Studies on yield improvement of High Melting Explosive (HMX)

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In India, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine, commonly known as HMX (High Melting Explosive), is manufactured by the modified Bachmann combination method using continuous nitrolysis of hexamine in a cascade of four stirred tank reactors. In this laboratory, the technology was established more than three decades ago with an overall yield of about 40%. However, as the reported yield of HMX is around 55%, it was considered essential to systematically study the Bachmann reaction system to improve the yield. As such a detailed study on quantities/ratios of raw materials and process conditions was carried out to improve the yield. Optimized ratios of raw materials, use of nitric acid having strength >99%, proper control of temperature and optimal nitration and residence time gave an yield of 60-65%.

Keywords: Explosive, Bachmann reaction system

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High Melting Explosive (HMX) is one of the most brisant military explosive and is used extensively in shaped charges, plastic bonded explosives and nitramine based propellants. HMX is the higher homologue of RDX. HMX was initially obtained as an impurity during yield improvement studies of RDX by Bachmann. Bachmann prepared RDX using hexamine, nitric acid, ammonium nitrate and acetic anhydride and obtained two moles of RDX from one mole of hexamine instead of one mole of former obtained in other approaches.

\[(CH_2)_6N_4 + 4HNO_3 + 2NH_4NO_3 + 6(CH_3CO)\_2O = 2(CH_2NNO_2)_3 + 12CH_3COOH \quad \cdots (1)\]

It was observed that RDX obtained from the above process was contaminated with HMX, whose melting point was more than that of RDX. The impurity level was about 10%. Later, it was found that HMX has superior qualities as compared to RDX, in terms of density (leading to higher loading), higher velocity of detonation (VOD), higher melting point and better chemical stability towards acids and alkalies. The reaction scheme, which is still not fully understood, is dealt in details by Feuer. Subsequent studies concentrated upon increasing the yield of HMX. The methods thus developed, were termed as modified Bachmann combination methods. In spite of the various advantages, the use of HMX has been limited due to its higher production cost. In India, the cost of acetic acid and anhydride, which are the main raw materials, are much higher compared to those prevailing globally, leading to still higher production costs.

Presence of numerous series and parallel reactions along with trivial knowledge about the mechanism and kinetics makes the modified Bachmann combination reaction system too complicated to be analyzed by a phenomenological model for improving the yield of HMX. Most of the studies resort to the heuristic approach. Even though in various papers, the yields have been claimed as high as 85% using the modified Bachmann route, the industrial scale production of HMX is reported to result in 55-60% yields.

Alternative approaches for synthesizing HMX have been reported. However, due to high corrosivity or toxicity of the raw materials involved or complicacy of the process, none have been realized in industrial scale.

Though a good amount of literature is available indicating effects of various factors on yield qualitatively, information in quantitative terms is limited. The objective of the paper is to provide quantitative data on the effect of various factors on HMX yield.

**Theoretical background of the modified Bachmann reaction system**

The exact route through which the reaction proceeds is not very clear and the available
literature gives broad and often contradictory mechanisms\textsuperscript{10,17-31}. The widely reported probable reaction scheme is presented in Fig. 1. It may be appreciated from the figure that the hexamine molecule cleaves at various locations depending upon the process conditions to result in intermediates required for formation of HMX, RDX or other open chain nitro bodies. For realizing higher yield of HMX, it is necessary to direct the reaction towards maximizing DPT formation and inhibit the formation of RDX as well as other nitro-bodies to as much extent as possible. The production of DPT and subsequently HMX is enhanced by proper control of temperature, proportional addition of the reactants and tuning the other operational parameters. Maximization of yield of desired product is virtually left to trial and error methods. As the reaction involved is nitrolysis (or solvolysis), the strength of nitric acid is one of the important criterion. Acetic acid medium helps to prevent the dissociation of nitric acid into nitrate and protonium ions and instead nitracidium ion ([H$_2$O$\cdot$NO$_2$]$^+$) generation takes place\textsuperscript{10}.  

\[ 4\text{HNO}_3 = 2[\text{H}_2\text{O}\cdot\text{NO}_2]^+ + 2[\text{NO}_3^-] \quad \ldots (2) \]

However, for slow and systematic nitrolysis, the nitracidium ion concentration needs to be controlled, and ammonium nitrate helps in this regard.  

\[ \text{NH}_4\text{NO}_3 = [\text{NH}_4]^+ + [\text{NO}_3^-] \quad \ldots (3) \]

The dissociation of ammonium nitrate leads to suppressing of dissociation of nitric acid to nitracidium and nitrate ion as is evident from equilibrium consideration, thus indirectly dictating the nitracidium ion concentration in reaction medium. Acetic anhydride acts as a media for removal of water and may also be responsible for acetolysis and subsequent nitrolysis.

**Experimental Procedure**

The experimental set-up consisted of a semi-batch jacketed glass reactor provided with a PID based heating and cooling system (Fig. 2). The semi-batch reactor has three inlets for continuous feeding of the reactants at a controlled rate. A four blade pitched turbine was used for agitation. Raw materials used for
these experiments were from commercial sources and the approximate raw material composition envelope for 50 g hexamine batch was - glacial acetic acid –400-500 g, acetic anhydride –330-485 g, ammonium nitrate –70-140 g, nitric acid –90-180 g and paraformaldehyde –0-8.5 g. All the three reactants viz., hexamine-acetic acid solution, ammonium nitrate-nitric acid (AN-NA) solution and acetic anhydride were fed at controlled rates to the reactor, which contained a heel of acetic acid and a little acetic anhydride. The feeds were maintained at a constant temperature throughout the reaction period by constant temperature bath. Feeding was carried out using peristaltic pumps. Catalyst, if required, was added to the heel. During the first addition cycle, all of the hexamine-acetic acid solution, 40% of both AN-NA solution and acetic anhydride were added at a predetermined rate. This step, where the major reaction was towards the formation of DPT along with small amount of precursor of RDX and other cyclic nitro/acetylated bodies, is called nitrolysis stage 1 (N-1). After completion of N-1, the reaction media was allowed to age (A-1) for a certain time to complete the reaction, after which the second nitrolysis (N-2) is carried out, wherein the rest AN-NA solution and acetic anhydride were added in a controlled manner. This was followed by ageing (A-2) for 60 min. The major reaction in N-2 and A-2 was formation of HMX along with minor amounts of RDX and open chain nitro bodies. A temperature of 45±2°C was maintained throughout the N-1, A-1, N-2 and A-2 stages. After the completion of ageing, the acid strength of the reaction mass was brought down to 60% by addition of water and the temperature raised to about 98°C. The reaction mass was allowed
to stay at 98°C for 30 min. This step decomposes off the open chain nitro bodies. The slurry was then filtered to obtain crude HMX, which was then crystallized from acetone to obtain β-HMX. All experiments were carried out at 50 g hexamine level. The process is illustrated in Fig. 3. The reported yields are based on quantity of HMX obtained after crystallization. A rough idea about the yield may also be obtained from the weight and melting point of crude HMX (melting point > 272°C).

**Results and Discussion**

Based on some prior studies, it has been observed that the yield of HMX primarily depends on, (a) nitrolysis and ageing periods (b) quantity of acetic anhydride (c) ratio of nitric acid to ammonium nitrate and concentration of nitric acid (d) reaction temperature and (e) catalyst and its quantity. As the number of variables is quite large, achieving globally optimized parameters is a difficult task. However, a large number of experiments were carried out changing certain critical factors, to obtain suitable conditions for realizing high yield of HMX.

**Effect of addition time**

The yield of HMX can only be increased by increasing the yield of its precursor, viz., DPT. Requisite residence time is an important factor for maximizing the yield of DPT. The HMX yield for various addition times is presented in Fig. 4. It is observed that addition time of 15-30 min gives the best yield. During scale up of this highly exothermic system, a major bottleneck is the provision of adequate heat transfer area and the only way of achieving a safe design is to increase the addition time to as much extent as possible without compromising much on the yield.

**Effect of ageing time**

It is observed that the reaction during N-1 is instantaneous. The hexamine is reported to disappear in the reaction very rapidly. However, the exothermicity of the reaction does not allow to carry out the reaction fast enough, further the rapid overshoot of temperature alters the product profile. Hence, the reaction is carried out in acetic acid medium with continuous addition of reactants instead of batch mode reaction to allow proper control of reaction temperature. Ageing time is provided to complete the reaction. Depending upon the nitration time, first ageing time is kept in between 0 and 30 min. It is seen from Fig. 5 that ageing time up to 30 min is acceptable, without affecting the yield.

**Effect of acetic anhydride**

Effect of variation of acetic anhydride quantity is shown in Fig. 6. 315 mL per 50 g hexamine seems to be the optimum quantity.

**Effect of ammonium nitrate and nitric acid**

The variation in yield of HMX with change in molar ratio of nitric acid (NA) to ammonium nitrate (AN) is shown in Fig. 7. From the plot it is clear that a ratio of 1:1.4-1:1.6 gives higher yield. These experiments were carried out with 80 mL nitric acid/50 g hexamine and varying the quantity of ammonium nitrate. After finalizing this ratio, quantity of nitric acid was varied. The test result is shown in Fig. 8. From the Figs 7 and 8, it can be concluded that 100-110 g of ammonium nitrate in 80 to 100 mL of nitric acid per 50 g hexamine gives the best result.
Concentration of nitric acid plays a vital role in the nitrolysis reaction. All the results quoted in this paper are for nitric acid strength above 98%, unless specified. The ammonium nitrate concentration in nitric acid should be such that the specific gravity of the ammonium nitrate-nitric acid solution is between 1.55 and 1.57. Figure 9 shows the variation of yield with various concentrations of nitric acid. Concentration in excess of 99% gives the best yield. Below 94%, oxidation takes precedence over nitrolysis. For lower strength (upto 96%) higher quantity of nitric acid is to be used, to realize the same yield (Table 1).

Effect of temperature

Table 2 presents the effect of temperature on yield of HMX on optimized composition of raw materials and addition and aging times. The reactions were carried out in Mettler Toledo RC1 reaction calorimeter for accurate temperature control. The general conception of very strict temperature control for higher yield is somewhat misplaced. The temperature control systems may be designed for achieving 45±3°C. The temperature should in no case exceed 50°C, as the rate of decomposition of DPT increases. The activation energy for formation of

**Table 1—Quantity of nitric acid to be used for various strengths (50 g hexamine batch)**

<table>
<thead>
<tr>
<th>Strength of nitric acid (%)</th>
<th>Quantity of nitric acid (mL)</th>
<th>Quantity of ammonium nitrate (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>96.0</td>
<td>100</td>
<td>135.0</td>
</tr>
<tr>
<td>97.5</td>
<td>90</td>
<td>121.5</td>
</tr>
<tr>
<td>98.0</td>
<td>80</td>
<td>108.0</td>
</tr>
</tbody>
</table>

**Table 2—Effect of reaction temperature on yield of HMX**

<table>
<thead>
<tr>
<th>Reaction temperature (°C)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1 43.5</td>
<td>55</td>
</tr>
<tr>
<td>A1 46.5</td>
<td>62</td>
</tr>
<tr>
<td>N2 47.5</td>
<td>61</td>
</tr>
<tr>
<td>A2 52.0</td>
<td>57</td>
</tr>
</tbody>
</table>
RDX and HMX are almost same\(^5\), viz., 15 kcal/mole. Hence, even though the emphasis is on accurate temperature control for minimizing RDX yield during production of HMX, actually it is the molar ratio of various reactants and the contacting pattern of the reactants that really affects the selectivity.

**Effect of catalyst**

Formaldehyde in the form of paraformaldehyde (pF) or trioxane (TO) was evaluated for similar raw material compositions. As has already been stated that pF/TO are not catalysts in a true sense and are consumed during the reaction, they are conventionally referred to as catalysts and the same nomenclature is retained. Formaldehyde helps in increasing the yield in two ways; first it stabilizes DPT by preventing its decomposition to formaldehyde and it seems to form an extra quantity of the nitramine. The yield obtained by using the above-mentioned catalysts is presented in Table 3. Figure 10 shows that 2 g of pF/50 g hexamine gives the best result. It may be appreciated that with the use of catalyst there is only slight improvement in the yield. However, the purity of crude HMX obtained was more than 90% for batches without catalyst. Trioxane has the advantage over paraformaldehyde of being soluble in the acetic acid medium, so that the intermittent solid dosing problem is circumvented.

**Conclusion**

Due to the large number of ingredients used in the manufacture of HMX, a number of side reactions compete with the main reaction. Concentration of nitric acid, reaction temperature, type of catalyst, nitrolysis time and quantities/ratios of various raw materials decide the course of nitrolysis reaction. The various raw material quantities and reaction conditions elaborated in this paper lead to an over all yield of about 60%. Efforts were made to find out the system response with the change in variables and also to fix the envelope of reaction conditions. Higher yields are very difficult to realize as many of the side reactions are favoured by the same conditions as required for the formation of HMX. This study has lead to a considerable reduction in the cost of HMX which is a key ingredient in many explosive and propellant formulations.

**Acknowledgement**

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**References**


**Table 3**—Effect of catalyst on yield of HMX

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraformaldehyde</td>
<td>60-63</td>
</tr>
<tr>
<td>Trioxane</td>
<td>58-61</td>
</tr>
<tr>
<td>Without catalyst</td>
<td>56-59</td>
</tr>
</tbody>
</table>

**Fig. 10**—Variation of yield with catalyst quantity.
30 Fang Z, Chen L, Wang S, Chen J & Li F, Conformation of intermediate HOCH$_2$NHNO$_2$ from nitrolysis of hexamethyleneamine as possible precursor for RDX formation by NMR spectrometry study, 3rd Int Symp on Pyrotechnic & Explosives, Peoples Republic of China, 1995, 121.