WASTE MINIMIZATION THROUGH EFFECTIVE CHEMICAL ENGINEERING

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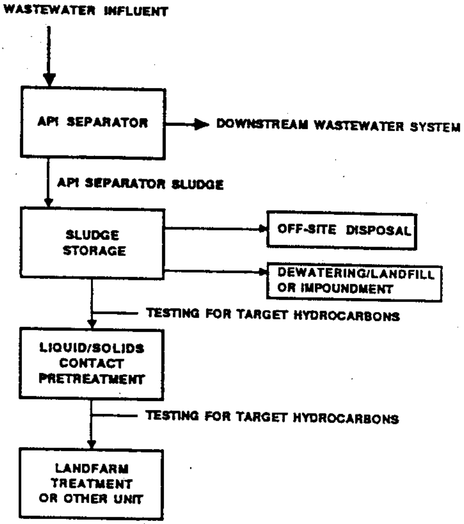
Successful waste minimization programs have existed since the early 1970's when they were part of prudent environmental management philosophies. These successful programs provide a blueprint for developing waste minimization programs because they have several elements in common including (1) Management commitment to encourage design and operating personnel to change the way waste generation is viewed so that it becomes an additional part of their jobs, (2) Defining the true source of wastes by examining processes from the point of view of discharges and (3) Applying effective chemical engineering principles to balance and integrate source control options with terminal treatment alternatives to optimize capital expenditures to meet short- and long-term environmental objectives.

This paper will describe a proven approach for waste minimization and how this approach was used to minimize the formation of isobutylene as an unwanted by-product from a process in which t-butyl alcohol was used to block a reactive site during a multi-step synthesis of an organic chemical. The emissions of isobutylene were reduced from three different process steps by identifying process conditions which (1) reduced the formation of isobutylene so that add-on emission controls were not needed and (2) significantly increased process yields of the desired products. The results from all three process steps are excellent illustrations of the concept that the formation of an unwanted by-product is not necessarily inevitable. Knowing why and how a by-product was formed led directly to the identification of methods to reduce the formation of the by-product.

FIGURE THREE-TREATMENT SCHEMATIC



Introduction

In the 1984 RCRA Reauthorization Bill, the U.S. Congress "declared it to be national policy of the United States that, wherever feasible, the generation of hazardous waste is to be reduced or eliminated as expeditiously as possible. Waste that is nevertheless generated should be treated, stored, or disposed of so as to minimize the present and future threat to human health and the environment."

Waste minimization technologies are available for two types of wastes: materials currently generated by industries that produce or use chemicals and accumulations of previously generated wastes.

Wastes currently produced can be minimized by applying resource recovery/source control (RR/SC) technologies as cost-effective alternatives to end-of-the-pipe treatment. Wastes generated by remediating remnants from previous disposal practices can be minimized by using mobile technologies and equipment to reduce the volume and/or toxicity of wastes that must be hauled off site. This paper addresses currently produced wastes.

Implementing this policy will require that firms reduce the volume and toxicity of hazardous wastes by applying effective chemistry and chemical engineering principles similar to those used by companies that manufacture chemicals. Indeed, the concept of waste minimization did not begin with the 1984 RCRA Amendments. Waste minimization has been an integral part (albeit sometimes a subtle part) of the function of many chemical engineers and chemists when they have designed, constructed, operated, and retrofitted chemical production processes. This means that the chemical engineers and chemists with industrial experience will be the most qualified professionals to implement waste minimization because they can best understand the sources of the wastes.

Waste minimization concepts and programs have had various titles over the years. They include waste reduction, waste minimization, source control, resource recovery, pollution prevention, and pollution control at the source. Many papers have been presented describing the methodology and benefits of waste minimization.[1,2,3] Even though the methodology was developed in the early 1970s as an extension of the effective chemical engineering approaches used by the chemical industry, this methodology is just as applicable today.

Elements of a Waste Minimization Program

The elements of successful waste minimization programs include:

- Management commitment to convince production personnel and process design engineers that considering process changes to reduce the generation of wastes and control pollution at the source is an important part of their jobs.

- Problem definition to establish the environmental and economic impact of existing discharges by examining processes from the point of view of process discharges (sewers, vents, or liquid/ solid residues) rather than products.

- Process definition to conceptualize and evaluate simple, as well as sophisticated, techniques for reducing waste formation.

- Implementation to develop, design, and install process modifications and/or recovery and treatment systems.

These elements are discussed below.

