

# Influence of the temperature rise time on pyrograms in analytical pyrolysis



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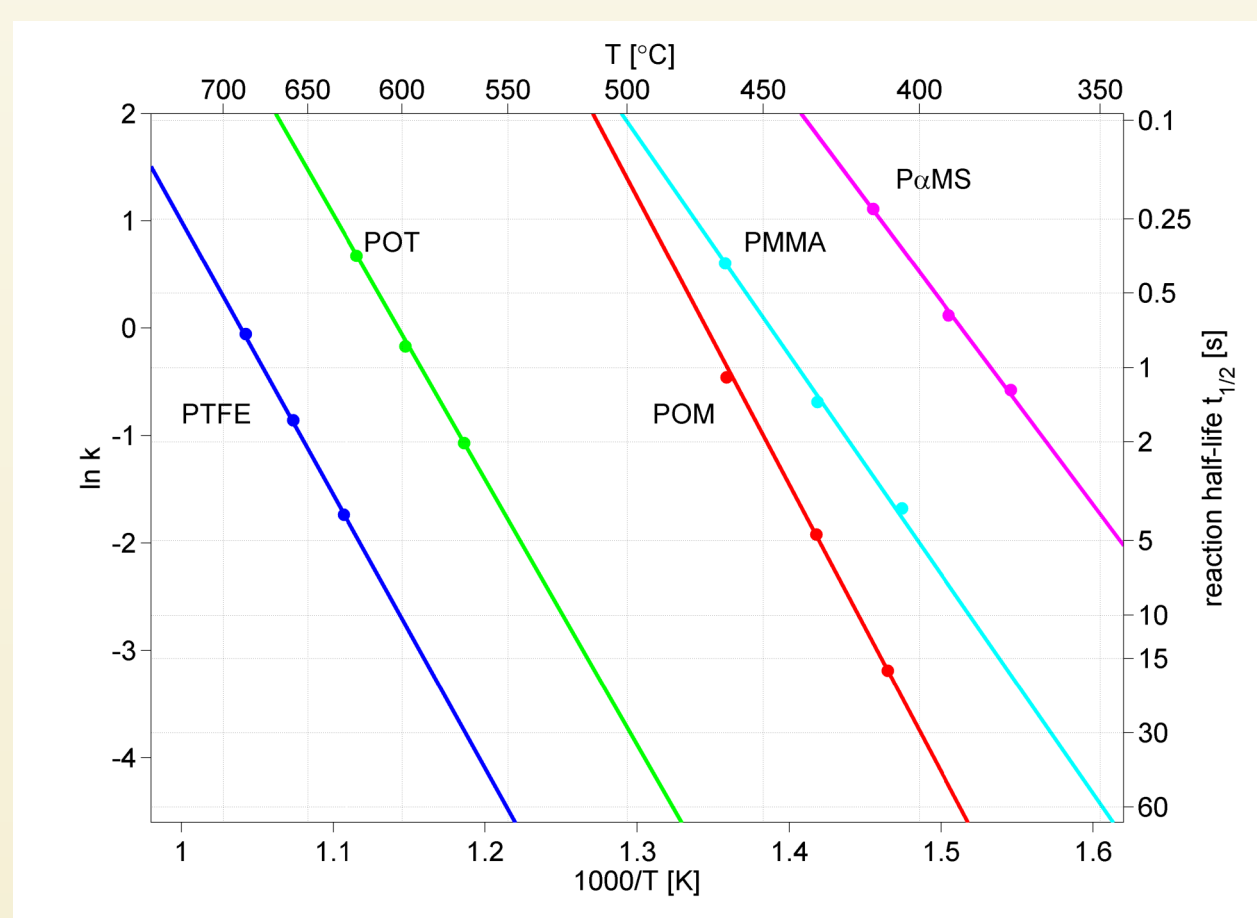
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## Introduction

