Introduction to Safety in Chemical Process Industry

- Chemical Process, Chemical Engineering, Safety/Risk/Hazard/Loss -

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Middle East Technical University - NCC
Sustainability

Community rights
Respecting the rights of the communities where we operate

Latest updates
July 2011
- BP investigation recommendations
  Update on our progress implementing BP report recommendations

Group performance data
- HSE charting tool
  Filter and analyze data on our group's health, safety and environmental performance

Highlights
Environment & Society

The energy we supply helps to support economic growth and development. At our operations we aim to address social concerns and work to benefit local communities, protecting our reputation as we do business.
### Rev. Processes Involving Ideal Gas

#### Summary

<table>
<thead>
<tr>
<th>Process</th>
<th>Isometric $(V = \text{const.})$</th>
<th>Isochoric $(P = \text{const.})$</th>
<th>Isothermal $(T = \text{const.})$</th>
<th>Adiabatic $(P\tilde{V}^\gamma = \text{const.})$</th>
</tr>
</thead>
</table>
| $P\cdot\tilde{V}\cdot T$ Relation | $\frac{P_1}{P_2} = \frac{T_1}{T_2}$ | $\frac{\tilde{V}_1}{\tilde{V}_2} = \frac{T_1}{T_2}$ | $\frac{P_1}{P_2} = \frac{\tilde{V}_2}{\tilde{V}_1}$ | $\frac{T_2}{T_1} = \left(\frac{\tilde{V}_1}{\tilde{V}_2}\right)^{\gamma^{-1}}$
|                      | $\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{(\gamma^{-1})/\gamma}$ |
| $\tilde{W}$ | $0$ | $-R\Delta T$ | $-R T \ln \left(\frac{\tilde{V}_2}{\tilde{V}_1}\right)$ | $\frac{R \Delta T}{\gamma - 1}$
|                      | $-P \Delta \tilde{V}$ | $-R T \ln \left(\frac{P_1}{P_2}\right)$ | $\frac{\Delta(P\tilde{V})}{\gamma - 1}$ |
| $\tilde{Q}$ | $\tilde{C}_V \Delta T$ | $\tilde{C}_V \Delta T$ | $RT \ln \left(\frac{\tilde{V}_2}{\tilde{V}_1}\right)$ | $0$
|                      | $RT \ln \left(\frac{P_1}{P_2}\right)$ |
| $\Delta\tilde{U}$ | $\tilde{C}_V \Delta T$ | $\tilde{C}_V \Delta T$ | $0$ | $\tilde{C}_V \Delta T$
| $\Delta\tilde{H}$ | $\tilde{C}_P \Delta T$ | $\tilde{C}_P \Delta T$ | $0$ | $\tilde{C}_P \Delta T$
Isentropic Expansion

Incorporate friction term:

\[ C_1^2 \int_{P_0}^{P} \frac{dP}{\rho} + \frac{\overline{u}^2}{2\alpha g_c} = 0 \]

Ideal gas, isentropic expansion:

\[ \frac{P}{\rho^\gamma} = a, \quad \gamma = \frac{C_p}{C_v} \]

Integrate and solve for \( \overline{u} \)

\[ Q_m = C_o A P_o \sqrt{\frac{2 g_c M}{R g T_o} \gamma} \sqrt{\left(\frac{P}{P_o}\right)^{2/\gamma} - \left(\frac{P}{P_o}\right)^{(\gamma+1)/\gamma}} \]
Exposure to Release

Predict effects of exposure near the surface.

Stages
1. Source
2. Acceleration, Diffusion
3. Gravity
4. Transition
5. Surface
6. Turbulence

Predict % affected by the exposure.
Gaussian Dispersion Pattern

A: stack height
B: effective height

$C_{max}$ at center

Along X $\bar{u}$
\[
\frac{p_o}{p_a} = \frac{1616 \left[ 1 + \left( \frac{z_e}{4.5} \right)^2 \right]}{\sqrt{1 + \left( \frac{z_e}{0.048} \right)^2} \sqrt{1 + \left( \frac{z_e}{0.32} \right)^2} \sqrt{1 + \left( \frac{z_e}{1.35} \right)^2}}
\]
Objective

Prevent the initiation of the fire or explosion and minimize the damage produced after it.

