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#### ABSTRACT

#### SUSTAINABLE GREEN MANUFACTURING OF ENERGETIC MATERIALS

#### by Ted Alex Formeza

Pollution from manufacturing processes of the major energetic materials currently used in the U.S., 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) was briefly evaluated. It was found that acetic acid was a major pollutant. It appeared that the British Process could be controlled to reduce the polluting effluents better than the Bachmann Process used in the U.S. Most of the effort for producing the next generation of energetic materials is currently centered around the production of 1,3,3-trinitroazetidine (TNAZ). We evaluated five synthetic routes for producing TNAZ. We reduced the number of potential processes by carefully considering possible changes in the schemes that would allow them to become a sustainable green manufacturing process are those due to Axenrod [1], [2], and Coburn and Hiskey [3], [4]. A methodology used to identify, assess, and prioritize pollution prevention approaches due to Pojascek [5] was applied to the two processes. It was found that both schemes could be improved substantially.

# SUSTAINABLE GREEN MANUFACTURING OF ENERGETIC MATERIALS

by Ted Alex Formeza

A Thesis Submitted to the Faculty of New Jersey Institute of Technology in Partial Fulfillment of the Requirements for the Degree of Master of Science in Applied Chemistry

Department of Chemical Engineering, Chemistry and Environmental Science

January 1999

#### APPROVAL PAGE

# SUSTAINABLE GREEN MANUFACTURING OF ENERGETIC MATERIALS

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# LIST OF ABBREVIATIONS AND ACRONYMS

DADN	1,5-diacetyl-3,7-dinitro-1,3,5,7-tetrazocine	
DANNO	1,5-diacety1-3-nitro-7-nitroso-1,3,5,7-tetrazocine	
DAPT	3,7-diacetyl-1,3,5,7-tetraazabicyclo-[3.3.1]-nonane	
DEAD	diethyl azocarboxylate	
DIAD	diisopropyl azocarboxylate	
DMF	dimethyl formamide	
DMSO	dimethyl sulfoxide	
DOD	Department of Defense	
HMX	1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane	
PPA	polyphosphoric acid	
РОР	Products Only Production	
RDX	1,3,5-trinitro-1,3,5-triazacyclohexane	
SGM	Sustainable Green Manufacturing	
TBDMS	tert-butyl-dimethylsilane	
THF	tetrahydrofuran	
TNAZ	1,3,3-trinitroazetidine	
TPP	triphenylphosphine	

#### **CHAPTER 1**

#### **INTRODUCTION**

#### 1.1 Objective

The objective of the research described in this thesis is to develop a guide to modification of laboratory results to make energetic material manufacturing facilities environmentally sustainable and economically viable. To achieve this objective, a procedure or model must be developed to critically evalute synthetic schemes in order to find the steps that cause pollution problems. This should then be followed by developing creative new procedures that replace one or more of the undesirable polluting steps with cleaner steps. Finally, a new scheme is developed on paper that shows promise of evolving into a sustainable green manufacturing process. The first step in ascertaining that the new scheme is viable has to be a semi-microscale laboratory verification. Clearly, if the chemistry does not work, then the scheme must be modified and new steps formulated and tested in a similar way until a viable scheme is developed. For the purpose of this research, the procedures outlined above will be tested with past and present scale up of laboratory results and manufacturing practices of energetic materials. These practices have been used to produce various energetic materials for many years, but were developed without today's level of concern for the environmental consequences associated with them.

The manufacturing processes examined include those used in the production of 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) (1), 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) (2) and in proposed processes for the production of 1,3,3-trinitroazetidine (TNAZ) (3).



#### **1.2 Background on Energetic Materials**

The three energetic materials, RDX (1), HMX (2), and TNAZ (3) can be categorized as cyclic nitramines (compounds consisting of R-N-NO<sub>2</sub> functionalities, where R represents an alkyl group). RDX is the trimer and HMX is the tertramer of  $CH_2$ -N-NO<sub>2</sub>. Long after RDX and HMX became the staple high explosives of many military establishments, researchers proposed that a four-membered analogue would possess higher density (density is an important property because explosive power is proportional to the density of the material) and energetic content than RDX or HMX. Attempts to make the dimer of  $CH_2$ -N-NO<sub>2</sub>, 1,3-dinitro-1,3-diazetidine (4)were not successful [6].



Nevertheless, as a result of this research, TNAZ (3) was synthesized and proved to possess properties desirable to the military.

