Industrial Organic Chemistry

- **Introduction**

1) Process Engineering & Economy

(1) Scale –Up : Bench Scale → Pilot Scale → Production

<Reactor Deign>

-Temp Control : Heating Mantle → Steam is used (<150℃)

-Rxtor Size : 1L → 1000L, 8000L for 500Kg product,

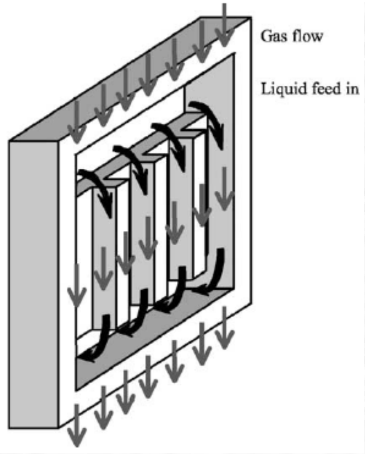
<70-80% charge

-Material : RB Flask → Carbon steel - GL for acidic condition

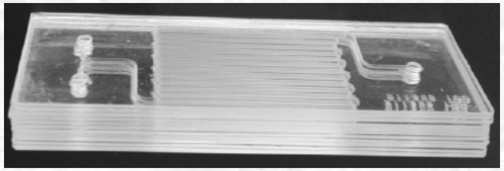
Stainless steel for basic condition

-Cooling vs. Reactor Vol : vol. increase ~ cooling efficiency

(2) Scale Down : Important features of Micro-channel reactor



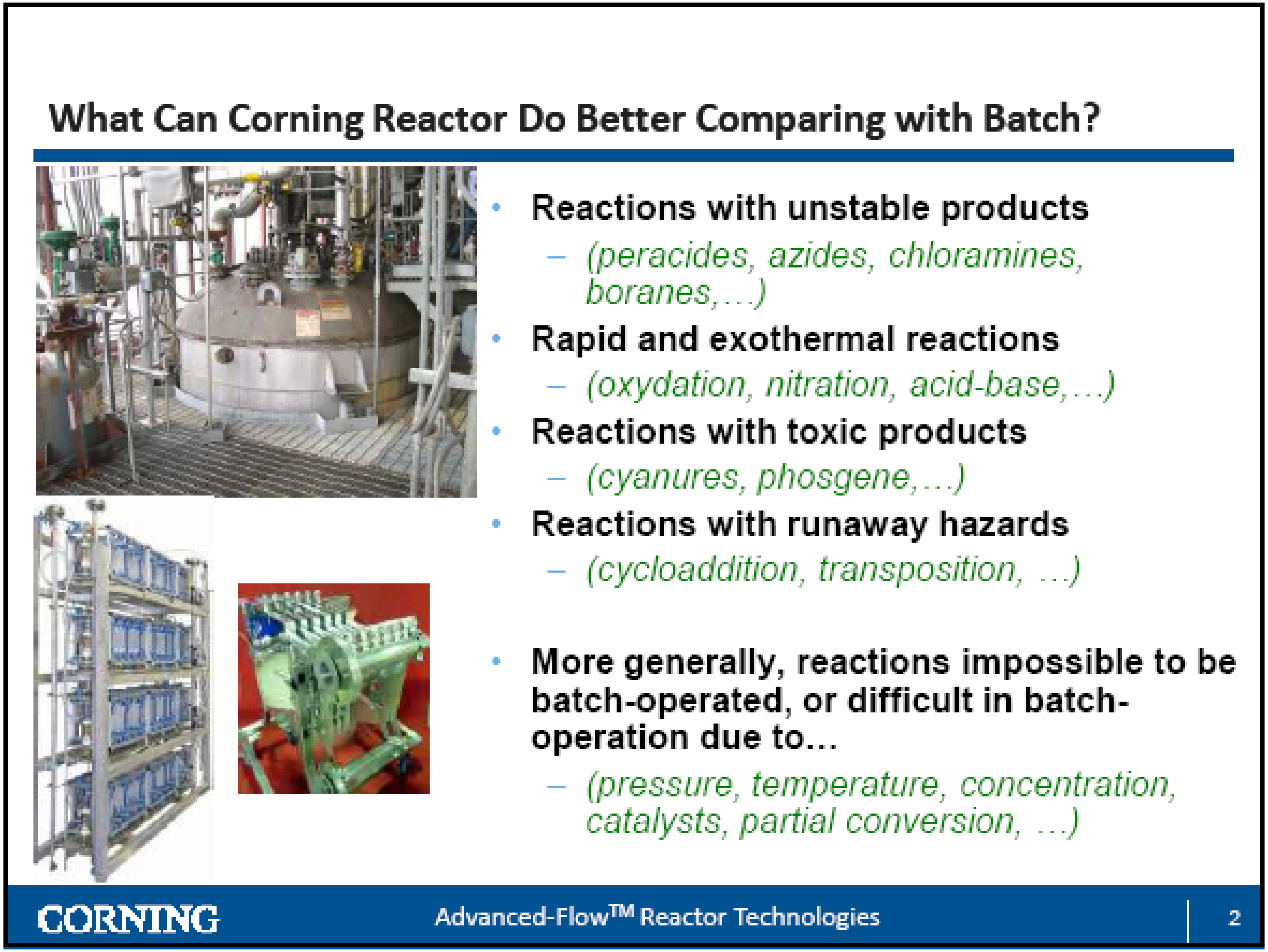
- **High Surface Area *vs* Volume Ratio**
- **Effective Mass Transfer between Different Phases**
- **Rapid Heat Exchange / Energy Transfer**
- **Short Molecular - Diffusion distance**
- **Highly Efficient Heat Transfer**
- **Easy Scaled - Up (Numbering - Up)**
- **Easy Isolation from Reactor (Efficient Solvent Extraction)**
- **Constant Flow of Products (Laminar Flow)**
- **Safe when Explosive compounds are used**



Recent Technology
for Effective, Smooth, Easy Organic Reaction

CORNING

continuous flow reactors



What Can Corning Reactor Do Better Comparing with Batch?

- **Reactions with unstable products**
  - *(peracides, azides, chloramines, boranes,…)*
- **Rapid and exothermal reactions**
  - *(oxydation, nitration, acid-base,…)*
- **Reactions with toxic products**
  - *(cyanures, phosgene,…)*
- **Reactions with runaway hazards**
  - *(cycloaddition, transposition, …)*

- **More generally, reactions impossible to be batch-operated, or difficult in batch-operation due to…**
  - *(pressure, temperature, concentration, catalysts, partial conversion, …)*

<Process Design >

✓ Safety Issue : LAH, NaBH4 → H_2

✓ Environmental Issue : Friedel Craft 촉매 ($FeCl_3$)

eg) Clean Nitration with NO_2 + [O]

✓ Laber Issue : Continuous vs. Batch

$2NO_2 + O_2 \rightarrow N_2O_5$

$N_2O_5 + H_2O \rightarrow HNO_3$

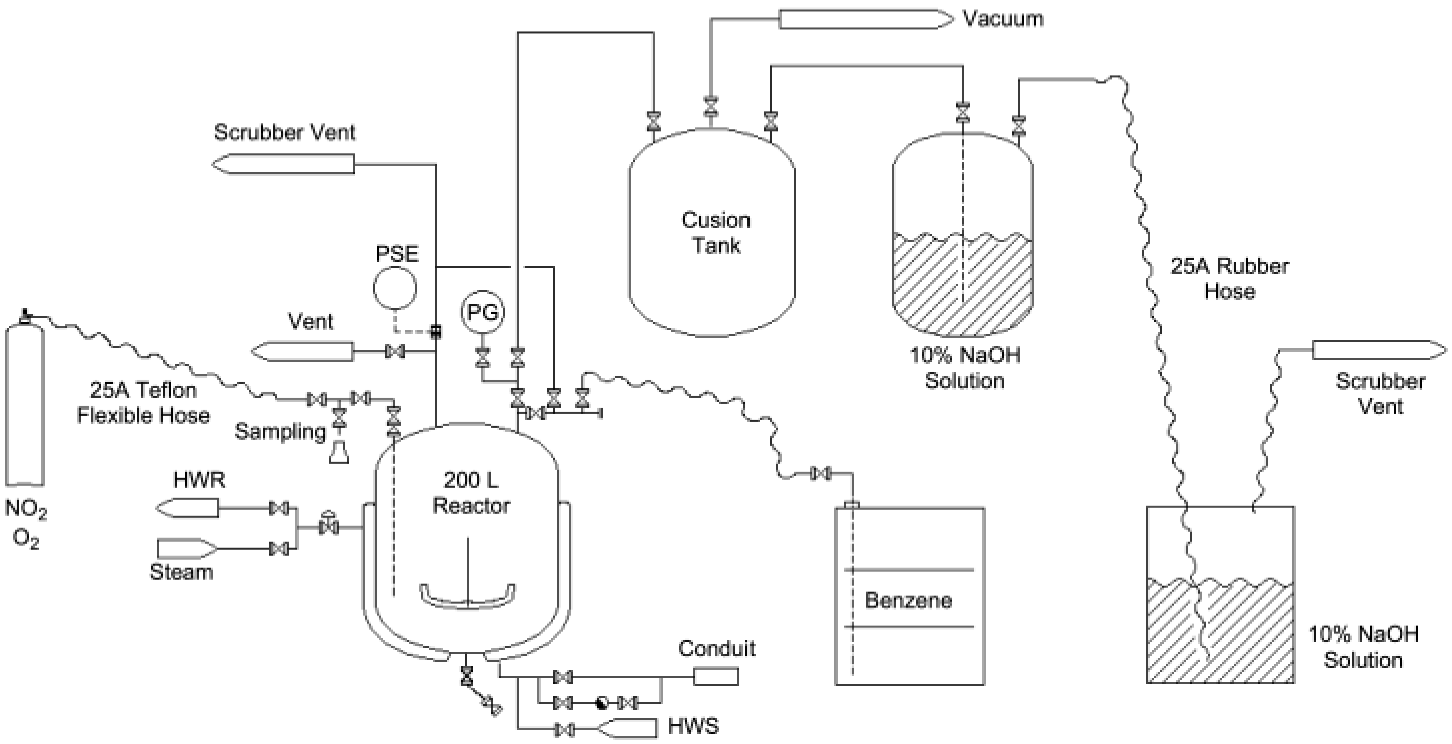
$C_6H_6 + HNO_3 + H_2SO_4 \rightarrow C_6H_5\text{-}NO_2 + H_2O + H_2SO_4$

To Green Process

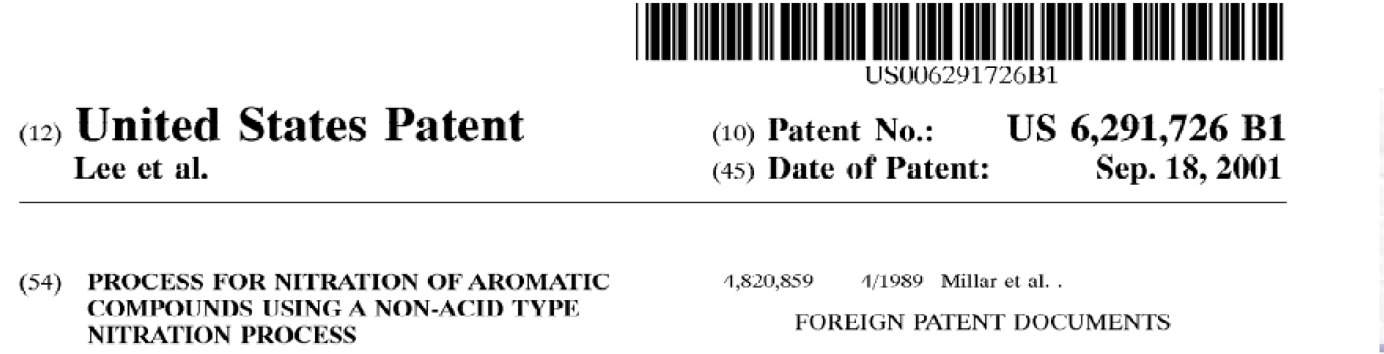
$C_6H_6 + 2NO_2 + O_2 \rightarrow C_6H_5\text{-}NO_2 + HNO_3$

Practical neutral aromatic nitration with NO2 in the presence of heterogeneous catalysts *Res. Chem. Intermed.*, (2006)

762



J. K. Cho et al.



US006291726B1

(12) **United States Patent**
Lee et al.

(10) **Patent No.:** **US 6,291,726 B1**
(45) **Date of Patent:** **Sep. 18, 2001**

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(54) **PROCESS FOR NITRATION OF AROMATIC COMPOUNDS USING A NON-ACID TYPE NITRATION PROCESS**

4,820,859 4/1989 Millar et al. .

FOREIGN PATENT DOCUMENTS

(2) Yield vs Conversion

(3) High cost when,..

- Labor cost ~ multi stage reaction
- High temp, high press reaction (Energy cost)
- Highly acidic reaction
- Extensive separation steps
- Pollution control : $FeCl_3$ as FC catalyst

(4) Terminology

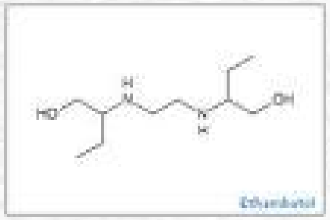
✓ **Unit Operation (단위조작) : "Physical Change"**

Filtration, Heat Transfer, Distillation, Extraction, ...

Heating is simple, But how about in scaling up?

Filtration is simple. But how about in scaling up?

eg): Ethambutol pilot (1976, KIST)



Ethambutol

✓ **Unit Process (단위공정): "Chemical Change"**

Akylation, Nitration, Sulfonation, Amination,..

Chlorination, Oxidation,

Hydrogenation,

✓ **Chemical Conversion : used in Petroleum Industry**

used same as Unit Process

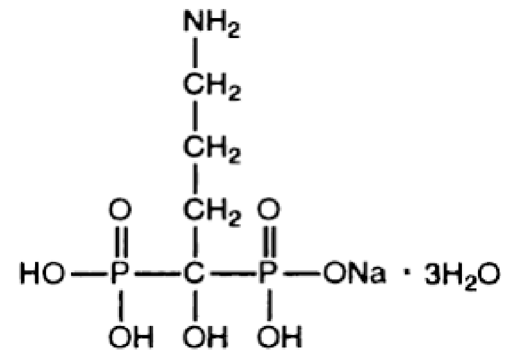
- **Batch Process (回分 공정)**
  - Similar to Lab process 와 유사
  - Reaction mixture in one reactor
  - More labor cost
  - Fine Chemical production : expensive drugs, explosive

- **Continuous Process (연속 공정)**
  - Flow processing
  - Automation-computer control
  - Energy saving process,
  - Short Reaction Time control:

eg) Acetylene production, Rxn time, 0.002 sec at 1600 C, Gas Phase Reaction

(6) Process Economics

- **High Cost Factors**



  - Labor : multi-step reactions
  - High Temp, High Press (high energy)
  - Acidic reaction: corrosion need special equipment
  - Complicate separation steps
    eg) Alendronate sodium salt: **crystal** form is important
    eg) Peptide products: filtration in weeks → 2-3 hours
  - Pollution control

- **Low Cost :** via Scale-Up

  eg) cost of CTC resin : $15,000/Kg → $1000?Kg

- **Plant Design** :

  -Technology and Economy (예) Phenol Plant

2) Carbon Source: Where organic chemicals come from?

(1) Coals : acetylene, water gas, BTX aromatics

– before WWII Chemical Industry

(2) Natural Gas & Petroleum : covers 95% of org compounds 📖 **94**

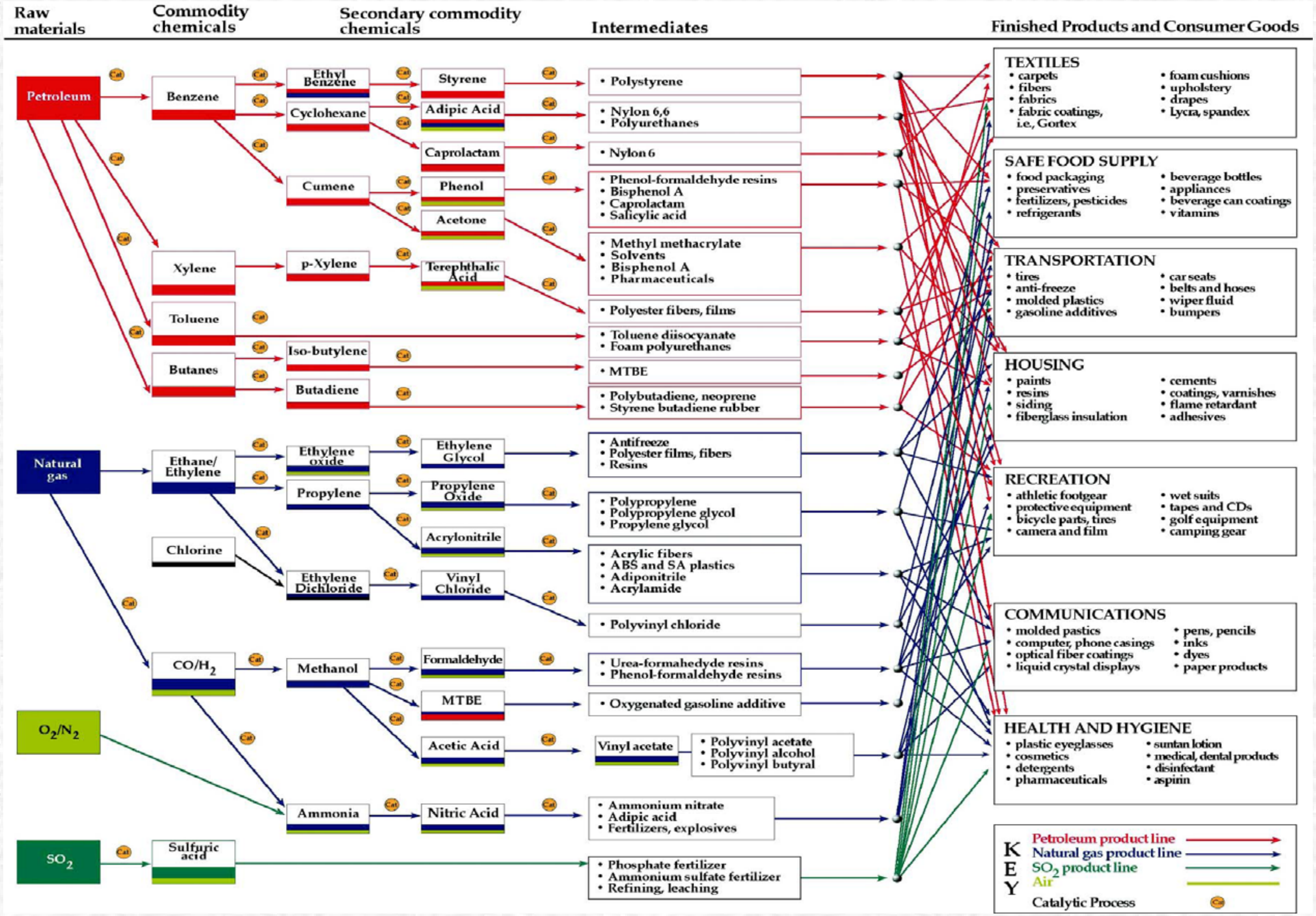
7 Major Chemical Building Blocks

- Ethylene : C2-Chemicals : Naphtha (Jpn, EU), Natural Gas → Shale gas(USA)
- Propylene : C3-Chemicals
- Butylene : C4-Chemicals
- Benzene, Toluene, Xylene : BTX
- Methane : C1-Chemicals

*50% of oil barrel is used for vehicles in US *petroleum will be drained in 50yrs ?

An Example of a Flow-Chart for Chemical Products

from Petroleum-based Feedstocks



Raw materials | Commodity chemicals | Secondary commodity chemicals | Intermediates | Finished Products and Consumer Goods

Petroleum

- Benzene
- Ethyl Benzene
- Styrene
- • Polystyrene
- Cyclohexane
- Adipic Acid
- • Nylon 6,6 • Polyurethanes
- Caprolactam
- • Nylon 6
- Cumene
- Phenol
- • Phenol-formaldehyde resins • Bisphenol A • Caprolactam • Salicylic acid
- Acetone
- • Methyl methacrylate • Solvents • Bisphenol A • Pharmaceuticals
- Xylene
- p-Xylene
- Terephthalic Acid
- • Polyester fibers, films
- Toluene
- • Toluene diisocyanate • Foam polyurethanes
- Butanes
- Iso-butylene
- • MTBE
- Butadiene
- • Polybutadiene, neoprene • Styrene butadiene rubber

Natural gas

- Ethane/ Ethylene
- Ethylene oxide
- Ethylene Glycol
- • Antifreeze • Polyester films, fibers • Resins
- Propylene
- Propylene Oxide
- • Polypropylene • Polypropylene glycol • Propylene glycol
- Acrylonitrile
- • Acrylic fibers • ABS and SA plastics • Adiponitrile • Acrylamide
- Chlorine
- Ethylene Dichloride
- Vinyl Chloride
- • Polyvinyl chloride
- CO/H_2
- Methanol
- Formaldehyde
- • Urea-formahedyde resins • Phenol-formaldehyde resins
- MTBE
- • Oxygenated gasoline additive
- Acetic Acid
- Vinyl acetate
- • Polyvinyl acetate • Polyvinyl alcohol • Polyvinyl butyral

O_2/N_2

- Ammonia
- Nitric Acid
- • Ammonium nitrate • Adipic acid • Fertilizers, explosives

SO_2

- Sulfuric acid
- • Phosphate fertilizer • Ammonium sulfate fertilizer • Refining, leaching

TEXTILES
- carpets
- fibers
- fabrics
- fabric coatings, i.e., Gortex
- foam cushions
- upholstery
- drapes
- Lycra, spandex

SAFE FOOD SUPPLY
- food packaging
- preservatives
- fertilizers, pesticides
- refrigerants
- beverage bottles
- appliances
- beverage can coatings
- vitamins

TRANSPORTATION
- tires
- anti-freeze
- molded plastics
- gasoline additives
- car seats
- belts and hoses
- wiper fluid
- bumpers

HOUSING
- paints
- resins
- siding
- fiberglass insulation
- cements
- coatings, varnishes
- flame retardant
- adhesives

RECREATION
- athletic footgear
- protective equipment
- bicycle parts, tires
- camera and film
- wet suits
- tapes and CDs
- golf equipment
- camping gear

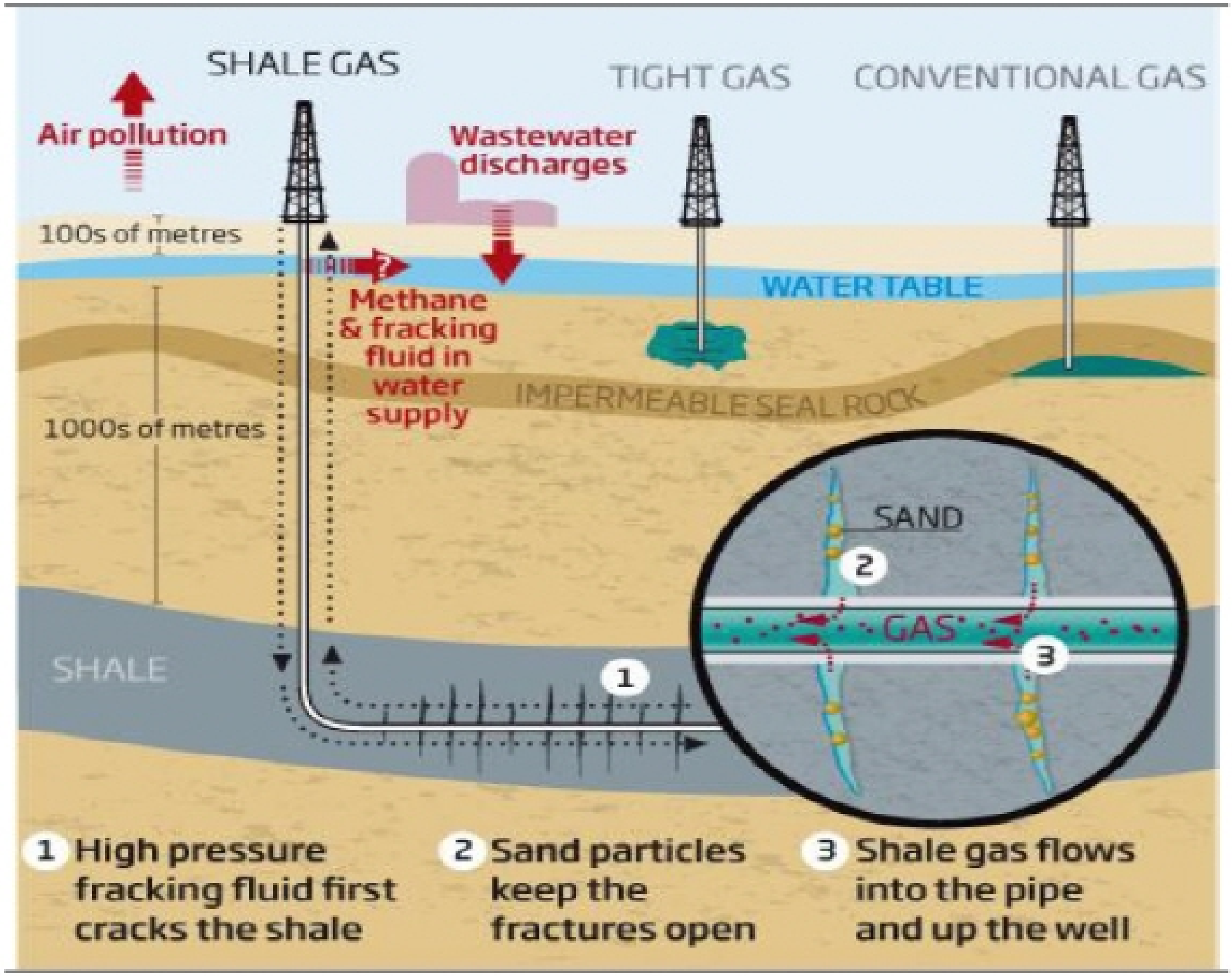
COMMUNICATIONS
- molded pastics
- computer, phone casings
- optical fiber coatings
- liquid crystal displays
- pens, pencils
- inks
- dyes
- paper products

HEALTH AND HYGIENE
- plastic eyeglasses
- cosmetics
- detergents
- pharmaceuticals
- suntan lotion
- medical, dental products
- disinfectant
- aspirin

KEY
- Petroleum product line
- Natural gas product line
- SO_2 product line
- Air
- Catalytic Process

National Renewable Energy Laboratory, August 2004

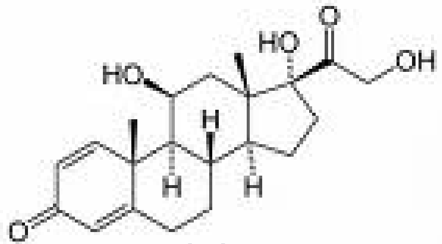
Shale Gas


SHALE GAS
TIGHT GAS
CONVENTIONAL GAS
Air pollution
Wastewater discharges
100s of metres
?
Methane & fracking fluid in water supply
WATER TABLE
IMPERMEABLE SEAL ROCK
1000s of metres
SAND
2
GAS
3
SHALE
1
1 High pressure fracking fluid first cracks the shale
2 Sand particles keep the fractures open
3 Shale gas flows into the pipe and up the well

(3) Biomass : Cellulose (C6), Hemicellulose(C5), Lignin (Aromatics)

(4) Fats, Oils & Carbohydrates

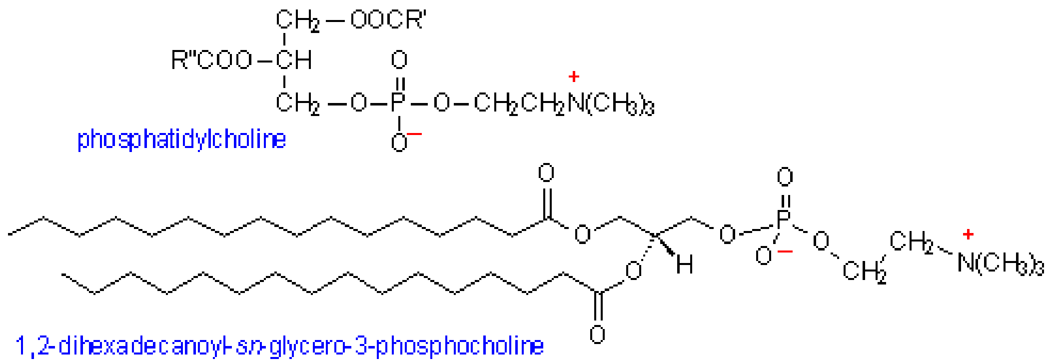
- Fatty acids (Palm oil, 우지(牛脂), Lad, ..)
- Sugars
- Fermentation Product:



Prednisolone

(5) Others

- Sterols, Alkaloids, Phosphatides (egg york,.. for DDS), ..
- Raw materials for expensive fine chemicals
- highly specialized field



phosphatidylcholine

1,2-dihexadecanoyl-*sn*-glycero-3-phosphocholine

An Example of a Flow-Chart for Chemical Products

from Biomass-based Feedstocks

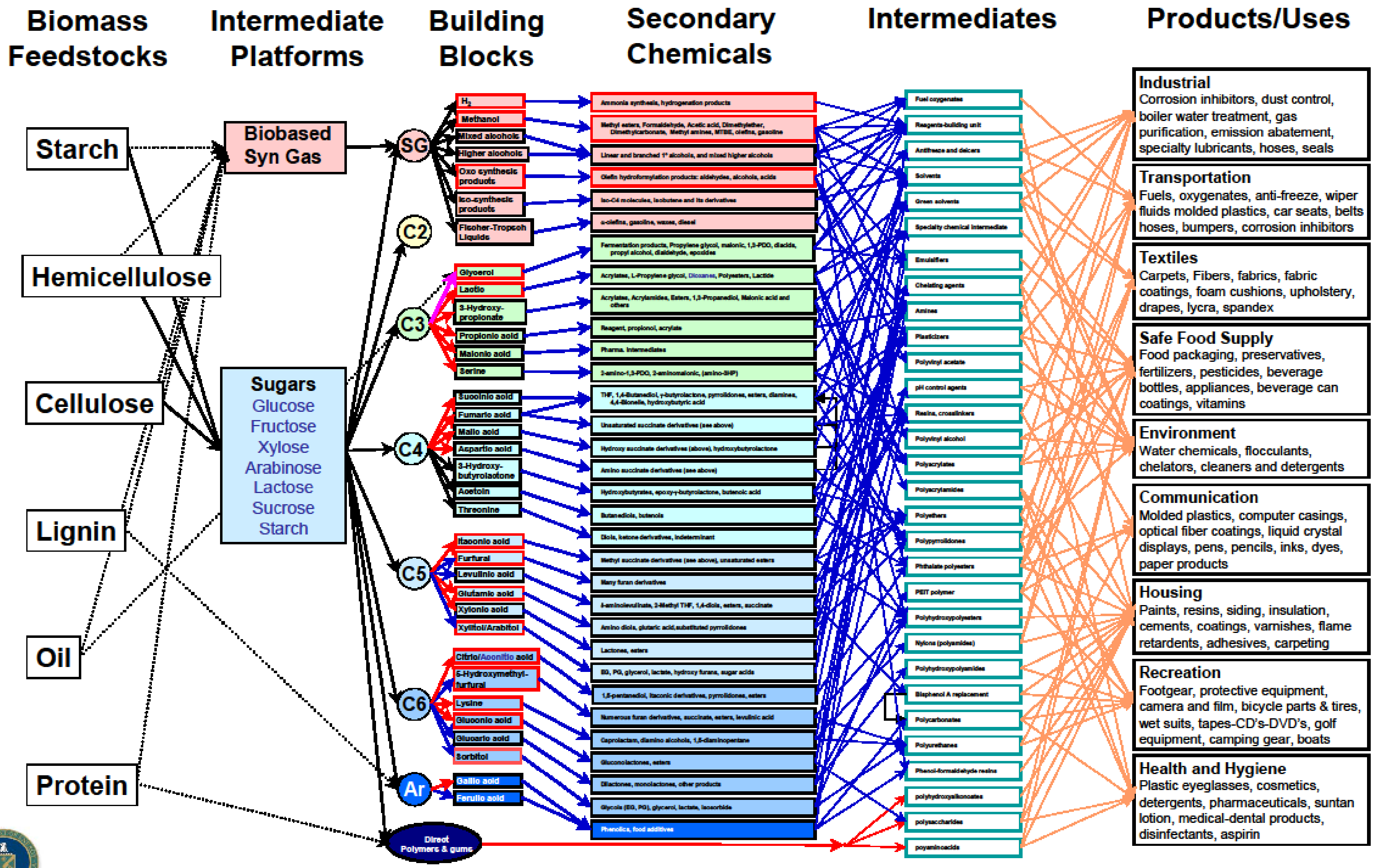
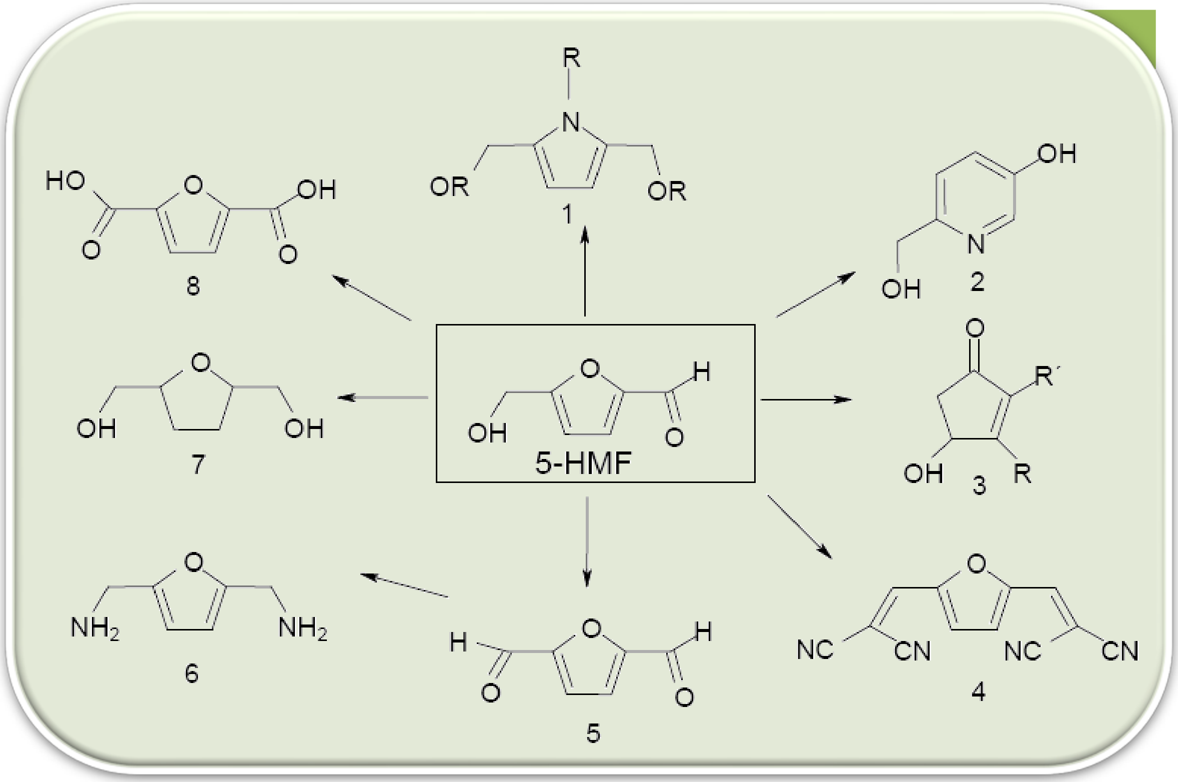


Figure 3 – Analogous Model of a Biobased Product Flow-chart for Biomass Feedstocks

National Renewable Energy Laboratory, August 2004

Cellulose (5-HMF) as Platform Chemical

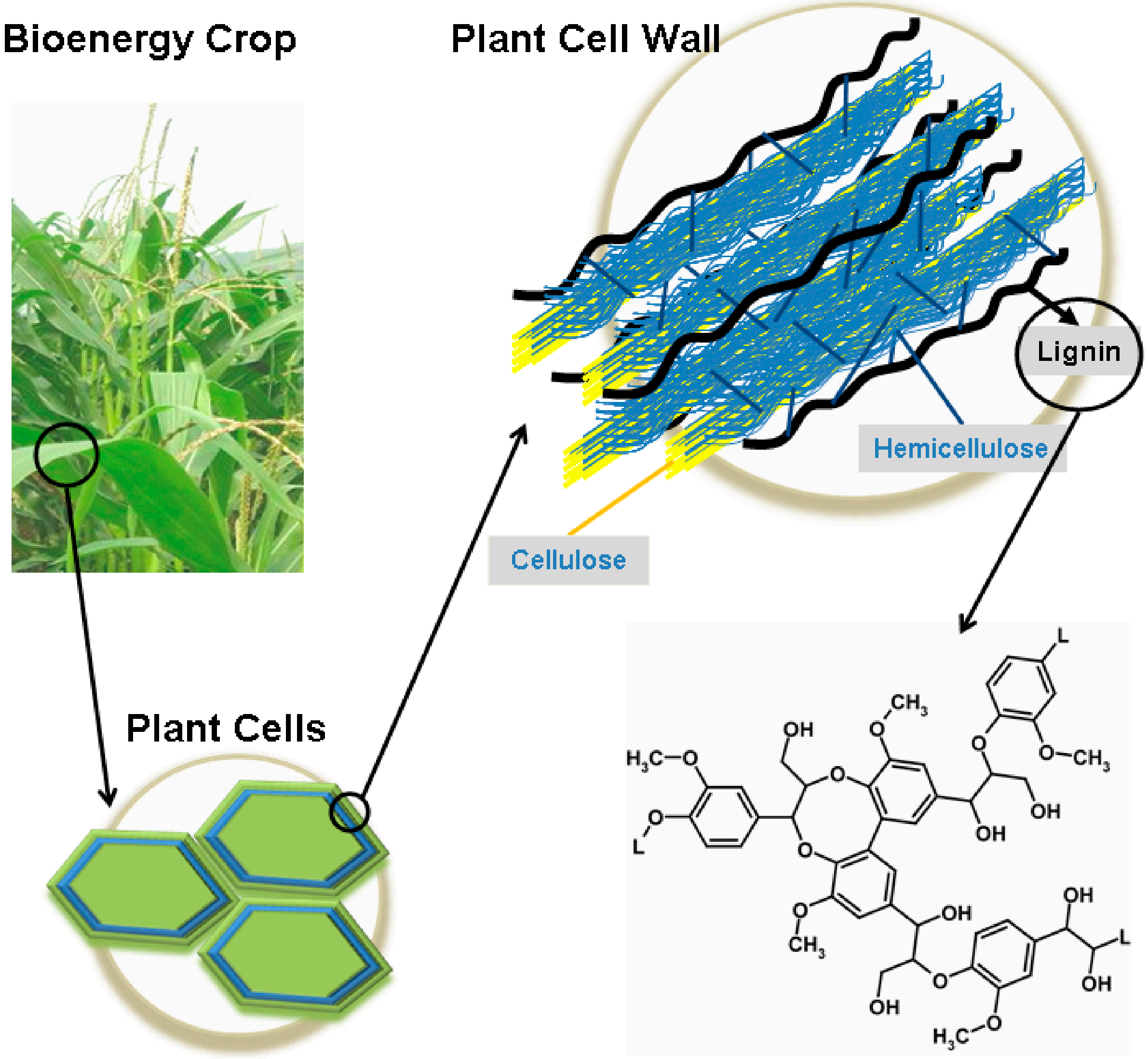
Highly Value-added Product



- **Polymers**
  - **- Polyesters**
  - **- Polyurethane**
  - **- Polyamides**
- **Bio-fuels**

1: 2,5-disubstituted pyrrols
2: hydroxymethyl-pyridinol
3: hydroxy-cyclopentenone
4: 2,5-diethyltetracyanofurane
5: 2,5-furandicarbaldehyde
6: 2,5-bis(aminomethyl)furan
7: 2,5-bis(hydroxymethyl)tetrahydrofuran
8: 2,5-furandicarboxylic acid

