Inherently Safer Design

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Inherently Safer Design and Green Engineering

- A common philosophy
  - Eliminate hazards from the manufacturing process rather than controlling hazards
  - Hazards to:
    - People
    - Environment
    - Property
    - Business

New paradigm for the environment

- Traditional environmental approach
  - "End of pipe" waste treatment
  - "Waste minimization" – an advance, but we can go further
- Green chemistry and engineering
  - Eliminate or dramatically reduce hazards to the environment

Many of us learned this as children

- Dr. Suess – *The Cat in the Hat Comes Back*

- **The message:**

Once you get something dirty, the only way to get it clean is to make *something else* dirty.

The best way to keep the world clean is to not get it dirty to begin with.

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New paradigm for safety

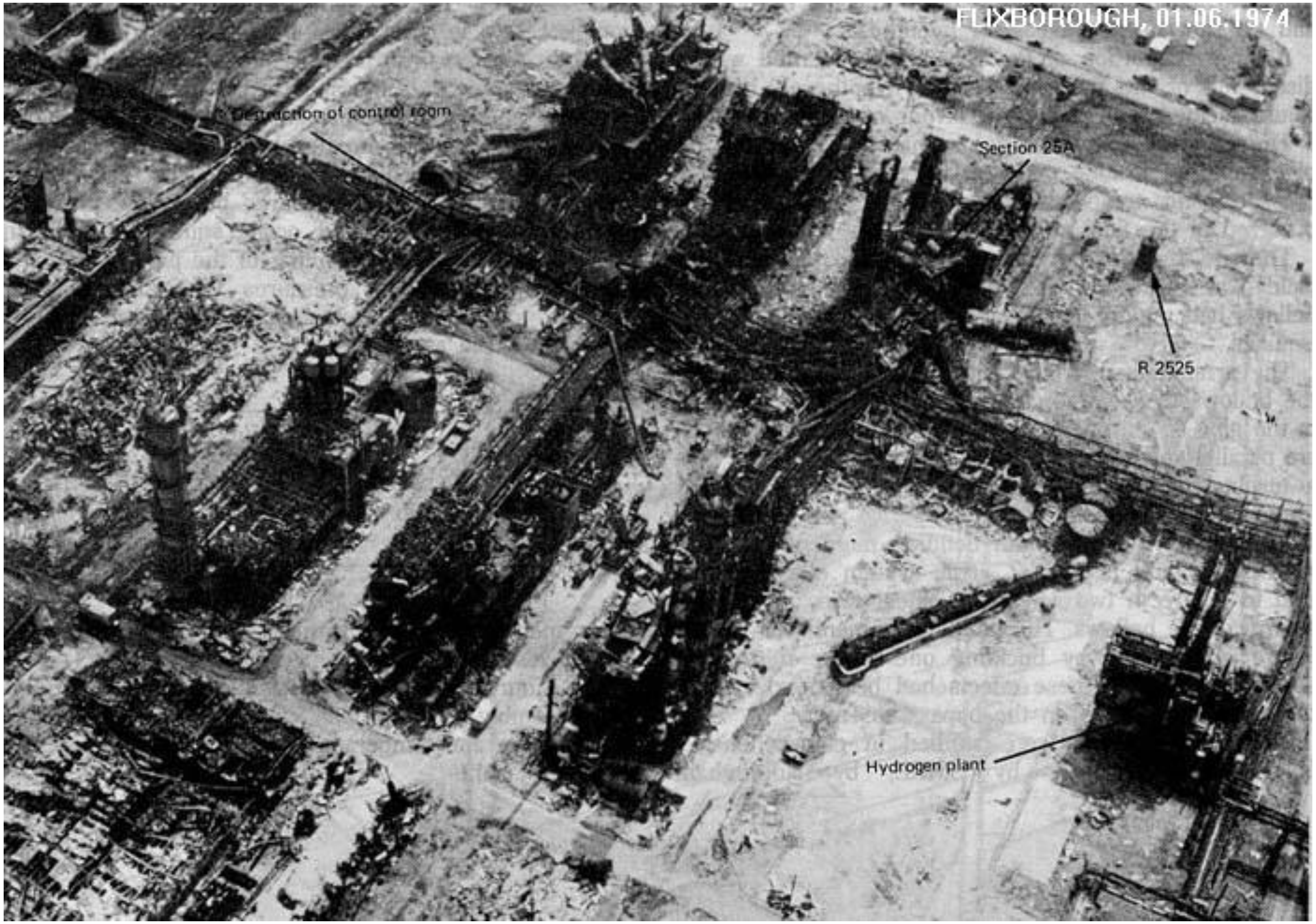
- Traditional safety approach
  - "Add on" safety features
    - Prevent - alarms, safety interlocks, procedures, training
    - Mitigate – sprinkler systems, water curtains, emergency response systems and procedures
- Inherently safer design
  - Eliminate or significantly reduce process hazards

Safety and the environment

- Safety – focus on immediate impacts of single events
  - Impact on people
  - Impact on property and business – "Loss Prevention"
- These single events do cause both short and long term environmental damage as well

Why are we interested in inherently safer design?

Flixborough, England (1974)



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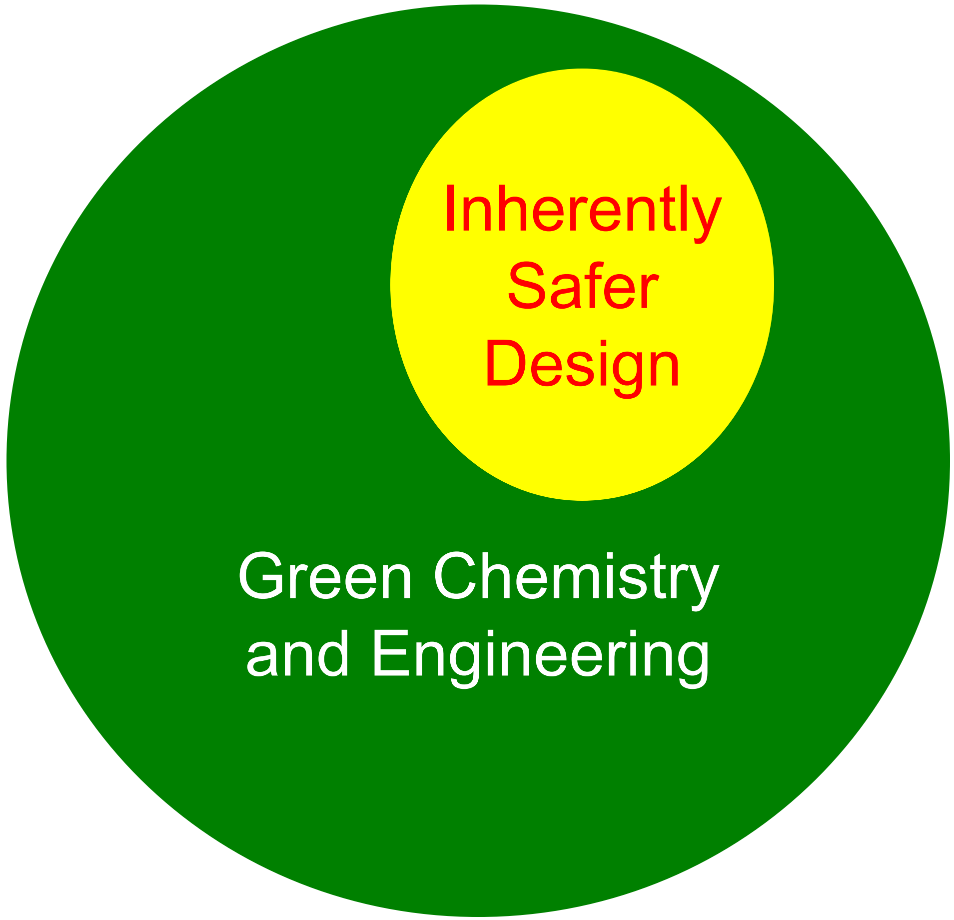
Pasadena, TX (1989)

Relationship of green chemistry, engineering, and inherently safer design

- Green chemistry and engineering – broad consideration of many human and environmental impacts
  - reaction paths, synthesis routes, raw materials and intermediates
  - implementation of selected synthesis routes
  - Requires fundamental knowledge of physical and chemical processes
- Inherently safer design – focus on "safety" incidents
  - Immediate consequences of single events (fires, explosions, immediate effects of toxic material release)
  - Includes consideration of chemistry as well as engineering issues such as siting, transportation, and detailed equipment design

Inherently safer design, green chemistry, and green engineering



History of inherently safer design

- **Technologists have always tried to eliminate hazards**
  - **Robert Stevenson – simplified controls for early steam locomotives (1820s)**
  - **James Howden – in-situ manufacture of nitroglycerine for the Central Pacific Railroad (1867)**
  - **Alfred Nobel – dynamite (1867)**
  - **Thomas Midgely – CFC Refrigerants – (1930)**
    - **Replacement for flammable (light hydrocarbons, ammonia) and toxic (ammonia, sulfur dioxide) refrigerants then in use**

Inherently safer design in the chemical industry

- Trevor Kletz, ICI, UK (1977)
  - Jubilee Lecture to the UK Society of the Chemical Industry
  - Reaction to Flixborough, England explosion
  - Named the concept
  - Developed a set of specific design principles for the chemical industry
  - Later published - original paper referring to "Inherently Safer Design"
    - Kletz, T. A. "What You Don't Have, Can't Leak." *Chemistry and Industry*, 287-292, 6 May 1978.

