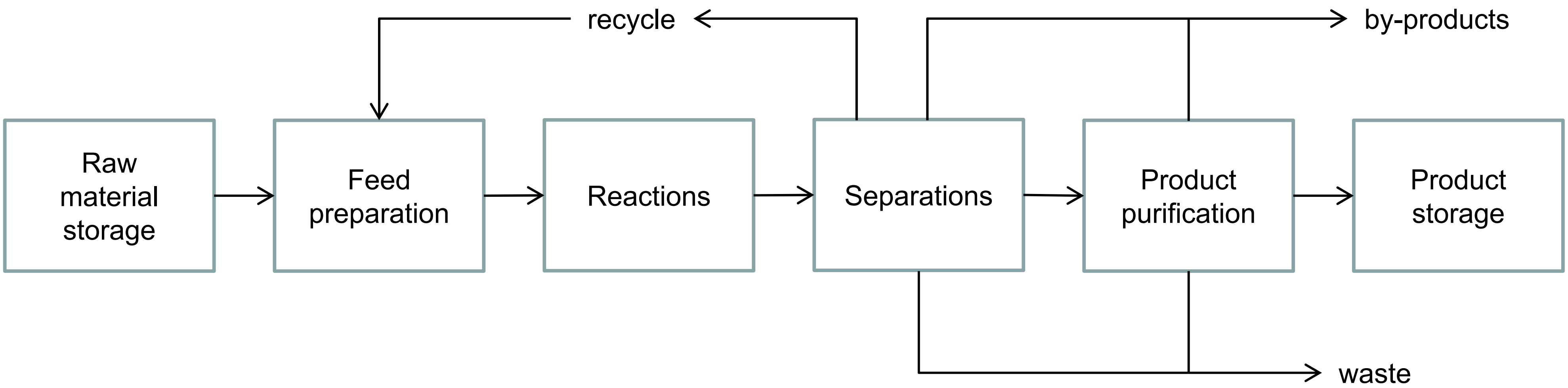
CH402 Chemical Engineering Process Design

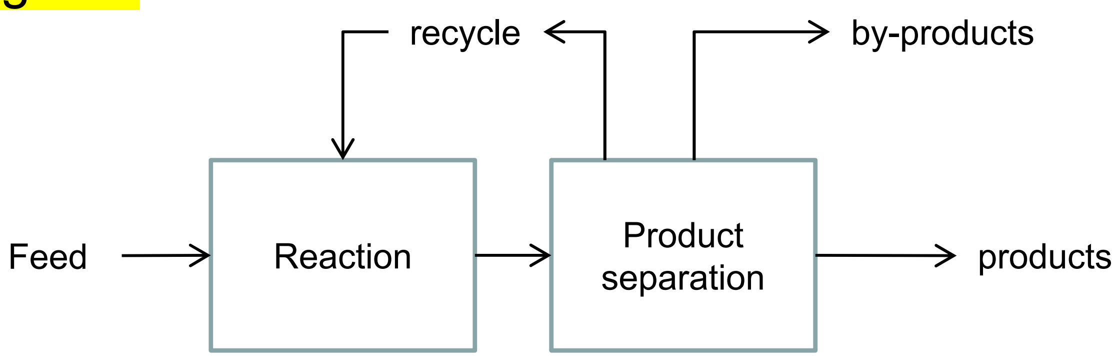
Class Notes L13

Flowsheet Synthesis

Block Diagram of (all) Chemical Processes



"Functions Diagram"



Q's may or may not be shown

Often simplified to this form.

Case Study - Vinyl Chloride Monomer (VCM) Production

Problem definition (market survey)

21,100,000 tons/y in 2000
40,000,000 tons/y in 2009

3.7% growth from 2000-2009
2.7% growth from 2009-2024

8,000,000 t/y in 2009
~10,000,000 t/y in 2020

12 US plants

Emissions are a problem
23 Feb 2023 East Palestine, OH

average US plant capacity is 667,000 t/y

1,334 million lbs/y per plant
604.8 million kg/y per plant

Known Vinyl Chloride Routes

Next step is a literature search – 5 Routes Identified

Kirk-Othmer, Wikipedia

(also CH383)

$$C_2H_2 + HCl \longrightarrow C_2H_3Cl$$

Route 1
direct reaction of acetylene
(acetylene hydrochlorination)

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

Literature Search

Kirk-Othmer, Wikipedia

CH383

$$C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2$$ 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

