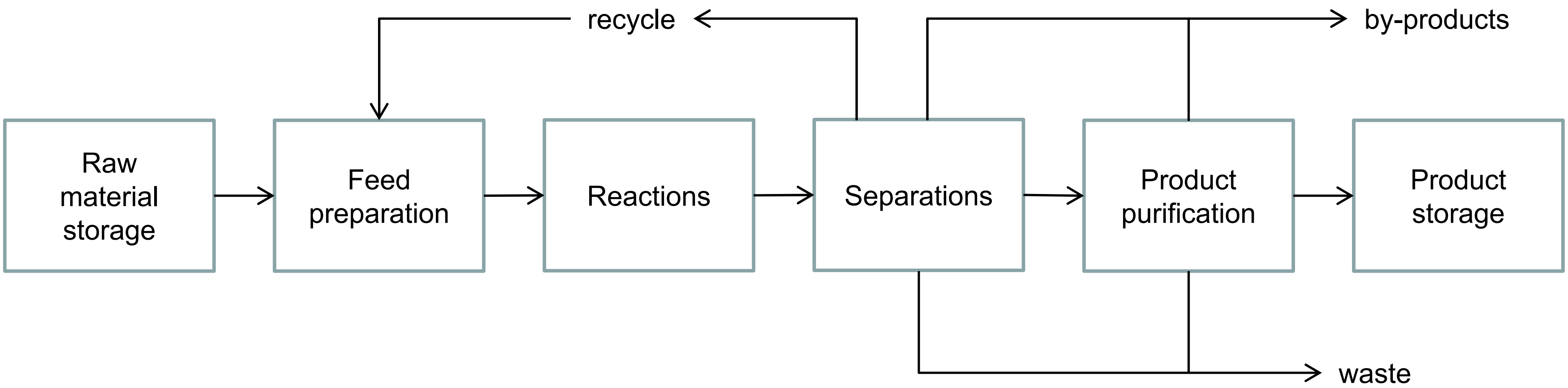
# CH402 Chemical Engineering Process Design

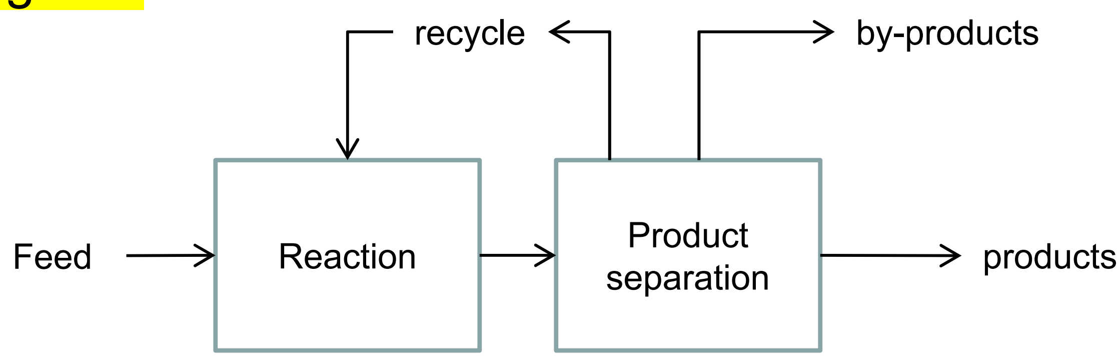
## Class Notes L13

### 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

Kirk-Othmer, Wikipedia

Literature Search

CH383

$C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2$ ethylene chlorination

$C_2H_4Cl_2 \longrightarrow C_2H_3Cl + HCl$ pyrolysis

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$C_2H_4 + Cl_2 \longrightarrow C_2H_3Cl + HCl$

**Route 3**
direct chlorination + pyrolysis

# Known Vinyl Chloride Routes



Kirk-Othmer, Wikipedia

$C_2H_4 + 2HCl + ½\,O_2 \longrightarrow C_2H_4Cl_2 + H_2O$ oxychlorination

$C_2H_4Cl_2 \longrightarrow C_2H_3Cl + HCl$ pyrolysis

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$C_2H_4 + HCl + ½\,O_2 \longrightarrow C_2H_3Cl + H_2O$ **Route 4**
oxychlorination + pyrolysis

# Known Vinyl Chloride Routes

Kirk-Othmer, Wikipedia

Literature Search

| | | | |
|---|---|---|---|
| $C_2H_4 + Cl_2$ | $\longrightarrow$ | $C_2H_4Cl_2$ | chlorination |
| | | | + |
| $C_2H_4 + 2HCl + \frac{1}{2}\,O_2$ | $\longrightarrow$ | $C_2H_4Cl_2 + H_2O$ | oxychlorination |
| | | | + |
| $C_2H_4Cl_2$ | $\longrightarrow$ | $C_2H_3Cl + HCl$ | pyrolysis |