- How can it be prevented?
  - Inerting
  - Control static electricity
  - Ventilation
  - Explosion-proof equipment
Flammability Diagram - OSFC

A contains pure fuel

Pure N\textsubscript{2} added till point S, OSFC

Requires a large amount of nitrogen ⇒ costly

Pure N\textsubscript{2} added till point S, OSFC

the air forms a flammable mixture at the entry point
Patterns of two phase flow
Chemical Process & Chemical Process Industry
Chemical Industry: Products

- Polyurethane mattress, polyester sheets
- Plastic clock, nylon carpet, phenolic switch
- Polyvinyl chloride insulated conductors
- Sanitized water, soap, refrigerants
- Fertilizers, printing inks, paper
- Electrical components in TV, radio

Chemical Product Groups

- Food, shelter, health
- Electronics, computing, communications
- Biotechnology, pharmaceuticals
- Automobiles, appliances, furniture
- Paper, textiles, paint
- Agriculture, construction
Chemical Industry: History I

Early to 5,000 BC

- First industrial chemical process: fire
- Burning wood for heat, cooking food
- Firing pottery, bricks

Chemical Industry: History II

3,000 - 4,000 BC

- Chemical: soda ash (sodium carbonate)
- Arabic name for soda: *al kali*
- Process: burning seaweeds & seashore vegetation including kali
- Hot water extraction to form brown lye
- Products: beads, glass ornaments, soap
Chemical Industry: History III

Prior to 3,000 BC

- Alcoholic fermentation
- Ale, wine (grapes, dates, palm), cider
- Egypt, Sumerian
Early Living Standards

10th Century in Europe

- Life expectancy: ~ 30 years
- Food scarce, monotonous, often stale or spoiled
- Much labor required with few rewards
- Gradually the practice of science reduced the burdens of existence
Chemical Industry: History IV

17th and 18th Centuries

• Food preservatives (inorganic chemicals)
• Dyes, fabrics, soap
• Gunpowder
• First American chemical plant in Boston, 1635, made saltpeter (potassium nitrate): gunpowder, tanning of hides
Chemical Industry: $\text{Na}_2\text{CO}_3$

18th Century

- Nicolas LeBlanc process (Paris, 1791) for soda ash from salt, NaCl. First large-scale process
- HCl: first large-scale industrial pollution
- From 1861-1880 was gradually replaced by Solvay Process (simpler & less expensive)
Chemical Industry: History V

Modern Era

• After 1850: coal-tar dyes, drugs, nitroglycerin explosives
• Celluloid plastics, fiber
• Lightweight metals
• Synthetic rubber
• Fuels
Chemical Industry: History VI

1930’s
- Neoprene, polyethylene, nylon, fiberglass

After 1945
- Rapid expansion of petroleum refining and chemical process industries
- Use, handling, & storage of chemicals presented more potential hazards
Chemical Industry: History VII

After 1950

- Chemical processing more disciplined
- **Larger inventories, higher T, P conditions**
- More emphasis on design & process changes
- More review of effects from modifications
- Today: U.S. & European chemical industries among safest of all industries
What is a Chemical Engineer?

a) An *Engineer* who manufactures chemicals
b) A *Chemist* who works in a factory, or
c) A glorified *Plumber*?
d) “None of the above”

(However, chemical engineering students bored with the relentless “pipe-flow example” during fluid dynamics class may begin to think of themselves as simply “glorified plumbers”)

All Right, So What is a Chemical Engineer?

- Who are comfortable with chemistry.
- But they do much more with this knowledge than just make chemicals.
- Who draws upon the vast and powerful science of chemistry to solve a wide range of problems.
- Sometimes described as the “universal engineer”
So What Exactly Does This "Universal Engineer" Do?

