MHSMP-75-40I

HNS Recovery from DMF Recrystallization Filtrate

Jacob Sandoval

DEVELOPMENT DIVISION

JULY - SEPTEMBER 1975

Normal Process Development
Endeavor No. 107

Mason & Hanger - Silas Mason Co., Inc.
Pantex Plant
P. O. BOX 647
AMARILLO, TEXAS 79177
806-335-1581

operated for the
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
under
U. S. GOVERNMENT Contract DA-11-173-AMC-487(A)

DISCLAIMER

HNS Recovery from DMF Recrystallization Filtrate

Jacob Sandoval

DEVELOPMENT DIVISION

July - September 1975
Endeavor No. 107

ABSTRACT

Low-cost recovery of HNS, retained by the filtrate during the recrystallization process, can be promoted by dilution of the mother liquor with a water-methanol solution.

DISCUSSION

A recrystallization process has been developed and documented, whereby 2,2', 4,4', 6,6'-hexanitrostilbene, HNS, with an approximate bulk density of 0.5 g/cc, can be reproducibly obtained from solution in N,N-dimethyl formamide, DMF(*1*). During the process, however, a portion of the solute is tenaciously retained by the filtrate. The high-cost of HNS warrants its extraction; consequently a low-cost recovery method was pursued.

From the HNS/DMF solubility curve (Fig. 1) it is noted that, near ambient temperature, the solubility of HNS in DMF is approximately 1.2 grams per 100 mℓ of solvent.

EXPERIMENTAL

Dilution of DMF filtrate with water causes the HNS to crystallize out of solution; however, the precipitated particles are so minute they make collection by filtration almost impossible as the filter pores become clogged. Collection can be effected through centrifugation, but this may prove impractical for recovery of large quantities of material. Dilution was attempted with varied volumes of water, over a wide temperature range, but no improvement in the size or mass of the precipitated particles was evidenced.

Cooling of the filtrate at 0 C for 48 hours and at -20 C for 3 hours failed to promote solute extraction. Addition of chipped ice to the filtrate had no immediate effect; it merely extended the dilution period. Introduction of granulated dry-ice (CO_2) caused the filtrate to freeze, but on thawing the filtrate remained unchanged.

Dilution of the filtrate with organic solvents, either full strength or in combinations with water, was also investigated. The effectiveness of the diluent, introduced under varied conditions in parts per 100 parts of filtrate, was evaluated with respect to product quality, particle size, filterability and yield. Also considered was the material cost of an extraction process. Varied results were obtained (see Table I). In all of the extraction endeavors, the diluent was poured into the filtrate in one operation without stirring.

---

(1) Jacob Sandoval, "HNS Crystallization Studies," MHSMP-75-24H (April-June 1975).

