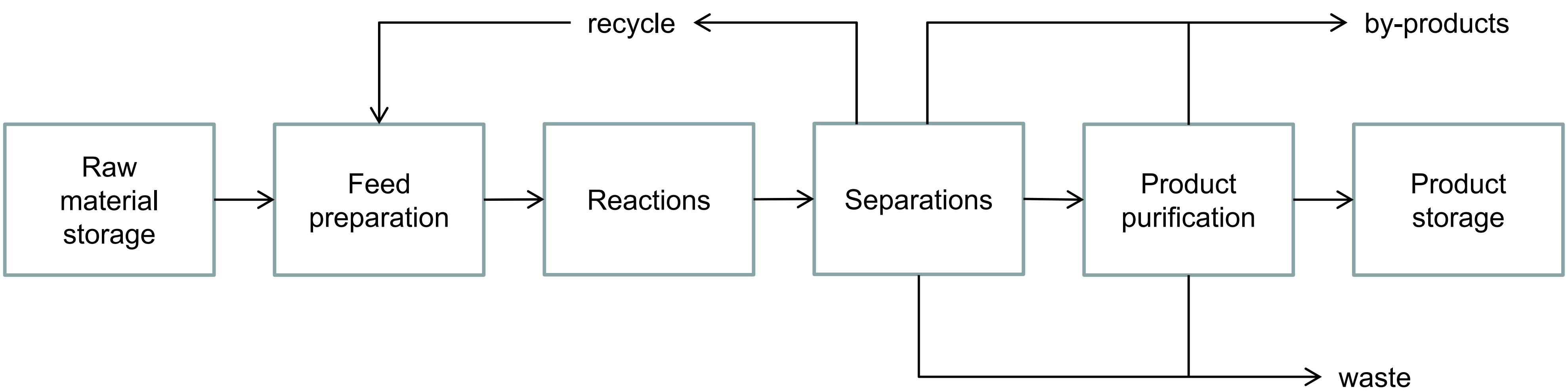
CH402 Chemical Engineering Process Design

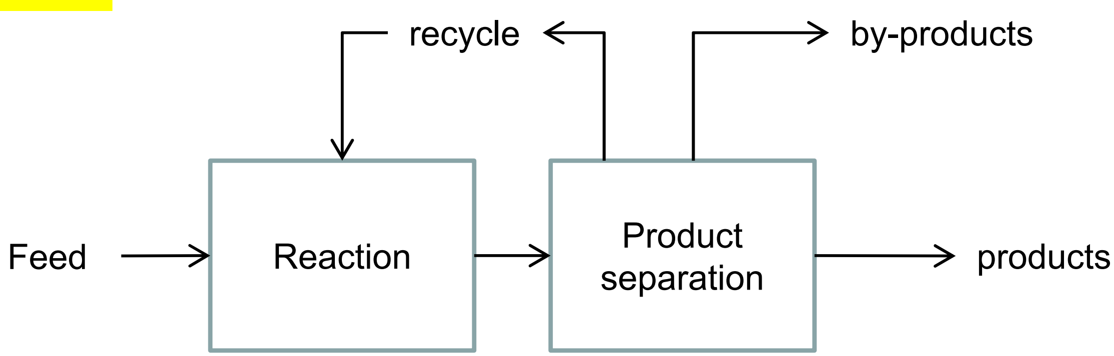
Class Notes L13

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

Known Vinyl Chloride Routes

Next step is a literature search – 5 Routes Identified

Kirk-Othmer, Wikipedia

(CH383)

