Energy-efficient production process

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Abstract: - Process production of the different products should be more economical. The fact is we target that more products are being produced more energy-efficient. Hexamethylenetetramine or hexamine is a white chemical compound known for over 100 years, which is formed as a product of the reaction between formaldehyde and ammonia. Hexamine use is widespread but it is only universally used in small quantities. Most of it is used for the production of explosives, and various resins. Hexamine is produced as a powder or a 42 % solution. Our aim is to simulate a more efficient continuous 42 % hexamine solution production process in order to operate with minimal cost, and to use exothermic heat flow rate and waste materials.

Key-Words: - hexamine, energy-efficient process, waste material, aqueous solution, utilities

1 Introduction

Energy-efficient processes are very important in the real chemical industry, because it can reduce energy losses and costs, and can improve the operation of energy and process systems.

Hexamine or hexamethylenetetramine is used in pharmaceutical industries as a primary feed material, and in chemical industries as an intermediate material. It is highly soluble in water and, as with some other tertiary amines, has an inverse solubility at low temperatures [1].

The Meissner process is an optimum method for producing hexamine from formaldehyde and gaseous ammonia in which the reaction and crystallization stages take place simultaneously in order to produce crystalline hexamine. The crystallization stage controls the Meissner process due to a high dissolution rate of ammonia and formaldehyde in the aqueous solution and a high reaction rate during hexamine production [2].

The values for those kinetic parameters regarding hexamine crystallization from aqueous solution that are necessary for controlling industrial crystallizers, have been calculated by Alamdari and Tabkhi [3].

2 Hexamine production

Hexamethylenetetramine or hexamine is a heterocyclic organic compound with the formula (CH₂)₆N₄. It was first prepared in 1859 by Butlerov of Russia [4, 6]. This white crystalline compound is highly soluble in water and polar organic solvents. It is useful in the synthesis of other chemical compounds, e.g. plastics, pharmaceuticals, rubber additives. It sublimes in a vacuum at 280 °C.

Hexamine is produced from ammonia and formaldehyde:

\[ 4 \text{NH}_3 + 6 \text{CH}_2\text{O} = (\text{CH}_2)_6\text{N}_4 + 6 \text{H}_2\text{O} \]
\[ \Delta H_r = -230 \text{ kJ / mol} \] (R1)

The are mainly two methods of obtaining hexamine in the world. In the first ammonia and formaldehyde are added into the reactor as an aqueous solution, and the second is the use of anhydrous ammonia, if we want to reduce the amount of water entering the reactor.

If you add ammonia to a gaseous reactant within a plural relationship of formaldehyde and ammonia between 3:2 and 3:3 when allowing the reactor to be an aqueous solution of formaldehyde, the composition is between \( w = 30-50 \% \) formaldehyde. This reaction is exothermic, so the temperature in the reactor is between 50 and 90 °C [7] or 102 °C [5]. The ammonia-formaldehyde reaction is highly exothermic. Conversion in the reactor is 97 % [7]. Passes expire at a pH of between 7 and 8. The reaction mixture is collected in a vacuum evaporator. Within it, the solution is concentrated until most of the water evaporates, therefore the hexamine is crystallized better. If solid hexamine is
required, concentrated aqueous solution is pumped into a crystallizer. The wet crystals are then separated by centrifugation or filtration. After centrifugation or filtration, those crystals are washed with water to produce pure hexamine. The crystals and then collected in a spray dryer, as the crystals contain less than 1 % water. After drying, the final product is ready for sale [6].

This paper presents a more efficient production producing continuous 42 % hexamine solution.

2.1 Continuous 42 % hexamine solution production

Hexamine is produced as a granular and free-flowing powder, as well as an approx. 42 % solution. Solution is cheaper because is not needed crystallizer.

Continuous hexamine water solution production is simulated using an Aspen Plus simulator [8]. Firstly, the outlet temperature of the reactor is simulated at 80 °C (chapter 2.1.1), and then for a second time at 102 °C (chapter 2.1.2). Continuous hexamine production is produced under a constant pressure of 1 bar. Both simulations are compared.

