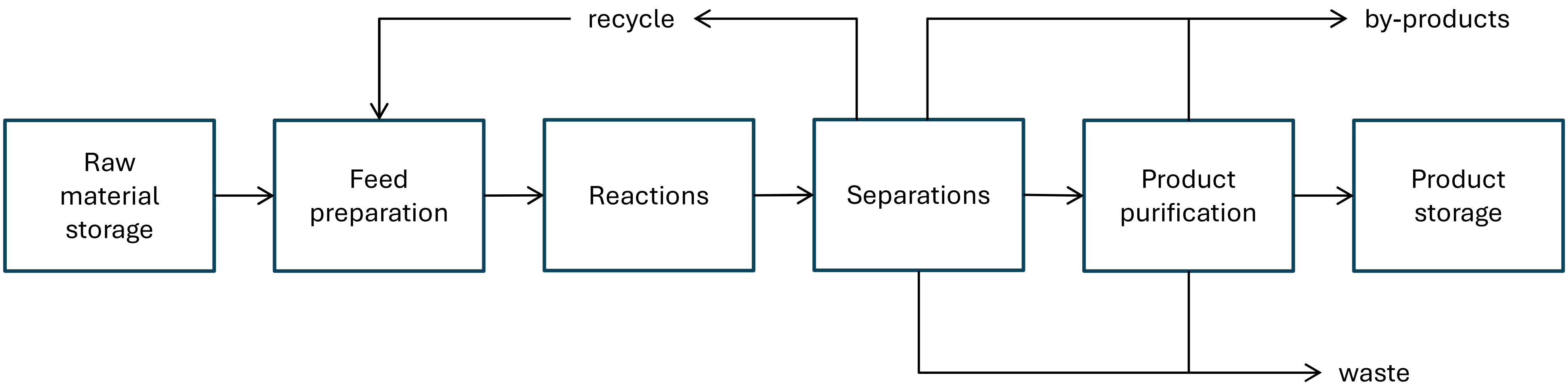
CH402 Chemical Engineering Process Design

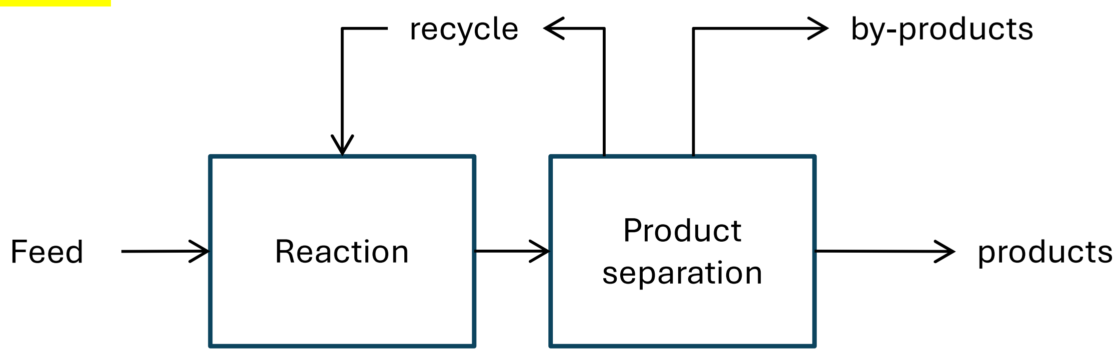
Class Notes L13

Flowsheet Synthesis and I/O Analysis

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 Encylcopedia of Chemical Technoilogy, 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)

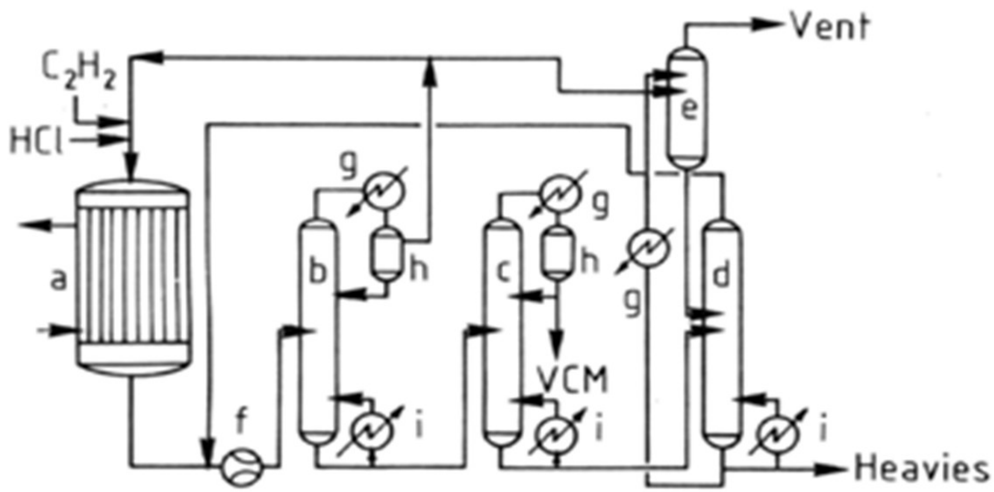
$$C_2H_2 + HCl \longrightarrow C_2H_3Cl$$

Route 1
direct reaction of acetylene
(acetylene hydrochlorination)

