

ASSESSMENT OF THERMAL SAFETY DURING DISTILLATION OF DMSO

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Distillations of unstable compounds carried out under vacuum can be quite dangerous in the case of a power failure and subsequent loss of vacuum, because heat is no longer removed by evaporation. The reaction mass may therefore self-heat and produce a runaway. During distillation and in the emergency case, heat accumulation conditions must therefore be avoided. A systematic approach to safe process conditions using the heat balance of the system is shown. The recovery of Dimethylsulfoxide by distillation is used as an example.

Key Words: Dimethylsulfoxide- distillation- heat accumulation - runaway reaction - heat balance - kinetics- cooling curves

INTRODUCTION

This paper deals with the risk of distillations of unstable compounds.

Distillations, especially when carried out under vacuum can be quite dangerous for different reasons:

during normal operation there is a high power throughput through the mass to be distilled. Heat is put into the mass through the heating mantle, on the other hand heat is dissipated by evaporation. For a considerable time the thermal load on the substance may be quite high. In the case of an energy failure, the vacuum and therefore the heat removal capacity can be lost, while the heating mantle is still hot. The mass in the distilling apparatus may therefore reach the temperature of the heat carrier, decompose and eventually undergo a thermal runaway.

For a long time it has been recognised in our company that tests to assess the thermal safety of distillations were needed (Lütolf [1]).

Using these tests, the temperature at which the first exotherm occurred was determined, from this a generous temperature safety margin was subtracted and thus the maximum temperature of the heating mantle fixed. The approach may seem to be primitive, but for a long time the method worked well, mainly because

- in the fine chemicals industry distillations were quasi exclusively performed in standardised batch equipment,
- the method covered just the case where solvent was distilled off and a comparatively small volume of a thermally unstable residue was left.

Today the situation has changed:

- distillation is very often an intrinsic part of a chemical process,
- distillation technology has changed: very often continuous and thin film evaporators are used and temperature gradients are usually higher to increase throughput.

We therefore felt that the risk of distillations could no longer be assessed by this type of standard test, but that a distillation process should be treated in the same way as a chemical process, i. e. an individual risk analysis should be made.

The following case study deals with the recovery of Dimethylsulfoxyde (DMSO).

DMSO is a very good solvent that solubilises many inorganic compounds and many other difficult-to-dissolve materials. It is therefore widely used in chemical industry [2]. It is a polar aprotic solvent that is high boiling and thus is easy to dry. However, these properties lead to some of the specific hazards of this material:

- DMSO is not inert; the reactivity of solvents that play only a physical role in reactions is easily forgotten. DMSO decomposes with a significant release of heat and gases. The decomposition is already evident at the boiling point; DMSO cannot be distilled at ambient pressure without decomposition. The decomposition is self accelerating and is further accelerated by both acid and base, particularly by even trace amounts of inorganic or organic halogens (Brogli et al [3]).
- The high boiling point prevents the dissipation of heat through vaporisation.
- Like other solvents, DMSO reacts with many reactive compounds, such as e.g. acid chlorides. However, in contrast to these other solvents, the reactions with DMSO involve a large release of heat that cannot be dissipated by vaporisation.

It is therefore understandable that quite a number of incidents during the recovery of DMSO has been reported (Bretherick [4]).

For this reason the recovery of DMSO by distillation was chosen as an example for the risk assessment of this operation.

Following an incident with DMSO at a Ciba production site, the safety aspects of the distillation of DMSO from a reaction mass - part of a process used in local production at two different sites - had been investigated and discussed in a report. Due to the high energy potential of the decomposition, the severity of an incident had been assessed to be high. The prob-

ability of an incident had been judged low, provided the jacket temperature T_a was kept below 130°C.

After the report had been sent to the production site, it was then found that in actual practice the jacket temperature was raised up to 168°C and that in case of a vacuum failure this could result in a critical state with very short runaway times. As a consequence, additional safety measures were judged to be necessary.

As a first precautionary consequence the production at the two sites was stopped.

Local production argued that this assessment was unnecessarily conservative and that during twenty years at neither of the two sites any accident had happened. We were therefore asked to review our assessment.

