3. CONVENTIONAL DSM STAMICARBON GAS-PHASE MELAMINE PRODUCTION PROCESS

3.1. Chemistry involved

In general, the formation of melamine from urea, via a catalytic process, is described by the following two consecutive reaction steps:

\[
\begin{align*}
6 \text{ urea} & \Rightarrow 6 \text{ isocyanic acid} + 6 \text{ ammonia} \quad (3) \\
6 \text{ isocyanic acid} & \Rightarrow \text{melamine} + 3 \text{ carbon dioxide} \quad (4)
\end{align*}
\]

which are combined to the following overall reaction:

\[
6 \text{ urea} \quad \Rightarrow \quad \text{melamine} + 6 \text{ ammonia} + 3 \text{ carbon dioxide} \quad (5)
\]

The reaction temperature and pressure for the formation of melamine are approx. 400 °C and 7 - 10 bar, respectively. The reaction is catalyzed by a solid silica and alumina containing catalyst. The first step, the decomposition of urea, is a highly endothermic reaction and the second step, the cyclization to melamine, is an exothermic one. The overall reaction itself is rather endothermic and requires approximately 5 GJ per metric ton of produced melamine.

In Table 1 some general information of melamine process is given.

<table>
<thead>
<tr>
<th>CAS No.:</th>
<th>108-78-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical name:</td>
<td>2,4,6-triamino-1,3,5-triazine</td>
</tr>
<tr>
<td>Chemical formula:</td>
<td>(\text{C}_3\text{N}_6\text{H}_6)</td>
</tr>
</tbody>
</table>

![Molecular structure of melamine](image)

Table 1. Melamine

Besides, the desired main reaction, several side-reactions occur, both in the reaction section during the synthesis of melamine and in the associated melamine recovery section. One important group of side-products is made by condensation of partial de-aminated melamine:

\[
\begin{align*}
2 \text{ melamine} & \Leftrightarrow \text{melem} + 2 \text{ ammonia} \quad (6) \\
2 \text{ melamine} & \Leftrightarrow \text{melam} + 1 \text{ ammonia} \quad (7) \\
6 \text{ melamine} & \Leftrightarrow \text{melone} + 8 \text{ ammonia} \quad (8)
\end{align*}
\]

In fact are these three de-amination reactions reversible, which means that the formation of these side-reactions can be suppressed by applying process conditions consisting of high ammonia pressures and temperatures. The structures of the dimers melem and melam and an example of a structure of melone, which is in fact a mixture of several components, are shown below in Figure 2.
Figure 2. Structures of dimers melem and melam and an example of a structure of melone.

Another important group of side-products is formed by partial or complete hydrolysis of the three amino groups of melamine:

\[
\text{melema} + 1 \text{ water} \rightarrow \text{ammeline} + 1 \text{ ammonia} \quad (9)
\]

\[
\text{melema} + 2 \text{ water} \rightarrow \text{ammelide} + 2 \text{ ammonia} \quad (10)
\]

\[
\text{melema} + 3 \text{ water} \rightarrow \text{cyanuric acid} + 3 \text{ ammonia} \quad (11)
\]

Figure 3. Structures of the side-products ammeline, ammelide and cyanuric acid.

3.2. Conventional Process description

A simple block diagram of a conventional DSM Stamicarbon gas-phase melamine process is shown in figure 4.

Figure 4. Block diagram of a conventional gas-phase melamine process. The bold lines show the heat flows; the thin lines show the process flows.
Molten urea from the urea plant is catalytically converted into melamine in the reactor at high temperature and medium pressure in the presence of additional ammonia gas. The reaction temperature and pressure are 360 – 440 °C and 7-10 bar, respectively. The reaction takes place in a fluidized catalytic bed reactor with only ammonia as fluidizing gas. The required heat, because the overall reaction is strongly endothermic, is supplied to the reactor by Heat Transfer Salt (HTS). About 2 tons of ‘byproduct’ gases (ammonia and carbon dioxide) are formed per ton of melamine according to the overall reaction, which is described as reaction (5).

The melamine is obtained as a vapor and is cooled with an aqueous medium in the quench vessel to obtain a melamine solution or slurry and a remaining gas containing NH₃, CO₂, and H₂O. The next steps are desorption of the dissolved carbamate out of the melamine slurry/solution and the down-stream processing of melamine. Down-stream processing comprises of dissolving of the melamine slurry, recrystallization, and finally drying of the melamine crystals. These steps require steam as energy input. The byproduct, gas out of the quench section, is partly condensed producing a lean carbamate solution and a water free ammonia gas (ammonia recovery section). The ammonia gas is recycled to the reactor. To be able to recycle the carbamate to the urea plant, water is removed from the lean carbamate solution is concentrated by evaporation followed by condensation using high-pressure steam for the evaporation. After concentration the carbamate solution still contains 20-24 wt% of water.

Water has a negative impact on the conversion in the urea reactor, since the urea formation is an equilibrium reaction. In addition water decreases the stripping efficiency in the urea process. Due to the presence of water in the process streams after the quench, the required steam consumption for the recovery of the melamine and the carbamate is high. The overall steam consumption of the melamine process ranges from 6 to 8 ton per ton melamine. In Table 2 more information on the utility consumption of a conventional gas-phase melamine process in given.

<table>
<thead>
<tr>
<th>Utilities (per metric ton of melamine):</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural gas:</td>
</tr>
<tr>
<td>Steam:</td>
</tr>
<tr>
<td>Electricity:</td>
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<tr>
<td>Cooling water:</td>
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<tr>
<td></td>
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<tr>
<td>8 – 13 GJ (reactor)</td>
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<tr>
<td>6 – 8 ton</td>
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<tr>
<td>0.4 – 0.6 MWh</td>
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<tr>
<td>700 ton</td>
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</tbody>
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Table 2. Utilities consumption of conventional Melamine process