

# Determination of $T_{D24}$ by ARC Instruments for Thermal Risk Assessment in Chemical Processes

Dr. Elena Moukhina, Software Neo Business Field Management, and Xu Liang, Senior Applications Scientist NSI

## Introduction

Chemical industrial processes based on exothermal reactions can be very dangerous. Lack of knowledge about the process may lead to incorrect process conditions and thus to thermal runaway in equipment or reactors. Furthermore, failure of the cooling device may also lead to an unplanned temperature increase in a reactor. In order to ensure safe processes, it is necessary to know beforehand whether this temperature increase is harmless or whether it is the beginning of thermal runaway.

In the chemical industry, highly energetic synthesis reactions with very intensive heat generation are often carried out. Such industrial processes require cooling devices which do not allow for the reactant to heat above the intended synthesis temperature. This temperature of reactants during industrial processing is called *Process Temperature*, or  $T_p$ . In order to know how intensive cooling must be to maintain the process temperature, it is necessary to know the heat of reaction, temperature increase and kinetics of reaction.

## The Solution: Measurements by Means of the Rate Accelerating Rate Calorimeter ARC 305

NETZSCH offers Accelerating Rate Calorimeters (ARCs, figure 1) for the study of self-heating reactions and their characteristics. The newest and most intelligent of them is the recently optimized ARC 305. The determination of characteristic temperatures like  $T_{D24}^{(1)}$  can either be performed using the standard software for simple  $n^{\text{th}}$ -order reactions, or the advanced Kinetics Neo software for complex multi-step reactions or for reactions with autocatalysis.



1 The new Accelerating Rate Calorimeter, ARC 305

<sup>(1)</sup>  $T_{D24}$  The initial temperature for an adiabatic process with Time to Maximum Rate (TMR) = 24 h is called  $T_{D24}$ .

## Determination of $T_{D24}$ by ARC Instruments for Thermal Risk Assessment in Chemical Processes

### Characteristic Temperatures of the Industrial Chemical Process – Avoiding Thermal Runaway

Knowledge of measured values like heat of reaction is very important, but not always enough for a safe chemical process. If cooling fails, the continuing reaction will increase the temperature in the reactor until the reactants are consumed. Then, the reaction and corresponding self-heating will have finished, and the final theoretical temperatures will have been reached. This temperature is called *Maximum Temperature of Synthesis Reaction* (MTSR). MTSR is an essential approach to assessing the thermal runaway risk and designing safe operating conditions.

The safety of industrial processes depends on how high the MTSR is. If it is too high, it can initialize secondary processes with further self-heating. Such consecutive reactions are usually decomposition reactions, which are exothermic and lead to a further temperature increase. In fact, if such secondary reactions are initialized, the risk of runaway and thermal explosion is very high.

During industrial processes in large-volume reactors, the reactants are under conditions close to adiabatic, where evolving heat of reaction leads to self-heating of reactants. In order to study the material behavior, the ARC system allows for creating adiabatic conditions for a small amount of sample material. Figure 2 shows an example of such a measurement.