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

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

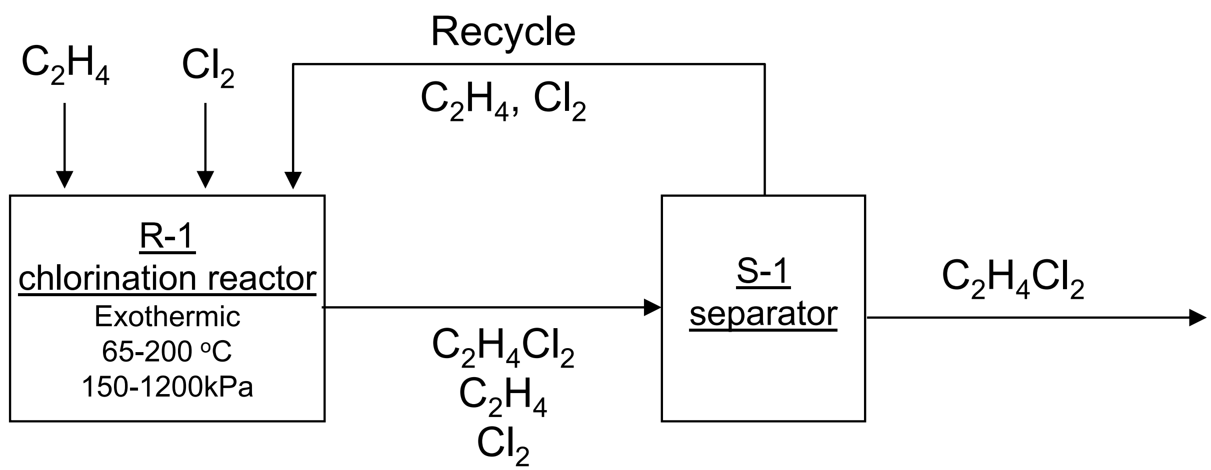
5 processes identified in literature survey

				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

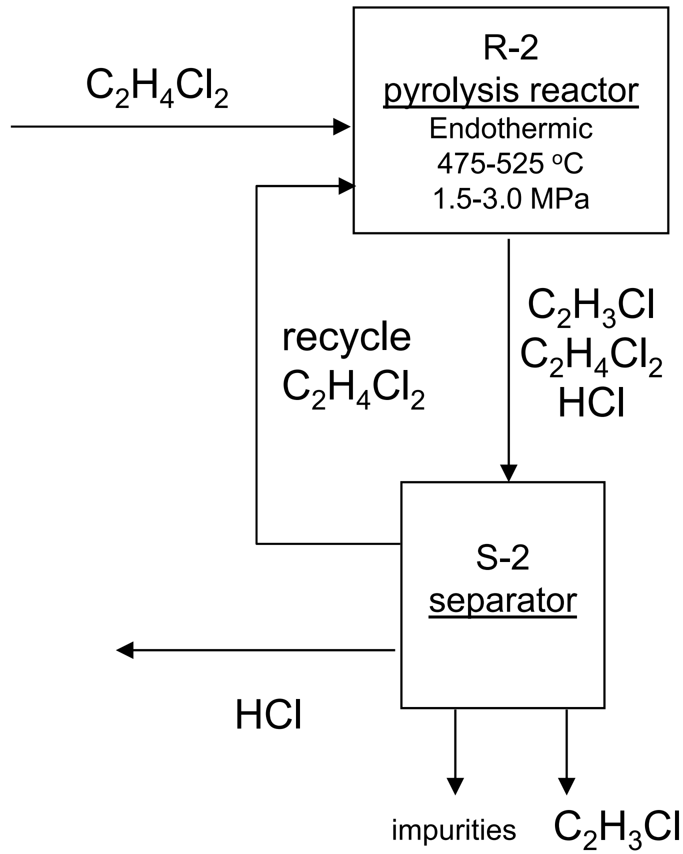
The utility of the functions diagram is that it can be used to build much larger processes.