RDX (1)was discovered in 1925 [7] by Hale, with HMX (2) as a trace by-product of the reaction. RDX (1) was an important military explosive during the second World War and subsequent 'Cold War' period, and methods for its synthesis were developed by both Allied and Axis powers. Some of these methods produced substantial amounts of HMX (2) which was also found to be a useful energetic material. Improved methods for the synthesis of HMX (2) were subsequently developed after the war and research has continued until the present. Development of TNAZ (3) has occurred much more recently [8], and there are currently five synthetic routes to TNAZ (3) which have been published in the open literature. Interest in TNAZ (3) has focused around its use as a melt-castable high performance explosive. [9]

#### **1.3 Sustainable Green Manufacturing**

Sustainable green manufacturing (SGM) incorporates concepts of sustainable development that can be defined as "Development that meets the needs of the present without compromising the ability of future generations to meet their own needs." (World Committee on Environment and Development, 1987) [10]. Past solutions towards environmental concerns and waste management have focused on end of pipe treatment, essentially processing wastes after they are produced. SGM seeks to address environmental concerns <u>before</u> they arise.

End of pipe involves two main practices: containment and treatment. Containment involves the storage of these by-products and wastes in various forms such as 'ponding'. This is not always desirable since these waste are often not recovered and remain in the environment. Treatment is the further processing of waste materials to produce more benign substances, or to recycle the wastes so that they can be reused in the original manufacturing process. Typically this involves the recycling of unreacted reagents and

solvents, regeneration or reconstitution of consumed reagents, and neutralization or breakdown of unrecoverable waste products such that they will not pollute the environment. However, these processes are not sustainable because some or all of the effluents are destroyed and cannot be reused in the process.

SGM is accomplished by process modification, which involves changing the actual manufacturing process so that less waste (or ideally none) is produced. This approach has become increasingly important, since it can eliminate potential end-of-pipe treatment costs, and is sometimes referred to as green by design. In other words, a process is blueprinted to meet the goals of sustainable green manufacturing before industrial production of the product has begun. An important concept in process modification is called products only production (POP). The philosophy behind POP is to produce (in addition to the desired product) only useful by-products, or to find uses for any by-products produced.

#### **CHAPTER 2**

#### EXAMINATION OF MANUFACTURING METHODS OF ENERGETIC MATERIALS

Initially, literature research focused on sustainable green manufacturing of RDX (1) and HMX (2), which are currently the primary high explosives employed by US military. After being informed by Picatinny Arsenal that modification of current manufacturing processes for RDX (1) and HMX (2) would not be logistically and financially feasible for the US Army, focus was shifted to TNAZ (3). This is a consequence of requiring new performance tests to verify that changes in manufacturing have not changed the existing properties needed in all Department of Defense applications.

#### 2.1 RDX Production Methods

Most methods for production of RDX (1) (and HMX (2)) begin with hexamethylenetetramine (hexamine) (5) and proceed by N-nitrolysis and cleavage of carbon-nitrogen bonds.



The oldest [6] and simplest method for the preparation of RDX (1) is by direct nitrolysis of hexamine with excess concentrated (92% or more) nitric acid, and is thought to proceed by a combination of the following reactions:

$$(CH_2)_6 N_4 + 4HNO_3 \rightarrow RDX + 3CH_2O + NH_4NO_3$$
Eq. (1)

$$(CH_2)_6 N_4 + 6HNO_3 \rightarrow RDX + 6H_2O + 3CO_2 + N_2$$
Eq. (2)

6

Additionally, some side reactions occur which produce NH<sub>3</sub>, HCOOH, NO and NO<sub>2</sub>.

Two industrial methods were developed using direct nitrolysis: the British Process [11] (also known as the Hale Process or Woolwich Process) is a continuous method, and the SH Process [12] (developed by Schurr in Germany) which is a batch process. We determined them to be the cleanest since they require no additional reagents, and the waste products can, to an extent, be controlled, recycled or treated. HMX (2) is produced only in trace amounts by these methods.

The Bachmann Process [13] was the primary method employed for the production of these energetic materials in the United States, and modifications of the Bachmann Process continue to be used today. The original Bachmann Process used hexamine, nitric acid, acetic anhydride and ammonium nitrate as the reactants. The somewhat milder conditions of the Bachmann Process lead to an increase in the amount of acetic acid produced as waste and also to the amount of HMX (2) produced. Initially, HMX (2) was considered an undesirable impurity in the production of RDX since it slightly reduces its power. The relative amounts of RDX (1) and HMX (2) produced can be varied by adjusting reaction conditions [14] in the Bachmann Process.

#### 2.2 HMX Production Methods

Production of HMX (2) in the US is by the same Bachmann Process used to produce RDX (1). As has been stated, modification of the reaction conditions in the Bachmann Process, can improve the yield of HMX (2). By varying parameters of temperature and acid strength, together with quantities of ammonium nitrate and acetic anhydride, it was shown that the ratios of RDX (1) to HMX (2) could be altered. These results led Bachmann and co-workers to prepare mixtures rich in HMX (2). The optimum yields obtained represented 82% conversion of hexamine to HMX (2) and RDX (1) containing 73% HMX

(2). [15] Other methods employ the use of various acylated and acylated/nitrated tetramines. These synthesis routes are summarized in **Scheme 1** [16].

