Lecture 6

Safety Practices in Chemical and Nuclear Industries

Chemical Process Safety

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Chemical Process Industry

- The chemical process industry is vast and varied, and the following is a list of major process industry.
  - Inorganic chemicals
  - Fertilizers
  - Organic chemicals
    - Soap, detergents, dyes, pharmaceuticals
  - Explosives
  - Plastics, resins, rubber, paper
  - Paints
  - Petrochemical processing

Requirements

- Industry and society are continuing to focus on reducing personnel and environmental damage resulting from accidents.
- **Business requirement**
  - Uninterrupted supply of regular products.
  - Scale-up, new process and new products.

Requirements

- **Government regulations**
  - Laws and regulation are major tools for protecting people and the environment.
  - If the requirement of legislation is ignored then prosecution is to be expected.
  - An employer who does not take due care of his or her employees is liable.

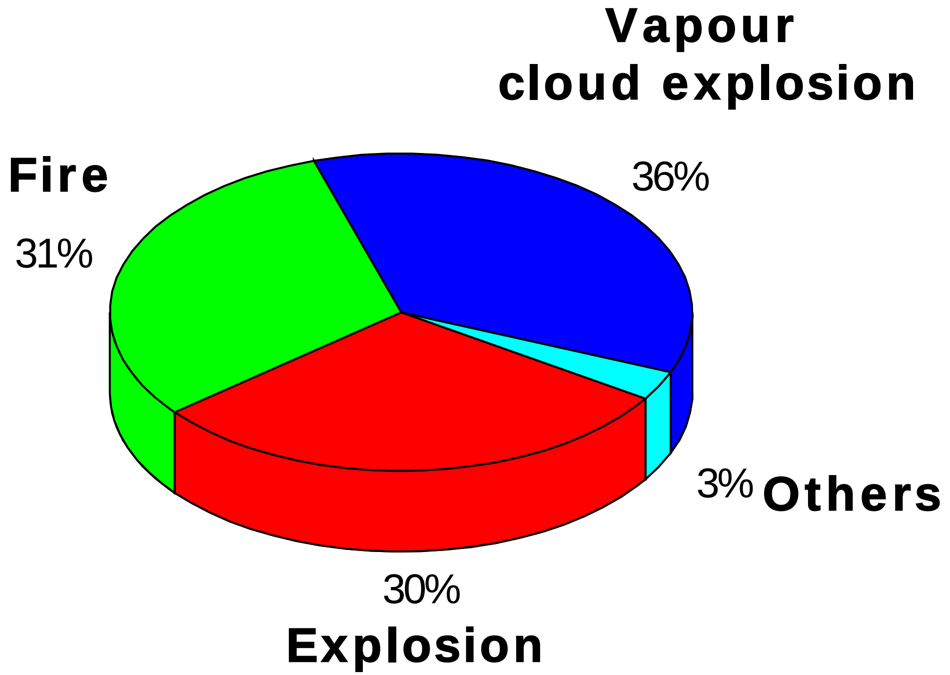
Requirements

A mishap on a process plant may have a variety of commercial implications:

- Loss of profit from production lost due to plant downtime.
- The cost of damage to equipment, comprising replacements costs of spares, etc. and labour.
- The costs resulting from injury or loss of life.
- The cost of environmental damage, including cleanup costs.
- The cost of damaged public image, including public opposition to further developments.

Accident Statistics

- Fire and explosion contribute substantially to the risk associated with the chemical plants.



Evaluation of the largest chemical plant accidents

Chemical reactions

- Endowed with inherent hazards (associated with a process)
  - Fire
  - Explosion
    - **BLEVE** (Boiling Liquid Expanding Vapor Explosion): This is a type of explosion that can occur when a vessel containing a pressurized liquid is ruptured. Such explosions can be extremely hazardous.
    - **Vapor cloud explosion**: Overpressure caused when a gas cloud detonates or deflagrates in open air rather than simply burn, *i.e.* extremely rapid flame front propagation.
    - **Detonation and Deflagration**
  - Toxic Chemicals Release
- Governed by system thermodynamics and kinetics of thermal process.

Decomposition & Runaway Reactions

- There are many reasons for explosions during chemical processing
    - Decomposition and runaway chemical reactions are the most common
    - Often these are either exothermic and/or gas producing reactions that go out of control
    - Can be avoided if reactions are understood and reactive chemicals are identified.

Decomposition & Runaway Reactions

- Identification of reactive chemicals
  - Chemical structure promoting either instability or susceptibility to other reactions
  - Decomposition energy
  - Affinity between different compounds.

Runaway Reaction

- In chemical engineering, runaway is a process by which an exothermic reaction goes out of control, often resulting in an explosion.
- Exothermic chemical reactions can lead to a thermal runaway if the heat generation rate exceeds the heat removal rate.

Runaway Reaction

- when the reaction rate increases due to an increase in temperature, causing a further increase in temperature and hence a further increase in the reaction rate.

- Thermal runaway may result from exothermic side reaction(s), and is characterised by an exponential increase in the rate of heat generation, temperature and pressure.

Initiating factors

Incorrect charging and inadequate cooling are the most important initiating factors for the runaway reactions followed by unknown exotherm/ decomposition, impurities and incorrect agitation/mixing resulting in hotspots.

- **Incorrect charging**
- **Inadequate cooling**

Initiating factors

Unknown exotherm/decompostion: In the manufacture of tetrachloro-ethane excess chlorine was reacted with acetylene at 100°C in the presence of ferric chloride catalyst. On one occasion, the temperature of the mix dropped to 60^{o}C and an explosion ruptured the bursting disc and also cracked the reactor. It was suggested that monochloroacetylene had decomposed, initiating the explosion.

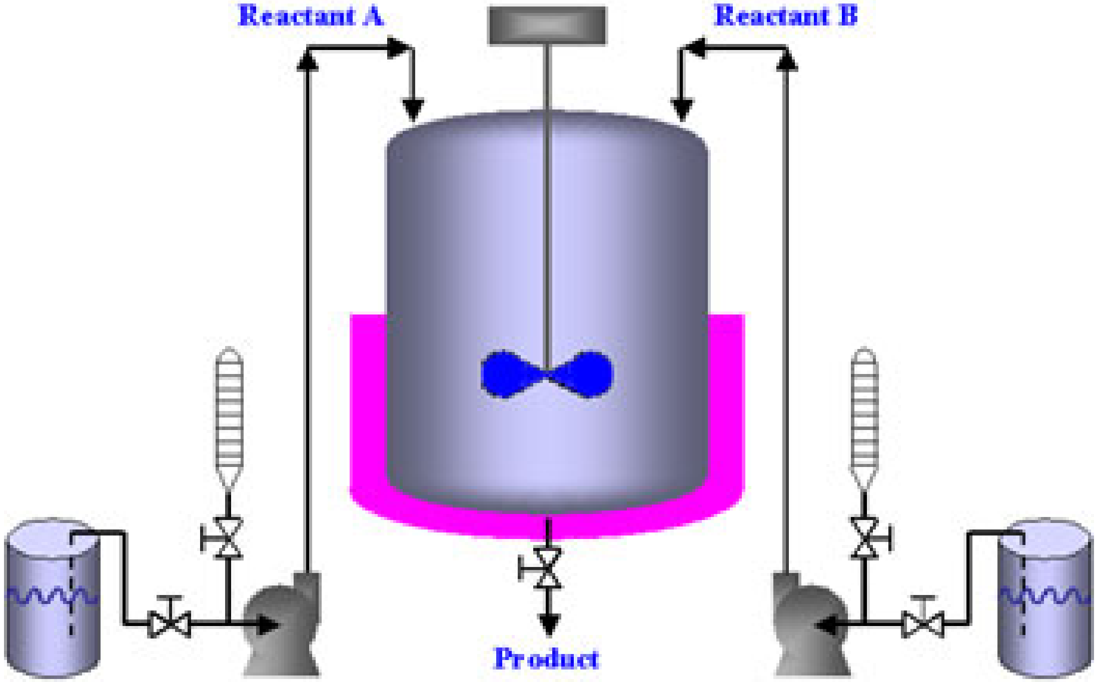
Initiating factors

- **Impurity exotherm**: An initiating mix of ether, butyl chloride, cyclohexane and butyl bromide for the preparation of a Grignard reagent was added to a reactor containing magnesium. Cyclohexane was added and immediately vapours emerged from the condenser vent and the bursting disc ruptured. The investigation revealed that the cyclohexane transfer line was wet and the Grignard reagent had reacted with the water to produce hydrogen and ethane.

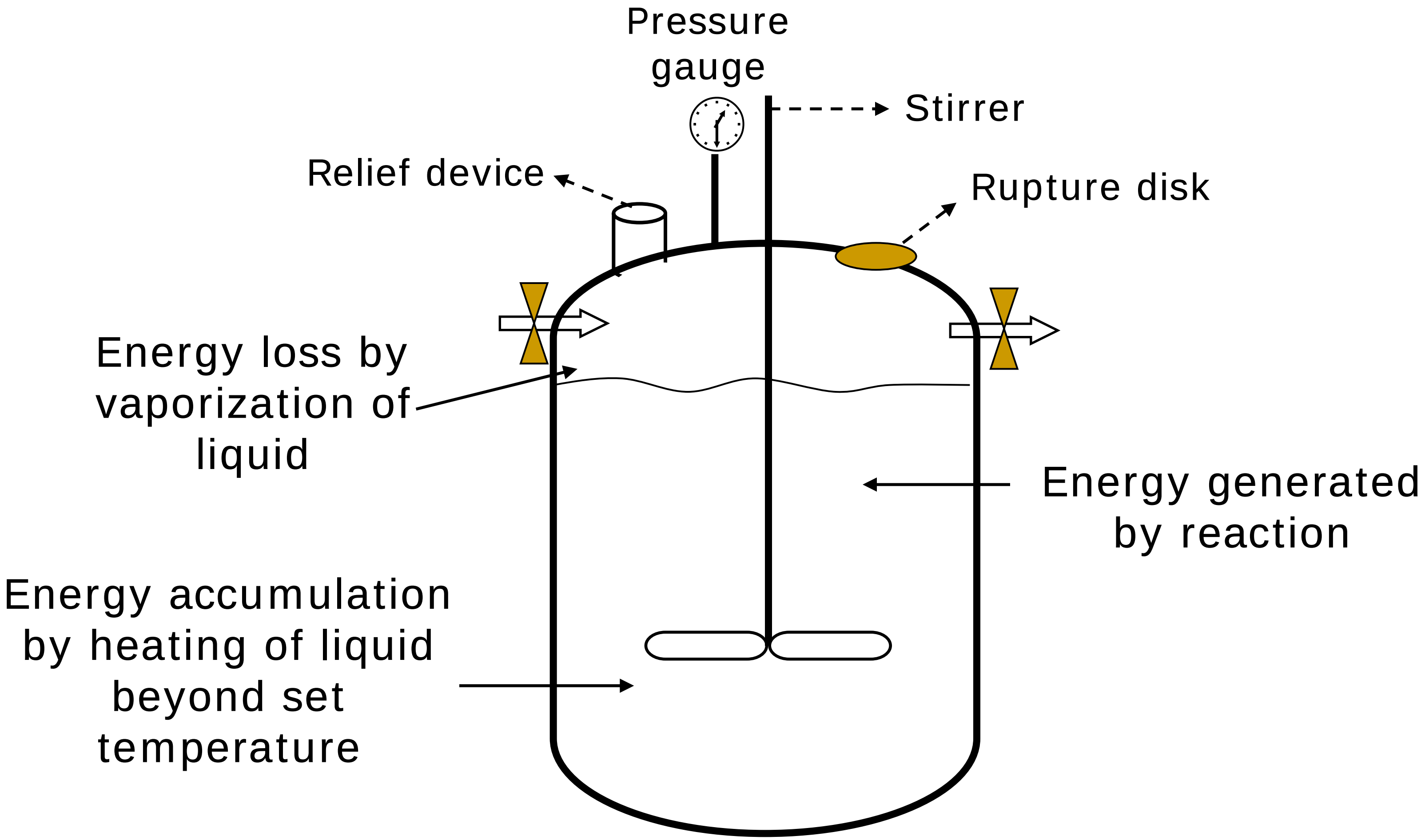
Initiating factors

- **Incorrect agitation**: Monoethanolamine was added slowly with stirring to 98% H_2SO_4 which was maintained at 110°C in a glass-lined reactor. The monoethanolamine and H_2SO_4 were immiscible. When the reaction was complete the mix was cooled and isopropyl alcohol was added to precipitate the product. On the day of the incident, the reactor was charged with H_2SO_4 and then there was a shift change. The oncoming shift did not realize that the stirrer had not been switched on and proceeded to add the monoethanolamine. When they realised the temperature was not rising and switched on the stirrer. The two liquids were mixed causing an instantaneous chemical reaction and explosion.

Batch Reactor



Reactor



Pressure gauge

Stirrer

Relief device

Rupture disk

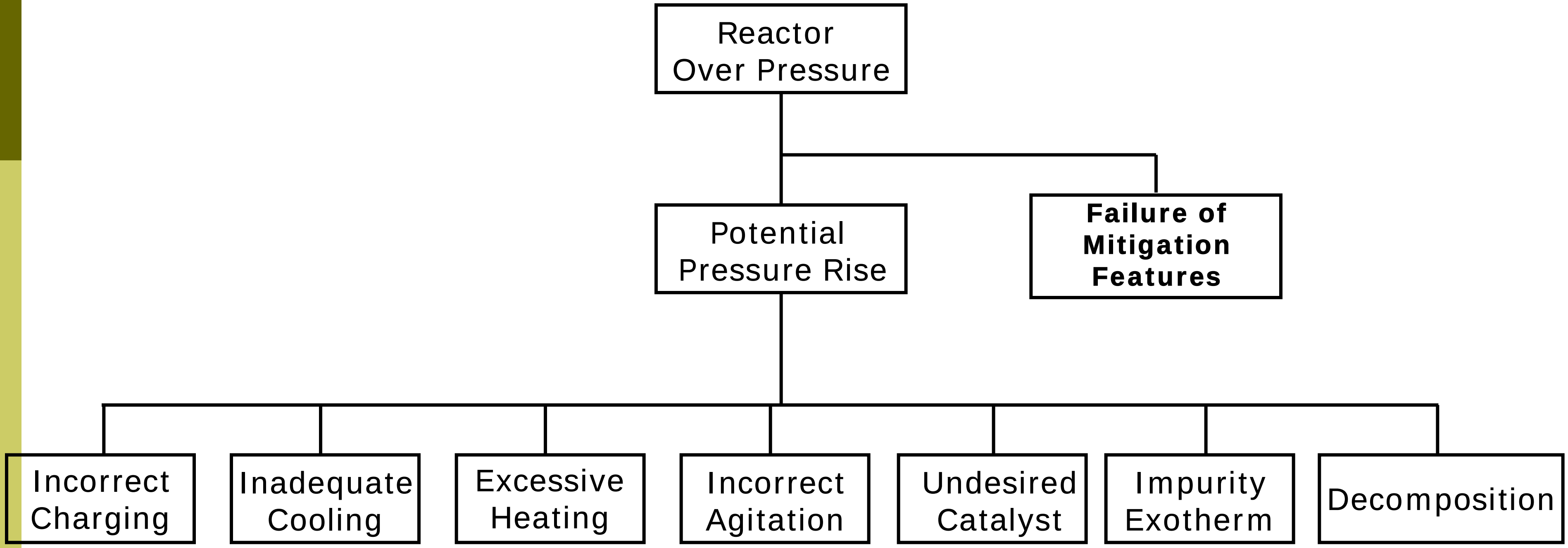
Energy loss by vaporization of liquid

Energy generated by reaction

Energy accumulation by heating of liquid beyond set temperature

Reaction system showing the important energy terms

Fault Tree



Reactor Over Pressure

Potential Pressure Rise

Failure of Mitigation Features

Incorrect Charging

Inadequate Cooling

Excessive Heating

Incorrect Agitation

Undesired Catalyst

Impurity Exotherm

Decomposition

Causes that may lead to reactor overpressure in a generic fault tree

Reactive Chemical Hazard

- Specific types of Chemical Structure lead to instability or high levels of reactive under appropriate conditions. Example of reactive functional groups are: Diazo, Diazonium, Nitroso, Nitrate, Nitrite, Chlorates, Ozonide.