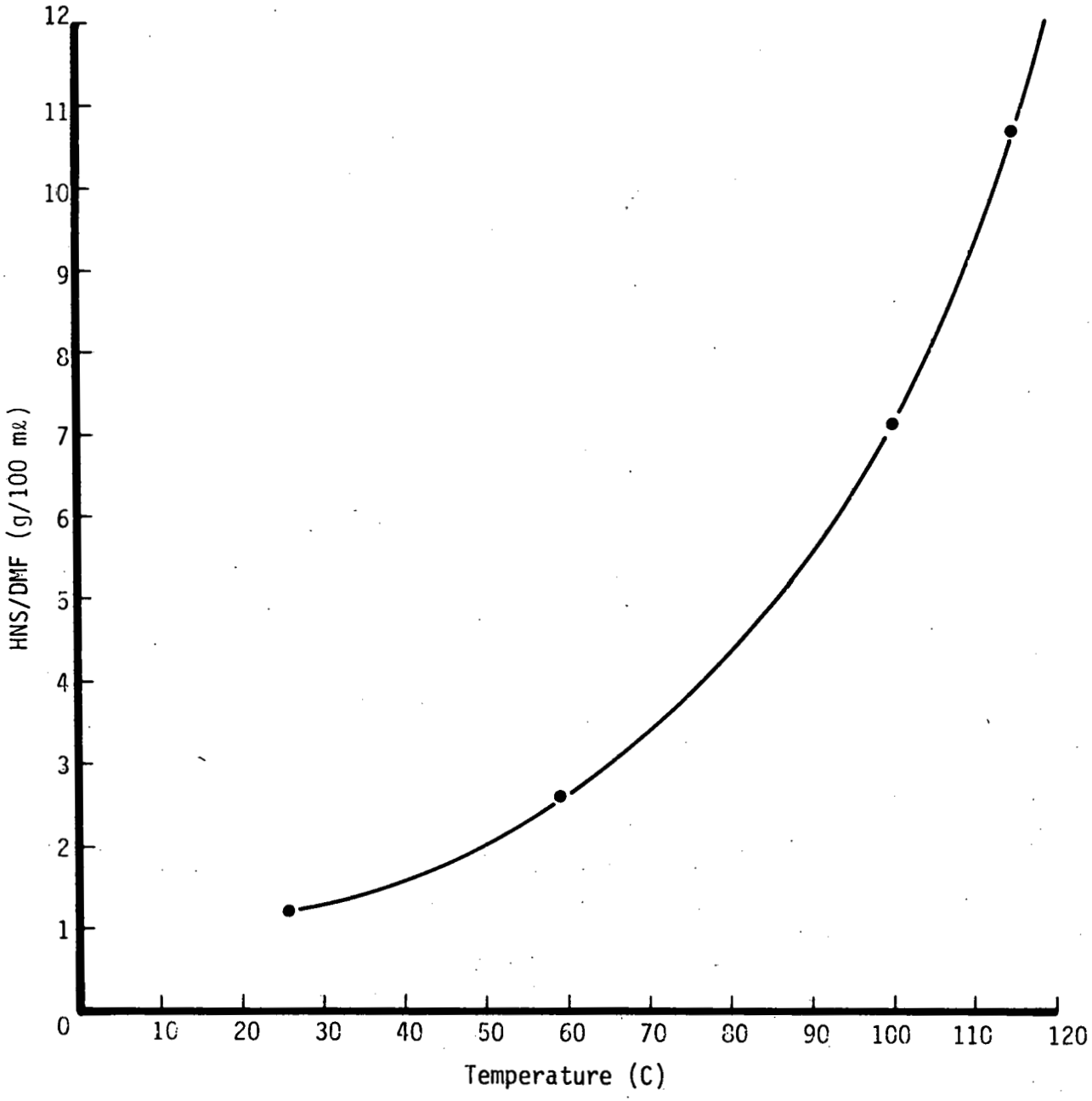


Fig. 1. Solubility of HNS in DMF as a Function of Temperature

Table I. HNS Recovery: Diluent Effect on Recrystallization Filtrate (HNS/DMF Process)

	Diluent (Solvent)	Cost/ℓ Filtrate ($)	Volume (mℓ)		Temperature (C)		Yield (%)	Comments
			Diluent	Filtrate	Diluent	Filtrate		
1	Ethylene Glycol	2.64	20	100	Amb	Amb	54	Light, Fluffy, Easy Filtering; Expensive
2	Petroleum Ether	1.32	20	100	Amb	Amb	2	Light, Poor Yield
3	Water		20	100	95	95	70	Very Small Particles; Poor Filterability
4	Water		20	100	Amb	75	65	Very Small Particles; Poor Filterability
5	Water		20	100	Amb	Amb	50	Minute Particles; Clog Filter
6	Water/Methanol		10/10	100	Amb	88	60	Minute Particles; Clog Filter
7	Water/Methanol		30/10	100	Amb/95	95	90	Small Particles; Poor Filterability
8	Water/Methanol		10/30	100	Amb/Amb	80	90	Small, Uniform Crystals; Easy Filtering
9	Water/Methanol		400/40	100	95/Amb	Amb	45	Minute Particles; Poor Filterability
10	Water/Methanol		80/80	100	95/Amb	Amb	50	Minute Particles; Slow Filtering
11	Water/Methanol		40/20	100	75/75	Amb	50	Miniscule; Almost Unfilterable
12	Water/Methanol		20/20	100	65/65	Amb	50	Miniscule; Almost Unfilterable
13	Water/Methanol		20/40	100	Amb/Amb	Amb	60	Miniscule; Almost Unfilterable
14	Methanol	0.40	80	100	Amb	Amb	45	Small Particles; Poor Filterability