The following reactants: 1,3,5,7-tetraacetyloctahydro-1,3,5,7-tetrazocine (TAT) (7), 1,5-diacetyloctahydro-3,7-dinitro-1,3,5,7-tetrazocine (DADN) (8), and 1,5-diacetyloctahydro-3-nitro-7-nitroso-1,3,5,7-tetrazocine (DANNO) (9) have all been converted to HMX (2). HMX (2) can be obtained from TAT (7) in 75%-80% yields when nitrated by phosphorous pentoxide and 96% nitric acid. DADN (8) can be converted to HMX in 81% yield and 100% purity by a mixture of nitric acid and polyphosphoric acid. Direct conversion of DANNO (9) to HMX (2) resulted in poor yields; high yields from DANNO occurred only when it was first converted to DADN (8).

Through personal communications with researchers at Picatinny Arsenal, it was determined that altering the manufacturing processes currently in use would lead to prohibitively high costs. The primary factor in this determination was recertification. When the production method of an energetic material is altered in any way, extensive testing is required by the DOD to insure that the material performs identically as the material produced by the unaltered method. This testing, known as recertification, is required because of the hazardous nature of military operations and the need to be certain that the energetic materials are compatible with the delivery systems. Recertification includes the need to test fire all weapons systems which employ the material in any quantity or form. Often these weapons systems are destroyed in the testing process; therefore, the high cost of some weapon systems makes development of new manufacturing methods for existing energetic materials prohibitively expensive. Accordingly, the focus of the project turned to new energetic materials being developed for future use.



Scheme 1 Alternative routes to HMX

#### 2.3 TNAZ Production Methods

The latest development in energetic materials has been in the so-called "second generation" high explosives, such as TNAZ (3). Development of TNAZ (3) is still in the early stages, and TNAZ (3) is not being used in any military weapon systems, therefore recertification is not at issue. Additionally, there is no existing infrastructure for production which might require expensive modification. Accordingly, TNAZ (3) appears to be a prime candidate for development into a potential SGM process. Currently there are five synthetic routes to TNAZ (3), that are published in the open literature.

The first method examined was the method proposed by Axenrod, et al., [1], [2]; the synthetic route is outlined in **Scheme 2**. A desirable feature of this synthesis is that all three nitro groups are placed on to the azetidine ring in the final step, an important safety benefit.

The method developed by Marchand [17] (Scheme 3) was examined. It involves the use of a 1-azabicyclo[1.1.0]butane [17] intermediate.

# $\left[ \bigoplus_{N} \right]$

This process involves the use of highly hazardous intermediates and has extremely poor yield. It will not be considered in this project as a likely candidate for further development into pilot plant scale.



Scheme 2 Axenrod synthesis of TNAZ



Scheme 3 Marchand synthesis of TNAZ

The original process proposed for synthesis of TNAZ (**3**) was developed by Archibald, et al., [18] at Flurochem, Inc. (**Scheme 4**) and is known as the Fluorochem process. Its major problem involves the use of epichlorohydrinas a starting material. Epichlorohydrin is a strong irritant, toxic, carcinogenic, and mutagenic [19].



Scheme 4 Archibald synthesis of TNAZ

Katritzky, et al., [20] examined two routes combining features of both the Fluorochem and Axenrod processes (**Scheme 5**). They begin with epichlorohydrin and benzhydrylamine, like the Fluorochem process, but then proceed through the same azetidinone **15** - azetidinone oxime **16** route as in the Axenrod Process. This method, along with the Marchand method, will not be considered furthur as a procedure worthy of development in this project.



Scheme 5 Katritzky synthesis of TNAZ

The process that has been used to produce the bulk of the TNAZ (3) used for testing by the military, is based on a process developed and patented by Coburn and Hiskey. It is also known as the Los Alamos Process. The process, as presented in the patent [3], is illustrated in **Scheme 6**. Its major advantage is that it uses simple starting materials: formaldehyde, nitromethane, and *t*-butylamine. However, the method requires the use of some expensive and undesirable reagents.

The Los Alamos process has been extensively modified by Coburn, Hiskey, and Archibald in attempts to reduce the amount of waste produced and increase yield. Their modified process is presented in **Scheme 7**. Their original method produced only a 20% overall yield and over 1200 kg of waste for every kg of TNAZ (**3**), whereas their modified method achieves an 80% overall yield and reduces chemical wastes to 15.7 kg (kg TNAZ)<sup>-1</sup> [4].