Vinyl Chloride Process Flow Diagram

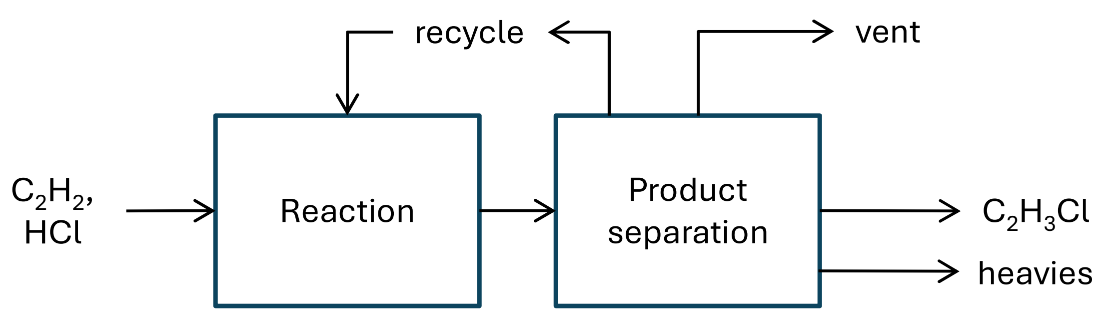
Ullmann's Encyclopedia of Industrial Chemistry
Dreher, L., Beutel, K.K., Myers, J.D., Lübbe, T., Krieger, S., & Pottenger, L.H., Chloroethanes and Chloroethylenes. 1-81.

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)

$$C_2H_4 + Cl_2 \xrightarrow[]{\text{thermodynamically unfavored}} C_2H_3Cl + HCl$$

Route 2
direct chlorination of ethylene (liquid phase)

$$C_2H_4 + Cl_2 \xrightarrow[]{\text{thermodynamically favored}} \cancel{C_2H_4Cl_2}$$

Not the product we want

Known Vinyl Chloride Routes

Kirk-Othmer, Wikipedia

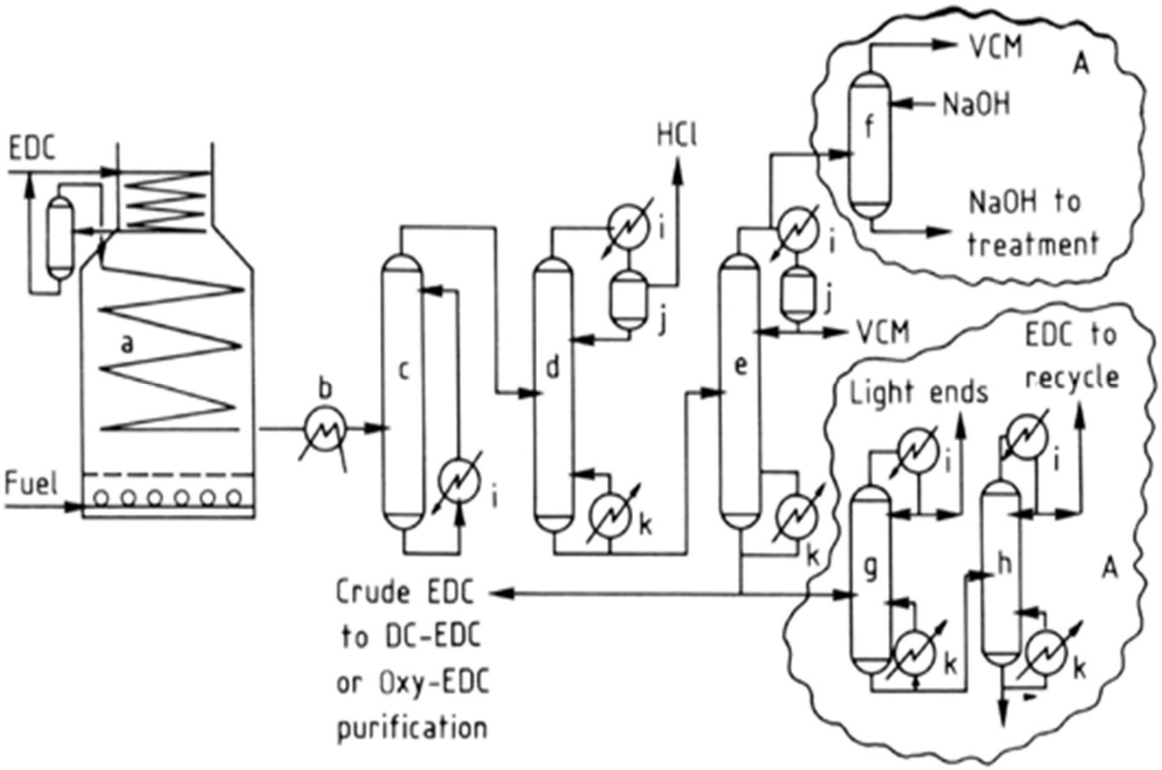
$C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2$ ethylene chlorination

$C_2H_4Cl_2 \longrightarrow C_2H_3Cl + HCl$ pyrolysis

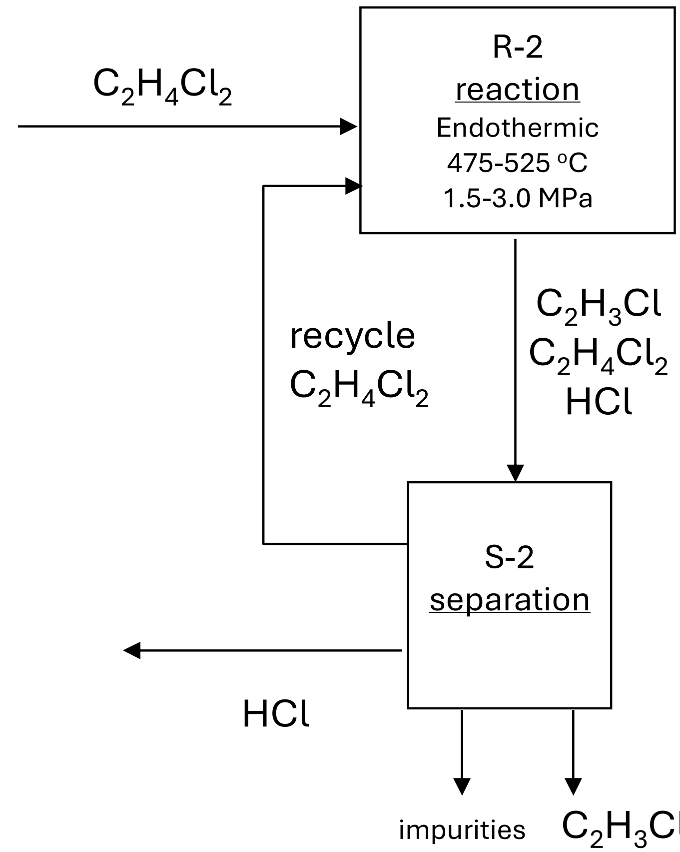
$C_2H_4 + Cl_2 \longrightarrow C_2H_3Cl + HCl$ **Route 3**
direct chlorination + pyrolysis