Table I. Cont'd

	Diluent (Solvent)	Cost/ℓ Filtrate ($)	Volume (mℓ) Diluent	Volume (mℓ) Filtrate	Temperature (C) Diluent	Temperature (C) Filtrate	Yield (%)	Comments
15	Methanol		40	100	Amb	Amb	50	Minute Particles; Poor Filterability
16	Methanol		20	100	Amb	Amb	45	Hair-Like Strands; Poor Filterability
17	Methanol		20	100	Amb	70	40	Hair-Like Strands; Poor Filterability
18	Benzene	1.45	20	100	Amb	Amb	2	Small Crystals; Poor Yield; Expensive
19	Chloroform	1.32	20	100	Amb	Amb	60	Small Crystals; Discolored
20	Acetonitrile	2.90	20	100	Amb	80	55	Small Uniform Crystals; Easy Filtering
21	Acetonitrile		20	100	Amb	Amb	50	Minute Particles; Slow Filtering
22	Propanol	1.58	20	100	Amb	70	60	Minute Particles; Slow Filtering
23	Water/Chloroform		200/40	100	Amb	Amb	-	HNS Coagulates; Poor Yield
24	Water/Hexane	0.45	200/20	100	Amb	Amb	-	Minute Particles; Poor Yield

Of the solvents, or solvent pairs, considered as extraction agents, the use of a methanol-water solution (75% CH_3OH) promoted the precipitation of HNS with the best particle characteristics. Introduction of 40 mℓ of this solution at ambient temperature into 100 mℓ of the filtrate at 80 C promoted the crystallization of small, uniform crystals. The particles, though small, were easily collected by filtration, yielding a 90% recovery of the estimated solute in solution. The melting point (DTA) was 319 C. This method gave similar results when repeated.

Although introduction of water as an extraction agent (at temperatures from ambient to its boiling point) was found to be ineffective, steam was considered as a diluent because it could be introduced at a constant rate and temperature. The filtrate was contained in a flask, equipped with a thermometer and a condensor, and steam was bubbled through it.

Plant steam was employed; consequently, a steam trap was engaged to retain line deposits and condensate. The steam train consisted of the trap, a glass transfer line (4 mm i.d.), the flask and an Allihn condensor (Fig. 2).

The initial contact of steam with the filtrate produced a temperature rise to ∿ 115 C within two minutes. Thereafter the temperature dropped to 98 ± 1 C in approximately 40 minutes and the precipitated HNS was collected by filtration. Analysis of the ensuing filtrate revealed total extraction of the HNS.

The temperature of the flask contents was monitored throughout the extraction period. A typical temperature history is given in Table II.

The recovered HNS solute (Fig. 3) consisted of small, uniform, free-flowing crystals with a melting point (DTA) of 320 C. Additional HNS extractions from the mother liquor produced similar results.

The simplicity and effectiveness of HNS extraction with steam from a dilute DMF solution suggested the application of the steam-dilution technique on a solution of higher concentration; consequently fresh solutions of HNS (Chemtronics, Lot 66-48) in DMF were prepared.

Three solutions of the same concentration (7 g HNS/100 mℓ DMF) were prepared by heating the respective mixtures, over an oil bath, to their dissolution temperature (104 C). Steam was bubbled at different but ungauged rates through these solutions. During each endeavor the temperature changes and distillate volumes were monitored (Table III).

For descriptive purposes the steam surge through the above samples were termed full, three-quarters, and half-flow. The respective percentage recoveries were 98, 94 and 73. The melting points (DTA) were 319, 319, 318 C, respectively.

