GREEN CHEMISTRY

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Designing Greener Processes

Design of 'greener' processes and products:

chemistry aspects
engineering aspects

- 1 Conventional Reactors
- 2 Inherently Safer Design
- 3 Process Intensification
- 4 In-process Monitoring

Conventional Reactors

- Reaction on the bench → Scale-up

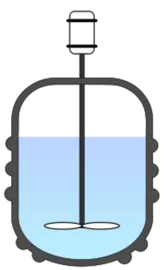
  correct choice of reactor and other plant equipment

- Chemical processes

Batch reactor: is filled with reactants in a single stirred tank at time zero and the reaction proceeds

Semi-batch reactor: allows partial filling of reactants with the flexibility of adding more as time progresses

Continuous reactor: Reactants are continuously fed into the reactor and emerge as continuous stream of product.



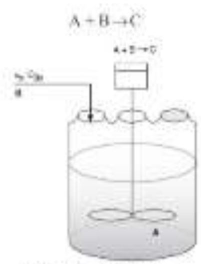
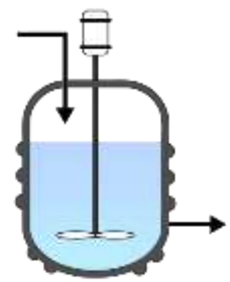


Figure 4-15 Semibatch reactor.



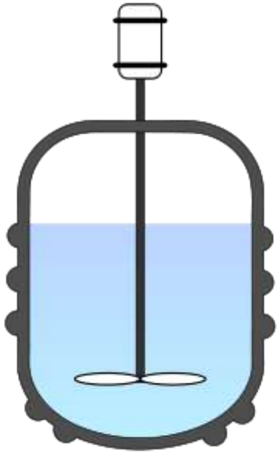
The design of an appropriate reactor system is the cornerstone of a green approach to process development.

1. minimal by-product formation and downstream processing requirements
2. optimal energy usage and costs reduction
3. minimal hazards and waste.

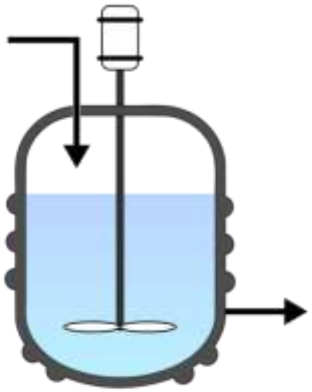
Conventional Reactors

(i) Batch Reactor: is filled with reactants in a single stirred tank at time zero and the reaction proceeds. it is mainly used in multi-purpose plants for fine chemicals and pharmaceuticals

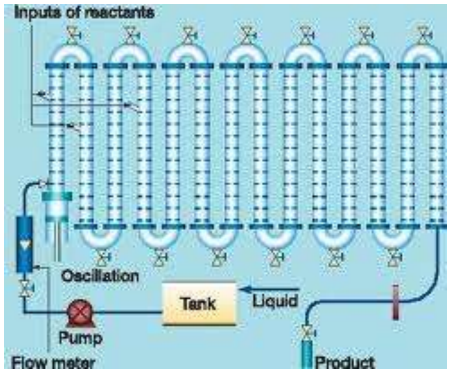
(ii) Continuous Reactor: Reactants are continuously fed into the reactor and emerge as continuous stream of product. It is used in dedicated plant for bulk chemicals



Continuous stirred tank reactor



Plug flow



Batch Reactors

Continuous Reactors

Batch Reactors

- Materials:
  - Stainless steel vessels: better heat transfer
  - Glass-lined steel vessels: superior fouling or corrosion properties
- Mixing: Internal agitator and baffles
- A variety of ports on the top of the reactor: sampling, instrumentation, reactant/product inlet/outlet and a venting line.
- The head of the reactor to a reflux condenser for additional heat removal or to a distillation column.
- At the bottom of the reactor is the drain valve, which often leads to a filter.

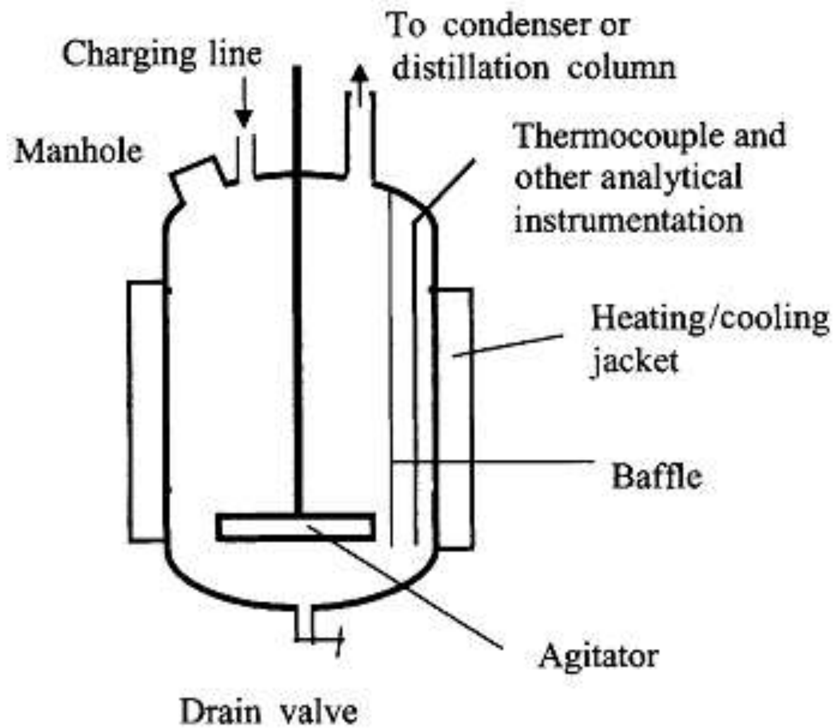


Figure 10.1 *A typical batch reactor*

Batch production is typically used for high-value added chemicals, e.g. pharmaceuticals, fine chemicals, pesticides, bio-products, foods, polymers etc.

Heat and mass transfer of batch Reactors

- Batch reactors are not just large versions of laboratory equipment laboratory: differences in heat transfer and mass transfer.
- Problems with mass transfer: the delay and subsequent generation of large and dangerous exothermic reactions.

The laboratory reaction rate can be monitored by varying agitator speed

The reaction rate is independent of speed.

- Problems with heat transfer: the safety and efficiency of a process, the economics.

$$Q = U \times A \times \Delta T$$

Q: the amount of heat transferred (W)

U: the heat-transfer coefficient ($W \cdot m^{-2} \cdot ℃^{-1}$)

A: the heat-transfer area (m^2)

ΔT: the temperature difference between the reactants and the heating or cooling medium

Heat and mass transfer of batch Reactors

- The heat-transfer area: surface area / volume

	volume	external surface area	
a laboratory flask	1 L=0.001 m^3	around 0.05m^2	50
a commercial reactor	10000 L=10 m^3	around 20 m^2	2

- The commercial reactor need prolonged heating or cooling periods, and will be slow to respond to external temperature changes (thermal lag).
- The adverse effects:

Probably reducing the yield and selectivity, and making purification more difficult, thus leading to more waste, increased energy usage and higher costs.

More by-products by further reaction of the product.

- Additional solvent can be used as a heat sink to control the temperature of exothermic processes in batch reactors, which cannot be recommended to the green chemist.

Scale-up problems met from lab bench to batch reactor

"Got a few problems going from lab scale up to full-scale commercial."

- heat transfer
- poor mass transfer

(i) resulting in the delay and subsequent generation of large and dangerous exothermic reactions.