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 Encylcopedia of Industrial Chemistry
Dreher, L., Beutel, K. K., Myers, J. D., Lübbe, 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

$C_2H_4 + 2HCl + \frac{1}{2}\,O_2$	$\longrightarrow$	$C_2H_4Cl_2 + H_2O$	oxychlorination
$C_2H_4Cl_2$	$\longrightarrow$	$C_2H_3Cl + HCl$	pyrolysis
$C_2H_4 + HCl + \frac{1}{2}\,O_2$	$\longrightarrow$	$C_2H_3Cl + H_2O$	**Route 4** oxychlorination + pyrolysis

Known Vinyl Chloride Routes

Literature Search

Kirk-Othmer, Wikipedia

$C_2H_4 + Cl_2$	$\longrightarrow$	$C_2H_4Cl_2$	chlorination
			+
$C_2H_4 + 2HCl + ½\, O_2$	$\longrightarrow$	$C_2H_4Cl_2 + H_2O$	oxychlorination
			+
$C_2H_4Cl_2$	$\longrightarrow$	$C_2H_3Cl + HCl$	pyrolysis

$2C_2H_4 + Cl_2 + ½\, O_2$	$\longrightarrow$	$2C_2H_3Cl + H_2O$	**Route 5** (overall)

Known Vinyl Chloride Routes

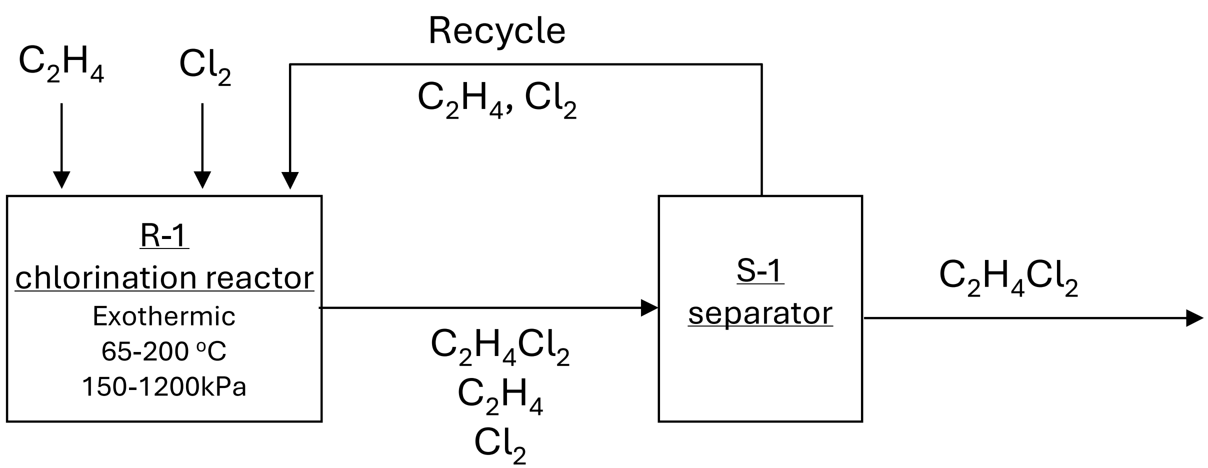
5 processes identified in literature survey

			Summary
$C_2H_2 + HCl \longrightarrow C_2H_3Cl$		A	acetylene hydrochl.
$C_2H_4 + Cl_2 \longrightarrow C_2H_3Cl + HCl$		C	direct chlorination
$C_2H_4 + Cl_2 \longrightarrow C_2H_3Cl + HCl$		C-P	chlorination + pyrolysis
$C_2H_4 + HCl + \frac{1}{2} O_2 \longrightarrow C_2H_3Cl + H_2O$		O-P	oxychlorination + pyrol.
$2C_2H_4 + Cl_2 + \frac{1}{2} O_2 \longrightarrow 2C_2H_3Cl + H_2O$		C-O-P	chlor. + oxychlor. + pyrol.

Functions Diagram – C – Direct Chlorination

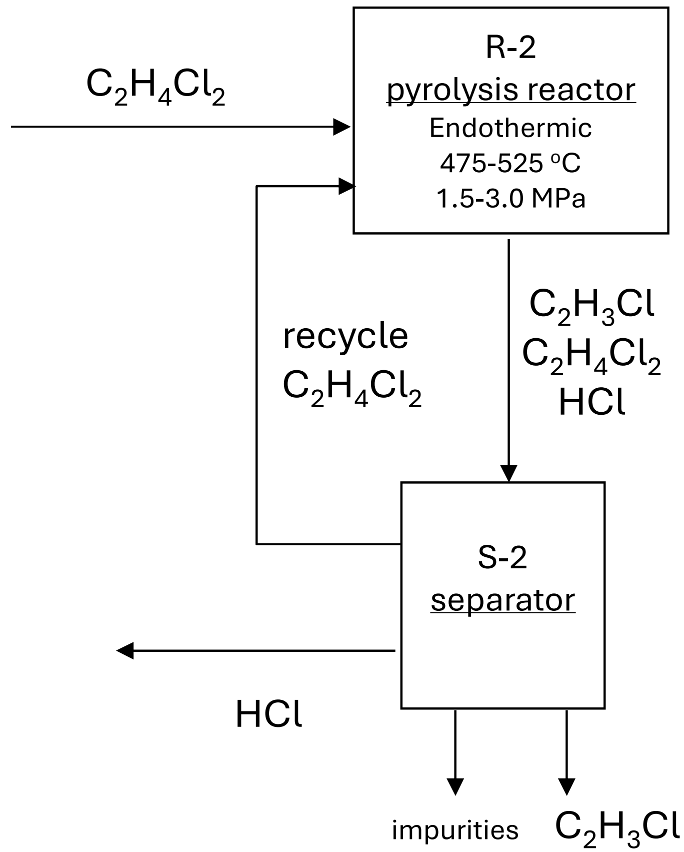
The utility of the functions diagram is that it can be used to build much larger processes.

