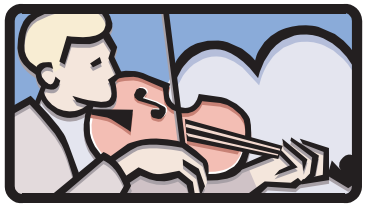
The Synthesis Step: From Ill-posed Problems to PFD



For every complicated problem, there is an answer that is short, simple and wrong

H.L. Mencken

Given: An ill-posed "word" problem

To develop a PFD which includes the following information:

- Unit operations
- Mass balances (flow rates in and out of each unit operation)
- Energy balances (heat requirements, enthalpies)
- Operating temperature and pressure of each unit operation
- Equipment size
- Equipment cost

This information is necessary for

- Feasibility analysis
- Detailed profitability analysis
- Generating P&IDs for construction

Basic Steps in Flowsheet Synthesis

- Gather information about the process chemistry
- Generate flow diagram based on Douglas Hierarchy
- Solve mass and energy balances
- Estimate equipment size based on flow rates from previous step
- Estimate equipment cost based on size from previous step
- Optimize process

Gather Information

- Patent Literature
  - US Patent Office
- Handbooks and Encyclopediae
  - Encyclopedia of Chemical Technology, Kirk and Othmer
  - Perry's Chemical Engineers' Handbook
- Online Data Bases
  - NIST Database
  - DECHMA Database

Case Study: Ethanol Synthesis

Main Reaction:

$$CH_2 = CH_2 + H_2O \rightarrow CH_3CH_2OH$$

5-7 % conversion

Other reactions:

$$2CH_3CH_2OH \leftrightharpoons C_2H_5 - O - C_2H_5 + H_2O$$

Equilibrium reaction

$$C_3H_6 + H_2O \rightarrow CH_3CH_2CH_2OH$$

0.5-0.7 % conversion

Trace amounts of croton aldehyde are formed.

Available process

- High temperature $(535K - 575K)$
- High pressure $(68\ atm)$
- Homogeneous, noncatalytic reactor

Coking considerations: Chemistry department advises that mole fraction of methane in the reactor feed should be less than 10% to prevent coking.

Equilibrium considerations: Excess water will push the equilibrium towards ethanol.

Physical Properties:

- At $1\ atm$, methane, ethylene and propylene boil at very low temperatures.
- It is not possible to condense methane and ethylene at room temperature.
- Propylene has a vapor pressure of $15\ atm$ at $310K$.
  $=>$ expensive distillation

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Generate Flow Diagram

The Douglas Hierarchy is a formal procedure for developing flow sheets and consists of the following steps:

- Step 1: Batch vs. Continuous Process
- Step 2: Input-Output Structure of the Process
- Step 3: Recycle Structure of the Process
- Step 4: General Structure of Separation System
- Step 5: Heat Exchanger Network or Process Energy Recovery System

This procedure works for a large number of chemical, bio-chemical, environmental, and materials processes.

Step 1: Batch vs. Continuous Process

When is batch process preferred?

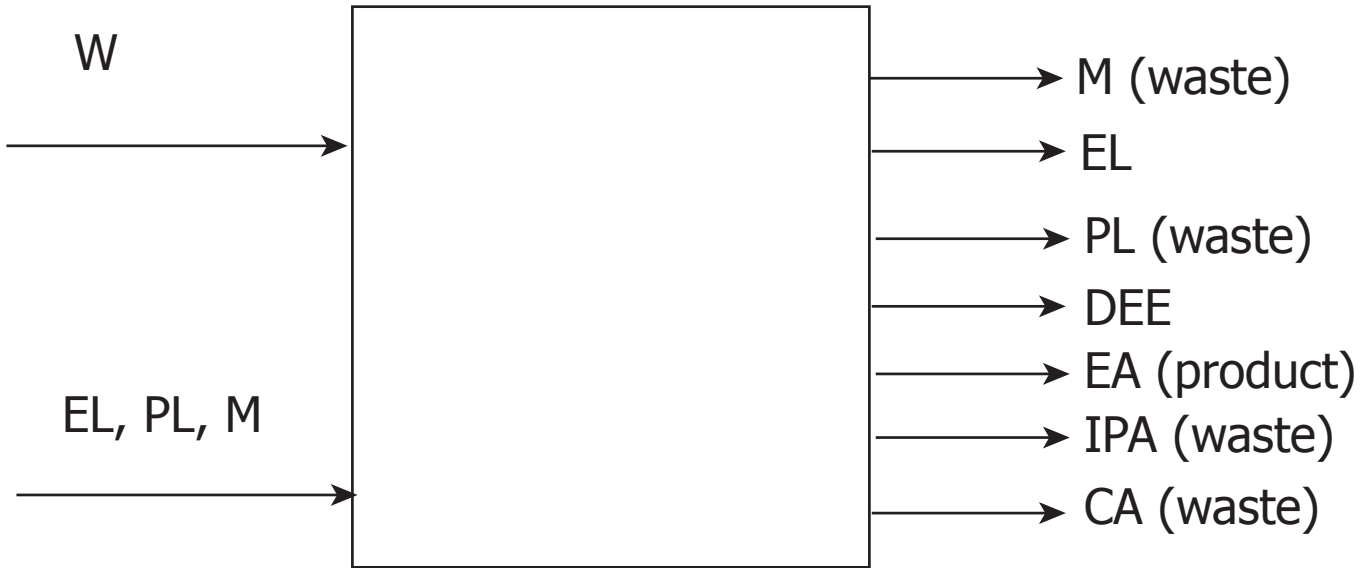
- Small quantity ($< 500\ tonnes/yr$), high quality, highly regulated
- New product, safety, sterility considerations
- Hard to handle chemicals and processes
- Large variation in feed, product and operating conditions

When is continuous process preferred?