APPROACH

The following approach was used:

1. Based on a valid process description, a possible incidents **scenario** had to be set up. In this case the scenario assumed the loss of vacuum and a subsequent runaway of the reaction mass.
2. The **heat production** of the reaction mass had to be determined by measuring samples by Differential Scanning Calorimetry (DSC). The choice, the correct description and in some cases the thermal history of these samples during transport was crucial as to the validity of the conclusions of the investigation.
3. **Heat dissipation** by convection and/or radiation to the surroundings as well as **heat storage** by the heat capacity of the system had to be determined.
4. A **heat balance** of the system had to be set up involving heat production by decomposition of the reaction mass (see point 2) and heat dissipation (see point 3). This allowed to predict the time-temperature-behaviour of the system.
5. The time available in the case of an emergency would then determine the nature of eventual **measures** to be taken.

SCENARIO

Process documentation was available from the two sites, as were samples drawn at defined stages (Figure 1 and table 1).

Table 1: Characterisation of the samples

Sample No.	total mass in reactor [kg], assumed density = 1000 kg/m ³	after distillation of lt. DMSO	T _i [°C]	T _a [°C]	Pressure [Torr] abs.
3	6430	600	124	130	140
4	5330	1000	150	150	150
5	4330	2000	150	170	100
6	3330	3000	160	170	120

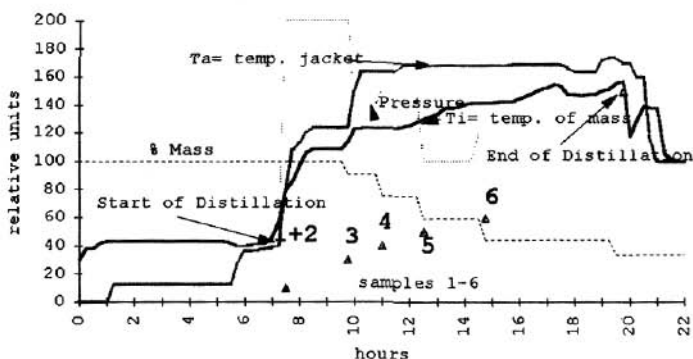


Figure 1: the distillation procedure is summarised in the graph, which is a linear representation of the circular temperature sheet from production site 1. Shown are the jacket and reaction mass temperatures T_a and T_i , the mass balance and the sampling times. The initial amount of reaction mass is 7000 kg and the reactor is made of stainless steel with 10 m³ capacity.

SAMPLES

Sample No. 6 from site 1 was chosen for further investigation of the heat production for the following reasons:

- it was drawn near the end of the distillation, where temperatures of both jacket and reaction mass were highest,
- it had therefore a long thermal history. This fact is important to the study of self accelerating reactions,
- it still contained about 10 % DMSO,
- it was very viscous. Therefore it could be assumed that heat transport in the corresponding reaction mass was by conduction only and therefore poor (see below).

The thermal behaviour of sample No. 5 was very similar. Furthermore, corresponding samples from the two sites were found to

behave similarly in the DSC. Thus errors due to a non-representative sample could be excluded. The assessment of the thermal safety of the operation was therefore based on the temperature-time runaway behaviour under adiabatic conditions of sample No. 6 from site 1.

HEAT PRODUCTION

Adiabatic assumption

Under conditions of no heat dissipation (adiabatic conditions) any sufficiently exothermic reaction will produce a thermal runaway characterised by an adiabatic temperature rise ΔT_{ad} and a time known as Time to Maximum Rate (TMR), as described for example by Townsend and Tou [5]:

$$TMR_{ad} = \frac{RT^2 E_a}{\dot{q}(T) c_p}$$

where

ΔT_{ad} = adiabatic temperature rise in K

ΔH = reaction energy in J/kg

c_p = specific heat capacity in J/kg/K

R = gas constant = 8.3143 J/Mol/°C

T = temperature in K

T_0 = initial, T_F = final temperature

E_a = activation energy in J/Mol

$\dot{q}(T)$ = heat release rate in W/kg at temperature T

All parameters needed for the determination of ΔT_{adiab} and TMR can in principle be determined by performing temperature programmed and isothermal Differential Scanning Calorimetry (DSC)-experiments. The thermal decomposition potential can be found by integration of such a curve. The decomposition potential ΔH of the sample No. 6 amounts to -450 kJ/kg, as measured by temperature-programmed DSC. This potential does not stem from the decomposition of DMSO alone, but also from other non volatile components of the mixture. In the adiabatic case, this potential would result in a temperature rise of 250 °C, using an estimated heat capacity c_p of 1.8 kJ/kg/K. This would raise the reacting mass to a final temperature of more than 400 °C. The severity of an incident is therefore high.

For the determination of the kinetic parameters such as the activation energy E_a of the decomposition, isothermal DSC-measurements at different temperatures are performed. E_a can then be found from the maximum heat release rates $\dot{q}_{max}(T)$ as function of T , using the Arrhenius relation:

$$\dot{q}_{\max}(T) = \dot{q}_{\max}(T_0) \cdot e^{-\frac{E}{R} \cdot \left(\frac{1}{T_0} - \frac{1}{T}\right)}$$

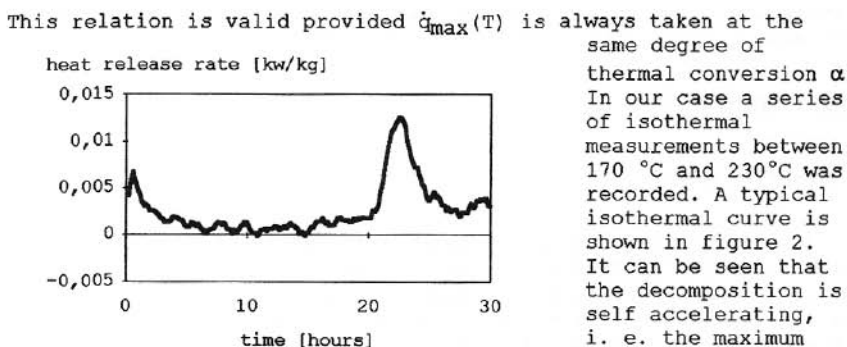


Figure 2: Isothermal DSC measurement of sample 6/site 1 at 170 °C

$$t_{\max}(T) = t_{\max}(T_0) \cdot e^{-\frac{E}{R} \cdot \left(\frac{1}{T_0} - \frac{1}{T}\right)}$$

In the special case discussed here it could be shown, that the activation energies for both \dot{q}_{\max} and t_{\max} were equal. The set of all isothermal curves could therefore be described by just one parameter, the activation energy as follows: In the adiabatic case the thermal conversion α is proportional to the temperature rise:

$$\alpha = \frac{T - T_0}{T_F - T_0}$$

For an isothermal DSC-measurement at temperature T , \dot{q} is a function of α , i. e. $\dot{q}(\alpha)$.

For a certain conversion α_0 all heat release rates \dot{q} which belong to the set of isothermal measurements and have the same conversion are related via the Arrhenius equation. Thus, if $\dot{q}(\alpha)$ is continuously known as function of time t and therefore conversion α for one temperature T , it is known for any other temperature and the adiabatic temperature time curve can be calculated by numerical integration.

$$T(t) = \frac{1}{c_p} \int_{t_0}^t \dot{q} dt$$

The numerical technique is discussed in more detail by Gyax [6]. Using an activation energy of 110kJ/Mol, the TMR_{ad} for various temperatures could be calculated (see table 2) The accuracy of the model could be further confirmed by comparison of calculated and measured temperature-programmed DSC- curves. For the specific heat capacity c_p a constant, temperature independent value of 1.8 kJ/kg/°C was assumed.

Heat balance

In order to determine the validity of the adiabatic assumption, one has to compare the initial heat production rate due to

Table 2: the table lists the estimated TMR_{ad} with an assumed heat capacity of 1800 J/kg/K

Temperature [°C]	TMR _{ad} [h]
150	10.5
160	5.5
170	2.8

decomposition $\dot{q}(T)$ to the heat dissipation rate due to cooling. If the heat dissipation rate is higher than the production rate, a runaway is not possible. On the other hand, if the heat production rate is greater than the heat dissipation rate a runaway reaction will occur

but can be stopped, if the TMR is sufficiently long, and countermeasures can be taken.

