

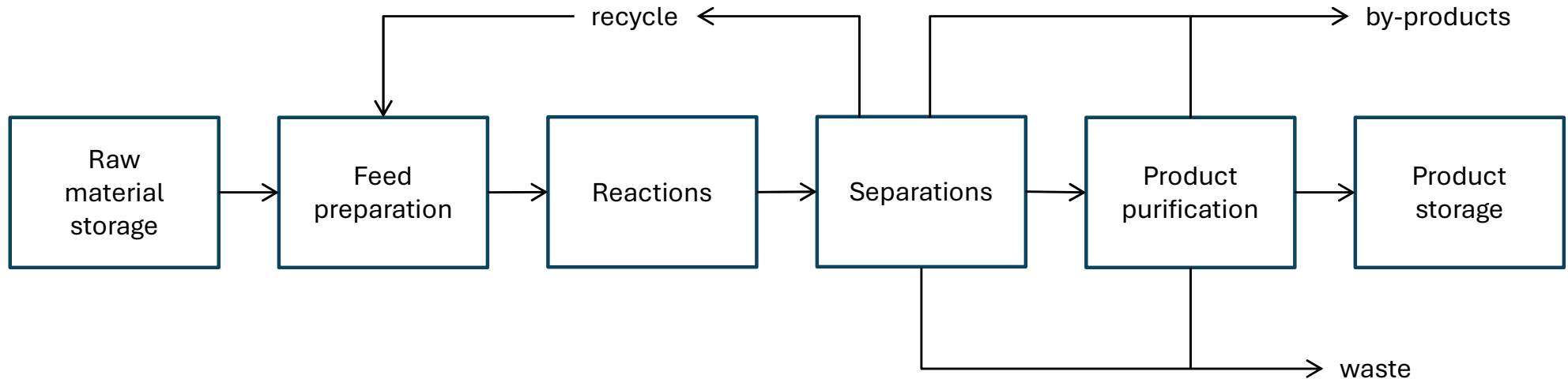
CH402 Chemical Engineering Process Design

Class Notes L13

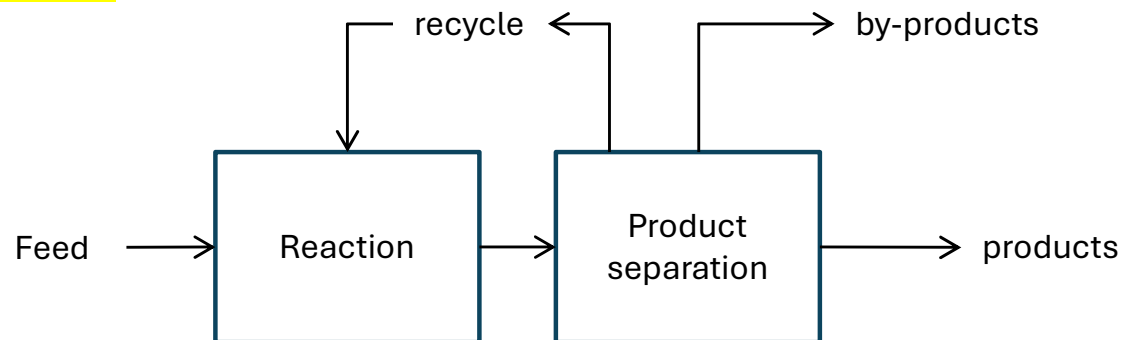
Flowsheet Synthesis and I/O Analysis

WPR1 Corrections – Due Friday 14 Feb 2359 at 40% recovery

Block Diagram of (all) Chemical Processes



“Function Diagram”



Q's may or may not be shown

Often simplified to this form.

Case Study - Vinyl Chloride Monomer (VCM) Production

47 million tons/y in 2025 worldwide

57 million tons/y in 2030 (est.)

3.87% growth to 2030

<https://www.mordorintelligence.com/industry-reports/vinyl-chloride-monomer-market>

12 US plants, average capacity is 667,000 t/y

J.A. Cowfer and M.B. Gorensek, 19 May 2006, Kirk-Othmer Encyclopedia of Chemical Technology,
<https://doi.org/10.1002/0471238961.2209142503152306.a01.pub2>

Emissions and toxicity

3 Feb 2023 East Palestine, OH

Vinyl chloride is highly flammable

Hydrogen chloride is highly corrosive

Continuous processing

page 132, > 50 mt/yr

Feedstocks are naphtha (50.8%), natural gas (27.2%), coal (17.2%), and other (4.7%)

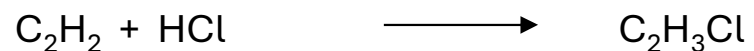
Kirk-Othmer, SRI, Wikipedia both have excellent articles

Known Vinyl Chloride Routes

Next step is a literature search – 5 Routes Identified

Kirk-Othmer, Wikipedia

(CH383)



Route 1

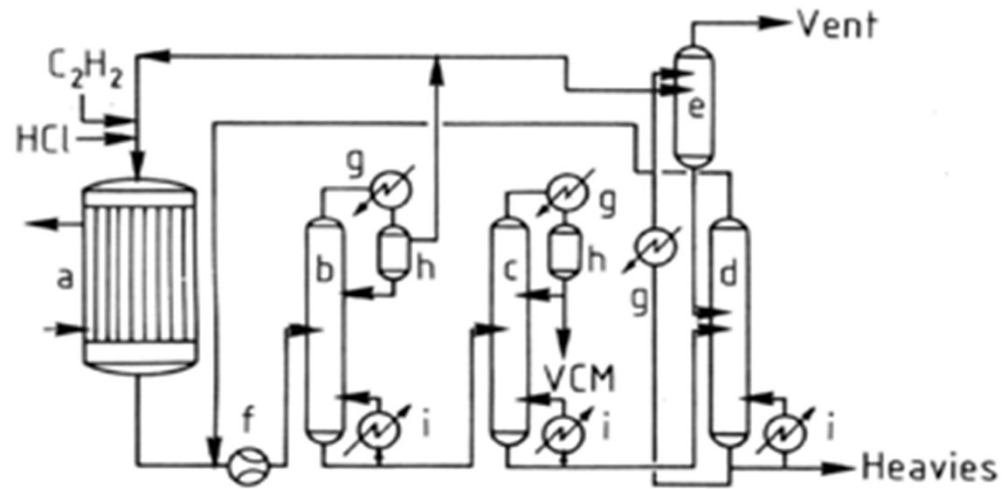
direct reaction of acetylene
(acetylene hydrochlorination)