(ii) allowing relatively high concentrations to build up which then start to react rapidly.

(iii) resulting in excessive hydrolysis when neutralizing agents were used.

Heat transfer of batch Reactors

$$Q = U \times A \times \Delta T$$

- Methods to improve the heat-transfer rate:
- To increase the temperature differential by using higher-pressure steam or a hot oil supply. (adverse effects: fouling and unwanted reactions)
- To increase the heat exchange area by the heating/cooling coils inside the reactor. (additional advantages: increasing the turbulence in the reactor; adverse effects: difficult cleaning and ‘dead spots’ or localized areas of poor mixing)

Buss loop reactor

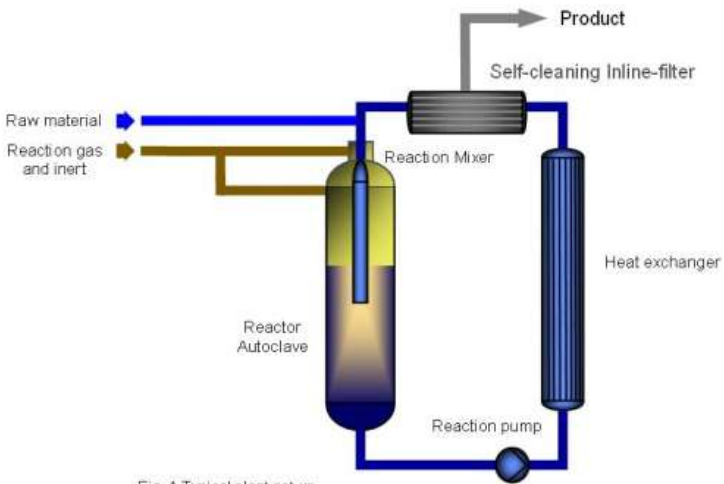
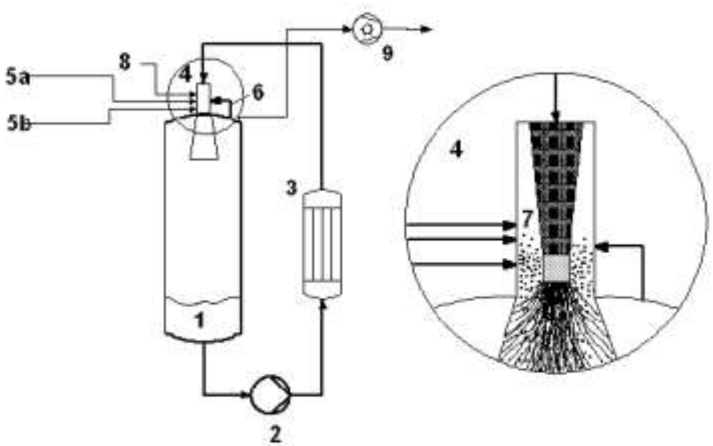


Fig. 1 Typical plant set-up



- A high performance gas/liquid ejector to achieve high mass transfer rates.
- An external heat exchanger with high surface area.
- The heat exchanger consists of many small diameter tubes or plates through which the heat-transfer medium flows, the tubes being often much thinner than the reactor walls, providing improved temperature response times.
- Separate mechanical stirring is not required in these reactors, adequate mixing being obtained by circulation through the heat.
- Such reactors are frequently used for hydrogenation oxidation, phosgenation, alkoxylation, amination processes.

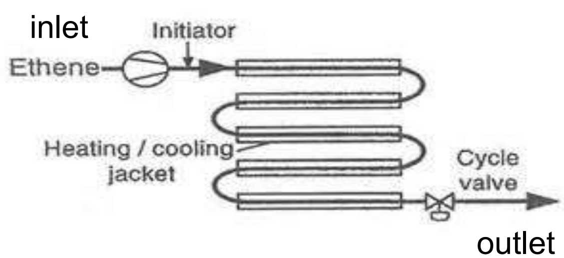
Batch reactors

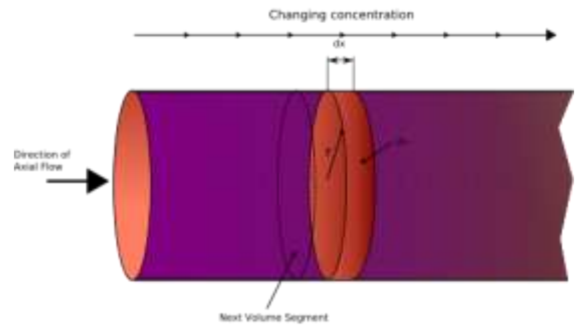
- An important advantage of a batch reactor is traceability. The product from a particular batch will have a uniform consistency, and can be uniquely labeled and readily traced.
- Batch reactors are, however, rarely the most efficient in terms of throughput and energy use when the reaction kinetics is fast.
- In contrast, the product from a continuous process may change gradually over time, and it is therefore more difficult to trace a particular impurity or fault in the material.

Continuous Reactors

Two categories of continuous reactors:

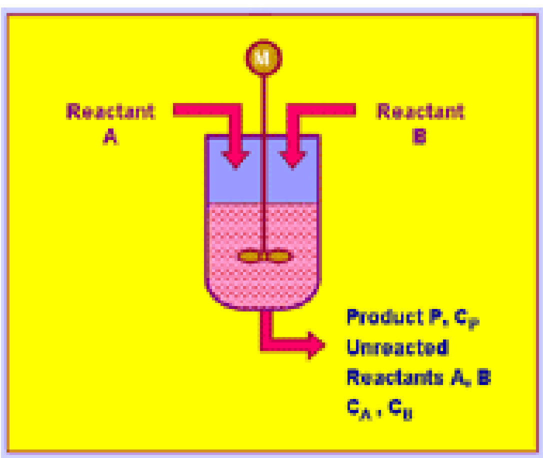
- Plug flow: tube-in-tube and fixed-bed reactors

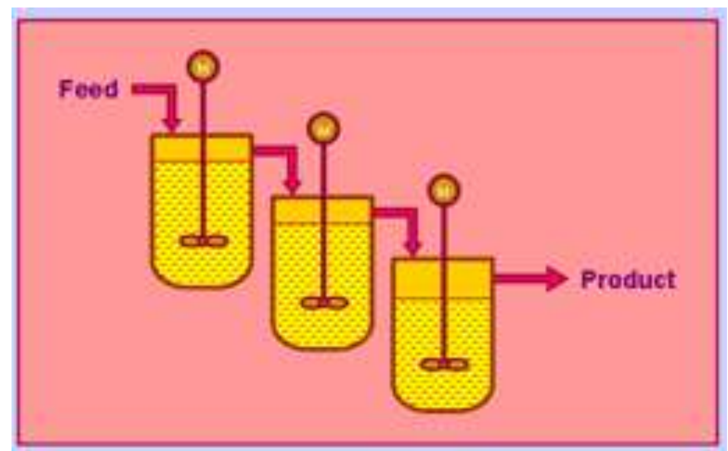




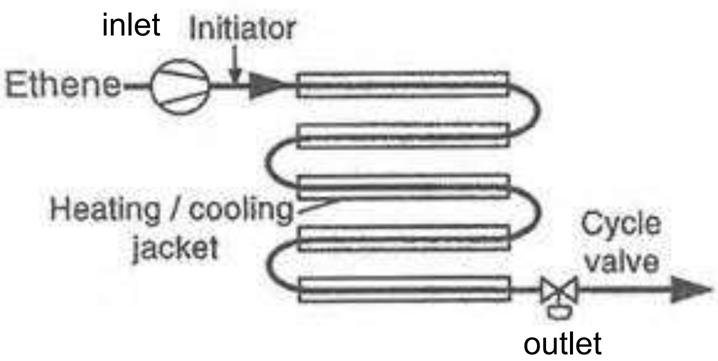
The composition of the reaction mixture changes along the length of reactor.

