Inherently Safer Process Design Strategies

Dennis C. Hendershot

Senior Technical Fellow
Rohm and Haas Company
Process Hazard Analysis and
Environmental Engineering Department
Engineering Division
P. O. Box 584
Route 413 and State Road
Bristol, PA 19007
U. S. A.

EMail: nagdh@rohmhaas.com
or dchendershot@hotmail.com

For presentation at the
Israel Institute of Petroleum and Energy Conference
Herzlia, Israel
5-6 May 1999

17 July, 1999

Inherently Safer Process Design Strategies

Dennis C. Hendershot
Rohm and Haas Company
Bristol, Pennsylvania, USA

ABSTRACT

There are four strategies for the development of inherently safer chemical manufacturing processes: Minimize, Substitute, Moderate, and Simplify. A few examples of each strategy are given to aid in understanding how that strategy can result in an inherently safer process.

Introduction

Approaches to inherently safer chemical process design have been categorized in many different ways. For purposes of this discussion, the categories described by the Institution of Chemical Engineers and the International Process Safety Group (IChemE and IPSG, 1995) and the Center for Chemical Process Safety (Bollinger, et. al., 1996) will be used. Strategies for inherently safer design can be considered as falling into four areas:

Minimize	Use small quantities of hazardous substances
Substitute	Replace a material with a less hazardous substance
Moderate	Use less hazardous conditions, a less hazardous form of a material, or facilities which minimize the impact of a release of hazardous material or energy
Simplify	Design facilities which eliminate unnecessary complexity and make operating errors less likely, and which are forgiving of errors which are made

A number of examples or each of these strategies will be discussed. Kletz (1991, 1998), IChemE and IPSG (1995), and Bollinger, et. al. (1996) provide many additional examples.

Minimize

To minimize is to reduce the quantity of material or energy contained in a manufacturing process or plant. Another common term for “minimize” is intensify, and there are many literature references for process intensification. We often think of process minimization as resulting from the application of innovative new technology to a chemical process — for example, tubular reactors with static mixing elements, centrifugal distillation techniques, or innovative, high surface area heat exchangers. However, plant inventories of hazardous material can be reduced significantly by applying good engineering principles with conventional technology. When designing a plant, every piece of process equipment should be specified to be large enough to do its job, and no larger. Minimize the size of raw material and in-process intermediate storage tanks, and question the need for in-process storage of hazardous materials.

Reactors

Reactors are often the major contributors to risk from a chemical process. A complete understanding of reaction mechanism and kinetics is essential to the optimal design of a reactor system. This includes both chemical reactions and mechanisms, as well as physical factors such as mass transfer, heat transfer, and mixing. A reactor may be large because the chemical reaction is slow. However, in many cases the chemical reaction actually occurs very quickly, but it appears to be slow due to inadequate mixing and contacting of the reactants. Innovative reactor designs which improve mixing may result in much smaller reactors. Such designs are usually cheaper to build and operate, as well as being safer due to smaller inventory. In many cases, improved product quality and yield also result from better and more uniform contacting of reactants. With a thorough understanding of the reaction, the designer can identify reactor configurations that maximize yield and minimize size, resulting in a more economical process, reducing generation of by-products and waste, and increasing inherent safety by reducing the reactor size and inventories of all materials.

Continuous Stirred Tank Reactors. A continuous stirred tank reactor (CSTR) is usually much smaller than a batch reactor for a specific production rate. In addition to reduced inventory, using a CSTR usually results in other benefits which enhance safety, reduce costs, and improve the product quality. For example:

- Mixing in the smaller reactor is generally better. Improved mixing may improve product uniformity and reduce by-product formation.
- Controlling temperature is easier and the risk of thermal runaway is reduced. Greater heat transfer surface per unit of reactor volume is provided by a smaller reactor.

- Containing a runaway reaction is more practical by building a smaller, but stronger, reactor rated for higher pressure.