Lignin as Aromatic Platform Chemical



Bioenergy Crop

Plant Cell Wall

Lignin

Hemicellulose

Cellulose

Plant Cells

FDCA as Platform Chemical

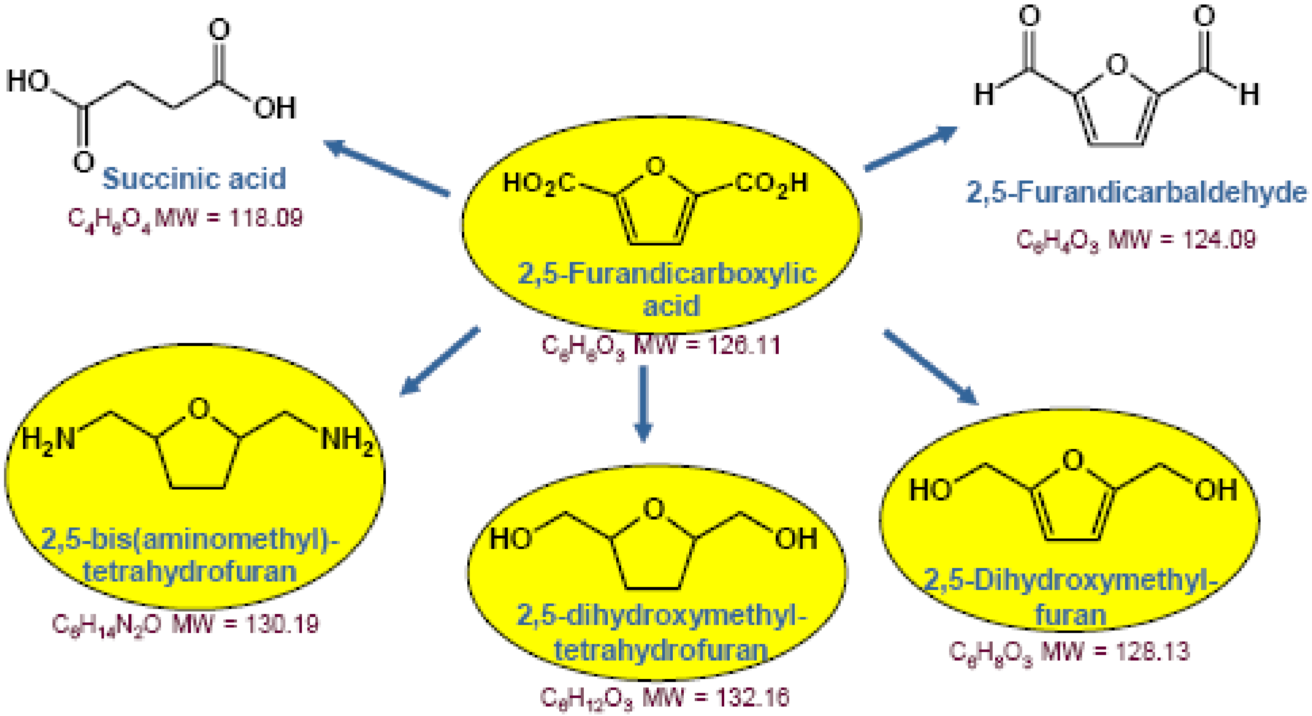


Figure 7 - Derivatives of FDCA

Hydroxypropionic Acid as Platform Chemical

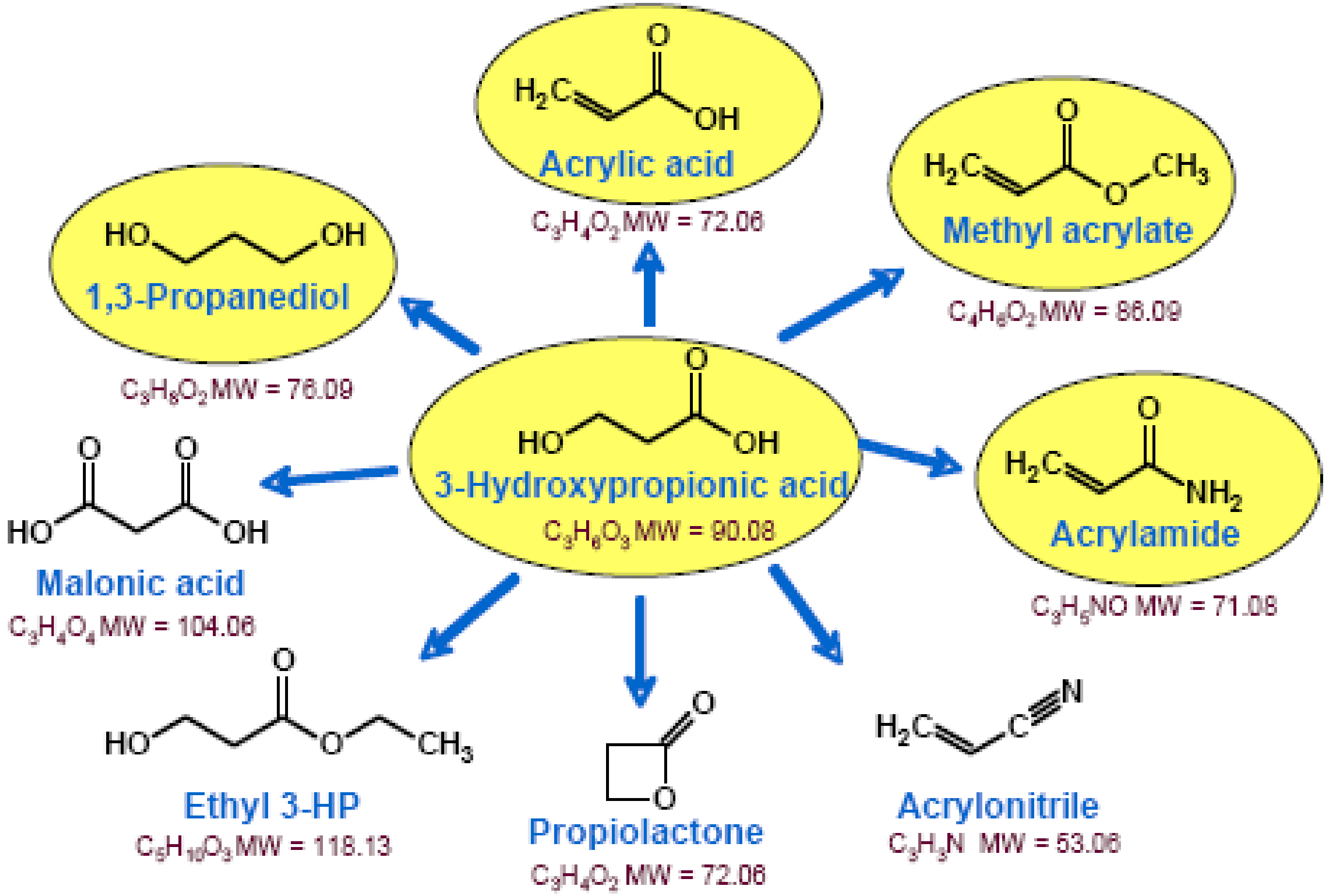


Figure 4 - Star Diagram of 3-Hydroxypropionic Acid

Succinic Aicd as Platform Chemical

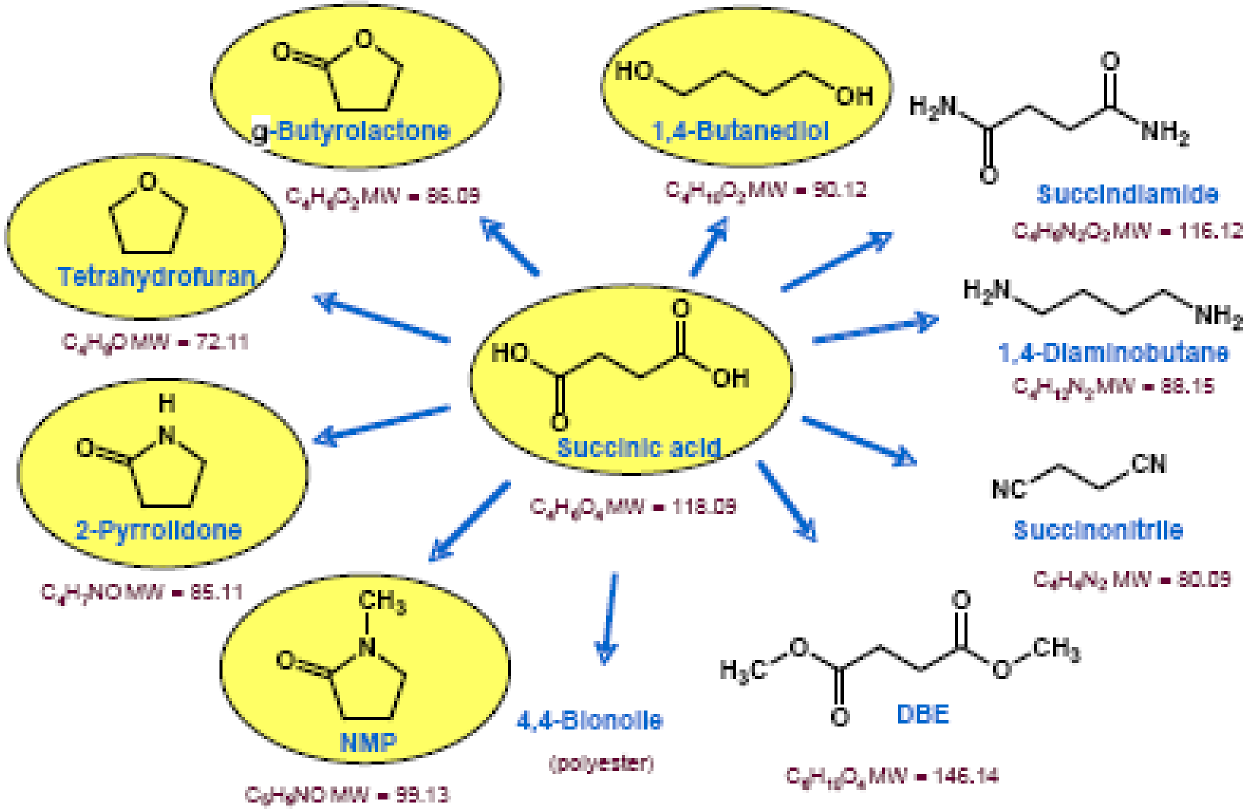


Figure 5 - Succinic Acid Chemistry to Derivatives

Aspartic Acid as Platform Chemical

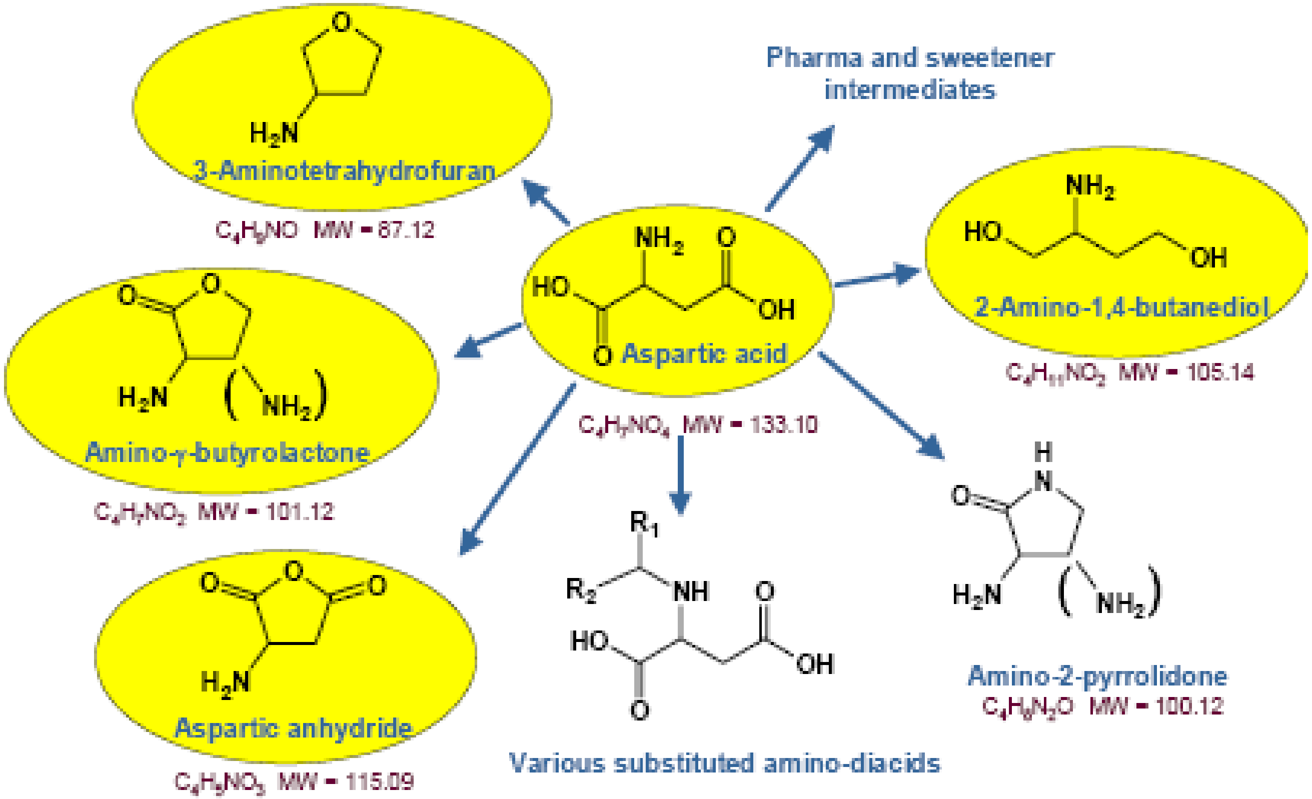


Figure 9 - Aspartic Acid Chemistry to Derivatives

Glycerol as Platform Chemical

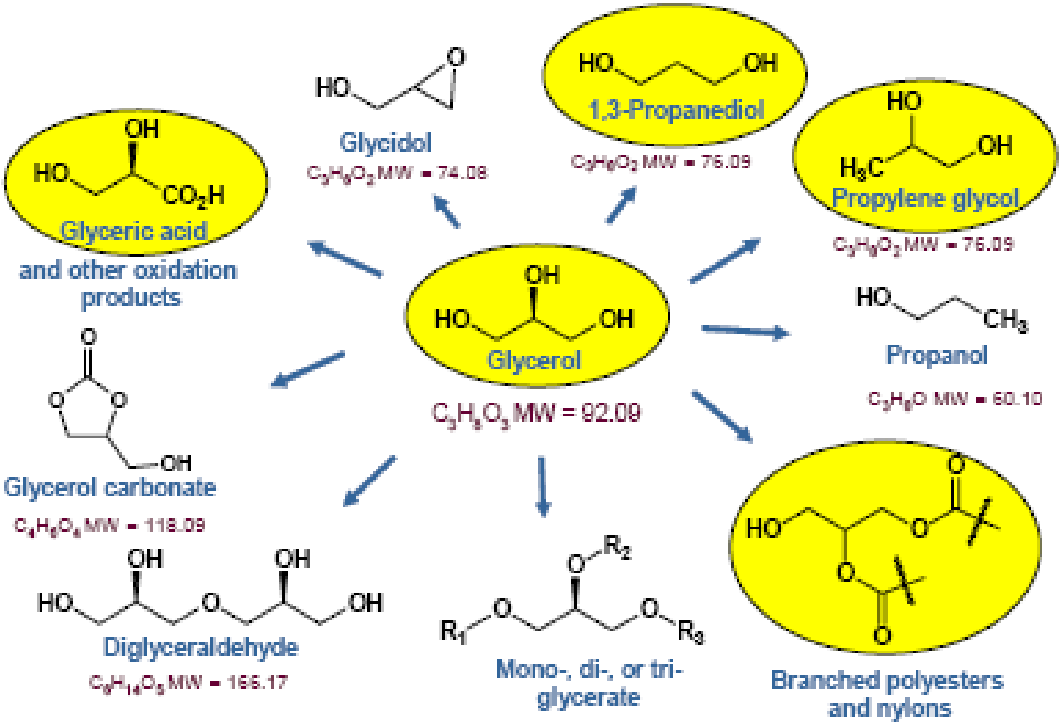


Figure 15 - Derivatives of Glycerol

Biodiesel Production

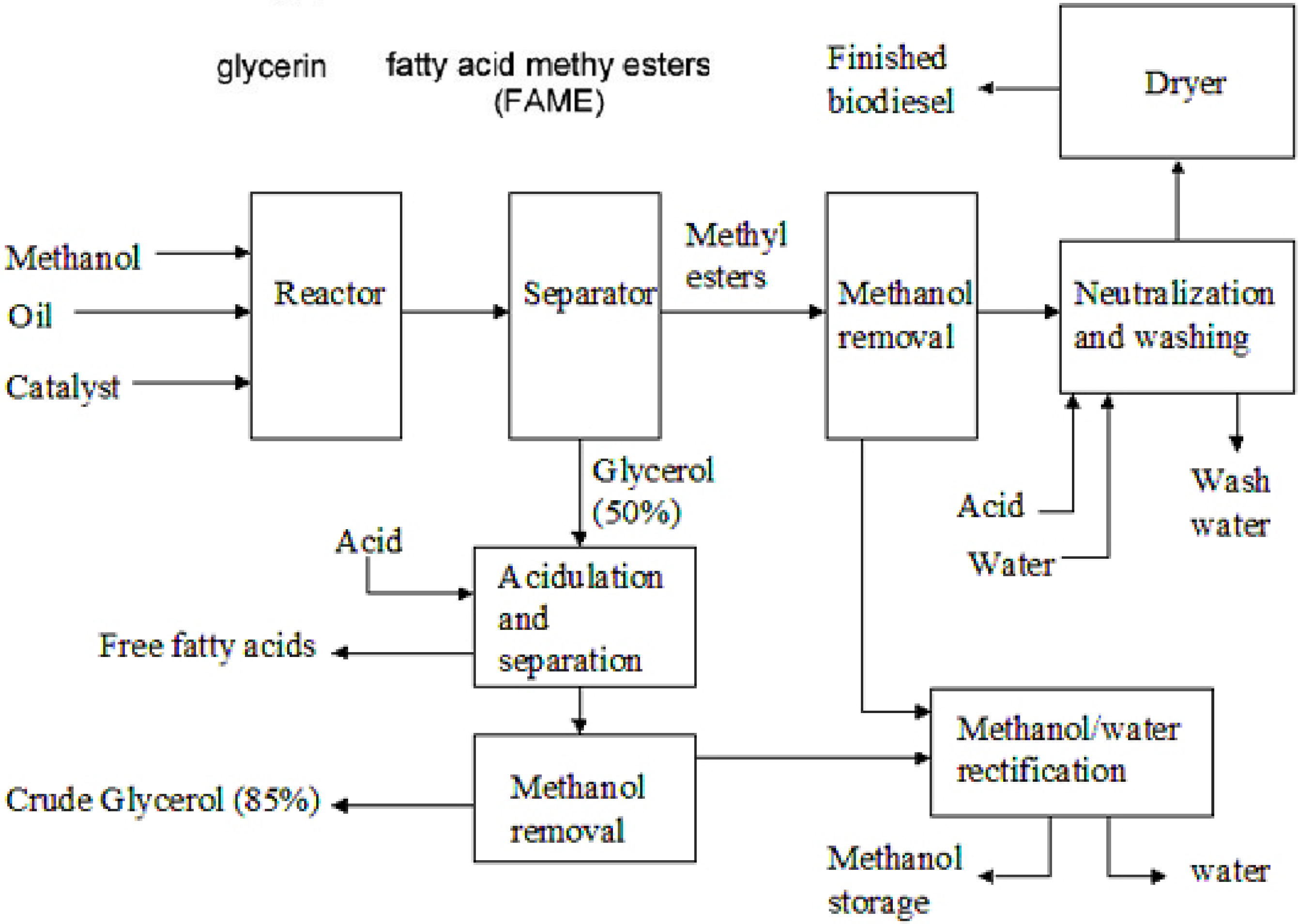
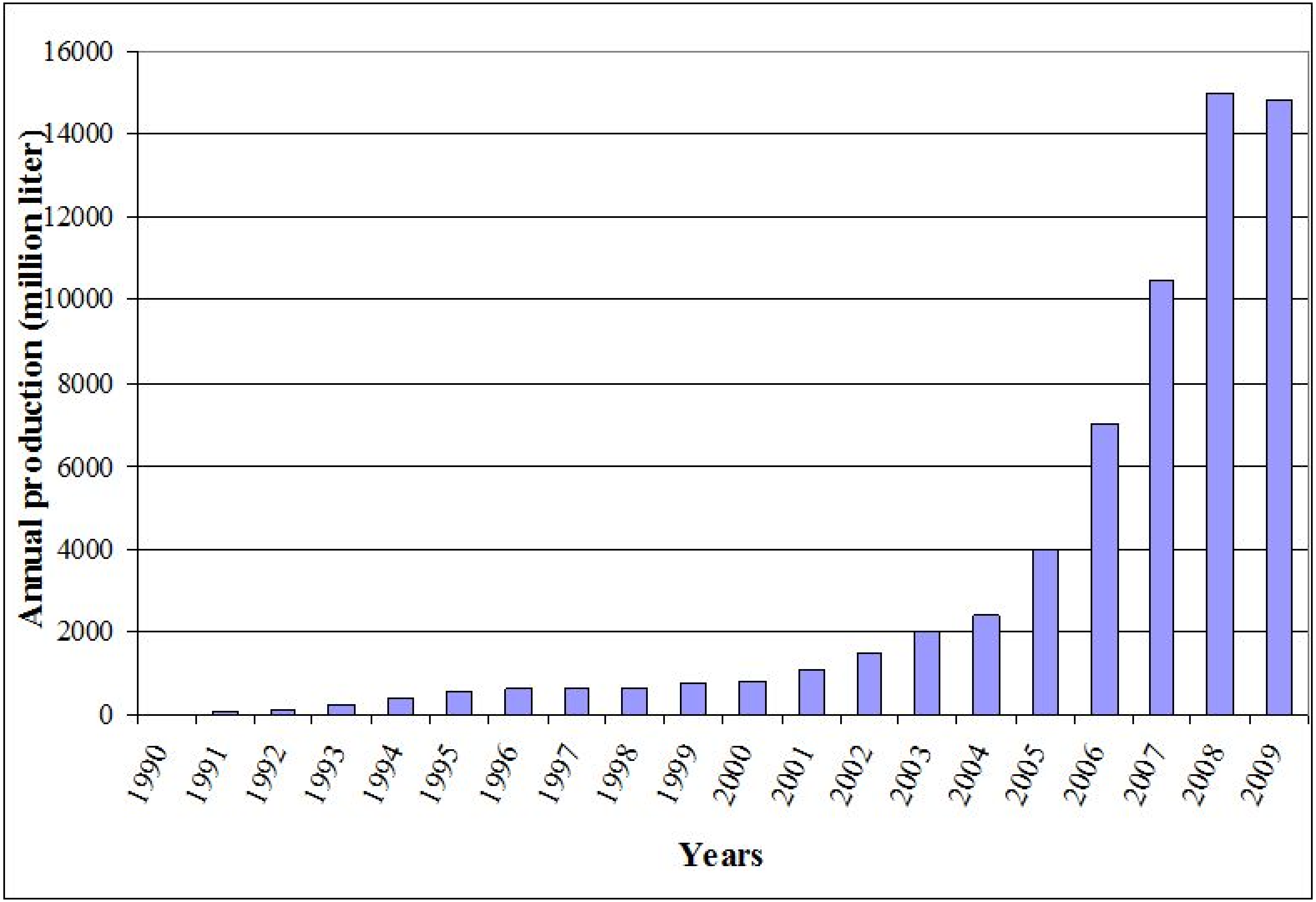


Figure 1. Process Flow Schematic for Biodiesel Production


Annual production (million liter)
16000
14000
12000
10000
8000
6000
4000
2000
0
1990
1991
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
2005
2006
2007
2008
2009
Years

Petroleum Refining

A. Introduction

1) Origin : Petro... (Latin: Peter, rock), Crude oil is found on Rocks

2) Composition C : 84–87%, H : 11–14%, N : 0–1%, S : 0->5%, O : 0–1%

Complex mixture HC 》 S, O, N, (tr.metal)

(Parafins) Alkanes : straight HC, branched HC, > CH_4

(Naphthens) Cycloalkanes : 5, or 6

(Aromatics) Aromatics : > C_6H_6

(Olefinics) Olefines

3) Classifications of Petroleum

(1) Depending on Composition

Paraffin base crude oil - open chain HC major

Naphtha base crude oil - cyclic HC major

Intermediate base crude oil

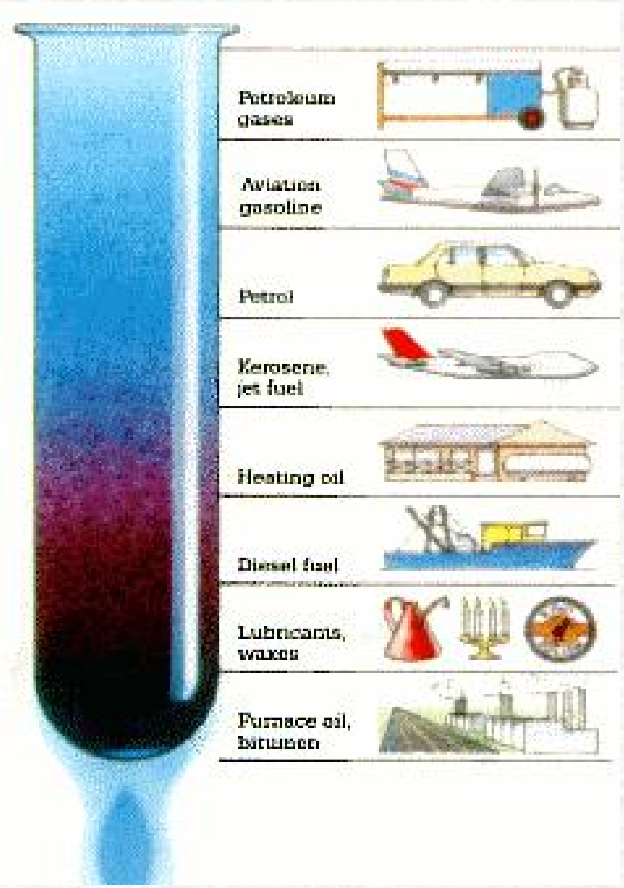
(2) Depending on M.W. distributions ~ Price

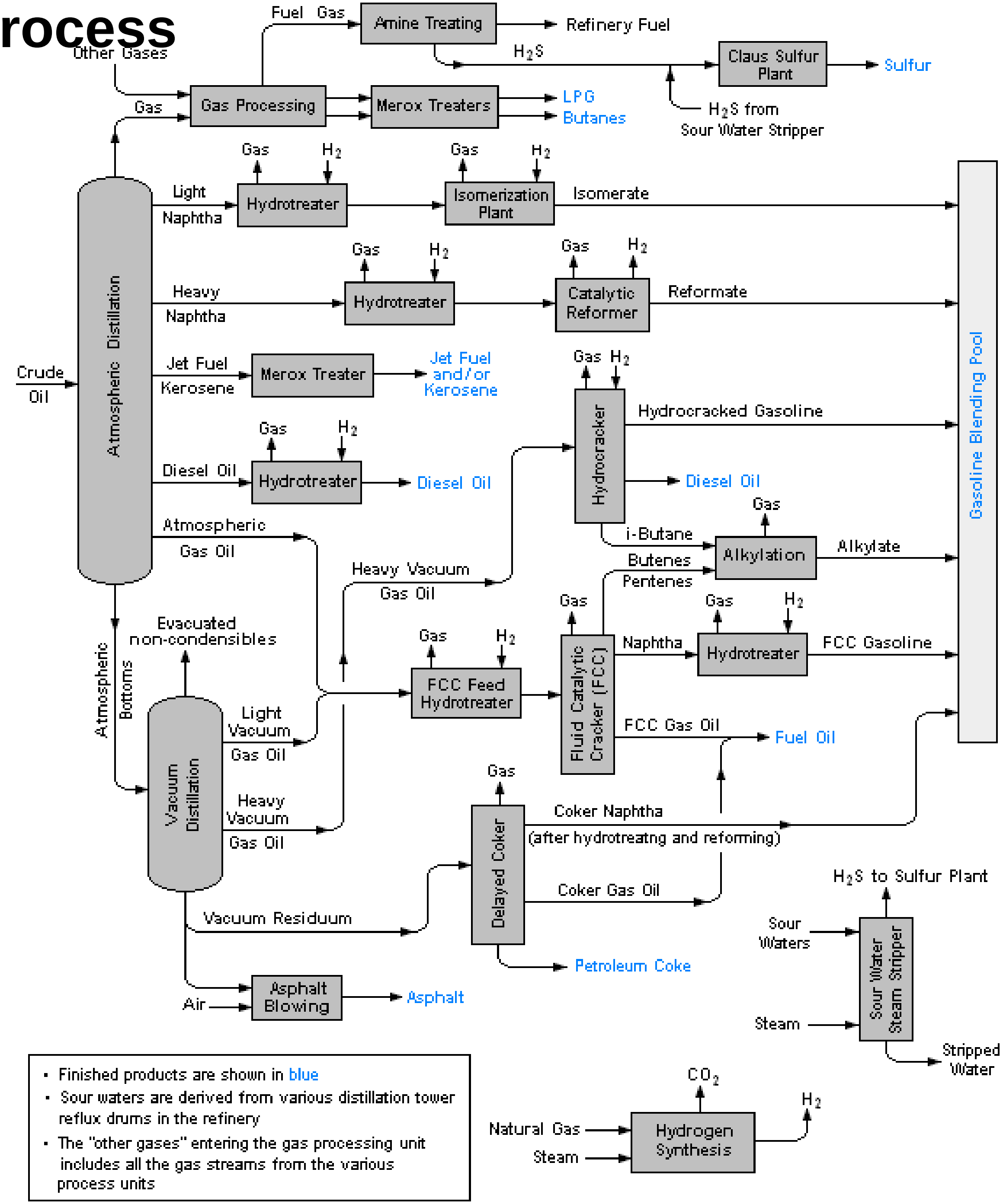
Light Crude : light M.W. major

Heavy Crude : high M.W. major

(3) Depending on Production Site: Dubai, Texas, North Sea

B. Petroleum Refining Process





- Finished products are shown in blue
- Sour waters are derived from various distillation tower reflux drums in the refinery
- The "other gases" entering the gas processing unit includes all the gas streams from the various process units

Some Historical Events

3000 BC	Sumerians use asphalt as an adhesive; Eqyptians use pitch to grease chariot wheels; Mesopotamians use bitumen to seal boats
600 BC	Confucius writes about drilling a 100’ gas well and using bamboo for pipes
1500 AD	Chinese dig oil wells >2000’ deep
1847	First “rock oil” refinery in England
1849	Canada distills kerosene from crude oil
1856	World’s first refinery in Romania
1857	Flat-wick kerosene lamp invented
1859	Pennsylvania oil boom begins with 69’ oil well producing 35 bpd
1860-61	Refineries built in Pennsylvania and Arkansas
1870	US Largest oil exporter; oil was US 2nd biggest export
1878	Thomas Edison invents light bulb
1901	Spindletop, Texas producing 100,000 bpd kicks off modern era of oil refining
1908	Model T’s sell for $950/T
1913	Gulf Oil opens first drive-in filling station
1942	First Fluidized Catalytic Cracker (FCC) commercialized
1970	First Earth Day; EPA passes Clean Air Act
2005	US Refining capacity is 17,042,000 bpd, 23% of World’s 73MM

1. **Fractional Distillation:**

   1^{st} operation in refining process by b.p. differences

2. **Cracking :**

   A. C_5-C_{12} from large size molecule

   B. Ethylene (or Propylene) from saturated HC

(1) Thermal cracking (for B) : so called steam cracking

(2) Catalytic cracking (for A) :

- also produces branched HC, aromatics

(3) Hydrocracking : " catalytic cracking + H_2 "

- prevents coking of catalyst
- Removal of S, N, O → H_2S, NH_3, H_2O (S- oil)

3. Polymerization

- low M.W. HC → gasoline-range molecule (via H^+ catalyst)
- not widely used today

4. Alkylation

- olefine + paraffin → branched HC
- under HF, or H_2SO_4 catalyst
- very important process for premium gasoline → high O.N.

5. Catalytic Reforming

- dehydrogenation of straight-chain, cyclic aliphatic HC
  → aromatic HCs (BTX)
- very important for high ON gasoline production
- most widely used refinery reaction

6. Dehydrogenation :

- occurs during Cracking, Reforming process

- for making others

eg) Butane → Butadiene, $PhCH_2CH_3 \rightarrow PhCH{=}CH_2$

7. Isomerization :

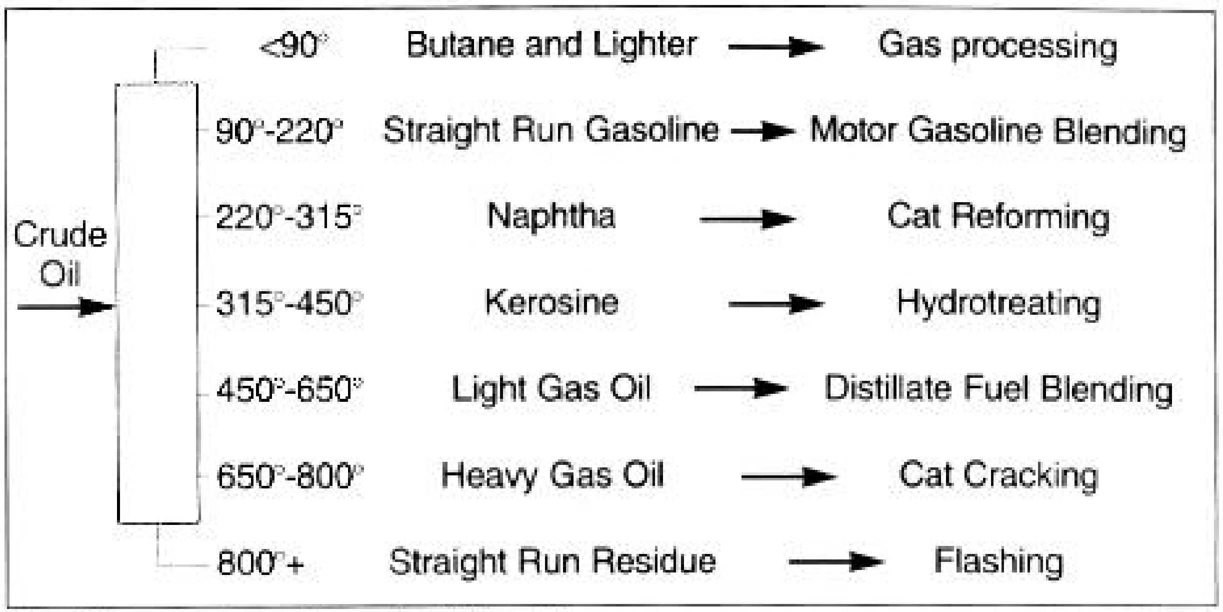
- straight chain → branched chain

eg) n-pentane → *i*-pentane (for alkylation)

eg) ethyl benzene, xylenes → *p*-xylenes → TPA

1) Fractional Distillation:

1sr operation in refining process by b.p. differences



<90°	Butane and Lighter	Gas processing
90°-220°	Straight Run Gasoline	Motor Gasoline Blending
220°-315°	Naphtha	Cat Reforming
315°-450°	Kerosine	Hydrotreating
450°-650°	Light Gas Oil	Distillate Fuel Blending
650°-800°	Heavy Gas Oil	Cat Cracking
800°+	Straight Run Residue	Flashing

Distilling crude and product disposition

1) Fractional Distillation 📖 98

(1) Gases (b.p 〈 20℃) : CH_4 (LNG)+C_2H_6 (lead gas)

$C_3H_8 + C_4H_{10}$ (LPG)

- refinery gas
- similar to Natural Gas : for fuels and chemical feed stock
- mostly flared because of recovery problem

(2) Light Naphtha (b.p. 70-140℃):

C_5-C_9 straight run gasoline

(3) Heavy Naphtha (b.p 140-200℃)

- C_7-C_9 aliphatic, cyclo-aliphatic + some aromatic
- For fuels, chemical feed stock

(4) Kerosine (燈油.석유) (b.p 175-275℃) : C_9-C_{16}

- first used as lightening, solvents
- Fuel for Jet, tractor, home heating

(5) Gas oil (輕油) (b.p 200-400℃) : C_{15}-C_{25}

- for diesel and heating fuel
- raw material for cracking to olefines

(6) Lub oil (b.p >350℃)

- used for lubrication
- maybe cracked to lighter fraction

(7) Heavy (Fuel) oil (重油) (b.p >350-450℃)

- Boiler fuel (bunker oil)
- Ship, Industrial furnace
- Needs vac distillation for further process
- Depending on Visocity: Bunker A, Bunker C

(8) Asphalt : for paving, coating etc...

* Knocking vs O.N.

* Block-Flow Diagram of Typical Petroleum Refinery

2) Cracking: catalytic cracking

- Thermal (Steam) cracking (1912-   )

- Catalytic cracking (1940-   ) : Si_2O_3/Al_2O_3, of Zeolite

(1) Purpose :

- **To Increase gasoline production:** can not by fully supplied by straight run gasoline

eg) gasoline production from heavy naphtha

total gasoline production > 50%

- Increase O.N.

(2) Reactions ： See 📖

- Condition : ~500℃(vaporize) → brief contact (1-3 sec) on catalyst

C_7H_{15}-$C_{15}H_{30}$-C_7H_{15} → C_7H_{15} + C_6H_{12}=CH_2 (High O.N. gasoline)

(Heavy G.O) (gasoline)

+ $C_{14}H_{28}$=CH_2 (recycle) (Endo, +Δ H)

-**Products : from middle east Oil (G.O.)**

Gasoline	36%	
Residue	23%	
G.O	15%	
*Coke	6%	… high MW carbonaceous materials: inactivate catalyst
Propane	4%	(need regeneration of catalyst process→ Fluidized - Bed Reactor: FCC)

Etc (no ethylene) !

- **Fluidized bed rxtor (see 📖 116)**

Regeneration of catalyst by burning deposited tar & coke

(3) Mechanism : Carbocation (R^+) mechanism

- **R^+ Formation by acidic site on catalyst**

$$C_{16}H_{34} + R^+ \rightarrow C_5H_{11}\text{-}CH^+\text{-}C_{10}H_{21} + RH$$

28 "CH_2" *vs* 6 "CH_3"

- **β-Scission**

$$C_5H_{11}CH^+\text{-}CH_2\text{-}CH_2C_8H_{17} \rightarrow C_5H_{11}CH{=}CH_2 + {}^+CH_2C_8H_{17}\ (1^\circ\ R^+)$$

$$C_8H_{17}CH^+ \rightarrow C_4H_9CH_2\text{-}CH^+\text{-}CH_2CH_3\ (C_9^+)$$

※ Smallest Unit of β-scission → “propene"

$RCH_2\text{-}CH_2\,CH_2^+ \rightarrow R\,CH_2^+ + CH_2{=}CH_2$: less possible

low conc. of 1° R^+ → low conc. $CH_2{=}CH_2$

$R\text{-}CH_2\text{-}CH^+\text{-}CH_3 \rightarrow R^+ + CH_3\text{-}CH{=}CH_2$: more possible

higher conc. of 2° R^+ → higher conc. > $CH_3\,CH_2{=}CH_2$

- **Further β-scission until $C3^+$**
- **Hydride ion abstraction → new R^+ (chain rxn)**

$$C_5H_{11}^+ + C_{16}H_{34} \rightarrow C_5H_{12} + C_{16}H_{33}^+$$

(4) Other Reactions

- Carbon skeletal rearrangement → branched HC

eg)

- Alkyl aromatics → Reverse F.C. alkylation

Alkyl Benzene → Benzene + Alkene

※ no change on aromatic ring itself under cracking condition

(*vs* hydro cracking)

- Double bond migration → increase O.N

eg) terminal olefin → internal olefin

(5) Side Reactions

- H^+ transfer : propylene + *t*-butyl $^+$ → → propane + *i*-butene
- Polymerization of alkene :

3) Hydrocracking

(1) combination : "cracking + hydrogenation"

- Cond : 340-420℃, 60-130atm, over dual-function catalyst

Cracking : Silica-Alumina, or Zeolite

Hydrogenation : Ni, W, Pt, Pd,

- Characteristics: less side rxn, no coke formation

no need for catalyst regeneration

(2) Reaction

$C_7H_{15}\text{-}C_{15}H_{30}\text{-}C_7H_{15} + H_2 \rightarrow n\text{-}C_7H_{16} + i\text{-}C_7H_{16} + C_{15}H_{32}$ (recycle)

Exo Therm Rxn : $-\Delta H$ (need cooling)

(3) Application

- In case of difficult in catalytic cracking such as ....

  cracking of polynuclear aromatic HC

- For production of low S containing jet fuel, diesel fuel

(3) Strong & Weak Points

- High press, large H_2 consumption
- More expensive process than catalytic cracking
- Rather low O.N product → need catalytic reforming

※ Octane Number : The higher the octane number, the more compression the fuel can withstand before detonating (igniting)

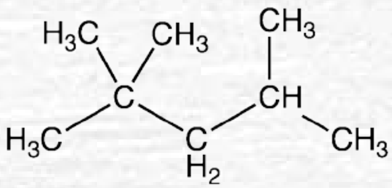
1) 2 Major quality of gasoline

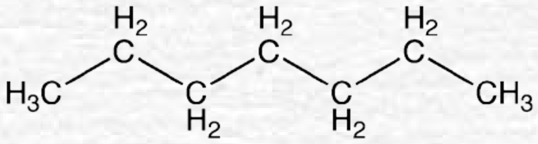
- appropriate volatility : bp 30-190℃
  - < 30 ℃ Loss by evaporation
  - > 190℃ fuel line locking
- Burning property : smooth burning

→ high O.N. (90-100℃)

2) Scale of O.N.

n-heptane(0) ↔ *i*-octane(100)
Burning property by the content of *i*-octane (%)





(eg)

n-pentane	62	2,2-dimethyl butane	92
n-hexane	25	Benzene, Tolune	>100
cyclohexane	83		
2-methyl butane	92		

3) Structure Requirement for high O.N

- Chain branching
- Unsaturation
- Aliphatic or Aromatic Ring

※ **Cetane number**: Cetane rating or CN is an indicator of the combustion speed of diesel fuel and compression needed for ignition. It is an inverse of the similar octane rating for gasoline.

4) Thermal cracking (steam cracking)

- Since 1912 (thermal cracking)
- Ethylene Production : “Major Objective"
- Free Radical mechanism : v. High Temp ~800℃ ~ rxtor material
- No **catalyst**

(1) Mechanism : FR mechanism

Thermal cracking of GO (n-Decane), ethane, and propane 🕮 118

- Mechanism drawing by fish hook -

- Initiation ~ BDE

$C_{10}H_{22}$ ------△→ $2\ CH_3CH_2CH_2CH_2CH_2.$

$CH_3CH_2CH_2 - CH_2CH_2 .$ → $CH_3CH_2CH_2.$

β-scission + $CH_2{=}CH_2$

$CH_3CH_2CH_2. \rightarrow CH_3. + CH_2{=}CH_2$

- **Propagation :**
  1) FR should be regenerated,
  2) Not much FR required, only for initiation (pyrolysis, smoking)

CH_3. or others + RH → R. + CH_4 or others

$CH_3CH_2CH_2CH_2CH_2CH_2$ - CH_2-CH.- CH_2CH_2 ------------→ β-scission

$CH_3CH_2CH_2CH_2CH_2$ -CH_2. + CH_2=$CHCH_2CH_3$

CH_3CH_2. → CH_2=CH_2 + H.

- Termination

1) RCH_2. + .CH_2R → RCH_2-CH_2R

2) Disproportionation : oxidaton/reduction

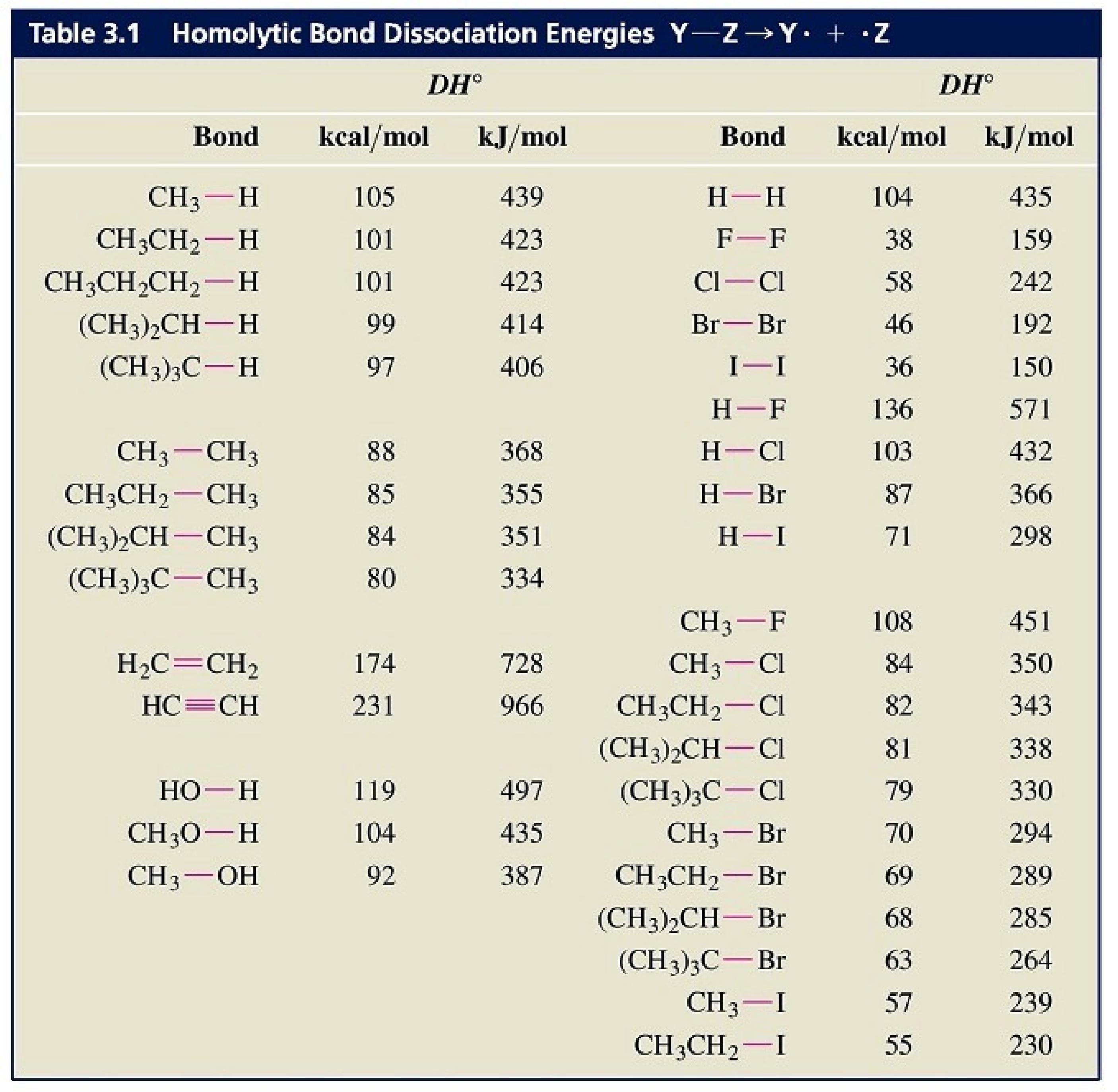


Table 3.1 Homolytic Bond Dissociation Energies $\mathrm{Y{-}Z \rightarrow Y\cdot + \cdot Z}$

	$DH°$			$DH°$	
Bond	**kcal/mol**	**kJ/mol**	**Bond**	**kcal/mol**	**kJ/mol**
$\mathrm{CH_3{-}H}$	105	439	$\mathrm{H{-}H}$	104	435
$\mathrm{CH_3CH_2{-}H}$	101	423	$\mathrm{F{-}F}$	38	159
$\mathrm{CH_3CH_2CH_2{-}H}$	101	423	$\mathrm{Cl{-}Cl}$	58	242
$\mathrm{(CH_3)_2CH{-}H}$	99	414	$\mathrm{Br{-}Br}$	46	192
$\mathrm{(CH_3)_3C{-}H}$	97	406	$\mathrm{I{-}I}$	36	150
			$\mathrm{H{-}F}$	136	571
$\mathrm{CH_3{-}CH_3}$	88	368	$\mathrm{H{-}Cl}$	103	432
$\mathrm{CH_3CH_2{-}CH_3}$	85	355	$\mathrm{H{-}Br}$	87	366
$\mathrm{(CH_3)_2CH{-}CH_3}$	84	351	$\mathrm{H{-}I}$	71	298
$\mathrm{(CH_3)_3C{-}CH_3}$	80	334			
			$\mathrm{CH_3{-}F}$	108	451
$\mathrm{H_2C{=}CH_2}$	174	728	$\mathrm{CH_3{-}Cl}$	84	350
$\mathrm{HC{\equiv}CH}$	231	966	$\mathrm{CH_3CH_2{-}Cl}$	82	343
			$\mathrm{(CH_3)_2CH{-}Cl}$	81	338
$\mathrm{HO{-}H}$	119	497	$\mathrm{(CH_3)_3C{-}Cl}$	79	330
$\mathrm{CH_3O{-}H}$	104	435	$\mathrm{CH_3{-}Br}$	70	294
$\mathrm{CH_3{-}OH}$	92	387	$\mathrm{CH_3CH_2{-}Br}$	69	289
			$\mathrm{(CH_3)_2CH{-}Br}$	68	285
			$\mathrm{(CH_3)_3C{-}Br}$	63	264
			$\mathrm{CH_3{-}I}$	57	239
			$\mathrm{CH_3CH_2{-}I}$	55	230

Environ Health Perspect. 1985 Dec; 64: 111–126

Free-radical chemistry of cigarette smoke and its toxicological implications.

Abstract

Cigarette smoke contains two very different populations of free radicals, one in the tar and one in the gas phase. The tar phase contains several relatively stable free radicals; we have identified the principal radical as a quinone/hydroquinone (Q/QH2) complex held in the tarry matrix. We suggest that this Q/QH2 polymer is an active redox system that is capable of reducing molecular oxygen to produce superoxide, eventually leading to hydrogen peroxide and hydroxyl radicals. In addition, we have shown that the principal radical in tar reacts with DNA in vitro, possibly by covalent binding. The gas phase of cigarette smoke contains small oxygen- and carbon-centered radicals that are much more reactive than are the tar-phase radicals. These gas-phase radicals do not arise in the flame, but rather are produced in a steady state by the oxidation of NO to NO2, which then reacts with reactive species in smoke such as isoprene. We suggest that these radicals and the metastable products derived from these radical reactions may be responsible for the inactivation of alpha 1-proteinase inhibitor by fresh smoke. Cigarette smoke oxidizes thiols to disulfides; we suggest the active oxidants are NO and NO2. The effects of smoke on lipid peroxidation are complex, and this is discussed. We also discuss the toxicological implications for the radicals in smoke in terms of a number of radical-mediated disease processes, including emphysema and cancer.

(2) Steam is Required

- Termination, Chain transfer reaction: bimolecular rxn
- Low partial Press → Inhibits bimolecular reaction

(3) High Temp is Required

- High Temp favors homolysis and β-scission
- High Temp : no effect on termination (∵ Ea ~ O)

$$RCH_{2}\cdot + \cdot CH_{2}R \rightarrow RCH_{2}\text{-}CH_{2}R$$

(4) Choice of feedstock 📖 110

- Ethylene % : highly depends on Feeds
  (Ethane > Naphtha > GO : MW of feed), propylene by product
- Little by product (propylene, 사생아?) from Ethane !
- Propylene surplus before → Propylene shortage in early 1990's
  EU/Jp is ok with naphtha feed
  USA is ok with catalytic cracking for gasoline production

5) Catalytic Reforming (Reforming)

(1) Purpose :

- Improve O.N. of gasoline (1950, UOP)
  40 ℃ < b.p. < 90 ℃ : O.N. of straight run gasoline, 40 → 95

- Production of aromatics from light Naphtha (C_6-C_8)
  ~ 50% production (w/w)

(cf) Production of H_2 : ~ 15% (w/w)

(2) Reactions : “dehydrogenation + isomerization + hydrogenolysis”

- Dehydrogenetion of cyclo-6 HC to aromatic compounds
  Methylcyclohexane → Toluene + 3 H_2

- Dehydroisomerization of cyclo-5 HC
  Methylcyclopentane → Benzene + 3 H_2

- Dehydrocyclization of alkanes to aromatic compounds

(minor reactions)

- Hydrocraking of Alkane (Hydrogenolysis)

$n\text{-}C_7H_{16} + H_2 \rightarrow C_3H_8 + C_4H_{10}$

- Isomerization of Alkane

$n\text{-}C_5 \rightarrow CH_3CH(CH_3)CH_2CH_3$

cf. High O.N. ← Aromatic compounds

(3) Process

※ Catalyst : Dual Function Catalyst (二元 촉매)

Catalyst effectiveness ∝ distance between two catal sites

Acidic site: (SiO_2/Al_2O_3) : RDS

Hydrogenation - Dehydrogenation site : (Pt/Re)

$A \rightarrow B \rightarrow C$

(good system when difficult to achieve
by successive beds of two catalyst)

- **Operation Temp. :** 450-550 ℃ … gas-phase reaction

  In the presence of H_2 (10-50 atm), Pt/Al_2O_3 - SiO_2

  equilibrium requires Low partial press H_2

  but, to prevent “coke"- formation

- **Platforming Process : Platinume + Reforming (UOP)**

  H_2 : HC = 5-10 : 1 (Feed Ratio)

  Series of diabetic Reactors (#3-5)

  Reheater between Reactors (∵) endotherm rxn

- **Rheniforming process : Pt-Re/Al_2O_3 - SiO_2**

- **Multi-metal Cluster Catalyst**

(4) Mechanism

- Dehydro-isomerization of Cyclopentane

Dehydrogenation + Carbocation reaction

eg) Methylcyclopentane → Cyclohexene → benzene

- Isomerization of Alkanes: paraffin to *iso*-paraffin

$CH_3CH_2CH_2CH_2CH_3$ == $CH_3CH_2CH=CHCH_3$ + H_2 (D)

$CH_3CH_2CH=CHCH_3$ + H^+ == $CH_3CH_2CH^{+}CH_2CH_2$ (A)

CH_3-$CH_2CH^{+}CH_2CH_2$ == == *iso*-pentane

- Paraffin to Aromatics

eg) Mechanism ?

(5) Byproduct

H_2 : large scale production
Raw material for Hydrocracking
Raw material for NH_3 production

(6) Separation of Products : Complicate and Difficult

(eg) Separation of Xylene

o-Xylene (bp 144.4, mp - 25 ℃)
m-Xylene (bp 139.1, mp - 47.9 ℃)
p-Xylene (bp 138.3, mp 13.2 ℃)

- Similar BPs→ need 200 plates for distilation column
- Isolated by crystallization at - 60 ℃

(eg) Recovery of Aromatics from Reforming Products

Cooling → (Gas + Liquid)

- Gas : HC (C_1-C_4), H_2

- Liquid : >C_5 Condensates
  → Aromatics recovered by extraction with
  Sulfolane, Glycol/H_2O, N-methylpyrolidone/EG

- To meet the market demand,

•Need isomerization of Xylenes

•Need dehydroalkyation of Toluene to Benzene 📖 121, Table 4.10

6) Alkylation (catalytic alkylation)

“olefin (C_3 or C_4) + paraffinic HC"

eg) *i*-butane (C4) + *i*-butene (C4) + strong H^+ → isooctane (C8)

(1) General characteristics

- To produce high O.N. gasoline contents (>90)
- For the production of best possible motor fuel
- should use isobutane only
  eg) isobutane, propene, butene, …
  (by products of catalytic cracking or oil distillation process gas)
- very important in U.S refinery process

(2) Reaction of isobutane + propylene → branched HC mixtures

✓ note: (2,3-C5 38% + 2,4-C5 19% + C3 25% + branched C8 15%)

- 96-98% H_2SO_4 : 0-10℃ (냉동장치 要… E cost)
- HF : 50℃ (high cost, safety!)

