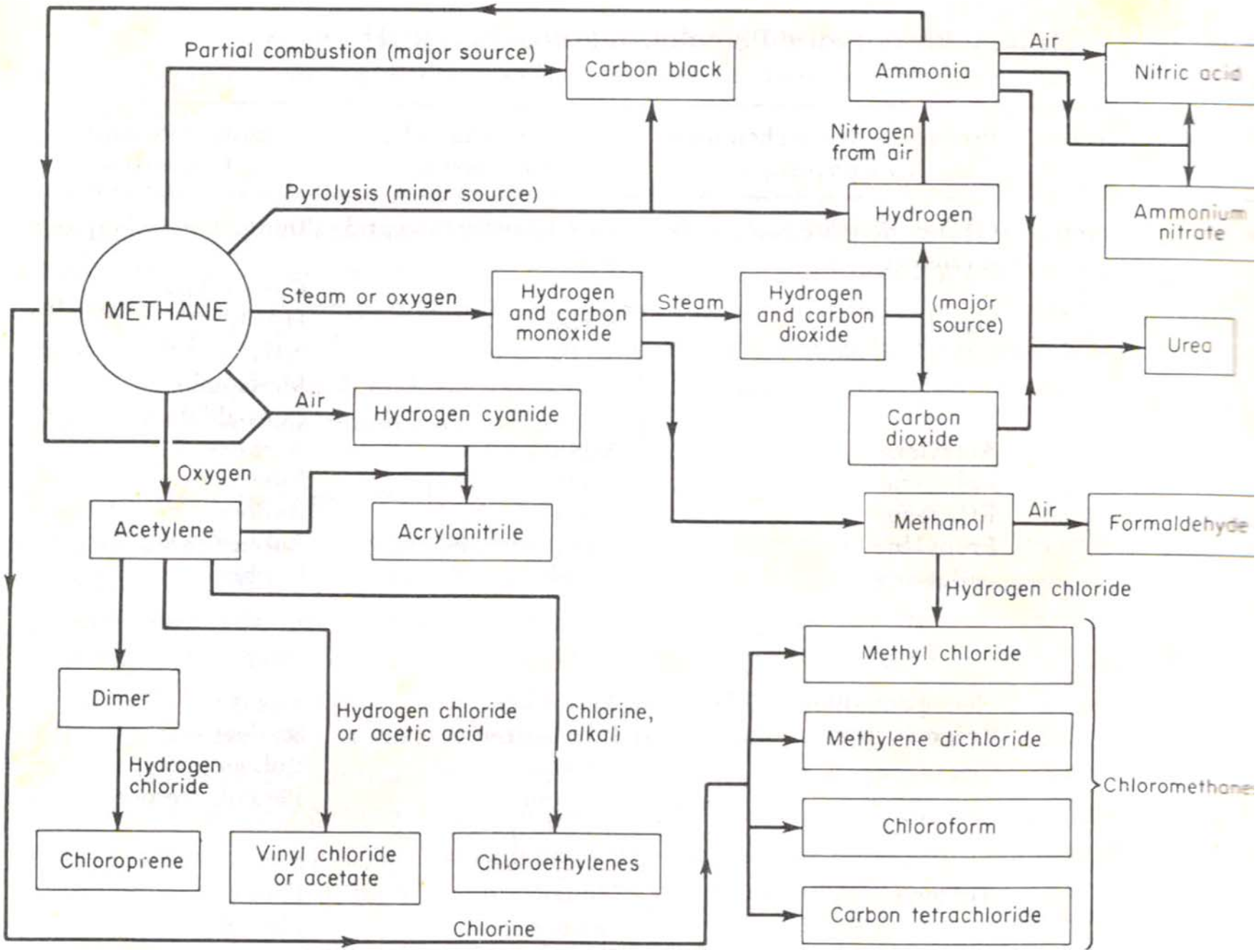
Petrochem / hydrocarbon based chemicals (organics)

Sourav Mondal

Department of Chemical Engineering

IIT Kharagpur


Partial combustion (major source)
Carbon black
Ammonia
Air
Nitric acid
Nitrogen from air
Pyrolysis (minor source)
Hydrogen
Ammonium nitrate
METHANE
Steam or oxygen
Hydrogen and carbon monoxide
Steam
Hydrogen and carbon dioxide
(major source)
Urea
Air
Hydrogen cyanide
Carbon dioxide
Oxygen
Acetylene
Acrylonitrile
Methanol
Air
Formaldehyde
Hydrogen chloride
Methyl chloride
Dimer
Hydrogen chloride or acetic acid
Chlorine, alkali
Methylene dichloride
Hydrogen chloride
Chloroform
Chloromethanes
Chloroprene
Vinyl chloride or acetate
Chloroethylenes
Carbon tetrachloride
Chlorine

Formaldehyde

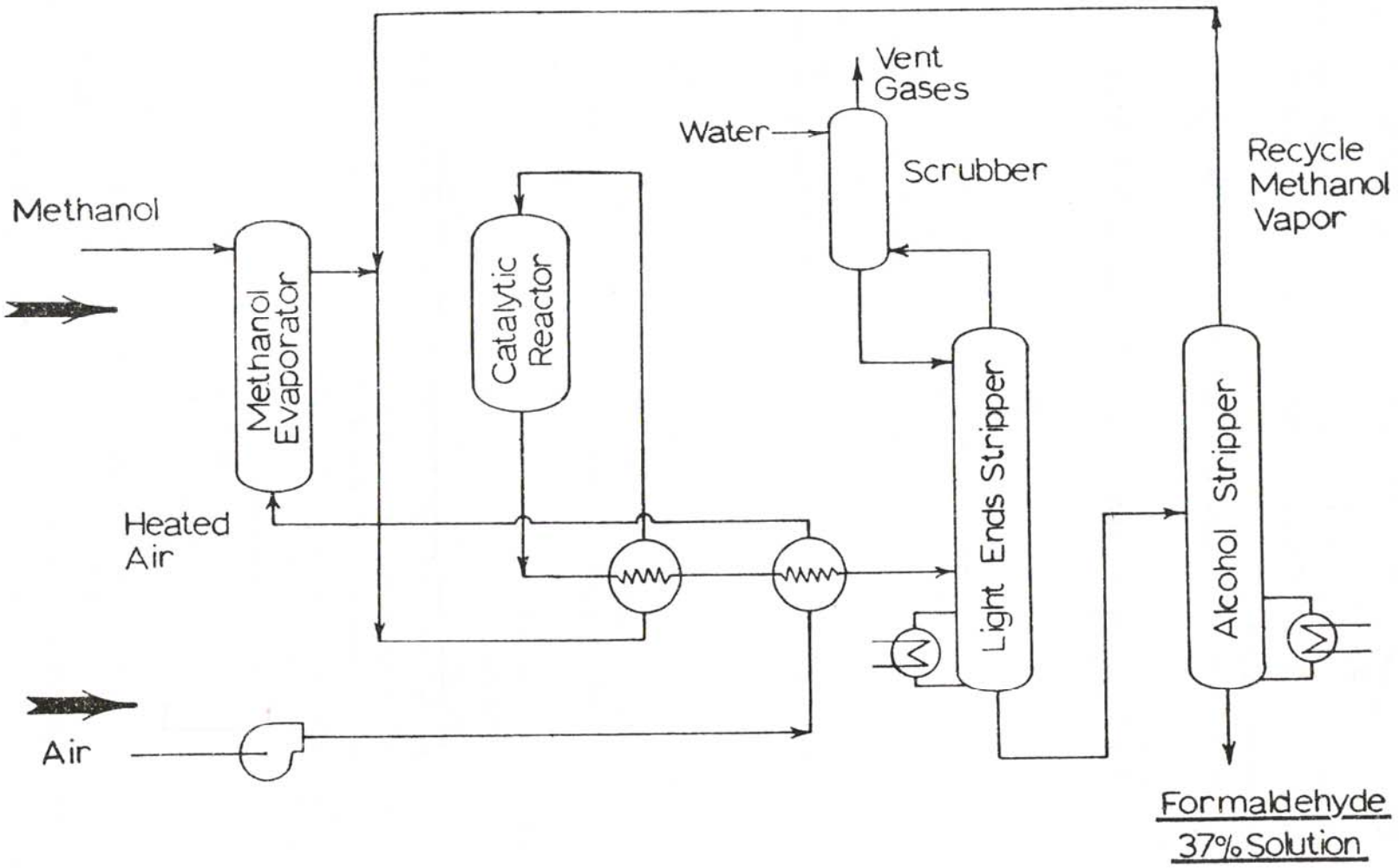
Catalytic oxidation of methanol:

$$CH_3OH + \frac{1}{2}O_2 \longrightarrow HCHO + H_2O \qquad \Delta H = -37 \text{ kcal}$$

Pyrolysis: $CH_3OH \longrightarrow HCHO + H_2$ $\qquad \Delta H = +20$ kcal

Side rxns: $CH_3OH + \frac{3}{2}O_2 \longrightarrow 2H_2O + CO_2$ $\qquad \Delta H = 160$ kcal

Catalytic oxidation of CH_4 or LPG can also produce HCHO, but separation of products is difficult & also the catalyst needed are expensive.


Vent
Gases
Water
Scrubber
Recycle
Methanol
Vapor
Methanol
Methanol
Evaporator
Catalytic
Reactor
Heated
Air
Light Ends Stripper
Alcohol Stripper
Air
Formaldehyde
37% Solution

Methanol

Catalytic hydrogenation of CO

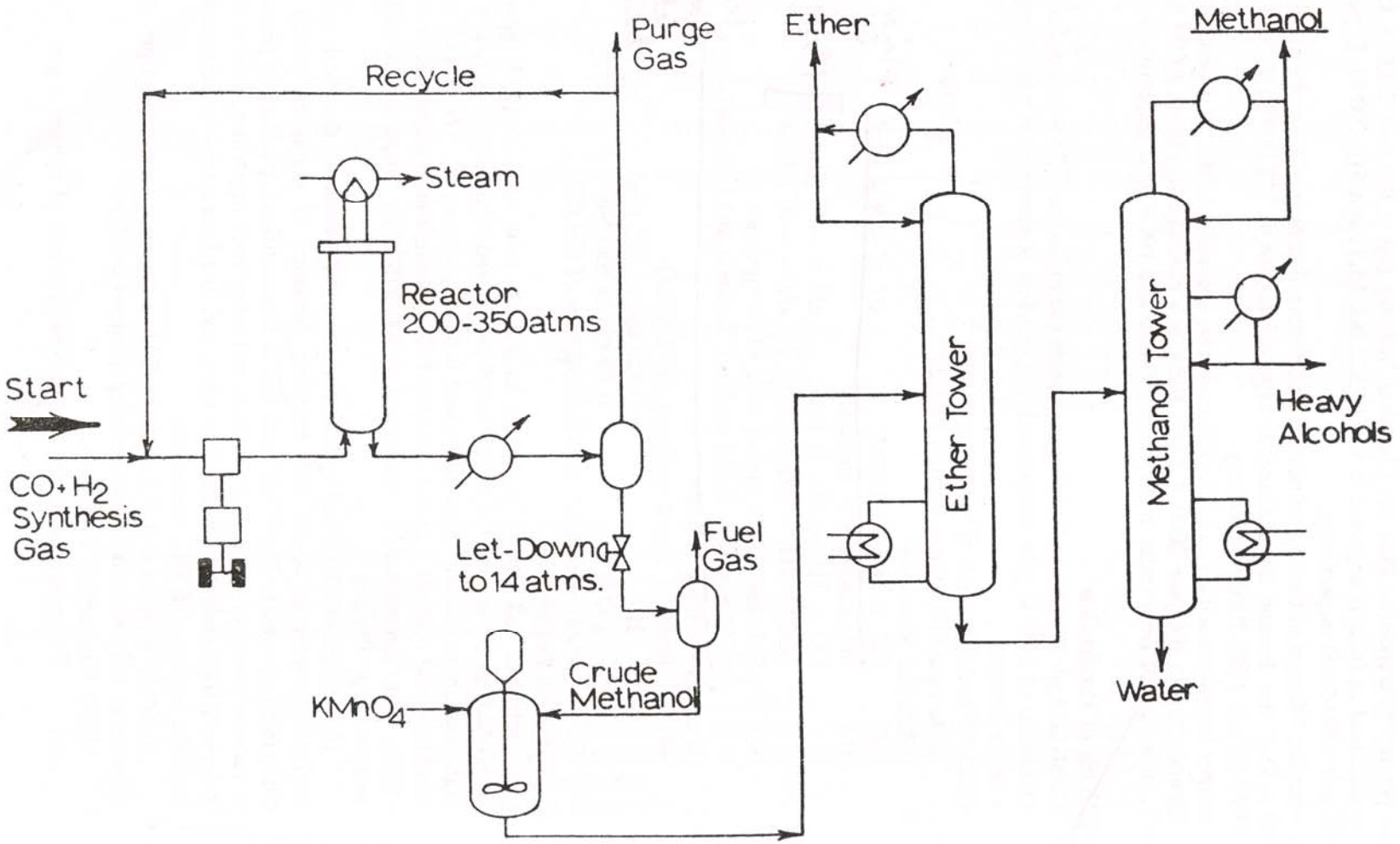
(+) $CO + 2H_2 \rightarrow CH_3OH$ $\Delta H = -26$ kcal

side rxns:

$CO + 3H_2 \rightarrow CH_4 + H_2O$ $\Delta H = -50$ kcal

$2CO + 2H_2 \rightarrow CH_4 + CO_2$ $\Delta H = -60$ kcal

$xCO + yH_2 \rightarrow$ higher MW HC organics



Question to think: $KMnO_4$ is a strong oxidising agent, so will it not affect/oxidise methanol?

Chloromethanes

Direct thermal methane chlorination

$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$ BP :- 24°C

$CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl$ BP 40°C

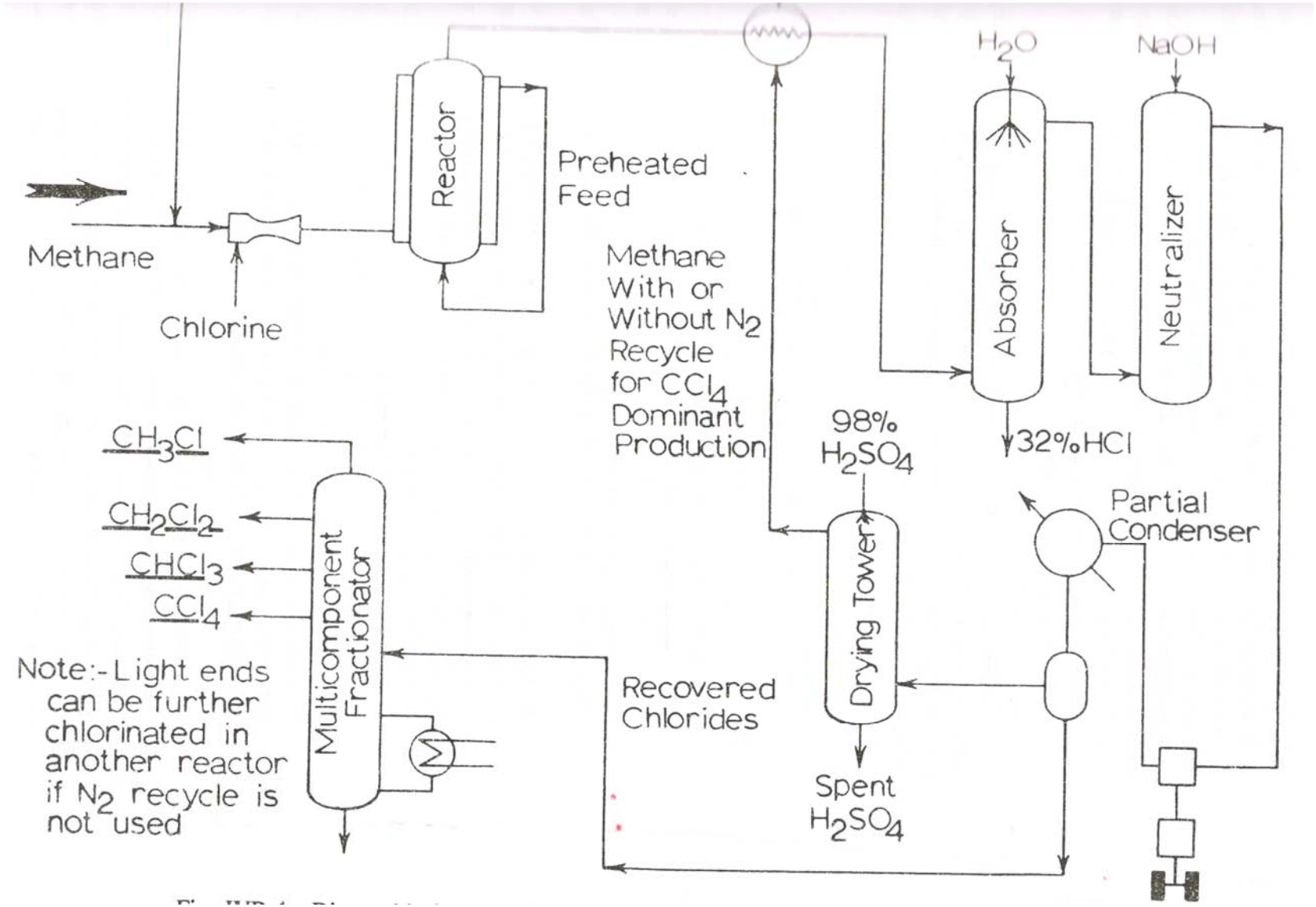
$CH_2Cl_2 + Cl_2 \rightarrow CHCl_3 + HCl$ BP 61°C

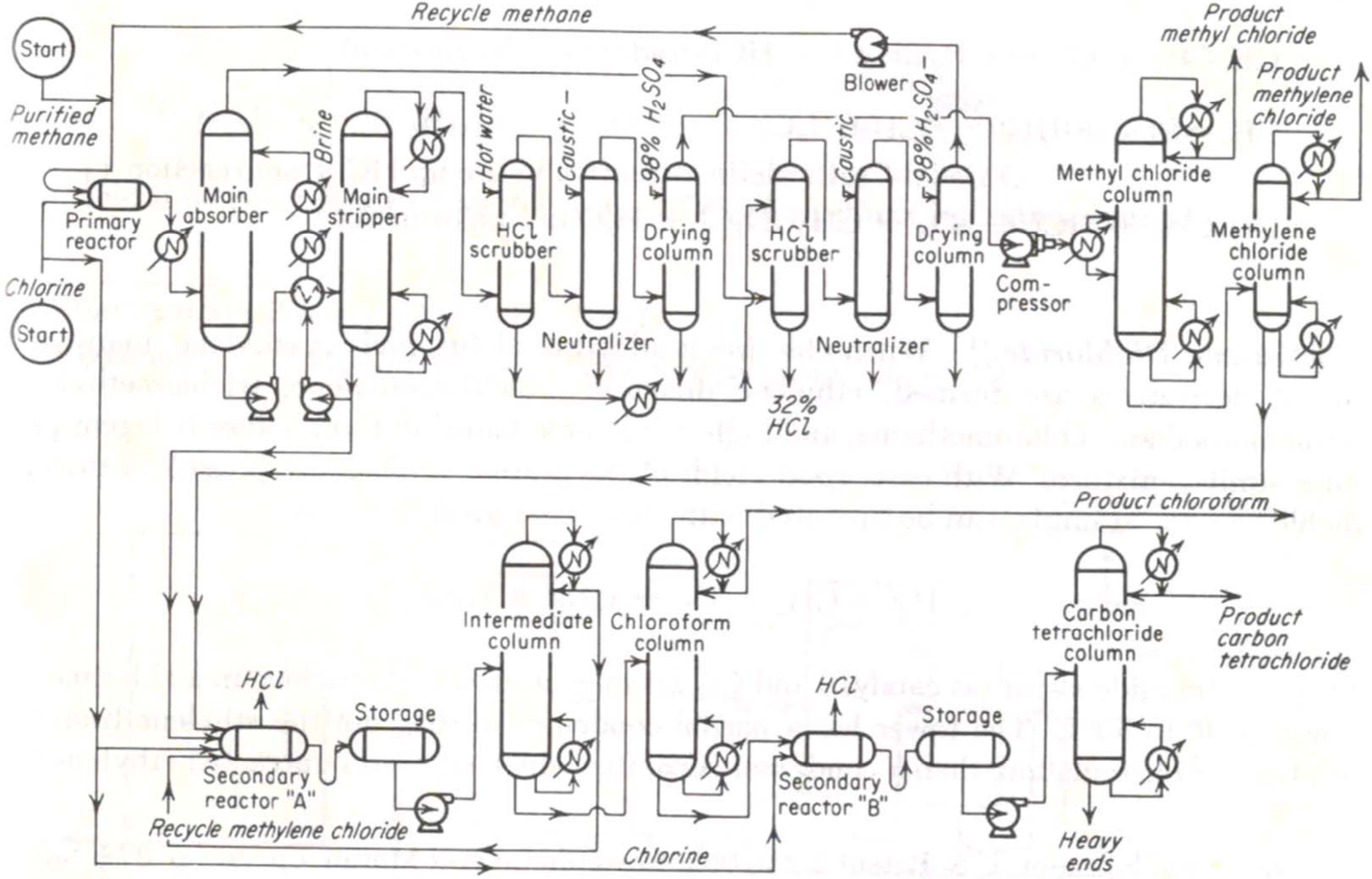
$CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$ BP 77°C

All rxns are exothermic: typically −24 kcal/mole of CH_4

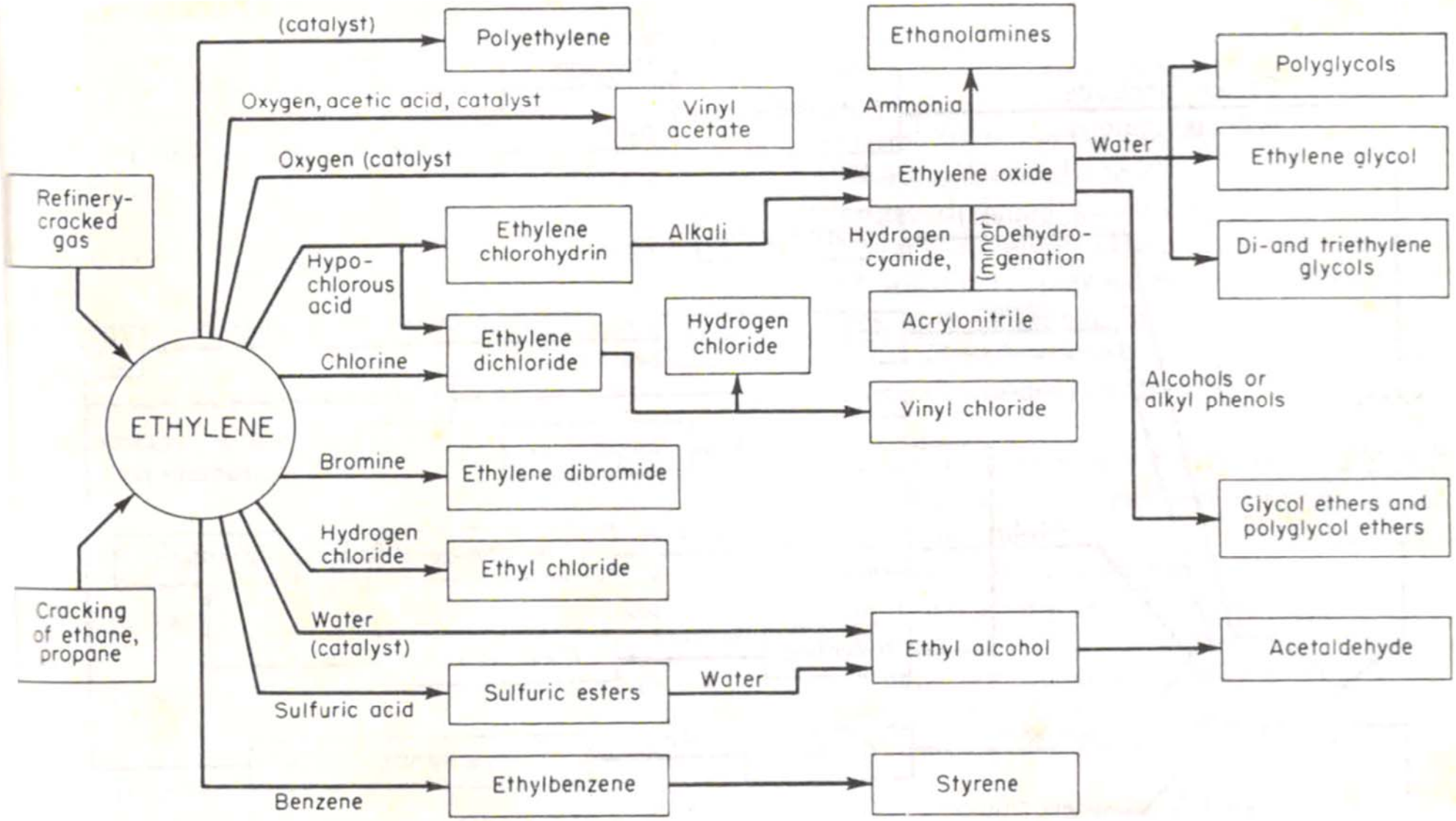
For a feed ratio of $CH_4 : Cl_2 = 1.8$, product compositions are:

CH_3Cl – 60% CH_2Cl_2 – 28% $CHCl_3$ – 9% CCl_4 – 3%


Methane
Chlorine
Reactor
Preheated Feed
Methane With or Without N_2 Recycle for CCl_4 Dominant Production
H_2O
NaOH
Absorber
Neutralizer
32% HCl
98% H_2SO_4
Partial Condenser
Drying Tower
Spent H_2SO_4
Recovered Chlorides
Multicomponent Fractionator
CH_3Cl
CH_2Cl_2
$CHCl_3$
CCl_4
Note:- Light ends can be further chlorinated in another reactor if N_2 recycle is not used


Recycle methane
Start
Purified methane
Primary reactor
Chlorine
Start
Main absorber
Brine
Main stripper
Hot water
HCl scrubber
Caustic
Neutralizer
98% H_2SO_4
Drying column
Blower
HCl scrubber
Caustic
Neutralizer
98% H_2SO_4
Drying column
Com-pressor
32% HCl
Product methyl chloride
Product methylene chloride
Methyl chloride column
Methylene chloride column
Product chloroform
Intermediate column
Chloroform column
Carbon tetrachloride column
Product carbon tetrachloride
HCl
Storage
Secondary reactor "A"
Recycle methylene chloride
HCl
Storage
Secondary reactor "B"
Chlorine
Heavy ends

Ethylene - Acetylene



Ethylene - Acetylene

Steam cracking / pyrolysis of LPG & naphtha

Dehydration of ethanol — not economically competitive in the long term

Thermal pyrolysis of ethane / propane — not attractive

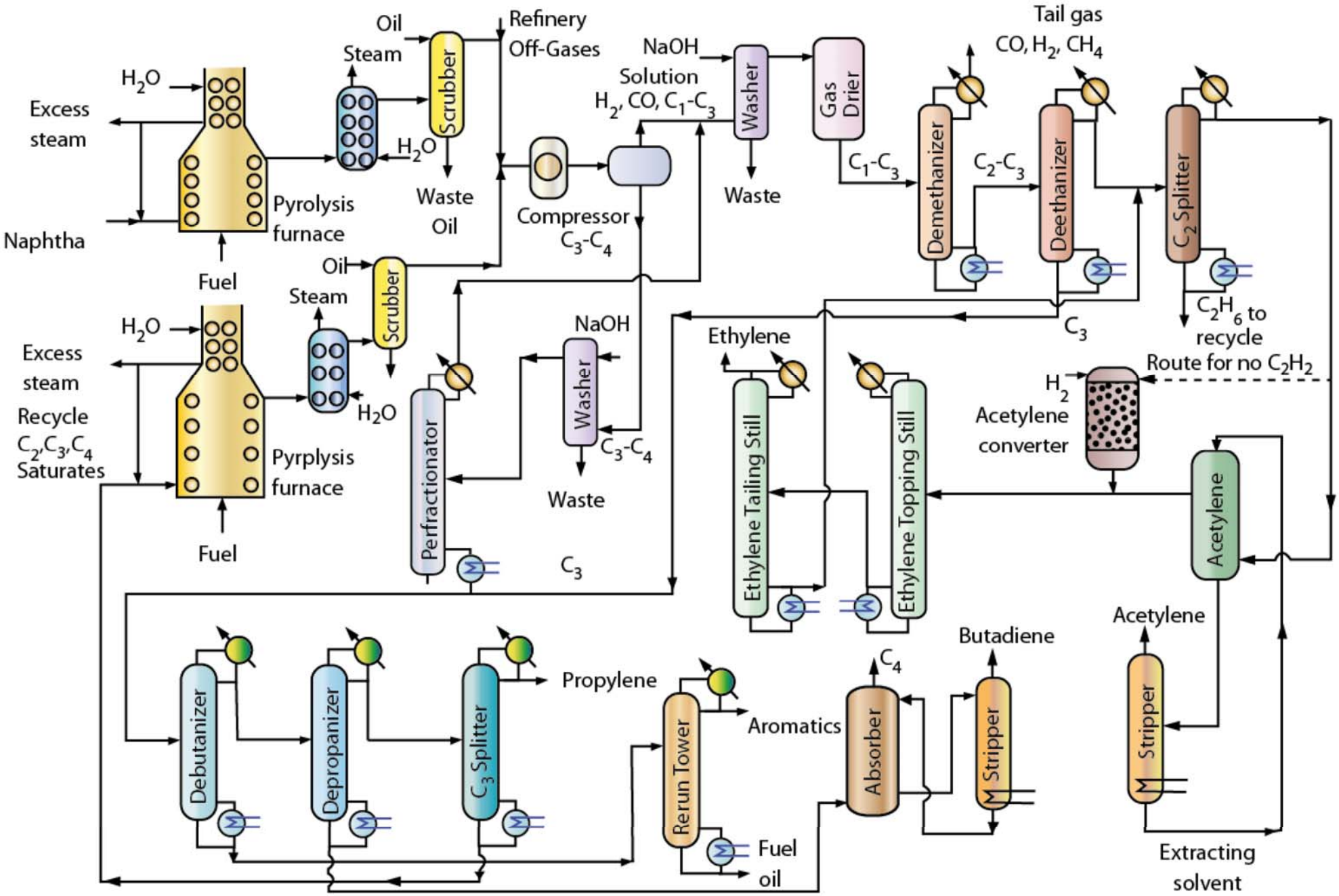
$C_nH_{2n+2} + H_2O + O_2 \longrightarrow C_2H_4\ (10\text{-}15\%) + C_2H_2\ (10\text{-}13\%)$

$+ H_2\ (25\text{-}30\%) + CO + CO_2$

$+ CH_4 + C_2H_6 + C_3H_6 + C_3H_8 + C_4H_{10}$

$+ C_4H_8 + C_4H_6 +$ Heavy HC (traces)

C_nH_{2n+2}: Naphtha feedstock in Indian context


H_2O
Excess steam
Naphtha
Fuel
Pyrolysis furnace
Oil
Steam
Scrubber
H_2O
Waste Oil
Refinery Off-Gases
Compressor C_3-C_4
NaOH Solution
H_2, CO, C_1-C_3
Washer
Waste
Gas Drier
C_1-C_3
Demethanizer
Tail gas CO, H_2, CH_4
C_2-C_3
Deethanizer
C_2 Splitter
C_2H_6 to recycle
C_3
Recycle C_2,C_3,C_4 Saturates
Pyrplysis furnace
Perfractionator
C_3-C_4
Ethylene
Ethylene Tailing Still
Ethylene Topping Still
Route for no C_2H_2
H_2
Acetylene converter
Acetylene
Debutanizer
Depropanizer
C_3 Splitter
Propylene
Rerun Tower
Aromatics
Fuel oil
C_4
Absorber
Butadiene
Stripper
Extracting solvent

Ethylene-dichloride

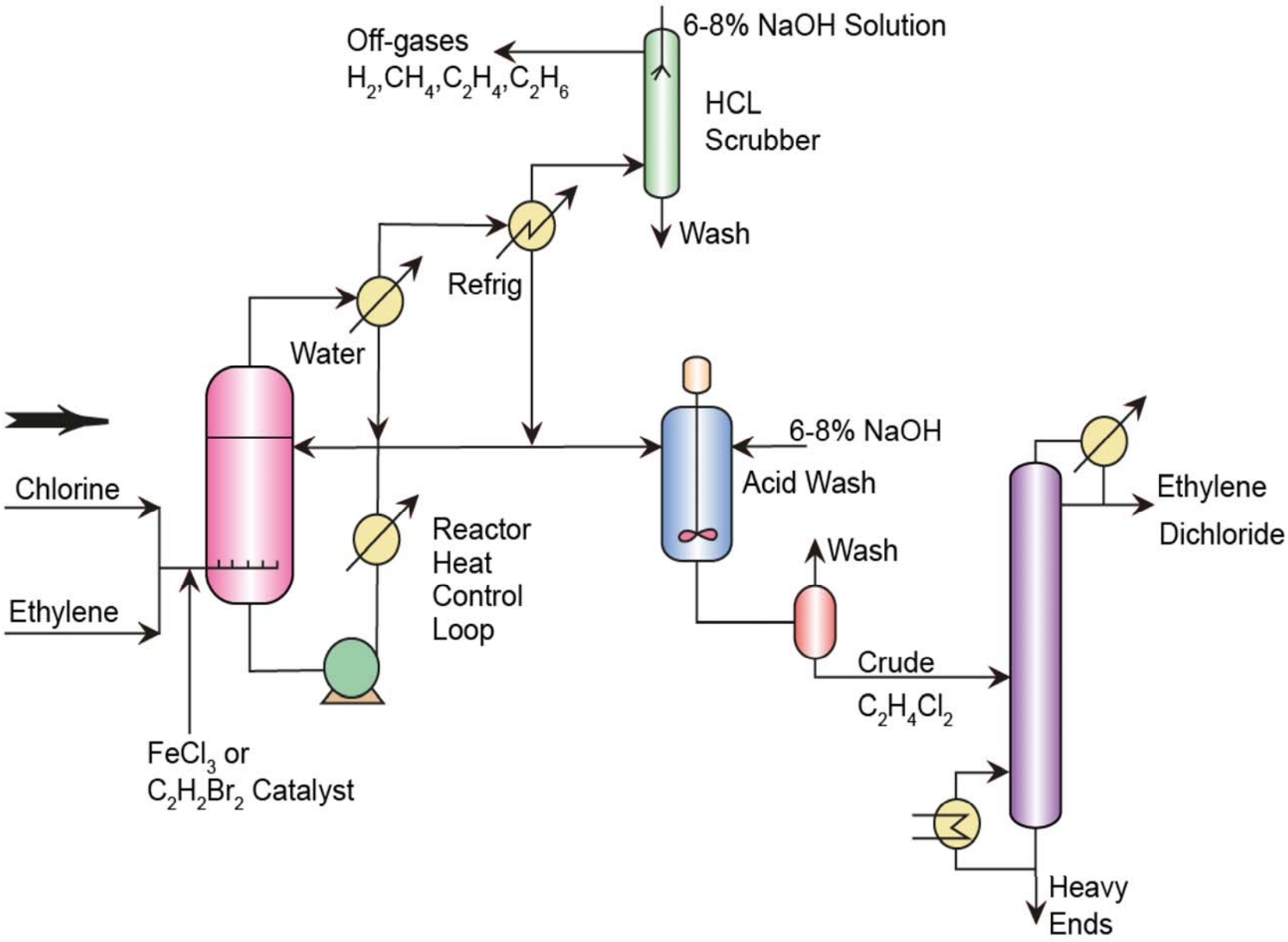
(1,2- Dichloroethane)