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| | | | |
|---|---|---|---|
| $2C_2H_4 + Cl_2 + \frac{1}{2}\,O_2$ | $\longrightarrow$ | $2C_2H_3Cl + H_2O$ | **Route 5** (overall) |

# Known Vinyl Chloride Routes

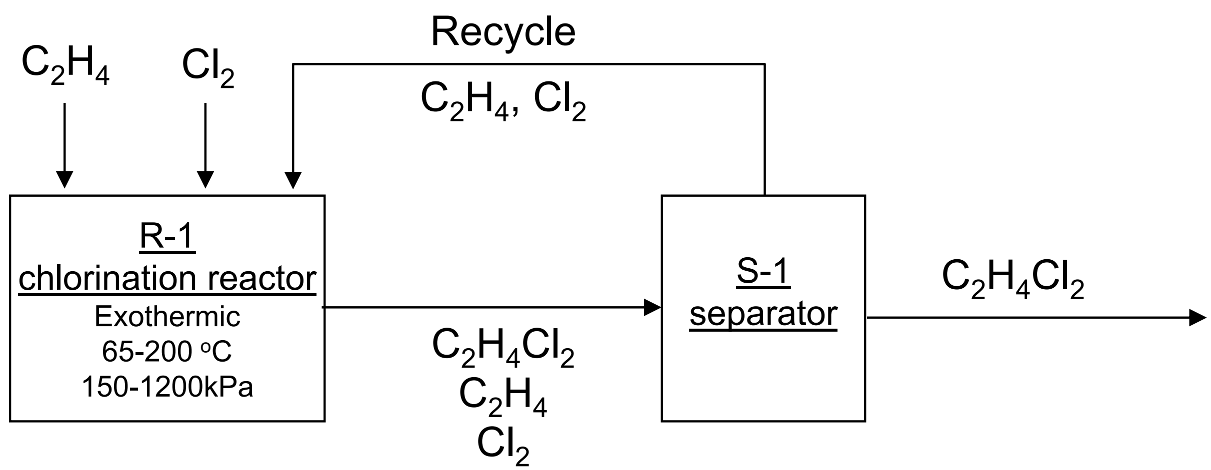
5 processes identified in literature survey

| | | | | 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

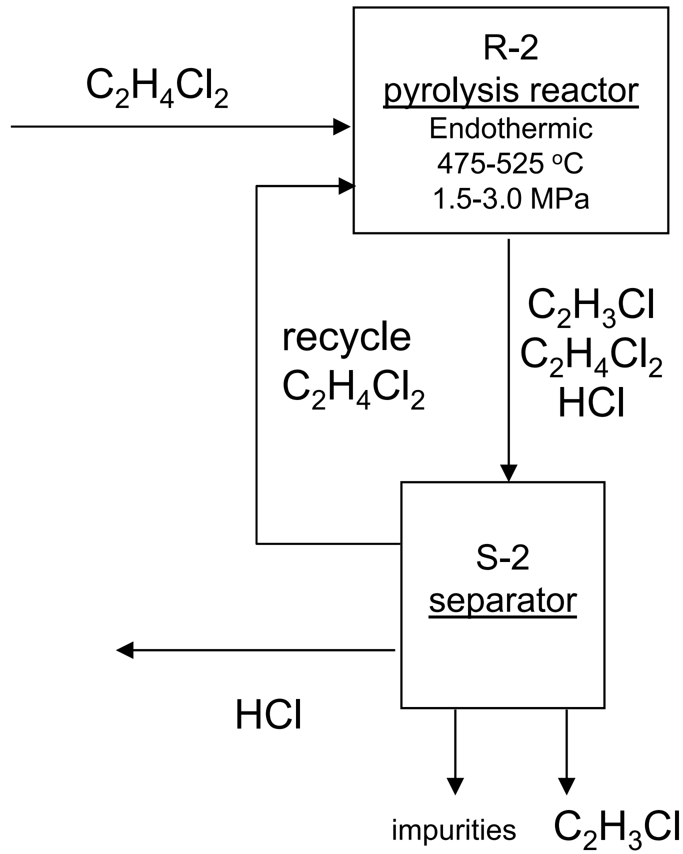
The utility of the functions diagram is that it can be used to build much larger processes.