Management Commitment

Management commitment is as important to a successful waste minimization program as it is to successful safety, quality, energy reduction or cost savings programs. In order to be successful, all of these programs usually require directives from management to encourage personnel to incorporate increased attention to these topics in their everyday jobs. For waste minimization, enthusiastic endorsement by management is often required to help people overcome the widespread opinion that no further improvements can be made to "mature" processes. Although resistance to considering process changes is often encountered, it often dissipates when the benefits that can accrue are recognized.

Problem Definition

A key element of an effective waste minimization program is to identify and define the waste problems before trying to solve them. The objective of problem definition is to determine the true sources of waste, i.e., whether they are related to the process chemistry or the way the process is engineered, operated, or maintained.

It is important to note that problem definition goes beyond a normal waste characterization which only determines "What and How Much" wastes are generated. Problem definition should also include determination of "How, Why, and When" wastes are generated in order to identify the true source of waste. The benefits of determining "How, Why, and When" wastes are generated (the difference between problem definition and a simple waste characterization) can be illustrated by a frequently encountered example concerning organic solvent losses. Calculated losses of solvents from known discharges often do not account for known consumption based on inventory and purchasing records. When the process is observed and reviewed from the specific viewpoint of discharges, the location and nature of previously unidentified losses can frequently be determined. Defining the problem (i.e., the location and nature of the losses) can make determining and then implementing the solution straightforward.

Understanding the environmental impact of existing and future production practices necessarily includes an assessment of the location, cost, and risk of current and future disposal operations.

The output of the problem definition step is a summary of the economic and environmental impacts of the process that was reviewed. This summary provides the basis for prioritizing the process definition activities so that the most significant problems are addressed first.

Process Definition

The selection of the optimum approach for managing a waste is usually based on a technical and economic evaluation of one or more alternatives.

For both currently generated and previously generated wastes, the alternatives usually fall into one of the following categories:

- Evaluate the capabilities of existing terminal treatment system versus the requirements

- Evaluate requirements for additional terminal treatment facilities

- Define on-site waste reduction options

- Analyze the cost/benefit of waste reduction versus terminal treatment.

For previously generated wastes, on-site waste reduction options are limited to changing the character of the wastes to reduce their volume or toxicity. For wastes generated by currently operating processes, additional RR/SC opportunities to change the process frequently can be identified based on the results of the problem definition. They usually fall into one of the following categories:

- Improvements requiring only equipment repairs or changes in operating procedures which become obvious after the specific source of discharge has been defined. Improved phase separations are one example.

- Simple improvements in operating procedures which require some form of simple testing. Reuse of kettle washes as the makeup water for the next batch or minor modification of a recipe to reduce the amount of excess raw material are two examples.

- Process changes requiring significant development work and/or capital expenditures. Providing additional capacity for chemical reaction, distillation, extraction, or stripping is an example. Another example is recovery of lost product which may require extensive testing to verify proper separation from unwanted by-products.

- Addition of an extra system to reduce the discharge of a specific component at the source. Separation and recovery of a valuable material or oxidation of a troublesome component are two examples.

Implementation

The activities to design, permit, construct and start up process modifications to reduce the generation of wastes from currently operating processes are well known in the chemical industry and need not be described in this paper. Dealing with remnants from past disposal practices provides another opportunity to apply effective chemical engineering techniques. Frequently the volume and/or toxicity of the wastes transported off site can be reduced by using mobile process equipment to assemble a temporary treatment process on site. Mobile treatment technologies will be discussed later.

Case History

Although few would argue with the overall concept that minimizing wastes is a prudent way to operate chemical plants, the value of this concept and ways to implement it can be illustrated through case histories. Our experiences over the last 16 years have shown that there are many fertile areas for reducing wastes through effective chemical engineering. These fertile areas include:

- Purer raw materials
- Improved liquid/liquid separation
- Improved solid/liquid separation
- Segregation
- Debottlenecking equipment to improve performance
- Vacuum system
- Countercurrent washing
- Leaking pump seals

Although numerous examples are available for each area, we would like to describe a more sophisticated case history which involves a series of process changes that eliminated the need for an emission control system.

Controlling Isobutylene Emissions via RR/SC

During the comprehensive problem definition, three significant sources of isobutylene emission from one organic synthesis process were identified. Isobutylene is a significant air pollutant because, as an unsaturated hydrocarbon, it is photochemically reactive and has been identified as an ingredient of smog-forming compounds. Figure 1 illustrates the batch process steps which were identified as isobutylene emission sources.