HEAT DISSIPATION OF THE PRODUCTION EQUIPMENT

Influence of heat capacity

If the distillation process is interrupted, for instance by loss of vacuum the temperatures of the reactor wall and of the reacting mass and within the reacting mass will equalize. Assuming conservation of heat content of the system reactor-reacting mass, the equilibrium temperature T_{eq} can be calculated from the relation of the heat which is accumulated in the apparatus to the heat accumulated in the reacting mass:

$$T_{eq} = \frac{m_i \cdot T_i \cdot c_{pi} + m_a \cdot T_a \cdot c_{pa}}{m_i \cdot c_{pi} + m_a \cdot c_{pa}}$$

where

m = mass

and subscript a, i corresponding to jacket and reaction mass respectively.

If the apparatus is only partially filled, the equilibrium temperature T_{eq} will be strongly determined by the temperature of the apparatus, i.e. the temperature of the jacket T_a , while T_{eq} of a completely filled vessel will approach T_i . Table 3 shows the relations, using values for normalised equipment [8].

Table 3: Calculation of equilibrium temperature

m_i	2450	kg
C_{pi}	2000	J/kg*°C
T_i	155	°C
m_a (mainly water in jacket)	300	kg
C_{pa}	4000	J/kg*°C
T_a	170	°C
T_{eq}	158	°C

6.2. Heat dissipation by convection

At site 1, as well as at site 2, cooling curves of a 10 m³ reactor partially filled

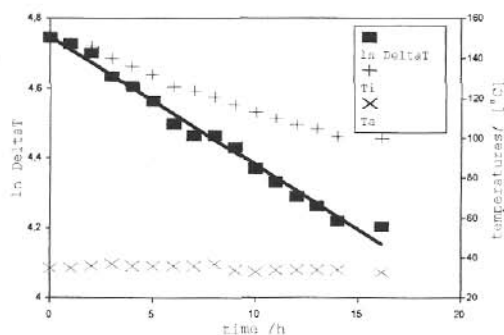


Figure 3: Temperature of reaction mass (+), of environment (x) and logarithm of temperature differences (■).

with 2450 l DMSO were measured. The reactor was heated to 150 °C, the heating mantle was not emptied and the reactor was let to cool down without stirring. Immediately before the temperature was measured, the stirrer was switched on to obtain homogeneous temperatures. Figure 3 shows the actual temperature of the reaction mass (+) and of the environment (x) together with the

natural logarithm of the temperature differences (■) as function of time. The latter is a linear function of time, indicating Newtonian cooling. From these measurements the heat dissipation rate in Watt/kg reaction mass could therefore be calculated (table 4).

Cooling behaviour of 10 m ³ reactor	
partially filled	
Dimensions	
Diameter (according to DIN [7])	2.40 m
liquid level of reaction mixture	0.54 m
area wetted by reaction mixture	8.61 m ²
mass of reaction mixture	2.45 t
heat capacity of reactant	1800.00 J/kg °C
estimated heat loss at 150 °C with surrounding temp.=35°C	3.19 W/kg °C
Heat transfer coefficient to outside	7.90 W/m ² °C
Half-life time	26.00 hours

Table 4: cooling behaviour of a 10 m³-reactor

The results in table 4 are based on the measurements from site 2. They are comparable to both those obtained without stirring and to those from site 1, also they compare well to other findings of Rogers [7].