- Large quantity ($> 500\ tonnes/yr$)
- Well defined process
- Small variation in feed, product and operating conditions

Step 2: Input-Output Structure

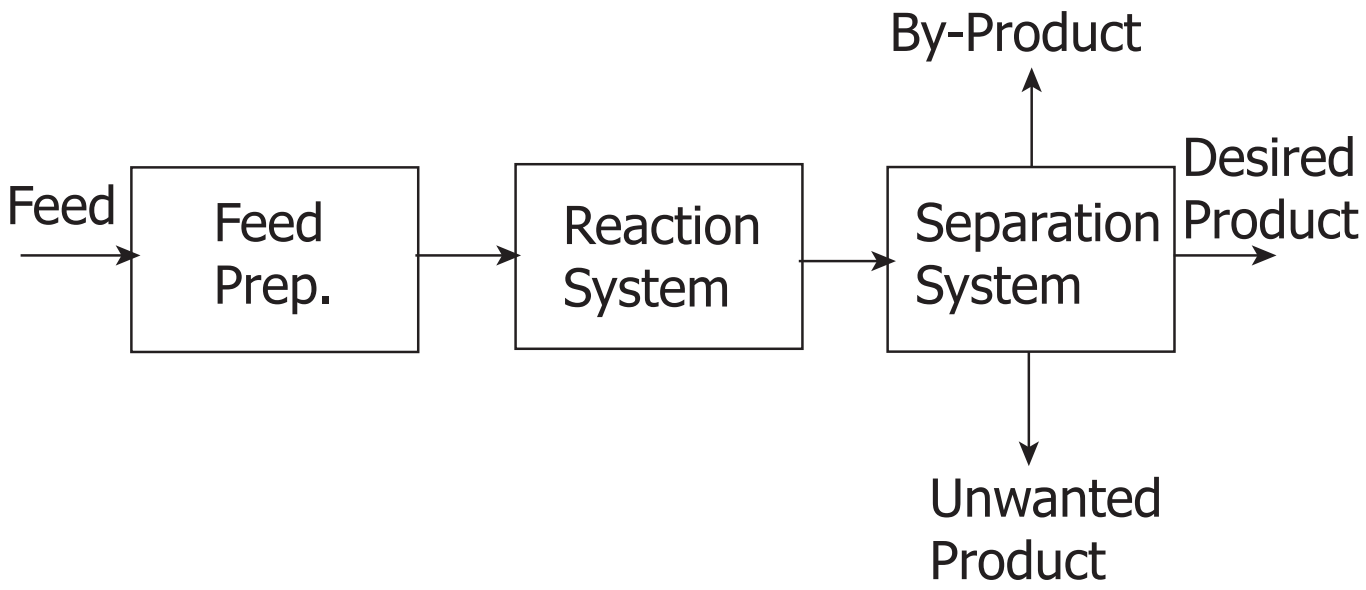
Process Concept Diagram

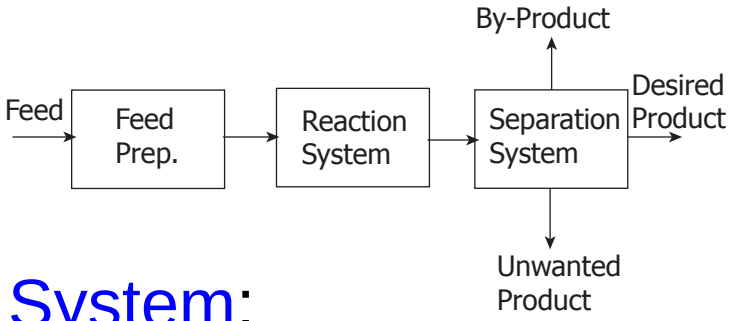


- Basic economic analysis on profit margin.
- What chemical components enter as feed and leave as product.
- All reactions, desired and undesired.

Generic Block Flow Diagram

A vast majority of processes can be represented by this generic BFD





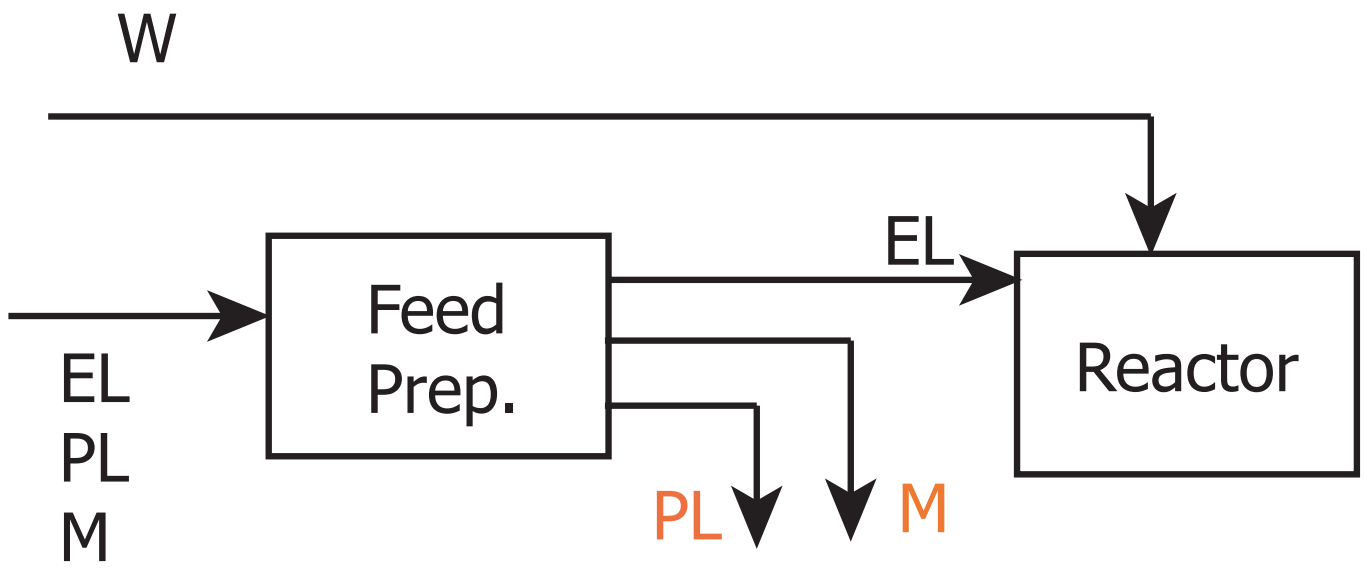
Feed Preparation System:

This system is required to adjust T, P, and composition in preparation for the reactor.

- If impurities are less than 10-20%, and these impurities do not react to form by-products, do not purify the feed.
- If separation of feed impurities is difficult (e.g. azeotropes are formed), do not purify the feed.
- If impurities foul the reactor catalyst or form hard-to-separate unwanted products, purify the feed.
- Add inert material to feed to control exothermic rxn.
- Add inert material to feed for favorable equilibrium rxn.

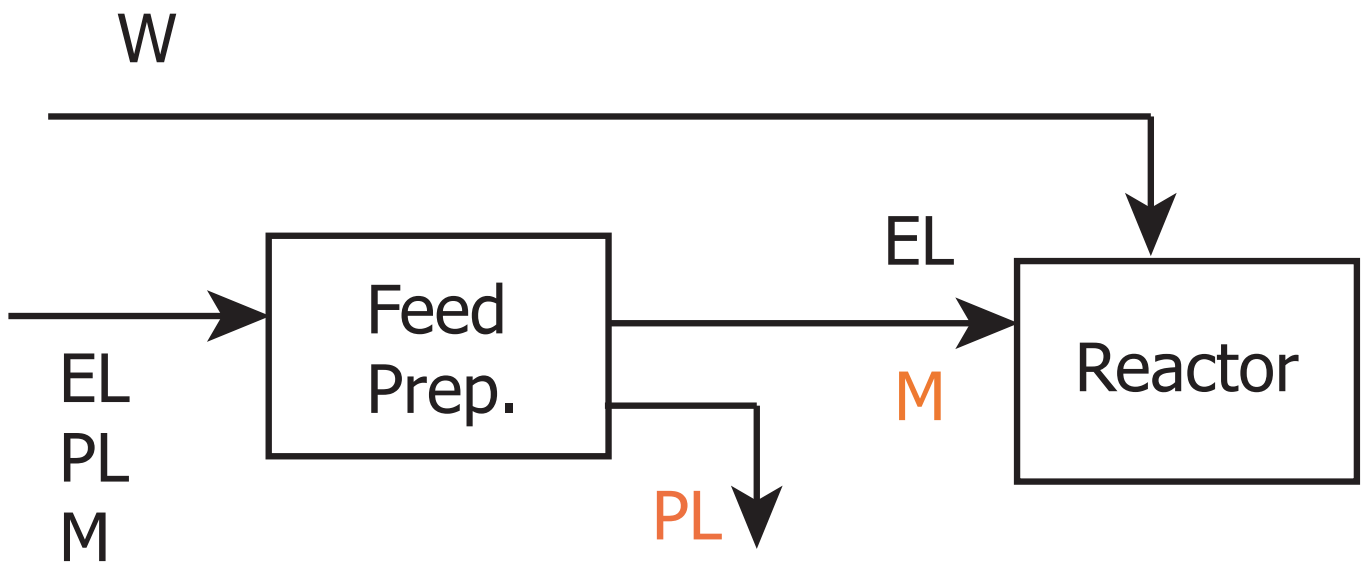
Case Study: Ethanol Synthesis

Alternative 1



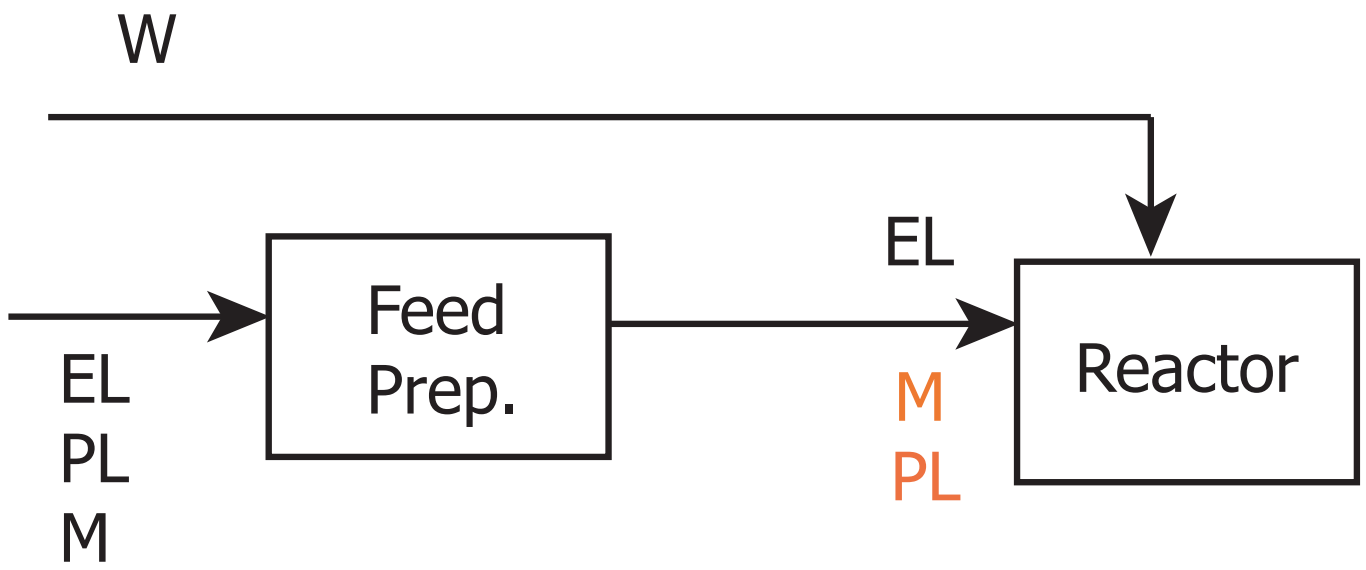
Case Study: Ethanol Synthesis

Alternative 2

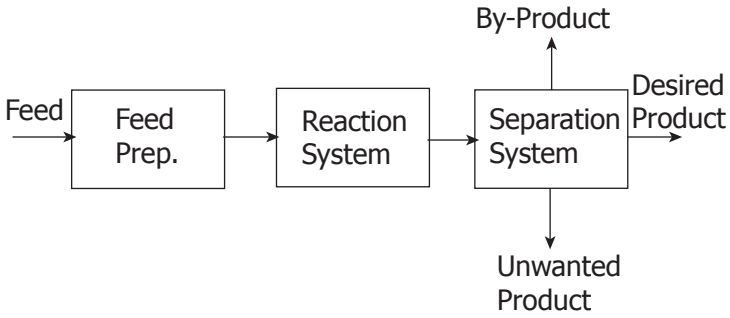


Case Study: Ethanol Synthesis

Alternative 3

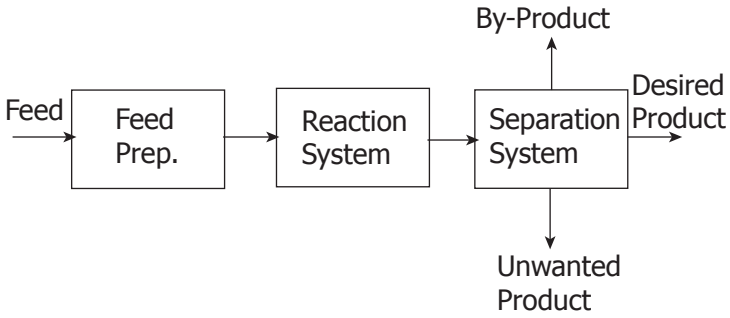


Which alternative would you choose?