Thermal degradation by pyrolysis is highly temperature dependent, and the distribution of pyrolysis products is dependent on the actual temperature at thermal decomposition. However it is not widely recognised that the time it takes to reach the equilibrium temperature of the pyrolyzer, the temperature rise time, can have a significant impact on the actual pyrolysis temperature of the sample, and thus on the pyrolysis results. The temperature rise time must be small in relation to the half-decomposition time in order to reach the intended pyrolysis temperature. Furthermore, with a cooling off time of the same order of magnitude it is possible to halt the pyrolysis, and the same sample can then be pyrolyzed again. This is the foundation of the methods of fractionated and sequential pyrolysis, as well as pyrotomy [2].

## Influence of temperature rise time

The pyrolysis degradation rate is highly temperature dependent, and generally follows the Arrhenius equation. This means that it is linear in a logarithmic scale versus the inverse of the temperature, see figure 1. The formation rate of monomers at different pyrolysis temperatures was determined experimentally for five polymers with a Pyrola pyrolyzer [1].



Alternatively the degradation rate may be expressed by the half-decomposition time, which is the time it takes for the half of the remaining to react. This gives the time scale of the reaction and is indicated to the right in figure 1. The temperature is given on top of the diagram for easier reading. Note the rapid decrease in half-decomposition time with increasing temperature.

Figure 1. Arrhenius plot of pyrolysis of 5 polymers: PTFE = poly(tetrafluoroethylene), POT = poly(octylthiophene), POM = poly(oxymethylene), PMMA = poly(methyl methacrylate), PaMS = poly( $\alpha$ -methylstyrene). Formation of monomers. Experimental data from [1].

The temperatures during a pyrolysis may be described by a temperature time profile, see figure 2. The temperature starts at a chamber temperature, increases to the equilibrium temperature. The time it takes is called the **temperature rise time**. The temperature increase may also be characterised by the temperature ramp, in  $^{\circ}\text{C}/\text{s}$ . The temperature is held constant, and then decreases during the cooling of time.