$$C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2$$



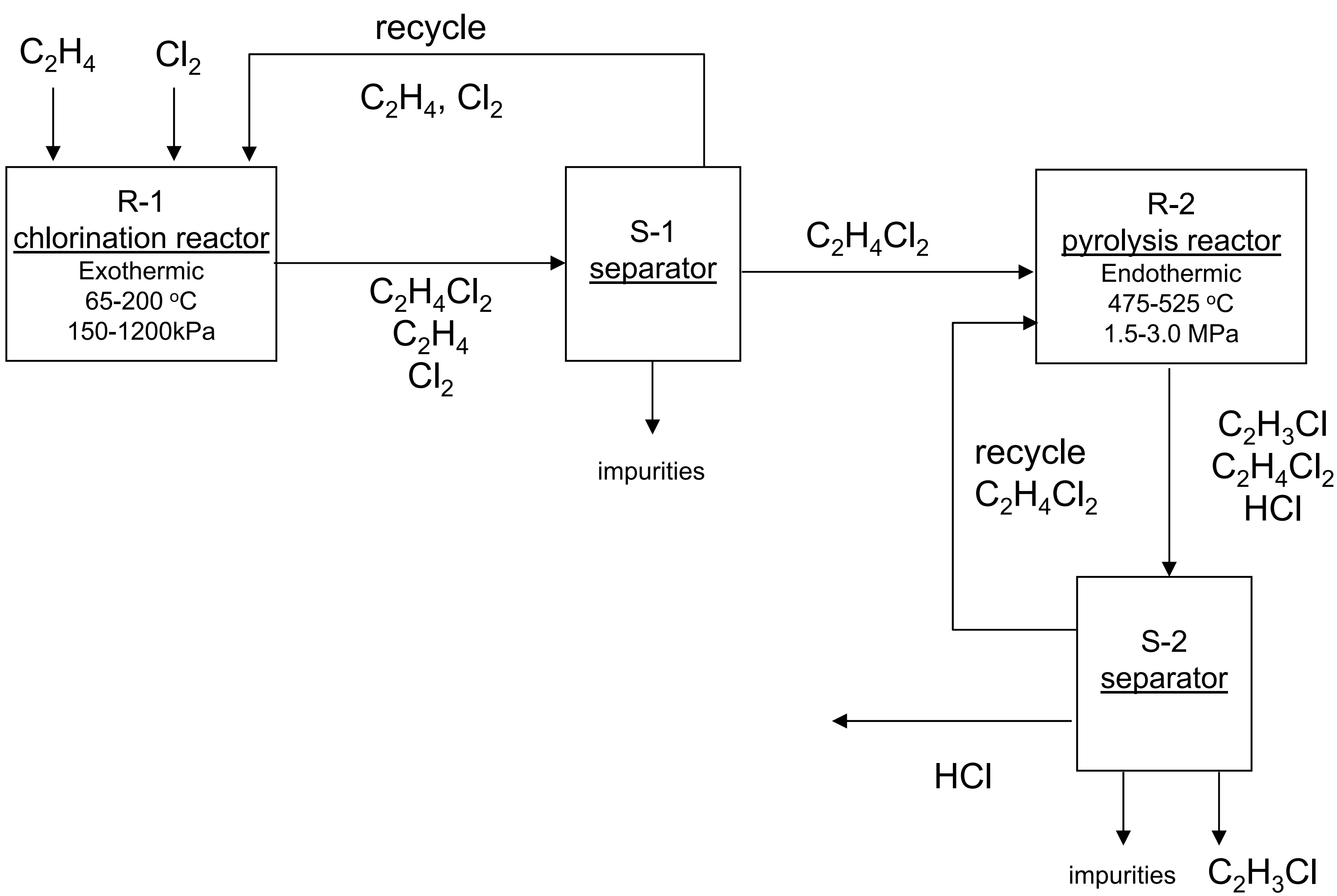
$C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2$ ethylene chlorination