Reaction System:
In this system, composition changes due to chemical reaction.

- Temperature and pressure ranges are set by reaction chemistry.
- Catalyst used is set by reaction chemistry.
- Reaction type (e.g. packed bed, fluidized bed, CSTR) are set by reactions occuring and reactor conditions (e.g. exothermic, endothermic)



Separation System:
In this system, the desired products are separated from by-products and unwanted products. The product stream may be further processed due to environmental, safety, or economic considerations.

This system is analyzed in detail in Step 4

Step 3: Recycle Structure

Unused reactants are recycled when:

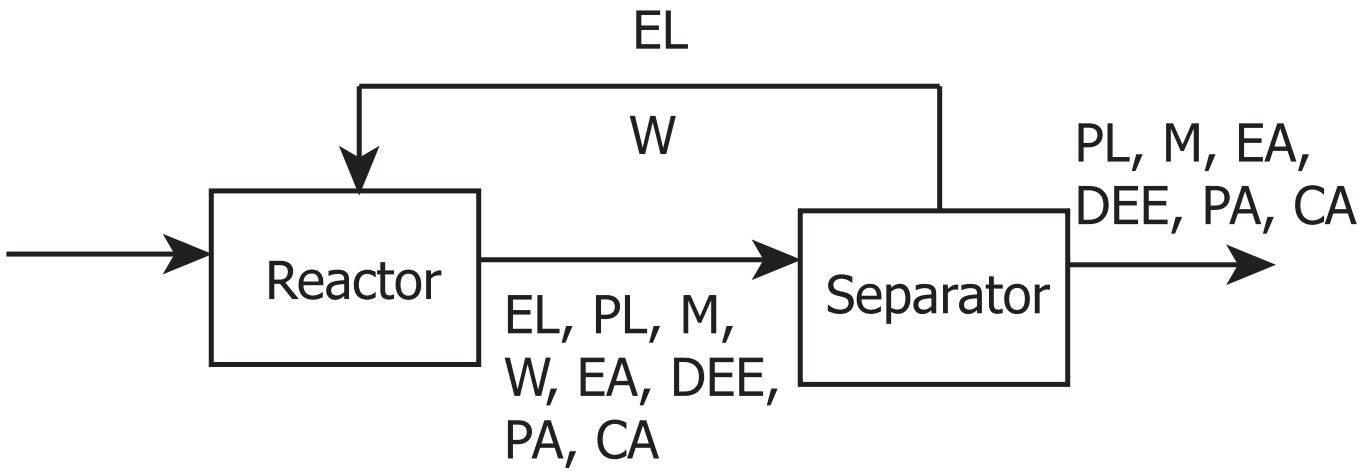
- Conversion is low.
- Raw material costs form a significant portion of operating costs.
- Unused reactants are easy to separate.
- Reactants are environmentally unfriendly.

