

CHEMICAL REACTION HAZARDS OF DISTILLATION PROCESSES

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Distillations are used for many reasons, including purification, solvent recovery, concentration and even reaction. There are a number of factors that should be considered when assessing the chemical reaction hazards associated with distillations. These include:

- thermal stability
- gas evolution
- peroxidation
- sublimation
- materials compatibility
- thermal history
- air ingress
- pyrophoricity
- control

This paper discusses the potential hazards associated with distillation processes on lab, pilot plant and production scale, by asking and answering pertinent questions, illustrated by using examples from the authors' experience.

INTRODUCTION

Consideration of reactive hazards normally focuses on loss of control of an exothermic reaction, or the decomposition of the reaction mass. The "runaway" scenario is usually the main consideration for the synthesis reaction stage; however this can occur in many other process operations, where undesired or unexpected exothermic reactions can result in severe incidents.

Distillation is one area which can give rise to both reactive and decomposition hazards in the one process operation and is the focus of this paper. The paper considers the potential hazards issues of distillation processes by asking and answering relevant questions to highlight the major concerns and stimulate thought. The questions posed include those frequently asked by hazards assessors when considering distillation process safety and also by those involved with distillation operations when requesting safety advice. In answering the questions, process details such as the following are considered:

- heating medium
- distillate temperature and composition
- scale of operation
- still design
- process conditions
- chemistry
- multiple distillations
- materials of construction
- maloperations

FREQUENTLY ASKED QUESTIONS (FAQS)

Is distillation the most appropriate technique?

Before embarking on a major assessment of potential distillation hazards, it is always important to ask

if distillation is the most appropriate technique for your process – could another method be better suited (e.g. crystallisation)?

What samples should be tested?

Initially, thermal stability screening should be carried out on relevant samples. Quite often the starting point will be the distillation residue as the residue is exposed to a higher temperature for a longer time than the feed or distillate and can contain more impurities (but bear in mind that the residue may be the product). However, consideration should also be given to the thermal stability of the feed and distillate.

Are there any special considerations for sample preparation?

Samples should be representative of the actual process. Initially, lab samples may need to be prepared, but plant samples should be tested as soon as they become available.

Distillation residues should be prepared at low temperature/high vacuum to ensure no thermal history prior to testing and to minimise decomposition during preparation so that the full potential heat output is realised and measured during the tests. Any re-cycles in the plant process should be simulated in the lab to determine the effect on residue stability.

Thermal history (heat aging) should also be simulated to see if this affects the stability – especially in the case of autocatalysis.

The effect of air ingress can be simulated by partial oxidation of the residues.

What are the key tests that should be carried out?

Some form of scanning calorimetry will normally be used to perform screening tests which will look at onset temperatures, heats of decomposition and potential gas

evolution (pressure data). A conservative estimation of TMR can also be made from e.g. dynamic DSC data. These tests should also give an indication of any autocatalytic character.

All tests should be performed with appropriate construction materials. Glass lined vessels are susceptible to damage so the consequences of this damage should also be examined by adding the appropriate material.

Compatibility of heat transfer fluid, coolants and lubricants with the batch should also be considered – for any reaction or effect on thermal stability – in case of leaks into the process from the heating coil/jacket, condensers, oil seal pumps etc.

When evaluating the screening test results, if the decomposition is not autocatalytic, the predicted onset temperature for full scale operation has an appropriate safety margin above the process temperature and/or TMRad at the process temperature is $\gg 24$ hrs then it should be possible to specify a basis of safe operation from the screening test data.

In terms of onset temperature approach, judgement is made based on the sensitivity of the test carried out and the scale of operation. Both the normal process temperature and the heating medium temperature should be considered, as the batch temperature may tend towards the heating medium temperature in case of maloperation (e.g. loss of agitation/vacuum). This is especially important in continuous distillations where the process is often operated at a temperature where some decomposition is occurring.

What further testing may be necessary

If the screening tests indicate a potential reaction hazard at or near to the process temperature then more sensitive testing will be required. This will normally involve some form of adiabatic testing. The technique and method employed will depend on the proposed distillation conditions, in particular the process operating pressure.