Tubular Reactors. Tubular reactors often offer the greatest potential for inventory reduction. They are usually extremely simple in design, containing no moving parts and a minimum number of joints and connections. A relatively slow reaction can be completed in a long tubular reactor if mixing is adequate. There are many devices available for providing mixing in tubular reactors, including jet mixers, eductors, and static mixers.

Loop Reactors. A loop reactor is a continuous steel tube or pipe which connects the outlet of a circulation pump to its inlet (Figure 1). Reactants are fed into the loop, where the reaction occurs, and product is withdrawn from the loop. Loop reactors have been used in place of batch stirred tank reactors in a variety of applications including chlorination, ethoxylation, hydrogenation, and polymerization. A loop reactor is typically much smaller than a batch reactor producing the same amount of product. Wilkinson and Geddes (1993) describe a 50 liter loop reactor for polymerization process which has a capacity equal to that of a 5000 liter batch reactor.

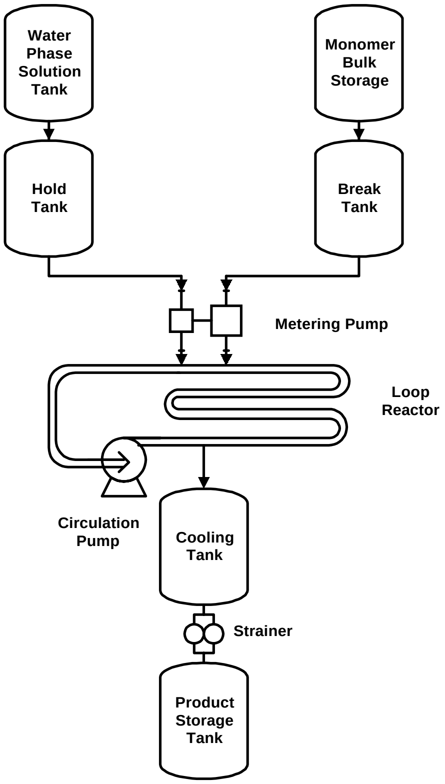

Figure 1: A Loop Polymerization Reactor System (Wilkinson and Geddes, 1993)

Reactive Distillation

Reactive distillation is a technique for combining a number of process operations in a single device. One company has developed a reactive distillation process for the manufacture of methyl acetate which reduces the number of distillation columns from eight to three, also eliminating an extraction column and a separate reactor (Agreda, et al, 1990; Doherty and Buzad, 1992; Siirola, 1995). Inventory is reduced

