Concentration and Mixing Effects on the Production of Amine Hydrochloride Salts in a Confined Impinging Jet Reactor

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Chemical precipitation from reactive solutions requires reactants to be mixed at smallest length scales to form fine particles. A Confined Impinging Jet Reactor (CIJR) was used to produce amine hydrochloride (AHC) salts which are by-products of a desired reaction sequence in manufacture of polyurethanes. This work investigates the effect of mixing intensity (flowrate) and local concentration (reactant concentration) on the formation of AHC salts. Results show that different AHC salts can be formed under different process conditions.

Introduction

Introduction to A Problem in Polyurethane Synthesis

Polyurethanes (PU) are ubiquitous in our everyday lives, where the total size of PU industrial activity was 8.4 million tons in 2008 and is expected to grow to 9.6 million tons by 2015.

In the phosgene step of PU synthesis, MDA (4,4'-Methyleneedianiline) reacts with phosgene to form MDI (Methyleneedianilinophosphorylchloride), but an undesired side reaction results in precipitation of highly insoluble and sticky AHC salts which are subject of study in this work. This side reaction causes loss of starting material and very expensive reprocessing.

Chemistry of the Process

AHC salts form as precipitated particles with following simplified reactions:

\[ CO + Cl_2 \rightarrow COCl_2 \]

Undesired Side Reactions: Phosgene

\[ R^-\cdot NH_2 + COCl \rightarrow R^-\cdot NHCOCl + HCl \]

MDA: Methyleneedianiline

\[ R^-\cdot NH^-\cdot COCl + HCl \rightarrow R^-\cdot NH\cdot CO\cdot N^+\cdot Cl^- \]

MDA: Methyleneedianilinophosphorylchloride

Where: \( R \) = 1 of MDA group; \( x \) between 0.5 and 1

Why is mixing important in Reactive Precipitation systems?

- Nucleation and aggregation rates are controlled by mixing and local concentration.
- Particle growth and agglomeration are dominated by supersaturation-generation and collisions.
- Particle morphology is controlled by mixing. Uniform mixing results in uniform particles.

Experimental

Why was the CIJR selected?

CIJR provides:
- Uniform mixing (initiates homogeneous nucleation)
- Fast mixing and small residence
- Continuous operation

In rapid reactions where uniform concentration and mixing intensity are important, the CIJR has advantages over the stirred tank, because stirred tanks have wide variation in dissipation across the mixing volume. Impinging jets can be used when the reaction time of the desired reaction is smaller than the reactor’s residence time, especially for crystallization and precipitations.

Highlights:
- Monochlorobenzene (MCB) used as the environment of photogeneration reaction.
- The MDA/MCB blend is mixed with dissolved anhydrous HCl(g) in MCB.
- System pressure is set at 4 bar to keep HCl dissolved in MCB.
- A vent is used to disperse HCl gas and dissolve it in MCB

CIJR design

Volume of CIJR: approx. 0.12 ml

Residence time range: 25-75 ms

Parameter

Value for flowrate of 300 ml/min

| Parameter                          | Value
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<tr>
<td>Energy Dissipation Rate (W/kg)</td>
<td>3.17</td>
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<tr>
<td>Maximum Velocity (m/s)</td>
<td>7.72</td>
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Process variables

- Blend Strength of MDA/MCB: MDA composition from 0.5 to 5 wt.
- HCl excess: 0-700%
- Flowrate: 100-300 ml/min

Which Analytical Techniques were considered and which ones were selected?

- FTIR
- SEM
- TEM
- EDX
- XRD

Results

Part 1. Characterising High Concentration compounds

Results show that filtered compound has a composition of MDA, MDA-HCl and MDA-2HCl, where more HCl availability to react with amines, results in a higher degree of chlorination. Five of the purest samples were characterized and used as a reference for the FTIR, DSC and CHN/Si Elemental Analyses.

Part 2. Studying Effects of Reaction Variables

2.1. Effect of Varying MDA Concentration on AHC salts

2.2. Effect of Varying Flowrate on AHC salts

Conclusions

- AHC structure depends on MDA concentration more than any other parameter.
- Increase in HCl excess and flowrate results in particles that are more even in shape and size.
- Higher HCl excess advances reaction to produce higher concentration AHC where unreacted MDA cannot be found in salts made with high HCl excess amounts.
- Faster mixing, i.e. higher flowrates, reduces the purity of AHC salts perhaps because of lower residence time in CIJR.
- Very high mixing intensity results in a lower conversion of MDA in the CIJR.

References and Acknowledgements

1. Ershad, N.F., Jones, R., Eaglesham, A., Kresta, S.M., “Chemical precipitation from reactive solutions requires reactants to be mixed at smallest length scales to form fine particles. A Confined Impinging Jet Reactor (CIJR) was used to produce amine hydrochloride (AHC) salts which are by-products of a desired reaction sequence in manufacture of polyurethanes. This work investigates the effect of mixing intensity (flowrate) and local concentration (reactant concentration) on the formation of AHC salts. Results show that different AHC salts can be formed under different process conditions.”

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