- Self Reaction
    - Nitro, Nitramino, Peroxide, Azide

Reactive Chemical Hazard

- Auto oxidation
  - Ethers (-O-), Isopropyl ($-CMe_2-H$), Allyl (-C=C-C-H), Vinyl (-C=C-H), Styrene (PhCH=C-H).

- Mutually Reacting
  - Metallic Sodium, Aluminium, Magnesium, Hydrazine, Hydrides, Propellants.

Reactive Chemical Hazard

- Pyrophoric & spontaneously combustible
  - e.g. aluminium alkyl, Grignard reagent,
- Peroxide forming
  - e.g. alkali metal, ethers
- Water-reactive chemicals
  - Na, acetic anhydride

Reactive Chemical Hazard

- Oxidizers
  - Chlorine, hydrogen peroxide, nitric acid
- Self-reactive
  - Polymerizing   e.g. acrolein, ethylene
  - Shock-sensitive   e.g. picric acid, NI_3, nitroglycerin, acetone peroxide
  - Thermally decomposing
  - Rearranging
- Incompatible materials

Decomposition energy

- Chemical compounds release energy by decomposition or combustion.
- Rapid energy release occurs when reacts with stoichiometric amount of oxygen.
- Reactive chemicals such as explosives contain enough of their own oxygen to give zero oxygen balance on decomposition. e.g. TNT.

Decomposition energy

Chemical Compounds	**Characteristic bond**	**Heat of decomposition** (KJ/mol)
Aromatic nitro	$R-NO_2$	220-410
Peroxides	C-O-O-	200-340
Aromatic Diazonium	$R-N_2$	130-165
Oximes	C=N-OH	110-170
Aromatic azo	R-N=N-C	100-180
Aromatic nitroso	R-N=O	90-290
Epoxides	$-CH-CH_2-O$	65-100

Organic nitro compounds

- Pure organic nitro compounds, i.e., aromatic or aliphatic nitro compounds, decompose at high temperatures. Their decomposition is rapid and highly exothermic. The thermal stability and decomposition exotherm are influenced by the type, position, and number of substituents.
- The decomposition of pure nitro compounds is rapid or explosive is due to the following factors:
  - The decomposition occurs at high temperatures (250−350 °C), where chemical reactions are fast anyway.

Organic nitro compounds

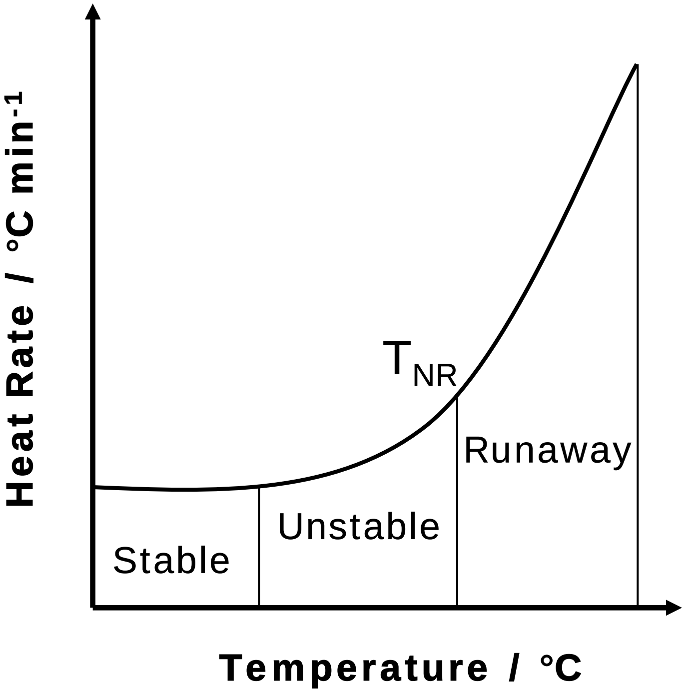
- The decomposition activation energy is very high (above 1050 kJ kg^{-1}). Consequently the thermal acceleration of the decomposition is large, due to a fast increase of the temperature in process situations.
  - Consequently the decomposition reaction, once initiated, becomes very fast even for a limited increase in temperature.
  - The decomposition may exhibit a chemical acceleration phenomenon.
  - The decomposition reaction of nitro compounds may be autocatalytic, i.e., exhibit a chemical acceleration under constant temperature conditions.

Hazardous Unit Processes

Process	**Energy**
Oxidation	Highly exothermic
Nitration	Highly exothermic
Reduction	Low
Halogenation	Highly exothermic
Sulphonation	Moderately exothermic
Hydrolysis	Mildly exothermic
Polymerization	Exothermic/highly exothermic
Condensation	Moderately exothermic
Hydrogenation	Mild to moderately exothermic
Alkylation	Mildly exothermic side reactions
Organometallics	Highly exothermic
Amination	Moderately exothermic

Thermal profile of exothermic reaction

- The following three cases can normally arise for the chemical reactions.
  - The heat production is less than the heat lost.
  - The heat production is same as the heat lost.
  - The heat production is greater than the heat lost.



Thermal profile of an exothermic reaction system

Example 1: T2 Laboratories, Florida

- On 19 December 2007, an explosion occurred at T2 Laboratories Inc. Jacksonville, Florida.

- The explosion killed four T2 workers and resulted in hospitalizing 14 other people. The blast was felt several miles away. Over 100 firefighters fought the ensuing blaze.

Example 1: T2 Laboratories, Florida

- T2 Laboratories is a small company employing about 12 people, and their facility in Jacksonville is their only production site.
- T2 Laboratories manufactured methylcyclopentadienyl manganese tricarbonyl (MMT) under the trade name Ecotane®.
- This chemical is used as a gasoline additive to boost octane rating of gasoline. It is also used in refinery processing to reduce emissions of nitrous oxide and increase the output of gasoline from crude oil. Over one million pounds per year are produced annually in the United States.

T2 Laboratories, Florida

The manufacturing process entails the following:

- Under a nitrogen atmosphere, methylcyclopentadienyl dimer is added to a dispersion of sodium metal in diethylene glycol dimethyl ether.
- A constant elevated reaction temperature is maintained to yield sodium-methylcyclopentadienyl, which is an intermediate in the reaction process. Manganese chloride is then added to the stirred mixture containing the sodium – methylcyclopendienyl intermediate.

T2 Laboratories, Florida

- An elevated temperature is maintained during the addition. Upon completion, the reaction gives bis (methylcyclopentadienyl) manganese, the second intermediate of the reaction process.

- The reaction vessel is then pressurized with carbon monoxide. The addition of CO results in MMT which is separated from the reaction mixture via vacuum distillation.

T2 Laboratories after the blast

Image courtesy: Google Images

U.S. Chemical Safety Board

An independent federal agency investigating chemical accidents to protect workers, the public, and the environment.

Safety videos @ www.csb.gov

Example 2. Synthron, North Carolina

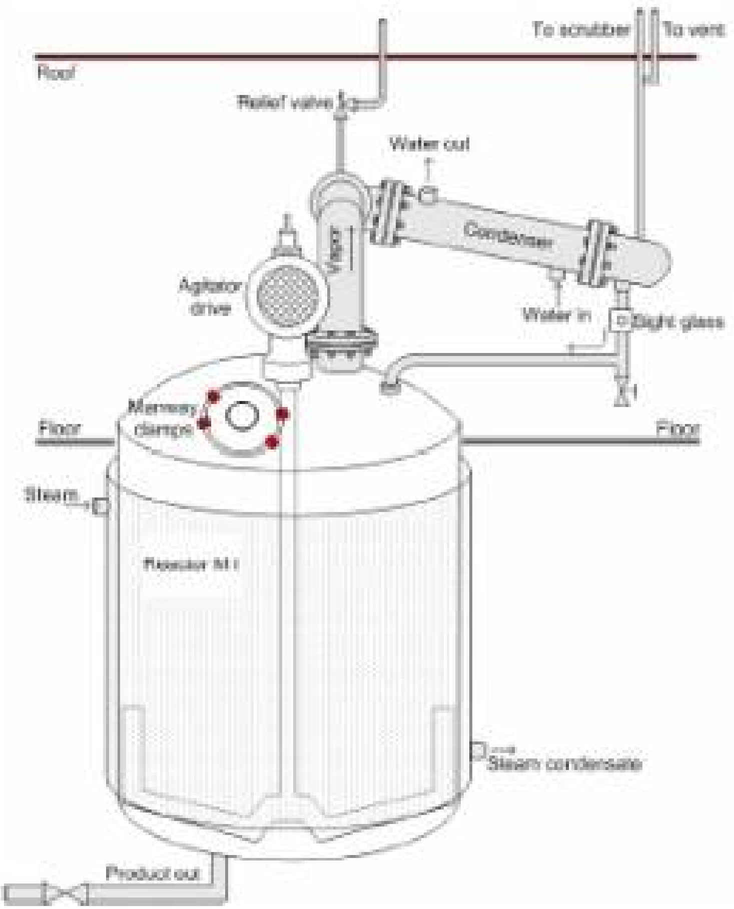
- On 31 January 2006, a runaway chemical reaction and subsequent vapor cloud explosion killed one worker and injured 14 people at the Synthron, LLC facility in Morganton, NC.

- The explosion destroyed the facility and damaged structures in the nearby community.

- The acrylic polymer products produced by Synthron are used for various coatings and paints.

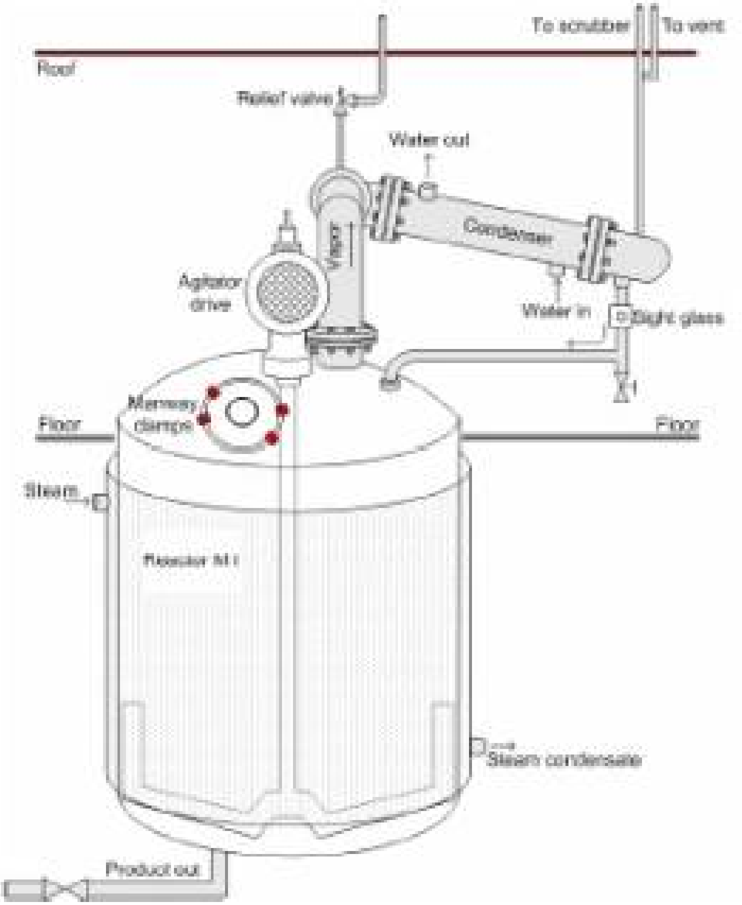
Polymerization

- The runaway chemical reaction at Synthron occurred in their reactor M1, which had a capacity of 1500 gallons.
- The reactor is used to produce acrylic polymers. In a typical operation, an acrylic monomer (purchased from a chemical supplier) is mixed with various flammable solvents in the reactor, and then steam is injected to heat the reaction mixture to a specified temperature (usually near the mixture boiling point).



Polymerization

- Then the steam is turned off, and a polymer initiating solution metered into the reactor. The heat given off by the reaction boils off the solvent which is condensed in the overhead watercooled condenser. Liquid solvent from the condenser is drained back to the reactor. The system operates near atmospheric pressure controlled by a vent on the condenser



Synthron, North Carolina

- The company had received an order for their product, liquid acrylic polymer, and the order was for a slightly greater amount of product than what the reactor was designed to produce in a single batch.
- Operators began preparing for the 6080 pound acrylic polymer batch the previous day which was 12 percent greater than normal.
- The chemical ingredients were scaled up to take care of the increased polymer product, but because there was insufficient aliphatic solvent on hand in storage the operator actually scaled back on the aliphatic solvent.

Synthron, North Carolina

- On the day of the explosion, operations appeared normal until after the steam was turned off and the polymer initiating solution was pumped into the reactor. The operator in charge noted that initially the reaction did not proceed as vigorously as expected, but later the solvent evaporated and the condensed solvent flow returning to the reactor appeared within normal range. A few minutes later, the operator heard a loud hissing and saw vapor venting from the reactor manway.
- A little latter the building exploded killing one and injuring many.

Synthron, North Carolina

The explosion occurred on the following combination of circumstances:

- Because there was a shortage of the aliphatic solvent in storage, the operator actually decreased the amount charged to the reactor by 12% compared with the standard recipe, and increased the acrylic monomer by 12%. With the adjustments made to the reactants to manufacture everything in one batch but with different proportions of chemicals, the heat release was at least 2.3 times that of the standard recipe.

