Inherently Safer Chemical Processes

Dennis C. Hendershot
Rohm and Haas Company, retired
dennis.hendershot@gmail.com

American Industrial Hygiene Association
Yuma Pacific-Southwest Section
43rd Annual Meeting
January 18, 2018
San Diego CA

ISD, ISP, IST?

- **ISD – Inherently Design**
- **ISP – Inherently Safety Process**
- **IST – Inherently Safer Technology**

They essentially mean the same thing. I think we really want IST, but the T means something different:

IST – Inherently Safer Thinking

History of inherently safer design concept

- **Technologists have always tried to eliminate hazards**
  - **Some examples:**
    - **In-situ manufacture of nitroglycerine in 1860s railroad construction**
    - **Alfred Nobel – dynamite in place of pure nitroglycerine for mining, construction**
- **Trevor Kletz, ICI, UK (1977)**
  - **Response to 1974 Flixborough, UK explosion**
  - **Named the concept**
  - **Developed a set of design principles for the process industries**


What you don't have, can't leak

Jubilee lecture

Trevor Kletz

Hazard

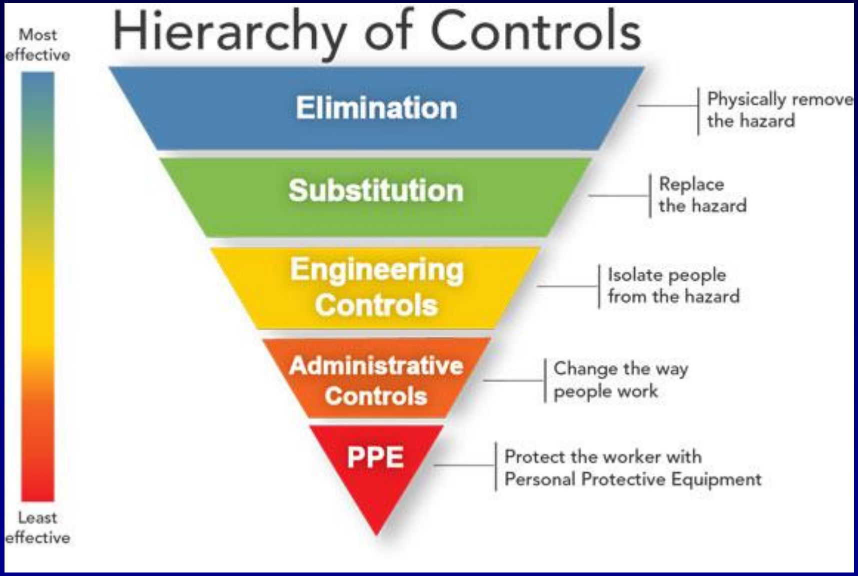
- An inherent physical or chemical characteristic that has the potential for causing harm to people, the environment, or property (CCPS, 1992).
- Hazards are intrinsic to a material, or its conditions of use.
- Examples
  - Chlorine - toxic by inhalation
  - Gasoline - flammable
  - High pressure steam - potential energy due to pressure, high temperature
- When we say something is "inherently safer," that is in the context of one or more of the multiple hazards in most technologies.