Scheme 6 Coburn and Hiskey synthesis of TNAZ



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Scheme 7 Modified Coburn and Hiskey synthesis of TNAZ (scale-up)

#### CHAPTER 3

#### PROPOSED GENERAL SUSTAINABLE GREEN MANUFACTURING APPROACH FOR ENERGETIC MATERIALS

While past pollution prevention efforts have focused on attacking a specific source of waste or have sought to produce a clean process for a single desired material, the goal of this research is to develop an approach that can be applied to the manufacturing of any energetic material. This is important because the future needs of the military can be subject to frequent and dramatic changes.

#### 3.1 Introduction

The general scheme developed stems from an application of the systems approach to pollution prevention developed by Robert B. Pojasek. [5] The approach developed by Pojasek seeks to address the problems of waste, pollution and sustainability for diverse industrial processes



Figure 1 General approach for Sustainable Green Manufacturing of energetic materials

not just chemical processes. The modified approach described here has been tailored and simplified for chemical processes typically found in the manufacturing of energetic materials. The approach follows a five step method diagrammed in **Figure 1**.

#### 3.2 The Process Map

The first step is to convert the synthetic scheme or existing process into a form that clearly shows the input of materials and resources and the output of wastes and products. To achieve this a process map is constructed. The process map is a simplified schematic which breaks the process down into its essential steps. "Process maps can be used to track the use and loss of all resources—materials, energy, and water. This enables the user of the process map to begin to look at efficiency at the work-step level" [21]. Water is singled out because it can be both a reagent, product , or a coolant affecting energy use and is often overlooked. A process map may have one step for each step in the chemical synthesis, but often it is more instructive to further simplify and combine steps. Each process will, of course, be unique, and which method is best will depend on the individual process. At any rate, if the process lends itself to a very simplified process map, each step in the process map can in turn be broken down into its own process map if necessary. A generic example of this is illustrated in **Figure 2**.

#### 3.3 Analysis of the Process Map

After a process map is created, attention can be turned to analyzing the information contained within it. This involves: (1) identifying the problems with the existing process and (2) determining the function of the problems within the process. The process map created in the first step not only elucidates these problems but can on occasion suggest possible solutions.

Identification of the problems, or as Pojasek calls them, opportunities [21], involves evaluating the inputs and outputs of the process map. For example, if a step is producing an output that is undesirable, then that output is a problem, or rather an



Figure 2 Generic process map

opportunity for improvement, that should be addressed. Typical opportunities are the elimination of organic solvents, the reuse of waste products from one step as an input material in another step, and the replacement of a toxic material with an environmentally benign material.

Once opportunities have been identified, the function that they serve in the process must be determined. This is necessary so that informed solutions can be generated later. If an opportunity lies in the elimination of a solvent, then the function the solvent plays in the chemical reaction needs to be determined. Questions such as: Is the chemical used only as a solvent?, Does it enhance nucleophilicity?, Is it used for extraction? etc. need to be answered. Additionally, the properties of the solvent are extremely important: Is it protic or aprotic, polar or nonpolar?, etc. When evaluating other chemical reagents typical functions are: oxidizing or reducing, catalysis, and use as a protecting group.

It may be that opportunities can be found in the elimination or replacement of an entire step in the process. This may lead to dramatic improvements since factors such as cost, yield, and waste are typically proportional to the number of steps in the process. In this case, the questions which need to be answered are somewhat more subtle since the obvious 'function' of any step in a process is simply to produce the next intermediate (or the final product) in the process. The substance of these questions includes:

- Does the step serve to increase the overall yield?
- Why is the product of the step an important intermediate?
- Is there an alternate route to the product of the step or directly to a further intermediate in the process?
- Do alternate methods with reduced cost or increased yields exist?

Once the analysis of the process has been carried out, and the function of each opportunity targeted for improvement has been determined, a list of alternatives must be generated.

#### 3.4 Brainwriting and Brainstorming

In the past, pollution prevention often has focused on applying a method that has been successful in a similar situation, typically giving a standard solution that may not, in fact, be the best solution for the particular problem at hand. "In reality, the only way to find the best pollution prevention solution ... is to consider as many alternatives as you can" [22]. To accomplish this a large list of ideas and alternatives must be generated, free from the possible constraints of past pollution prevention measures. Typically, the method used to generate a free flow of ideas was brainstorming. While this method is still viable and valuable, Pojasek suggests the concept of brainwriting as a better less restrictive method.

In brainwriting, team members are are instructed to write down alternatives on separate sheets of paper. These papers are then randomly distributed to other team members and more ideas and alternatives are written down. This process is repeated until the emergence of possible new alternatives is exhausted. If a member cannot generate a new alternative then he is free to criticize or compliment another member's idea and suggest an improvement. "It is intersting to watch someone pick up a sheet on which a tearmate has criticized one of his ideas... We are much more apt to write down honest feelings than we are to speak it. Brainwriting offers an outlet for criticism and comments" [23]. In order to avoid confrontation and defensive posturing, the comments can be couched into what one likes about the idea and how he or she would like to see it modified. In the end a master list of all the alternatives is compiled by the team. A detailed discussion with examples of the brainwriting method was published by Robert B. Pojasek [24] in *Pollution Prevention Review / Autumn 1996*.

