

Venting – Or How to Regain Control of a Reactor in Cases Where “Thermal Runaway” Has Already Started

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Inherently Safe Process Control

Reactions must remain controllable at all times, not only on a laboratory scale of usually less than one liter, but also – and especially – in large reactors that produce on a ton scale. Even if unplanned events like the failure of a pump in the cooling cycle of a reactor occur, precautions need to already have been taken at the planning stage of the production plant to prevent reactors from getting out of control. This forward-looking planning, which also takes unforeseeable events into account, enables inherently safe operation of production plants at all times [1].

Worst-Case-Scenario

Already before planning production plants, it is essential to assess the chemicals used and the planned reactions in terms of their hazard potential. In order to avoid unpleasant surprises in the size and capacity of the plants, in upscaling, or even in the order in which the reactants are added, studies are often carried out to this end describing the worst-case scenario. Knowledge of the worst case makes it easier to control all real production conditions. The worst case with regard to the temperature control of a reactor is exceeding the planned process temperature due to, for example, the failure of a pump in the cooling cycle. If the cooling system fails and the heat of reaction can no longer be balanced, the temperature in the reactor rises above the planned reaction temperature. This can lead to undesirable side reactions or secondary reactions. In the worst case, temperature and/or pressure increases can cause the reactor to burst. In order to investigate what happens when the temperature in the reactor rises uncontrollably, how fast the temperature rises and how much pressure builds up in the reactor, such reactions are simulated on a small scale in the laboratory. An instrument designed to investigate this worst case is the NETZSCH ARC® 254.

The NETZSCH ARC® 254

The NETZSCH ARC® 254 (figure 1) is an accelerating rate calorimeter capable of carrying out so-called thermal runaway tests. The objective of this measurement technology is to find the hazardous potential with respect to the temperature of a sample or a reaction mixture under adiabatic conditions. Adiabaticity in particular means no heat exchange occurs. If all the heat of reaction remains inside a reaction vessel and is not able to dissipate to the environment, the temperature will rise and thus cause the speed of reaction to increase. This will result in a self-accelerating reaction mechanism. By studying such scenarios, any real-world conditions – which as a rule are not fully adiabatic, since some heat is always lost to the surroundings – can be calculated and classified.



1 NETZSCH ARC® 254

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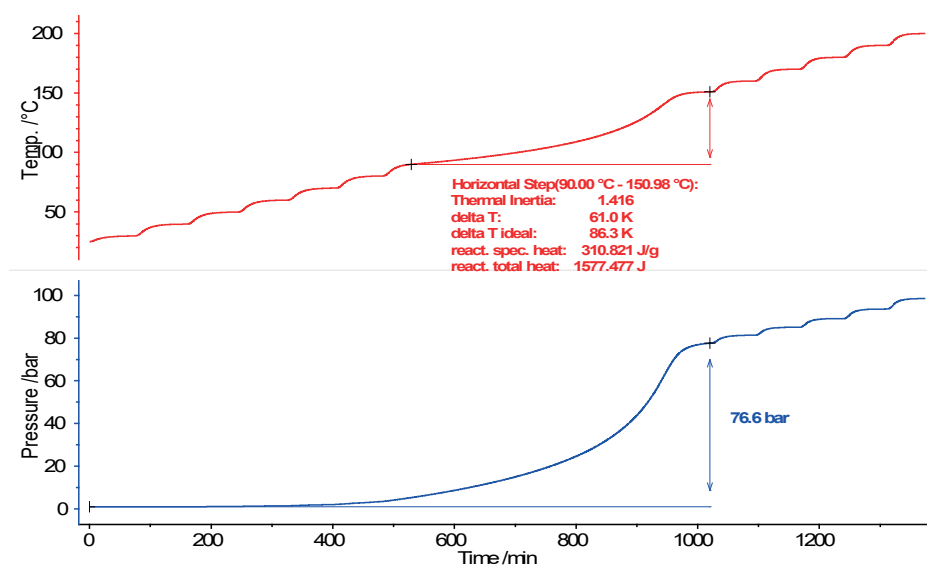
How is the Detection of an Exothermal Self-Decomposition Reaction Detected?