$$C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2$$



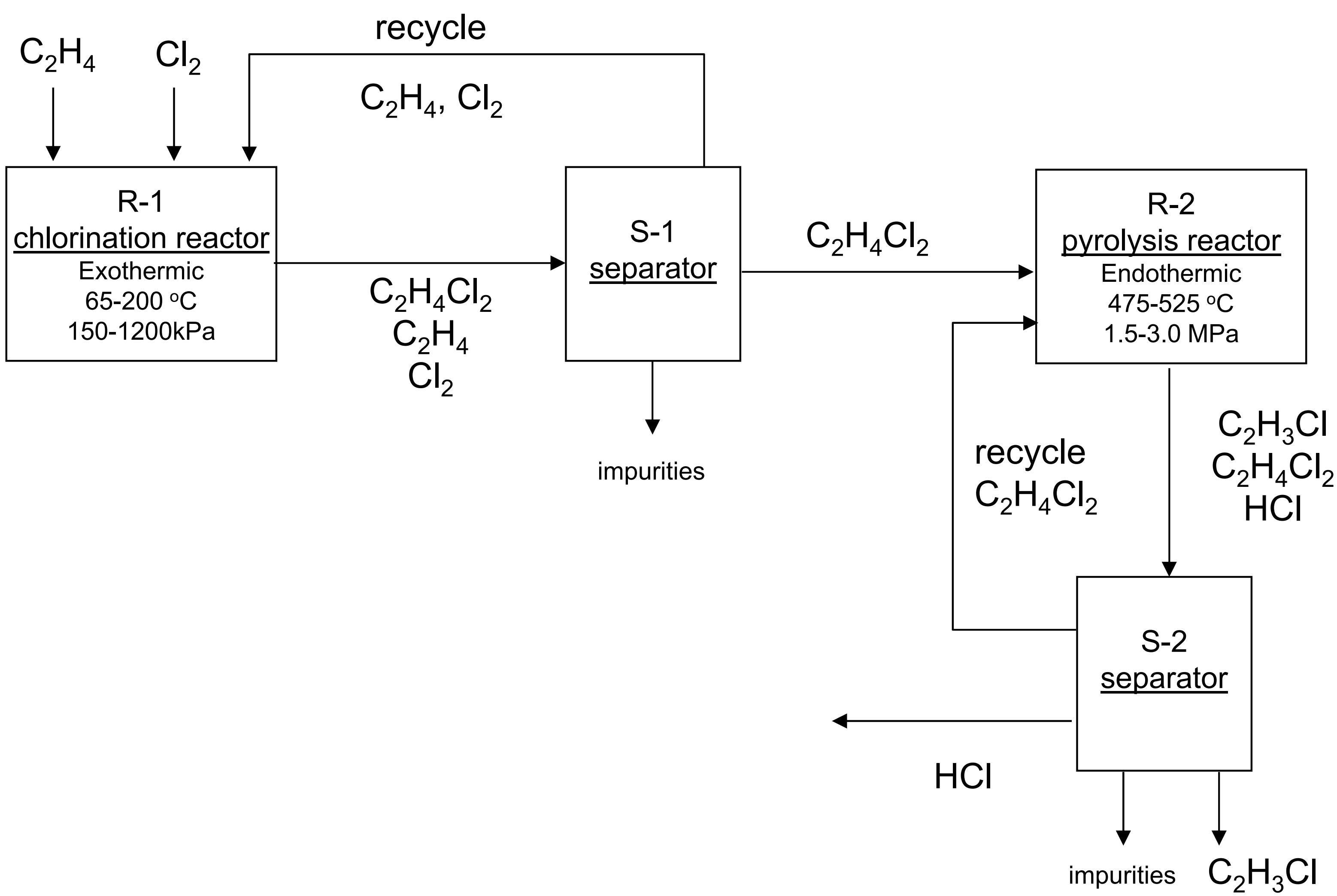

$$C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2$$ ethylene chlorination

