CHEMICAL PROCESS INDUSTRY

- **LECTURE 2**
- **Process Creation**

Process Creation

- **Preliminary Database Creation**
  - to assemble data to support the design.
- **Experiments**
  - often necessary to supply missing database items or verify crucial data.
- **Preliminary Process Synthesis**
  - top-down approach.
  - to generate a "synthesis tree" of design alternatives.
  - illustrated by the synthesis of processes for the manufacture of VCM.
- **Development of Base-case Design**
  - focusing on the most promising alternative(s) from the synthesis tree.

Ref: Seider, Seader and Lewin (1999), Chapter 2

Preliminary Database Creation

- Thermophysical property data
  - physical properties
  - phase equilibria (VLE data)
  - Property prediction methods
- Environmental and safety data
  - toxicity data
  - flammability data
- Chemical Prices
  - e.g. as published in the *Chemical Marketing Reporter*
- Experiments
  - to check on crucial items above

Literature and Information Sources

Company context - employees, company files, open literature provide :

Product info (related), thermophysical properties, transport data, flowsheets, equipment descriptions, process models.

National Laboratories and Research Institute Reports e.g. SRI International, NIST, NIOSH.

Encyclopedias (technical, chemical process and technology).

Handbooks and Reference Books (Perry's Chemical Engineer's Handbook, CRC Handbook of Physics and Chemistry)

Journals (Book format, electronic format)

Indexes (INSPEC, COMPENDEX, SCIENCE CITATION INDEX)

Patents (U.S. Patent Office www.uspto.gov/patft)

Auxiliary Studies (e.g. technical feasibility, marketing, business related)

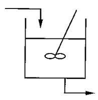
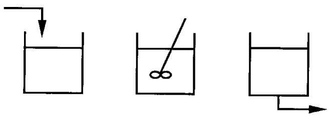
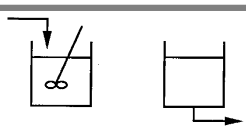
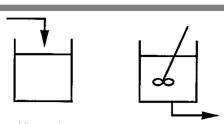
Innovation (e.g 3M)

Preliminary Process Synthesis

Synthesis of chemical processes involves:

- Selection of processing mode: continuous or batch
- Fixing the chemical state of raw materials, products, and by-products, noting the differences between them.
- Process operations (unit operations) - flowsheet building blocks
- Synthesis steps -
  1. Eliminate differences in molecular types
  2. Distribute chemicals by matching *sources* and *sinks*
  3. Eliminate differences in composition
  4. Eliminate differences in temperature, pressure and phase
  5. Integrate tasks (combine *tasks* into *unit operations*)

Continuous or batch processing?

	Continuous
	Batch
	Fed-batch
	Batch-product removal

The Chemical State

- Decide on the raw material and product specifications (*states*):
  - ✧ Mass (flow rate)
  - ✧ Composition (mole or mass fraction of each chemical species having a unique molecular type)
  - ✧ Phase (solid, liquid, or gas)
  - ✧ Form (e.g., particle-size distribution and particle shape)
  - ✧ Temperature
  - ✧ Pressure

Process Operations

- Chemical reaction
  - – Positioning in the flowsheet involves many considerations (conversion, rates, etc.), related to T and P at which the reaction are carried out.
- Separation of chemicals
  - – needed to resolve difference between the desired composition of a product stream and that of its source. Selection of the appropriate method depends on the differences of the physical properties of the chemical species involved.
- Phase separation
- Change of temperature
- Change of pressure
- Change of phase
- Mixing and splitting of streams and branches

Synthesis Steps

Synthesis Step	Process Operation
❶ Eliminate differences in molecular types	Chemical reaction
❷ Distribute chemicals by matching *sources* and *sinks*	Mixing
❸ Eliminate differences in composition	Separation
❹ Eliminate differences in temperature, pressure and phase	Temperature, pressure and phase change
❺ Integrate tasks (combine *tasks* into *unit operations*)	