Process Safety Strategies

- **Inherent**
- **Passive**
- **Active**
- **Procedural**

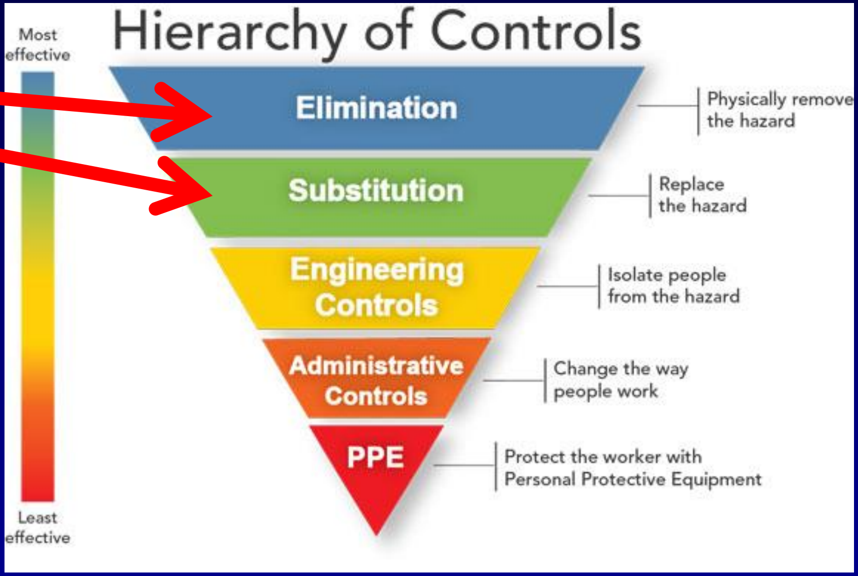
Process Safety Strategies

- Inherent
- Passive
- Active
- Procedural



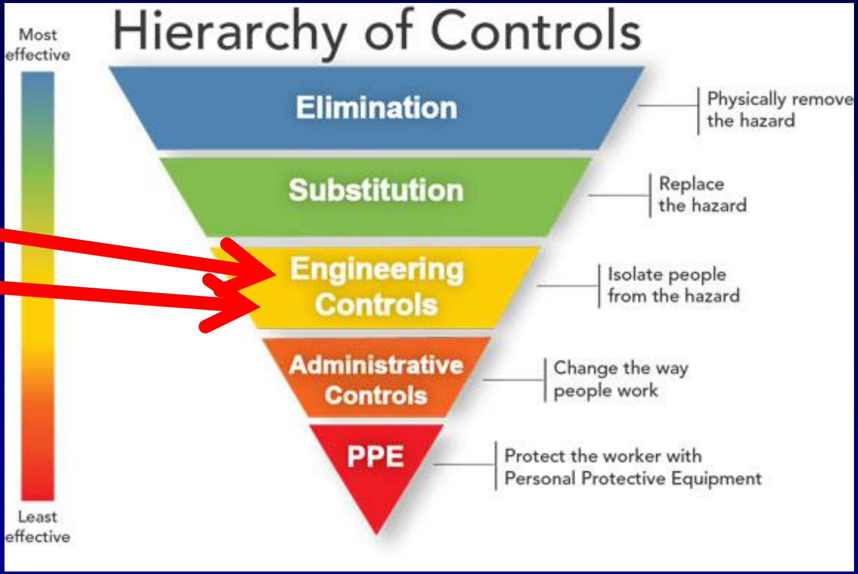
Process Safety Strategies

- Inherent
- Passive
- Active
- Procedural



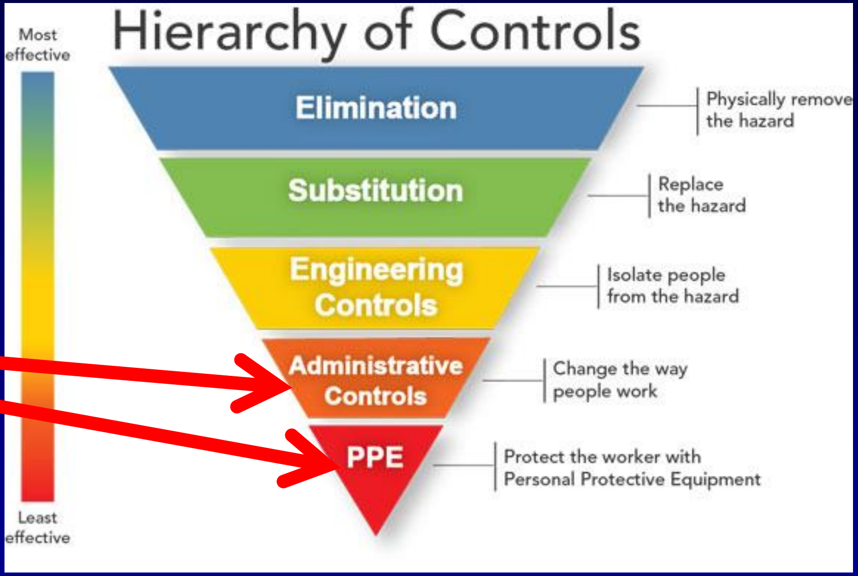
Process Safety Strategies

- Inherent
- Passive
- Active
- Procedural



Process Safety Strategies

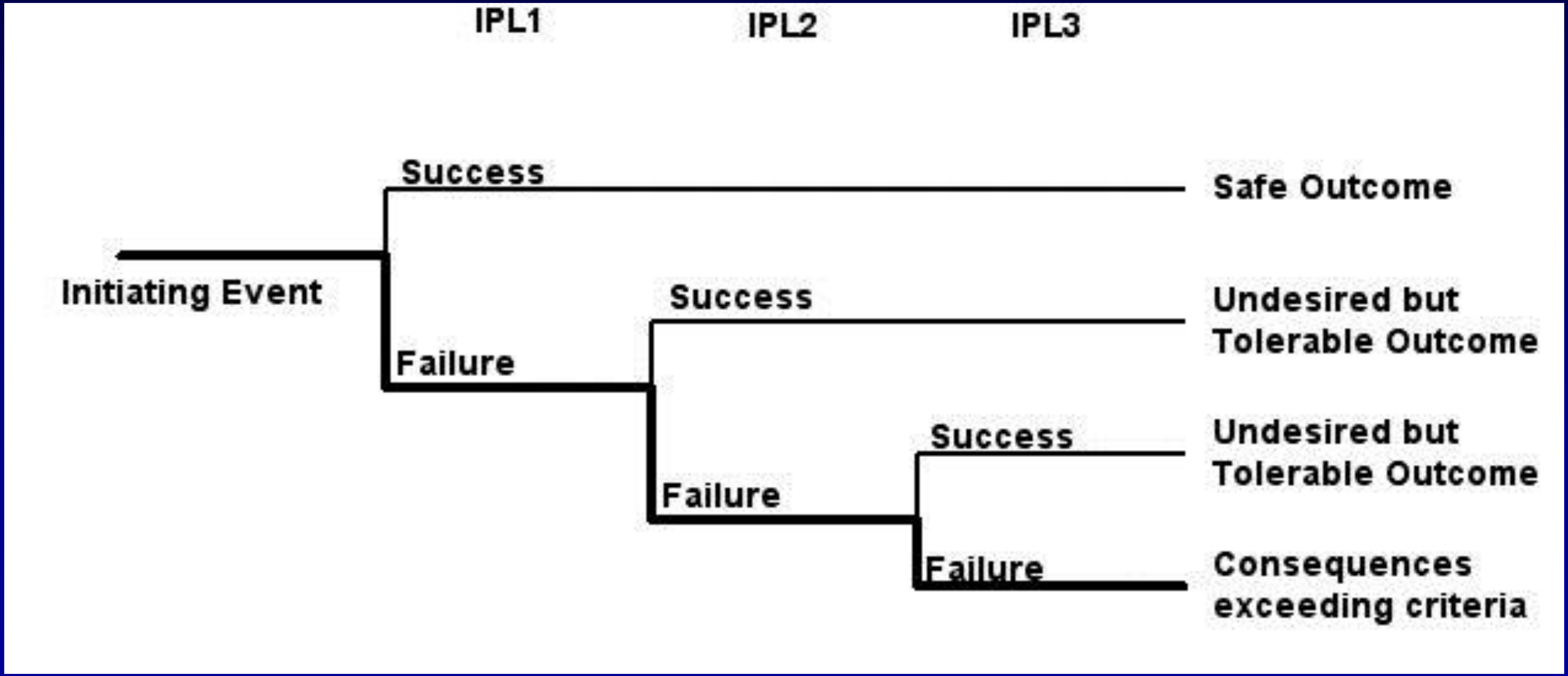
- **Inherent**
- **Passive**
- **Active**
- **Procedural**



Event tree model to understand ISD

- **Focus of ISD – reduce need for “add on” protective systems**
- **These are “layers of protection”**
- **Event tree logic model shows layers of protection**
- **An inherently safer design will require fewer layers of protection (fewer branches in the event tree) meet risk tolerance criteria**