Vinyl Chloride Process Flow Diagram

Ullmann's Encyclopedia of Industrial Chemistry

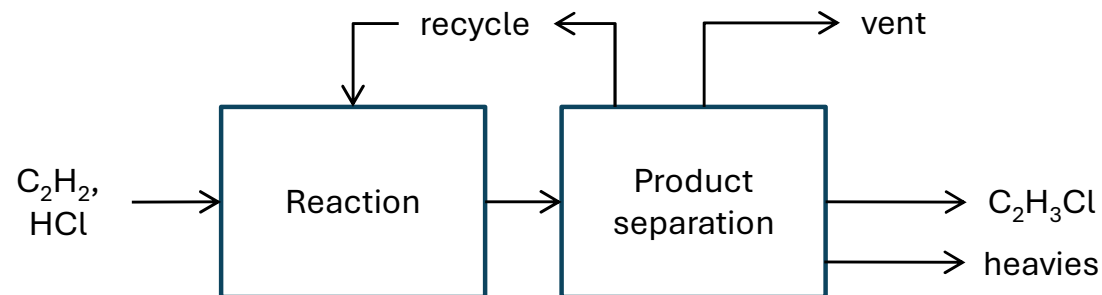
Dreher, L., Beutel, K.K., Myers, J.D., Lübke, T., Krieger, S., & Pottenger, L.H., Chloroethanes and Chloroethylenes. 1-81.

Process Flow Diagram (PFD)
Similar to CHEMCAD



- a) Reactor
- b) Lights column
- c) VCM column
- d) Heavy stripper
- e) Vent wash tower
- g) Condenser
- h) Reflux drum
- i) Reboiler

Function Diagram

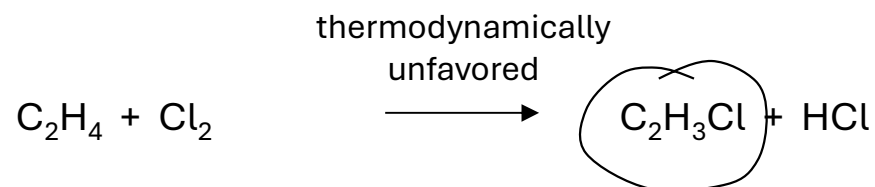


Known Vinyl Chloride Routes

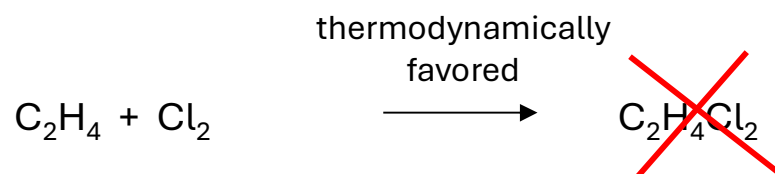
Kirk-Othmer, Wikipedia

Literature Search

(also CH383)



Route 2
direct chlorination of
ethylene (liquid phase)



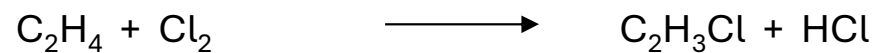
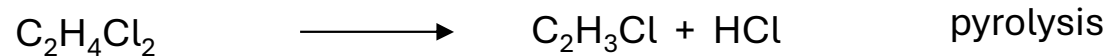
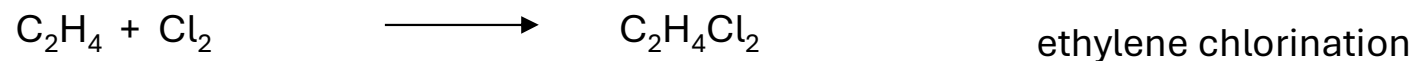
Not the product we want

