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Impact of Basic Process Chemistry Issues on Process Safety

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> "Many molecules, even complex ones, can be *made*, but this is not really the issue any more, and perhaps never was. The daunting challenge now is whether complex targets can be *made well*."
>
> — Wender, Handy and Wright (1997)

Abstract

The greatest opportunities for development of an inherently safer chemical manufacturing process occur at the earliest stages of research and development, in the selection of the chemical synthesis route for the product. Research and development chemists need to be aware of the safety, health, and environmental

(SHE) consequences that their early decisions will have on the ultimate SHE characteristics of a commercial manufacturing plant. Inherent SHE characteristics of manufacturing process options must be measured and evaluated at an early stage in development, and these characteristics must be included in the route selection decision process. Examples of the potential benefits of inherently safer chemical synthesis routes will be discussed.

Introduction

What do we mean by inherently safer? Perhaps the best short definition is given by Trevor Kletz: "An inherently safer design is one that avoids hazards instead of controlling them" (Kletz, 1997). In recent years, the concept of inherently safer design has been enlarged to include health and environmental considerations, and this broader vision is often referred to as Inherent SHE (Safety, Health, and Environment). One might expand Kletz's definition to state that inherent SHE avoids hazards to safety, health and the environment instead of controlling them. This integrated vision recognizes that SHE characteristics of a process are inextricably linked, and it is necessary to consider all aspects of the process in order to make the best process and plant design decisions.

Inherent SHE is most effectively addressed early in process development, although it is never too late. However, as a process evolves through its life cycle, certain choices are made, resources expended or committed, and other stakeholders (including potential customers who test and evaluate new products) brought into the process. Changes in basic technology become more difficult. They also become more expensive, and the product or process may not be able to afford the extra development time necessary to go back and develop an alternate manufacturing scheme. Thus it is very important that the ultimate SHE characteristics of a manufacturing process be considered at the earliest stages of development. For the chemical process industries, this means that inherent SHE must be considered when selecting the chemical synthesis route.

Early, seemingly minor, choices in the development of technology can have major impacts later on in the life of that technology. In many cases those choices become so embedded in the overall technology that it is virtually impossible to change them. Thus we continue to use the "QWERTY" keyboard for computer input, despite its acknowledged deficiencies. Better arrangements of keys are available (and, perhaps, better mechanisms for getting character input into a computer), but the QWERTY keyboard is so deeply embedded in the technology of computers that it is unlikely to change for many years, if ever. Similarly, a particular chemistry may become so embedded in the technology of an industry, with a large capital investment commitment and an industrial infrastructure built around a particular technology, that it is nearly impossible to change. For this reason, we must be fully aware of the ultimate SHE impacts of the choices we make in selecting chemistry and technology early in product and process design.

This is certainly not news. In 1988, the National Research Council stated that "few basic decisions affect the hazard potential of a plant more than the initial choice of technology." (Design, 1988). In the chemical process industry, the selection of the process chemistry is the basis of that choice of technology. Selection of technologies and chemistries which avoid hazards rather than controlling them offers the greatest potential for the chemical process industries to continue to cost effectively meet the ever increasing expectations of society for improvements in safety, health, and the environment.

Risk Management Strategies

Chemical process risk management strategies are often grouped in four categories (Bollinger, et al., 1996):

> ***Inherent*** – eliminating the hazard by using materials or processing conditions which are non-hazardous
>
> ***Passive*** – eliminating or minimizing the hazard by process or equipment design features which do not eliminate the hazard, but reduce risk without the need for any device to actively function
>
> ***Active*** – using controls, safety interlocks and emergency shutdown systems to detect potentially hazardous deviations and take corrective action before the deviation becomes serious enough to result in an incident
>
> ***Procedural*** – using operating procedures, administrative controls, emergency response and other management approaches to prevent incidents or minimize the impact of an incident after it occurs

All these categories have their place in a complete risk management program. The approaches in the inherent and passive categories are generally regarded as inherently safer than active and procedural. Marshall (1990) categorized safety approaches as "strategic" and "tactical." Inherent and passive approaches are strategic, must be implemented early in the facility development, and have broad and wide ranging impacts on the process design. Tactical approaches, including the active and procedural categories, can be implemented late in the design process and are characterized by repetition and high costs associated with maintenance and ongoing operation.

