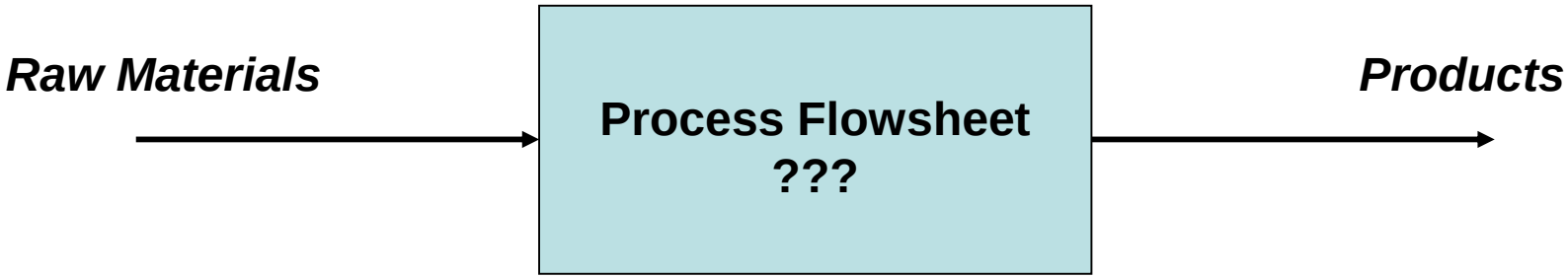
Conceptual Process Design: Process Synthesis



Process Flowsheet Synthesis: Method to determine a process flowsheet that satisfies all product, operational and other requirements

Case Study: Utilize 75 million kg/y of excess ethylene

What can we produce from Ethylene that can be sold profitably?

One alternative – Ethanol

Questions

How pure is ethylene source? 96%EL, 3%PL, 1%M

What are the consequences of impurities?

By-products (DEE, IPA, W, CA) & purge?

How much ethanol to make and at what purity?

150000m3/y at 190 proof (85.44% mole) of ethanol

What is the next step?

Make a quick cost evaluation & establish the flowsheet requirements (see section 2.4.1 of textbook) - $72 - $82 million/y (profit), but operating cost/y and annualized capital cost/y needs to be subtracted.

Case Study: Utilize 75 million kg/y of excess ethylene

Reaction information? (Task 2)

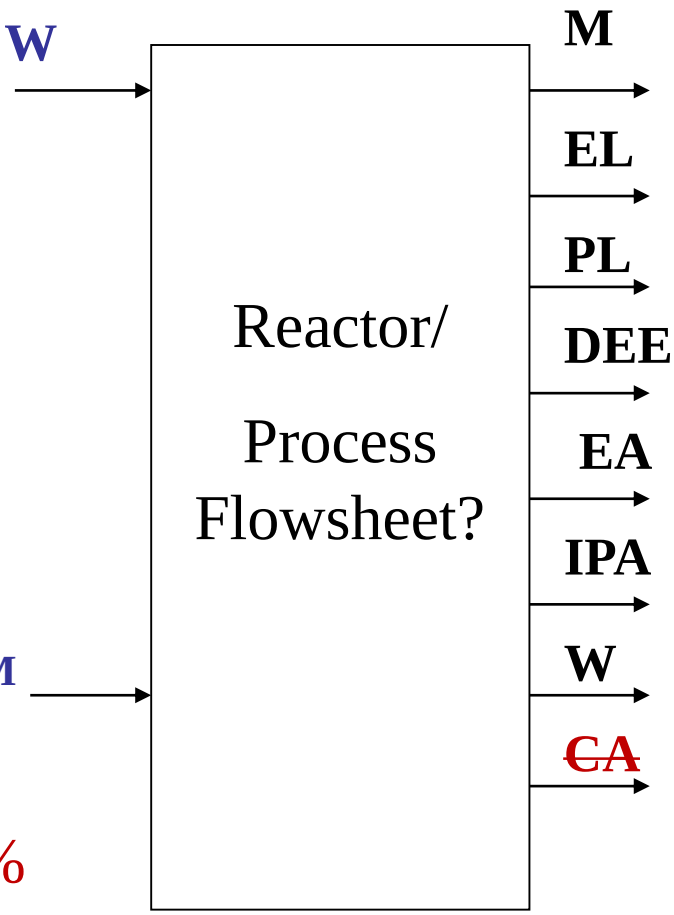
$CH_2=CH_2 + H_2O \rightarrow CH_3CH_2OH$

535 K < T < 575; P approx 68 atm; homogeneous noncatalytic reactor; low conversion 5-7% of ethylene to ethanol

$2CH_3CH_2OH \rightarrow C_2H_5OC_2H_5 + H_2O$

Keep concentration of methane < 10%

Conversion of propylene approx 0.5-0.7%



Properties: M_w, density, T_m, T_b, H_{vap}, $P_{vap}(T)$, T_c, P_c

Case Study: Utilize 75 million kg/y of excess ethylene to produce 150000 m3/y at 85.44%mole purity ethanol

Task 3: Generate a process flowsheet (chapter 2) – process synthesis

Next: Task 4 (perform a simple mass balance)

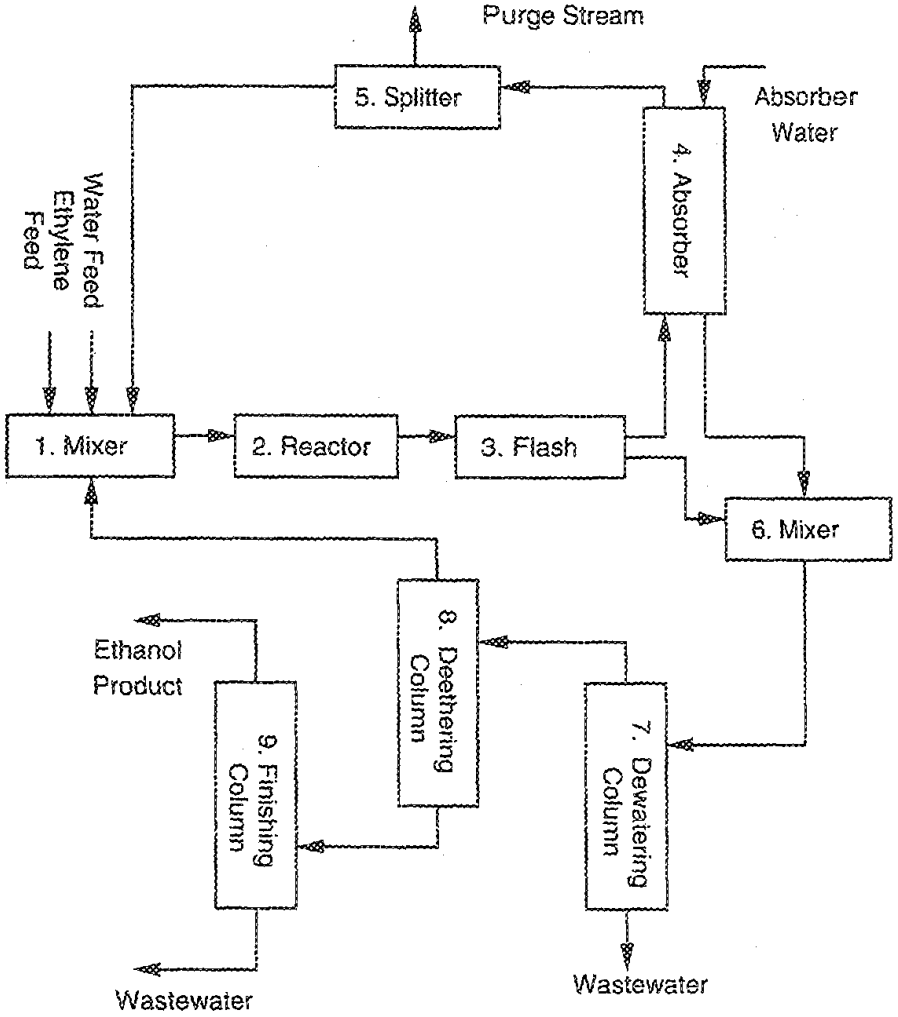


FIGURE 3.1 Ethanol flowsheet.

Basic Steps in Flowsheet Synthesis

* **Gathering Information (tasks 1-2)**
* **Representing Alternatives (e.g., by flow-diagrams)**
* **Criteria for Assessing Preliminary Designs**
  - **Economic evaluation**
  - **Environmental concerns**
  - **Safety analysis**
  - **Flexibility & controllability**
* **Synthesis method (generate and test alternatives)**

Synthesis Method: Generate & test alternatives

* **Total enumeration**
* **Evolutionary methods**
* **Mathematical programming**
* **Hybrid**

Establish targets for the design

Generate (feasible) alternatives that will match the targets

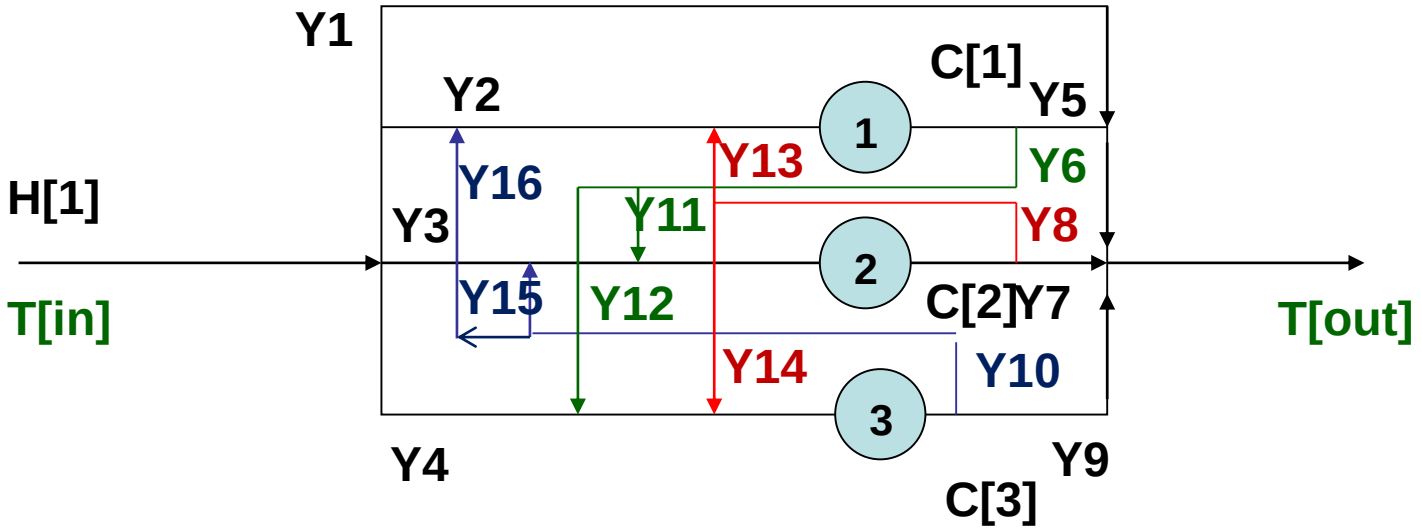
Order all the feasible alternatives and select the most appropriate