Event tree model



IPL – Independent Protection Layer

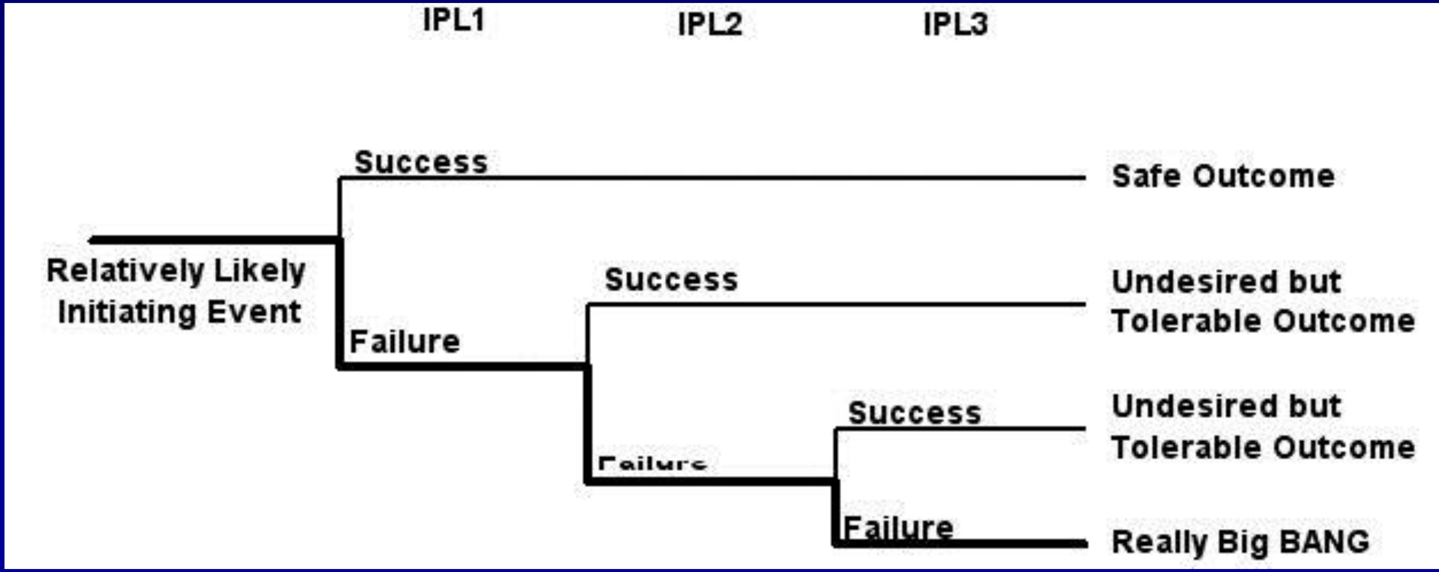
ISD as a consequence reduction tool

- **Initial situation - unacceptable**

IPL – Independent Protection Layer

Reducing Risk

- **TRADITIONAL APPROACH: Add additional layers of protection to meet risk criteria**
- **Consequence is not changed, likelihood is reduced**

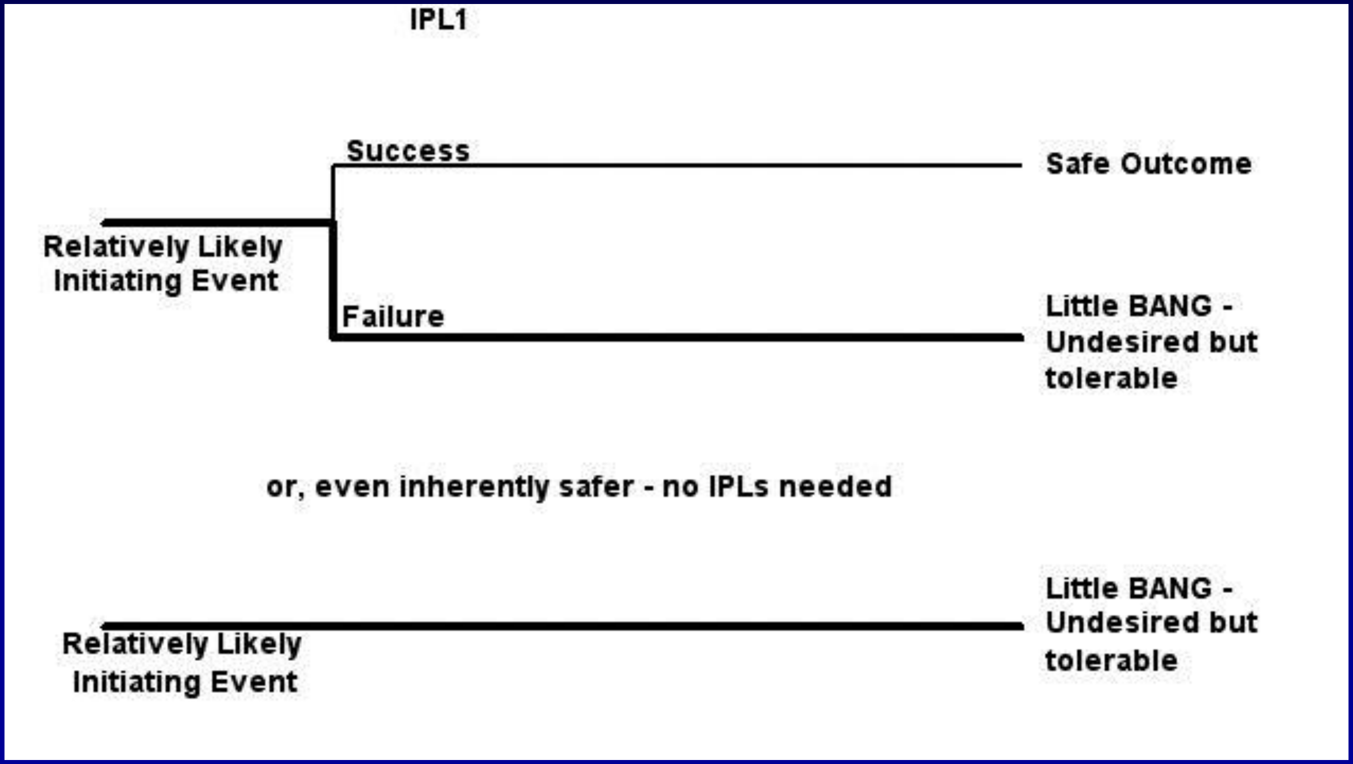


IPL – Independent Protection Layer

ISD Approach – Reduce Consequences

- **ISD approach – reduce consequence so additional layers of protection are not needed**
- **Ideally, consequence would be reduced sufficiently that no layers of protection are needed at all!**

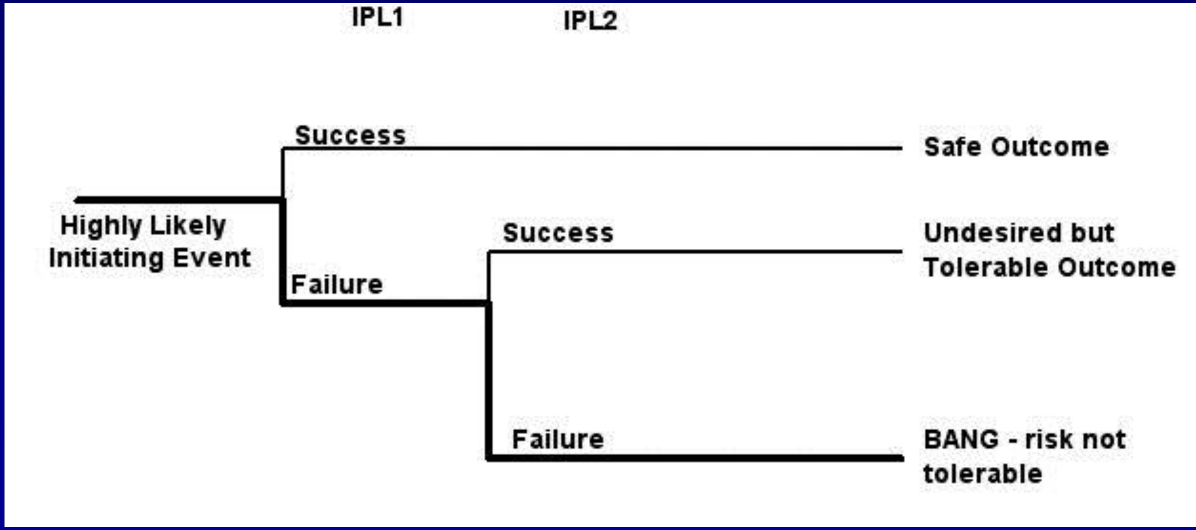
ISD as a consequence reduction tool



IPL – Independent Protection Layer

ISD as a frequency reduction tool

- **Initial situation – relatively likely initiating event with two layers of protection, risk is not tolerable**