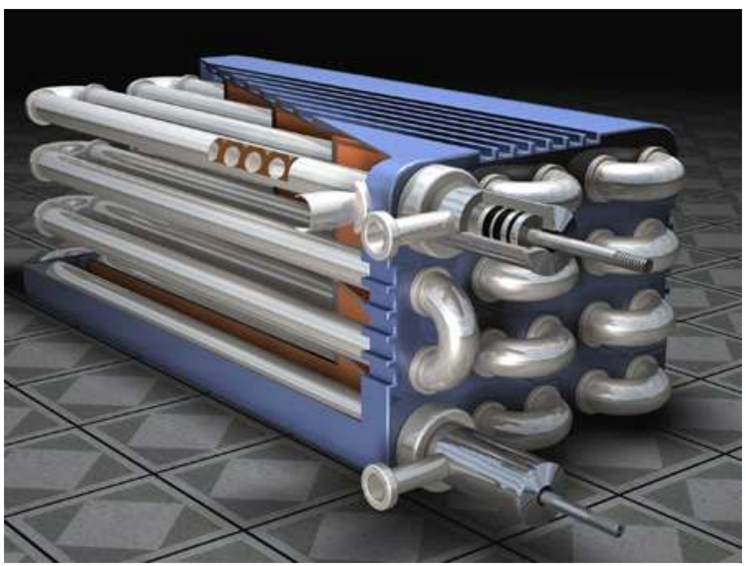
- Mixed flow: a Continuous Stirred Tank Reactor (CSTRs)





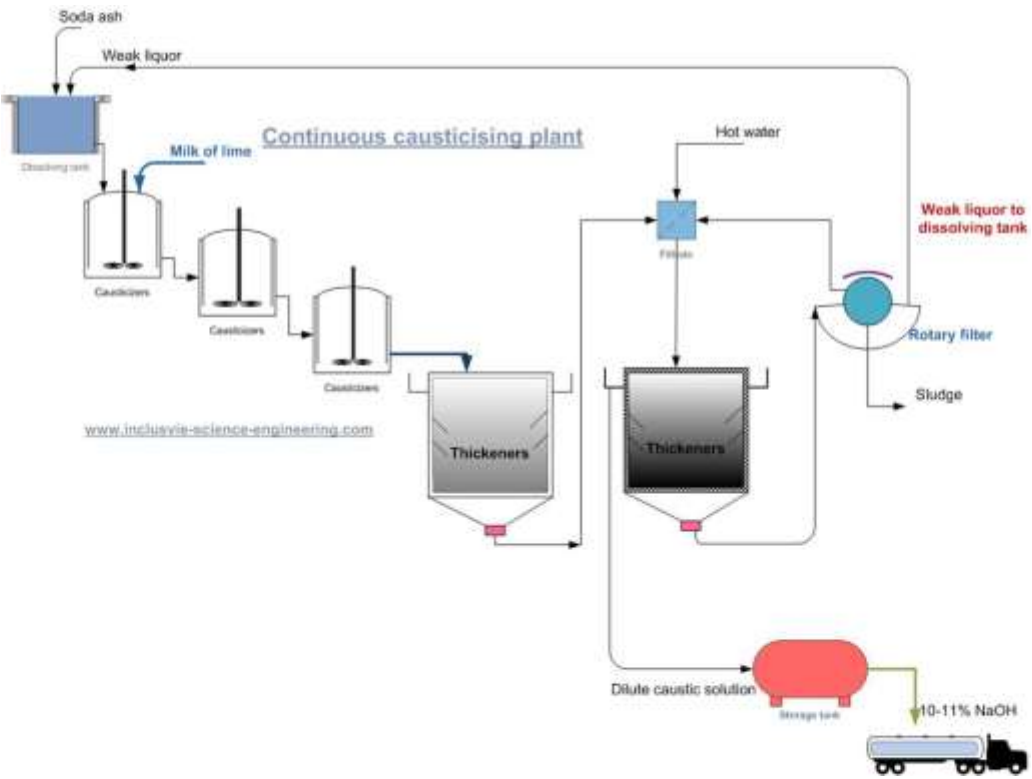
Plug Flow Reactors





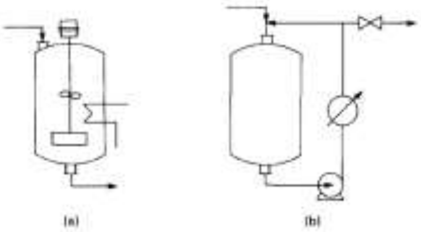
- **Advantages**
- Easily maintained since there are no moving parts.
- High conversion rate per reactor volume.
- Mechanically simple.
- Unvarying product quality.
- Good for studying rapid reactions.
- Efficient use of reactor volume.
- Good for large capacity processes.
- Low pressure drops.
- Tubes are easy to clean.
- **Disadvantages**
- Reactor temperature difficult to control.
- Hot spots may occur within reactor when used for exothermic reactions.
- Difficult to control due to temperature and composition variations.

Continuous Reactors



- The greater the number of CSTRs in series, the closer the overall behavior will be to a plug flow reactor.
- Safety advantages in terms of relatively low individual reactor inventory may be important as may the faster heat-transfer rates associated with smaller reactors.
- Flexibility is another great advantage, for example additional reagents which would react adversely with one starting material can be added further downstream.

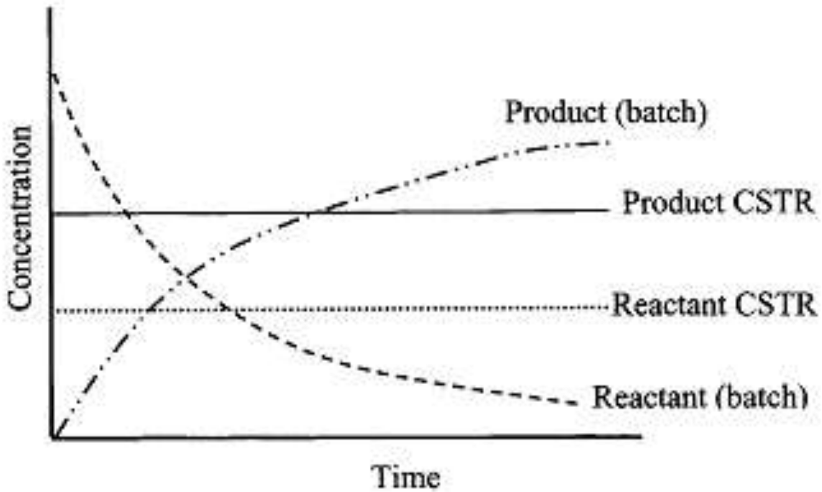
Continuous Stirred Tank Reactors (CSTRs)