Synthesis Method: Generate & test alternatives

* **Total enumeration**
* **Evolutionary methods**
* **Mathematical programming**
* **Hybrid**

Concepts:

Superstructure & Alternatives



Synthesis Method: Generate & test alternatives

* **Total enumeration**
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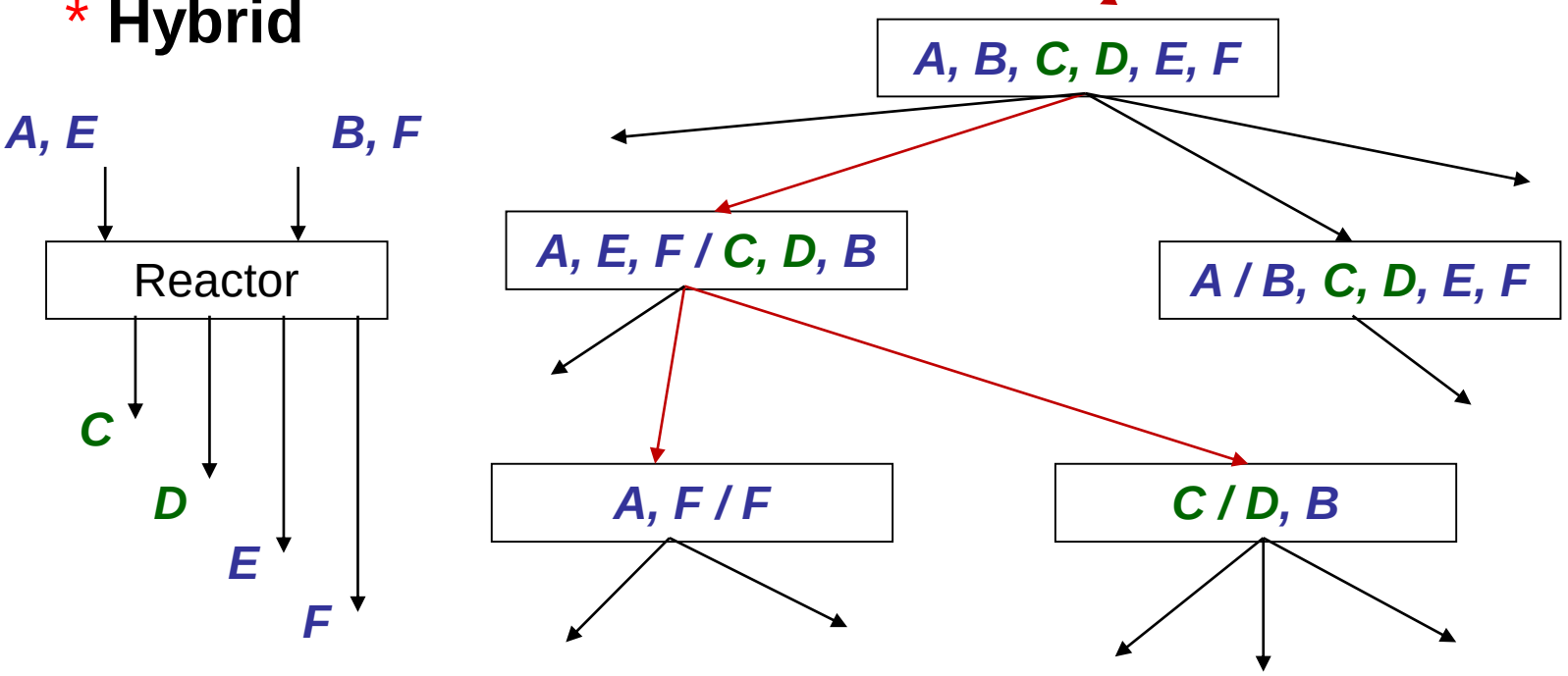
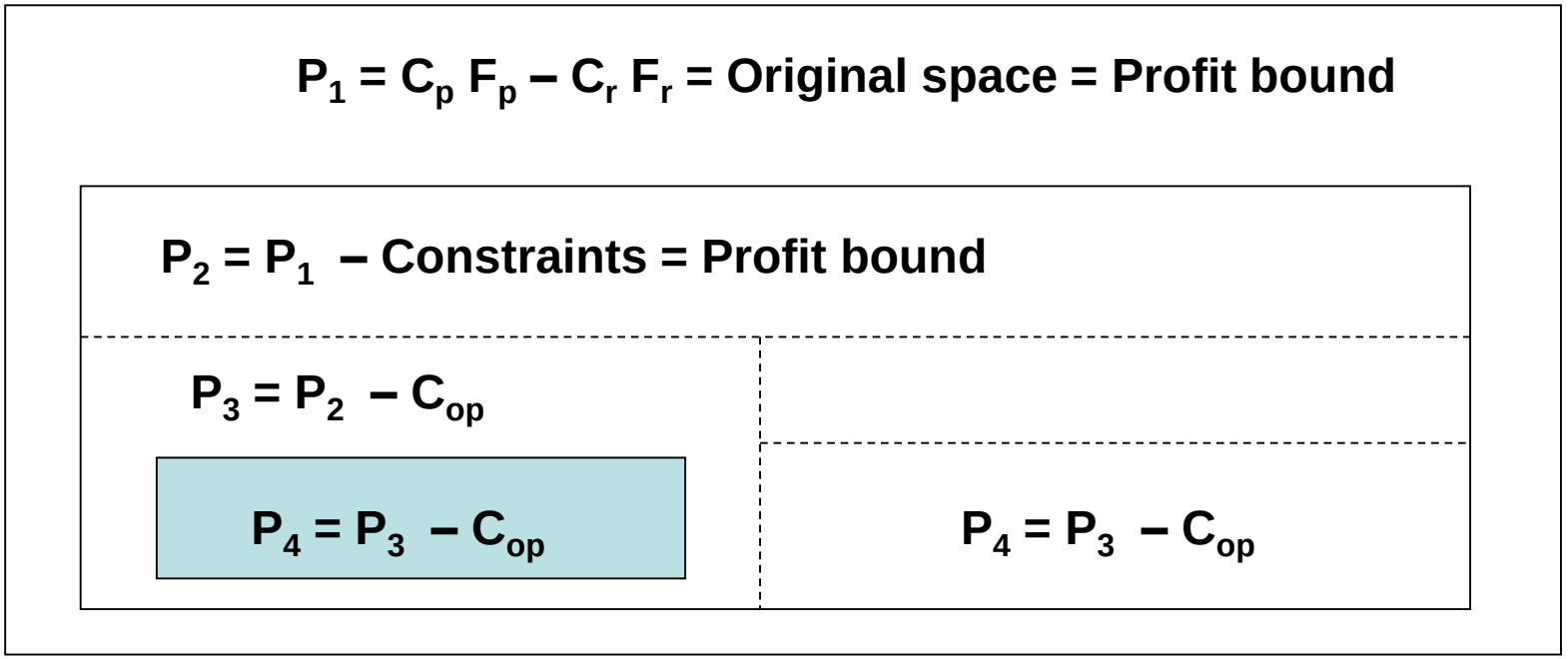


Decomposition Strategies for Process Synthesis

- ***Bounding Strategies for Process Synthesis***
- ***Hierarchical Decomposition for Process Synthesis***



Decomposition Strategies for Process Synthesis

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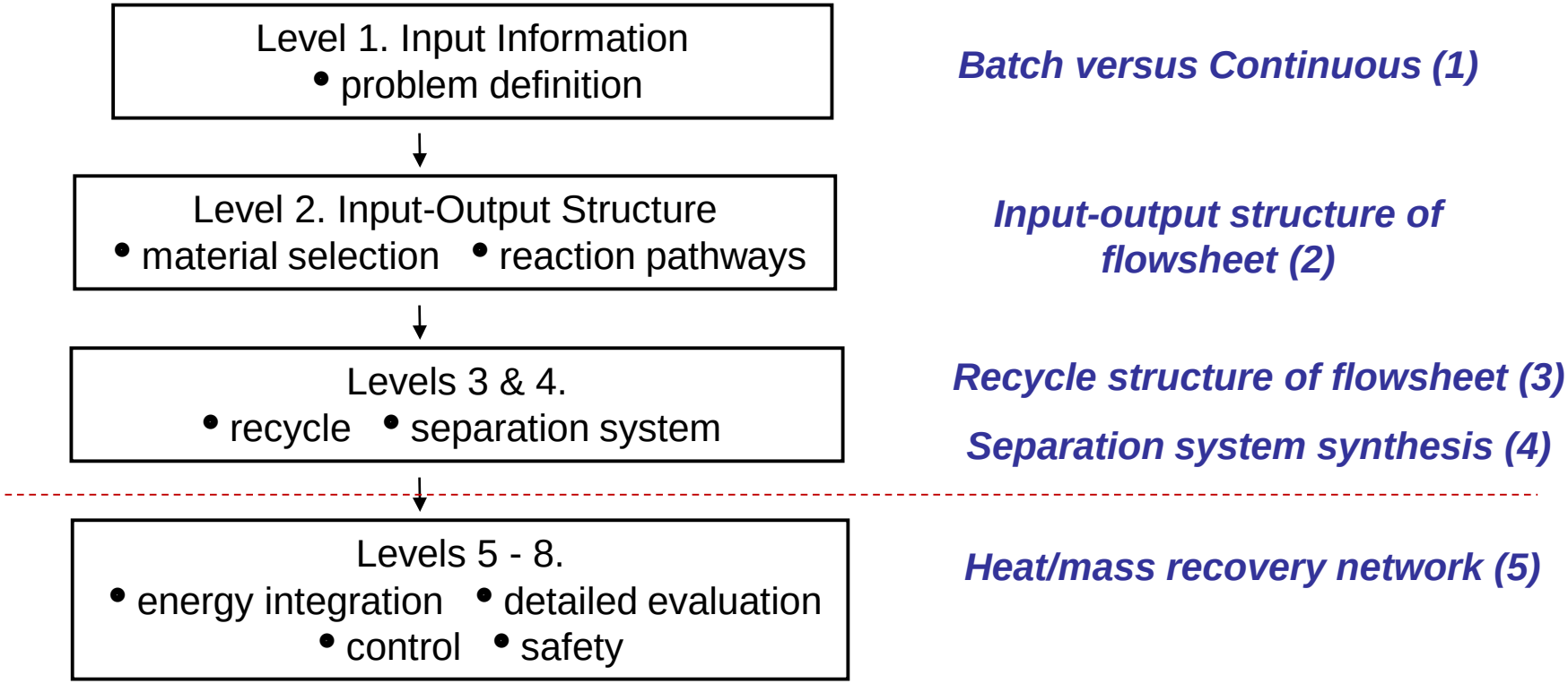


