

Case study: FIRE IN A DRIER

Incident:

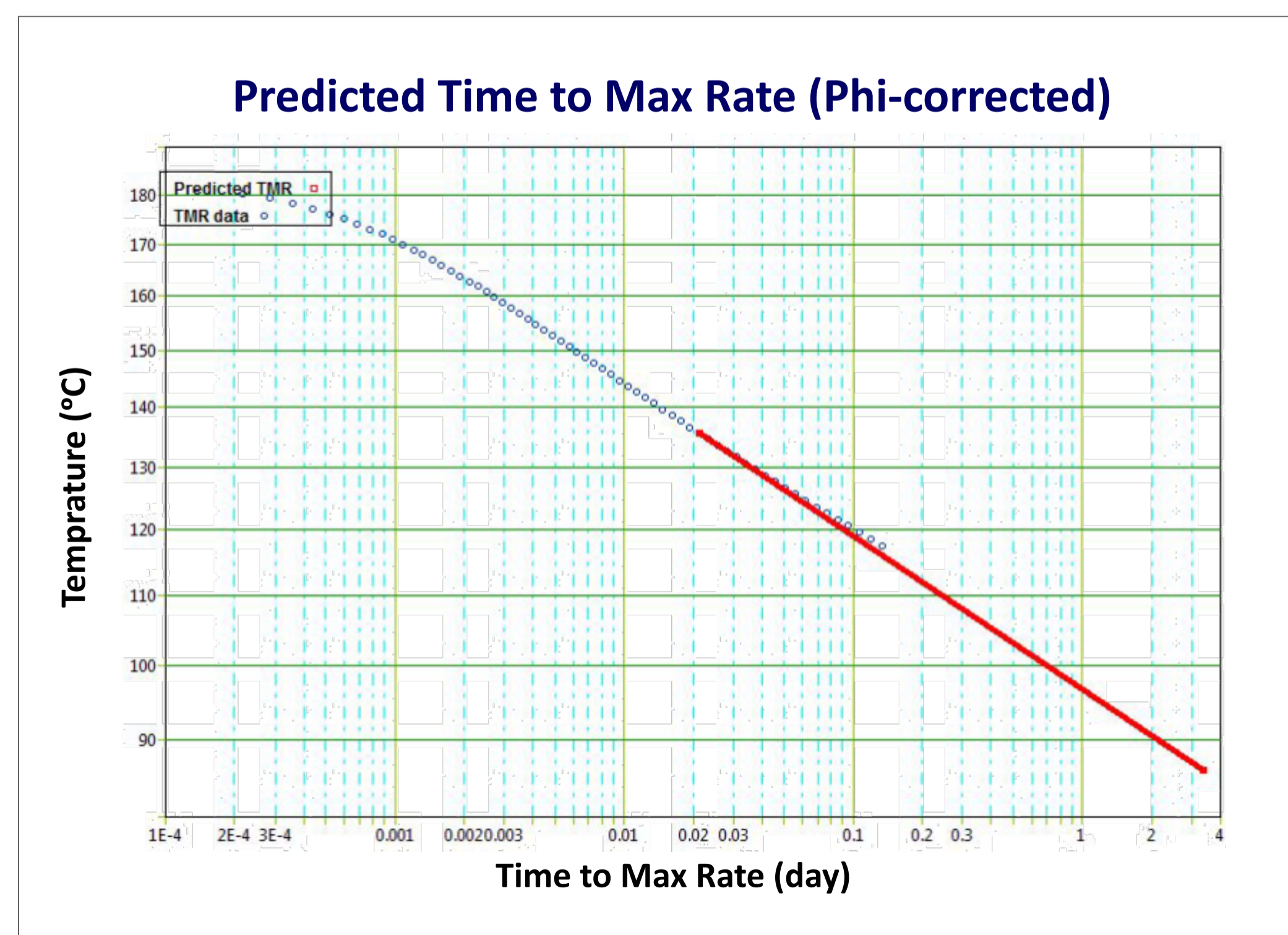
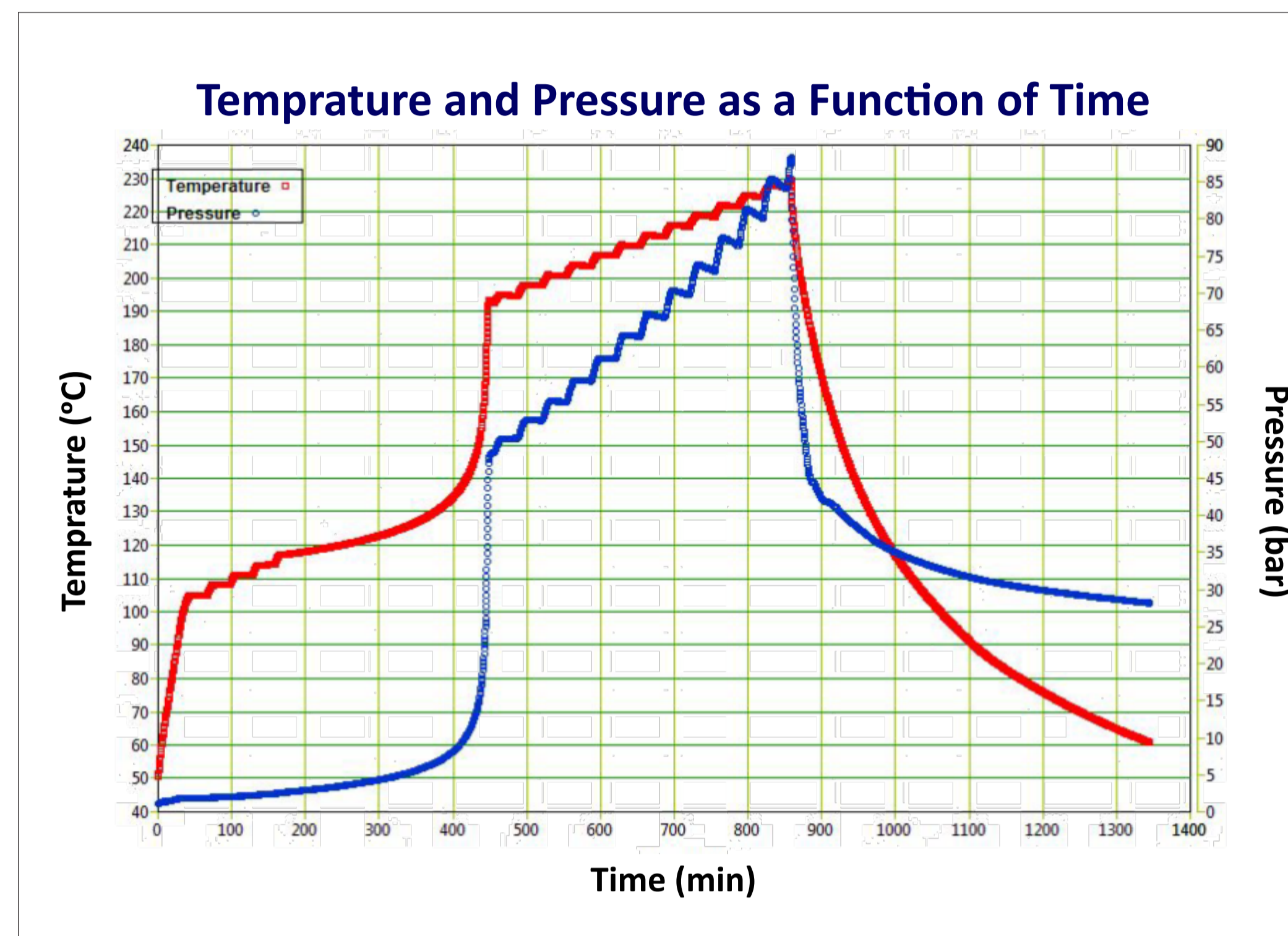
- RMR-Intermediate is dried in Rotary Vacuum Dryer for 24 hours per batch.
- Drying Temp is 80 – 85°C. Heating media temperature ?
- RVD was running for more than 3 days for campaign batches.
- There was a major explosion in RVD and the entire material in dryer was decomposed.

