

# Predesign With Safety in Mind

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This article will help you develop strong safety instincts that will guide you in making critical decisions in the preliminary design phase.

**S**afety has become an indispensable requirement for any manufacturer to be granted society's "license to operate." Because a process module's intrinsic safety is shaped in the predesign stage, safety could be improved if greater expertise and more attention were dedicated to safety early in a project. In this respect, preliminary designers have a profound influence on ultimate plant safety.

Safety in predesign presents a dilemma. Traditional hazard and operability studies (HAZOPs) require detailed engineering specifications, such as piping and instrumentation diagrams (P&IDs), that are not available during a preliminary analysis. Yet, it is too late to gain many of the benefits of inherent safety once a project has reached the P&ID stage (1).

HAZOP typically involves a team of six to eight people who spend from 25 to 50 total person-hours per P&ID. Considering the cost of professional time, including overhead, this represents an additional \$5,000–\$10,000 per evaluation above and beyond the cost of preparing the P&ID (2). Since most study estimates cannot justify this time and cost, preliminary designers must have strong safety instincts. Thus equipped, they can make critical early decisions geared toward safe design.

## Hazard versus risk

The terms *hazard* and *risk* are often used interchangeably, but there are subtle differences. An appropriate definition for hazard is "a source of danger," whereas risk reflects "the degree of peril that one or more hazards create(s)."

Risk is defined generically as the product of the chance

that a particular hazard may actually cause injury or damage (frequency) and the impact of an event if it occurs (consequence) (3). A hazard's risk can be expressed in the following mathematical equation:

$$\text{Risk} = \text{Frequency} \times \text{Consequences} \quad (1)$$

One can reduce risk by designing so that an occurrence becomes extremely rare, or so that if it does happen, little damage would result.

## Where do hazards lie?

Wherever there is latent energy of any kind, there is danger. The greater the energy, the greater the danger. Risk lurks in each term — kinetic energy, potential energy, work, heat, enthalpy and internal energy — of the fundamental energy balance that chemical engineers use almost every day.

- *Kinetic energy* — Although more prominent for its damage to people traveling in high-speed vehicles, kinetic energy present in rotating equipment or other machines causes many isolated personal casualties in the chemical industry.

- *Potential energy* — More commonly a source of danger in civil engineering projects, structural failures can release this form of stored energy with disastrous consequences.

- *Work* — Pent-up work, stored in springs, electrical circuits (sidebar, p. 28) or other devices, powers many machine accidents and can cause havoc in chemical process situations.

- *Heat* — Strictly defined as energy crossing a boundary, heat from the rapid release of internal or other forms

## Work Stored in an Electrical Circuit

Forty years ago, one of the authors was responsible for the design and construction of a pilot plant. The bag filter was heated with an external electrical resistance system, but the filter would not reach its design temperature. (It turned out that the design calculations were correct, but during plant shakedown, the newly applied insulation was still damp, and extra heat was consumed in drying it.)

An electrician who happened to be passing by was asked to check the electrical connections. He borrowed a test meter from a nearby bench and opened the circuit box to check the voltage.

When he touched the probes to the terminals, the box exploded as though it had been struck by lightning, accompanied by thunder. Both men were driven backward. The electrician suffered third-degree burns on both hands and arms. Partially shielded by him, the engineer escaped with a few holes in his clothing and molten spots embedded in his safety lenses (caused by fiery liquid copper droplets spewn from the circuit box).

Investigators believe there was a loose strand of wire on one of the meter's probes. It somehow formed a short-circuit and then vaporized from the intense current driven by the 440-V power supply. This evidently created an arc path that allowed even more current to flow, melting and vaporizing the copper wiring in the box, and causing the explosion. The engineer gained great respect that day for work stored as electricity.

of energy is a factor in many serious incidents that occur in the process industries, such as runaway reactions and boiler explosions.

- *Enthalpy or internal energy* — This source powers most chemical reactor runaways and destructive fires. In one such incident, a runaway reaction blew the inspection cover off a reactor and spewed a jet of atomized liquid through the third floor and roof of the building, splattering the adjacent neighborhood. The aerosol plume ignited, forming a fireball with an explosion that drove the 7,500-L (2-m I.D. by 2.7-m tall) jacketed vessel from its moorings and against a cement wall. Nine employees were injured, two seriously with second- and third-degree burns. (For insight into the drama and trauma of this incident, as well as photos of the scene, see U.S. Chemical Safety and Hazard Investigation Board Report 1998-06-I-NJ, NTIS Report No. PB2000-107721, [www.csb.gov/index.cfm?folder=completed\\_investigations&page=info&INV\\_ID=18](http://www.csb.gov/index.cfm?folder=completed_investigations&page=info&INV_ID=18)).

## Risk hot spots in a plant

Before discussing how to design for safety, it makes sense to review what, in a plant, causes a disaster.

*Piping*, including valves, flanges, threaded joints, drains, traps, strainers and other elements, is the largest single source of failure (4). Preliminary designers don't

have much to do with piping, except in choosing construction materials for process equipment, which are almost always matched in process piping. Responsibility for safe piping design is ultimately in the hands of final plant designers. Many piping failures, however, are caused by corrosion and faulty upkeep. Therefore, predesign manufacturing cost estimates should include generous allowances for maintenance in plants that process hazardous substances.