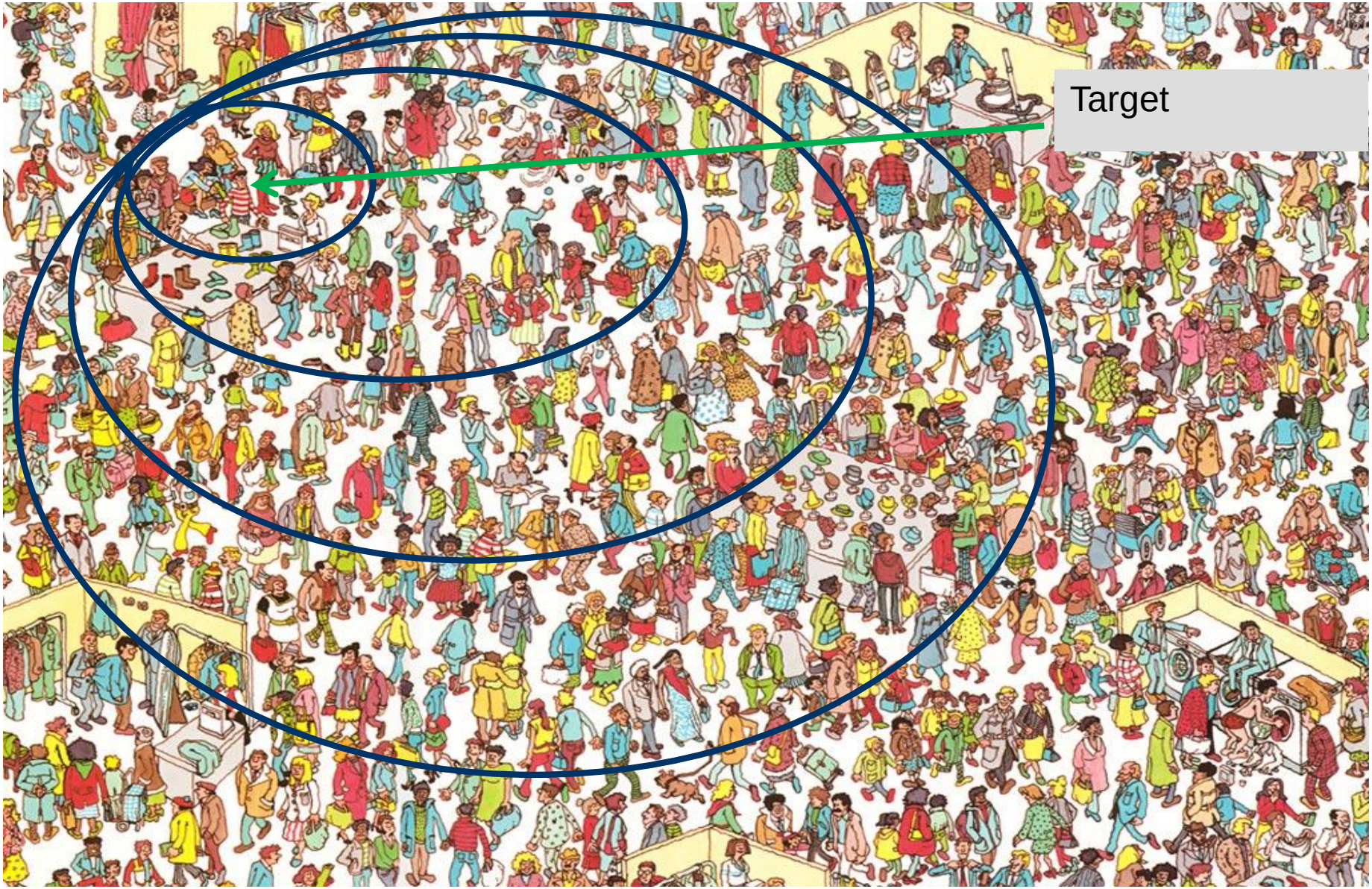
Design problem decomposed into a hierarchy of decisions

Another view of how to find the target process flowsheet!

Where is Wally?
Donde esta Waldo?
Hvor er Holger?
.....
.....

Our target process flowsheet

Another view of how to find the target process flowsheet!



Case Study: Utilize 75 million kg/y of excess ethylene

Reaction information? (Task 2)

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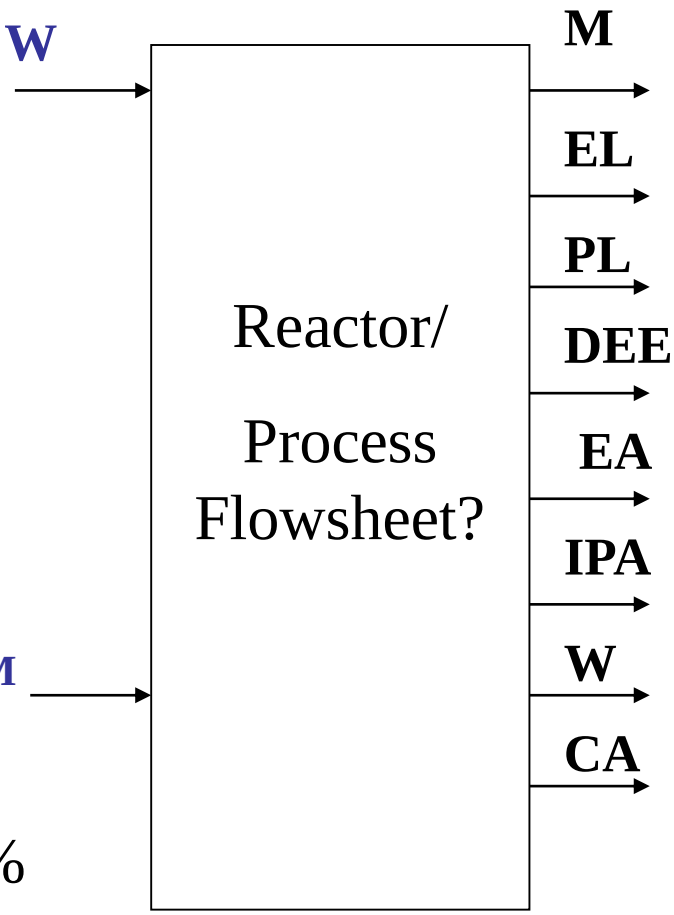


Properties: M_w, density, T_m, T_b, H_{vap}, $P_{vap}(T)$, T_c, P_c

Properties of the compounds found in the process

TABLE 1.3 Physical Property Data for Species

Species	W water	EA ethyl-alcohol	EL ethylene	DEE diethyl-ether	M methane	PL propylene	IPA isopropyl-alcohol	CA croton aldehyde
Formula	H_2O	CH_3CH_2OH	$CH_2=CH_2$	$(C_2H_5)_2O$	CH_4	$CH_3CH=CH_2$	$CH_3CH-OHCH_3$	$CH_3CH=CH-CH=O$
MW	18.02	46.07	28.05	74.12	16.04	42.08	60.10	70.09
Sp. Gr.	1.0	0.789	0.56	0.708	-	0.609	0.785	
Melt Pt, °C	0	−114.5	−169.2	116.3(c)	−182.5	−185.3	−89.5	159–160
BP, °C	100	78.4	−103.7	34.6	−161.5	−47.7	82.4	
ΔH_v (kcal/mo)	539.55	204.3	115.4		121.9	104.6	159.4	
VP A[1]	8.10765	8.04494	6.74756	7.4021	6.61184	6.81960	6.66040	
VP B	1750.286	1554.3	585.00	1391.4	389.93	785.00	813.055	
VP C	235.0	222.65	255.00	273.16	266.00	247.00	132.93	
t_c, °C	374.14	243.5	9.6	193.8	−82.1	91.4	235.16	
P_c, atm	217.6	63.1	50.7	35.5	45.8	45.4	47.02	

[1] $VP(\text{mm Hg}) = 10^{A-B/(C+t(^\circ C))}$ where VP is vapor pressure and t is temperature.

Check if all the listed values are correct!

Hierarchical Decomposition for Process Synthesis

Level 1: Decisions on Batch versus Continuous

Consider,

- **Technical Information**
  - ***Does any apparatus work in batch mode? Is process sensitive to upsets & variations?*** ***No batch mode***
  - **Production Rate**
  - ***High or low production rate? Only few days production needed? Few days operational notice?*** ***High production rate***
  - **Product Lifetime**
  - ***One or two years or longer?*** ***Longer***
  - **Value of Product**
  - ***Product value >> manufacturing cost?*** ***Yes***

Note: Several batch units can be combined to give a continuous production! – Conclusion: continuous process

Hierarchical Decomposition for Process Synthesis

Level 2: Decisions on Input-Output Structure

Consider,

- **Raw materials – what to do with impurities ?**
- **How many product streams?**
- **Recycle streams? Purge streams?**
- **Reversible by-products? Recycle or recover?**
- **Selectivity versus cost**

Three Types of Decisions (Assumptions)

1. **Decision that fix parts of the flowsheet**
2. **Decisions that fix some of the design variables**
3. **Decisions that fix connections to the environment**

Hierarchical Decomposition for Process Synthesis

Level 2: Decisions on Input-Output Structure

Raw Materials - Impurities?

- ***If the impurities are inert, remove them after reaction, if they are valuable –*** ***OK***

- ***If the impurities are inert, present in large amounts, and, can be easily separated, remove them before the reactor -*** ***No***

- ***If the impurities have boiling points lower than reactants and products, and, they are also inert, recycle them (note: purge unit will be needed!) -*** ***OK***

- ***If the impurities are also products from the reactor, place the feed stream before the unit that will remove the impurities -*** ***No***

Hierarchical Decomposition for Process Synthesis

Level 2: Decisions on Input-Output Structure

Product streams?