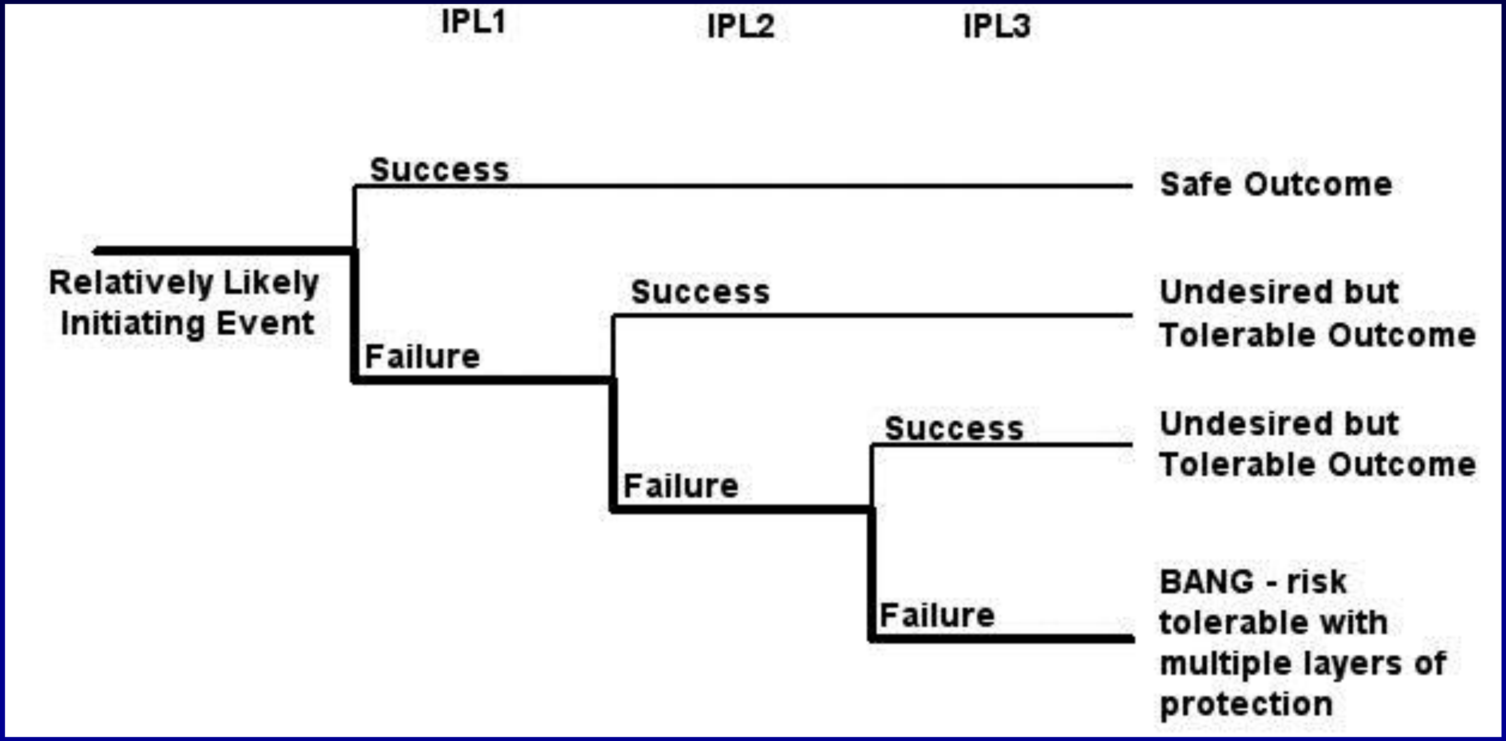


IPL – Independent Protective Layer

ISD as a frequency reduction tool

- **TRADITIONAL APPROACH: Add additional layers of protection to meet risk criteria**
- **Consequence is not changed, likelihood is reduced**