What is inherently safer design?

- Inherent - "existing in something as a permanent and inseparable element..."
  - safety "built in", not "added on"
- Eliminate or minimize hazards rather than control hazards
- More a philosophy and way of thinking than a specific set of tools and methods
  - Applicable at all levels of design and operation from conceptual design to plant operations
- *"Safer,"* not *"Safe"*

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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
  - Phosgene - toxic by inhalation
  - Acetone - flammable
  - High pressure steam - potential energy due to pressure, high temperature

To eliminate hazards:

- Eliminate the material
- Change the material
- Change the conditions of use

Chemical Process Safety Strategies

Inherent

- **Eliminate or reduce the hazard by changing the process or materials which are non-hazardous or less hazardous**
- **Integral to the product, process, or plant - cannot be easily defeated or changed without fundamentally altering the process or plant design**
- **EXAMPLE**
  - **Substituting water for a flammable solvent (latex paints compared to oil base paints)**

Passive

- **Minimize hazard using process or equipment design features which reduce frequency or consequence without the active functioning of any device**
- **EXAMPLE**
  - **Containment dike around a hazardous material storage tank**

Active

- Controls, safety interlocks, automatic shut down systems
- Multiple active elements
  - Sensor - detect hazardous condition
  - Logic device - decide what to do
  - Control element - implement action
- Prevent incidents, or mitigate the consequences of incidents
- EXAMPLE
  - High level alarm in a tank shuts automatic feed valve

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Procedural

- Standard operating procedures, safety rules and standard procedures, emergency response procedures, training
- EXAMPLE
  - Confined space entry procedures

Batch Chemical Reactor Example

- **Hazard of concern – runaway reaction causing high temperature and pressure and potential reactor rupture**

Inherent

- **Develop chemistry which is not exothermic, or mildly exothermic**
  - **Maximum adiabatic exotherm temperature < boiling point of all ingredients and onset temperature of any decomposition or other reactions**

Passive

- Maximum adiabatic pressure for reaction determined to be 150 psig
- Run reaction in a 250 psig design reactor
- Hazard (pressure) still exists, but passively contained by the pressure vessel

Active

- Maximum adiabatic pressure for 100% reaction is 150 psig, reactor design pressure is 50 psig
- Gradually add limiting reactant with temperature control to limit potential energy from reaction
- Use high temperature and pressure interlocks to stop feed and apply emergency cooling
- Provide emergency relief system

Procedural

- Maximum adiabatic pressure for 100% reaction is 150 psig, reactor design pressure is 50 psig
- Gradually add limiting reactant with temperature control to limit potential energy from reaction
- Train operator to observe temperature, stop feeds and apply cooling if temperature exceeds critical operating limit

Which strategy should we use?

- Generally, in order of robustness and reliability:
  - Inherent
  - Passive
  - Active
  - Procedural
- But - there is a place and need for ALL of these strategies in a complete safety program

Inherently Safer Design Strategies

Inherently Safer Design Strategies

- Minimize
- Moderate
- Substitute
- Simplify

Minimize

- Use small quantities of hazardous substances or energy
  - Storage
  - Intermediate storage
  - Piping
  - Process equipment
- "Process Intensification"

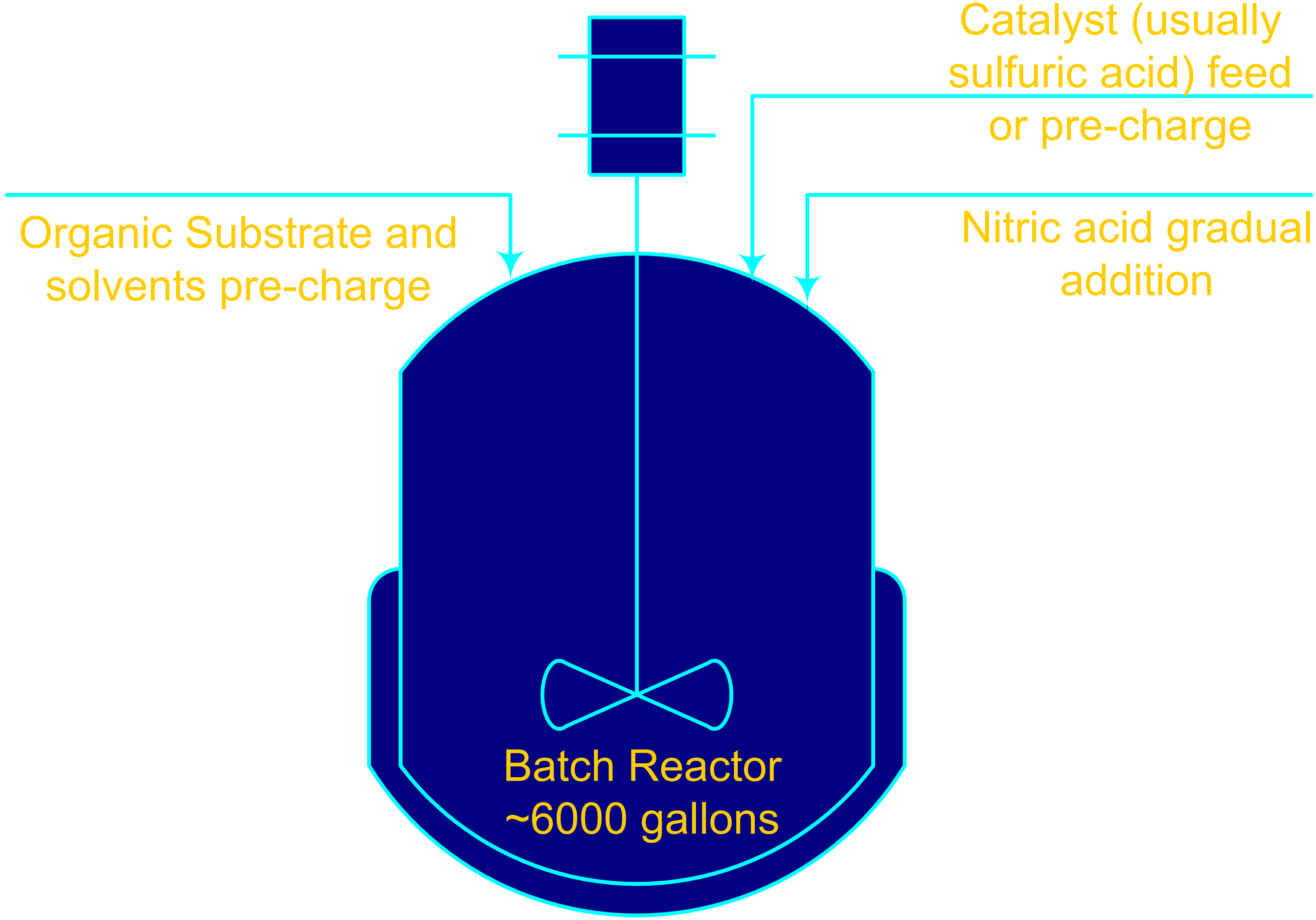
Benefits

- Reduced consequence of incident (explosion, fire, toxic material release)
- Improved effectiveness and feasibility of other protective systems – for example:
  - Secondary containment
  - Reactor dump or quench systems

