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A New Recycling Technique of Trifluoroacetic Acid in Synthesis of LLM-105 Explosive

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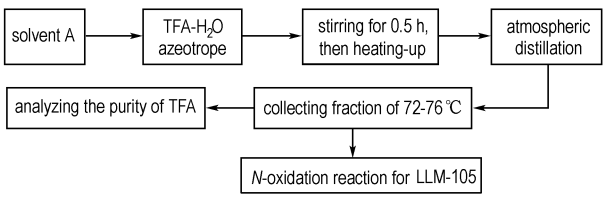
Trifluoroacetic acid (TFA) is corrosive and toxic, which is hard to decompose by chemical reaction and micro-biological degradation[1-2]. However, TFA is largely used for the nitrogen oxidation reaction to obtain 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105). Common industrial separation methods such as distillation can not be utilized for recovery of TFA because of a maximum boiling azeotrope (20.6 wt % water, boiling at 105.5 ℃ [3]) formed by TFA and water. Till now, there is few report about the separation method of TFA-H_2O. Deng[4] et al. studied the recovery of TFA liquid in the synthesis of LLM-105 explosive, the operation processes included neutralization using strong base, concentration, acidation and distillation. Mahajan[5] et al. investigated the feasibility of using reactive distillation to recover TFA through esterification with 2-propanol, but this method was aimed to dilute aqueous solution, which is unsuitable for concentrated aqueous solution.

Considering above, we explored a new broken azeotropic technique to recover TFA by adding solvent A, and then employ atmospheric distillation to recove TFA for synthesis of LLM-105. The process diagram is shown in Scheme 1.



Scheme 1 The flow process diagram of recovery

(1) Separation of TFA-H_2O azeotrope

A is a strong hydrophilic solvent, and does not react with TFA. At room temperature, 372.2 g solution containing TFA (70 wt %) was added to the three-necked bottle, then solvent A was added slowly. After stired for 0.5 h, the mixture was heated to reflux, and distilled at atmospheric condition. The fraction was collected at 72－76 ℃, and 248.0 g TFA was obtained with a yield of 88%. The purity of TFA was 93% by GC-MS quantitative analysis (see in Figure 1).

(2) *N*-oxidation for LLM-105 with fresh/recovered TFA

5.0 g 2,6-diamino-3,5-dinitropyrazine, 50 mL TFA were added to the three-necked bottle, 15 g 50% H_2O_2 was dropwised to the mixture in ice bath. It was stirred for 6 h at 25－30 ℃, and the precipitation was filtrated, washed with water, dried at 60 ℃ in vacuum. The experimental results were listed in Table 1, which indicating that the purity of LLM－105 using recovered TFA can be paralleled to that of fresh TFA.

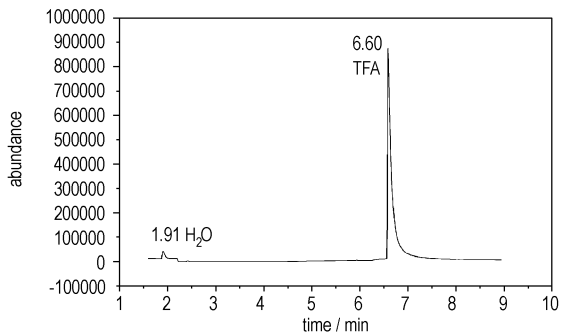


Fig. 1 The purity of recovery TFA

Table 1 Comparison of experimental results between fresh and recovered TFA

TFA	yield/%	purity (HPLC)/%
fresh	93.52	98.90
recovered	90.74	98.45

A new recovered technique of TFA in the synthesis of LLM-105 explosive was obtained. The yield and purity of recovered TFA were 88% and 93%. The recovered TFA was used in the synthesis of LLM-105 with good yield and purity.

Key words: organic chemistry; trifluoroacetic acid; LLM-105; azeotrope; separation
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