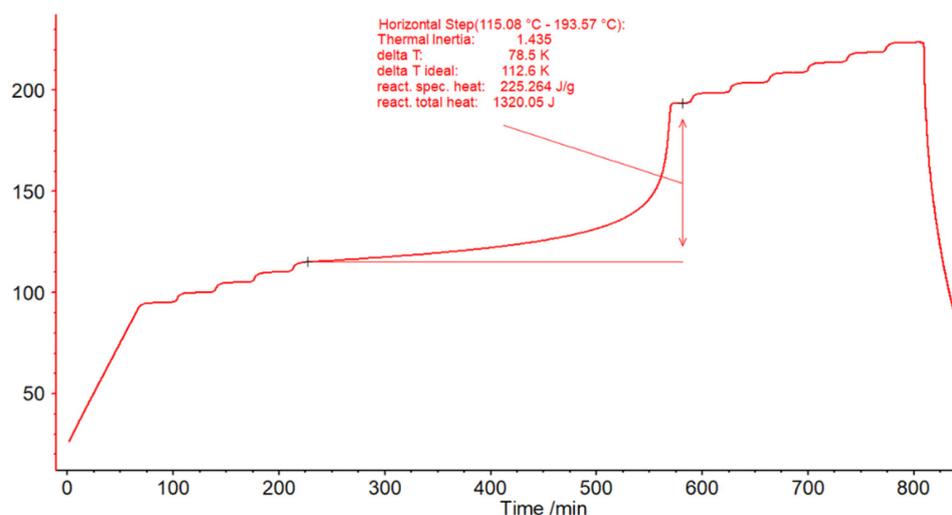
### Time to Maximum Rate

The temperature increase of reactants during exothermic reactions under adiabatic conditions accelerates with time; then reaches its maximum rate. The time from the beginning of an adiabatic process to the maximum reaction rate is called *Time to Maximum Rate* (TMR). This time value depends on the initial temperature: The lower the initial temperature, the longer this time period is.

The initial temperature for an adiabatic process with TMR=24 hours is called  $T_{D24}$ . This corresponds to the temperature at which the time to maximum rate of the runaway reaction (the speed of thermal runaway) is 24 hours. This temperature characterizes the process and is used for thermal risk assessment.

### Comparison of Characteristic Temperatures

If the value of MTSR is lower than  $T_{D24}$ , this means that the temperature is not sufficient for initiating a secondary process such as a decomposition reaction, and the risk of a runaway reaction is thus low. If MTSR is higher than  $T_{D24}$ , the secondary reaction starts already during the primary reaction and it is impossible to avoid the runaway, with dangerous consequences. There are several intermediate classes of risk levels between these two cases [1], which depend on the relationship between MTSR,  $T_{D24}$  and MTT (Maximal Technical Temperature).



2 Decomposition of 20-% DTBP in toluene; measurement in Heat-Wait-Search mode (ARC 305 instrument).

## Determination of $T_{D24}$ by ARC Instruments for Thermal Risk Assessment in Chemical Processes

### Kinetic Methods for Calculation of $T_{D24}$

Temperature  $T_{D24}$  can be calculated by means of different kinetic methods based on the experimental data from ARC instruments.

#### Linear TMR-Extrapolation

This is a traditional linear algorithm. It is based on the assumption of a one-step adiabatic process with approximation to a zero-order reaction, where in the main kinetic equation (1) the reaction type  $f(\alpha)=1$

$$c_p \cdot \phi \frac{dT}{dt} = \Delta H \cdot A \cdot f(\alpha) \cdot \text{Exp} \left[ \frac{E_a}{RT} \right] \quad (1)$$

Here,  $\phi$  is the thermal inertia factor, i.e. the ratio of the specific heat capacity of the material with the vessel to the specific heat capacity of the material,  $c_p$ . In the absence of a container,  $\phi=1$ .

$\Delta H$  is the enthalpy,  $A$  is the pre-exponent,  $E_a$  is the activation energy and  $R$  is the gas constant.

Under this assumption, the following linear approximation can be used:

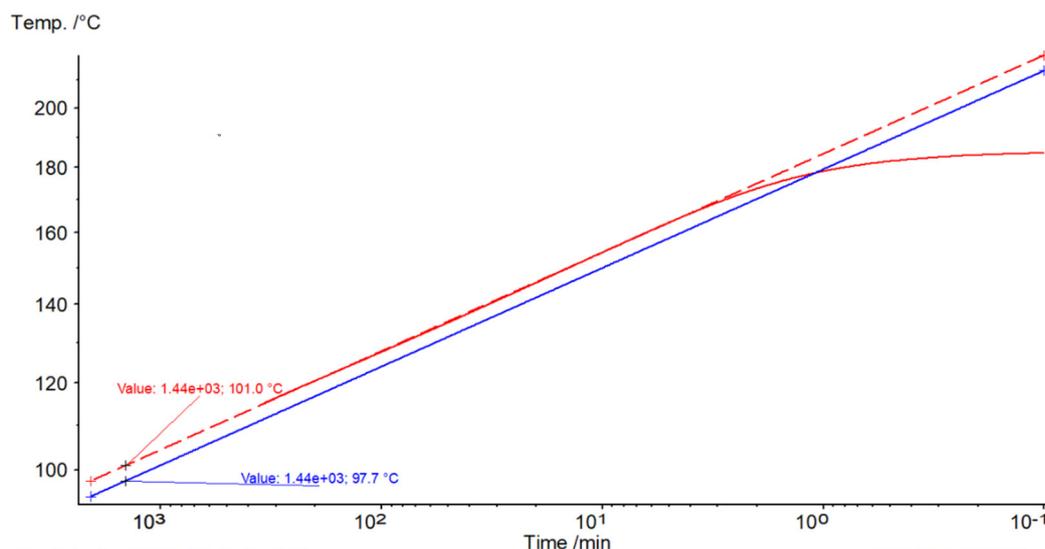
$$\log(\text{time}) = \frac{E_a}{RT} + \text{Const} + \log \phi$$

