Applications of reaction calorimetry for process development, scale up and physical properties measurements

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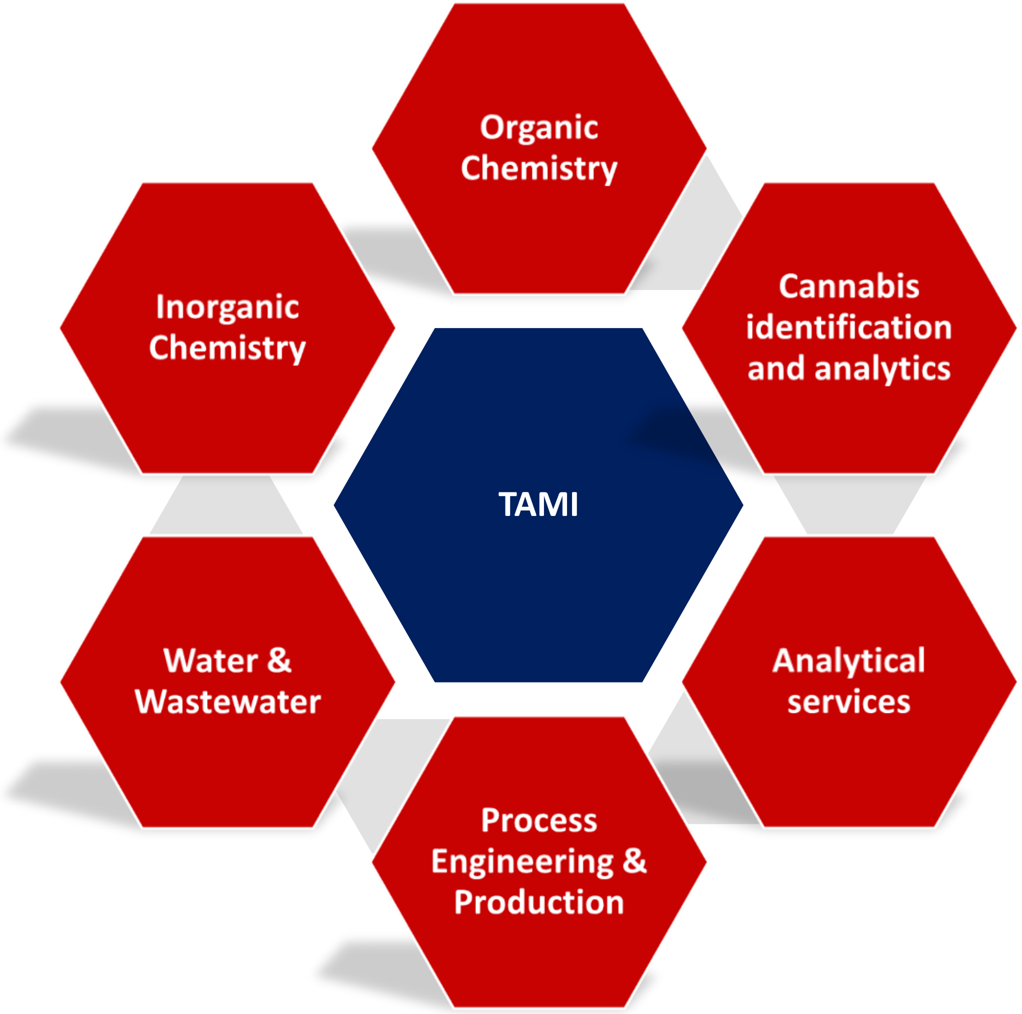
AEAI – The Association of Engineers, Architects and Graduates in Technological Sciences in Israel

Who is IMI-TAMI ?

- The largest Institute for Industrial R&D in Israel (Founded in 1952)
- Owned by ICL Corp. since 1975
- Central R&D for ICL Group
- Contract R&D for External Clients, including sample preparation
- Development of new processes and products
- Safe scale up and examination of existing processes
- Wide range of analytical services



Why do we need reaction calorimetry?

- Understanding the process and the control parameters
- Impact of changing current parameters and procedures
- Safe scale-up of the process
- Avoiding runaway reactions that may lead to loss of control on process parameters and in some cases to disastrous results!

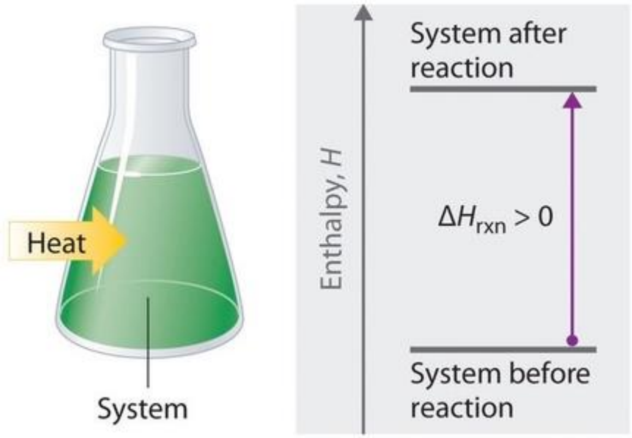
What do we get?

- Thermal profile of chemical reactions
- Estimation the risks and hazard potential of chemical processes
- Tools for safe and efficient scale up of chemical processes
- Advanced process development
- Determination of physical properties

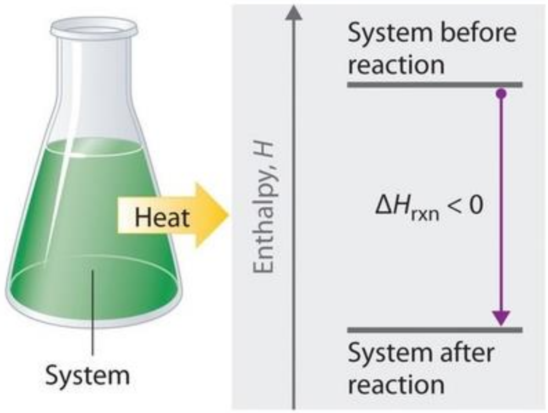
Theoretical background

- **Reaction Enthalpy, ΔHr -** the enthalpy change that occurs when substances are transformed by a chemical reaction. The enthalpy changes produce heat
- **Heat of Reaction, Qr-** related to the overall enthalpy of the reaction, but considers **how** the energy is released as a function of time

Theoretical background



(b) Endothermic reaction



(a) Exothermic reaction

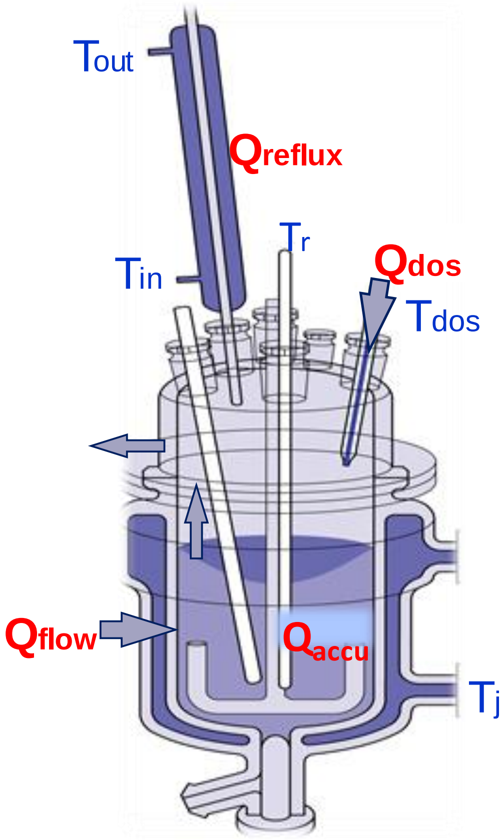
Heat flows from the surrounding to the system