Known Vinyl Chloride Routes

Kirk-Othmer, Wikipedia

Literature Search

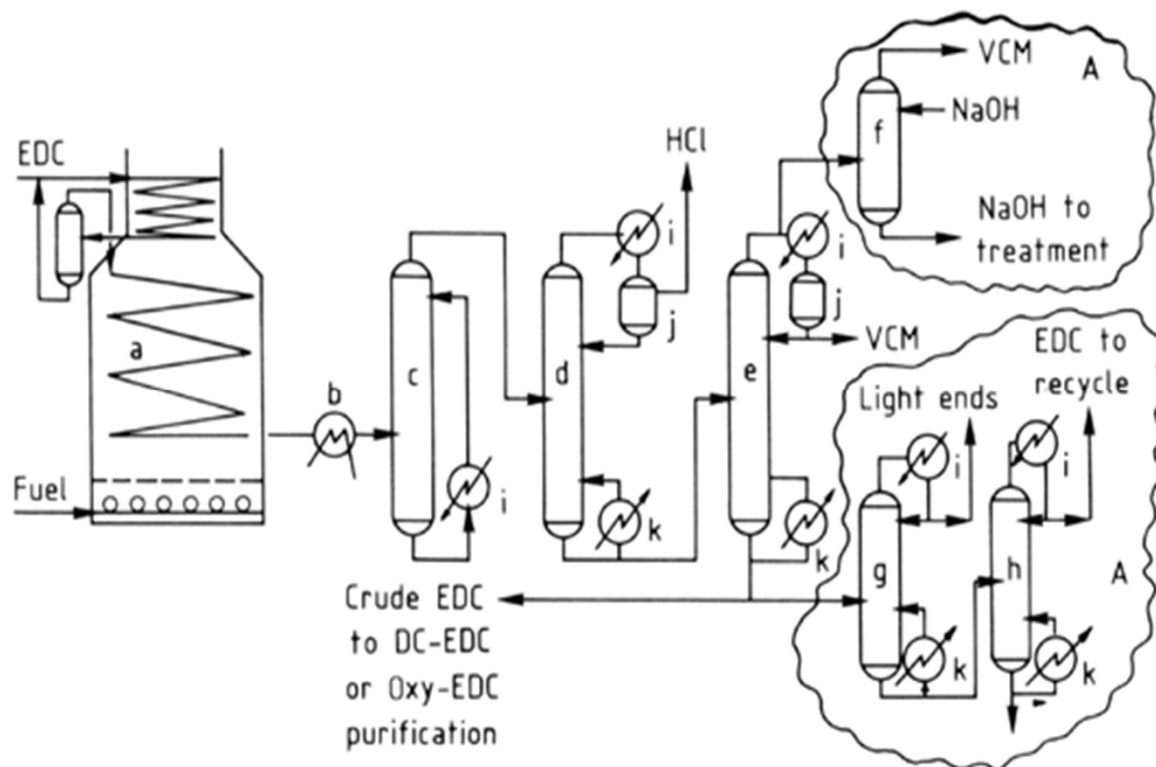
CH383



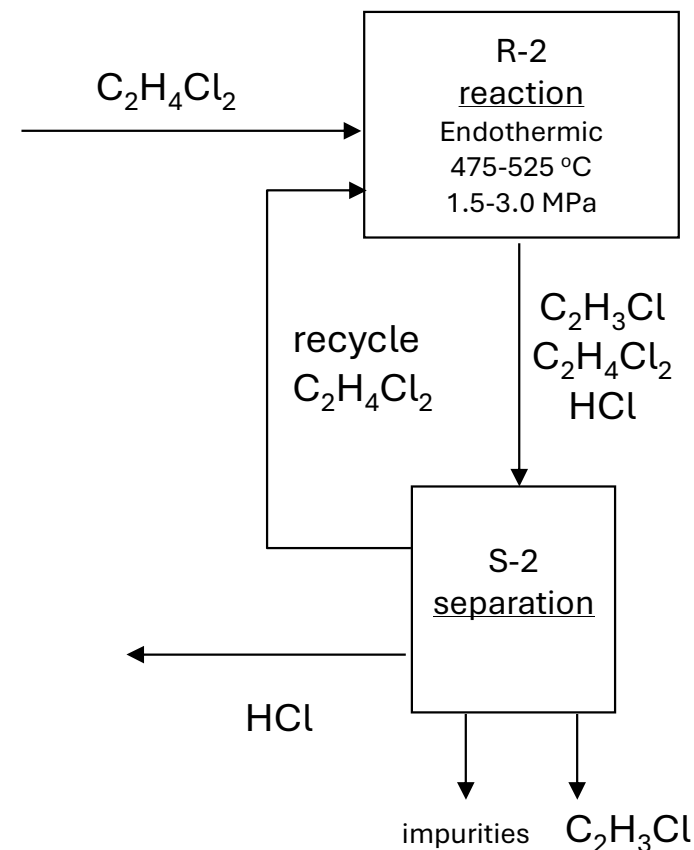
Route 3
direct chlorination + pyrolysis

Ethylene Dichloride (EDC) Pyrolysis

Process Flow Diagram (PFD)



Function Diagram



a) Crack furnace; b) Heat exchanger; c) Quench tower; d) HCl distillation tower; e) VCM purification tower; f) VCM wash tower; g) Light-end tower; h) EDC-heavy-end tower; i) Condenser; j) Reflux drum; k) Reboiler

Ullmann's Encyclopedia of Industrial Chemistry

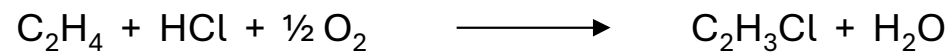
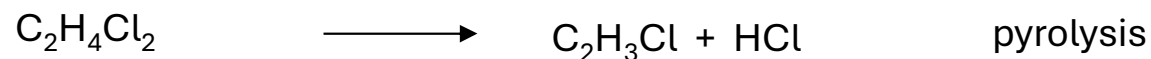
Dreher, L., Beutel, K. K., Myers, J. D., Lübke, T., Krieger, S., & Pottenger, L. H. Chloroethanes and Chloroethylenes. 1-81.

https://doi.org/10.1002/14356007.o06_o01.pub2

Known Vinyl Chloride Routes

Kirk-Othmer, Wikipedia

Literature Search



Route 4
oxychlorination + pyrolysis

Known Vinyl Chloride Routes

Kirk-Othmer, Wikipedia

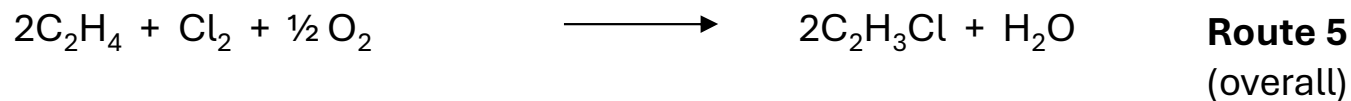
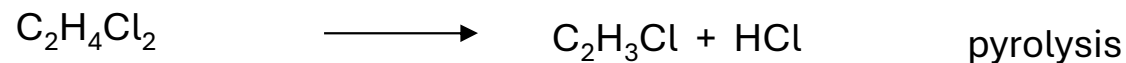
Literature Search



+



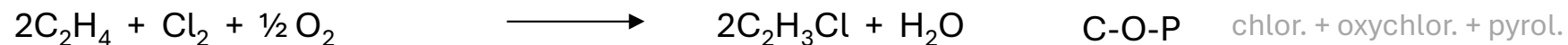
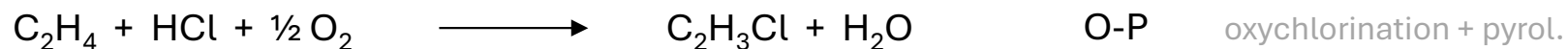
+



Known Vinyl Chloride Routes

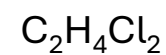
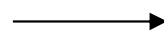
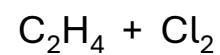
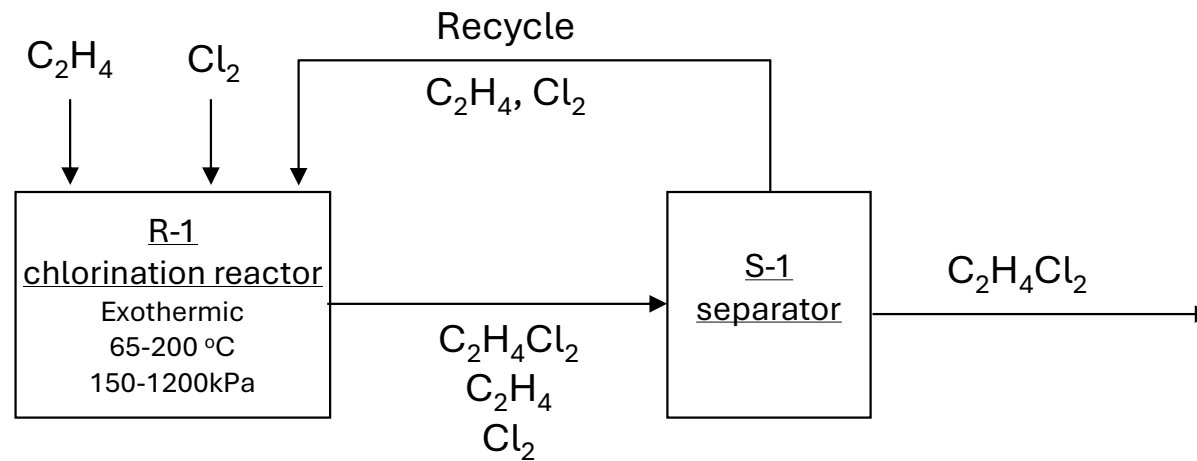
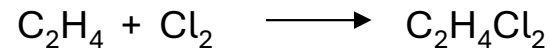
5 processes identified in literature survey

