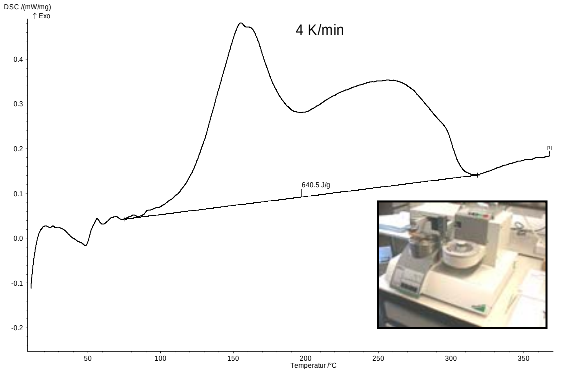
Comparing different methods to define a TMRad for a complex decomposition

F. Abbiati, Safety Lab Dottikon Exclusive Synthesis AG

1) Challenge

To define the safety temperature of 65° for a distillation residue for at least 18 hours. The DSC from the residue showed a complex, multi-steps decomposition with a high energy of 650 J/g with an onset at 90°C.



TMRad estimation

$$q_0 = q_{onset} * \exp(\frac{Ea}{R} * (\frac{1}{T_{onset}} - \frac{1}{T_0}))$$

$$TMR = \frac{cp*R*T_0^2}{q_{T_0}*Ea}$$

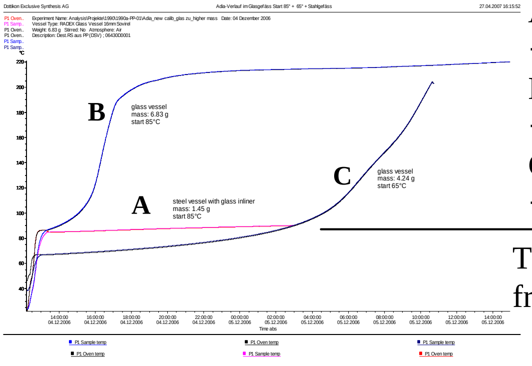
gives for the maximum wall temperature of 65°C a TMRad time of 4 h, needed was > 18 h !

Is it possible to gain a more realistic TMRad ? More measurements with other equipments and methods of the safety lab of Dottikon ES were performed.

TMRad estimation; Safety and Environmental Technology Group, ETH Zürich

2) Results

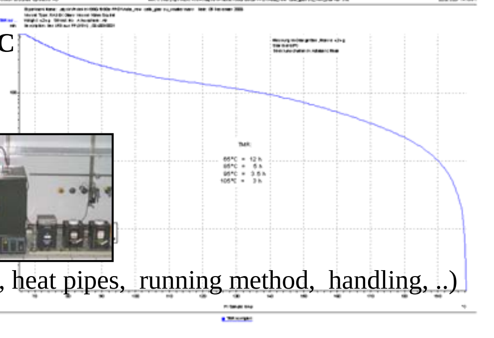
2a) Adiabatic run; heat loss compensation



Radex-FlexyTSC; Systag System Technik AG

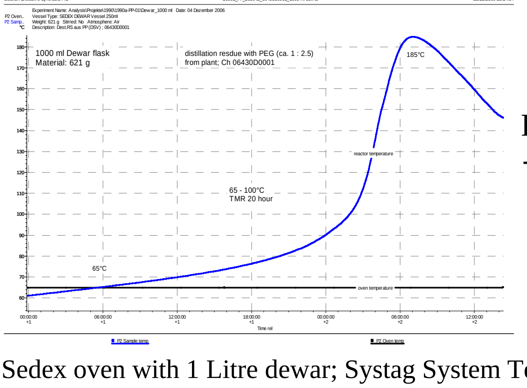
A. Run in steel vessel with glass inliner, at 85°, m: 1.45 g
→ no detection, sensitivity to low
B. Run in glass vessel closed, at 85°, m: 6.83 g
→ adiabatic run
C. Run in glass vessel closed, at 65°, m: 4.24 g
→ adiabatic run

TMR-Plot from run by 65°



Critical points for adiabatic calorimetry were amount of sample, bottle material, behaviour of sample (one or multi-step decomposition), heat pipes, running method, handling, ..)

2 b) Dewar run; heat loss prevention



Run in 1 litre Dewar vessel (glass), at 65°, m: 621 g
→ runaway in 20 h

Sedex oven with 1 Litre dewar; Systag System Technik AG

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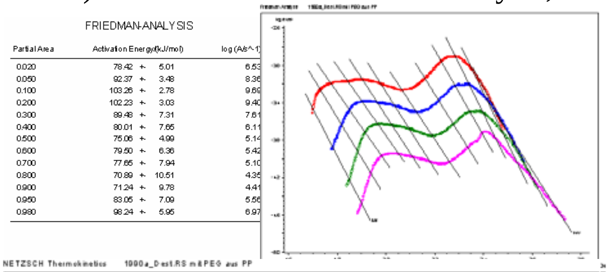
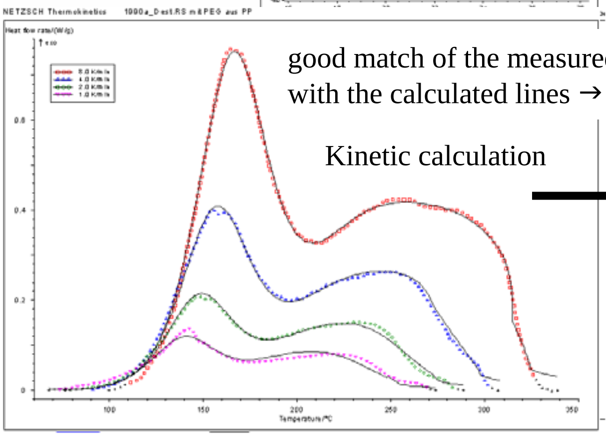
2c) more DSC's → Friedman analysis, kinetic and simulation



DSC runs with 8, 4, 2, 1 K/min
Kinetic with multivariate, non-linear regression

5-steps reaction model: independent and follow reaction type: nth order
every step with different kinetic parameters



good match of the measured data points with the calculated lines → correlation 0.9988

Kinetic calculation → Adiabatic simulation

Netzsch Thermokinetics and Simulation by J.Opfermann†

Kinetic parameters for every step

Step	Concentration [%]	Pre-exponential factor	Activation energy [kJ/mol]	order
first	29	7.3	94	2.6
second	42	11.3	112	1.8
third	7	4.4	71	0.8
fourth	16	-1.5	13	0.19
fifth	6	4.3	72	0.47

Reasonable kinetic values

3) Comparing TMRad results for 65°C

Estimation from one DSC run; target → safety margin	**4 h**	conservative
TMR plot from adiabatic mode, run at 85°C → extrapolation	**6 h**	
TMR plot from adiabatic mode, run at 65°C	**12 h**	
1 Litre dewar run in Sedex oven	**20 h**	
DSC with kinetic and simulation software	**20 h**	more realistic

4) Conclusions

- Never trust only one equipment or method
- Sophisticated software are good tools, if match with measurement is reached
- Macrocalorimetry, used under specific conditions → simple method for realistic results
- Adiabatic calorimetry, if accurate applied, good method to gain less conservative views

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