ISD as a frequency reduction tool

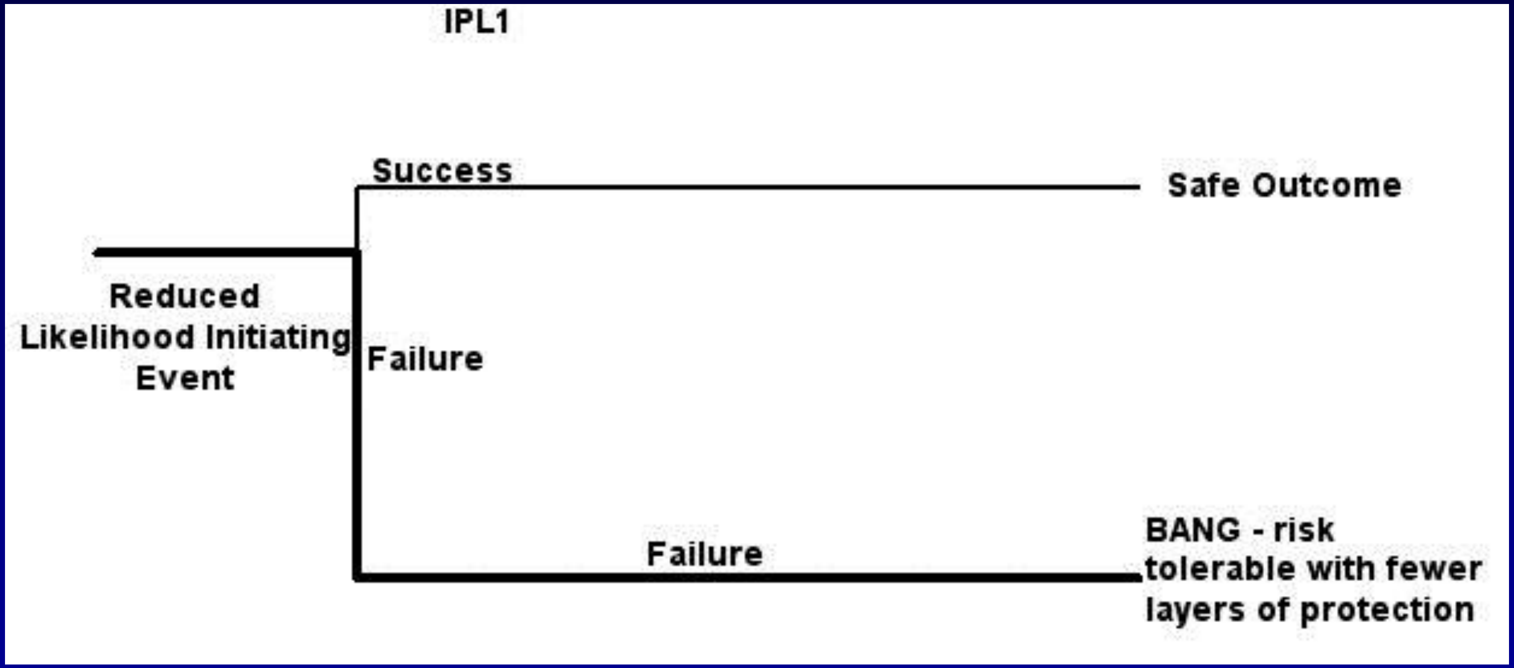


IPL – Independent Protective Layer

ISD as a frequency reduction tool

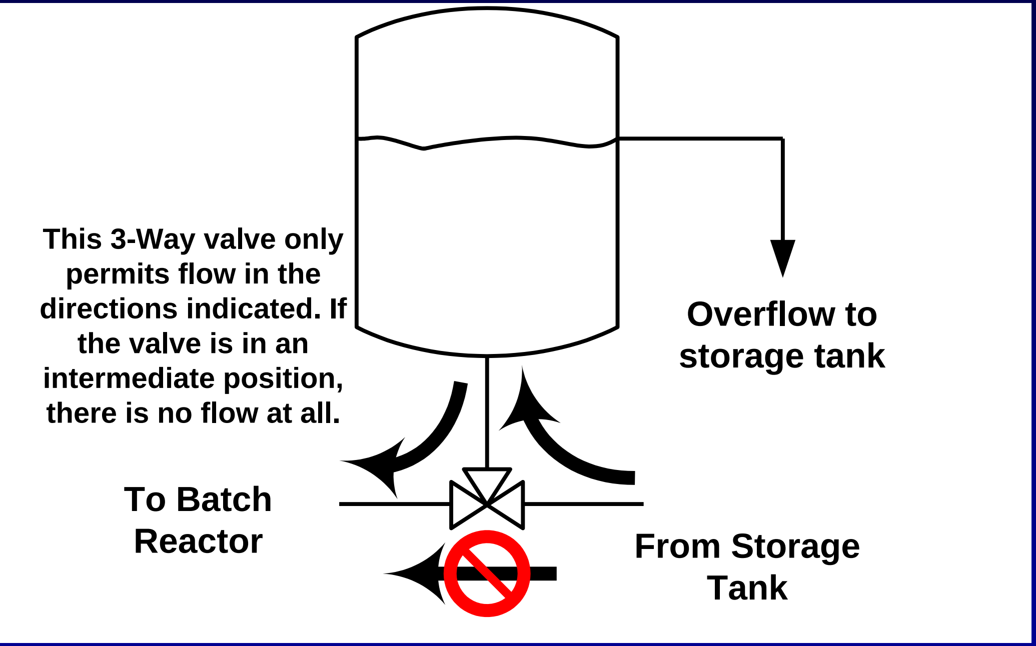
- **ISD approach – make the initiating event extremely difficult or unlikely (ideally, impossible!) so layers of protection are not needed**

ISD as a frequency reduction tool



IPL – Independent Protective Layer

Example of inherent frequency reduction



- **If the material in the feed tank is overcharged to the downstream vessel, a runaway reaction can occur**
- **The charge tank holds exactly the correct charge, and overflows to the supply tank if overfilled**
- **The tank would have to be filled and emptied many times to get sufficient raw material into the reactor for a runaway**
- **If you do this, the *consequence* is the same, but the *likelihood* (frequency) is inherently lower – it is really difficult to overcharge the batch reactor**

Inherently safer design strategies for the process industries

- **Substitute**
- **Minimize**
- **Moderate**
- **Simplify**

IST – Throughout the process life cycle

- **Selection of basic technology**
  - **Chemistry**
  - **Catalysts**
  - **Process conditions**
- **Preliminary design**
  - **Unit operations**
  - **Site selection**

IST – Throughout the process life cycle

- **Detailed design**
  - **Specific process equipment**
  - **Plant layout**
  - **Piping design**
- **Operation and Management of Change**
  - **Much of the consideration of IST is focused on the technology R&D, process design, and plant design stages of the life cycle. But, it is never too late!**

Example – a nitration process

Understand your process!

- **Basic chemical engineering – know what physical and chemical parameters are important in the process**
  - **Mass transfer**
  - **Heat transfer**
  - **Mixing**
  - **Chemical reaction**
  - **……**