During the past Century, chemical engineers have made tremendous contributions to our standard of living. To celebrate these accomplishments, the American Institute of Chemical Engineers (AIChE) has compiled a list of the “10 Greatest Achievements of Chemical Engineering.”
The Atom, as Large as Life:

- Ability to split the atom and isolate isotopes
  - Biology, medicine, metallurgy, and power generation
  - Production of the atomic bomb
  - Use isotopes to monitor bodily functions
  - Accurately date historical findings
The Plastic Age:

Mass produced polymers = Plastic Age

A viable economic reality

Bakelite -1908

- Electric insulation, plugs & sockets, clock bases, iron cooking handles, and fashionable jewelry
The Human Reactor:

- “Unit operations” consisting of heat exchangers, filters, chemical reactors and the like = Human body.
- Improve clinical care
  - Diagnostic and therapeutic devices
  - Artificial organs
Wonder Drugs for the Masses:

- Mutation and special brewing techniques
- Increase antibiotics’ yields
- Low price, high volume, drugs enables.
Synthetic Fibers, a Sheep's Best Friend:

- Keep us warm, comfortable, and provide a good night's rest
- Help reduce the strain on natural sources of cotton and wool tailored to specific applications.
- Nylon stockings make legs look young and attractive
- Bullet proof vests keep people out of harm's way.
Liquefied Air, Yes it's Cool:

Air separation

- Purified nitrogen; to recover petroleum, freeze food, produce semiconductors, or prevent unwanted reactions

- Oxygen; to make steel, smelt copper, weld metals together, and support the lives of patients in hospitals.
INDUSTRIAL AIR SEPARATION METHODS

ADSORPTIVE

SELECTIVE ADSORPTION

A

A

A+B

B

B

A+B

MEMBRANE

SELECTIVE MEMBRANE PERMEABILITY

A+B

A

A

A+B

CRYOGENIC

HEAT AND MASS EXCHANGE
The Environment

- Provide economical answers to clean up yesterday's waste and prevent tomorrow's pollution.
- Catalytic converters
- Reformulated gasoline
- Smoke stack scrubbers
- Synthetic replacements
- More efficient processing, and new recycling technologies
Food, "It's What's For Dinner":

- Chemical fertilizers can help provide these nutrients to crops
- Forefront of food processing where they help create better tasting and most nutritious foods
Petrochemicals, "Black Gold, Texas Tea":

Form many useful products from petroleum by developing processes like catalytic cracking

- gasoline, lubricating oils, plastics, synthetic rubber, and synthetic fibers
Running on Synthetic Rubber:

- Developing today's synthetic rubber industry
- During World War II, synthetic rubber capacity suddenly became of paramount importance.
- Tires, gaskets, hoses, and conveyor belts (not to mention running shoes)
Chemical Engineering Today & Tomorrow

- The highest paid of the "Big Four" (civil, mechanical, electrical, chemical)
- Upper management position
  - 3M, Du Pont, General Electric, Union Carbide, Dow Chemical, Exxon, BASF, Gulf Oil, Texaco, and B.F. Goodrich
- 70,000 practicing chemical engineers in the United States
Safety & Process Safety
The superior man, when resting in safety, does not forget that danger may come.... When all is orderly, he does not forget that disorder may come.

Confucius (551 BC – 479 BC)
Basic Terms I

**Safety**: prevention of loss incidents by identification, control, or elimination of hazards

**Hazard**: A physical situation with a potential for human injury, damage to property, damage to the environment, or some combination of these

**Risk**: The likelihood of a specified undesired event occurring within a specified period or in specified circumstances.

*Nomenclature for Hazard and Risk Assessment in the Process Industries* - David Jones, UK Institution of Chemical Engineers, 1992
Risk deals with well defined events about which norms have been negotiated amongst different stakeholders. Technology must be designed such that these norms are met.
True and Perceived Risks 0
True and Perceived Risks 0
True and Perceived Risks I

Probability of deaths by disaster (tornado, plane crash) overestimated by the public

More ordinary risks (auto accident, smoking, stroke, heart attack) are underestimated

Public ranks disease and accidents ~ equally, but disease causes ~ 15 times more deaths.
True and Perceived Risks II

- 400,000 smoking-related deaths/year
- 40,000 deaths/year on U.S. highways
- An airline crash with 300 deaths draws far more attention over a longer time.
True and Perceived Risks III

Example: Three years old kid killed in water knee-deep by an alligator: reported nationally

Only 7 recorded fatalities by alligator

Primary hazards were minimum supervision and shallow water.