$$C_2H_2 + HCl \longrightarrow C_2H_3Cl$$

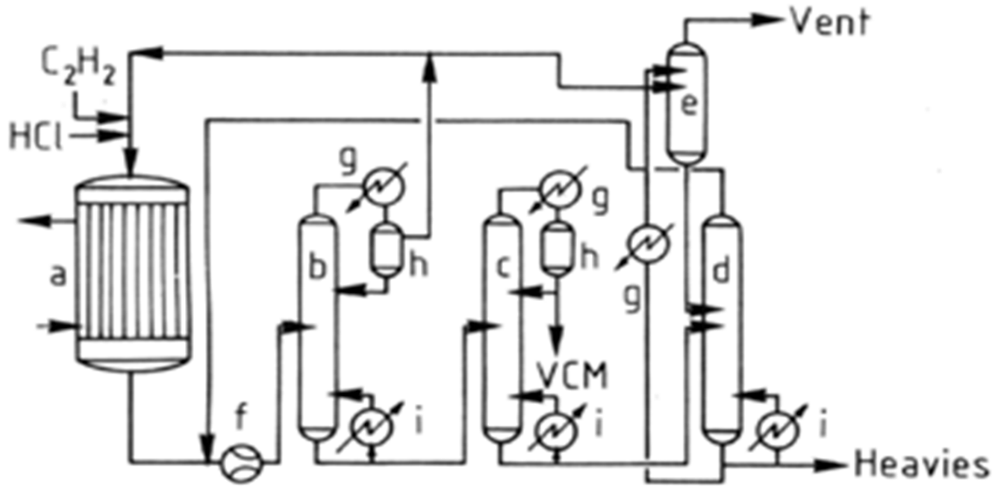
Route 1
direct reaction of acetylene
(acetylene hydrochlorination)

Vinyl Chloride Process Flow Diagram

Ullmann’s Encylcopedia of Industrial Chemistry

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

Surfhvv#Iorz#Gldjudp#+SIG,
Vlplodu#wr#FKHPFDG



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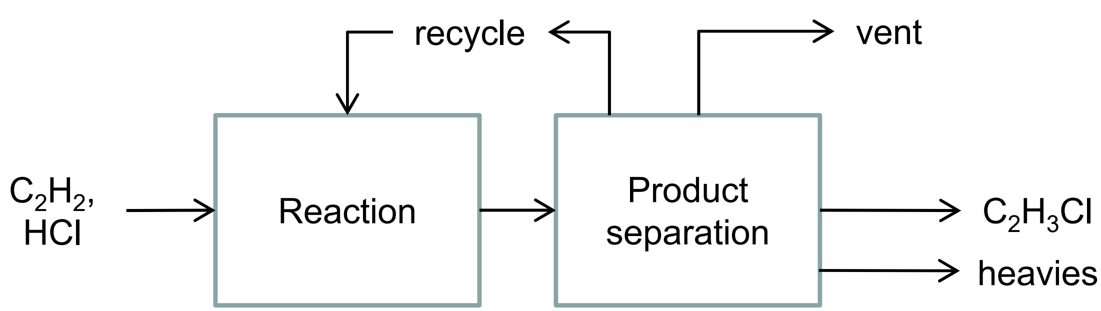


Known Vinyl Chloride Routes

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

$$C_2H_4 + Cl_2 \longrightarrow C_2H_3Cl + HCl$$

Route 3
direct chlorination + pyrolysis

Known Vinyl Chloride Routes

Kirk-Othmer, Wikipedia

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

$$C_2H_4Cl_2 \longrightarrow C_2H_3Cl + HCl$$ pyrolysis

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

Route 4
oxychlorination + pyrolysis

Known Vinyl Chloride Routes

Kirk-Othmer, Wikipedia

Literature Search

$C_2H_4 + Cl_2$	$\longrightarrow$	$C_2H_4Cl_2$	chlorination
			+
$C_2H_4 + 2HCl + ½ O_2$	$\longrightarrow$	$C_2H_4Cl_2 + H_2O$	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

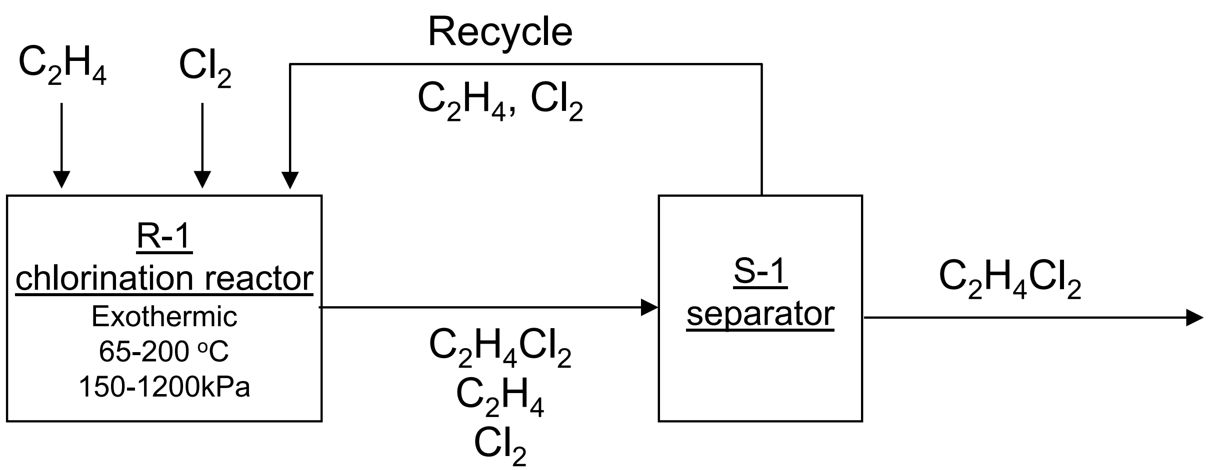
5 processes identified in literature survey