$$C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2$$



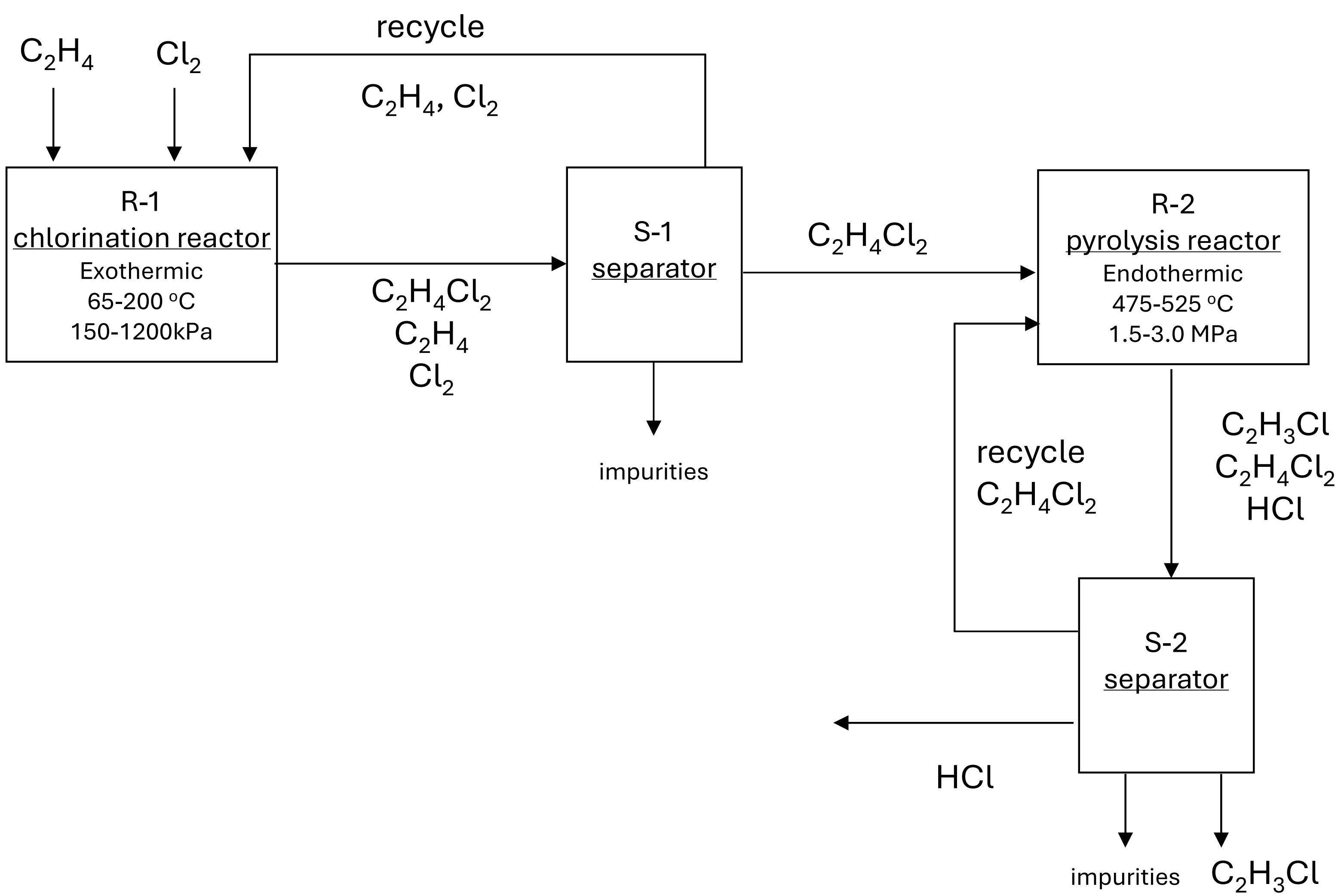
$C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2$ ethylene chlorination