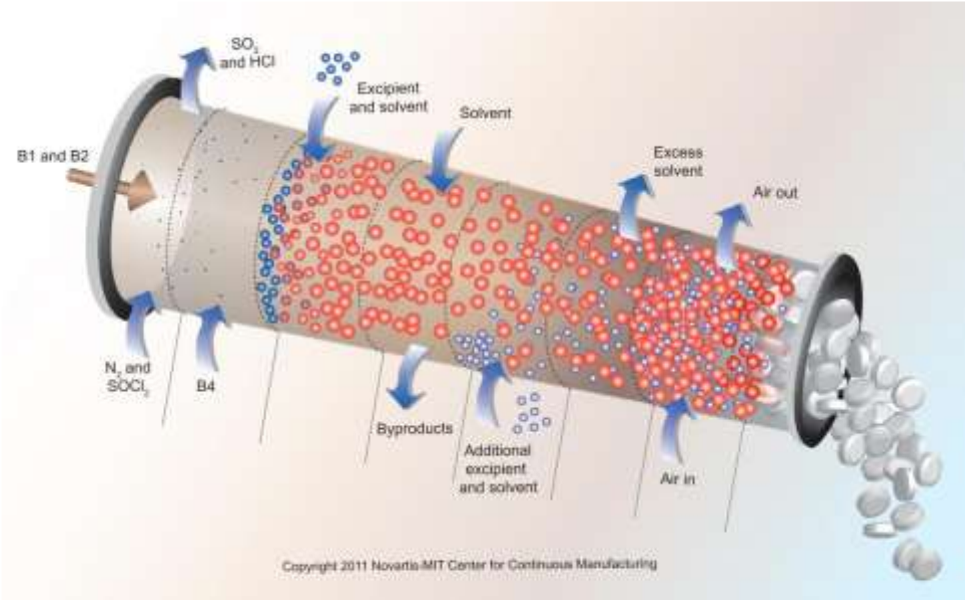
- The physical similarities of CSTRs and batch reactors:
  - large stainless steel vessels with an agitator, possibly baffles
  - a jacket or internal coils for heating and cooling.
- The differences: a constant in and out flow of materials, the constant concentrations of all the components and the constant reaction conditions for the CSTR.

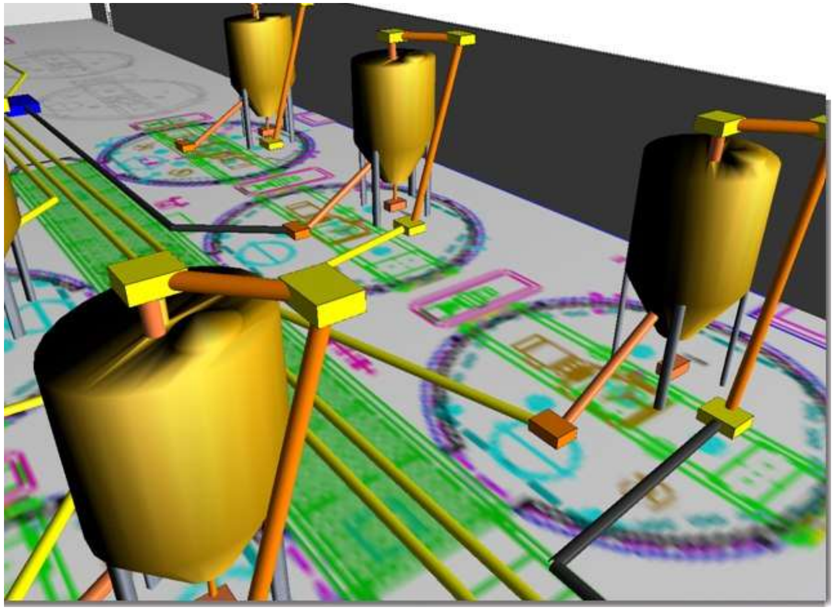
Minimization of by-product.
Significant starting materials to separate from product for recycle.

- CSTRs in series:
  - more costly.
  - Safety.
  - Flexibility.



Reaction profile of batch and CSTR reactors





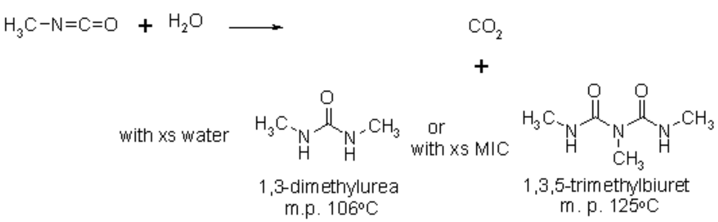
- **Continuous production** is a flow production method used to manufacture, produce, or process materials without interruption.

- Continuous production is used in oil refining, fine chemicals, synthetic fibers, fertilizers, pulp and paper, power stations, natural gas processing, sanitary waste water treatment.

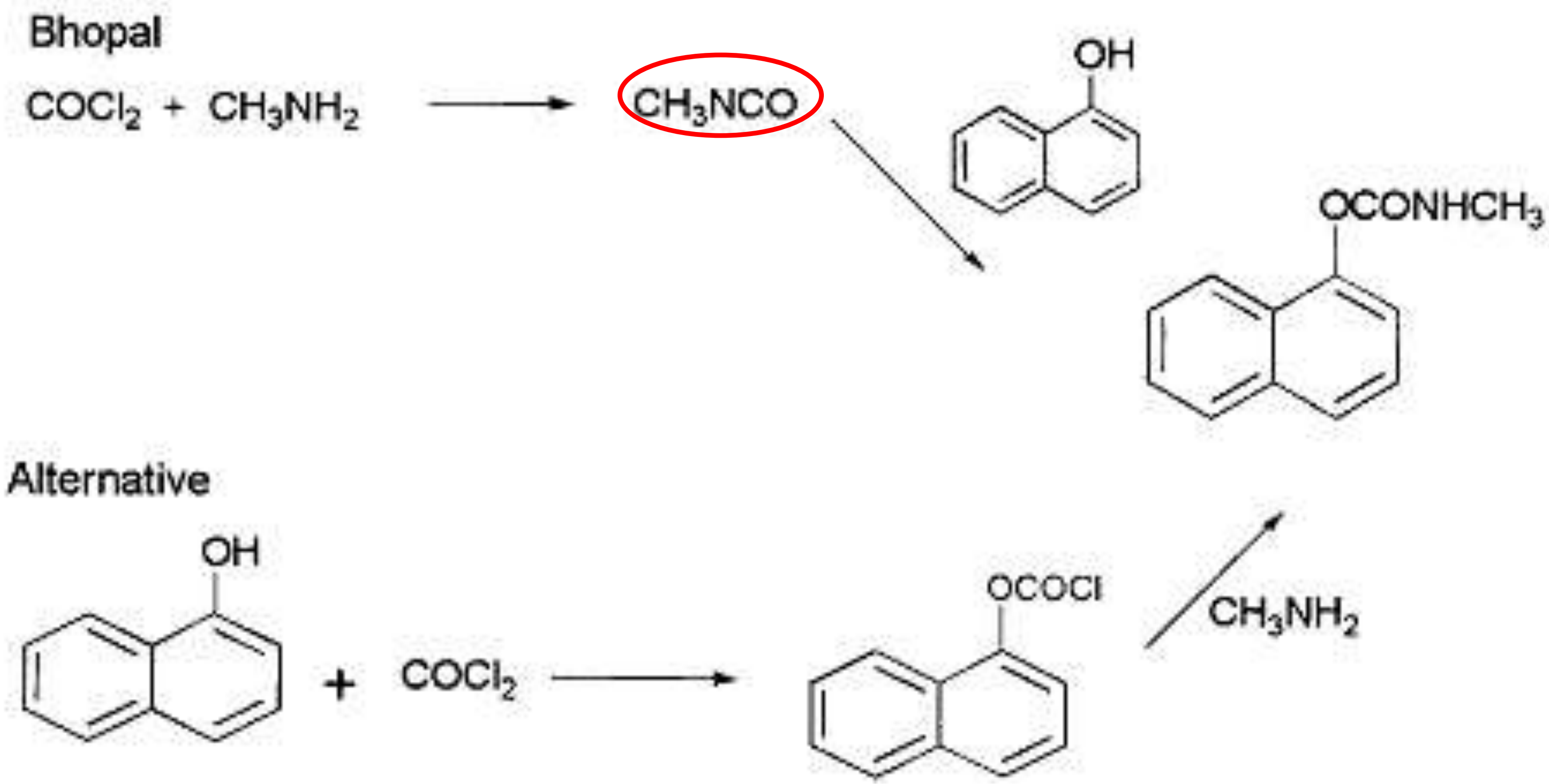
Inherently Safer Design

- The concept of inherently safer design arose as a consequence of the incident at Bhopal.
- Over 60% of all accidents at chemical manufacturing plants are caused by either mechanical failure or operational error.