This dependence corresponds to the straight line  $\log(\text{time})$  vs.  $1/T$ , where slope  $E_a/R$  is independent from the thermal inertia factor  $\phi$ .

Fig. 3 demonstrates the example of the simplest linear approximation for evaluation of  $T_{D24}$ .

If the experiment is carried out in the ARC with  $\phi > 1$  (red solid line), extrapolation to 24 hours results in the red dashed line. The extrapolated straight line for  $\phi = 1$  (blue line) runs parallel but is shifted by  $\log(\phi)$  to lower temperatures. Then on the new red-dashed line, the temperature  $T_{D24}$  can be found for time=24 hours.

For this type of analysis and evaluation of  $T_{D24}$  only one experimental data set of an ARC measurement is required.



3 Linear TMR extrapolation for decomposition of 20% DTBP in toluene. Solid red curve: experimental data for  $\phi=1.4$  (figure 1); dashed red line: linear extrapolation for  $\phi=1.4$ ; blue line: simulated linear extrapolation for  $\phi=1.0$  with  $T_{D24}=97.7^\circ\text{C}$

## Determination of $T_{D24}$ by ARC Instruments for Thermal Risk Assessment in Chemical Processes

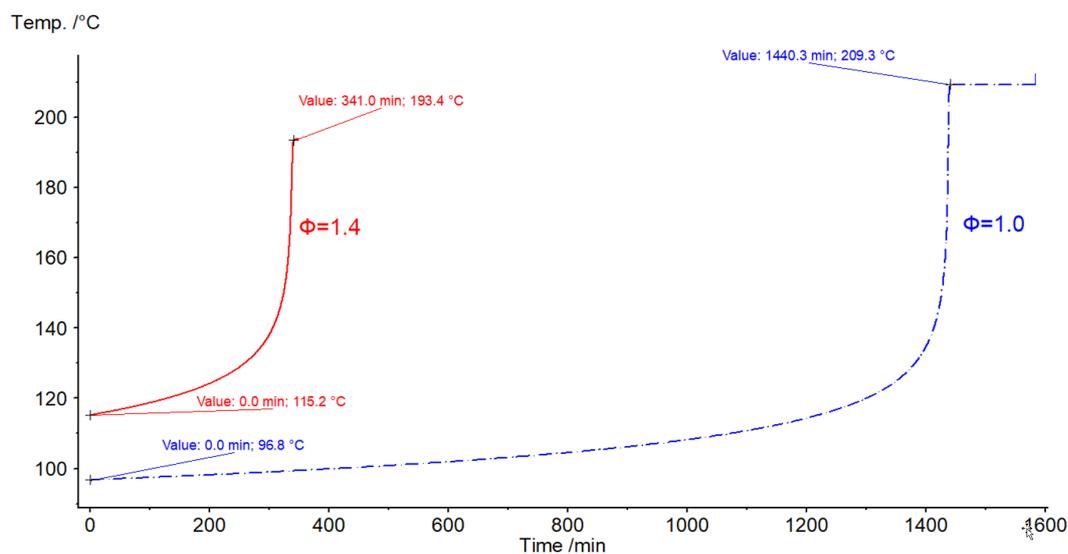
### Non-Linear TMR Extrapolation

In reality, however, the decomposition reaction may have other reaction orders in addition to zero order and, besides a single-step mechanism, also multiple reaction steps.