Summary



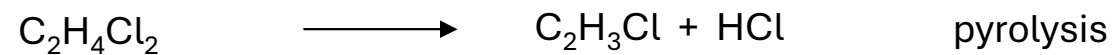
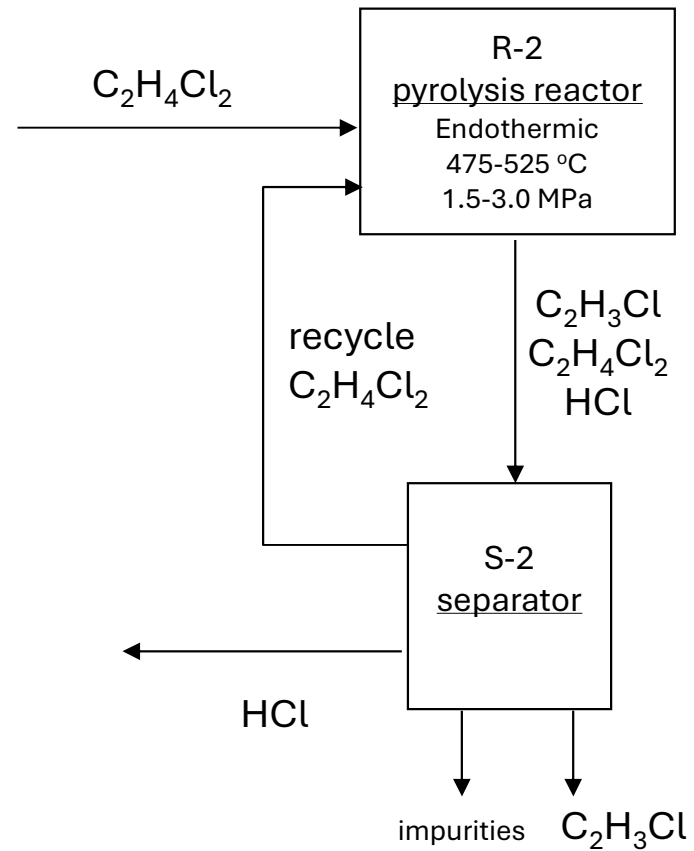
Functions Diagram – C – Direct Chlorination

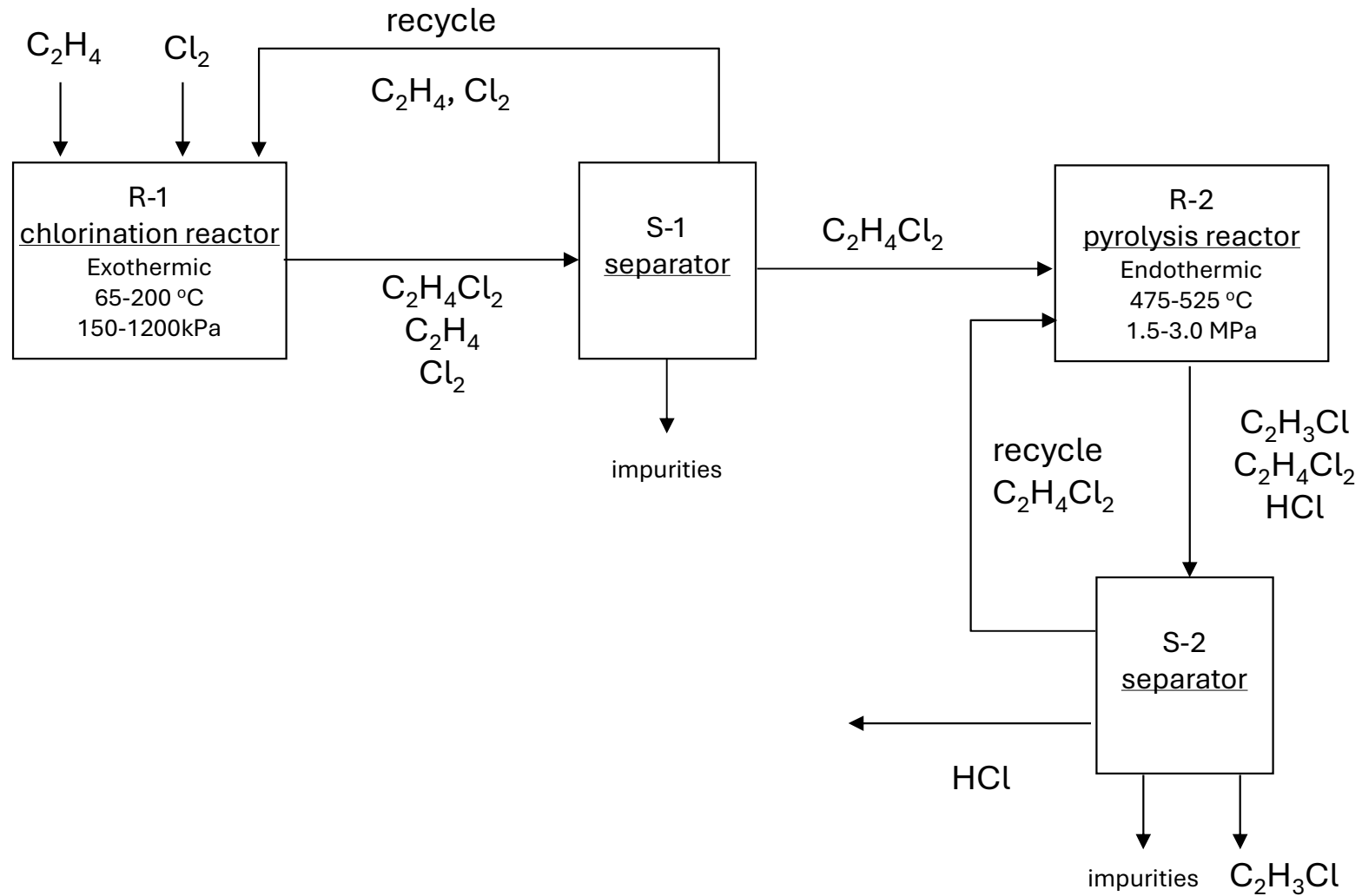
The utility of the functions diagram is that it can be used to build much larger processes.