Reactants		Products		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

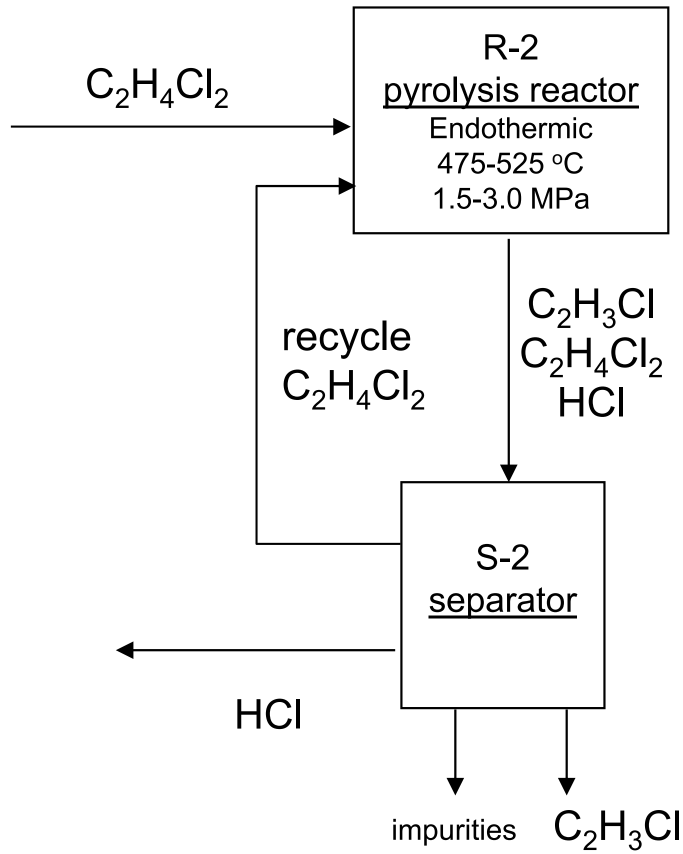
The utility of the functions diagram is that it can be used to build much larger processes.