For such cases, we developed the second, more precise non-linear method [2]. This method assumes that the initial part of the reaction runs according to an  $n^{\text{th}}$ -order reaction and allows the activation energy,  $E_a$ , to be found. Then, the model-free method is used for the calculation of adiabatic self-heating for  $\phi=1$  from the experimental data, with  $\phi>1$  obtained by the measurement shown in figure 2.

This method works both for reactions with any reaction type having an initial part resembling an  $n^{\text{th}}$ -order reaction, and for reactions having multiple consecutive reaction steps.

In figure 4, two temperature curves with self-heating are shown: the original experimental data with  $\phi=1.435$  (red curve), and the newly calculated curve with  $\phi=1$  (blue curve). An important temperature for safety assessment is the so-called  $T_{D24}$ . This corresponds to the temperature at which the time to maximum rate of the runaway reaction is 24 hours. The time it takes to reach the maximum rate under adiabatic conditions is known as TMR, the time to maximum rate. This second curve, corrected to  $\phi=1$  (blue), is used to find the temperature  $T_{D24}$ .



4 Non-linear TMR extrapolation for decomposition of 20-% DTBP in toluene. Red solid curve: experimental data for  $\phi=1.4$ . Blue dashed curve: simulated, non-linear extrapolation for  $\phi=1.0$  with  $T_{D24}=96.8^{\circ}\text{C}$ .

## Determination of $T_{D24}$ by ARC Instruments for Thermal Risk Assessment in Chemical Processes

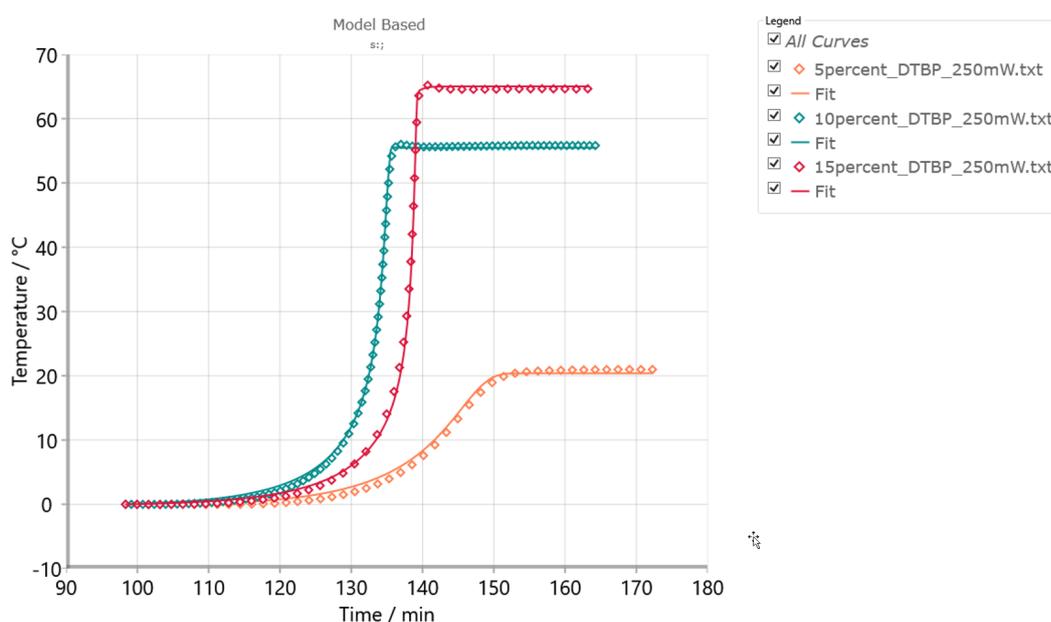
### Advanced Kinetics by Kinetics Neo Software

Both methods described above are based on the assumption that the activation energy is a constant value. However, the process can contain steps with different activation energies and reaction steps different from the reaction of nth-order. The most accurate kinetic analysis with a more precisely predicted value of TD24 requires data sets from several experiments, carried out under different conditions. Having data from multiple experiments is a mandatory condition for an accurate kinetic analysis, as recommended by ICTAC [3].