Synthron, North Carolina

- The waterside of the condenser had apparently never been cleaned and was fouled and could not remove the excess heat release as the solvents boiled. Once the heating rate exceeded the condenser cooling capacity, control of the reaction was lost resulting in a runaway reaction.
- Only 4 of the 18 clamps specified by the manufacturer were tightened for the manway cover. This was a labor-saving step as it was long-standing practice to open and clean reactor tank after every batch. The manway began to leak vapors (the hissing sound reported) when the pressure reached approximately 23 psig. The flammable vapors filled the room and ignited.

Synthron site

after the blast

Image courtesy: Google Images

Example 3: Phenol-formaldehyde reactions

- Phenol-formaldehyde reactions are common industrial processes. The reaction of phenol or substituted phenol with an aldehyde, such as formaldehyde, in the presence of an acidic or basic catalyst is used to prepare phenolic resins.
- Phenolic resins are used in adhesives, coatings, and molding compounds.

Example 3: Phenol-formaldehyde reactions

- Typically, phenol-formaldehyde reactions are highly exothermic. Once a reaction is initiated, heat generated by the reaction increases the reaction rate generating more heat. Because the reaction rate is typically an exponential function of temperature, the rate of heat generation will accelerate. Without intervention, a thermal runaway will occur, producing a large amount of heat in a very short time.

Example 3: Phenol-formaldehyde reactions

- Once the reaction begins to accelerate, the pressure of the system will typically increase suddenly due to gas production and/or the vigorous evaporation of liquid. If the reaction continues to accelerate, the pressure buildup may reach and exceed the ultimate strength of the reactor and cause it to explode.
- The heat of reaction is removed by the evaporation of water or other liquid from the process, condensation of the liquid in the overhead condensation system, and return of the liquid to the reactor vessel. Emergency relief on the reactor is usually provided by rupture disks. For safety reasons, slow continuous or stepwise addition of formaldehyde is preferred.

Phenol-Formaldehyde Reaction Incidents

Phenol-Formaldehyde Reaction Incidents at Various Companies in USA.

Date of incident	State, USA	Description	Effects
September 10, 1997	OH	A 8,000 gallon reactor exploded during production of a phenol-formaldehyde resin.	1 worker fatality, 4 employees injured, 3 firefighters treated for chemical burns. Evacuation of residents for several hours.
August 18, 1994	OH	Pressure buildup during manufacture of phenolic resin, pressure increased, rupture disks popped. Product was released through emergency vent. The cause of accident was reported as failure to open condensate return line.	Residents evacuated for 5 hours.
February 29, 1992	GA	A 13,000 gallon reactor exploded during production of a phenol-formaldehyde resin. Explosion occurred during initial stages of catalyst addition.	4 employees injured, 1 seriously. 1 firefighter treated for chemical burns. Evacuation of 200 residents for 3 hours.

Georgia-Pacific, 1997.

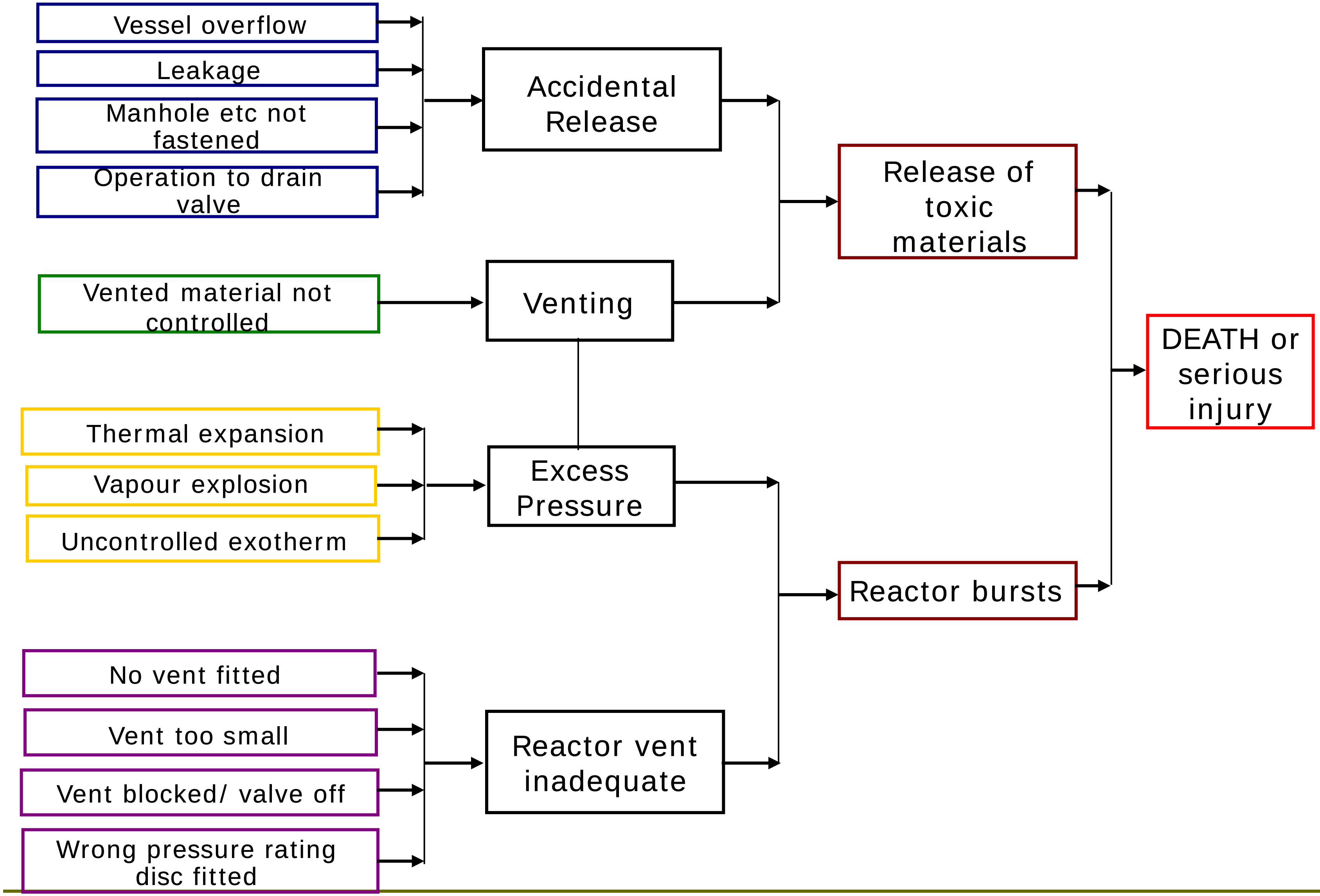
- Georgia-Pacific was manufacturing a phenolic resin in an 8,000-gallon batch reactor when the incident occurred.

- An operator charged raw materials and catalyst to the reactor and turned on steam to heat the contents. A high temperature alarm sounded and the operator turned off the steam. Shortly after, there was a large, highly energetic explosion.

Georgia-Pacific, 1997.

- The investigation revealed that the reactor explosion was caused by excessive pressure generated by a runaway reaction. The runaway was triggered when, contrary to standard operating procedures (SOP), all the raw materials and catalyst were charged to the reactor at once followed by the addition of heat.
- Under the runaway conditions, heat generated exceeded the cooling capacity of the system and the pressure generated could not be vented through the emergency relief system causing the reactor to explode

Fault tree for reactor overpressure



Chemical Reactivity Hazard

- A chemical reactivity hazard is a situation with the potential for an *uncontrolled chemical reaction* that can result directly or indirectly in serious harm to people, property, or the environment.
- The resulting reaction may be violent, releasing heat, large quantities of toxic, or flammable gases or solids.

Chemical Reactivity Hazard

- If the reaction is confined in a container, the pressure within the container may increase resulting in an explosion.
- Common materials that we use routinely by themselves with negligible hazard may react violently when mixed with other common materials, or react violently when the temperature or pressure is changed.

Components of intrinsic safety

- The basic parameters that have to be considered for assessing the chemical reaction systems are

Thermodynamics

- Reaction energy
- Adiabatic temperature and pressure rise
- Quantum of gas generated

Kinetics

- Activation energy
- Reaction rate
- Rate of heat generation
- Rate of pressure rise
- Time to maximum rate

Physical

- Heat capacity
- Thermal conductivity

- In addition to the above parameters the safe limits of temperature, feed rate and concentration have to be defined as a function of operating conditions.

Reaction Hazard

- Analysis indicates that incidents occur due to:
  - Lack of proper understanding of the thermo-chemistry and chemistry
  - Inadequate engineering design for heat transfer
  - Inadequate control systems and safety back-up systems
    - Including venting arrangements
  - Inadequate operational procedures, including training.

Assessing Reaction Hazard

- Controlling an exothermic reaction depends on the interaction among:
  - the kinetics and reaction chemistry
  - the plant equipment design
  - the operating environment.

- Chemical process industry must consider the following factors to better understand and address the potential hazards and consequences of reactive systems:

Assessing Reaction Hazard

- **Thorough hazard assessment:** The chemical & process hazards and the consequences of deviations must be thoroughly understood, evaluated, and appropriately addressed through preventive measures. Several layers of safety systems, whether complementary or redundant should be considered to enhance reliability.

Assessing Reaction Hazard

- **Complete identification of reaction chemistry and thermochemistry:** For some exothermic reactions, the time to runaway is very short. Over-pressurization can occur when gas or vapor is produced as a byproduct of the reaction or any decomposition reactions. The kinetics of the runaway reaction will be reaction specific and may differ in various runaway situations. The characteristics of the particular reactions must be determined experimentally. Experimental data should be used to define process boundaries in terms of the pressure, temperature, concentration, and other parameters as well as the consequences of operating outside of these boundaries.

Assessing Reaction Hazard

- **Addition of raw materials:** Frequently, the reaction rate is controlled by the addition rate of one reactant or the catalyst and should be determined based on chemistry studies. Process industries must pay attention to the order of ingredients, the addition rates, under- or over-charging, and loss of agitation.

Assessing Reaction Hazard

- **Emergency relief:** Runaway reactions may lead to the rapid generation of gas or vapor. Under certain conditions, the vapor generation rate may be large enough to cause the vapor-liquid mixture to swell to the top of the vessel, resulting in two-phase flow in the relief venting system. Relief system capacity should be evaluated in conjunction with the hazard analysis to ensure that sizing is based on an appropriate worst case scenario.

Assessing Reaction Hazard

- **Administrative controls:** If administrative controls, such as training and standard operating procedures (SOP), are used as a safeguard against process deviation and accidental release, consideration must be given to human factors to ensure reliability.

Characterization using Calorimeters

- Chemical plants produce products using a variety of complex reactive chemistries.
- It is essential that the behavior of these reactions be well characterized prior to using these chemicals in large commercial reactors.
- Calorimeter analysis is important to understand both the desired reactions and also undesired reactions.

Characterization using Calorimeters

Important questions that must be asked for the characterization of reactive chemicals:

- At what temperature does the reaction rate become large enough
- What is the maximum temperature increase
- What is the maximum pressure during the reaction.
- At what time and temperature does the maximum self-heat rate or pressure rate occurs
- Are there any side reactions
- Can the heat generated by chemical reactions (desired or undesired) exceed the capability of the vessel/process to remove heat

Tools for evaluating thermal explosion

- Calorimetric techniques are excellent tools for evaluating thermal explosion hazards of chemicals/chemical process.

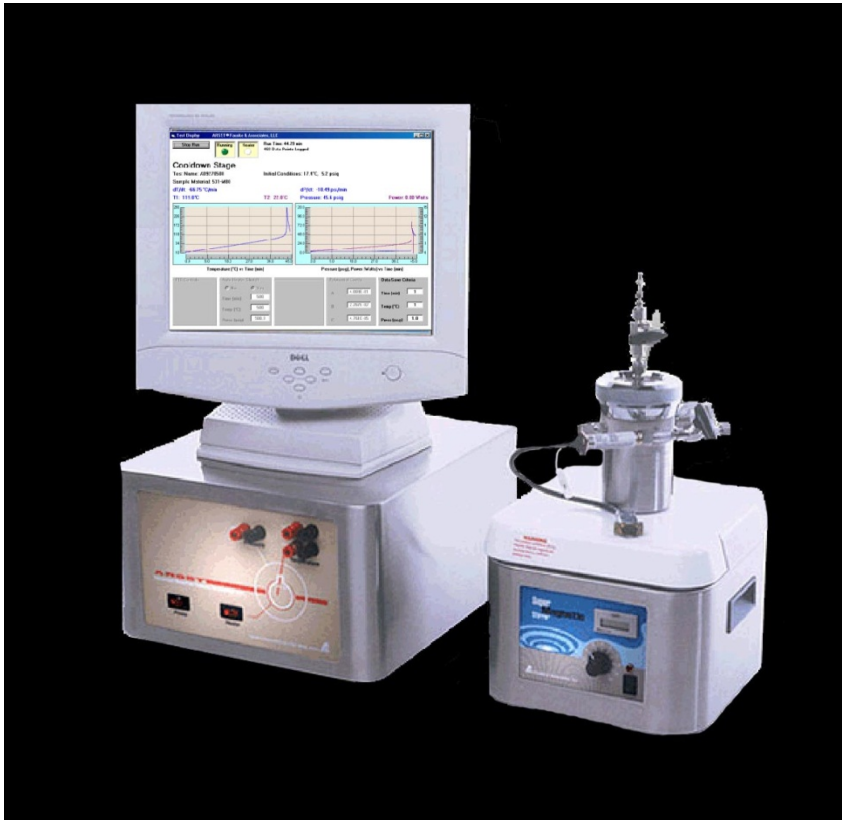
- They measure the thermal instability of a compound which is the root cause for runaway and decomposition reactions.

Tools for evaluating thermal explosion

- The following techniques have attained scientific importance due to their novelty in determining the instability and thermal runaway potential of a chemical compound.
  - Thermal analysis
    - Differential Scanning Calorimeter (DSC),
    - Thermo Gravimetric Analyzer (TGA),
    - Differential Thermal Analyzer (DTA).
  - Advanced Reactive Systems Screening Tool (ARSST).