$$C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2$$



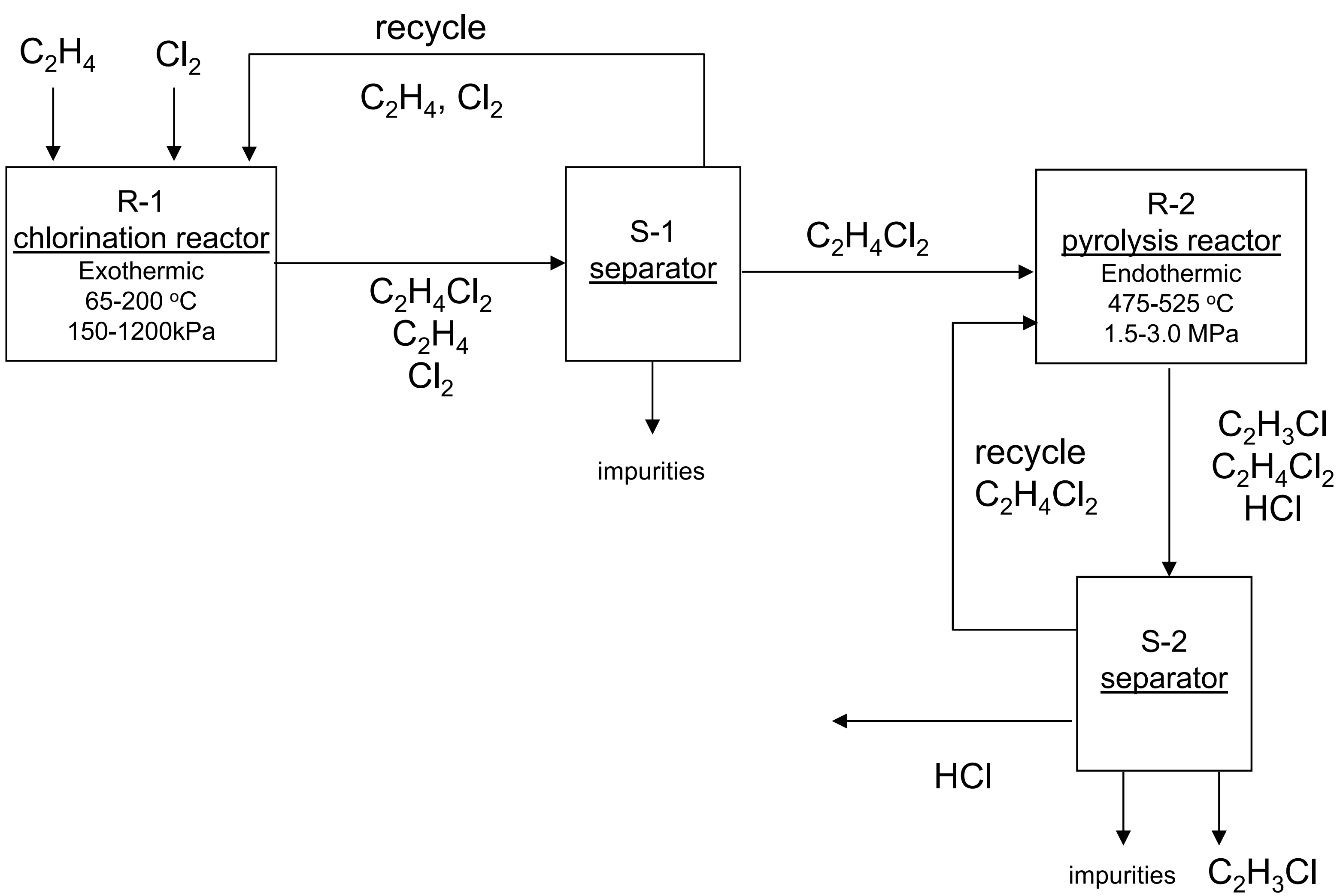
$C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2$ ethylene chlorination