For this advanced evaluation, several ARC experiments can be carried out at different  $\phi$ -factors. For these experiments, different values of conversion are obtained by different measurements at the same temperature. The tool for this accurate kinetic analysis is NETZSCH Kinetics Neo software, which includes both model-free and model-based kinetic methods. Model-based methods can help

determine the number of reaction steps as well as kinetic parameters for each individual reaction. The application of advanced kinetic analysis includes the creation of a single kinetic model which mathematically consists of the system of differential kinetic equations with the set of kinetic parameters independent of time and temperature. If the curves simulated by this one model are in good agreement with the experimental data measured under different conditions, this model can be used for the simulation of the material behavior and reaction rate under temperature conditions other than those of the previous experiments, such as for calculation of the temperature increase under adiabatic conditions, and  $T_{D24}$ .

Figure 5 shows the set of ARC experiments under different conditions and simulated curves for these conditions. The good agreement between the model and experiments allows for using this model for other temperatures and thermal inertia.

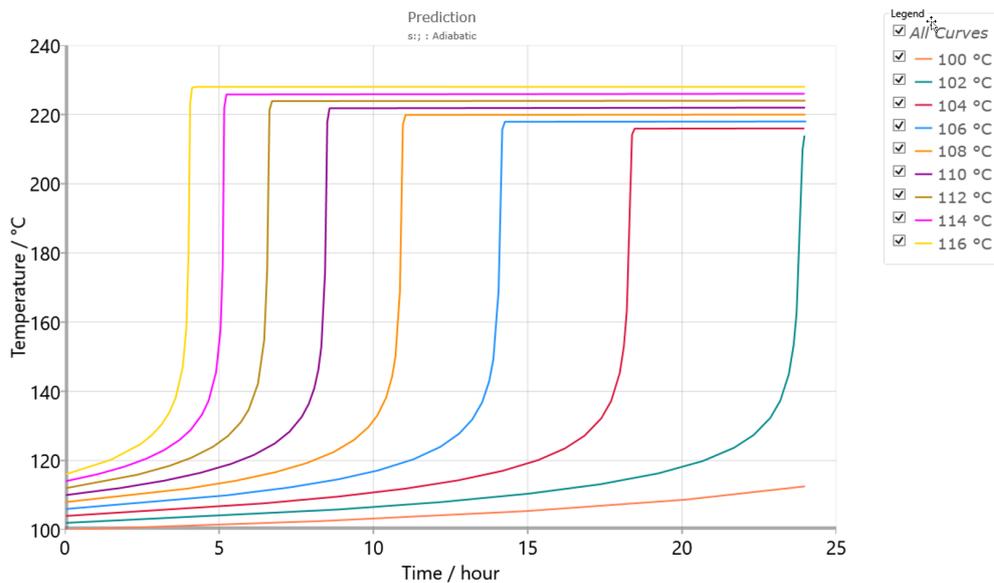


5 Temperature increase from ARC experiments (points) and simulations (solid lines) for DTBP in toluene for 5%, 10% and 15% solution under constant power of 250 mW. The one-step kinetic model of first order is found by model-based kinetic analysis.