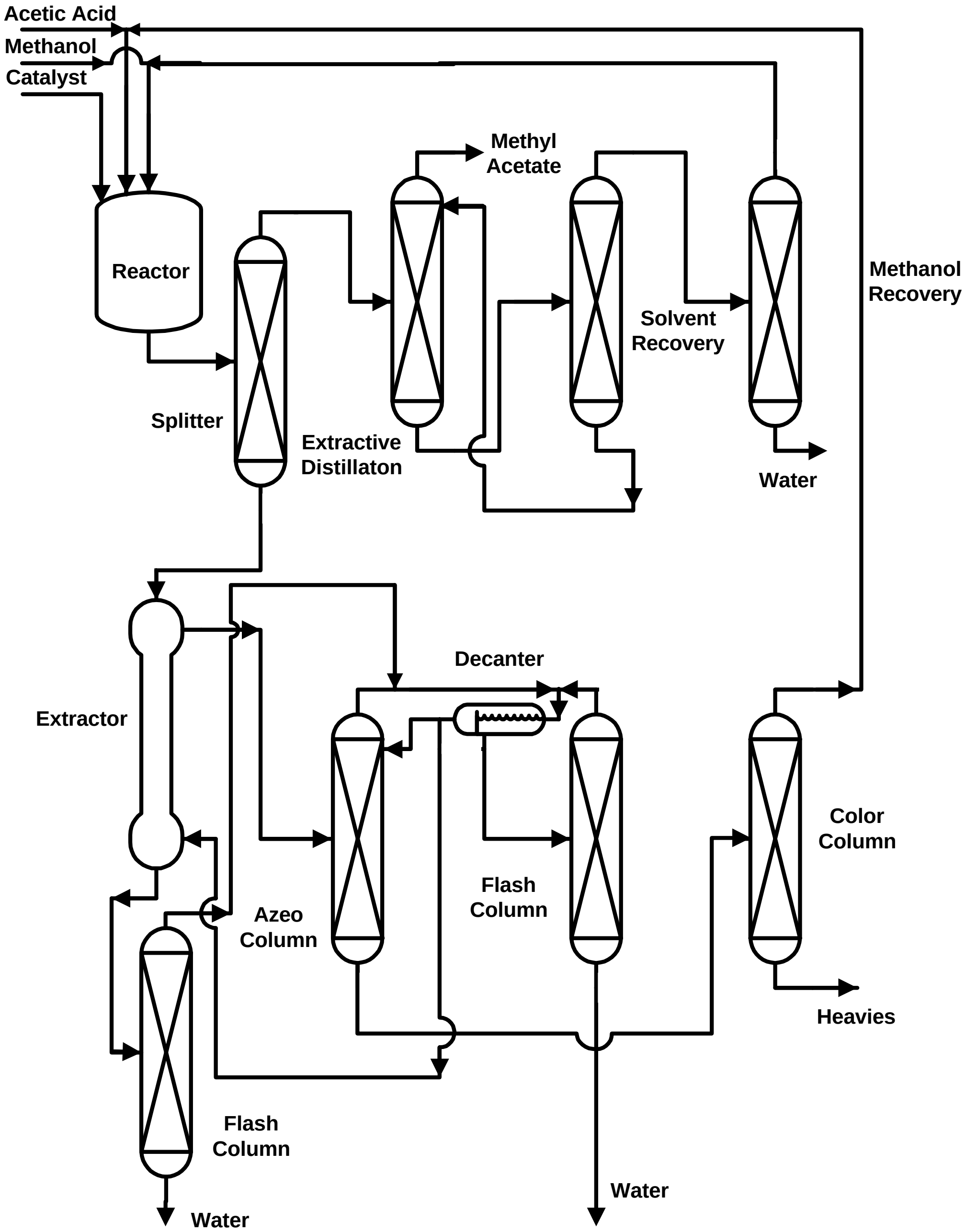

Figure 2: Conventional Design for Manufacture of Methyl Acetate (Based on Siirola, 1995)