Functions Diagram – Pyrolysis

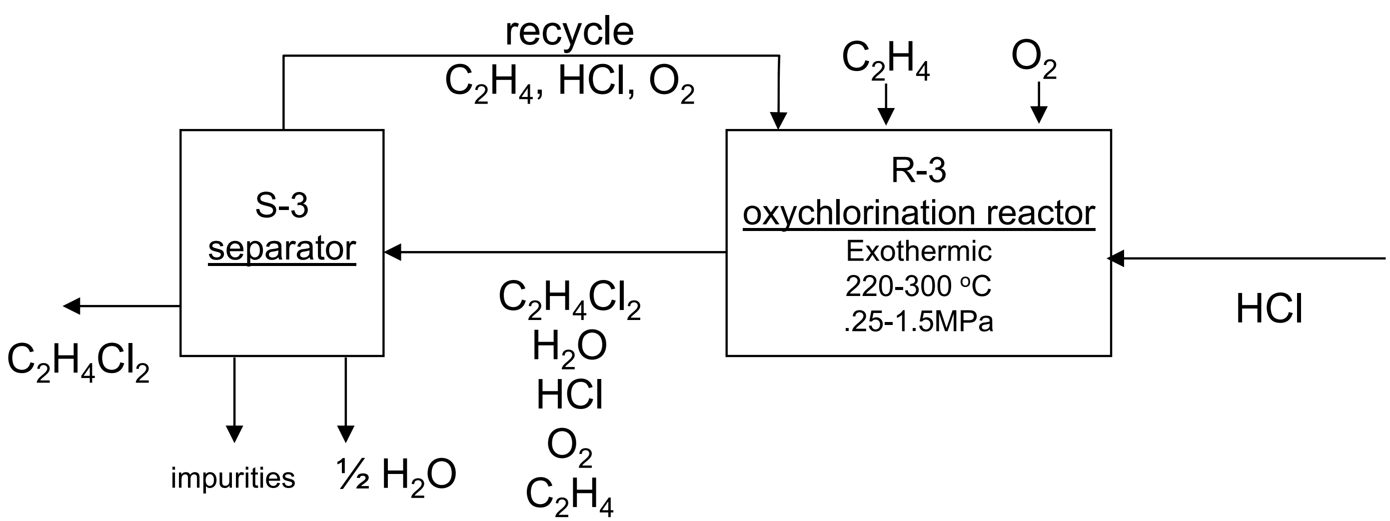


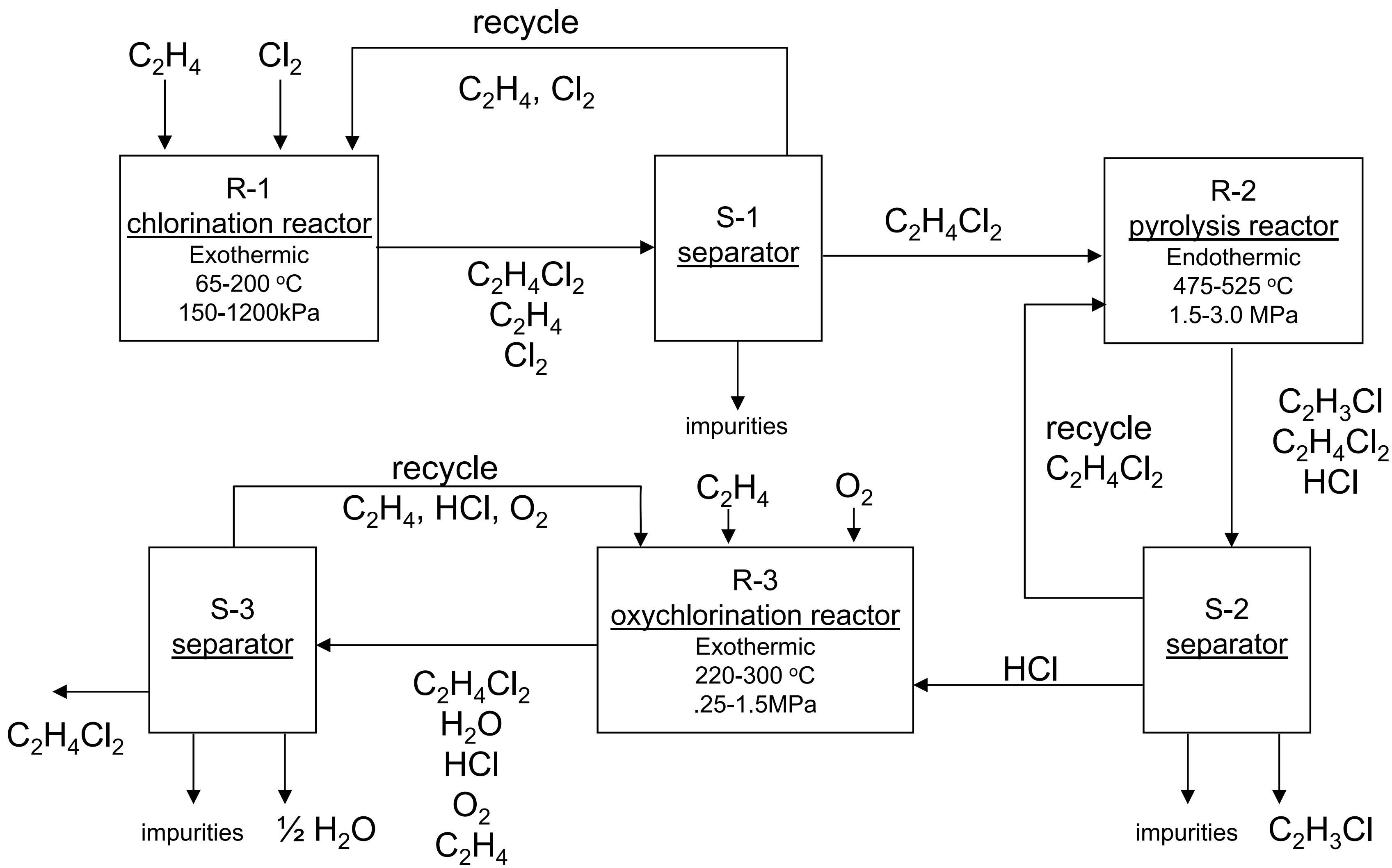
$$C_2H_4Cl_2 \longrightarrow C_2H_3Cl + HCl$$ pyrolysis