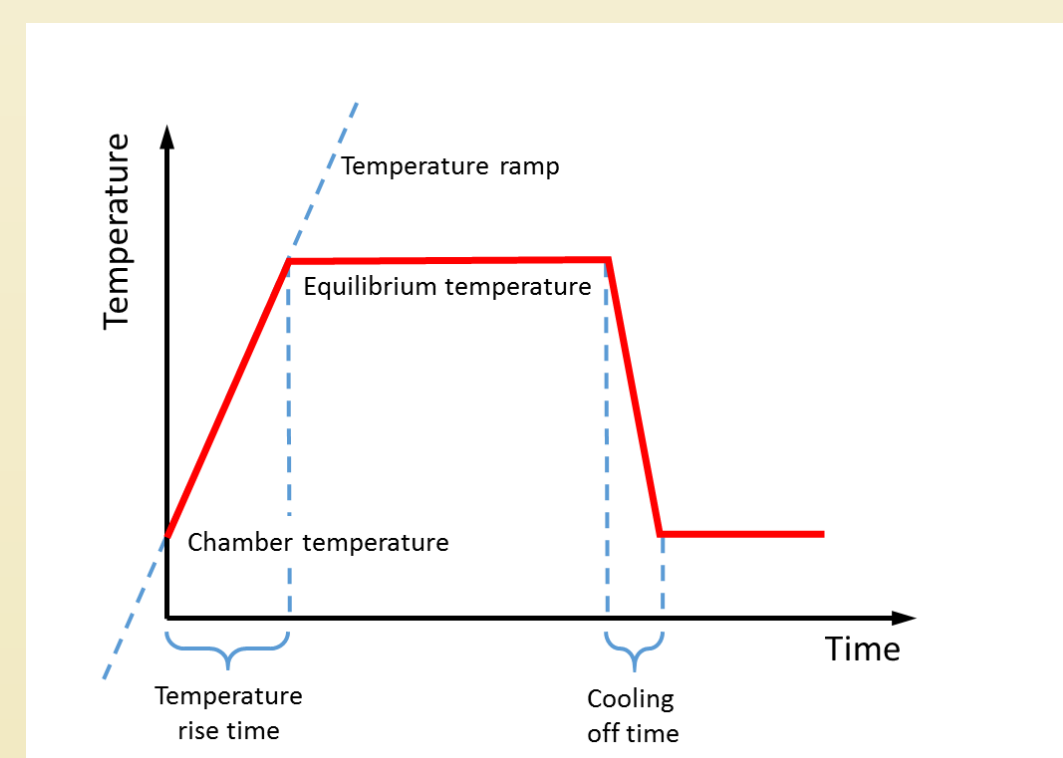


Figure 2. Temperature time profile. Typical values for Pyrola is 8 ms temperature rise time, 2 s pyrolysis.

The influence of the temperature rise time may be investigated by a numerical experiment, with the following assumptions:

- The pyrolysis is a first-order reaction.
- The reaction rates given by the Arrhenius equation are valid for all temperatures.
- The temperature is the same in the whole sample and follows a given temperature time profile.

The thermal degradation is calculated by solving the first-order differential equation.

The result of a calculation for pyrolysis of POM, poly(oxymethylene), is shown in figure 3. An isothermal pyrolysis with 8 ms temperature rise time is compared to three temperature ramps. The temperature and the formation of pyrolysis products are shown in the same diagram.

Two effects may be observed: With the slower temperature ramps the sample is **pyrolysed before the equilibrium temperature is reached**. A slower ramp also has the consequence that the pyrolysis products are formed at a lower intensity over a longer period of time, **making the peaks wider**.

Experimental results with the same temperature time profiles are shown in figure 4, although with a different sample than in figure 3, pyrolysis of a lacquer. The output from the mass spectrometer (TIC) gets wider and lower as predicted by the theoretical result.