(3) Mechanism

- Initiation : by protonation

  $CH_3CH{=}CH_2 + HF \rightarrow CH_3CH^+CH_3 + F^-$

- Hydride abstraction :

  $(CH_3)_3C\text{-}H + CH_3CH^+CH_2 \rightarrow$ t-butyl cation + $CH_3CH_2CH_3$

  (only *i*-butane 을 쓰는 이유 : very stable cation)

- Rearrangement :

  ~ 1,2 H shift or ~1,2 alkyl shift for further branching

7) Polymerization

- Converts C_3, C_4 olefine → olefinic gasoline

- Important process during WWII : aviation fuel
  C_3, C_4 olefine (by-prod of cracking) → polymerized gasoline

- Propylene trimer, tetramer → alkylbenzene → [sulfonation]
  detergents (hard surfactant)

8) Isomerization (Catalytic Isomerization)

(1) Purpose

- n-butane + $AlCl_3$ → isobutane (as a feedstock for alkylation)
  if , >C_5, tar formation, etc side rxn
- straight run gasoline → branched gasoline (high O.N)

(2) Reaction

$C_4H_{10} + HCl + AlCl_3 \rightarrow C_4H_9^+ + AlCl_4^- + H_2$

$R^+ + CH_3CH_2CH_2CH_3 \rightarrow RH + CH_3\text{-}CH^+\text{-}CH_2\text{-}CH_3$ → 1,2 H shift

→ 1,2 Alkyl shift → t-butyl cation → *i*-butane

- Chain rxn → needed small amount C^+

Unleaded gasoline & Clean Air Act

- Catalytic cracking, TEL/EDB → High ON gasoline
- lead bromide emission : toxic

Unleaded gasoline w/ high ON needs

- Oligomerization: reactivated process
- Alkylation
- Catalytic cracking catalyst developed
- Catalytic reforming →? Clean Air Act

Clean Air Act (1991) demanded lower aromatics & oxygenate source

- Benzen contents (3 % → 1%)
- Aromatics (36 % → 25 %) by EPA
- New demand for MTBE (MeOH and isobuten)
  (same amount as Ethylene)

Olefin Metathesis reaction

1) Metathesis

$2\ CH_2{=}CHCH_3 \rightarrow$ W (Mo, or Re) $\rightarrow CH_2{=}CH_2 + CH_3\text{-}CH{=}CH\text{-}CH_3$

- Phillips Tri-olefin Process *Hydrocarbon Process*, 46, 232, Nov, 1967

- Usually get equilibrium mixture of three olefin

- Driving force for the product → $CH_2{=}CH_2 \uparrow$

2) Economy

- Cheap propylene → Expensive products

- Butene as butadiene feed stock:

  @ difficult to separate from C4 cracking product

3) Mechanism

4) Other applications

① $CH_2=CH_2$ + PhCH=CH-Ph → 2 Ph-$CH_2=CH_2$

- Stilbene to Styrene (Monsanto)

2 Ph-CH_3 → PhCH=CHPh (stilbene, *via Oxidative Coupling*)

② 1,7-Octadiene → Cyclohexne + $CH_2=CH_2$

※ driving force : "formation of cyclohexene" – poor substrate

③ 2 Cyclopentene → 1,5-Cyclodecadiene

n Cyclopentene → Pentenomer (ROM polymerization product)

$-[CH_2CH_2CH_2-CH=CH-]_n$

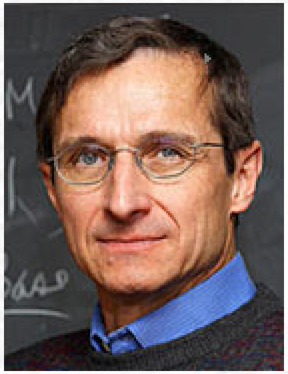
※ Grubbs Catalyst: Ruthenium Complex, Nobel 상 (2005)

2005 Nobel Prize

Chauvin Yves

Institute Francais du Petrole

Organic synthesis for AIDS drug, bio-pesticide, contact lens via metathesis reaction



Richard R. Schrock

Department of Chemistry
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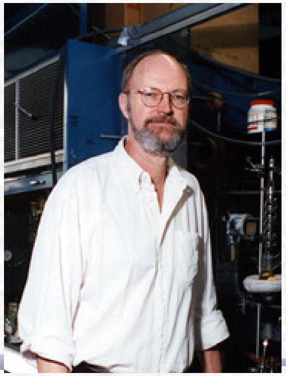
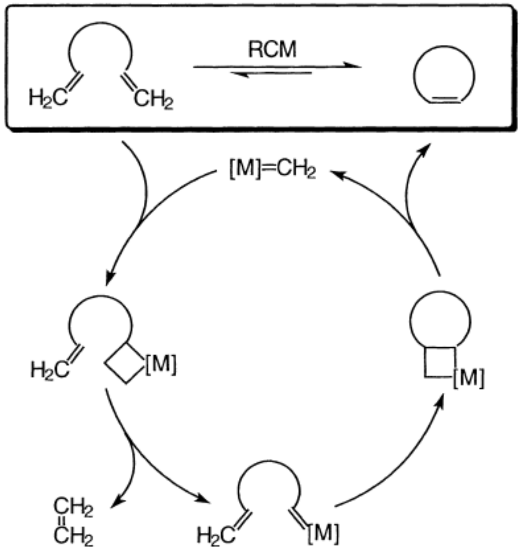


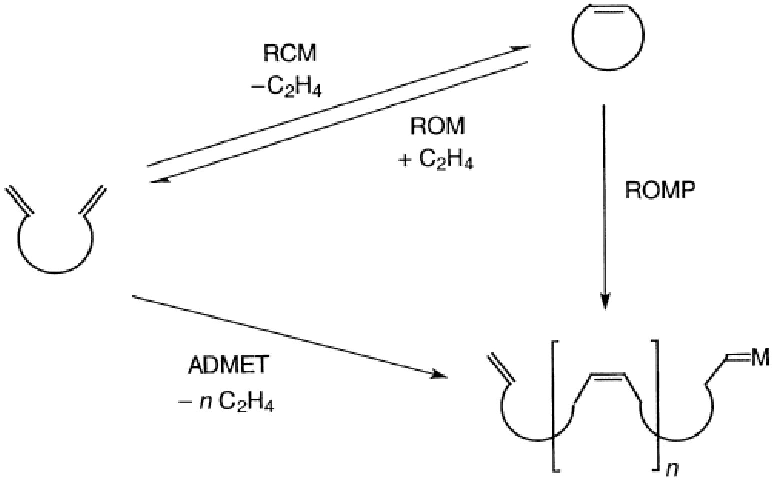
Robert H. Grubbs

Division of Chemistry and Chemical Engineering
California Institute of Technology

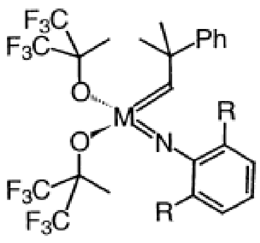
Olefin Metathesis

- **Yves Chauvin (Chauvin mechanism)**





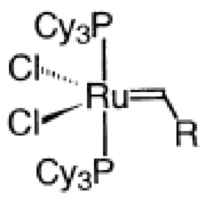
- **Richard R. Schrock**

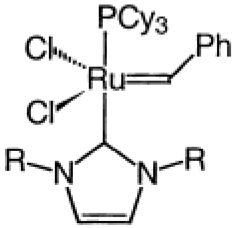


1 (M = Mo, W)

Molybdenum and Tungsten catalyst

- **Robert H. Grubbs**





Ruthenium catalyst

④ pheromone synthesis

$CH_2{=}CHC_8H_{17}$(1-decene) + $CH_2{=}CHC_{13}H_{27}$(1-pentadecene)

→ $CH_2{=}CH_2$ + $C_8H_{17}CH{=}CHC_{13}H_{27}$

- *cis*-compound … housefly pheromone
- simple rxn, but separation difficult

*** Other applications : See 📖 130**

- ethylene + stilbene → styrene
- Ring opening metathesis polymerization (ROMP)
- C4 raffinate (isobutene + 2-butene) →

  → isoprene + propylene
- Ring Closure Metathesis (RCM) → stapled peptide

5) Industrial Application (SHOP)

- Olefin Metathesis reaction : Shell Higher Olefin Process (SHOP)

See 📖 158

① Oligomerization of ethylene

n C_2H_4 → $(C_2H_4)_{n-1}CH=CH_2$: α-olefins (cond: Ni, 100C, 40 atm, EG)

C_4-C_8 41 %

C_{10}-C_{18} 40.5% → separation of C_{10}-C_{18} olefins by distill

C_{20} ~ 18.5%

② Isomerization of others (C_4-C_8 + C_{20} ~) to Internal Olefins

C_4-C_8 (low boiling)

C_{10}-C_{18} (high boiling)

③ Metathesis

$$\mathbf{CH_3\text{-}CH{=}CH\text{-}CH_3 \quad + \; C_{10}H_{21}CH{=}CH\text{-}C_{10}H_{21} \rightarrow 2\, CH_3CH{=}CHC_{10}H_{21}}$$

C_4 C_{22} C_{13}

④ Hydroformylation

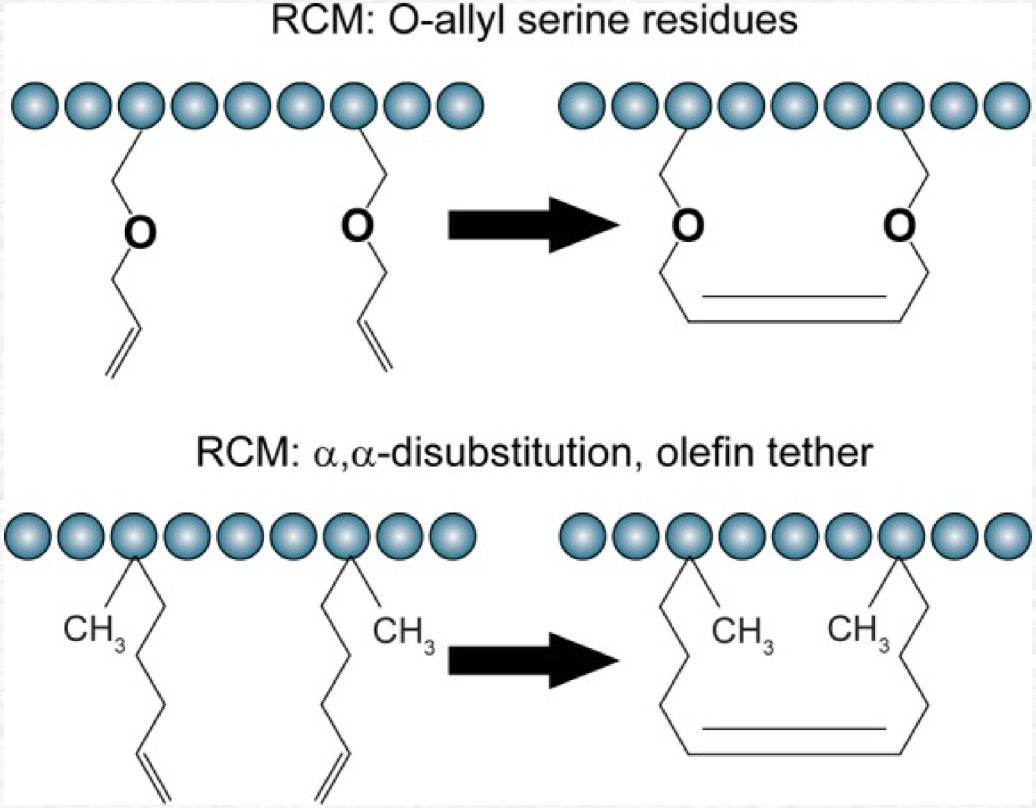
$CH_3CH{=}CHC_{10}H_{21} \rightarrow CH_2{=}CHCH_2C_{10}H_{21} \rightarrow CO/H_2 \rightarrow$

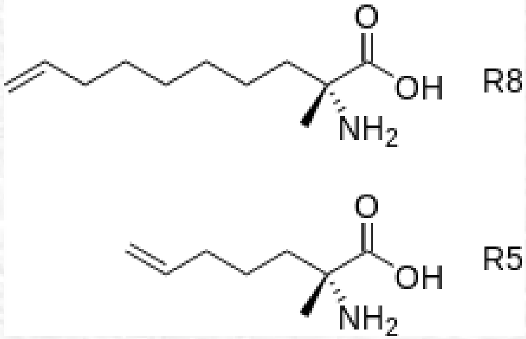
$HCOCH_2CH_2CH_2C_{10}H_{21} \rightarrow HO(CH_2)_{14}H$ (OXO alcohols)

< Block Diagram for SHOP>

※ **Linear alcohol :** Used for biodegradable detergent

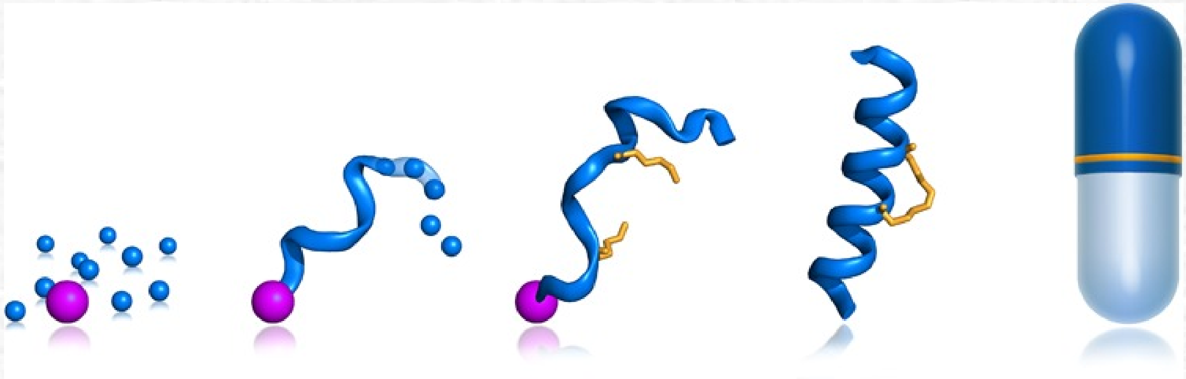
Stapled Peptides by RCM

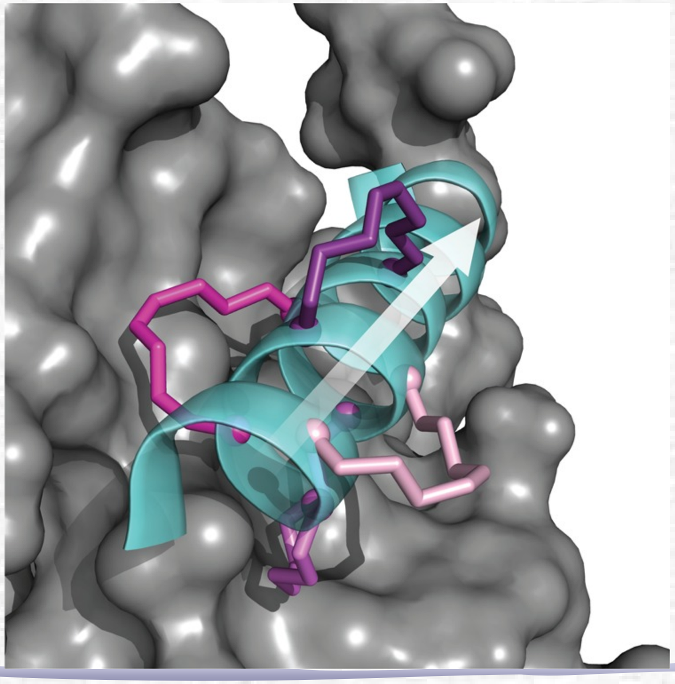


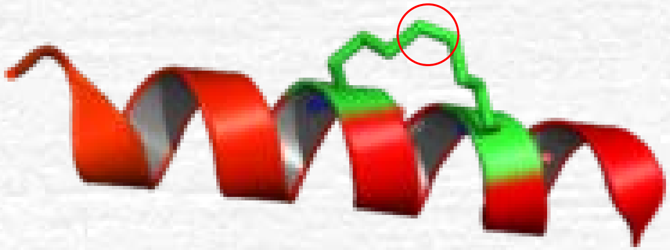


J Med Chem. 2014 Aug 14; 57(15): 6275–6288.

Protein-Protein Interaction for drug development







J Med Chem. 2014 Aug 14; 57(15): 6275–6288.

Petrochemicals

A. Top Chemicals

1) Top 12 Chemicals

- Sulfuric Acid
- Lime (CaO)
- Ammonia
- Oxygen
- Ethylene
- Nitrogen
- Chlorine

1) Top 29 Organic Chemicals

(1) C2-Chemicals: Ethylene, EO, EG, AcOH, EtOH, EDC, EB, VCM

(2) C3-Chemicals: Propylene, Acetone, *i*-Propanol, PO, AN, Cummen, Phenol

(3) C4-Chemicals: Butadiene

(4) BTX : Benzene, EB, ST, CH, Phenol, Acetone, Adipic acid, Cummen
Toluene
Mixed Xylene, TPA, *p*-Xylene

(5) C1-Chemicals: Methane, Methanol, Urea, Formaldehyde, AcOH

B. Petrochemical Process Economy

1) Petrochemical Process 🕮 103

Natural Gas
Refiner Gas
*Gas oil
↓
Cracking
↓
C_2 : $CH_2=CH_2$
C_3 : $CH_2CH=CH_2$
C_4 : butylenes

* Naphtha → Gasoline (USA)
straight run gasoline → Gasoline (USA)
↙ ↓
↙ Catal Reforming
↙
↓
B.T.X → → → Gasoline (USA)

*(JAPN, EU, Korea)

-

2) Source of Ethylene 📖 110

Coproduct yield per 100Kg Ethylene

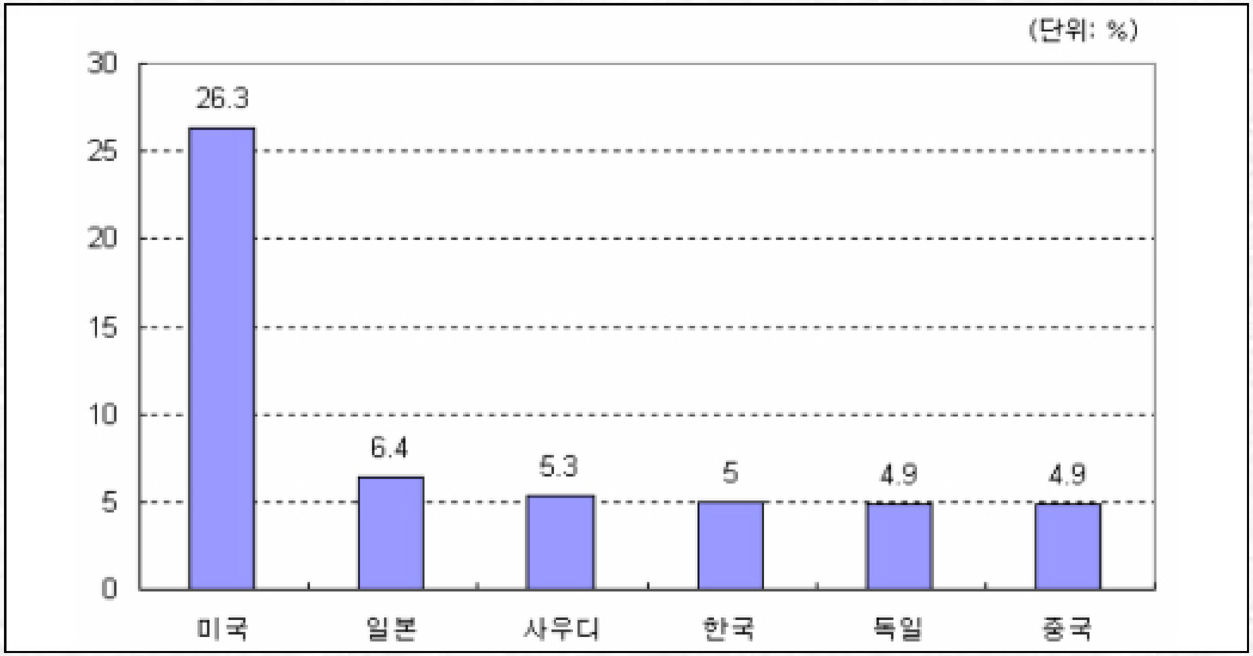
		<Feed Required>
Ethane	**80%**	**120**
Propane	**42%**	**240**
Butane	**38%**	**250**
Naphtha	**31%**	**320**
G.O	**26%**	**380**
vac. G.O	**23%**	**430**

3) Value of Oil

Crude : Fuel : Petrochemical : Consumer Product

Value 1 : 2 x : 13 x : 55 x

WW Ethylene Production



2012, 840 M TON

C. Ethylene

1) Production

-Thermal Cracking ·· Ethane / Propane (USA)
·· Naptha (EU, Jpn, Korea)

- Tubular furnace : NCC
※ Intial Temp : 750-930℃, then cooled to 300-400℃ in <1sec

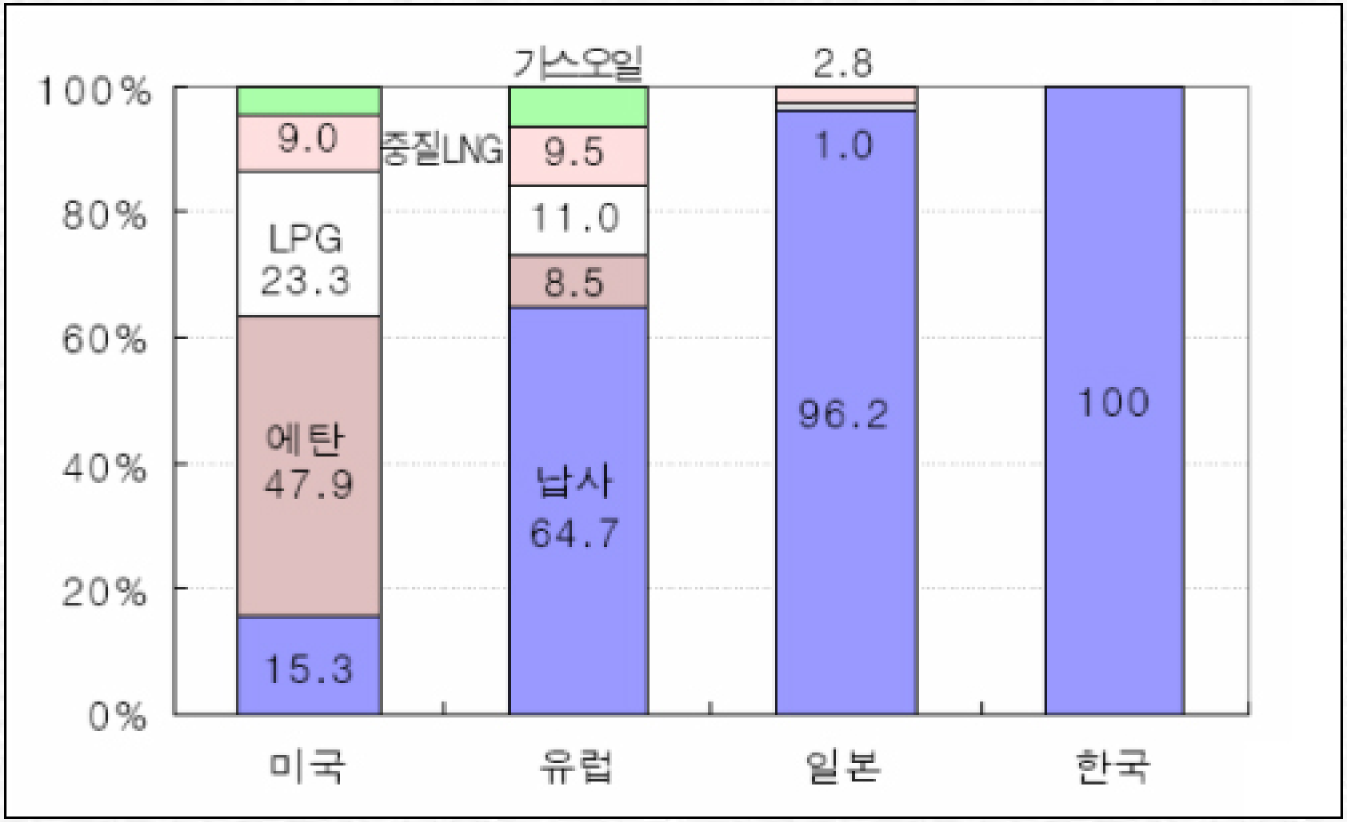
- **Ethane-based plant**
  - Simple separation sections, require high Temp

- **Naphtha-based plant**
  - Complex separation, require multiple distillation columns
  - Low Temp OK, and Flexible to the market

2) Product Distributions

	Feed	Ethylene	Propylene	Butadiene	BTX	Others
	C2	84	1.4	1.4	0.4	12.8
	C3	44	15.6	3.4		34
(Severe)	Naptha	31.7	13.0	4.7	13.7	36
(Mild)	“	25.8	16.0	4.5	10	43
	GO	28.3	13.5	4.8	10.9	42
	Crude	32.8	4.4	3.0	14.4	45

Feed for Ethylene Production



3) Mech of Ethane Cracking

〈Free Radical Rxn〉

(1) Initiation

CH_3-CH_3 → CH_3. + CH_3. (fast) homolysis △H 90Kcal

CH_3CH_2 -H → CH_3CH_2. + H. (slow) △H 100Kcal

(∵) stronger C-H bond

CH_3. + CH_3CH_2 -H → CH_3CH_2. + CH_4

(2) Propagation

CH_3CH_2. → CH_2=CH_2 + H.

H. + CH_3CH_2 -H → CH_3CH_2. + H_2

(3) Termination

$2\ CH_3CH_2\cdot \rightarrow C_4$ (Higher HC's)

$CH_3CH_2\cdot + H\cdot \rightarrow CH_3CH_3$

- Side Reactions

$CH_3CH_2\cdot + CH_2{=}CH_2 \rightarrow CH_3CH_2{-}CH_2CH_2\cdot$

$\rightarrow CH_3CH_2CH{=}CH_2 + CH_3CH_2CH_2CH_3$ (*via* +H. or - H.)

4) Mech of propane cracking : Complicate

- $CH_3CH_2CH_3 \rightarrow .CH_3 + .CH_2CH_3$

$CH_3CH_2. \rightarrow CH_2{=}CH_2 + H.$

Statistically
↙

$$\begin{array}{llllll} & CH_3. & & CH_3CH_2CH_2. & & CH_4 \\ CH_3CH_2CH_3 + & CH_3CH_2. & \rightarrow & CH_3CH.\,CH_3 & + & C_2H_4 \\ & H. & & \nearrow & & H_2 \end{array}$$

Energetically

- β-Scission

terminal FR : $CH_3{—}CH_2CH_2. \rightarrow CH_2{=}CH_2 + .CH_3$

internal FR : $CH_3{—}CH.\,CH_2{—}H \rightarrow CH_3CH{=}CH_2 + H.$

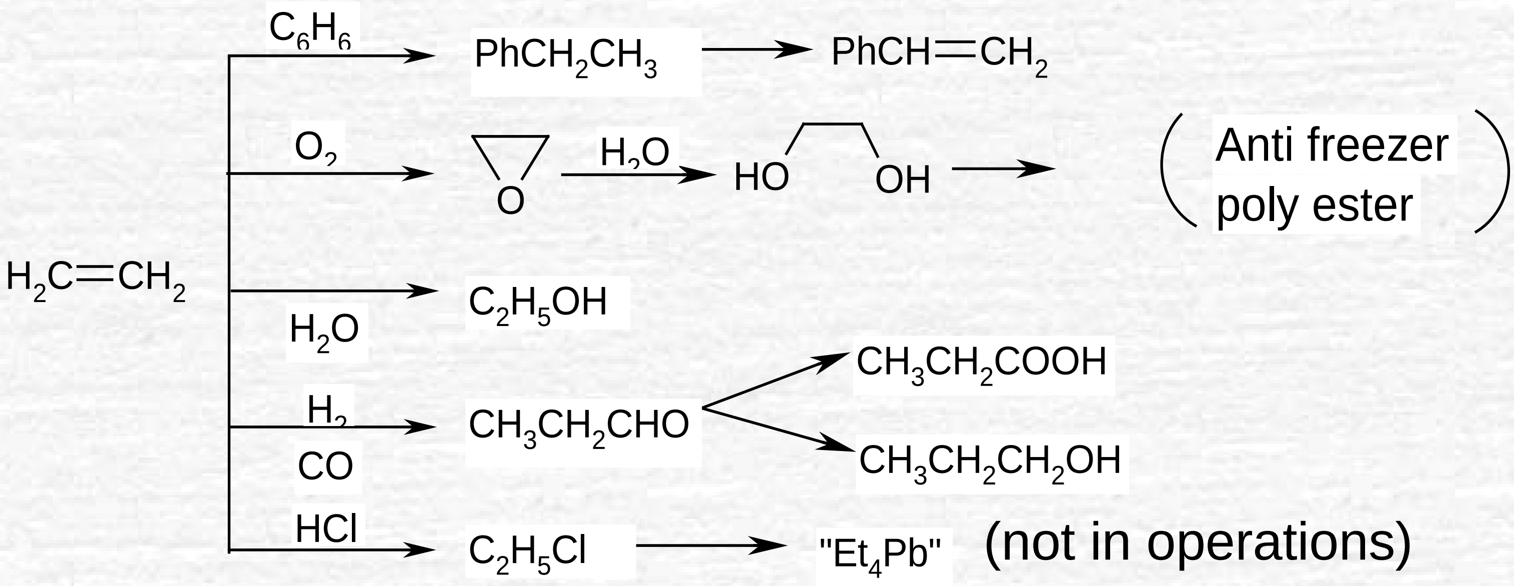
propylene is formed

-Termination : higher carbon number 생산(by-prod)

Major Chemicals from Ethylene

A. Chemistry of Ethylene 📖 **141** (different classification)

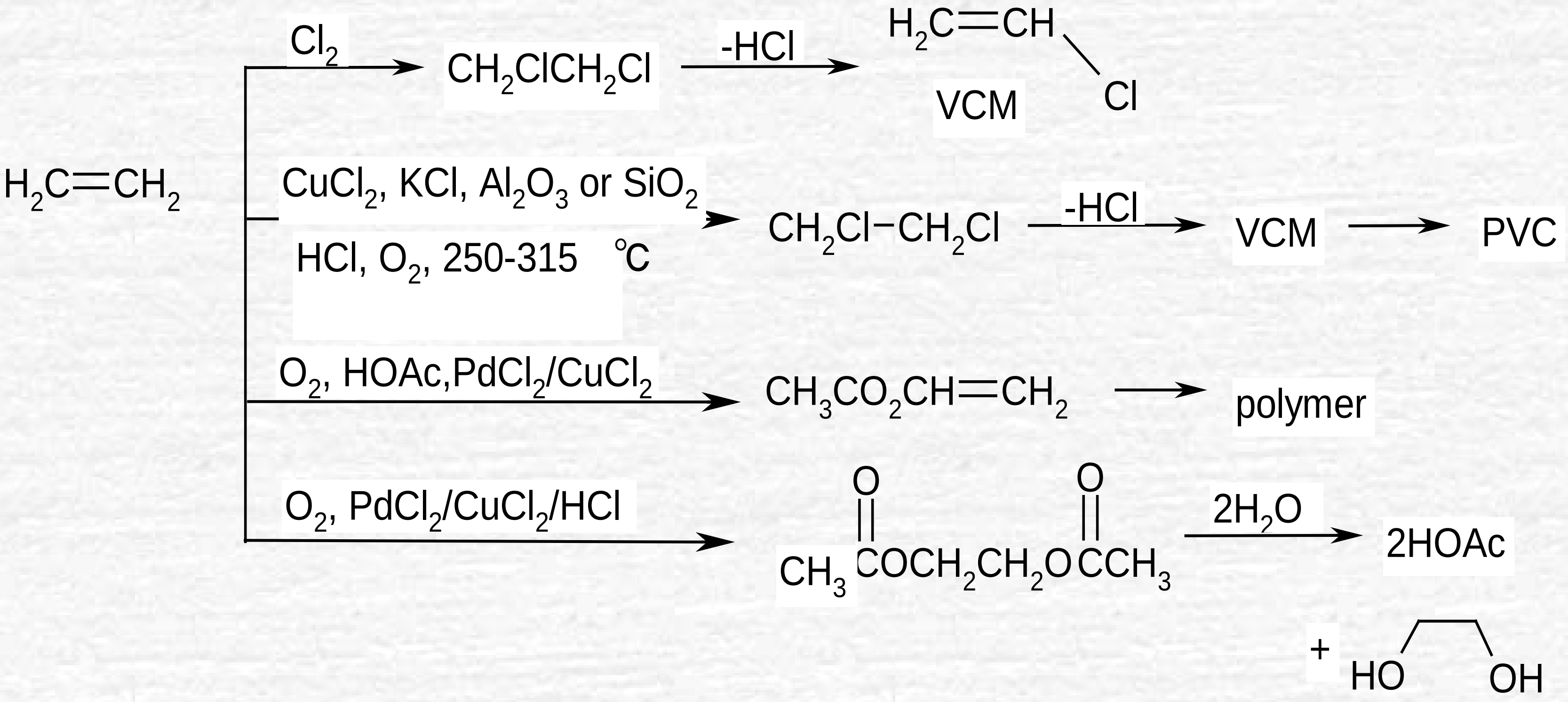
① “Classical" Reactions



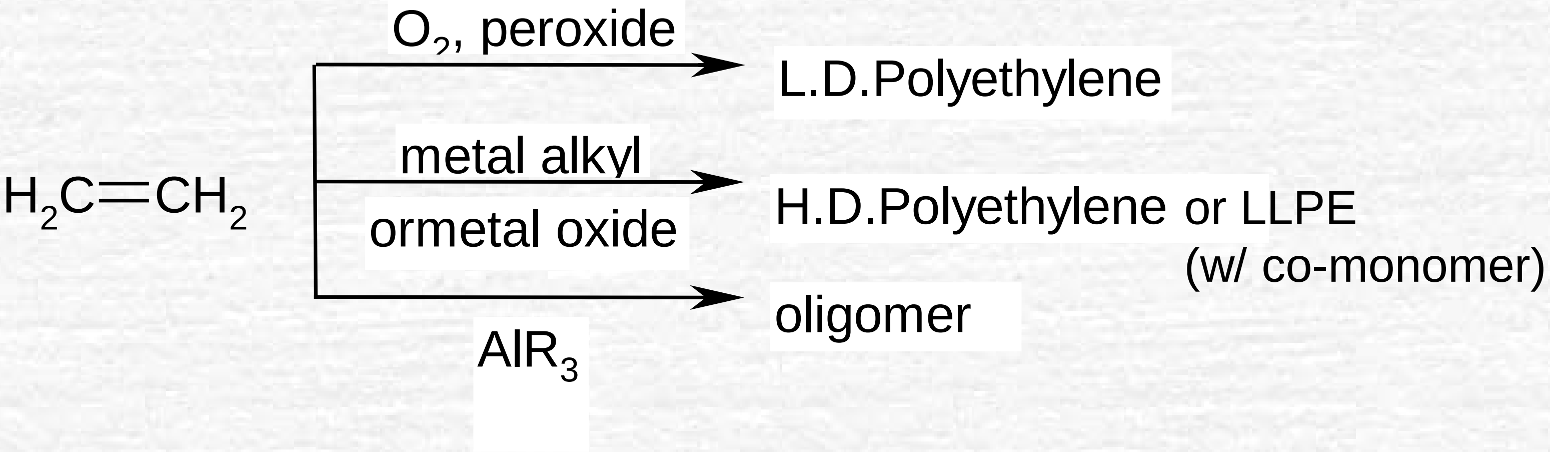
(Anti freezer
poly ester) [Oxidation]

(not in operations)

② Replacement of one or more Ethylene → Oxidation



③ Polymerization and Oligomerization

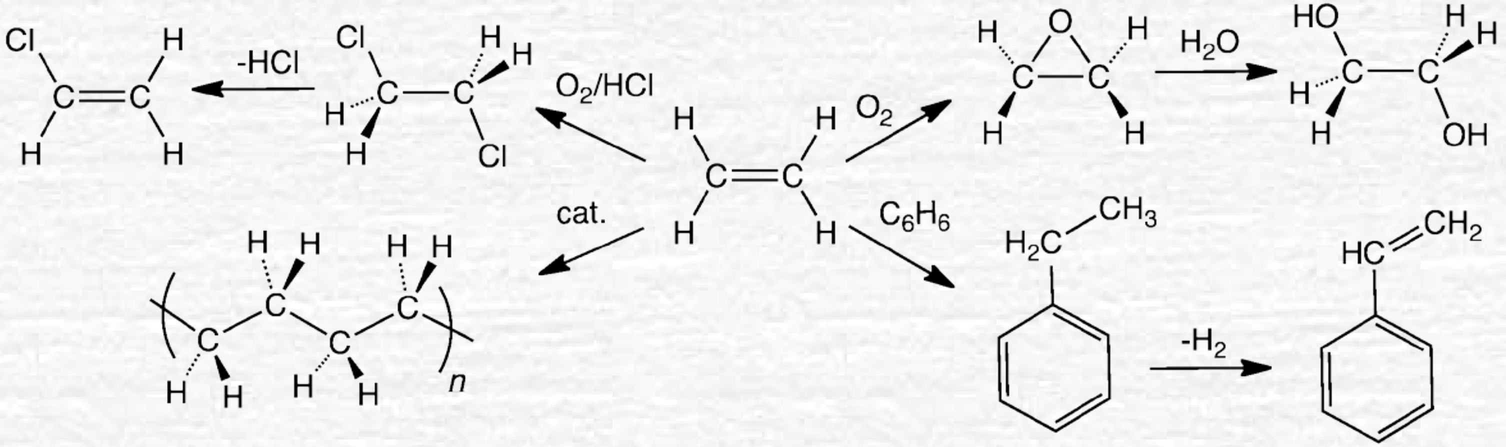


$H_2C{=}CH_2$

$\xrightarrow{O_2\text{, peroxide}}$ L.D.Polyethylene

$\xrightarrow[\text{ormetal oxide}]{\text{metal alkyl}}$ H.D.Polyethylene or LLPE (w/ co-monomer)

$\xrightarrow[AlR_3]{}$ oligomer



B. Importance of Ethylene

- 12 M TON → 50 M TON Chemicals (1977)

  20M TON (1980) → ??

- USA(2,900), Jp(700), Saudi(600), Kr(570), DE(540) (1990~)
- Total production : 1.2 B TON including EU+USA (60 M TON) (2008)
- 60% of Ethylene are used for Polymer Production (1999)

	(EU)	(USA)
LDPE/HDPE	56%	50 %
VCM	14%	11 %
EO +	10%	12 %
Acetaldehyde +	2%	0.5%
EB/ST	7%	6 %

ETHYLENE FACTS

Ethylene is a natural plant hormone. It affects the growth, development, ripening, and aging of all plants. It is normally produced in small quantities by most fruits and vegetables. Many fruits produce larger quantities of ethylene and respond with uniform ripening when exposed to an external source of ethylene.

C. Chemicals from Ethylene

1) Vinyl Chloride

(1) Production

① Acetylene-based 1930~1960`s

$HC{\equiv}CH + HCl \rightarrow CH_2{=}CH\text{-}Cl$ $\triangle H$ (exotherm, no heat supply)

- Side Rxn : $CH_2{=}CHCl + HCl \rightarrow CH_3CHCl_2$
- HCl : can be obtained from chlorination of HC
- economy : acetylene, expensive raw material

② Ethylen-based : Direct chlorination (1940-)

$$CH_2{=}CH_2 + Cl_2 \rightarrow CH_2Cl\text{-}CH_2Cl \rightarrow \triangle \rightarrow CH_2{=}CHCl + HCl$$

- **Mechanism: pyrolysis of dichloroethane**

Initiation : $CH_2ClCH_2Cl \rightarrow CH_2ClCH_2\bullet + Cl\bullet$

Propagation : $Cl\bullet + CH_2ClCH_2Cl \rightarrow CH_2ClCH(Cl)\bullet + HCl$

$CH_2ClCH(Cl)\bullet \rightarrow CH_2{=}CHCl + Cl\bullet$ (chain rxn)

Termination : $Cl\bullet + \bullet CH_2CH_2Cl \rightarrow CH_2{=}CHCl + HCl$

- Side rxn :

$$CH_2{=}CHCl \rightarrow CH{\equiv}CH + HCl$$

(∴) op. in low conversion < 50%

- Economy

- **Cl_2 (expensive raw material) → HCl (cheap by-product)**
- **until 1960`s co-operated with "acethylene-based process " : why?**
- **Economy of HCl ∝ Environmental problem**

HCl value : "0.0 $" if no outlet

"- $" if disposal problem

HCl(gas) : hard to mass transpot

HCl(l) : saturated market → ($\therefore$) need for consumption site near by

③ Ethylen-based : "Oxychlorination Process"

- **Ethylene based w/ HCl** (Du Pont)

$CH_2=CH_2 + 2HCl + O_2 \rightarrow CH_2ClCH_2Cl \rightarrow CH_2=CHCl + HCl$

- **History : Oxidation of Cl^-** (Deacon, 1858)

$2HCl \rightarrow [O_2, CuCl_2, 450] \rightarrow Cl_2 + H_2O$

*bricks@copper chloride : 1st heterogeneous catalyst

- Characteristics:

HCl (by product) can be utilized in process

eg) TDI/MDI process poduces 4 HCl/TDI or MDI

. “USA” : 1/2 of CH_2ClCH_2Cl produced by "Oxychlorination"

. Recent trends:

Combination of “Direct Chlorination” + "Oxychlorination"

- Mechanism :

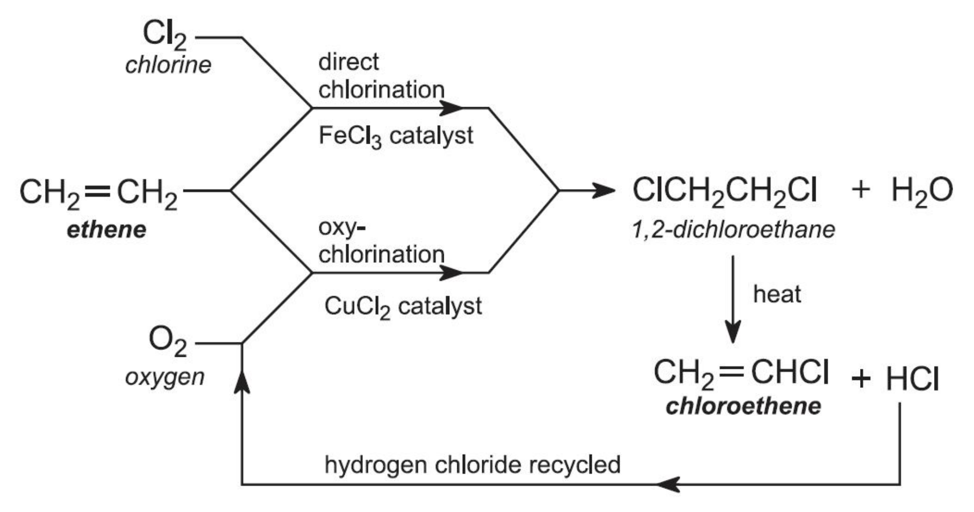
$CH_2{=}CH_2 \rightarrow CH_2ClCH_2Cl \rightarrow CH_2{=}CHCl + HCl$

$CH_2{=}CH_2 + 2CuCl_2 \rightarrow CH_2ClCH_2Cl + Cu_2Cl_2$ (*via* Cu^{+2} mediate oxidation)

$Cu_2Cl_2 + 1/2\ O_2 + 2HCl \rightarrow 2CuCl_2 + H_2O$

- Two kinds of processes

(depending on HCl source)



- Application : Cheap raw material for Polymer (PVC and copolymer ...)

* Environmental problem? (VCM Gas → ozone depletion)

* When PVC get fired → fume gas contains HCl gas → Fire retardant needed

2) Acetaldehyde

- important source of n-butanol, acetic acid (past)

(1) Production

① Hydration of Acetylene

$CH{\equiv}CH + H_2O \rightarrow CH_3CHO$

- Mech? : 50% conversion, 95% yield
- appeared once in Text Book process, never operated in full scale

② Oxidation of Ethyl Alcohol (Dehydration of Ethanol)

. Ethanol became cheaper than acetylene (~1960)

$$C_2H_5OH(g) + 1/2\ O_{2(9)} \ + \ \text{catal} \ \rightarrow \ CH_3CHO(g) + H_2O(g) \quad \triangle H = -43\text{kcal}$$

-Ethanol source :

- . Fermentation of starch/bio mass → Ethanol → Gasohol (Bio fuel, Biomass)
- . Hydration of ethylene

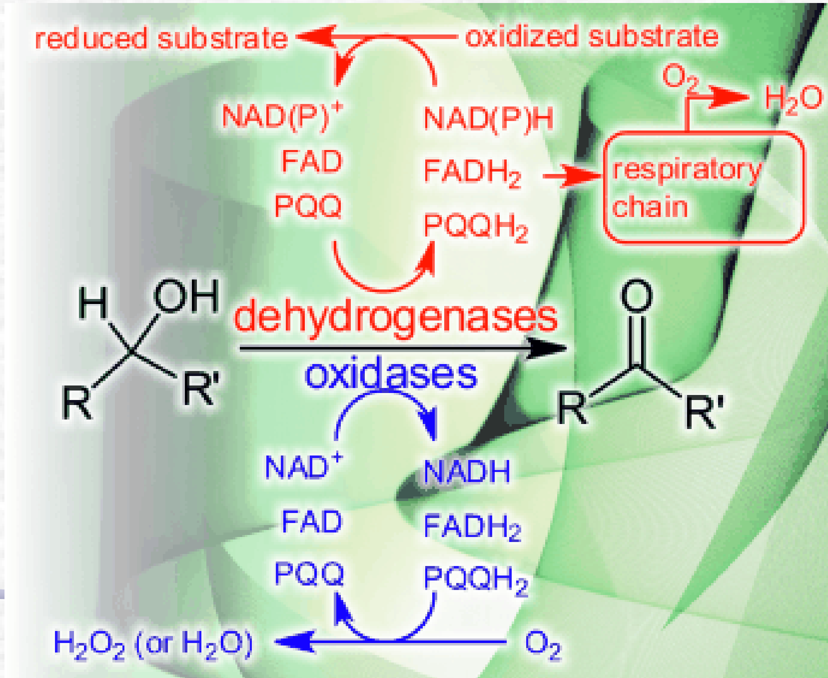
- Catalyst :

AD enzyme removes EtOH in body by oxidation

Ag : oxidation - dehydration

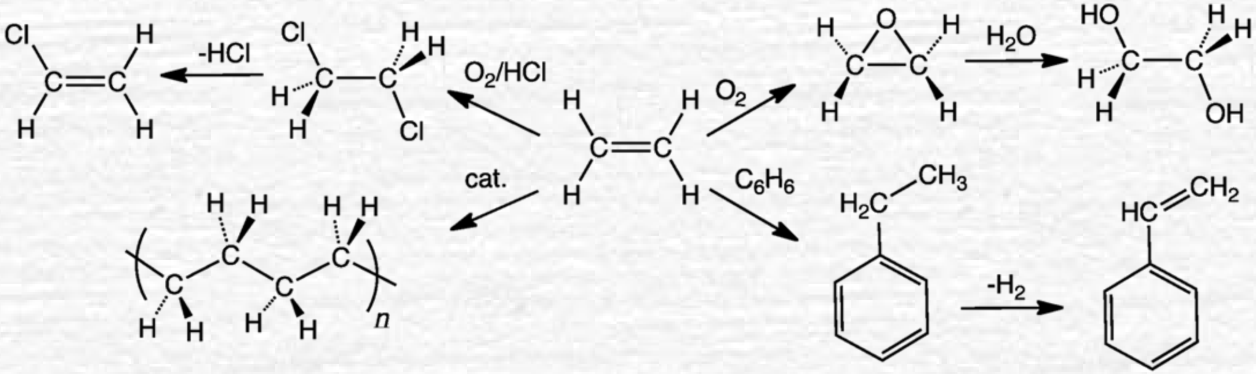
Cu/CrO_3 : promotor, dehydration, 260-290°

- 15% production in USA (1974), 현 : 전무



※ Oxidation State of Carbon/Nitrogen

- Ethane : CH_3-CH_3
- Chloroethane :
- Dichloroethane :
- Trichlorethane :
- CO_2



- NH_3 → NO_2 → NO_3 → HNO_3

③ Wacker Process (Direct oxidation of ethylene)

$CH_2{=}CH_2 + PdCl_2 + H_2O \rightarrow CH_3CHO + Pd[0] + 2HCl$

$Pd[0] + 2HCl + 1/2\ O_2 \rightarrow PdCl_2 + H_2O$

"$CH_2{=}CH_2 + O_2$: bubbling thru acidic catalyst"

- Conversion and yield are both ~95%
- Accidental finding → Technological process

. 1950`s Wacker Chemie

“$CH_2{=}CH_2 + Pd/C + O_2 \rightarrow CH_2(O)CH_2$” (N.R)

sometimes, smells “aldehyde” (?) found from batches using impure Pd(?)

→ Contains “$PdCl_2$” impurity in Pd/C catalyst

. Preparation process of Pd/C

$PdCl_2$ Soln + Charcoal → [reduction] → Pd/C

※ When Reduction is not complete : small amount of $PdCl_2$ exist

. Literature survey : (1894)

$CH_2{=}CH_2 + PdCl_2 + H_2O \rightarrow CH_3CHO + Pd + 2HCl$ (high yield)

※ Difficult in large scale commercial process because …

- Pd, expensive material as Pt
- Used as reagent, not as catalyst

. Engineering R & D → process for Pd recycling

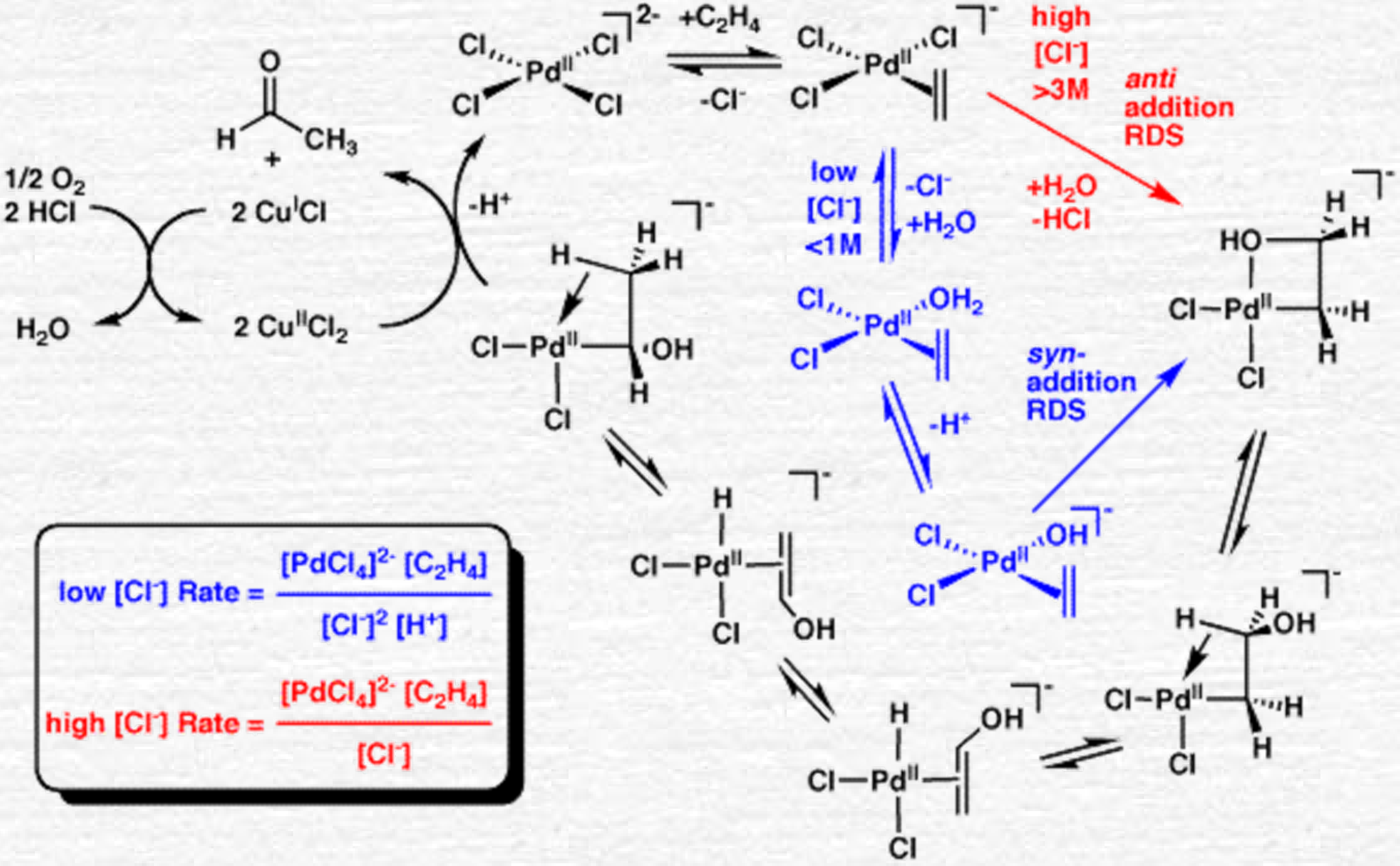
$Pd[0] + 2CuCl_2 \rightarrow PdCl_2 + Cu_2Cl_2$

$Cu_2Cl_2 + 2HCl + 1/2\ O_2 \rightarrow 2CuCl_2 + H_2O$ (fast)

※ **Mechanism** : 🕮 166

∏ -bonded complex + oxidative addition + reductive elimination

"One of industrial process, the catalyst role is understood"



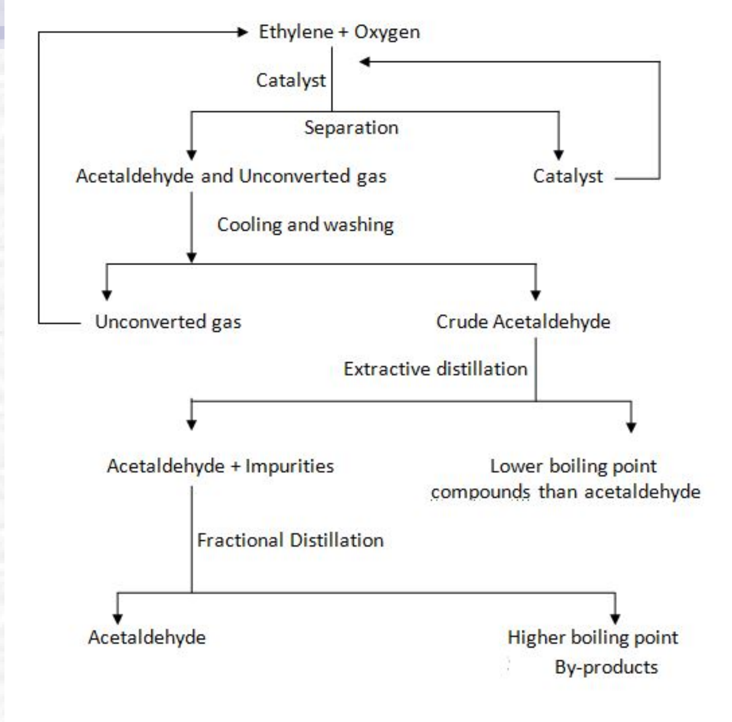
$$\text{low } [Cl^-] \text{ Rate} = \frac{[PdCl_4]^{2-}\,[C_2H_4]}{[Cl^-]^2\,[H^+]}$$

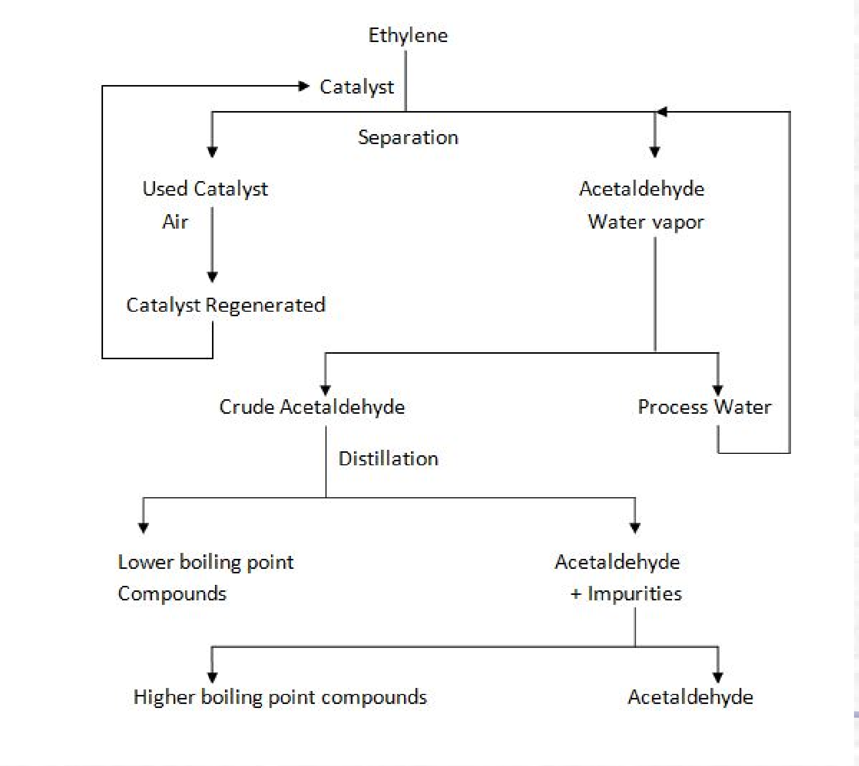
$$\text{high } [Cl^-] \text{ Rate} = \frac{[PdCl_4]^{2-}\,[C_2H_4]}{[Cl^-]}$$

Two Processes

<single-stage process>

- excess C2 used → need recycling
- 99% O_2 used
  → need separate O_2 plant





<two-stage process>

- oxidation in separate process
  → air can be used
- No recylcing of C2
  → C2 mixture can be used.

