Mass loss of climate-controlled unstabilized NC

If mass loss is regarded as a function of weekday, measurements are consistent

Decomposition occurs over period with no gas exchange

Probably accumulation of reactive species (NO_x)

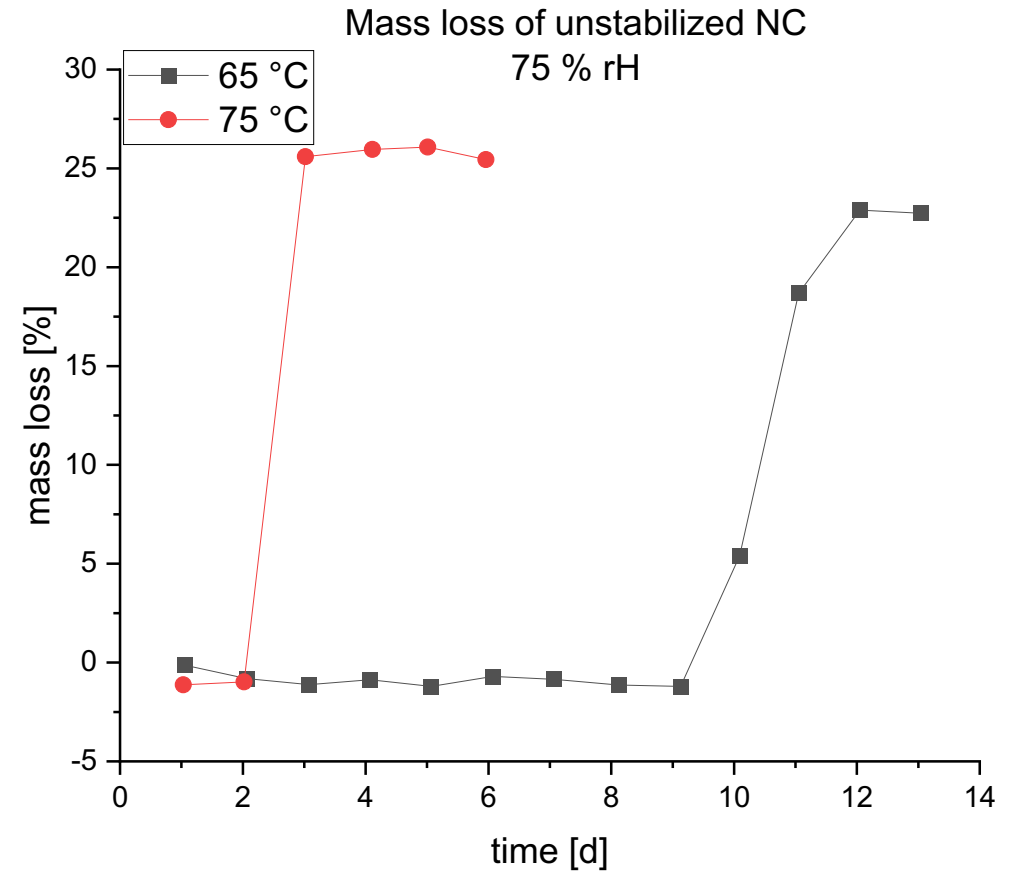
- New measurement procedure:
 - Each time point is a sample that is stored for a pre-defined time, mass loss is determined and the sample then discarded
 - Huge increase in needed NC



Influence of humidity

Interpretation

- Experimental control (sample handling, measurement intervals) have a very large influence on results
- Extrapolation to lower temperatures difficult:
 - 25 % rH at 80 °C correspond to (theoretical) 400 % at RT
 - Realistic humidity levels @ RT between 40 % and 60 %
- Effect of experimental control could be much larger than humidity fluctuation



Part 03

Decomposition at low temperatures

Decomposition at low temperatures

Experimental

- Mass loss measurements are conducted in glass vials with 1 g of NC
- Each measurement is conducted five-fold
- Temperatures from 40 °C to 80 °C in steps of 5 °C
- Mass loss is retrieved, cooled to RT and then weighed