#### 3.5 Prioritization of Alternatives: Bubble Up/Bubble Down

Ideally, a large list of alternatives is generated by the brainwriting step and an efficient method to choose the best alternatives is needed. To accomplish this, a simple comparison method, a bubble sort algorithm, is used. In a bubble sort, alternatives are compared two

at a time and the better of the two "bubbles up" to the top and the other "bubbles down." The bubble sort is completed when all of the items in the list are in decending order relative to each other. "Alternatives that are inexpensive and easy to implement tend to rise to the top of the list. Implementing these alternatives can provide some quick wins. The middle tier of altenatives generally are those that need additional study or are more expensive" [21]. The strength of this method lies in the fact that many comparisons are carried out. Rather than picking what appears at first glance to be the best choice, this method allows for more unbiased choices and rank ordering.

#### **3.6** Testing and Further Improvement

Armed with the best alternatives, the process can now be modified. A good method is to create an entirely new process map with all of the improvements implemented. Not only does this provide a good basis for testing the new process, but it may give insight into additional improvements that may have been overlooked. Each improvement must be evaluated in the laboratory and if successful, tested in the pilot plant. This makes it possible to (1) determine if the improvements will indeed work as intended and (2) determine the optimal conditions to implement the improvements. The importance of literature research at this point should not be overlooked, since at times experiments similar to the suggested alternatives may have already been conducted, possible in a completely unrelated field.

#### CHAPTER 4

#### APPLICATION OF PROPOSED GENERAL SUSTAINABLE GREEN MANUFACTURING APPROACH: TNAZ CASE STUDY

#### 4.1 Introduction

The five methods developed to produce TNAZ (3) were evaluated and ranked. This was done to determine which methods were most likely to lead to a SGM process. A simple and general method of evaluation and ranking was used, in which we assigned a relative score, ranging from 1 to 5 (with 5 being the best), to the factors we felt were most relevant to SGM and a total score was calculated. The most likely processes to be chosen for production are the ones with the higest sum. The results are displayed in **Table 1**.

	Process				
	Axenrod	Coburn- Hiskey	Archibald	Marchand	Katritzky
Yield	4	5	3	1	2
Cost	3	4	2	1	2
Environment	3	3	2	1	2
Solvents	1	3	1	1	1
Heavy Metals	3	3	3	3	3
Halogens	1	4	2	1	2
Waste	1	1	1	1	1
Toxicity of					
Materials	4	3	1	1	1
Sum	2 0	26	15	1 0	14

**Table 1** Evaluation of TNAZ processes

In developing a set of criteria to evaluate the production method, cost of production immediately became a very important factor because military budgets in the US have been drastically reduced since the fall of the Soviet Union. Additionally, EPA guidelines for reduction of many volatile organic compounds provided definite environmental constraints. The elimination of these chemicals was given a high priority. From this evaluation, it was evident that the Axenrod and the Coburn-Hiskey methods were most the likely to lead to a SGM process. Therefore, the general procedures outlined in Chapter 3 were applied to these methods.

#### 4.2 Examination of the Axenrod Process

A process map for the Axenrod method was made (Figure 3). To provide a reference to the synthetic scheme (Scheme 2), the reference numbers of the intermediates involved were included in the process map. The main problem areas in the Axenrod method, as illustrated by the process map, are the use of many organic solvents (such as pyridine, THF, DMF, and methanol), the large amounts of waste acids produced, and the use of chromium. These chemicals account for the bulk of the wastes generated. The functions of these materials in the process were then determined, and the results are detailed in Table 2.

Process Step	Problem Material	Function
Tosylation	Pyridine	Used to form alkoxide which then can react
		with the los-ci to form the tosylate ether.
		Protects the secondary alcohol during the ring
Alcohol Protection	TRDMS-CI	closure. Produces HCI as a by-product leaves
	1 DDIVIO-OI	as a waste material during the deprotection
		step.
Bing Cleaure	тис	Used as a polar-aprotic solvent which solvates
ning Closure	th	the Li⁺ cations.
Deprotection	THF	Used to disolve the azetidine into the acid.
	AcOH	Proton source for the deprotection.
Ovidation	Chromic Acid	Standard laboratory reagents used to oxidize
Oxidation	Reagents	the alcohol to a carbonyl.
<b>Oxime Formation</b>	MeOH	Used to disolve the azidinone.
	Nitric Acid,	
Nitration	Ammonium	Source of NO <sub>2</sub> <sup>+</sup>
	Nitrate, Urea	