Inherent Safety Strategies

Strategies for the design of inherently safer processes have been classified in several different ways. In this discussion, I will use the four categories described by the International Process Safety Group (IChemE and ISPG, 1995) and the Center for Chemical Process Safety (Bollinger, et al., 1996):

> ***Minimize*** – Use smaller quantities of hazardous substances (also called "intensify")
>
> ***Substitute*** – Replace a material with a less hazardous substance

Moderate – Use less hazardous conditions, a less hazardous form of a substance, or facilities which minimize the impact of the release of hazardous material or energy (also called "attenuate")

Simplify – Design processes and facilities which eliminate unnecessary complexity and are forgiving of operating errors

The choice of process chemistry can impact any or all of these categories, and examples will be discussed in the following sections.

Minimize

Inherent safety of a chemical manufacturing process can be improved by minimizing the amount of hazardous material and energy in the process. How can chemistry contribute to this objective? The chemist should be consider chemical synthesis routes that:

Produce product of high purity at high yield, generating few or no by-products which would have to be removed through downstream purification steps

Use reactions which occur rapidly when the materials come into contact, reducing the residence time required in the reactor and making the process amenable to continuous operation

Use single phase reaction systems of low viscosity, avoiding the need to transport reactants across phase boundaries and facilitating the rapid contact of reactants

Operate as closely to ambient temperature and pressure as possible, reducing the potential energy from elevated temperature and pressure in the reactor system

Use reactions which are not highly exothermic

Use reactions which are not highly sensitive to operating conditions – reactions which are very tolerant of variations in raw material composition, changes in temperature, pressure, and concentration, and the presence of common contaminants such as water, air, rust, and oil.

Development of chemistry alternatives with these characteristics requires a fundamental understanding of reaction mechanism and of the factors which control the chemical reaction. What actually determines the rate of a particular reaction? Is it the actual rate of reaction once the molecules come into contact with each other? Or, are physical factors such as mass transfer across phase boundaries, diffusion into solid particles, or mixing in a fluid phase the most important factors in determining reaction rate? The chemist must understand what controls the behavior of the reaction, so that the chemical engineer can design a reactor which optimizes that chemistry on an industrial scale.

The well known and often discussed example of the manufacture of nitroglycerin is an excellent example of the inherent safety benefits which can be realized by an understanding of the mechanism and controlling factors in a chemical reaction system (Kletz, 1991). The reaction of nitric acid and glycerin is actually quite rapid, but early industrial implementation of this chemistry used large batch reactors which were far from optimal for bringing the reactants, which are present in separate liquid phases, into contact with each other. Current technology focuses on efficiently contacting the reactants so that the reaction can occur very rapidly. Today's continuous reactors are orders of magnitude smaller than the old batch reactors, greatly reducing the potential hazard from this extremely hazardous reaction.

Some other examples in which a good understanding of the process chemistry and chemical reaction mechanism resulted in significant reduction of reactor size include:

> Osterwalder (1996) describes a continuous process to manufacture "phosgene on demand," supplying batch process phosgene users, and eliminating the storage of liquid phosgene. The quality control issues, understanding of transient reactor operation, and process control issues associated with this process were successfully resolved by an excellent fundamental understanding of the chemical reaction, which allowed process engineers to design a system which met all of the user's requirements. Interfacing a continuous process for manufacturing phosgene with batch processes which consumed the phosgene represented a particular challenge, imposing requirements for rapid startup and steady state operation on the continuous phosgene plant.
>
> The rate and efficiency of a chlorination reaction was determined to be controlled by mixing and gas-liquid phase mass transfer. Replacement of a stirred tank reactor with a loop reactor designed to optimize mixing and gas-liquid phase transfer significantly reduced the reactor size, reduced processing time, and reduced chlorine usage (CCPS, 1993).
>
> In another case, a 50 liter loop reactor replaced a 5000 liter

batch reactor in a polymerization process (Wilkinson and Geddes, 1993).

A process for the small scale, distributed manufacture of hydrogen cyanide using microwave catalysis has been reported (Koch, et al., 1995).

Substitute

Substitution of a chemical synthesis route using less hazardous raw materials and in-process intermediates, or less energetic reactions has great potential inherent SHE benefits. Examples of completely different chemical synthesis routes include:

Manufacture of acrylic esters by oxidation of propylene to produce acrylic acid, followed by esterification to manufacture the various esters is inherently safer than the old Reppe process, which used acetylene, carbon monoxide, and nickel carbonyl (Bollinger, et al., 1996).