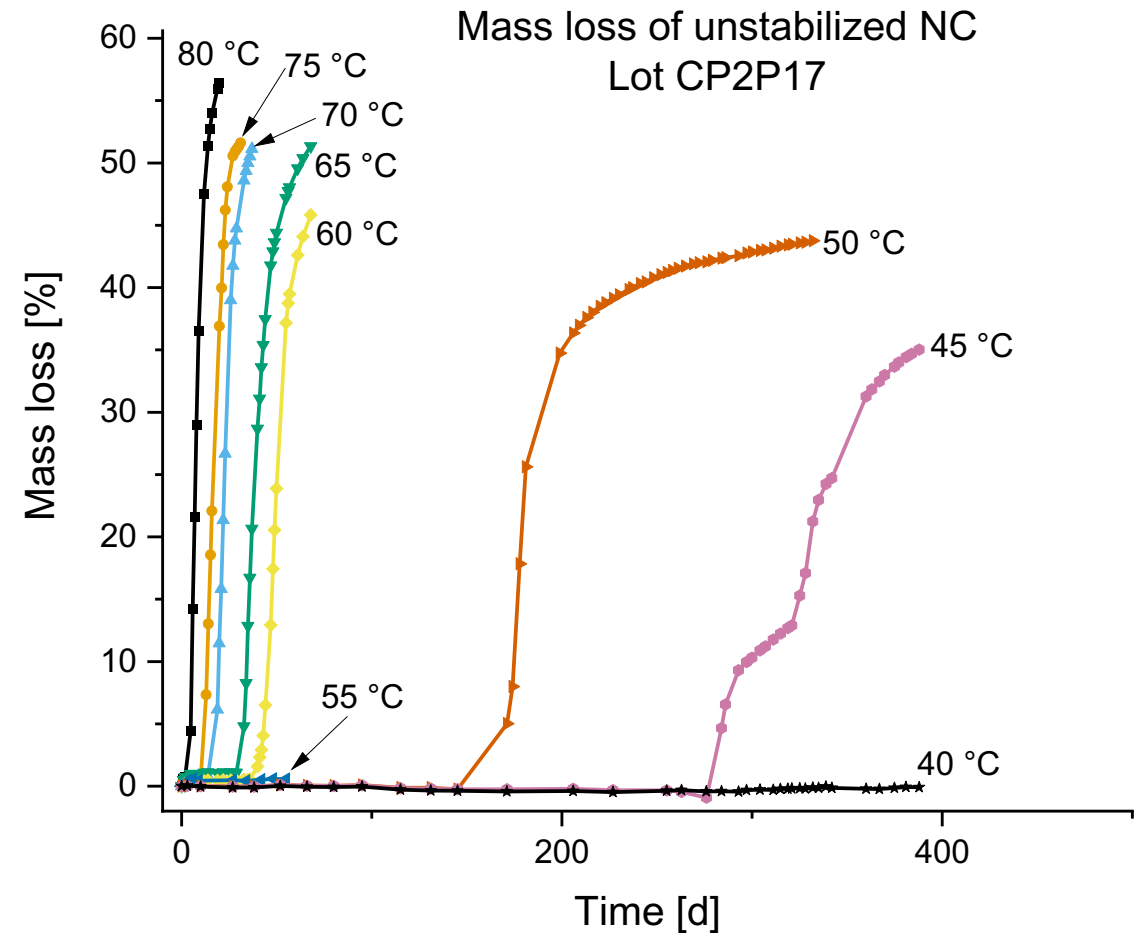


Decomposition at low temperatures

Mass loss

- As expected, autocatalytic decomposition is observed with decreasing with increasing temperature
- STANAG assumes change of activation energy for decomposition at 60 °C
- Time until fast decomposition occurs can be used to calculate activation energy via Arrhenius equation

