BCl_3-amine adduct preparation and purification: a Process Hazard Study

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The industrial preparation of a Lewis acid-amine adduct has been analyzed within the frame of a PHR (Process Hazard Review). Process deviations have been experimentally explored, allowing to define safe operation conditions and to dimension adequate safety trips.

The analysis focused at first on the synthesis step, carried out by dosing of gaseous BCl_3 on the liquid amine. The reaction, highly exothermic and irreversible in the process conditions, is completely dosing-controlled. A control loop based on the measure of the internal temperature of the reaction medium acts on the regulation valve of the gas inlet, limiting the BCl_3 entry flow.
DSC analysis showed that the product has no significant decomposition potential, actually presenting an endothermic behavior at high temperature, when analyzed at constant volume (in a DSC high pressure crucible). On the other hand, autoclave measurement shows that the reaction, highly endoenthropic, reaches equilibrium with temperature increase. The experimental T-P data were the fitted with the Van t'Hoff law, in order to describe the scenario in case of failure of the dosing loop, with a consequent increase of temperature and pressure. In turn, this allowed sizing the pressure relief device and the determination of the nominal relief pressure.

The process includes a wash step which, after decantation, causes the separation of a water-rich intermediate layer that has to be treated by water distillation to be recovered.
This treatment is delicate, since the hydrolysis of BCl_3 leads to a degradation of the product and, potentially, to the release of heat and gaseous HCl.
The first deviation studied was the loss of heat exchange during distillation. Through AKTS[1] modeling of the DSC measured on the intermediate product, it has been determined that the decomposition potential was not negligible, but with TMR_{ad} at the process temperature longer than 24 h; this situation corresponds to a low risk scenario.
The second deviation study concerned the possibility of loss of vacuum, with simultaneous failure of the safety trip monitoring the product temperature. Due to constant temperature of the jacket this deviation corresponds to isoperibolic conditions. The maximum reaction power at different temperatures, obtained by AKTS modeling, was coupled with an estimation of the heat exchange coefficient to constitute a Semenov diagram. This analysis established a upper limit for the jacket temperature, under which the heat release is allowed despite the loss of vacuum.
In both cases, a linear correspondence was assumed between the gas and heat release peaks measured in the autoclave[2], in order to generate data for pressure relief sizing.

[1] AKTS AG, http://www.akts.com (AKTS - Thermokinetics software and AKTS – Thermal Safety software).
[2] F. Stoessel, (2008). *Thermal Safety of chemical Processes, 10.6 – Design of technical measures*. Weinheim: Wiley-VCH

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Introduction and goals

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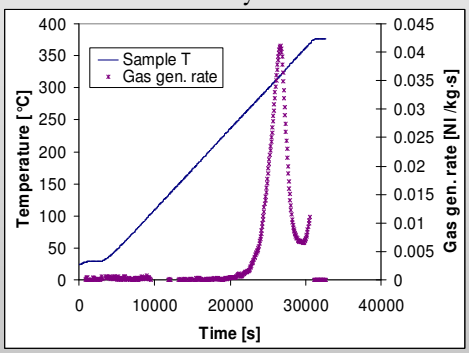
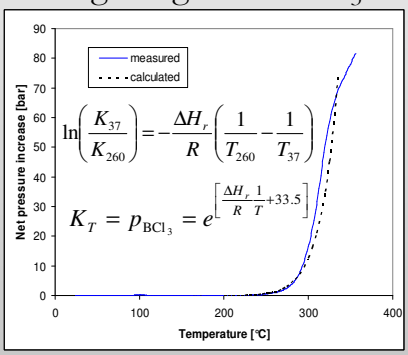
Preparation

Desired reaction: $NR_{3(l)} + BCl_{3(g)} \longrightarrow R_3N\text{-}BCl_{3(l)} + \Delta H$

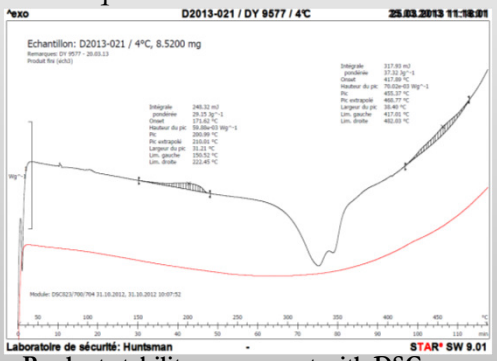
The exothermicity is controlled by dosing the gaseous BCl_3 onto the liquid amine substrate.



Gas release at constant volume (autoclave)



Fitting data with Van t'Hoff equation



Product stability assessment with DSC scan

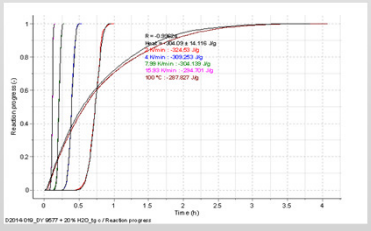
The decomposition potential of the product is low. A failure of the control loop for BCl_3 dosing would lead to T and P increase. The dimensioning of the P relief system was based on this study.

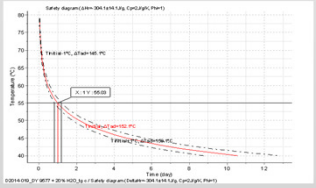
Drying of intermediate layers from wash step

After washing the product with water and separating by decantation, a certain amount of intermediate layers (up to 20% water content) have to be dried through water distillation

Unwanted hydrolysis reaction: $R_3N - BCl_3 \xrightarrow{H_2O} NR_3 + B(OH)_3 + HCl$

Loss of cooling (power failure) / Adiabatic





TMR evaluation

AKTS® modelling of hydrolysis reaction[1]

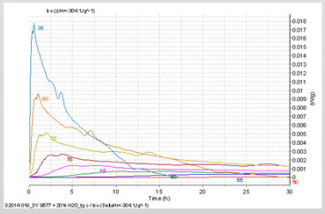
Evaluation of process risk

	TMR_{ad}< 8h	8h<TMR_{ad}< 24 h	TMR_{ad}>24 h
ΔT_{ad}>200° C	high	intermediate	low
50° C<ΔT_{ad}<200° C	intermediate	intermediate	[LOW]
ΔT_{ad}<50° C	low	low	low

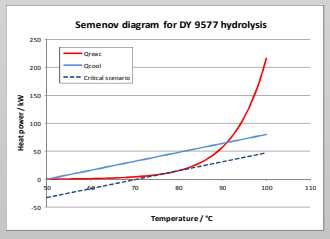
The loss of heat exchange is not critical due to long TMR_{ad} at the process temperature.

Gas release rate has been estimated correlating the peak heat release to max gas release rate[2]

Loss of vacuum (pump failure)/Isoperibolic



Maximum heat release vs. T from AKTS ® model[1]



Semenov diagram for determination of critical jacket T

Semenov analysis coupled with AKTS results allowed determining the critical T_{jacket}

[1] AKTS AG, http://www.akts.com (AKTS - Thermokinetics software and AKTS – Thermal Safety software).

[2] F. Stoessel, (2008). *Thermal Safety of chemical Processes, 10.6 – Design of technical measures.* Weinheim: Wiley-VCH.