Three ways to recycle unused reactants

- Separate and purify unreacted feed material from products and then recycle the reactants.
- Recycle feed and product together and use purge stream.
- Recycle feed and product together and do not use purge stream.

Recycle in Ethanol Synthesis

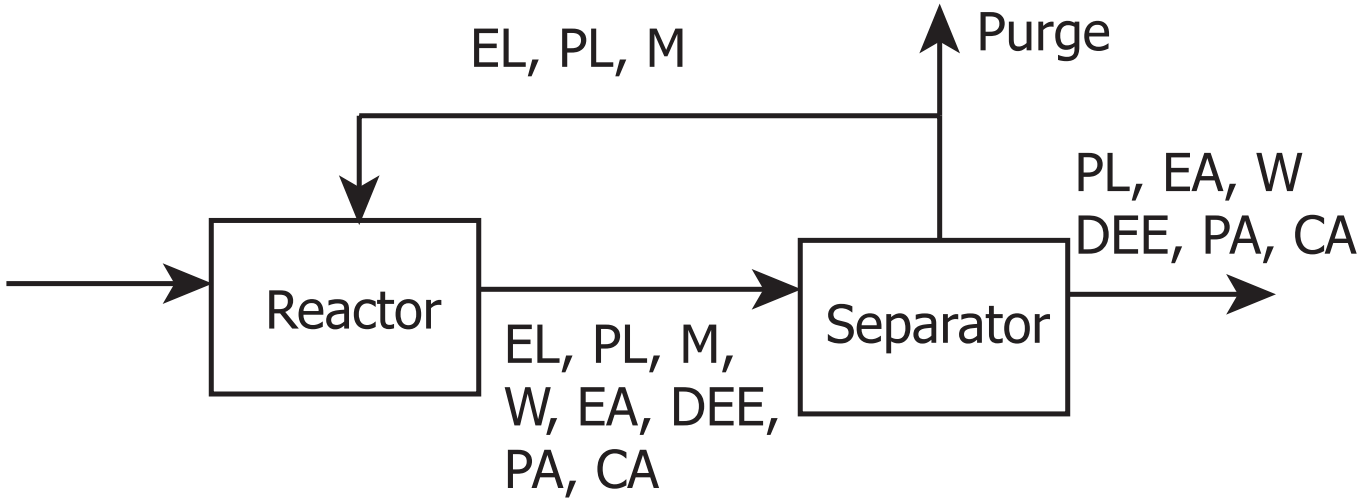
Alternative 1



How to separate EL and W from the reactor outlet?

Recycle in Ethanol Synthesis

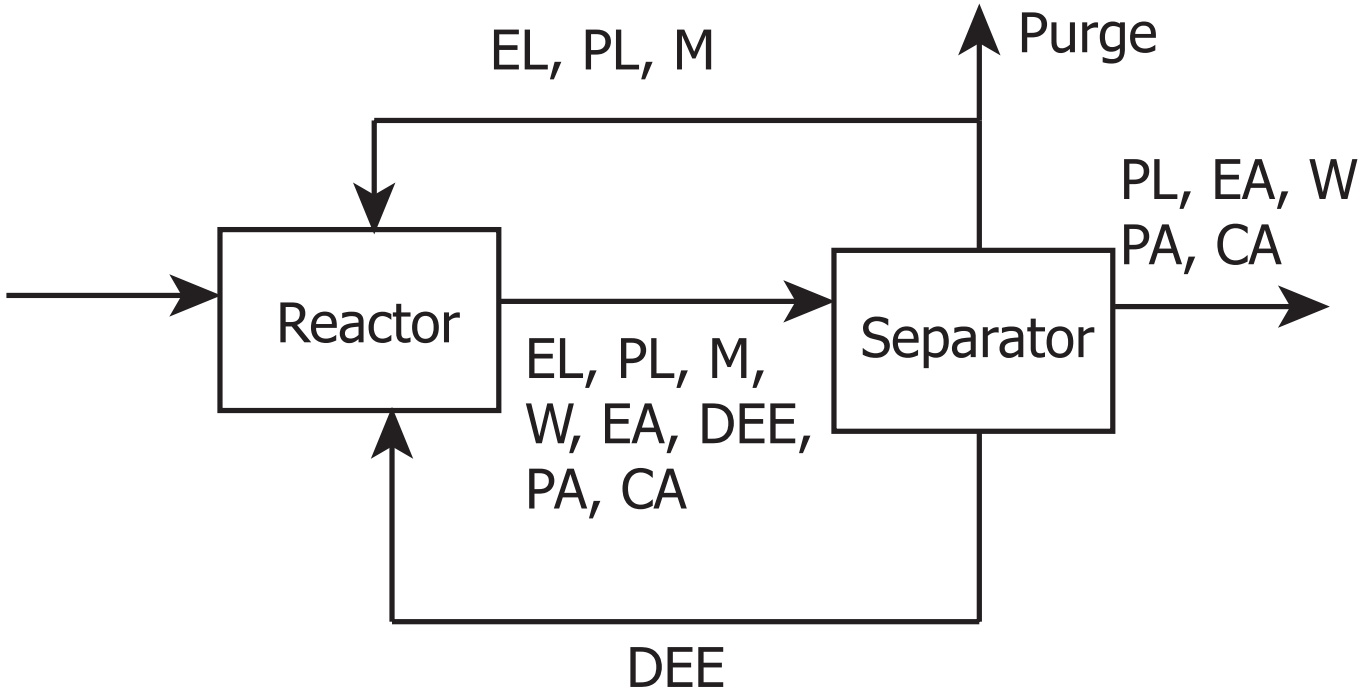
Alternative 2



What should be the purge fraction?
What happens to the DEE reaction which is an equilibrium reaction?