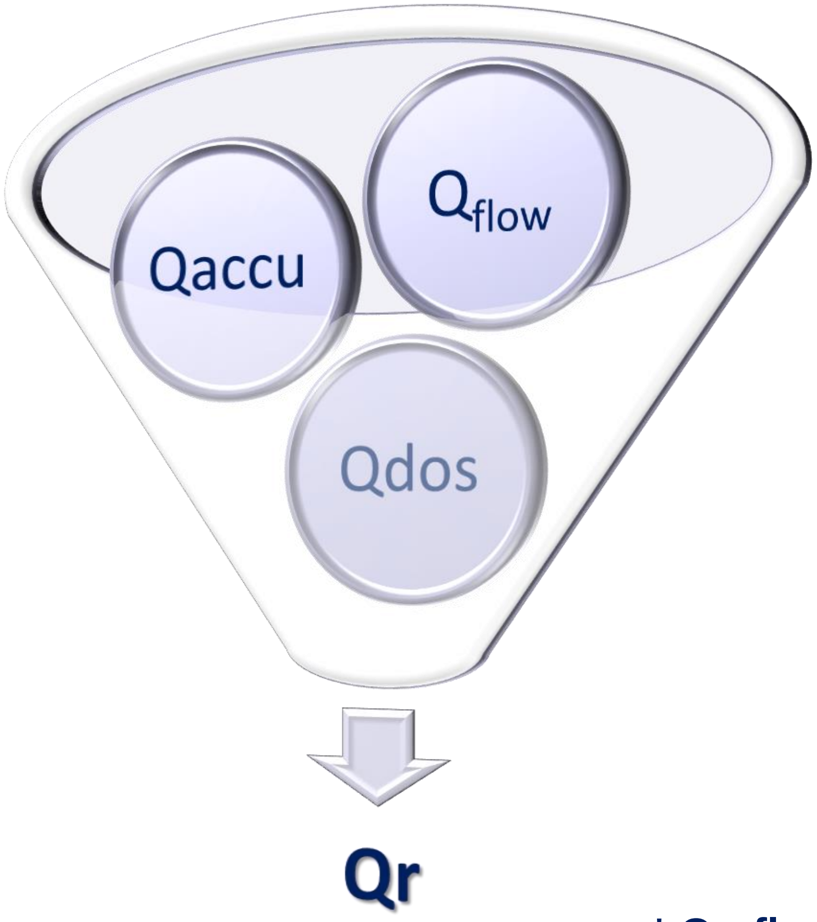
ΔHr>0 the reaction is endothermic

Heat flow from the system to the surrounding

ΔHr<0 the reaction is exothermic

Heat of reaction measurement





Q_{flow}- The heat flow across the reactor wall

Q_{dos}- The heat flow due to reagents addition

Q_{accu}- The heat accumulated during the reaction

***Q_{reflux}**- The heat flow across the reflux condenser

*** Qreflux should be added in case of working in reflux conditions**

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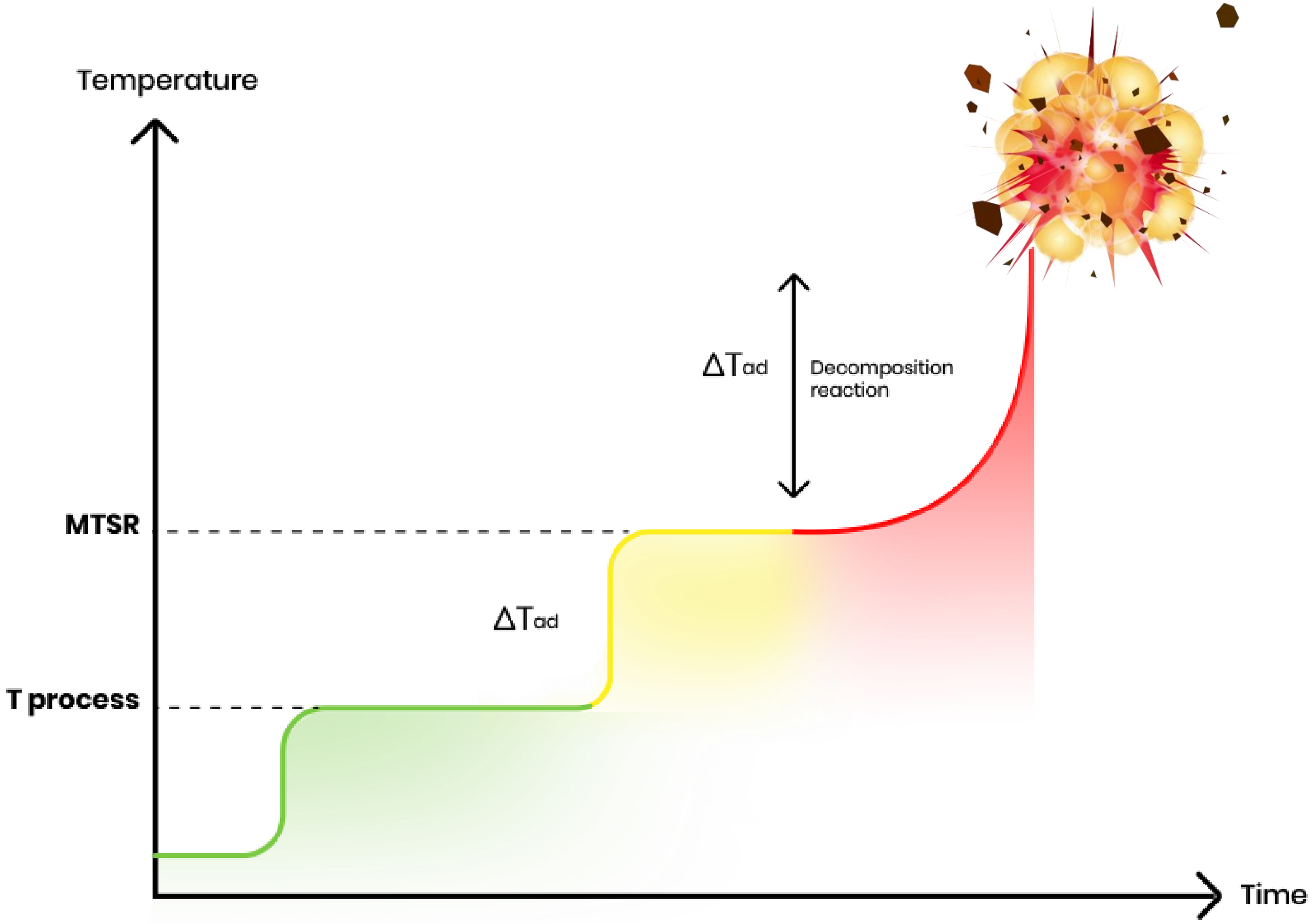
Measurements goals

- The goals of the measurements are:
  - ✓ Establish key process parameters
  - ✓ Determine safety parameters and the criticality of the process
  - ✓ Determine scale up parameters such as dosing rates and times
  - ✓ Detect non-scalable processes
  - ✓ Avoid runaway scenarios and failure conditions

Runaway reaction stages



Where the problem pops up?

- Surface/ volume ratio
  - In scale up, the increase of the volume is not proportional to the increase of the surface area of the reactor.
  - Larger reactor have smaller surface/ volume ratio which leads to lower cooling capacity

$$Q_{removal} = U \cdot A \cdot (T_r - T_j)$$

Reactor volume V, L	Heat transfer area S, m²	Surface/volume ratio S/V, m^{-1}	Tr-Tj, K
0.5	0.0323	65.0	3.0
5	0.135	27.0	7.1
50	0.633	12.7	15.3
100	1.000	10.1	19.3
250	1.85	7.4	26.2
500	2.90	5.8	31.3
1,000	4.67	4.7	41.6
5,000	13.6	2.7	71.0
10,000	21.7	2.2	90.0

x20

x 7.4

The laboratory of calorimetry in TAMI

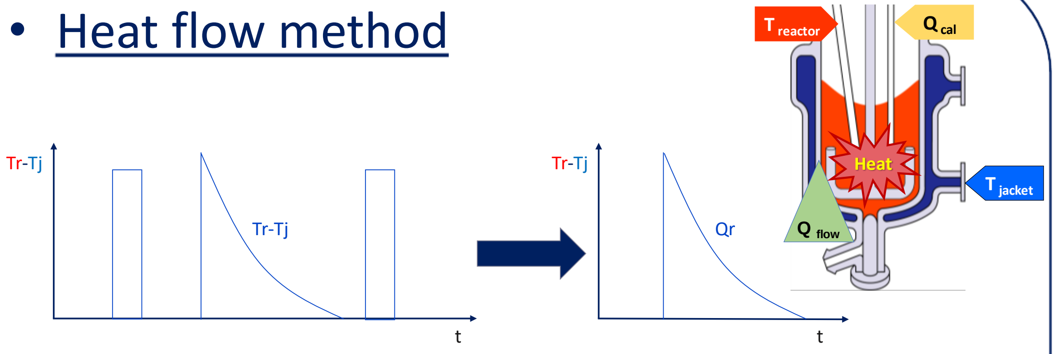
- Different volumes (0.5 and 2 L), structure materials (Stainless steel/ glass) and pressures (up to 60 bar) are available
- The RC1 0.5L glass reactor is equipped with a **real time calorimetry (RTCal)** systems which allows online measurement of the reaction heat

What can we measure?

- **Q**- The heat of the reaction, kJ
- **Cp**- The heat capacity of the mixture before and after the reaction, kJ/kg·K
- **U**- Heat transfer coefficient through the RC1 reactor wall, $W/m^2 \cdot K$
- Integral conversion at the end of the reaction,%
- **ΔH**- The enthalpy of the reaction, kJ/mol reactant
- Heat of dilution/ crystallization/ melting, kJ/mol
- Specific reaction heat, kJ/kg (or liter) reaction mass
- **ΔT adiabatic**- Possible temperature raise in case all the reagents were loaded simultaneously (the reactor is isolated)

Heat flow measurements

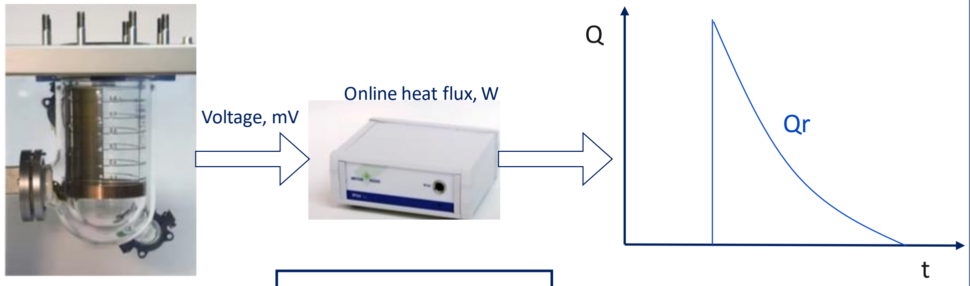
- Heat flow method



$$Q_{flow} = U \cdot A \cdot (Tr - Tj)$$

- System **calibration**- Heat transfer coefficient (U) calculation and heat capacity (Cp) determination
- Integration of the heat release during the reaction
- Calculation of the total heat release at the reaction Q