A series of papers by Edwards and various associates at Loughborough University in England compares inherent safety and environmental characteristics of six alternative chemical routes for the manufacture of methyl methacrylate (Edwards, et al., 1996; Cave and Edwards, 1997).

Disodium iminodiacetate (DSIDA), an intermediate used for agricultural chemicals, was traditionally manufactured using a process requiring ammonia, formaldehyde, hydrogen cyanide, and hydrogen chloride. Monsanto developed a new process for DSIDA which eliminates the use of hydrogen cyanide and formaldehyde, has a higher yield, is simpler, and produces a product of sufficiently high purity that purification is not required (Franczyk, 1997). Monsanto won a "Presidential Green Chemistry Challenge" Award for this process in 1996.

A number of other innovative chemistries offer potential for inherently safer and more environmentally friendly processes, including electrochemical techniques, "domino" reactions, reactions controlled with external energy sources such as microwaves and laser light, supercritical processing, use of enzymes and "extremozymes" – enzymes which can tolerate relatively harsh conditions, and various innovative catalytic processes (Bollinger, et al., 1996).

Another area for potential improvement is in the substitution of less hazardous solvents. Reaction solvents can be both beneficial and detrimental in terms of the inherent safety of a process. A solvent does moderate the potential impact of hazardous reactants, intermediates, or products. However, if the solvent itself is toxic or flammable, it will introduce new hazards into the process. In many cases, it is possible to identify less hazardous solvents which will realize the benefits of moderation from the use of the solvent while minimizing the hazards of the solvent itself. Some examples include:

> Use of water-based emulsion paints in place of solvent based paints reduces hazards to the final user, and also in the manufacturing facilities.
>
> Many cleaning and de-greasing operations have eliminated the use of organic solvents, substituting water-based systems.
>
> A polymerization process was done in an organic solvent using a gradual addition batch process. A large quantity of organic solvent was required to keep the system viscosity low enough for effective mixing and heat transfer. In the event of an uncontrolled (runaway) polymerization, a large quantity of flammable and toxic material would be ejected through the reactor rupture disk, requiring an expensive and elaborate emergency relief discharge system. Instead of designing an elaborate system to control the potential hazard, the basic process chemistry was re-considered. It was found that it was possible to make the product using a suspension polymerization process in water, with only a small amount of solvent present. With the new process, in case of a runaway reaction most of the material released would be water (with a small amount of solvent and unreacted monomer). A runaway was also less likely because of the higher heat capacity of water, allowing it to absorb more of the heat of reaction in case of a process upset which might lead to a runaway.
>
> Dittmer (1997) discusses research on "no solvent" organic synthesis, including the use of catalysts and solid phase reactions to carry out various reactions.

Moderate

Understanding of process chemistry, and what ultimately controls reaction paths and rates, allows us to design processes which operate at lower temperature and pressure. Catalysis, in particular, offers potential for inherent SHE by improving process yields, making reactors and associated equipment smaller and eliminating or reducing the size of downstream purification equipment, and by allowing reactions to be conducted at less severe temperature and pressure conditions. Examples of moderation in processing conditions include:

> In the 1930s, ammonia plants typically operated at pressures as high as 600 bar. Over the years, improved understanding of the chemistry has resulted in a downward trend in the operating pressure of ammonia plants, and in the 1980s, plants operating in the range of 100-150 bar were being built. The newer, low pressure plants were also cheaper and more efficient (Kharbanda and Stallworthy, 1988).
>
> Catalysis, including phase transfer catalysis, solid catalysts of various types, and enzymes and related compounds, is an area receiving a great deal of attention with the recent focus on "green chemistry." Bollinger, et al. (1996) provides some references related to inherent safety, and there is a lot of discussion on this topic in papers presented at "Design for the Environment" sessions sponsored by the American Chemical Society’s Division of Environmental Chemistry at various ACS meetings and conferences.

Simplify

An understanding of basic process chemistry allows the process chemist and engineer to design simpler reaction systems and plants. "One pot" and "in-situ" processes allow the designer to generate a hazardous intermediate in the vessel where it will be used, eliminating the need to store it, or to move it around the plant in piping systems. The inventory of hazardous material will be limited to a maximum of one batch.