Advanced Reactive Systems Screening Tool (ARSST)

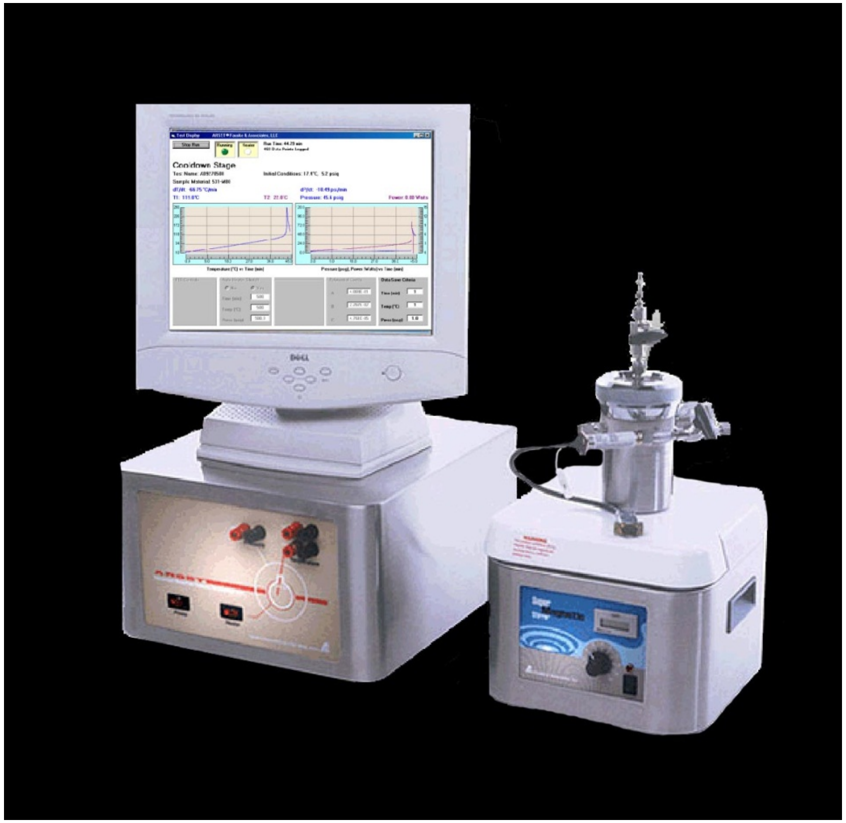
- ARSST is a low thermal inertia calorimeter used to obtain critical upset process design data.
- ARSST tests are used to model such upset scenarios as loss of cooling, loss of stirring, mischarge of reagents, batch contamination and fire exposure heating.



(www.fauske.com)

Advanced Reactive Systems Screening Tool (ARSST)

- This can quickly and safely identify potential reactive chemical hazards in the process industry.
- ARSST data yields critical experimental knowledge of the rates of temperature and pressure rise during a runaway reaction, thereby providing energy and gas release rates which can be applied to full scale process conditions.



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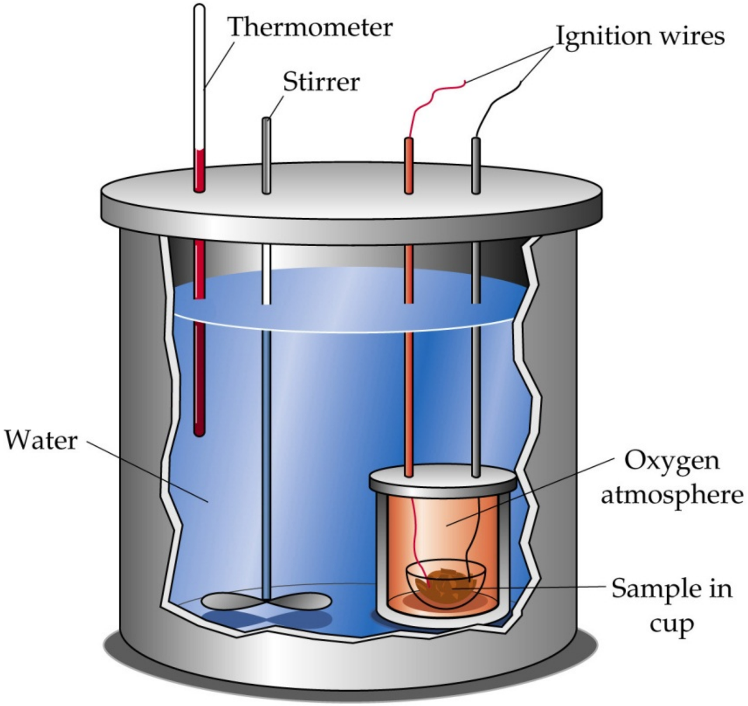
Calorimeter

- Calorimetry is the science of measuring the heat of chemical reactions or physical changes as well as heat capacity.
- Adiabatic calorimeters
  - Accelerated Rate Calorimeter (ARC)
- Reaction calorimeters
  - Heat flow calorimetry
- Bomb calorimeters



Bomb calorimeter

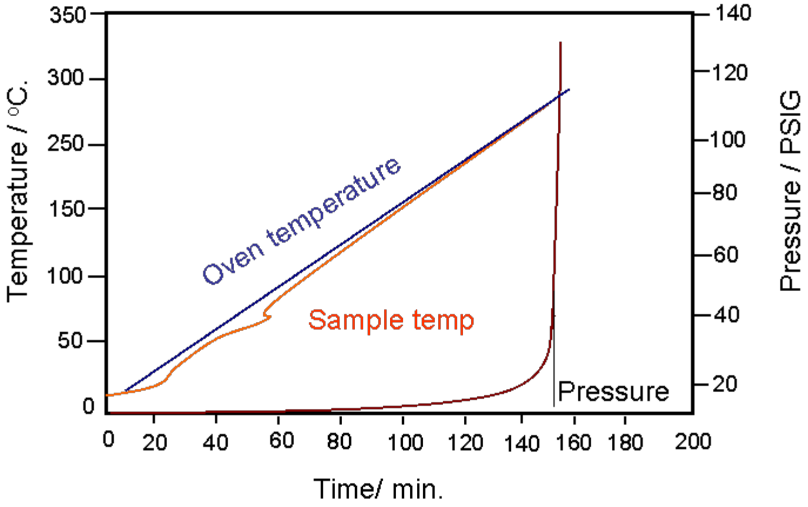
Reaction Calorimeter (RC)

A computer controlled batch reactor to monitor the course of chemical or physical reactions at process-like conditions

Image courtesy: Google Images

Carius Tube

- The test is designed to provide a relatively low cost screening of thermal stability and pressure generation capacity. With an appropriate safety margin, the maximum safe exposure temperature of a material can be specified.



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Decomposition rate of DNT

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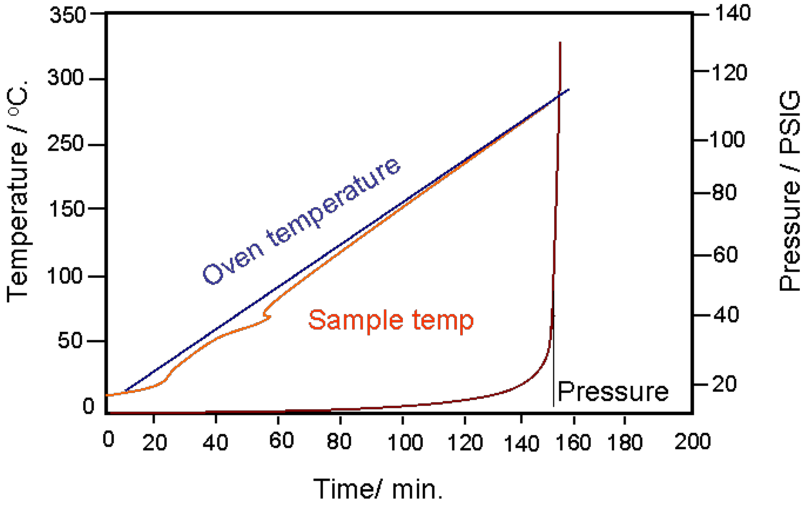
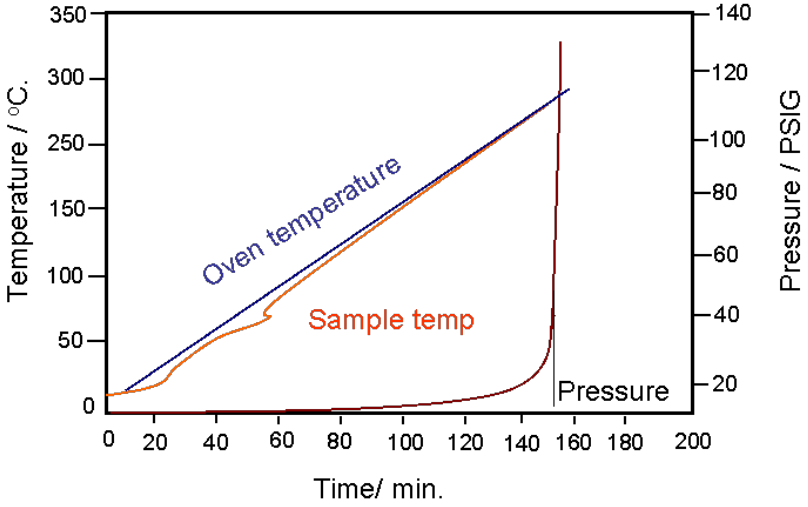
- The test is a form of Differential Thermal Analysis (DTA). This is a high heat loss thermal screening technique. The test measures the onset temperature and magnitude of thermal activity and any pressure events when a material is exposed to elevated temperatures.



Decomposition rate of DNT

Carius Tube

- Typical temperature and pressure plot for the decomposition of dinitrotoluene (DNT) is shown in the figure. DNT is not normally considered as an explosive material but it can undergo very high rate decomposition. The high rate occurs above its atmospheric boiling point ~300°C, therefore confinement is necessary before propagative deflagration will occur.



Decomposition rate of DNT

Calorimeter

- Measuring Procedure
  - Heat Production rate
  - Reaction enthalpy
  - Specific heat
  - Heat of dissolution & crystallization
  - Heat of mixing
  - Enthalpy of phase changes
- Measuring
  - Process variables, e.g. temperature, stirrer speed, mass, pH, pressure, etc.
  - Heat transfer coefficient
  - Heat production rate

- Control
  - Temperature, stirrer speed,
  - Dosing, pressure, pH, etc.

Steps to Reduce Reactive Hazards

- The consequences of a runaway reaction can be severe. Therefore, facilities must focus on prevention of conditions favorable to a reaction excursion through process design control, instrumentation, and interlocks to prevent recurrence of similar events.

Steps to Reduce Reactive Hazards

- Facilities should take the following steps to prevent runaway reactions:
    - Modify processes to improve inherent safety.
    - Minimize the potential for human error.
    - Understand events that may lead to an overpressure and eventually to vessel rupture.
    - Use lessons learned.
    - Evaluate Safe Operating Procedures.
    - Evaluate the effectiveness of the emergency relief system.
    - Evaluate employee training and oversight.

Controlling Reactive Hazards

Through Inherent Safety

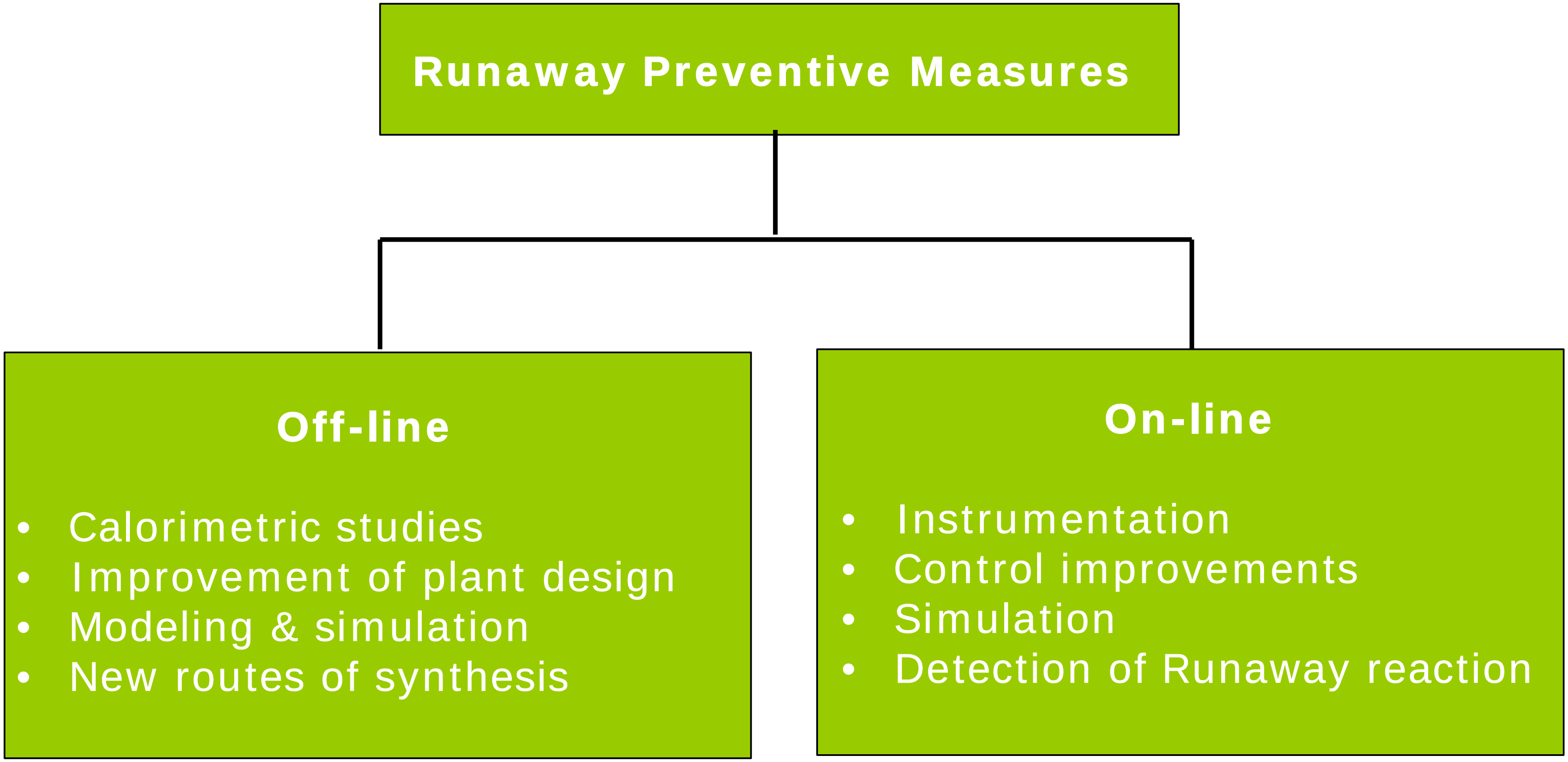
- Use a reaction pathway that uses less hazardous chemicals
- Use reaction pathway that is less energetic, slower or easier to control
- Use smaller inventories of reactive chemicals both in process and in storage

Controlling Reactive Hazards

Through Inherent Safety

- Reduce shipping of reactive chemicals – produce on site on demand.
- Design equipments or procedures to prevent an incident in the event of a human error.
- Control reactor stoichiometry and charge mass so that in the event of a runaway reaction the pressure rating of the vessel will not be exceeded.