※ Overall costs : very similar

<one-stage process>

- Excess Ethylene → recycling required (need pure feed)
- If air is used , N_2 should be separated before recycling
- low temp distillation or solvent extraction for product recovery
- If O_2 is used to avoid there problems → “need oxygen plant”

<two-stage process>

- Oxidation in separate process → air can be used
- No recycling of Ethylene → (Ethane + Ethylene) mixture can be used
- Catalyst solution is circulating (acidic), corrosive → need special reactor

  “rubber-lined reactor” "titanium pipe, pump"

④ Oxidation of Naptha (propane or butane or lower paraffins)

C_4H_{10} → CH_3CHO + CO + CO_2

$HCHO$

CH_3COOH

CH_3OH

Mechanism

- FR oxidation (gas phase)
- less selective → higher separation cost: requires special distillation

- Mixtures of products *vs.* Simple operation

Cheap raw material but expensive separation

- 15-20% of HC is oxidized to CO, CO_2 → waste of C resources

※ **CO_2 = money !! (Tokyo protocol 2002.11, 2013-17 CO_2 emmision should be reduced)**

(2) Application & Economy

① Acetic acid production

$CH_3CHO \rightarrow CH_3COOH \rightarrow Ac_2O$

- Strong competition w/ " Oxidation of Butane or Naphtha",
"Carbonylation of MeOH"

② n-Butanol production : important solvent

$2CH_3CHO \rightarrow CH_3CH{=}CHCHO \rightarrow CH_3CHCH_2CHO$

$\rightarrow [H_2] \rightarrow CH_3CH_2CH_2CH_2OH$

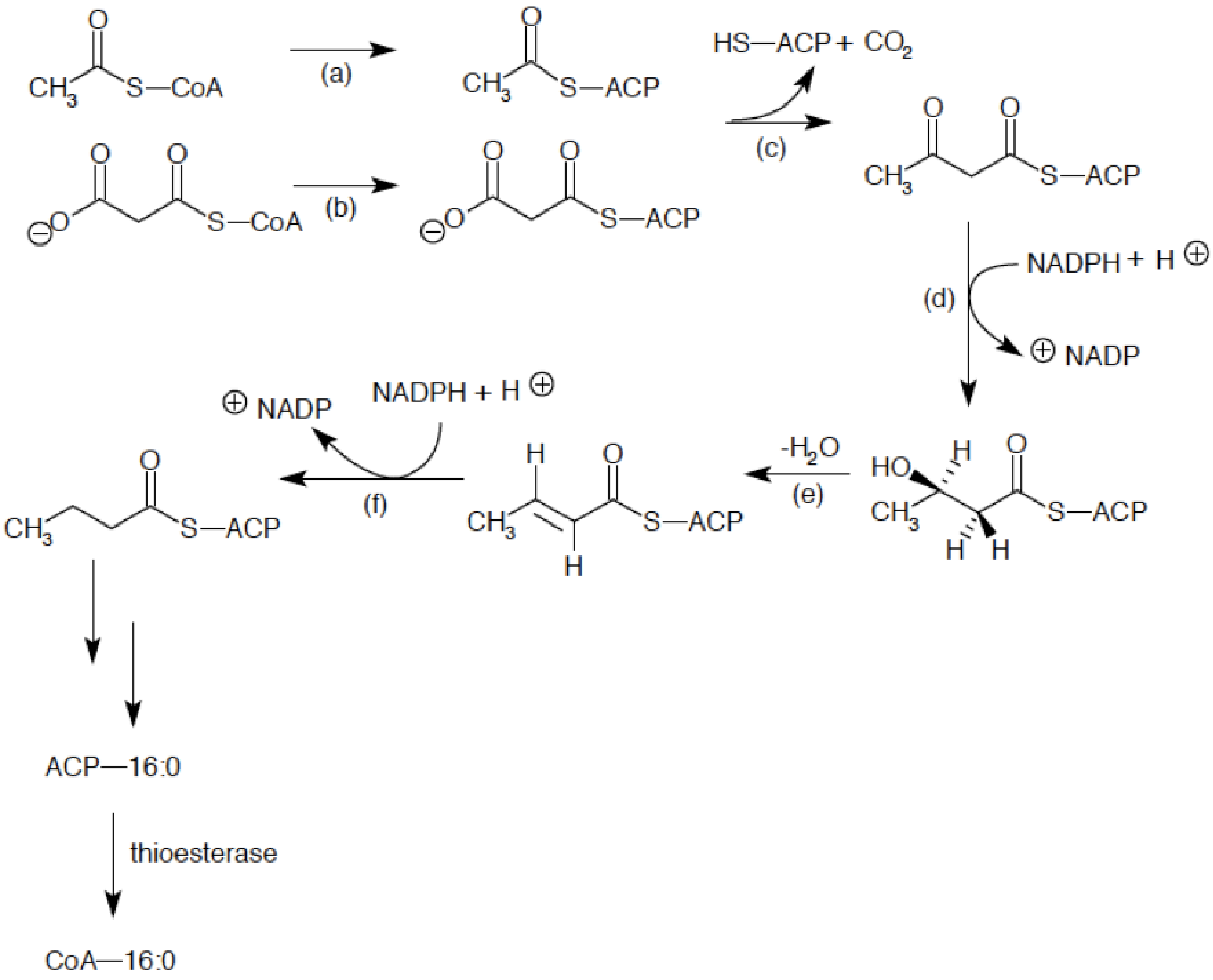
- MMA ester (monomer), phthalate (plasticizer, DEHP or DOP)

$CH_3CH{=}CHCHO \rightarrow CH_3CH_2CH_2CHO \rightarrow$ EH:2-ethylhexanol

→ DOP(plasticizer for PVC plastics)

※Synthetic method for long carbon chain

※ Natural method : Biosynthesis of fatty acids (Name Rxn?)


(a)
(b)
(c)
HS—ACP + CO2
(d)
NADPH + H ⊕
⊕ NADP
(e)
-H2O
(f)
NADPH + H ⊕
⊕ NADP
S—CoA
S—ACP
ACP—16:0
thioesterase
CoA—16:0

- No more by this route (from acetaldehyde)
- "OXO" process (Hydroformylation) 로 n-Butanol 제조

$$\text{"}CH_2{=}CHCH_3 + CO + H_2\text{"} \rightarrow CH_3CH_2CH_2CHO$$

③ 기타

$$CH_3CHO + Cl_2 \rightarrow Cl_3CHO \text{ (chloral)} \rightarrow \text{[chlorobenzne]} \rightarrow \text{DDT}$$

$$CH_3CHO + 4HCHO \rightarrow HOCH_2C(CH_2OH)_3 + HCOOH$$ (Mech?)

pentaerythritol

* SM of Alkyd Resin, Riqid PU form

* Nitration → Pentin (tetranitrate)

④ Production Drugs

3) Vinyl Acetate $CH_2=CH-O-C(O)CH_3$

(1) Production :

① Acetylene-Based ~ 1967

$CH≡CH + CH_3CO_2H +$ Catalyst $(Zn(OAc)_2\text{-}C)$ → $CH_2=CH-O_2CH_3$

- USA : only 10% by this way (1975)

- UK : closed at 1972

② Ethylene-Based

Modified "Wacker Process" : HOAc used instead of (H_2O, HCl)

$$CH_2=CH_2 + 2\ CH_3CO_2Na + \text{catal} \rightarrow CH_2=CHO_2CCH_3 + H_2O + NaCl + Pd + CH_3CO_2H$$

- Acetaldehyde production : if by-product water is used

- By adjusting H_2O → Acetaldehyde can be also produced

"Two" for "One" Process

(2) Application:

- Adhesives
- Emulsion Paints (Latex for Coatings)
- Polyvinyl alcohol (PVA) after saponification

  Fiber (U High MW, Jpn) : PVA -*co*-formaldehyde (Vinylon fibers)
- PVA + butyraldehyde → Poly(vinyl butyral) : for safety glass film

(4) Production capacity :

- Samsung BP : 150,000 TON (1996, 10)
- World Wide : 33M TON (96)

4) Acetic acid

(1) Production

① Oxydation of Acetaldehyde

$CH_3CHO + O_2 \rightarrow CH_3COOH$

- One of the major route for HOAc, AC_2O but declining.

- Mechanism : liquid phase, FR Mech

initiation :

$CH_3COH + X\bullet \rightarrow CH_3CO\bullet + HX$

$CH_3CO\bullet + O_2 \rightarrow CH_3COOO\bullet$

< •O-O• : triplet ground state, biradical>

$CH_3COH + CH_3COOO\bullet \rightarrow CH_3CO\bullet + CH_3COOOH$

peracetic acid

propagation

$CH_3COOOH \rightarrow CH_3COO\bullet + \bullet OH$

$CH_3COH + CH_3COO\bullet \rightarrow CH_3COOH + CH_3CO\bullet$

<main route>

$CH_3COH + CH_3COOOH \rightarrow$ a-hydroxyethyl peracetate

→ 2 CH_3COOH

② **Oxidation of Naphtha (or Butane)**

$C_4H_5 \rightarrow \triangle \rightarrow CH_3CO_2H + \text{Others} + CO_2 + CO + H_2O$

(Ca 50% yield, in theory)

- Mechanism : (liquid phase / air oxidation) F.R. mech

i) $CH_3CH_2CH_2CH_3 + X\bullet \rightarrow CH_3CH_2CH\bullet\text{-}CH_3 + HX$

$CH_3CH_2CH\bullet\text{-}CH_3 + O_2 \rightarrow CH_3CH_2CH(OO\bullet)CH_3$

$CH_3CH_2CH(OO\bullet)CH_3 + C_4 \rightarrow CH_3CH_2CH(OOH)CH_3 + C_4\bullet$

$CH_3CH_2CH(OOH)CH_3 + Co\bullet^{+2} \rightarrow CH_3CH_2CH(O\bullet)CH_3 + -OH + Co^{+3}$

$CH_3CH_2CH(O\bullet)CH_3 \rightarrow CH_3CH_2\bullet + HC(O)CH_3$

↳ CH_3COOH

ii) $CH_3CH_2\bullet + O_2 \rightarrow CH_3CH_2OO\bullet \rightarrow C_4 \rightarrow CH_3CH_2OOH + C_4\bullet$

$CH_3CH_2OOH + Co^{+2} \rightarrow CH_3CH_2O\bullet + -OH + Co^{+3}$

$CH_3CH_2O\bullet + X\bullet \rightarrow CH_3COH + HX$

↳ CH_3COH

- Raw Materials :

USA : Butane as SM: simple procedure (from CH_3COH, 45% production)

EU : light Naphtha (C_4-C_5) as SM: more complex, get mixture of products (formic, propionic, succinic...), higher cost for purification

③ Carbonylation of Methanol (by Monsanto) – C1 chemistry

$CH_3OH + CO \rightarrow [I_2\text{-}Rh] \rightarrow CH_3COOH$

- Dramatic new process : applied in many new plant
- Major cause of drop of acetaldehyde production
- High yield : ~99% based on CH_3OH, ~90% based on CO
- High purity : energy savings/avoiding extensive separation
- Cheap raw material: CH_3OH from syn gas (from Natural gas)

$CH_4 + H_2O \rightarrow CO + 3H_2$ $CO/H_2 = 1:3$

* ($CO_2 + H_2 \rightarrow CO + H_2O$) reverse shift rxn for adjusting CO/H_2

$CO + 2H_2 \rightarrow CH_3OH$ $CO/H_2 = 1:2$ $\triangle H = -22\text{kcal}$

※ CO can be also obtained from coal, can reduce oil dependency

(2) Application - various acetate

i) Cellulose acetate for film, package, molding ii) Vinyl acetate for polymer

5) Acetic Anhydride

(1) Production

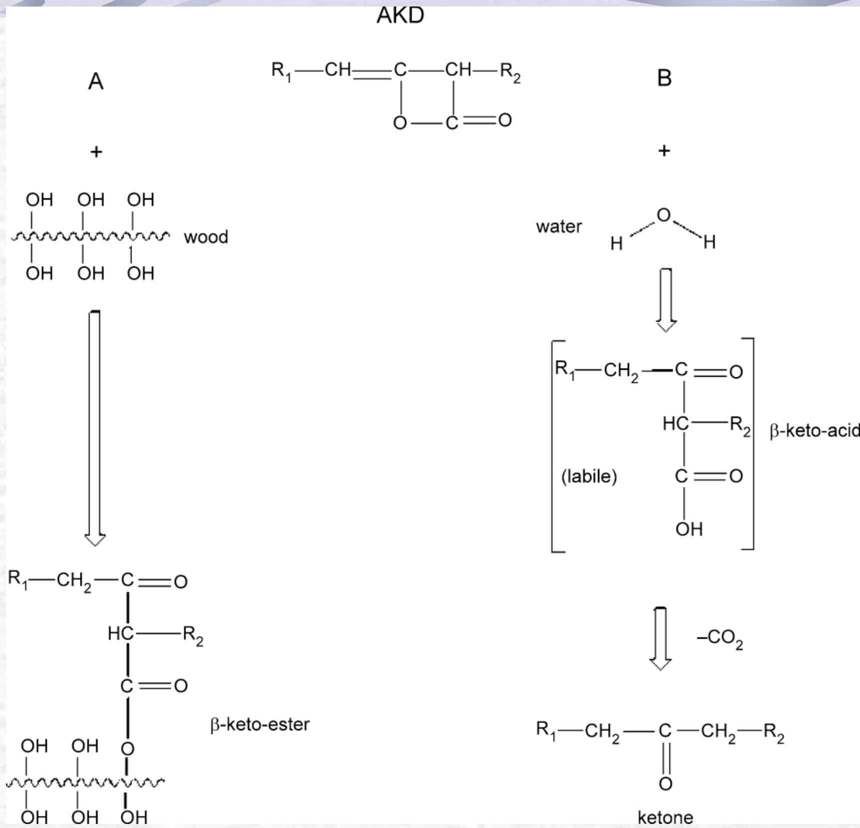
① **from acetic acid** thru Keten

$CH_3COOH \rightarrow CH_2{=}C{=}O + H_2O$

$CH_2{=}C{=}O + CH_3COOH \rightarrow Ac_2O$

- uneconomical process

※ Alkyl Ketene Dimer (AKD) for sizing agent in paper mill



② ***in situ* production from Acetaldehyde** w/modified oxidation

$CH_3CHO + O_2 \rightarrow CH_3CO\bullet \rightarrow CH_3CO+$

$+ HOAc \rightarrow Ac_2O + H_2O$

(2) 용도 :

- various acetate (esp: cellulose acetate), aspirin

6) Ethylene Oxide (EO)

- Most important C_2 chemical (except polymer product)

(1) Production

① Chlorohydrin process

$CH_2{=}CH_2 + Cl_2 + H_2O \rightarrow HOCH_2CH_2Cl + HCl$

$2HOCH_2CH_2Cl + Ca(OH)_2$ (Lime) $\rightarrow 2\ CH_2(O)CH_2 + CaCl_2 + 2H_2O$

- Mechanism :

$Cl_2 + H_2O \rightarrow HO^- Cl^+$ (hypochlorous acid) $+ HCl$

$CH_2(Cl+)CH_2 + HO^- \rightarrow HOCH_2CH_2Cl \rightarrow 2\ CH_2(O)CH_2$

- Lime, cheapest industrial inorganic base.
- Ammonia, cheapest industrial organic base

- EO selectivity (yield) : 80% (75% of cost from Ethylene → yield is important!)

- Cl_2 → $CaCl_2$ 300-350 kg/100kg EO *High salt load

$ClCH_2CH_2Cl$ 10-15kg by-products

$ClCH_2CH_2OCH_2CH_2Cl$ 7-9kg

※ High Cl_2 consumption (simply lost as $CaCl_2$) → no more used except PO

② Direct Oxidation (15 atm, 250°C)

$CH_2{=}CH_2 + 1/2\ O_2 \rightarrow Ag \rightarrow \triangle\ CH_2(O)CH_2$ $\triangle H = -25 kcal$

※ (side rxn) : complete oxidation!! More heat than EO production

$CH_2{=}CH_2 + 3O_2 \rightarrow 2CO_2 + 2H_2O$ $\triangle H = -317 kcal$

$CH_2(O)CH_2 + 21/2O_2 \rightarrow 2CO_2 + 2H_2O$ $\triangle H = -292 kcal$

△E is 10~14x higher: temp control ↔ "run-away" rxn

※ Inhibitor : $ClCH_2CH_2Cl$ (ppm) added to chemisorb •Cl on Ag

- Mechanism

$[Ag] + O_2 \rightarrow [Ag]\,O_2^{ads} \rightarrow CH_2=CH_2 \rightarrow CH_2(O)CH_2 + [Ag]\,O^{ads}$

$4\,[Ag]\,O^{ads} + CH_2{=}CH_2 \rightarrow 2\,CO + 2\,H_2O + 4\,[Ag]$

$[Ag]\,O_2^{ads} + 2\,CO \rightarrow 2\,CO_2 + [Ag]$

max selectivity >82% of E.O

- Process operation

- Low conversion : maintains <10%
- Careful heat removal, to avoid local hot spots & to prevent sintering of Ag
- Fixed-bed tubular reactor (gas-phase)

※ Fluidized-bed rxtor has been tried (excellent heat removal)

- Selectivity (yield) : ~ 65-70% (Ag/alumina)

small amount of K, Ru, Ce ions increase yields (IP)

③ Newer process

※ New catalyst : "Ag-NP cluster as catalyst"

Ag_2C_2O → Ag◦ (crystallographic Ag ◦ metal)

- 50-60% conversion,
- <80% E.O. selectivity

(2) Application

① Minor importance of its own

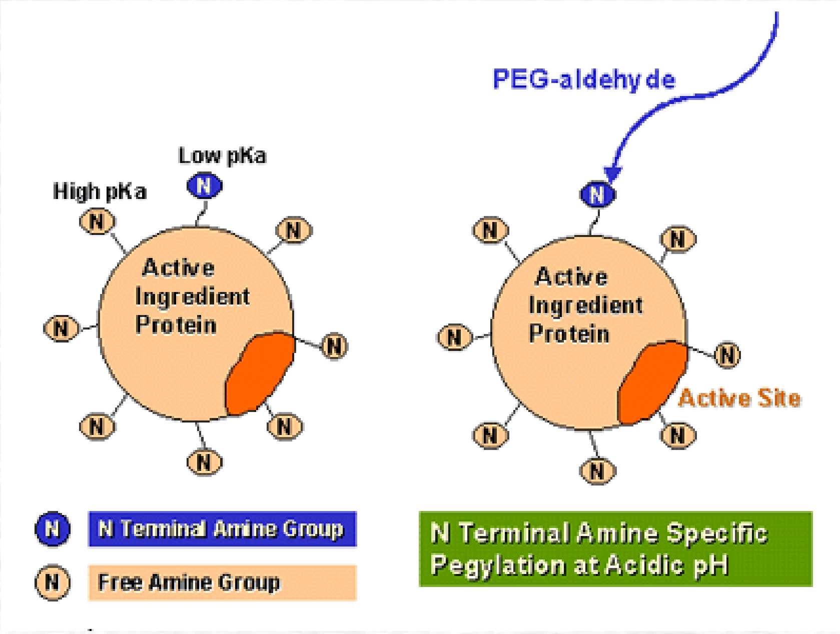
※ fumigant (~%) in grain stores

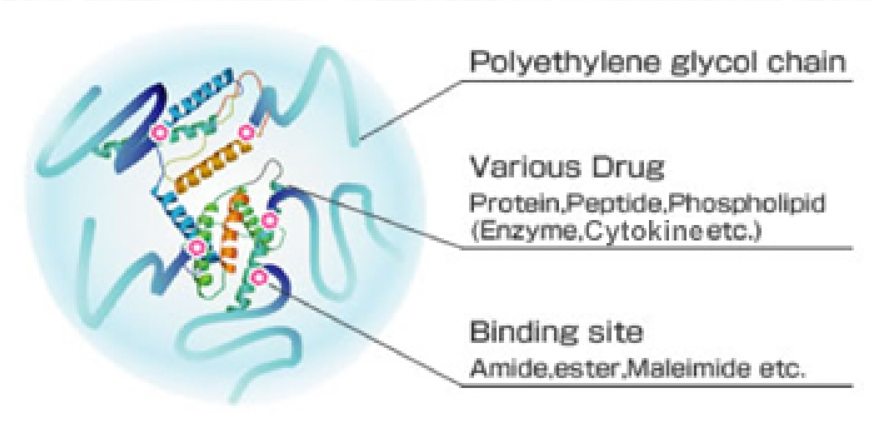
② Intermediate for Ethoxylation:

eg) Production of HEMA

③ PEG & PEGylation for Bio Drug

PEGylation for Bio Drug

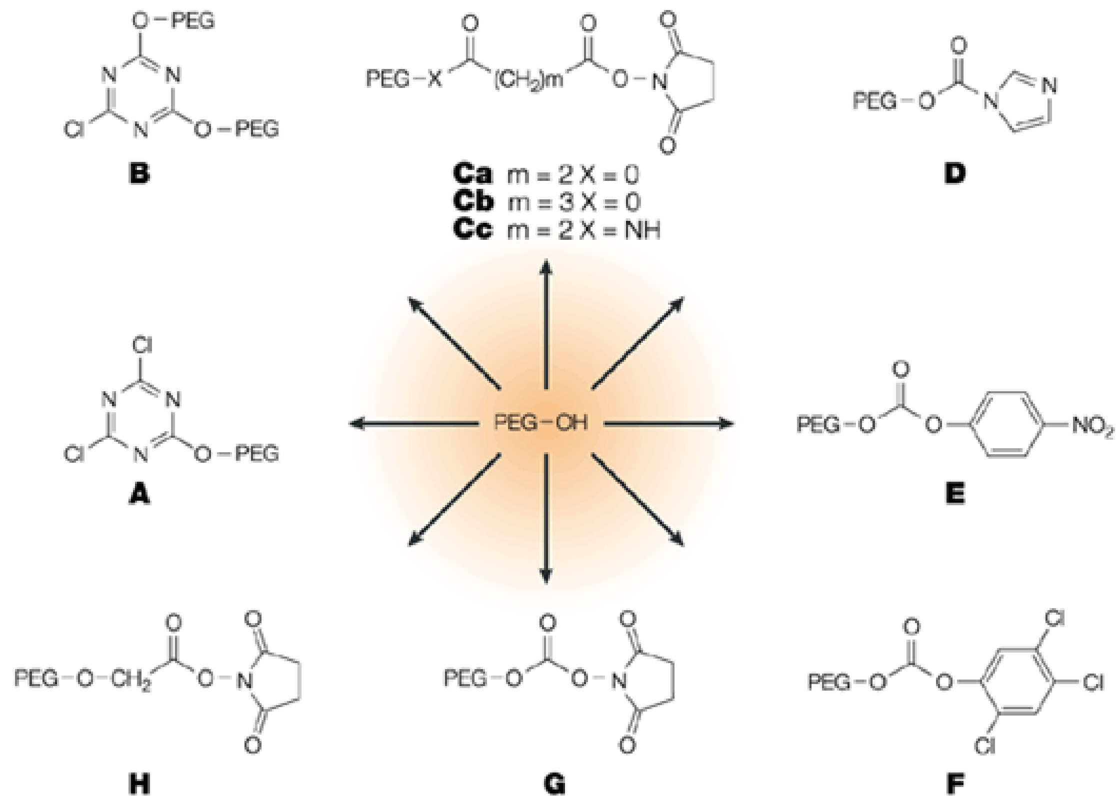




※ PEGylated Long-Acting Human Growth Hormone Possesses a Promising Once-Weekly Treatment Profile, and Multiple Dosing Is Well Tolerated in Adult Patients with Growth Hormone Deficiency (March, 2011)

※ pKa of N-terminal NH_3^+ 9.8 → 8.0 vs side chain 10.5 : Why pKa is different?

PEGylation Reagents



Nature Reviews | Drug Discovery

- Major Out-put of EO in USA (%)

Ethylene glycol	60
Non-ionic surfactants	14
Ethanol amine	6
기타	20

eg) Ethoxylated fatty alcohols, and fatty amide

Ethoxylated alkylphenol → wetting agent for washing

(Nonionic surfactant: used in semiconductor industry)

eg) ※ Nonylphenol-EO9 + TMAH for etching agent.

Ethoxylated starch, cellulose

→ HEC (cellusizer): thick, protective layer for colloid

→ HE-starch: used for paper and food industry

※ Surfactant

- Long hydrophobic tail (C8-C18) with hydrophilic head group

- Surface active agent → Surfactant, Lowering surface energy

- CMC

- classes

- Cationic Surfactant :
- Anioinic Surfactant :
- Nonionic Surfactant :

7) Ethylene Glycol

- High selectivity is important

(1) Production :

① Hydration of E.O. via " chlorohydrin process"

$$CH_2(O)CH_2 + H_2O \rightarrow HOCH_2CH_2OH$$

- **Neutral condition** : more popular
  - fairly high temp (~200℃)
  - pressure (~14 atm)
- **Acidic condition** :
  - 0.5% H_2SO_4 , 50-70℃, 1 atm (no press equipment)
  - requires corrosion-resist material
  - need separation of acid

- **Basic condition :**

not used for EG production

used for higher ethylene glycol : glycolysis 〉 hydrolysis

※ Side rxn : affected by water/EO ratio → complex purification

EO/H_2O (molar ratio)	EG	di-EG	tri-EG	polyEG
** 1 : 10	82%	13%		
* 1 : 4.2	66%	27%		
1 : 2.1	47%	34%	13%	0.3%
1 : 0.61	16%	26%	20%	33%

* Excess water → large rxtor vol needed

→ high dilution, higher separation cost

* Purity is very important for PET (high MW) production

② Halcon Process (1974) → 1978 (1st operation)

- None EO based process (acetoxylation of ethylene)

$CH_2{=}CH_2 + 2HOAc + 1/2\ O_2 \rightarrow [Br_2/Te^{+4}] \rightarrow AcOCH_2{=}CH_2OAc + H_2O$

$AcOCH_2CH_2OAc + H_2O \rightarrow HOCH_2CH_2OH + 2HOAc$

- Overall rxn :

$CH_2{=}CH_2 + 1/2\ O_2 + H_2O \rightarrow HOCH_2CH_2OH$

- High yield : 95%~98% (reagents, similar to Wacker for vinyl acetate)
- Reactor: acidic condition, corrosion problem !!
- Mechanism

$CH_2{=}CH_2 + Br_2 \rightarrow BrCH_2CH_2\ Br$

$BrCH_2CH_2Br + 2AcOH \rightarrow AcOCH_2CH_2OAc + 2HBr$

$HBr + 1/2\ O_2 \rightarrow [Te^{+4}] \rightarrow H_2O + Br_2$

③ Ethylene Carbonate Process (UC)

EO + CO_2 → Ethylene Carbonate → [H_2O] → EG + CO_2 (acidic!)

- No excess of water used;

$Et_4N^+Br^-$/KI catalyst → new solid-phase catalyst possible?

- Only EG, no dimer or trimer in product

- **Similar process (Texaco) : two-for-one reaction**

Ethylene Carbonate + $2CH_3OH$ → EG + $(CH_3O)_2C=O$ (DMC)

※ **Can eliminate the use of phosgene or CO in DMC production**

<기존의 DMC process>

$COCl_2 + 2CH_3OH \rightarrow (CH_3O)_2C=O + 2HCl$

$CH_3OH + 0.5O_2 + CO \rightarrow (CH_3O)_2C=O + H_2O$

※ DMC → as substitute of phosgene in polycarbonate production

④ Newer process $\propto$ price of $CH_2{=}CH_2$

- Single step oxidative C_2 hydration

$CH_2{=}CH_2 + H_2O + 1/2\ O_2 \rightarrow HOCH_2CH_2OH$

Catalyst : TiO_2/HCl ; I_2/Cu; $CuBr_2$/CuBr/HBr

- Catalytic hydrolysis of EO : Va^{+n} or Mo^{+n} /IE resin

$CH_2(O)CH_2 + 2.5\ H_2O \rightarrow HOCH_2CH_2OH$ (100%)

- 'CO' Utilizing Process (C1 chemistry)

- From Syn Gas (UCC process)

  $CO + H_2 \rightarrow$ EG (64%) + (CH_3OH + PO + glycerol)

- Carbide + Ube Process: hydrogenolysis of oxalate

  $2\,ROH + CO + 1/2O_2 \rightarrow R\text{-}OCOCOOR \rightarrow [H_2] \rightarrow EG + 2\,ROH$

- Single step oxidative C_2 hydration

  $HCHO + CO + H_2O \rightarrow HOCH_2COOH$ (glycolic acid)

  $HOCH_2COOH + MeOH \rightarrow HOCH_2COOMe + H_2O$

  $HOCH_2COOMe + H_2 \rightarrow EG + MeOH$

  (Overall Rxn) $2H_2 + HCHO + CO \rightarrow EG$

- Monsanto Process : Hydroformylation

  $HCHO + CO + H_2 \rightarrow HOCH_2CHO \rightarrow [H_2] \rightarrow EG$

- FR reaction with $HCHO + CH_3OH$

$HCHO + CH_3OH \rightarrow \rightarrow HOCH_2CH_2OH$

<Mechanism>

- (In) $CH_3OH + \bullet X \rightarrow \bullet CH_2OH + HX$
- (P) $\bullet CH_2OH + HCHO \rightarrow HOCH_2CH_2O\bullet$
- $HOCH_2CH_2O\bullet + CH_3OH \rightarrow EG + \bullet CH_2OH$
- (T) $2 \bullet CH_2OH \rightarrow EG$ (in fact, major rout)

※ In fact, too short chain rxn →

requires more Initiator (expensive process)

- **Electro-hydrodymerization** : $2HCHO + 2H + 2e \rightarrow EG$

(2) Application :

① Antifreezer ~ 50% (USA)

② Polyester 원료 : ~ 50%(USA)

- Fiber: "Dacron" “Terylene” “Mylar”

  - Purity is very important factor for high MW: PTPA, DMTA, EG

- Plastic Bottle: PET for Coke

③ Others : As Esters : brake fluids plasticizer, lubricant

PUs, ...

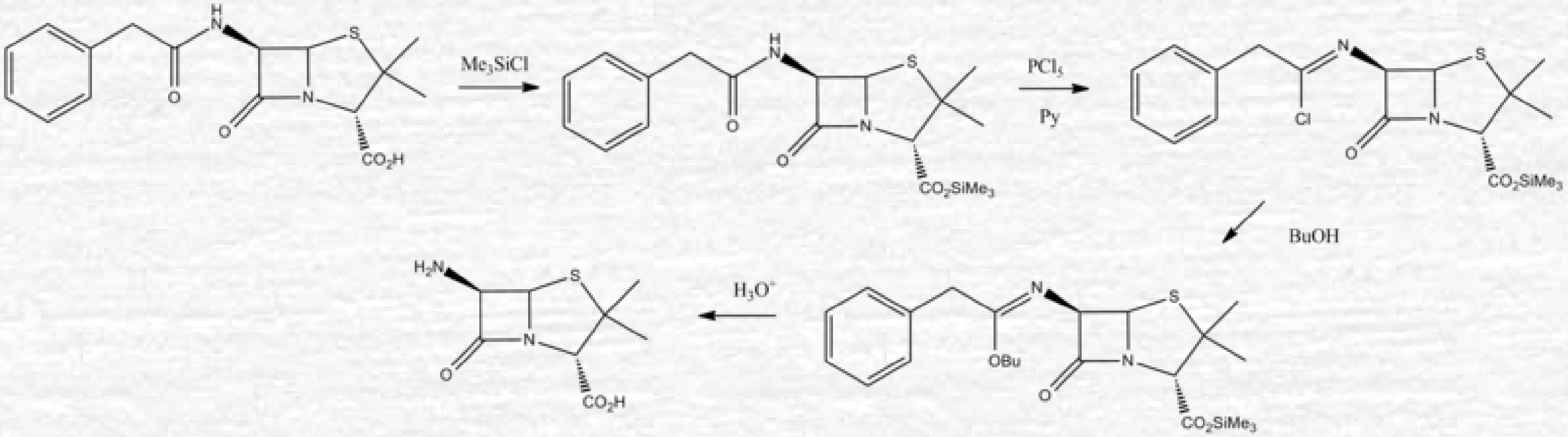
④ oxidation product → glyoxal, glycolic acid

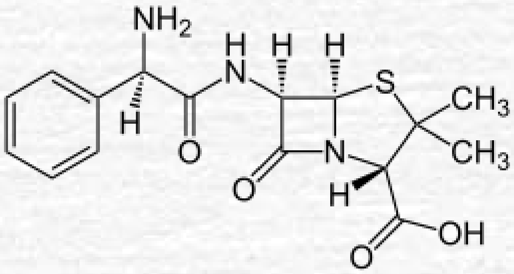
* glycolic acid + phenol → → 4-hydroxyphenylGly

* glyoxal + phenol + urea → 4-hydoxyphenyl hydantoin

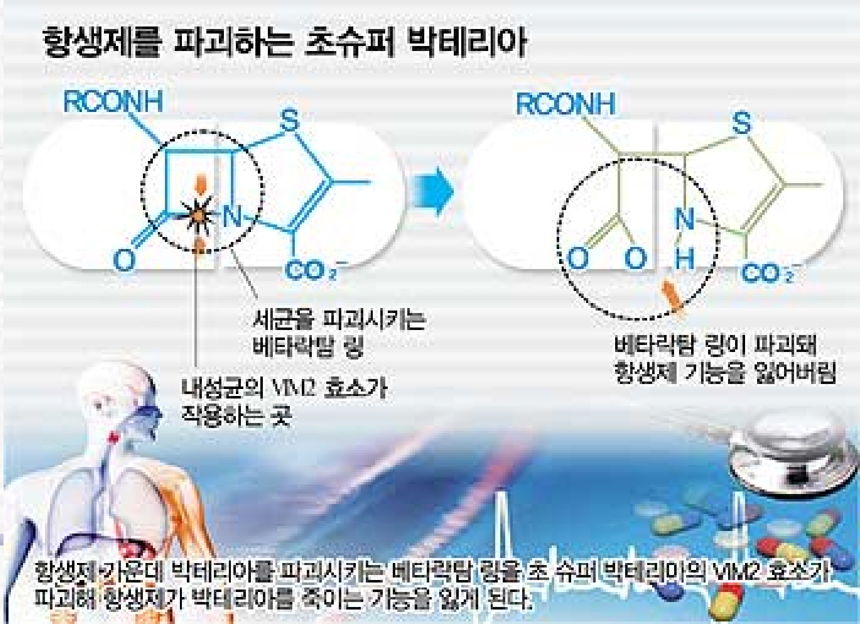
→ 4-hydroxyphenyl-Gly : 6-APA → Amoxicillin production

6-APA





Ampicillin : how to synthesize
from 6-APA ?



항생제를 파괴하는 초슈퍼 박테리아

항생제 가운데 박테리아를 파괴시키는 베타락탐 링을 초 슈퍼 박테리아의 VIM2 효소가 파괴해 항생제가 박테리아를 죽이는 기능을 잃게 된다.

8) Ethanol

(1) Production

- $CH_2=CH_2 + H_2SO_4$ → Ethyl sulfate + Diethyl sulfate → hydrolysis

- Direct hydration over catalyst

- Fermentation : w/ government subsidy → Gasohol (1980’s in US)

(2) For Abs. Ethanol

① Azeotropic distil w/ benzene

② countercurrent extraction w/ glycerol or EG (via H-Bond intxn)

(3) Application：

- solvent, EtOAc

- Acetaldehyde, Acetic acid, Ethylene,,.

※ Alcohol vs EtOH? : Whisky (Grain, Molt, Blend), Cognac

9) Styrene

(1) Production

① **CH_2=CH_2 + Benzene + HCl+ $AlCl_3$ → Ethylbenzene**

Ethylebenzene → Styrene + H_2

- Mechanism:

② **Dimerization of butadiene → Vinyl cyclohexene → Styrene**

(2) Production condition

① Friedel-Craft Alkylation (in liquid phase, 85~95 ℃, 1 atm)

② Continuous vapor-phase reaction (400 ℃, 18 atm)

. Zeolite ZSM-5 catalyst

(3) Application ： 3rd largest use of Ethylene (PE>PVC>PS)

① Polystyrene, Styrofoam : packing material (1st use, 1/2 use)

② Rubber & Plastic

- SBR Rubber : Styrene(24%, w/w) + Butadiene (2nd use)
  - Synthetic rubber (2/3 of rubber) for tire
  - “Buna S” rubber: developed by Germany (WW II), 1st use of styrene
- ABS resin: acrylonitrile + butadiene + styrene (3rd use)

  Plasitic for appliance
- SAN : styrene + acrylonitrile
- styrene + MA copolymer

10) Ethanolamines

(1) Production：

n EO + NH_3 → MEA + DEA + TEA (Ratio ∝ mole Ratio of SM)

(2) Application

① Acidic gas scrubber

$$CO_2 + MEA \rightleftarrows CO_2 . MEA$$

② Surfactant

. $RCO_2H + HOCH_2CH_2NH_2 \rightarrow \rightarrow R\text{-}CONHCH_2CH_2OH + H_2O$

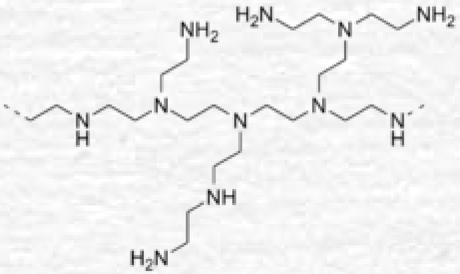
additive as foam stabilizer, booster

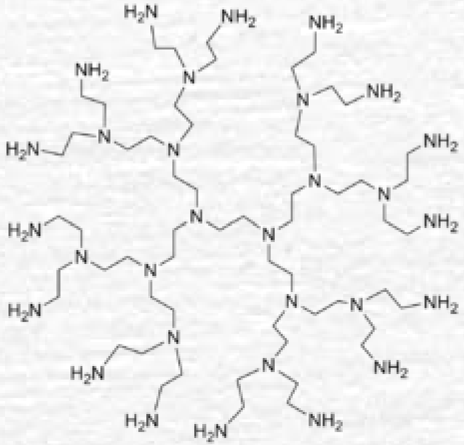
. RCO_2^{-} $MEAH^{+}$ (weak alkaline soap, for baby) → cosmetics

③ Ethyleneimine

$HOCH_2CH_2NH_2$ + H_2SO_4 → $H_2NCH_2CH_2OSO_3H$ →[NaOH]→ $CH_2(NH)CH_2$

- PEI : flocculant (esp. for paper mill waste water), transfaction agent for gene delivery





- Fire retardant for textile:

$CH_2(NH)CH_2$ + $POCl_3$ → tris-(1-aziridinyl phosphine oxide) 🕮 200

11) Ethyl Chloride

(1) Production ：

① Chlorination of Ethane

$C_2H_6 + Cl_2$ (excess) → C_2H_5Cl + HCl↑ (by product 이용?)

- Gives high yield (∵) further rxn is slow; $C_2H_5Cl + Cl_2 \rightarrow$ slow

② $CH_2{=}CH_2 + HCl \rightarrow CH_3CH_2Cl$ (USA)

(2) Process

- EU : Integrated process

Ethane + Ethylene is used as raw material (EU)

- USA : Ethylene-based process

(3) Application： TEL (80% USA)

$4NaPb + 4C_2H_5Cl \rightarrow Pb(C_2H_5)_4 + 4NaCl + 3Pb$

12) ECH(ethylene chlorohydrin)

$CH_2(O)CH_2 + HCl \rightarrow HOCH_2CH_2Cl$

- >1000$/TON, high value product
- Application : paint, epoxy
- Production capacity : Hanwha 25,000 t/y; Samsung 30,000 t/y (98)

Ethylene Polymers : Largest use of Ethylene

1) LDPE

- 1932 : Found by Fawcett and Gibson (ICI)
During study w/ "ethylene + benzaldehyde" (for Syn rubber)
(trace of Oxygen impurities added to the autoclave)

- Conditions: 200~300 ℃, ~2000 bar
  Oxygene or Organic Peroxide

- Density : 0.915~0.925, low crystallinity (55%) → translucent
- Application : Greenhouse films for agriculture

2) HDPE

- **1950 : Phillips Petroleum / (Standard Oil)**
  During study w/ “ethylene” (for gasoline size oligomers)
  Cr_2O_3 /silica catalyst & mild condition was used → HDPE

- **1954 Ziegler : AlR_3** + metal salt impurity → **HDPE**
  - Ziegler catalyst : $AlEt_3 + TiCl_4$
  - Can be applied to PP
- **Conditions: 60℃, 1-300 bar, less energy intensive**
  < 4% 1-butene used for copolymerization to prevent High MW
  - Cr based catalyst in US
  - Ziegler process in EU
  - Metallocene catalyst recently used
- Density : 0.945~0.965

- Application : Bottles, PE bags

2) LLDPE

※ During research for energy saving condition for LDPE

- Copolymer of Ethylene + 1-butene (6-8%)

known before, but recognized later for energy saving production of LDPE → compensates high cost of 1-butene

- high branching point → reduces crystallinity

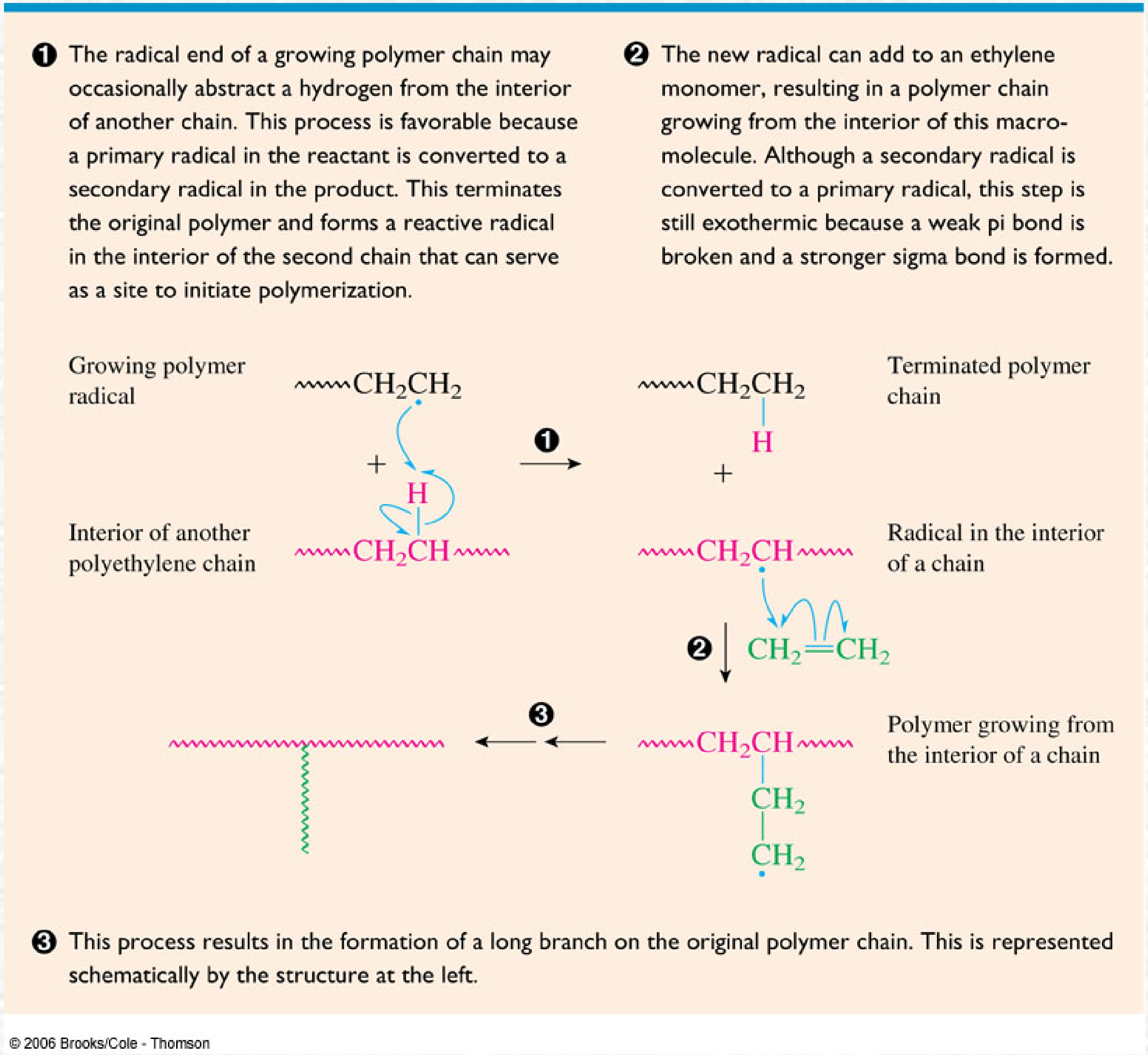
- regular branching than LDPE → higher tensile strength

- Used in wrap films (clean wrap w/out using plasticizer)

- **Mechanism for the Formation of Long Branch**

Linear Structure *vs* Branched Structure

Chain transfer Mechanism



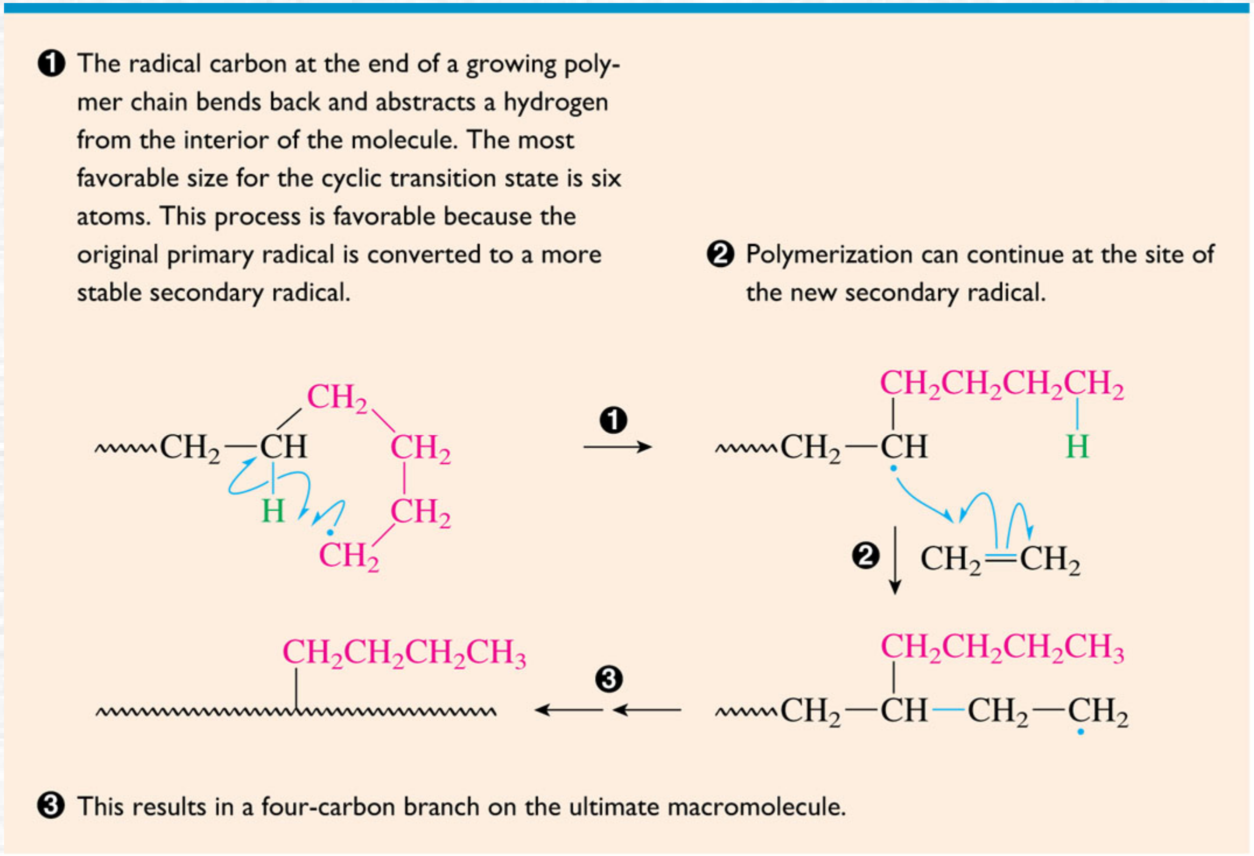
❶ The radical end of a growing polymer chain may occasionally abstract a hydrogen from the interior of another chain. This process is favorable because a primary radical in the reactant is converted to a secondary radical in the product. This terminates the original polymer and forms a reactive radical in the interior of the second chain that can serve as a site to initiate polymerization.