In 1995, 300 children under 4 years old drowned at home: reported locally
Voluntary or Involuntary

Choice affects perceived risk.

Accept risk by coercion vs. by choice
Accept the risk of smoking
Voluntarily drive a motorcycle
Protest a plant with a much smaller risk
Moral or Immoral

- Deaths by moral means are more acceptable than by immoral means.
- Far more driving deaths than murders per year but murder is much less acceptable.
Detectable vs Undetectable Risks

People fear the undetected or the risks that may take years to appear.

Collapse of a dam in India (1979) killed thousands and perhaps more than killed in the Bhopal tragedy (1984).

People are concerned far more about chemical engineering than civil engineering disasters.
Detectable vs Undetectable Risks II

- Water is a familiar chemical, so hazards are less noticed or are accepted.
- Pesticides and radioactivity poorly understood, so they are feared.
- NIMBY, BANANA
- PIMFY
Safety Program

System
- To record what needs to be done to have an outstanding safety program

Attitude
- Positive attitude

Fundamentals
- Understand and use the fundamentals of chemical process safety in the design, construction and operation of their plants

Experience
- Read and understand case histories of past accident

Time
- Time to study, time to do work, time to share experience

You
- Take the responsibility to contribute to the safety program

9/28/2011
METU
Impact of Accidents

○ All for the want of a nail…..

For want of a nail, the shoe was lost,
For want of a shoe, the horse was lost,
For want of a horse, the rider was lost,
For want of a rider, a message was lost,
For want of a message, the battle was lost,
For want of a battle, the kingdom was lost,
And all for the want of a nail…..

George Herbert, in outlandish proverbs(1640)
Oppau

- Location: Oppau, Germany
- Company: BASF
- Date: September 21, 1921
- Killed: 430
- Injured: unknown
- Financial: N/A
- Type of Plant: Fertilizer
- Trigger: Blasting Powder being used to break up a 50:50 mixture of ammonium sulfate and ammonium nitrate
Texas City

- Location: Texas City, Texas, USA
- Company: Monsanto
- Date: April 16, 1947
- Killed: 552
- Injured: about 3000
- Financial: N/A
- Type of Plant: petrochemical
- Trigger: fire on ship at dock – ammonium nitrate
Flixborough

• Location: Flixborough, UK
• Company: Nypro
• Date: June 1, 1974
• Killed: 28
• Injured: 104
• Financial: $635,900,000
• Type of Plant: cyclohexane oxidation (→Nylon)
• Trigger: Vapor Cloud Explosion
Beek

- **Location:** Beek, NL
- **Company:** Dutch State Mines (DSM)
- **Date:** November 7, 1975
- **Killed:** 14
- **Injured:** N/A
- **Financial:** $114,700,000
- **Type of Plant:** petrochemical
- **Trigger:** propylene
Westwego

- Location: Westwego, La, USA
- Company: Continental Grain
- Date: December 23, 1977
- Killed: 35
- Injured: 9
- Financial: N/A
- Type of Plant: Grainery
- Trigger: Corn dust explosion in grain elevator
Bhopal

- Location: Bhopal, India
- Company: Union Carbide
- Date: December 3, 1984
- Killed: 4000 – 20,000
- Injured: 100,000 + asymptomatic
- Financial: ($470,000,000 settlement)
- Type of Plant: pesticide
- Trigger: Release of MIC
Phillips

- Location: Pasadena, Texas, USA
- Company: Phillips 66
- Date: October 23, 1989
- Killed: 23
- Injured: 130-300
- Financial: $623,500,000 – 1,770,000,000*
- Type of Plant: polyethylene
- Trigger: isobutane
Accidental Flow

Proactive Management  Reactive Management

Prevention  Control  Protection  Mitigation

Hazard
- Material/energy Contained and controlled during normal operation
  - Toxicity
  - Flammability
  - Reactivity
  - Elevated pressure etc.

Cause
- Initiating event of process upset; Start of accident event sequence
  - Mechanical failure
  - Procedural error
  - External force
  - Fouling etc.