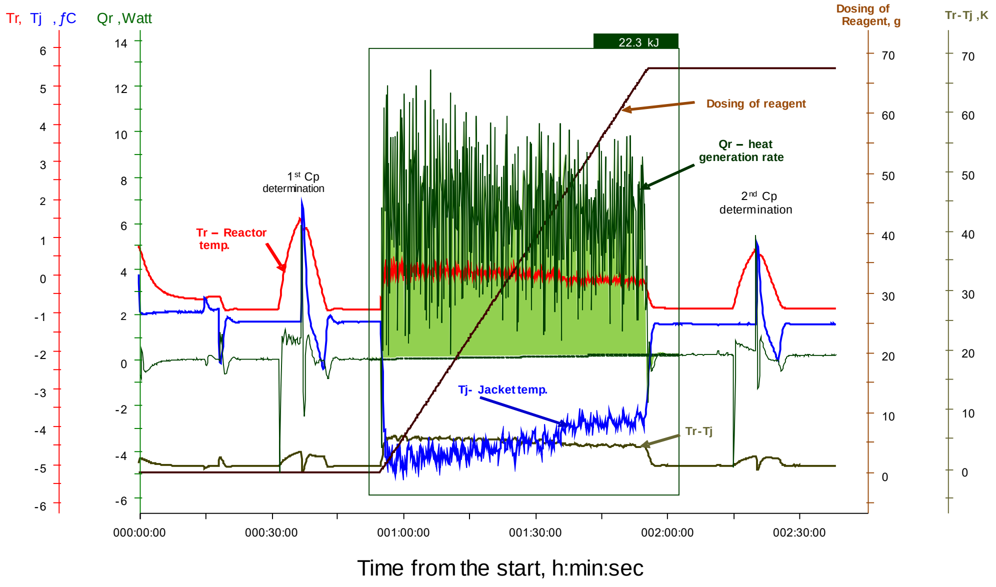
- RTCal (real time calorimetry) method

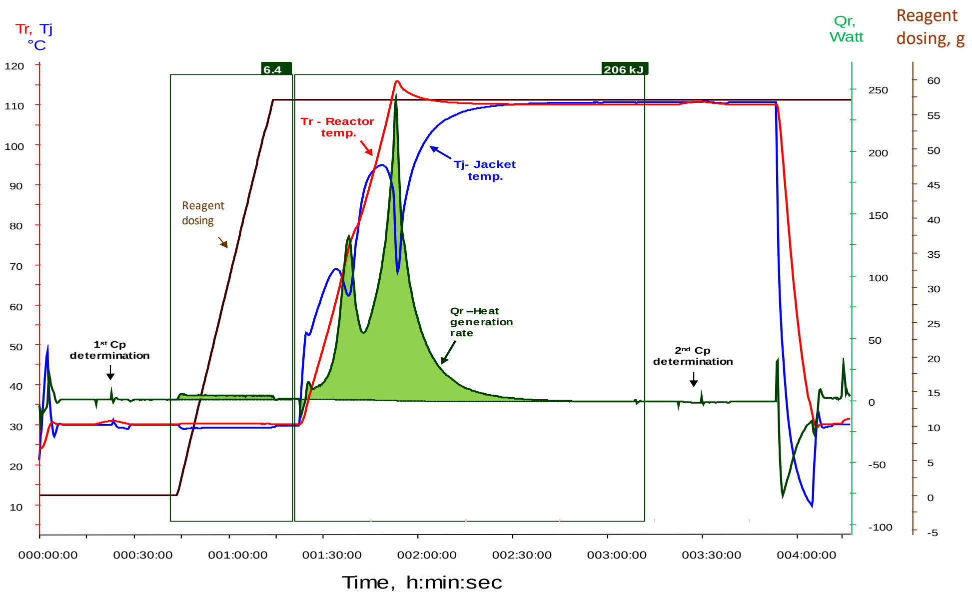


$$Q_{rtc} = A \cdot q_{band}$$

- Using 2 sensors attached to the reactor wall
  - Horizontal at the bottom of the reactor
  - Vertical sensor band
- Online heat flux measurement by multiplying the specific heat through the low band ($q_{band}, W/\mathrm{m}^2$) and the wetted reactor area measured through the vertical sensor band (A, m^2)

Results analysis and process risk evaluation





The heat release is Proportional to the dosing (**well controlled reaction**)

No heat release during the dosing. The heat release starts **after** the dosing (**uncontrolled, dangerous reaction**)

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Criteria for severity of the desired reaction

Criterium	Severity
200 K < Δtad 400 kJ/kg < Qr	High
50 K < Δtad < 200 K 100 kJ/kg < Qr < 400 kJ/kg	Medium
Δtad< 50 K Qr< 100 kJ/kg	Low

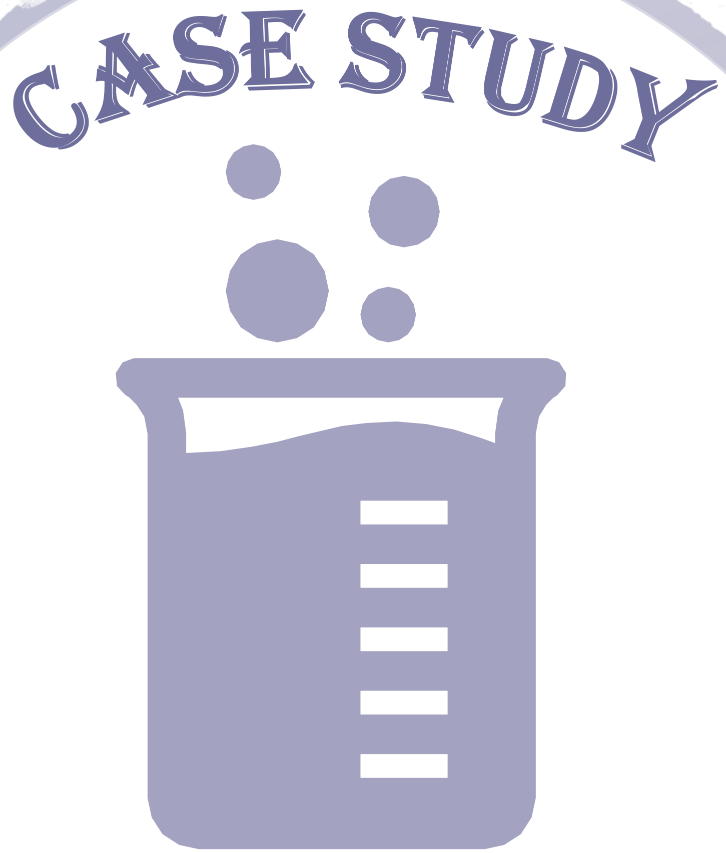
Ways to control the heat release

- Dosing rate (reagents/catalyst)
- Controlled dosing (interlocks, etc)
- Stirring rate (in case more then 1 phase are involved)
- Solvent addition for better heat absorption
- Using reflux condenser
- Absorption tower (for gases)

Results and recommendations

- After the process analysis, recommendations for wise scale up are given according to the reactor size, heat release during the dosing and the cooling capacity

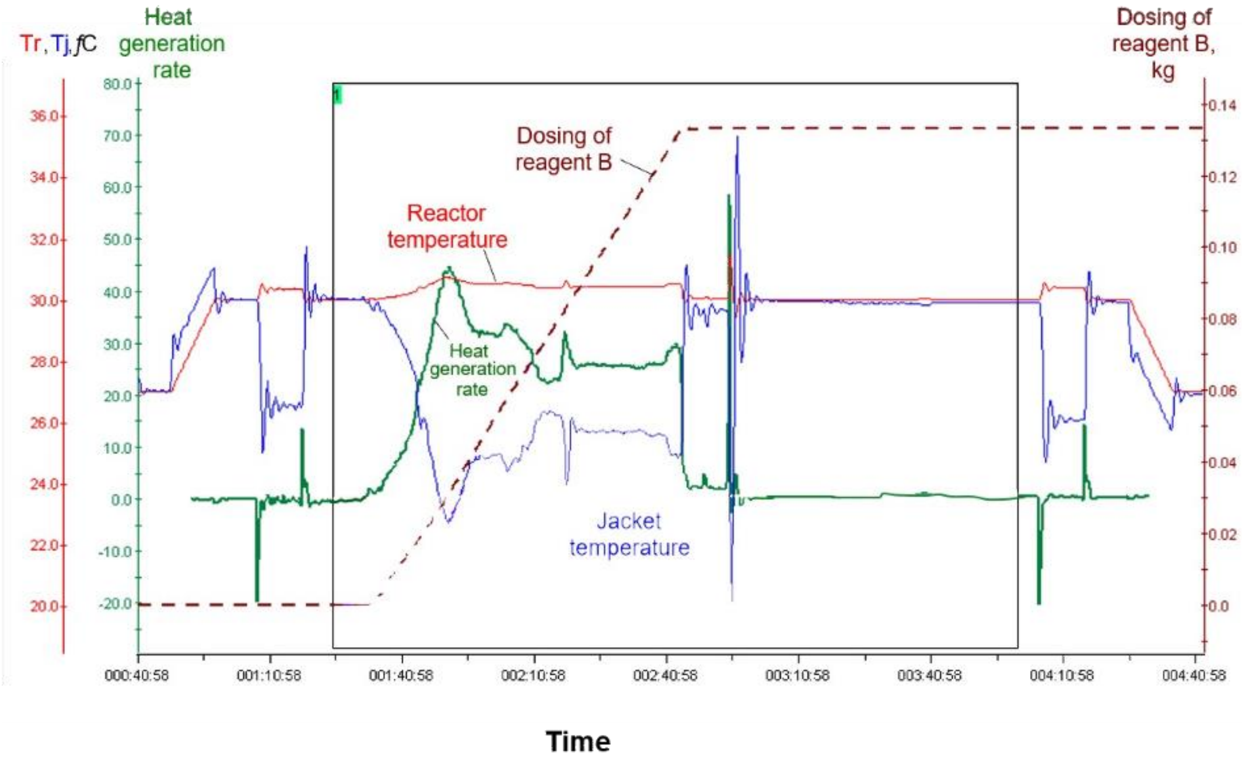
Parameters	Unit	25 liter (glass-lined)	250 liter (glass-lined)	2000 liter (glass-lined)	2000 liter (Hastelloy)
Scaling factor		50	500	4,000	4,000
Average heat exchange area	m^2	0.28	1.29	5.15	5.15
Heat release during the dosing	kJ	4,455	44,550	356,400	356,400
Average heat generation rate	kW	0.8	3.5	13.7	13.7
Recommended duration of the dosing in different reactors (constant Tr-Tj)	**hour**	**1.7**	**3.6**	**7.3**	**3.0**