Observe the following Rules

- ***Recycle unreacted reactants -*** **OK**
- ***Recycle intermediate reactants (products) -*** **??**
- ***Recycle/remove azeotropes with reactants* -*** **??**
- ***Remove (recover) the main product -*** **OK**
- ***Remove (recover) the valuable by-products -*** **OK**
- ***Remove (as waste)/recycle by-products that are not valuable -*** **OK**

Hierarchical Decomposition for Process Synthesis

Level 2: Decisions on Input-Output Structure

Recycle? Purge Units? Consider *the following:*

- ***For < 100% conversion of reactants and reaction in the gas phase,***
  - ***Recycle of gases will be necessary -*** **YES**
  - ***If impurities are present, purge units will be necessary -*** **YES**
- ***For < 100% conversion and reaction in the liquid phase,***
  - ***Recycle of liquids (reactants) will be necessary***
  - ***If impurities are present, purge units will be necessary***

Hierarchical Decomposition for Process Synthesis

Level 2: Decisions on Input-Output Structure

Reversible by-products? Selectivity versus cost?

EP_2 = Product value + Byproduct value – Raw material value

Function of conversion, selectivity, reaction T & P, ….

Hierarchical Decomposition for Process Synthesis

Level 2: Decisions on Input-Output Structure

Reversible by-products? Selectivity versus cost?

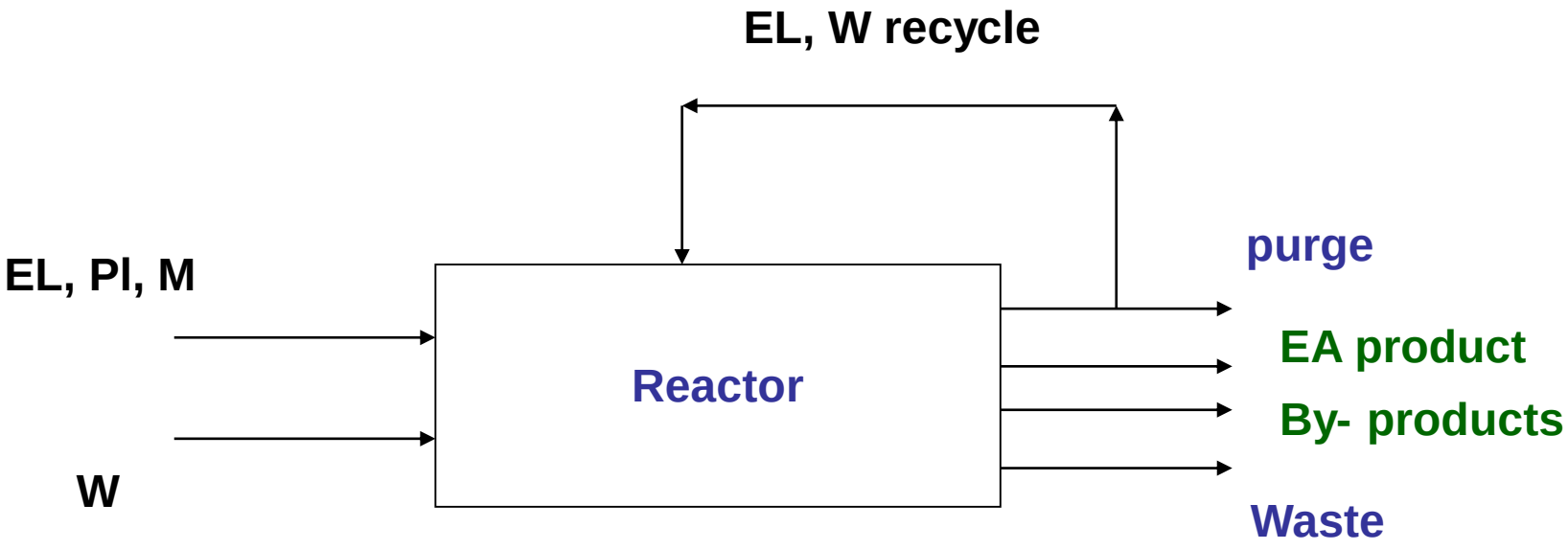
EP_2 = Product value + Byproduct value + Raw material value

Function of conversion, selectivity, reaction T & P, ….

EP2 is approximately $(US) 82 million (see chapter 2)

Note: Since you know the amount of product you will make and the raw materials needed, EP_0 (product value – raw material value) can be calculated already at the start and then refined at level-2

Ethanol Process Flowsheet at the end of Level 2



Hierarchical Decomposition for Process Synthesis

Level 3: Decisions on Recycle Structure & Reactor

Consider,

- **Number of reactors?**
- **Number of recycle streams?**
- **Need for compressor/pump?**
- **Reactor type? Adiabatic or Isothermal?**
- **Reaction equilibrium or kinetics?**
- **Reactor cost (capital & operating)?**

Hierarchical Decomposition for Process Synthesis

Level 3: Decisions on Recycle Structure & Reactor

- **Number of reactors?**
  - ***If more than one reaction is needed to get the desired product, more than one reactor will be needed if the conditions are very different –***

1 reactor??

- **Number of recycle streams?**
  - ***Depends on the number of raw materials and conversion of all reactants –***

2 recycles??

- **Need for compressor/pump?**
  - ***Compressor for gas recycle; pump for liquid recycle -*** **OK**
- **Reactor type? Adiabatic or Isothermal?**
  - ***If temperature change is too high or low, heating or cooling will be needed –***

Isothermal – heating is necessary

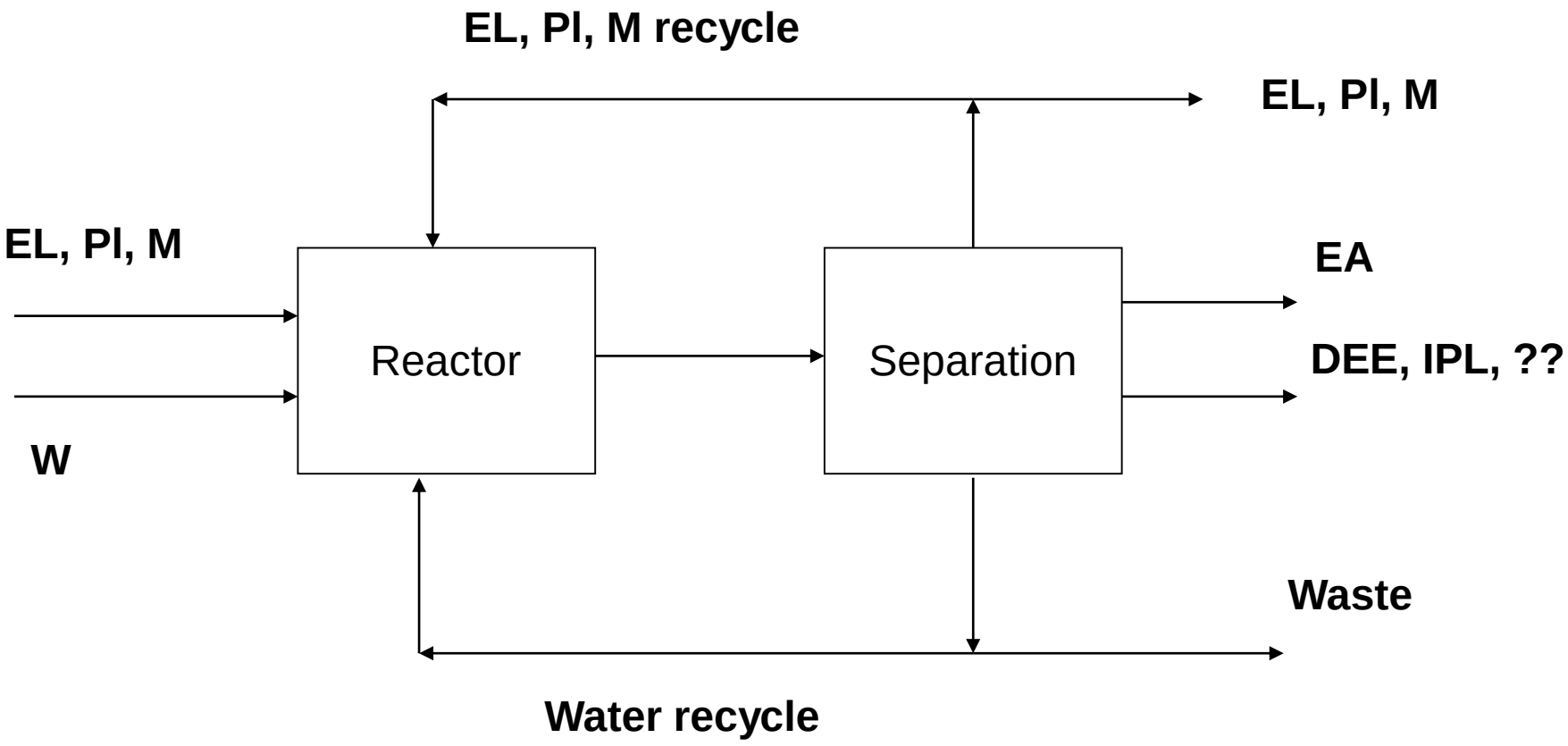
  - **Reaction equilibrium or kinetics?**
  - ***Kinetically controlled or equilibrium reached? –***

Kinetically controlled

- **Reactor cost (capital & operating)?**

$EP_3 = EP_2$ – Compressor/pump cost – Reactor cost

Ethanol Process Flowsheet at the end of Level 3



Hierarchical Decomposition for Process Synthesis

Level 4: Decisions on Separation System

Vapour recovery and/or Liquid recovery? - Rules

- **If reactor stream is in liquid phase, use liquid recovery**
- **If reactor stream has 2 phases (separate the 2 phases first)**
  - ***Use vapour recovery for vapour phase***
  - ***Use liquid recovery for liquid phase***
- **Reactor stream is gas (vapour) phase**
  - ***Perform phase split (if possible) by reducing temperature (ie., condenser) and then separate the 2-phase. Otherwise, use vapour recovery***