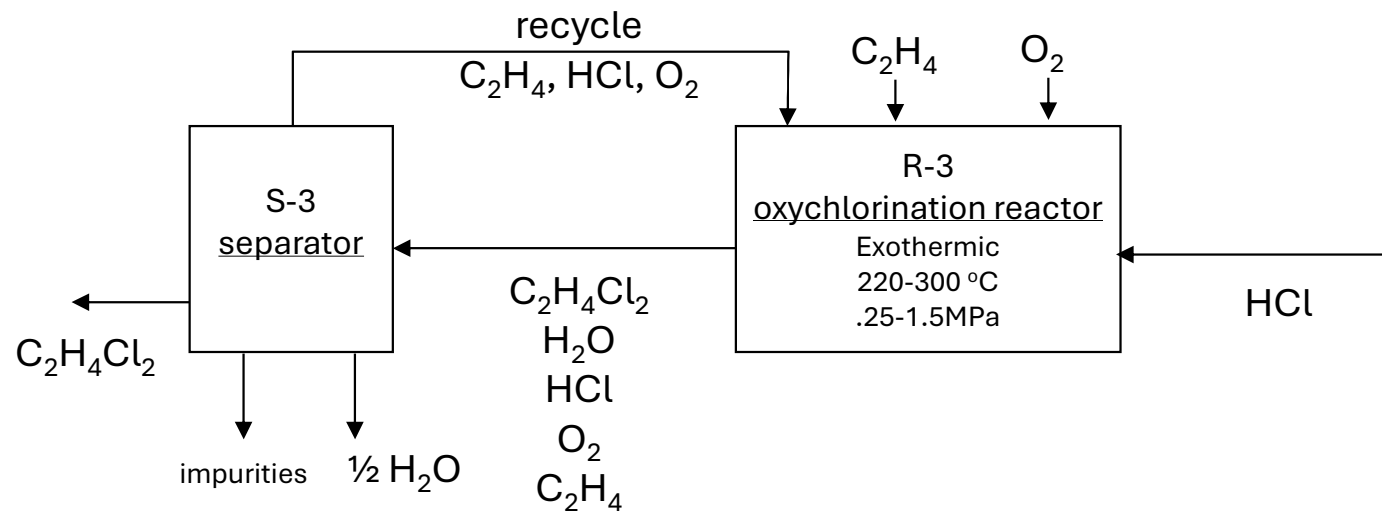
ethylene chlorination

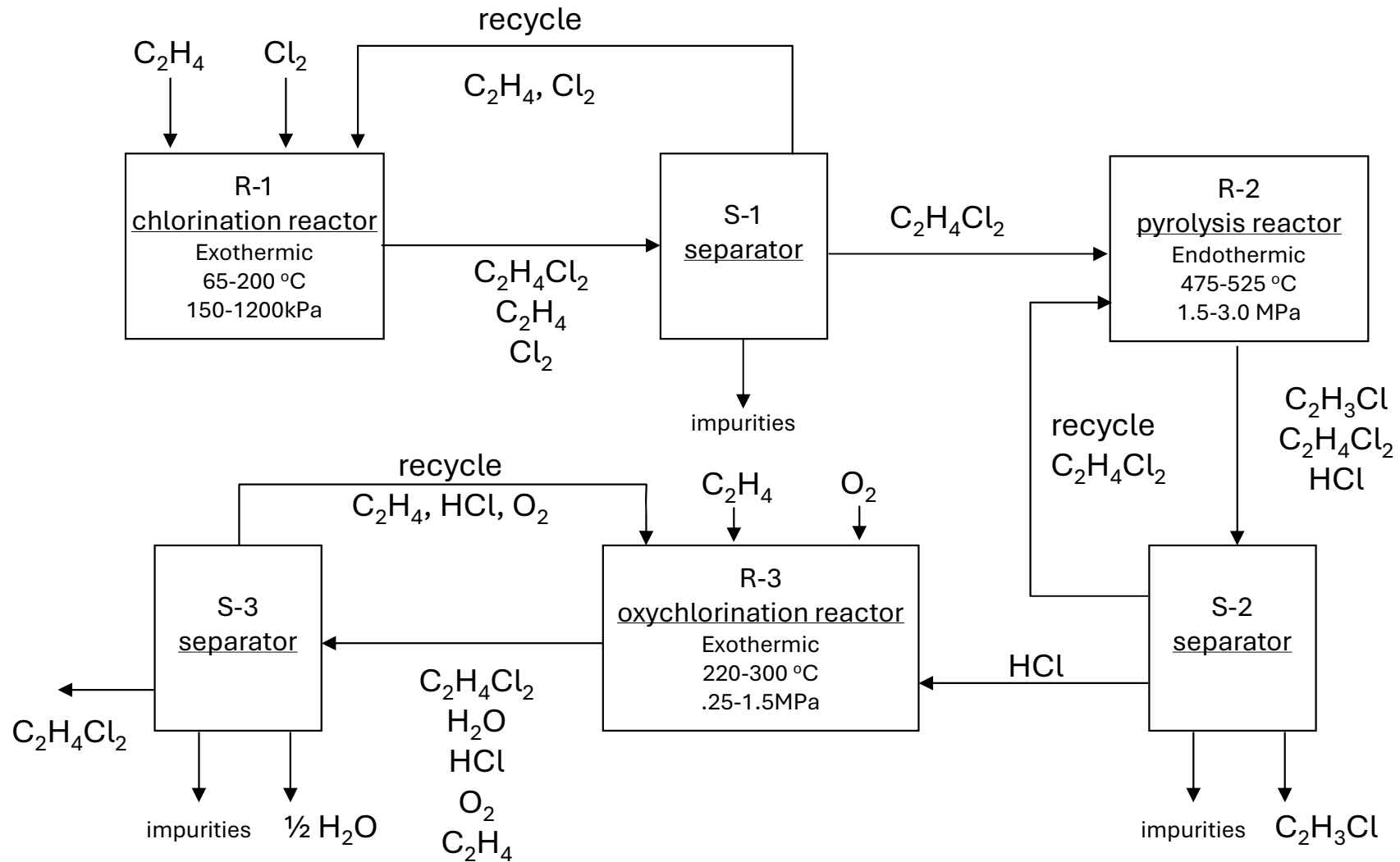
Functions Diagram – Pyrolysis

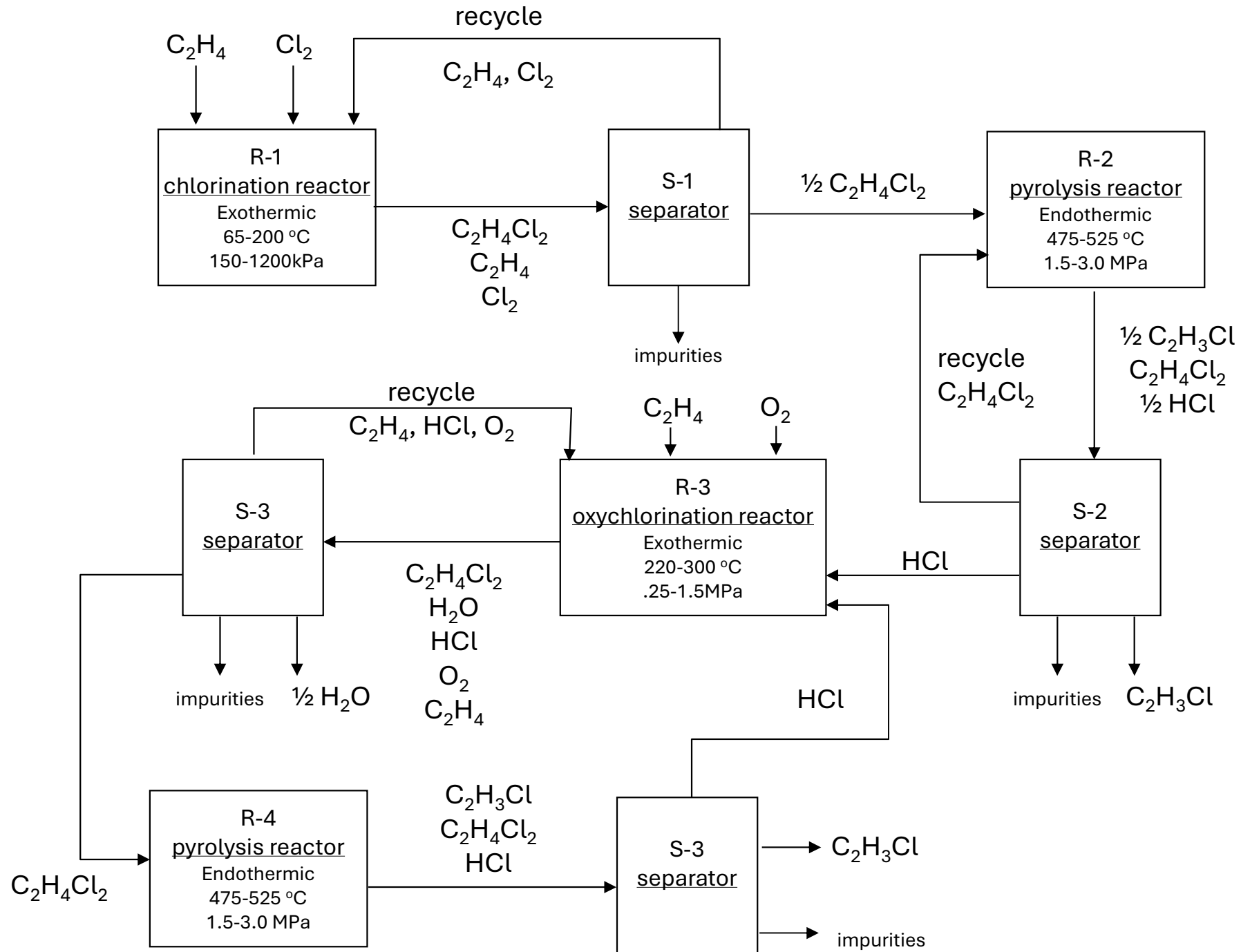


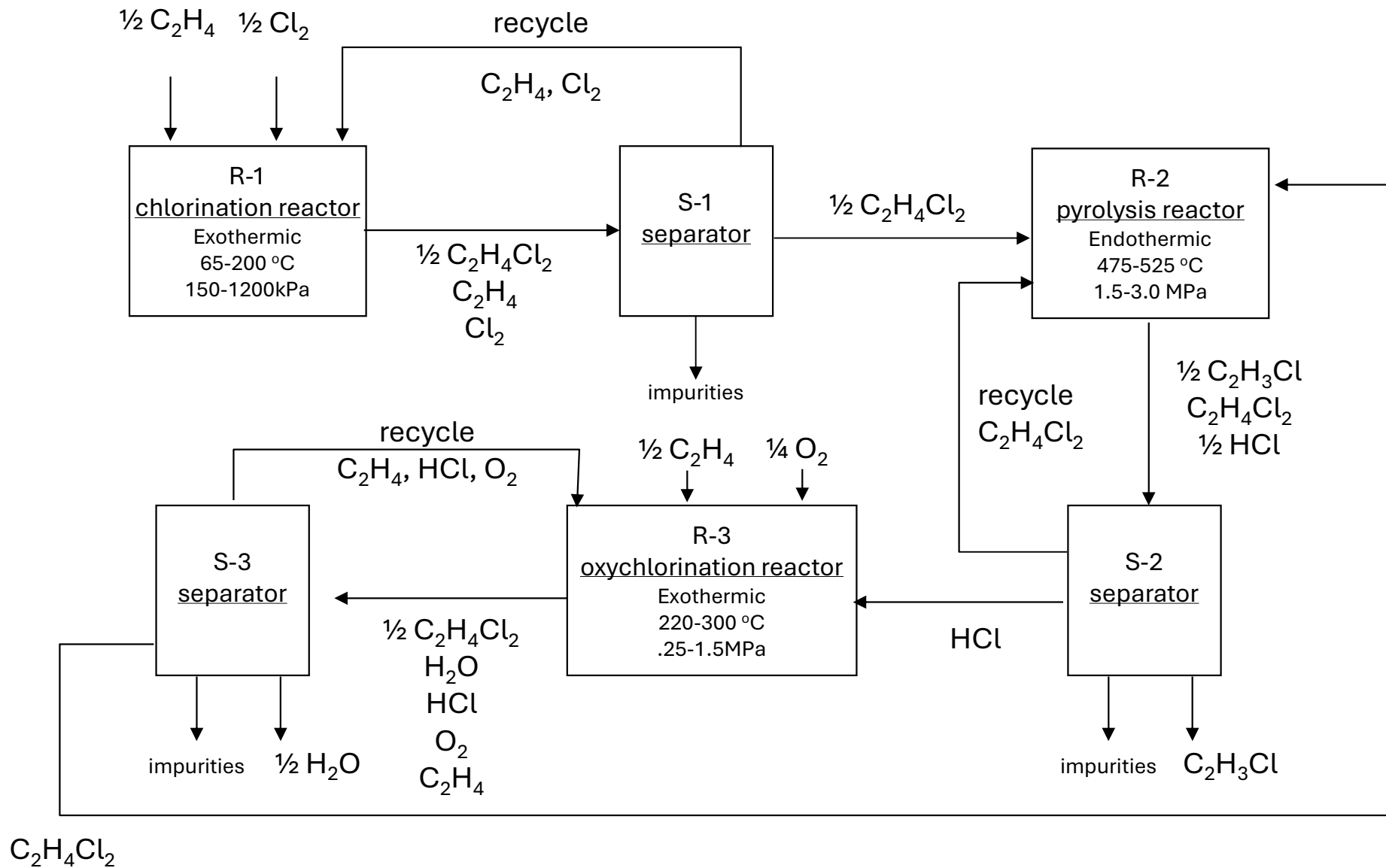


Functions Diagram – Oxychlorination



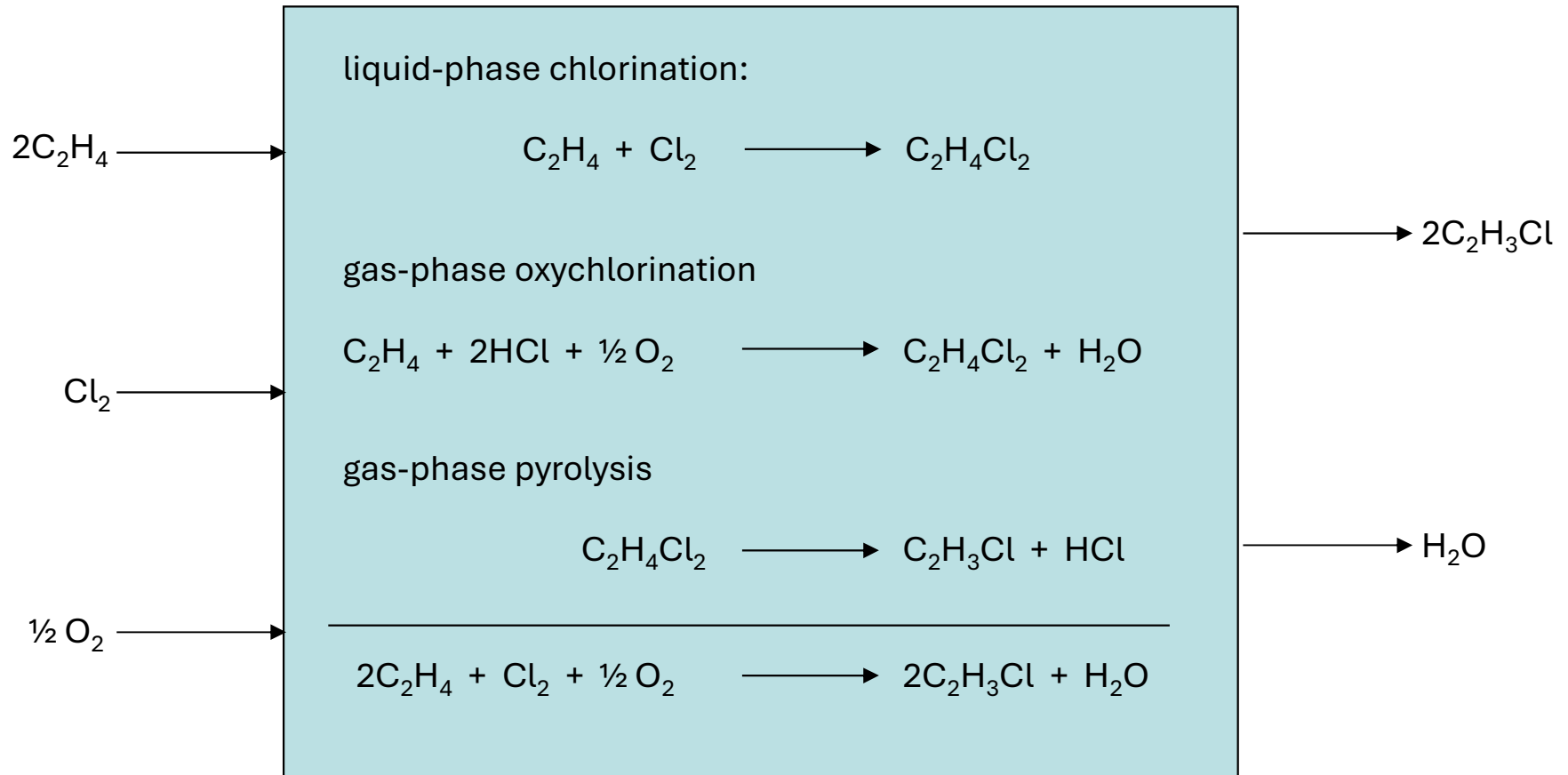






Input/Output Structure - Route 5 - COP

I/O box is frequently left blank



The I/O analysis allows us to assess the overall economics of the process.

Known Vinyl Chloride Routes

5 processes

				Reaction Path
$\text{C}_2\text{H}_2 + \text{HCl}$	\longrightarrow	$\text{C}_2\text{H}_3\text{Cl}$	A	1
$\text{C}_2\text{H}_4 + \text{Cl}_2$	\longrightarrow	$\text{C}_2\text{H}_3\text{Cl} + \text{HCl}$	C	2