Opportunities for process intensification in reactors

- Understand what controls chemical reaction to design equipment to optimize the reaction
  - Heat removal
  - Mass transfer
    - Mixing
    - Between phases/across surfaces
  - Chemical equilibrium
  - Molecular processes

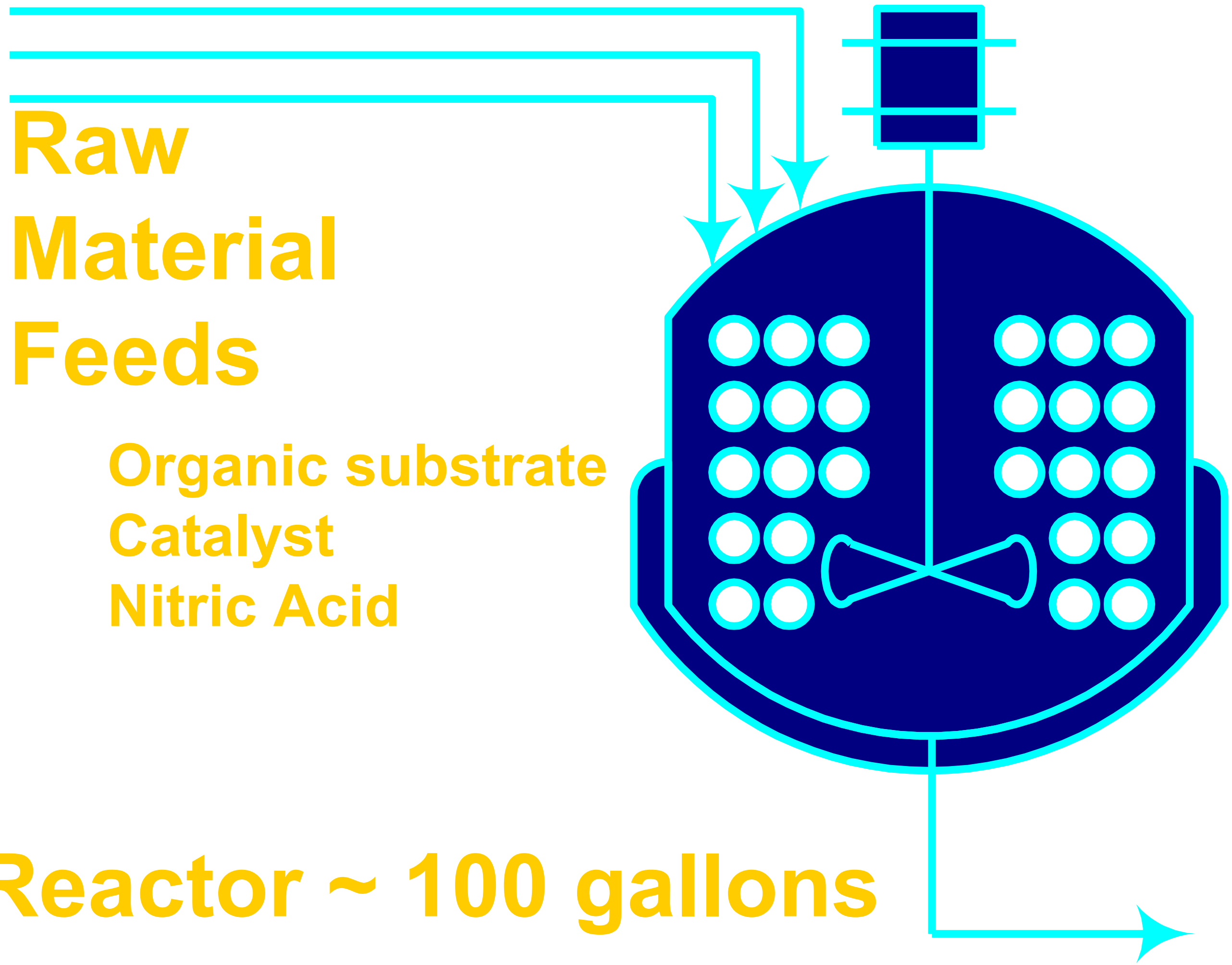
Semi-batch nitration process



What controls the rate of this reaction?

- Mixing – bringing reactants into contact with each other
- Mass transfer – from aqueous phase (nitric acid) to organic phase (organic substrate)
- Heat removal

CSTR Nitration Process



Raw Material Feeds

- Organic substrate
- Catalyst
- Nitric Acid

Reactor ~ 100 gallons

Product

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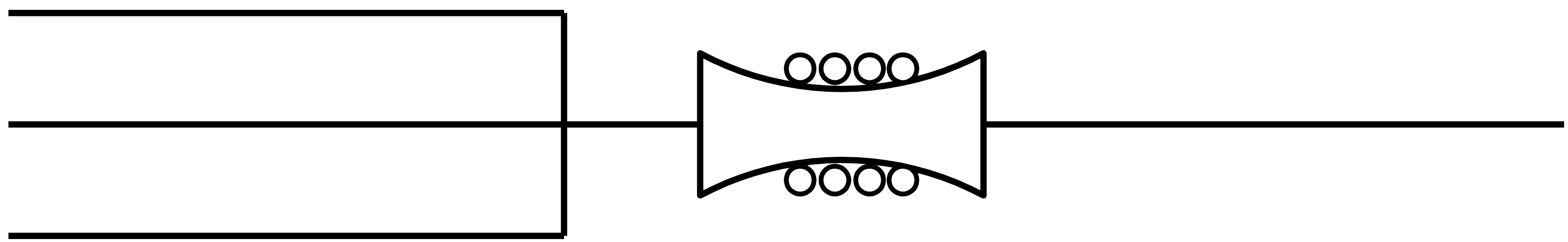
Can you do this reaction in a pipe reactor?

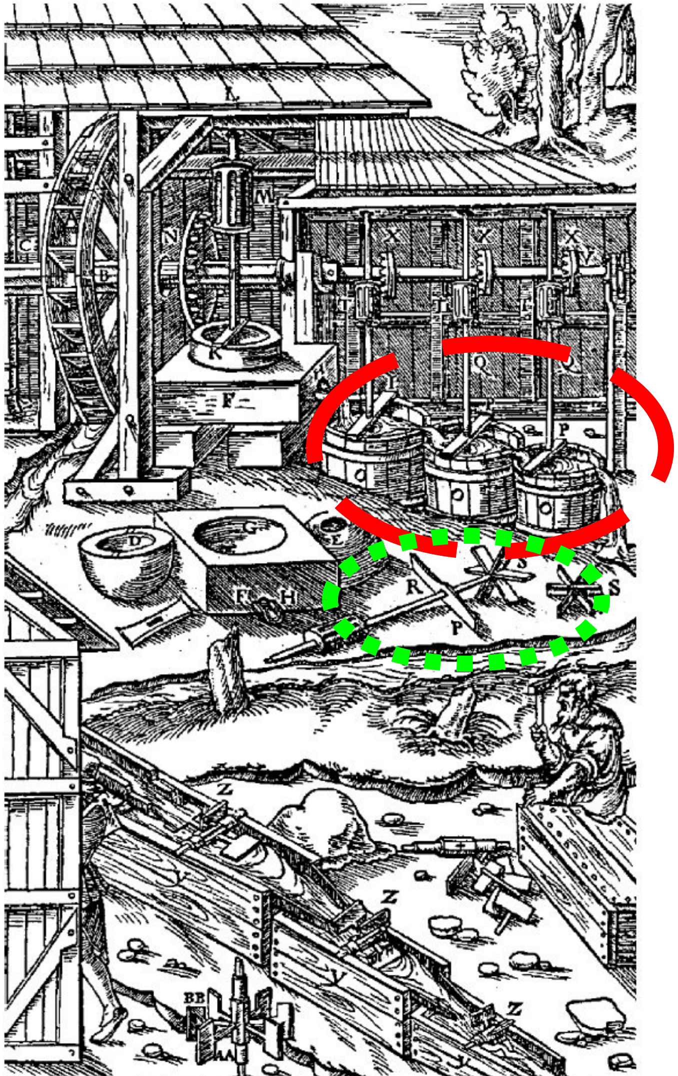


Raw Material Feeds

- Organic substrate
- Catalyst
- Nitric Acid

Cooled continuous mixer/reactor

How much progress have we made since this 16th Century gold plant?



From A. I. Stankiewicz and J. A. Moulijn, “Process Intensification: Transforming Chemical Engineering,” *Chemical Engineering Progress* **96** (1) (2000) 22-34.