To detect thermal runaway, the temperature of the substance or reaction mixture to be investigated is increased stepwise. At each temperature step, a sufficient amount of time is waited in order to temper the sample to that temperature. Then, a detection is carried out as to whether the sample temperature remains constant at this temperature or whether it rises slowly, i.e., whether self-heating of the sample occurs or not. If no self-heating is detected, this sequence of stepwise temperature increase (Heat-Wait-Search) will be continued. When exceeding the self-heating rate of 0.02 K/min, the instrument changes into the so-called adiabatic mode. This measurement mode prevents heat loss to the sample environment, since all heaters surrounding the sample chamber follow the sample temperature now. If all heaters have the same temperature as the sample, i.e., there is no temperature gradient, no heat can be lost to the environment. This way, the ARC ensures an adiabatic sample environment to the greatest extent possible. This, in turn, is an important prerequisite for investigating a worst-case scenario such as thermal runaway.

How is a Thermal Runaway Reaction Measured?

If thermal runaway begins to occur during a reaction, it is desirable to determine this critical point in time or temperature as early as possible. Carried out sequentially, the sample temperature will initially increase only very slowly at the beginning of self-heating. 0.02 K/min is a very low self-heating rate, corresponding to only 1.2 K per hour. The decomposition reaction starts slowly, but continuously increases in speed with rising temperature until it reaches its maximum self-heating rate and finally the maximum temperature. Figure 3 shows the results for temperature (red) and pressure (blue) for an HWS test on a 17.5% hydrogen peroxide solution (H_2O_2). To this end, a volume of 5.0757 g of the hydrogen peroxide solution was placed into a spherical titanium container (8.7 ml).

As mentioned earlier, the criterion for recognizing an exothermal decomposition reaction is a self-heating rate of > 0.02 K/min. This threshold value was exceeded at 90°C (onset), and then the sample temperature rose to 151°C under adiabatic conditions. During the decomposition reaction, the pressure inside the sample vessel increased to 76.6 bar.



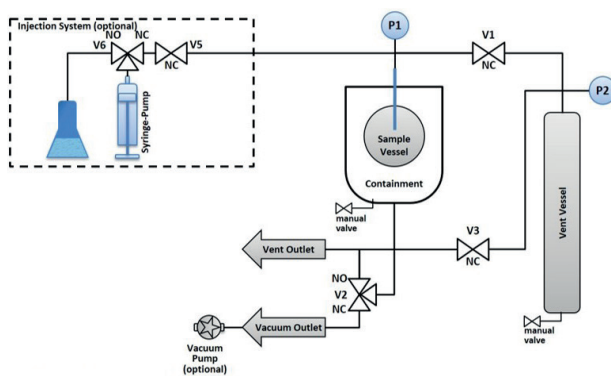
2 HWS results for hydrogen peroxide (17.5%), temperature (red) and pressure (blue).

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Is There a Way to Stop Thermal Runaway?

The question as to whether thermal runaway can be stopped or not is, of course, strongly related to the self-heating rate. It is necessary to detect the critical temperature or the start of thermal runaway, but maybe it is not always desirable to allow the decomposition reaction to fully run its course. It would be much more important to know the temperature or pressure up to which a reaction that has already begun to undergo runaway can be stopped again and brought under control. The possibility of detecting the beginning of a reaction’s thermal

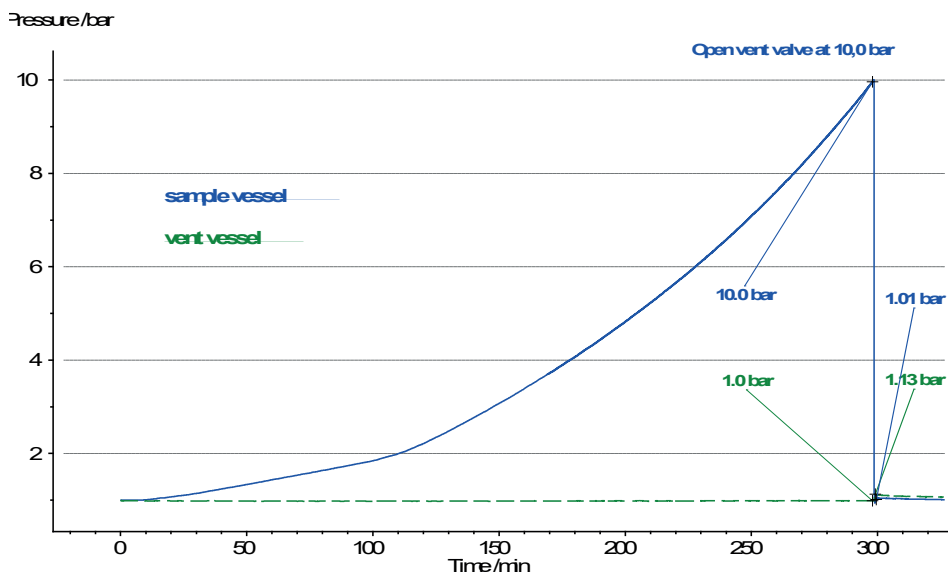
runaway and then preventing further self-heating by shutting off the adiabatic environment, thus avoiding the decomposition reaction, has already been reported about elsewhere [2]. Here, an attempt should be made to show another way to stop a decomposition reaction that has just started by pursuing a different strategy. The reaction vessel is connected via a pressure line and a valve to another vessel, the so-called vent vessel (figure 3). When a freely selectable sample pressure is reached, the measuring software will open the valve to the vent vessel. By venting into this vessel, the pressure in the reaction vessel should also decrease. This could be sufficient to stop self-heating and thus uncontrolled consecutive and side reactions.