**Table 2** Problem materials and their function in the Axenrod process



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Figure 3 Process map for Axenrod synthesis of TNAZ

Process Step	Problem Material	Alternatives		
Tosylation	Pyridine	<ol> <li>Use triethylamine or other teriary amine</li> <li>Use an ion exchange resin</li> <li>Recycle HCI</li> </ol>		
Alcohol Protection	TBDMS-CI	<ol> <li>Use an alternate protecting group such as ethylene glycol</li> <li>Recycle HCI</li> </ol>		
Ring Closure	THF	<ol> <li>Use a crown ether (12-crown-4 solvates Li<sup>+</sup></li> <li>Use another ether such as diethyl ether or dimethoxyethane.</li> </ol>		
Deprotection	THF	<ol> <li>Use another polar aprotic solvent such as diethyl ether or dimethoxyethane</li> <li>Use of a solvent blend with sililar properties to THF</li> <li>Use of agitation without organic solvent</li> </ol>		
Oxidation	Chromic Acid Reagents	1) Use of CuO and heat. 2) Use Pt 3) UseMnO <sub>2</sub>		
Oxime Formation	MeOH	1) Use of water and agitation		
Nitration	Nitric Acid, Ammonium Nitrate, Urea	1) Use nitrogen pentoxide/nitric acid 2) Use nitric acid/ammonium nitrate only		

 Table 3
 Alternative suggestions for problem materials in the Axenrod process

Following the next step in the general SGM approach outline in Chapter 3, the information generated in **Table 2** was used to develop ideas in the brainwriting step. A listing of alternative solution to the problems presented in **Table 2** are displayed in **Table 3**.

After the list of alternative solutions was compiled, each of the possible alternatives was evaluated and prioritized by the "bubble-up/bubble-down" method described in Chapter 3. A prioritized list is shown in **Table 4**. For example, in the first step of the process, pyridine is used as the reaction medium for the tosylation of the starting material. It is know that other tertiary amines may be used for this purpose, but the most common substitute, triethylamine, is also a hazardous substance, therefore use of triethylamine is given a low priority. On the other hand, recycling the HCl is given a high priority, since

Process Step	Problem	Prioritized Alternatives
	Wateriai	1) Recycle HCl
Tosylation	Pyridine	2) Use an ion exchange resin
		3) Use triethylamine or other teriary amine
		1) Use an alternate protecting group such as
Alcohol Protection	TBDMS-CI	ethylene glycol
		2) Recycle HCI
		1) Use another ether such as diethyl ether or
Ring Closure	THF	dimethoxyethane.
		2) Use a crown ether (12-crown-4 solvates
		Li <sup>+</sup>
		1) Use another polar aprotic solvent such as
		diethyl ether or dimethoxyethane
Deprotection	THE	2) Use of a solvent blend with sililar
Deprotection		properties to THF
		3) Use of agitation without organic solvent
	Aroh	1) Use of other acid such as HCl generated in
	70011	previous steps
	Chromic Acid	1) Use CuO and heat
Oxidation	Reagents	2) Use MnO <sub>2</sub>
		3) Use Pt
Oxime Formation	MeOH	1) Use of water and agitation
	Nitric Acid,	1) Lise nitrogen pentoxide/nitric acid
Nitration	Ammonium Nitrate, Urea	2) Lise nitric acid/ammonium nitrate only
		2) Ose mult actorationormalit multate only

Table 4 Prioritized list of alternatives in the Axenrod process

HCl will always be generated when tosylating the starting material, and it is relatively easy to implement. The recycled HCl may then be sold or if necessary used in another step in the process.

Another important area to address, is the use of TBDMS-Cl as a protecting group in the second step of the process. TBDMS-Cl is toxic, and its use leads to the generation of HCl and a silane waste when it is removed. It is obvious that an alternative protecting group could possibly lead to a significant waste reduction. After examining the process, it is clear that the alcohol functionality is needed since it leads to the azetidinone intermediate. This suggests a possible alternative: if the carbonyl functionality can be protected, then it would not be necessary to protect the alcohol. A common, and inexpensive method of protecting carbonyls is to use ethylene glycol. This is a good alternative since it can be accomplished in aqueous solution and the byproduct of the protection is water. The problem is that the product of the first step (the tosylation) is an alcohol not a ketone. The solution is to perform the oxidation step <u>before</u> protection. Whereas the original process followed a protection  $\rightarrow$  ring-closure  $\rightarrow$  deprotection  $\rightarrow$  oxidation route, the alternative route using ethylene glycol would follow an oxidation  $\rightarrow$  protection  $\rightarrow$  ring-closure  $\rightarrow$  deprotection  $\rightarrow$  protection  $\rightarrow$  ring-closure  $\rightarrow$  deprotection  $\rightarrow$  protection  $\rightarrow$  ring-closure  $\rightarrow$ 