Hybrid Functions Diagram - Route 3 - CP

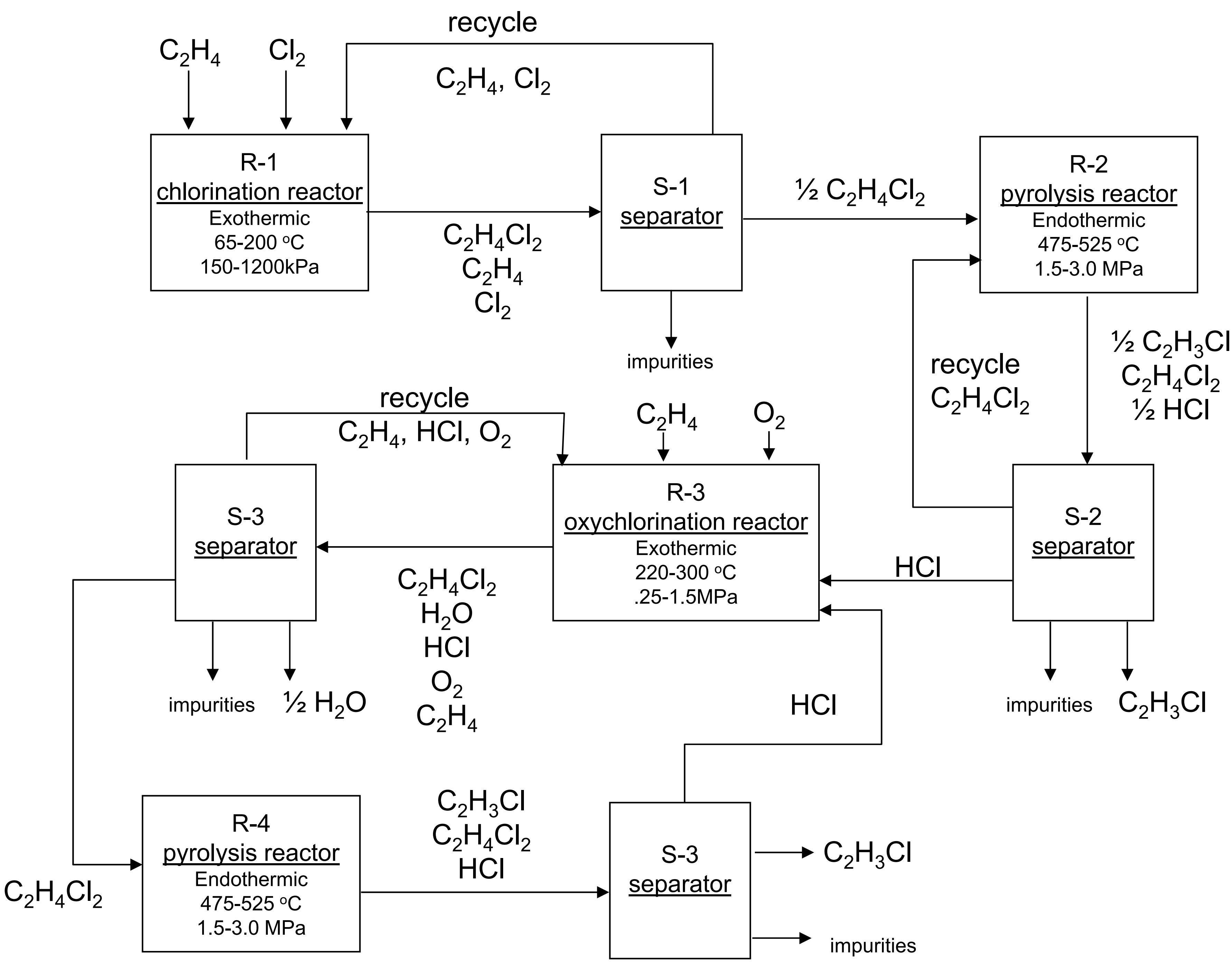


Functions Diagram – Oxychlorination

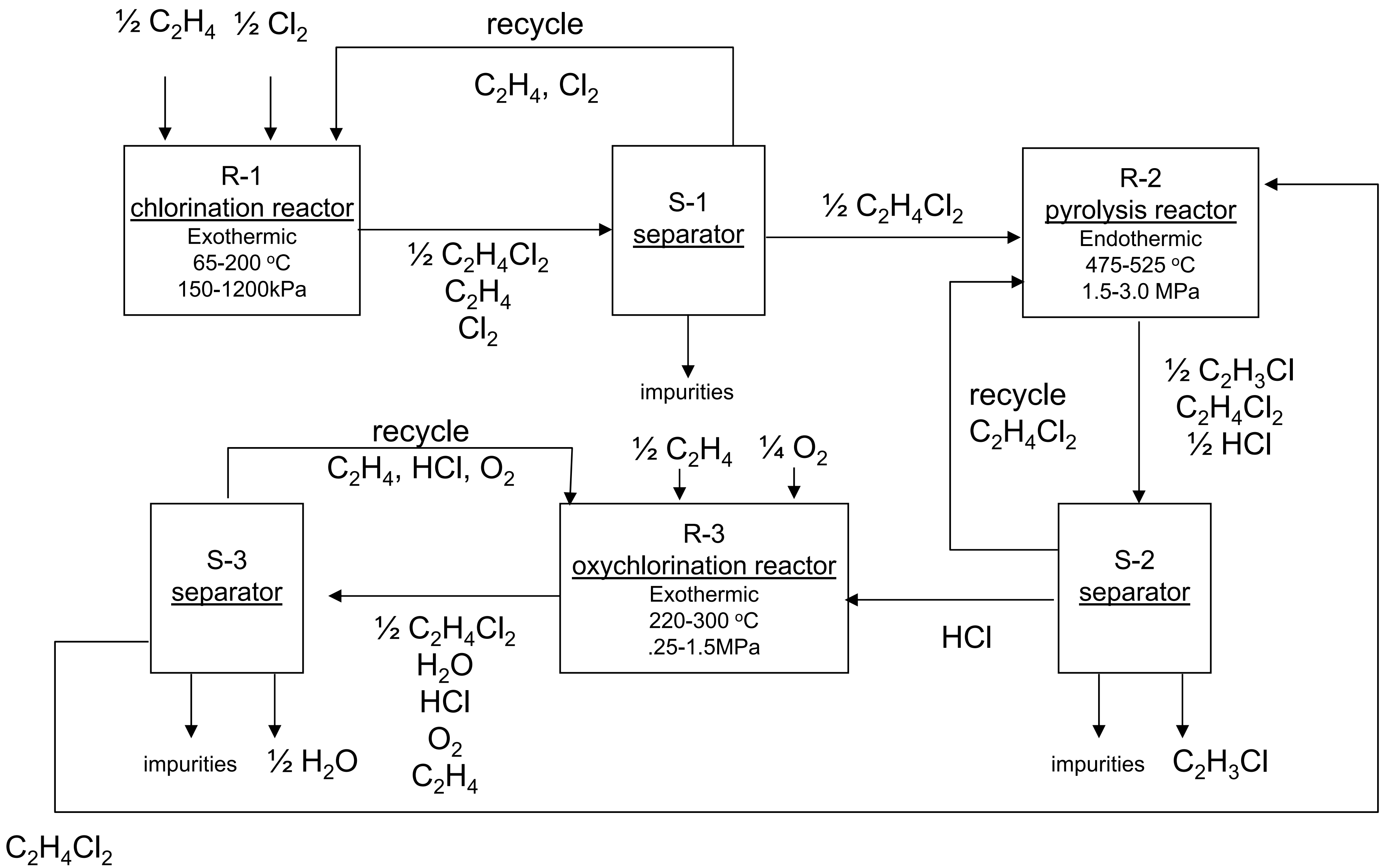




recycle
C_2H_4
Cl_2
C_2H_4, Cl_2
R-1
chlorination reactor
Exothermic
65-200 °C
150-1200kPa
$C_2H_4Cl_2$
C_2H_4
Cl_2
S-1
separator
impurities
$C_2H_4Cl_2$
R-2
pyrolysis reactor
Endothermic
475-525 °C
1.5-3.0 MPa
C_2H_3Cl
$C_2H_4Cl_2$
HCl
recycle
$C_2H_4Cl_2$
S-2
separator
impurities
C_2H_3Cl
HCl
recycle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


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
$C_2H_4Cl_2$
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
S-2
separator
HCl
$C_2H_4Cl_2$
H_2O
HCl
O_2
C_2H_4
impurities
½ H_2O
HCl
impurities
C_2H_3Cl
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



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

				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

			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.