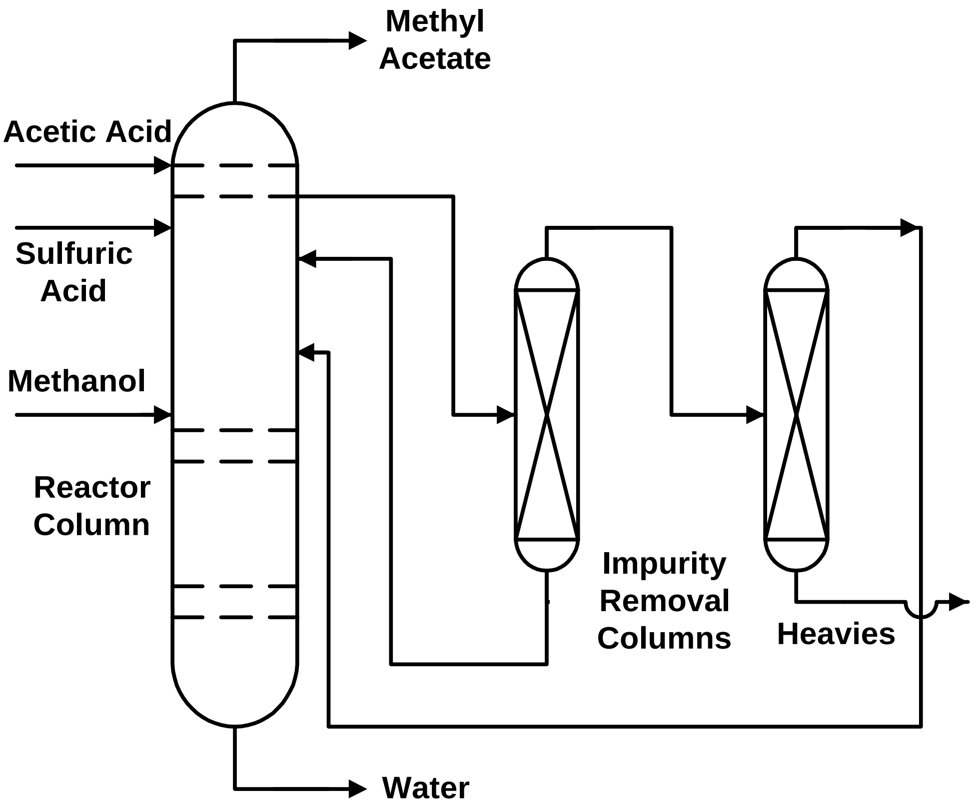

Figure 3: Reactive Distillation Process for Manufacture of Methyl Acetate
(based on Agreda, et. al., 1990)

and auxiliary equipment such as reboilers, condensers, pumps, and heat exchangers are eliminated. Figure 2 shows the conventional design, and Figure 3 shows the reactive distillation design.

Substitute

Substitution means the replacement of a hazardous material or process with an alternative which reduces or eliminates the hazard. Process designers, line managers, and plant technical staff should continually ask if less hazardous alternatives can be effectively substituted for all hazardous materials used in a manufacturing process. Examples of substitution in two categories are discussed - reaction chemistry and solvent usage. There are many other areas where opportunities for substitution of less hazardous materials can be found, for example, materials of construction, heat transfer media, insulation, and shipping containers.

Reaction Chemistry

Basic process chemistry using less hazardous materials and chemical reactions offers the greatest potential for improving inherent safety in the chemical industry. Alternate chemistry may use less hazardous raw material or intermediates, reduced inventories of hazardous materials, or less severe processing conditions. Identification of catalysts to enhance reaction selectivity or to allow desired reactions to be carried out at a lower temperature or pressure is often a key to development of inherently safer chemical synthesis routes. Some specific examples of innovations in process chemistry which result in inherently safer processes include:

- The Reppe process for manufacture of acrylic esters uses acetylene and carbon monoxide, with nickel carbonyl catalyst having high acute and chronic toxicity, to react with an alcohol to make the corresponding acrylic ester:

  $$CH \equiv CH + CO + ROH \xrightarrow[HCl]{Ni(CO)_4} CH_2 = CHCO_2R$$

  The propylene oxidation process uses less hazardous materials to manufacture acrylic acid, followed by esterification with the appropriate alcohol (Hochheiser, 1986):

  $$CH_2 = CHCH_3 + \frac{3}{2}O_2 \xrightarrow{Catalyst} CH_2 = CHCO_2H + H_2O$$

  $$CH_2 = CHCO_2H + ROH \xrightarrow{H^+} CH_2 = CHCO_2R + H_2O$$

- The chemistry of side reactions and by-products may also offer opportunities for increasing the inherent safety of a process. For example, a process involving a caustic hydrolysis step uses ethylene dichloride (EDC, or 1,2-dichloroethane) as a solvent. Under the reaction conditions a side reaction between sodium hydroxide and EDC produces small but hazardous quantities of vinyl chloride:

  $$C_2H_4Cl_2 + NaOH \longrightarrow C_2H_3Cl + NaCl + H_2O$$

  An alternative non-reactive solvent has been identified which eliminates this hazard (Hendershot, 1987).
- New chemical synthesis procedures have been proposed as safer and more environmentally friendly manufacturing routes. For example:

  - Phase transfer catalysis, which may reduce or eliminate the need for hazardous organic solvents, and may allow the use of less hazardous reactants (Tavener and Clark, 1997).
  - Supercritical processing, allowing the use of less hazardous solvents such as carbon dioxide or water in chemical reactions.