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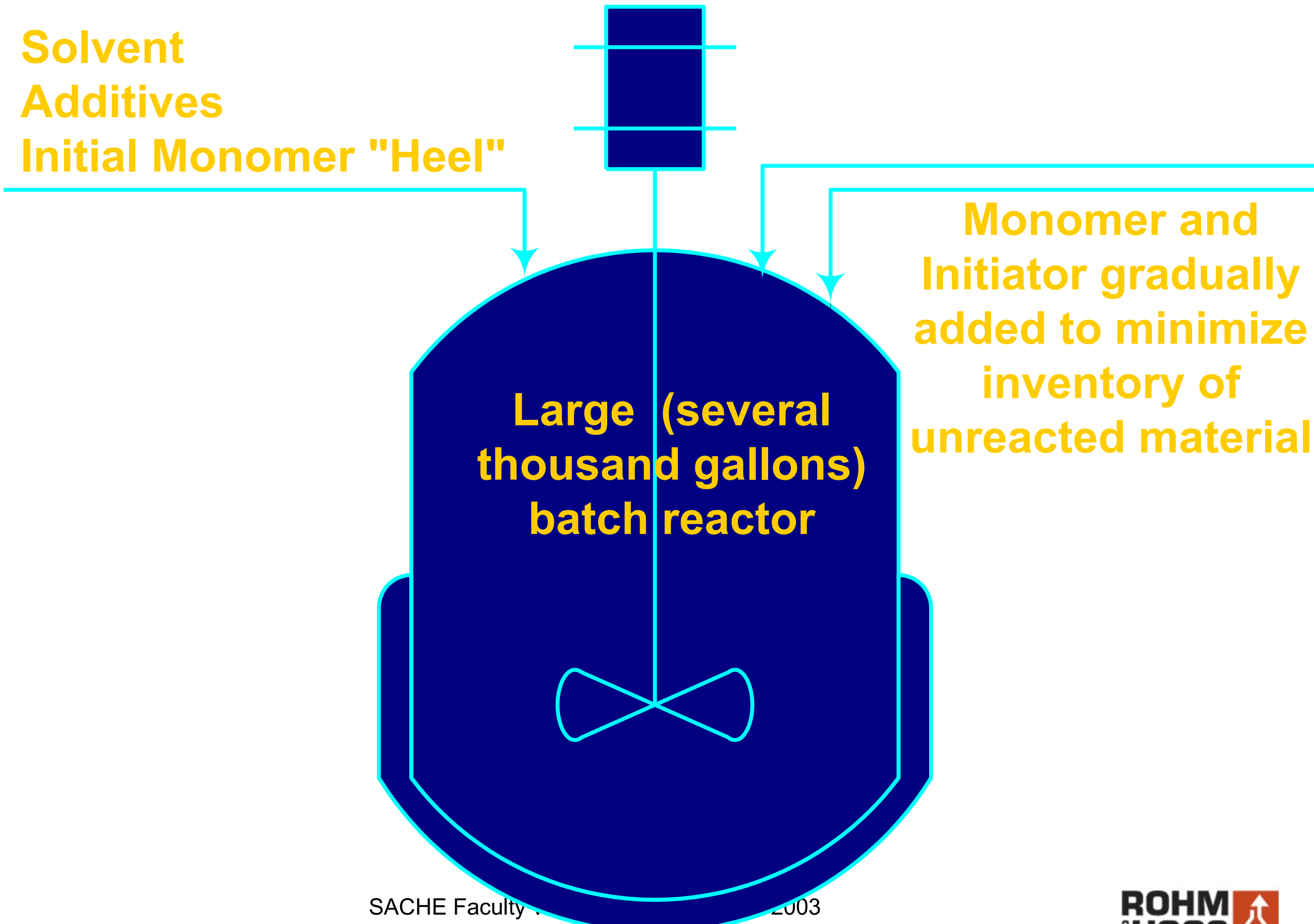
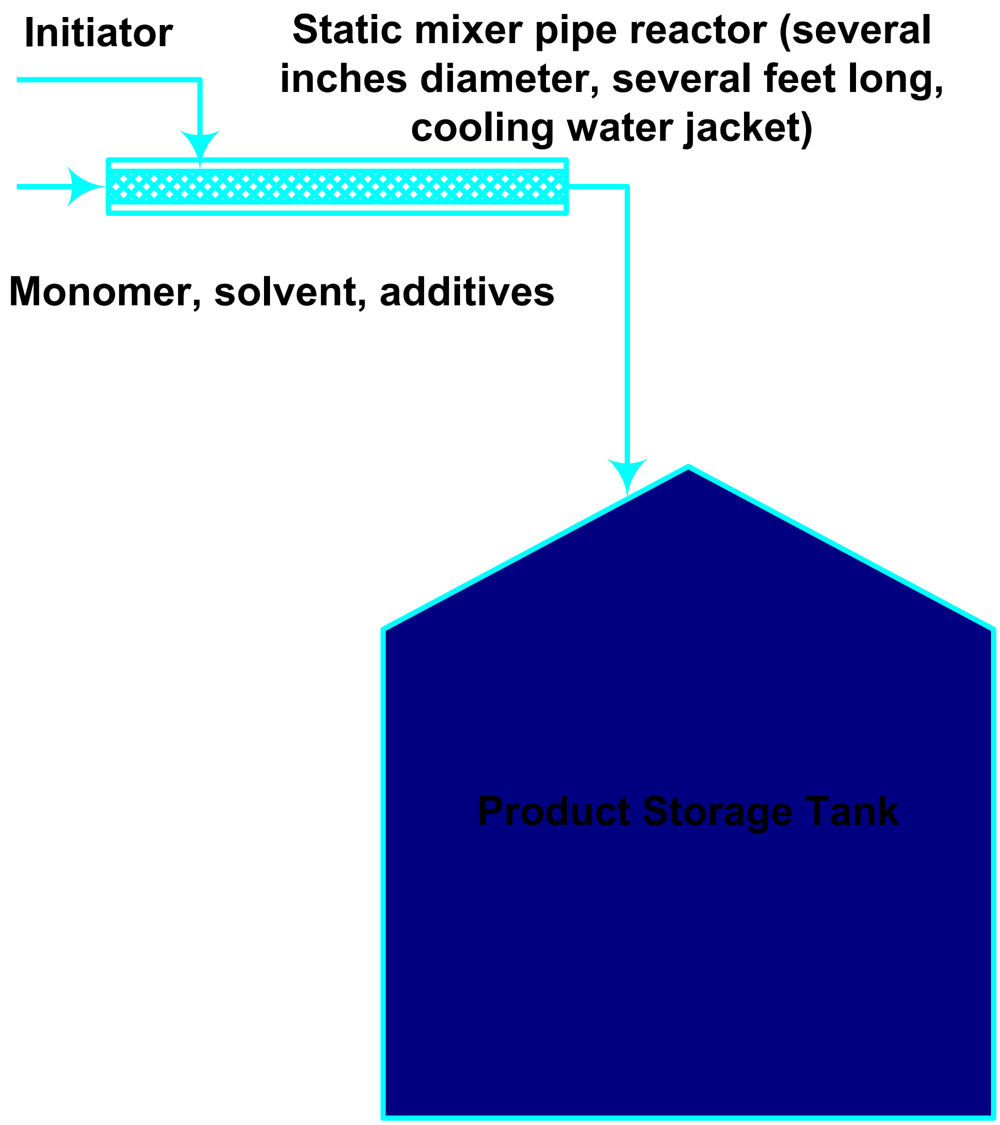
"Semi-Batch" solution polymerization