As a highly toxic and irritating material, methylisocyanate is extremely hazardous to human health. It was the principal toxicant involved in the Bhopal disaster, which killed nearly 3787 people initially and officially 19787 people in total.



At 25 ^{o}C, in excess water, half of the MIC is consumed in 9 min, if the heat is not efficiently removed from the mixture, the rate of the reaction will increase and rapidly cause the MIC to boil.



- Do we need to use phosgene? Yes
- Do we need to use MIC ? No
- Do we need to store MIC or phosgene? No

Methylamine
phosgene
methylisocyanate
α-naphthol
carbamate

Inherently Safer Design

How to prevent hazardous occurrences in designing chemical plants?

- By mechanical safety devices and documented procedures?
- Or by Inherently Safer Design ? 'What you don't have can't harm you.'

storage

- Minimization: use small quantities of hazardous substances or energy

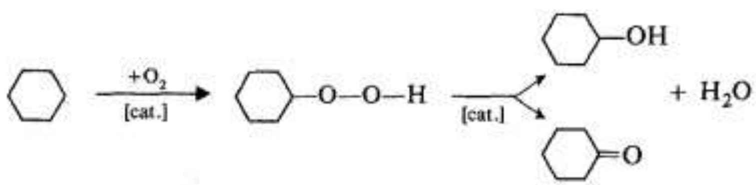
Intermediate storage

- Simplification: eliminating problems by design rather than adding additional equipment or features to deal with them
- Substitution: replacing one material with another of less hazard, e.g. cleaning with water and detergent rather than a flammable solvent
- Moderation: using material in a dilute rather than concentrated form
- Limitation: minimizing the effects of failure (of equipment or people) or an incident, by design.

Minimization

- Minimization of hazardous material inventories, ‘just in time’ production.
- No storage: hazardous materials such as phosgene and hydrogen cyanide through the development of small portable generators.
- Slow reaction rates→large reactor volumes $\begin{cases} \text{an inherently slow rate} \\ \text{poor heat and mass transfer.} \end{cases}$
- Reduction of reactor size: through radical reactor design whilst throughput is maintained→Process Intensification
- The Flixborough disaster in 1974

- The oxidation of cyclohexane with air using a boric acid catalyst.
- Slow formation of the intermediate hydroperoxide owing to poor mixing of air and hydrocarbon.
- Reaction conversion was limited to under 10% per pass.
- Six reactors in series and high hydrocarbon inventories.



$$\left(\Delta H = -\frac{70\ \text{kcal}}{294\ \text{kJ}}/\text{mol}\right)$$

- Large reactor volumes are often employed because of slow reaction rates. Essentially there are two causes of this, either an inherently slow rate or, more commonly, poor heat and mass transfer.
- By minimizing inventories of hazardous material, for example through 'just in time' production the consequences of any accident will inevitably be reduced.

Simplification

- A simplified plant with less mechanical equipment and fewer joints
- Addition of further safety devices and frequent modification→complex plants.
- Simplification by a detailed safety study early in the design process

Some possible examples of over-complexity include:

Running long lengths of pipe with many flanges.

Using solvent as a heat sink in a batch reaction.

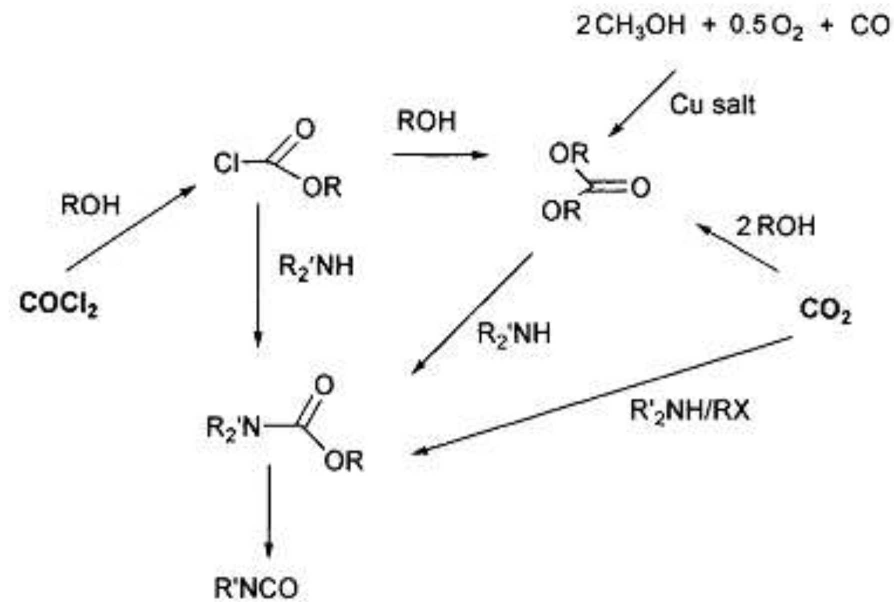
Installing an excess of analytical equipment and sample ports.

Substitution

- The substitution of hazardous materials by more benign ones is a core principle of green chemistry, and a key feature in Inherently Safer Design.

  - a flammable solvent → a non-flammable one
  - a harmful material → a safer one, phosgene →carbon dioxide

Approximately 8 million tpa of phosgene are used in the synthesis of isocyanates, urethanes and carbonates.



Scheme 10.2 *Replacement of phosgene by CO_2*

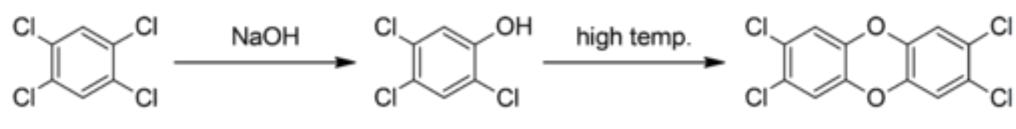
10.2.4 Moderation

- By using the hazardous material in a less hazardous form or under less hazardous conditions.
- *e.g.*

  - Hydrogen→Powerball in fuel cells. (The sodium comes in the form of metal pellets, 1.3 inches in diameter, wrapped in plastic. A tanker truck could carry 24 tons of sodium powerballs, enough to generate 2,100 pounds of hydrogen.
  - Chlorine stored in pressurized containers→ refrigerated at atmospheric pressure.
  - Chlorine→sodium hypochlorite to disinfect swimming pools.