Rxn of Cl_2 with C_2H_4 in liq./vap. phase

By-product of direct chlorination of ethane to ethyl chloride

Byproduct of chlorinated HC

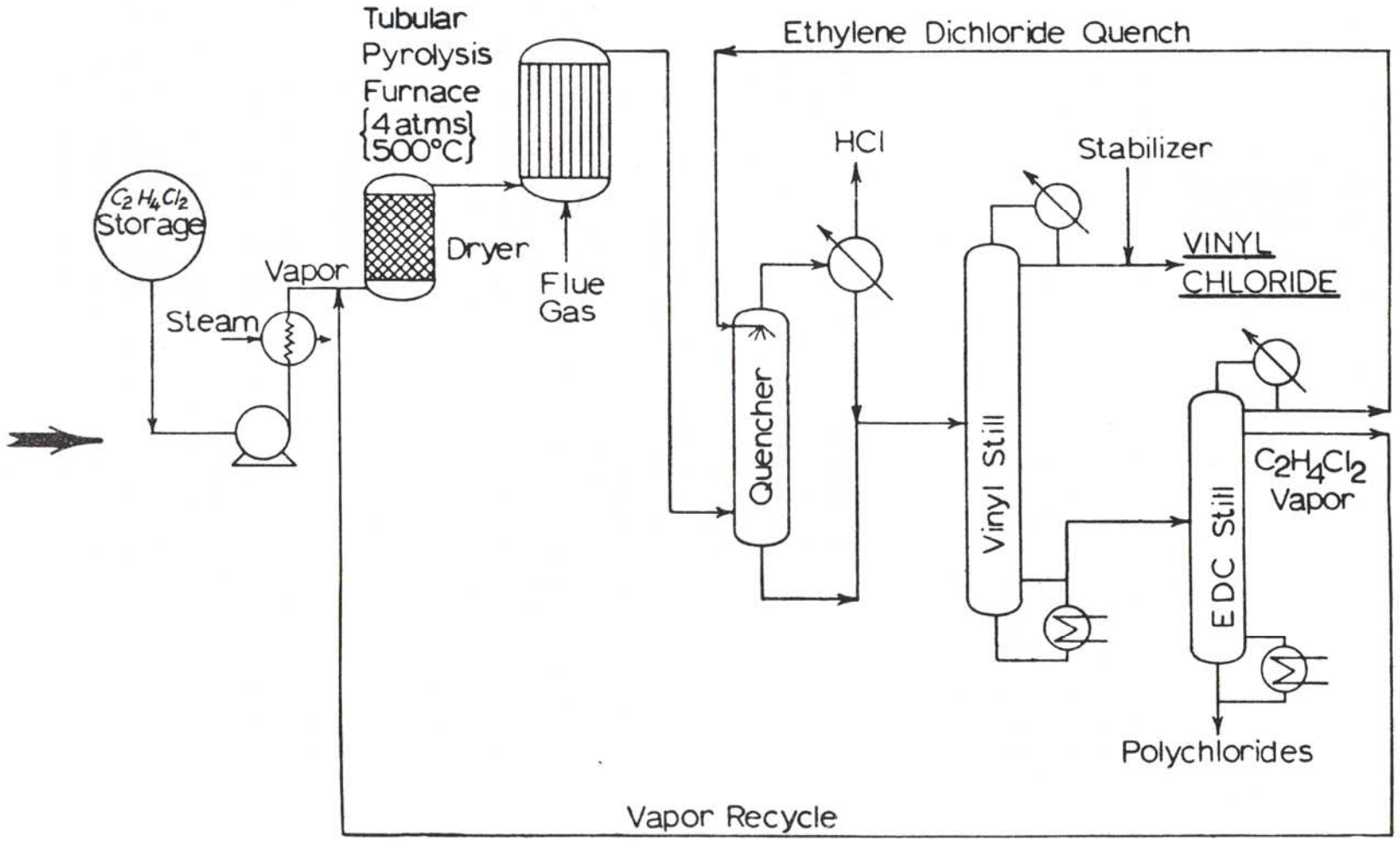
$$C_2H_4 + Cl_2 \longrightarrow ClH_2C-C_2Cl$$

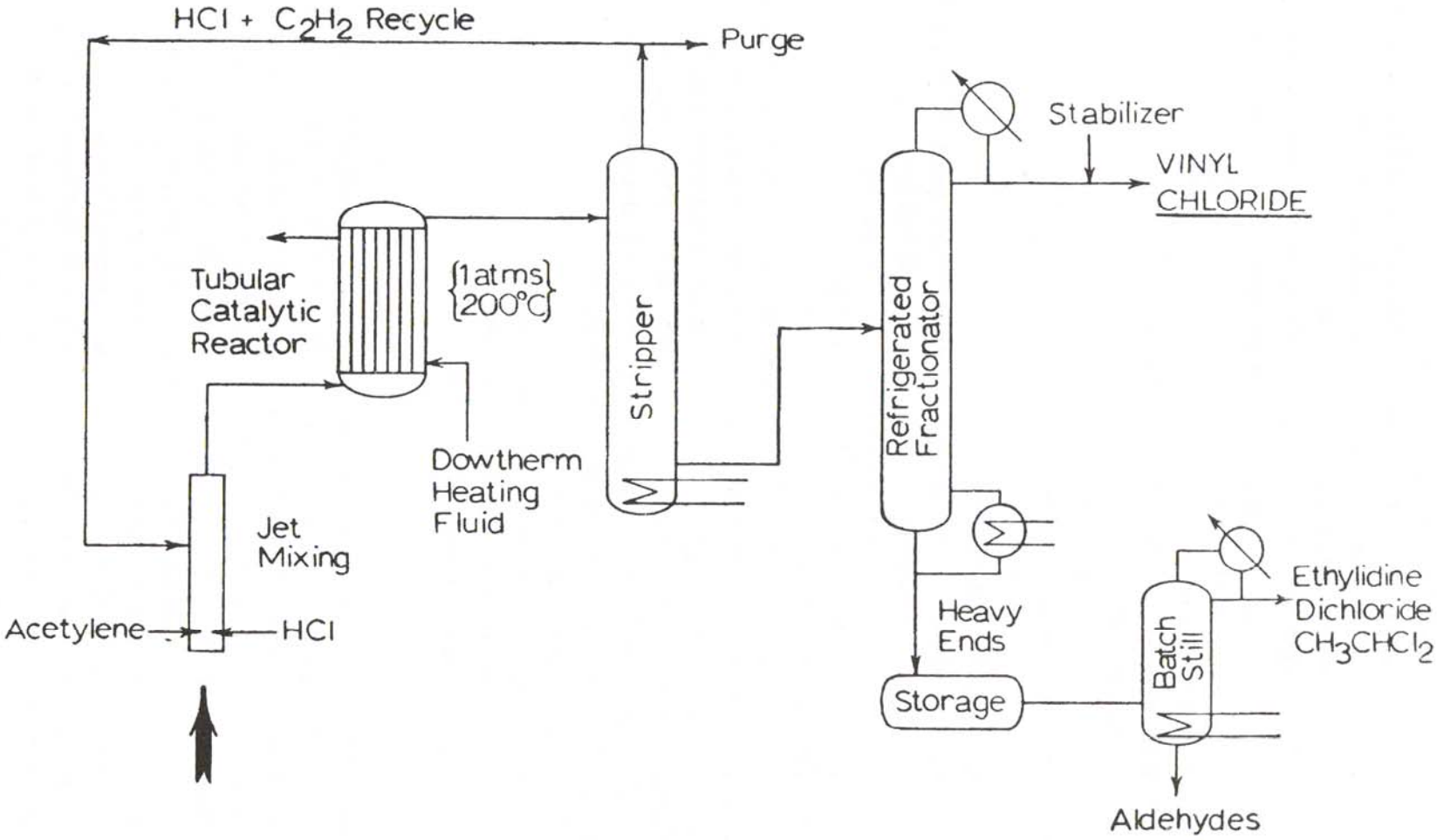

Off-gases
$H_2, CH_4, C_2H_4, C_2H_6$
6-8% NaOH Solution
HCL
Scrubber
Wash
Refrig
Water
Chlorine
Ethylene
$FeCl_3$ or
$C_2H_2Br_2$ Catalyst
Reactor
Heat
Control
Loop
6-8% NaOH
Acid Wash
Wash
Crude
$C_2H_4Cl_2$
Ethylene
Dichloride
Heavy
Ends

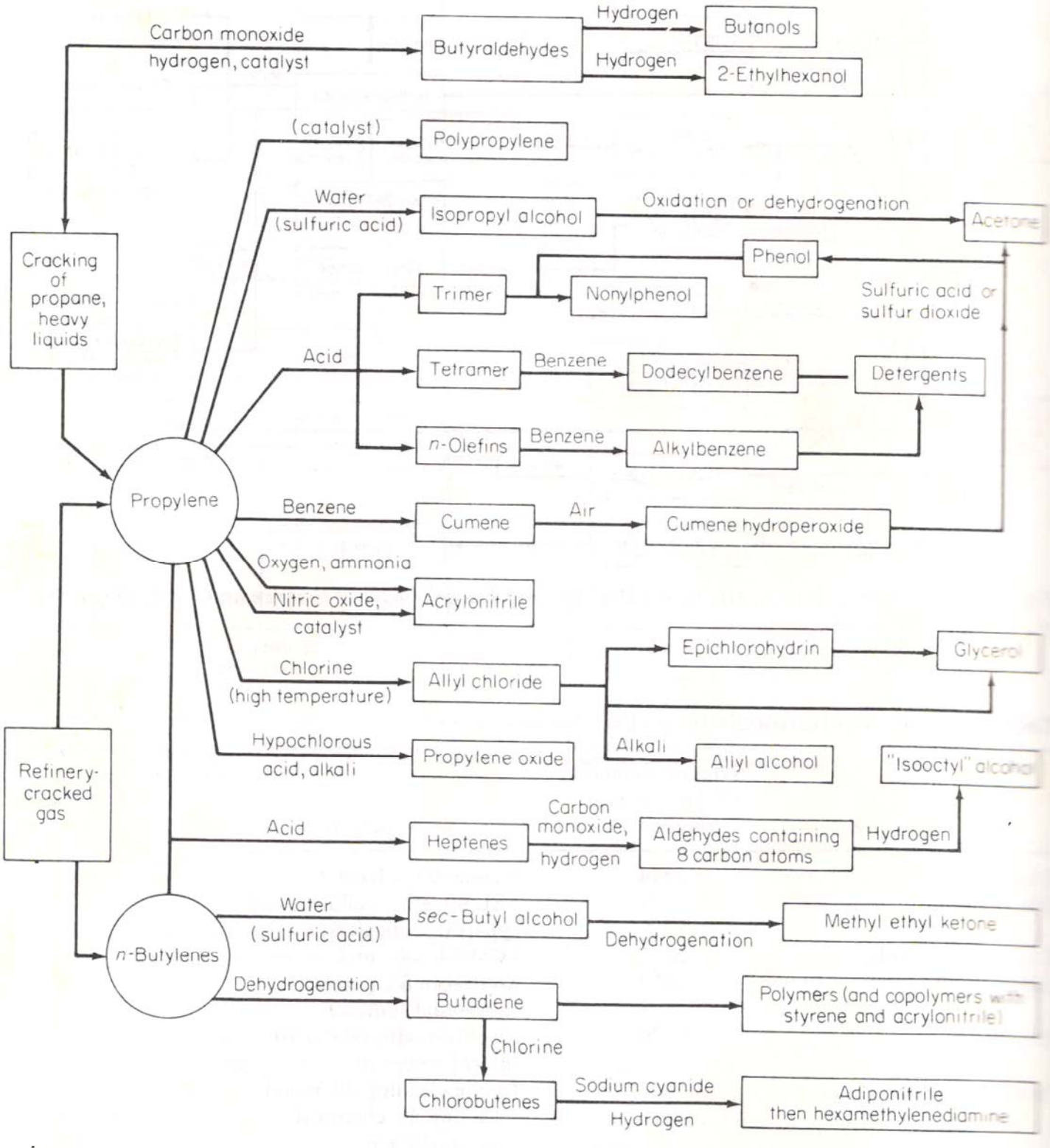
Vinyl dichloride

Ethylene dichloride thermal pyrolysis :