In the case of gassing systems, an accurate gas evolution rate should be determined. In terms of the maximum gas rate, an appropriate safety factor is often used when recommending a vent/scrubber capacity (e.g. 1.5–2 x the measured value).

A large proportion of decompositions have some autocatalytic character. For autocatalytic decompositions, high rate/high energy decompositions would cause the greatest concern. The onset temperature or TMR approaches are not usually sufficient in these cases – induction time and time/temperature relationship should be determined.

It is also important in cases of autocatalysis to try to determine the nature of the catalyst (e.g. acidic species produced in DMSO decomposition (Ciba Geigy et al, 1978–79). It may be possible to add a catalyst scavenger (e.g. carbonate for acidic species) which could increase induction time.

Are there any particularly “problematic” materials with respect to distillation?

Certain materials are particularly hazardous in terms of thermal stability e.g. nitrochloro compounds, peroxides (HSE, 1999; McCloskey, 1989), peroxyacids (Manly,

1982). Ethers may form peroxides (Jackson et al, 1970; Steere, 1964) during distillation. Some materials such as tetrahydrofuran (BASF, 1970) may undergo auto-oxidation.

Stabilisers are often added to prevent peroxidation, but the fate of the stabiliser during distillation should be determined (i.e. does it go with the distillate or stay with the residues?). Additional stabiliser may need to be added if it is lost e.g. in THF recovery, the stabiliser stays with the residue (typical of peroxidisable solvents). In this case, stabiliser should be charged to the distillate receiver and the solvent distilled into it.

It is important to know what effect the stabilizer has e.g. does it affect thermal stability or prevent oxidation? Does the stabilizer need oxygen to work? e.g. some monomer stabilizers need oxygen but this can affect the basis of safety in terms of flammability.

Before distilling materials that have been in contact with peroxides or peroxidisable/auto-oxidisable materials it should be checked that the batch is peroxide-free and that the distillation is carried out under a strictly inert atmosphere.

Residues of nitro-compounds can be very unstable (particularly with some materials of construction) and especially if subjected to thermal history (i.e. repeated heating/cooling) e.g. distilling several batches without removing the residues, as in the 1992 Hickson & Welch incident (HSE 1994) (see Fig. 1).

If sublimation can occur then vents/pumps etc. can become blocked and loss of vacuum and/or pressurisation can result. Amine hydrochlorides, urea, acetamide and ammonium carbamate often sublime.



Figure 1. Photo of 60 Still Base from the Hickson & Welch Incident, 1992

Often, materials can be liquid when impure but then can solidify as the solvent is distilled off (e.g. tertiary butanol and DMSO), which can also lead to blockages.

Should there be a different approach for batch and continuous distillation processes

The approach to batch/continuous processing is usually the same at first. Batch processing is usually preferred on economic grounds and this is the starting point for testing. If decomposition occurs at the process temperature, the consideration will be whether the loss is acceptable and/or whether the loss constitutes a hazard. Continuous processing may then be the preferred option as the distillation can be run at temperatures where decomposition occurs – the rate of decomposition is balanced against residence time.

The main difference between batch and continuous processes is the variation of temperature/pressure over time. In terms of thermal effects, for batch distillations determination of the decomposition onset temperature or time to maximum rate (TMR) of the decomposition can usually be used to specify safe operating conditions. For continuous operations it may be more appropriate to use TMR, as the important parameter in terms of thermal stability will be residence time, notwithstanding any gas evolution issues. In terms of gas evolution, the rate of gas (e.g. l/min/kg) may be a significant problem for batch processes (e.g. 20 te), but may be less of a problem for the low inventories used in continuous processing (e.g. 20 kg). However, low gas rates may still be enough to overcome the vacuum.

Loss of vacuum or vent blockages are important considerations for both batch and continuous operations, but for continuous distillations loss of vacuum or blockages can also effectively result in a batch situation, with the effect of build up of material, raised temperatures/pressures and increased residence time. Process controls should limit the maximum build up of feed to minimise the impact.

What specific hazards arise from the distillation process, equipment problems or design?