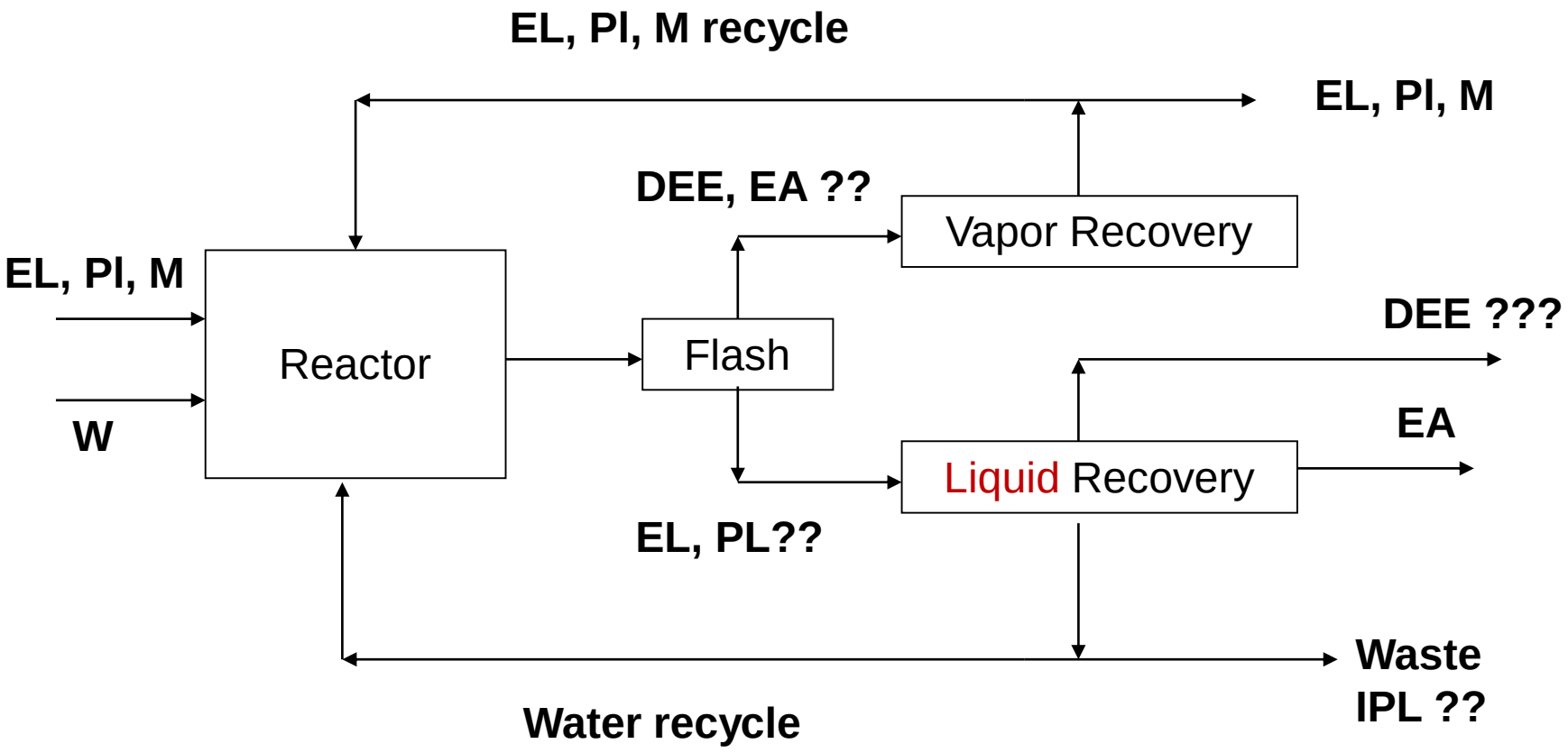
OK

How to locate & perform the separation?

Evaluate properties of compounds

$EP_4 = EP_3$ – Vapour recovery cost – Liquid recovery cost

Ethanol Process Flowsheet during Level 4



Level 4: Decisions on Separation System

Vapour Recovery System (VS) - Location

- **If vapour stream contains significant amount of valuable material (reactants, impurities, product), place VS after purge unit ??**
- **If vapour stream contains components that may slow down the reaction or destroy or affect the catalyst, place VS on the recycle stream**
- **If both the above criteria are satisfied, place VS after a "phase split" unit ??**
- **If none of the above are satisfied, VS is most likely not necessary!**

How to perform the separation?

Condensation *(high pressure and/or low temperature)*

Absorption *(needs solvent and solvent recovery – try water!)* ??

Adsorption *(needs adsorbent and regeneration of adsorbent)*

Membrane separation *(suitable membrane, low flux, etc.)*

Hierarchical Decomposition for Process Synthesis

Level 4: Decisions on Separation System

Liquid Recovery System (LS) - Decisions on …

- Which separations can be made with distillation? All ?
- Sequence of distillation columns Order compounds in terms of Tb
- Removal of light ends (send to VS if valuable, otherwise, waste disposal) Yes
- Other types of separations possible? Yes – but not necessary now

Rule for selecting separation by distillation or phase split (V-L)

- If $\alpha > 1.1$, between two key components, use distillation provided the key components do not form azaotrope Yes, there are azeotropes
- If $\alpha >>> 1.1$, try phase split (condensation or vaporization)

Tb of ethanol, IPA & azeotrope have values very close to each other

Rules for sequencing of distillation columns

- Recover lightest component first OK
- Recover most plentiful component first OK
- Make the most difficult separation last
- Always try equimolar separations

Ethanol Process Flowsheet

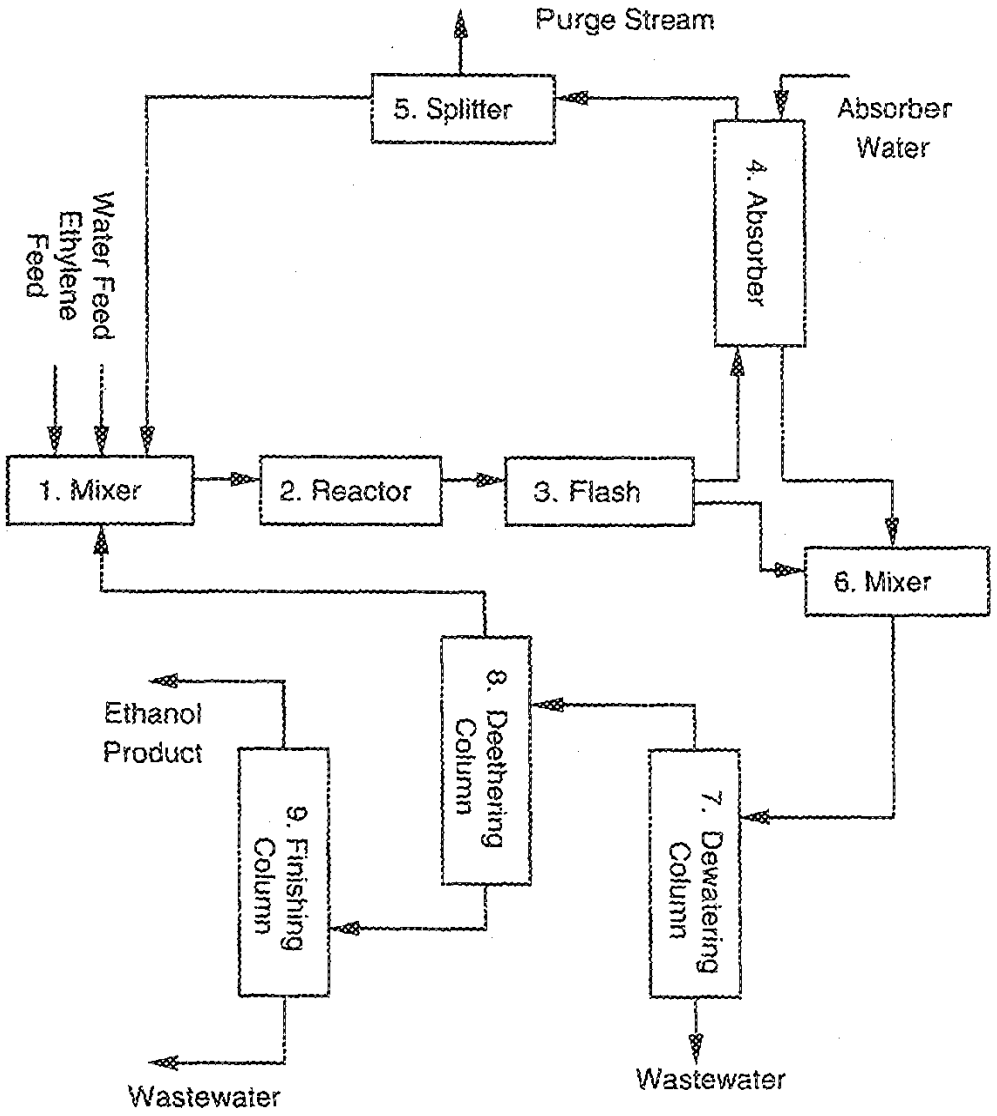
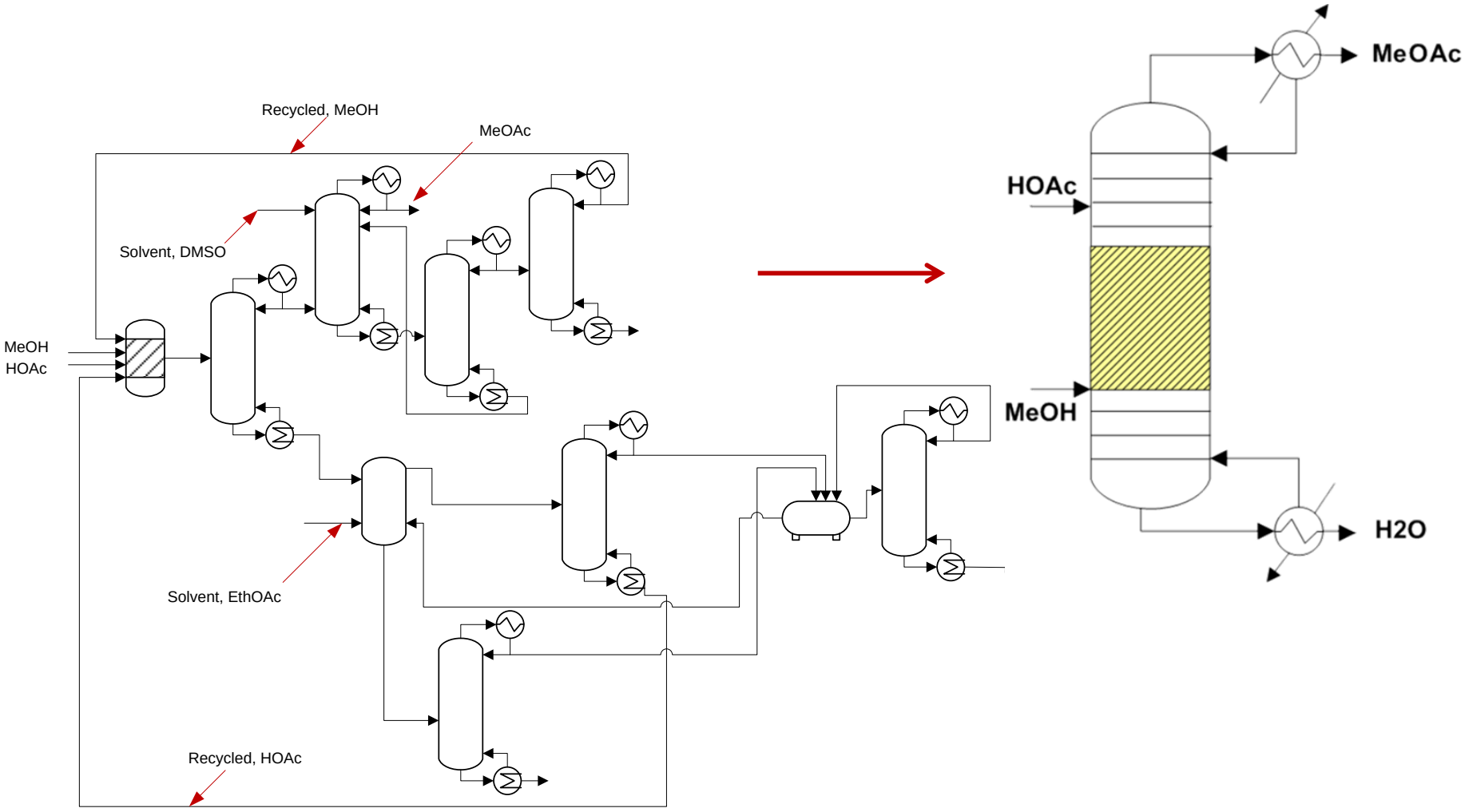