Runaway Preventive Measures



Runaway Preventive Measures

Off-line

- Calorimetric studies
- Improvement of plant design
- Modeling & simulation
- New routes of synthesis

On-line

- Instrumentation
- Control improvements
- Simulation
- Detection of Runaway reaction

Safety Aspects in Process Plant Design

Process plant safety

Process plant

- Receive, store, process chemicals in controlled manner
- Most chemical are flammable, toxic
- Unsafe conditions will result in uncontrolled release of materials.

Process plant safety is ensured by

- Design of inherent safe plant
- Constructional facility as designed
- Operational controls.

Chemical Plant Design

- In plant design, normally less than 1% of ideas for new designs become commercialized.
- During this process, typically, cost studies are used as an initial screening to eliminate unprofitable designs.
- If a process appears profitable, then other factors such as safety, environmental constraints, controllability, etc. are considered.

Chemical Plant Design

- Generally, small chemical plant called a pilot plant is built to provide design and operating information before construction of a large plant.
- From data and operational experience obtained from the pilot plant, a scaled-up plant can be designed for higher or full capacity.

Design

- Design of the facility shall be
  - To meet & withstand external & internal conditions
  - Provide passive and active protections

Design

- External conditions
  - Site selections, environment
  - Metrological data
  - Site elevation
  - Max, Min temperature
  - Seismic data
  - Wind speed
  - Tide, Tsumani

- All these factors are taken into account for P & ID.

Flow Diagrams

- The units, streams, and fluid systems of chemical plants or processes can be represented by Block Flow Diagrams which are very simplified diagrams, or Process Flow Diagrams which are somewhat more detailed.
- **Block Flow Diagrams (BFD)** is a schematic illustration of the major process. Shows overall processing picture, flow of raw materials and products may be included. Unit operations such as mixers, separators, reactors, distillation columns, etc. are usually denoted by a simple block or rectangle.

Flow Diagrams

- **Process Flow Diagrams (PFD)** use more detailed symbols and show pumps, compressors, and major valves. Likely ranges of material flow rates for the various streams are determined based on desired plant capacity using material balance calculations.
- Energy balances are also done based on heats of reaction, heat capacities, expected temperatures and pressures at various points to calculate amounts of heating and cooling needed in various places and to size heat exchangers.

e.g. Biodiesel Process Block Diagram

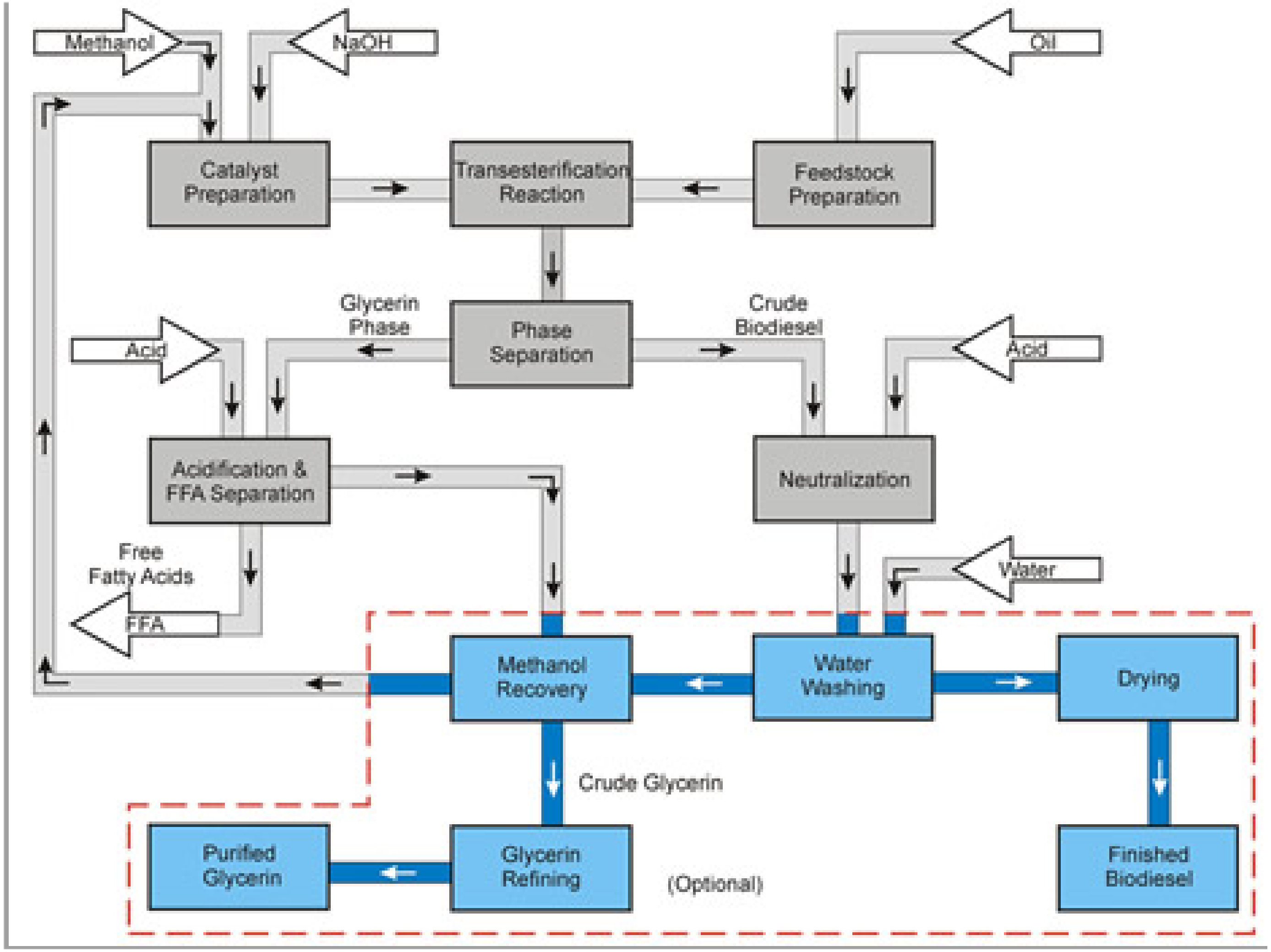
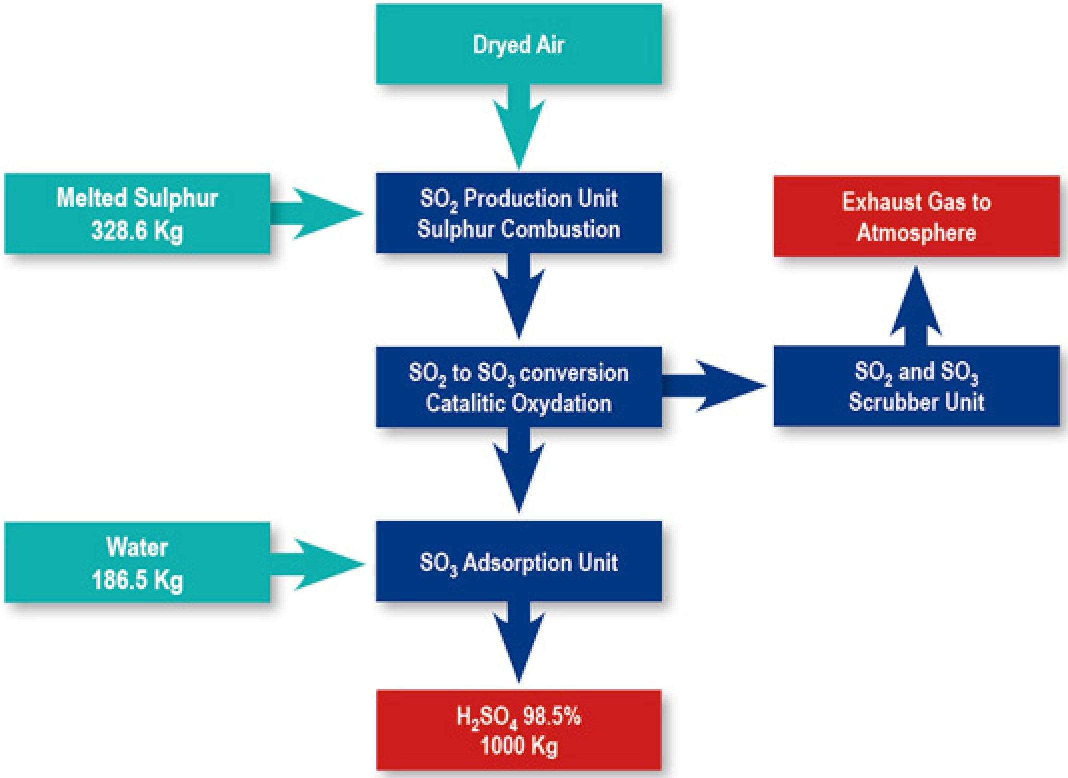