Functions Diagram – Pyrolysis

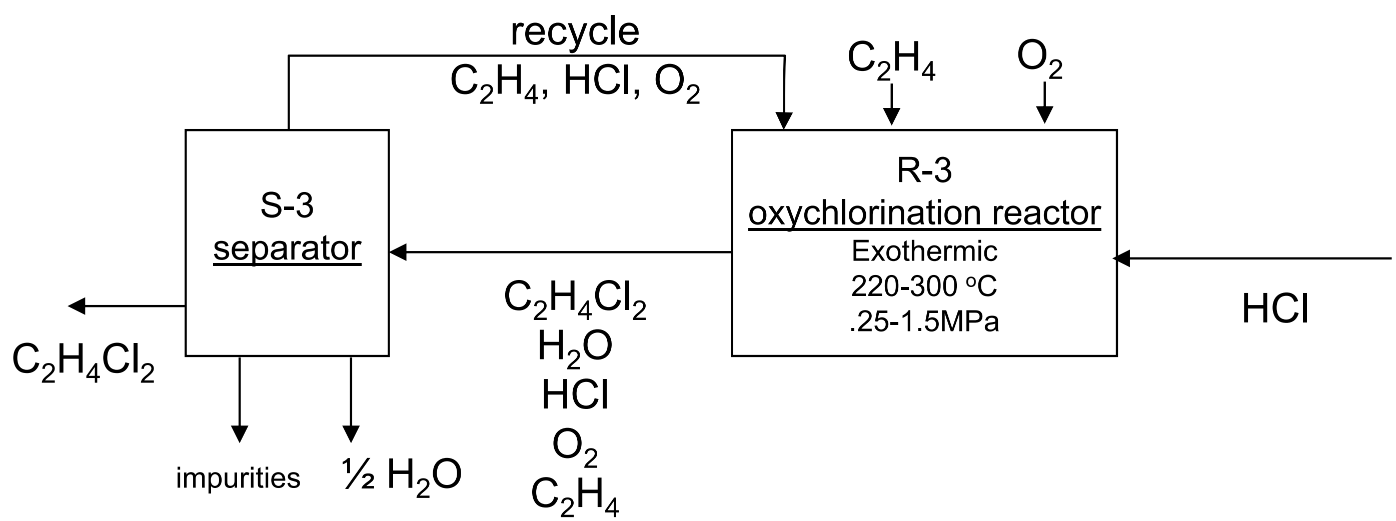


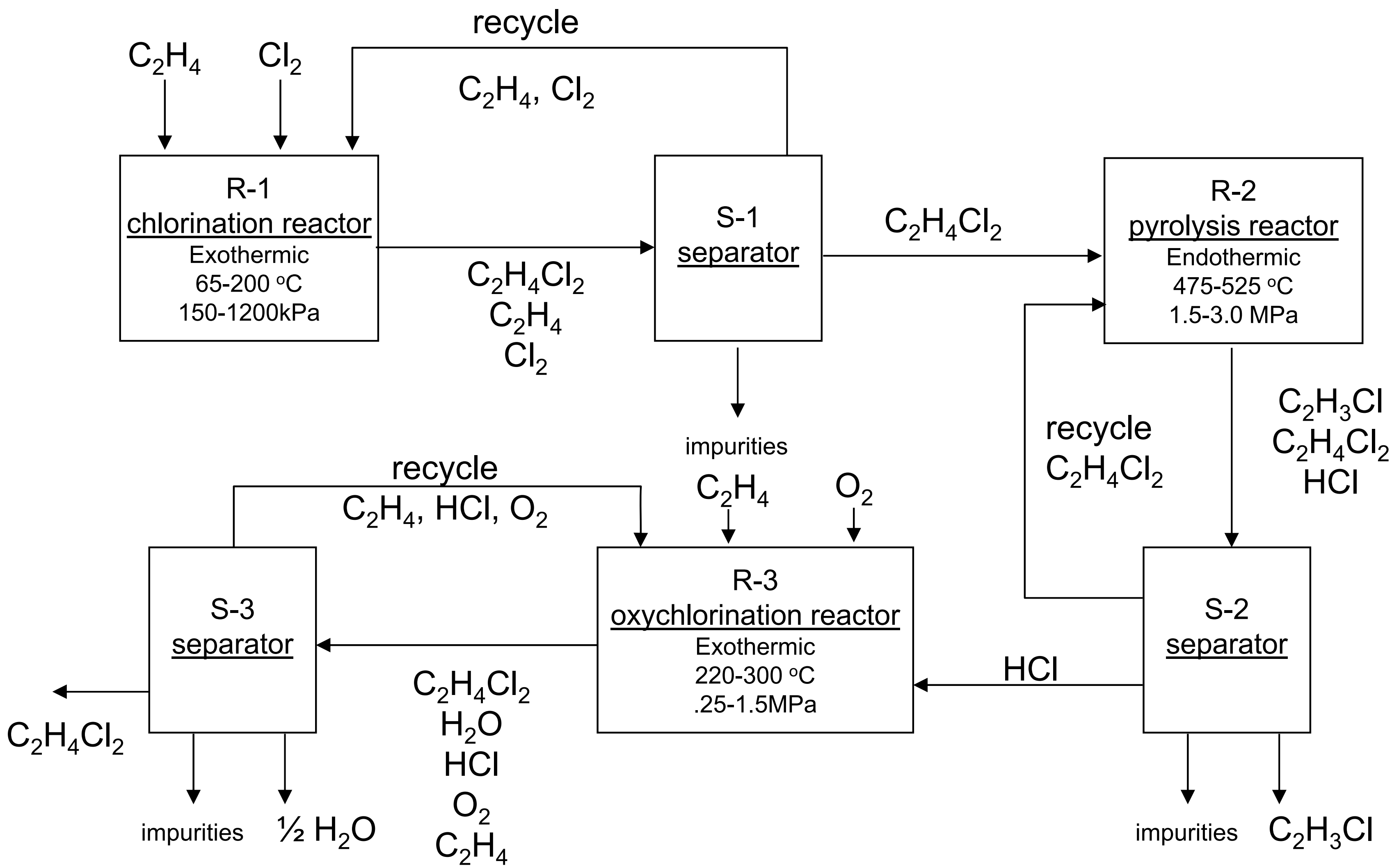
$C_2H_4Cl_2 \longrightarrow C_2H_3Cl + HCl$ pyrolysis