Deviation
- Excursion Beyond design/Operating limits
  - No flow
  - High temperature
  - Low level
  - Impurities
  - Wrong material
  - Step omitted etc.

Accidental Event
- Loss of containment of process material/energy
  - Fire
  - Explosion
  - Hazardous material release etc.
  - Other energy releases

Impact
- Loss of containment of process material/energy
  - Illnesses/injuries/Death
  - Property damage
  - Business interruption
  - Environmental damage etc.
Flixborough

The Chemistry

cyclohexane → cyclohexanone → cyclohexanol

caprolactam
The Reactor Train

Temporary Pipe Section

Bellows
Problems with New Process

- Serious technical and financial problems
- Hazardous process to produce cyclohexanone
- Office building close to plant
- Control room was within plant
Events of June 1, 1974

- Cyclohexane circulated
- Pipe assembly ruptured
- Uncontrolled vapor cloud explosion
The Possible Causes

- No qualified engineer on the site
- Connections between 4 and 6 were expedient
- "Hurry up" attitude of management ← Only Profit!
BHOPAL DISASTER

MIC Released at Bhopal, India

December 3, 1984

Over 2000 Fatalities
The Chemistry

OH
α-Napthol

+ CH₃-N≡C=O

MIC

→

O−CNHCH₃
Carbaryl

Critical Properties of MIC

- Boiling point: 39.1°C
- Molecular weight: 57
- PEL (p.54): 0.02 ppm
- IDLH (p.56): 3 ppm
- Odor threshold: 2 ppm
Exothermic Reactions with Water and Itself

\[
\text{MIC} + H_2O \rightarrow 1,3,5 \text{ Trimethyl Biuret} + CO_2
\]
Runaway Scenarios

- Loss of cooling or refrigeration
- Loss of Agitation
- Unexpected addition of heat
- Human error
Condition before Accident

- Refrigeration turned off.
- Flare down for maintenance.
- Scrubber in standby mode.
Accident

- Vessel vented at 180 psig
- Released for 2 hours
- MIC heavier than the air
- 2000 fatalities
The traditional method of identifying hazards was to build the plant and see what happens - ‘every dog is allowed one bite’. Until it bit someone, we could say that we did not know it would do so. This method is no longer acceptable now that we keep dogs as big as Flixborough.

-Kletz and Lawley
To Prevent Accidents We Need Knowledge In

- Design (inherently safe)
- Thermodynamics
- Kinetics
- Control
- Management and ethics
Routes to Carbaryl, Bhopal

\[ \text{CH}_3 \text{NH}_2 + \text{COCl}_2 \rightarrow \text{CH}_3 \text{OCN} \]
Routes to Carbaryl, Alternative

\[
\text{OH} + \text{COCl}_2 \xrightarrow{\text{CH}_3\text{NH}_2} \text{O.CO.NH.CH}_3 \xrightarrow{\text{O.CO.Cl}}
\]
Measurement of Safety

How to measure safety of a process?

Is a safety procedure effective?

Incident and loss statistics models

Perspective of risk, real and perceived, is needed for assessment of results of these models
Measure Danger of a Job

1. Number of fatalities in a job or group

2. Fatality Rate (FR): \[ \frac{\text{fatalities/year}}{\text{population}} \]
   Independent of exposure time

3. Relative Risk Index (RRI): \[ \frac{FR\text{ group}}{FR\text{ all}} \]
   Compare risk to average job
Measure Danger of a Job

RRI (fatalities), 1995

- Finance, insurance, real estate: 0.4
- Chemical industry: 0.6
- Average job: 1.0
- Petroleum refining: 1.8
- Truck driving: 5.3
- Metal workers: 13.1
Measure Danger of a Job

Fatal accident rate (FAR)

\[ FAR = \frac{10^8 \times \text{# fatalities}}{\text{hours worked}} \]

Dependent on exposure time, unlike FR
Fatal Accident Rate

- The FAR period of time, $10^8$ hours, is based on 1,000 employees working for a lifetime.
- Work lifetime is assumed to be 50 years
- One work year is 2,000 hr\([250\cdot8]\)
- $1,000(2,000 \text{ hr/yr})(50 \text{ yr}) = 10^8 \text{ hours}$
FAR Statistics for Industry

Chemical industry improved from a FAR of 4.0 in 1986 to 1.2 in 1990 (Crowl, Tab. 1-3, p. 8)

Causes of fatalities divided about equally between physical accidents and chemical exposures.