This new process may also lead to further waste minimization in the replacement of the chromium reagents used in the original oxidation. This is important because chromium is a water soluble carcinogen and is an expensive material as well. Catalytic oxidation by CuO and air is often used in industrial oxidations since it is inexpensive. Unfortunately, it requires harsh conditions (the intermediate contacts CuO at high temperature) which may decompose the organic intermediate. It is known that this technique was tried in the original process [6], but the strained azetidine ring would decompose. It is possible that since the oxidation in the revised process occurs before the ring-closure, this intermediate may survive the high temperature conditions. If the oxidation cannot be carried out with CuO, other alternatives such as  $MnO_2$ , though it is preferentially used to oxidize allylic alcohols, or platinum, which is expensive but works under milder conditions, may be tried. Replacement of the oxidation step with any of these reagents also elminates the need to use sulfuric acid.

Implementing all of the prioritized alternatives results in a new process map, Figure 4, which leads to a new synthetic route, Scheme 8. The optimal reaction conditions have been left out of Scheme 8. Determination of these optimal reaction conditions as well as the applicability of the suggested modifications requires verification in the laboratory and scale-up.



Figure 4 Process map for our suggested revision of the Axenrod synthesis of TNAZ



Scheme 8 Our proposed revision of the Axenrod synthesis of TNAZ

#### 4.2 Examination of the Coburn-Hiskey Process

After consulting with the researchers at Picatinny Arsenal, we were informed that development of TNAZ (**3**) had proceeded to pilot-plant scale using the Coburn-Hiskey (Los Alamos) process and that much work had been done to increase yields and "clean up" the process. Nevertheless, we applied the general SGM methods to the process as presented in the patent. Ideally, this should lead to the same conclusions generated. The process map for the original process is presented in **Figure 3**. **Table 5** shows the functions of the materials targeted in the waste minimization analysis, and **Table 6** is the prioritized list of alternatives generated during the "brain writing" and "bubble-up / bubble-down" phases.

Process Step	Problem Material	Function	
<b>Oxime Formation</b>	Dimethoxyethane	Used as a reaction media and solvent	
Ring Opening	Ethanol	Used as a solvent	
	Formaldehyde	Byproduct of reaction	
		Used to initiate nucleophilic attack by the	
Ring Closure	DEAD / PPh <sub>3</sub>	weak base (R <sub>2</sub> N ) on a carbon with a poor leaving group (OH)	
First Nitration	Methanol / NaOMe	Used as a base and solvent for deformulation	
	Formaldehyde	Byproduct of reaction	
De-alkylation	Benzyl Chloroformate	Used to convert the t-butyl functionality to a funtionality that can be easily removed	
	Nitric Acid,		
Final Nitration	ZnCl <sub>2</sub> , Acetic Anhydride	Source of NO₂ <sup>+</sup>	

Table 5 Problem materials and their function in the Coburn-Hiskey process





Process Step	Problem Material	Prioritized Alternatives
<b>Oxime Formation</b>	Dimethoxyethane	1) Use an aqueous base solution
	Ethanol	2) Use water
Ring Opening	Formaldehyde	<ol> <li>Recycle the formaldehyde as a raw material</li> </ol>
Bing Closure		1) Tosylate the hydroxyls so that they are
	DEAD / FFII3	better leaving groups
First Nitration	Methanol / NaOMe	<ol> <li>Use an aqueous base solution</li> <li>Use the solvent from the Ring Closure step</li> </ol>
	Formaldehyde	<ol> <li>Recycle the formaldehyde as a raw material</li> </ol>
De-alkylation	Benzyl Chloroformate	1) De-alkylate by direct nitrolysis
	Nitric Acid, ZnCl <sub>2</sub> ,	1) Use HNO <sub>3</sub> only
Final Nitration	Acetic Annhydride	2) Use HNO <sub>3</sub> / N <sub>2</sub> O <sub>5</sub>
	Ammonium Nitrate	3) Use HNO <sub>3</sub> / NH <sub>4</sub> NO <sub>3</sub>

Table 6 Prioritized list of alternatives in the Coburn-Hiskey process

The process map shows many potential waste elimination opportunities. It was immediately noted that the de-alkylation step is unnecessary and can be eliminated entirely, the final product being accomplished through direct nitrolysis of **27**. Through the literature research that was conducted earlier, it was established that a simple alkyl group (such as a t-butyl group) can be replaced by a nitro group through nitrolysis with nitric acid and ammonium nitrate. [8] By proceeding directly from **27** to **3**, the use of the benzyl chloroformate, triflouromethanesulfonate, zinc(II) chloride and the solvents involved in the additional reactions of the original method can be eliminated, resulting in a substantial reduction of waste and cost. Additionally, this immediately shows that, as suggested in **Table 6** as an alternative to the original nitration mixture, a simpler nitration mixture may be used to accomplish the final nitration.