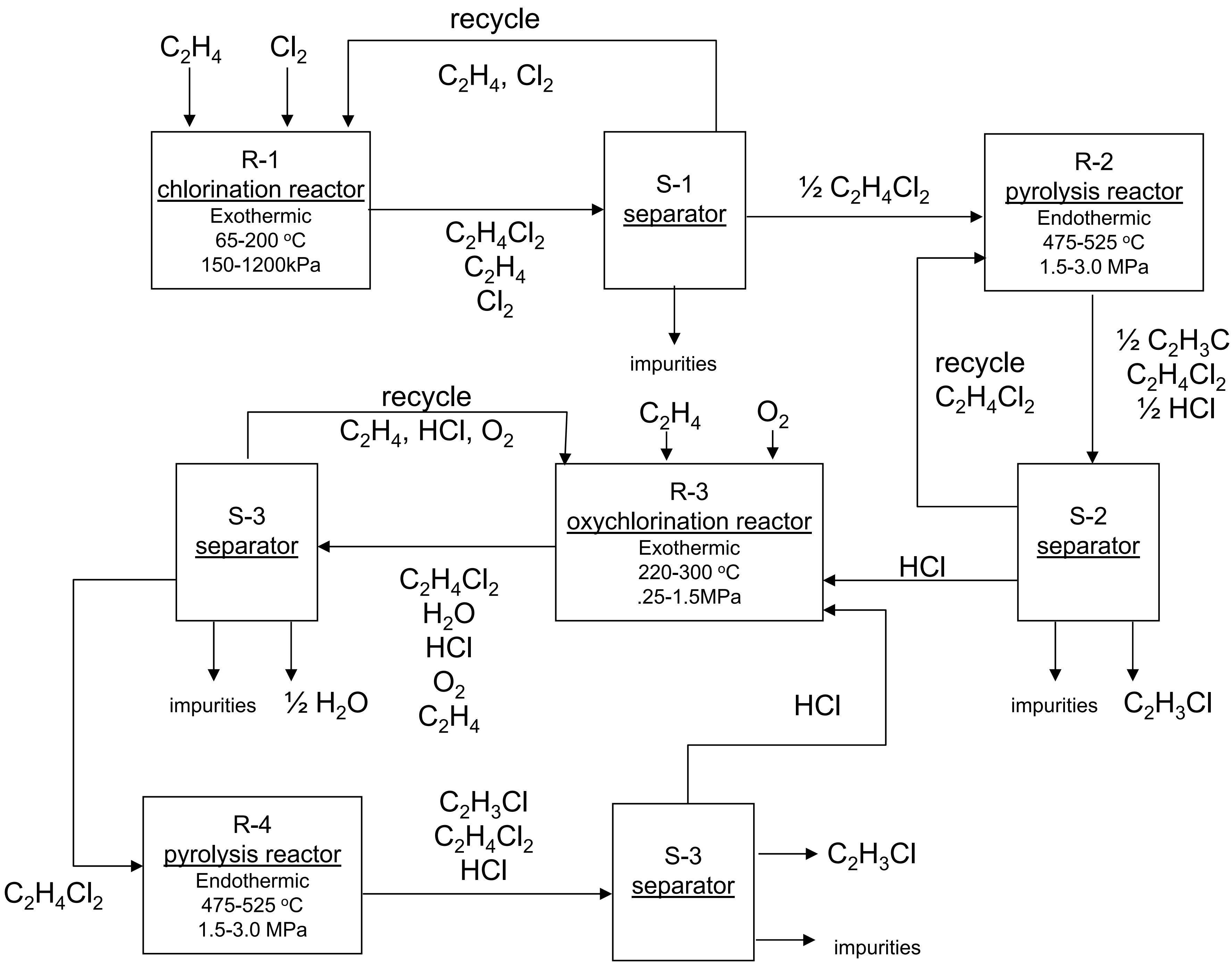
Hybrid Functions Diagram - Route 3 - CP



Functions Diagram – Oxychlorination

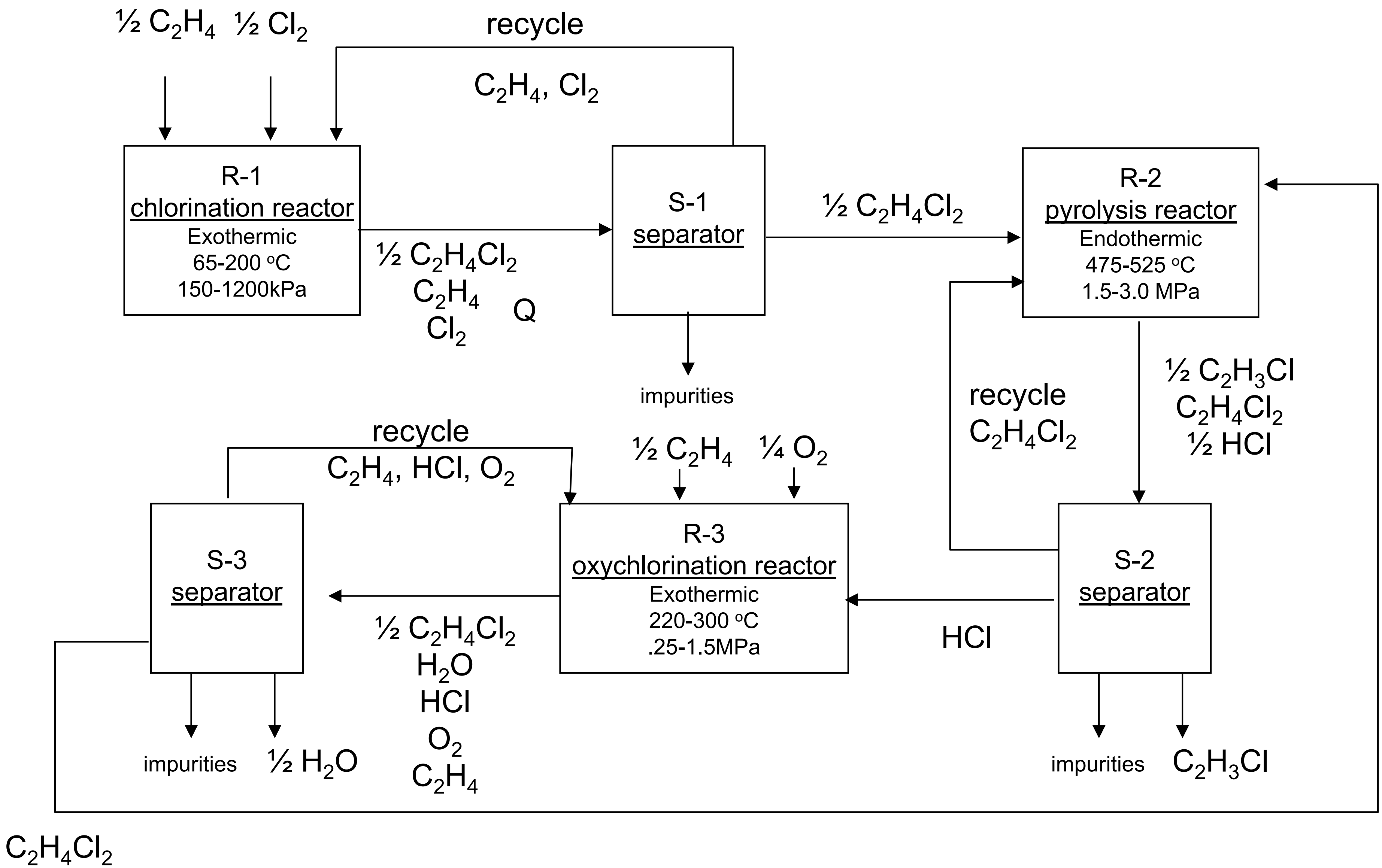


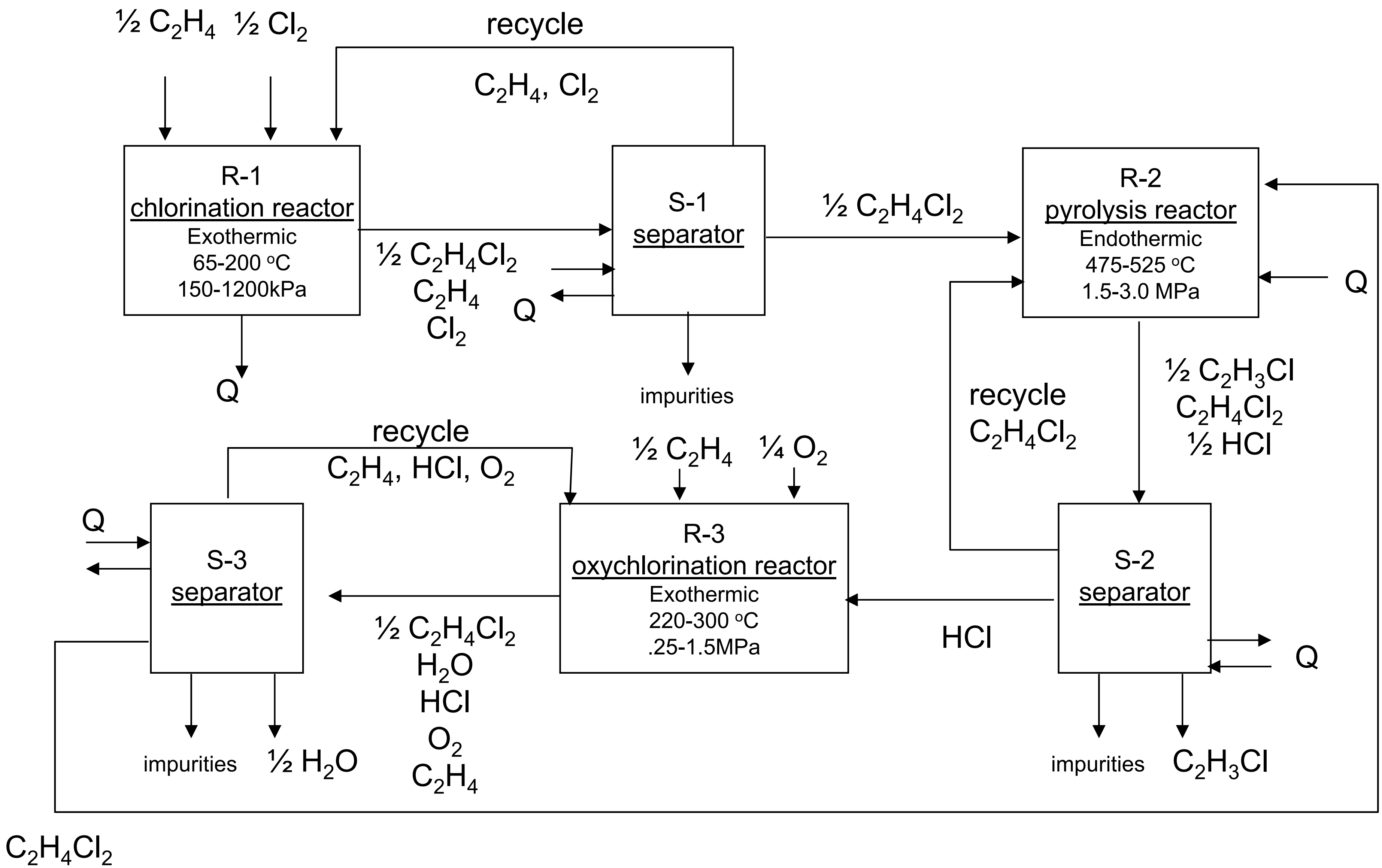

recycle
C2H4 Cl2
C2H4, Cl2
R-1
chlorination reactor
Exothermic
65-200 oC
150-1200kPa
C2H4Cl2
C2H4
Cl2
S-1
separator
C2H4Cl2
R-2
pyrolysis reactor
Endothermic
475-525 oC
1.5-3.0 MPa
impurities
recycle
C2H4Cl2
C2H3Cl
C2H4Cl2
HCl
recycle
C2H4, HCl, O2
C2H4 O2
S-3
separator
R-3
oxychlorination reactor
Exothermic
220-300 oC
.25-1.5MPa
S-2
separator
HCl
C2H4Cl2
C2H4Cl2
H2O
HCl
O2
C2H4
impurities ½ H2O
impurities C2H3Cl



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
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
$C_2H_4Cl_2$
H_2O
HCl
O_2
C_2H_4
impurities
½ H_2O
impurities
C_2H_3Cl
HCl
R-4
pyrolysis reactor
Endothermic
475-525 °C
1.5-3.0 MPa
$C_2H_4Cl_2$