FIGURE 3.1 Ethanol flowsheet.

Flowsheet alternatives versus new developments



Method for Separation Process Synthesis

Separation Process Identification

Step 1: Mixture Analysis (*number of components in mixture, mixture type, mixture state, temperature, pressure, number of binary pairs, azeotrope pairs, etc.)*

Step 2: Generate binary ratio matrix

$R = r_{ij} = p_{iA} / p_{iB}$ ***for property I, binary pair j***

compounds A & B in pair j

Step 3: Identify separation technique

If, $r_{min} < r_{ij} < r_{max}$ for separation technique k, select this technique for separation of the compounds in the binary pair j

Step 4: If more than one separation technique is feasible for binary pair j, select the separation technique with the largest r_{ij} value

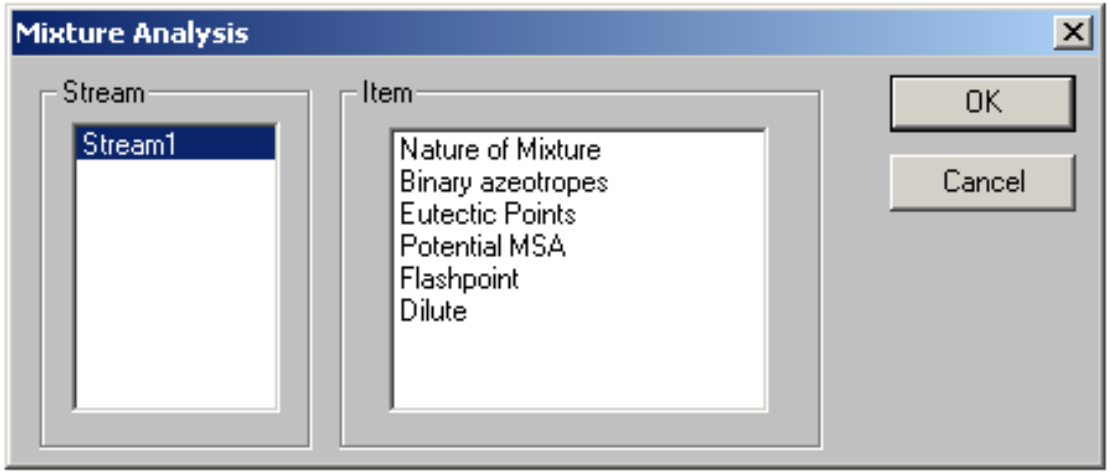
Principle for separation is a driving force created by a difference in property; different separation techniques employ different properties!

Method for Separation Process Synthesis

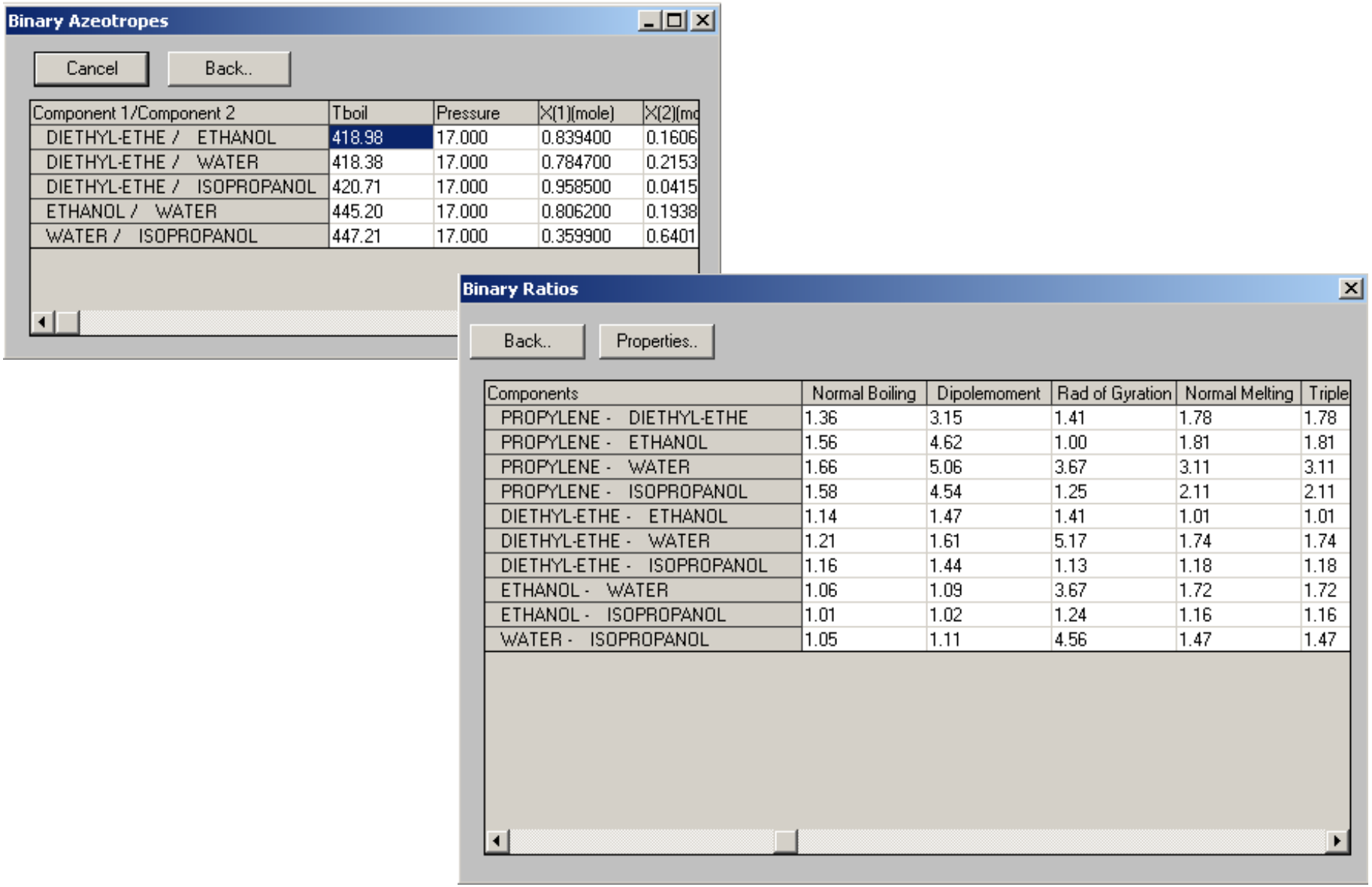
Separation Process Identification

```
****** Mixture Analysis Report:

* A multi component mixture property is to be calculated.
* Based on simple mixture analysis (no use of thermo. model) the mixture at the specified
condition is probably of GLE.
* The property probably does not have composition extremes.
* Pressure is in the very high range.
* At least one component is in its critical/super critical region.
* Mixture is of the AQUEOUS type.
* This is a SUPERCRITICAL system.
* The mixture is probably non-ideal.
```