# Functions Diagram – Pyrolysis

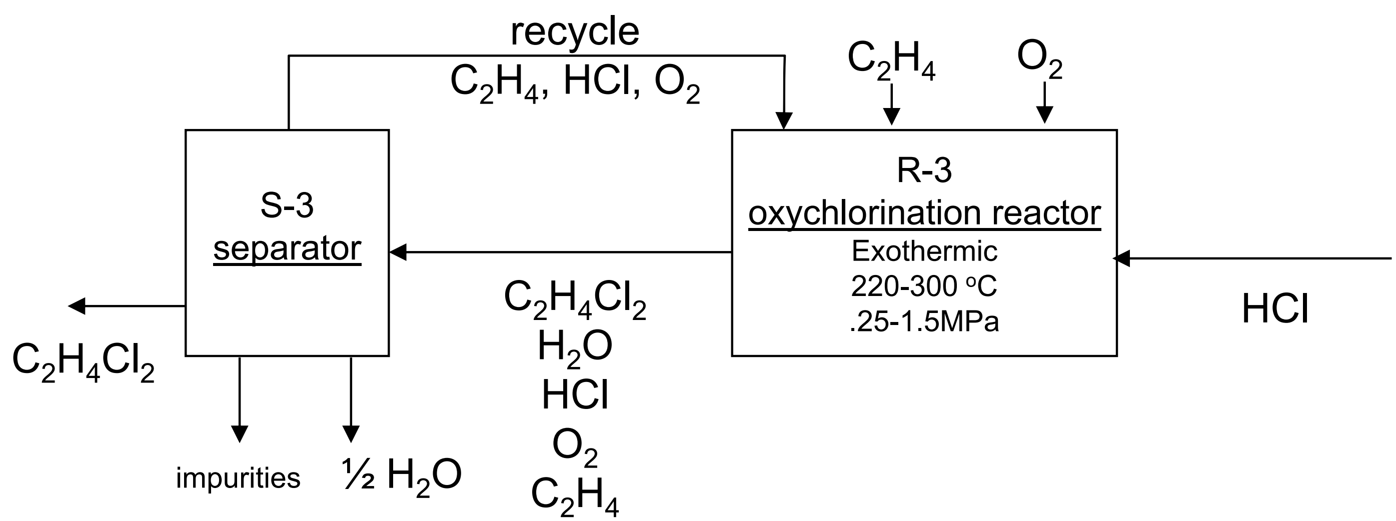


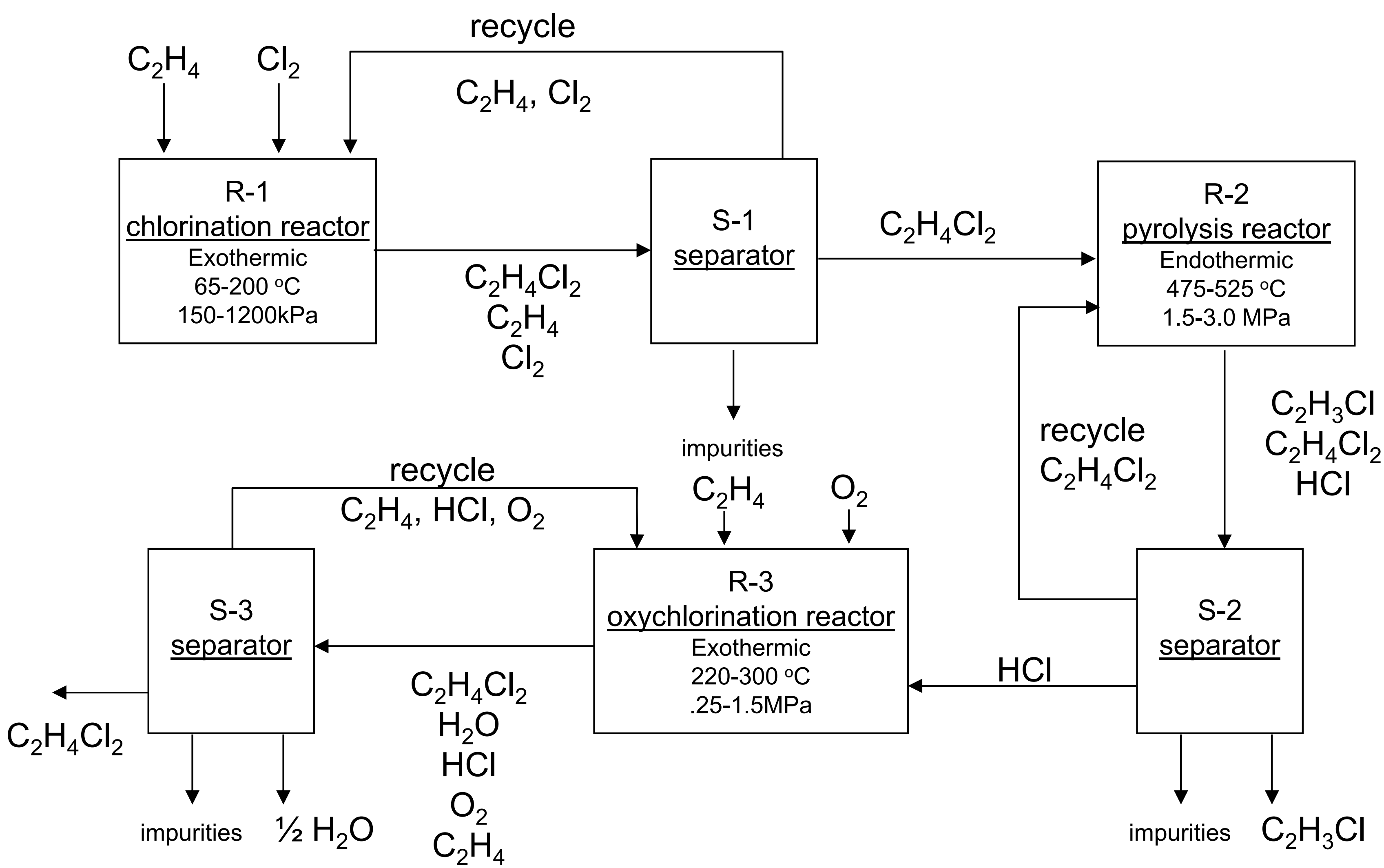