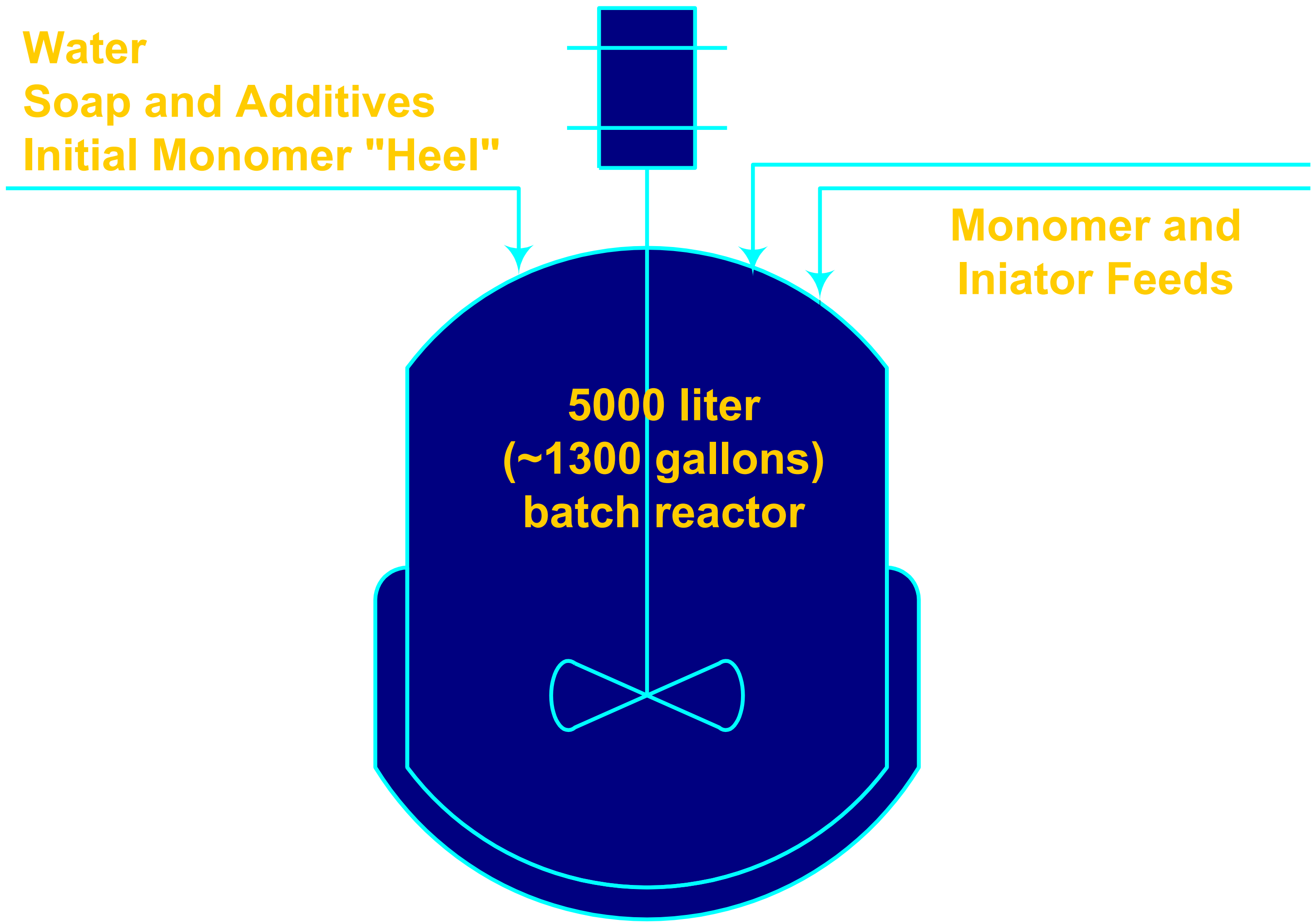
What controls this reaction

- Contacting of monomer reactants and polymerization initiators
- Heat removal
  - Temperature control important for molecular weight control

Tubular Reactor



Reducing the size of an emulsion reactor



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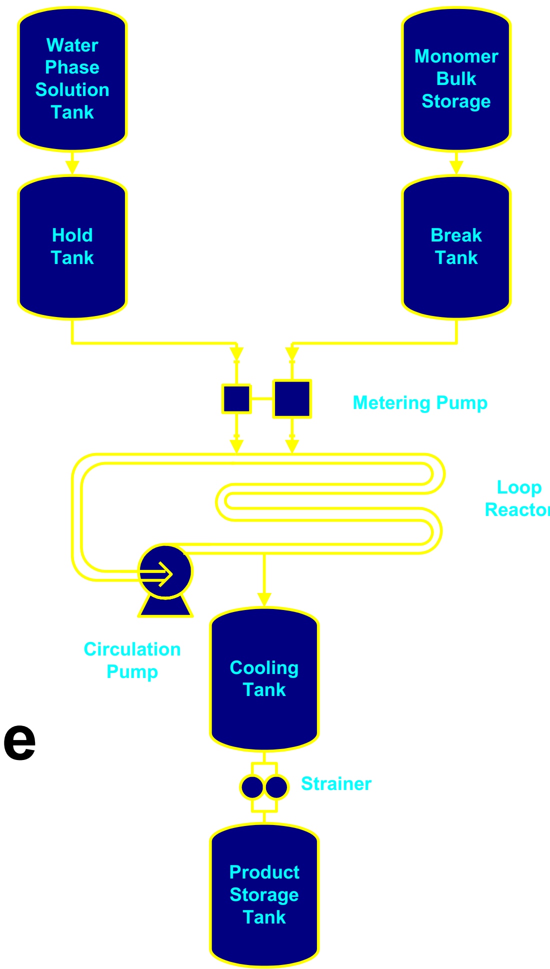
Loop Reactor - Emulsion Polymerization



Cooling Tank "Reactor" Volume

~ 50 liters

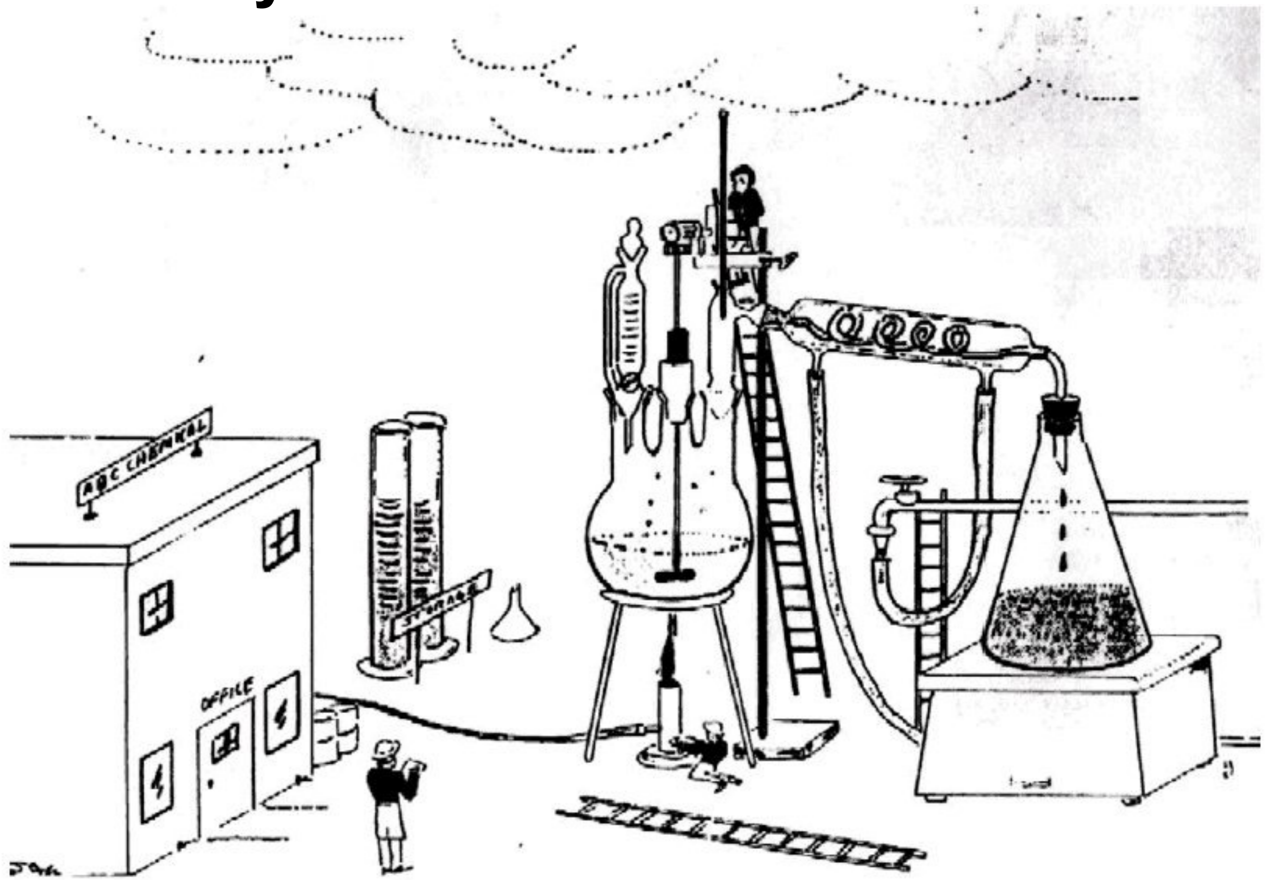
(~13 gallons)

Good engineering makes existing chemistry "Greener"

- Chlorination reaction – traditional stirred tank reactor
- Mixing and mass transfer limited
  - Chlorine gas → liquid reaction mixture → solid reactant particle → rapid reaction
- Loop reactor – similar design to polymerization reactor in previous slide
  - Reduce:
    - Chlorine usage from 50% excess to stoichiometric
    - Reactor size by 2/3
    - Cycle time by ¾
    - Sodium hydroxide scrubber solution usage by 80%

We can do better!