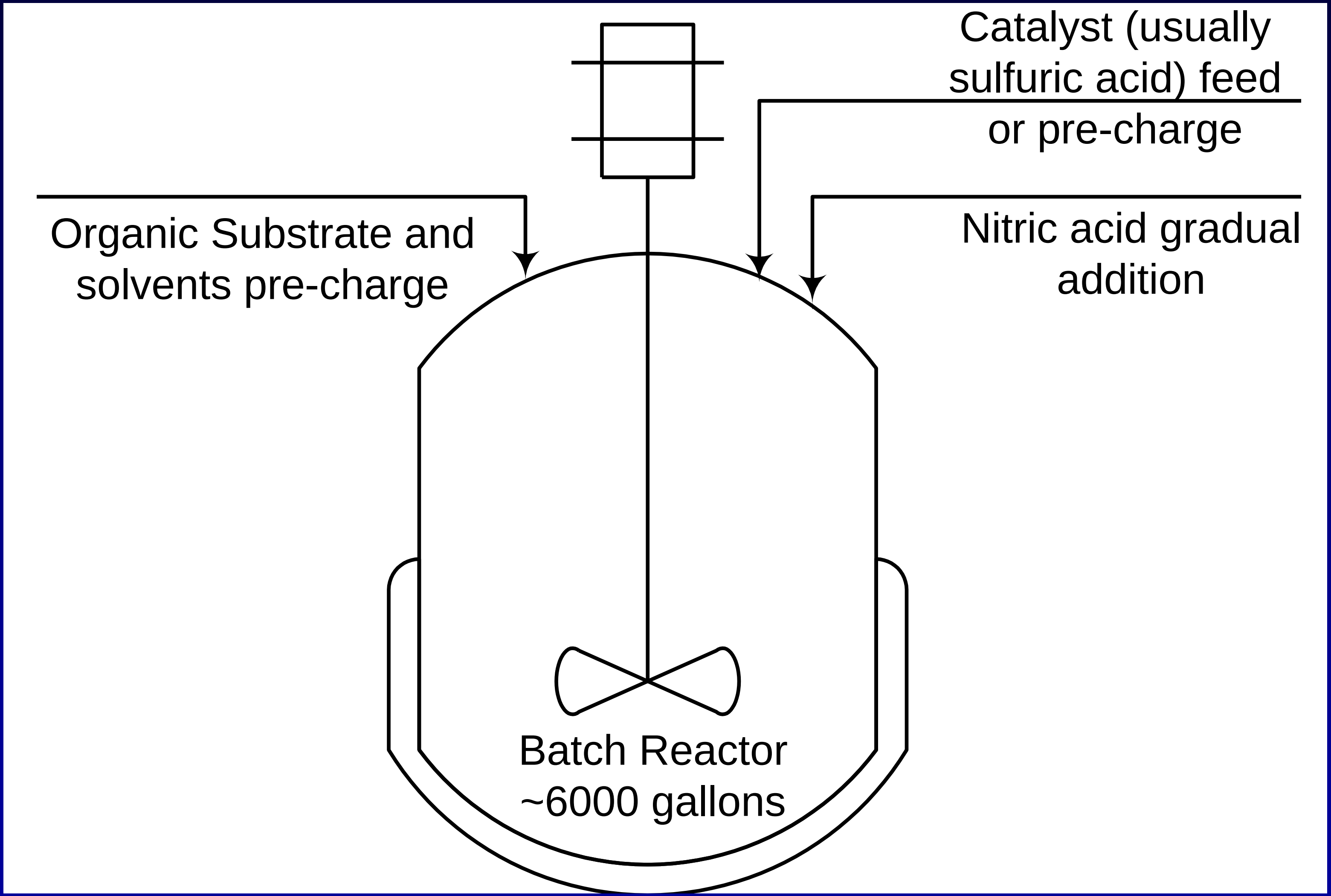
Minimize – A batch nitration process

$$\text{Organic substrate (X -H)} + HNO_3 \xrightarrow[\text{Solvent}]{H_2SO_4}$$

$$\text{Nitrated Product (X -NO}_2\text{)} + H_2O$$

+ a lot of HEAT!

Batch nitration process



What controls the nitration reaction?

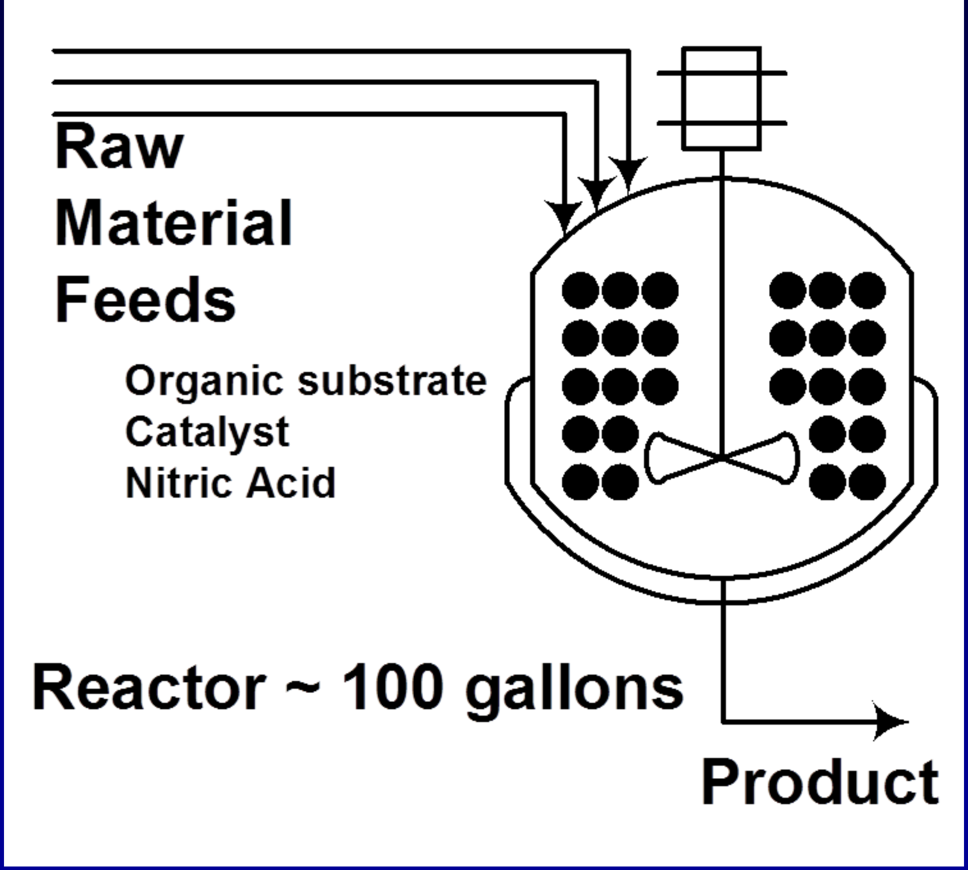
- **Bulk mixing of the nitric acid feed into the reaction mass**
- **Mass transfer of nitric acid from the aqueous phase to the organic phase where the reaction occurs**
- **Removal of the heat of reaction**

- **To design a smaller reactor, focus on these chemical and physical processes.**
- **Do you want a fast reaction or a slow reaction? Why?**

To minimize reactor size

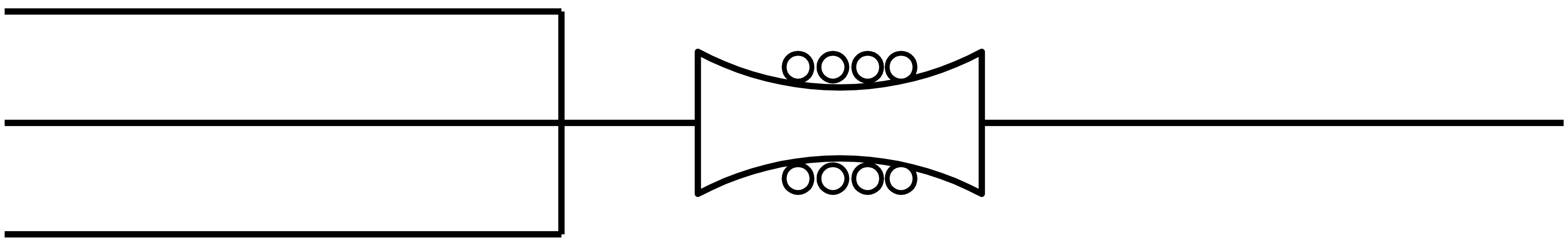
- **Good bulk mixing of materials (“macromixing”)**
- **Large interfacial surface area between the aqueous and organic phase to maximize mass transfer (and therefore maximize the *rate of reaction*.**
  - **create smaller droplets of the suspended phase (high shear mixer, good “micromixing”**
- **Large heat transfer area in the reactor**

CSTR Nitration Process



Why is smaller potentially safer?

Will a pipe reactor work?