❷ The new radical can add to an ethylene monomer, resulting in a polymer chain growing from the interior of this macromolecule. Although a secondary radical is converted to a primary radical, this step is still exothermic because a weak pi bond is broken and a stronger sigma bond is formed.

❸ This process results in the formation of a long branch on the original polymer chain. This is represented schematically by the structure at the left.

- **Mechanism for the Formation of Shorter Branch**

Irregularity →
 Polymer property change



❶ The radical carbon at the end of a growing polymer chain bends back and abstracts a hydrogen from the interior of the molecule. The most favorable size for the cyclic transition state is six atoms. This process is favorable because the original primary radical is converted to a more stable secondary radical.

❷ Polymerization can continue at the site of the new secondary radical.

❸ This results in a four-carbon branch on the ultimate macromolecule.

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Thru 6-Member TS → Butyl Branch

Irregularity:
- from Branched Polymer
- from Tacticity

Chemicals from Propylene: C_3 - Chemistry

A. Source of Propylene

- Source : From olefin mixture

25% from Thermal Cracking for Ethylene

75% from Catalytic Cracking + Refinery Gas

- Economy

① Not produced only for Propylene, but as byproduct for Ethylene

② As byproduct for gasoline production

③ Much cheaper than Ethylene

- Application: 50% used for chemicals

50% used for alkylation with *i*-butane → gasoline production

B. Chemistry of Propylene 📖 218

① **“Classical" Reactions :** oxo reaction, alkylation, cummene to actone

② **“Oxidation” Reaction :**

③ **“Polymerization” & “Oligomerization”**

- Reactivity of Propylene *vs* Ethylene

Active Allylic hydrogene *vs* Double bond

1) Acrylonitrile (AN)

(1) Production

① Acetylene based

HC≡CH (excess) + HCN → [aq. Cu_2Cl_2] → CH_2=CH-CN (80%)

recovered as 2% aq. solution

② Sohio Process – Ammoxidation

CH_2=CH-CH_3 + NH_3 → [O_2] → CH_2=CH-CN + HCN + CH_3CN + H_2O

- New C-N bond formation, exotherm (need cooling)
- High conversion
- Useful by-product : major source of HCN (USA)

0.1 MT of HCN and CH_3CN/MT AN

※ HCN → melamine, MMA, adiponitrile

③ Union Carbide Process

$CH_2(O)CH_2 + HCN \rightarrow HOCH_2CH_2CN \rightarrow CH_2{=}CH\text{-}CN + H_2O$

④ Two stage “Sohio" process : Dupont

$CH_2{=}CH\text{-}CH_3 + O_2 \rightarrow [Ag] \rightarrow CH_2{=}CH\text{-}CHO$ acrolein

$CH_2{=}CH\text{-}C(O)H + NH_3 \rightarrow [air/catal] \rightarrow CH_2{=}CH\text{-}CN + H_2O$

(2) Application :

① Polyarylonitrile co-polymer

② ABS polymer (terpolymer): "Acrylonitrile + Butadiene + Styrene"

- cheap, strong → metal substitution for auto parts, pipe,.. etc

③ HMDA(hexamethylene diamine) via Hydrodimerization

$2\ CH_2{=}CH\text{-}CN \rightarrow [e] \rightarrow NC\text{-}CH_2CH_2\text{-}CH_2CH_2\text{-}CN$

$\rightarrow H_2NCH_2(CH_2)_4CH_2NH_2 \rightarrow$ Nylon 6,6

2) Acrolein or Acrylic Acid

(1) Production

① Oxidation of Propylene : major source

$CH_2=CH\text{-}CH_3 \rightarrow CH_2=CHCHO \rightarrow CH_2=CHCOOH$

- Two step/low conver for control → very pure feed needed

② $CH\equiv CH$ + HCN → $CH_2=CH\text{-}CN$ →hydrolysis→ $CH_2=CHCOOH$

- has been major source before ① in USA

③ $CH_2(O)CH_2$ + HCN → $HOCH_2CH_2CN$ → $CH_2=CHCOOH$

④ CH_3CHO + HCN → $CH_3CH(CN)OH$ → $CH_2=CHCOOH$

※ Cyanohyrin → Ala

⑤ $CH_2=C=O$ + HCHO → $CH_2=C=O$ →[H^+/ROH]→ $CH_2=CH\text{-}COOR$

$CH_2=O$

**** Biorenewable process for AA** 📖 **225**

① Fumaric acid ② Lactic acid ③ Glycerol

(2) Application :

① **Acrylic ester: polymer or co-polymer/emulsion for paint**

② **Glycerol: “Shell Process"**

$CH_2{=}CHCH_3 \rightarrow CH_2{=}CHCHO$

$CH_2{=}CHCHO + CH_3CH(OH)CH_3 \rightarrow CH_2{=}CHCH_2OH + CH_3C(O)CH_3$

$CH_2{=}CHCH_2OH + H_2O_2 \rightarrow CH_2(OH)\text{-}CH(OH)\text{-}CH_2OH$

$CH_3CH(OH)CH_3 + O_2 \rightarrow CH_3C(O)CH_3 + H_2O_2$ (v. expensive)

$CH_2{=}CHCH_3 + H_2O + H^+ \rightarrow CH_3CH(OH)CH_3$

※ production of bio-disel vs glycerol price

③ **Methionine: “Dow Chemical"** 📖 **268**

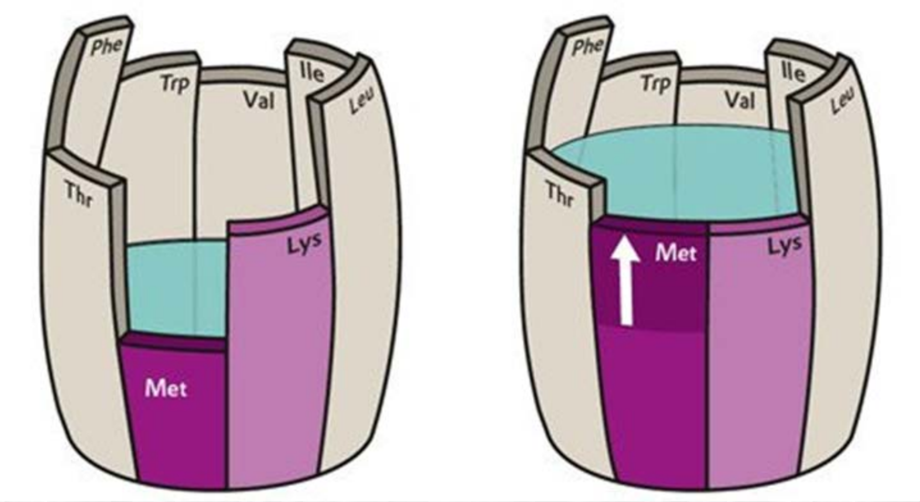
$CH_2{=}CHCHO + CH_3SH \rightarrow CH_3SCH_2CH_2CHO$

$CH_3SCH_2CH_2CHO + HCN + (NH_4)_2CO_3 \rightarrow$

$CH_3SCH_2CH_2\text{-Hydantoin} + NH_3 + 2H_2O$

$CH_3SCH_2CH_2\text{-Hydantoin} \rightarrow CH_3SCH_2CH_2CH(COOH)\text{-}NH_2$

- Animal feed supplement (Lys, Met, Trp)



Liebig (1840), Law of Minimum

※ Lysine (BASF)

3) Propylene Oxide(PO)

(1) 제법 Production

① **chlorohydrin process:** once used for EO production

$CH_2=CH\text{-}CH_3 + HOCl \rightarrow CH_2(O)CH\text{-}CH_3 + CaCl_2 + H_2O$

"$Cl_2 + H_2O \rightarrow HOCl + HCl$" *in situ generation*

- Chlorine consumption 1.59t of Cl_2/TON of prod.

$Cl_2 \rightarrow CaCl_2$ “recycle ??”

- Direct oxidation ??, why not? What is the product of direct oxidation?

$CH_2=CHCH_3 + H_2 + O_2 \rightarrow CH_3CH(O)CH_3 + H_2O$ 🕮 249

② Halcon International Process 1960~ 📖 244

"two-for-one rxn" - via peroxide

- $(CH_3)_3CH$ → $(CH_3)_3COOH$ →(propylene) → $CH_2(O)CH\text{-}CH_3$ (95%)

  t-butyl hydroperoxide $(CH_3)_3COH$

- $PhCH_2CH_3$ → $PhCHOOH$ → $CH_2(O)CH\text{-}CH_3$ + $PhCH(CH_3)OH$

  $PhCH(CH_3)OH$ → Styrene + H_2O

※ Future process for PO

- Isopentane →→ Isopentanol → Isoprene
- Isobutyraldehyde →→ *Isobutyric acid → MMA

(*Unwanted Oxo roduct before)

※ Oxo reaction: Hydroformylation

Propylene + CO + H_2 → n-butyaldehyde (4) + $CH_3\text{-}CH(CH_3)CHO$ (1)

unwanted side prod

$CH_3CH(CH_3)CHO$ → $CH_3CH(CH_3)COOOH$

→ $CH_2(O)CH\text{-}CH_3$ + $CH_3CH(CH_3)COOH$

→ $CH_2{=}CH(CH_3)\ COOCH_3$ (MMA) + H_2O

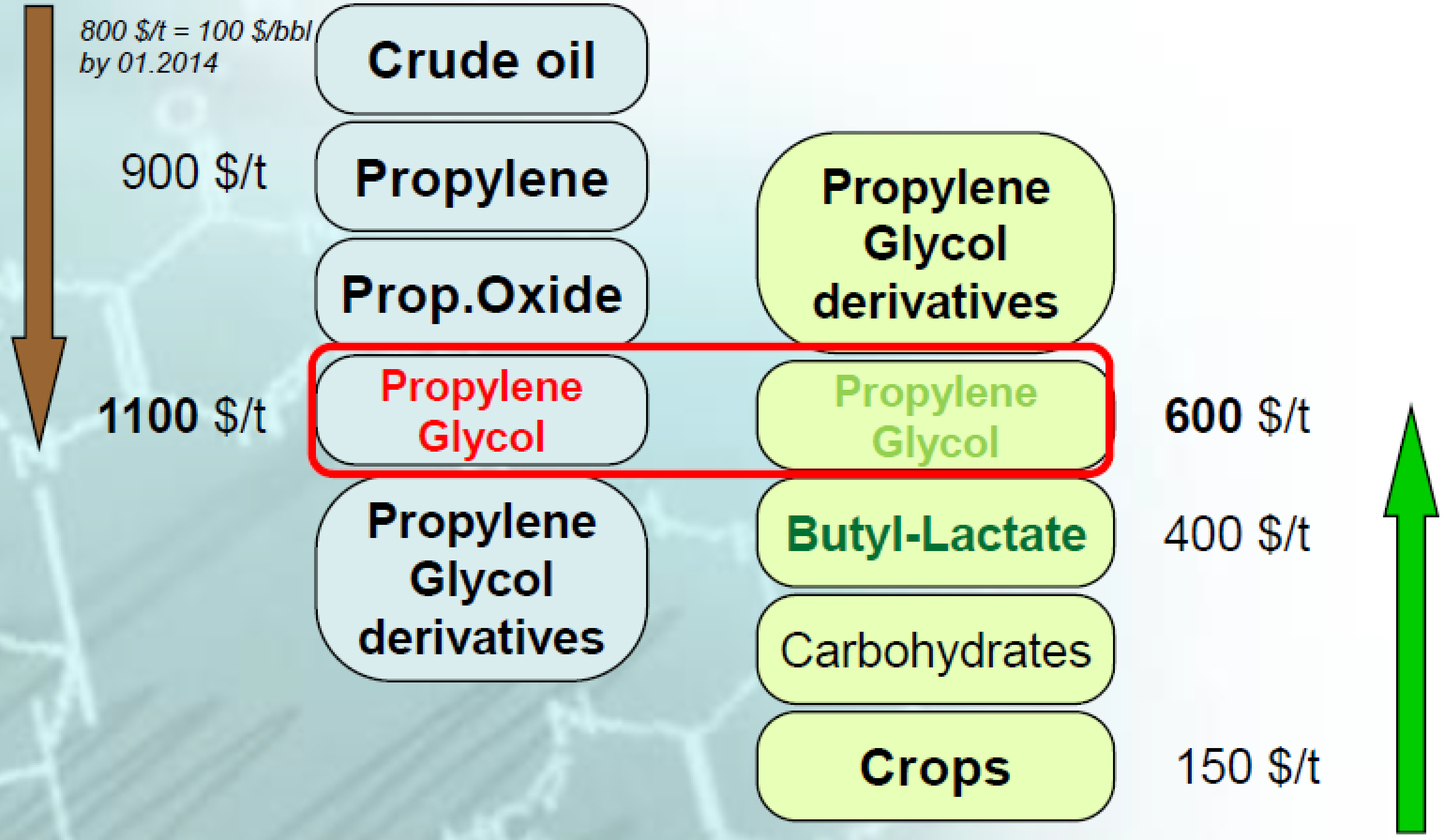
- Mechanism for Halcon?

③ BioTech Process Proposed 📖 252

D-Glucose + O_2 + Propylene + H_2 → D-Fructose + PO + H_2O

3 kinds of immobilized Enzs and & supported catalyst (glucose-2-oxidase, bromoperoxidase, halohydrin epoxidase) and Pd

C3: Petro- versus Nordbiochemistry™



50 $/bbl, by 01.2015

800 $/t = 100 $/bbl by 01.2014

Crude oil

900 $/t **Propylene**

Prop.Oxide

1100 $/t **Propylene Glycol**

Propylene Glycol derivatives

Propylene Glycol derivatives

600 $/t **Propylene Glycol**

400 $/t **Butyl-Lactate**

Carbohydrates

150 $/t **Crops**

Price-difference: 1100-600=500 $/t = 45%

2) Economy ※ Expensive by-product

① **t-BuOH:** solid, mp 25.6, small market by itself.

- **2.2kg/kg PO**

- t-BuOH → Isobutene → alkylation for gasoline

  Isobutene → MMA (?) ! (Japan)

  Isobutene → $(CH_3)_3C\text{-}OCH_3$ (TBME)

  $(CH_3)_3C\text{-}OAc$: additives for high ON gasoline

② Phenyl methyl carbinol → Styrene

- **2.5kg Sytrene /kg PO**
- **Become major source of styrene**

※ US PO plant (200 MT?) → Styrene (500 MT, 1/7 total production)

③ **Others :** Isoprene, MMA production possible

Isopentane → Isoprene

i-butyryaldehyde → i-butyric acid → MMA

(3) Application :

① propylene glycol

$CH_3CH(O)CH_2 \rightarrow [H_2O] \rightarrow CH_3CH(OH)CH_2OH$ **(PPG)**

- cellophane plastisizer
- SM for polyurethane

② Poly propylene glycol (PPG) + TDI → rigid PU

※ **PPG** (production in 97: 54,000TON/year : Domestic demand 110,000t/y)

4) Cumene

(1) Production: Benzene + $CH_2{=}CH{-}CH_3$ → $AlCl_3$ → Cumene

(2) Application : for Phenol, Acetone

(3) Mechanisim : 📖 **233**

5) Butylaldehyde & n-Butanol

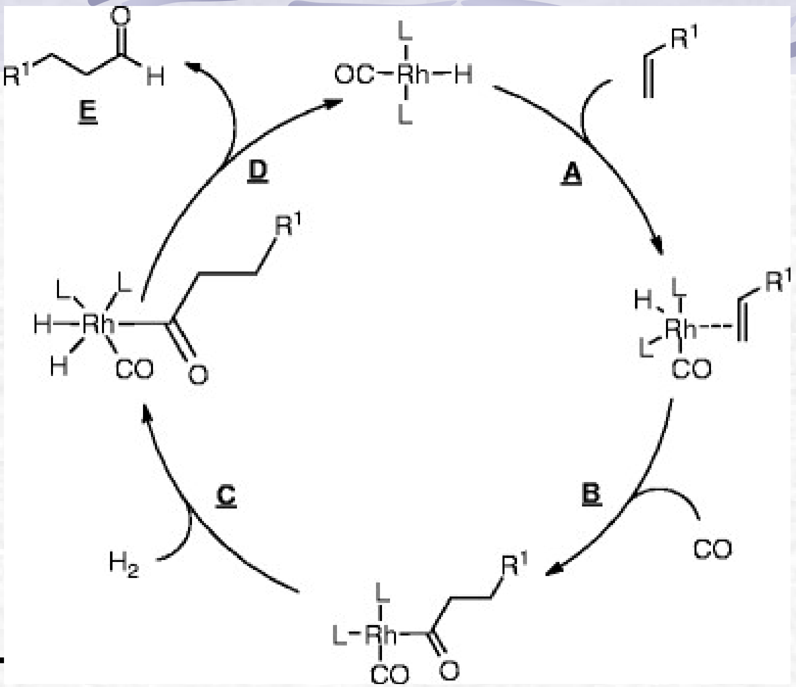
(1) Production : “Hydroformylation" or "Oxo Rxn"

$CH_3CH{=}CH_2 + H_2/CO \rightarrow CH_3CH_2CH_2CHO$ (4) + $CH_3CH(CHO)CH_3$ (1)

- Original Catalyst : $Co_2(Co)_8$ Straight/Branched = 4:1
- New catalyst for : $HRh(CO)(PPh_3)_3$ Straight/Branched = 16:1

→ Can compete w/ aldol synthesis

(2) Mech : 🕮



(3) Application :

① n-Butanol production

$CH_3CH=CH_3$ → $CH_3CH_2CH_2CHO$ → n-BuOH

- n-BuOH → Butyl ester : Good solvent

※ n-butyl acetate: "Lacguer" solvent

※ Old process : Acetaldehyde → n-BuOH

② 2-Ethylhexanol (2-EH)제조

$CH_3CH_2CH_2CHO$ → $C_3H_7CH=CH(Et)\text{-}CHO$ → $C_4H_9CH(Et)CH_2OH$

- Plastisizer alcohol → Dioctylphthalate (DOP)

- 2-Ethylhexanoic acid : “Isootanoic acid"

6) Acetone

(1) Production :

① Cumene process : ~60% world wide production

② $CH=CHCH_3 \rightarrow CH_3CH(OH)CH_3 \rightarrow CH_3C(O)CH_3$

$CH_3CH(OH)CH_3 \rightarrow CH_3C(O)CH_3 + H_2$

$CH_3CH(OH)CH_3 + O_2 \rightarrow CH_3C(O)CH_3 + H_2O_2$ (Shell process)

< 40% world wide production before (run as a buffer process)

(2) Application : production of MMA (major)

Aceton + HCN $\rightarrow (CH_3)_2C(OH)CN \rightarrow CH_2=C(CH_3)CN$

$\rightarrow CH_2=C(CH_3)COOCH_3$ (MMA)

7) MMA

(1) Production : 📖 236

① Aceton + HCN → $(CH_3)_2C(OH)CN$ → $CH_2=C(CH_3)CN$

→ $CH_2=C(CH_3)CONH_2$ →[MeOH, H^+] → $CH_2=C(CH_3)COOCH_3$ (MMA)

*1.5 MT of ammonium bisulfate/MT (because acid is used)

- short fall of HCN source (because of other route for acrylonitrile)

※ Methyl formate as other source for HCN :

$HCOOCH_3$(methyl formate) → $HCONH_2$ → HCN + H_2O

Aceton + HCN → $(CH_3)_2C(OH)CN$ → $(CH_3)_2C(OH)CONH_2$
→[$HCOOCH_3$] → $(CH_3)_2C(OH)COOCH_3$ + $HCONH_2$ → MMA

- **$HCONH_2$ → HCN (to recycle) + H_2O** (via dehydration)
- CO + CH_3OH → $HCOOCH_3$ (via C1 chemistry)

② t-BuOH [or Isobutene] → [ox] → $CH_2=C(CH_3)CHO$ (methacrolein)

→ $CH_2=C(CH_3)COOH$ → $CH_2=C(CH_3)COOCH_3$

- Tried commercially in 1960`s → sounds attractive

- Contains two allylic hydrogens !! (Jpn)

③ Halcon process

$CH_2=CHCH_3$ + CO + H_2 → Isobutylaldehyde

Isobutylaldehyde + $CH_2=CHCH_3$ → MMA + PO

④ Other method for MMA 📖 236

- C_4 -Ammooxidation Process (Asahi) : Isobutene based
  Isobutene → Methacrylonitrile → Methacrylamide sulfate → MMA

- Ethylene based
  Ethylene + CO + H_2 → Propionaldehyde → Propionic Acid
  →[HCOH]→ Methacrylic Acid → MMA

- Propylene Based (Atochem)
  Propylene + CO → [HF, H_2O] → Methacrylic acid → MMA

- Methylacetylene(Propyne) Based Process (Shell)

  $CH{\equiv}CCH_3 + CO + H_2O$ → MA → MMA

  ($CH{\equiv}CCH_3$ == $CH_2{=}C{=}CH_2$) from C3 (steam cracking)

(2) Application : PMMA, high refractive index optical material (fiber optics), water based paint

C_1-Chemistry

A. Synthesis Gas

- Gas mixture of **$CO + H_2$** (or $N_2 + H_2$)
- Used as chemical feedstock
- Classification / according to Origin or Application

※ Origin: any carbon source (coal > petroleum > gas.. peat, wood, biomass)

📖 425

1) According to Origin

① Water gas : from steam of coal : $CO + H_2$

② Crack gas : from steam reforming of CH_4: $CO + 3H_2$

2) According to Application

③ Methanol synthesis gas : $CO + 2H_2$

④ Oxo gas : for hydroformylation : $CO + H_2$

⑤ 기타 : Ammonia synthesis gas : $N_2 + 3H_2$

Fischer-Tropsch process : $CO + 2H_2$

B. Generation of Synthesis Gas

1) Raw materials for Syn Gas

(1) Coal : H/C ratio = 1 : 1

(2) Mineral oil : H/C " = 2 : 1 WWⅡ 이후

(3) Natural gas : H/C " = 4 : 1 WWⅡ 이후

C. Purification of Syn Gas (for NH_3 production)

- Main impurities : H_2S, COS, CO_2, … etc

1) Chemical process

(1) Girbotol process

$CO_2 + MEA \rightarrow CO_2.MEA$

$CO_2 + H_2O + NH_2CH_2CH_2OH \rightarrow (HOCH_2CH_2NH_3)_2CO_3$

- CO_2 〈 0.01% v/v
- also can remove H_2S

(2) Hot potassium carbonate process

- Pressurized wash with K_2CO_3
- Good for large amount of CO_2 〈 1% v/v

2) Physical Process

(1) Rectisol process

- **Pressurized washing w/ MeOH (-60℃)**

  (solubility depends on press, temp)

(2) Adsorption (ie, molecular sieve)

CO_2, H_2O, CH_4, C_2H_6, N_2, …etc

Fixed Bed + impurity → Fixed Bed ⇄ imp

high temp → low temp, high press → low press

3) CO removal process (esp, for NH_3 production)

- to adjust CO/H_2 ratio
- for catalyst protection → complete **CO** removal required

(1) Water-gas shift rxn

"$CO \rightarrow CO_2$"

$CO + H_2O \rightarrow CO_2 + H_2$ ※ Good for CO_2 production

“ H_2O reduction w/ CO”

(2) Mathanation : for compete removal of trace CO after (1)

"$CO \rightarrow CH_4$ "

$CO + 3H_2 \rightarrow CH_4 + H_2O$

Industrial Gases (CO, H_2, O_2, CO_2 ...)

A. H_2 Gas

※World wide H_2 production

1) Source : as by product of

- Cracking/Reforming of crude oil : 48% (petrochemical process)
- Cracking/Reforming of natural Gas : 30% (petrochemical process)
- Coal gasification: 16%
- Electrolysis : 3% → will be up via “solar energy”
- Others (refineries, etc): 3%

2) Production

(1) Steam Reforming process

① Steam Reforming process

$CH_4 + H_2O \rightarrow 3\,H_2 + CO$ $\triangle H = 49\text{kcal}$

1/3 H_2 comes form water

"H_2O reduction w/ carbon of organic" (large endotherm)

② Water-gas shift rxn

$CO + H_2O \rightarrow CO_2 + H_2$ $\triangle H = -10\text{kcal}$ (mod exotherm)

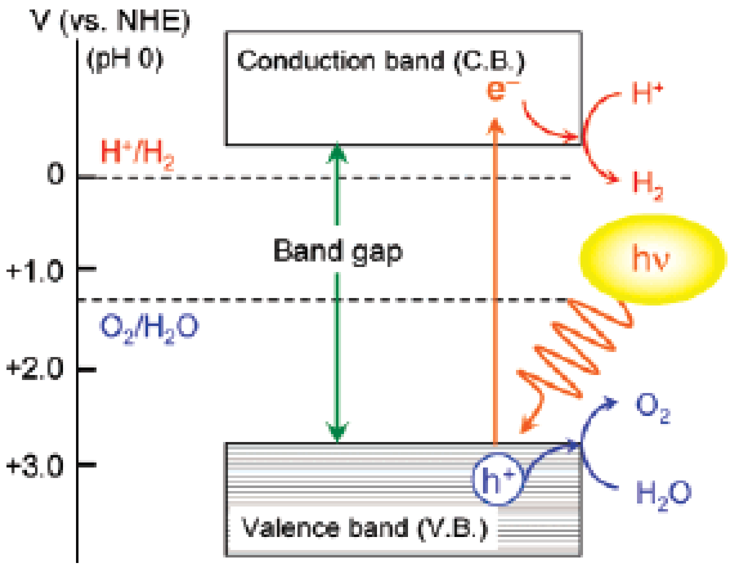
③ removal of CO_2

④ Fine purification by Methanation

(2) Eletrochemical process

$2H_2O \rightarrow 2H_{2(9)} + O_{2(9)}$ △H = +136kcal (Purity 〉 99% v/v)

- Cheap electrical power 요구
- Solar Energy/photocatalysts 개발 중



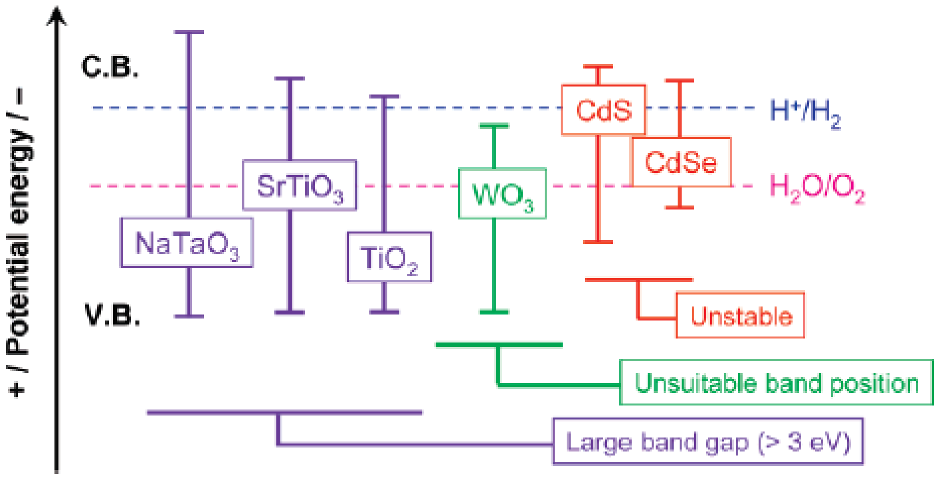
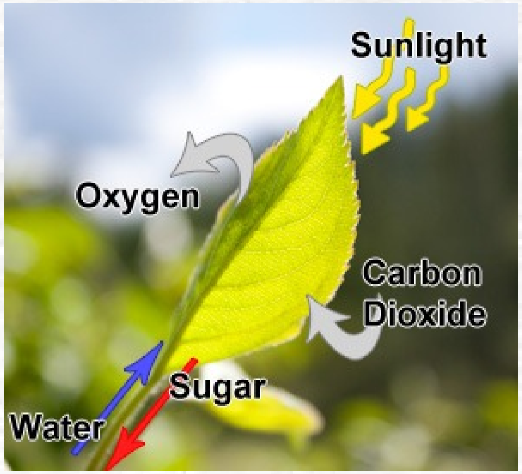
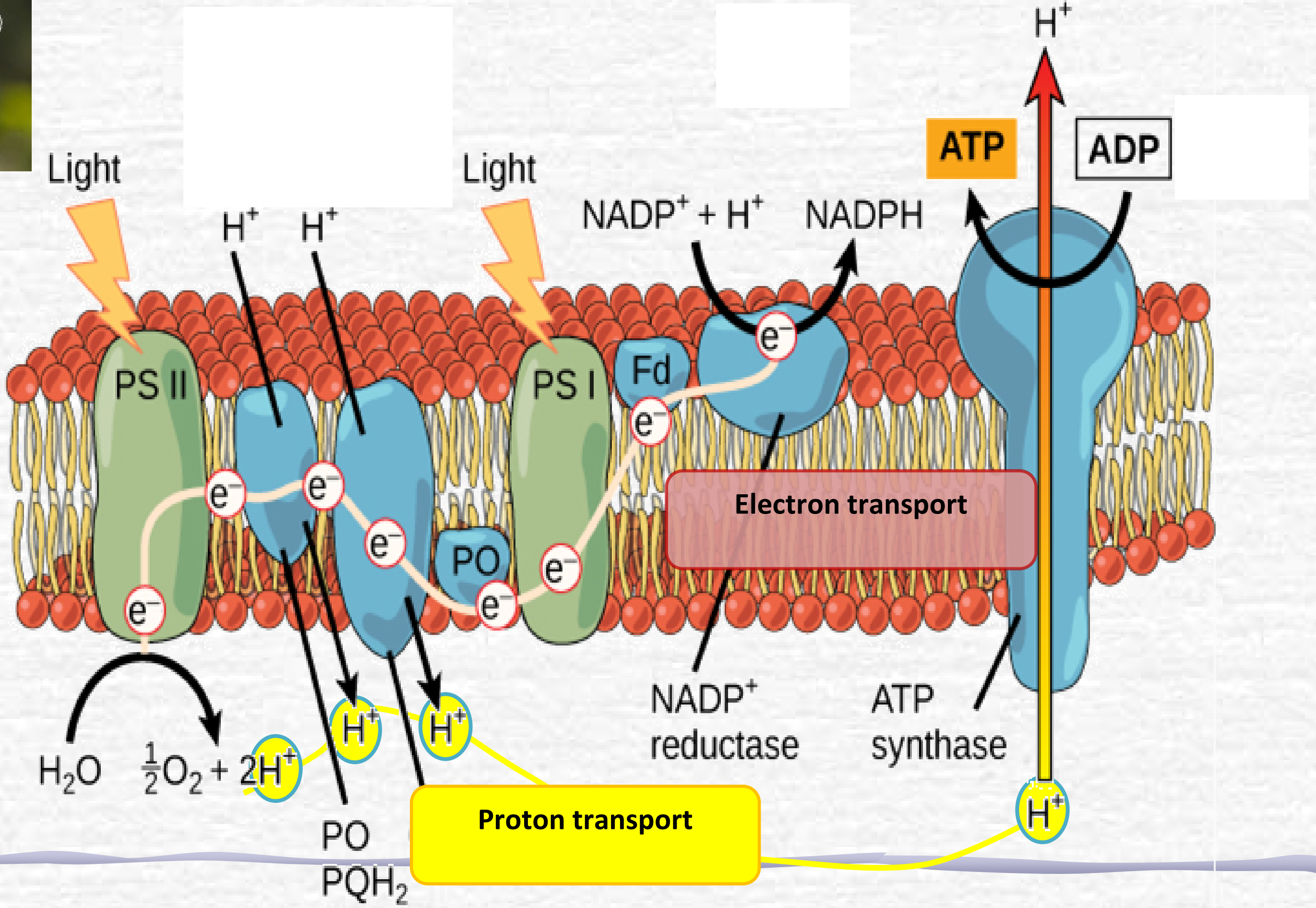


Figure 1. Basic principle of overall water splitting on a heterogeneous photocatalyst.

J. Phys Chem (2007)

Photosynthesis in nature





3) Application : Exclusively for NH_3, CH_3OH production

NH_3 Production	60
Hydrotreating/Hydrocracking/Desulfunzation	15
Hydrocracking	9
Methanol Production	7
Oxo alcohol of hydrogenation	6
others (cooking oil hydrogenation, missile production)	4

* Trans fatt thru hydrogenation

Trans Fat

Essential fatty acids :

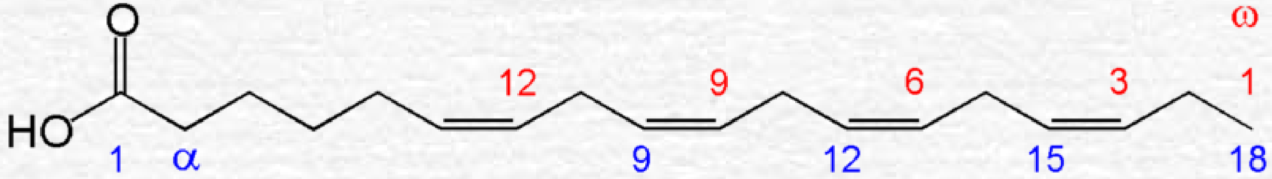
The first position from the last is important for physical property

- ✓ **Omega-3 : α- linoleic acid**
  ALA (18:3)
- ✓ **Omega-6 : linoleic acid**
  LA (18:2)
  → → GLA (18:3)

2005년 식약청 발표 트랜스지방 함량 모니터링 결과

단위:g

초콜릿 입힌 과자 1봉지	3.2g (평균 100g)
크루아상 1개	4.6g
꽈배기 1개	0.8g
페이스트리 1개	4.6g
스낵 1봉지	1.0g (평균 80g)
감자튀김 1봉지	4.6g (평균 100g)
전자레인지용 팝콘 1봉지	24.9g (평균 100g)
도넛 1개	0.7g
마가린 · 쇼트닝 1작은술	0.7g
햄버거 1개	0.7g
식빵 1장	0.4g
비스킷 1봉지	2.2g
오징어 튀김 1개	0.6g
파이 1조각	1.6g
치킨 1조각	0.4g
마가린 발라 구운 토스트 1장	2.8g
케이크 1조각	3.1g
핫도그 1개	0.4g



B. NH_3

1) NH_3 Gas : most important chemical for Syn Gas

(1) Source : 1970

① **Coal … 40%**

- Coke Oven gas from Steel plant → NH_3 scrubber by H_2SO_4
- Keep deceasing recovered as $(NH_4)_2SO_4$

② **Natural Gas … 40%**

- Ammonia Syn Gas

③ **Other source for Ammonia Syn Gas … 20%**

- Oil refinery off-gas
- Catal reforming of HC
- Partial oxidation of HC
- Steam reforming of HC

(2) NH_3 Synthesis - “Haber(1918)-Bosch(1931) process"

$1/2\ N_2 + 3/2\ H_2 \rightarrow NH_3(_9)$ (Fe catalyst)

$\triangle H_{18}$℃ = - 11.0kcal

$\triangle H_{569}$℃ = - 13.3kcal

- Highly exo-therm reaction, favoreable

  increase of Temp → desrease of NH_3

- Requires high press “1000 bar (original) → 250bar"

- S, CO → catalyst poisoning → 〈 10ppm

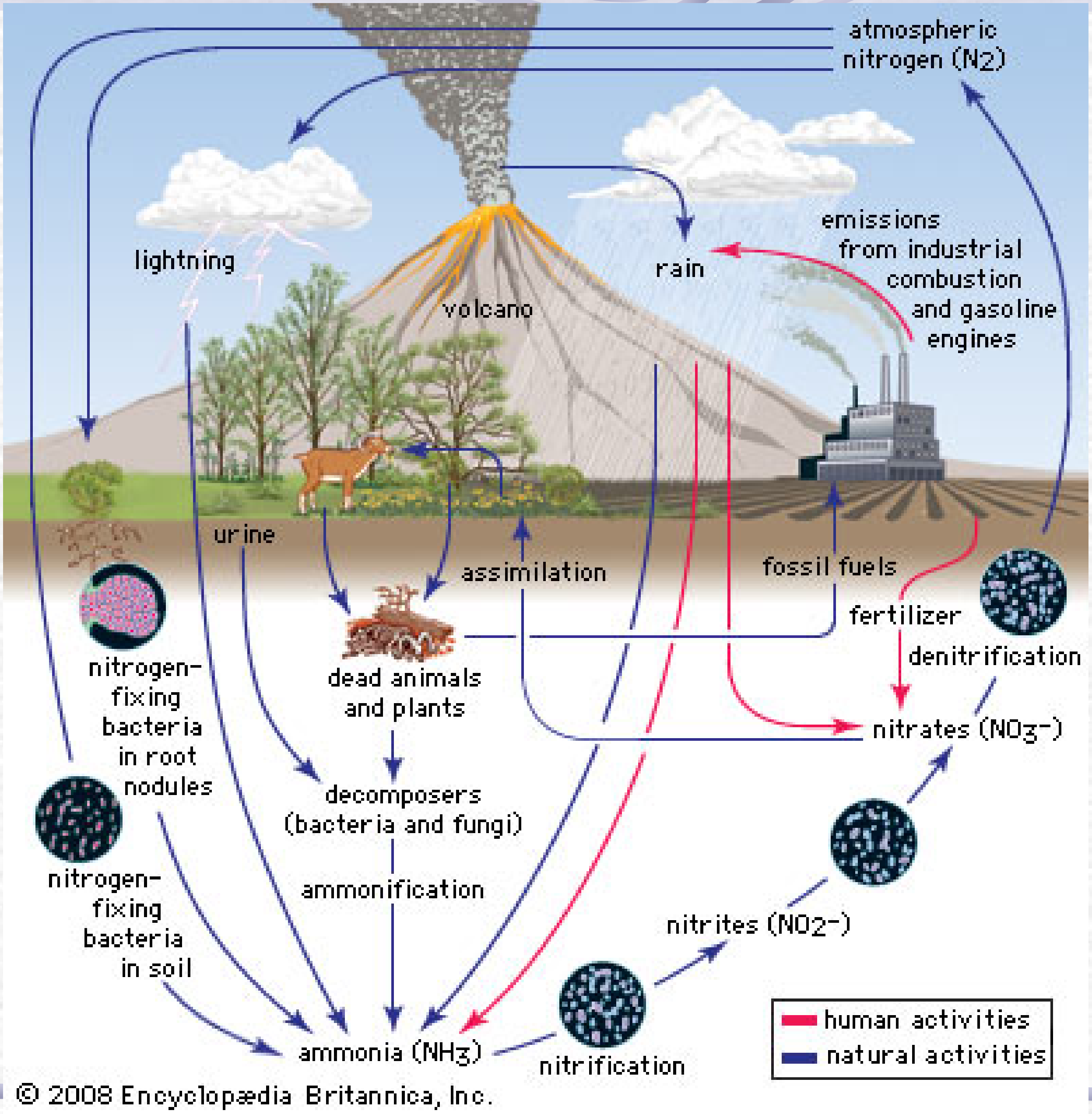
- H_2 source : steam reforming of HC (natural gas, naphtha)

📖 430

※ Crisis in fertilizer (N) source (1898) → great starvation expected by 1930

→ 50% of N in our body from Harber

Nitrogen Circulation



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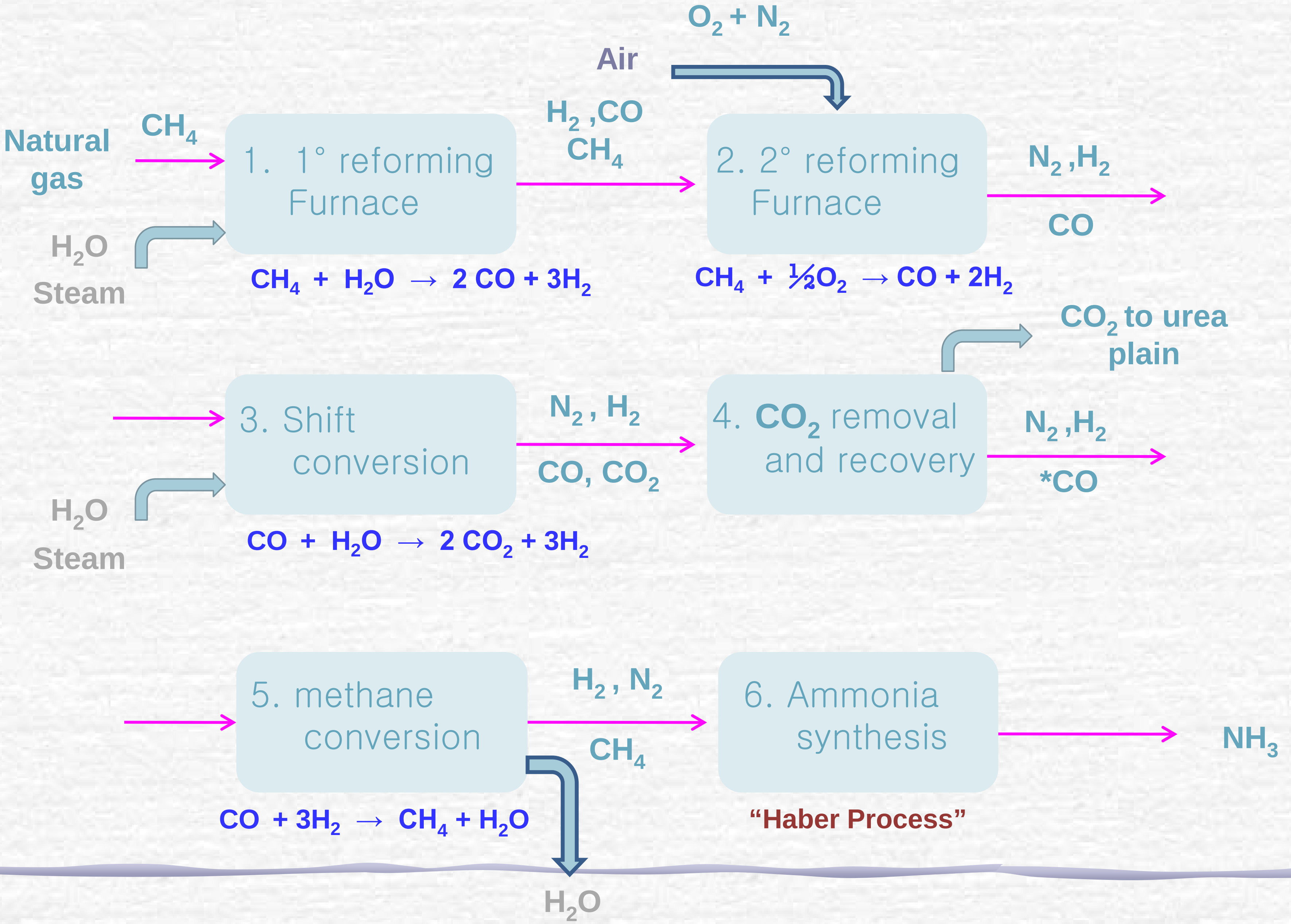
Industrial Ammonia Process



$O_2 + N_2$

Air

Natural gas

CH_4

1. 1° reforming Furnace

H_2O

Steam

$CH_4 + H_2O \rightarrow 2\,CO + 3H_2$

H_2 ,CO

CH_4

2. 2° reforming Furnace

N_2 ,H_2

CO

$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2$

CO_2 to urea plain

3. Shift conversion

H_2O

Steam

$CO + H_2O \rightarrow 2\,CO_2 + 3H_2$

N_2, H_2

CO, CO_2

4. CO_2 removal and recovery

N_2 ,H_2

*CO

5. methane conversion

$CO + 3H_2 \rightarrow CH_4 + H_2O$

H_2O

H_2, N_2

CH_4

6. Ammonia synthesis

"Haber Process"

NH_3

※ Industrial Ammonia Process

① **Primary Reformer**

$CH_4 + H_2O \rightarrow CO + 3H_2$

② **Secondary Reformer : adiabatic rxtor**

$CH_4 + 1/2\ O_2 \rightarrow CO + 2H_2$

- Partial oxidation reaction

Adjust Ratio of H_2/N_2 to 3:1

- Completion of reforming

(3) Application : 75% as fertilizer

* Biological N fixation → Green revolution

2) Chemicals from NH_3

(1) Ammonium Nitrate (AN)

① $NH_3 + HNO_3 \rightarrow (NH_4)NO_3$

② Application :

- Most "important" fertilizer (33%) : cheap

- “Safety-type" explosives w/TNT (eg) $(NH_4)ClO_4$

$$2\,NH_4NO_3 \rightarrow 2N_2 + 4H_2O + O_2$$

- Anesthesia gas

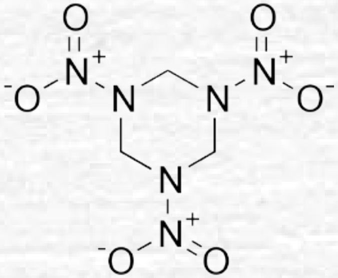
$$NH_4NO_3 \rightarrow \triangle \rightarrow 2N_2O$$

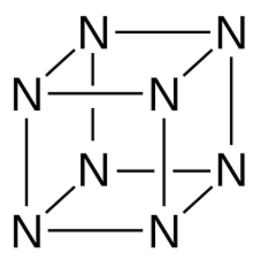
(alternative route) $NH_3 + 2O_2 \rightarrow N_2O + 3H_2O$

(2) HNO_3

① Production

※ **Nitric Acid via oxidation of NH_3**





② Application :

. **Nitrating agent with H_2SO_4**

. **Explosives :** 📖 433

AN (ammonium nitrate), cellulose nitrate, nitroglycerine

TNT, Tetyrl, Picric acid, Penta

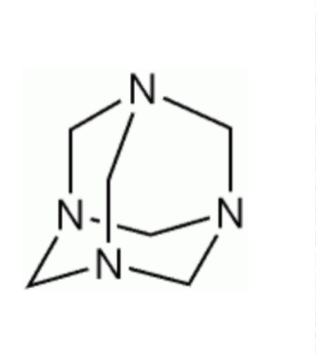
RDX

HMX, TNTAC

. **Propellants :** Nitromethane, Nitroethane

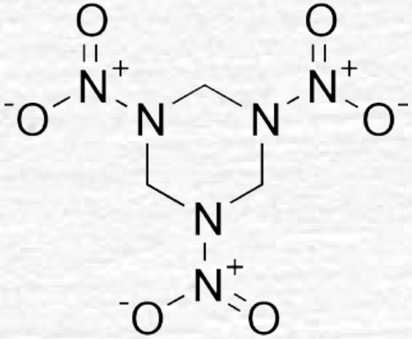
RDX: Cyclotrimethylenetrinitramine

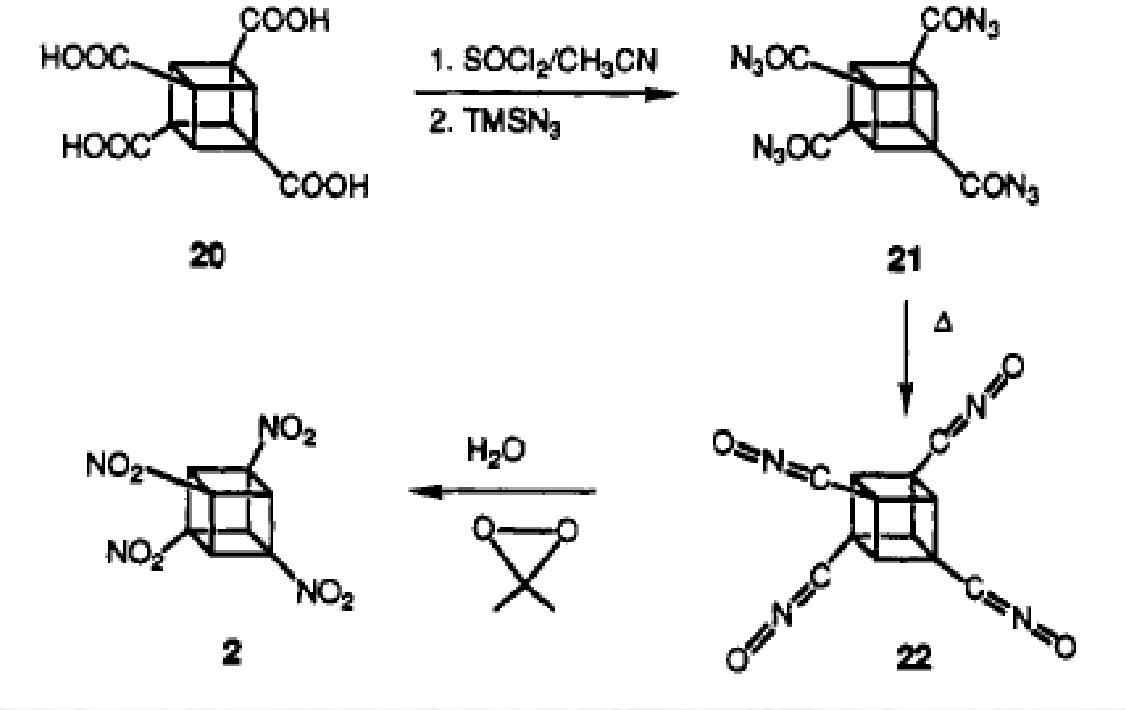
Thru Nitration of hexamine



hexamine

→ [Nitration] →





(3) Urea

※ **History Woehler (1828)**

$KOCN + NH_4Cl \rightarrow NH_4OCN$

$NH_4OCN \rightarrow NH_2CNH_2$

① **Commercial Process**

"syn gas plant" → CO_2

$CO_{2(9)} + 2NH_3(l) \rightarrow$ high P $\rightarrow NH_2CO_2NH_4(l)$ Ammonium Carbamate

$NH_2CO_2NH_4(l) \rightarrow NH_2CONH_2 + H_2O$ (Dehydration)

② **Application :**

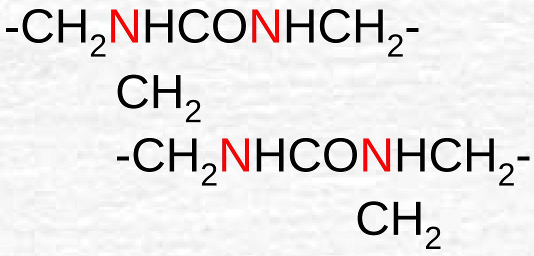
- Fertilizer : High content of N (45%) *vs* $(NH_4)NO_3$ (35%)

- Animal Feed supplement: 86 Lb / yr. head

③ Amino-Resin : " Urea-Formaldehyde" (U/F) Thermosetting resin

$NH_2CONH_2 + CH_2O \rightarrow HOCH_2NHCONHCH_2OH$ dimethylol urea

$HOCH_2NHCONHCH_2OH + CH_2O \rightarrow$



$$\begin{array}{l} -CH_2NHCONHCH_2- \\ \quad CH_2 \\ \quad -CH_2NHCONHCH_2- \\ \qquad\qquad CH_2 \end{array}$$

- fly wood, paper, fiber industry

(4) Melamine

① Production

- 1960`s : cheap "electric power"

"CaC_2" + $N_2 \rightarrow$ C + CaNCN calcium cyanamide

CaNCN → [H_2SO_4] → $CaSO_4$ + NH_2CN cyanamide

2 NH_2CN → [80 C, pH 9] → NH_2CNHCN dicyandiamide

3 NH_2CNHCN → 330 C→ Melamine

- Obsolete process now

< New process>

- **From Urea → 330 C, 100atm → Melamine +** [6 NH_3 + CO_2] (recycle)
- **From HCN**

** HCN : from Sohio process (Ammoxidaton)

◎ $CH_2=CHCH_3 + NH_3 \rightarrow CH_2=CHCN + 3H_2O + HCN + CH_3CN$

$HCN + Br_2 \rightarrow HBr + BrCN$ (cyanogen bromide)

$BrCN + NH_3 \rightarrow NH_2CN$ (cyanamide)

$3\ NH_2CN \rightarrow \triangle, P \rightarrow$ Melamine (cyanamide trimer)

② **Application :** thermo-setting resins

- Amino-resin : "Melamine-Formaldehyde" (M/F) resin

similar to U/F resin

strong to heat & hydrolysis

. Molding powder w/ cellulose : dinner ware

. corrosion resistant coating materials : washer, stove, house ware

(5) Hydrazine

① **Prpoduction**

- **NH_2CONH_2 + NaOCl → NH_2NH_2 + NaCl + CO_2**
- **Rasching process (indirect oxidation of NH_3)**

  NH_3 + NaOCl → NaOH + NH_2Cl (chloramine)

  NH_2Cl + NH_3 → NH_2-NH_2 + HCl

  NaOH + HCl → NaCl (by product ?!?!)