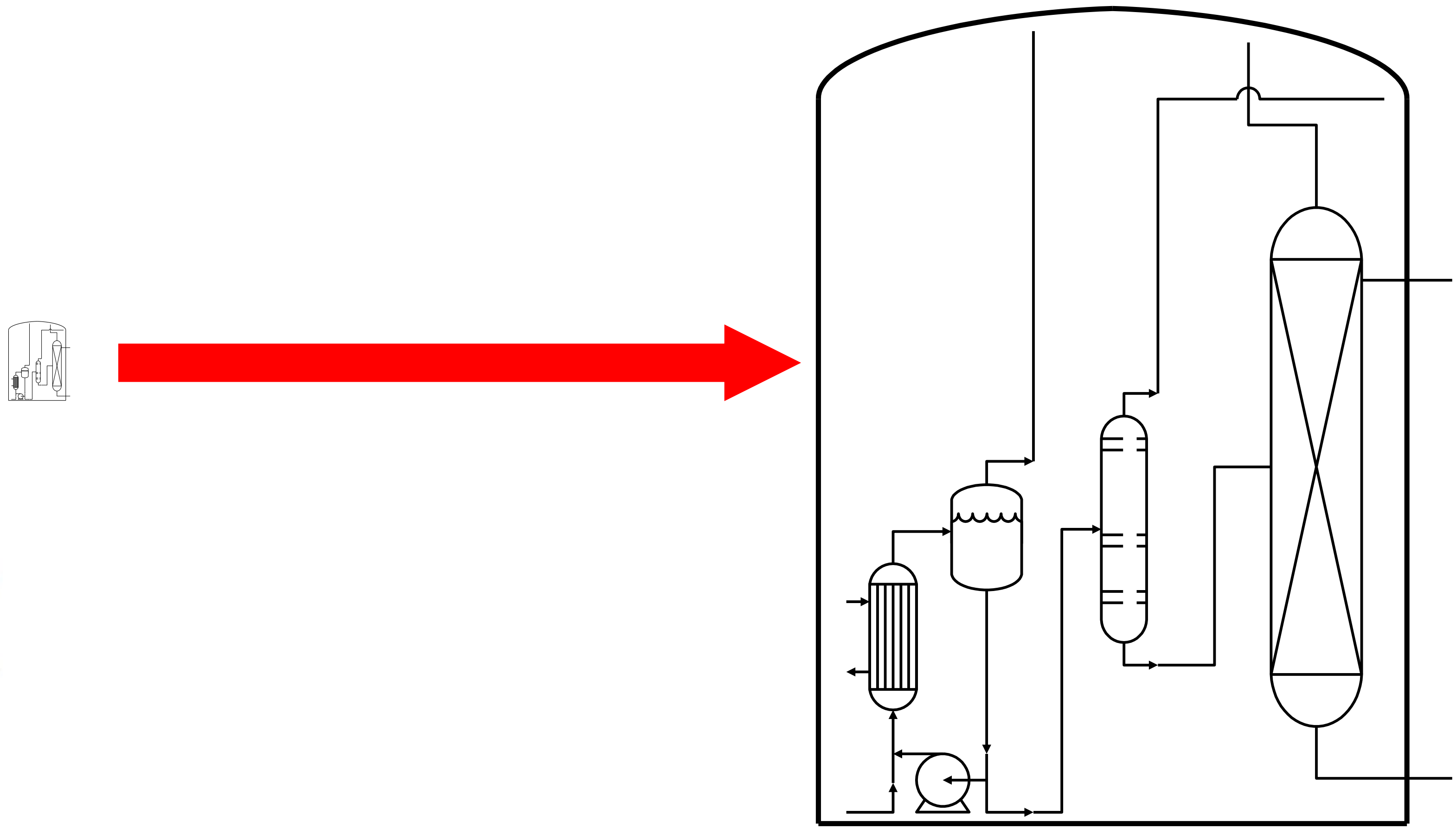
Why so many batch stirred tank reactors?



"The bench scale results were so good that we by-passed the pilot plant."

From E. H. Stitt, "Alternative multiphase reactors for fine chemicals: A world beyond stirred tanks," *Chemical Engineering Journal* **90** (2002) 47-60.

Scale up



Scale out

On-demand phosgene generation

- Reported by Ciba-Geigy/Novartis Crop Protection in 1996/1998
- Continuous process to produce phosgene
- Phosgene consumers are batch processes
- No phosgene storage
- Engineering challenges
  - Rapid startup and shutdown
  - Quality control
  - Instrumentation and dynamic process control
  - Disposal of "tail gas" and inerts

Substitute

- Substitute a less hazardous reaction chemistry
- Replace a hazardous material with a less hazardous alternative

Substitute materials

- **Water based coatings and paints in place of solvent based alternatives**
  - Reduce fire hazard
  - Less toxic
  - Less odor
  - More environmentally friendly
  - Reduce hazards for end user and also for the manufacturer

Substitution - Refrigeration

- Many years ago (pre-1930)
  - Toxic, flammable refrigerants
    - Ammonia, light hydrocarbons, sulfur dioxide
    - Quantity – often several kilograms
- Inherently safer alternative (1930s)
  - CFCs
- Discovery of environmental problems (1980s)
  - “Green” alternatives include light hydrocarbons
  - Require re-design of home refrigerators to minimize quantity of flammable hydrocarbon (currently as little as 120 grams of hydrocarbon refrigerant)

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.**

By-products and side reactions

- Organic intermediate production
  - Intended reaction - hydrolysis

  Organic raw material + sodium hydroxide --->

    product + sodium salt
- Reaction done in ethylene dichloride solvent

Hazardous side reaction

- **Sodium hydroxide + ethylene dichloride solvent:**

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

- **The product of this reaction is vinyl chloride (health hazard)**
- **A different solvent (perchloroethylene) was used**

The next step – "Green" but inherently safer?

- Replace perchloroethylene with a biodegradable hydrocarbon
- Reactants and products are highly soluble in chlorinated hydrocarbon solvents
- Chlorinated hydrocarbon solvents are relatively inert in all reaction steps
- New engineering problems with "green" solvent
  - Reduced solubility (solids handling, coating of heat transfer surfaces, fouling and plugging, mixing and fluidity problems)
  - Solvent can react exothermically with reactants in some process steps
  - These hazards can be managed, but the engineering is not ***INHERENT***