- Solid superacid catalysts, proposed as replacements for catalysts such as hydrogen fluoride and aluminum chloride for processes such as alkylation and acylation.
- New catalysts which improve the yield and selectivity of chemical reactions, resulting in smaller reactors and other processing equipment (Sheldon, 1997). Another important benefit is that product is of higher purity, reducing the size of downstream equipment to purify the product, or perhaps even eliminating the need to purify the reactor product at all.
- Other new chemical synthesis technologies such as electrochemical techniques, enzymatic synthesis, biocatalysis, domino reactions, and laser light "micromanaged" reactions are being investigated in the laboratory and offer potential future inherently safer industrial processes.

Bollinger, et. al. (1996) and Hendershot (1998) discuss these and other examples of chemical approaches to inherent safety, and provide many literature references. A United States Environmental Protection Agency report (Lin, et al, 1994) contains an extensive review of inherently safer process chemistry options which have been discussed in the literature.

Solvents

Replacement of volatile organic solvents with aqueous systems or less hazardous organic materials improves safety of many processing operations and final products. Some examples of solvent substitutions include:

- Water based paints and adhesives, replacing solvent based products.
- Less volatile solvents with a higher flash point, used for agricultural formulations. In many cases, aqueous or dry flowable formulations for agricultural chemicals may be used instead of organic formulations.
- Aqueous and semi-aqueous cleaning systems, used for printed circuit boards and other industrial degreasing operations.

An understanding of the relationship between chemical structure and hazardous properties of materials is valuable in identifying inherently safer material substitutions. For example, hydrocarbons of higher molecular weight are generally less of a fire hazard than lower molecular weight materials of a similar structure. Benzene is a greater fire hazard than toluene, and toluene is more of a fire hazard than xylene. Similarly, longer chain aliphatic hydrocarbons are less of a fire hazard than shorter chain materials. Structure-property relationships can be developed for toxicological and other properties, and these can provide useful guidance in selecting potential alternate materials for use in a chemical manufacturing process. For example, DeVito (1996) reviews relationships between chemical structure and toxicological effects, with the objective of using this knowledge to design safer chemicals. Ashby and Paton (1993) discuss the relationship of chemical structure to carcinogenic effects in rodents and humans.

Moderate

Moderate means using materials under less hazardous conditions. This is also called attenuation. Moderation of conditions can be accomplished by physical means such as lower temperature or dilution, and by chemical means such as using a different reaction chemistry which requires less severe conditions.

Dilution

Dilution reduces the hazards associated with the storage and use of a low boiling hazardous material in two ways — by reducing the storage pressure, and by reducing the initial atmospheric concentration if a release occurs. Materials which boil below ambient temperature are often stored in pressurized systems. The pressure in the storage system can be lowered by diluting the material with a higher boiling solvent. This reduces the pressure difference between the storage system and the outside environment, reducing the rate of release in case of a leak in the system. If there is a leak, the atmospheric concentration of the hazardous material at the spill location is reduced. The reduced atmospheric concentration at the source results in a smaller hazard zone downwind of the spill.

Examples of materials which have been handled in a dilute form to reduce the risk of handling and storage include:

- Aqueous ammonia or methylamine in place anhydrous
- Muriatic acid in place of anhydrous HCl
- Sulfuric acid in place of oleum (SO_3 solution in sulfuric acid)

The area impacted by a leak of hazardous material can be reduced significantly by dilution. Figure 4 (Carrithers, et. al., 1996) shows the centerline concentration of ammonia as a function of distance for two ammonia release scenarios for both anhydrous ammonia and aqueous ammonia solution. At any given distance, the concentration is much lower for the aqueous ammonia system.