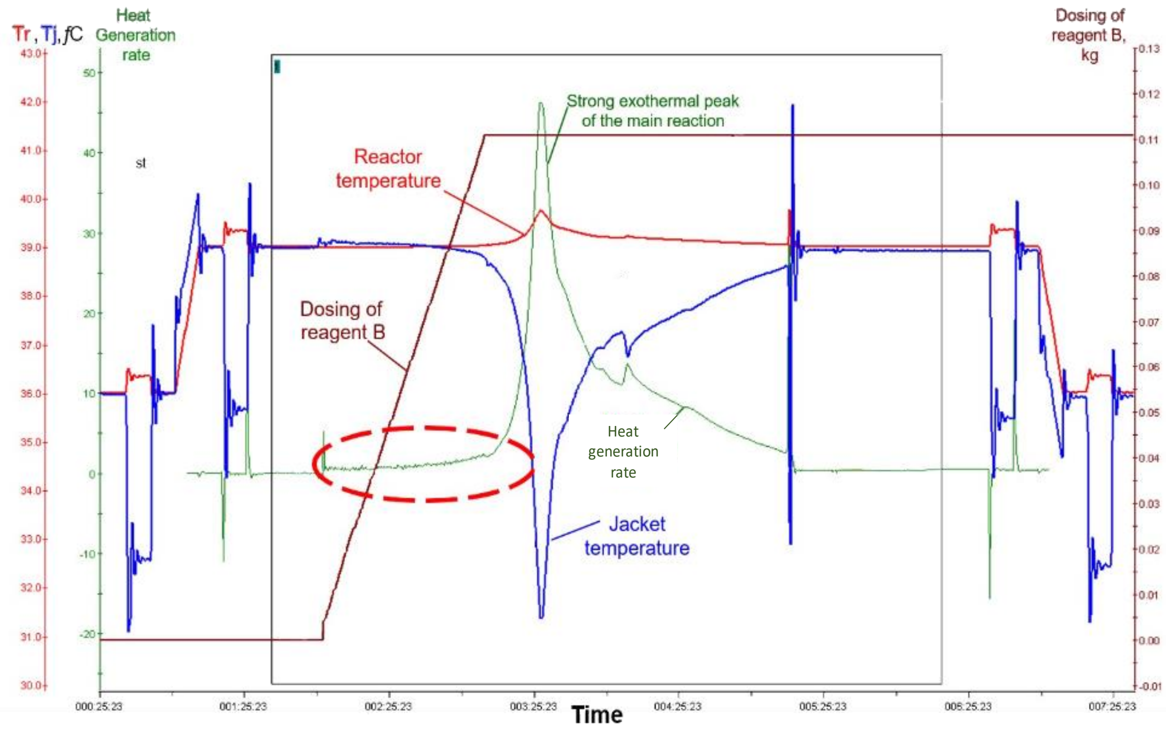


Unexpected reactor explosion

- In one of the processes at a large industrial company, it was decided to change the supplier of the solvent
- The COA of both solvent was similar
- The change was tested in the lab
- **Runaway reaction caused an explosion in the reactor**
- The TAMI team was requested to examine possible reasons for the explosion

Comparison of the solvents





- <u>Old solvent</u>
  - Short induction period
  - Heat release is almost proportional to the feed of reagent B
  - Safe process, the temperature is well controlled by the dosing rate

- <u>New solvent</u>
  - Long induction period
  - Spontaneous exothermic reaction <u>after</u> the dosing of the reagent
  - High heat generation rate and low cooling capacity probably led to a runaway reaction
  - A new procedure was proposed by TAMI and successfully applied in the plant

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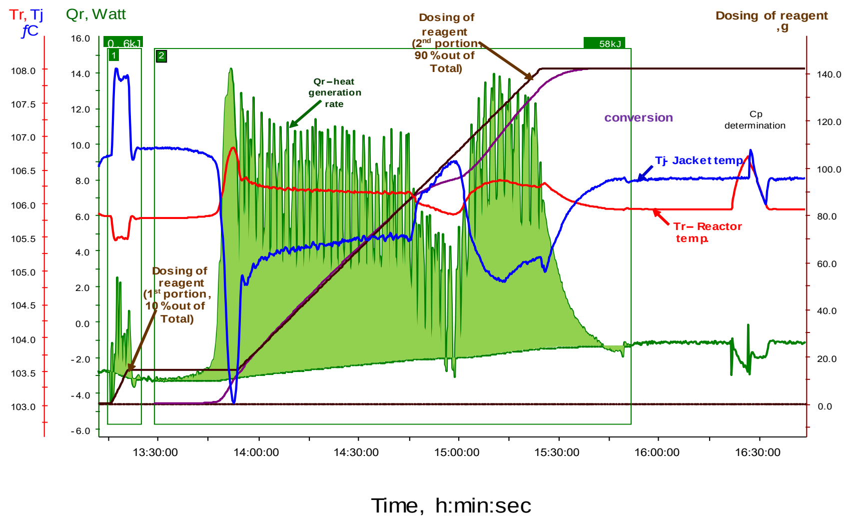
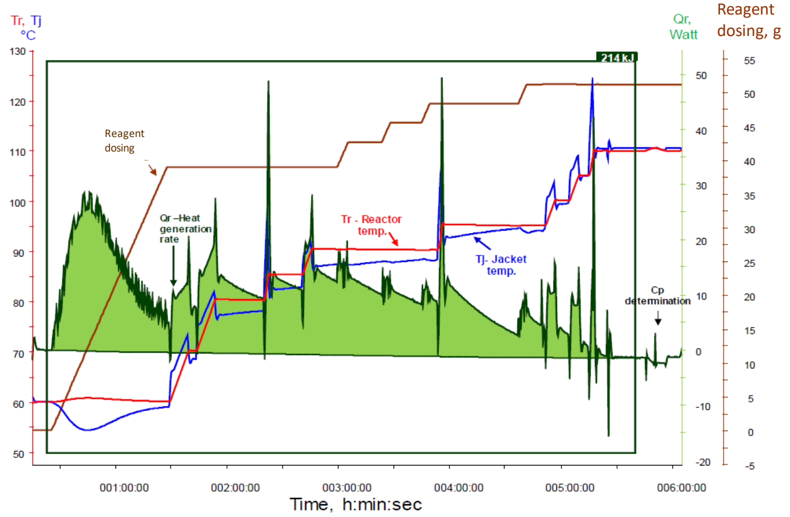
Case study conclusions

- In this type of reactions the recommendations will include:
  - Portioned dosing, reaction initiation, temperature stabilization and completion of dosing
  - Considering parameters change (temperature, catalyst, etc.)
  - Controlled dosing with different dosing rates