C_2H_3Cl
$C_2H_4Cl_2$
HCl
S-3
separator
C_2H_3Cl
impurities

Hybrid Functions Diagram - Route 5 - COP




½ C_2H_4 ½ Cl_2
recycle
C_2H_4, Cl_2
R-1
chlorination reactor
Exothermic
65-200 °C
150-1200kPa
Q
½ $C_2H_4Cl_2$
C_2H_4
Cl_2
Q
S-1
separator
impurities
½ $C_2H_4Cl_2$
R-2
pyrolysis reactor
Endothermic
475-525 °C
1.5-3.0 MPa
Q
recycle
$C_2H_4Cl_2$
½ C_2H_3Cl
$C_2H_4Cl_2$
½ HCl
S-2
separator
Q
impurities
C_2H_3Cl
HCl
recycle
C_2H_4, HCl, O_2
½ C_2H_4 ¼ O_2
R-3
oxychlorination reactor
Exothermic
220-300 °C
.25-1.5MPa
½ $C_2H_4Cl_2$
H_2O
HCl
O_2
C_2H_4
Q
S-3
separator
impurities
½ H_2O
$C_2H_4Cl_2$

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 make an assessment of the overall economics of the process.

Known Vinyl Chloride Routes

5 processes

				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 + ½ O_2	$\longrightarrow$	C_2H_3Cl + H_2O	O-P	4
$2C_2H_4$ + Cl_2 + ½ 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

			Reaction Path, kg/kg VC				
Species	MW, kg/kgmol	Price, $/kg	1	2	3	4	5
Cl_2	70.9	0.03	---	-1.13	-1.13		-0.57
HCl	36.5	0.22	-0.58	0.58	0.58	-0.58	---
C_2H_2	26.0	1.39	-0.42	---	---	---	---
C_2H_4	28.1	0.45	---	-0.45	-0.45	-0.45	-0.45
C_2H_3Cl	*62.5*	*0.45*	*1.00*	*1.00*	*1.00*	*1.00*	*1.00*
O_2	32.0	0.04	---	---	---	-0.26	-0.13
product value			$0.45	$0.58	$0.58	$0.45	$0.45
reactant cost			-$0.71	-$0.24	-$0.24	-$0.34	-$0.22
excess value			-$0.26	$0.34	$0.34	$0.11	$0.23

I/O diagram for process 5 is shown on slide 24

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

2 pts bonus – complete table in Excel – submit with PS6 - (pdf of table only)

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 used to obtain production rates of $2x10^7$ and $1x10^8$ kg/y? (batch or continuous?)