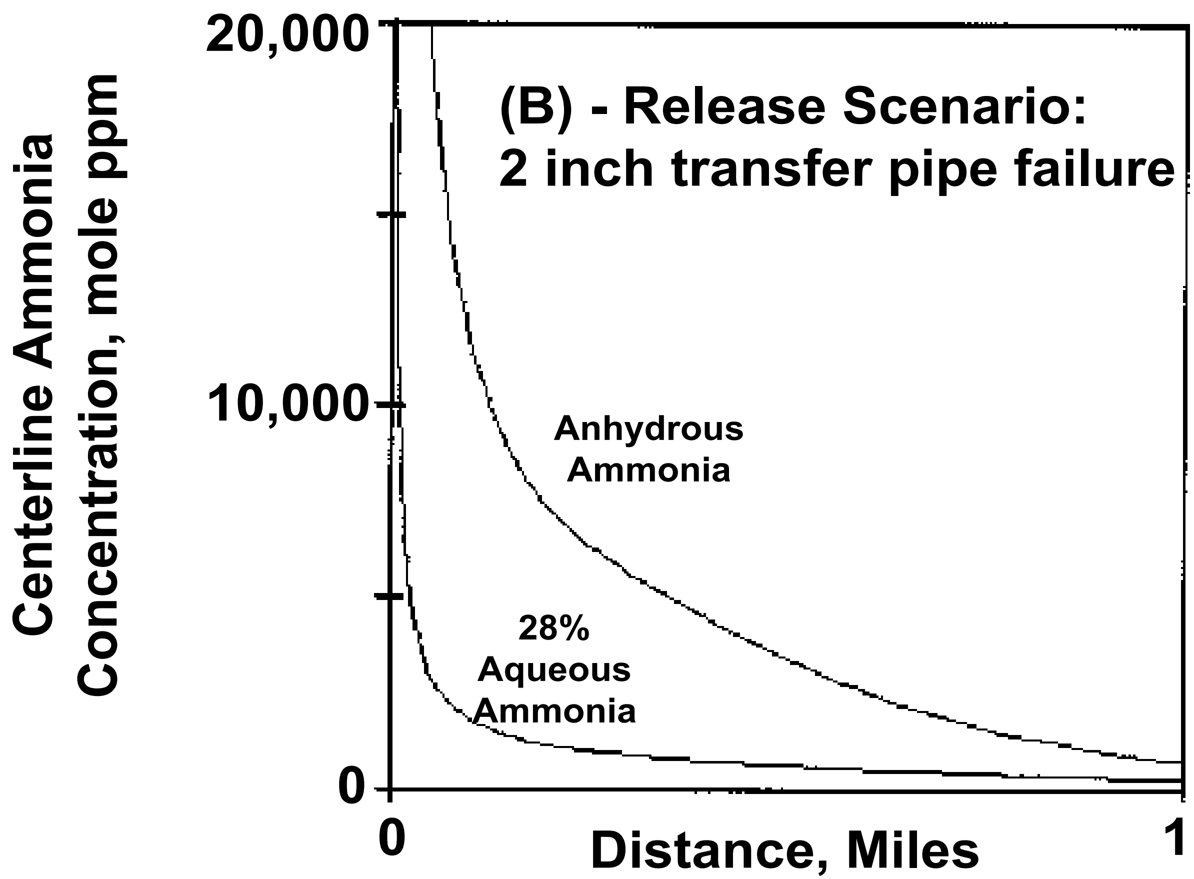
Moderate

- Dilution
- Refrigeration
- Less severe processing conditions
- Physical characteristics
- Containment
  - Better described as “passive” rather than “inherent”

Dilution

- Aqueous ammonia instead of anhydrous
- Aqueous HCl in place of anhydrous HCl
- Sulfuric acid in place of oleum
- Wet benzoyl peroxide in place of dry
- Dynamite instead of nitroglycerine

Effect of dilution



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Impact of refrigeration

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

Less severe processing conditions

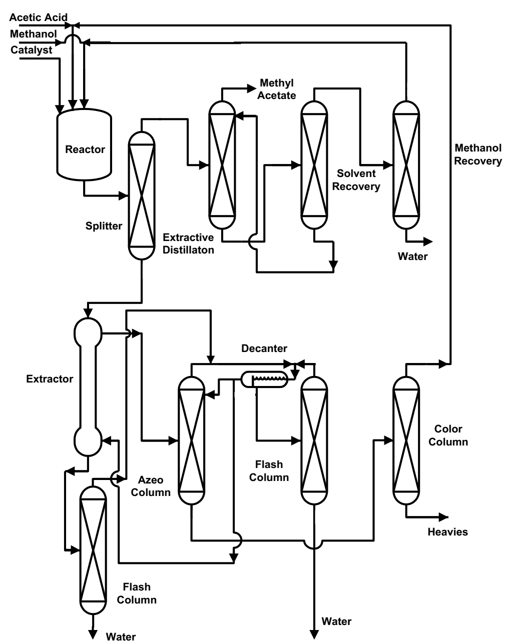
- Ammonia manufacture
  - 1930s - pressures up to 600 bar
  - 1950s - typically 300-350 bar
  - 1980s - plants operating at pressures of 100-150 bar were being built
- Result of understanding and improving the process
- Lower pressure plants are cheaper, more efficient, as well as safer

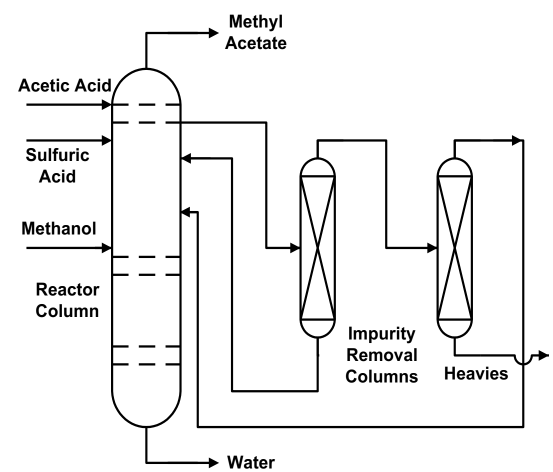
Simplify

- Eliminate unnecessary complexity to reduce risk of human error
  - QUESTION ALL COMPLEXITY! Is it really necessary?

Simplify - eliminate equipment

- Reactive distillation methyl acetate process (Eastman Chemical)
- Which is simpler?





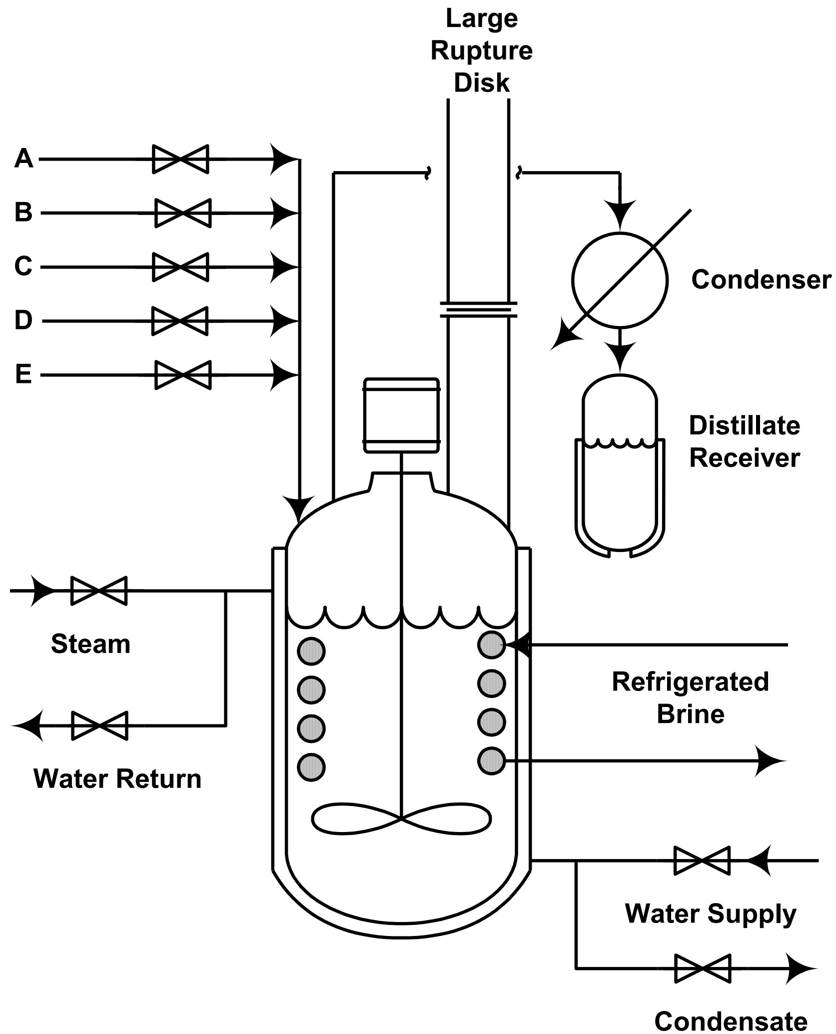
Modified methyl acetate process

- Fewer vessels
- Fewer pumps
- Fewer flanges
- Fewer instruments
- Fewer valves
- Less piping
- ……