$\text{C}_2\text{H}_4 + \text{Cl}_2$	\longrightarrow	$\text{C}_2\text{H}_3\text{Cl} + \text{HCl}$	C-P	3
$\text{C}_2\text{H}_4 + \text{HCl} + \frac{1}{2} \text{O}_2$	\longrightarrow	$\text{C}_2\text{H}_3\text{Cl} + \text{H}_2\text{O}$	O-P	4
$2\text{C}_2\text{H}_4 + \text{Cl}_2 + \frac{1}{2} \text{O}_2$	\longrightarrow	$2\text{C}_2\text{H}_3\text{Cl} + \text{H}_2\text{O}$	C-O-P	5

Economic Analysis is Based on I/O

Measures the economic “driving force”

Example 4-2, page 135

	A	B	C	D	E	F	G	H
1	Example 4-2. Compare product and raw material values based on 1kg of vinyl chloride							
2								
3				Reaction Path, kg/kg VC				
4	Species	MW, kg/kgmol	Price, \$/kg	1	2	3	4	5
5	Cl ₂	70.9	0.03	---	1.13	1.13	---	0.57
6	HCl	36.5	0.22	0.58	0.58	0.58	0.58	---
7	C ₂ H ₂	26.0	1.39	0.42	---	---	---	---
8	C ₂ H ₄	28.1	0.45	---	0.45	0.45	0.45	0.45
9	C ₂ H ₃ Cl	62.5	0.45	1.00	1.00	1.00	1.00	1.00
10	O ₂	32.0	0.04	---	---	---	0.26	0.13
11								
12	product value			\$0.45	\$0.58	\$0.58	\$0.45	\$0.45
13	reactant cost			\$0.71	\$0.24	\$0.24	\$0.34	\$0.22
14	excess value			-\$0.26	\$0.34	\$0.34	\$0.11	\$0.23

The bottom line represents \$/kg. If we know the kg/year, then we know the annual cash flow.

The I/O diagram for process 5 is shown in slide 19.

Bonus Op – 2 points – Complete the spreadsheet and submit pdf with PS6

Problem 4.13

- (a) Analyze the basic economics and show an I/O diagram for producing hydrogen from water, coal, and natural gas.
- (b) What production mode (batch or continuous) should be used to obtain production rates of 2×10^7 and 1×10^8 kg/y?