Electricity:	\$.05/kW·h
H_2:	\$.67/kg (Kirk-Othmer)
O_2:	\$.04/kg (Kirk-Othmer)
Coal:	\$.055/kg
Steam:	\$.008/kg
NG:	\$.13/kg

References are Kirk-Othmer and Ullman's

basis: 1kg of H_2

Use same approach as Example 4-13

Continuous versus Batch

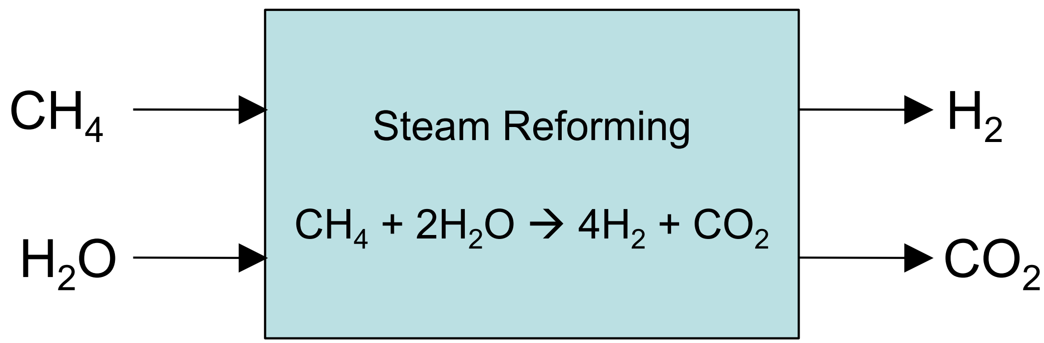
page 132-133

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

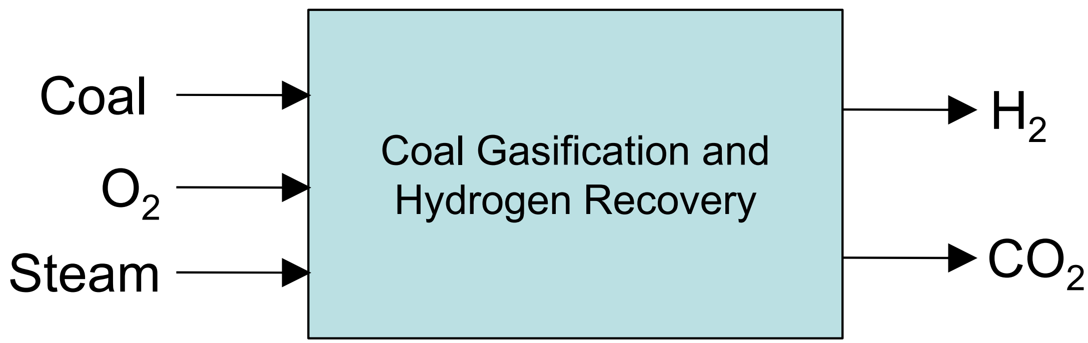
H_2:	\$.67/kg (Kirk-Othmer)
O_2:	\$.04/kg (Kirk-Othmer)
Steam:	\$.008/kg
NG:	\$.13/kg

Problem 4.13

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

hint 1: need stoichiometry (reaction coefficients).

hint 2: need an empirical formula for coal (coal is not “C”).



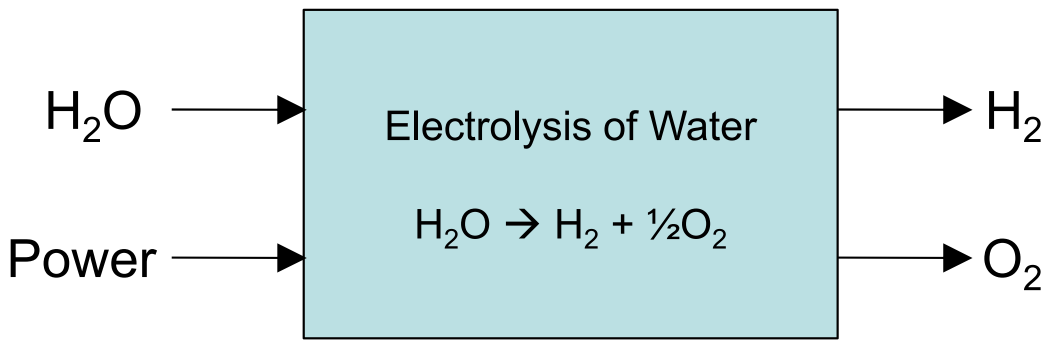
basis: 1kg of H_2

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.

hint: need a relationship between electrical power and stoichiometry



basis: 1kg of H_2

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 ~1.1 V

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

Questions?