*Storage vessels* are the second-riskiest equipment in a plant. Most storage vessel incidents result from complacency. Ancillary areas like this don't demand much attention from operators, so they tend to receive less maintenance — which is not a design problem, but an operations problem.

On the other hand, some storage tank incidents result from overpressurization. This is especially true of slops tanks used for waste storage. Fluids with vapor pressures that unexpectedly exceed design specifications sometimes accumulate in these vessels. Tanks burst, often causing explosions or fires.

In some incidents, liquid levels fall below tank heaters, which subsequently overheat and ignite combustible mixtures in the vapor phase. Other events stem from floating tank roofs that develop leaks, thereby allowing air to enter and create an explosive mixture. Tanks are sometimes mistakenly overfilled. Careless workers or faulty equipment create hazardous conditions during loading and unloading.

Based on these statistics, most storage risks are the responsibility of operations, maintenance and final mechanical design personnel. Preliminary designers, on the other hand, should specify storage vessels that are large enough and strong enough for any anticipated need. As with piping, one must be cautious in choosing materials of construction. Inert-gas blanketing should be seriously considered for slops tanks or any vessel that contains combustible liquids.

*Vacuum operations* involving any chemical that can react with air require caution. Air in-leakage is difficult to detect and may create unexpected explosive mixtures. (At pressures greater than atmospheric, on the other hand, the leak is outward, and sight, sound, smell or special instruments can detect it for repair.)

*Furnaces* are risky by nature, because combustible mixtures and ignition sources are essential to their function. A key consideration in furnace design is to avoid large volumes of reactive mixtures. For example, most furnaces employ burners with small mixing chambers of special design where intense turbulence, temperature and geometry assure dependable ignition and flame stability. Special instrumentation is provided to shut off fuel if a flame goes out, so that unreacted mixtures do not accumu-

late in the combustion chamber and explode. These safeguards are integrated into the purchased equipment package, so furnace safety requires little of a preliminary designer other than normal vigilance.

*Pump* failures are common because pumps are ubiquitous in a chemical process plant. Demands on a pump are also broad and severe with regard to pressure, temperature, exposure and other service conditions. Seal failure is by far the most common defect in operation. As a result, toxic or reactive mixtures can escape. This is compounded by friction-induced overheating from a corroded bearing, which can vaporize and ignite the leaking fluid. Engineers involved in detailed or mechanical design might specify magnetically coupled or canned pumps for especially hazardous situations. Mechanics and operators must provide proper maintenance and effective inspections. In preliminary design for hazardous service, one should be conservative in choosing the material of construction and pump type.

*Heat exchangers* do not have the mechanical complications and moving parts of pumps, nor do they have the safety protection of furnaces. Normally, safe design respects the same criteria as for pressure and process vessels. But when heat exchangers operate at extreme temperatures or pressures, observance of rules for safe furnace design may be more appropriate.

*Gas movers and compressors* exhibit the same mechanical demands as pumps, but these demands are usually more extreme. Heat generation is larger in gas compression, and vapors ignite more readily than liquids. Thus, compressors are intrinsically more hazardous than pumps. Gas movers fall below pumps in incident frequency because they are less ubiquitous, but compressor-triggered damage is often more deadly and catastrophic. Safety guidelines for all of the items discussed above should be considered when designing gas movers.

*Chemical reactors* are the next-most common type of equipment after storage vessels that initiate chemical process disasters. This is not surprising, since most commercial reactions are controlled explosions, often involving poisonous reagents or products.

Runaway batch reactions top the list of violent incidents (13% of all reactor incidents). Specific causes include loss of utilities (*e.g.*, electricity or cooling water), flow reversal, carryover in feed or product streams, incorrect reagent charging procedures, plugging and fouling of heat exchange or instrument surfaces, poor mixing or agitator failure, and external fires. Most of these stem from careless, poorly trained operators or mechanics, and faulty control systems. Major engineering errors involve selection of inappropriate materials of construction, superficial equipment inspection, failure to anticipate destructive side

### Water as a Hazard

As a graduate student, one of the authors was working on a high-temperature electrochemical experiment. To hurry things up, he poured molten salt from a tube furnace into a pail of cold water. The resulting explosion drenched the ceiling of the lab, but, fortunately, caused no harm to himself other than well-deserved embarrassment. There was no chemical reaction, but the intense energy transfer generated steam at a fast enough rate to create a shock wave.

A similar phenomenon is believed to explain the destructive explosions that were once quite common in Kraft recovery boilers used in paper/pulp plants. Steam tubes rupture and discharge water into a hot smelt reservoir at the base of the boiler.

reactions, and following risky operating procedures. Backup safety systems, such as vents, dump tanks and quenches, also fail, and thus serve their intended purpose with only about 80% reliability.

One guideline for preliminary design is to follow the furnace strategy: Avoid large batch reactors or large reactor vessels of any type, including continuously stirred tank reactors (CSTRs), especially if exothermic reactions are possible (5–7). This is a severe and often impossible limitation, since exothermic main or side reactions occur with high-energy feedstocks in most commercial processes, ranging from foods, plastics, fertilizers and pharmaceuticals to chemicals and fuels. Almost 90% of commercially important chemical reactions (Table 4-21 of Ref. 8) are highly exothermic.