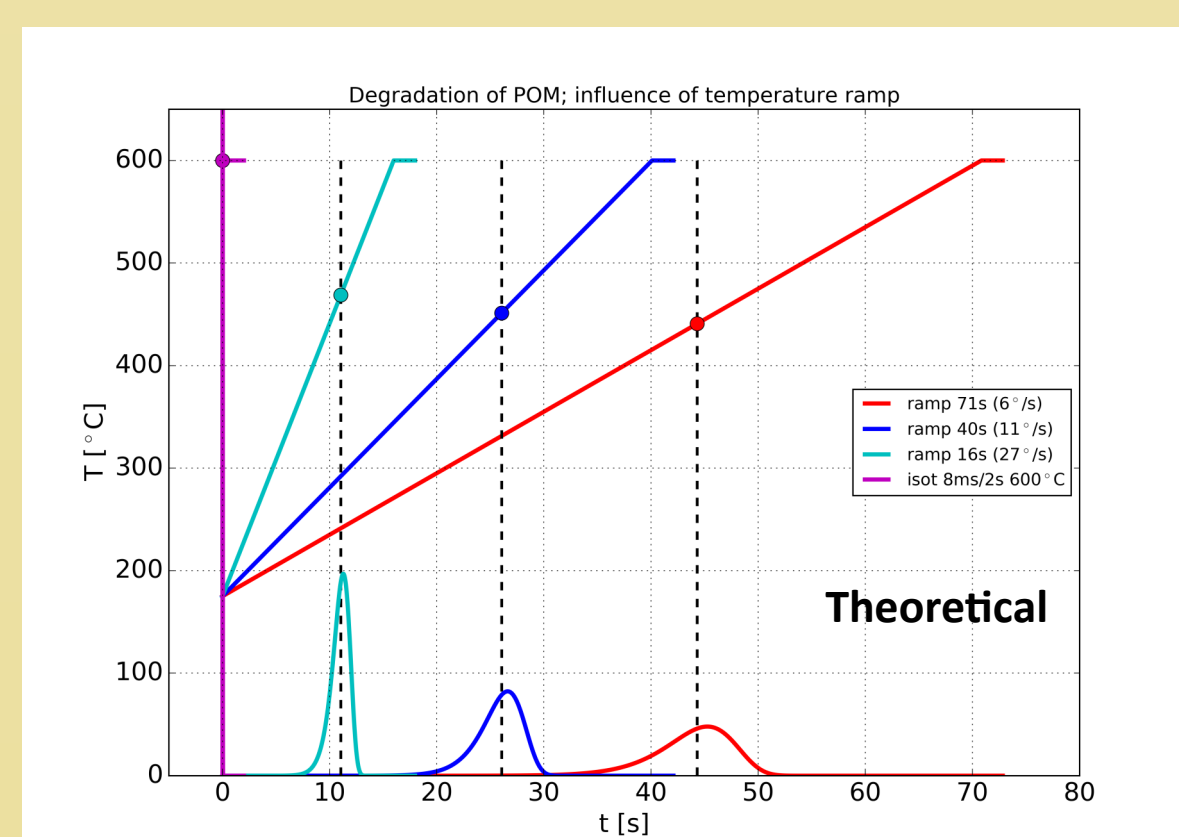


Figure 3. Influence of temperature rise time on pyrolysis of POM. Theoretical result.