FAR of 1.2 for all manufacture vs 3.7 for agriculture (synthetic vs natural fibers)
Accident Statistics for Various Selected Industries

<table>
<thead>
<tr>
<th>Industry</th>
<th>OSHA incident rate (cases involving days away from work and deaths)</th>
<th>FAR (deaths)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1985(^1)</td>
<td>1998(^2)</td>
</tr>
<tr>
<td>Chemicals and allied products</td>
<td>0.49</td>
<td>0.35</td>
</tr>
<tr>
<td>Motor vehicles</td>
<td>1.08</td>
<td>6.07</td>
</tr>
<tr>
<td>Steel</td>
<td>1.54</td>
<td>1.28</td>
</tr>
<tr>
<td>Paper</td>
<td>2.06</td>
<td>0.81</td>
</tr>
<tr>
<td>Coal mining</td>
<td>2.22</td>
<td>0.26</td>
</tr>
<tr>
<td>Food</td>
<td>3.28</td>
<td>1.35</td>
</tr>
<tr>
<td>Construction</td>
<td>3.88</td>
<td>0.6</td>
</tr>
<tr>
<td>Agricultural</td>
<td>4.53</td>
<td>0.89</td>
</tr>
<tr>
<td>Meat products</td>
<td>5.27</td>
<td>0.96</td>
</tr>
<tr>
<td>Trucking</td>
<td>7.28</td>
<td>2.10</td>
</tr>
<tr>
<td>All manufacturing</td>
<td></td>
<td>1.68</td>
</tr>
</tbody>
</table>
FAR for Chemical Worker

- For 1000 workers during lifetime (50 years) in chemical industry†
- 2 work deaths (1 physical and 1 chemical)
- 20 non-work accident deaths
- 370 non-work disease deaths
- Some common activities more dangerous than chemical plant work (Crowl, Tab. 1-4, p. 9)

# Fatality Statistics for Common Nonindustrial Activities

<table>
<thead>
<tr>
<th>Activity</th>
<th>FAR (deaths/10^8 hours)</th>
<th>Fatality rate (deaths per person per year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Voluntary activity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Staying at home</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Traveling by</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Car</td>
<td>57</td>
<td>17 × 10^{-5}</td>
</tr>
<tr>
<td>Bicycle</td>
<td>96</td>
<td></td>
</tr>
<tr>
<td>Air</td>
<td>240</td>
<td></td>
</tr>
<tr>
<td>Motorcycle</td>
<td>660</td>
<td></td>
</tr>
<tr>
<td>Canoeing</td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>Rock climbing</td>
<td>4000</td>
<td>4 × 10^{-5}</td>
</tr>
<tr>
<td>Smoking (20 cigarettes/day)</td>
<td></td>
<td>500 × 10^{-5}</td>
</tr>
<tr>
<td>Involuntary activity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Struck by meteorite</td>
<td></td>
<td>6 × 10^{-11}</td>
</tr>
<tr>
<td>Struck by lightning (U.K.)</td>
<td></td>
<td>1 × 10^{-7}</td>
</tr>
<tr>
<td>Fire (U.K.)</td>
<td></td>
<td>150 × 10^{-7}</td>
</tr>
<tr>
<td>Run over by vehicle</td>
<td></td>
<td>600 × 10^{-7}</td>
</tr>
</tbody>
</table>
OSHA Incident Rate (IR)

Based on work-related injuries, illness, and fatalities or lost workdays for 100 worker years

- 50 weeks/yr x 40 hr/wk = 2,000 hr/yr
- 100 yr x 2,000 hr/yr = 200,000 hr
OSHA Incident Rate (IR)

Deaths, injuries, and illnesses:

\[ OSHA\ IR = \frac{\text{# incidents}}{\text{hours worked}} \times \frac{1}{2 \cdot 10^5 \text{ hr}} \]