Process Creation

Example 1:

Vinyl Chloride Manufacture

Assess Primitive Problem

- Process design begins with a primitive design problem that expresses the *current situation* and provides an *opportunity* to satisfy a societal need.
- Normally, the primitive problem is examined by a small design team, who begins to assess its possibilities, to refine the problem statement, and to generate more specific problems:
  - Raw materials - available in-house, can be purchased or need to be manufactured?
  - Scale of the process (based upon a preliminary assessment of the current production, projected market demand, and current and projected selling prices)
  - Location for the plant
- Refined through meetings with engineering technical management, business and marketing.
- *Brainstorming* to generate alternatives

Example: VC Manufacture

- To satisfy the need for an additional 800 MMlb/yr of VCM, the following plausible alternatives might be generated:

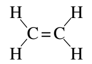
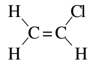
  Alternative 1. A competitor's plant, which produces 2 MMM lb/yr of VCM and is located about 100 miles away, might be expanded to produce the required amount, which would be shipped. In this case, the design team projects the purchase price and designs storage facilities.

  Alternative 2. Purchase and ship, by pipeline from a nearby plant, chlorine from the electrolysis of NaCl solution. React the chlorine with ethylene to produce the monomer and HCl as a byproduct.

  Alternative 3. Since the existing company produces HCl as a byproduct in large quantities are produced, HCl is normally available at low prices. Reactions of HCl with acetylene, or ethylene and oxygen, could produce 1,2-dichloroethane, an intermediate that can be cracked to produce vinyl chloride.

❶ Eliminate differences in molecular types

Chemicals participating in VC Manufacture:

Chemical	Molecular weight	Chemical formula	Chemical structure
Acetylene	26.04	C_2H_2	H-C≡C-H
Chlorine	70.91	Cl_2	Cl-Cl
1,2-Dichloroethane	98.96	$C_2H_4Cl_2$	Cl Cl | | H-C-C-H | | H H
Ethylene	28.05	C_2H_4	
Hydrogen chloride	36.46	HCl	H-Cl
Vinyl chloride	62.50	C_2H_3Cl	

Selection of pathway to VCM (1)

❶ Direct chlorination of ethylene:

$$C_2H_4 + Cl_2 \rightarrow C_2H_3Cl + HCl \qquad (2.1)$$

Advantages:

- Attractive solution to the specific problem denoted as Alternative 2 in analysis of primitive problem.
- Occurs spontaneously at a few hundred °C.

Disadvantages:

- Does not give a high yield of VC without simultaneously producing large amounts of by-products such as dichloroethylene
- Half of the expensive chlorine is consumed to produce HCl by-product, which may not be sold easily.

Selection of pathway to VCM (2)

❷ Hydrochlorination of acetylene:

$$C_2H_2 + HCl \rightarrow C_2H_3Cl \qquad (2.2)$$

Advantages:

- This exothermic reaction is a potential solution for the specific problem denoted as Alternative 3. It provides a good conversion (98%) of C_2H_2 VC in the presence of $HgCl_2$ catalyst impregnated in activated carbon at atmospheric pressure.
- These are fairly moderate reaction conditions, and hence, this reaction deserves further study.

Disadvantages:

- Flammability limits of C_2H_2 (2.5 ⟶100%)

Selection of pathway to VCM (3)

❸ Thermal cracking of $C_2H_4Cl_2$ from chlorination of C_2H_4:

$$C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2 \qquad (2.3)$$
$$C_2H_4Cl_2 \rightarrow C_2H_3Cl + HCl \qquad (2.4)$$
$$C_2H_4 + Cl_2 \rightarrow C_2H_3Cl + HCl \qquad (2.1)$$

Advantages:

- Conversion of ethylene to 1,2-dichloroethane in exothermic reaction (2.3) is ≈98% at 90 °C and 1 atm with a Friedel-Crafts catalyst such as $FeCl_3$. This intermediate is converted to vinyl chloride by thermal cracking according to the endothermic reaction (2.4), which occurs spontaneously at 500 °C with conversions as high as 65% (Alternative 2).