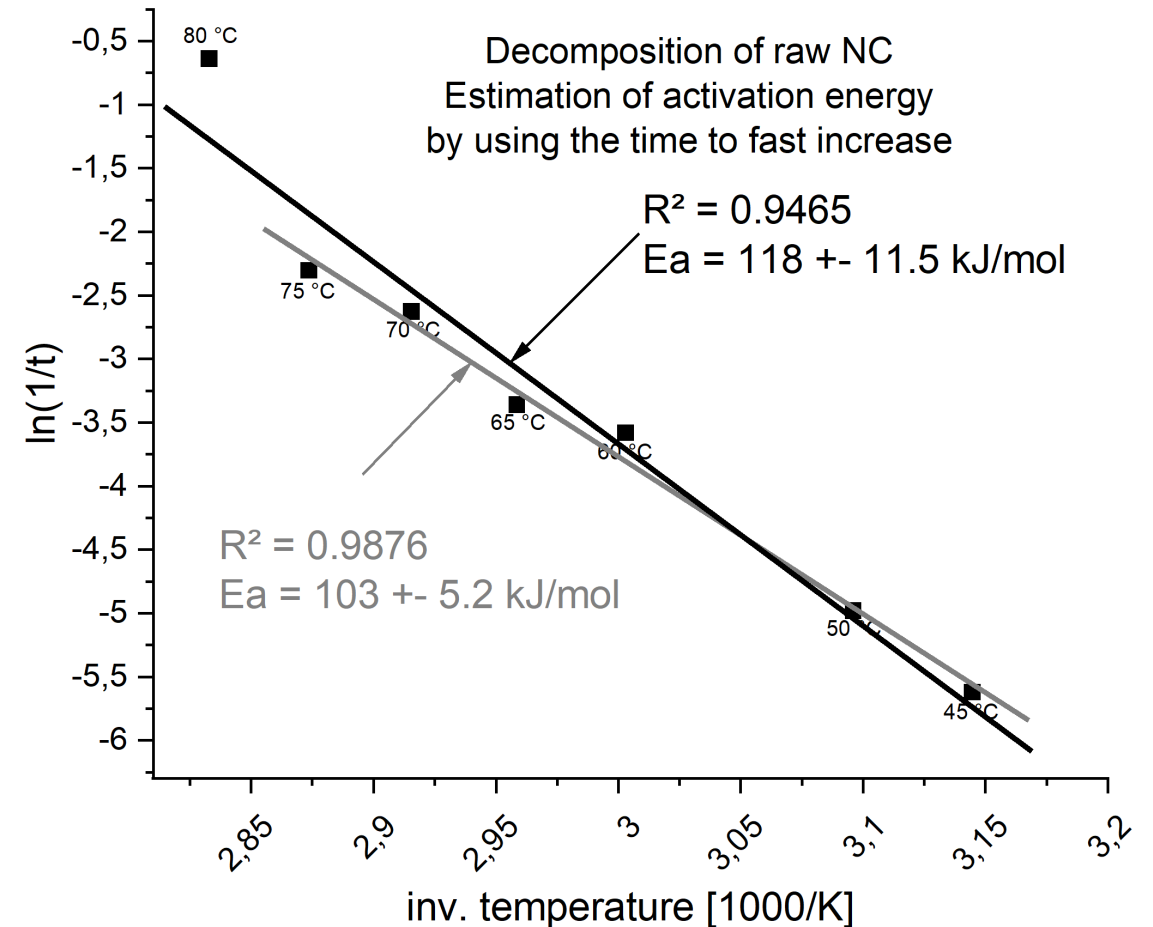
$$\ln k = \ln \frac{1}{t_{fastIncrease}} = \ln A - \frac{E_a}{R \cdot T}$$