Lost workdays:

\[ IR = \frac{\text{# lost workdays}}{\text{hours worked}} \times 2 \cdot 10^5 \]

Dependent on exposure time, like FAR
# The Nature of the Accident Process

<table>
<thead>
<tr>
<th>Type of Accident</th>
<th>Probability of occurrence</th>
<th>Potential for fatality</th>
<th>Potential for economic loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fire</td>
<td>High</td>
<td>Low</td>
<td>Intermediate</td>
</tr>
<tr>
<td>Explosion</td>
<td>Intermediate</td>
<td>Intermediate</td>
<td>High</td>
</tr>
<tr>
<td>Toxic release</td>
<td>Low</td>
<td>High</td>
<td>Low</td>
</tr>
</tbody>
</table>
Safety in the Chemical Industry

- Risks, perceptions often misunderstood
- Chemical industry is held to a higher than average safety standard.
- This responsibility must be accepted to work for an accident free workplace.
- Continuous improvement is necessary for credibility and the public trust.
Losses in Chemical Industry

- Largest causes of loss: mechanical failure and operator error (Crowl, Fig. 1-7, p.16)

- Losses are sometimes divided into mechanical failure (#1) and operator error (#2).
Causes of losses in the largest hydrocarbon-chemical plant accident

Hardware associated with largest losses

Piping systems
Miscellaneous or unknown
Storage tanks
Reactor piping systems
Process holding tanks
Heat exchangers
Valves
Process towers
Compressors
Pumps
Gauges

Loss Trends in Industry

Number and magnitude of losses from the 1960’s have increased.

Consistent with trend of larger & more complex plants and processes. Also higher pressures and temperatures.

Drop is shown in Crowl, Fig. 1-9, p. 18, for 1992-1996 period, but trend is not clear.
Figure 1-9  Loss distribution for onshore accidents for 5-year intervals over a 30-year period. (There were also 7 offshore accidents in this 30-year period.) Source: Large Property Damage Losses in the Hydrocarbon-Chemical Industries: A Thirty-Year Review (New York: J & H Marsh & McLennan Inc., 1998), p. 2. Used by permission of Marsh Inc.
Program to Prevent Incidents

Safety involves many levels: design, management, control systems, interlocks, detectors, alarms, shutdown systems, protective systems, emergency response procedures, Table 5-10, p. 214.

For safer and more economical processes, it is much better to eliminate rather than to control hazards.
<table>
<thead>
<tr>
<th>Major area</th>
<th>Examples</th>
</tr>
</thead>
</table>
| Inherent safety            | Inventory reduction: Less chemicals inventoried or less in process vessels  
                              | Chemical substitution: Substitute a less hazardous chemical for one more hazardous  
                              | Process attenuation: Use lower temperatures and pressures  |
| Engineering design         | Plant physical integrity: Use better seals or materials of construction  
                              | Process integrity: Ensure proper operating conditions and material purity  
                              | Process design features for emergency control: Emergency relief systems  
                              | Spill containment: Dikes and spill vessels  |
| Management                 | Operating policies and procedures  
                              | Training for vapor release prevention and control  
                              | Audits and inspections  
                              | Equipment testing  
                              | Maintenance program  
                              | Management of modifications and changes to prevent new hazards  
                              | Security  |
| Early vapor detection and warning | Detection by sensors  
                              | Detection by personnel  |
| Countermeasures            | Water sprays  
                              | Water curtains  
                              | Steam curtains  
                              | Air curtains  
                              | Deliberate ignition of explosive cloud  
                              | Dilution  
                              | Foams  |
| Emergency response         | On-site communications  
                              | Emergency shutdown equipment and procedures  
                              | Site evacuation  
                              | Safe havens  
                              | Personal protective equipment  
                              | Medical treatment  
                              | On-site emergency plans, procedures, training, and drills  |