10.2.5 Limitation

- Limitation is the process of minimizing the effects of failure (of equipment or people) or an incident, by design.
- One important aspect of the design process should be to limit the available energy to an appropriate level.
- The Seveso accident in Italy:



1 2 3

1,2,4,5-tetrachlorobenzene

2,4,5-trichlorophenol

2,3,7,8-tetrachlorodibenzo-p-dioxin

10.3 Process Intensification

- Process intensification '*Technologies and strategies that enable the physical sizes of conventional process engineering unit operations to be significantly reduced.*'

Improving mass-transfer rates to match that of the reaction.
Improving heat-transfer rates to match the exothermicity of a reaction.
Having an appropriate residence time for the reaction.

Process Intensification

- Originally, process intensification is devised as a cost reduction concept, such as reactors, distillation columns, pipework, instrumentation, labour and engineering charges, *etc.*

- As a result of the development of novel smaller reactors and ancillary equipment, process intensification is now recognized as a way of providing safety improvements, greater throughput and improved product quality through better control by using novel pieces of key equipment.

Process Intensification

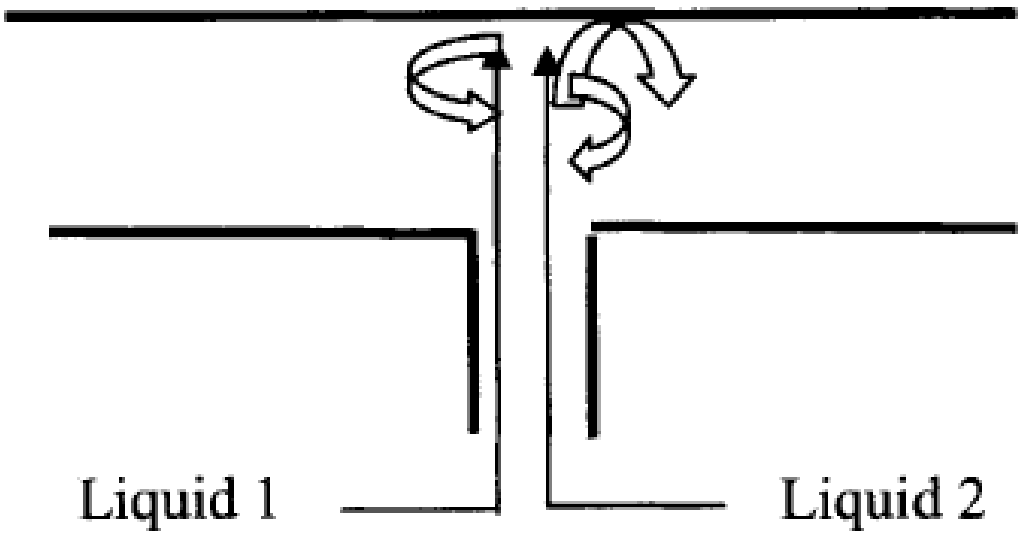
Table 10.1 *Scope of process intensification*

PI	Equipment	Reaction	Examples: Spinning disc reactor, Supercritical fluids reactor, Static mixer reactor, Static mixing catalysts operation, Monolithic reactors, Microreactors, Heat exchange reactors, Supersonic gas/liquid reactor, Jet-impingement reactor, Rotating packed-bed reactor
		Non-reaction	Examples: Static mixers, Compact heat exchangers, Rotor/stator mixers, Rotating packed-bed, Centrifugal absorber, Microchannel heat exchangers
	Methods	Multi-functional reactors	Examples: Reverse-flow reactors, Reactive distillation, Reactive extraction, Reactive crystallization, Chromatographic reactors, Periodic separating reactors, Membrane reactors, Reactive extrusion, Reactive comminution, Fuel cells
		Hybrid separations	Examples: Membrane absorption, Membrane distillation, Adsorptive distillation
		Alternative energy sources	Examples: Centrifugal fields, Ultrasound, Solar energy, Microwaves, Electric fields, Plasma technology
		Other methods	Examples: Dynamic

Example of some process intensification

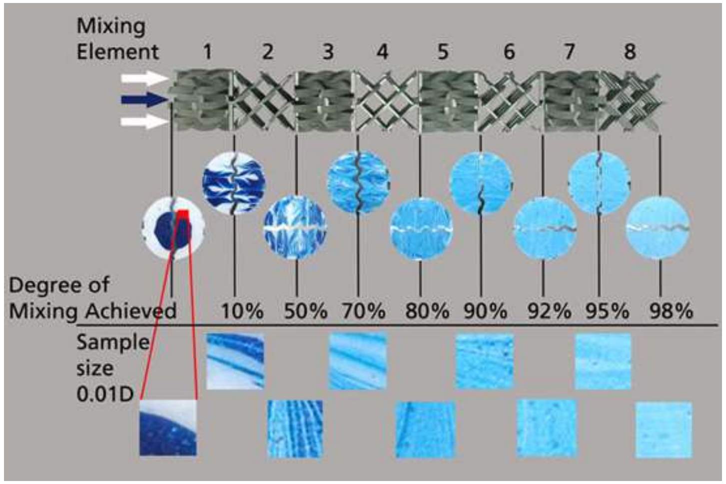
- Ensuring the efficient mixing of viscous or non-miscible liquids or of gases and liquids is a common problem which, if not solved, can lead to mass-transfer-limited reactions.
- Traditionally, mechanical mixers, as well as sometimes being inefficient, are prone to breakdown and the sealing arrangements on pressurized reactors can be complex and prone to leaking.

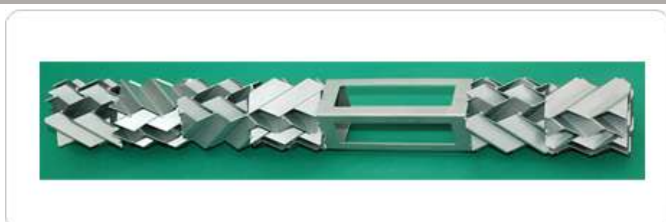
The radial jet mixer



- The radial jet mixer, is perhaps the simplest device for efficient liquid-liquid mixing; when the liquid mixture hits the opposite tube wall, fluid-flow patterns are established which cause rapid mixing.
- This is a particularly good method of mixing in a tubular reactor with multiple injection points.