- **Cl_2 + 4 NH_3 + RCOR → diaza-CP + NH_4Cl + H_2O**

  diaza-CP + H_2O + H_2SO_4 → $NH_2NH_2\,H_2SO_4$ + RCOR

- **"Non chlorine" process (Atochem process)**

  $2NH_3$ + H_2O_2 + CH_3COCH_3 → NH_2-NH_2 + H_2O

  - Mechanism:

- **Strong points :**

  Low energy cost : 1/3 of "Rashing"

  High yield : ~90% *vs* 70% “Rashing”

  No by-product *vs* NaCl “Rashing”

② **Application : WW production (1980), 99×10^6 Lb. (10% increased/yr)**

. Agrochemicals (40%): herbicides, pesticides

. Blowing agent (30%) : $NH_2CON=NCONH_2 \rightarrow N_2 + H_2O + CO$

  For foamed plastics, rubbers ($N_2\uparrow$)

. Boiler additives (15%)

  Reduce oxygen from boiler water → Reduce corrosion

. Fine chemicals, pharmaceuticals, Rocket fuel (toxic, 12%)

C1- Chemicals

1) Methanol

(1) Production

① ~1913 BASF: During NH_3 production, impurity "CHO“ found

② Chemistry ; 1923

$CO + 2H_2 \rightarrow CH_3OH \quad \triangle H = -22 kcal/mol$

③ From Natural gas : Syn Gas $CO + 3H_2$

Adjust ratio with CO_2 gas (*→ recent new process)

$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \quad \triangle H = -12 kcal$

. Operation:

$CuO\text{-}ZnO\text{-}Cr_2O_3$ 230-260 C, 100-150bar

$CuO\text{-}ZnO\text{-}Al_2O_3$ 200-350 C, 50-250 bar

. Purity : 99.99 wt %

(2) Application : Chemicals (70%) + Fuel (30%)

① MTBE : Gasolin additive for high O.N

② Formaldehyde

③ HOAc, AC_2O MMA ④ Dimethyl Terephthalate (DMT)

⑤ Solvent

(3) Future Application

① Feed for Synthesis of gasoline : Mobile MTG (methanol to gasoline)process

$$CH_3OH \rightarrow H_2O + CH_3OCH_3$$

$$CH_3OH \rightarrow [\text{ZSM-5}] \rightarrow CH_3(CH_2)_nCH_3 + (\text{Aromatics} + H_2O)$$

※ Geometry of zeolite prevents formation of aromatics

- $CH_3OH + CH_3OCH_3 \rightarrow CH_2{=}CH_2 / C_3H_6$
- $CH_3OH + CO + H_2 \rightarrow C_2H_5OH + H_2O$

  $C_2H_5OH \rightarrow CH_2{=}CH_2 + H_2O$

② Energy Source :

- Feed for SNG

  $4\,CH_3OH \rightarrow CH_4 + CO_2 + 2H_2O \qquad \triangle H = 71\text{kcal/mol}$

- Methyl fuel : for power station,

  for gasoline carburator fuel additive

※Problems : high $\triangle H_{vap}$, low E content

③ SCP (single cell protein)

MeOH (or CH4, CnOH,..) → [micro-org] → protein

2) Formaldehyde

(1) Physical Property

① aq solution (35-55%)

$HCHO.\ H_2O = HO\text{-}CH_2\text{-}OH$ (99%) + $H\text{-}(OCH_2)n\text{-}OH$: n 〈10

② Trioxan : MP 64 degree

3 HCHO → trioxane

③ Paraformaldehyde :
n HCHO → $H\text{-}(OCH_2)n\text{-}OH$: n >10

(2) Source

① CH_3OH ; 92%

② C_1-C_4 Alkane ; 8%

(3) Production

※ Two route :

- Oxidative dehydration of MeOH / [Ag or Cu]
- Oxidation of MeOH / [Fe-MoO_3]

$$CH_3OH + O_2 \rightarrow HCOH + H_2O$$

① $CH_3OH \rightarrow HCHO + H_2$ △H = +20kcal

$H_2 + ½ O_2 \rightarrow H_2O$ △H = -58kcal

- Net Reaction

$CH_3OH + 0.5O_2 \rightarrow HCOH + H_2O$ △H = -38kcal

. By product : CO, CO_2 : no formic acid !

. Reaction condition

- Temp ; 600 ~720 ± 5℃
- O_2 addition ; little less than stoichiometry
- H_2O added to complete reaction

(advantage) - increase CH_3OH conversion

- Ag sintering 제어 (2-4 mouth life)
- lowers C deposition on Ag

② CH_3OH + air → HCOH + Others (CO, CO_2, formic acid)

. Reaction condition

- Temp ; 350 ~450 ℃
- Fe_2O_3/MoO_3 95-99% conversion, 91-94% selectivity

③ CH_4 or C_3/C_4 + air → HCOH, CH_3COH, ...

(4) Applicaition

① Formaldehyde condensation product , thermosetting product (-OCH_2-)

② Trioxan (from water free HCOH)

③ Aldol product:

eg) Pentaerythritol, etc

④ Glycolic acid (Dupont)

$HCHO + CO + H_2O \rightarrow HOCH_2COOH \rightarrow HOCH_2COOCH_3 \rightarrow$ EG (NG)

3) Formic acid

(1) Production

① **$CO + H_2O \rightarrow HCOOH$**

$CO + ROH \rightarrow HCOOR$

. 35% of world production

. Base catalyzed reaction of CO (under press)

with H_2O to acid

with ROH to ester (ROH = MeOH ; 70 ℃, 20-200 bar)

. Free HCOOH obtained via

- Direct ester hydrolysis
- Ammonolysis & hydrolysis

eg) $CH_3OH + CO \rightarrow HCOOCH_3 \rightarrow [NH_3] \rightarrow HCONH_2 + CH_3OH$

$HCONH_2 + H^+ \rightarrow HCOOH + (NH_4)_2SO_4$ ※prevents retro-esteritication

② As by-prod of "HC" Oxidation

- Light naphtha or butane for HOAc production
- ~ 60% of world production

(2) Application

① Fermentation : pH adjusting agent

Na, Al Salt : 가죽, textile industry

② $2\ HCOONa + NaOH \rightarrow (COONa)_2 + H_2$

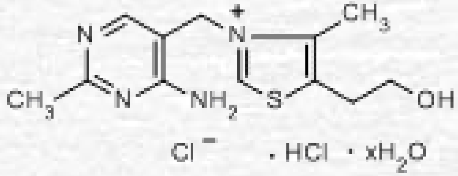
③ Introduction of formyl group in Org Synthesis

eq) Vitamine B_1

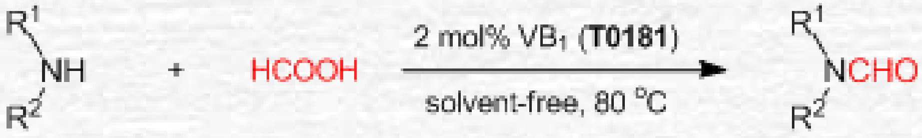
④ Amides (as solvents)

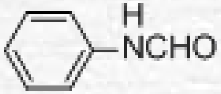
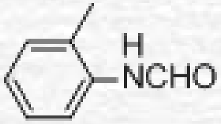
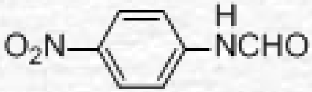
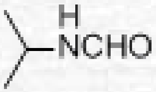
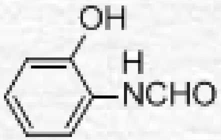
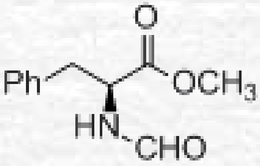
- $HCO_2CH_3 + NH_2CH_3$ (or $NH(CH_3)_2$) → $HCONHCH_3$ (or DMF)

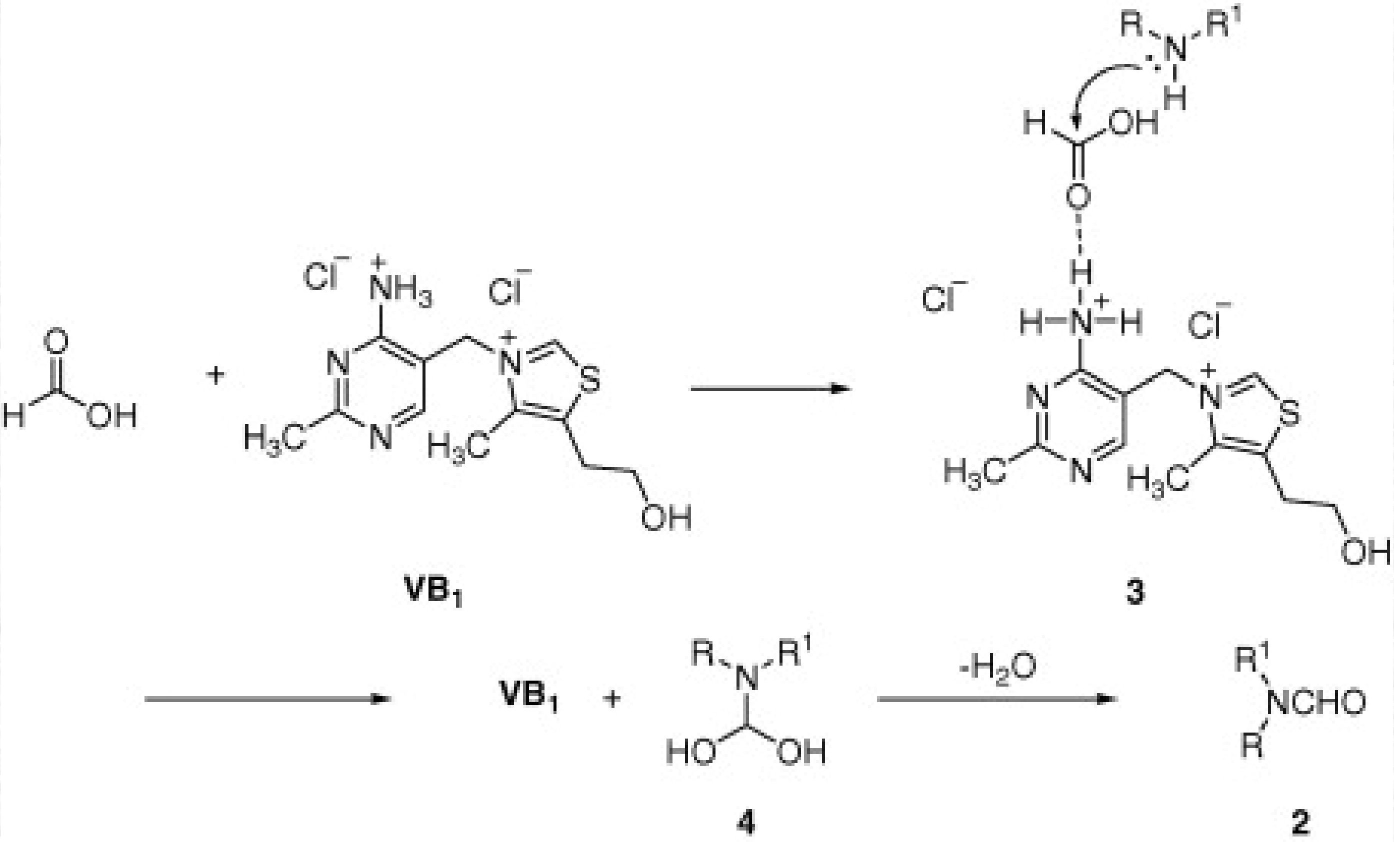
cf: $NH(CH_3)_2 + CO \rightarrow [NaOCH_3] \rightarrow HCON(CH_3)_2$ (DMF)



Thiamine Hydrochloride Hydrate
(Vitamin B_1 Hydrochloride Hydrate = VB_1)
(**T0181**)



Product	Time (min)	Yield (%)	Product	Time (min)	Yield (%)
	10	96		30	87
	20	92		30	90
	40	94		15	92
	30	88		40	85



Tetrahedron Letters Volume 51, Issue 32, 11 August 2010, Pages 4186–4188

4) Acetic Acid

※ **Monsanto process: Carbonylation of MeOH** (dramatic new process)

(1) Production

① **$CH_3OH + CO \rightarrow CH_3CO_2H$ 99+% (selectivity) (삼성 BP)**

- Catalyst : I_2-Rh

- CH_3OH from Syn Gas

※ Old process : CoI_2 catalyst (BASF), 250℃, 60 bar, lower selectivity

. USA : Monsanto process (60%)

. EU (1992) : Monsanto process (43%)

CH_3COH 산화 process (33%)

Naphtha oxidation process (18%)

② **$2CO + 2H_2 \rightarrow CH_3COOH$** (BP, Not commercial?)

③ **$CH_2{=}CH_2 \rightarrow CH_3COOH$** (Shiowha Denco process, can avoid Wacker)

5) Acetic Anhydride

(1) Production

① Ketene process ② Peracetic acid process

③ Estman-Halcon process: Coal mine near by (at Tennessee)

$HOAc + CH_3OH \rightarrow CH_3COOCH_3 + H_2O$

$CH_3COO\text{-}CH_3 + CO \rightarrow CH_3COOCOCH_3 \rightarrow \text{cell-OAc} + HOAc$

※ Ketene → Diketen 📖 **445**

Diketen + MeOH → methyl acetoacetate (pKa ??)

Aniline → acetoacetanilide

※ Alkyl Ketene → AKD (sizing agent in paper mill)

AKD + Cell-OH → Cell-O-dialkyl

(2) Application → Various acetates

※ First & only process /replaced petroleum based process 📖 **444**

Coal + O_2 + H_2O → CO + H_2

CO + H_2 → CH_3OH

HOAc + CH_3OH → CH_3COOCH_3 + H_2O

CH_3COO-CH_3 + CO → $CH_3COOCOCH_3$ (Ac_2O)

Ac_2O + Cell-OH → Cell-OAc + HOAc

cf: High cost of Gasifies (3×Expensive) ↔ cheap Coal

6) HCN

(1) Production

① Direct Synthesis:

. Dehydration of formamide

$HCONH_2 \rightarrow HCN + H_2O$

. Oxidative or dehydrogenative rxn of NH_3 w/ “HC” (esp CH_4)

$CH_4 + NH_3 + 1.5O_2 \rightarrow HCN + 3H_2O$

$CH_4 + NH_3 \rightarrow$ [Catal, w/out O_2] $\rightarrow HCN + 3H_2$

. $CO + NH_3 \rightarrow HCN + H_2O$ (C: same oxidation state)

② As by product : "Sohio Process"

- Acrylonitrile by-product from propylene
- 100,000t/y vs 183,000t/y (USA) by "direct synthesis"

(2) Application

① Production of ClCN :

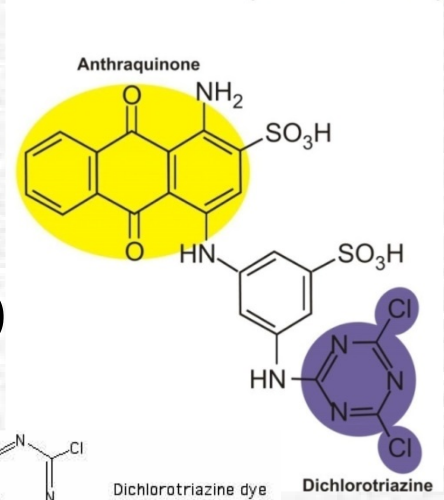
HCN + Cl_2 →[H_2O]→ ClCN + HCl 📖 410

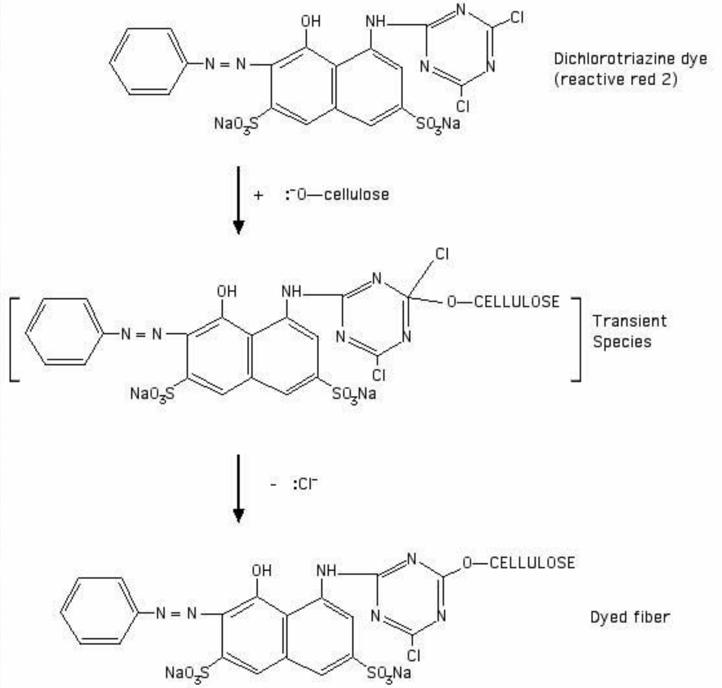
(cyanogen chloride)

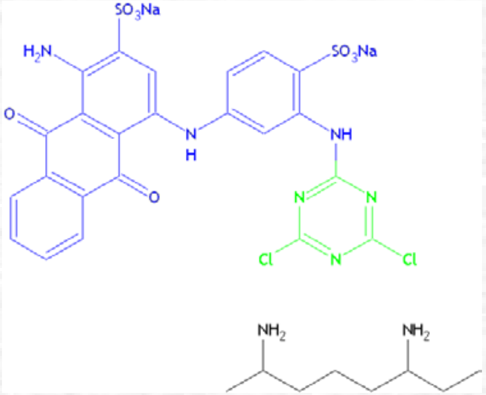
※ **3 ClCN → cyanuric chloride** (3 different reactivity)

- Starting material for agrochemicals
- Rxtive Dyes (coupling agent)

Procion Blue MX-R (reactive blue 4)



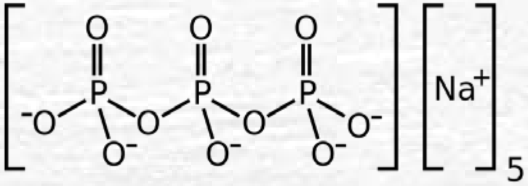


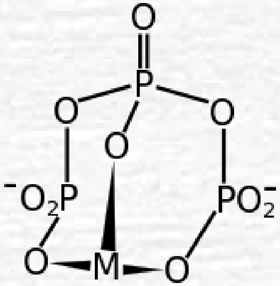


② **$3\ HCHO + 3HCN \rightarrow 3\ HOCH_2CN \quad \rightarrow [NH_3] \rightarrow \quad N(CH_2CN)_3$**

→ **NTA** (nitrilotriacetic acid)

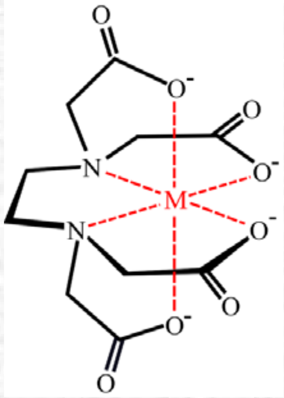
- Detergent builder as STP substitute 📖 **409**



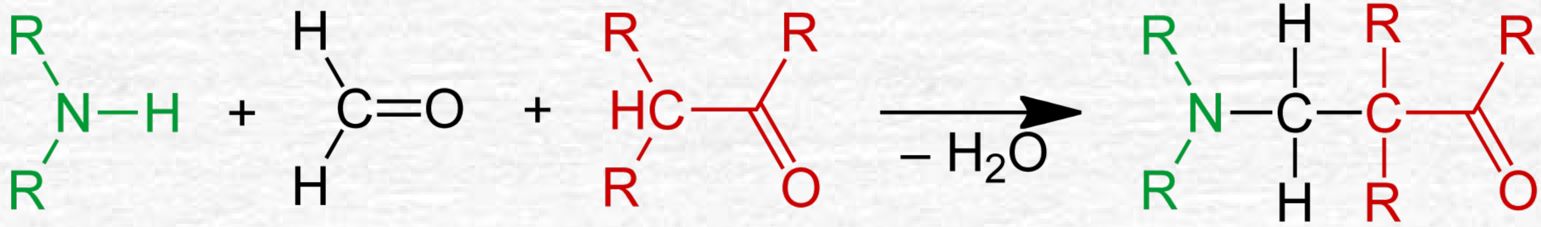


EDA + 4 HCHO + HCN → → EDTA (thru Mannich type rxn)

📖 **410**



Mannich Reaction



※ Reactions of stabilized Nu with carbonyl containing E+

- 1,3 di carbonyl
- 1,4 di carbonyl
- β-hydroxy carbonyl
- β-amino carbonyl

7) Methyl Amine, Dimethyl Amine, Trimethylamine

(1) Production

$$CH_3OH + NH_3 \rightarrow CH_3NH_2 + (CH_3)_2NH + (CH_3)_3N$$

13% 7.5% 10.5%

※ Compare with the following process: (Cost)

$$CH_4 \rightarrow CH_3Cl \rightarrow CH_3NH_2$$

※ Separation: $(CH_3)_2NH$ by HCl extraction: pKa 10.64 > 10.62 > 9.76

$(CH_3)_3N$ by NH_3 azeotrope separation

(2) Application

① **Solvent**

$(CH_3)_2NH$ + CO → $(CH_3)_2NCOH$ (DMF) (Samsung, 1999)

$(CH_3)_2NH$ + HOAc → $(CH_3)_2NCOCH_3$ (DMA) + H_2O

② **CH_3NH_2 + $COCl_2$ → $CH_3N{=}C{=}O$ (MIC) + 2HCl**

MIC + ROH → carbamate agrochemicals

※ What will happen when water is added to MIC ? (Bhophal Disaster)

③ **$(CH_3)_3N$ + EO → Choline chloride** (choline, animal feed supp)

8) Dimethyl carbonate

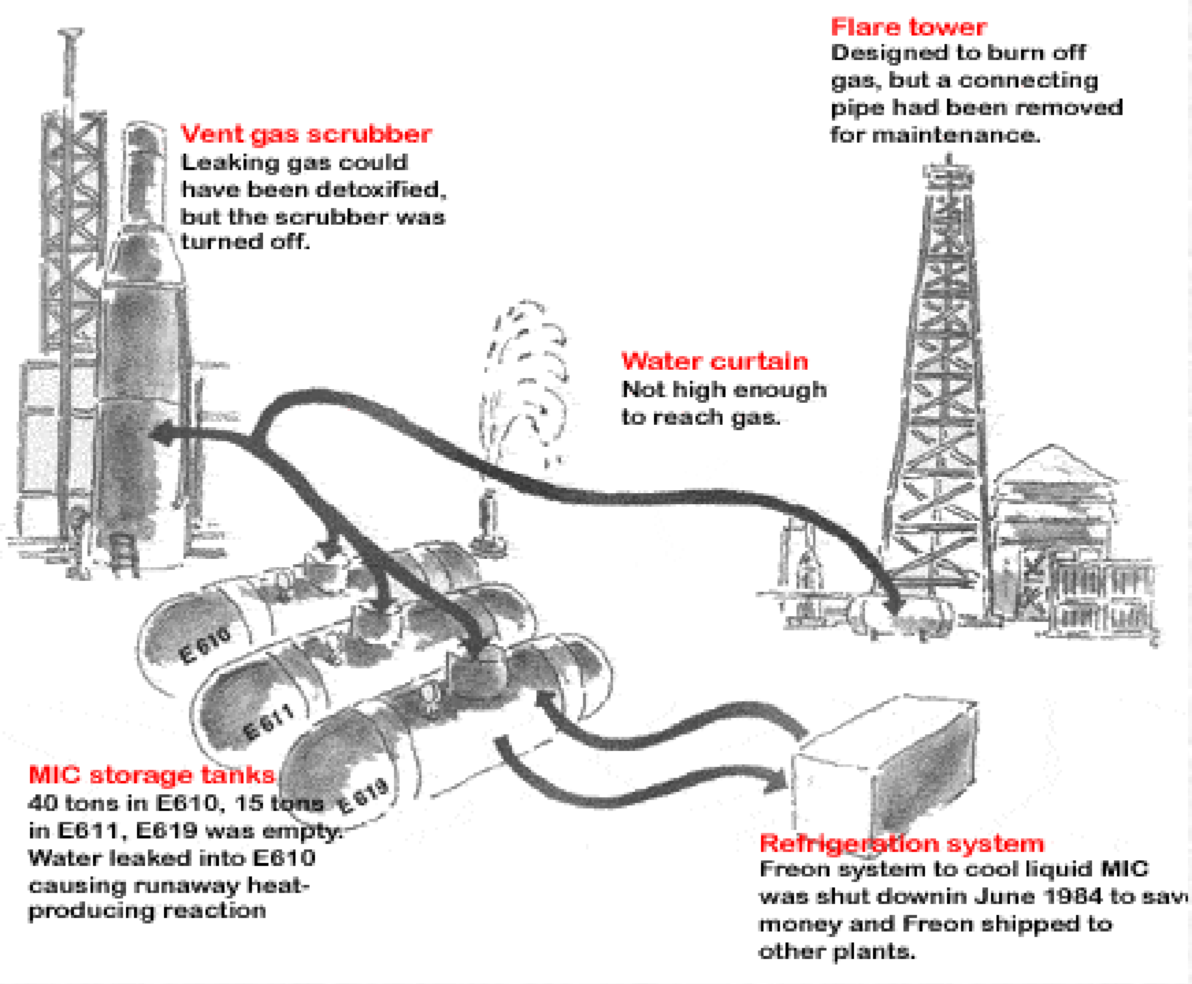
(1) Production : 2 CH_3OH + 1/2O_2 + CO → $CH_3O\text{-}CO\text{-}OCH_3$

(2) Application: substitute of phosgene, dimethylsulphate (for isocyanate, alkylation)

① Polycarbonate w/out phosgen ② Alkylation agent

Bhophal Disaster

Worst disaster in Chem Ind. History (1984,12, 2-3 📖 327)



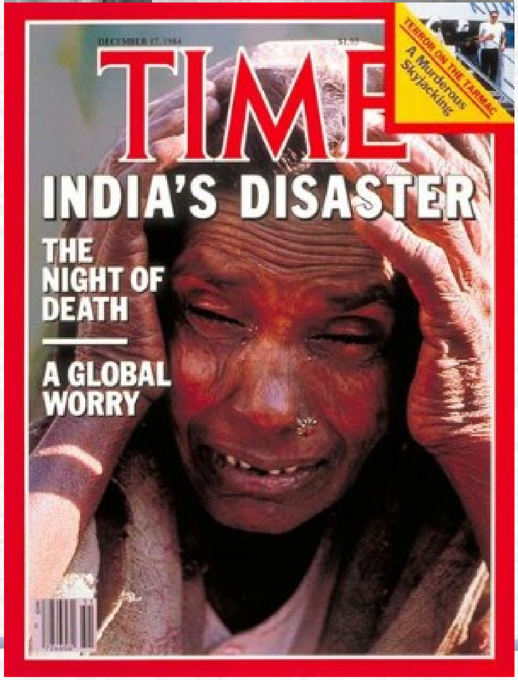
Flare tower
Designed to burn off gas, but a connecting pipe had been removed for maintenance.

Vent gas scrubber
Leaking gas could have been detoxified, but the scrubber was turned off.

Water curtain
Not high enough to reach gas.

MIC storage tanks
40 tons in E610, 15 tons in E611, E619 was empty. Water leaked into E610 causing runaway heat-producing reaction

Refrigeration system
Freon system to cool liquid MIC was shut downin June 1984 to sav money and Freon shipped to other plants.



9) Chemicals from CO

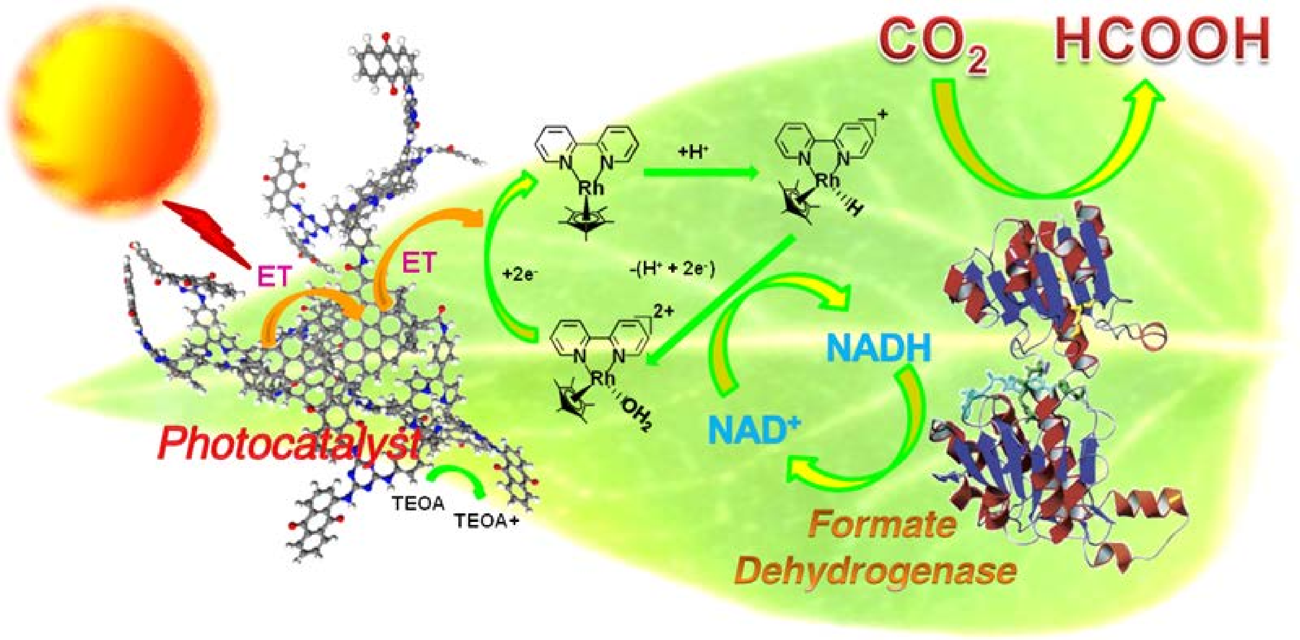
(1) Phosgene

$CO + Cl_2 \rightarrow COCl_2$ (Used for diisocyanate)

(2) Formic acid

$CH_3OH + CO \rightarrow CH_3OCOH \rightarrow HCO_2H$ (60% world production

※ Photocatalyst−Enzyme Coupled Artificial Photosynthesis



Scheme 1. Graphene-Based Photocatalyst Catalyzed Artificial Photosynthesis of Formic Acid From CO2 under Visible Light

dx.doi.org/10.1021/ja3009902 | J. Am. Chem. Soc. 2012, 134, 11455−11461

(3) Phenyl acetic acid/Phenyl pyruvic acid

Conditions: phase transfer carbonylation : 40% aq NaOH/$Co_2(CO)_8/N_4^+$

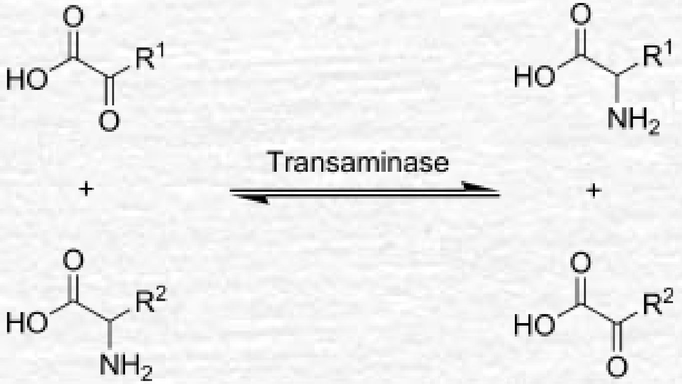
Benzyl chloride + CO + H_2O → Phenyl acetic acid + HCl

※ Benzyl chloride + 2CO + H_2O

→ Phenylpyruvic acid (*via* bis carbonylation)

→[trans-aminase]

→ L-Phe (cheapest way for L-Phe) 🕮 **458**



(4) Malonic ester form Ethyl Acetate thru carbonylation

Cl-$CH_2CO_2C_2H_5$ + CO + C_2H_5OH → Diethyl Malonate

10) Acetylene

※ Acetylene vs Ethylene (Olefine)

Olefins are

- Cheap, mass products
- Transportable by pipeline, Safe
- Less reactive than acetylene

(1) Production : keep declining 🕮 **419**

(2) Substituted by Olefin

① $CH_2{=}CH_2$: CH_3COH ($CH{\equiv}CH + H_2O$); VCM ($CH{\equiv}CH + HCl$)

$CH{=}CHOAc$ ($CH{\equiv}CH + HOAc$), $CCl_2{=}CHCl$, $CCl_2{=}CCl_2$

② Propylene : $CH_2{=}CHCN$ ($CH{\equiv}CH + HCN$)

$CH_2{=}CHCOOH$ ($CH{\equiv}CH + ROH + CO$) acrylate

③ Butadiene : $CH_2{=}C(Cl){-}CH{=}CH_2$ ($CH{\equiv}C{-}CH{=}CH_2$)

※ Increase of Butanediol production

(3) Production : CaC_2 Based Process 🕮 418

CaO(lime) + C(coke) → $CaC_2 + CO$ (→ origin of Union Carbide)

$CaC_2 + 2H_2O \rightarrow CH{\equiv}CH + Ca(OH)_2$

※ pKa value of acetylene ?

※Main cost factors

- Batch process, Coal (solid)

- Labor intensive(solid raw material)

- Waste problem:

~ 2.8t $Ca(OH)_2$(slurry in 28 ton H_2O) per 1 MT of CH≡CH

- Life time of furnace is short

- High E. cost : 10kwh/kg CH≡CH

(4) Production :Thermal process

- Feed : CH_4 ↔ Crude oil
- Very high Temp pyrolysis : 〉 1400℃
- Very Short Reation Time : 0.01 ~0.001 sec
- Rapid quenching

① **Electric arc process**

- Allothermal process w/ direct heat transfer
(electrical heating)

- Feed : HC(b.p up to 200℃) → Cracked in 1m long electric arc

② **Partial Oxidation Process** (Direct Autothermal Cracking)

O_2 (pre heated) + CH_4(pre heated)

→ (incomplete Ox, pyrolysis, 10^{-3}sec) → Quenching

(5) 용도:

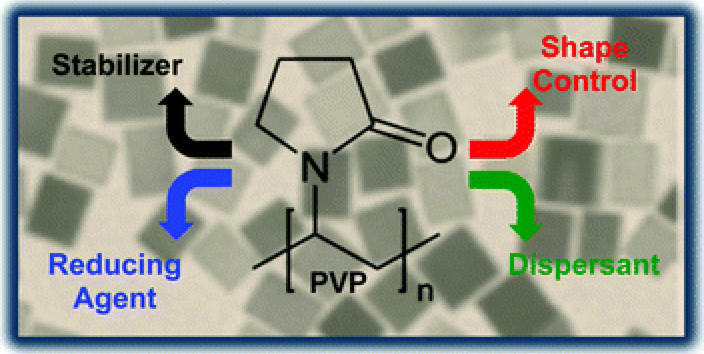
① **Welding**

② **1,4-Butandiol (BD)** 📖 420-422

$CH\equiv CH + HCHO(aq) \rightarrow HOCH_2\text{-}C\equiv C\text{-}CH_2OH \rightarrow HOCH_2\text{-}C{=}C\text{-}CH_2OH$

→ 1,4 Butandiol (Reppe process)

- ✓ 1,4 Butandiol → THF → Poly(tetramethylene ether glycol) → PU (Spandex)
- ✓ *N*-Vinylpyrrolidone : 1,4 butandiol → γ-butyrolactone →[NH_3]→ pyrrolidone →[$CH\equiv CH$]→ *N*-vinylpyrrolidone → PVP
- ✓ PVP : water soluble polymer for hair, drug excipients, NP's stabilizer



※**Other route for BD :** fast growing market

- MA →[H_2]→ butandiol
- Furfural →[-CO]→ Furan → 1,4 Butandiol
- Butadiene + Cl_2 →
- Butadiene + 2 HOAc →
- PO → ally alcohol → [H_2, CO] → $OHCCH_2CH_2OH$ → BD

  Mech?
- MA → THF (DuPont)
- Sugars → BD (Genomica)

C4 Chemicals

A. Overview

1) C4 olefines & others from Cracker

C3	0.5	
n-Butane	3	
Isobutane	1	
Isobutene	23	
1- Butene	14	
2- Butene	11	
*Butadiene	47	→ extract by aprotic solv (CH_3CN, NMP, DMF)
C5, others	0.5	

2) Separation Process:

Physical & Reactive Separation

(1) **Physical separation** : seperation of i-butene by molecular sieves

(2) Reactive separation of *i*-butene

① Oxidation to methacrolein (MAL) or MMA

② Conversion to TBME for anti-knocking agent

③ Reversible hydration to n-BuOH

B. Chemicals form C4

1) Maleic Anhydride (MA)

(1) Production

① from Benzene

- 2C atoms are wasted, benzene is burned out
- Cost of Benzene → variable factor

② Oxidation of Butadiene

③ Oxidation of n-Butene

④ Oxidation of n-Butane → Cheap raw material from refinery (since 1980), unexpectedly successful since MA is stable 🕮 304

(2) Application

① Unsaturated Polyester resin :

EG + MA → condensation polymer (*via* crosslinking by heat)

② THF

MA + H_2 → SA → γ-butyrolactone →THF → **1,4-Butandiol (BD)**

→ Oligomer → flexible PU 📖 **305**

※ Other source for 1,4-butandiol (BD)

- Acetylene → Reppe Process
- Butadiene + 2 HOAc + O_2 → $AcO\text{-}CH_2CH{=}CHCH_2OAc$ →
  $[H_2/H_2O]$ → 1,4-butandiol + HOAc
- Butadiene + Cl_2 →
- PO → allyl alcohol → hydroformylation <ARCO>

2) HMDA (& Adipic acid)

(1) Production of HMDA

① from Adipic Acid (AA)

(a) Adipic acid:

Two step oxidation : cHx → [air] → Mixed oil → [Nitric acid] → AA

- One step Ox gives low yield w/ by-product → needs a lot of nitric acid

Mechanism to mixed oils →

- Side reactions from beta-scission

Cyclohexane from benzene : depending on the cost of benzene

(b) Adipic acid + NH_3 → adiponitrile → [H_2 + NH_3] → HMDA 📖 **285**

- original propaganda : “coal + air + water” ???
- expensive raw material (AA)

② **From Butadiene** (Dupont)

Butadiene + Cl_2 → [NaCN/CuCl] → **adiponitrile** → **HMDA**

- cheaper raw material
- expensive Cl_2 → cheap NaCl and toxic (+CuCl) waste
- 1, 4-dichloro-2-butene: possible carcinogenic

③ **From Acrylonitrile** (Monsanto, from 1960's)

(a) Electric hydrodimerization

2 CH_2=CH-CN + $2H^+$ + 2e → adiponitrile → HMDA

- yields are very high, no toxic waste, no C waste
- high cost of electricity

(b) Chemical dimerization (phosphine catalyst) 📖 **286**

$2\ CH_2{=}CH\text{-}CN \rightarrow NCCH_2CH{=}CHCH_2CN$ + isomer + etc

→ HMDA

④ From Butadiene again (Dupont's new process, form 1977)

Empire strikes back!!