Disadvantage:

- Half of the expensive chlorine is consumed to produce HCl by-product, which may not be sold easily.

Selection of pathway to VCM (4)

❹ Thermal Cracking of $C_2H_4Cl_2$ from Oxychlorination of C_2H_4:

$$C_2H_4 + 2HCl + \tfrac{1}{2}O_2 \rightarrow C_2H_4Cl_2 + H_2O \quad (2.5)$$
$$C_2H_4Cl_2 \rightarrow C_2H_3Cl + HCl \quad (2.4)$$
$$C_2H_4 + HCl + \tfrac{1}{2}O_2 \rightarrow C_2H_3Cl + H_2O \quad (2.6)$$

Advantages:

- Highly exothermic reaction (2.5) achieves a 95% conversion to $C_2H_4Cl_2$ in the presence of $CuCl_2$ catalyst, followed by pyrolysis step (2.4) as Reaction Path 3.
- Excellent candidate when cost of HCl is low
- Solution for specific problem denoted as Alternative 3.

Disadvantages:

- Economics dependent on cost of HCl

Selection of pathway to VCM (5)

❺ Balanced Process for Chlorination of Ethylene:

$$C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2 \quad (2.3)$$
$$C_2H_4 + 2HCl + \tfrac{1}{2}O_2 \rightarrow C_2H_4Cl_2 + H_2O \quad (2.5)$$
$$2C_2H_4Cl_2 \rightarrow 2C_2H_3Cl + 2HCl \quad (2.4)$$
$$2C_2H_4 + Cl_2 + \tfrac{1}{2}O_2 \rightarrow 2C_2H_3Cl + H_2O \quad (2.7)$$

Advantages:

- Combination of Reaction Paths 3 and 4 - addresses Alternative 2.
- All Cl_2 converted to VC
- No by-products!

Evaluation of Alternative Pathways

- Reaction Path ❶ is eliminated due its low selectivity.
- This leaves four alternative paths, to be compared first in terms of Gross Profit.

Chemical Bulk Prices

Chemical	Cost (cents/lb)
Ethylene	18
Acetylene	50
Chlorine	11
Vinyl chloride	22
Hydrogen chloride	18
Water	0
Oxygen (air)	0

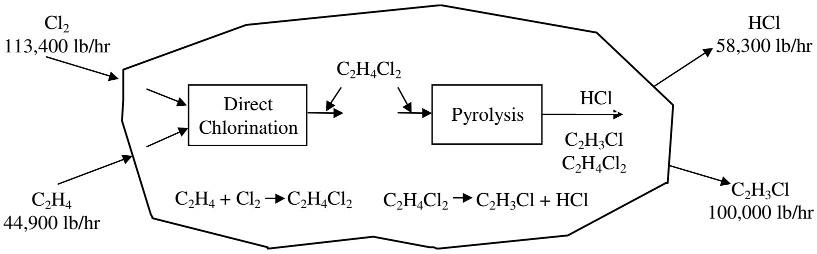
Computing Gross Profit

Reaction path ❸	C_2H_4	+	Cl_2	=	C_2H_3Cl	+	HCl
lb-mole	1		1		1		1
Molecular weight	28.05		70.91		62.50		36.46
lb	28.05		70.91		62.50		36.46
lb/lb of vinyl chloride	0.449		1.134		1		0.583
cents/lb	18		11		22		18