Acetylene – HCl reaction:

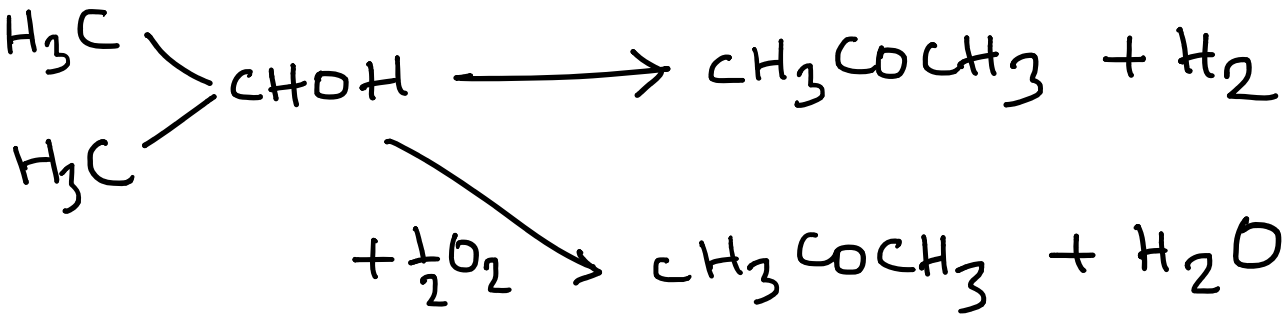

Tubular
Pyrolysis
Furnace
{4 atms}
{500°C}
Ethylene Dichloride Quench
HCl
Stabilizer
$C_2H_4Cl_2$
Storage
Dryer
Vapor
Flue
Gas
VINYL
CHLORIDE
Steam
Quencher
Vinyl Still
EDC Still
$C_2H_4Cl_2$
Vapor
Polychlorides
Vapor Recycle


HCl + C_2H_2 Recycle
Purge
Stabilizer
VINYL
CHLORIDE
Tubular
Catalytic
Reactor
{1 atms
{200°C
Stripper
Refrigerated
Fractionator
Dowtherm
Heating
Fluid
Jet
Mixing
Acetylene
HCl
Heavy
Ends
Batch
Still
Ethylidine
Dichloride
CH_3CHCl_2
Storage
Aldehydes


Carbon monoxide
hydrogen, catalyst
Butyraldehydes
Hydrogen
Butanols
Hydrogen
2-Ethylhexanol
(catalyst)
Polypropylene
Water
(sulfuric acid)
Isopropyl alcohol
Oxidation or dehydrogenation
Acetone
Cracking of propane, heavy liquids
Phenol
Trimer
Nonylphenol
Sulfuric acid or sulfur dioxide
Acid
Tetramer
Benzene
Dodecylbenzene
Detergents
n-Olefins
Benzene
Alkylbenzene
Propylene
Benzene
Cumene
Air
Cumene hydroperoxide
Oxygen, ammonia
Nitric oxide, catalyst
Acrylonitrile
Chlorine
(high temperature)
Allyl chloride
Epichlorohydrin
Glycerol
Refinery-cracked gas
Hypochlorous acid, alkali
Propylene oxide
Alkali
Allyl alcohol
"Isooctyl" alcohol
Acid
Heptenes
Carbon monoxide, hydrogen
Aldehydes containing 8 carbon atoms
Hydrogen
Water
(sulfuric acid)
sec-Butyl alcohol
Dehydrogenation
Methyl ethyl ketone
n-Butylenes
Dehydrogenation
Butadiene
Polymers (and copolymers with styrene and acrylonitrile)
Chlorine
Chlorobutenes
Sodium cyanide
Hydrogen
Adiponitrile then hexamethylenediamine

Acetone

Catalytic dehydrogenation of isopropanol



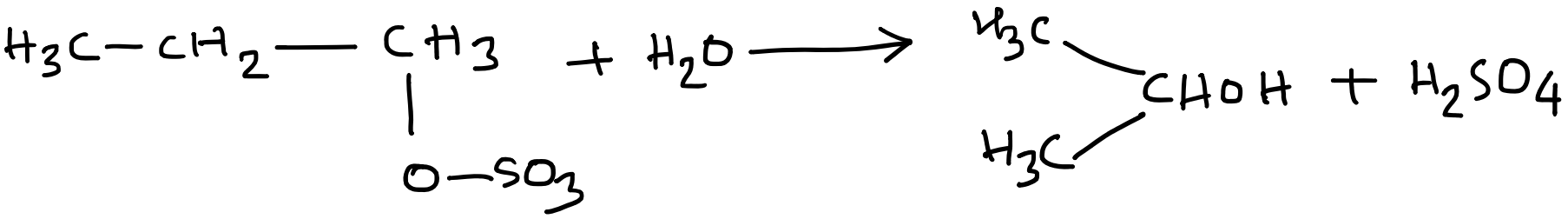
Iso-propanol

Methods of production:

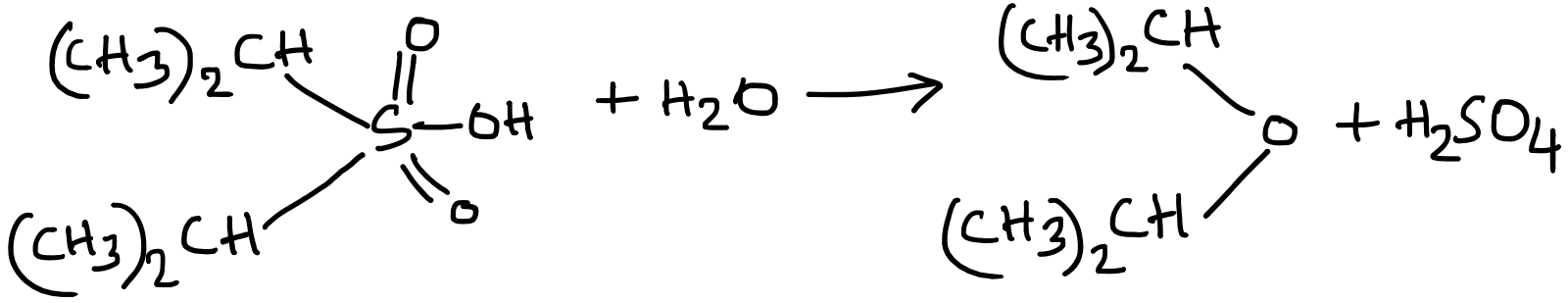
→ Direct catalytic hydration of propylene

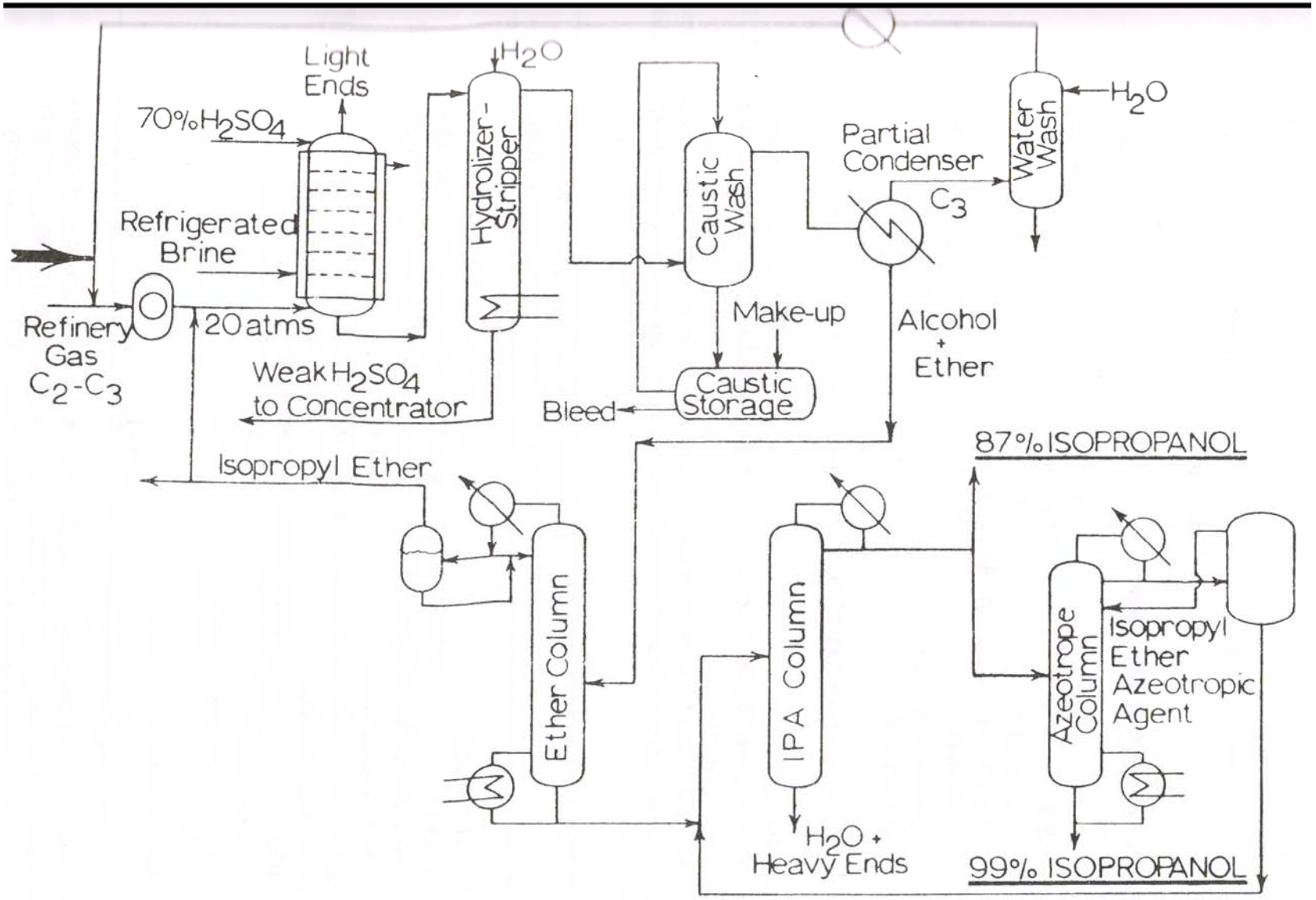
→ Hydration of propylene via sulponation & hydrolysis