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:	\$.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

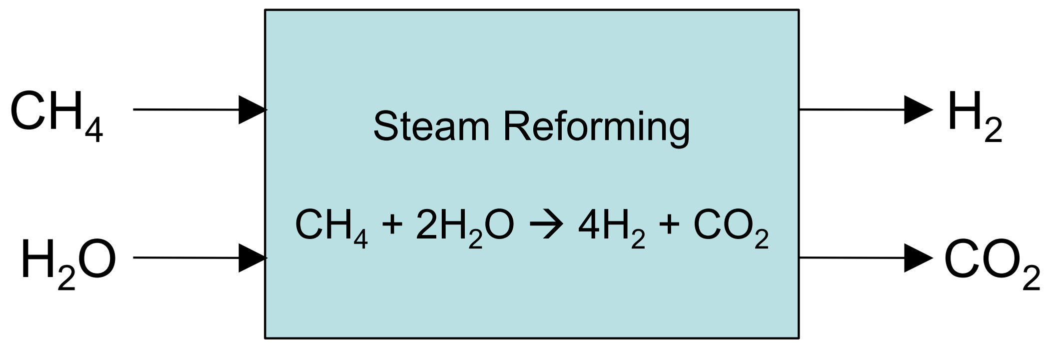
page 132-133

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

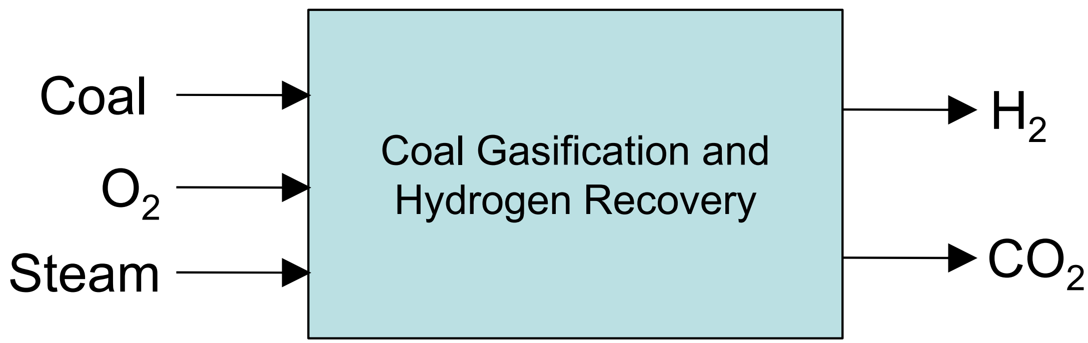
H_2:	\$.67/kg (Kirk-Othmer)
O_2:	\$.04/kg (Kirk-Othmer)
Steam:	\$.008/kg
NG:	\$.13/kg

Problem 4.13

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

Need stoichiometry (reaction coefficients).

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



basis: 1kg of H_2

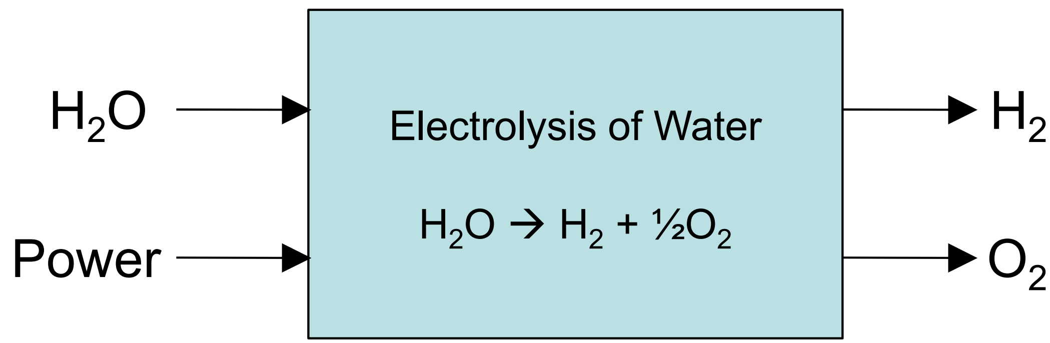
H_2:	$.67/kg (Kirk-Othmer)
O_2:	$.04/kg (Kirk-Othmer)
Coal:	$.055/kg
Steam:	$.008/kg

Problem 4.13

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

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:

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

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

Overall (water electrolysis):

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

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?