Recycle in Ethanol Synthesis

Alternative 3



At steady state, DEE is at equilibrium and no reactant is consumed.

Step 4: Separation System Synthesis

Flash	Filtration	Crystalization
Distillation	Chromatography	Drying
Gas Absorption	Centrifugation	.
Extraction	Membrane Separation	.

Guidelines for Choosing Separation Units

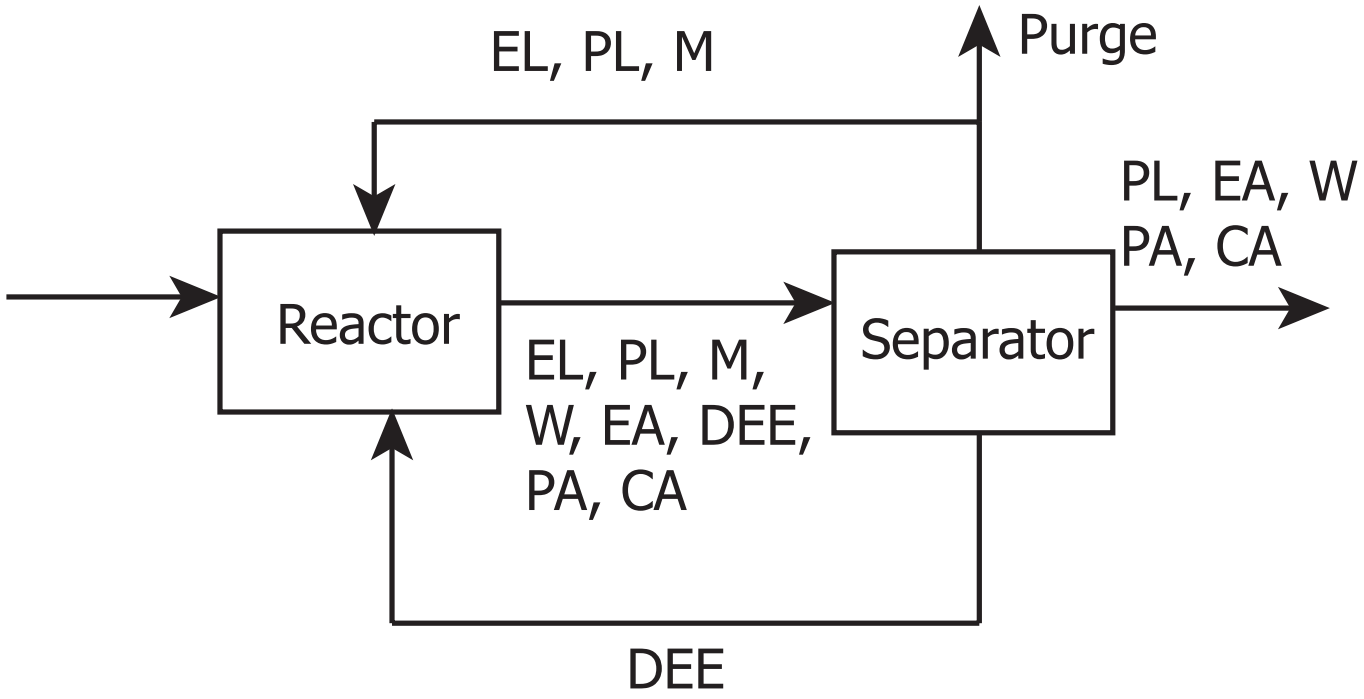
- Use distillation when purity of both products is required.
- Use gas absorption to remove one trace component from a gas stream.
- Use membrane seperation to separate gases of cryogenic boiling points and relatively small flowrates.
- Choose an alternative to distillation if the boiling points are very close or if the heats of vaporization are very high.
- Use crystallization to purify a solid from a liquid solution.
- Use extraction to purify a liquid from another liquid.

Please see Table 10.1 (page 360, TBWS)