isopropyl acid sulfate

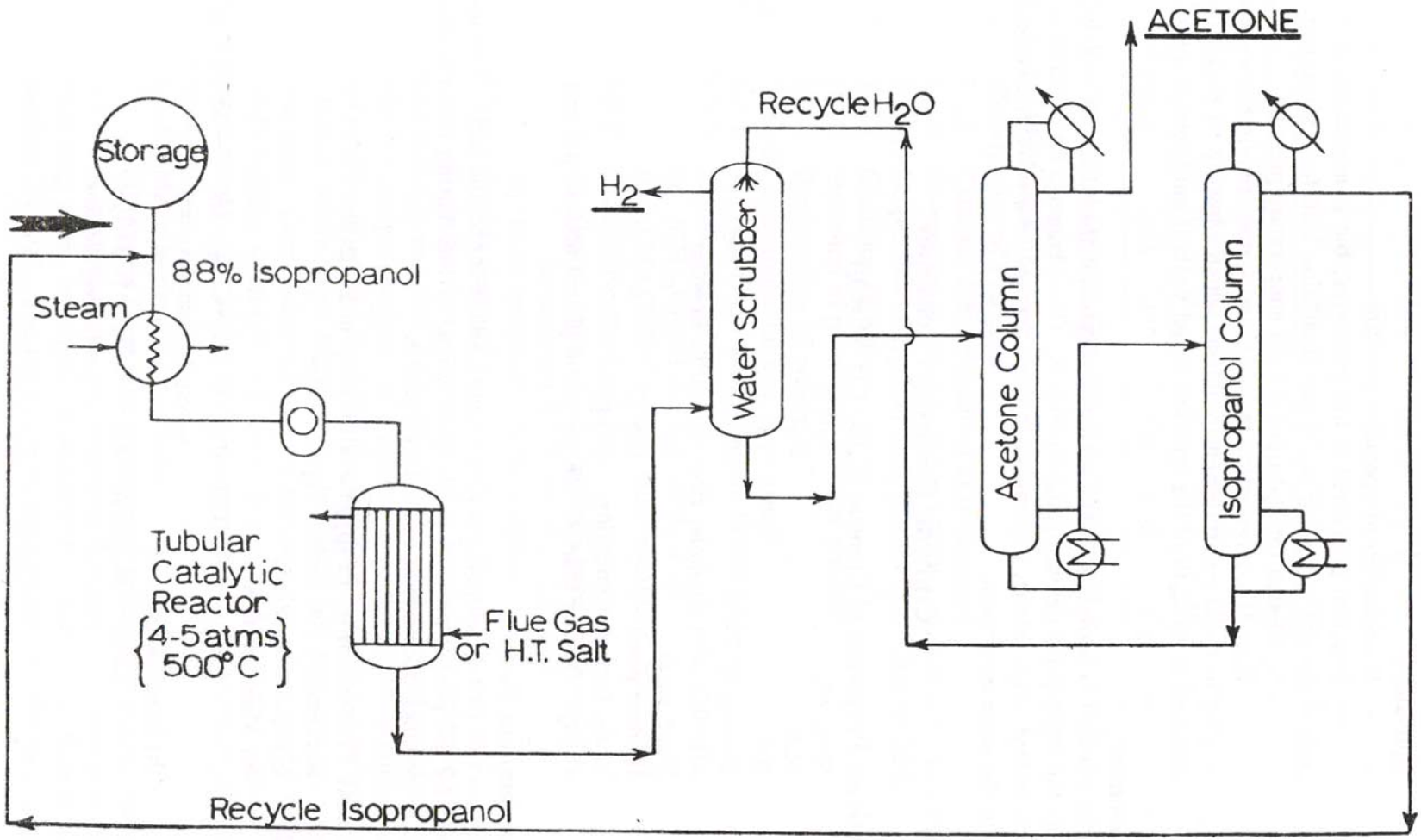


Side reactions:





Isopropanol by indirect hydration of propylene.



Acetone production by dehydrogenation of Isopropanol.

Cumene (Isopropyl benzene)

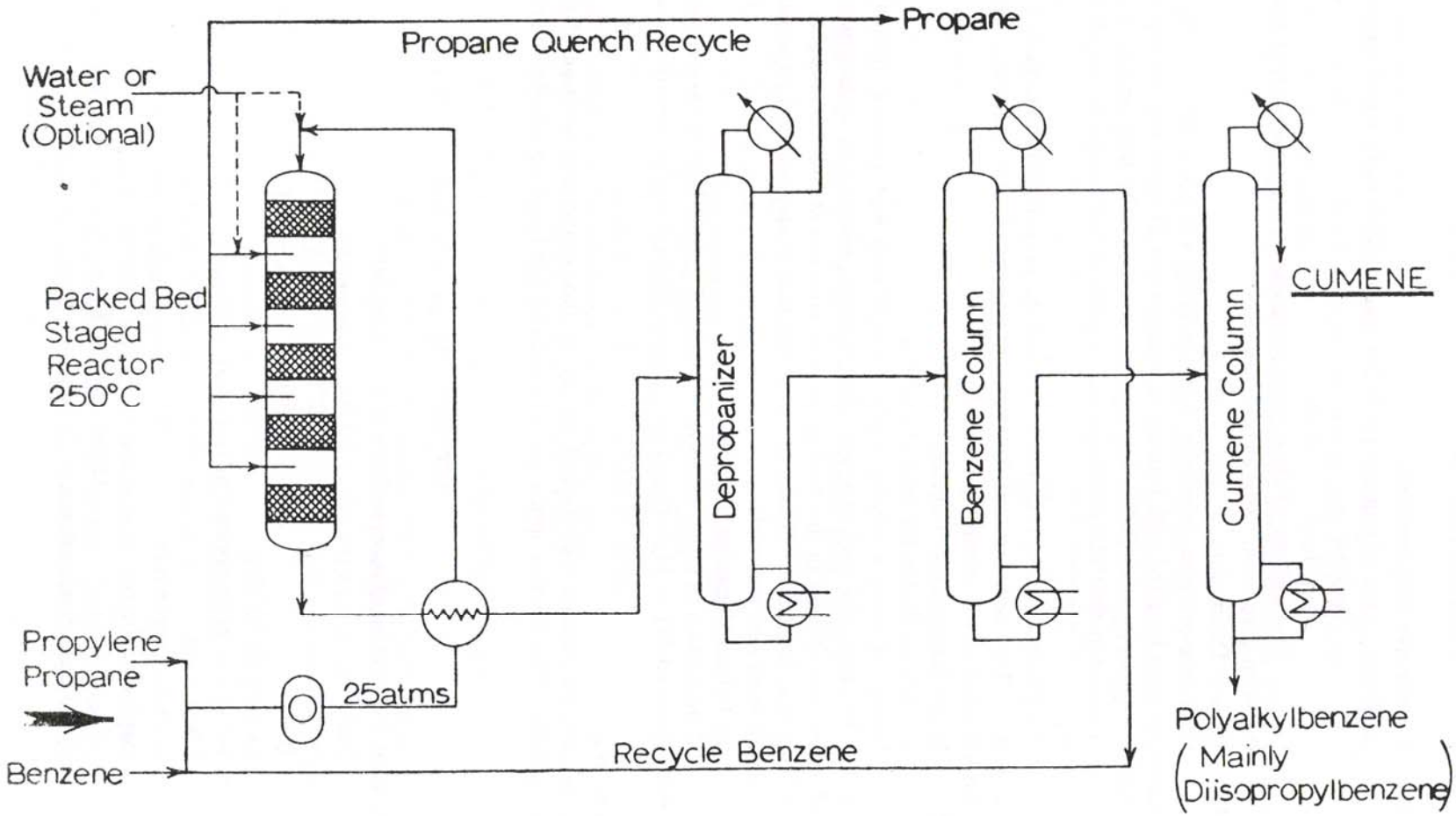
Propylene alkylation of Benzene

$$C_6H_6 + CH_3 \cdot CH = CH_2 \longrightarrow C_6H_5 \cdot C_3H_7$$

Cumene

Side rxn: $C_6H_6 + n\,CH_3CH = CH_2 \longrightarrow C_6H_{6-n} (C_3H_7)_n$

poly-isopropyl benzene



Cumene production by propylene alkylation of benzene.

Acrylonitrile

Possible methods of production:

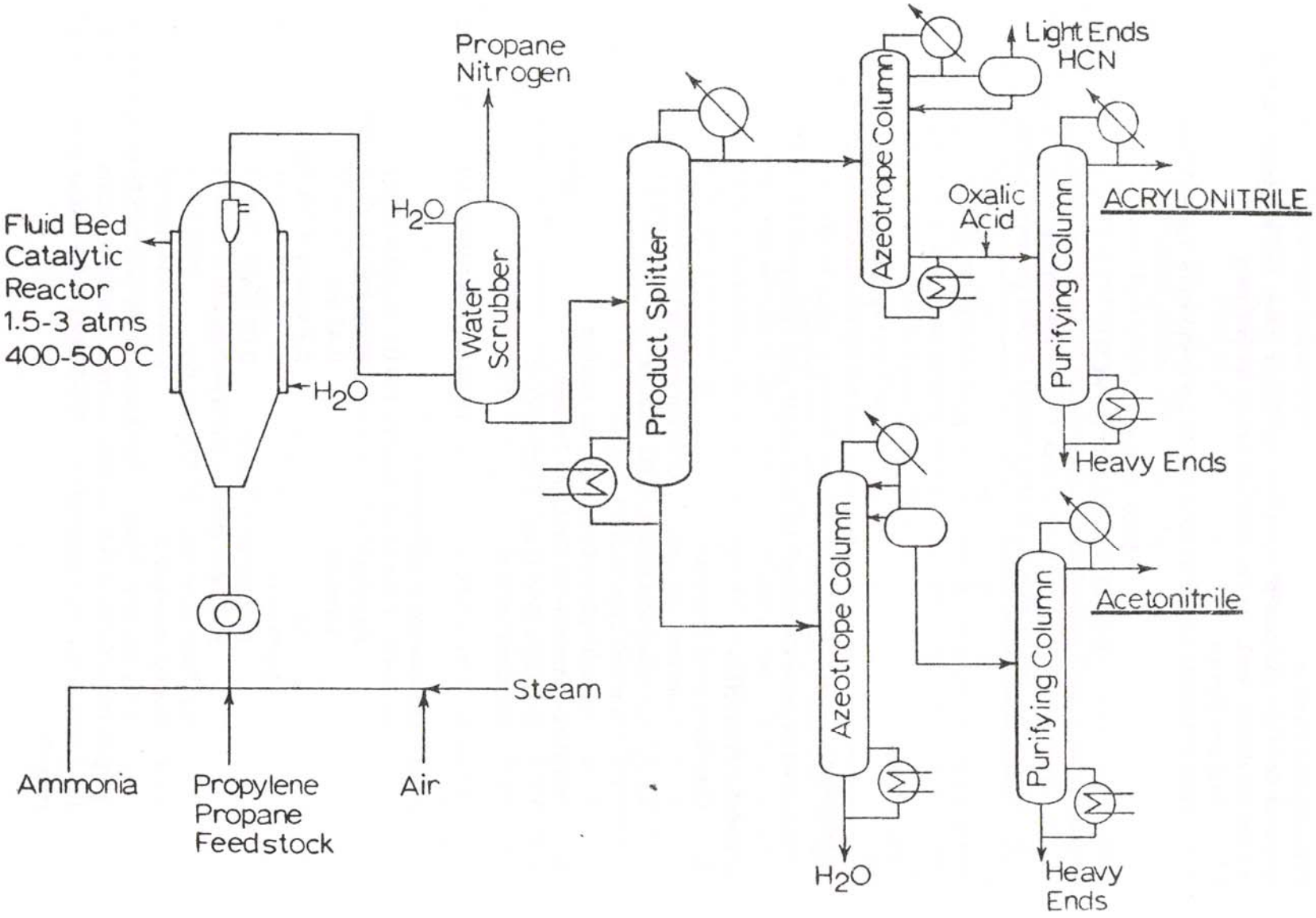
Propylene – ammonia-air oxidation

Acetylene – hydrogen cyanide rxn

Acetyldehyde – HCN rxn

$$H_2C{=}CH{-}CH_3 + NH_3 + \frac{3}{2}O_2 \longrightarrow H_2C{=}CHCN + 3H_2O$$

$$\Delta H \sim -136 \text{ kcal}$$



Acetonitrile production from propylene ammonia oxidation

Butadiene

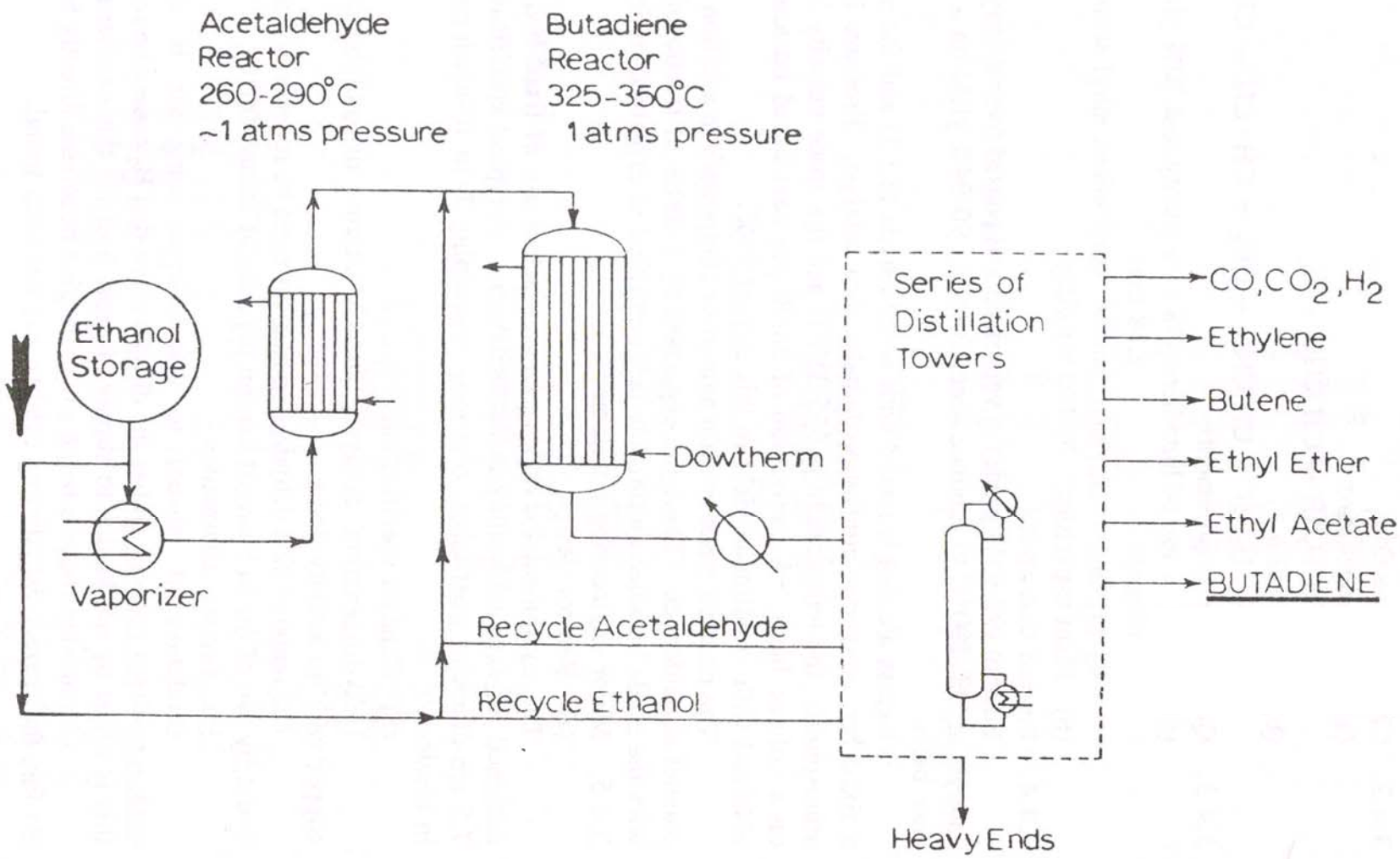
Dehydrogenation Dehydration of ethanol

$$CH_3CH_2OH \longrightarrow CH_3CHO + H_2$$

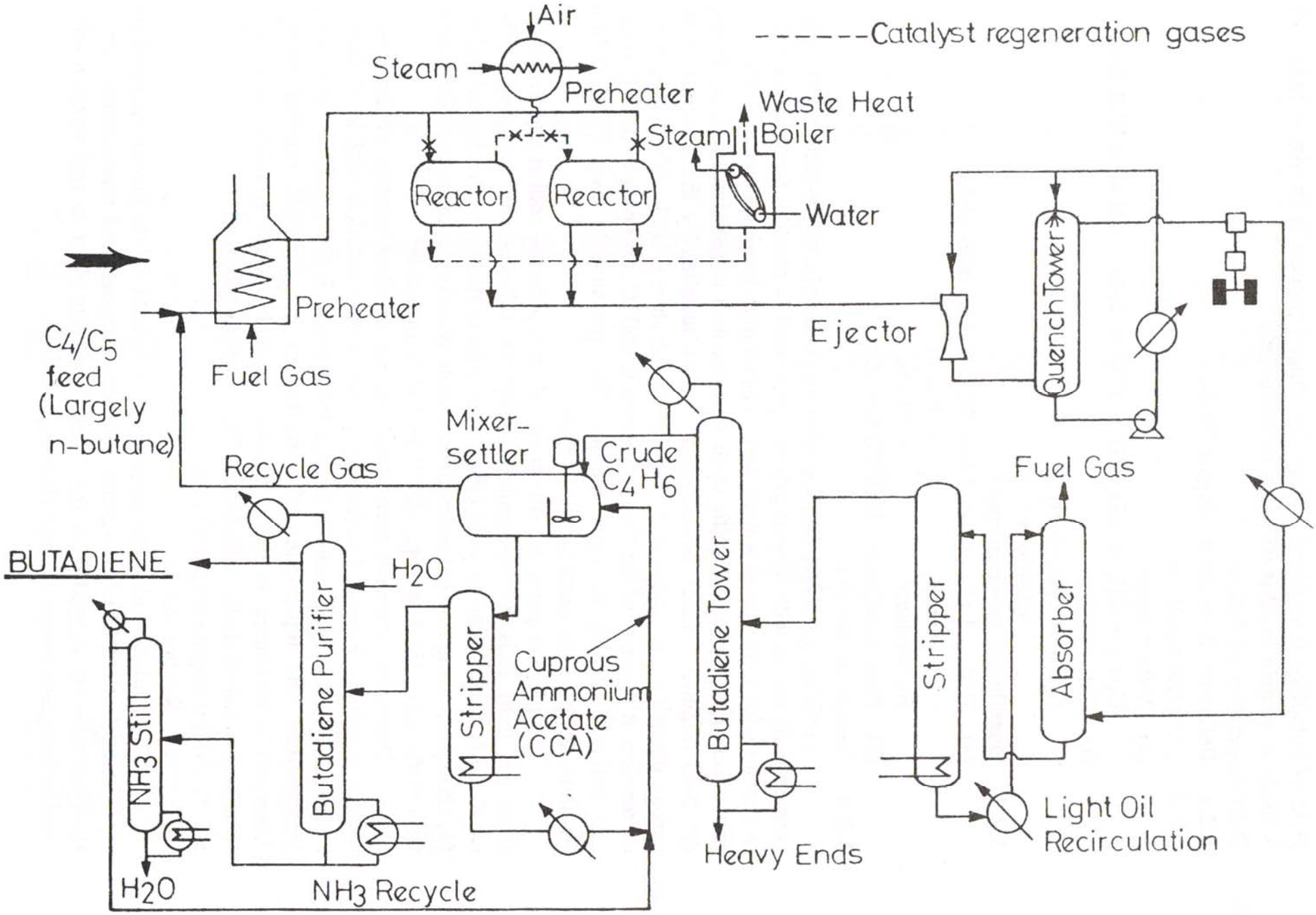
$$CH_3CH_2OH + CH_3CHO \longrightarrow H_2C{=}CH{\cdot}CH{=}CH_2 + 2H_2O$$