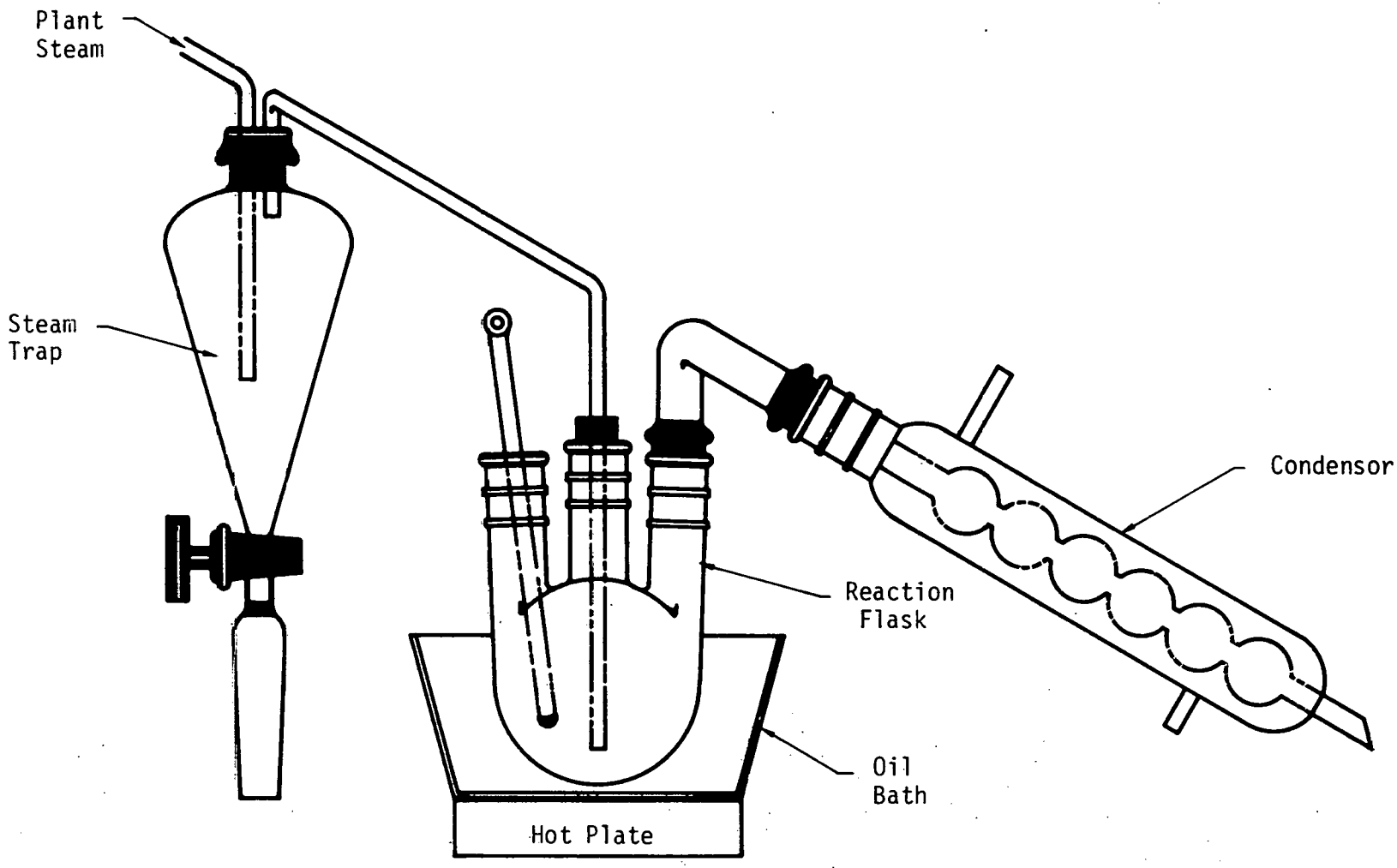
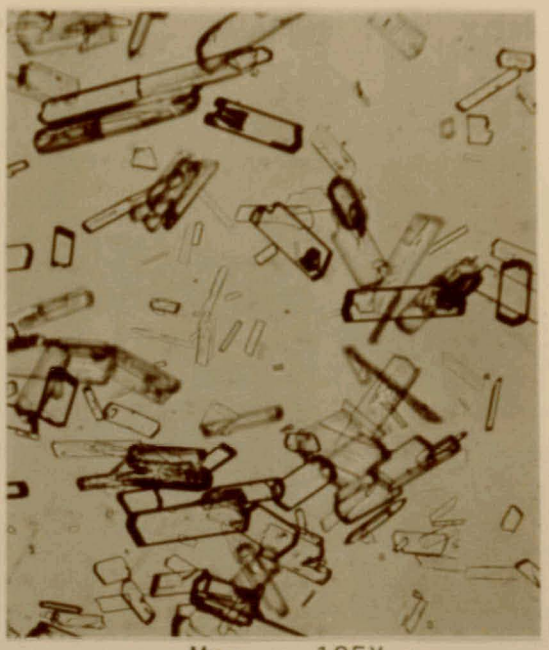