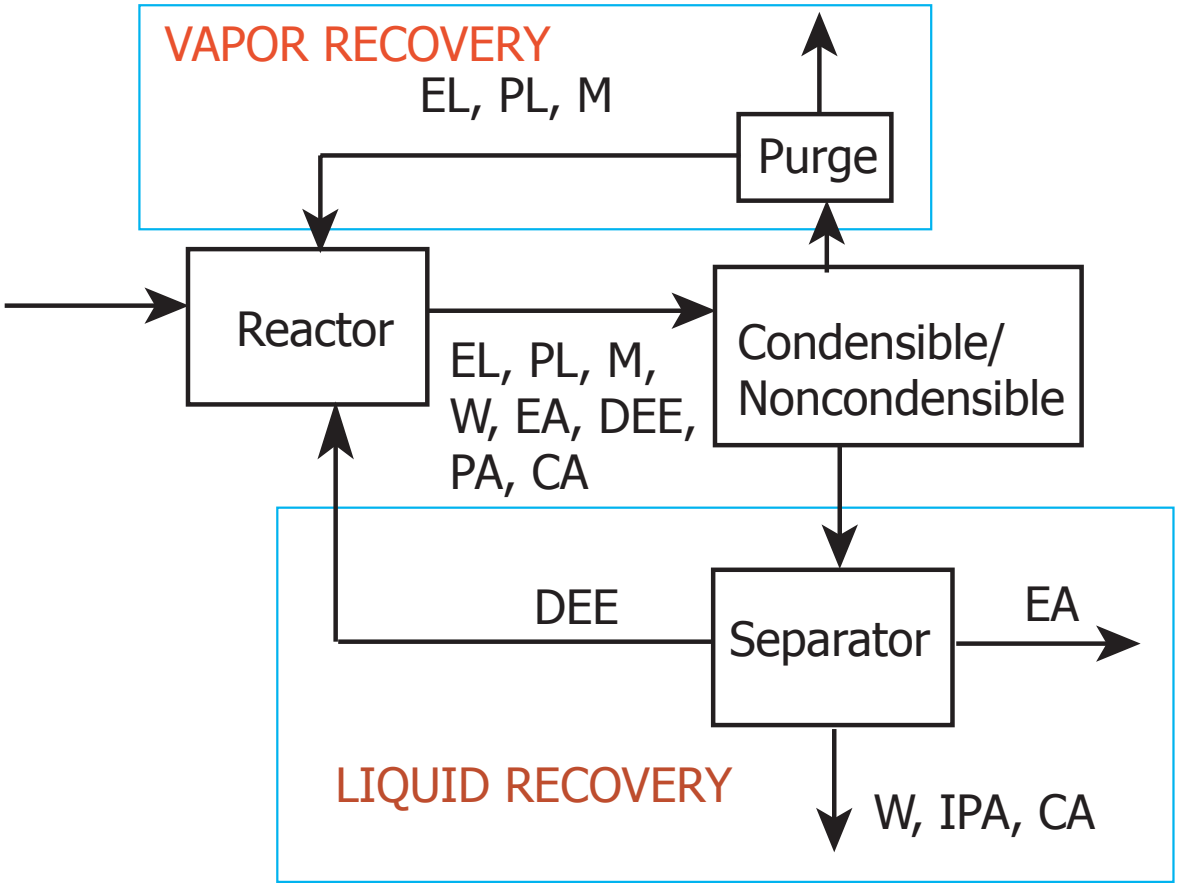
Sequencing Separation Units

- Remove the largest product stream first.
- For distillation, remove the product with the highest heat of vaporization first.
- Do not recombine separated streams.
- Do the easy separation first.
- Do not overpurify streams based on their use.
- Remove hazardous or corrosive materials first.

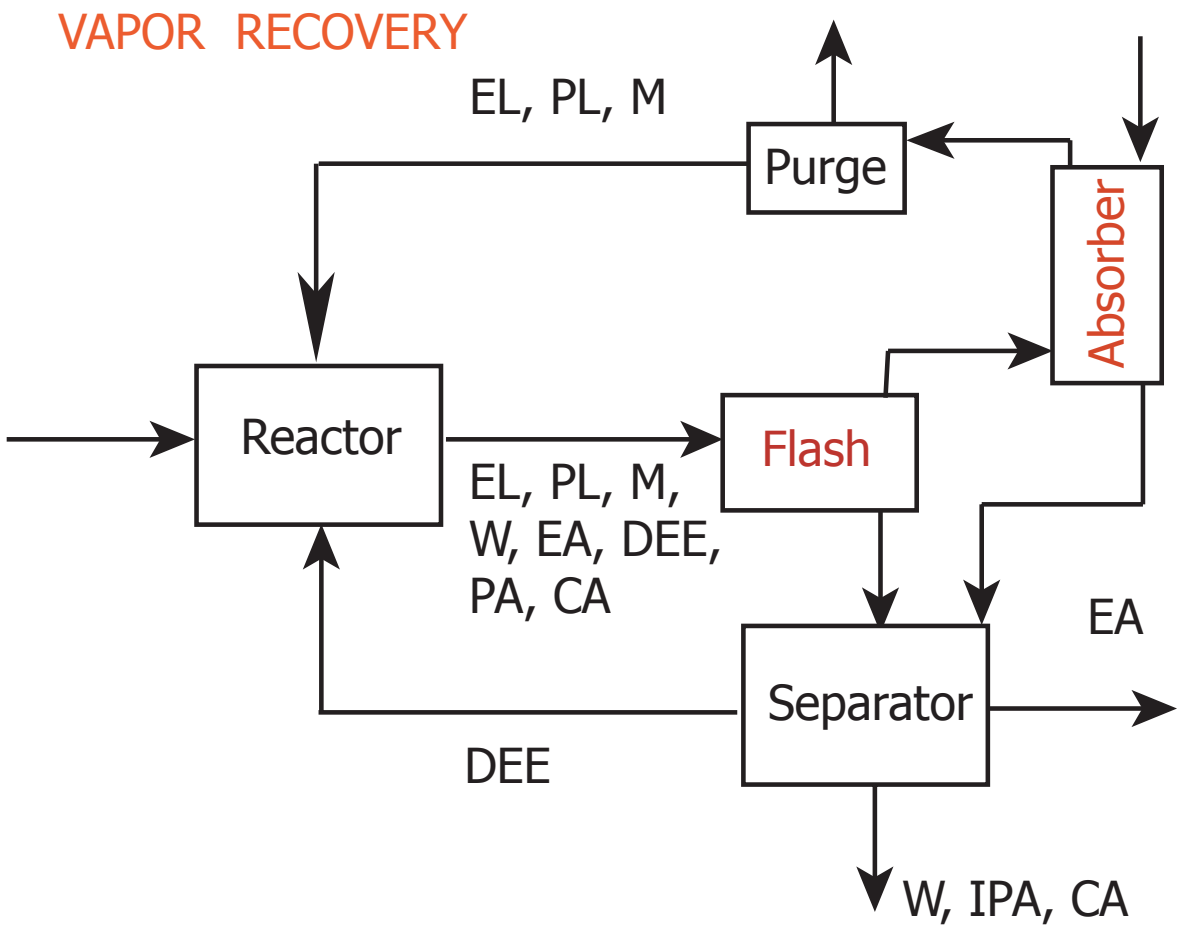
Separation System for Ethanol Synthesis



- Separate the reactor products into a liquid phase and vapor phase.
- Design vapor recovery system and liquid recovery system separately.