The original method begins by the formation of an oxazine **37** by reaction of nitromethane with formaldehyde and *t*-butylamine in dimethoxyethane. This reaction and the subsequent ring opening can be conducted in an aqueous solution, thereby eliminating the use of two solvents: dimethoxyethane and ethanol. The net result is that the first three

steps of the synthesis can be conducted in water, and since there is no need for separation or extraction, can be carried out as a "one pot" process. This greatly simplifies the process. Also the formaldehyde produced in this step and in the first nitration step should be recycled so that it can be reused as a starting material.

To form the dinitroazetidine (the precursor to TNAZ (**3**)), 1-*tert*-butyl-3hydroxymethyl-3-nitroazetidine needs to be deformylated and nitrated. Originally, sodium methoxide in methanol is used as the base for deformylating, but the deformylation can also be accomplished with sodium hydroxide and performed in the same reaction vessel as the ring closure once the Mitsunobu reagents are removed.

Therefore, the only remaining step in the process which is not conducted in an aqueous solution is the Mitsunobu reaction used in the ring closure and the first nitration. Without the Mitsunobu reaction, the ring closing would involve nucleophilic substitution of a very poor leaving group (OH), by a weak nucleophile, which will not occur. The Mitsunobu reagents strengthen the nucleophile and make the leaving group more labile. Tosylation of the alcohols, followed by ring closure with potassium carbonate or lithium hydride as in the Axenrod Process may be a viable alternative. This alternative would require the protection of the amine functionality by forming a carbamate by reaction with benzyl chloroformate before tosylation. This would be followed by removal of the carbamate with  $H_2/Pd$ , and ring closure with potassium carbonate. The removal of the extra tosylate and the subsequent deformylation can both be accomplished with sodium hydroxide. Laboratory verification of these suggestions has not yet been conducted. A process map including the suggested modifications is shown in **Figure 6.** Our reaction sequence incorporating further changes to Coburn-Hiskey's own modified scheme (Scheme 7) is shown in Scheme 9.

It is important to note that the synthetic routes of common reagents have not been examined. Certainly, the life cycle waste generation in their production should also factor into any decision making process.



Figure 6 Process map for our suggested revision of the modified Coburn-Hiskey synthesis of TNAZ



Scheme 9 Our proposed revision of Coburn-Hiskey's modified (scale-up) synthesis of TNAZ

#### **CHAPTER 5**

#### CONCLUSIONS AND RECOMMENDATIONS

As shown in Chapter 4, the general SGM approach developed in Chapter 3 yields intriguing results. In the Axenrod Process, an entirely new approach was devised which shows promise for reducing acid wastes, eliminating the use of some of the toxic organic solvents (pyridine) and replacing two toxic reagents, chromium oxide and TBDMS-Cl with CuO and ethylene glycol. When the approach was applied to the Coburn-Hiskey process, the results generated were in line with the waste minimization measures that have been implemented in the pilot plant. Additionally, except for laboratory and pilot plant verification, the approach generates these potential SGM alternatives quickly and efficiently.

As stated earlier, further study is needed. Testing of the suggested modification to the Axenrod and Coburn-Hiskey processes needs to be conducted on a laboratory scale. If promising results are obtained, then scale-up of the modifications can proceed. Of course, if a suggested alternative does not yield the desired results, other alternatives need to be tried. For example, in addition to the possibility of replacing the Mitsunobu reaction with a tosylation to accomplish the ring closure in the Coburn-Hiskey process, other methods of converting the alcohol to a better leaving group (such as forming a triflate) can be tried. It has also been shown that azetidines can sometimes be formed from halogenated intermediates. [25]

As a result of this research, it is recommended that the experimental procedures suggested be tried in the laboratory. It appears possible that concrete recommendations for the sustainable green manufacturing of TNAZ (3) can be developed in less than a year. This would be followed by an economic comparison of the envisioned new process with the existing pilot plant.

Although the TNAZ (3) was used as a case study to illustrate the application of the methods developed, it bears noting that these same methods can be applied to any laboratory synthesis route of future energetic materials or other chemicals. Most importantly, laboratory researchers seeking to develop new materials should approach their research with a similar methodology, thereby producing sustainable green synthetic procedures. Often the synthetic chemist is concerned only with obtaining the final product. Yet, as the level of concern for the environmental consequences associated with the production of new materials increases, the importance of designing new syntheses which take into account factors such as waste, the environment, and sustainability also increases. By applying ideas such as process mapping and brainwriting, the development of new materials can be designed green and sustainable from the laboratory phase right through development and commercialization.

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