As Eq. 1 demonstrates, the greatest risk lies with those common processes that handle the most volatile and reactive materials. More than 90% of the process fluids involved in incidents in one database were petroleum fractions (4). Liquefied petroleum gas (LPG) topped the list, followed by gasoline/naphtha, hydrogen, heavy hydrocarbons, hydrocarbon gases, crude oil and diesel fuel. Water, on the other hand, was involved in the most non-petroleum incidents (sidebar above), followed by chlorine and ethylene oxide.

### Principles of safe design

A popular and successful modern movement toward greater safety in the chemical processing industries is known as inherently safer design (ISD). The goal of this concept is to design production modules so safe that catastrophic failure cannot occur. ISD was pioneered by Trevor Kletz in 1976, who summarized the philosophy in his famous statement, “What you don’t have, can’t leak” (9). The Bhopal tragedy would not have occurred had this rule been rigorously applied to that pesticide plant.

Reference 10 (p. 26-5, authored by Kletz) lists a dozen principles of ISD, although more than half apply to plant assembly and operation, not design. The following five

## Fail-Safe Design

At a safety workshop for chemical engineering faculty (2), participants worked in teams to identify various safety issues related to exothermic batch reaction-polymerization. As mentioned previously, reactor runaways that occur under these circumstances are notoriously dangerous — for example, a U.K. Health and Safety Executive study reported 134 batch-process accidents (an average of more than five per year) between 1962 to 1987 (14).

Common worst-case scenarios for reactor runaways include (3):

- loss of cooling water
- agitator failure
- heat-exchange-surface fouling
- unexpected phase separation
- unexpected energetic side reactions
- unexpected introduction of reagent/catalyst or depletion of inhibitor.

One workshop team was asked to envision an electric power failure, formulate a response to this emergency, and report its conclusions to the larger audience. The discussion became intense as the group presented and defended its findings before the body. When asked to define the ultimate danger, the group replied, “runaway reaction.” The questioner, who had helped design the actual reactor, then explained that it was a fail-safe system, and that if any or all of the worst-case conditions were to occur, operators could simply walk away and the reactor would shut itself down safely.

A reaction can’t “run away” unless it can get out of the reactor. Reagent feed limits, interlocking controls, integrated heat balances, and other precautions keep an inherently safer reactor in check. (Reference 3 explains fail-safe design for exothermic reactions.) Combined with redundant back-up provisions (e.g., purges, vents, dump tanks and quenches), regular inspections and rigorous operator training, risk — though it can never be reduced to zero — becomes infinitesimal.

principles (11–13) apply to preliminary process design.

1. *Use fewer hazardous substances, and smaller quantities of them (minimize).* Methylisocyanate (MIC) was only an intermediate in the production of a less toxic pesticide at Bhopal. If a continuous reactor had been used, only a small quantity of MIC would have needed to exist at any point in the process.

Kletz describes how shifting from a batch reactor to a thousand-fold-smaller continuous one decreased the dangers of nitroglycerine manufacture by an even greater magnitude. Added to this dramatic safety gain was a marked reduction in capital and operating costs with the smaller reactor (10).

2. *Use substances that are less hazardous (substitute).* Gupta and Edwards argue that a different reaction scheme could have been used at the Bhopal MIC plant, one that substituted a much less toxic intermediate for MIC (9).

3. *Use moderate operating conditions (moderate, attenuate).* As an example of this principle, Gupta and Edwards point to ammonia production, a source of many chemical processing disasters (9). With the aid of better catalysts,

reactor conditions have become less severe, from 1,000 atm and 500°C in 1920, to 100 atm and 300°C today. (The accompanying 20% gain in equilibrium yield (7) was undoubtedly the major incentive for this migration.)

As an example of attenuation or weakening a danger, Kletz points out that it is generally safer to store large quantities of a hazardous volatile chemical as refrigerated liquid than as gas under pressure.

4. *Use simple plant designs (simplify).* Similar to minimizing the amount of hazardous substances, simplifying equipment often produces a less expensive, more efficient and safer plant.

5. *Design equipment so the effects of an incident are minimized (limit effects).* Similar to attenuation, this principle may sometimes go beyond weakening to sidestepping of a danger (see sidebar at left).

## Steps for inherently safer predesign

Reference 15 provides an excellent blueprint for identifying and defusing hazards, including an important initial step — hazard identification. Table 1 outlines a framework for inherently safer predesign (ISPD) analysis based on Sheppard’s (15) and Kletz’s (13) recommendations. Kletz’s rules for ISD are noted in parentheses in the first column. Note that the use of “safer” rather than “safe” is intentional, since no human activity can be made perfectly safe.

### 1. Identify

A useful tool for hazard identification is the fire triangle (Figure 1), which illustrates that three quantities — fuel, oxidizer and an ignition source — are needed to support combustion and cause a chemical explosion. It might appear from Figure 1 that these three factors are physically separate. With many compounds that chemical engineers encounter (explosives, for example), fuel and oxidant are combined, and a minor impact can cause ignition. Reference 10 (p. 26-51) provides a useful list of known unstable violent compounds.