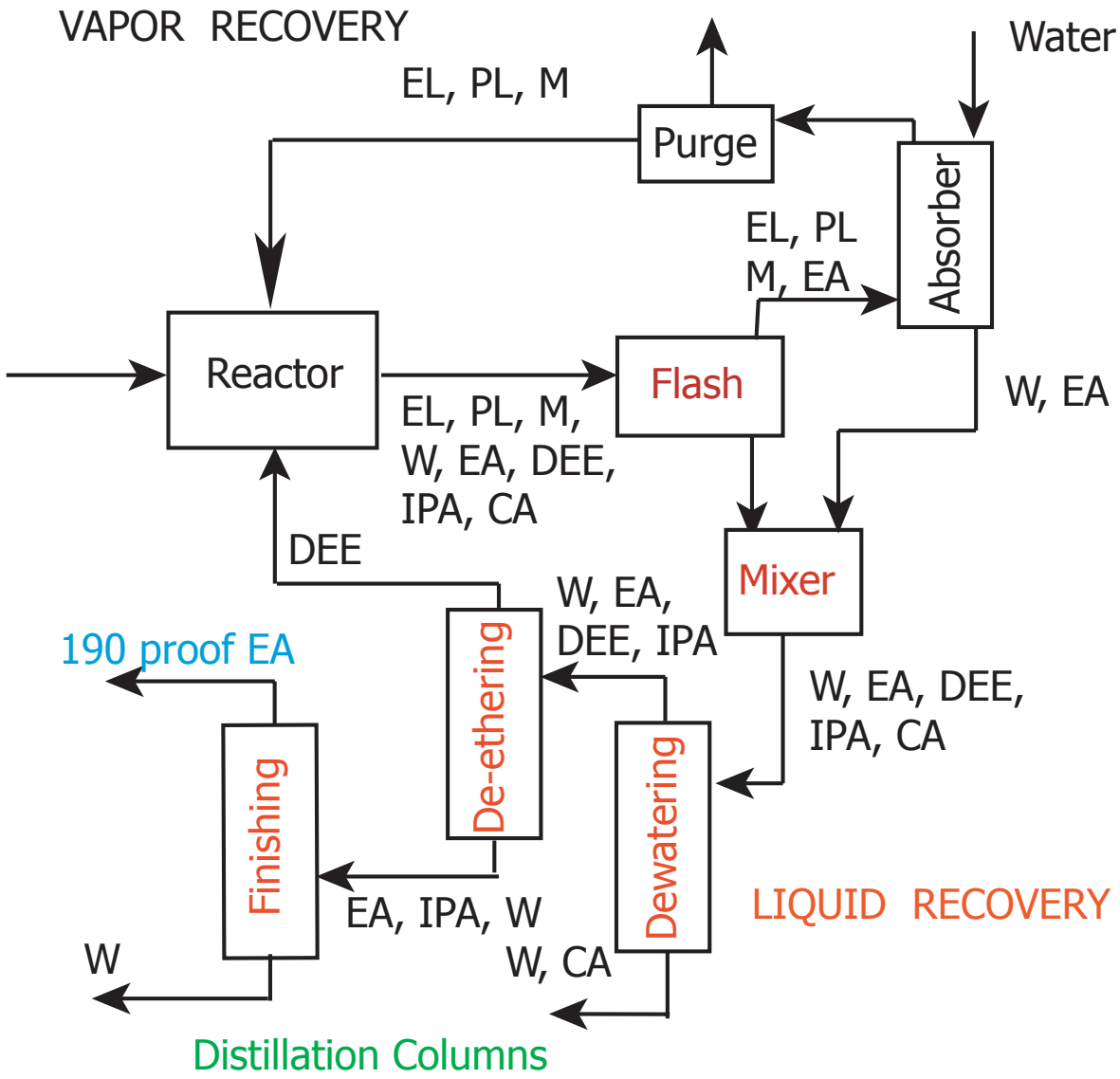


- Flash the reactor products to get a vapor stream and liquid stream.
- The vapor stream is mainly EL, PL, and M and is recycled back.
- Some EL will leave in the vapor stream which can be recovered via an absorber.



- Increasing the purge stream results in loss of reactants but reduces the amount of methane going into the reactor (M has to less than 10% to prevent coking).
- The liquid recovery system is designed as a series of distillation columns.

Final Design



- Distillation is carried out in order of decreasing volatility of species.

Step 5: Heat Exchange

Every flowsheet has hot streams that need cooling and cold streams that require heating.

- Option 1: Use separate utility streams for each heating/cooling process stream.
  Advantage: Easy to set-up and operate.
  Disadvantage: Expensive to build and maintain.
- Option 2: Exchange energy between process streams.
  Advantage: Saves cost.
  Disadvantage: More complex process, difficult to control.

Which option to use depends on process economics.

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