Functions Diagram – Pyrolysis

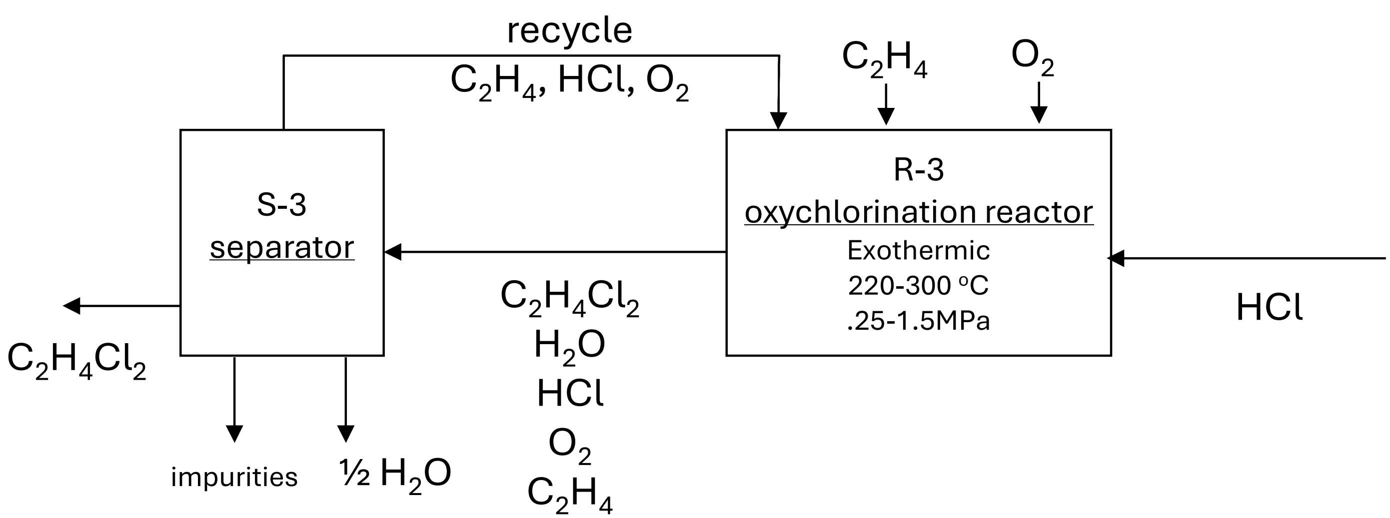


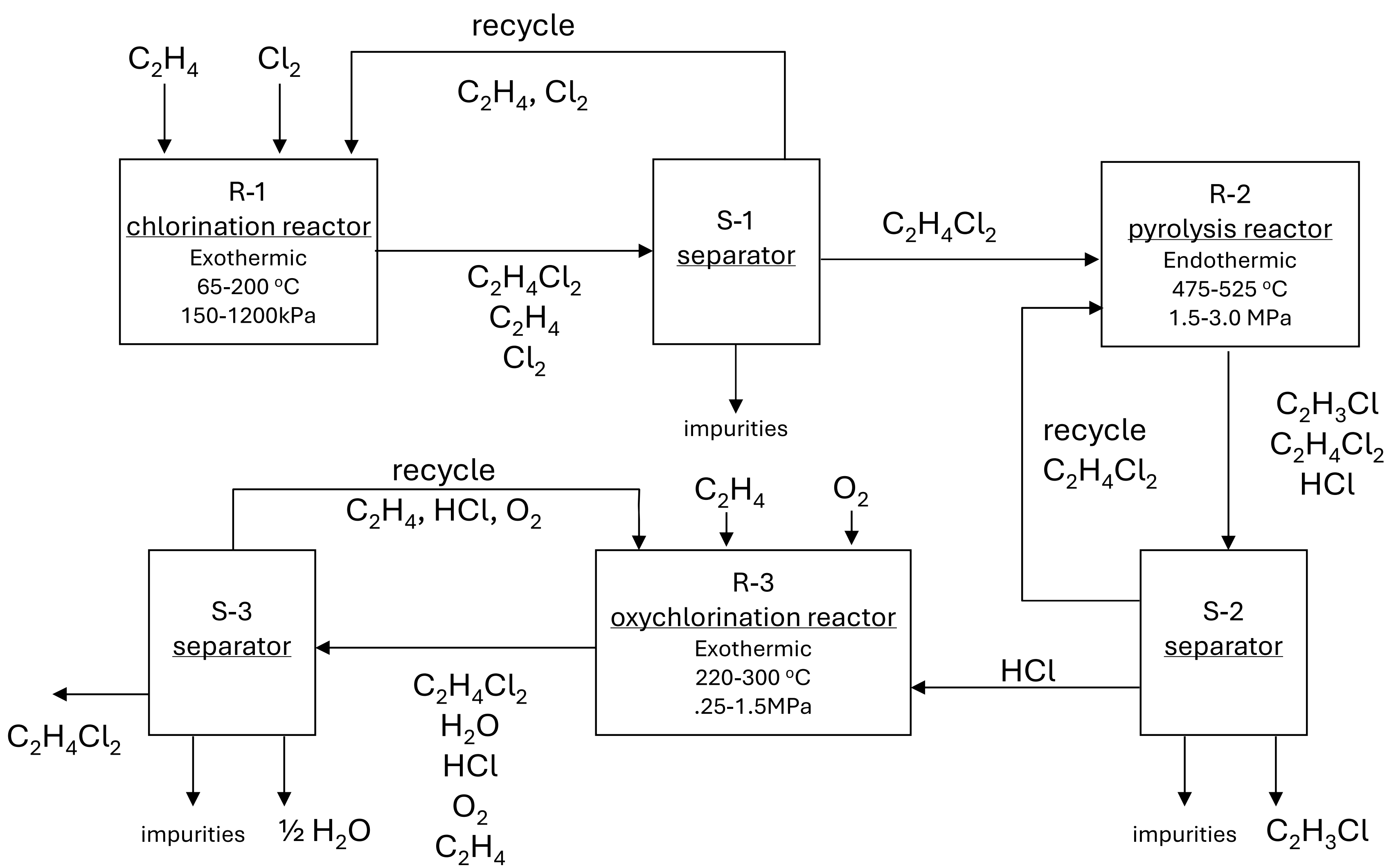
$C_2H_4Cl_2 \longrightarrow C_2H_3Cl + HCl$ pyrolysis