3 Schematic diagram of the setup of the NETZSCH ARC® 254

Venting

Both the reaction vessel and vent vessel are equipped with an individual pressure gauge. Thus, the pressure increase can be tracked after opening the valve (see V1 in figure 3). The volume of the vent vessel at 250 ml, however, is many times larger than the volume of the sample vessel, where typically approx. 5 ml of gas volume remain above the sample. For this reason, the pressure in the vent vessel increases only from 1.0 bar to 1.13 bar after opening the valve, while the pressure in the sample vessel decreases from 10.0 bar to 1.0 bar at the same time (figure 4).



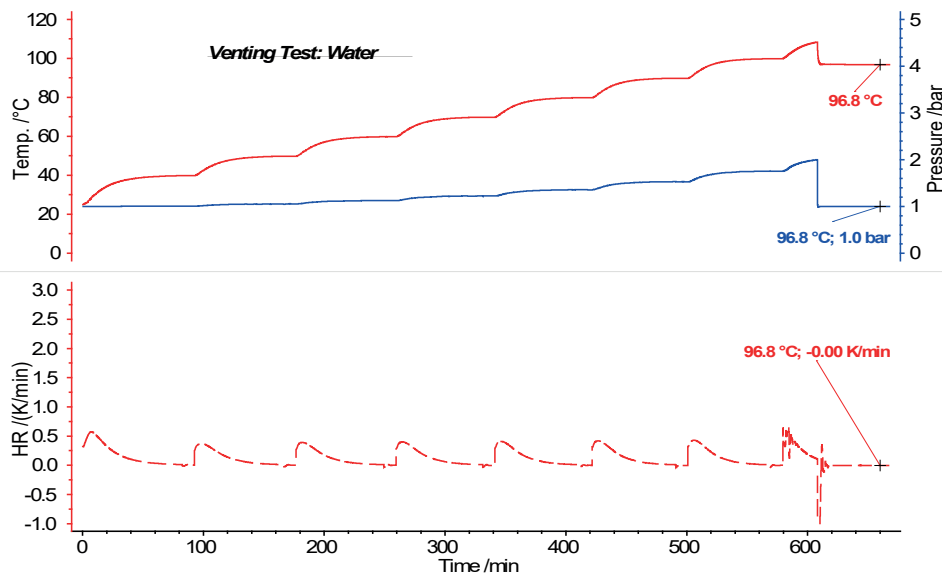
4 Results of a measurement with venting at 10.0 bar. Pressure course in the sample vessel (blue) and in the vent vessel (green).

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Figure 5 shows the results of an HWS measurement with water as the sample substance, in which the pressure signal increases analogously to the temperature signal and according to the temperature steps of the HWS program. In this example, opening of the vent valve was programmed via the measurement software at 2.0 bar. It can easily be seen that by opening the vent vessel, not only does the pressure in the sample vessel decrease from 2.0 bar to 1.0 bar, but the temperature in the sample vessel also strongly decreases. Over a period of 60 min in which the vent valve remains open, the heaters surrounding the calorimeter also follow the sample temperature. This decreases from 108.4°C to 96.8°C and – although the adiabatic measurement mode remains activated during this time, i.e., the surrounding heaters follow the sample temperature – no further increase in sample temperature can be determined.

Now, when investigating water as a sample substance, it can be expected that there will be no exothermal reaction. Instead, it was confirmed that when there is no exothermal reaction by the sample, the sample temperature decreases after opening the vent valve and then remains constant due to the adiabatic surrounding. This is also confirmed by the self-heating rate of the sample in the lower part of the figure.