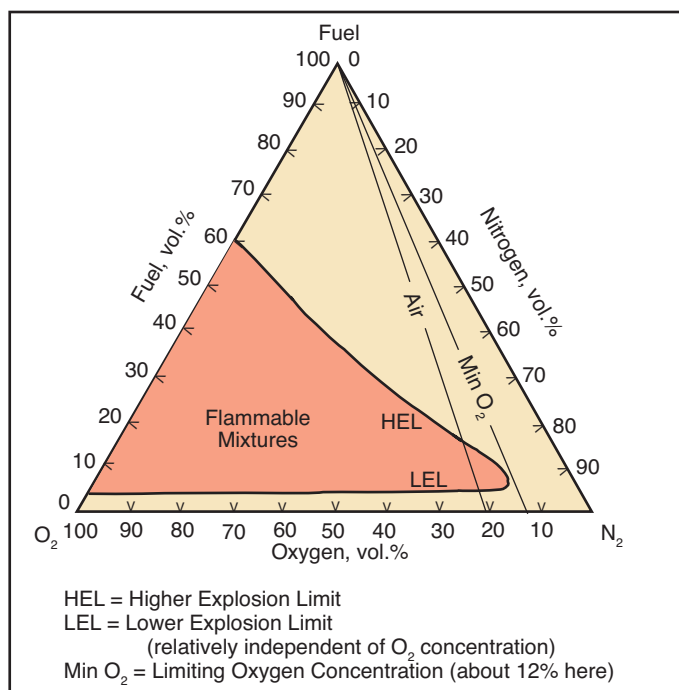
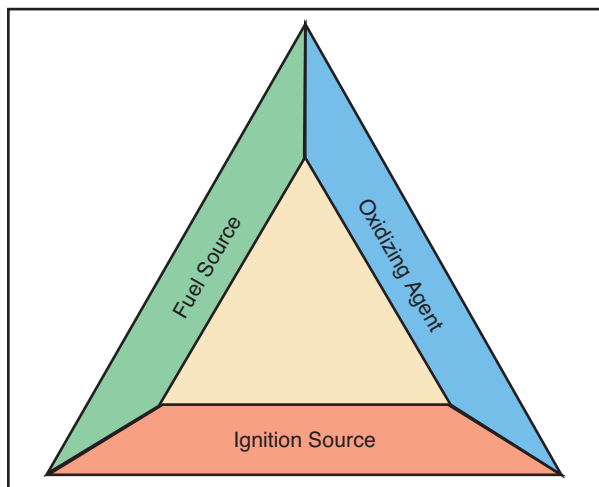
The identities of fuels and oxidizers will be obvious in most design situations. Sometimes, the combustibility of a chemical combination may be uncertain. Several resources are available to resolve that question.

First, as shown in the third column of Table 1, one can perform thermodynamic calculations using heats of formation. Basically, any mixture capable of exothermic reaction can be dangerous. However, there are composition ranges that do not support combustion. These are well-defined in flammability limit charts, which are available for common combustible mixtures. Figure 2 is a flammability limit chart for methane/oxygen/nitrogen mixtures.

Even with such a chart, one must be wary, because com-

bustibility limits change with temperature, pressure, the presence of impurities, and other factors. And, in real processes, incomplete mixing can create pockets that will burn even when a chart developed from carefully controlled laboratory experiments says the uniform mixture will not.

Many new and interesting projects involve proprietary reactions for which there are few published data. Most corporations that deal with hazardous exothermic reactions have their own laboratory with sophisticated calorimetric test equipment. To define danger zones,



■ (Left) Figure 1. The fire triangle illustrates the three elements needed to support combustion.

■ (Above) Figure 2. Flammability diagram for methane/oxygen/nitrogen mixtures. (Courtesy R. French, Exxon Corp., SACHE, "Safety and Chemical Engineering Education Workshop for Faculty on Safety and Process Design," Baton Rouge, LA (Sept. 24, 2003).)

**Table 1. Inherently Safer Predesign (ISPD) involves four basic steps.**

Step/Rule	Tools	Experimental and Analytical Resources	Literature References
1. Identify	Fire triangle Flammability-limit chart Chemical reactivity chart Safety compatibility chart Safety stream chart Toxicity ratings	Thermodynamic calculations Reactor design equations Calorimetry Flammability charts	Perry's Handbook (10) Table 26-10 and associated pages Lees (16) Crowl and Louvar (17) Urban and Bretherick (18) Pohanish and Sittig (19) Shanley and Melhem (20) Kirk-Othmer Encyclopedia (21)
2. Eradicate (ISD Rule 2)	Inert-gas blanketing Failsafe design		
3. Minimize — Simplify, Moderate, Attenuate (ISD Rules 1, 3, 5)	Control and eliminate ignition sources Keep reactive volumes small Safety equipment and instruments fall within this category, but these items are not usually defined in preliminary design	Sound chemical engineering analytical and computational skills	Merck Index Material Safety Data Sheets (MSDSs) Chemical engineering textbooks and monographs
4. Isolate (ISD Rule 4)	Segregate hazardous operations Encase in an impenetrable structure	Sound chemical engineering judgment and common sense	

Sources: (13, 15).