Decomposition at low temperatures

Mass loss

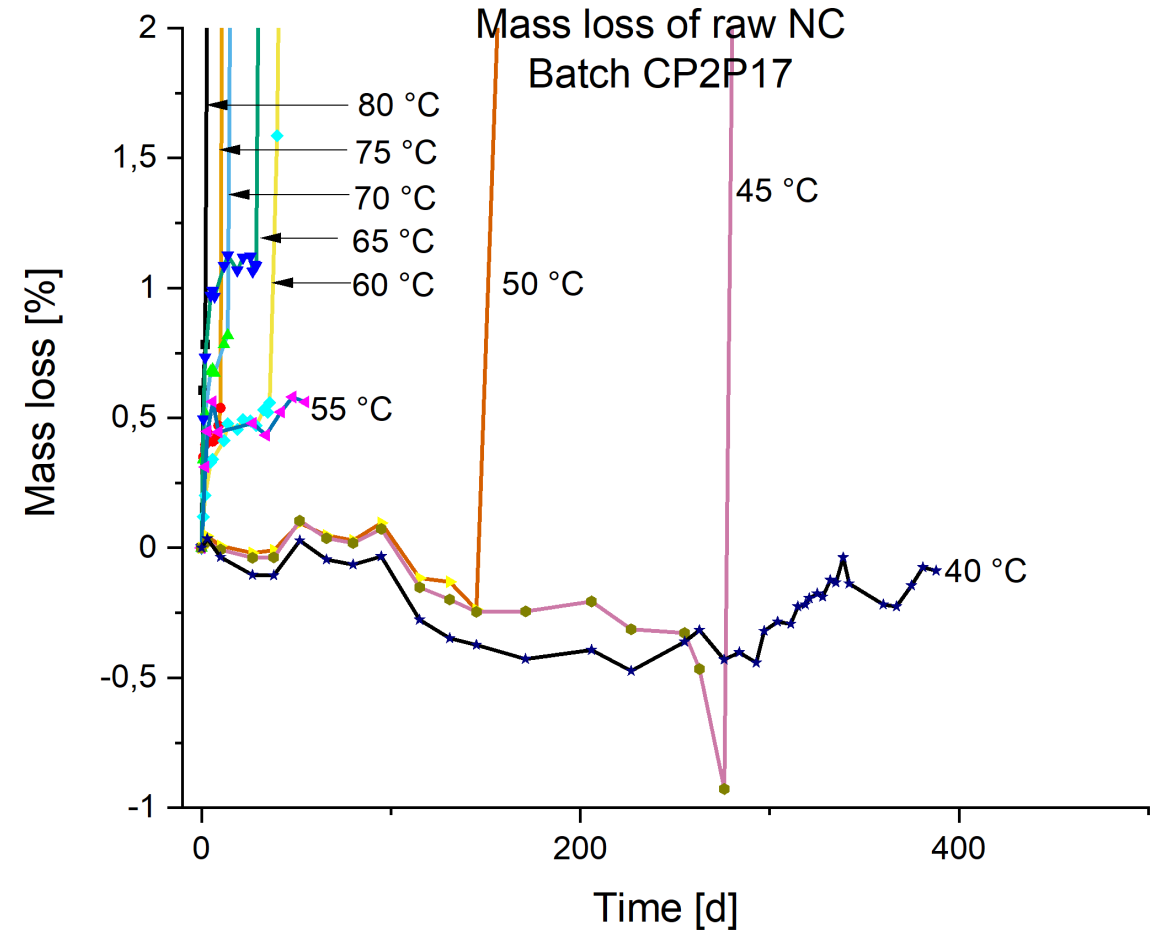
- Arrhenius equation shows good linear fit
- Activation energy between 100 and 120 kJ/mol, which is well within literature range
- No change of activation energy can be observed in this plot
- Value at 80 °c is off, but it is difficult to determine fast increase due to rapid decomposition