Hybrid Functions Diagram - Route 3 - CP

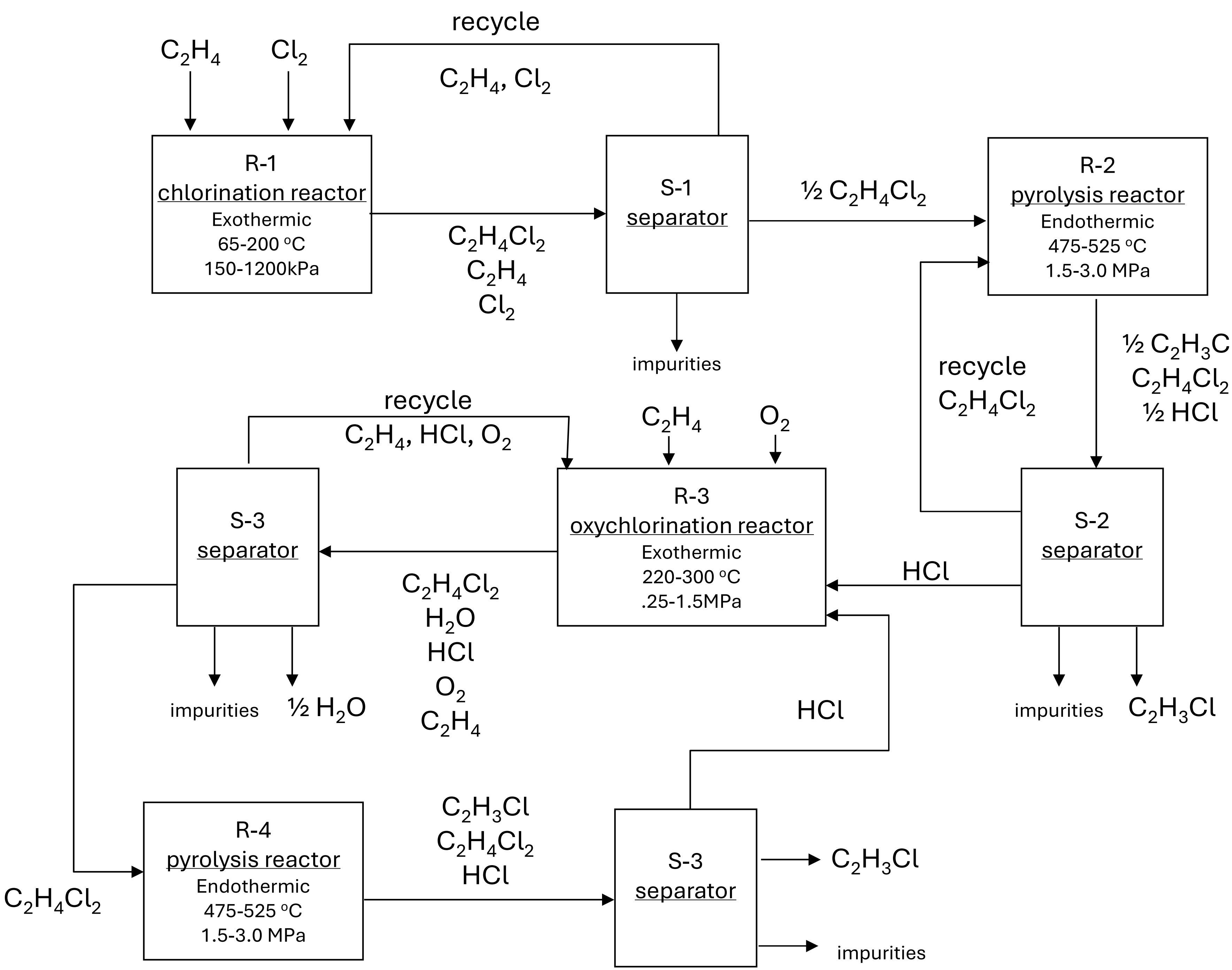


Functions Diagram – Oxychlorination



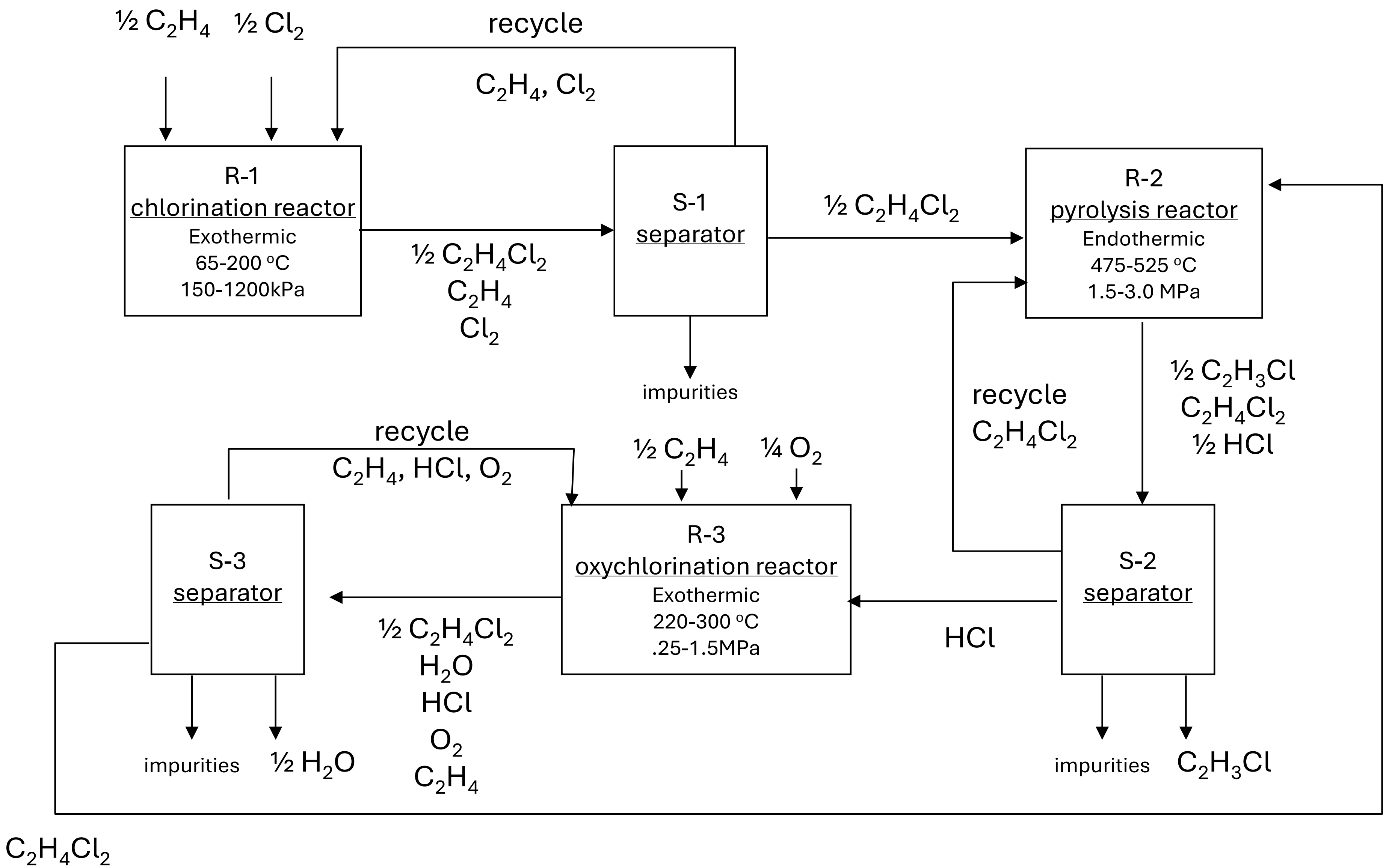


recycle
C_2H_4
Cl_2
C_2H_4, Cl_2
R-1
chlorination reactor
Exothermic
65-200 °C
150-1200kPa
$C_2H_4Cl_2$
C_2H_4
Cl_2
S-1
separator
impurities
$C_2H_4Cl_2$
R-2
pyrolysis reactor
Endothermic
475-525 °C
1.5-3.0 MPa
recycle
$C_2H_4Cl_2$
C_2H_3Cl
$C_2H_4Cl_2$
HCl
recycle
C_2H_4, HCl, O_2
C_2H_4
O_2
S-3
separator
R-3
oxychlorination reactor
Exothermic
220-300 °C
.25-1.5MPa
HCl
S-2
separator
$C_2H_4Cl_2$
$C_2H_4Cl_2$
H_2O
HCl
O_2
C_2H_4
impurities
½ H_2O
impurities
C_2H_3Cl



recycle
C_2H_4
Cl_2
C_2H_4, Cl_2
R-1
chlorination reactor
Exothermic
65-200 °C
150-1200kPa
$C_2H_4Cl_2$
C_2H_4
Cl_2
S-1
separator
impurities
½ $C_2H_4Cl_2$
R-2
pyrolysis reactor
Endothermic
475-525 °C
1.5-3.0 MPa
recycle
$C_2H_4Cl_2$
½ C_2H_3Cl
$C_2H_4Cl_2$
½ HCl
S-2
separator
impurities
C_2H_3Cl
HCl
recycle
C_2H_4, HCl, O_2
C_2H_4
O_2
R-3
oxychlorination reactor
Exothermic
220-300 °C
.25-1.5MPa
S-3
separator
impurities
½ H_2O
$C_2H_4Cl_2$
H_2O
HCl
O_2
C_2H_4
HCl
$C_2H_4Cl_2$
R-4
pyrolysis reactor
Endothermic
475-525 °C
1.5-3.0 MPa
C_2H_3Cl
$C_2H_4Cl_2$
HCl
S-3