Dehydrogenation of butane

$$C_4H_{10} \longrightarrow H_2C{=}CHCH{=}CH_2 + 2H_2 \qquad \Delta H > 0$$

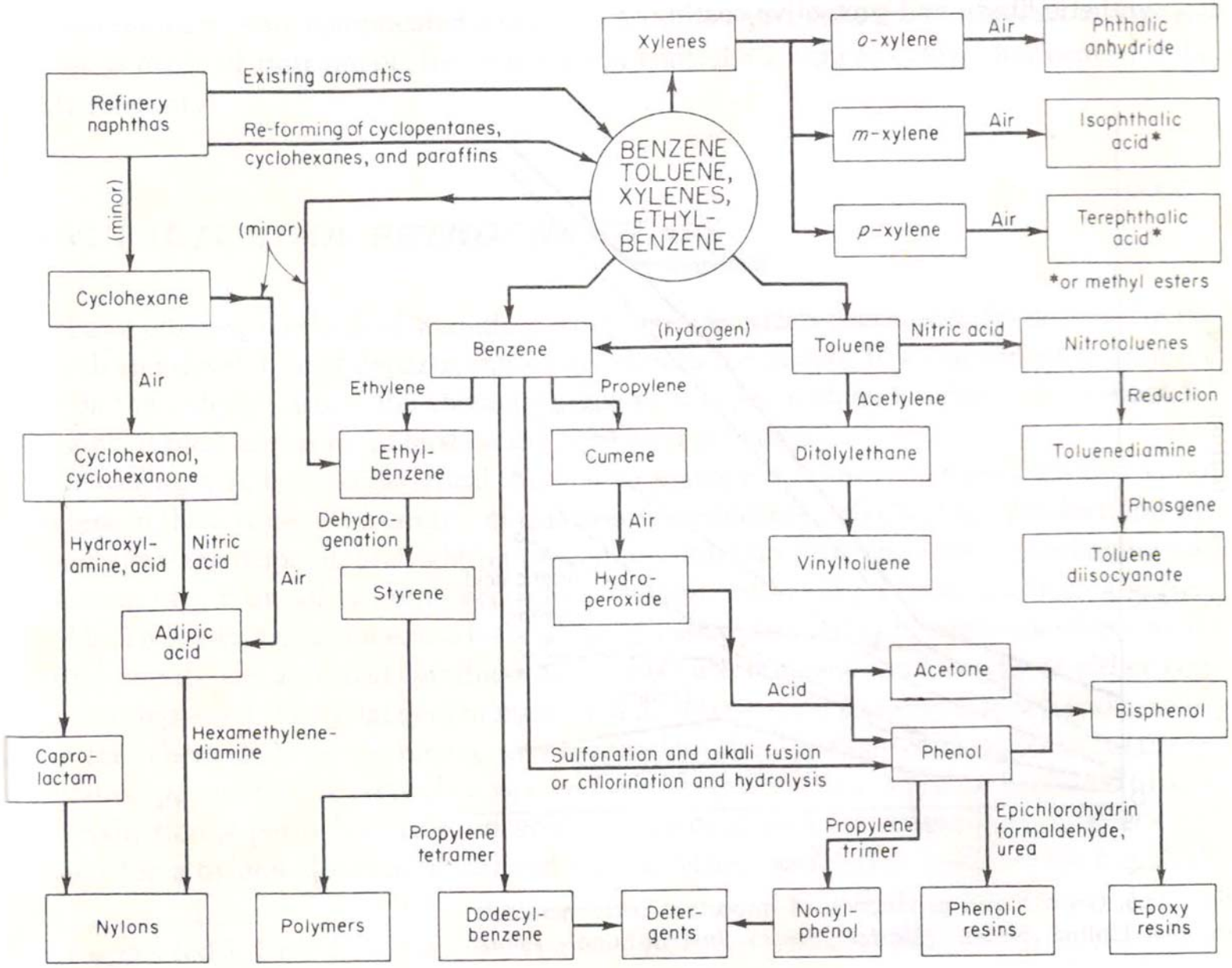


Butadiene production by dehydrogenation / dehydration of ethanol



Butadiene production by dehydrogenation of butane

Aromatics

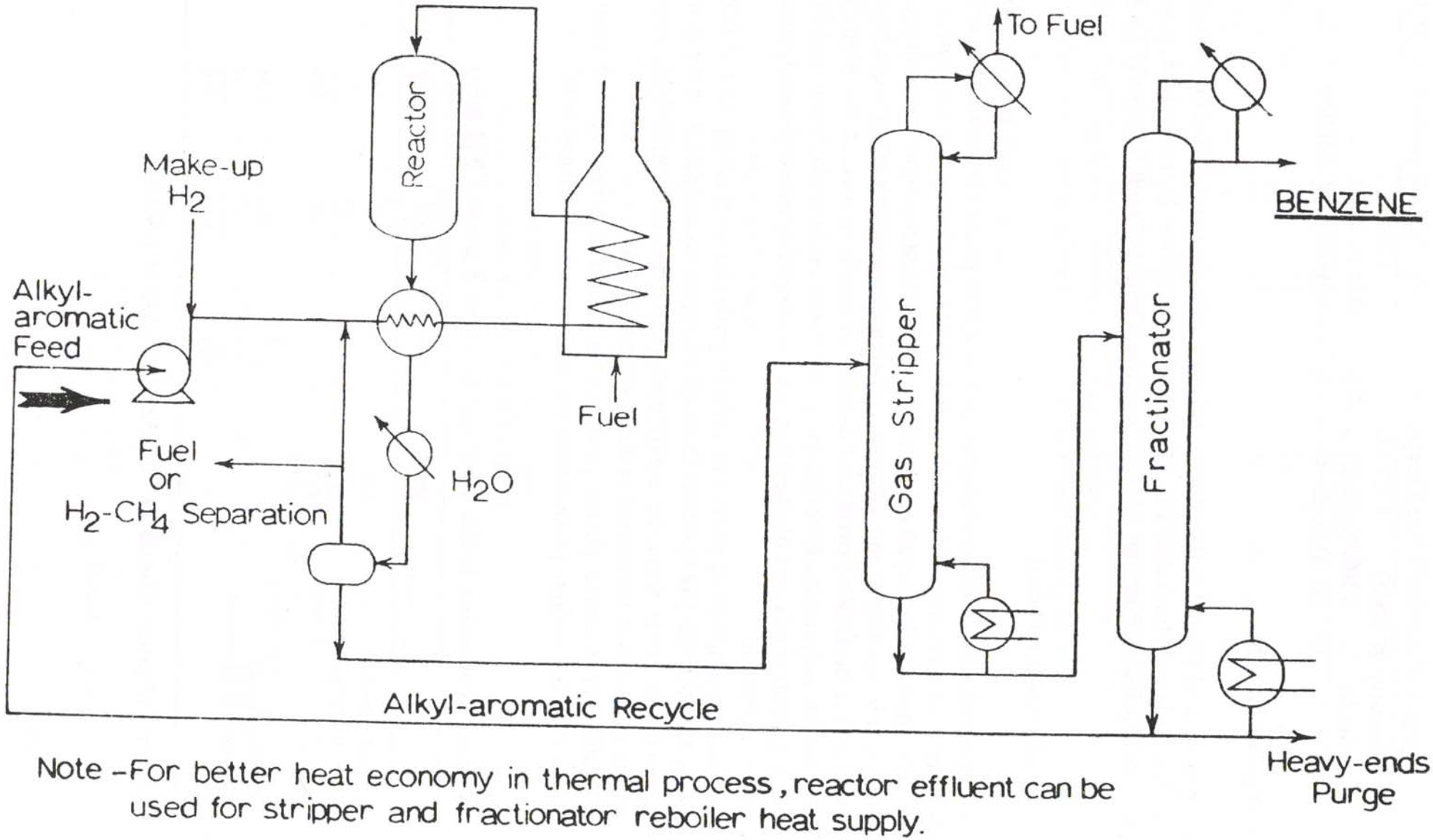

Xylenes
o-xylene
Air
Phthalic anhydride
m-xylene
Air
Isophthalic acid*
p-xylene
Air
Terephthalic acid*
*or methyl esters
Refinery naphthas
Existing aromatics
Re-forming of cyclopentanes, cyclohexanes, and paraffins
BENZENE TOLUENE, XYLENES, ETHYL-BENZENE
(minor)
(minor)
Cyclohexane
Air
Cyclohexanol, cyclohexanone
Hydroxyl-amine, acid
Nitric acid
Air
Adipic acid
Hexamethylene-diamine
Capro-lactam
Nylons
Benzene
(hydrogen)
Toluene
Nitric acid
Nitrotoluenes
Ethylene
Propylene
Acetylene
Reduction
Ethyl-benzene
Cumene
Ditolylethane
Toluenediamine
Dehydro-genation
Air
Phosgene
Styrene
Hydro-peroxide
Vinyltoluene
Toluene diisocyanate
Acid
Acetone
Bisphenol
Phenol
Sulfonation and alkali fusion or chlorination and hydrolysis
Propylene tetramer
Propylene trimer
Epichlorohydrin formaldehyde, urea
Polymers
Dodecyl-benzene
Deter-gents
Nonyl-phenol
Phenolic resins
Epoxy resins

Hydroalkylation

Method of converting toluenes & dialkyl benzenes to benzene

$$C_6H_5CH_3 + H_2 \longrightarrow C_6H_6 + CH_4$$

$$C_6H_4(CH_3)_2 + 2H_2 \longrightarrow C_6H_6 + 2CH_4$$



Note –For better heat economy in thermal process, reactor effluent can be used for stripper and fractionator reboiler heat supply.

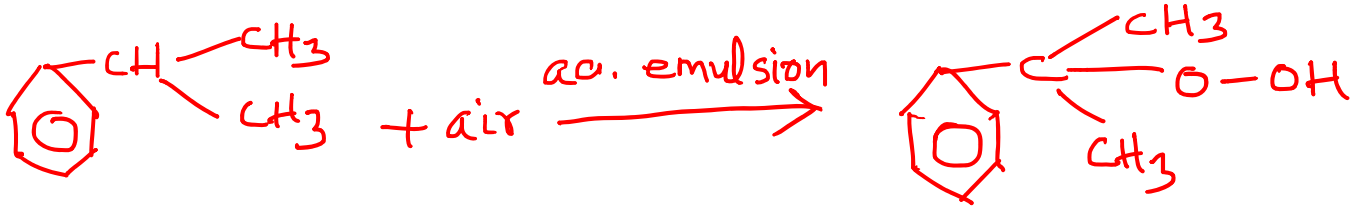
Hydroalkylation process to manufacture benzene from alkyl-aromatics

Phenol

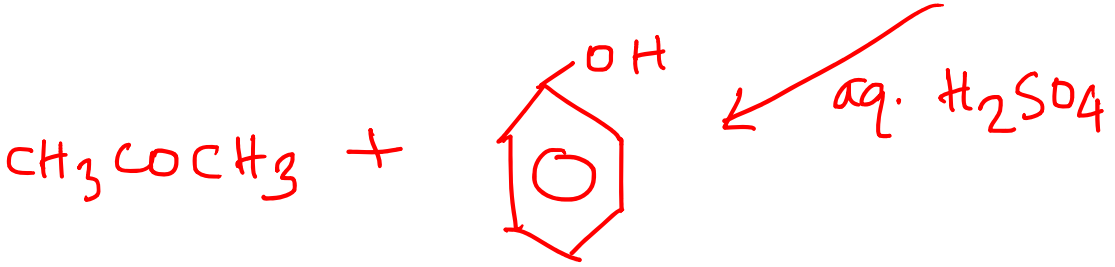
Several processes are available

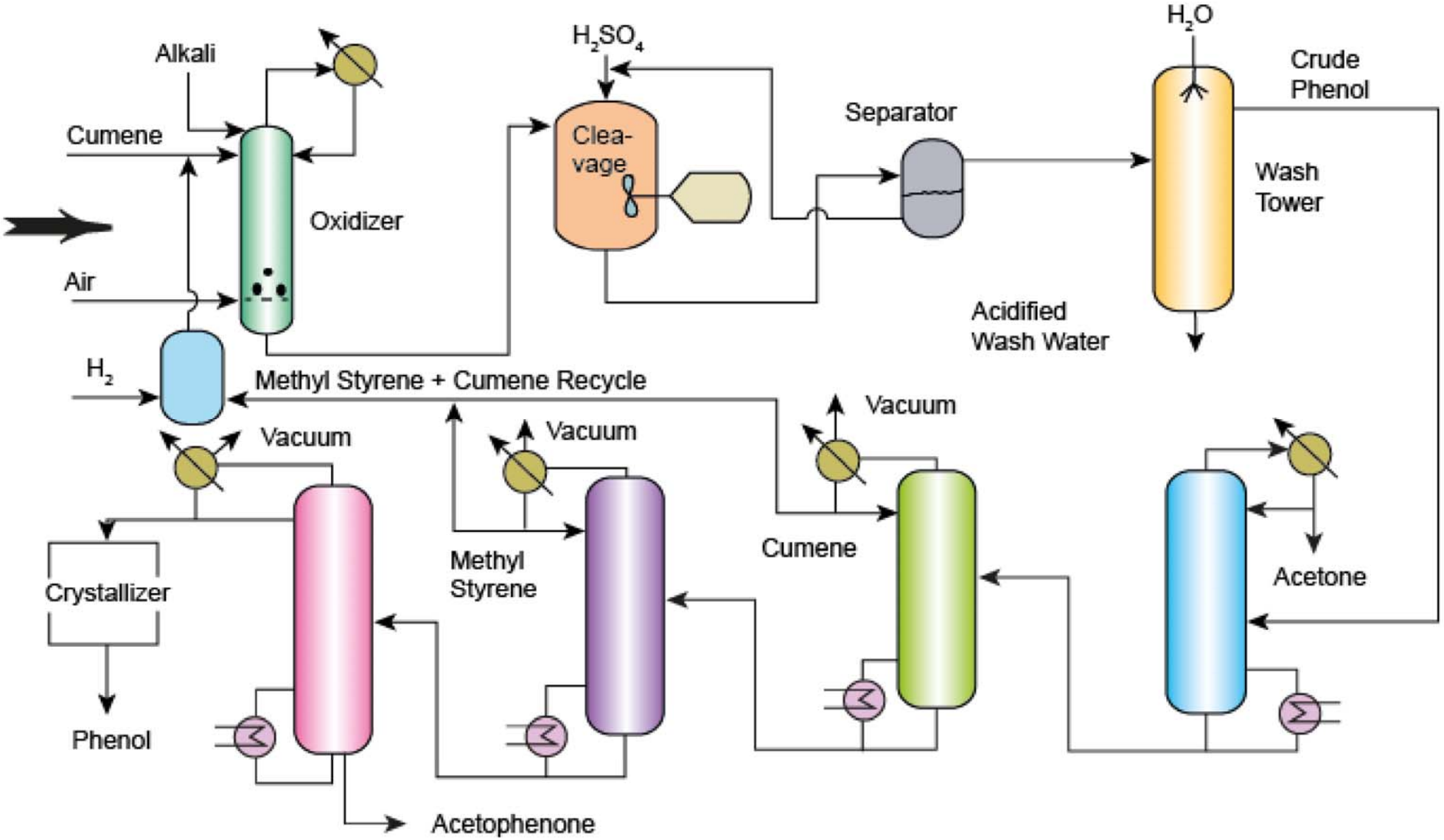
- Cumene peroxidation – hydrolysis
- Toluene two-stage oxidation
- Chlorobenzene – caustic hydrolysis
- Benzene sulfonate – caustic fusion
- Benzene – direct oxidation (oldest)

Peroxidation:



Hydrolysis:




Alkali
Cumene
Air
Oxidizer
H_2SO_4
Clea-
vage
Separator
H_2O
Crude
Phenol
Wash
Tower
Acidified
Wash Water
H_2
Methyl Styrene + Cumene Recycle
Vacuum
Vacuum
Vacuum
Crystallizer
Phenol
Methyl
Styrene
Cumene
Acetone
Acetophenone