Other examples of simplification involve a trade-off between the complexity of an overall plant and complexity within one particular device or piece of equipment. For example, a new process for methyl acetate using reactive distillation requires only three columns and the associated support equipment. The older process required a reactor, an extractor, and eight other columns, along with the associated support equipment. The new process is simpler, safer, and more economical, but the operation of the reactive distillation is itself more complex, and requires a thorough understanding of the chemistry and process for successful operation (Agreda, et al., 1990; Siirola, 1995; Bollinger, et al., 1996).

Inherent SHE Conflicts

No discussion of inherent SHE would be complete without a recognition of the potential for conflicts in attempting to attain multiple, sometimes incompatible goals. In an ideal world, we would be able to identify processes which generated no waste, used no hazardous raw materials or intermediates, operated at ambient temperature and pressure, operated robustly with little sensitivity to variation in feed quality or operating conditions, and were economical both in terms of initial capital investment and also operating costs. Unfortunately, we do not live in that ideal world, and we must constantly resolve conflicts among our conflicting needs and desires when selecting manufacturing technology. The non-flammable solvent for our process turns out to have chronic toxicity hazards, so which option is inherently safer? The new process eliminates a toxic raw material, but it operates at high temperature and pressure. Which of these is the better option? These are difficult issues to resolve, and there are many decision analysis tools available to help understand and resolve such issues. Hendershot (1995) and Bollinger, et al. (1996) discuss inherent safety conflicts specifically, and CCPS (1995) discusses the use of formal decision making tools in the broader chemical process safety field.

The Future

So, what are we asking for the chemical industry of the future? Not much, really. All we want is to invent chemical manufacturing processes which:

use non-hazardous raw materials and intermediates

operate at ambient temperature and pressure

produce no waste or undesirable by-products of any type

have low capital investment and life cycle operating costs

have an "atomic efficiency" of 100%; i.e., we want to sell every atom of raw material that we purchase to a customer! (Sheldon, 1997)

have a low "E Factor", defined as the weight ratio of all of the raw materials purchased by the purchasing manager to the weight of all of the product sold by the sales manager (Sheldon, 1997)

We have a long way to go, but we can get there, or, at least, a lot closer than we are now. Somebody once described chemistry to me as a mature science, where all of the important discoveries have already been made. Nothing could be further from the truth. Drexler (1994) used a good analogy to describe our current practice of chemistry. He likened it to the electronics industry taking a cement mixer and filling it with a mixture of capacitors, resistors, wires, chips, transistors, and other bits of electronic components, turning on the cement mixer, and hoping that occasionally a radio would fall out of the chute. That is not a bad description of how we practice chemistry on an industrial scale. We have a long way to go in understanding the basic mechanism of chemical reactions, so that we can manipulate molecules to give us the specific structures that we want.

It can be done, and we know it is physically possible. Each of us, in our own body, is constantly creating complex, elegant, and useful chemical structures from simple raw materials, at ambient temperature and pressure. But I am not necessarily thinking about biotechnology as the route to achieving our desired future state, although there is a lot of potential in this field. Again, borrowing an analogy from Drexler (1994), assume that the Wright brothers and their successors had not invented the airplane, and we now wished to build a flying machine to transport large quantities of cargo across the ocean. The biotechnology approach might be likened to breeding, and perhaps genetically engineering, a much larger and more powerful carrier pigeon. Perhaps a better approach would be to understand the basic scientific principles which allow a carrier pigeon to fly, and then to use that knowledge and understanding to build a Boeing 747. Both the pigeon and the airplane fly based on the same physical principles, but the design, material of construction, propulsion system, and other design features differ dramatically. We need to understand the scientific principles which allow fine manipulation and control of molecules, and then develop systems to do this on a large scale.

When I was a child, my father kept frozen food in a locker at the Harrisburg (PA) Cold Storage Company. It was a large, refrigerated warehouse (probably using an ammonia refrigeration system) which rented lockers to individuals for storing frozen food. It no longer exists, having been driven out of business long ago by home refrigerators and freezers (using small quantities of safer refrigerants). So, where is the alleged benefit of "economies of scale" in this business? Shouldn’t the large, central facility be much more economical? Actually, there are economies of scale in the modern system, but they are in the manufacture of refrigerators and freezers. It probably does cost more to operate all of the small freezers in everybody’s house, but they can be manufactured and sold cheaply, and we are willing to pay a higher operating cost for the convenience of having the frozen food in our own homes.