Fig. 2. Steam Flow Through HNS Solution

Table II. HNS Recovery: Steam Treated Filtrate

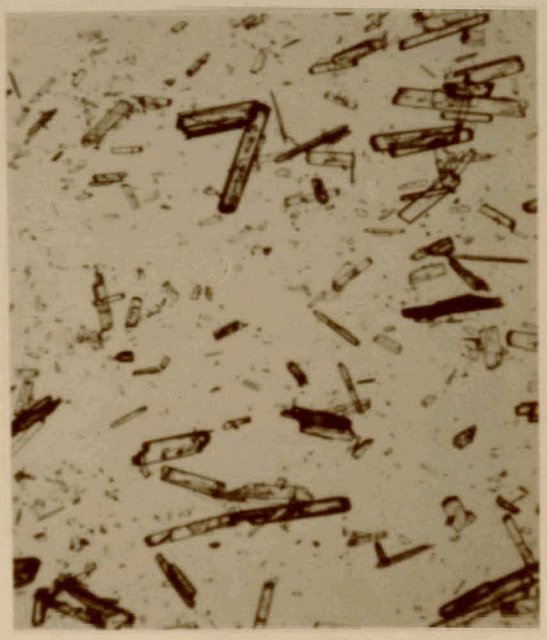
Time (Min)	Temperature (C)	Distillate (mℓ)
0	23	0
1	110	
2	113	
2.5	110	25
3.5	109	45
5	108	66
10	105	115
15	102	170
20	100.5	220
25	100	
28	99.5	
45	98	250

Mag. ~ 50X

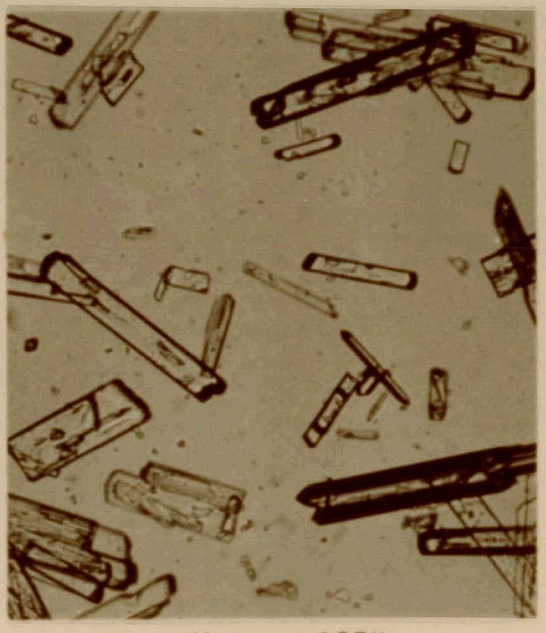


Mag. ~ 125X

Fig. 3. HNS - Filtrate Recovery Product by Steam Treatment



Mag. ~ 50X



Mag. ~ 125X

Fig. 4. HNS - Extracted from Solution by Steam Treatment

Table III. HNS Recovery: Steam-Treated Solution

Time (Min)	Temperature (C) (Run) 1	2	3	Distillate (mℓ) (Run) 1	2	3
0.5	114					
1.0	125	114	110			
1.5	120					
2.0		121	113			
2.5			110			25
3.0		116			25	
4.0	115					
5.0	113	112	108	60	96	60
6.0						
7.0	110			90		
8.0		108				
9.0	108			105		
10.0			105			115
11.0	106			120		
12.0						
13.0		105			104	
14.0	105			155		
15.0			102			173
16.0		103				
18.0		102			300	
19.0	102			193		
20.0			100			220
24	101			225		
25.0						243
26.0		99		240	450	
28.0			99			250
32		98		300	500	
34.0						
35.0		97			535	
39.0	99			350		
40.0		97			550	
44.0	98		98	380		
45.0						

The highest yield crop (98%) had an initial bulk density of 0.39 g/cc. This sample showed a slight discoloration and was washed successively in water and methanol followed by an acetone rinse. This treatment promoted the removal of 0.8 g of product, and eliminated the discoloration. This HNS (Fig. 4) was found to have a bulk-density of 0.59 g/cc.

CONCLUSIONS

Recovery of the HNS solute can be effected by either of two procedures: (a) one method promotes the precipitation of the solute by passing steam through the filtrate, and (b) the other technique involved the dilution (4/10) of the filtrate at 80 C with a water-methanol (75 volume % methanol) solution at ambient temperature.

Recovery of HNS in crystalline form can also be promoted through steam dilution of a concentrated HNS/DMF solution.