Separation Process Identification



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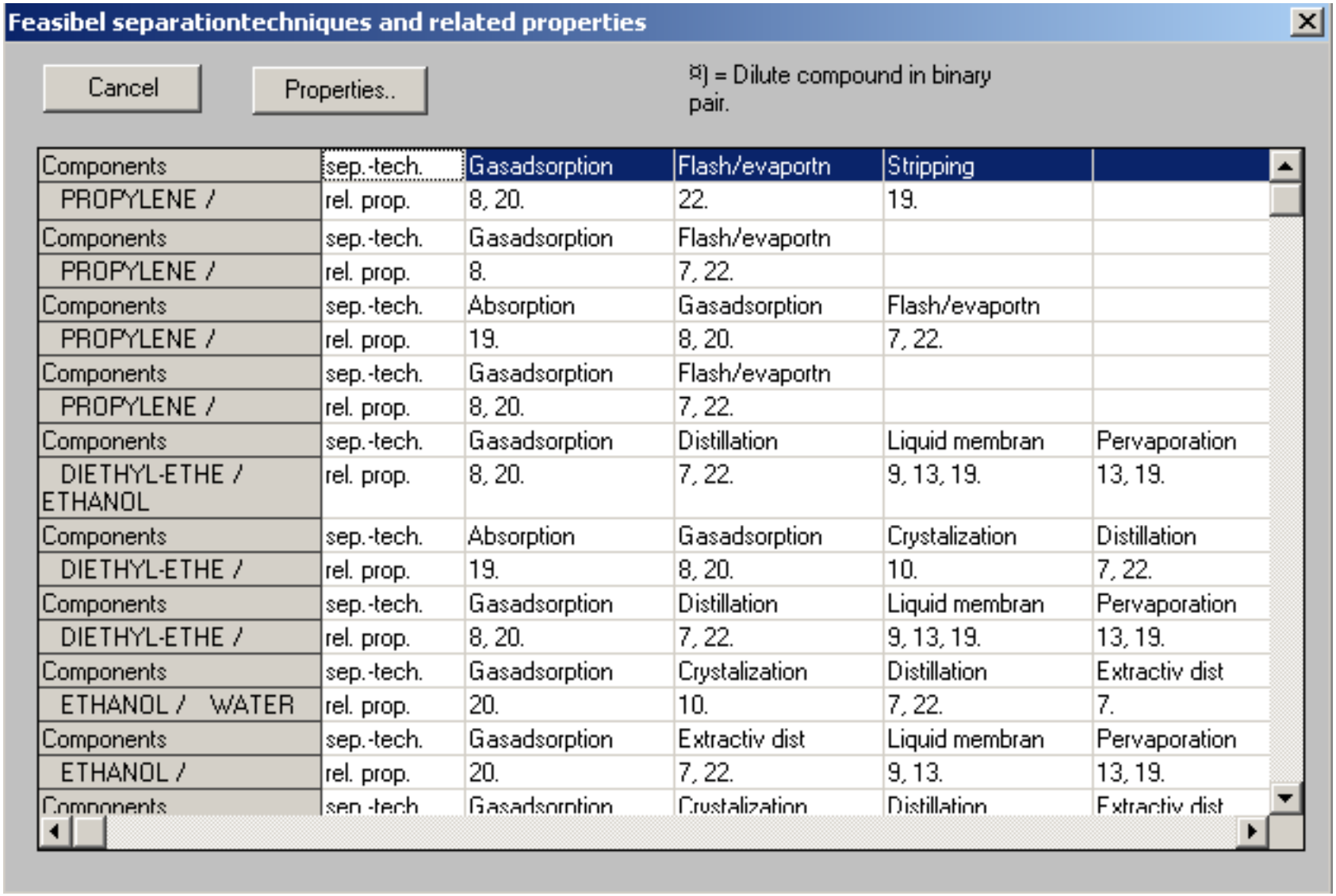
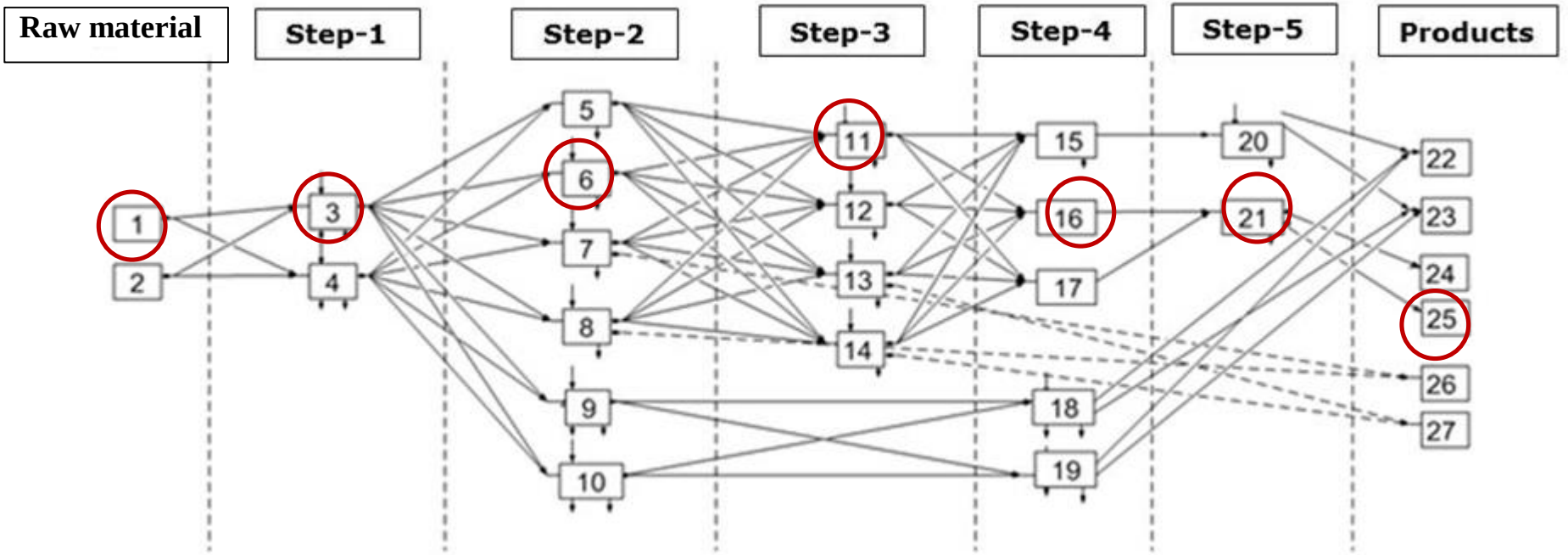
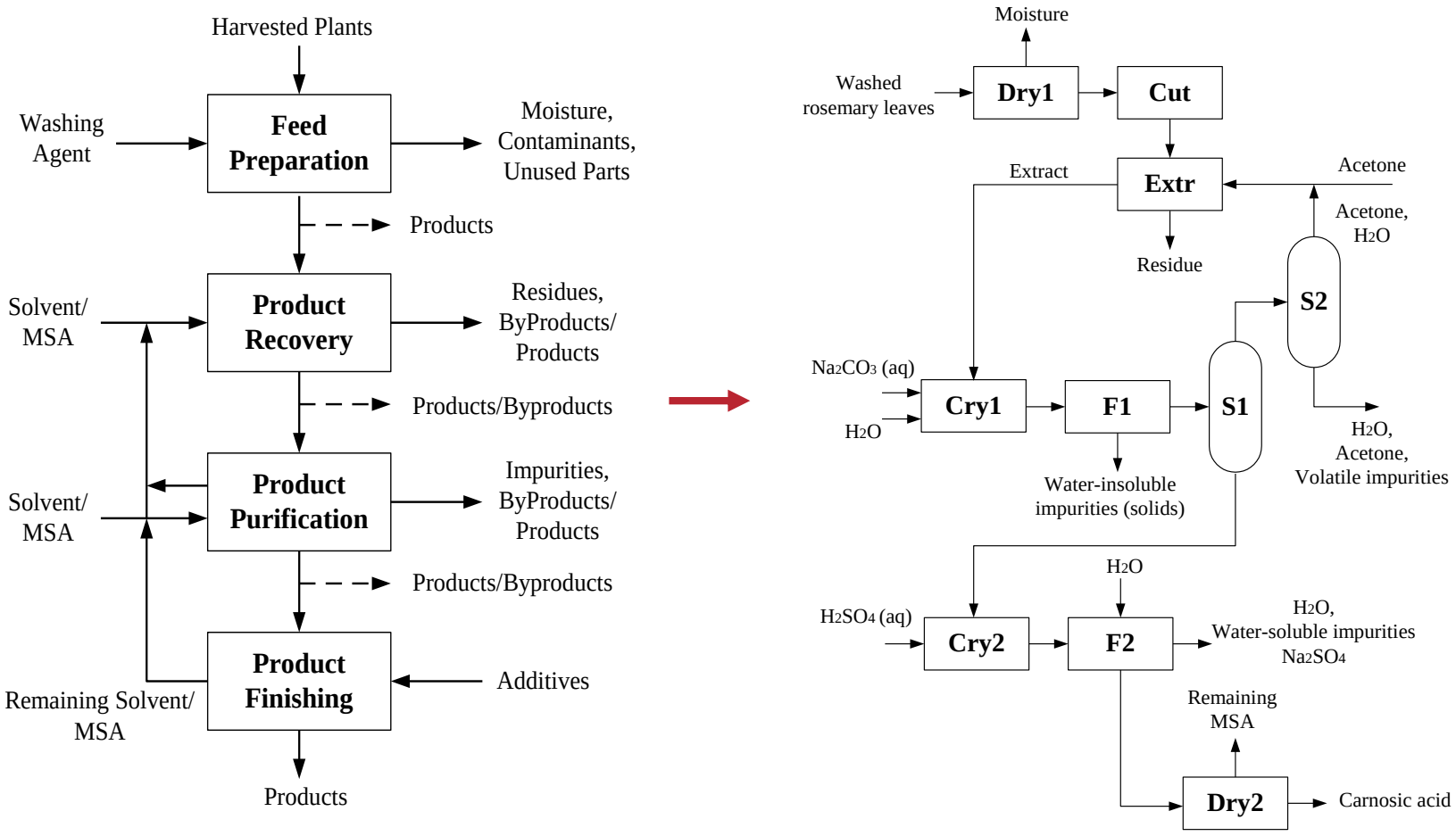


Components	sep.-tech.	Gasadsorption	Flash/evaportn	Stripping	
PROPYLENE /	rel. prop.	8, 20.	22.	19.	
Components	sep.-tech.	Gasadsorption	Flash/evaportn		
PROPYLENE /	rel. prop.	8.	7, 22.		
Components	sep.-tech.	Absorption	Gasadsorption	Flash/evaportn	
PROPYLENE /	rel. prop.	19.	8, 20.	7, 22.	
Components	sep.-tech.	Gasadsorption	Flash/evaportn		
PROPYLENE /	rel. prop.	8, 20.	7, 22.		
Components	sep.-tech.	Gasadsorption	Distillation	Liquid membran	Pervaporation
DIETHYL-ETHE / ETHANOL	rel. prop.	8, 20.	7, 22.	9, 13, 19.	13, 19.
Components	sep.-tech.	Absorption	Gasadsorption	Crystalization	Distillation
DIETHYL-ETHE /	rel. prop.	19.	8, 20.	10.	7, 22.
Components	sep.-tech.	Gasadsorption	Distillation	Liquid membran	Pervaporation
DIETHYL-ETHE /	rel. prop.	8, 20.	7, 22.	9, 13, 19.	13, 19.
Components	sep.-tech.	Gasadsorption	Crystalization	Distillation	Extractiv dist
ETHANOL / WATER	rel. prop.	20.	10.	7, 22.	7.
Components	sep.-tech.	Gasadsorption	Extractiv dist	Liquid membran	Pervaporation
ETHANOL /	rel. prop.	20.	7, 22.	9, 13.	13, 19.
Components	sep.-tech.	Gasadsorption	Crystalization	Distillation	Extractiv dist