Raw Material Feeds

- **Organic substrate**
- **Catalyst**
- **Nitric Acid**

Cooled continuous mixer/reactor

Reaction Chemistry - Acrylic Esters

- **Reppe Process**

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

Acetylene - flammable, reactive

Carbon monoxide - toxic, flammable

Nickel carbonyl - toxic, environmental hazard (heavy metals), carcinogenic

Anhydrous HCl - toxic, corrosive

Product - a monomer with reactivity (polymerization) hazards

Alternate chemistry

- **Propylene Oxidation Process**

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

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

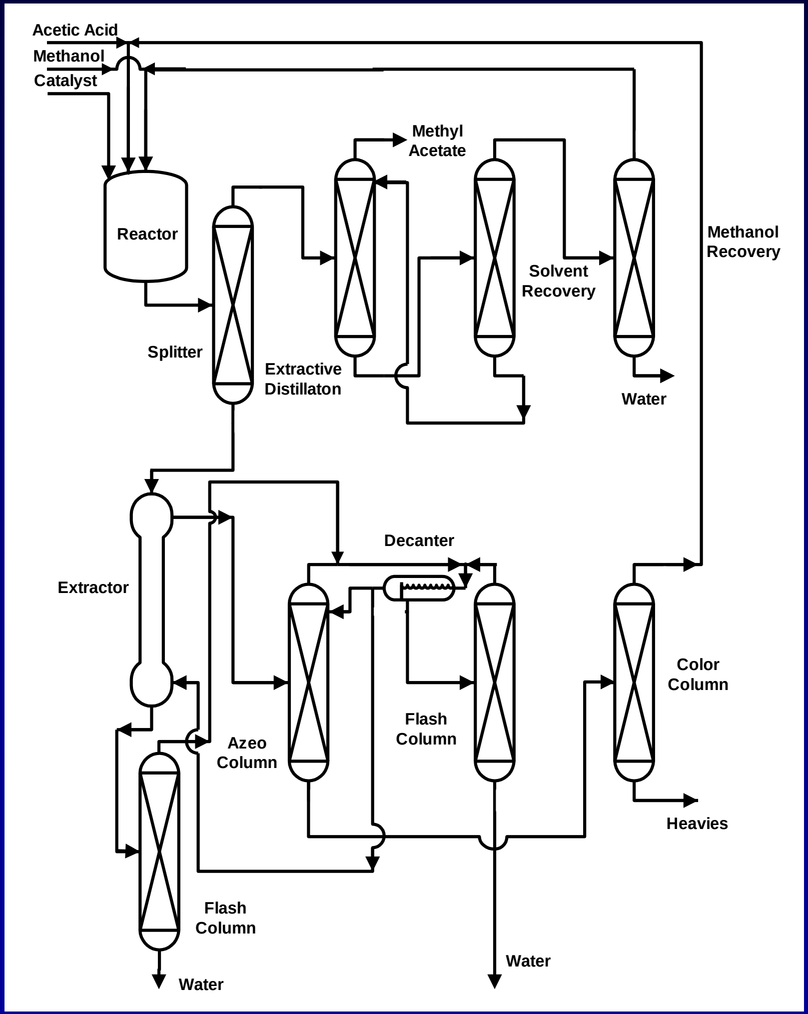
Inherently safe?

No, but inherently *safer*. Hazards are primarily flammability, corrosivity from sulfuric acid catalyst for the esterification step, small amounts of acrolein as a transient intermediate in the oxidation step, reactivity hazard for the monomer product.

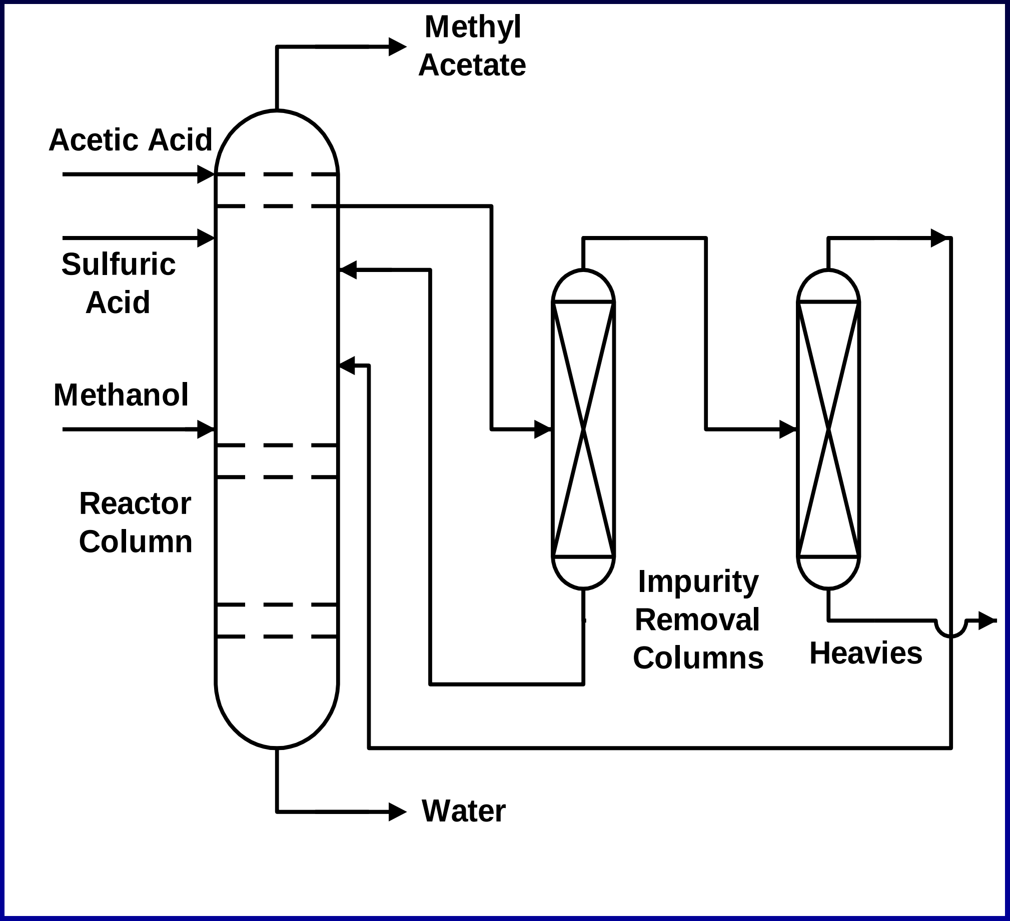
Recent Refining Alkylation Example

- **Alkylation processes for refineries**
  - **HF**
  - **Sulfuric acid**
- **In the fall of 2016 Chevron announced plans to commercialize a new alkylation process at their Salt Lake refinery using ionic liquid catalyst (*Chemical and Engineering News*, Oct. 3, 2016)**

Traditional Methyl Acetate Process



Reactive Distillation Process - Eastman Chemical



How do we get people to practice Inherently Safer Thinking?

We do a lot of things in the design and operation of process facilities which identify hazards – for example:

- **Process hazard analysis (PHA) and other formal hazard identification tools at all stages in the life cycle**
- **Management of Change (MOC)**
- **Pre-Startup Safety Review (PSSR)**
- **Incident Investigation**
- **Writing operating procedures**
- **Job safety analysis for a specific job**
- **"Walk around" safety inspection of a plant by a small group of people (operator, foreman, engineer, manager, etc.)**

How do we get people to practice Inherently Safer Thinking?