It is important to know the normal still heating medium temperature and the maximum temperature that it can reach as this is normally the maximum temperature that the distillate and residues can be exposed to. Typical values of maximum heating medium temperatures are:

Water/condensate:	100° C
Low pressure (LP) steam:	135° C
Intermediate pressure (IP) steam:	160° C
High pressure (HP) steam:	180° C
Oil:	300° C

When carrying out batch distillations, it is usually ensured that the residue volume is sufficient to cover the agitator and thermocouple. Incidents have happened when the residue temperature was not measured and so overheating occurred. Problems can arise prior to maintenance when distillations are carried out on reduced batch sizes to use up residual stock. However, safety can be based on maintaining heating medium temperature below the decomposition temperature of the batch.

In an agitated process, if the residue can solidify on cooling then care should be taken to switch off agitation before solidification occurs to avoid breaking the agitator. Agitation may be critical to the process for heat transfer.

Repeated heating of residues (i.e. failure to remove residues regularly) can lead to thermal instability due to thermal history (HSE 1994).

If vacuum is lost during distillation, the temperature of the batch/feed can increase to the heating medium temperature. Loss of the vacuum could be due to blockage in the line – this can in turn lead to a sealed system with increasing pressure. A failing vacuum pump can have the same effect because the pump is usually sealed.

When using a distillation column, the column design should allow for effective separation without it being liable to flooding. An undersized column will be liable to flooding, which may result in high pressures and therefore higher temperature in the still. Flooding will also affect separation and can result in delayed problems (e.g. water/solvent separation in reactive distillations).

Compatibility of materials of construction is particularly important as there is an increased surface area in column packing. Thermal stability screening can be carried out on materials doped with relevant materials of construction.

Corrosion products from the column/packing may catalyse decompositions or reactions on the column (e.g. fires have been known in packing due to reaction with e.g. NO_x gases; anhydrous ammonia recovery distillations can be susceptible to corrosion due to acidic ammonium carbamate sublimation and solidification in the column).

Maloperations upstream of the distillation, such as an overcharge of one of the components, or an incomplete reaction, may affect the feed composition and consequently the thermal stability of the batch.

Are there any specific fire and explosion considerations for distillations?

Fire and explosion hazards should always be considered alongside chemical reaction hazards when assessing safety of distillation processes. Some specific distillation issues include the generation of distillate with an auto-ignition temperature below its boiling temperature or even below the heating medium temperature. In such cases an alternative solvent would be preferable but vacuum distillation is an option. Operating under inert atmosphere may be possible but not for all vapours as some are too sensitive (e.g. acetylenic compounds (Forshey et al, 1969), phosphines (Taylor, 1976)).

If an azeotropic mixture is to be distilled then inerting may be necessary if any of the fractions are flammable.

Air ingress can cause flammability issues – leaking may let in oxygen to the process, giving a flammable atmosphere or possible reaction. Normally, vacuum is let down at the end of distillation using inert gas (e.g. nitrogen) to avoid generation of a flammable atmosphere. Residues may also be pyrophoric.

A leak of high temperature heat transfer medium to the atmosphere can result in a flammability hazard. Often the material is above its flash point in the condenser.

What is the most appropriate basis of safety?

Prevention is better than cure; therefore use of inherently safer operations should be the first consideration (e.g. heating medium temperature below the decomposition temperature, continuous distillation to reduce inventory, vacuum distillation to reduce batch temperature).

Process control measures should be the next consideration (e.g. limiting time/temperature/pressure of the process).

For most distillation processes, decomposition of the residues is the major concern. These can be very rapid, with high energy output and significant gas evolved. If inherent safety and/or process control measures are not of sufficient integrity, then protective measures will be required. Quench, drown-out and relief venting are some of the usual options. For rapid, high energy, gaseous decompositions, relief venting is not the obvious choice in the case of batch distillations as the required vent size will often be unfeasibly large. Batch-to-batch variations in residues samples also makes accurate vent sizing difficult. However, relief venting may often be successfully employed for continuous processes. Problems arising from rapid decompositions and residue variability become less significant due to the low inventory of materials.

Care needs to be taken to maintain adequate batch size to cover temperature probes to ensure no loss of control.

SUMMARY

There is no "generic" method for determining the hazards of all types of distillation processes due to the wide range

of possible uses, such as purification, solvent recovery, concentration and even reaction. The assessment process will depend on all the factors discussed in the above list of questions/answers, but this list is not exhaustive. . .

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