$$C_2H_4Cl_2 \longrightarrow C_2H_3Cl + HCl$$ pyrolysis

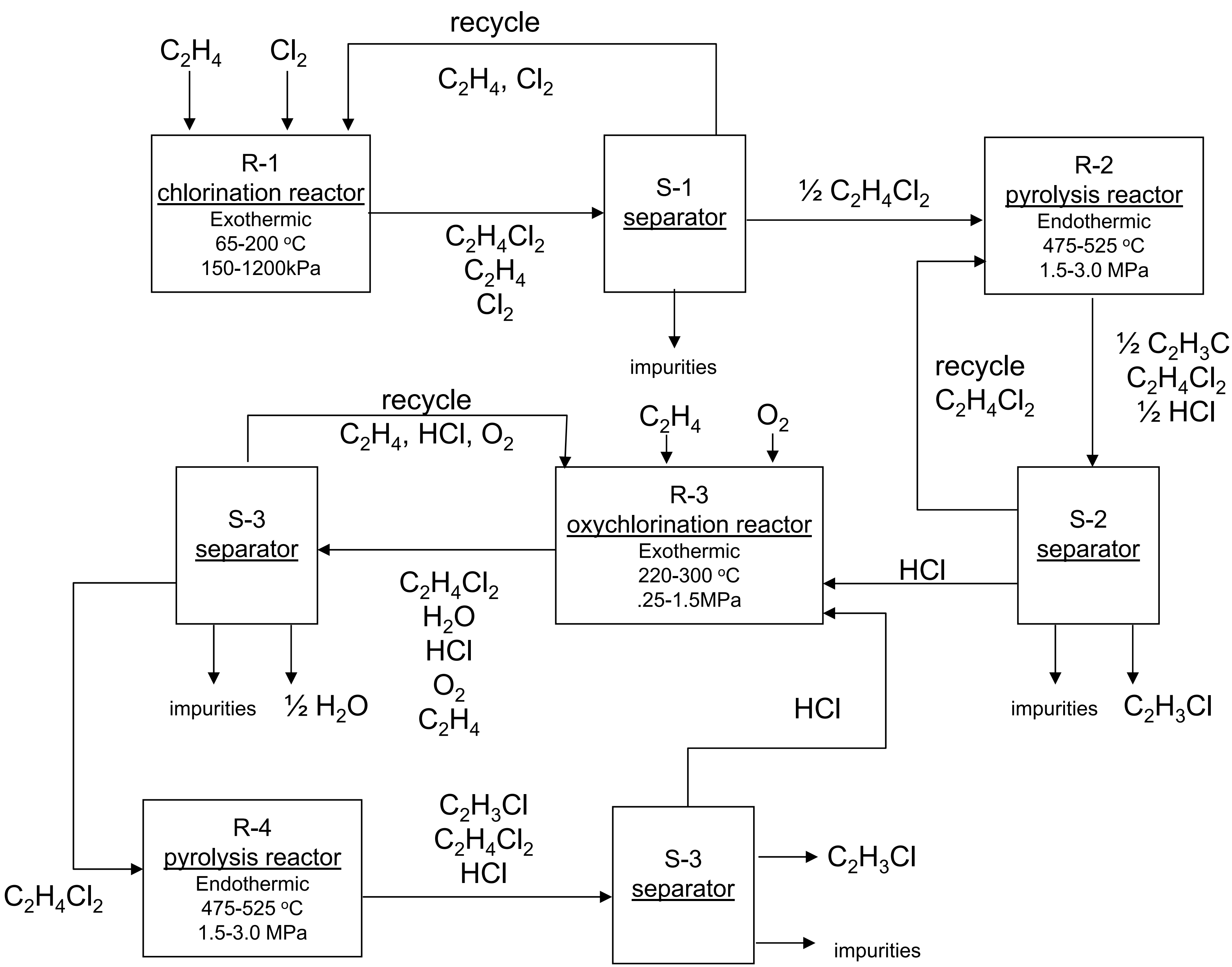
# Hybrid Functions Diagram - Route 3 - CP