The investigation of a one-percent hydrogen peroxide solution also shows no further temperature increase after opening the vent valve at a pressure of 3 bar in the sample vessel. In the case of a two-percent hydrogen peroxide solution, it can already be seen that the exothermal decomposition reaction caused by opening the vent valve and depressurizing the system to atmospheric pressure is not sufficient to entirely suppress further

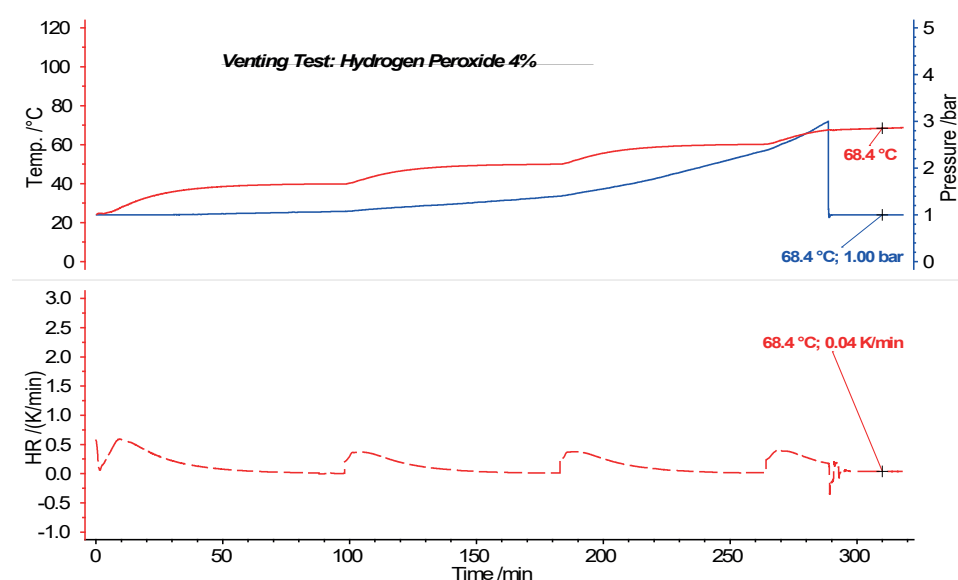


5 Results of a measurement with venting at 10.0 bar. Pressure course in the sample vessel (blue) and in the vent vessel (green).

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decomposition. This results in a self-heating rate of 0.02 K/min. For a four-percent hydrogen peroxide solution (figure 6), a self-heating rate of 0.04 K/min is still

detected after opening the vent valve. The temperatures and self-heating rates for the hydrogen peroxide solutions discussed are summarized in table 1.



6 Results of a measurement on a hydrogen peroxide solution (4%) with venting at 3.0 bar. Pressure curve in the sample vessel (blue), temperature curve in the sample vessel (red), self-heating rate (red dashed).

Table 1 Summary of the temperature and self-heating rate for various hydrogen peroxide solutions

Sample	Temperature during venting	Self-heating rate after venting
H ₂ O	108.4°C (2 bar)	0.00 K/min
H ₂ O ₂ (1%)	81.8°C (3 bar)	0.00 K/min
H ₂ O ₂ (2%)	70.8°C (3 bar)	0.02 K/min
H ₂ O ₂ (4%)	67.6°C (3 bar)	0.04 K/min

Summary

The NETZSCH ARC® 254 offers two possibilities for regaining control, if necessary, of reactions where thermal runaway has already started. One possibility is that in which the surrounding heaters are switched off when the sample reaches a given self-heating rate, thus eliminating the adiabatic environment of the sample and making heat losses possible again; further runaway of the reaction is then staved off via these heat losses [2]. The other possibility, in which pressure can be removed from the sample vessel into another sample vessel (vent vessel) by opening a pressure relief valve (vent valve), was presented in this application note. By measuring

the pressure independently, the pressure increase in the vent vessel can be monitored. It was shown that further progress in weakly exothermal decomposition reactions can be stopped by this, while more strongly exothermal reactions continue to show detectable self-heating even after the pressure has been released.

Literature

- [1] F. Stöbel, „Thermal Safety of Chemical Processes“, WILEY-VCH, Weinheim, 2008
- [2] NETZSCH Application Note 207, E. Füglein, “Is There a Way to Stop Thermal Runaway“, 2021