Gross profit = 22(1) + 18(0.583) - 18(0.449) - 11(1.134) = 11.94 cents/lb VC

Reaction Path	Overall Reaction	Gross Profit (cents/lb of VC)
❷	$C_2H_2 + HCl = C_2H_3Cl$	-9.33
❸	$C_2H_4 + Cl_2 = C_2H_3Cl + HCl$	11.94
❹	$C_2H_4 + HCl + \frac{1}{2}O_2 = C_2H_3Cl + H_2O$	3.42
❺	$2C_2H_4 + Cl_2 + \frac{1}{2}O_2 = 2C_2H_3Cl + H_2O$	7.68

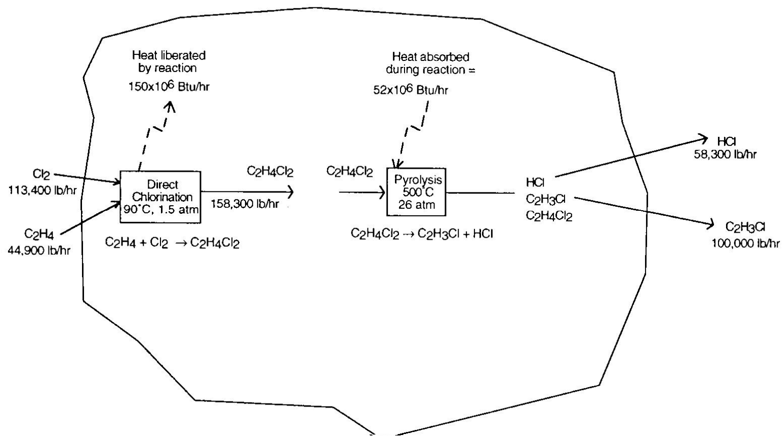
Preliminary Flowsheet for Path ❸



- 800 MM lb/year @ 330 days/y ⇒ 100,000 lb/hr VC
- On the basis of this principal *sink*, the HCl *sink* and reagent *sources* can be computed (each flow is 1,600 lbmol/h)
- ◎ Next step involves distributing the chemicals by matching *sources* and *sinks*.

❷ Distribute the chemicals

- A conversion of 100% of the C_2H_4 is assumed in the chlorination reaction.

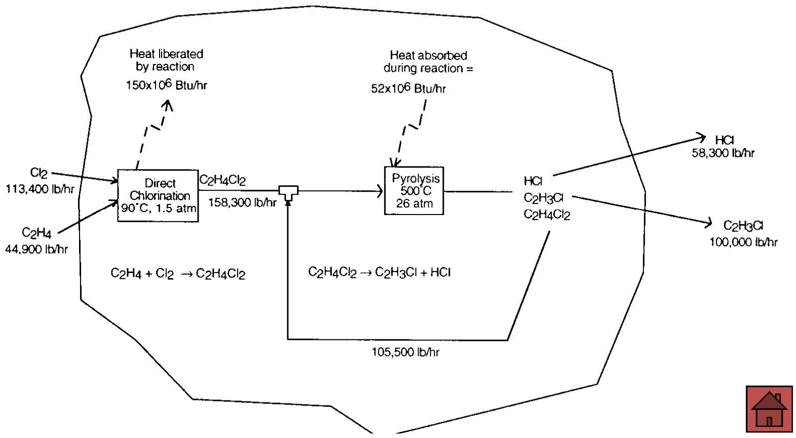


❷ Distribute the chemicals

- Only 60% of the $C_2H_4Cl_2$ is converted to C_2H_3Cl with a byproduct of HCl, according to Eqn. (2.4).
- To satisfy the overall material balance, 158,300 lb/h of C_2H_4Cl must produce 100,000 lb/h of C_2H_3Cl and 58,300 lb/h of HCl.
- But a 60% conversion only produces 60,000 lb/h of VC.
- The additional $C_2H_4Cl_2$ needed is computed by mass balance to equal: [(1 - 0.6)/0.6] x 158,300 or 105,500 lb/h.
- Its source is a recycle stream from the separation of C_2H_3Cl from unreacted $C_2H_4Cl_2$, from a mixing operation, inserted to combine the two sources, to give a total 263,800 lb/h.