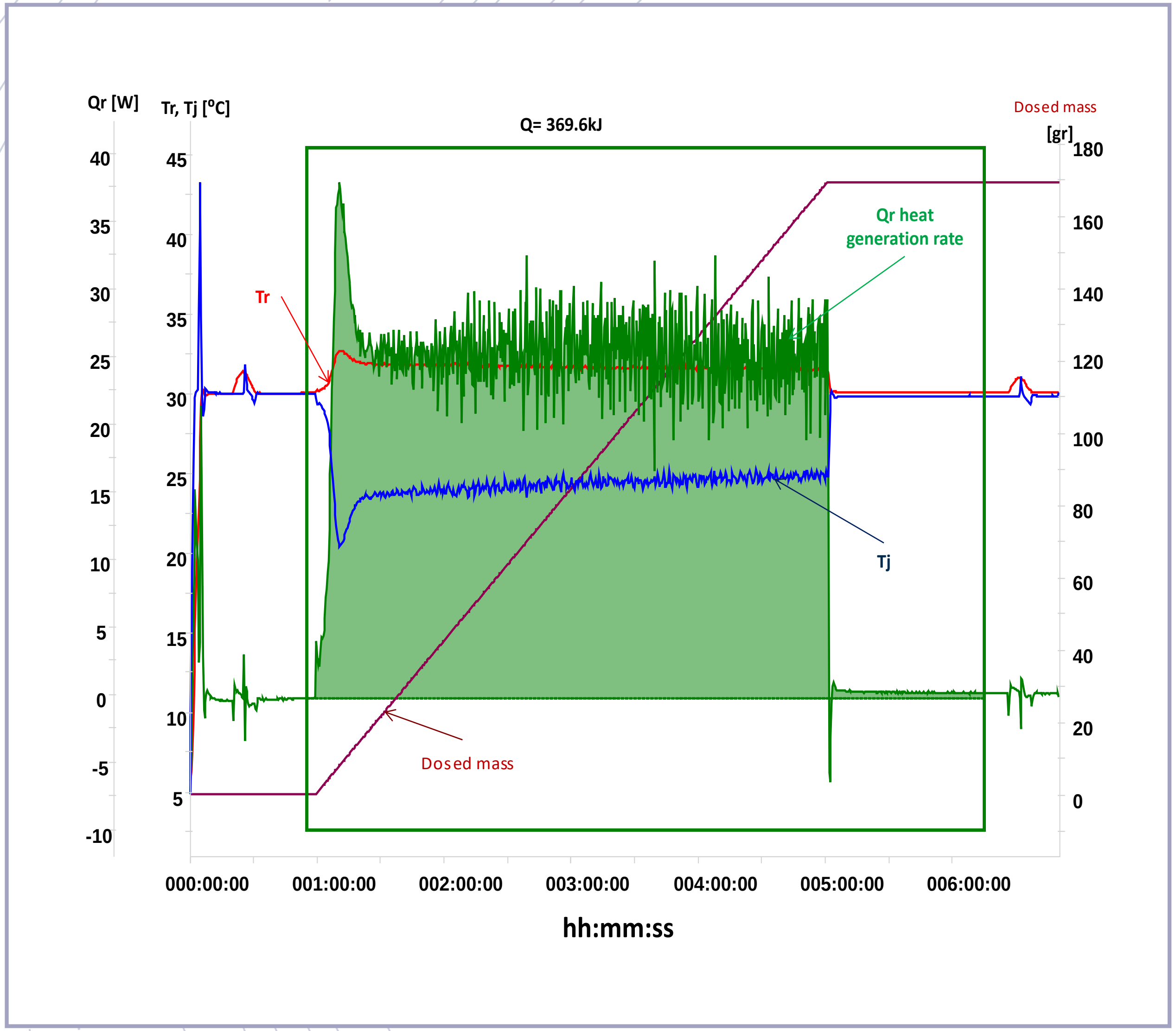




Process development

- Initial thermal analysis in the RC1 reactor showed dosing controlled reaction
- During the scale up in 100L reactor unexpected temperature increased led to dosing pause
- **The temperature kept rising for additional 3 hours**
- Further process development was carried out in the 0.5L RC1

Process development in RC1 reactor

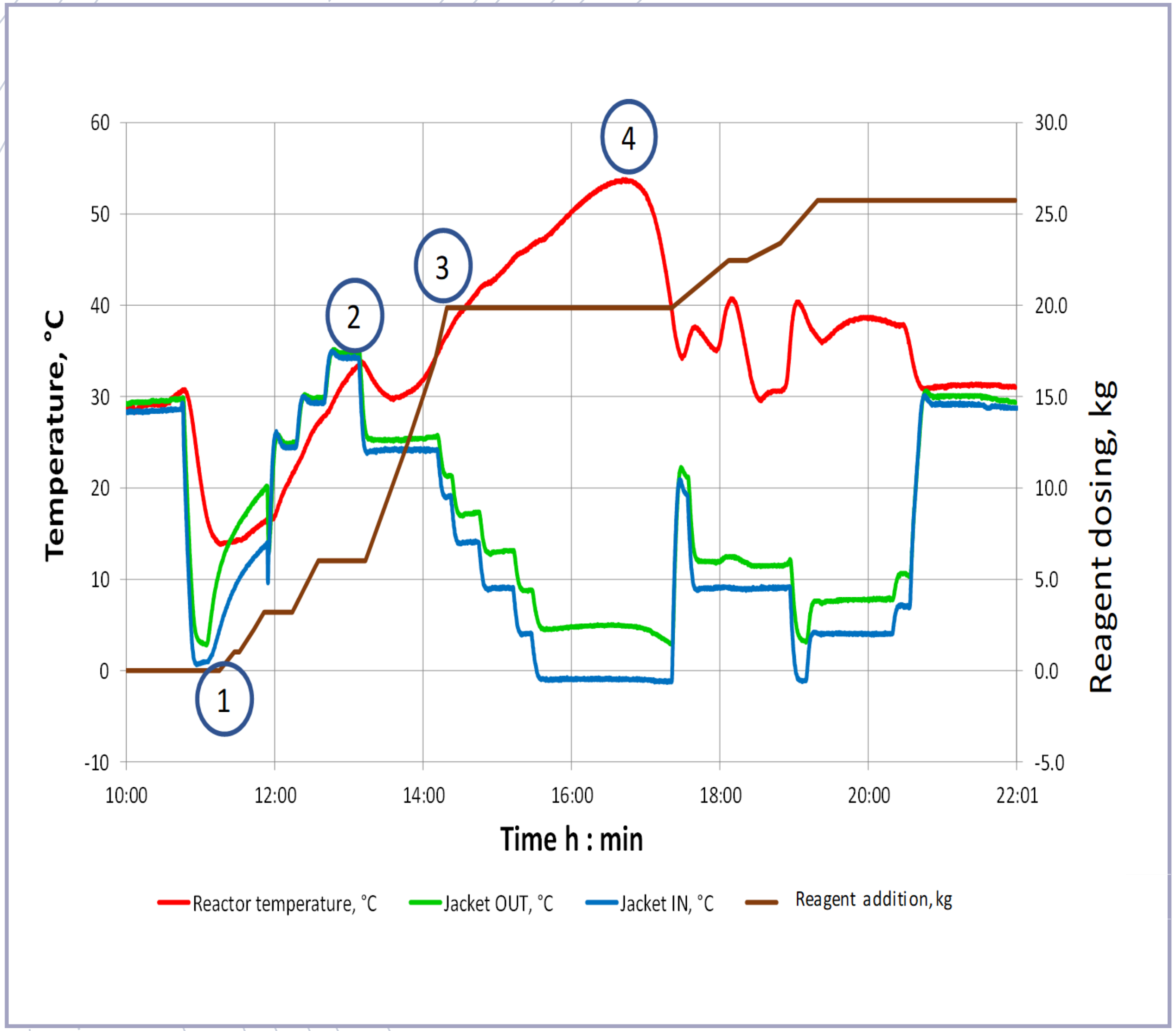


- RC1 study (reaction at 30°C):
  - Low heat release rate at the first 10 minutes
  - A sharp peak of ~40W (indicating accumulation in the reactor)
  - The heat release was proportional to the dosing until the end of the reaction

Process development in RC1 reactor

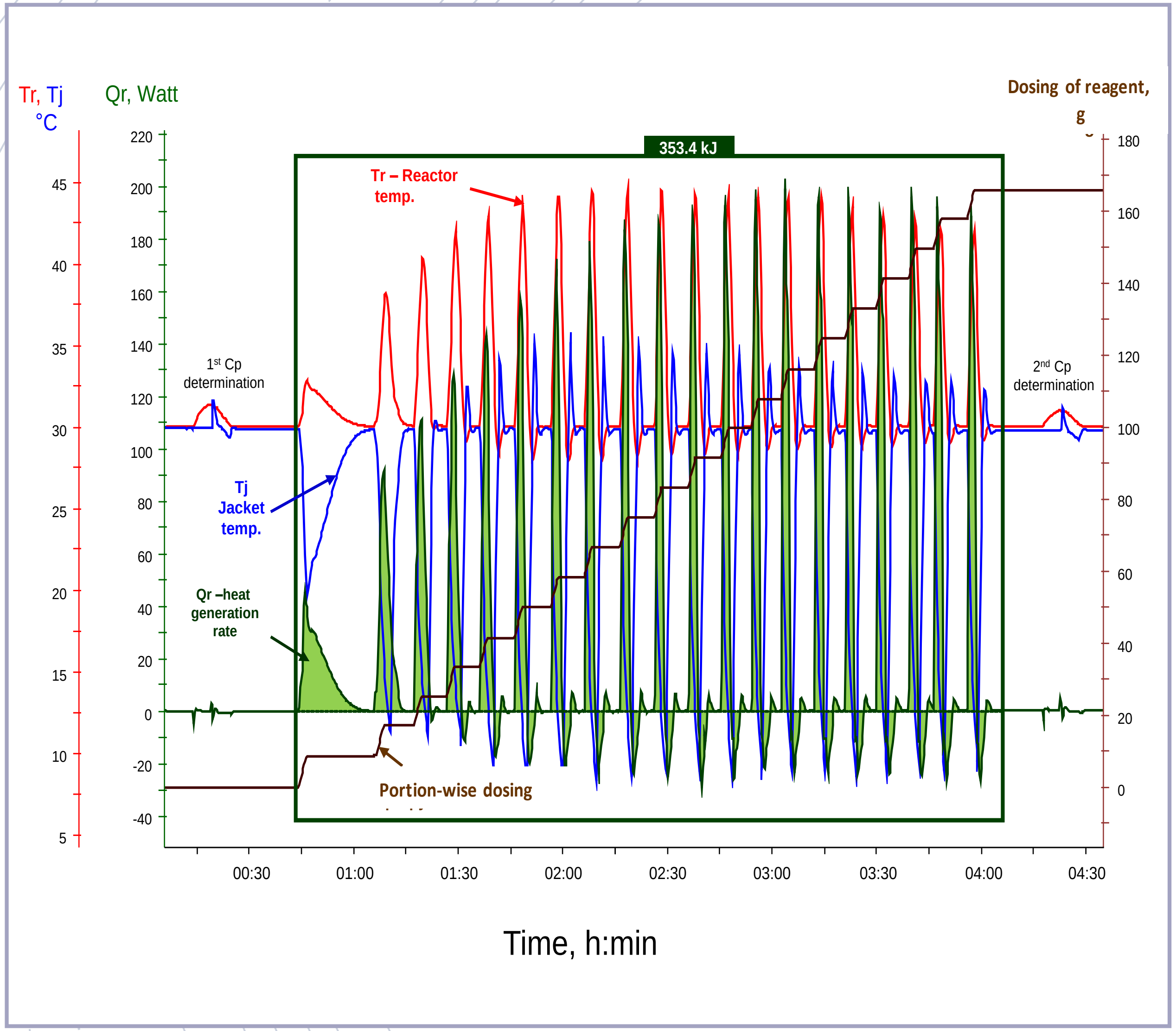
- Strongly exothermic reaction
- The enthalpy of the reaction was -126 kJ/mol
- Low heat capacity of the reaction mixture, Cp=1.23 J/g·K
- High adiabatic temperature increase, **ΔTad=522K**
- Scale up recommendations:
  - Dosing of 5% of the reagent, waiting for temperature stabilization and further dosing
- Scale up was performed in 100 L reactor
  - Material of construction- Hastelloy C