separator
C_2H_3Cl
impurities

Hybrid Functions Diagram - Route 5 - COP



Input/Output Structure - Route 5 - COP

I/O box is frequently left blank

Inputs: $2C_2H_4$, Cl_2, $\frac{1}{2}\,O_2$

liquid-phase chlorination:

$$C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2$$

gas-phase oxychlorination

$$C_2H_4 + 2HCl + \tfrac{1}{2}\,O_2 \longrightarrow C_2H_4Cl_2 + H_2O$$

gas-phase pyrolysis

$$C_2H_4Cl_2 \longrightarrow C_2H_3Cl + HCl$$

$$2C_2H_4 + Cl_2 + \tfrac{1}{2}\,O_2 \longrightarrow 2C_2H_3Cl + H_2O$$

Outputs: $2C_2H_3Cl$, H_2O

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

Known Vinyl Chloride Routes

5 processes

Reactants		Products		Reaction Path
$C_2H_2 + HCl$	$\longrightarrow$	C_2H_3Cl	A	1
$C_2H_4 + Cl_2$	$\longrightarrow$	$C_2H_3Cl + HCl$	C	2
$C_2H_4 + Cl_2$	$\longrightarrow$	$C_2H_3Cl + HCl$	C-P	3
$C_2H_4 + HCl + \frac{1}{2}O_2$	$\longrightarrow$	$C_2H_3Cl + H_2O$	O-P	4
$2C_2H_4 + Cl_2 + \frac{1}{2}O_2$	$\longrightarrow$	$2C_2H_3Cl + H_2O$	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_2H_2	26.0	1.39	0.42	---	---	---	---
8	C_2H_4	28.1	0.45	---	0.45	0.45	0.45	0.45
9	*C_2H_3Cl*	*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 $2x10^7$ and $1x10^8$ kg/y?