Superstructure representation & flowsheet selection

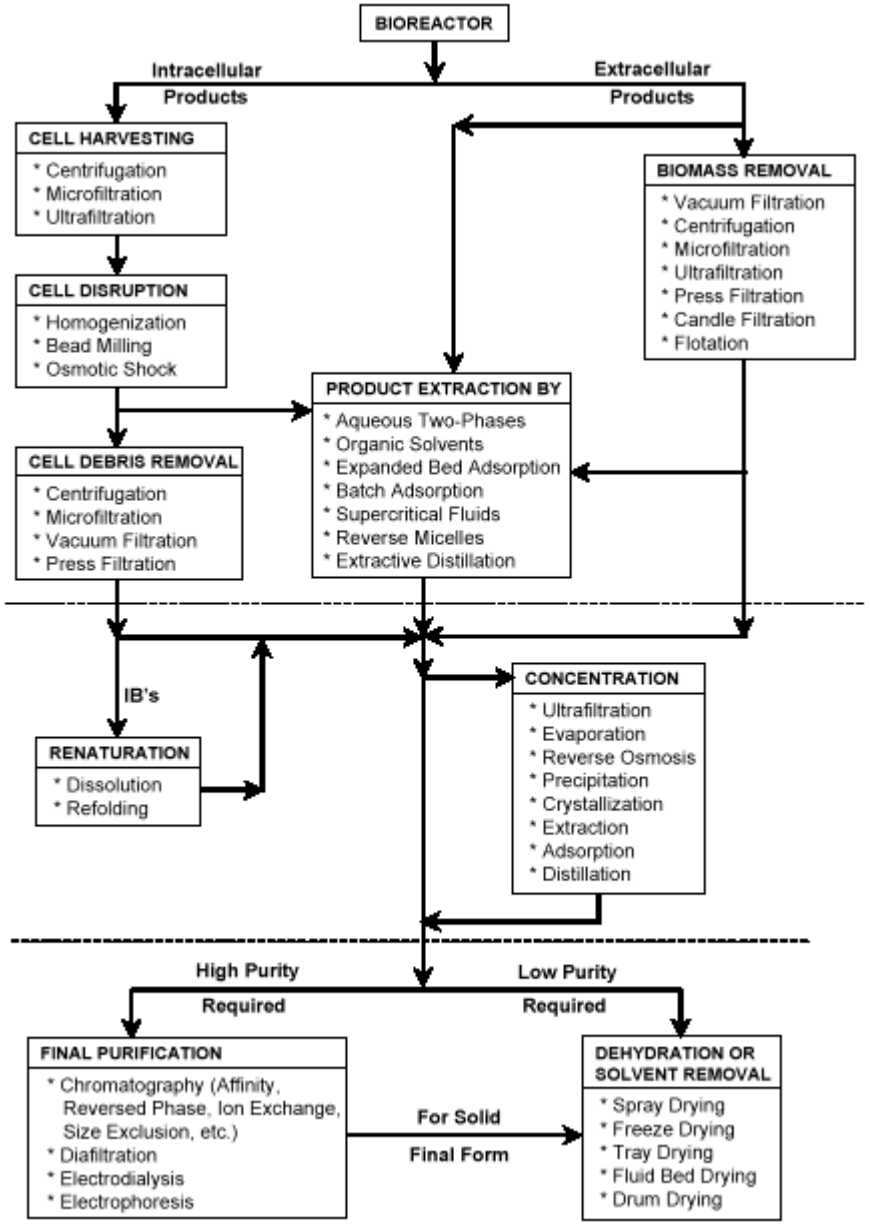


Special Flowsheet Generation for Specialty Chemical Products



Example: Manufacture of Carnosic acid by recovering it from popular herbs (Harjo et al 2004)

Generalized block diagram for downstream processing (bioprocess)



Downstream Processing: Recovery & purification of Insulin

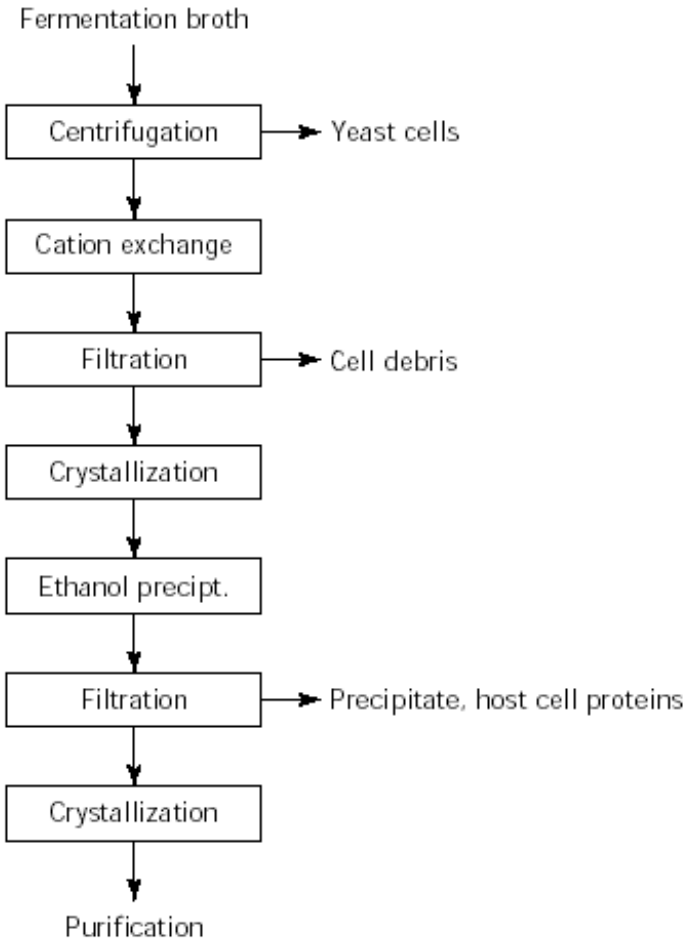


Figure 1. Flow chart of recovery process.

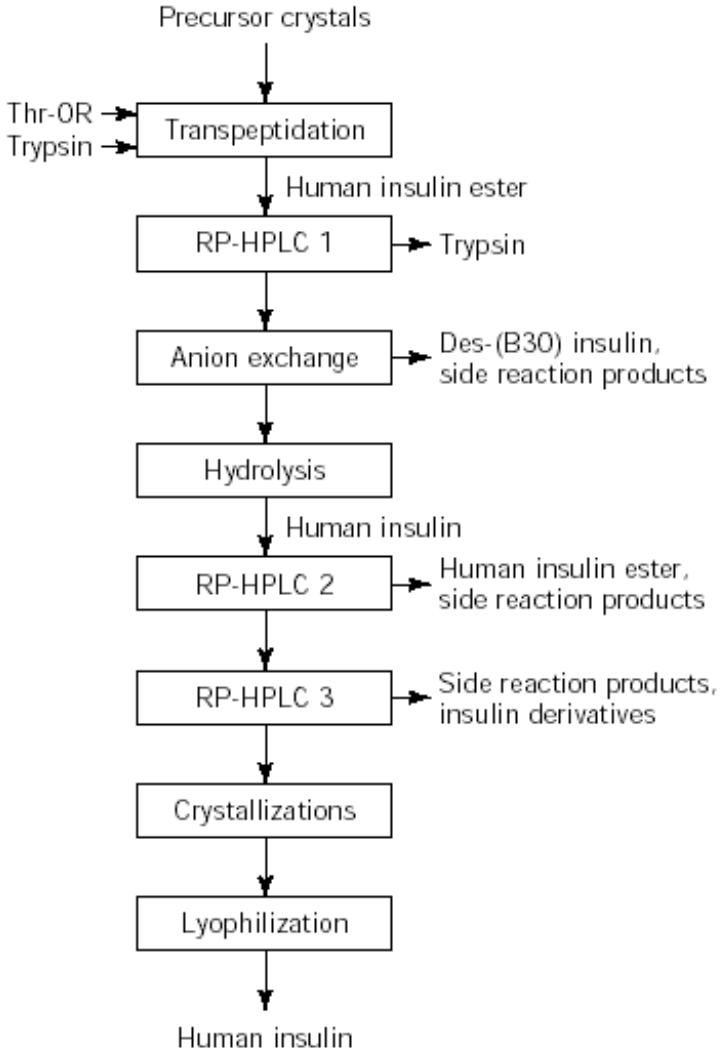


Figure 4. The purification process.

Example of process synthesis: HDA-process

- **Hydroalkylation of Toluene to Benzene – generate flowsheet using the hierarchical decomposition approach**

Benzene from Toluene Process

Tutorial exercise in class

Reactions:

Toluene + H2 $\rightarrow$ Benzene + CH4

2 Benzene $\leftrightarrow$ Biphenyl + H2

Benzene production = 265 kmol/h
Product purity > 99.9%
Toluene feed, liquid at 300 K
H2 feed (95% H2, 5% CH4 at 311 K
Toluene conversion, 75%
Selectivity, 0.9694
H2/aromatics = 5 reactor inlet
Temperature, 639 K
Pressure, 34 atm

	Tb	Tc	ρ_L	Pv	Tm
	K	K		at 300 K	K
H2	20.39	33.19	0.03	4×10^7	13.95
CH4	111.66	190.56	0.04	1.8×10^7	90.69
B	353.24	562.16	0.09	14000	278.68
T	383.78	591.80	0.10	4158	178.18
BP	529.25	789.26	0.15	-	342.37

ρ_L is molar liquid density in kmol/m3

Pv is vapor pressure at 300 k in Bar

Home Exercise

- **Production of Maleic Anhydride – generate flowsheet using the hierarchical decomposition approach**
- **Downstream separation of a bio-process**

MA from n-Butane Process

Catalyst VPO

$$2C_4H_{10} + 7O_2 \rightarrow 2C_4H_2O_3 + 8H_2O$$
$$2C_4H_{10} + 9O_2 \rightarrow 8CO + 10H_2O$$
$$2C_4H_{10} + 13O_2 \rightarrow 8CO_2 + 10H_2O$$
$$C_4H_2O_3 + 3O_2 \rightarrow 4CO_2 + H_2O$$
$$C_4H_2O_3 + O_2 \rightarrow 4CO + H_2O$$

n-butane conversion, 85%
MA Yield, 60%
Air/n-butane, ~ 62 (moles)
Temperature, 400°C
Pressure, 150 kPa

	Tb	Tm	D_L	Pv(300)
MA	475	326	13.8	-
CO	82	68	-	252
CO2			15	66
O2	90	54	-	274
H2O	373	273	55	0.035
N-C4	274	134	9.8	2.6

D_L is liquid density at 300 K in kmol/m3

Pv is vapor pressure at 300 k in Bar