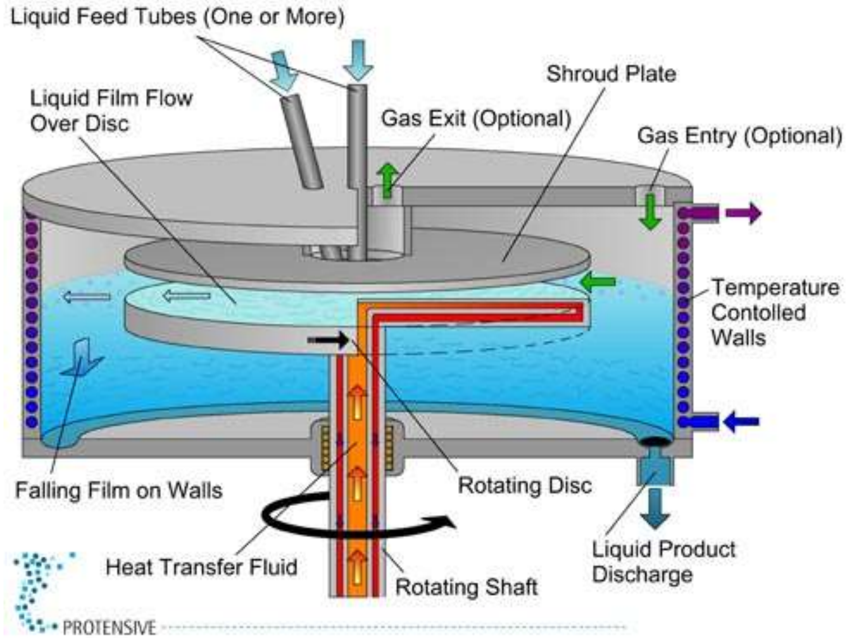
Sulzer mixer

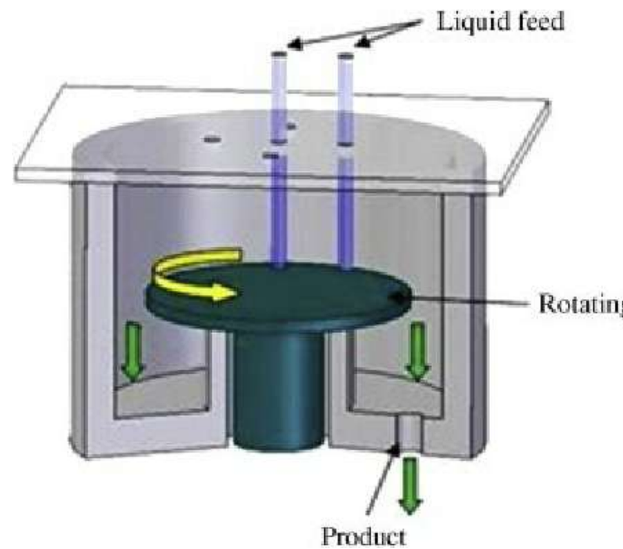




- Another type of static mixer frequently used is one containing structured packing, often referred to as a **Sulzer mixer**.
- There are several different arrangements of **structured packing** available;
- Simply the mixers can be viewed as a column packed with a **high-surface-area, honeycomb-like, structure** that **disrupts liquid flow.**
- In certain systems these can be prone to **fouling**, and may therefore be unsuitable. In other systems the **honeycomb surface** can be impregnated with a **catalyst** to produce a small **efficient catalytic reactor**.

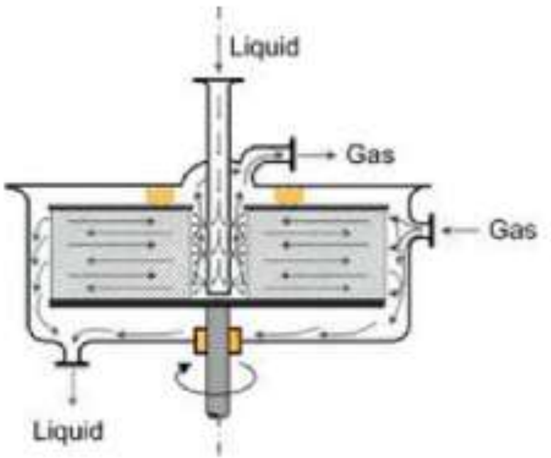
spinning disc reactor





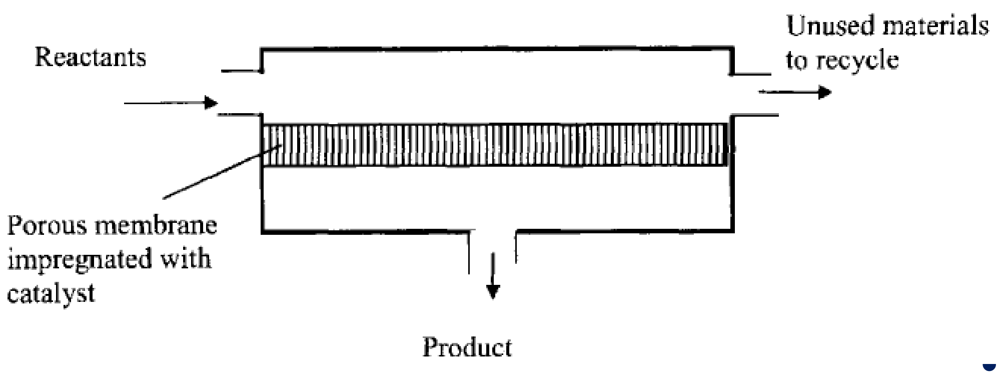
- Spinning disc reactors consists of a disc rotating at speeds up to 5000 rpm or more, developed at Newcastle University.
- The disc may be smooth or contain ridges to aid mixing; acting as a source of heat or have a catalytic surface.
- The reactant liquids are pumped onto the center of the disc, the resulting flow patterns causing intense mixing as the liquids move towards the edge of the disc.
- Because the liquid forms a thin film on the disc surface, heat transfer is rapid, which, together with the intense mixing, overcomes any heat- and mass-transfer limitations, allowing the reaction to run under kinetic control.

Rotating packed bed reactor



- Another form of related reactor is the **rotating packed bed**, which can generated high centrifugal force in rotation.
- This reactor consists of a rotating bed containing packing, often metal gauze, but structured packing similar to those used in static mixers can be employed.
- These reactors are particularly efficient at gas-liquid mixing, the liquid being fed to the center of the reactor and the gas coming in from the side.
- Although rotating packed beds provide exceptionally good mass transfer; heat transfer is not as efficient as in the spinning disc reactor.

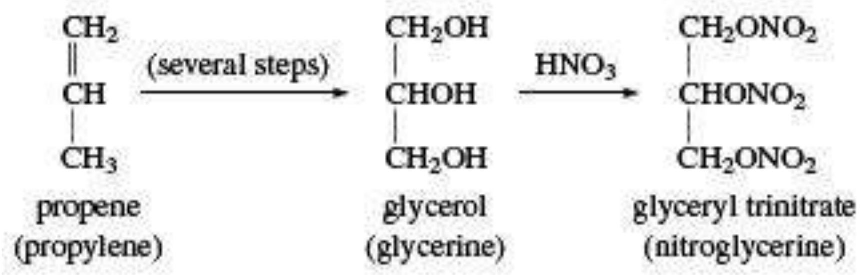
catalytic membrane reactor

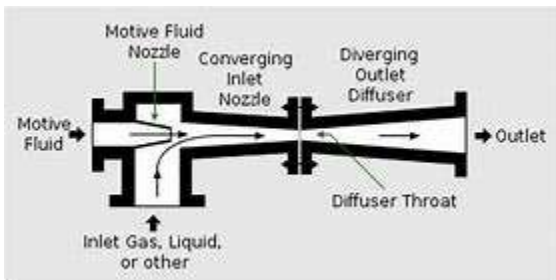


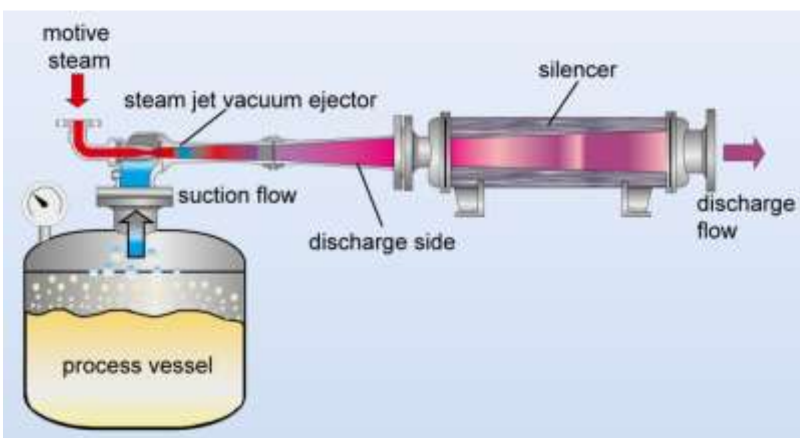
A wide variety of inorganic membranes are now commercially available, many being designed for fuel-cell applications, such as alumina, zirconium oxide, thorium oxide, silicon carbide, glass and even stainless steel.