Image courtesy: Google Images

Block Diagram for H_2SO_4 Production



Dryed Air

Melted Sulphur
328.6 Kg

SO_2 Production Unit
Sulphur Combustion

Exhaust Gas to
Atmosphere

SO_2 to SO_3 conversion
Catalitic Oxydation

SO_2 and SO_3
Scrubber Unit

Water
186.5 Kg

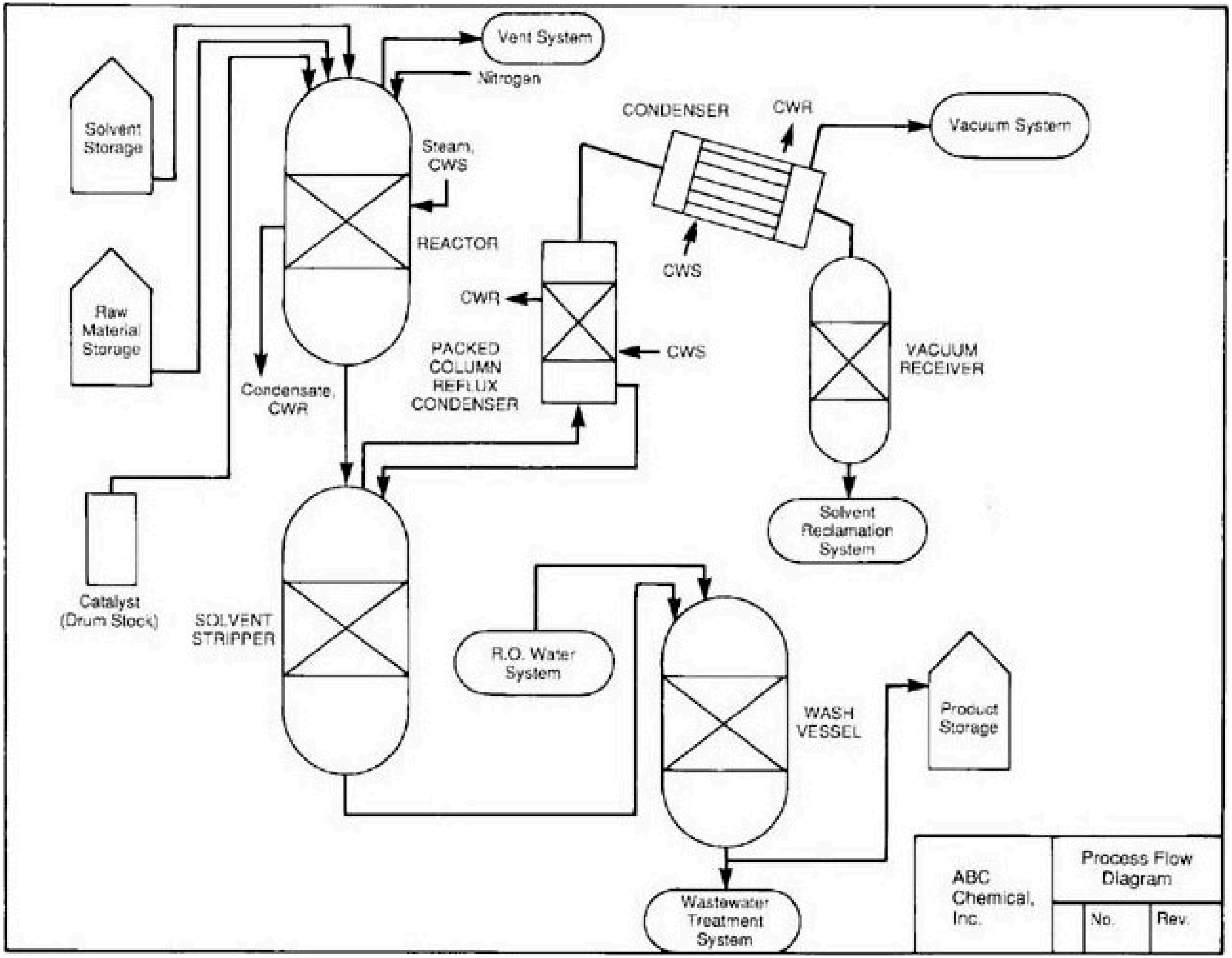
SO_3 Adsorption Unit

H_2SO_4 98.5%
1000 Kg

Plant block diagram and overall material balance

Image courtesy: Google Images

e.g. Process flow diagram

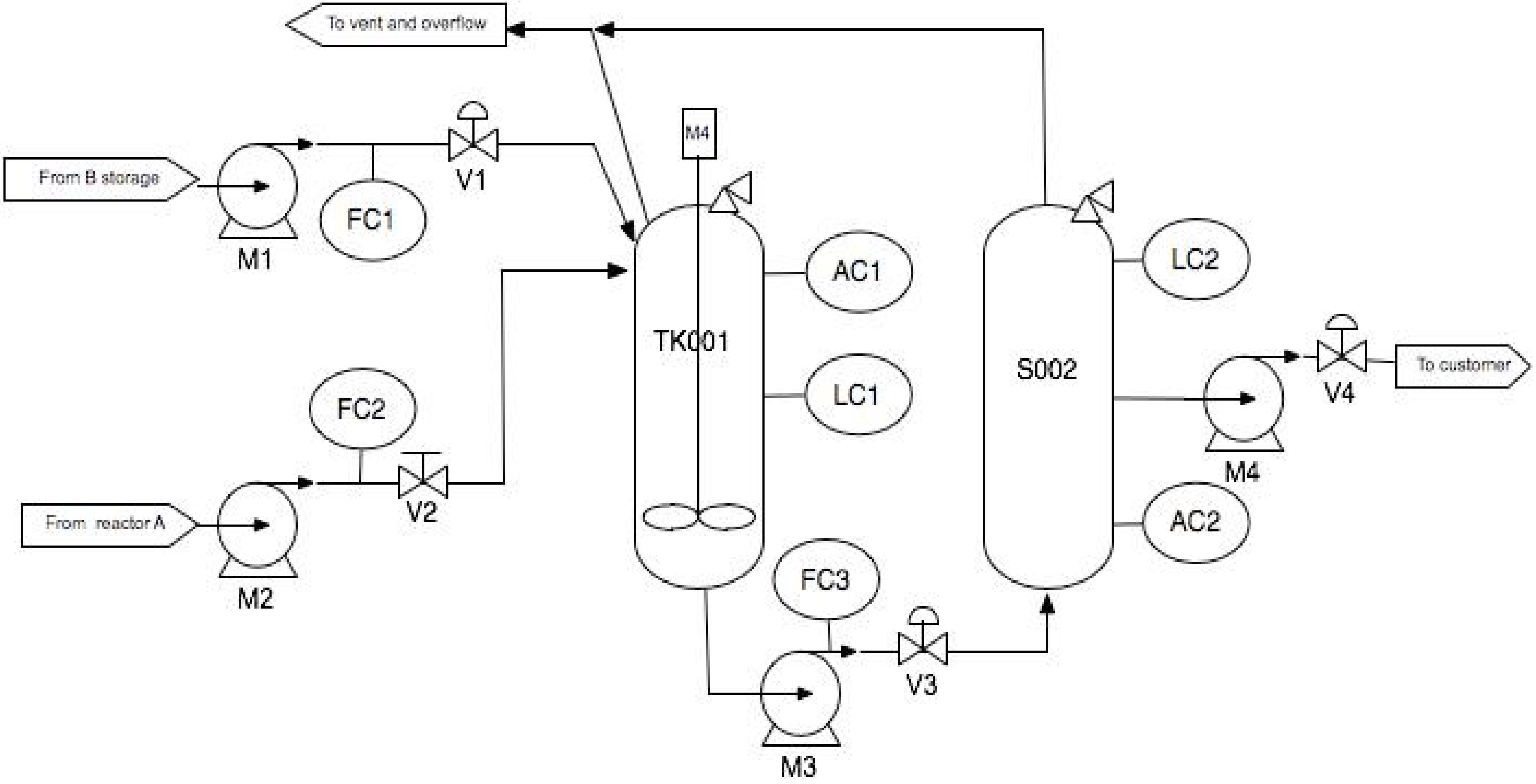


P&I D

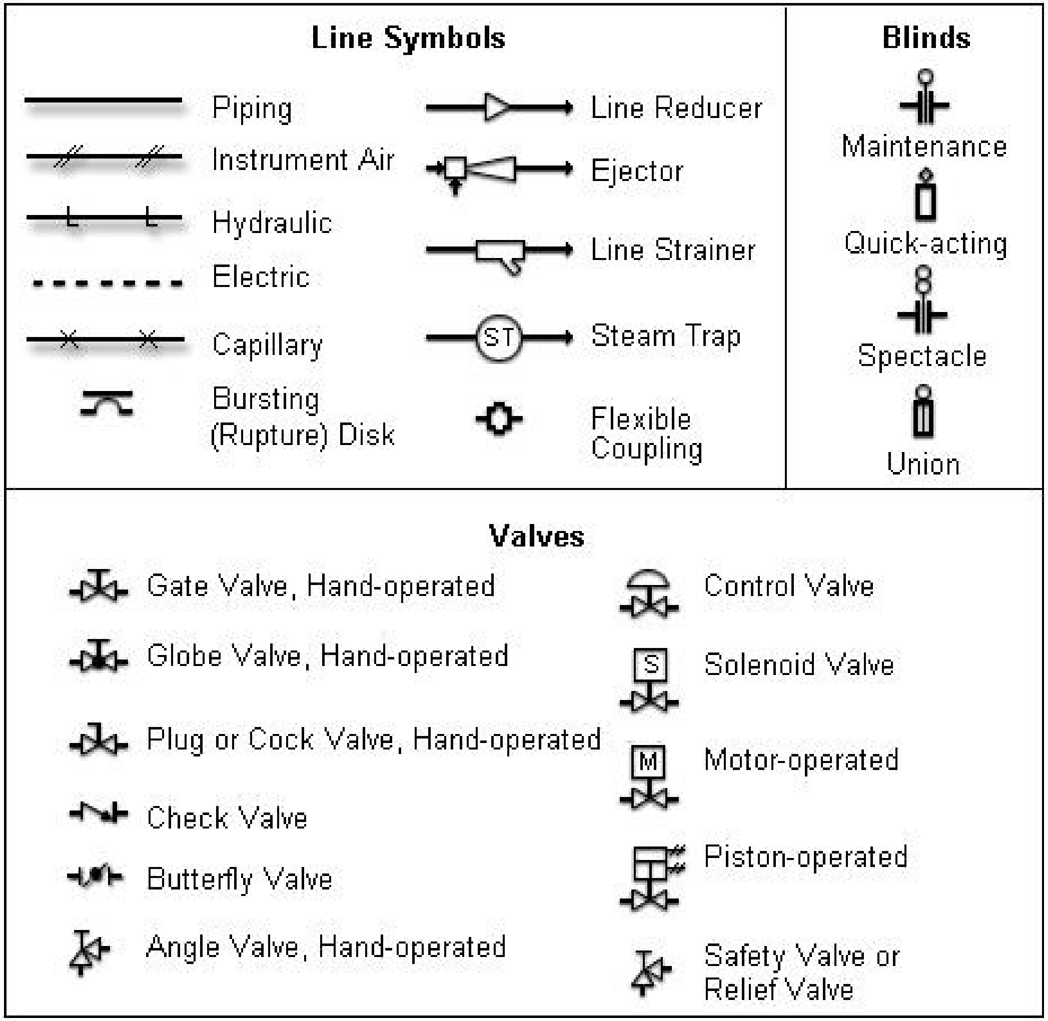
- Chemical plant design can be shown in full detail in a **Piping and Instrumentation Diagram/Drawing** (P&ID) which shows all piping, tubing, valves, and instrumentation, typically with special symbols.

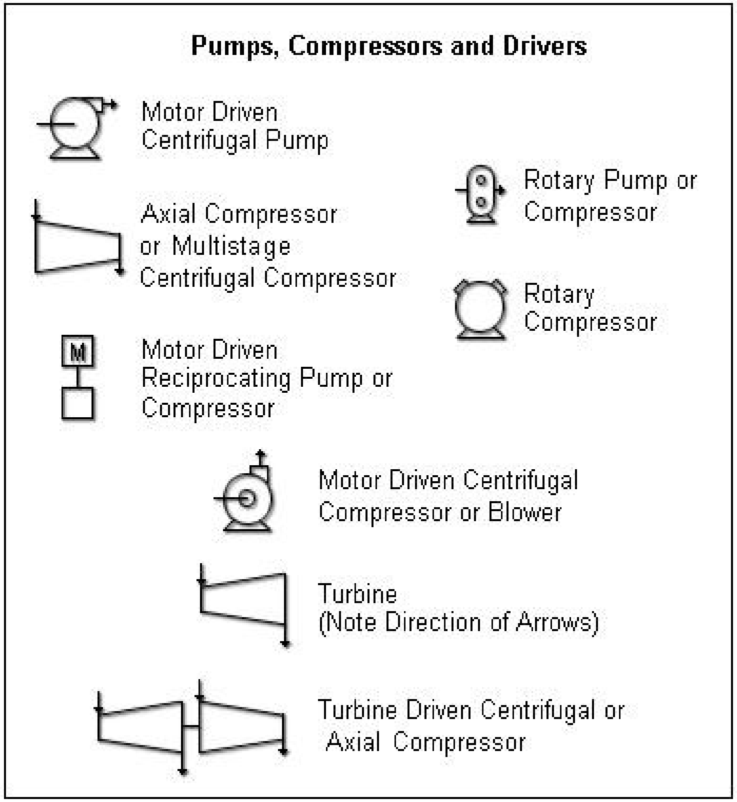
- It is a pictorial representation of
    - Key piping and instrument details
    - Control and shutdown schemes
    - Safety and regulatory requirements

e.g. Piping and Instrumentation Diagram

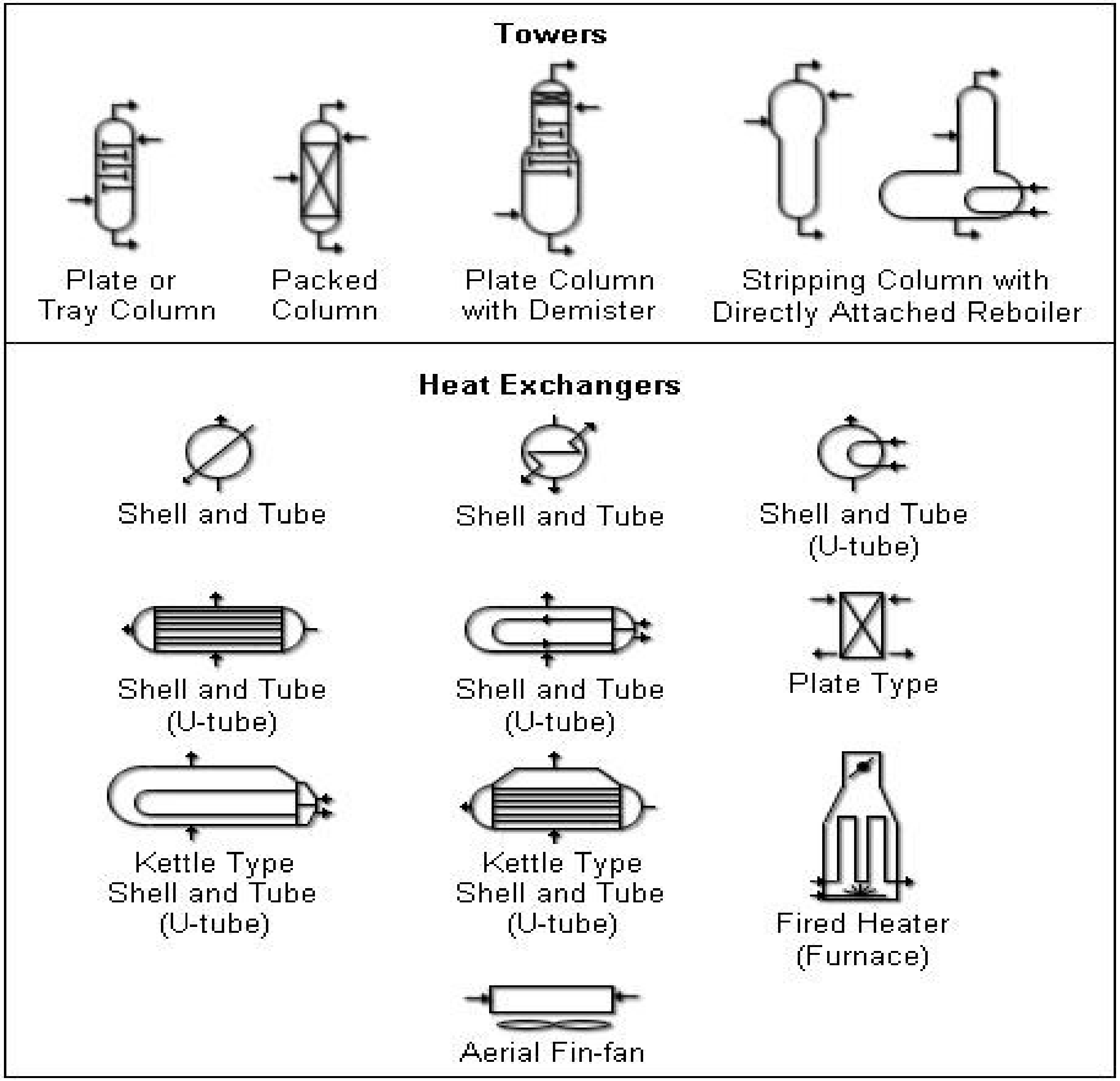


P & ID Symbols

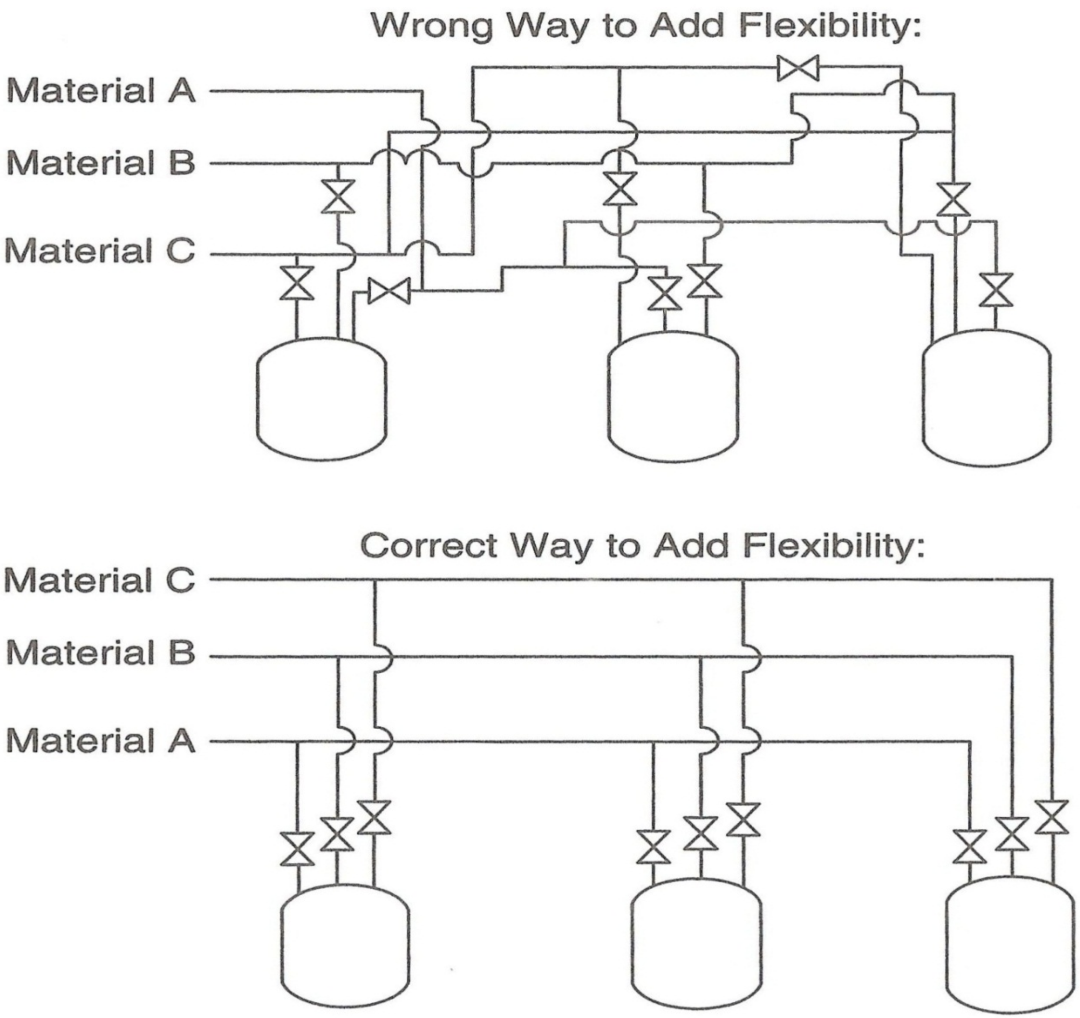

Line Symbols
Piping
Instrument Air
Hydraulic
Electric
Capillary
Bursting (Rupture) Disk
Line Reducer
Ejector
Line Strainer
ST
Steam Trap
Flexible Coupling
Blinds
Maintenance
Quick-acting
Spectacle
Union
Valves
Gate Valve, Hand-operated
Globe Valve, Hand-operated
Plug or Cock Valve, Hand-operated
Check Valve
Butterfly Valve
Angle Valve, Hand-operated
Control Valve
S
Solenoid Valve
M
Motor-operated
Piston-operated
Safety Valve or Relief Valve