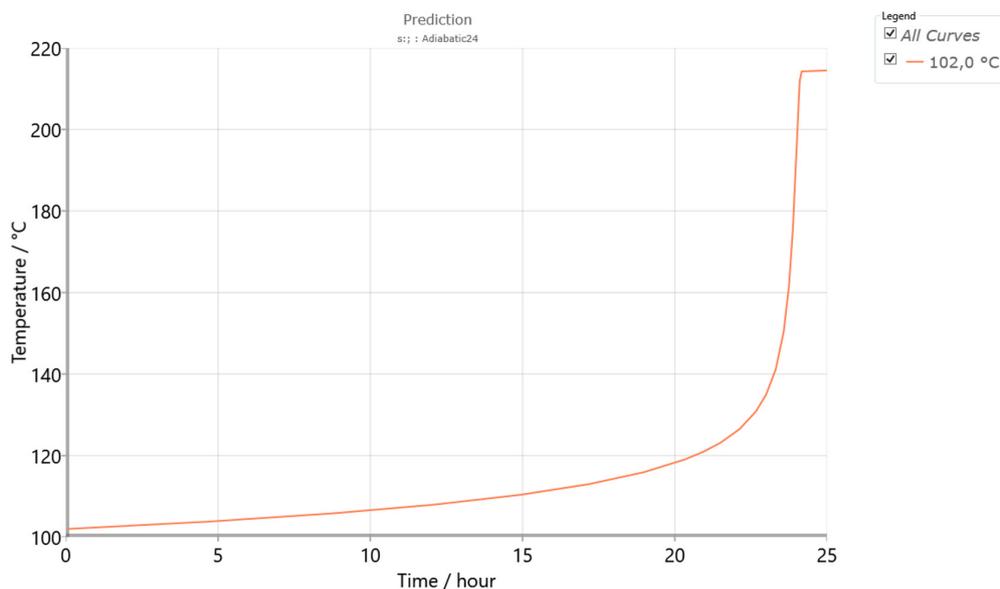
## Determination of $T_{D24}$ by ARC Instruments for Thermal Risk Assessment in Chemical Processes

In figure 6, a simulation is shown in which the substance being investigated is subjected to isothermal treatment at different exposure temperatures, which were calculated with the kinetic model from figure 5. Besides the simulated adiabatic curves, the software can calculate  $T_{D24}$ , which is the initial temperature of the adiabatic process needed in order to achieve TMR in 24 hours.

Figure 7 shows the self-heating course of the sample under adiabatic conditions for removal from thermal treatment at 102°C for 24 hours.



6 Simulation of the adiabatic self heating at different temperatures for  $\phi=1.0$ .



7 Calculation of  $T_{D24}$  for  $\phi=1.0$  and simulation of adiabatic self-heating at this temperature.

# Determination of $T_{D24}$ by ARC Instruments for Thermal Risk Assessment in Chemical Processes

## Conclusion

Self-heating reactions can be studied through experiments with NETZSCH ARC instruments – from simple linear Proteus analysis software results to more advanced calculations using the Kinetics Neo software. This allows for the calculation of temperature  $T_{D24}$  even in the case of more complex courses of reaction, which is essential in assessing thermal risk. A comparison of the results obtained with various methods allows for assumptions about the linear and non-linear predictions to either be confirmed or rejected, and for additional experiments to be carried out. These, in turn, allow for increasing the depth of the study and refining the results via advanced kinetic analysis in the Kinetics Neo software.

## Literature

- [1] Thermal Safety of chemical processes: Risk Assessment and Process Design, by Francis Stoessel (Switzerland 2008)
- [2] HarsNet. Thematic Network of Hazard Assessment of highly reactive systems. 6. Adiabatic calorimetry. <https://documents.net/document/6-adiabatic-calorimetry-calorimetrypdfharsnet-thematic-network-on-hazard-assessment.html?page=1>
- [3] S.Vyazovkin, ICTAC Kinetics Committee recommendations for analysis of multi-step kinetics, Thermochimica Acta, V689, July 2020, 178597  
<https://doi.org/10.1016/j.tca.2020.178597>

## The Authors

**Dr. Elena Mouhkina** studied physics and mathematics at the Yaroslavl State University in Russia and has a Phd in physics. She has been part of the NETZSCH Analyzing & Testing family for over 20 years now and has gained lots of experience in our R&D department, before taking over the position of the Business Field Manager for the Software Neo in 2021.

**Liang Xu** studied fine chemical engineering and got his bachelor's degree from the East China University of Science and Technology in 1997. After working in a local material company's analytical test center for 5 years, he joined NETZSCH Instruments (Shanghai) in March 2002 as a lab engineer. Based on a work experience of 20 years, he accumulated extensive knowledge of various thermal analysis methods, application fields and corresponding background theories. Currently, he holds the position as senior application scientist at NETZSCH Instruments (Shanghai) Ltd.