- Catalytic membrane reactors are now being developed in which the reaction and separation are carried out in a single process, greatly intensifying the process.
- Since reaction and separation are being carried out together, membrane reactors offer potential for improved yield, selectivity and increased overall rate due to the driving of equilibrium reactions through product removal.
- This often has the additional advantage of preventing by-product formation from further reaction of the product.

Examples of intensified processes



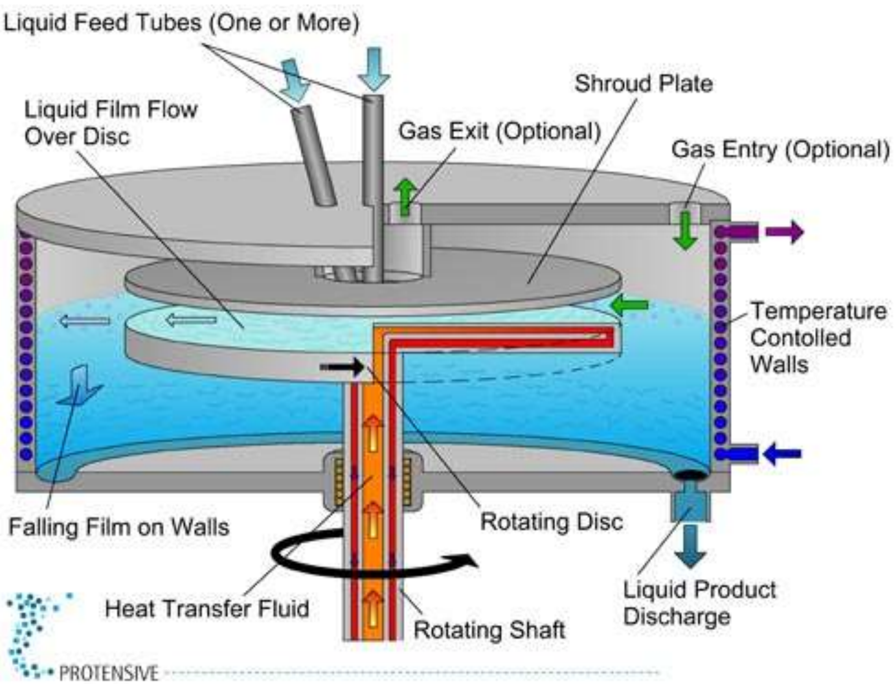




- The reaction, originally carried out in large stirred batch reactors, involves the nitration of propylene glycol with a mixture of concentrated nitric and sulfuric acid, and is highly exothermic.
- If the heat is not removed quickly enough, the nitroglycerine can decompose explosively.
- The reaction was slow because mixing was poor.
- There were by now many ways in which mixing could be improved; the method developed in the 1950s involved having a rapid flow of acid into a small reactor. This created a partial vacuum which sucked glycerine into the acid stream, ensuring good mixing.

Examples of intensified processes

$$x\mathrm{HO(CH_2)}_n\mathrm{OH} + x\mathrm{HO_2C(CH_2)}_m\mathrm{CO_2H} \rightarrow$$
$$-[\mathrm{O(CH_2)}_n\mathrm{OC(O)(CH_2)}_m\mathrm{C(O)}]_x- + x + 1\mathrm{H_2O}$$



- The synthesis of polyesters from a dibasic acid and a diol is normally carried out in large batch reactors, the reaction being driven by water removal.
- Typical reaction times are over 12 h owing to low water removal rates, in turn attributed to mass-transfer limitations which result from the increase in viscosity brought about by the formation of high molecular weight polyester.
- With the application of spinning disc reactor, the required degree of polymerization could be achieved, potentially reducing reactor time by several hours.

10.4 In-process Monitoring

- In-line or on-line process monitoring
- In-line analysis: no removal of the sample from the reaction vessel
- On-line analysis: does involve removing a sample, usually as a side stream

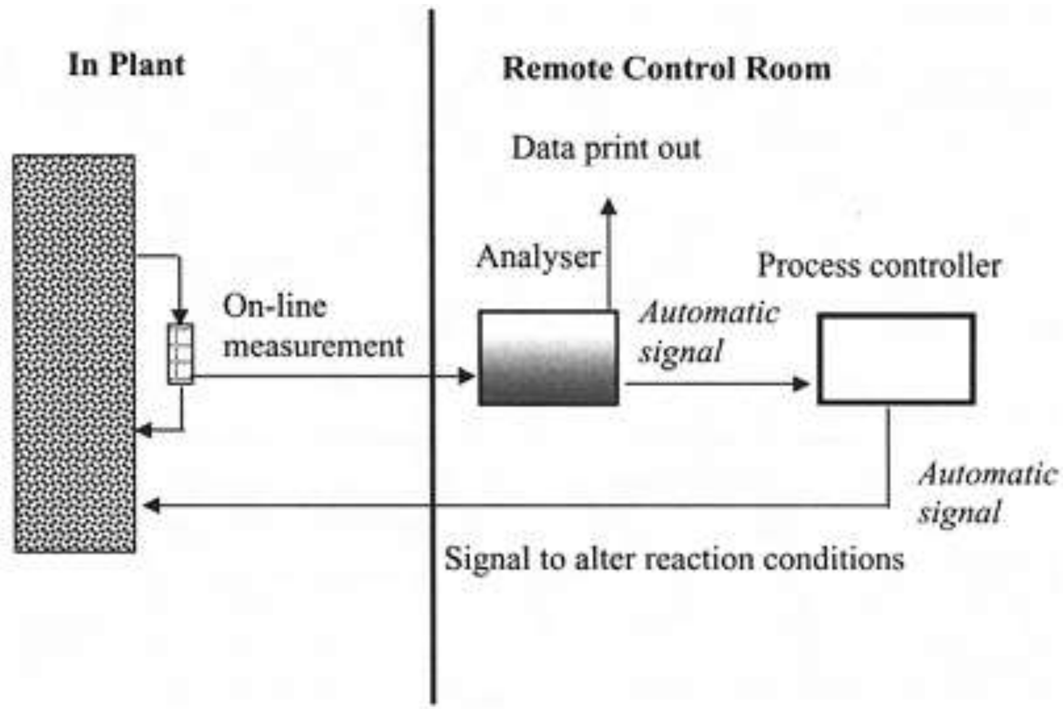


Figure 10.8 *In-process analysis concept*

In-process Monitoring

- There are four common techniques employed:
- ***Titration.*** requires physical removal of a sample from the plant.
- ***Chromatography.*** Like titration the sample is destroyed in the analysis process.
- ***Spectroscopy.*** IR, microwave, Raman and X-ray spectroscopy. real-time analysis.
- ***Sensor-based methods.*** temperature measurement, viscosity, pH, oxygen and humidity determination, *etc*. true in-line techniques and offer rapid, inexpensive real-time analysis.

Near-infrared Spectroscopy

- Electromagnetic radiation
- Transition from the ground state to the first excited state
- NIR region of the spectrum, 780-2500 nm: transitions from the ground state to the second or third excited level, O-H, C-H and N-H bonds
- NIR spectroscopy as an in-process monitoring technique
- Two important reasons: NIR signals can be transmitted over long distances through fibre optic cables, the sample path for NIR can be much larger than for IR
- A negative aspect: very sophisticated and expensive data analyzers are required to interpret the basic data and convert it into meaningful spectra.

Thank you