- **Requirements for new process**

✓ no waste of elements,

✓ no harmful intermediate,

✓ no byproduct,

NaCN → replaced by "HCN"

Butadiene + HCN →[1,4 add]→ $CH_3CH{=}CHCH_2CN$ →[isomer'n]→ $CH_2{=}CHCH_2CH_2CN$ →[anti Markof add of HCN]→ Adiponitrile → HMDA

- **Mechanism** : TM catalyst 🕮 **288**

- **Production cost for HMDA ?**

※ **Butadiene to nylon 6 and nylon 6,6** (Two for One process) 🕮 **289**

Butadiene + 2 HCN → Adiponitrile →[partial H_2]→ Aminocarpronitrile + HMDA

✓ Aminocarpronitrile → Carprolactam

✓ HMDA → nylon 6,6

(2) Other production methods of HMDA

① Newer Butadiene process

Butadiene + 2 HCN → adiponitrile

- op. at 30-150 C, 1 atm

② Obsolete processes 📖 **235**

- Adipic acid ester →[H_2]→ 1,6-hexanediol →[NH_3] → HMDA

- Cyclohexanone →[B-V oxidation] → caprolactone →
  6-hydroxy CA → methyl ester → 1,6-hexanediol → HMDA
- Methyl-ch →[ammoxidation]→
  adiponitril + glutaronitrile + succinonitrile

③ from Biomass (furfural)

- Furfural → THF → hexamethylene dichloride →

④ Double carbonylation of Butadiene 📖 **294**

3) Other C4 Chemicals

(1) BHT(butylated hydroxytoluene), **BHA** (butylated hydroxyanisol) 📖 **300**

- p-Cresol + 2 Isobutene → BHT
- Hydoxyquinone monomethyl ether + Isobutene → BHA

- Oil-soluble antioxidants for rubbers, plastics, fatty foods

(2) D-A Products

- Sulfolane 📖 **293**

Butadiene + SO_2 →[DA] → Sulfolene → Sulfolane

- Extraction solvent for aromatics

C5 Chemicals

Separation of C5 stream 📖 309

Removing cyclopentadiene by DA rxn (endo product)

1) Isoprene

(1) Separation from C5 cut

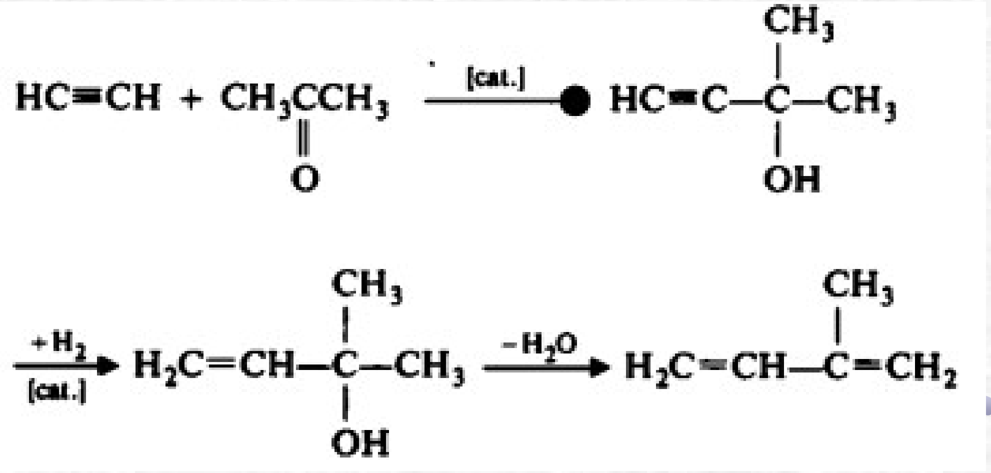
① Isolation : extractive distillation w/ aprotic solvent from C5 cut
② Dehydrogenation of isopentene
③ Dehydrogenation of isopentane

(2) Synthetic Routes

① From Acetylene

CH:CH + acetone → reduction
→ dehydration

- high price of acetylene



$$HC\equiv CH + CH_3\underset{\underset{O}{\|}}{C}CH_3 \xrightarrow{[cat.]} HC\equiv C-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_3$$

$$\xrightarrow[{[cat.]}]{+H_2} H_2C=CH-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_3 \xrightarrow{-H_2O} H_2C=CH-\overset{\overset{CH_3}{|}}{C}=CH_2$$

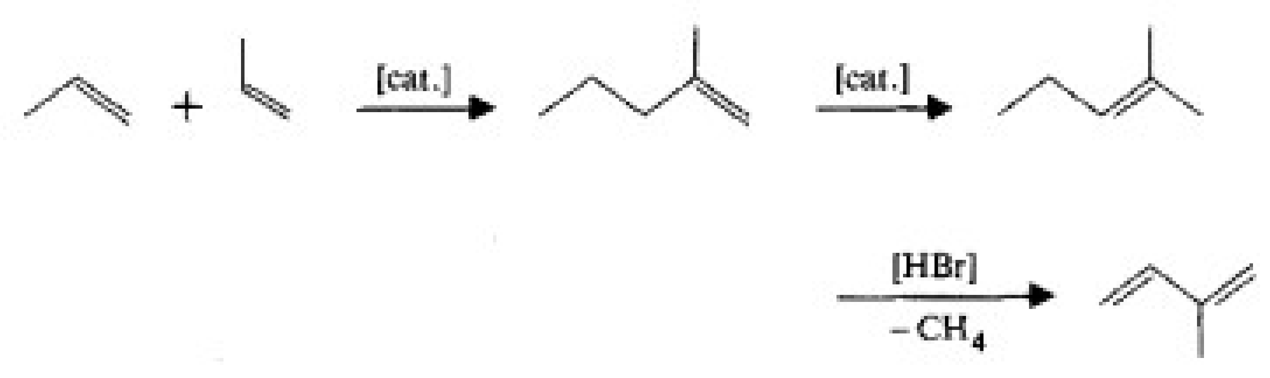
② From Isobutylene (Isobutene) via Prince reaction

Isobutene + 2 CH_2O → [H^+] → 4,4-dimethyl-*m*-dioxane
→ [thermal decomp] → Isoprene + CH_2O(recycle) + H_2O

- Mixture 중 ter-olefin 만 반응 → no need for pure isobutene feed
- very low production cost; raw material, cheap, plentiful
- 단점 : low isobutene contents in C4 cut
- formaldehyde from methanol (C1 chemical)

③ From Propylene

CH_3-CH=CH_2 → propylene dimer → isomerization
→ decomposition → isoprene + CH_4



④ Hydroformaylation of 2-butene (possible process)

$CH_3CH=CHCH_3$ + CO + H_2 → 2-Methylbutanal →

Isoprene + H_2O

- * Rh catal → branched aldehyde;
- * Co catal → linear aldehyde

⑤ Methathesis reaction (possible process)

isobutene + 2-butene → 2-methyl-2-butene → isoprene

(3) Application :

① Synthetic rubber :

- Polymerization to *cis*-1,4-polyisoprene with Ziegler-Natta catalyst

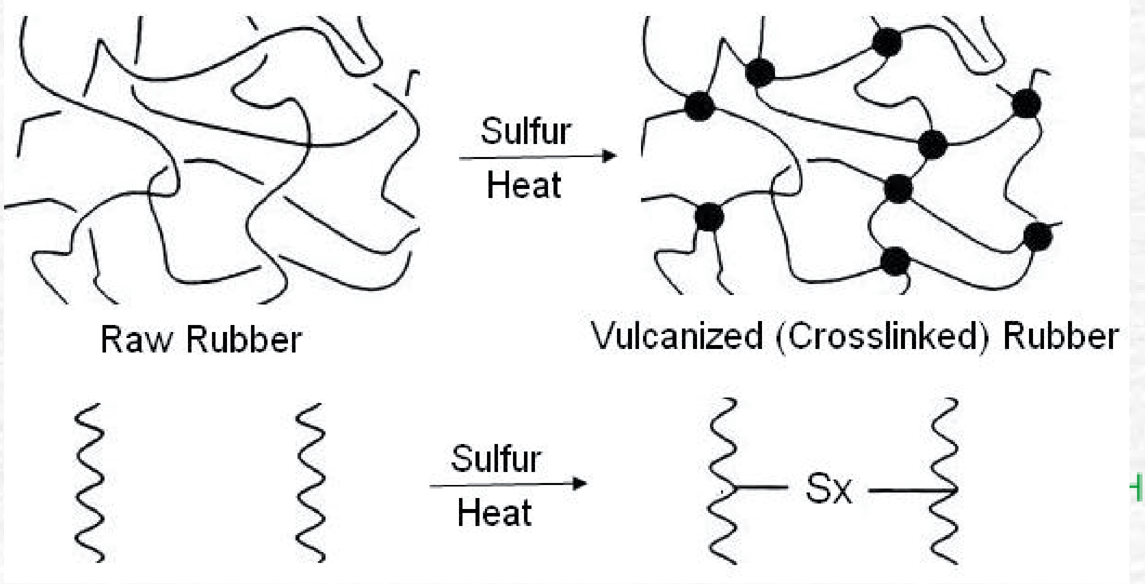
② Styrene-isoprene-styrene block (S-I-S) copolymer : elastomer

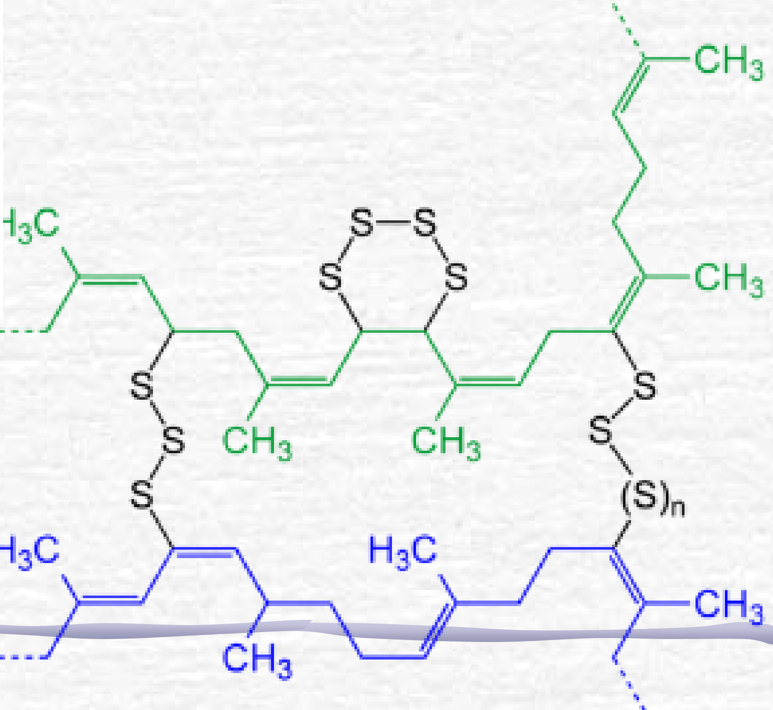
③ Butyl rubber : co-poly[isobutene + isoprene (3~5%)]

※ Rubber

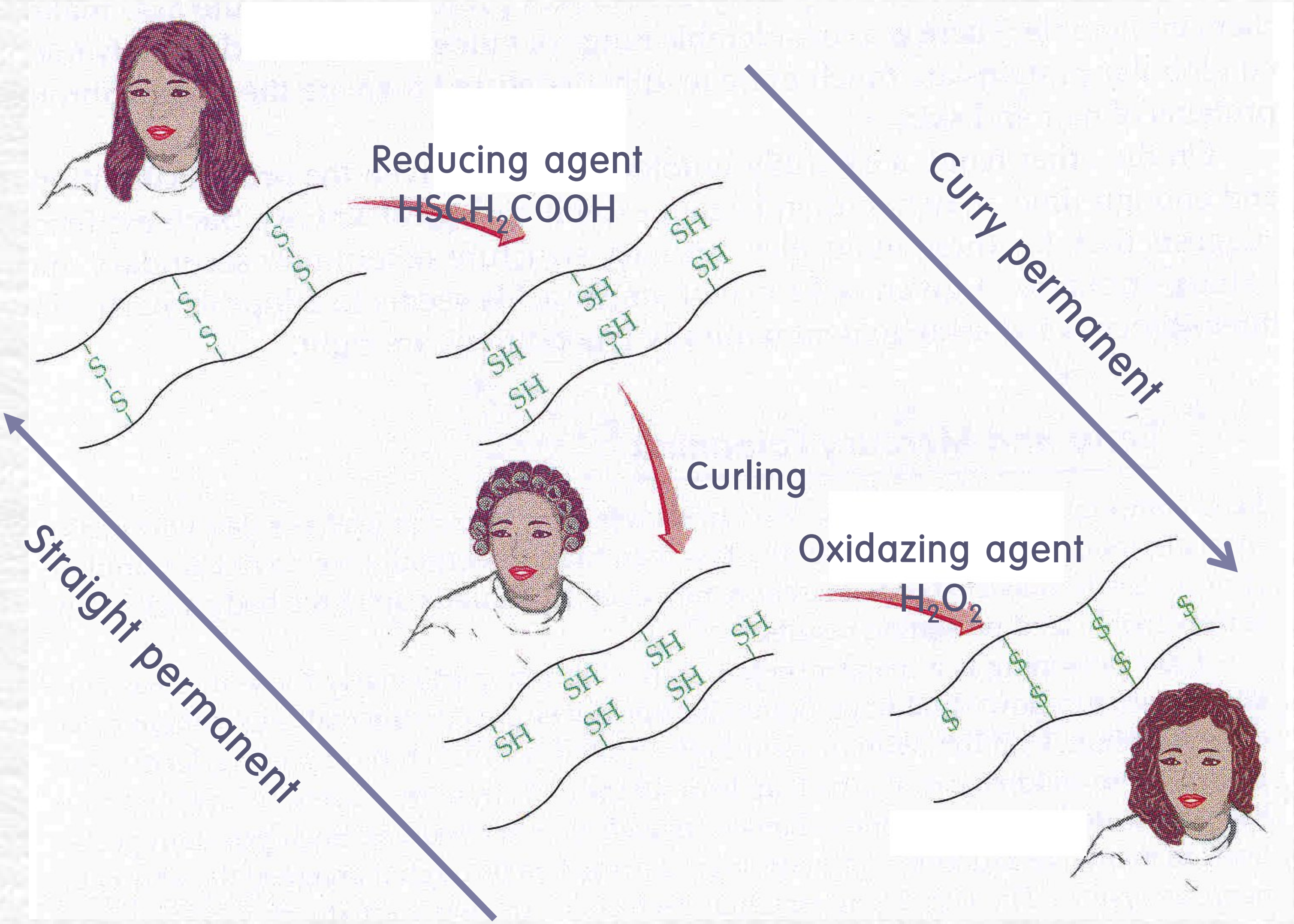
- SBR rubber : copoly[butadiene-styrene(24%)], Buta-S(1930)→SBR
- Natural rubber :
- Polychloroprene
- Nitrile rubber (NBR) : butadiene-acrylonitrile ; oil compatible
- Butyl rubber (IIR) :
- Polyisoprene : identical to natural rubber (Shell Isoprene Rubber)
- Polybutadiene
- Ethylene-Propylene rubber

Vulcanization





Hair permanent



Reducing agent $HSCH_2COOH$

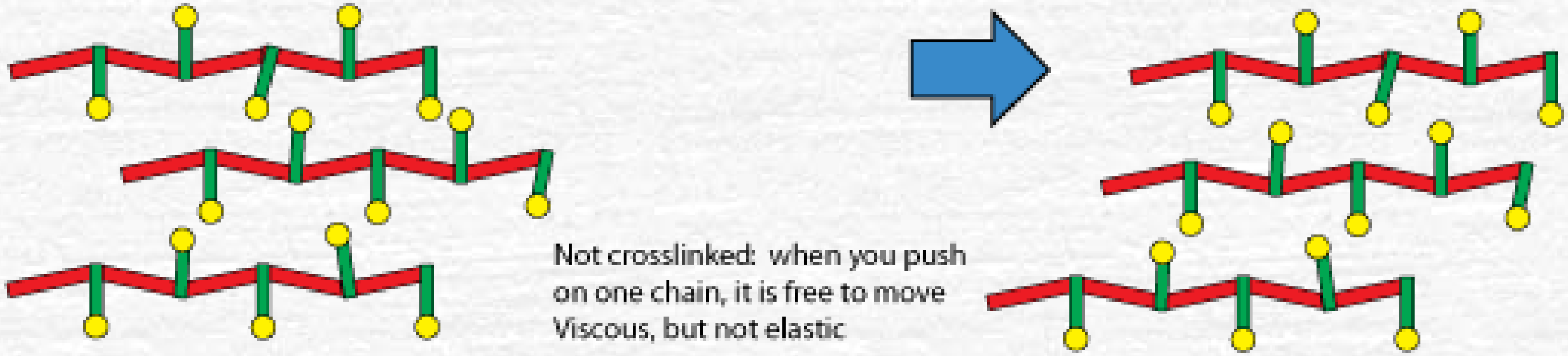
Curling

Oxidazing agent H_2O_2

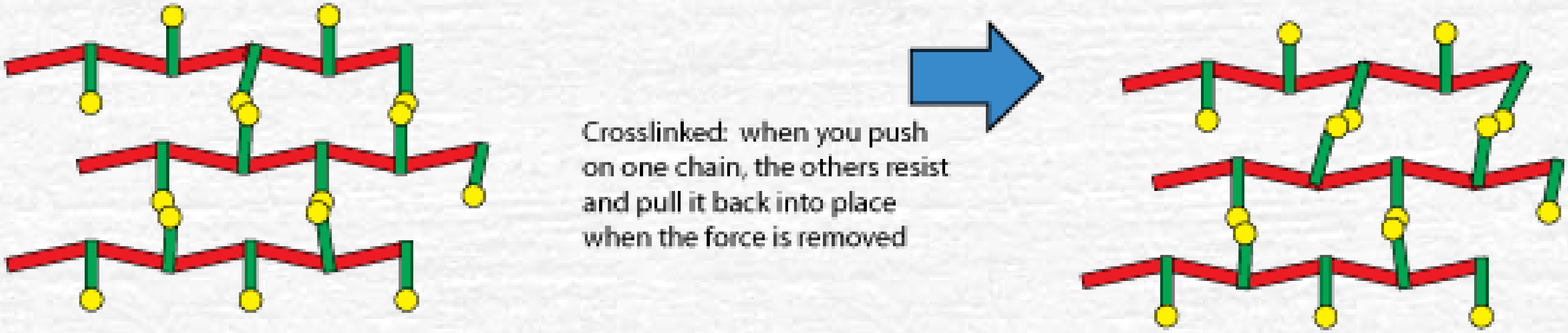
Curry permanent

Straight permanent

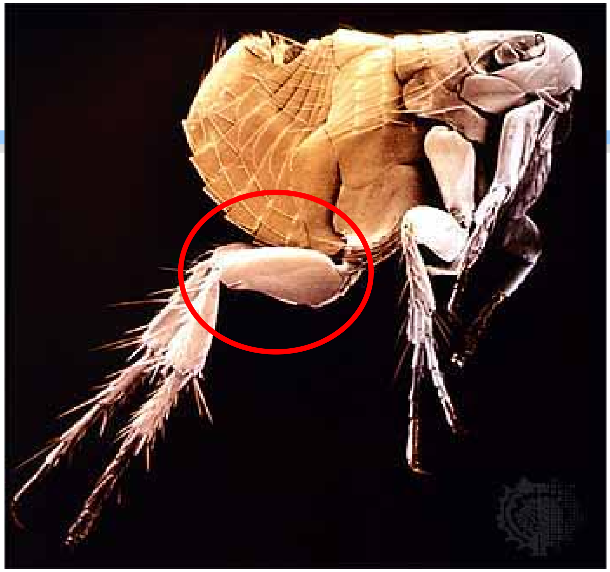
Gluten crosslinking in Food

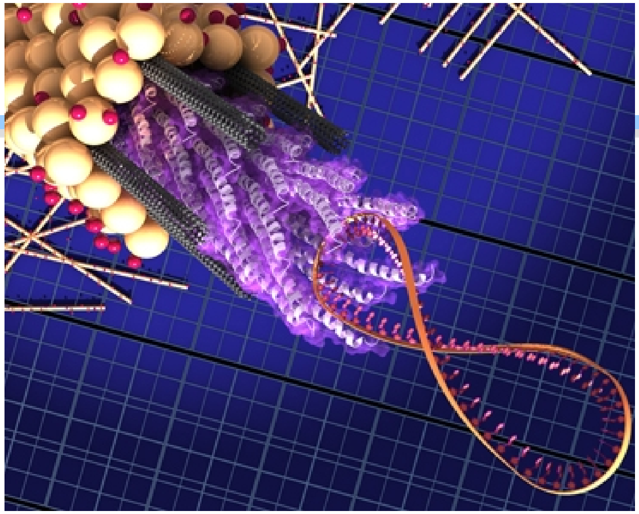


Not crosslinked: when you push on one chain, it is free to move Viscous, but not elastic

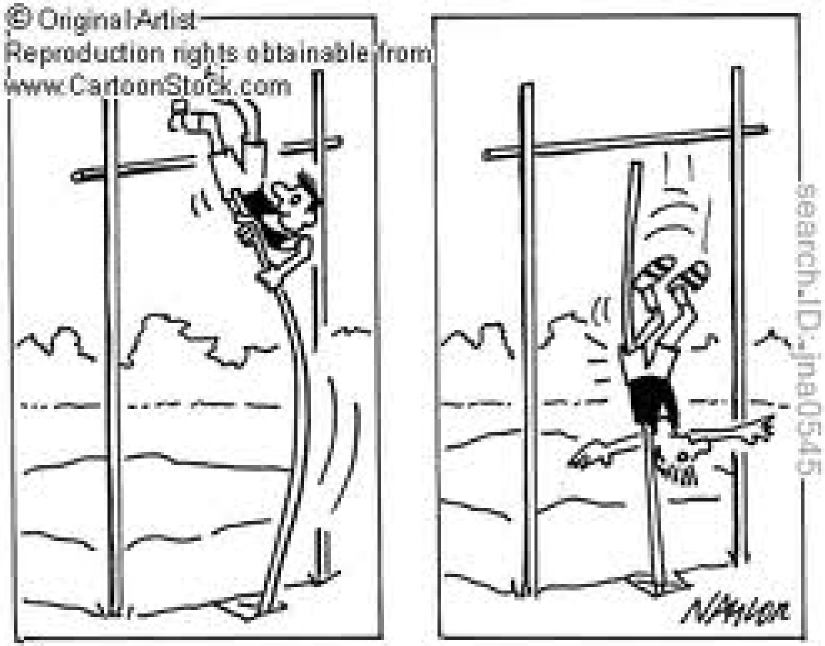


Crosslinked: when you push on one chain, the others resist and pull it back into place when the force is removed





Random coiled structure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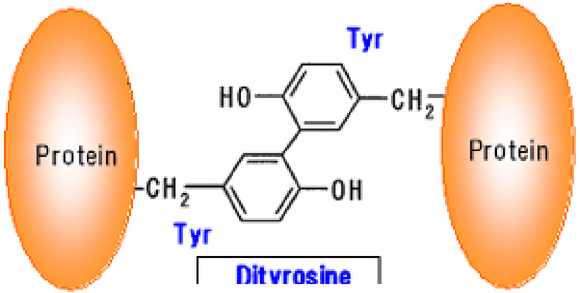
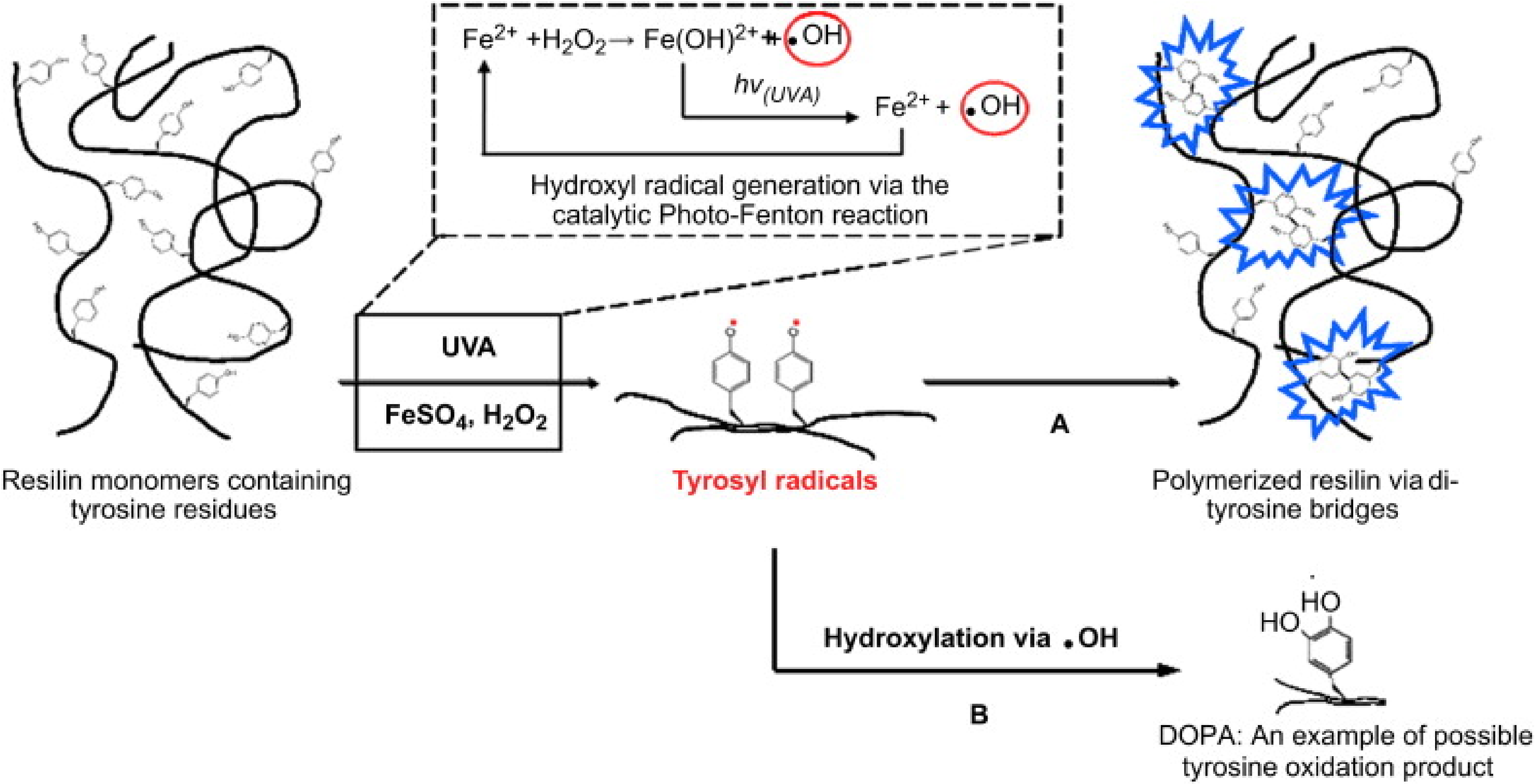


Dityrosine X-link

- ✓ High Elasticity
- ✓ High Strain
- ✓ Effficient Energy Storage

Mechanism of Resilin



$Fe^{2+} + H_2O_2 \rightarrow Fe(OH)^{2+} + {\bullet}OH$

$\xrightarrow{h\nu_{(UVA)}} Fe^{2+} + {\bullet}OH$

Hydroxyl radical generation via the catalytic Photo-Fenton reaction

UVA

$FeSO_4$, H_2O_2

Resilin monomers containing tyrosine residues

Tyrosyl radicals

A

Polymerized resilin via di-tyrosine bridges

Hydroxylation via •OH

B

HO HO

DOPA: An example of possible tyrosine oxidation product

BTX Chemicals

1) Benzene

(1) 제법

① Catalytic reforming

C_6 ~ C_{14} cut from naphtha → Reforming
(dehydogenation + isomerization)

- Major products: Benzene, Toluene, Xylene (isomeric)
- Distillation separates benzene

② Hydrodealkylation of Toluen

2 Toluene + H_2 → 2 Benzene + 2 CH_4

- Waste of C1
- Due to large excess of toluene → once major outlet
- Now, toluene is used as Octane booster → became higher value

③ **Thermal cracking of Naphtha** → for “Ethylene” production

<Steam Cracking>

ethylene (31%), ethane (3%), methane(15%), propylene(15%), gasoline (28%), etc

- pyrolysis gasoline contains lots of aromatics (5~15 ton/100 ton of ethylene)

④ **Disproportionaltion of toluene**

2 toluene → benzene + xylene

2) TDI (Toluene Diisocyanate)
MDI (Methylenephenyl Diiocyanate, Diphenylmethane Diisocyanate)

- TDI : volatile, toxic? - MDI : less volatile

(1) Production : OCI → BASF(China)

① **Toluene → DNT → [H_2] → [$COCl_2$] →[-HCl]→ TDI**
[CO + Cl_2 → Phosgene]

② **Benzene →[nitration] → [H_2] → Aniline → Ph-NCO**
Ph-NCO + CH_2O → MDI + (trimer + tetramer)
- Product as mixtures
- Aniline used as SM of dye stuff
- Environmental Problems : Nitration, Phosgene, HCl

③ Other method w/out phosgene 📖 **358**

Nitobenzene + 3 CO + ROH → Ph-$NHCO_2R$ (carbamate)
→[CH_2O]→ →[heat]→ MDI + ROH(recycle)
Op. condition for carbamate: Se or S catalyst, 100-200 C, ~100 atm
not yet commercialized.. Se removal?

④ Other method w/out nitrobenzene?

- Phenol + NH_3 → Aniline + H_2O ?
- Benznene + NH_3 → Aniline ?
- etc 📖 **356**

(2) Application

① PU Rigid Foam: Insulating material for refrigerator, housing

PU Flexible Foam: Automobile seat, mattress, etc

TDI + polyhydroxy compound + H_2O + etc → Foam

- foaming agt : low bp liquid; gas generation by heat (i.e., CCl_3F)
- foam stabilizing agent; silicone surfactant

- H_2O + isocyanate → carbamic acid → amine + CO_2 gas released
  (density of foam ~ CO_2 ~ H2O)
  Amine + isocyanate → crosslinking or branching occur

② Elastomers

③ Surface Coating agent

④ Fibers (ie., spandex, artificial leather)

3) Caprolactam 🕮 349

(1) From cyclohexanone

- Beckmann rearrangement of cH-oxime → carprolactam + $(NH_4)_2SO_4$
- NH_3 → NH_4NO_2 (explosive) → NH_2OH + $(NH_4)_2SO_4$
- 4.5 Ton of 비료/ Tone of product
- 비료 market 이 경제성 좌우 → need alternative route

(2) From cyclohexane (Japan, Toray Process)

- Cyclohexane + NOCl →[UV]→ Oxime HCl (one step)
- Photonitrosation: need engineering/UV light source (mercury lamp ~ electricity)

(3) Thru Nitrocyclohexane (Dupont)

Cyclohexane + Nitric acid → Nitrocyclohexane → cH-oxime

- can reduce the amount of by-product fertilizer
- nitration is difficult for high selectivity <one time only process>

(4) From Toluene (Italy)

Toluene → Benzoic acid → cyclohexane carboxylic acid
→ [$NOHSO_4$] Nitrosylsulfuric acid
→ caprolactam H_2SO_4 + CO_2

[SO_2 + HNO_3 → in situ Nitrosylsulfuric acid]

- Most economic process before higher price of Toluene

(5) From Cyclohexanone

- *via* B-V oxidation → caprolactone → [NH_3]→ caprolactone 📖 **351**

- “Ammoximation”
  cyclohexanone + NH_3 + H_2O_2 → ch-oxime 📖 **354**

4) Phenol 🕮 326

(1) Benzene sulfonation process :Oldest Process

- 1899~1902 picric acid needed during War
- first organic chemical process in TON scale
- large amounts of by products (sulfite & bisulfite salt)

(2) Mono Cholrobenzene Process

- high T, high P; need expensive Cl_2, NaOH → high yield
- US plant (10MT) closed

(3) Regenerative Chlorobenzene Process

- similar to oxychlorination process for VCM
- used HCl, air are used to produce chlorobenznene
- low conversion, w/ byproducts
- highly corrosive

(4) Cumene Process

- Cumene: by product of petrolium refinery
- most attractive process
- Phenol + Aceton (1:1) → not flexible to market need

(5) Toluene Oxidation process (Dow Process)

Toluene → Benzoic Acid → Phenol + CO_2 📖 **327**

- motivate by surplus toluene (low cost raw material)
- CO_2 waste(15% C), but benzoic acid by product, high selectivity
- Mechanism ? thru decomposition of phenyl benzoate or salicylic acid/p-hydroxybenzoic acid 📖 **329**

(6) Direct air oxidation of benzene

Benzene → Phenol ??

(7) Others

- Benzene + HOAc + 1/2O_2 →[Pd]→ PhOAc + H_2O 📖 **329**
  PhOAc + H_2O → phenol + HOAc
  similar to Wacker process

- Ethylbenzene hydroperoxide →[Ni]→ phenol + acetaldehyde

- Benzene + N_2O → phenol + N_2 📖 **330**

- Benzene + H_2 + O_2 → phenol + H_2O 📖 **331**

Soap and Detergents

A. Surfactants : Surface active agents

1) Definition : Hydrophobic tail (C_8-C_{18})과 hydrophilic functional group

- soluble in water → reduce surface tension
- reduce interfacial tension between two immiscible liquids (at interface)

(1) Soap

- Simple salts of alkali and fatty acid
- Less powerful cleaning action: easily protonated as weak acid
- Precipitate in hard water with Ca^{+2} or Mg^{+2}

(2) Detergents :

- Powerful cleaning action : (strong acid derivatives)
- Complex mixtures :

  eq) Builders (inorganic chemicals), corrosion inhibitor,

  anti-microbial agent, bleach, perfum, color, enzyme (lipase)
- various applications

  surface coating additive

  shampoo, hair conditioner (rinse)

  fire extinguisher, fabric softener,

  emulsifying agent, cosmetics, etc ...

2) Functions of surfactant

(1) Solubilization: for hydrophobic materials

(2) Emulsification**:** between two immiscible liquids less than 0.1 um size

(cf): colloid 10um, suspension (100nm)

(3) Dispersion **:** gas/liquid (foam), solid/liquid (dispersion)

(4) Wetting: needed in coating process

(5) Cleaning: laundering

(6) Anti forming: waste water treatment, dyeing process, painting (preventing pin hole), fermentation (food industry)

3) Classes and Production

① Anionic Surfactant

. $C_{12}H_{25}OH + SO_3 \rightarrow C_{12}H_{25}OSO_3H \rightarrow C_{12}H_{25}OSO_3Na$

(major component of detergent)

. Alkyl Benzene Sulfonate (ABS surfactant)

. Triglyceride (Fat, oil)

Fatt → $C_{17}H_{35}COO^{-}$ Na^{+} + glycerine

‘Stearate' (soap)

② Cationic Surfactant

$C_{12}H_{25}Br(Cl) + N(CH_3)_3 \rightarrow C_{12}H_{25}N^+(CH_3)_3\ Br^-\ (Cl^-)$

TMA

eg) CTAB

③ Zwitterionic Surfactant

◎Cleaning soap for babies: similar to membrane component

④ nonionic surfactant

$C_{12}H_{25}OH + (2\text{-}3)CH_2(O)CH_2 \rightarrow C_{12}H_{25}CH_2O(CH_2CH_2O)_nH$

cf: Nonyphenyl PEG for semiconductor industry

B. Production of ABS detergent (hard detergent)

1) Synthesis method ① Propene oligomerization

$CH_2CH{=}CH_2 \rightarrow \langle R\text{-}CH{=}CHCH_3 \rangle$

propylene tetramer or trimer

② Alkylation w/ Benzene

③ Sulfonation :

2) Problems

- ABS detergent is not fast biodegradable

(∵) numerous branched side chain)

- Severe pollution in river & lakes: Sud problem

- Banned since 1965 (USA)

→ LAS (substituted by Linear Alkyl Sulfonate; LAS)

C. Production of LAS detergent

1) Linear primary alcohol (or α-olefines)

① Oligomerization of Ethylene "by Shell"

- Shell process (Shell Higher olefin process ; SHOP)
- by Olefin Metathesis reaction and hydroformylation
- can get α-olefins (C_{10}-C_{18}) or oxo alcohol (C_{10}-C_{18})

② Oligomerization of Ethylene by Ziegler Catalyst

- Ziegler catalyst : $Al(Et)_3$

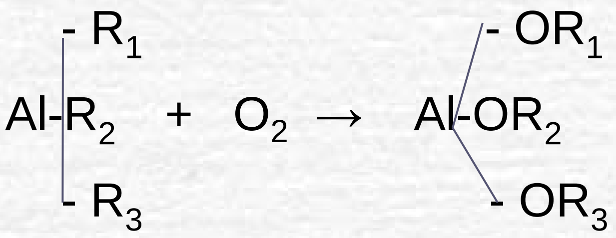
- growth reaction or "Build up reaction" of Ethylene

$$
\begin{array}{llll}
 & -\ CH_2CH_3 & & -(CH_2\text{-}CH_2)_{x+1}H \\
.\ Al & -CH_2CH_3\ +\ CH_2{=}CH_3 & \rightarrow & Al\text{-}(CH_2\text{-}CH_2)_{y+1}H \\
 & -\ CH_2CH_3 & & -(CH_2\text{-}CH_2)_{z+1}H
\end{array}
$$

**chain length is proportional to press

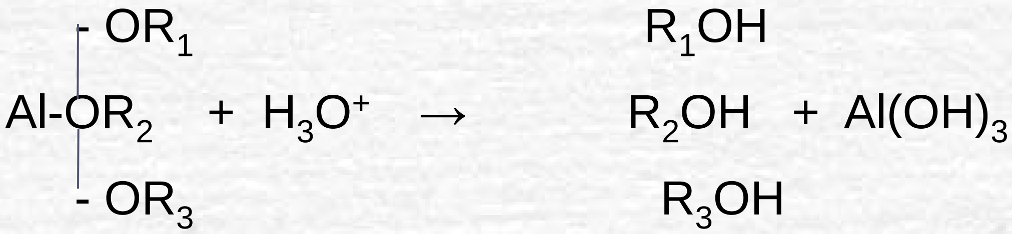
$$
\begin{array}{llll}
 & -(CH_2\text{-}CH_2)_{x+1}H & & -\ (CH_2\text{-}CH_2)_{x+1}H \\
.\ Al & \text{-}(CH_2\text{-}CH_2)_{y+1}H & \rightarrow & Al\text{-}(CH_2\text{-}CH_2)_{y+1}H\ +\ CH_2{=}CH(CH_2CH_2)_zH \\
 & -(CH_2\text{-}CH_2)_{z+1}H & & -\ H \qquad\qquad \text{"side rxn"} \\
 & \downarrow CH_2{=}CH_2 & & \downarrow CH_2{=}CH_2 \\
 & Al(Et)_3\ +\ \alpha\text{-olefines} & & -\ (CH_2\text{-}CH_2)_{x+1}H \\
 & & & Al\text{-}(CH_2\text{-}CH_2)_{y+1}H \\
 & & & -\ CH_2CH_3
\end{array}
$$

- Oxidation of trialkyl Aluminum



$$\mathrm{Al}\begin{cases}-R_1\\-R_2\\-R_3\end{cases} + O_2 \rightarrow \mathrm{Al}\begin{cases}-OR_1\\-OR_2\\-OR_3\end{cases}$$

- Hydrolysis of aluminum alkoxides



$$\mathrm{Al}\begin{cases}-OR_1\\-OR_2\\-OR_3\end{cases} + H_3O^+ \rightarrow \begin{matrix}R_1OH\\R_2OH\\R_3OH\end{matrix} + \mathrm{Al(OH)_3}$$

③ Wax caracking

- Paraffin wax : n-alkanes(C_{18}-C_{56})
- Wax → C_5-C_{20} alkanes

  95% are α-olefines
- Cheap source → AOS 세제

④ Seperation of branched HC from Kerosine(~ C_{12})

- by Zeolite(5 A diameter, clay mineral) or Molecular Sieves
- by Urea crystals : complex formation with urea : only straight alkyl chain

2) Alkylation with benzene :

3) Sulfonation

※AOS(α-olefines sulfonate) :

$R`CH=CH_2 \rightarrow [SO_3] \rightarrow R\text{-}(CH=CH)CH_2SO_3Na$ or

$RCH(OH)\text{-}CH_2CH_2SO_3Na$ + isomer "mixture"

D. Detergent and Environment

1) Builders : Inorganic Chemicals

- boost foam, cleaning action
- for less use of detergent affording similar properties

※ Classed : $NaSO_4$, $NaCO_3$, Na Borate(Boxax), Sodium sillicate,
Sodium tripolyphosphate(STPP)

(1) polyphosphate : PO_4^{-3} (orthophosphate)

esp) sodium tripolyphsophate ; $Na_5P_3O_{10}$ <u>STPP</u>

① Structures and Functions

- strong chelating agent : reduce Ca^{+2}, Ma^{+2} ions in hard water

  → no water spotting "in dish washer"

eq) $Ca^{+2} + HPO_4^{-2} \rightarrow CaHPO_4$ $K = 5.02 \times 10^2$

$Ca^{+2} + P_3O_{10}^{-5} \rightarrow [CaP_3O_{10}]^{-3}$ $K = 1.25 \times 10^8$

esp) P_3O_{10} forms tridentate, six member complex

- by increasing basicity of water → completely ionize detergent's functional groups → boosting detergent power

② cheap, non toxic:

contains 35-50% in household detergent

③ Environmental Effect

- slowly hydrolyze into simple phosphate
- good nutrient ; esp for algae
- eutrophiacation : “decomposing algae"

→ proliferation of algae & microorganism → reduce dissolved O_2 contents

- increase B.O.D (Biological oxygen demand)
- Banned in USA & Canada since 1970-

*Eutrophic : rich in dissolved nutrients but often defficient in oxygen

(Cf) *mesotrophic : having moderate amounts of dissolved nutrient

*oligotrophic : having abundant DO w/out plant nutrient

Halogen Compounds

A. Chloromethanes

CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4 (+ simple chloro HC)

1) general methods : Chlorination of methane

$CH_4 \rightarrow [Cl_2] \rightarrow CH_3Cl + CH_2Cl_2 + CHCl_3 + CCl_4 + HCl$

- get mixtures : (redical phathways : $Cl_2 \rightarrow Cl.$)
- depends on the economy of HCl by product ($Cl_2 \rightarrow HCl$)
- price of methane ?

2) Classes

(1) Methyl chloride

① Production

$$CH_3OH + HCl \rightarrow CH_3Cl + H_2O$$

vapor(or liq) phase, ~400℃ /catal

- HCl sink for another process
- CH_3OH : expensive raw material

② Application 📖 **412**

- Chloromethlysilane → Silicone resin

$$CH_3Cl + Si(Cu) \rightarrow (CH_3)_2SiCl_2 + Cu$$

$$(CH_3)_2SiCl_2 + H_2O \rightarrow (CH_3)_2Si(OH)_2 \rightarrow \text{polysiloxane (silicone)} + H_2O$$

- Freezer

(2) Methylene chloride

- direct chlorination of methane
- $CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 +$ etc
- powerful solvent

(3) Chloroform

- direct chlorination of methane
- old days : anesthesia
- solvent (may be carcinogen)
- raw material for "Fleon" production

(4) CCl_4

① Production

- Chlorination of CS_2

$$CS_2 + 3Cl_2 \rightarrow [Fe, 30℃] \rightarrow CCl_4 + S_2Cl_2$$
$$CS_2 + S_2Cl_2 \rightarrow CCl_4 + 6S$$

cf) Production process of CS_2

$C + 2S \rightarrow CS_2$

$CH_4 + 2S + O_2 \rightarrow CS_2 + 2H_2O$

- Chlorinolysis of Hydrocarbon

C3 “CH” + $Cl_2 \rightarrow CCl_4$ + other chloro HCs

eg) $CH_3CH{=}CH_2 + Cl_2 \rightarrow CCl_4 + Cl_2C{=}CCl_2 + 6HCl$

Perchloro dry cleaning

② Application

- solvent, fire extingisher, etc
- raw material for "Fleon"

(5) Others

CH_3Br

- used as soil fumigant (against termite)
- life time 1.5-2 yrs, class I ozone depleter

3) Environmental Issues

(1) carcinogens : $CHCl_3$, Cl_3CCH_3, Cl_2HCCH_3, CCl_4

(2) chlorination of drinking water: How safe at HOT summer?

Humic acid + Cl_2 → THM

(3) vinylchloride(VCM) gas

VOC from 2억 lb/yr from PVC plant → liver cancer, birth defects

B. Freon : Fluorochlorocarbons

1) General :

(1) Strong C-F bond : BE = 116kcal

(cf: C-C 83 kcal, C=C 146 kcal, C-Cl 81 kcal)

→ No reaction like SN1/SN2 or E1/E2

Short C-F bond distance ; 1.3-1.4 Å (cf: C-Cl ~1.8 Å)

→ steric repulsion

(2) Thermal & chemical stable, low toxicity

2) Freon nomenclature (industry)

Freon (xyz) : Z = #F, Y = #H+1, X = #C-1

eg) CFC (w/out Hs) *vs* HCFC (w/ Hs)

- CFC : Cl_3CF (Freon 11), Cl_2CF_2 (Freon 12)
- HCFC : CF_3CHCl_2 (HCFC-123)

3) Production : Chloro “HC” + HF → Freon + HCl

*condition : $SbCl_5$ (catalyst), 50℃

- $CCl_4 + 2HF \rightarrow CCl_2F_2 + 2HCl$

* Mechanism for $SbCl_5$ (Antimony pentachloride)

① $SbCl5 + HF \rightarrow SbCl_XF_y + HCl$

(X+Y=5)

② Cl Cl

C Sb → CCl_3F + $Cl\text{-}SbCl_4$ ($SbCl_{X+1}F_{Y-1}$)

Cl F

Cl/F exchange rxns

③ $SbCl_{X+1}F_{Y-1} + HF \rightarrow SbCl_XF_Y + HCl$

- $CHCl_3$ + HF → $CHClF_2$ + 2HCl

$CHClF_2$ →[△, 600-800℃] → $CF_2=CF_2$ + 2HCl

Thru "difuluorocarbene" mechanism

$CHClF2 \rightleftharpoons :CF2 + HCl$

$2 :CF2 \rightleftharpoons CF2=CF2$

4) Application

(1) Aerosol propellants or refrigerant fluids
(low b.p., non-flammable, non-toxic)

eg) CCl_2F_2, Freon12 *largest use in aerosol, freezer
PU blowing agents

eg) refrigerant fluidics: Freon22, Freon13, Freon23
CHClF2, CClF3, CHF3

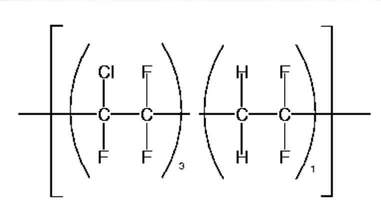
eg) aerosol : $CClF_2CClF_2$ (1,2- dichlorotetrafluoroethane)

(2) Thermal, chemical resistant polymer

eg) "Teflon"

$CF_2=CF_2$ → $(CF_2\text{-}CF_2)n$ (polytetrafluroethylene)

eg) Kel-F : polyvinylidene foluoride



5) Properties and environmental effect

(1) colorless, oderless, essentially stable *, no toxic(?)

* eg) CF_2Cl_2 →[△, 800℃]→ only 1%만 decompose/yr

* nonbiodegradable

* used as wafer cleaning solvent

(2) Released to air (as aerosol, refrigerant)

eg) Freon11 + Freon12 : 48×10^8kg/yr : 1973

(3) Photo-dissociate in stratosphere → ozone layer → melanoma

* **Nobel Prize in Chemistry** 1995 (P.Crutzen, **M.Molina**, S.Rowland) 🕮 **415**

$CCl_2F_2(g)$ + uv light (<260nm) → $CF_2Cl(g)$ + $Cl(g)$ 🕮 **739**

$Cl(g) + O_3(g) \rightarrow ClO(g) + O_2(g)$ (destroy ozone via chain reaction)
$ClO(g) + O_3(g) \rightarrow Cl(g) + 2O_2(g)$

$NO_2(g) \rightarrow NO + O$ (under UV)
$ClO(g) + NO(g) \rightarrow Cl\text{-}ONO \rightarrow 2\,NO_2(g) + Cl$

*one chlorine atom has an atmospheric lifetime of one to two years and may destroy 100,000 ozone

$NO_2(g) \rightarrow NO + O$ (under UV)
$NO + O_3(g) \rightarrow NO_2 + O_2(g)$
$NO_2 + O \rightarrow NO + O_2(g)$ (Now, major route for ozone layer depletion) 🕮 **739**

* Banned in production (1978) → as substitutes : CF_3CHCl_2 (HCFC-123) 🕮 **416**

(2) Some comp`ds are quite stable

① VCM : very stable in air → half life 15 years

② CCl_4 : not susceptible to environmental degradation

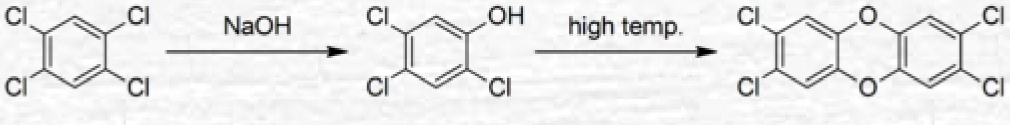
Pollution and Green Chemistry

A. Dioxine (2,3,7,8-tetrachloro-dibenzo-p-dioxine, TCDD)

1) Seveso disaster (Italy, 1976)
  - 2kg of TCDD was released by accident

2) Toxicity : one of the most poisonous substances ever known
  - Vietnam war (as an impurity in agent orange), Incinery plant
  - 3 μg/g soil kills bird, fish, ..
  - accumulate thru food chain,

3) Mechanism of formation
  - during herbicide production



1 2 3

  - during incineration of chlorine-containing waste? 📖 **755**

B. PCB (polychlorinated biphenyl)

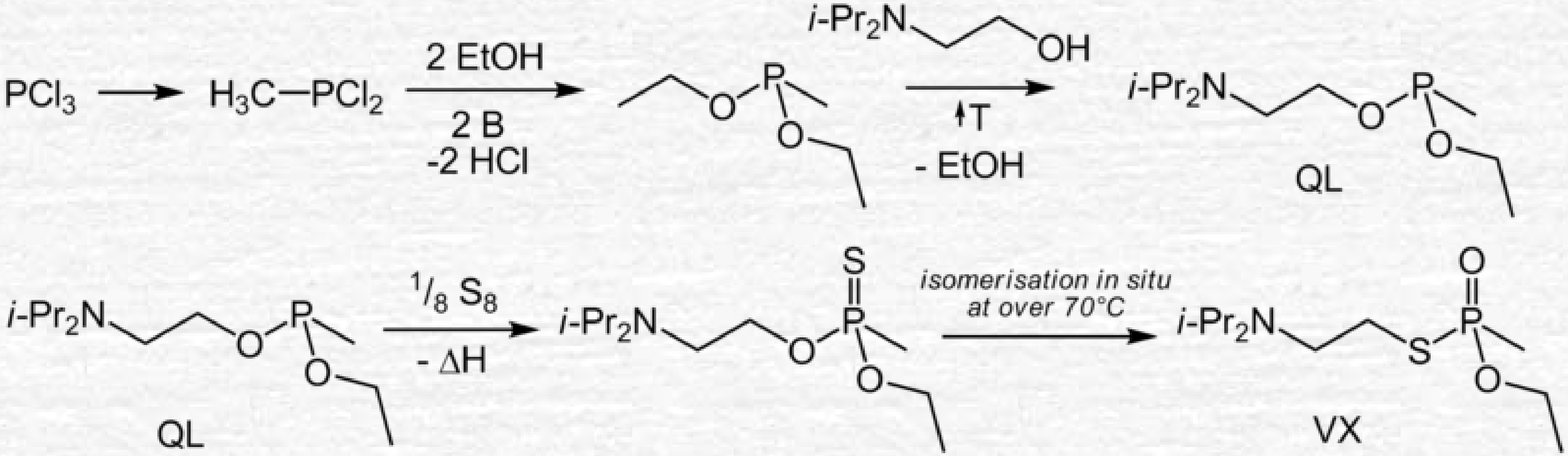
1) Production : direct cholrination of biphenyl

2) Application :
- resistant to acid, base, heat, oxygen
- dielectric material for capacitors or transformer
- plascicizer

3) Toxicity :

Chemical Weapon & Chemical Demilitarization

VX (nerve agent)



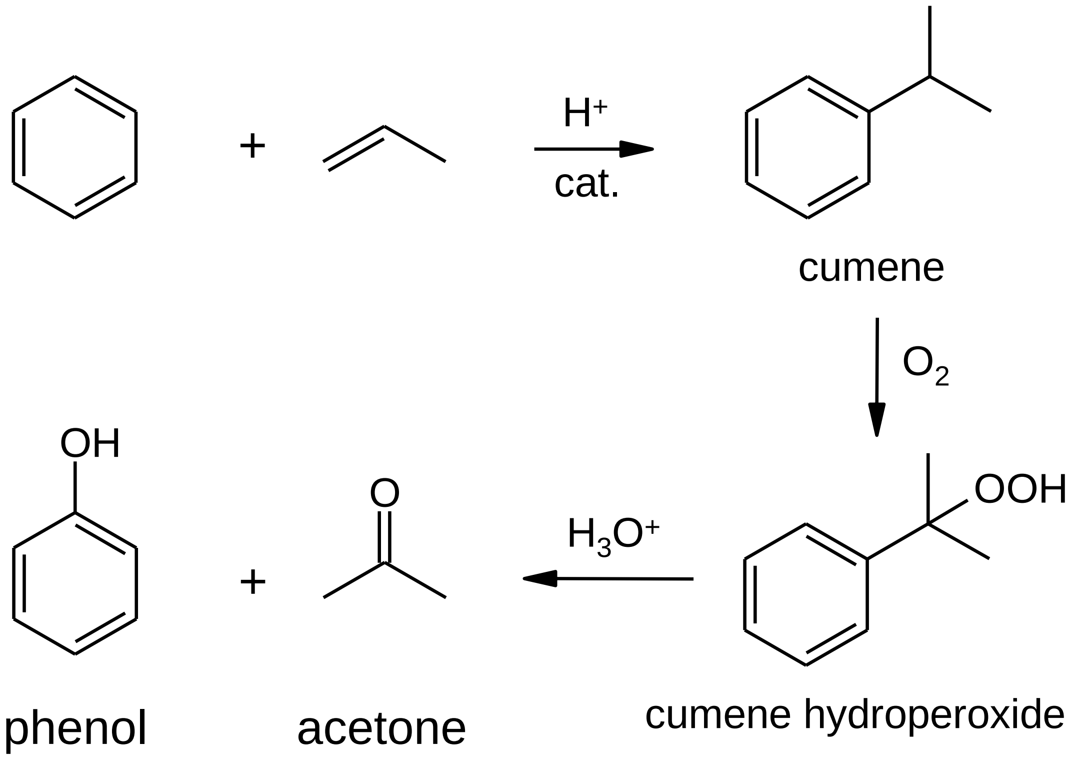
Detoxification Mechanism

Organic Synthesis to Fine Chemicals

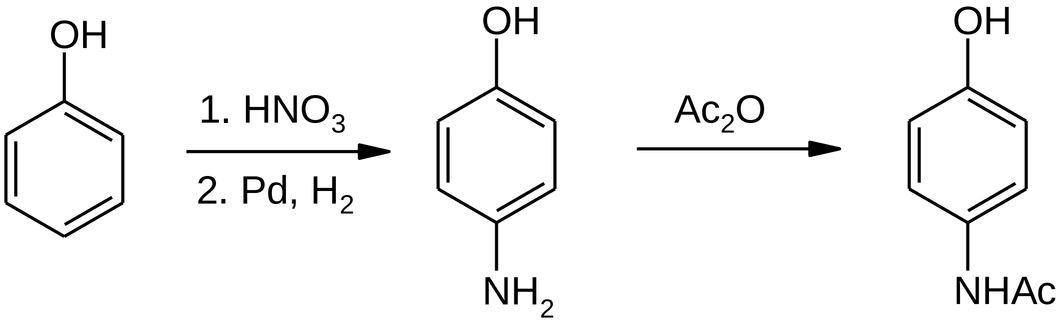
☐ Broad applications to Fine chemicals

- Petrochemicals
- Pharmaceuticals
- Agrochemicals
- (Bio)Polymers
- Dyes & Pigments
- Cosmetics
- Food (Additives)
- Household products
- Electrochemicals
- Display materials
- Semiconductors
- Organic electronics
- and so on…..