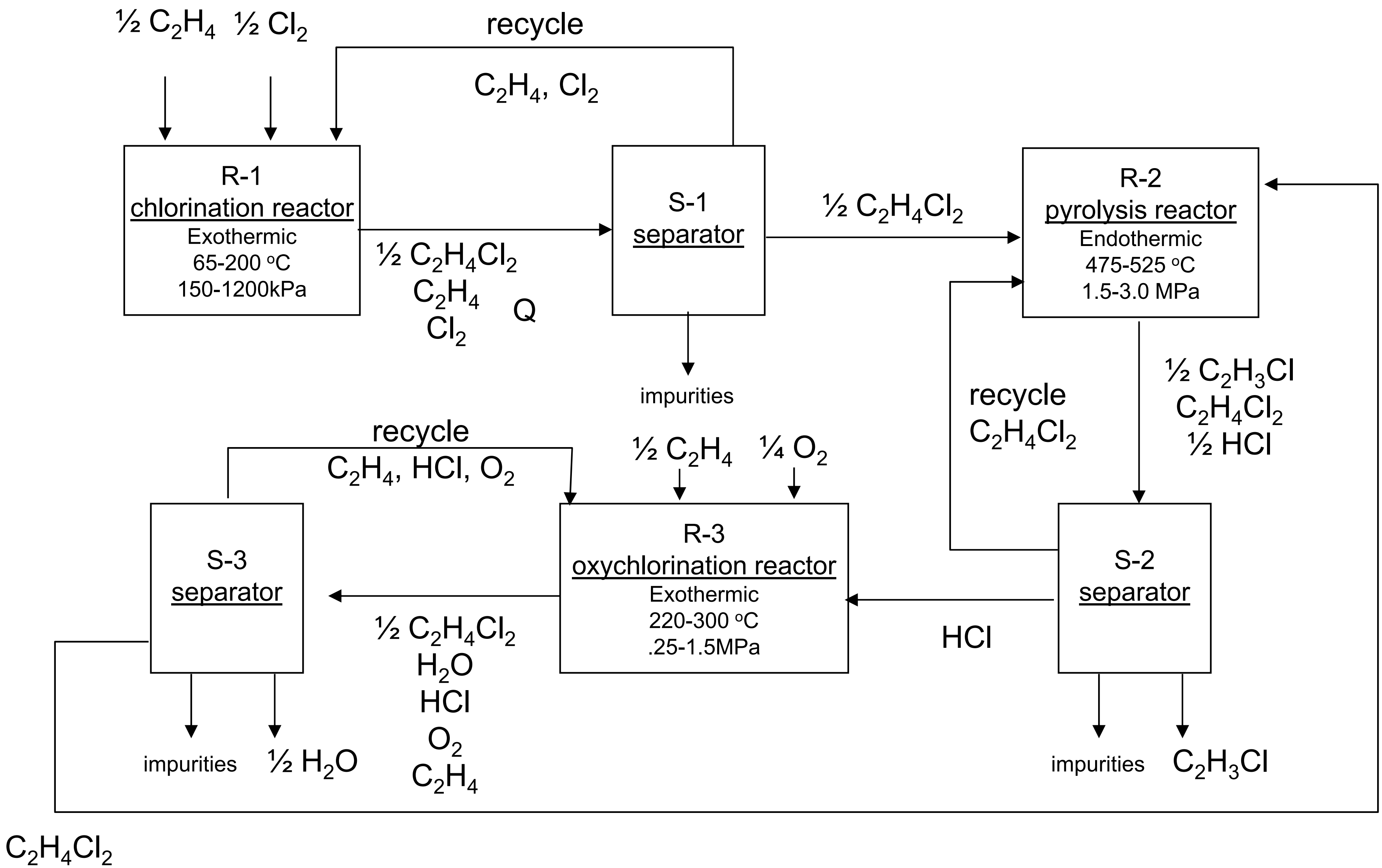
# Functions Diagram – Oxychlorination

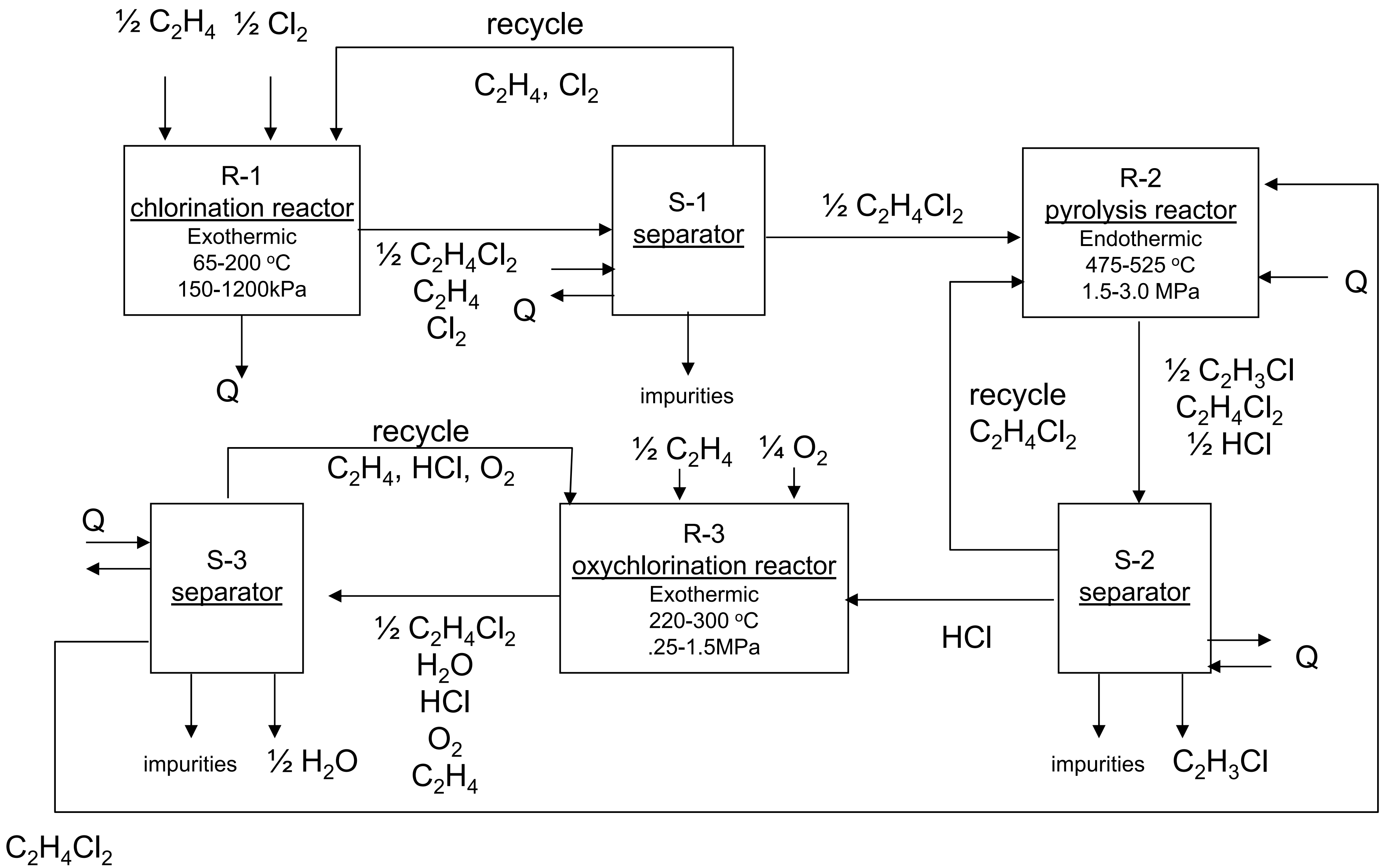



recycle
$C_2H_4$
$Cl_2$
$C_2H_4$, $Cl_2$
R-1
chlorination reactor
Exothermic
65-200 °C
150-1200kPa
$C_2H_4Cl_2$
$C_2H_4$
$Cl_2$
S-1
separator
$C_2H_4Cl_2$
R-2
pyrolysis reactor
Endothermic
475-525 °C
1.5-3.0 MPa
impurities
recycle
$C_2H_4Cl_2$
$C_2H_3Cl$
$C_2H_4Cl_2$
HCl
recycle
$C_2H_4$, HCl, $O_2$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





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
recycle
$C_2H_4$, HCl, $O_2$
½ $C_2H_4$ ¼ $O_2$
Q
S-3
separator
R-3
oxychlorination reactor
Exothermic
220-300 °C
.25-1.5MPa
½ $C_2H_4Cl_2$
$H_2O$
HCl
$O_2$
$C_2H_4$
impurities ½ $H_2O$
HCl
S-2
separator
Q
impurities $C_2H_3Cl$
$C_2H_4Cl_2$