Pumps, Compressors and Drivers
Motor Driven Centrifugal Pump
Axial Compressor or Multistage Centrifugal Compressor
M
Motor Driven Reciprocating Pump or Compressor
Rotary Pump or Compressor
Rotary Compressor
Motor Driven Centrifugal Compressor or Blower
Turbine (Note Direction of Arrows)
Turbine Driven Centrifugal or Axial Compressor

P & ID Symbols

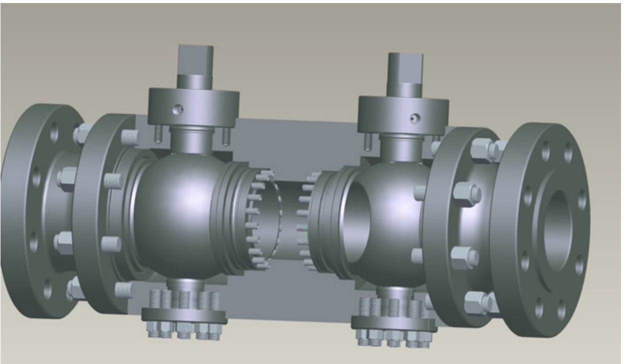

Towers
Plate or Tray Column
Packed Column
Plate Column with Demister
Stripping Column with Directly Attached Reboiler
Heat Exchangers
Shell and Tube
Shell and Tube
Shell and Tube (U-tube)
Shell and Tube (U-tube)
Shell and Tube (U-tube)
Plate Type
Kettle Type Shell and Tube (U-tube)
Kettle Type Shell and Tube (U-tube)
Fired Heater (Furnace)
Aerial Fin-fan

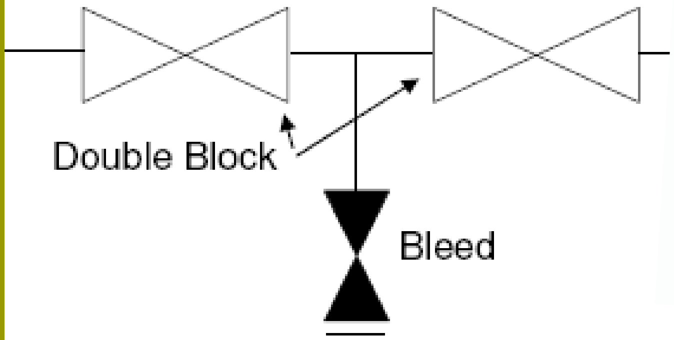
Sketch of a simple vs. complex design

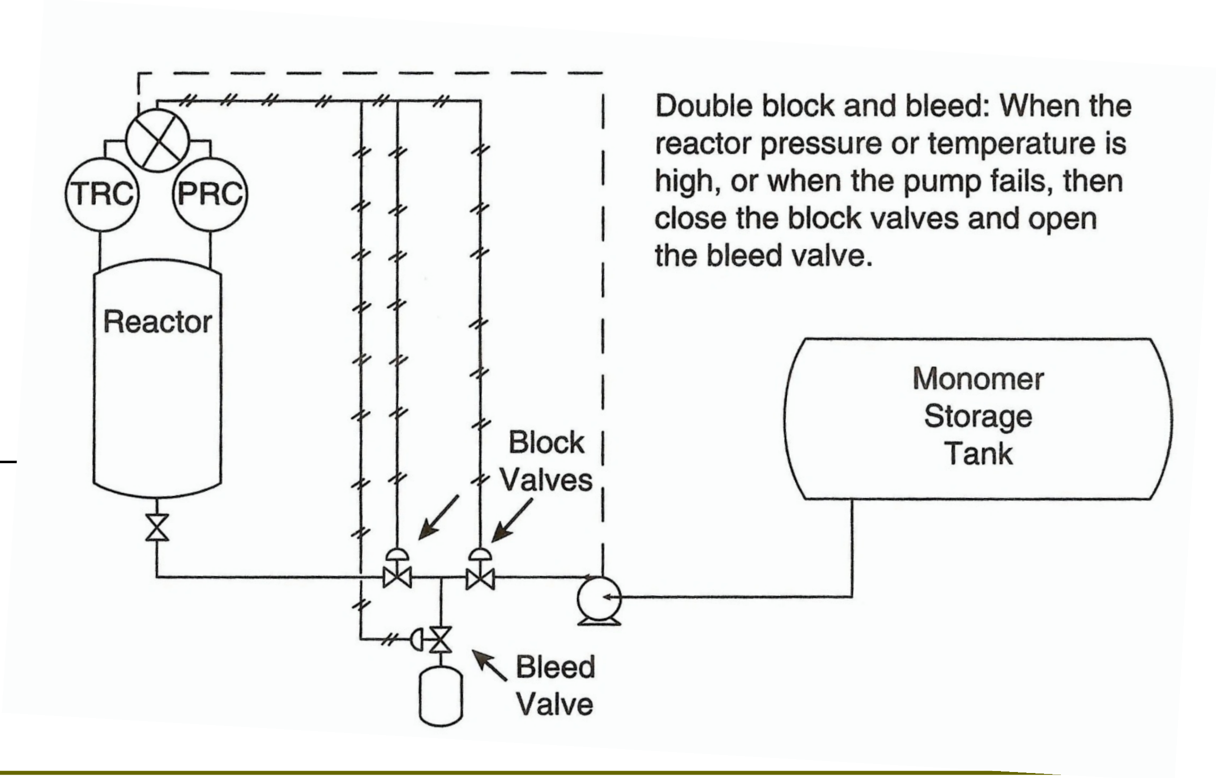


Controls: Block and Bleed

- A block and bleed manifold is a hydraulic manifold that combines one or more block/isolate valves, for interface with other components. The purpose of the block and bleed manifold is to isolate or block the flow of fluid in the system.






Double block and bleed: When the reactor pressure or temperature is high, or when the pump fails, then close the block valves and open the bleed valve.

Control System

- Control systems monitor, record and log plant status and process parameters.
- Provides provision for operator to control changes to the plant status.
- Detect onset of hazard and automatic hazard termination (i.e. control within safe operating limits).
- Prevent automatic or manual control actions which might initiate a hazard.

Control System

- Control system may be independent, or share elements such as plant interface and human interface.
- The plant interface comprises inputs (sensors), outputs (actuators), and communications (wiring, fibre optic, analogue/digital signals).
- The human interface may comprise a number of input and output components, such as controls, keyboard, mouse, indicators, audible alarms and charts.

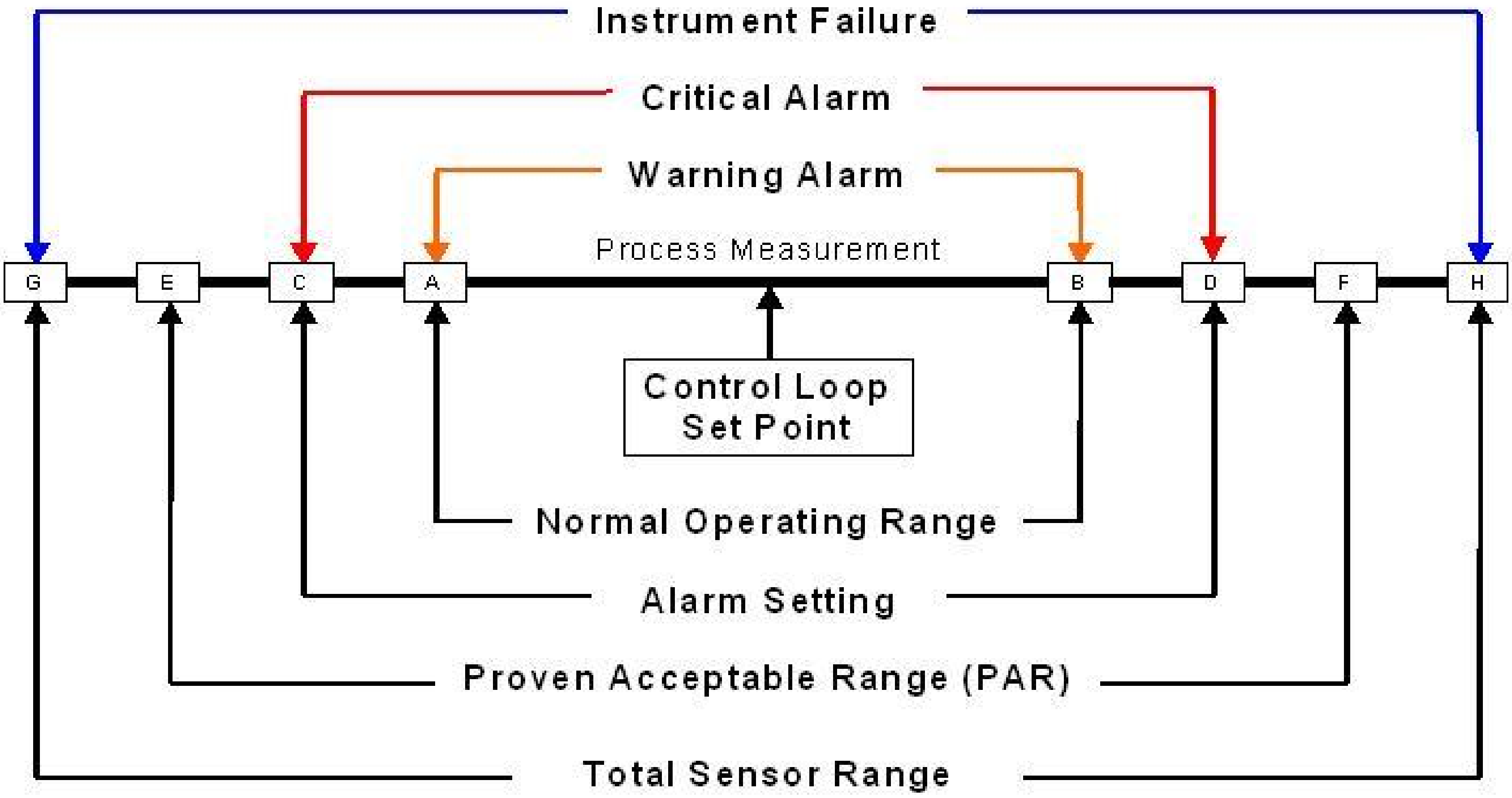
Alarms in Processes

- Alarms are implemented in a process design to aid in the control of the process.
- In all processes, disturbances occur that can shift a plant's operation away from normal. When this happens, measures are usually taken by computers, with the use of P&ID control loops, to keep the process under control.
- With the control systems, processes are designed to fall within a range of acceptable normal operating limits. When a process deviates beyond these normal limits, an alarm should be triggered.

Alarms in Processes

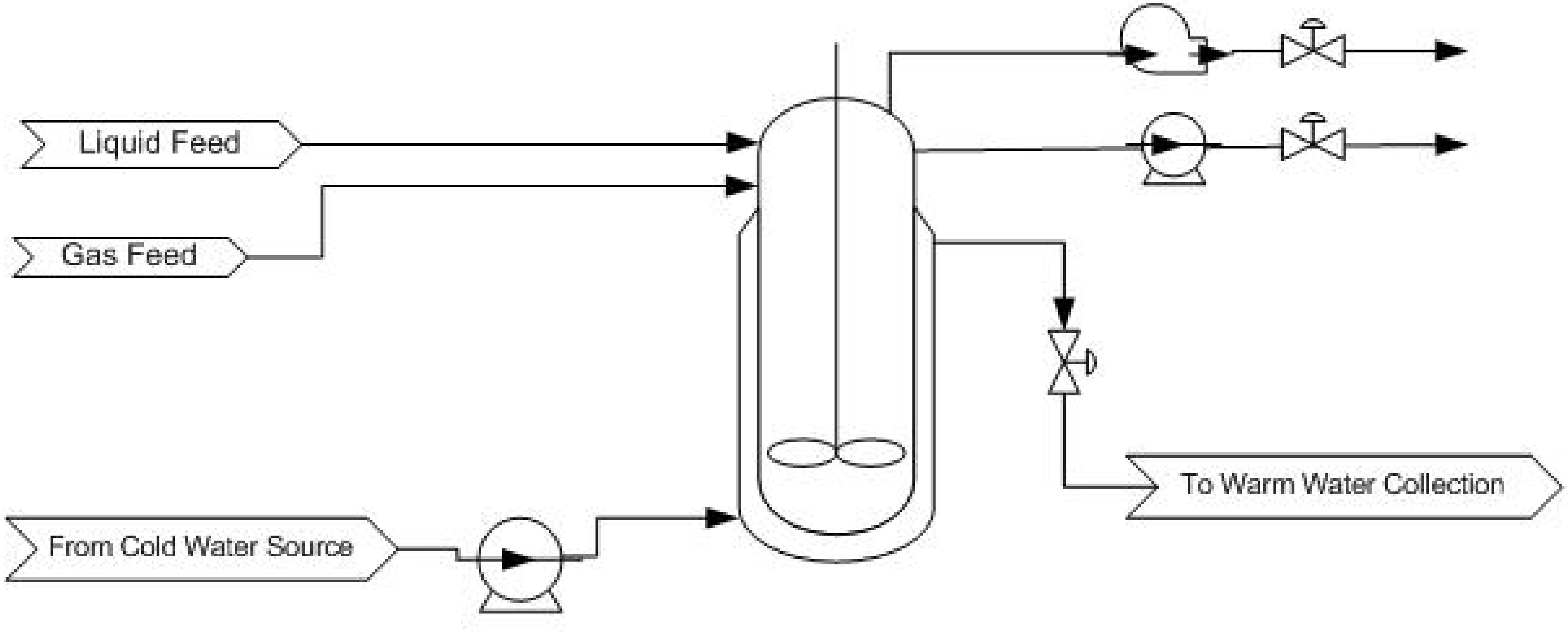
- For most processes, the minimum for safe operation is two levels of alarms: **Warning and Critical**.
    - The warning alarm tells plant operators that the process has deviated beyond the acceptable limits and provides them with the time and ability to take corrective action so that the product quality is not affected and environmental and safety regulations are not exceeded.
    - If the right actions are not taken quickly enough to correct the problem, a critical alarm may then be triggered. The critical alarm tells the plant operators that conditions are dangerously close to breaching what is allowed. In many cases, the critical alarm will call for a systematic shut-down of the operation.