Decomposition at low temperatures

Mass loss – close-up

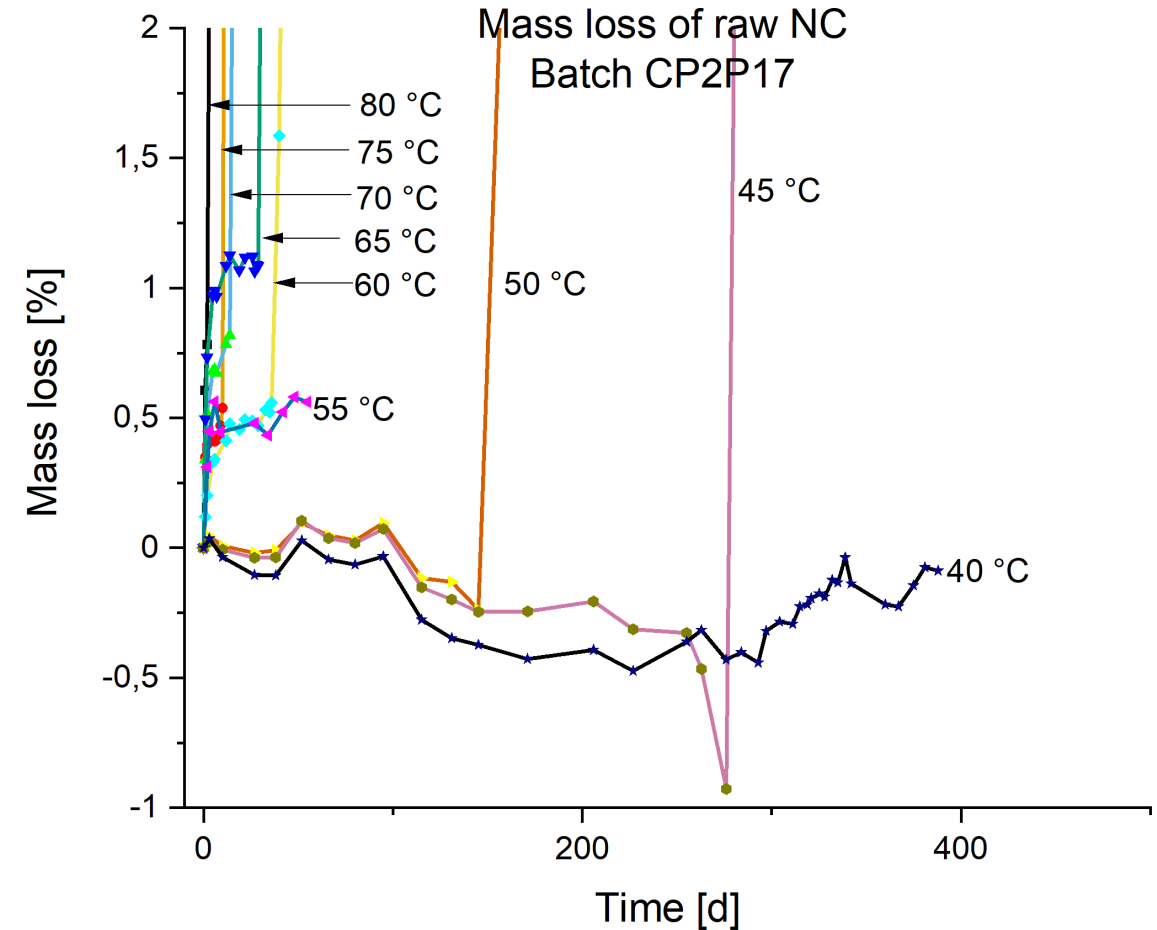
- Samples $\geq 55\text{ °C}$ show initial mass loss
- This is usually attributed to evaporation of water, solvents or other volatile compounds
- Below 55 °C , a mass increase is observed with unclear reason
- Low temperature samples show parallel tendency, all measured at the same days → maybe day-to-day fluctuation due to changes in ambient conditions
- Samples at low temperatures show an additional mass increase before decomposition
- For higher temperatures this is not observable but could be hidden by fast mass losses



Decomposition at low temperatures

Interpretation

- Process solvent (water?) might evaporate at 55 °C under these conditions
- If mass loss below 55 °C is a different reaction, this might be an indication of the reaction that is assumed by STANAG to change at 60 °C
- Reason for mass increase is unclear as is sharp mass increase before decomposition



Part 05



Summary

Summary and conclusions

Oxygen

- Oxygen linearly decreases decomposition temperature of NC by 0.1 °C per % synthetic air
- Possible interpretation is oxidation of NO to NO₂ which autocatalytically decomposes NC
- Oxidation is the speed determining step in this reaction

Humidity

- NC decomposes faster as humidity increases
- Exchange of reactive species can heavily influence decomposition behavior and might partially negate the influence of humidity
- At low temperature, the effect of humidity will be concealed by experimental control
- Comparison of different experiments is therefore difficult

Low temperature

- Change of activation energy at 60 °C can neither be confirmed nor disproved
- NC shows a mass increase under 55 °C
- Activation energy of the start of autocatalytic decomposition is between 100 and 120 kJ/mol
- NC shows additional mass increase before decomposition

Thank you for your attention!