The people involved in these activities need to learn to ask these questions, in this order:

1. **Can I eliminate this hazard?**
2. **If it cannot be eliminated, can I reduce the magnitude of the hazard (or the frequency of the hazardous operation)?**
3. **Do the alternatives identified in questions 1 and 2 increase the magnitude of any other hazards, or create new hazards?**
   - **(If so, consider all hazards in selecting the best alternative.)**
4. **At this point, what technical and management systems are required to manage the hazards which inevitably will remain?**
   - **How can I make those systems inherently more robust and reliable?**

Usually people go directly to Question 4, without challenging the existence of the hazard.

How to approach ISThinking

- Not a meeting or series of meetings, but rather an ACTIVITY and a way of thinking
- Not really different than any other engineering activity
  - I am using the term "engineering design activity" with the broad definition of "engineer" in mind
    - "to arrange, manage, or carry through by skillful or artful contrivance" (dictionary.com)
    - "to plan or do something in a skillful way" (Cambridge English Dictionary on line)
  - Not based on a person's college degree or job title
  - Many people in the process industries "engineer" by this definition – operators, maintenance workers, chemists, industrial hygienists, even people with "engineer" in their college degrees or job titles, etc.
  - Apply inherently safer thinking in all "engineering" activities

Be an engineer!

- Identify hazards
- Establish Inherently Safer Design goals
- Use all of your knowledge of the technology to identify options to meet those goals
  - Not just your own knowledge – use all the knowledge and expertise of others to help!
- Decide on the design that best meets all of the design objectives

The importance of establishing goals in design

(for inherently safer design, as well as other important objectives for the technology)

A process example - domestic “green” home refrigerators

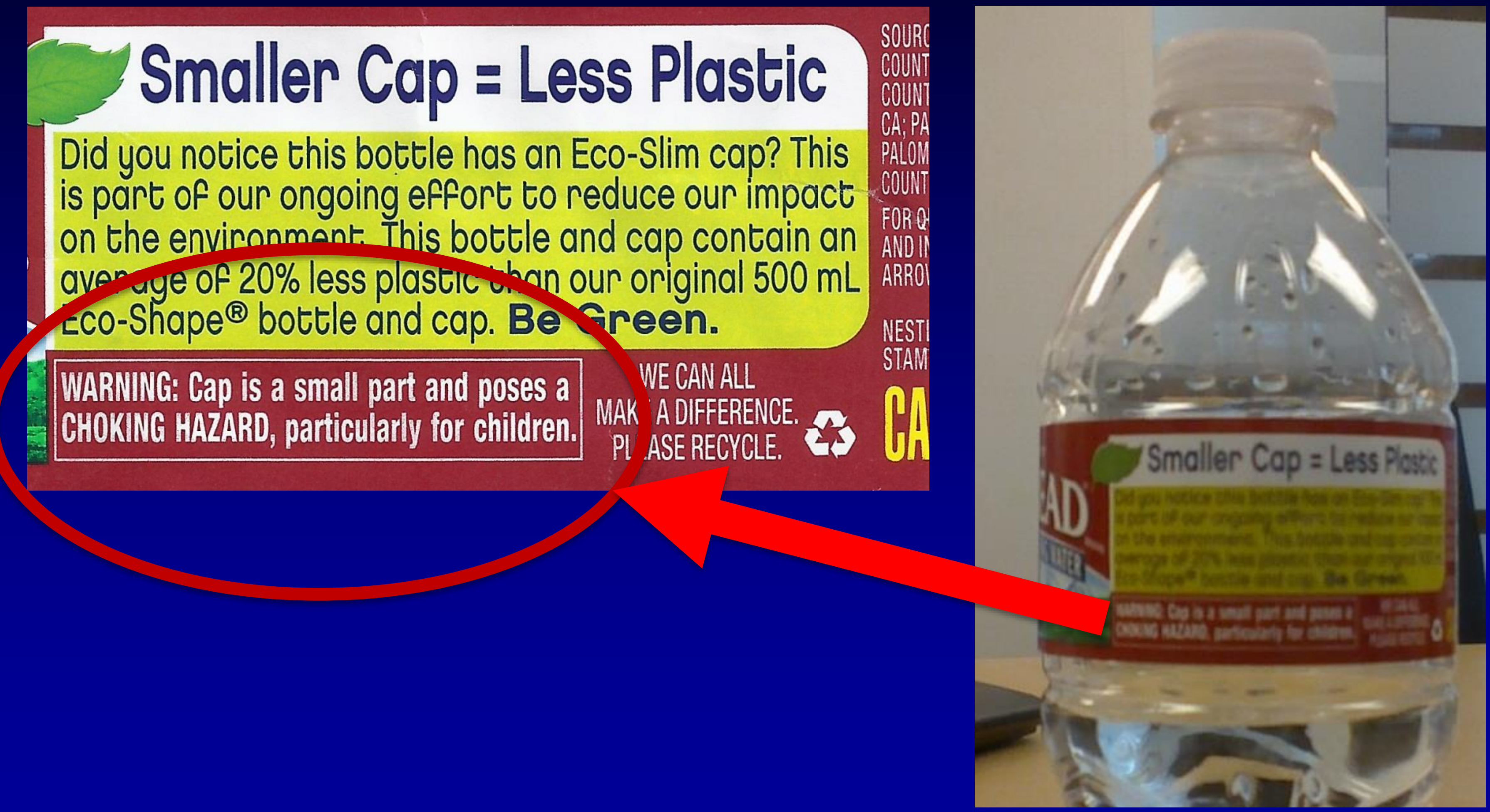
- **Hazard – flammability of hydrocarbon refrigerant (you don’t want a refrigerant leak to create an explosive atmosphere in the kitchen!)**
- **Design objective: Inventory of refrigerant in a domestic refrigerator < 150 grams**
- **Given this goal, experts in home refrigeration technology were able to design safe “green” home refrigerators**

ISD Conflicts

"The true rule, in determining whether to embrace, or reject, any thing, is not whether it have any evil in it; but whether it have more of evil than of good. There are few things wholly evil, or wholly good. Almost every thing ... is an inseparable compound of the two; so that our best judgment of the preponderance between them is continually demanded."

Trade offs – an inherently more environmentally friendly design

No good deed goes unpunished!



Finally - Inherently safer = “safe enough”?

- **Maybe not!**
- **You still have to answer the question “How safe is safe enough?”**
- **Example**
  - **Union Carbide and successor owners of the pesticide plant in Institute WV that handled methyl isocyanate (MIC, the material released at Bhopal) significantly reduced the inventory of MIC after 1984 (Inherent Safety strategy - minimize).**
  - **The inventory reduction was not sufficient to satisfy the community, and following years of protest, litigation, and other community obstacles, the final owner, Bayer Crop Sciences, shut the facility down in 2012.**

Thank you for your attention!

Scooter, an engineer who can "carry through by skillful or artful contrivance." He has invented a procedure to get dog biscuits out of his "biscuit ball" by tossing the ball down the hardwood steps so the biscuits break and fall out through the holes in the ball.