Scale up in the 100L reactor, 1st batch



- Initial temperature was 15°C to “be on the safe side”
- 5% of material was added and reaction started
- The reagent was added continuously
- The temperature increased and the dosing was stopped
- The temperature kept rising for 3 additional hours

Portion-wise dosing



- The reagent was dosed in 20 equal portions
- Each portion was dosed over 2 minutes
- Each dosing was followed by waiting time to obtain temperature stabilization

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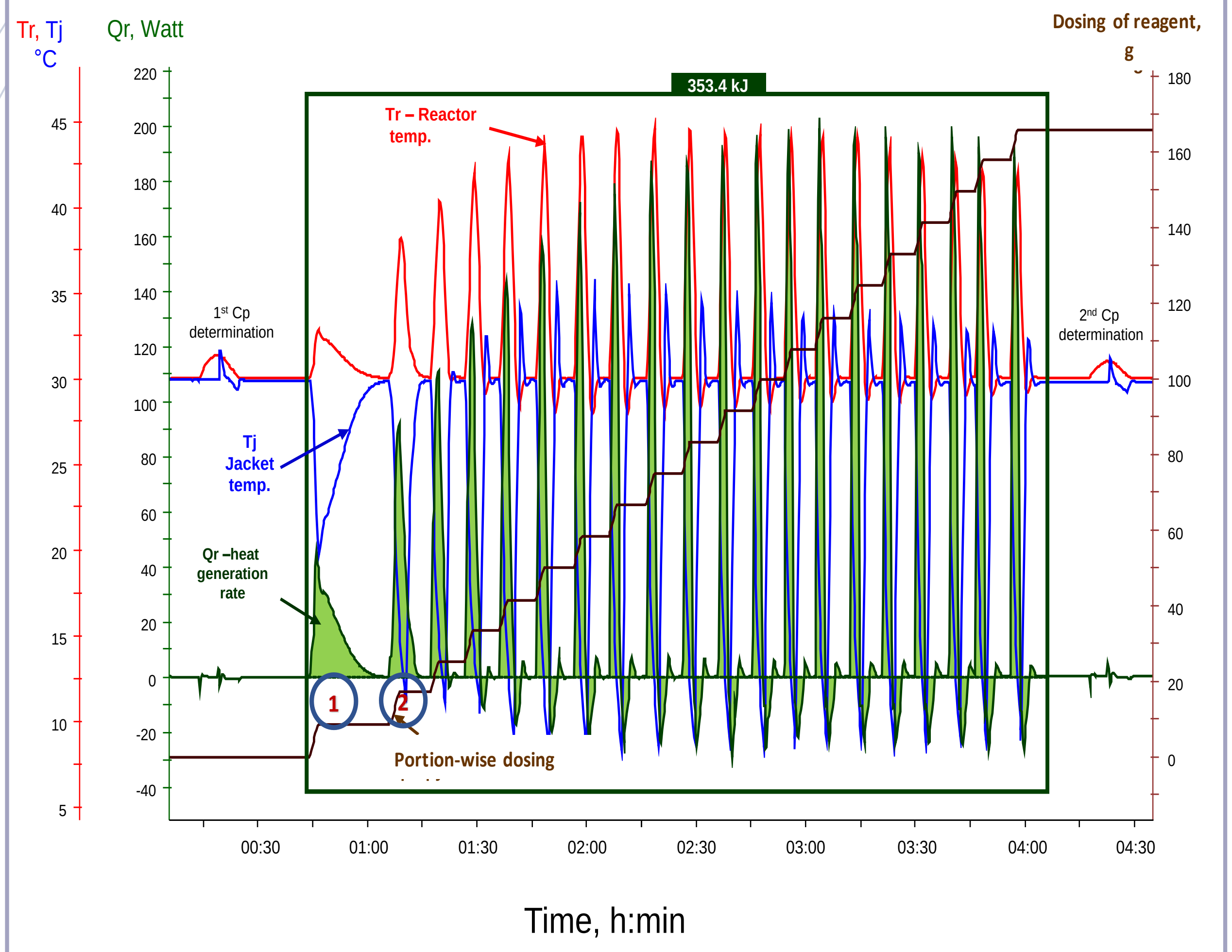

Portion-wise dosing

- The waiting time for stabilization was long at the beginning and became shorter after the 3rd dose
- The reaction rate accelerates during the dosing
- When 45-50% < of the reagent was dosed, the reaction started immediately at a very fast rate and ended with the dosing

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Portion-wise dosing of the reagent-conclusions

- The kinetics of the reaction strongly depends on the mixture composition
- The reaction mixture works as a catalyst to accelerate the reaction
- The dosing should be very slow at the first stages of the reaction until ~ 45% of the reagent is dosed
- When > 45% of the reagent is dosed, the heat release is almost in direct proportion to the dosing and can be well controlled by the dosing rate

- **The process should be run at the same temperature as the RC1 study**
- **Even in extremely exothermic reactions, temperature can strongly affect the kinetics**

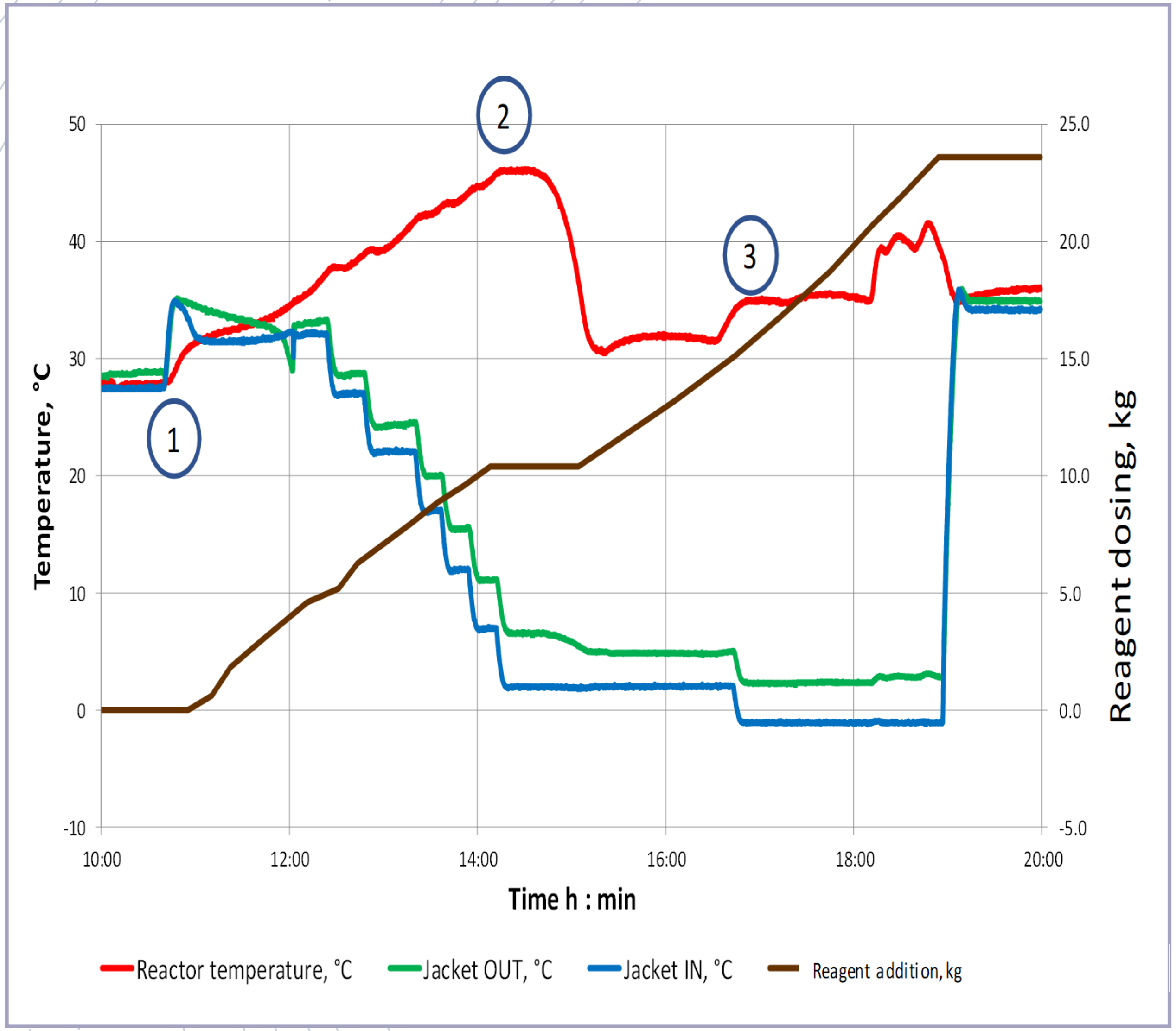
Portion-wise dosing - Scale up recommendations

- The estimated dosing times at each step of the process at a 100L reactor:

Step	Amount of reagent dosed (%)	Dosing time (Hours)
1st portion	5%	1-1.2
2nd portion	5%	0.5-0.6
3rd portion	10-40%	2-2.5
4th portion	60%	4

- Working on higher scale reactor will demand longer duration of the initial dosing step

Scale up in the 100L reactor, 2nd batch



- Initial dosing temperature was 28°C
- The dosing rate was adopted to cooling rate
- Dosing was stopped at 45-46°C and the reactor was cooled
- Temperature relatively constant during the rest of the dosing
- Portion wise dosing was recommended to be applied in the plant

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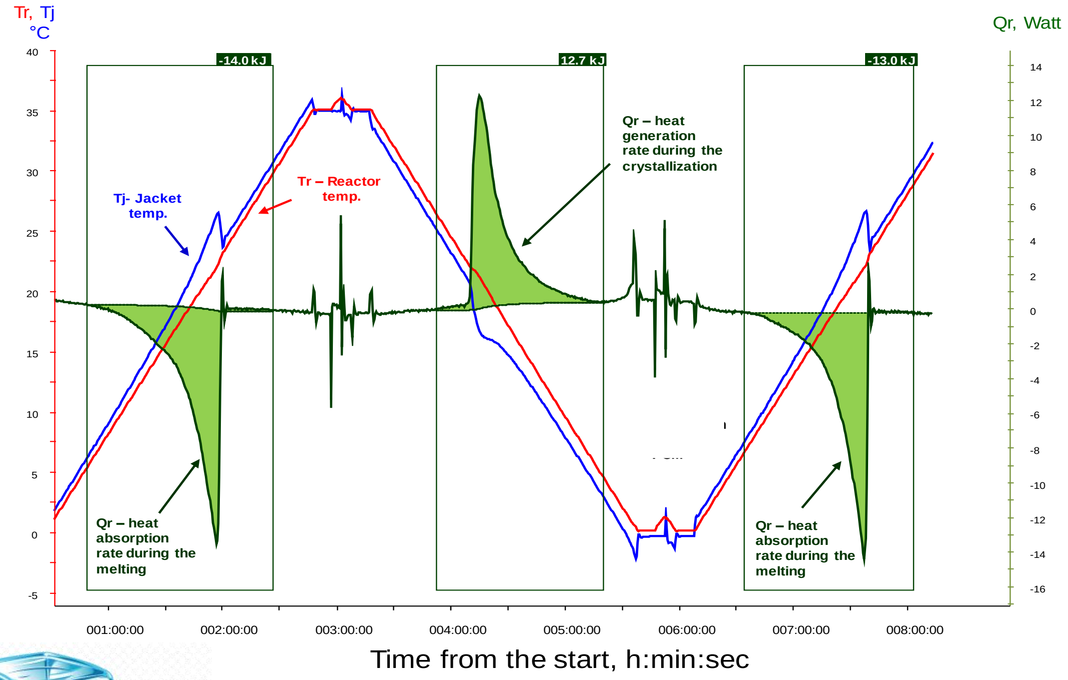
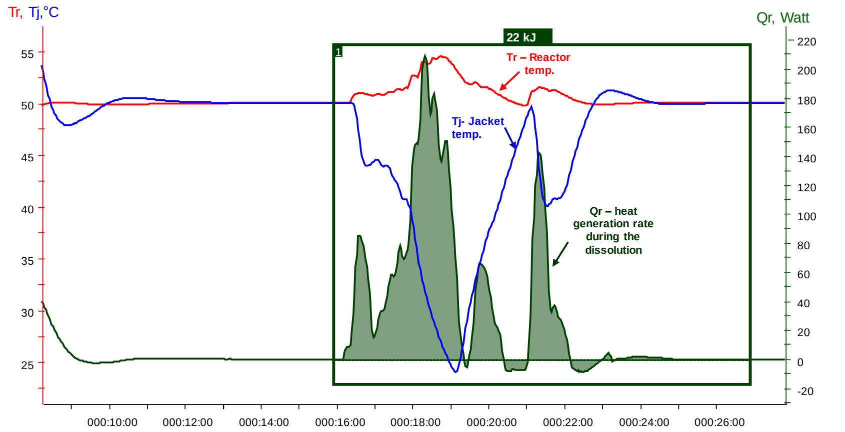
Measurements of physical properties in the RC1 reactor

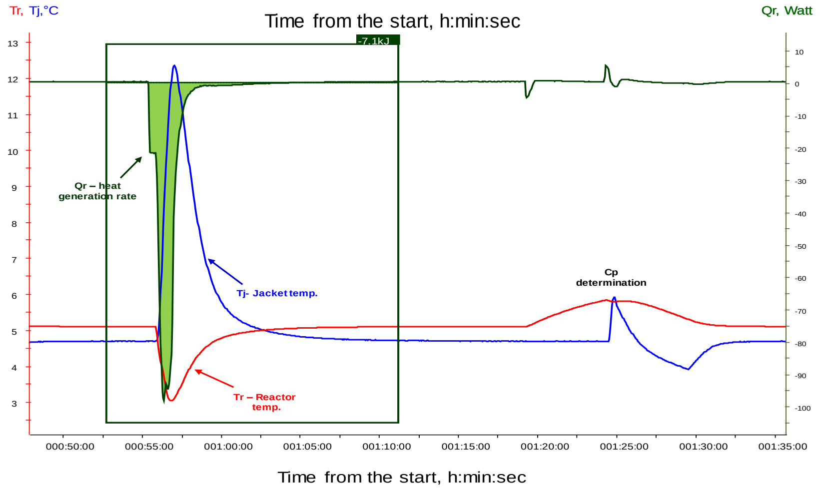
Physical properties that can be measured in the RC1

- Melting/ Crystallization temperature and heat



- Heat of dissolution





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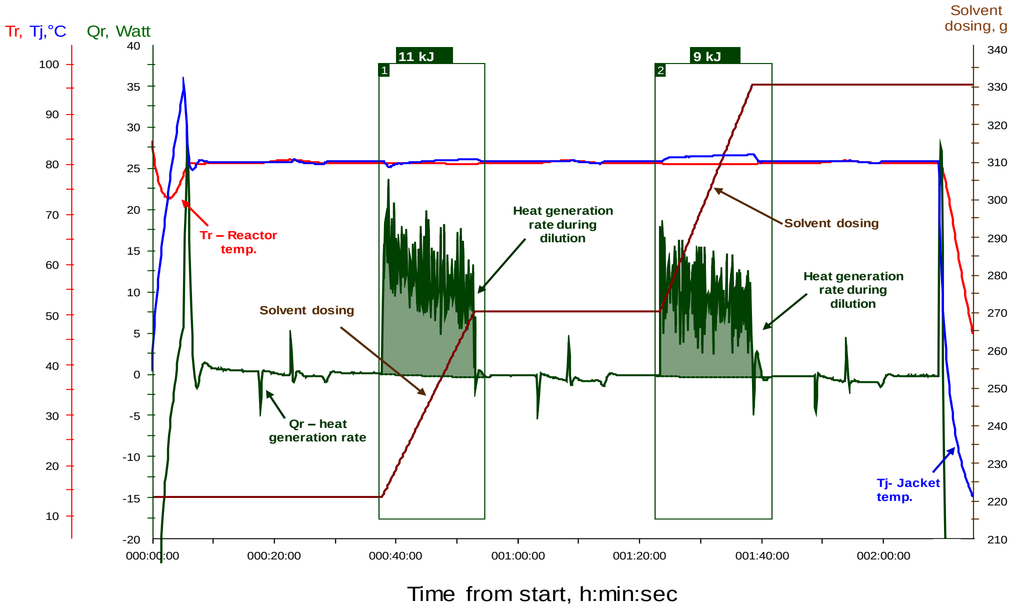
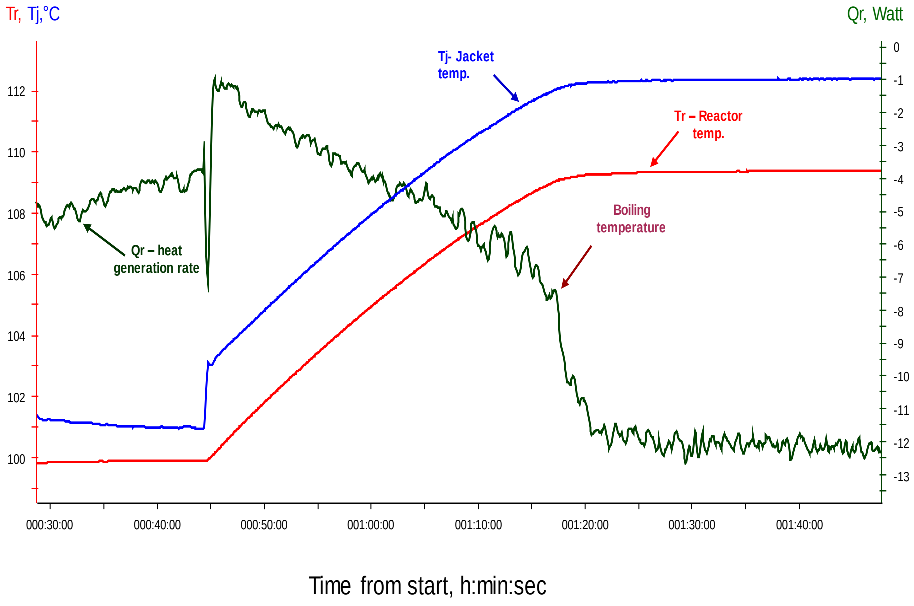
Physical properties that can be measured in the RC1