**Table 2. Chemical reactivity chart for acrylonitrile production.**

Reaction Type	Reactants	Expected Reaction	Endothermic or Exothermic?
Main	Propylene Oxygen Ammonia	Partial Combustion	Exothermic
Side	Propylene	Polymerization	Exothermic
Side	Oxygen	None	—
Side	Ammonia	None	—
Side	Propylene Oxygen	Combustion	Exothermic
Side	Oxygen Ammonia	Combustion	Exothermic
Side	Propylene Ammonia	None	—
Side	Propylene Oxygen Ammonia	Combustion	Exothermic

Source: (15).

researchers can measure the reactivity of various feed mixtures over all probable composition, temperature and pressure ranges. If your organization has such a resource, you should exploit it to the maximum extent possible. (For more information on calorimetry, see Refs. 3, 14 and 15.)

Thermochemistry is an important area of ISPD diagnosis. One-fourth of batch reactor runaway incidents stem from ignorance in this area, rivaling human-caused operating errors in importance (14). Remember that most chemicals can ultimately go to their most extreme oxidation states (hydrocarbons to CO<sub>2</sub> and H<sub>2</sub>O, for example). And,

one must not overlook the potential for dust to self-combust and produce an explosive mixture (10).

Another tool for identifying hazards is the chemical reactivity chart, such as the one for the production of acrylonitrile from propylene, air and ammonia illustrated in Table 2. The chemical reactivity chart provides useful insight into some consequences, expected and unexpected, of mixing these reagents.

A good place for a novice designer to begin is the chemical process hazard analysis matrix (Table 3), which includes other critical risk factors. Components are listed in one column and in the top row. Interactions among the various chemicals are rated according to a National Fire Protection Association (NFPA) code. A more-detailed version of this interaction checklist (22) can be constructed with columns and rows for steam, people, dirt, grease and other hazards, using chemical compatibility information (such as from Ref. 18). This type of matrix serves as the basis for a chemical hazard analysis (CHA) review similar to the HAZOP conducted during later project stages. As more information becomes available during construction and operation, the hazard analysis matrix matures into a permanent plant safety document.

Tables 2 and 3 are decision charts that make a process designer's thinking public and transparent. With these diagnostic tools, we move through the next steps of ISPD.

## 2. Eradicate

One might look at the fire triangle and conclude that eradicating risk is easy — merely prevent ignition. If it were that simple, many lives and billions of dollars would not have been wasted. The references in Table 1 (and others) enumerate the many sources of reaction initiation. Most destructive fires, reactions and explosions are initiated by:

- auto- or spontaneous ignition caused by heating
- friction, *e.g.*, heat from a failed bearing on pump or compressor
- static electricity
- repair activities, such as arc welding, cutting, grinding and impact, that could generate sparks
- open flames, which are often unavoidable around furnaces, reactors and heaters
- unprotected or faulty electrical fixtures or switches
- lightning and other natural causes.

**Table 3. Chemical process hazard analysis matrix for acrylonitrile production based on NFPA ratings.**

Health	Fire	Reactivity	Component	Propylene	Ammonia	Oxygen	Acrylonitrile
1	4	1	Propylene	P	—	—	—
3	1	0	Ammonia	0	0	—	—
0	0	0	Oxygen	4	1	0	—
?	?	?	Acrylonitrile	P	?	4	P

National Fire Protection Association (NFPA) Ratings:

0 = No hazard    1 = Minimal hazard    2 = Caution    3 = Danger    4 = Extreme danger

P = Polymerization

? = Yet to be determined

Source: (15).

Given the widespread presence of so many ignition sources, it is impossible for them to be eradicated.

To eliminate risk and ensure a safe design approach, avoid flammable mixtures. This can be done, for example, by blanketing storage tanks with nitrogen, carbon dioxide or some other appropriate inert gas. Reactors, where possible, should be designed as fail-safe vessels, as described earlier.

### 3. Minimize

When reactive mixtures cannot be avoided, keep volumes small. If reaction is the goal, ignition must be reliable and certain to assure that complete combustion occurs (see the previous discussion of furnaces).

### 4. Isolate

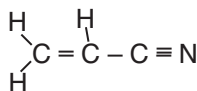
As a final line of defense, limit the effects of an incident by segregation. In the U.S., for instance, solid rocket facilities were placed in a Utah desert, miles from civilization, and a nuclear reactor test site was built in a remote area of Idaho.

The risk can also be confined. Reactor containment vessels in nuclear power plants represent this type of quarantine.

### Putting ISPD into practice

Starting with the safety documents introduced by Sheppard (15), a preliminary flow diagram for acrylonitrile production will be developed using ISPD concepts.

The raw materials — propylene, air and ammonia — are well known to most chemical plant designers. Acrylonitrile is less familiar, but a great deal about its properties can be surmised from its molecular formula,  $C_3H_3N$ , and its structure:



This simple information raises several red flags:

- double- and triple-bonded carbon atoms indicate pent-up energy
- $-C \equiv N$  denotes membership in the deadly cyanide family
- the highly unsaturated structure almost guarantees the potential for spontaneous exothermic polymerization
- hydrocarbon character assures combustibility
- small molecular size indicates a gas at ambient conditions or a highly volatile liquid
- the cyano group suggests water-solubility.