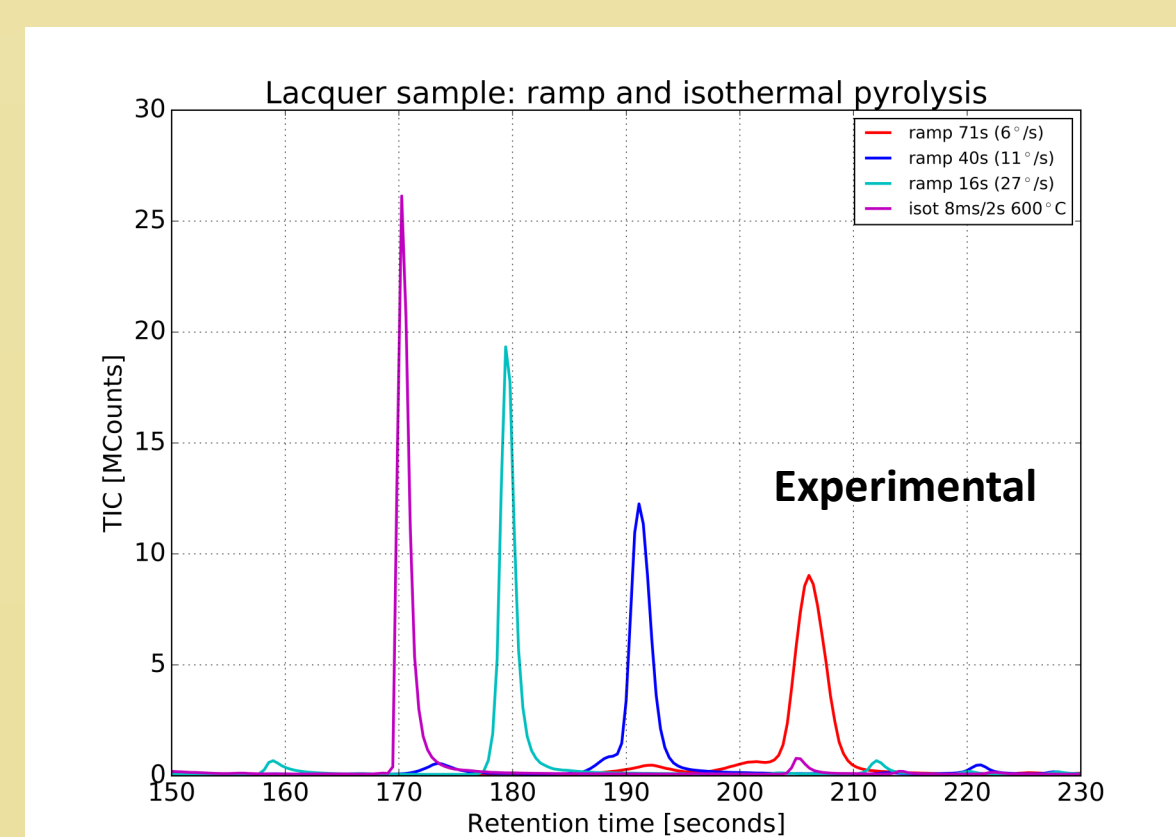


Figure 4. Influence of temperature rise time on pyrolysis products from lacquer sample. Same temperature time profiles as in figure 4. Same tests as in figure 7.