- Heat of dilution



- Boiling point



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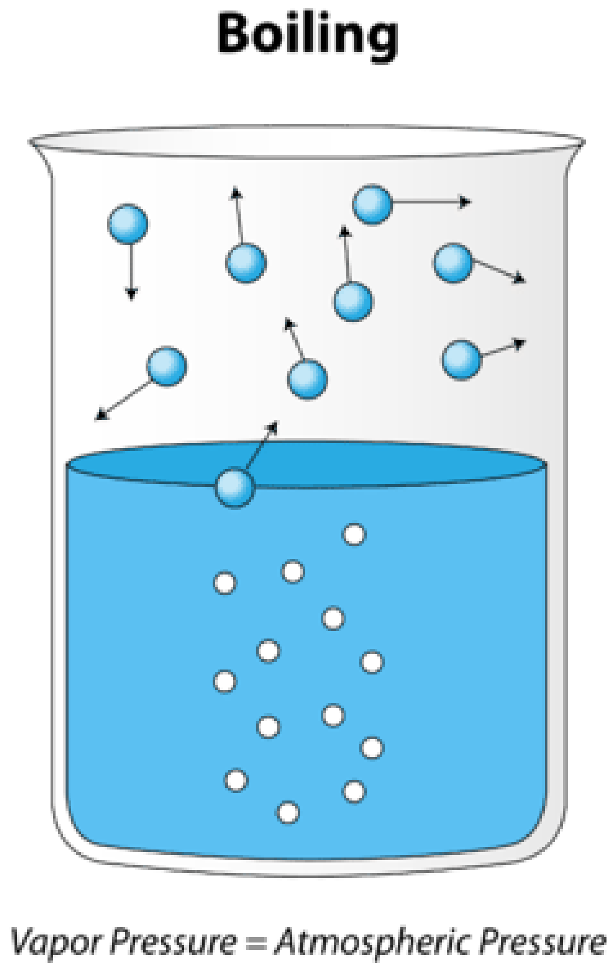
Vapor pressure measurements in the RC1



- Common method:
  - Heating the solution to the desired temperature
  - Changing the pressure until boiling is observed in the vessel
  - Method disadvantages
    - ✗ Transparent vessel is required (usually glass)
    - ✗ Not suitable for turbid solutions
    - ✗ “False” boiling may appear
  - A new method for vapor pressure measurements in the RC1 reactor was developed

New method developed in TAMI for the measurement of vapor pressure in the RC1

- The desired pressure is set via the vacuum pump
- The solution is heated until its boiling point
- At the boiling point, the pressure in the vessel is the vapor pressure
- Measurements of the vapor pressure and the boiling points at different concentrations by gradual dilution of the mixture.

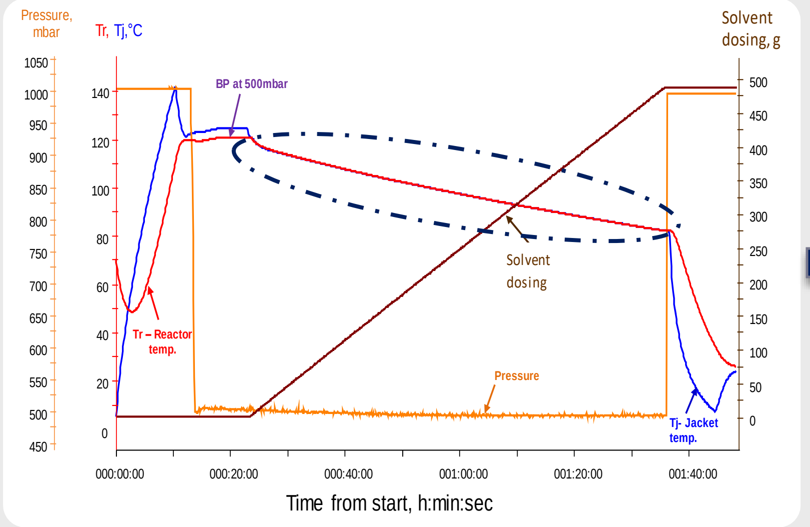
Vapor pressure measurements- Example

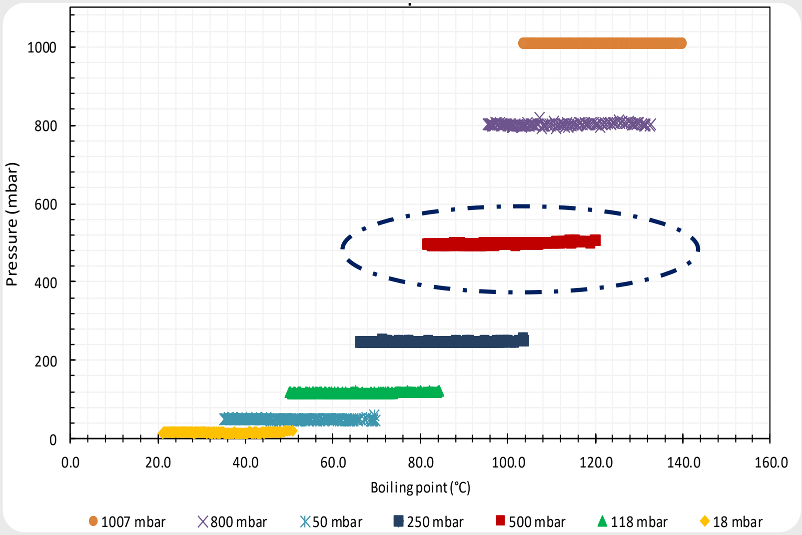
The pressure was set with the vacuum pump

The solution was heated until its boiling point

The solution was gradually diluted maintaining the boiling in the reactor

The results were translated to BP at different concentrations (at constant pressure)





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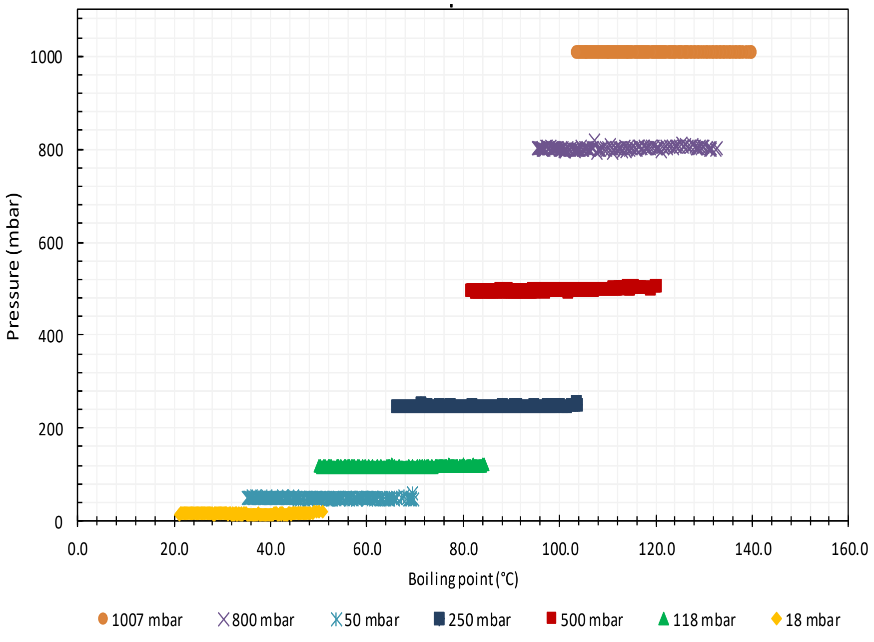
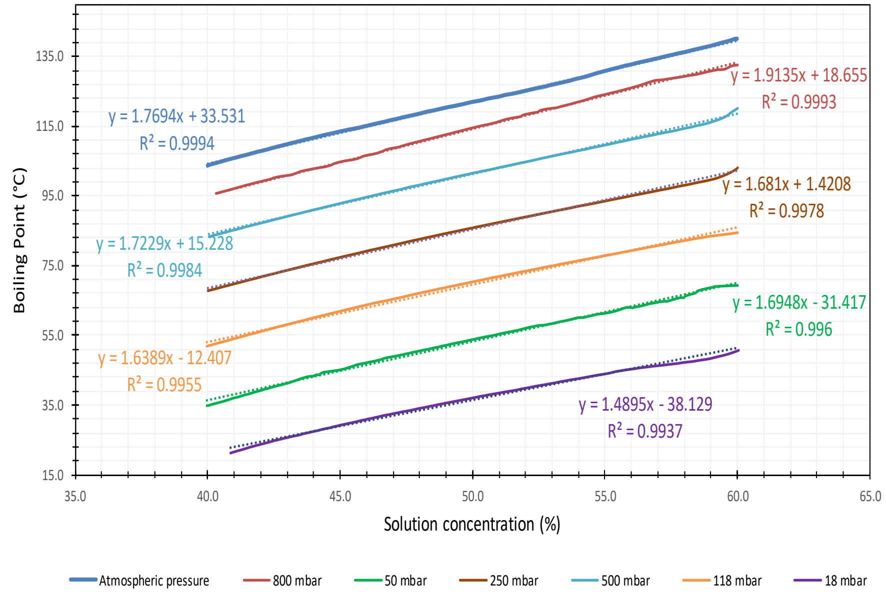
Vapor pressure measurements- Results Analysis





BP of solutions at different concentrations (at constant pressure)

Vapor pressure of solutions at different concentrations

Boiling points of solutions at different pressures

Summary

- The RC1, is an essential tool in the development, safety and scale up of chemical processes
- Various thermochemical and physical properties can be measured
- The RC1 allows the safe scale up of processes from a lab to industrial scale
- **Scaling should be done in small steps, and precautions should be taken in every process step**

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