Inherent Safety

Inherent safety involves prevention or reduction of hazards

Applies throughout the plant at any time but best at the design stages

Minimize amounts, substitute for safer, moderate to reduce hazards, simplify to limit error, Crowl, Tab. 1-9, p. 22
<table>
<thead>
<tr>
<th>Type</th>
<th>Typical techniques</th>
</tr>
</thead>
</table>
| Minimize (intensification) | Change from large batch reactor to a smaller continuous reactor  
Reduce storage inventory of raw materials  
Improve control to reduce inventory of hazardous intermediate chemicals  
Reduce process hold-up |
| Substitute (substitution) | Use mechanical pump seals vs. packing  
Use welded pipe vs. flanged  
Use solvents that are less toxic  
Use mechanical gauges vs. mercury  
Use chemicals with higher flash points, boiling points, and other less hazardous properties  
Use water as a heat transfer fluid instead of hot oil |
| Moderate (attenuation and limitation of effects) | Use vacuum to reduce boiling point  
Reduce process temperatures and pressures  
Refrigerate storage vessels  
Dissolve hazardous material in safe solvent  
Operate at conditions where reactor runaway is not possible  
Place control rooms away from operations  
Separate pump rooms from other rooms  
Acoustically insulate noisy lines and equipment  
Barricade control rooms and tanks |
| Simplify (simplification and error tolerance) | Keep piping systems neat and visually easy to follow  
Design control panels that are easy to comprehend  
Design plants for easy and safe maintenance  
Pick equipment that requires less maintenance  
Pick equipment with low failure rates  
Add fire- and explosion-resistant barricades  
Separate systems and controls into blocks that are easy to comprehend and understand  
Label pipes for easy “walking the line”  
Label vessels and controls to enhance understanding |
Trend of Chemical and Energy Industries

More dangerous operating conditions
  – high pressure, low temperature
• More toxic and environment-dependent products
• Increased work and information overload for human operators
• The public and the international society are more sensitive and regulation-minded about the safety
Future Features of Chemical Plant Accidents

- More severe personal injuries
- More potential for major accidents
  - Fire, explosions and toxic material releases
- Greater economic loss
- International environmental damage
- Human casualties in the wider surrounding area
Goals for Safety and Environment in the 21st Century

- Handle disasters with local communities
- Prevent pollution
- Operate safe plants
- Distribute products in a way that reduces hazards to people and the environment
- Protect the health of people at plant sites
- Promote the safe use of chemicals from manufacture to recycling and disposal
Present Safety Problems

- Complex & diverse energy facilities
- Lower priority to safety-related investment
- Inspection only for facilities
- Present safety management reached its limit.
The Nature of the Accident

The Nature of the Accident II

Petrochemical Plants

Others
Columns
Furnaces
Compressors
Piping
Tankage
Vessels
Reactors

0 10 20 30 40 50

The Nature of the Accident III

Examples of Loss by Accident

**Direct Loss (Cost)**
- Recovery of facility and equipment
- Off-spec.
- Compensation for the contractors
- Legislation fees for suit
- Increase in insurance

**Indirect Loss (Cost)**
- Production & Selling Interruption
- Cost for Accident Investigation
- Loss of customers & buyers
- Disrepute
Safety Pyramid, Crowl, Fig, 1-3, p. 11

※International Safety Rating System, DNV, 5th Ed.(1993)
A + B → AB

Bhopal

A + C → AC

Alternative

C

ABC

B
An INHERENTLY SAFER DESIGN is one that **avoids hazards instead of controlling them**, particularly by removing or reducing the amount of hazardous material or the number of hazardous operations.
Layer of Protection Analysis (LOPA)

Community emergency response

Plant emergency response

Fire protection, steam/water curtain

Passive physical protection - walls, dikes, bunds, zoning

Pressure relief device

Automatic action, ESD

Critical alarm/Operator supervision
Manual intervention

Basic controls/ Process alarms
Operator supervision

Inherent safer process design

Independent Layer of Protection “Onion”
SAVINGS

1. Less protective equipment needed, say 5-10% of capital.

2. Less maintenance of plant & systems.

3. SMALLER SIZE.
Inherent Safety
esp Intensification

Simplification

Less Energy

Lower Cost
Avoid a Narrow Focus

Bad Science!

Human

Environment

Machine
• Many accidents occur as the result of interactions between matrix elements