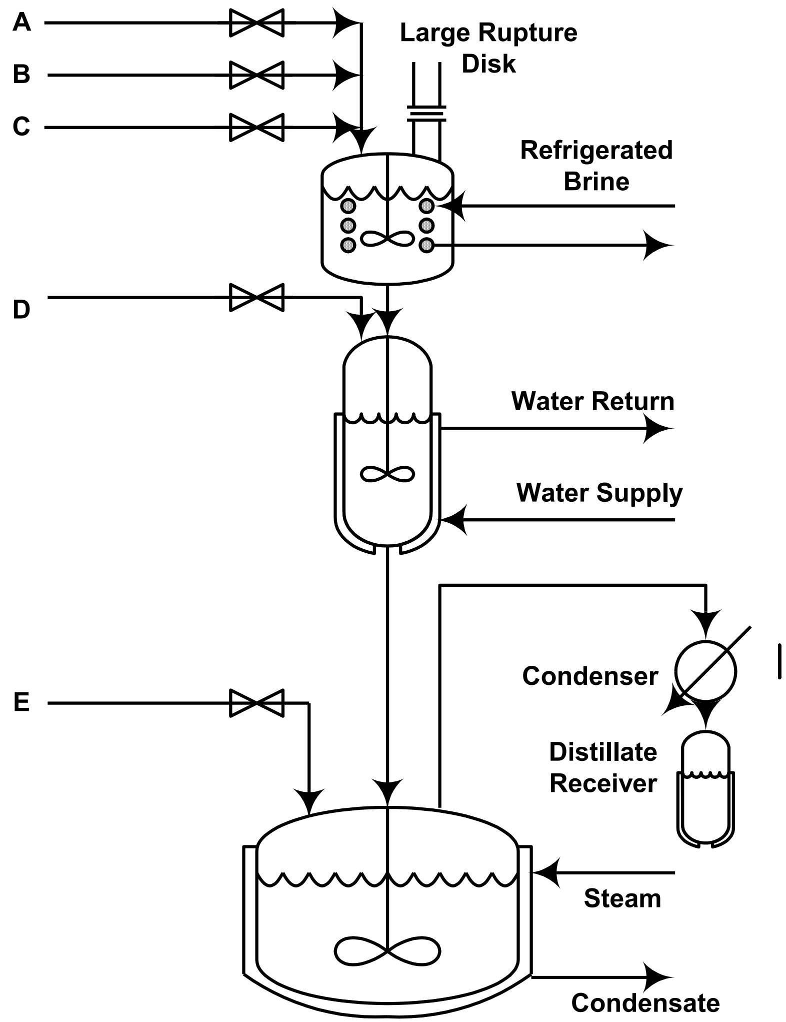
But, it isn't simpler in every way

- Reactive distillation column itself is more complex
- Multiple unit operations occur within one vessel
- More complex to design
- More difficult to control and operate

Single, complex batch reactor



A sequence of simpler batch reactors for the same process



Inherent safety conflicts

- In the previous example
  - Each vessel is simpler
- But
  - There are now three vessels, the overall plant is more complex in some ways
  - Compare to methyl acetate example
- Need to understand specific hazards for each situation to decide what is best

Conflicts and Tradeoffs

Some problems

- The properties of a technology which make it hazardous may be the same as the properties which make it useful
  - Airplanes travel at 600 mph
  - Gasoline is flammable
    - Any replacement for gasoline must have one similar characteristic - the ability to store a large quantity of energy in a compact form
      - a good definition of a hazardous situation
  - Chlorine is toxic
- Control of the hazard is the critical issue in safely getting the benefits of the technology

Multiple hazards

- Everything has multiple hazards
  - Automobile travel
    - velocity (energy), flammable fuel, exhaust gas toxicity, hot surfaces, pressurized cooling system, electricity......
  - Chemical process or product
    - acute toxicity, flammability, corrosiveness, chronic toxicity, various environmental impacts, reactivity.......

What does inherently safer mean?

- Inherently safer is in the context of one or more of the multiple hazards
- There may be conflicts
  - Example - CFC refrigerants
    - low acute toxicity, not flammable
    - potential for environmental damage, long term health impacts
    - Are they inherently safer than alternatives such as propane (flammable) or ammonia (flammable and toxic)?

Inherently safer hydrocarbon based refrigerators?

- Can we redesign the refrigeration machine to minimize the quantity of refrigerant sufficiently that we could still regard it as inherently safer?
  - Home refrigerators – perhaps (<120 grams)
  - Industrial scale applications – probably not, need to rely on passive, active, procedural risk management strategies

- Which is inherently safer?
- What is the hazard of concern…

  …if you live on top of a hill in Philadelphia?

  …if you live on the ocean front at the shore?

Multiple impacts

- Different populations may perceive the inherent safety of different technology options differently
- Example - chlorine handling - 1 ton cylinders vs. a 90 ton rail car
  - What if you are a neighbor two miles away?
    - Most likely would consider the ton cylinder inherently safer
  - What if you are an operator who has to connect and disconnect cylinders 90 times instead of a rail car once?
    - Most likely would consider the rail car inherently safer
- Who is right?
- How can you measure relative risks?

Inherently safer ≠ safer

- Air travel
  - several hundred people
  - 5 miles up
  - control in 3 dimensions
  - 600 mph
  - thousands of gallons of fuel
  - passengers in a pressure vessel
  - ....
- Automobile travel
  - a few people
  - on the ground
  - control in 2 dimensions
  - 60 mph
  - a few gallons of fuel
  - might even be a convertible
  - ....

- Automobile travel is inherently safer
- But, what is the safest way to travel from Washington to Los Angeles?
- Why?

Inherently safer design – at what stage in development and design

- Use acrylate manufacture as an example
  - Basic technology
    - Reppe process vs. propylene oxidation
    - Other alternatives?
  - Implementation of selected technology
    - Catalyst options (temperature, pressure, selectivity, impurities)
      - Propylene oxidation step
      - Esterification step

Inherently safer design – at what stage in development and design

- Acrylate manufacture example
  - Plant design
    - Plant location
    - Plant layout on site (location relative to people, property, environmentally sensitive locations)
    - Equipment size
      - Storage of raw materials
      - One large train vs. multiple smaller trains
      - …..

Inherently safer design – at what stage in development and design

- Acrylate manufacture example
  - Detailed equipment design
    - Inventory of hazardous material
    - Heat transfer media (temperature, pressure, fluid)
    - Pipe size, length, construction (flanged, welded, screwed pipe)
    - Leak potential of equipment
    - ….

Inherently safer design – at what stage in development and design

- Acrylate manufacture example
  - Operation
    - "User friendly" operating procedures
    - Management of change
      - consider inherently safer options when making modifications
      - Identify opportunities for improving inherent safety based on operating experience, improvements in technology and knowledge

At what level of design should engineers consider inherently safer design?

- My answer – at all levels!
- Inherently safer design *is not* a meeting, or a review session.
- Inherently safer design *is a way of thinking*, a way of approaching technology design at every level of detail – part of the daily thought process of a chemist, engineer, or other designer as he goes about his work.

Questions a designer should ask when he has identified a hazard

In this order

1. Can I eliminate this hazard?
2. If not, can I reduce the magnitude of the hazard?
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?

Better may be harder to invent

"There are two ways of dealing with this problem: one is complicated and messy, and the other is simple and elegant. We don't have much time left, so I'll show you the complicated and messy way."

- Richard P. Feynman

Nobel Prize winning physicist, discussing approaches to understanding a physics problem

The future of inherently safer design

Inherently safer design

- Some hazardous materials and processes can be eliminated or the hazards dramatically reduced.
- The useful characteristics of other materials or processes make their continued use essential to society for the foreseeable future.
  - Continue to manage risks
  - Similar to air travel – we understand the hazards, but the activity is so essential to our way of life that we will continue to fly. We will put up with, and pay for, the active and procedural design features required to maintain acceptable safety and security.

What is needed to promote inherently safer design?

- Research
  - Chemical engineering technology
    - Process intensification
    - Physical and chemical phenomena
    - Novel energy sources
    - Biological and biochemical synthesis
    - Catalysis
  - Chemistry
    - Green chemistry – safer synthesis routes considering raw materials, intermediates, products, reaction conditions, solvents and by-products…

What is needed to promote inherently safer design?

- Measurement
  - Consideration of all hazards
  - Different tools at different levels of design
    - Simple, fast, high level tools for early evaluation of alternative technologies
  - Relative importance of conflicting hazards transparent to decision maker
  - Decision tools for inherently safer design and green chemistry and engineering

What is needed to promote inherently safer design?

- Education of chemists, engineers, all technologists
  - Inherently safer design is the way they think
    - How many good ideas are lost because they are not pursued? The inherent safety/green benefits are not recognized.
  - First focus on eliminating and reducing hazards rather than managing and controlling them