HEAT BALANCE

It can be seen from figure 4 that below ca. 155 °C cooling prevails, whereas over 155 °C the reaction mass will undergo a

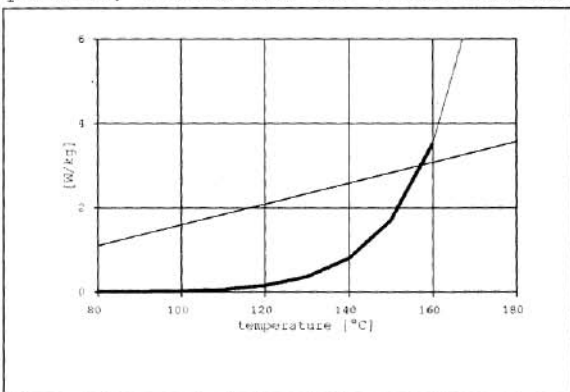


Figure 4: Summary of the heat balance of the system, based on the decomposition heat release rate measured by isothermal DSC (curved, solid line) and the heat dissipation rate (thin line) by natural cooling as measured in site 2. Data are given per unit mass and as as function of the temperature.

runaway reaction. As long as therefore the temperature of the system is below 155 °C, there is no risk of runaway in the case of an emergency. The cooling experiments were made with pure DMSO. In this case stirring is not necessary, as the movement of the liquid

created by convection is sufficient to give a high heat transfer coefficient.

In the case of forced convection, i.e. for a stirred solution, similar results would be expected. Unlike pure DMSO, the reaction mass No. 6 is highly viscous. Without stirring, the mechanism of heat transfer will therefore be limited to heat conduction and cooling will be much slower. Under these circumstances, the vessel can be considered as adiabatic.

RISK ASSESSMENT

The risk of a runaway of the reaction mass is considerable: An adiabatic runaway will theoretically raise the temperature of the reacting mass to more than 400 °C. The **severity** of an incident is therefore high. The most critical stage in case of a power failure occurs after 14 hours. If at this moment stirring and heat release by distillation will come to a standstill, the temperature of the reacting mass will equilibrate at ca. 160 °C. The vessel will behave adiabatically and a runaway will occur within a few hours as shown in table 2. As the TMR_{ad} is quite short, the runaway can hardly be stopped, and therefore its **probability** is high.

Measures must therefore be taken to prevent a runaway.

MEASURES

In an intrinsically safe process heat accumulation conditions are avoided altogether. In our example heat accumulation and a possible runaway are prevented by defining time and temperature limits. In addition emergency measures to stop an ongoing runaway can be taken. The nature of these is defined by the available time, therefore by the probability of the incident.

The following measures were recommended to production:

The heat release rate of the decomposition should be controlled

- by limiting the normal operating temperature to below 150 °C,
- by limiting the wall temperature T_a to 170 °C,
- by limiting the time, during which the reaction will be held at temperatures higher than 130 °C to 12 hours maximum. This measure takes into account the self accelerating nature of the decomposition .

Also good and constant heat dissipation conditions should be maintained

- by guaranteeing stirring under any circumstances, even in the case of an external power failure. This can be accomplished by using a stand-by generator.
- by maintaining the cooling characteristics of the reactor. Any change in insulation will change these characteristics. If the

cooling characteristics of the reactor are changed, a new heat balance and subsequently a new temperature limit has to be determined.

As an additional emergency measure it was proposed to quench the reaction mass with cold water or DMSO. The quenching should reduce the temperature to 130 °C within 40 minutes, whenever 165 °C are reached.

As a long term measure, the vacuum should be improved, so that the distillation can be accomplished in shorter time.

As the problem is caused by both the instability of DMSO and the high viscosity of the solution, installation of a short path distillation apparatus has been considered, as well as replacing DMSO by another solvent. Both possibilities are currently under study.

9. CONCLUSION

The procedure described above delivers also a safe temperature. However, unlike the empirical procedure, it is based on a physical model taking in account the heat balance, i.e. both heat production of the substance and heat dissipation of the distillation vessel. A successful use of the heat balance requires a close cooperation between the physical chemist of the measuring laboratory and the process engineer. A heat balance, both heat production and heat dissipation are taken into account and can be treated separately.

The **heat production** of decompositions is an exponential function of the temperature. Therefore it must always be determined experimentally by the measuring laboratory.

The **heat dissipation** and heat storage can either be directly measured in the plant, but in many cases it can be estimated by engineering data.

This approach is more flexible than the traditional one: whenever the scale of the vessel or its insulation is changed, it is sufficient to determine the heat loss of the vessel and from this and the heat balance a new safe temperature can be determined.

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