Refrigeration

Many hazardous materials, such as ammonia and chlorine, can be stored at or below the atmospheric boiling points with refrigeration. Refrigerated storage reduces the magnitude of the consequences of a release from a hazardous material storage facility in three ways:

- lower storage pressure
- reduced immediate vaporization of leaking material, and subsequent evolution of vapors from the spilled pool of liquid
- reduced or no liquid aerosol formation

Table 1 illustrates the reduction in hazard distance, as defined by the distance to the Emergency Response Planning Guideline 3 (ERPG-3) concentration, which can be obtained by refrigeration of monomethylamine (Carrithers, et. al., 1996). Marshall, et al (1995) provide a series of case studies which evaluate the benefits of refrigerated storage for six materials – ammonia, butadiene, chlorine, ethylene oxide, propylene oxide, and vinyl chloride. They conclude that "refrigerated storage is generally safer than pressurized storage" for all of the chemicals studied except ammonia. Ammonia was reported to be an exception "due to a density shift with temperature making it heavier than the surrounding air." Other materials may give similar results, and it is essential that the designer fully understand the consequences of potential incidents.

Monomethylamine Storage Temperature (°C)	Distance to ERPG-3 (500 ppm) Concentration, km
10	1.9
3	1.1
-6	0.6

Table 1: Effect of refrigeration on distance to ERPG-3 concentration for a 5.1 cm. monomethylamine pipe rupture (from Carrithers, et. al., 1996)

Less Severe Processing Conditions

Processing under less severe conditions, close to ambient temperature and pressure, increases the inherent safety of a chemical process. Some examples include:

- Improvements in ammonia manufacturing processes have reduced operating pressures. In the 1930's ammonia plants operated at pressures as high as 600 bar. In the 1950's, process improvements had reduced operating pressures to 300-350 bar. By the 1980's, ammonia processes operating in the 100-150 bar range were being built. Besides being safer, the lower pressure plants are also cheaper and more efficient (Kharbanda and Stallworthy, 1988).

- Semi-batch or gradual addition batch processes limit the supply of one or more reactants, and increase safety when compared to batch processes in which all reactants are included in the initial batch charges. For an exothermic reaction, the total energy of reaction available in the reactor at any time is minimized.
- Advances in catalysis will result in the development of high yield, low waste manufacturing processes. Catalysts frequently allow the use of less reactive raw materials and intermediates, and less severe processing conditions.

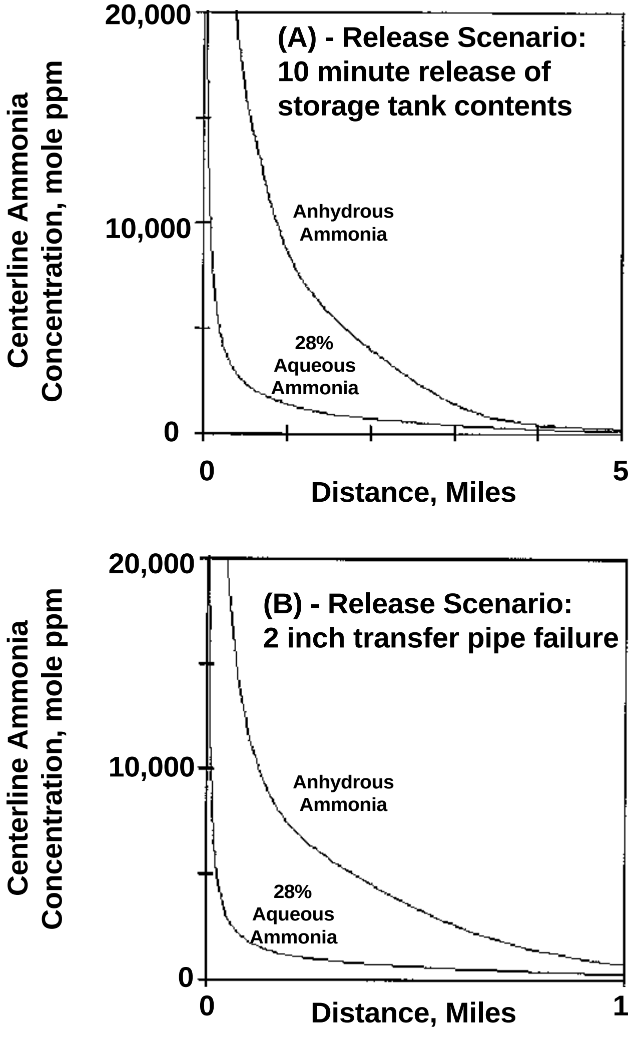

Figure 4: Comparison of centerline vapor cloud concentration as a function of distance from the release for anhydrous and 28% aqueous ammonia storage for two release scenarios (Weather - D Stability, 3.4 mph wind speed) (from Carrithers, et. al., 1996)