As shown in Figure 1, this process consisted of four batch operations. In the first reaction, a t-butyl group supplied by t-butyl alcohol was added to temporarily block an active site on the primary molecule (W) during the second reaction. Following the second reaction, from which no significant emissions were detected, the t-butyl group was removed as t-butyl chloride by hydrolysis with HCl. The recovered t-butyl chloride was then hydrolyzed to recover the t-butyl alcohol which was recycled to the first reaction step. The isobutylene formed in three of the four steps resulted from the decomposition of t-butyl alcohol and t-butyl chloride.

The characterization of the emissions not only identified three significant air pollution sources but also pinpointed the sources of most of the t-butyl lost from the process which resulted in substantial t-butyl alcohol makeup requirements in Step 1. (Part of the t-butyl loss was identified during the characterization of liquid waste effluents from the process.)

Since it was not anticipated that the emissions could be totally eliminated through source process changes, the following alternative solutions were considered: (1) installation of piping to collect and transfer isobutylene to the steam generation plant for combustion in the boilers, or (2) the installation of a recovery process to either generate purified isobutylene for resale, or to convert isobutylene to t-butyl alcohol for use in the process. The capital cost for the installation of a t-butyl alcohol recovery process (the most attractive alternative) was estimated at approximately $200,000.

The initial thrust of this project was to characterize the isobutylene emissions from the three batch processes in order to define the design bases for an isobutylene emission control system. Since isobutylene was not an inevitable by-product of the process, it was hoped that an additional benefit of this project would be the identification of operating conditions that would reduce the quantity of isobutylene generated.

First Reaction. This step combined three liquid components: concentrated sulfuric acid, t-butyl alcohol, and W, the product from the previous step. The temperature of the mixture was raised and the elevated temperature maintained for a period to "ensure completeness of the reaction." The characterization of emissions from the plant operation indicated that most of the isobutylene was emitted as the temperature of the batch was increased, and emissions continued at a lower rate throughout the hold period.

Laboratory scale tests discovered that the reaction:

$$W + TBA \rightleftarrows X$$

was significantly reversible and that although higher temperatures accelerated the achievement of equilibrium, acceptable reaction rates could be achieved even if the reactor were not heated. The tests also showed that higher temperatures and extended hold times increased the conversion of t-butyl alcohol to isobutylene. This combination of facts demonstrated that heating the reactor and holding the reactor contents not only increased the quantity of isobutylene emitted but also decreased the yield of X because the irreversible loss of t-butyl alcohol (as isobutylene) shifted the equilibrium back toward W.

When the revised conditions (lower temperature and shorter residence time) were incorporated in the plant operation, isobutylene emissions were reduced by 99 percent, primary product yield (from W) was increased from approximately 94.5 to 99.7 percent, batch cycle time was reduced from approximately 8 hours to less than 4 hours, and steam requirements were eliminated. These improvements were attained with virtually no capital expenditure.

Hydrolysis. In this operation the product from the second reaction (Y, a crystalline solid) was dissolved in HCl solution and heated to the boiling point. During the reaction, a mixture of t-butyl chloride, HCl, water vapor, and isobutylene (formed from the decomposition of t-butyl chloride) was vented from the reactor as an overhead vapor stream. Heating of the reactor was continued until the reaction was essentially complete and all the t-butyl chloride formed was vaporized. The overhead vapor passed through water- and brine-cooled condensers in series, condensing most of the t-butyl chloride, HCl, and water vapor.

The characterization of emissions showed a pattern similar to the first reaction, where the emissions were high as the reaction mixture was heated, and then more moderate once the maximum temperature had been attained.

A series of laboratory experiments were conducted, aimed simultaneously at reducing emissions and increasing primary product yield. The most favorable combination of conditions found was:

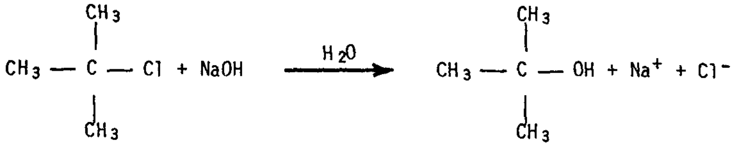
- Higher HCl concentration (higher normality and mole ratio to the primary reactant)
- Slower heating rate
- Lower final temperature
- Shorter residence time at maximum temperature.

When these changes were incorporated in the plant operation,

- Isobutylene emissions were virtually eliminated and the yield of Z was increased by 8-10 percent.
- T-butyl chloride yield from this step was increased equivalent to the reduction in isobutylene loss.