Electricity: \$0.05/kW·h
H₂: \$4.67/kg (Kirk-Othmer)
O₂: \$0.04/kg (Kirk-Othmer)
Coal: \$0.055/kg
Steam: \$0.008/kg
NG: \$0.13/kg

References are Kirk-Othmer and Ullman's

basis: 1kg of H₂

Use same approach as Example 4-13

Continuous versus Batch

page 132-133

Batch if:

production rate < 50 m.t./y

heavy fouling

biological processes

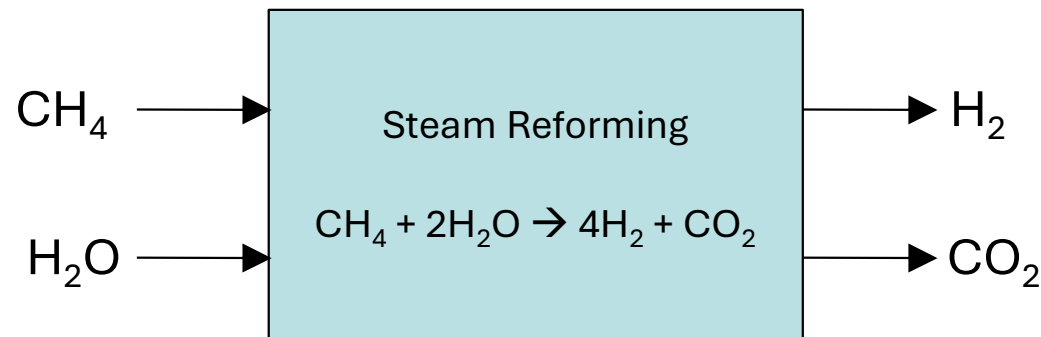
pharmaceutical processes

short product life spans, 1-2 y

product value \gg product cost

Problem 4.13

(a) Analyze the basic economics and show an I/O diagram for producing hydrogen from water, coal, and natural gas. (b) What production mode should be utilized to obtain production rates of 3×10^7 and 1×10^8 kg/yr?



basis: 1kg of H_2

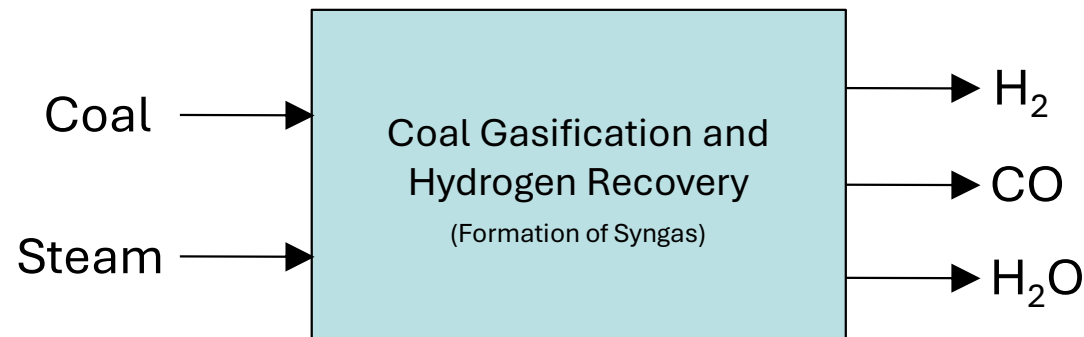
H_2 :	\$.67/kg (Kirk-Othmer)
O_2 :	\$.04/kg (Kirk-Othmer)
Steam:	\$.008/kg
NG:	\$.13/kg

Problem 4.13

Analyze the basic economics and show an I/O diagram for producing hydrogen from water, coal, and natural gas.

Need stoichiometry (reaction coefficients).

Also need an empirical formula for coal (coal is not “C”).



basis: 1kg of H₂

This is an incomplete combustion.

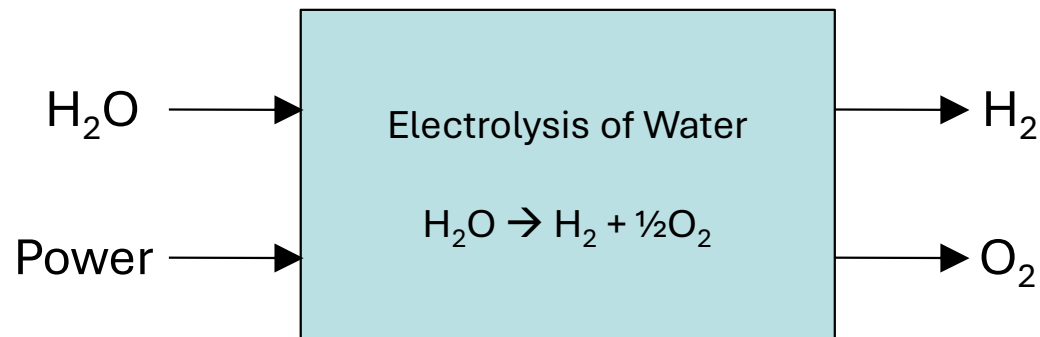
H ₂ :	\$.67/kg (Kirk-Othmer)
O ₂ :	\$.04/kg (Kirk-Othmer)
Coal:	\$.055/kg
Steam:	\$.008/kg

Problem 4.13

Analyze the basic economics and show an I/O diagram for producing hydrogen from water, coal, and natural gas.

Need a relationship between electrical power and stoichiometry

electrolysis is a cathode/anode process with 2 mol e⁻ flowing per mol H₂
think electrochemical (Daniel) cell from general chemistry with a voltage of ~1.23 V



basis: 1kg of H₂

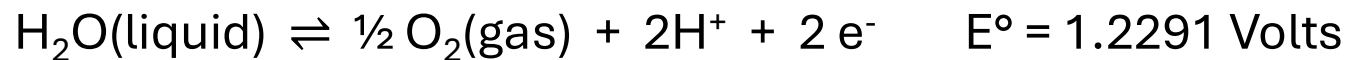
Electricity: \$.05/kW·h

H₂: \$.67/kg (Kirk-Othmer)

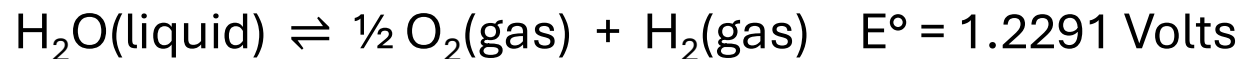
O₂: \$.04/kg (Kirk-Othmer)

Balancing Electrochemical Reactions (General Chemistry)

Adding half-reactions:



Overall (water electrolysis):



In[1]:= (*Electric Power*)

$$\left(\frac{1 \text{ kmol_H2}}{2.0158 \text{ kg_H2}} \right) \left(\frac{2 \text{ kmol_e}}{1 \text{ kmol_H2}} \right) \left(\frac{1000 \text{ mol_e}}{1 \text{ kmol_e}} \right) \left(\frac{96485 \text{ C}}{1 \text{ mol_e}} \right) \left(\frac{1 \text{ Amp}}{1 \text{ C / s}} \right) * 1.2291 \text{ V} \left(\frac{1 \text{ W}}{1 \text{ V} * \text{Amp}} \right) \left(\frac{1 \text{ kW}}{1000 \text{ W}} \right) \left(\frac{1 \text{ h}}{3600 \text{ s}} \right)$$

Out[1]= $\frac{32.68339 \text{ h kW}}{\text{kg_H2}}$

Questions?