Simplify

Simplify means designing to eliminate unnecessary complexity, reducing the opportunities for error and incorrect operation. A simpler plant is generally safer and more cost effective than a complex one. Many of the examples discussed in the previous sections will also result in a simpler plant. For example, the reactive distillation methyl acetate process in Figure 3 greatly simplifies the plant. The processes in these examples eliminate process equipment, and also eliminate the need for complex safety interlocks and equipment.

Containment Within Process Equipment

In many cases it is possible to design process equipment strong enough to contain the maximum or minimum pressure resulting from a process incident. Containment within the process vessel simplifies the design by eliminating high pressure interlock systems. Emergency relief devices such as rupture disks or relief valves may still be required by regulations and codes, but the size may be reduced and the hazards associated with opening of the relief devices may be considered to be eliminated. Catch tanks, scrubbers, flare stacks, or other devices to dispose of the effluent from emergency relief systems safely may also be eliminated.

- **Combustion.** The maximum pressure resulting from a deflagration of a combustible dust or flammable vapor in air initially at atmospheric pressure is often less than 10 bar. It may be feasible to build equipment strong enough to contain this type of event. When designing a system for combustion containment, the engineer must consider factors such as highly reactive materials, oxygen or other oxidant enriched atmospheres, and congested geometry inside vessels or pipelines which could result in transition to detonation. All of these factors can significantly increase the maximum pressure of a combustion reaction.

- **Vacuum.** Designing vessels for full vacuum eliminates the risk of vessel collapse due to vacuum. Many storage and transport vessels have been imploded by pumping material out with the vents closed.

Reactor Geometry

Reactor geometry can limit the magnitude of potential temperature excursions in a chemical process. For example, maleic anhydride is manufactured by partial oxidation of benzene in a fixed catalyst bed tubular reactor. There is a potential for extremely high temperatures due to thermal runaway if feed ratios are not maintained within safe limits. Catalyst geometry, heat capacity, and partial catalyst deactivation have been used to create a self-regulatory mechanism to prevent excessive temperature (Raghaven, 1992).

Human Factors

The literature contains many examples of how plants can be simplified and better designed to fit with human capabilities to improve inherent safety. Kletz (1991) and Bollinger, et. al. (1996) provide many examples from the chemical industry. Norman (1988, 1992, 1994) discusses human centered design from a more broad perspective, considering issues in a range of industries and technologies.

Summary

This discussion has reviewed a few examples of the four basic strategies for implementation of inherently safer chemical processes:

- Minimize
- Substitute
- Moderate
- Simplify

There are many other examples, and those presented are intended to aid in understanding the four inherent safety strategies.

One thing that all of these examples, and others, have in common is that they have been developed based on a thorough understanding of the manufacturing process. This enables the designer to understand the factors which control the hazards of the process and identify ways of reducing and eliminating them. ***All*** hazards associated with a chemical process must be fully understood in order to make good decisions on selection of process technology. Chemical processes have multiple potential hazards, and the process designer must not fall into the trap of focusing on one particular hazard, minimizing or eliminating it, and possibly increasing or introducing another hazard of greater importance. ***There is no substitute for a full and complete understanding of how a system works.*** This understanding will allow the designer to make intelligent decisions on the selection of inherently safer process technology.

References

Agreda, V. H., L. R. Partin, and W. H. Heise (1990). “High-Purity Methyl Acetate Via Reactive Distillation.” *Chemical Engineering Progress*, (February), 40-46.

Ashby, J., and D. Paton (1993). "The Influence of Chemical Structure on the Extent and Sites of Carcinogenesis for 522 Rodent Carcinogens and 55 Different Human Carcinogen Exposures." *Mutation Research* 286, 3-74.