We see similar changes in many other industries – replacement of rail transportation for passengers and much non-bulk freight with cheap automobiles and trucks; replacement of large mainframe computers with networks of cheap personal computers; the shutdown of many large, integrated steel mills contrasting with the great success of "mini-mills". Where does the chemical industry stand with respect to this trend? We are still at the stage of the large, world scale centralized facility. I believe that this will change in the future, and that the future chemical industry will consist of small, dedicated plants producing specific materials at the site of the product consumer, on demand, highly automated and largely unstaffed, using commonly available and relatively non-hazardous raw materials. We will replace the economies of scale in operation of a large, centralized plant with the economies of scale of building small, cheap, perhaps disposable or recyclable plants which can be set down where they are needed, used, and then taken away or recycled. This future vision of the chemical industry has been described in articles by Benson and Ponton (1993), Ponton (1996), and others. We do not know enough about the chemistry and other technologies required to realize this vision yet, but we are learning fast. I believe this vision does represent the future state of the chemical industry, and I hope, in my retirement years, to be able to serve as a National Park Service interpreter at the Houston Ship Channel National Historic Park!

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.

Benson, R. S., and J. W. Ponton (1993). "Process Miniaturisation - A Route to Total Environmental Acceptability?" *Trans. IChemE* 71, Part A (March), 160-168.

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.

Cave, S. R., and D. W. Edwards (1997). "Chemical Process Route Selection Based On Assessment of Inherent Environmental Hazard." *Computers Chem. Engng.* 21, S965-S970.

Center for Chemical Process Safety (CCPS) (1993). *Guidelines for Engineering Design for Process Safety*. New York: American Institute of Chemical Engineers.

Center for Chemical Process Safety (CCPS) (1995). *Tools for Making Acute Risk Decisions With Chemical Process Safety Applications*. New York: American Institute of Chemical Engineers.

The Design of Inherently Safer Plants (1988). *Chemical Engineering Progress*, (September), 21.

Dittmer, D. C. (1997). " ‘No Solvent’ Organic Synthesis." *Chemistry & Industry*, (6 October), 779-784.

Drexler, K. E. (1994). Unpublished remarks to the 208th American Chemical Society National Meeting, August 21-25, 1994, Washington, DC.

Edwards, D. W., D. Lawrence, and A. G. Rushton (1996). "Quantifying the Inherent Safety of Chemical Process Routes." *5th World Congress of Chemical Engineering*, July 14-18, 1996, San Diego, CA, Vol. II, 1113-1118. New York: American Institute of Chemical Engineers.

Franczyk, T. S. (1997). "The Catalytic Dehydrogenation of Diethanolamin." *Preprints of Papers Presented at the 213th ACS National Meeting*, April 13-17, 1997, San Francisco, CA, 342. Washington, DC: American Chemical Society, Division of Environmental Chemistry.

Hendershot, D. C. (1995). "Conflicts and Decisions in the Search for Inherently Safer Process Options." *Process Safety Progress* 14, 1 (January), 52-56.

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: Taylor and Francis.

Kletz, T. A. (1997). "Inherently Safer Design - The Growth of an Idea." *Conference on Inherent SHE: The Cost Effective Route to Improved Safety, Health and Environmental Performance*, 16-17 June 1997, London, London: IBC Conferences Limited.

Koch, T. A., K. R. Krause, and M. Mehdizadeh (1996). "Improved Safety Through Distributed Manufacturing of Hazardous Chemicals." *Process Safety Progress* 16, 1 (Spring), 23-24.

Marshall, V. C. (1990). "The Social Acceptability of the Chemical and Process Industries." *Trans. IChemE* 68, Part B (May), 83-93.

Osterwalder, U. (1996). "Continuous Process to Fit Batch Operation: Safe Phosgene Production on Demand." *Symp. Pap. - Inst. Chem. Eng., North West. Branch*, 6.1-6.6. Rugby, Warwickshire, England: IChemE.

Ponton, J. (1996). "The Disposable Batch Plant." *5th World Congress of Chemical Engineering*, July 14-18, 1996, San Diego, CA, Vol. II, 1119-1123. New York: American Institute of Chemical Engineers.

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, 222-233.

Wender, P. A., S. T. Handy, and D. L. Wright (1997). "Towards the Ideal Synthesis." *Chemistry & Industry*, (6 October), 765-769.

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

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