❷ Distribute the chemicals

- The effluent stream from the pyrolysis operation is the source for the C_2H_3Cl product, the HCl by-product, and the $C_2H_4Cl_2$ recycle.



❷ Distribute the chemicals

- **Reactor pressure levels:**
  - Chlorination reaction: 1.5 atm is recommended, to eliminate the possibility of an air leak into the reactor containing ethylene.
  - Pyrolysis reaction: 26 atm is recommended by the B.F. Goodrich patent (1963) without any justification. Since the reaction is irreversible, the elevated pressure does not adversely affect the conversion. Most likely, the patent recommends this pressure to reduce the size of the pyrolysis furnace, although the tube walls must be considerably thicker and many precautions are necessary for operation at elevated pressures.
  - The pressure level is also an important consideration in selecting the separation operations, as will be discussed in the next synthesis step.

❸ Eliminate Differences in Composition

- The product of the chlorination reaction is nearly pure $C_2H_4Cl_2$, and requires no purification.
- In contrast, the pyrolysis reactor conversion is only 60%, and one or more separation operations are required to match the required purities in the C_2H_3Cl and HCl sinks.
- One possible arrangement is given in the next slide. The data below explains the design decisions made.

	Boiling point (°C)				Critical constants	
Chemical	1 atm	4.8 atm	12 atm	26 atm	T_c, °C	P_c, atm
HCl	-84.8	-51.7	-26.2	0	51.4	82.1
C_2H_3Cl	-13.8	33.1	70.5	110	159	56
$C_2H_4Cl_2$	83.7	146	193	242	250	50

Chemical	Boiling point (°C)				Critical constants	
	1 atm	4.8 atm	12 atm	26 atm	T_c,°C	P_c, atm
HCl	-84.8	-51.7	-26.2	0	51.4	82.1
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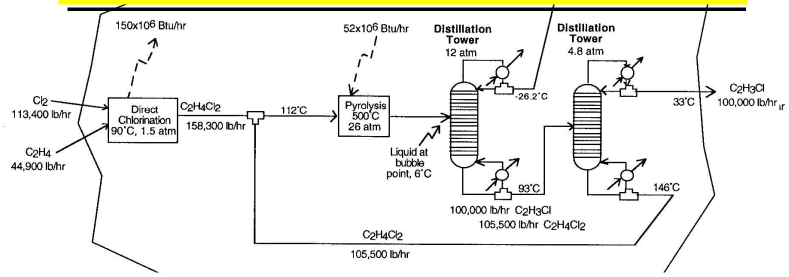
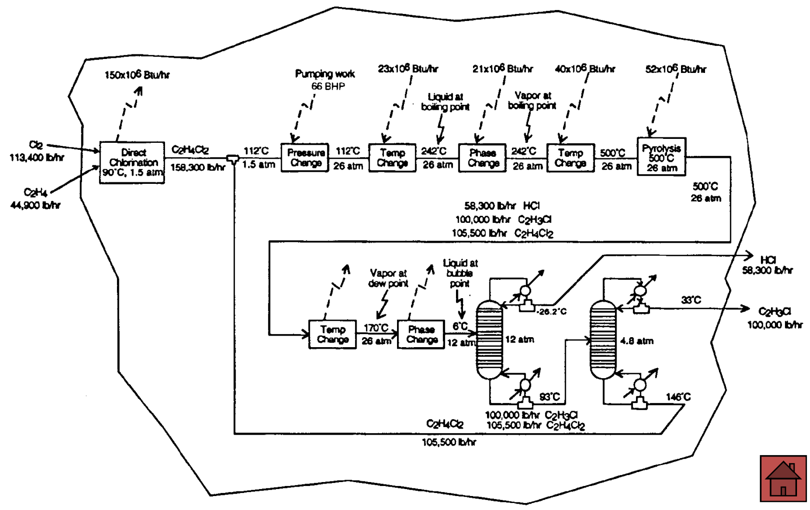
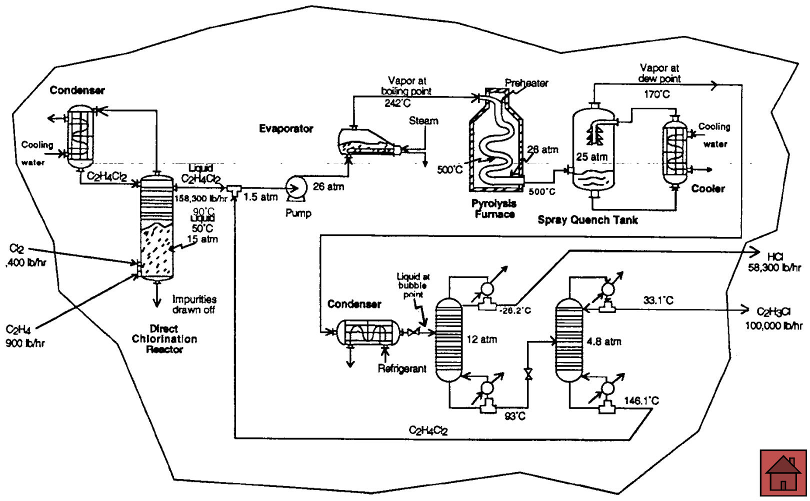


There may be other, possibly better alternative configurations, as discussed in Lecture 4 (Chapter 5).

❹ Eliminate differences in T, P and phase

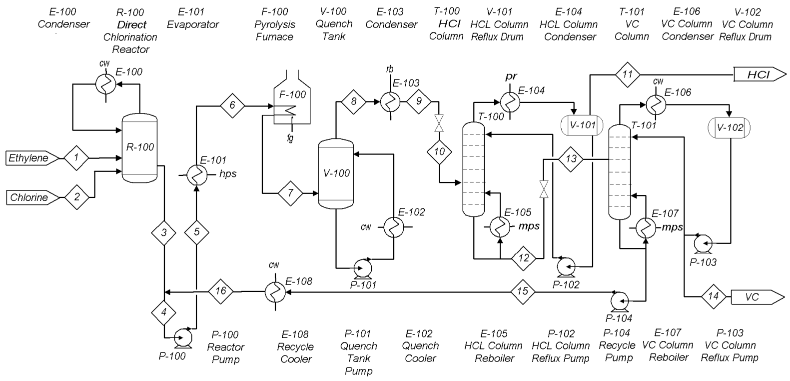


❺ Integrate tasks (*tasks ⇒ unit operations*)



Development of Base-case Design

Develop one or two of the more promising flowsheets from the synthesis tree for more detailed consideration.



Homework II

- Review assigned projects, form the project team, and submit the project design constraints and criteria

Project design: UMORE park is a 5,000-acre property located 25 miles southeast of the Twin Cities in Dakota County. The university is envisioned to build an environmental friendly community in the next two to three decades focusing on innovations in many areas for example renewable energy. Instead of changing agricultural land to metro blocks, we are making this fake projects to study the feasibility of producing ethanol, butanol or PLA from this agricultural land. Students are requested to estimate the annual agricultural products that can be generated from this land and provide an engineering design of a process to produce the targeted product. Please work in a big team to generate the overall economic feasibility study.

1. ethanol fermentation
2. ethanol distillation
3. butanol fermentation (ABE fermentation)
4. Butanol distillation
5. lactic acid fermentation
6. PLA production

Project design: Minnesota State Fair is one of the largest state fairs in the US and it attracts over one million visitors every year. The organization committee "wants" to build a demonstration process to teach the general public how we can convert our food waste oils to biodiesel. Please provide an engineering design of this project, working in a big team to generate the overall economic feasibility study.

1. biodiesel proudction --- oil transesterification
2. biodiesel separation
3. glyceral utilization