Bollinger, R. E., D. G. Clark, A. M. Dowell, R. M. Ewbank, D. C. Hendershot, W. K. Lutz, S. I. Meszaros, D. E. Park, and E. D. Wixom (1996). *Inherently Safer Chemical Processes: A Life Cycle Approach*, ed. D. A. Crowl. New York: American Institute of Chemical Engineers.

Carrithers, G. W., A. M. Dowell, and D. C. Hendershot (1996). “It's Never Too Late for Inherent Safety.” *International Conference and Workshop on Process Safety Management and Inherently Safer Processes*, October 8-11, 1996, Orlando, FL, 227-241. New York: American Institute of Chemical Engineers.

DeVito, S. C. (1996). "Designing Safer Chemicals: Toxicological Considerations." *Chemtech*, (November), 34-47.

Doherty, M., and G. Buzad (1992). “Reactive Distillation by Design.” *The Chemical Engineer*, (27 August), s17-s19.

Hendershot, D. C. (1987). “Safety Considerations in the Design of Batch Processing Plants.” *Proceedings of the International Symposium on Preventing Major Chemical Accidents*, February 3-5, 1987, Washington, D. C., ed. J. L. Woodward, 3.2-3.16. New York: American Institute of Chemical Engineers.

Hendershot, D. C. (1998). “Inherent Safety Strategies for Process Chemistry.” *Chemical Health and Safety* 5, 4 (July/August), 18-22.

Hochheiser, S. (1986). *Rohm and Haas: History of a Chemical Company*. Philadelphia, PA: University of Pennsylvania Press.

The Institution of Chemical Engineers (IChemE), and The International Process Safety Group (IPSG) (1995). *Inherently Safer Process Design*. Rugby, England: The Institution of Chemical Engineers.

Kharbanda, O. P., and E. A. Stallworthy (1988). *Safety in the Chemical Industry*. London: Heinemann Professional Publishing, Ltd.

Kletz, T. A. (1991). *Plant Design for Safety*. Bristol, PA, USA: Taylor & Francis.

Kletz, T. A. (1998). *Process Plants: A Handbook for Inherently Safer Design*. Bristol, PA, USA: Taylor & Francis.

Lin, D., A. Mittelman, V. Halpin, and D. Cannon (1994). *Inherently Safer Chemistry: A Guide to Current Industrial Processes to Address High Risk Chemicals*. Washington, DC: Office of Pollution Prevention and Toxics, U. S. Environmental Protection Agency.

Marshall, J., A. Mundt, M. Hult, T. C. McKealvy, P. Myers, and J. Sawyer (1995). “The Relative Risk of Pressurized and Refrigerated Storage for Six Chemicals.” *Process Safety Progress* 14, 3 (July), 200-211.

Norman, D. A. (1988). *The Psychology of Everyday Things*. New York: Basic Books.

Norman, D. A. (1992). *Turn Signals Are the Facial Expressions of Automobiles*. Reading, MA: Addison-Wesley Publishing Company.

Norman, D. A. (1994). *Things That Make Us Smart: Defending Human Attributes in the Age of the Machine*. Reading, MA: Addison-Wesley Publishing Company.

Sheldon, R. A. (1997). "Catalysis and Pollution Prevention." *Chemistry & Industry*, (6 January), 12-15.

Siirola, J. J. (1995). “An Industrial Perspective on Process Synthesis.” *AIChE Symposium Series* 91, 222-33.

Tavener, S. J., and J. H. Clark (1997). "Recent Highlights in Phase Transfer Catalysis." *Chemistry & Industry*, (6 January), 22-24.

Wade, D. E. (1987). “Reduction of Risks by Reduction of Toxic Material Inventory.” *Proceedings of the International Symposium on Preventing Major Chemical Accidents*, February 3-5, 1987, Washington, D. C., ed. J. L. Woodward, 2.1-2.8. New York: American Institute of Chemical Engineers.

Wilkinson, M., and K. Geddes (1993). “An Award Winning Process.” *Chemistry in Britain*, December, 1050-1052.