In contrast to both the first reaction (t-butyl addition) and the TBA recovery, there is no direct relationship between primary product (Z) yield and isobutylene emissions from this step. It was fortunate, in this case, that the conditions which were found to be favorable for minimum isobutylene emission and maximum t-butyl chloride yield (i.e., high HCl concentration, lower temperature) were compatible with the conditions which improved primary product yield (i.e., higher initial HCl concentration, slower heating rate, shorter residence time, and lower temperature).

<u>TBA Recovery</u>. In this operation the t-butyl chloride formed in the hydrolysis step was converted to t-butyl alcohol, as shown by the following summary equation:



$$CH_3 - \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}} - Cl + NaOH \xrightarrow{H_2O} CH_3 - \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}} - OH + Na^+ + Cl^-$$

In the original process, after transferring t-butyl chloride to a jacketed, stirred reactor, a slight stoichiometric excess of NaOH was added, resulting initially in a strongly basic water phase in the two-phase mixture. The solution was heated to the boiling point (initially 50°C) and was then refluxed until conversion of the t-butyl chloride was complete. Laboratory tests focussed on determining the effect of pH on the conversion of t-butyl chloride to t-butyl alcohol, because information from the literature indicated that a pH of 7 or less was more favorable for the formation of the intermediate t-butyl carbonium ion. The literature also indicated that high pHs would enhance the formation of isobutylene. The results showed that although a stoichiometric quantity of NaOH was required to complete the reaction, order of addition and the rate of NaOH addition was critical. If NaOH were added at a controlled rate to maintain the pH between 1 and 2, the reaction would proceed rapidly at ambient temperature. These conditions strongly favored the formation of t-butyl alcohol, in preference to isobutylene, almost eliminating isobutylene formation. As pH was increased, the reaction rate became much slower, requiring higher temperatures for practical reaction times and causing increased isobutylene formation.

When the most favorable conditions as determined from the laboratory experiments (pH 1-2, temperature 30-35°C) were incorporated in the plant operation, the emission of isobutylene was almost entirely eliminated and the yield of t-butyl alcohol was increased. The only capital requirement for the revised process was the installation of a pH control loop.

This case history vividly demonstrated that even though this organic synthesis was a mature process, product yields could still be increased, and the generation of an unwanted by-product was not inevitable. Understanding the conditions under which isobutylene was created identified three different, easily implemented, and obvious chemical engineering solutions. These three solutions eliminated the need for an expensive air pollution control device with concurrent savings of $500,000 a year in operating costs at a total capital cost of less than $50,000.

Summary

The objective of a waste minimization program should be to optimize capital expenditures required to meet short- and long-term environmental objectives and to minimize future liabilities. For currently operating plants, this objective is met by integrating and balancing in-plant RR/SC options with terminal treatment alternatives. For previously generated wastes, on-site treatment options to reduce the volume or toxicity should be compared to off-site treatment and disposal alternatives.

Our experience as well as the experiences of other successful waste reduction programs in the chemical industry have shown that (1) the production of waste is not necessarily inevitable and (2) defining the <u>true</u> source of the waste is the critical step in considering ways to reduce the formation of waste.

We hope that this paper will help stimulate managers in the chemical industry to direct their staffs to seriously consider waste minimization and the technical staffs to create their own successful case histories by examining their processes from the perspective of the waste streams.

References

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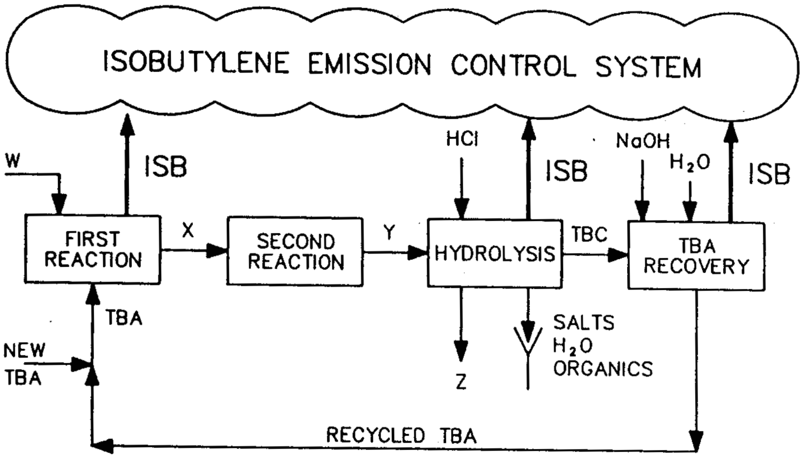

FIGURE 1
ORGANIC CHEMICAL SYNTHESIS