Visual representation of alarm ranges



Problem: Alarms in P&ID

- A P&ID appears below for the production of a chemical compound. The reaction taking place in the CSTR is highly exothermic.
- After examining the P&ID for this part of the process, describe a possible alarm and control system.



Answer

The CSTR for the exothermic reaction is jacketed with a cooling water stream. An alarm should be in place to monitor the reactor temperature.

A warning alarm can notify the operator that the temperature is too high and corrective action needs to be taken.

A critical alarm should be in place to warn that the reactor is nearing runaway conditions and an immediate response is needed.

.

Answer

Flow controller and valve for the liquid feed and gas feed can be placed.

If the necessary action is not taken for warming/critical alarm, systematic shutdown of the reactor need to occur. This would involve closing the valves, flooding the jacket with cooling water.

Another possibility for an alarm, is in a composition measurement of the product containing chemical compound. As, too high a concentration could be dangerous if no other concentration-altering steps occur before the finished product goes out to consumers.

Equipment and Piping

- Material of construction is selected based on process parameter

- Equipment and piping are designed
  - For maximum operational pressure plus 10%
  - Operational temperature -5°C (for temperature below 0°C) or +30°C (for temperature above 0°C)

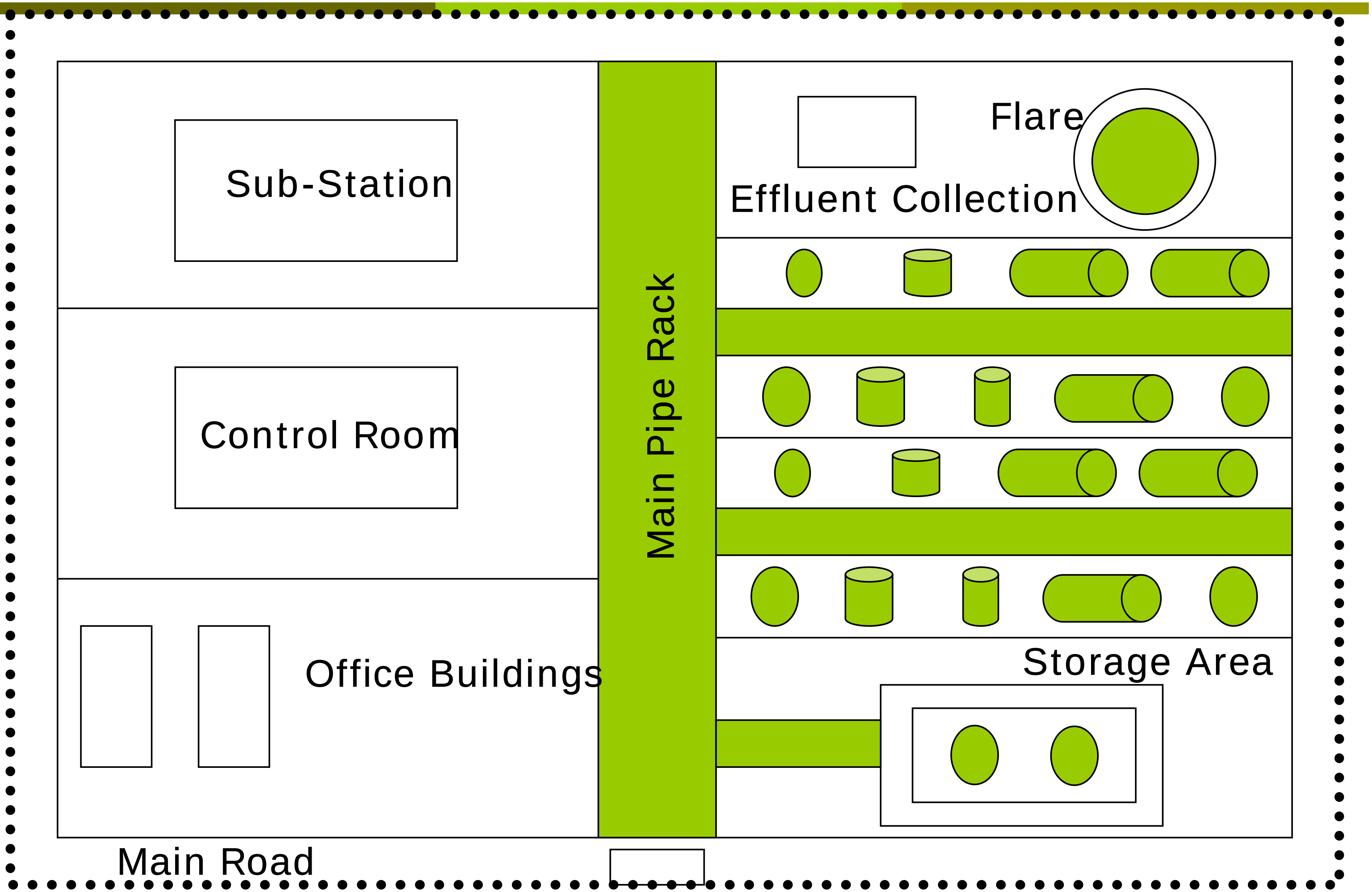
Equipment and Piping

- Engineering Materials - Types and Properties
  - Metals - Ferrous and non-ferrous
  - Carbon steel
  - Alloying elements added to iron base - carbon, manganese, and silicon
  - Impurities and their effect - sulfur, phosphorus
  - Alloy steel
  - Stainless steels
  - Corrosion resistant alloys
  - High temperature alloys

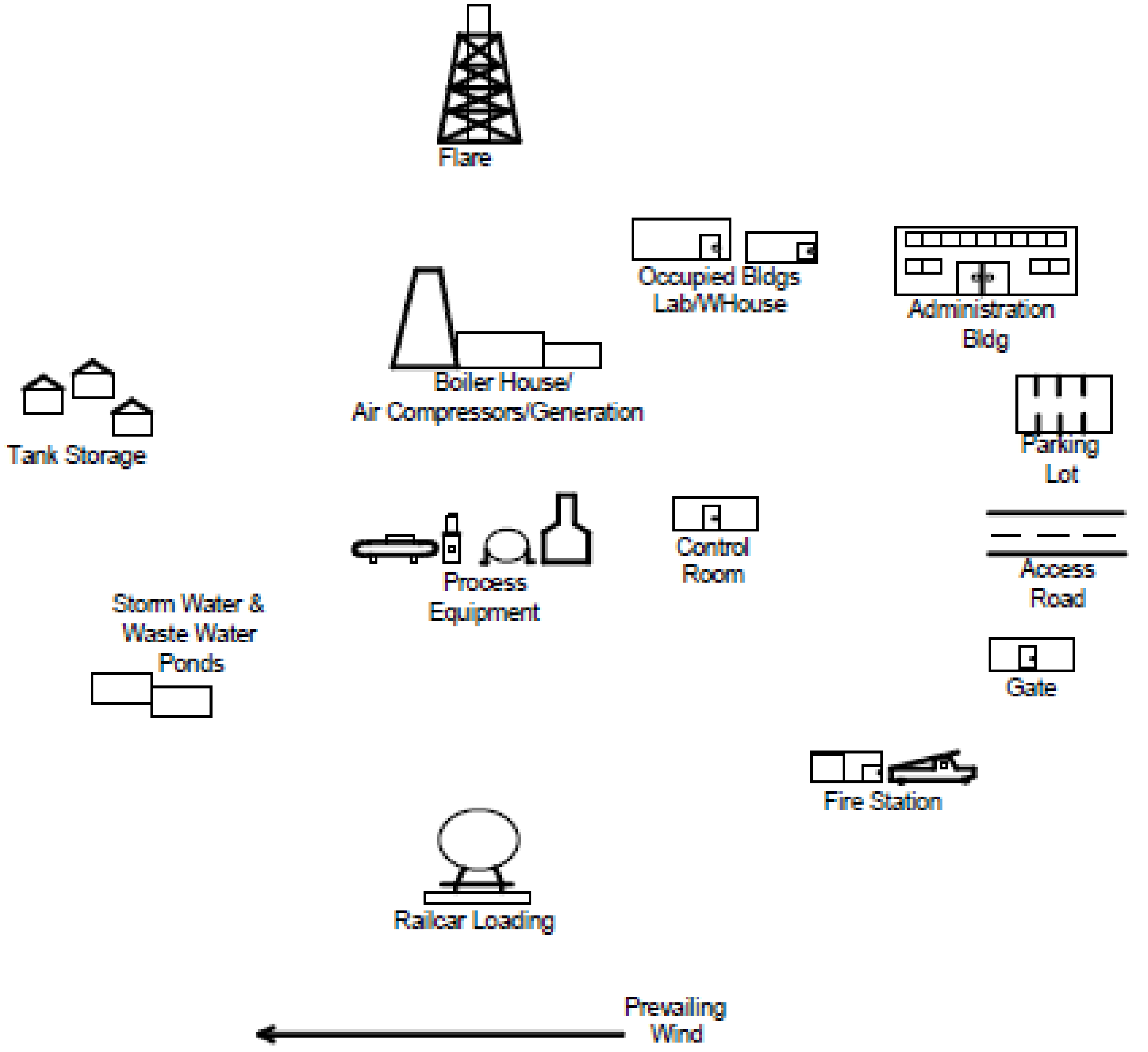
Passive protection

- First and foremost is a good layout
  - There are guidelines which specify the distance between units, buildings and roads.
- Plant is designed to
  - Minimize involvement of adjacent facility in fire
  - To permit access for fire fighting
  - Ensure emergency facility will be accessible for operators to perform emergency shutdown in event of fire or explosion
  - To segregate high risk facility or equipment from less hazardous operation and equipment.
  - To permit access to plant personnel for normal operation & maintenance of equipment.

Chemical Plant Layout



Chemical Plant Layout



Active Protection

Active fire protection

Image courtesy: Google Images

- Fire water storage and supply
- Hydrants and monitors
- Deluge system
- Foam systems
- Fire and smoke detect
- Manual call point

Fire Hydrants

Foam systems

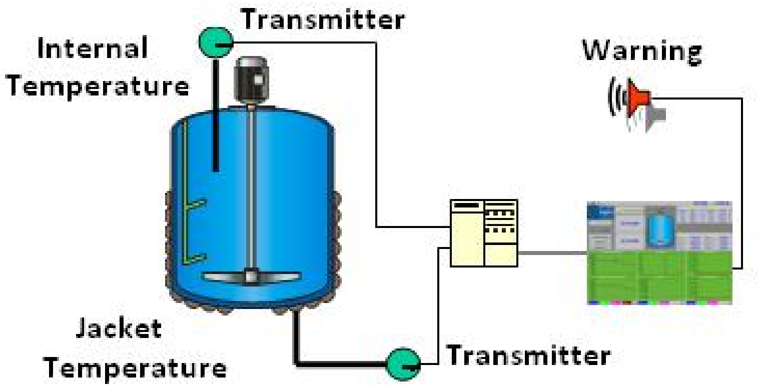
Emergency Shutdown System

- During the development of P&ID, emergency shutdown system are identified.

- Emergency Shutdown System (EDS) are segregated from normal shutdown system.
  - Heat inputs are stopped
  - Equipments are stopped
  - Depressurization done.

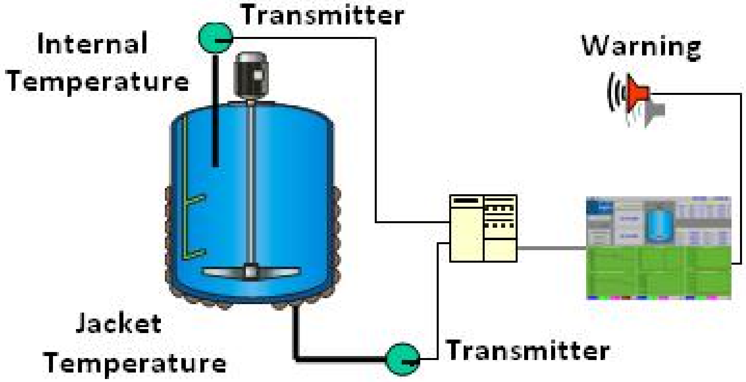
Early Warning Detection System (EWDS)

- EWDS was intended to improve the quality, safety and reliability of production operations and reduce accidents in chemical plant by developing new devise for early warning of runaway events..



Early Warning Detection System (EWDS)

- EWDS interface with the process to acquire data (monitoring); criteria to distinguish between dangerous situations and non-dangerous ones (detection); procedure for triggering off the alarms (diagnosis and evaluation).
- EWDS should allow counter measures to be taken for the runaway events, whilst protecting the environment.



Safety Integrity

- Safety Integrity = Ability of a safety function to continue to be effective in spite of deterioration of its implementation.
- Things can go wrong, so we need additional functionality
  - Safety functions to reduce the risks
- Safety functions can have varied implementation measures
    - active functionality
    - design properties
    - administrative measures
    - any combination of the above
- Safety Integrity Level (SIL) is a relative level of risk-reduction provided by a safety function.

Safety Integrity Level (SIL)

- Degree of Safety Integrity is determined by
  - number of implementation measures
  - how effective they are
  - how vulnerable they are
  - how independent they are

Safety Integrity Level (SIL)

- Many different degrees of safety integrity, grouped into 5 levels:

  SIL 0 = no safety integrity at all

  …

  …

  SIL 4 = highest possible level

- For "important" safety functions, a high SIL will be demanded

- **Safety Integrity Levels depend on Risk Acceptability**

Inherent Safety Techniques

1. Minimize
    - Change from large batch reactor to a smaller continuous reactor
    - Reduce storage inventory of raw materials
    - Improve control to reduced inventory of hazardous intermediate chemicals
    - Reduce process hold-up

Inherent Safety Techniques

2. Substitute
   - 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.

Inherent Safety Techniques

3. Moderate
   - Use vacuum to reduce boiling point
   - Reduce process temperatures and pressures
   - Refrigerate storage vessel
   - Dissolve hazardous materials in safe solvents
   - Operate at conditions where reactor runaway is not possible
   - Place control rooms away from operations
   - Barricade control rooms and tanks

Inherent Safety Techniques

4. Simplify
    - ❑ Keep piping system neat and visually easy to follow
    - ❑ Design Plant for easy & safe maintenance
    - ❑ Pick equipment with low failure rates
    - ❑ Add fire and explosion resistant barricade
    - ❑ Label vessels and controls to enhance understanding

References

- Daniel Crowl and Joseph Louvar

  “Chemical Process Safety: Fundamentals with Applications”, Prentice Hall, 2001.

- U.S Chemical Safety Board

  www.csb.gov