Investigation:

Safety Test Result of Powder:

- Burning class: 5
- D.T.A: Decomposition onset 131 °C; $\Delta T=74$ °C at 172 °C.
- Grewer: Decomposition onset 127 °C; $\Delta T=55$ °C at 166 °C.
- ARC
 - Onset of decomposition: 115 °C
 - Heat of decomposition: 215.6 kJ/kg (Tad 103 °C)
 - Maximum Pressure : 47 bar
 - Residual pressure : 28 bar
 - 8 hr TMRad : 107 °C
 - 24 hr TMRad : 96 °C
 - TMRad at 85 °C : 3.4 days

ARC Thermogram:



Conclusion:

- As campaign batches were going on, cleaning of RVD after each batch was not done thoroughly.
- TMRad at 85 °C (by ARC) is around 3 days. Hence if product remaining in RVD would decompose after 3 days. This will trigger further decomposition in RVD.

ARC study is required when operating temperature and decomposition onset are close.

RVD to be thoroughly cleaned prior to next batch when product decomposition is close to operating temperature.

Case study: Runaway --Oxidation using Hydrogen Peroxide

Situation:

- Oxidation of an organic compound using H_2O_2 is carried out in batch mode.
- Water, starting compound and sulphuric acid are charged to reactor.
- H_2O_2 is charged to reactor over 5hrs under vacuum maintaining temp between 37- 43C – (at aprox 35-40 mm Hg abs pressure)

Reaction was carried out in **SS316 reactor (3kL)**– H_2O_2 quantity ~450 litres

- Manual rate control of H_2O_2 addition through ball valve and an orifice plate.
- Operators not fully aware of risks involved with H_2O_2 handling and its reactions
- Temperature was manually controlled via jacket cooling.

Situation:

During “**this batch**” the reaction mass temperature was below 300C for considerable time (about 2 hours) before it was restored to above 380C.

The rate of addition at this time was about 60 litre/hr. To compensate for slower addition the rate of addition was increased may be more than 120 kg/hr.

Because of this temperature started increasing (38 to 52 in 5minutes and then to 62 in two minutes) then later it took off in an uncontrolled manner (**runaway** reaction) to much more than 140C as indicated by temperatures recorded.

EXPLOSION SCENARIO –DECOMPOSITION



Information to Toll Manufacture

SOP Data

3KL reactor – (2700kg rxn mass, 450kg H_2O_2)
heat transfer area ~6m², U ~ 1000kj/m² 0C
 H_2O_2 addition rate ~90kg/hr for 5hours
water evaporated during rxn. ~120kg/hr

Safety related information

1. Reaction heat control with only jacket cooling is not sufficient.
2. Maximum addition rate of 125kg/hr is ok under present rxn. Conditions.
3. Vacuum of > 720mm Hg required through out reaction.
4. At 60 C stoppage of H_2O_2 and full cooling recommended.
5. At 70C quenching of reaction.
6. Impurities trigger decomposition of H_2O_2 at low temperatures.

Calorimetric data

Heat of reaction ~490kj/kg rxn mass (by RC1)
~2960 kj/kg of H_2O_2 (0.6C rise/kg of H_2O_2)

Reaction is dosing controlled.

Onset of decomposition 600C and very fast above 70°C (by DSC)

Cooling capacity

1. Jacket cooling = $UA \Delta T = 1000 \times 6 \times (40-10) = 180,000$ kj/hr

2. Evaporative cooling ~2420kj/kg of water evaporation.

Heat generation (@ 90kg/hr) =266400kj/hr

1. jacket cooling: $180000 / 2960 = 60$ kg/hr of H_2O_2 - hence unsafe

2. Evap. cooling: $120 \times 2420 = 290400$ kj/hr hence Safe

At rate of addition above 140 kg/hr would lead to temperatures of 70 C which lead to runaway.

Heat generation rate and cooling capacity in reactor are needed to assess possibility of runaway.