The purpose of this study was to simulate the production of hexamine solution using an Aspen Plus simulator [8]. This simulator is very common for any engineer assisting in the planning process. The Aspen Plus simulator calculates the mass flows and energy balances during hexamine production, and analyzes the process at different temperatures by using an ideal thermodynamic model that includes Raoult's and Henry equations of state.

Aspen Plus is used for the simulation of arbitrary processes, which are comprised of a processing unit associated with continuous mass and energy flows. As a proven software package, it has a wide range of applications for simulating processes within the chemical and petrochemical industries, petroleum refining, the production of fuels and fuel products, industrial metals and minerals, the paper and food industries, pharmaceuticals and biotechnology, etc. The programs in the software package are written in Fortran, so it is also useful for advanced users who want Aspen Plus to complement their knowledge [8].

2.1.1 Reactor outlet temperature of 80 °C

The reactor releases 321 kW of heat flow rate (Table 1; Fig. 1). The evaporator was assumed to have a temperature of 101 °C, and needed 163 kW of heat flow rate. A temperature of 101 °C is best for the evaporator, when producing hexamine, which contains 42 % aqueous solution. A temperature of 100 °C gives 35.0 % aqueous hexamine solution, but at 102 °C, this is 50.3 %. Table 1 shows the mass flows of the entire process and the composition of the flow simulations at an evaporator temperature of 101 °C. The final product (stream 4; 711.1 kg/h), when cooled with water, releases 47 kW of heat flow rate in the cooler.

![Flowchart of process](image)

**Fig. 1: Basic simulation process of 42 % hexamine solution production.**

<table>
<thead>
<tr>
<th>q_m (kg/h)</th>
<th>AM</th>
<th>MO</th>
<th>FOR</th>
<th>MA</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>formaldehyde</td>
<td>0.0</td>
<td>400.0</td>
<td>10.6</td>
<td>10.0</td>
<td>0.5</td>
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</tr>
<tr>
<td>water</td>
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<td>400.0</td>
<td>633.6</td>
<td>224.7</td>
<td>408.9</td>
<td>408.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ammonia</td>
<td>151.0</td>
<td>0.0</td>
<td>3.8</td>
<td>3.6</td>
<td>0.1</td>
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</tr>
<tr>
<td>hexamine</td>
<td>0.0</td>
<td>0.0</td>
<td>302.9</td>
<td>0.8</td>
<td>302.2</td>
<td>302.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature, °C</td>
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<td>20</td>
<td>80</td>
<td>101</td>
<td>101</td>
<td>25</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.1.2 Reactor outlet temperature of 102 °C

The reaction takes place at an outlet temperature of 102 °C from the reactor, as in the literature [4]. The reactor releases a 99 kW heat flow rate. A partial condenser was analyzed by running at 101 °C, with an entrained heat flow rate of 57 kW, thus producing a 42 % aqueous hexamine solution (Fig. 2). Table 2 shows the mass flows of the entire process, and the compositions of the flow simulations at a flash temperature of 101 °C. The final product (stream 4; 711.1 kg/h) was cooled in a cooler with a released heat flow rate of 47 kW.
Any available heat may be used for the heating of ionized water: first into the cooler, followed by into the reactor, and then into the flash. The water separated in the flash can be combined with ionized water, because it contains minimal impurities (Fig. 3).

### 3 Conclusion

Hexamine has a wide use in the military, the pharmaceutical industries, and in the production of resins. The economic and operational hexamine solution production was more favourable than the powder production. The most favourable is the process that operates at a maximum temperature of 102 °C, because of the total available heat flow rate, and without the need for heat flow rate. Energy-efficient continuous 42 % hexamine solution production is very simple, and uses only a small number of processing units. The process itself can heat the hot utilities within all process units, separately. No materials are discarded during the process. The water, after separation, could be used as utility or material.

### References:


