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Recovery of Ammonium Nitrate and Reusable Acetic Acid from Effluent Generated during HMX Production

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ABSTRACT

Production of HMX on commercial scale is mainly carried out by modified Bachmann process, and acetic acid constitutes major portion of effluent/spent liquor produced during this process. The recovery of glacial acetic acid from this spent liquor is essential to make the process commercially viable besides making it eco-friendly by minimising the quantity of disposable effluent. The recovery of glacial acetic acid from spent liquor is not advisable by simple distillation since it contains, in addition to acetic acid, a small fraction of nitric acid, traces of RDX, HMX, and undesired nitro compounds. The process normally involves neutralising the spent mother liquor with liquor ammonia and then distillating the neutralised mother liquor under vacuum to recover dilute acetic acid (strength approx. 30 %). The dilute acetic acid, in turn, is concentrated to glacial acetic acid by counter current solvent extraction, followed by distillation. The process is very lengthy and the energy requirement is also very high, rendering the process economically unviable. Hence, a novel method has been developed on bench-scale to obtain glacial acetic acid directly from the mother liquor after the second ageing process.

Keywords: HMX, glacial acetic acid, RDX, ammonium nitrate, spent liquor, waste recovery, effluent treatment

1. INTRODUCTION

HMX also known as octogen (1,3,5,7 tetranitro-1,3,5,7 tetraazacyclooctane) is one of the most powerful high explosive for military use. On a large scale, HMX is produced by modified Bachmann[1] process, ie, by nitrolysis of hexamine in acetic acid medium using ammonium nitrate-nitric acid solution, acetic anhydride and paraformaldehyde (Fig.1). After the reaction is over, the reaction mass is diluted with two times the volume of water and the product simmered at 96-98 °C.

The effluent (mother liquor) obtained after the separation of crude HMX is found to contain: acetic acid (28-30 %), nitric acid (1.0-1.5 %), ammonium nitrate (2.0-2.5 %), RDX/HMX [0.05 % (max)], and water (remaining).

The concept of the recovery of acetic acid from waste streams is gaining momentum due to economic and environmental reasons. The high worth of acetic acid in chemical industry has virtually given birth to a concept of augmenting the commercial production of acetic acid and also the recovery of whatever small amount of this acid that flows into the waste streams. Brown[2] has aptly described the economics of recovering acetic acid from the waste streams. In short, the reasons for the recovery are: (i) viability of the technology, (ii) safety and

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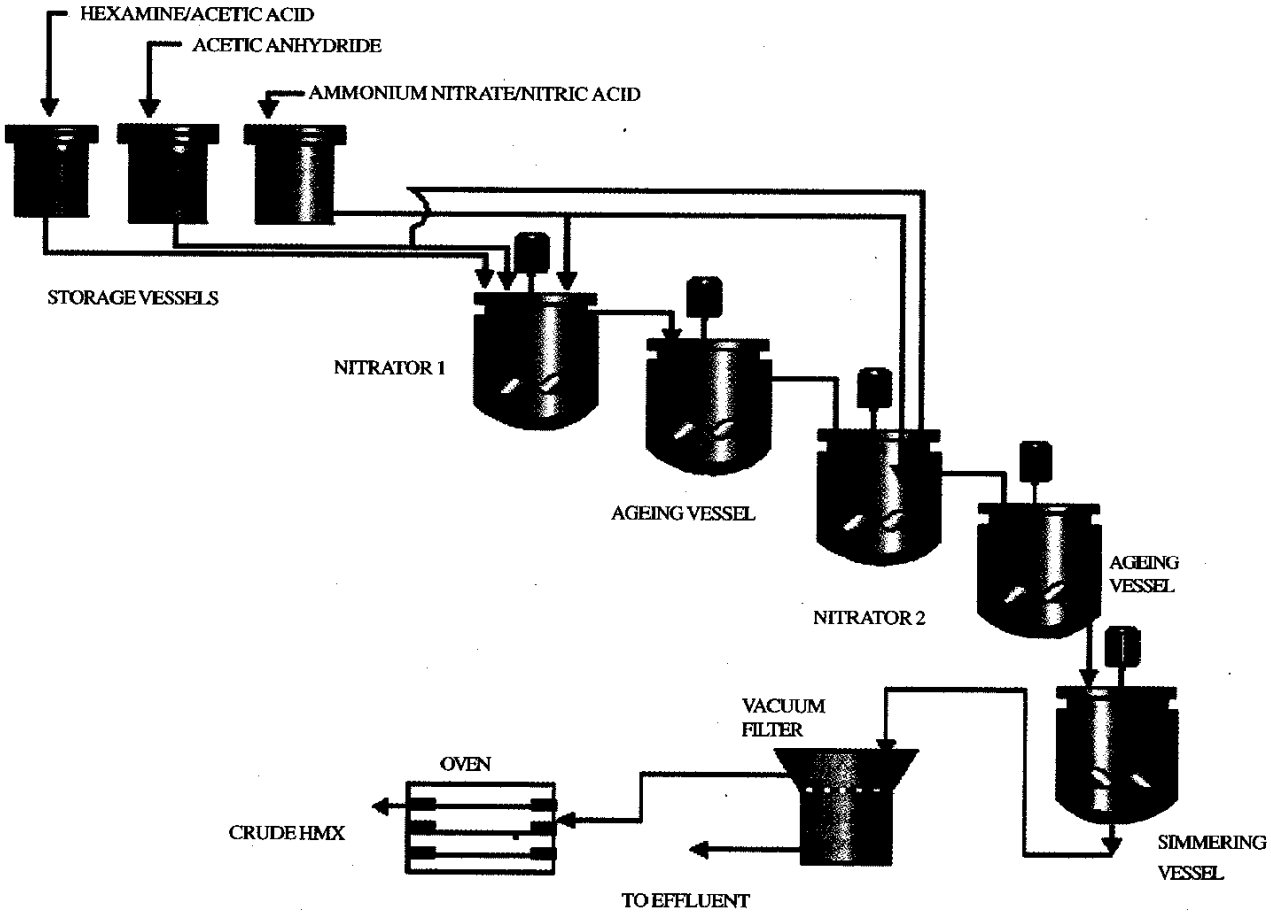

Figure 1. Production of HMX on commercial scale

environmental aspects, (iii) economic importance, and (iv) overall efficiency and logistics of the process. Moreover, waste water containing carboxylic acids poses problems during treatment when biologically oxidised, since these acids are converted into activated sludge having poor settling characteristics. Presence of organic acids increases the biochemical oxygen demand (BOD). Very often, it becomes obligatory to remove these carboxylic acids to meet a certain acidity specification. Due to their toxic nature, these acids are not considered eco-friendly by the environmental engineers.

Saxena[3], *et al.* have suggested a process for the recovery of glacial acetic acid, which involves neutralisation of nitric acid with liquor ammonia. The neutralised mother liquor is then vacuum distilled to recover dilute acetic acid, which, in turn, is converted into glacial acetic acid by counter current solvent extraction, followed by distillation.

A study on similar lines was carried out earlier by Rajopadhye[4], *et al.* and a pilot plant for the recovery of acetic acid (Fig. 2.) has been setup at the High Energy Materials Research Laboratory (HEMRL), Pune. However, the process of the recovery of acetic acid is quite complex, time-consuming, and also requires a lot of space, machine, and energy input, which is obvious and unavoidable, considering the nature and quantity of effluent generated during the process (1 kg crude HMX generates 100 kg effluent). Also, the separation of ammonium nitrate from residual part of effluent, ie, black liquor obtained after recovery of dilute acetic acid, involves an additional process since presence of ammonium nitrate hampers

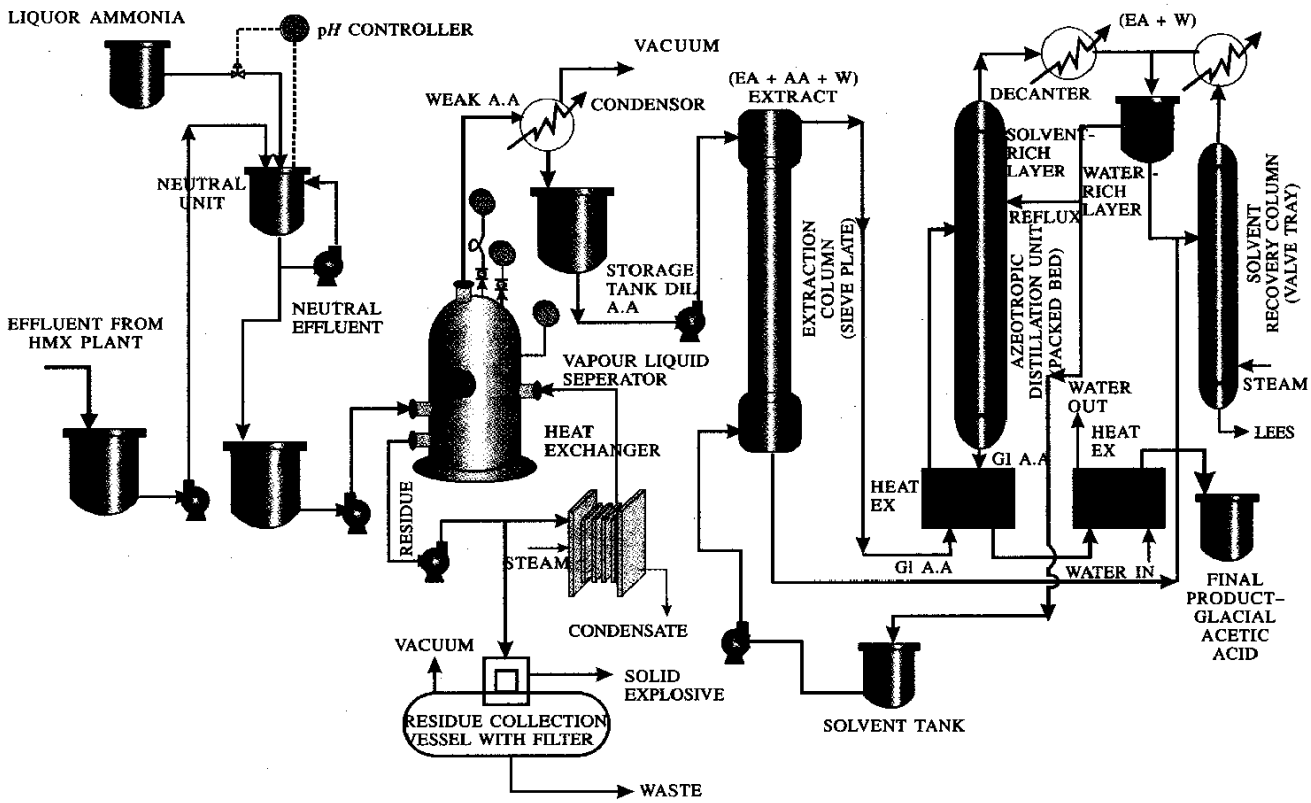

Figure 2. Schematic process flow diagram for the recovery of glacial acetic acid

biodegradation of residual mother liquor. Hence, an attempt was made to regenerate glacial acetic acid directly and to separate RDX and ammonium nitrate during the process.

A process has been developed to generate acetic acid in its glacial form, directly from the mother liquor obtained after filtration of crude HMX after second ageing process, ie, before simmering the crude HMX. This makes the process one step ahead towards eco-friendliness by minimising the quantity of effluent. Besides this, it also reduces the process time, energy input, raw material consumption, and total cost of the recovery of reusable raw material.

Furthermore, the recovered raw material can be reused in the process directly, which reduces the cost of production. Some quantity of ammonium nitrate formed during treatment of mother liquor with ammonium acetate is also separated. RDX formed along with HMX gets separated when simmering of crude HMX is carried out with 60 per cent acetic acid. This recovered RDX is found to be 10-15 per cent by weight of HMX produced.

2. EXPERIMENTAL PROCEDURE

2.1 Nitrolysis of Hexamine

Two-stage nitrolysis of hexamine is carried out in acetic acid (medium) using ammonium nitrate, nitric acid, acetic anhydride, and paraformaldehyde at 44 ± 2 °C. After the second stage of nitrolysis, ageing of the contents is carried out. The contents are crash cooled to 10 °C. Filtration is then carried out at ambient temperature to separate the crude HMX from the mother liquor. The crude HMX and the mother liquor (I) are treated separately in the following manner:

2.1.1 *Treatment of Crude* HMX

The crude HMX is simmered using 60 per cent acetic acid and filtered while hot. HMX is then washed with sufficient quantity of hot water to remove the acidity and the filtrate is crash cooled to obtain RDX, which is separated by filtration at ambient temperature.

2.1.2 *Treatment of Mother Liquor*

The nitric acid content in the mother liquor is estimated by titrimetric method. Nitric acid is eliminated by adding stoichiometrically calculated quantity of ammonium acetate, which converts it to ammonium nitrate and acetic acid. The conversion of nitric acid into ammonium nitrate and acetic acid follows the p*H* profile as shown in Fig. 3. The complete neutralisation of nitric acid takes place at a p*H* of 2.8 to 3.0.

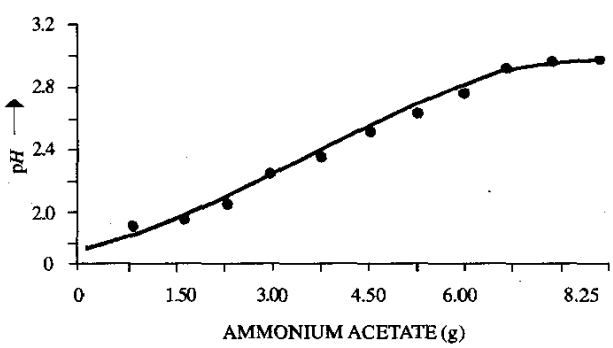

Figure 3. p*H* profile showing progressive elimination of nitric acid in the spent mother liquor.

The ammonium nitrate precipitated out is separated by filtration. The excess quantity of acetic anhydride remaining unreacted is converted to acetic acid by adding water. The mother liquor, which is now free from nitric acid, is subjected to distillation under reduced pressure (600 - 630 mm of mercury) to obtain glacial acetic acid directly. The recovery of acetic acid is made up to 85 per cent of total volume of the mother liquor. The strength of the acetic acid obtained is checked by titrimetric method and the purity is checked by the GC analysis. The liquid residue after the recovery of glacial acetic acid is crash cooled to 10 °C to separate out ammonium nitrate. The overall process is illustrated in the block diagram (Fig. 4).

3. RESULTS & DISCUSSION

The present process of production of HMX involves dilution of the contents obtained after the second ageing stage with two times the volume of water. This makes the concentration of acetic acid approx. 30 per cent. The simmering is carried out at 96-98 °C for an hour. In the new procedure, contents are filtered after completion of second ageing, without dilution. The mother liquor contains glacial acetic acid, besides some nitric acid and unutilised acetic anhydride along with small amounts of RDX, HMX, and nitro compounds in the solution. This mother liquor can be subjected to fractional distillation to recover nitric acid and acetic acid. However, it has been reported by Henry and Paquette[5] that nitric acid when heated in a certain proportion with acetic anhydride forms an explosive product, namely acetyl nitrate as follows:

$$\left.\begin{matrix} CH_3CO \\ CH_3CO \end{matrix}\right\rangle O + 2HNO_3 \longrightarrow 2NO_2OCOCH_3 + H_2O$$

To avoid this, nitric acid present in the spent mother liquor is first treated with ammonium acetate so that ammonium nitrate and acetic acid are formed.

$$CH_3COONH_4 + HNO_3 \longrightarrow NH_4NO_3 + CH_3COOH$$

After the removal of ammonium nitrate, the excess acetic anhydride present is converted to acetic acid by adding requisite quantity of water.

$$\left.\begin{matrix} CH_3CO \\ CH_3CO \end{matrix}\right\rangle O + H_2O \longrightarrow 2CH_3COOH$$

The mother liquor at this stage contains mainly acetic acid, besides small quantities of RDX, HMX, ammonium nitrate, and nitro compounds in dissolved state. This is then subjected to distillation under reduced pressure. Due to the presence of dissolved

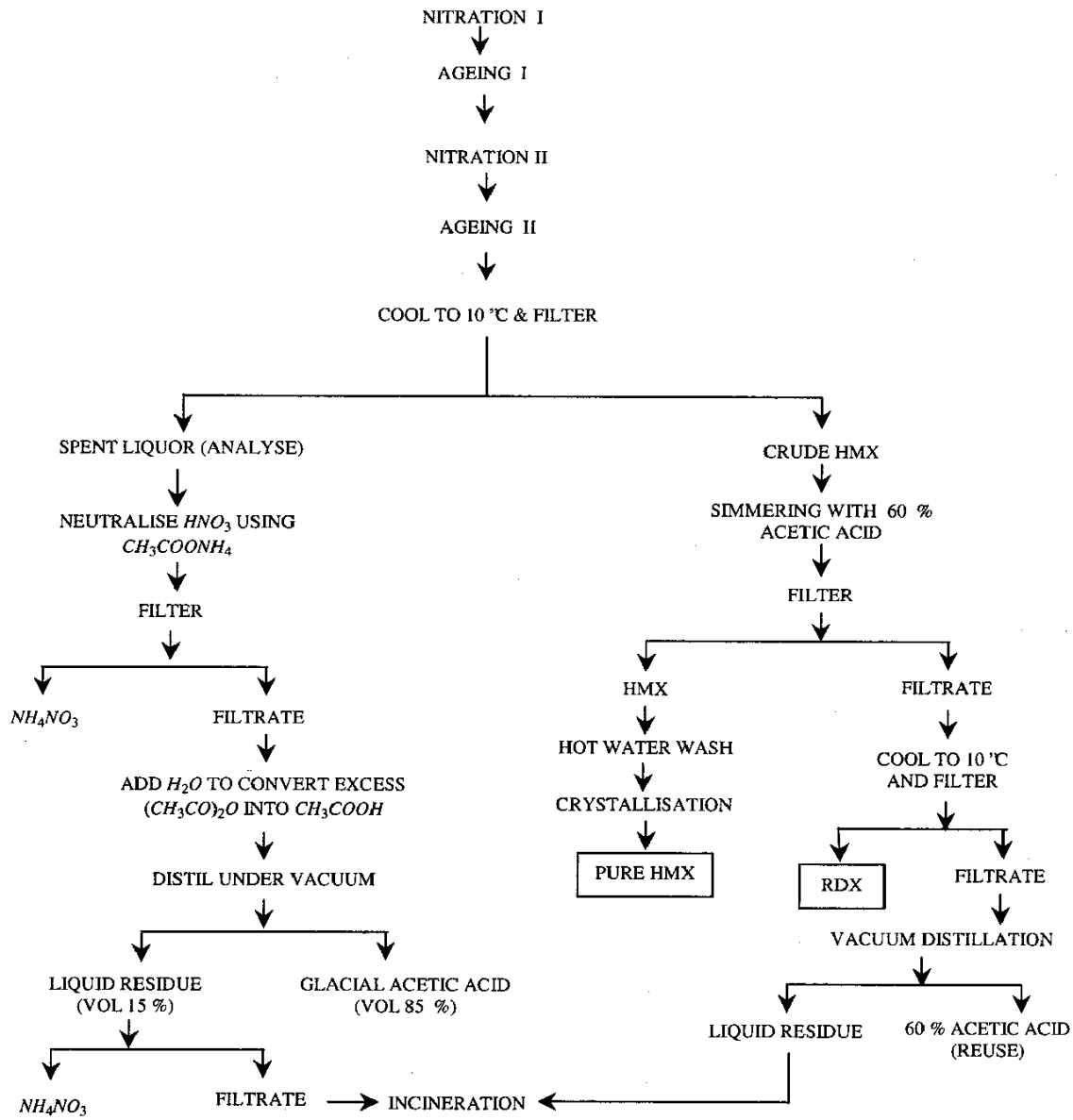

Figure 4. Flow chart of the effluent treatment of HMX–nitrolysis

explosive, the recovery of acetic acid is restricted to 85 per cent to prevent explosive hazard[6]. The liquid residue after the recovery of glacial acetic acid is crash cooled to 10 °C. This separates out the ammonium nitrate present in it.

The results of five sets of experiments indicating strengths of the acetic acid obtained after distillation are given in Table 1. Details of ammonium nitrate obtained during processing of the mother liquor are given in Table 2.

It has been observed that for a 50 g batch, the quantity of effluent (mother liquor) after the recovery of glacial acetic acid is about 80 ml, which is quite moderate (compared to the 100 kg effluent generated per kg of HMX in the original method) and can be easily disposed off. The available routes for

Table 1. Recovery of acetic acid*

Initial volume of mother liquor (I) (ml)	Acetic acid obtained by distillation (ml)	Mother liquor (residue) (ml)	Acetic acid obtained by distillation of mother liquor (% strength) Assay
520	442	78	98.75
500	425	75	98.90
530	450	80	99.40
490	416	74	99.70
480	408	72	99.60

* 50 g batch of hexamine

Table 2. Recovery of ammonium nitrate*

AN obtained after treatment of mother liquor (I) with ammonium acetate (g)	AN obtained after recovery of acetic acid from mother liquor (II) (g)
13	4
15	3
14	3
15	3
15	4

* 50 g batch of hexamine

disposing off this mother liquor are incineration and biode gradation.

Ammonium nitrate is separated during two different stages as mentioned above. This ammonium nitrate is, however, contaminated with acetic acid and nitro compounds, which obviously rules out the possibility of its reuse for the production of HMX. It can, however, be used elsewhere.

4. CONCLUSION

Reusable glacial acetic acid can be generated directly from the mother liquor of HMX effluent. Acetic acid (60 %) used for simmering can be reused after purification. Excess glacial acetic acid generated from acetic anhydride can either be sold or converted to acetic anhydride.

Recovery of glacial acetic acid directly saves not only in energy costs but also reduces the quantity of cfflucnt significantly. Spent mother liquor generated during various stages can be disposed off either by incineration or by biodegradation.

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REFERENCES

1. Bachman, W.E.; Horton, W.J.; Jenner, E.L.; Mac Naughton, N.W. & Scott, L.B. *J. Am. Chem. Soc.*, 1951, **73**, 2769.

2. Brown, M.V. Economics of acetic acid recovery, *Chem. Engg. Progress*, 1963, **59**(10), 65.

3. Saxena, R.C.; Sahu, D.K. & Sarkar, S.K. Separation and recovery of acetic acid in HMX production. *Chemical Weekly*, March 24, 1998, 167-69.

4. Rajopadhye, M.V.; Hima Prasanth & Syal, R.K. Recovery of acetic acid from spent of cyclotetramethylene tetranitramine plant. *Chem. Engg. World,* 1999, **34**, 81-86.

5. Henry, Feuer. *In* The chemistry of the nitro and nitroso groups, Part-I. Purdue University, Lafayette, Indiana, Inter Science Publishers, New York. pp. 316.

6. Paquette Leo, A. *In* Encyclopedia of reagents for organic synthesis, Vol. 1, Ohio State University, Columbus, OH, USA, 1995. pp 75.