Electricity:	\$0.05/kW·h
H_2:	\$4.67/kg (Kirk-Othmer)
O_2:	\$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 H_2

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

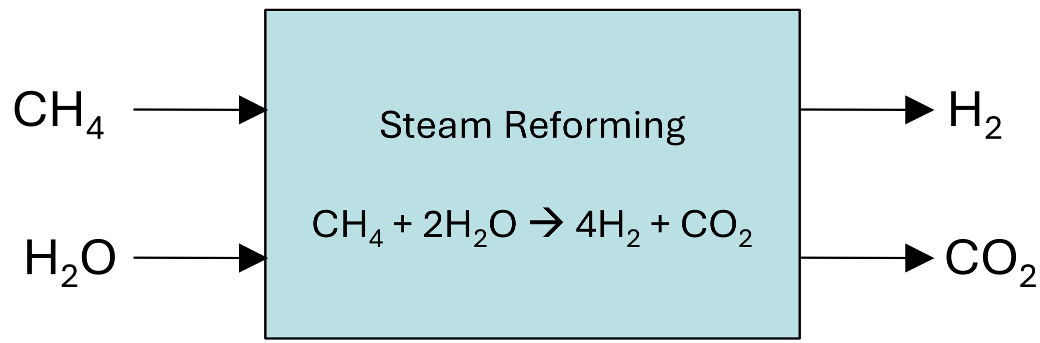
pharmaceutical processes

short product life spans, 1-2 y

product value >> 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

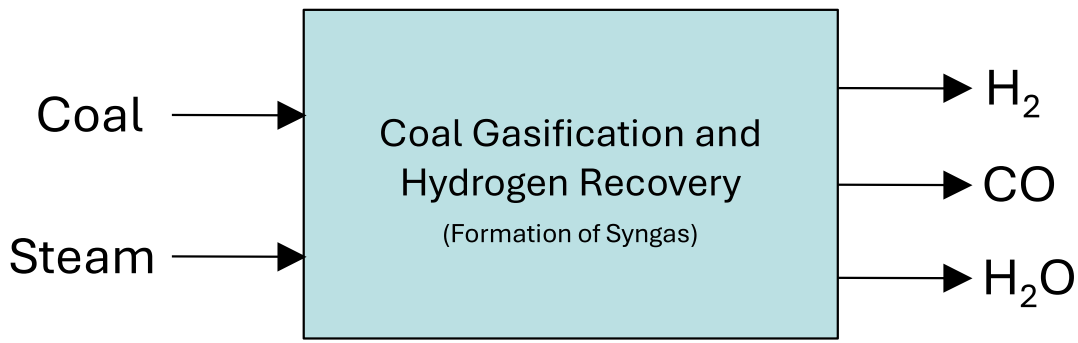
H_2:	$.67/kg (Kirk-Othmer)
O_2:	$.04/kg (Kirk-Othmer)
Steam:	$.008/kg
NG:	$.13/kg

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 H_2

This is an incomplete combustion.

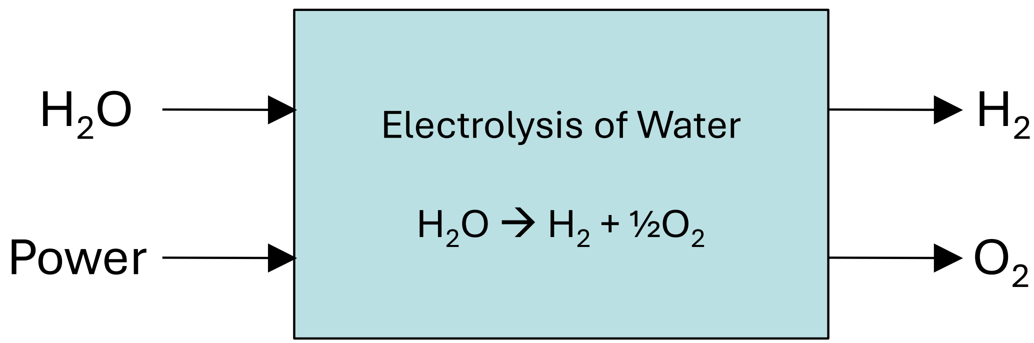
H_2:	\$4.67/kg (google- average market price of hydrogen)
CO:	\$0.20/kg (google- average market price of carbon monoxide)
Coal:	\$0.055/kg
Steam:	\$0.008/kg

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 H_2
think electrochemical (Daniel) cell from general chemistry with a voltage of ~1.23 V



basis: 1kg of H_2

Electricity: $.05/kW·h
H_2: $.67/kg (Kirk-Othmer)
O_2: $.04/kg (Kirk-Othmer)

Balancing Electrochemical Reactions
(General Chemistry)

Adding half-reactions:

$$2\,H^+ + 2e^- \rightleftharpoons H_2(\text{gas}) \qquad E° = 0.0000 \text{ Volts}$$

$$H_2O(\text{liquid}) \rightleftharpoons \tfrac{1}{2}\,O_2(\text{gas}) + 2H^+ + 2\,e^- \qquad E° = 1.2291 \text{ Volts}$$

Overall (water electrolysis):

$$H_2O(\text{liquid}) \rightleftharpoons \tfrac{1}{2}\,O_2(\text{gas}) + H_2(\text{gas}) \qquad E° = 1.2291 \text{ Volts}$$

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

$$\left(\frac{1\ \text{kmol\_H2}}{2.0158\ \text{kg\_H2}}\right)\left(\frac{2\ \text{kmol\_e}}{1\ \text{kmol\_H2}}\right)\left(\frac{1000\ \text{mol\_e}}{1\ \text{kmol\_e}}\right)\left(\frac{96\,485\ \text{C}}{1\ \text{mol\_e}}\right)\left(\frac{1\ \text{Amp}}{1\ \text{C / s}}\right) * 1.2291\ \text{V}\left(\frac{1\ \text{W}}{1\ \text{V} * \text{Amp}}\right)\left(\frac{1\ \text{kW}}{1000\ \text{W}}\right)\left(\frac{1\ \text{h}}{3600\ \text{s}}\right)$$

Out[1]= $\frac{32.68339\ \text{h kW}}{\text{kg\_H2}}$

Questions?