**Table 4. Key chemical and physical properties of acrylonitrile.**

Property	Data	Comments
Formula	$C_3H_3N$	Clear, colorless liquid at room temperature with a faintly pungent odor
Molecular Weight	MW = 53	
Boiling Point	$77.3^\circ\text{C}$	
Freezing Point	$-83.5^\circ\text{C}$	
Density @ $20^\circ\text{C}$	$806 \text{ kg/m}^3$	
Vapor Pressure @ $20^\circ\text{C}$	0.115 bara	Dangerously high vapor pressure at room temperature
Vapor Density (Air = 1)	1.8	Unlike hydrogen, vapors will not dissipate in air; leaked gas may accumulate in low spots
Solubility in Water @ $20^\circ\text{C}$	6.0–7.5wt. %	Severe potential for pollution; all wastewater will require treatment
Viscosity @ $25^\circ\text{C}$	$3.4 \times 10^{-4} \text{ Pa}\cdot\text{s}$	Viscosity is about one-third that of water; watch for seal leakage
Flash Point	$0^\circ\text{C}$	Absolutely no sparks or open flames are permitted near liquid
Autoignition Temperature	$481^\circ\text{C}$	Avoid hot surfaces
Flammability Limits in Air @ $25^\circ\text{C}$	Lower: 3vol. % Higher: 17vol. %	Flammability limits are about the same as those of methane
Enthalpy of Formation @ $25^\circ\text{C}$	Gas: 185 MJ/kgmole Liquid: 150 MJ/kgmole	Risk of spontaneous decomposition or combustion
Heat of Combustion, Liquid @ $25^\circ\text{C}$	1,762 MJ/kgmole	This is about two-thirds the heat of combustion of gasoline and natural gas
Heat of Vaporization @ $25^\circ\text{C}$	32.7 MJ/kgmole	This is about one-fourth the latent heat of water

Source: (21) and others.

All these factors point to a highly dangerous process. Indeed, nitroalkanes, and *c*-nitro and polynitroaryl compounds tend to undergo violent or explosive decomposition (10).

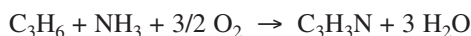
The table of thermodynamic data in Perry's Handbook (Table 2-221 in Ref. 10) does not include acrylonitrile; however, enthalpies of formation for its siblings, acetonitrile ( $C_2H_3N$ ) and propionitrile ( $C_3H_5N$ ), are both positive, denoting the potential for spontaneous exothermic decomposition. Acrylonitrile is related to TNT and nitroglycerine, although its lack of molecular oxygen makes it less hazardous than the latter two.

Table 5. Stream hazard chart.

Compound	Molecular Weight	Melting Point, °C	Flash Point, °C	Boiling Point, °C	Liquid Density kg/m <sup>3</sup>	Flammability	Deadly Poison?	Toxin?	Carcinogenic?	Genetic Damage?	Irritating?	Corrosive?
C <sub>3</sub> H <sub>6</sub>	42					High		Suffocation Hazard			No	No
NH <sub>3</sub>	17					Moderate		Yes			Strongly	Moderately
O <sub>2</sub>	32					Powerful Oxidant					No	Sometimes
N <sub>2</sub>	28					Non		Suffocation Hazard			No	No
C <sub>3</sub> H <sub>3</sub> N	53	-83	0	77	806	High	Yes	Deadly	Yes			
HCN	27	-14		26	700		Yes	Deadly				
C <sub>2</sub> H <sub>3</sub> N	41	-88	5	82	786	High		Yes				
CO	28					High	Yes	Deadly			No	No
CO <sub>2</sub>	44					Non		Suffocation Hazard			No	No
H <sub>2</sub> SO <sub>4</sub>	98					Powerful Oxidant		Yes			Strongly	Strongly
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	132											

The Kirk-Othmer Encyclopedia (21) contains more details and a flow sketch that provide the basis for a tentative process flow diagram. Facts relevant to this analysis are:

- over 4 million metric tons of acrylonitrile are produced per year worldwide, more than 90% of which is made by heterogeneous vapor-phase synthesis from propylene, ammonia and air over a bismuth-molybdate catalyst according to the reaction:



- acrylonitrile is a basic raw material for fibers and textiles, acrylonitrile-butadiene-styrene (ABS) and styrene-acrylonitrile (SAN) plastics, nitrile rubber, bottles/packaging, transparent and opaque plastics, and resins for many specialty applications

- it is among the top 50 tonnage chemicals in the U.S.
- it is miscible with a wide range of organic solvents
- it undergoes spontaneous polymerization in the presence of light.

The properties of acrylonitrile are listed in Table 4. Production occurs in a fluid-bed reactor at a temperature of 400°C–510°C and pressure of 0.5–2 barg, where conversions of up to 98% are achieved in a single pass. A

starting quantity of 1.1 kg of propylene yields about 1.0 kg of acrylonitrile, 0.1 kg of hydrogen cyanide and 0.03 kg of acetonitrile.

**A more-detailed hazard evaluation.** Further reading reveals acrylonitrile is highly toxic if ingested, moderately toxic when inhaled, extremely irritating and corrosive to skin and eyes, readily absorbed through skin, carcinogenic and mutagenic. The average allowable 8-h exposure limit in the U.S. is 2 ppm, with a 10-ppm maximum for no more than 15 min. Acrylonitrile combustion can produce HCN, a deadly gas.