## Limit temperatures and peak broadening

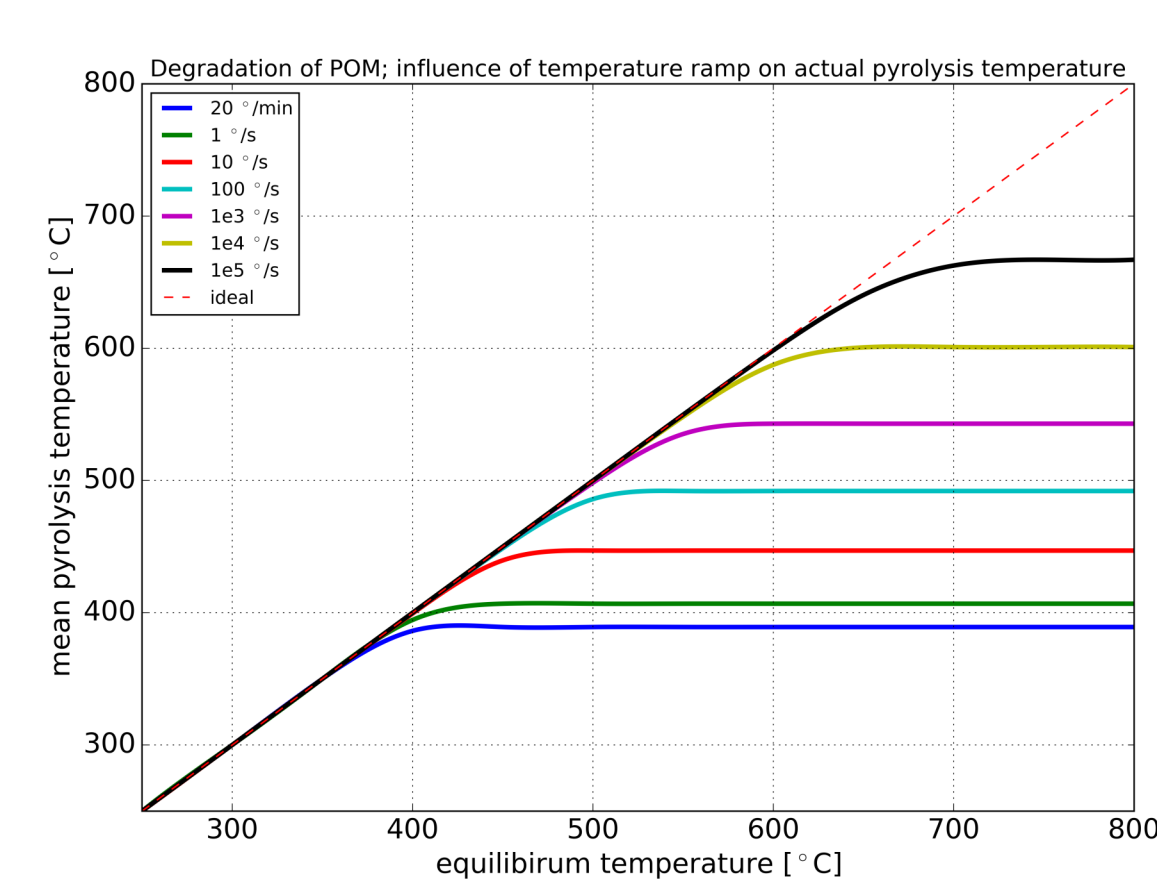


Figure 5. Mean pyrolysis temperatures for degradation of POM for different temperature ramps.