# 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

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

gas-phase pyrolysis

$$C_2H_4Cl_2 \longrightarrow C_2H_3Cl + HCl$$

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

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: | \$0.05/kW·h |
| $H_2$: | \$6.00/kg (Google current price of hydrogen) |
| $O_2$: | \$0.04/kg (Kirk-Othmer) |
| Coal: | \$0.055/kg |
| Steam: | \$0.008/kg |
| NG: | \$0.13/kg |

basis: 1kg of $H_2$

Use same approach as Example 4-13

# Continuous versus Batch

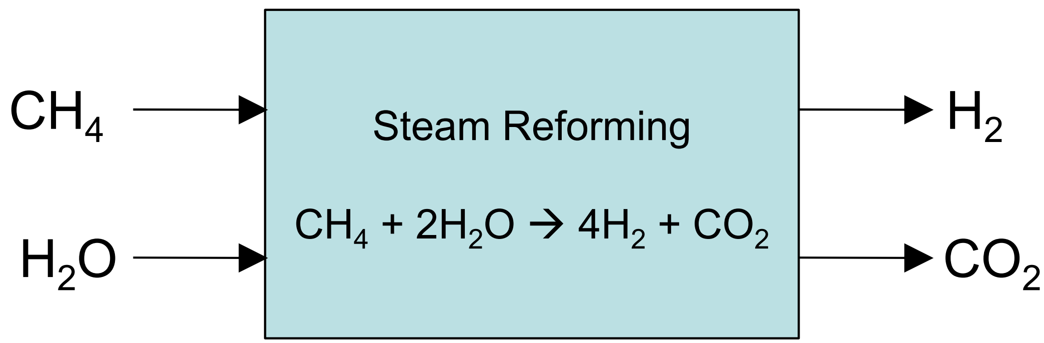
page 132-133

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 $3\times10^7$ and $1\times10^8$ kg/yr?




basis: 1kg of $H_2$

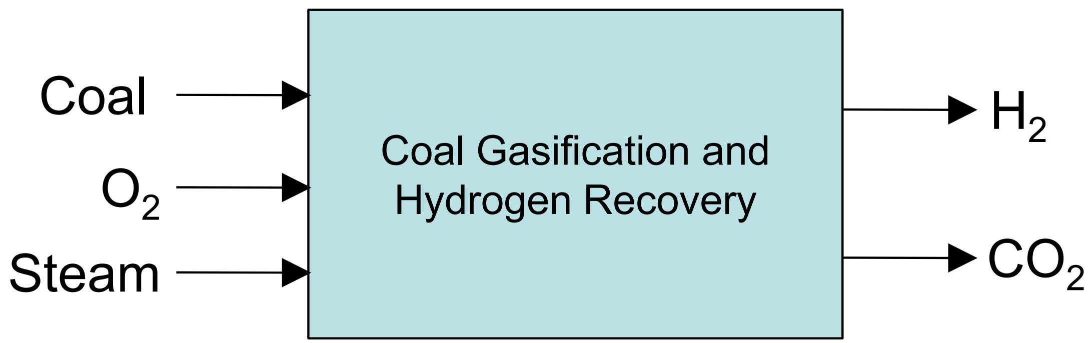
| | |
|---|---|
| $H_2$: | \$6.00/kg (Google current price of hydrogen) |
| $O_2$: | \$0.04/kg (Kirk-Othmer) |
| Steam: | \$0.008/kg |
| NG: | \$1.295/kg |

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”).



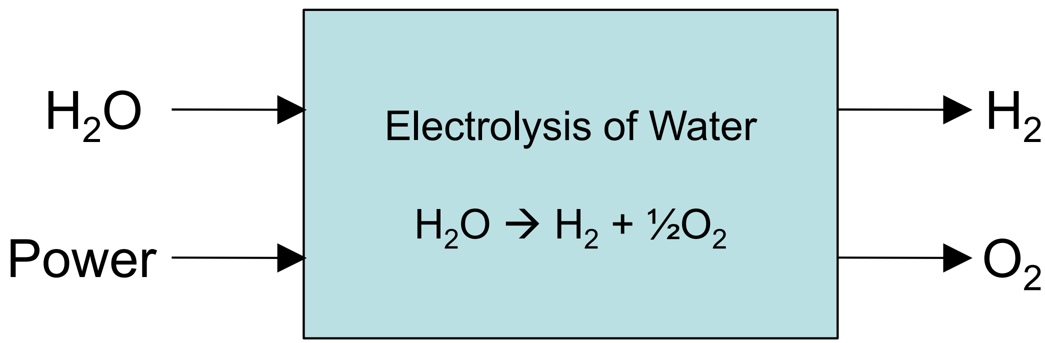

basis: 1kg of $H_2$

| | |
|---|---|
| $H_2$: | \$6.00/kg (Google current price of hydrogen) |
| $O_2$: | \$0.04/kg (Kirk-Othmer) |
| Coal: | \$0.0675/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.

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: | \$0.05/kW·h |
| $H_2$: | \$6.00/kg (Google current price of hydrogen) |
| $O_2$: | \$0.04/kg (Kirk-Othmer) |

# Questions?