Since more than half of North American and Western European production goes to the export market, it seems that manufacturers already compromise Kletz's first rule of ISD, minimize. With large quantities of acrylonitrile stored and shipped around the world, any tanker accident would be worse than a conventional oil spill because of the compound's solubility in water. Ideally, acrylonitrile production would be integrated with final product manufacture, but markets and economics evidently do not favor this. (To the credit of acrylonitrile makers, only one of the incidents in Duguid's database (4) occurred in this industry.)

Based on *identification* (Step 1 of ISPD, Table 1), *eradication* (Step 2) is not truly possible with this prod-

uct, unless its manufacture is abandoned altogether. Therefore, inherently safer predesign must focus primarily on Step 3, *minimization*. A predesigner might also recommend that *isolation* (Step 4) be considered in ultimate plant siting.

In developing the preliminary process design, safety considerations are formalized by constructing a comprehensive stream hazard chart like the abbreviated version shown in Table 5. This chart includes byproducts and other chemicals present beyond those in Tables 2 and 3. In the predesign report, this document would be located, along with the stream chart ledger, at the bottom of the process flow diagram (PFD). Space does not allow inclusion of the comprehensive PFD here (a full-scale version appears on pp. 512–518 of Ref. 8 and on the web at [www.ulrichvasudesign.com/ACN.pdf](http://www.ulrichvasudesign.com/ACN.pdf)). Table 5 is an incomplete stream hazard chart presented to illustrate how a comprehensive one would be constructed; it should not be cited as an authoritative source.

To illustrate how ISPD principles are applied to equipment selection and design, a section of the reactor module from the PFD is shown in Figure 3. At first glance, it looks like any other process flow segment. Closer examination reveals that several important design concessions were made for the sake of safety.

A natural opportunity for regenerative heat recovery is not exploited. Without considering safety, one might be tempted to preheat the propylene and ammonia with the reactor effluent. But that is risky, because a broken heat exchanger seal could create premature combustion in the feed line.

Instead, reagents are injected into the reactor without preheating. This is a solid yet simple design strategy for CSTRs that minimizes the risk of premature feed ignition. Reactor and effluent heat-recovery chores are shifted to steam generation and feed vaporization through safer heat-transfer fluid intermediaries. The heat-transfer fluid is circulated between the E-113 heat exchangers and the vaporizers to avoid direct contact between the reagents and the hot reactor effluent. At the predesign stage, the heat-transfer fluid is not yet specified. Water is an obvious candidate, although a pump failure might lead to freezing and the formation of ice in the vaporizer tubing, causing it to burst. Heat-transfer oil is an alternative, but it also has drawbacks. Thus, the selection of a heat-transfer fluid is an issue that might await final design to be resolved.

In keeping with Kletz's third rule, attenuate, propylene and ammonia are stored as liquids under refrigeration rather than as gases or liquids under pressure.

To minimize adverse effects (Rule 3, Table 1), reactants

are fed to the reactor as gases. Propylene and ammonia could easily be sprayed into the bed as cold liquids to eliminate vaporizers E-110 and E-115. As liquids, however, their energy density and potential for causing damage are a thousand times larger.

On the other hand, the feed system in Figure 3 conflicts with Kletz's admonition to simplify. Vaporization adds complexity to the process and increases the risk of failures due to the extra equipment, not to mention its higher capital costs. This dilemma of which reactant phase is best should be revisited in discussions with safety experts and other designers on the project. Direct liquid injection might be chosen, in which case special fail-safe instrumentation and operating procedures must be in place to assure that it is done safely.

Reactor R-120, an exothermic CSTR, is a candidate for disaster. To avoid the risk of an ignition surge, reactor design and operation must exclude any chance of classic CSTR multi-stability (see Ref. 7, p. 184 for details on this phenomenon). The reactor should be as small as possible. Fortunately, the hot solid catalyst is a reliable reaction initiator. Start-up procedures must be designed to heat the bed to a temperature that guarantees the immediate ignition of fresh feed when it enters the reactor.

A more subtle ISPD characteristic of Figure 3 is that key mechanical devices, like pumps and compressors, are provided in multiples (equipment numbers followed by letters — A, B, etc.). This is done because most high-risk incidents, such as device failures, occur during shutdown and startup activities. With multiple units, a plant can still be operated, albeit at reduced capacity, when one device fails. The faulty unit can be isolated, purged, repaired,