The temperature rise time will limit the maximum temperature that can be reached during pyrolysis. This is illustrated in figure 5, which shows a calculation of the mean pyrolysis temperature as a function of the equilibrium temperature of the pyrolyzer for different temperature ramps. At low temperatures the actual pyrolysis temperature will be equal to the equilibrium temperature. However, if the temperature increase is slow, the sample will be pyrolyzed completely before reaching the equilibrium temperature. In general the temperature de-

pendence of the degradation rate is not known, which means that the limit temperature for a given temperature ramp is unknown. For slow ramps the actual pyrolysis temperature will remain uncertain. In order to have **well-defined pyrolysis conditions it is important to have a very short temperature rise time**.

The other effect of longer temperature rise time is that the pyrolysis will take place during a longer time. If the pyrolysis products are analysed by GC this means that the resulting peaks will be broader. In figure 6 the peak width is shown as a function of the temperature ramp. The actual pyrolysis temperature will depend on the temperature ramp. The coloured markers correspond to the coloured lines in figure 5, where the pyrolysis temperature can be read.

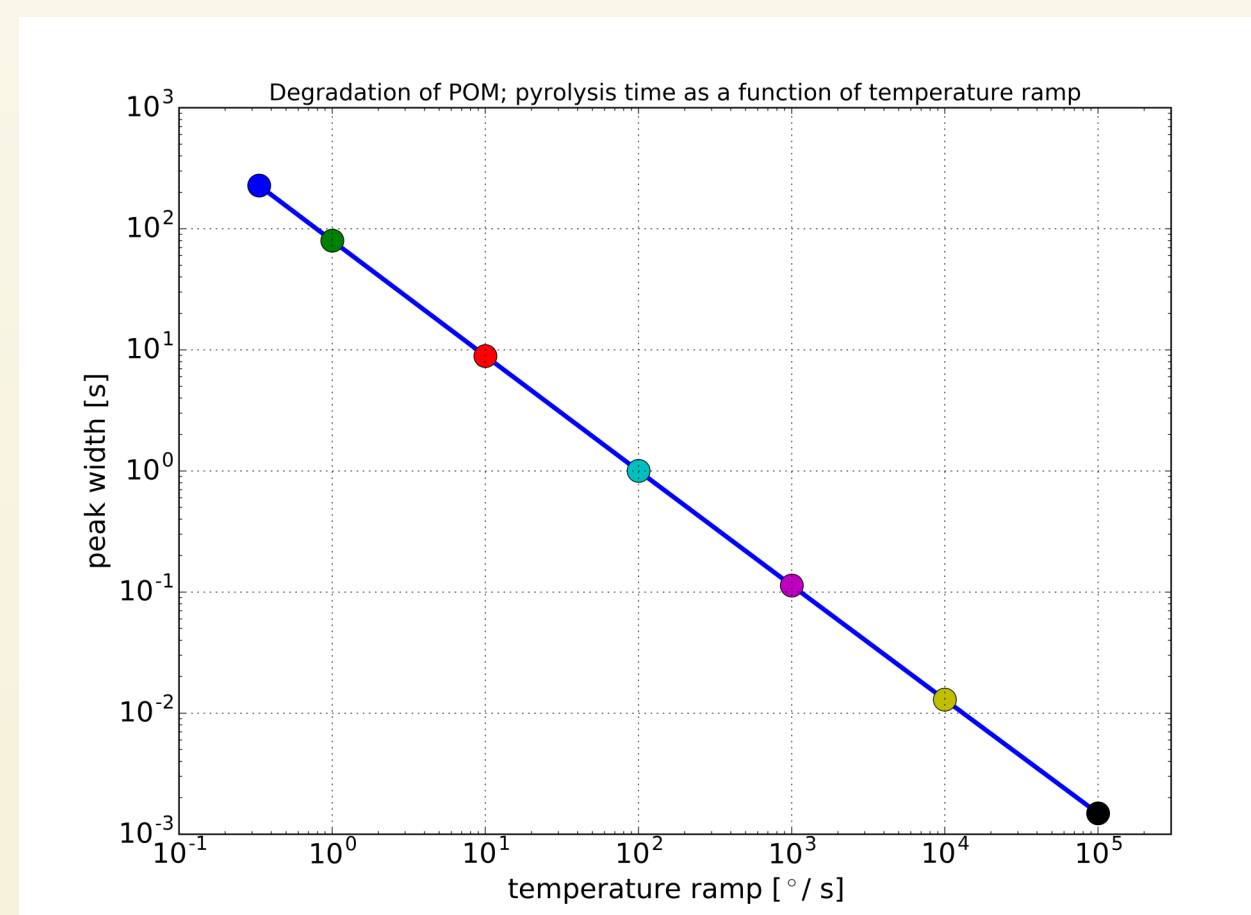


Figure 6. Peak width of POM as a function of temperature ramp. The peak width is defined as the time it takes to pyrolyze 95% of the sample.

## Fractionated pyrolysis vs temperature ramp

A lacquer of polyurethane-vinyl hybrid polymer was pyrolyzed with different temperature time profiles, see figure 7. The upper diagram shows the fractionated pyrolysis of the same piece of sample at 200, 400 and 600  $^{\circ}\text{C}$ . The lower diagram shows the pyrolysis of four different samples:

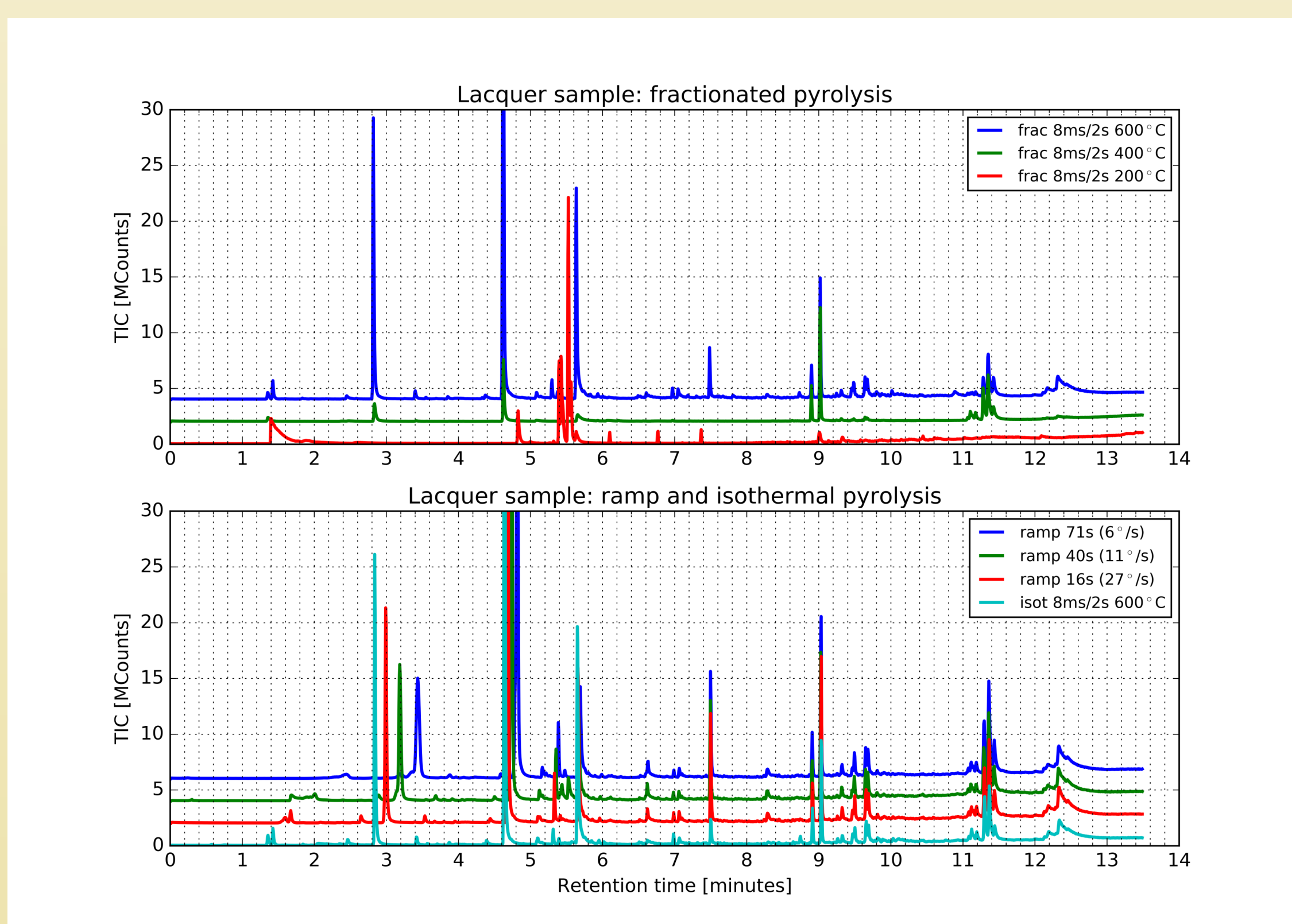


Figure 7. Pyrolysis of lacquer sample. Upper diagram: fractionated pyrolysis of one sample (8ms rise time, 2s pyrolysis). Lower diagram: four samples pyrolyzed: isothermal (8ms rise time, 2s pyrolysis) and temperature ramps 175-600  $^{\circ}\text{C}$  at 16 s, 41 s and 71 s.

Conditions:  
Pyrolyzer: Pyrola 2000  
GC: Varian 3800  
MS: Varian 4000  
Column: DB5 30.025  
Column temp: 40 $^{\circ}\text{C}$  (2)-320 $^{\circ}$  (25 $^{\circ}\text{C}/\text{min}$ )  
Carrier gas: He  
Flow: 1 ml/min  
Split: 1:40  
Chamber temp: 175  $^{\circ}\text{C}$

isothermal pyrolysis with 8 ms rise time, and three different temperature ramps to 600  $^{\circ}\text{C}$ . The fractionated pyrolysis shows the volatile components at 200  $^{\circ}\text{C}$ , and separates the fractions at higher temperatures compared to the isothermal pyrolysis. The ramps show a delay and widening of the early peaks, see also figure 4. There are some additional peaks, such as at 8.2 minutes, that may be secondary effects.

## Summary

The temperature rise time will influence the actual pyrolysis temperature of the sample, and may be as important as the equilibrium temperature of the pyrolyzer. Long rise times will give undefined pyrolysis temperature and broader peaks, whereas a short rise time and cooling off time will make advanced pyrolysis techniques such as fractionated pyrolysis possible.

## References

- [1] Inger Ericsson, Analysis of Polymers by Py-GC/MS, Pittcon 1986.
- [2] H. Jönsson, I. Ericsson, Analytical pyrolysis beyond fingerprinting techniques. Poster presented at Pyro2014, Birmingham, UK.