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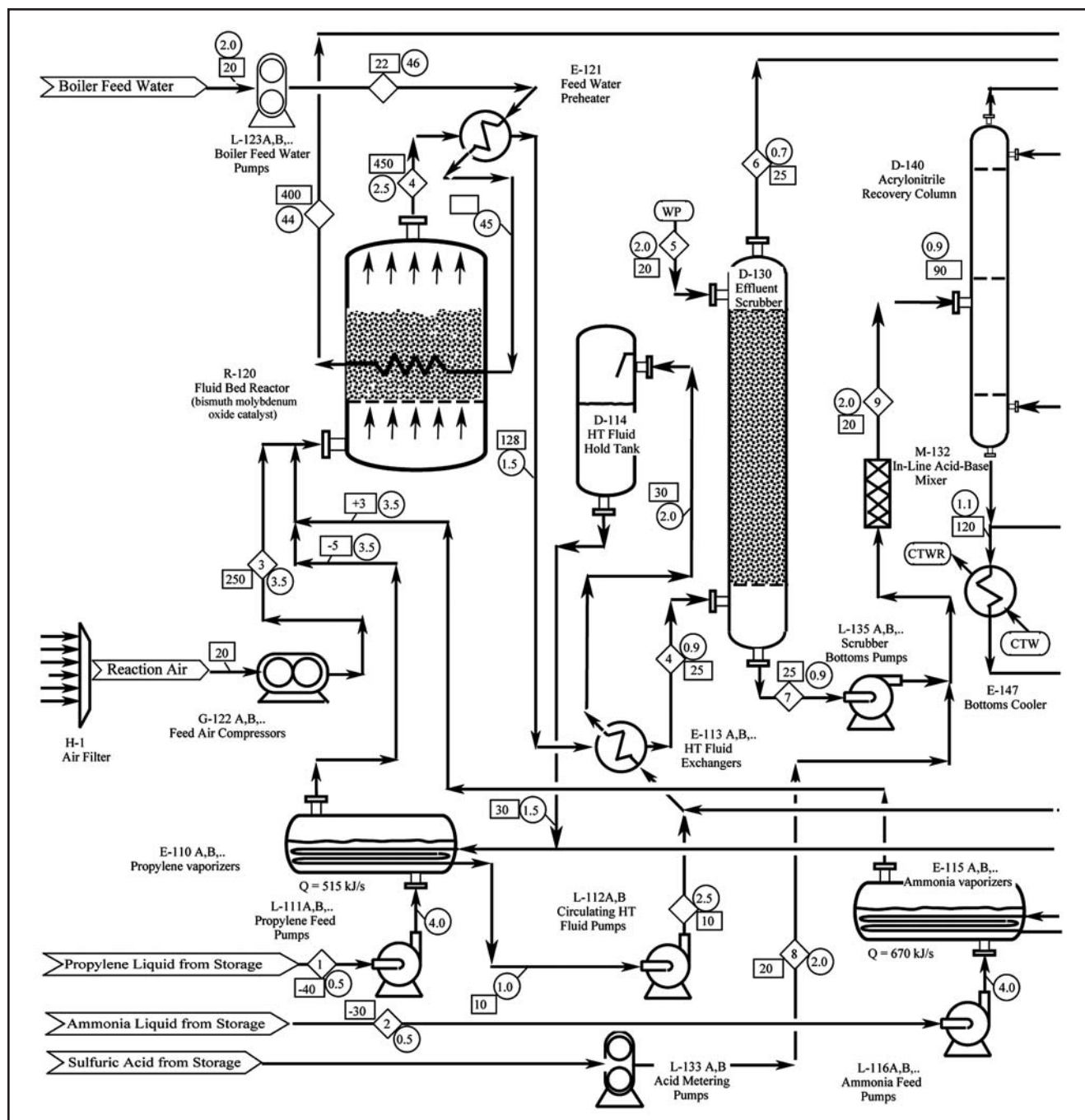


Figure 3. Portion of the acrylonitrile process flow diagram. (The complete version is available on pp. 512–515 of Ref. 8 or at [www.ulrichvasudesign.com/ACN.pdf](http://www.ulrichvasudesign.com/ACN.pdf).)

inspected, tested, purged again and returned to service, while its twin continues to operate — thereby avoiding a total plant shutdown.

Kletz recommends the use of non-continuous spares, *i.e.*, equipment that remains idle until it is needed (13). One may argue that idle equipment is more likely to dete-

riorate than functioning equipment. For that reason, the authors favor multiple items that operate continuously unless one is under repair.

The development of detailed safe startup and shutdown procedures are reserved for the final design stage and its hazards and operability analysis. Nonetheless,

any preliminary designer should be aware of the concerns that HAZOPs will raise.

A major issue with a process like the acrylonitrile plant is ensuring safety inside lines and vessels when they are idle. For example, upon cool-down, vapors inside heat exchangers, condensate drums, vaporizers and other equipment are prone to condense, thereby creating a vacuum; consequently, any leak (from a faulty isolation valve, for instance) allows atmospheric air to enter and create a combustible mixture. To prevent this, final designers should provide fill lines to blanket equipment with either an inert gas (e.g., nitrogen or carbon dioxide, or, for some vessels in a process like that shown in Figure 3, a hydrocarbon gas). Such practices avoid the creation of combustible mixtures at all times.

Unfortunately, history has recorded many deadly examples of failures in blanketing systems, since even successful inert-gas blanketing has its hazards. For example, cases have been documented where isolation procedures were

carried out properly to leave a vessel ready for repair, except that the vessel was full of inert gas. Maintenance workers, unaware of the need for breathing apparatus, subsequently entered the equipment, only to collapse and die from suffocation.

By the principles of inherently safer design, vessels should be strong enough to avoid implosion or collapse under vacuum and rupture if an explosion occurs inside. To the predesigner, this generally means “small is good.” Guidance for designing inherently safer vessels can be found in Refs. 15 and 23.

### Closing thoughts

Documents like Tables 2–5 can be woven seamlessly along with the process flow diagram into a design report. Upon such integration, safety, like economics and environmental protection, becomes a vital element of the pre-design package — and an issue that cannot be overlooked or ignored.

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