Petrochemicals



Pharmaceuticals & Medicinal Chemistry



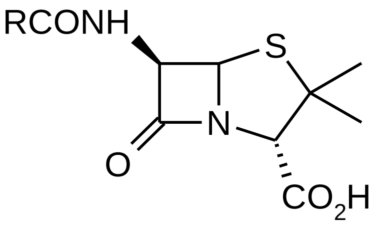
Tylenol

Antibiotics

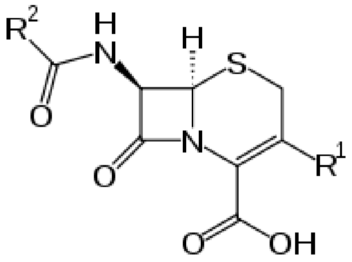
■ Beta Lactams

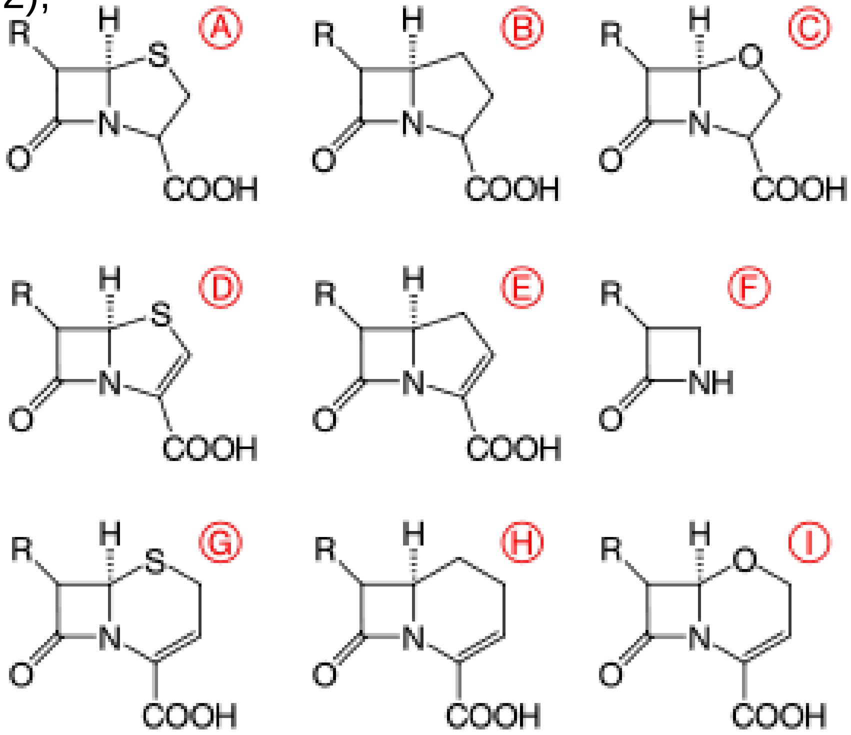
Production of Anitbiotics (penicillins, cephalosporins)

- ➢ Fermentation + Organic Syntheis



R = $PhCH_2$; Pen G
R = $PhCH(NH_2)$; ampicillin
R = (4-OH)-PhCH(CH2);
amoxycillin

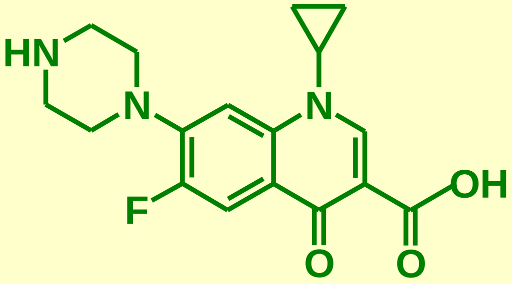




(A) penam. **(B)** carbapenam. **(C)** oxapenam. **(D)** penem. **(E)** carbapenem. **(F)** monobactam. **(G)** cephem. **(H)** carbacephem. **(I)** oxacephem

Antibiotics

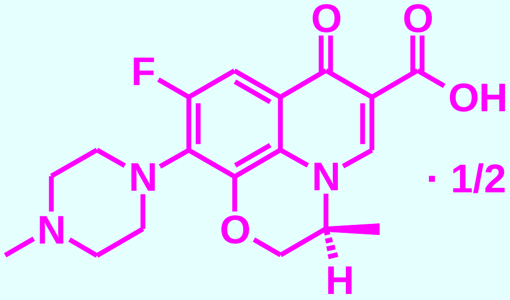
■ Quinolones



Cipro ™(Ciprofloxacin)

96 FDA approved

Bayer

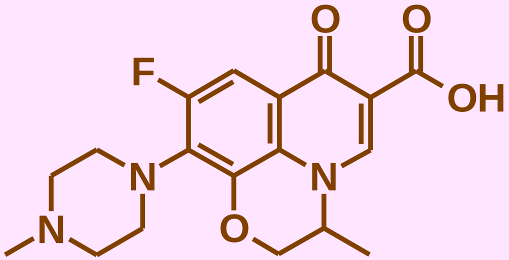


$\cdot$ 1/2 H_2O

Levaquin ™(Levofloxacin)

97 FDA approved

Ortho-McNeil Pharmaceutical

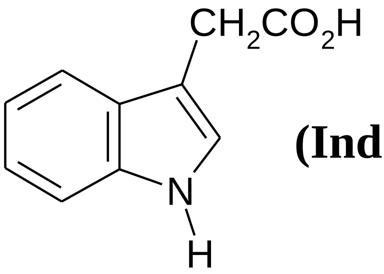


Floxin ™(Ofloxacin)

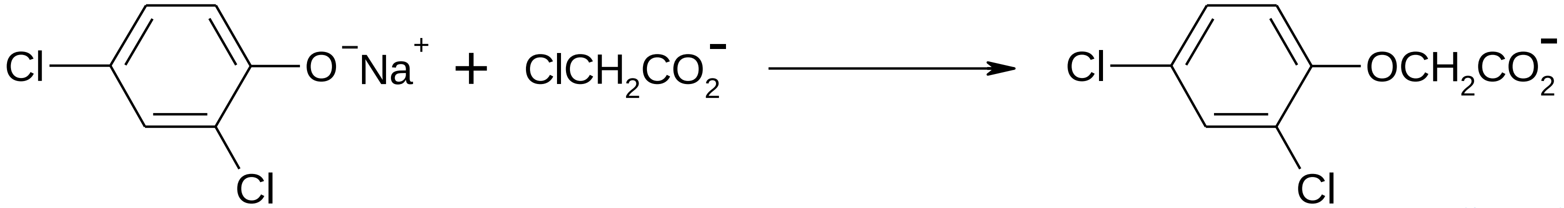
97 FDA approved

Ortho-McNeil Pharmaceutical

Agrochemicals: Herbicide

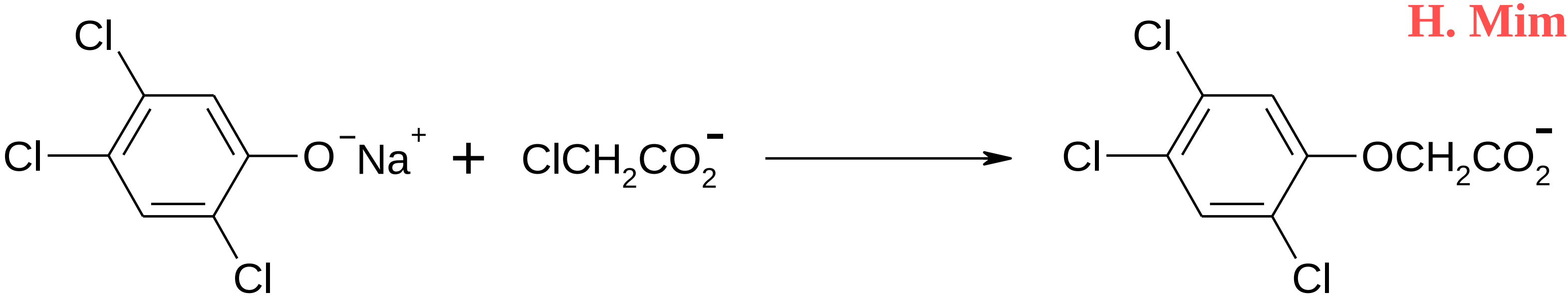


(Indoleacetic acid) **Plant Growth Hormon**



2,4-D (제초제)

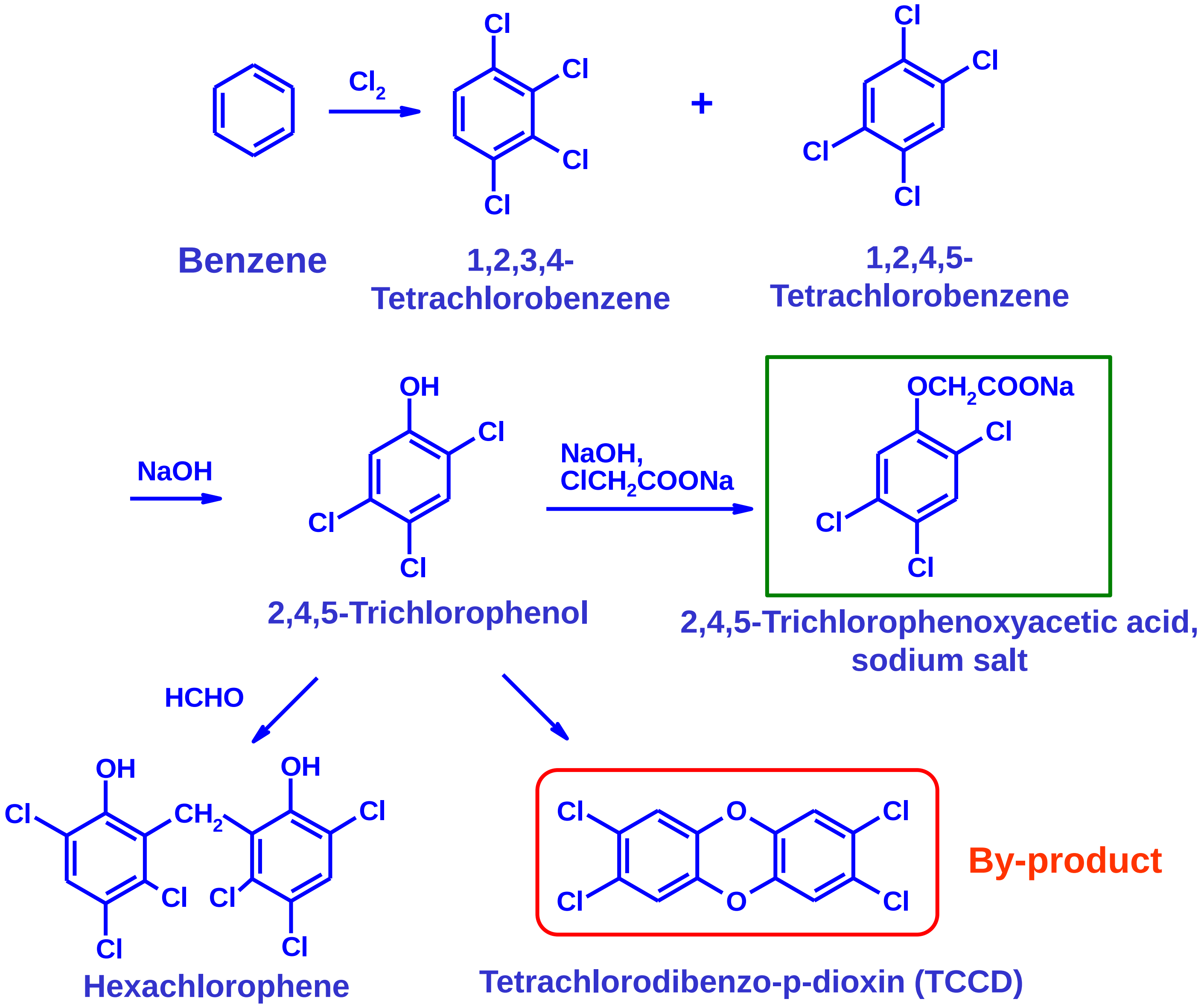
H. Mimic



*** H_20 Material Balance**

2,4,5-T (제초제)

Manufacturing Process



Benzene

1,2,3,4-Tetrachlorobenzene

1,2,4,5-Tetrachlorobenzene

2,4,5-Trichlorophenol

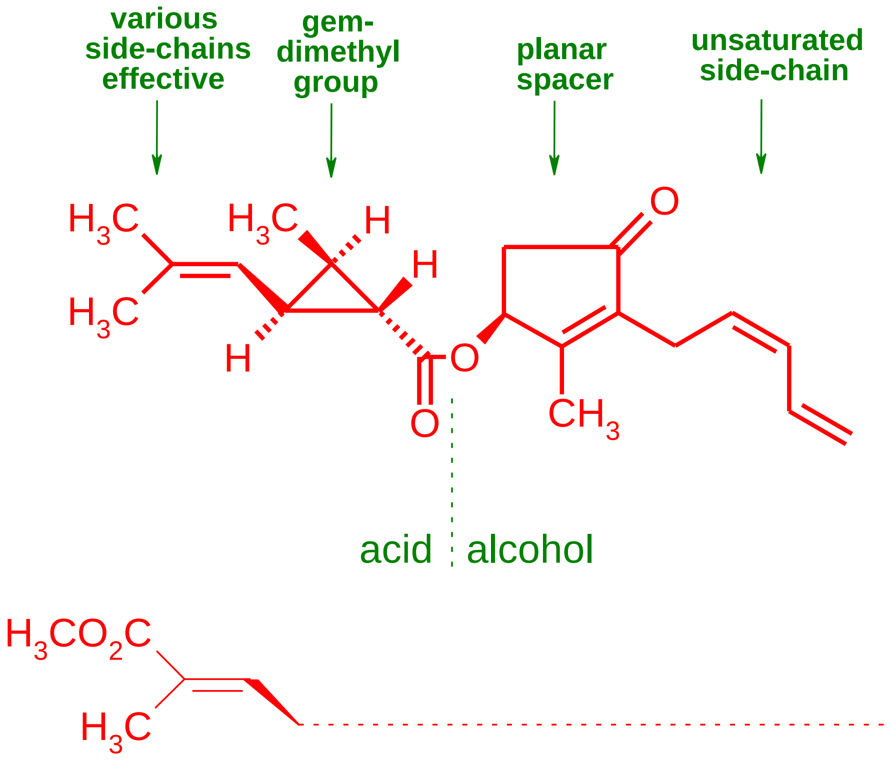
2,4,5-Trichlorophenoxyacetic acid, sodium salt

Hexachlorophene

Tetrachlorodibenzo-p-dioxin (TCCD)

Non Toxic Natural Pesticide

Structure & Acitivity of pyrethroids

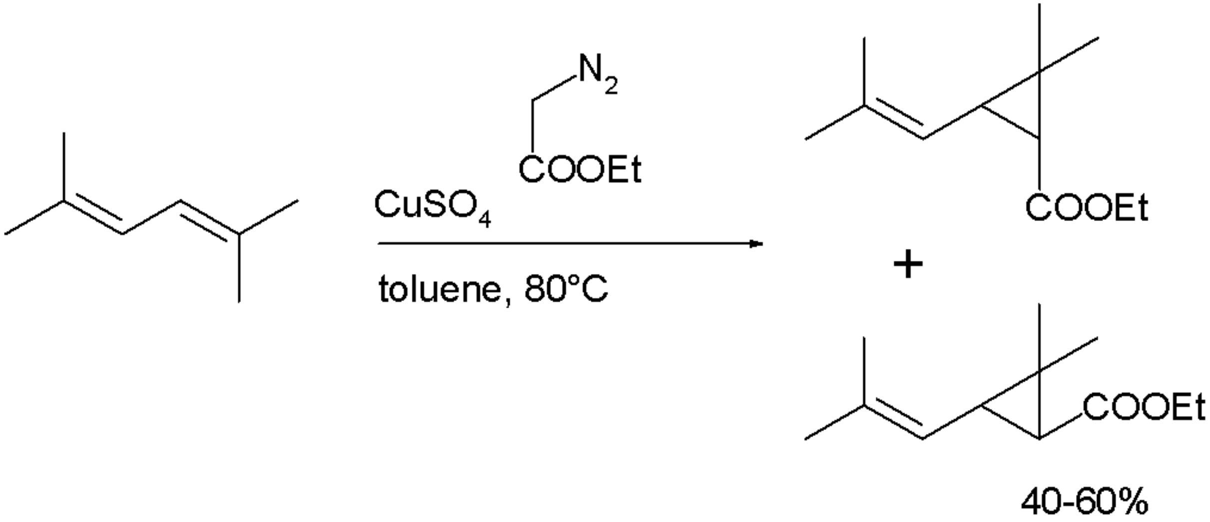


PYRETHRIN I

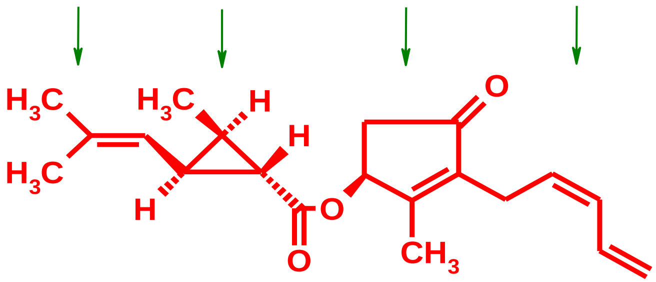
PYRETHRIN II

Chrysanthemic ester synthesis

Chrysanthemic acid : produced industrially in a cyclopropanation reaction of a diene as a mixture of cis- and trans isomers followed by hydrolysis of the ester

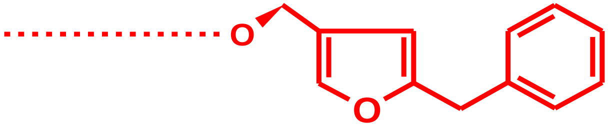


Typical pyrethroid pesticides

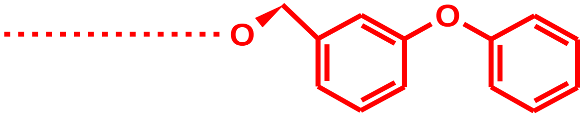


PYRETHRIN I

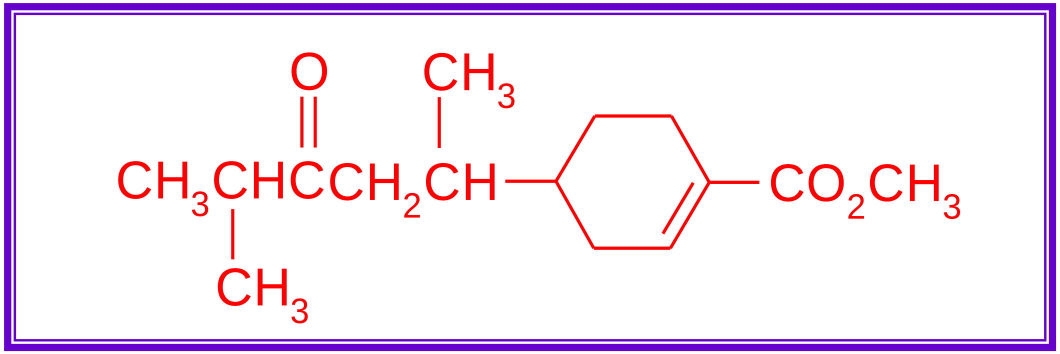
S-BIOALLETHRIN



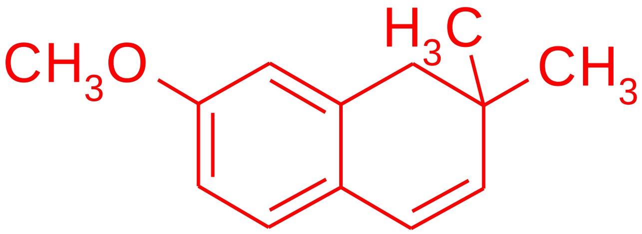
BIORESMETHRIN



PHENOTHRIN
((+)-trans)

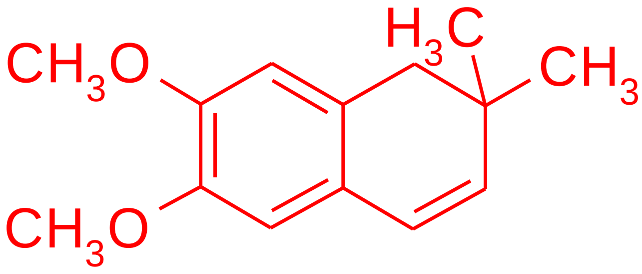


Juvabione (from natural plant)
Juv. H. mimic (N. America 전나무)



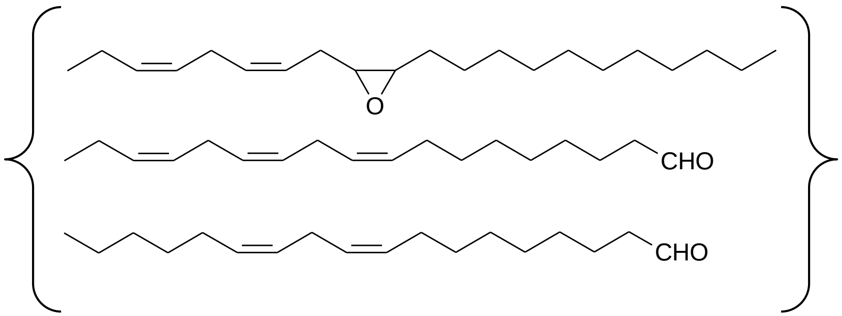
Precocene I

No Resistance !

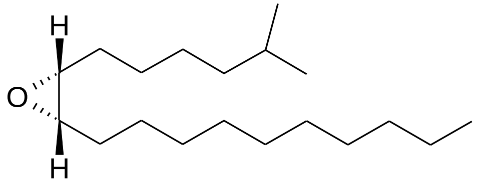


Precocene II
(juv. Inhibitor)

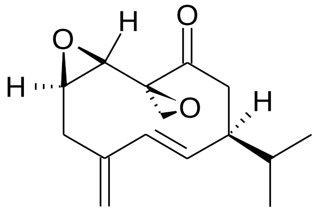
Agrochemicals: Pheromones



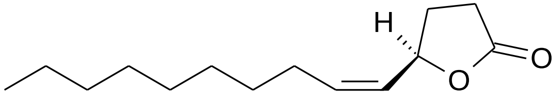
흰불나방



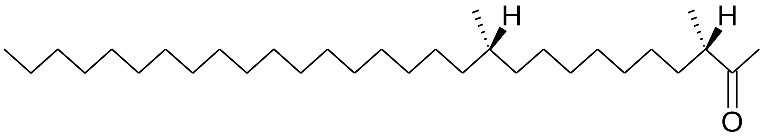
(+)-disparlure (Gypsy moth)



periplanone-B (American cockroach)



(R,Z) - Japanese beetle



German cockroach

"Since you started doing pheromone research you've become hideously ugly, yet I still find you irresistible."

Classification of Pheromones

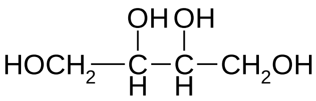
- Aggregation pheromones
- Alarm pheromones
- Epideictic pheromones
- Releaser pheromones
- Signal pheromones
- Primer pheromones
- Territorial pheromones
- Trail pheromones
- Information pheromones
- Sex pheromones

Sweetener

Examples of natural and synthetic sweeteners

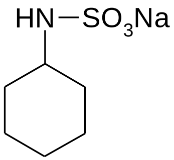
$H_3\overset{+}{N}CH_2COO^-$

Glycine
MW 75

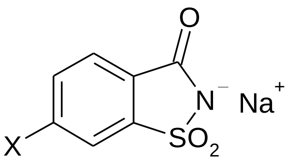


$HOCH_2-\underset{H}{\overset{OH}{C}}-\underset{H}{\overset{OH}{C}}-CH_2OH$

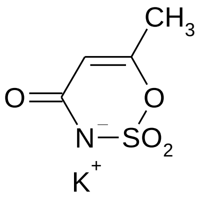
Erythritol
MW 122



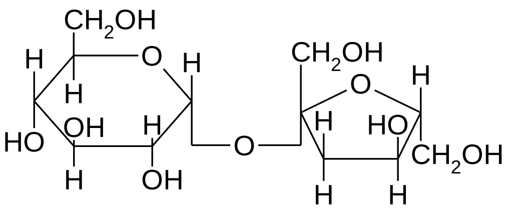
Cyclamate
MW free acid 179



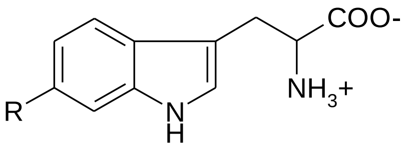
Saccharin (X=H)
MW free acid 183
X=OH, sweet
X=OCH_3, tasteless



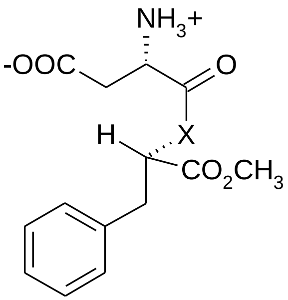
Acesulfame-K



Sucrose
MW 342



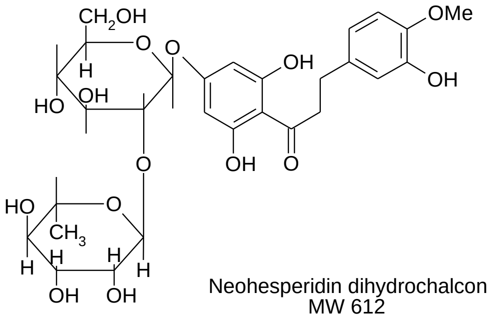
(+)-Tryptophan (R=H)
MW 204
(R=Cl is 37X more
potent than R=H)



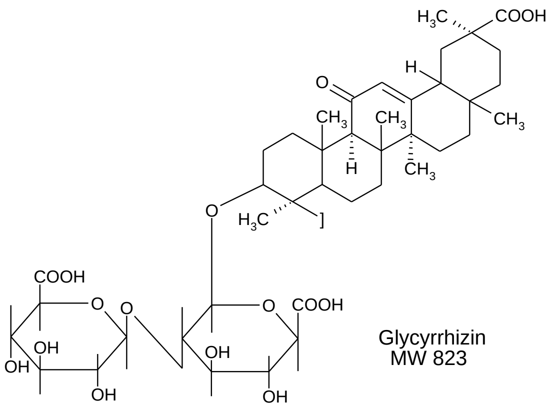
Aspartame (X=NH)
MW 280
(X=O, tasteless)

Sweetener

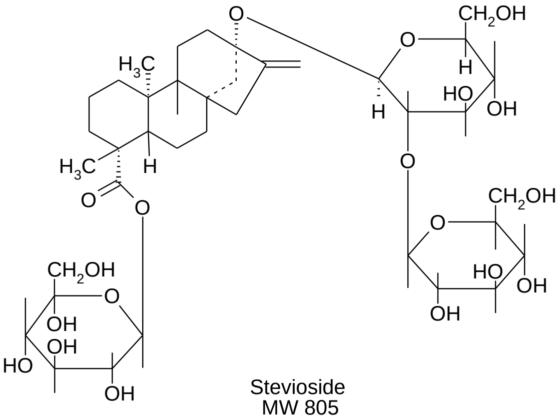
Examples of natural and synthetic sweeteners



Neohesperidin dihydrochalcone
MW 612



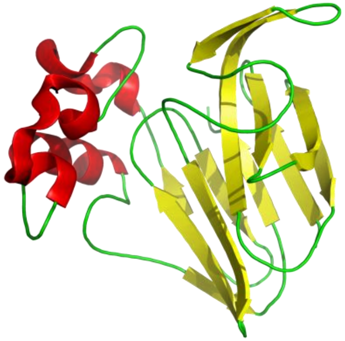
Glycyrrhizin
MW 823



Stevioside
MW 805

Proteins

monellin	MW 10,700
thaumatin I and II	MW 22,000



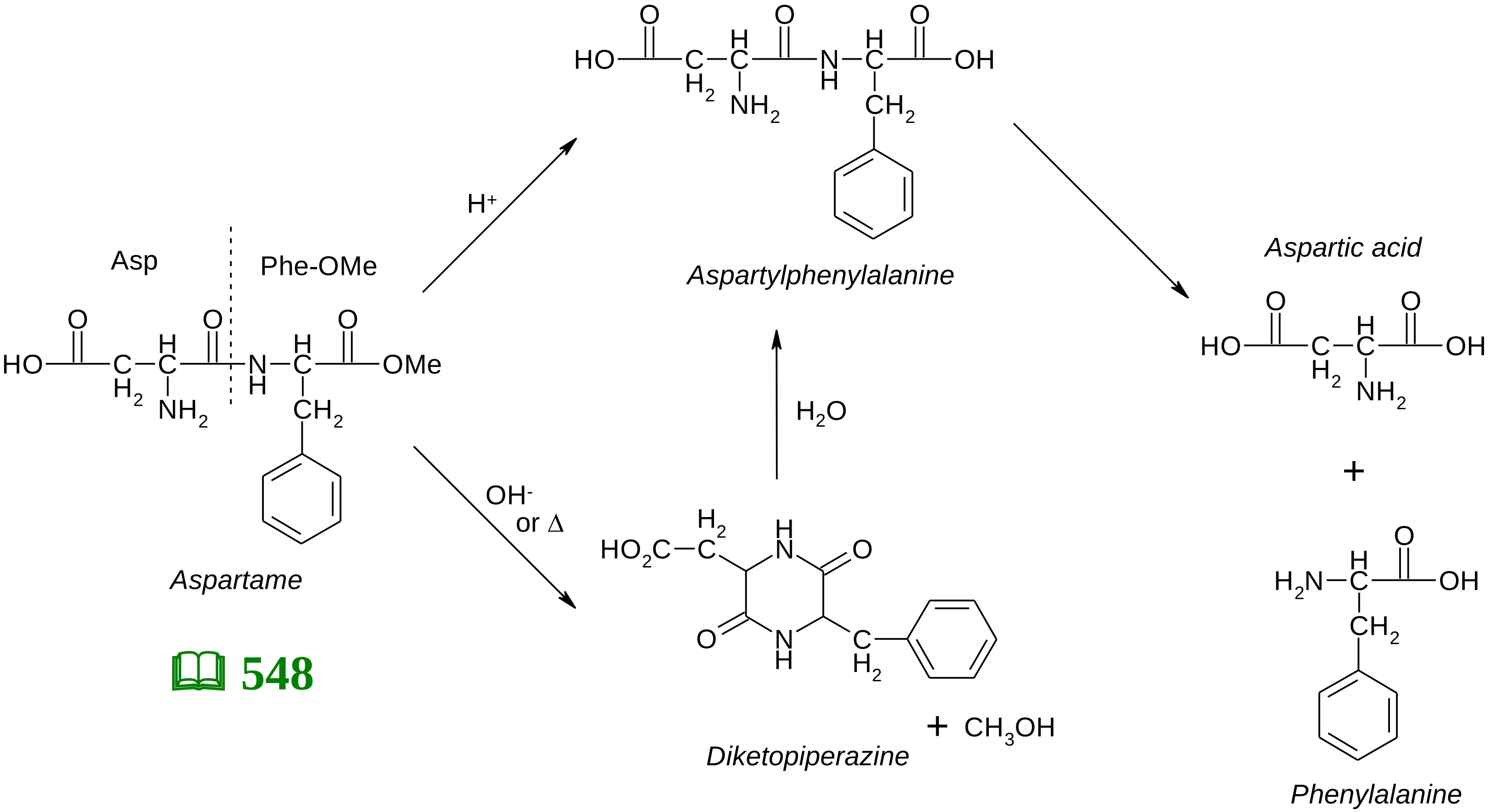
Sweetener

각종 감미료의 맛의 특성과 기타 기능

감미료	감미도	감미의 질	기타기능
설 탕	**1.0**		**50%**이상의 당도가 되면 식품의 보존성을 높인다.
과 당	**1.2**	강하고 고상한 감미	습윤성
포도당	**0.7**	진한 용액일수록 달고 저온에서 상쾌한 맛	착 색
솔비트	**0.5**	상쾌한 감미, 한랭감	보습효과
글리실리진	**200**	특유의 뒷맛	큰 염혼합효과, 풍미조정
스테비오사이드	**100**	쓴맛을 동반한 감미	변색방지, 이상발효 억제
크실로오스	**0.7**	무칼로리, 저흡습성	지질산화방지
글리신	**0.6**	시원한 맛	균 제거작용
이성화당	**1.1**	연한 감미질	액화당 원료사용에 의한 공정 합리화
물 엿	**0.4**	곡물냄새 나는 감미	고점도, 습윤작용

Synthetic Sweetener

Pathway of Aspartame Degradation



548

Super APM

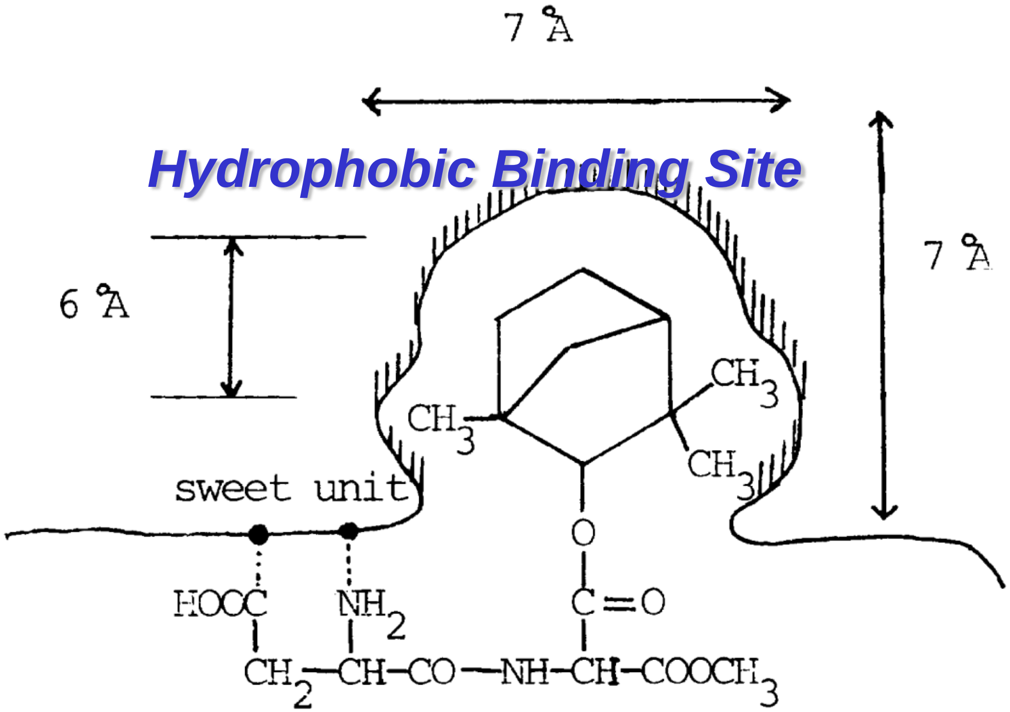
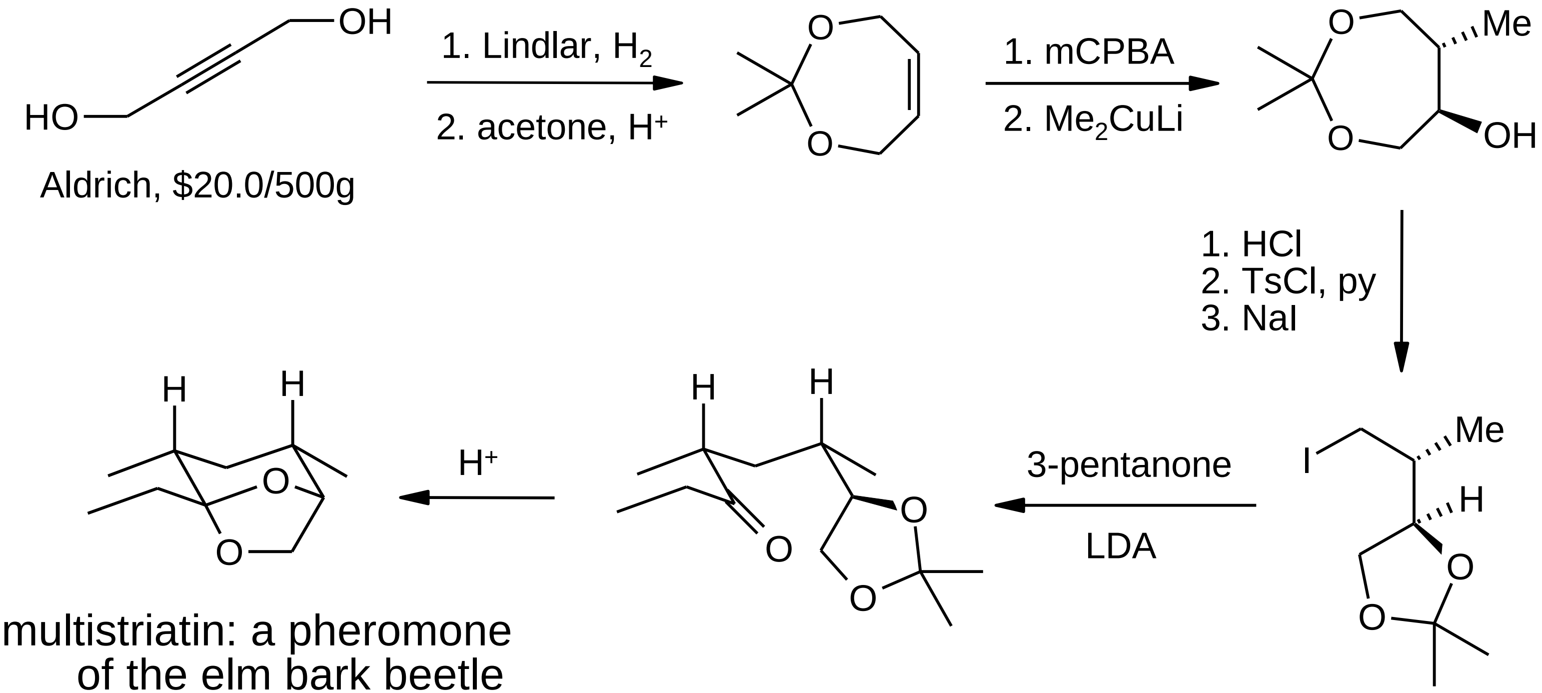


Fig. Gross Model of the Hydrophobic Binding Site of a “Taste Receptor” and L-Asp-Ama Diester(22000-33000 X sweeter than sucrose)
Fujino, et al (1976)

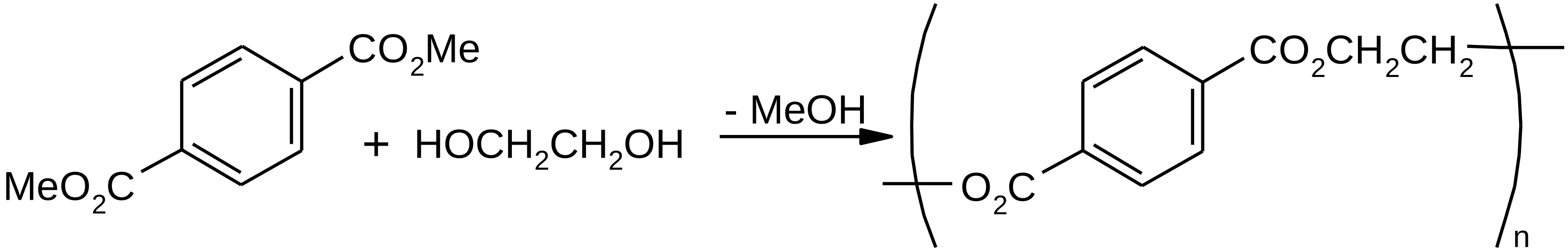
Industrial Production of Feromones



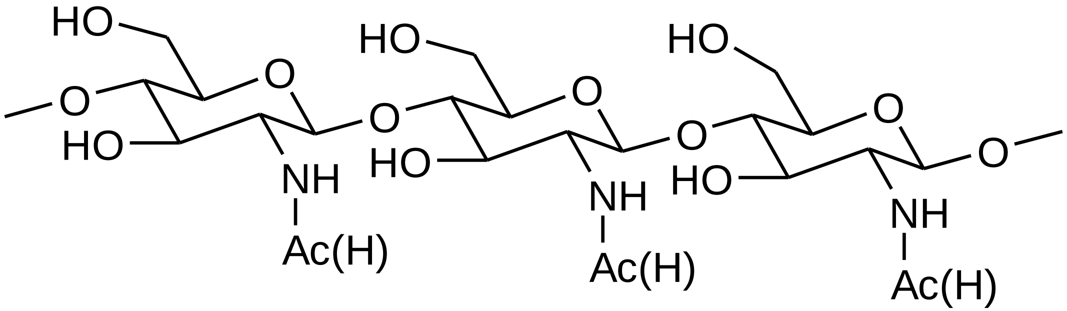
Aldrich, $20.0/500g

multistriatin: a pheromone
of the elm bark beetle

Polymers & Biopolymers

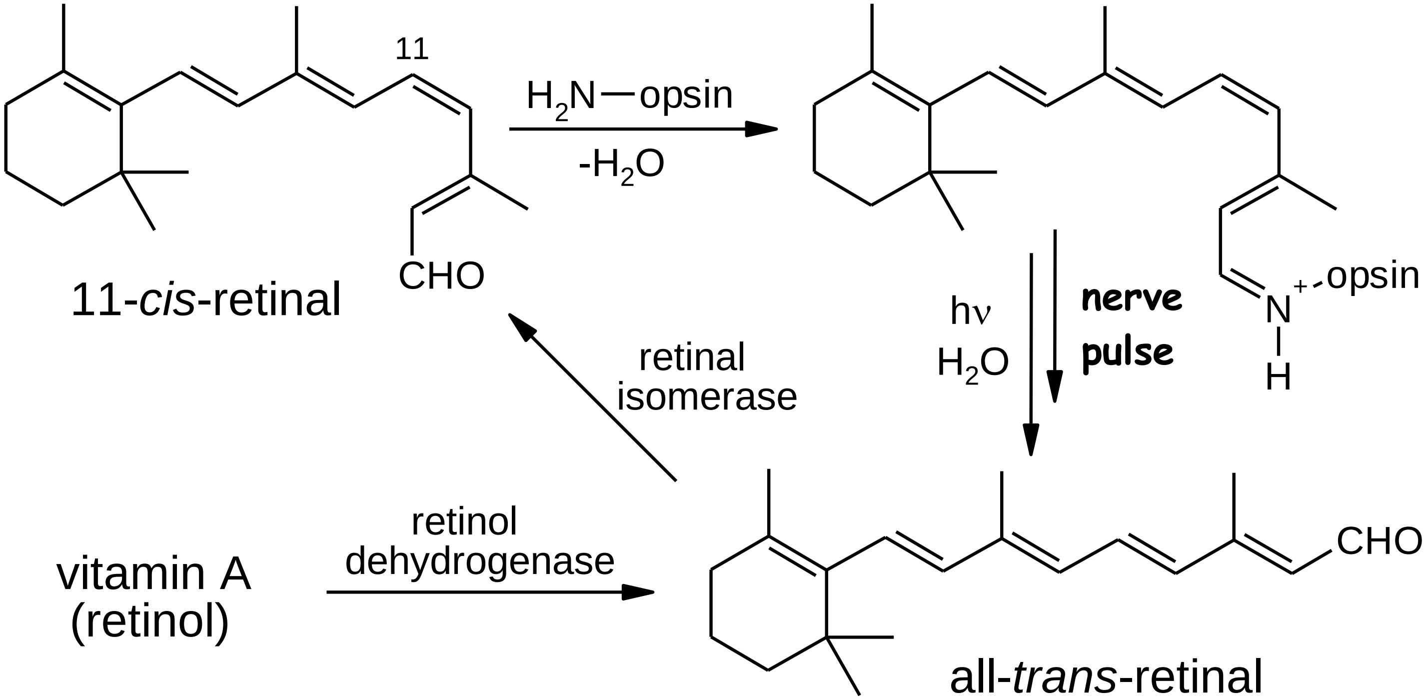


polyester (Dacron)



chitin (chitosan)

Biology & Biochemistry



11

11-*cis*-retinal

CHO

H_2N—opsin

$-H_2O$

$^+$-opsin

N

H

hν

H_2O

nerve pulse

retinal isomerase

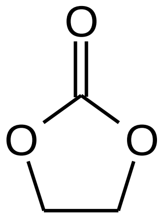
vitamin A (retinol)

retinol dehydrogenase

CHO

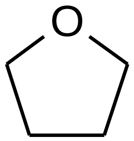
all-*trans*-retinal

Electrochemicals



ethylene carbonate

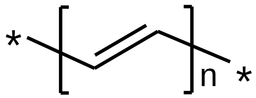
(better electrolyte)



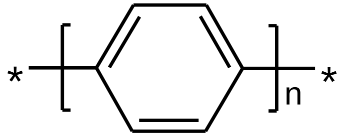
THF

(poor electrolyte)

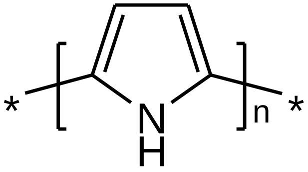
Display Materials



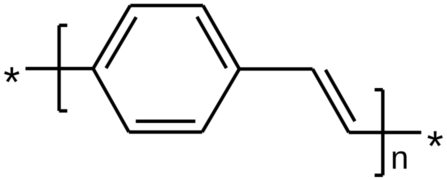
polyacetylene



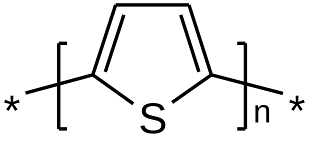
PPP



polypyrrole

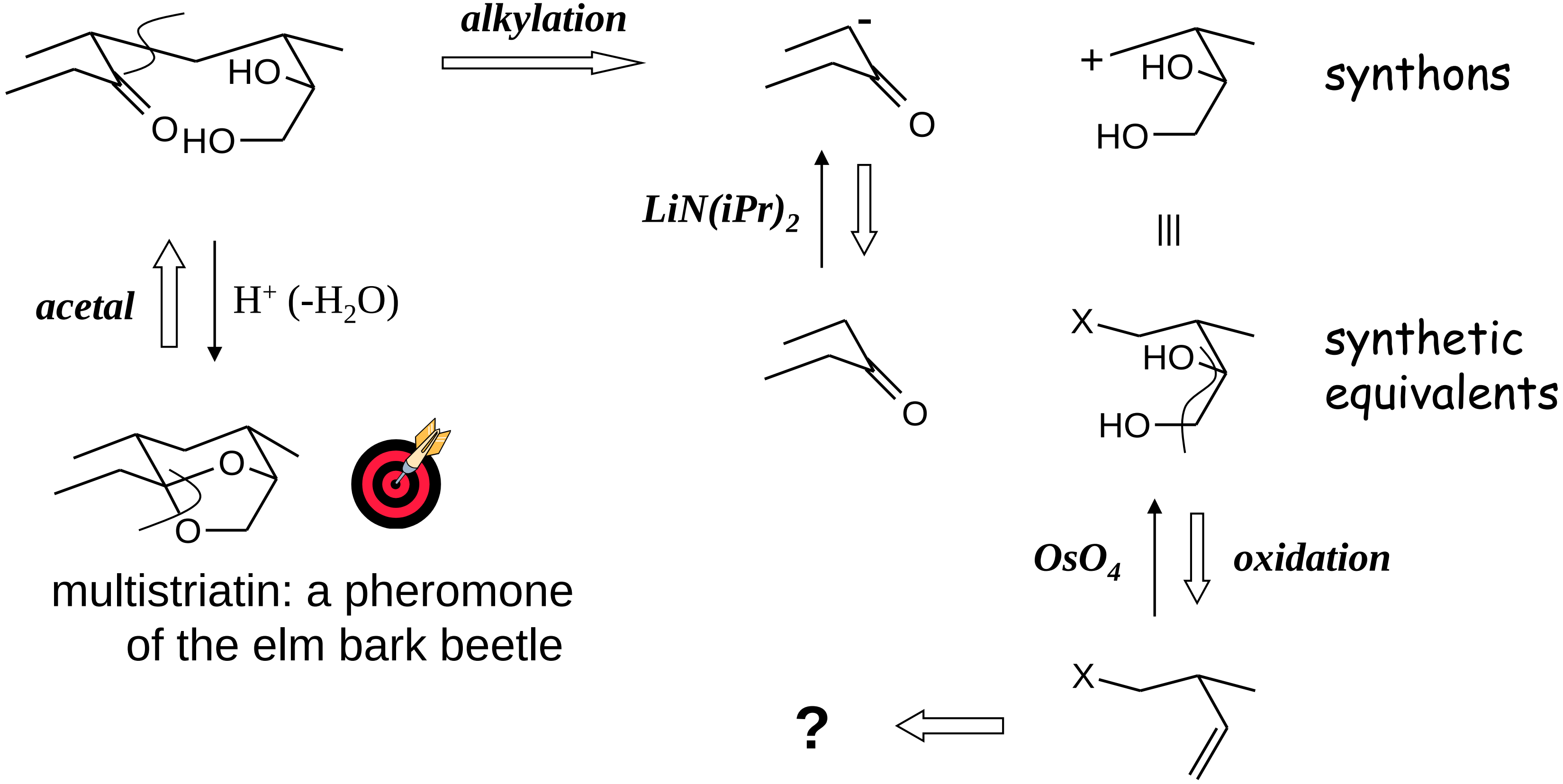


PPV



polythiophene

Disconnection Approach: An Example



alkylation

synthons

LiN(iPr)$_2$

≡

acetal

H$^+$ (-H$_2$O)

synthetic equivalents

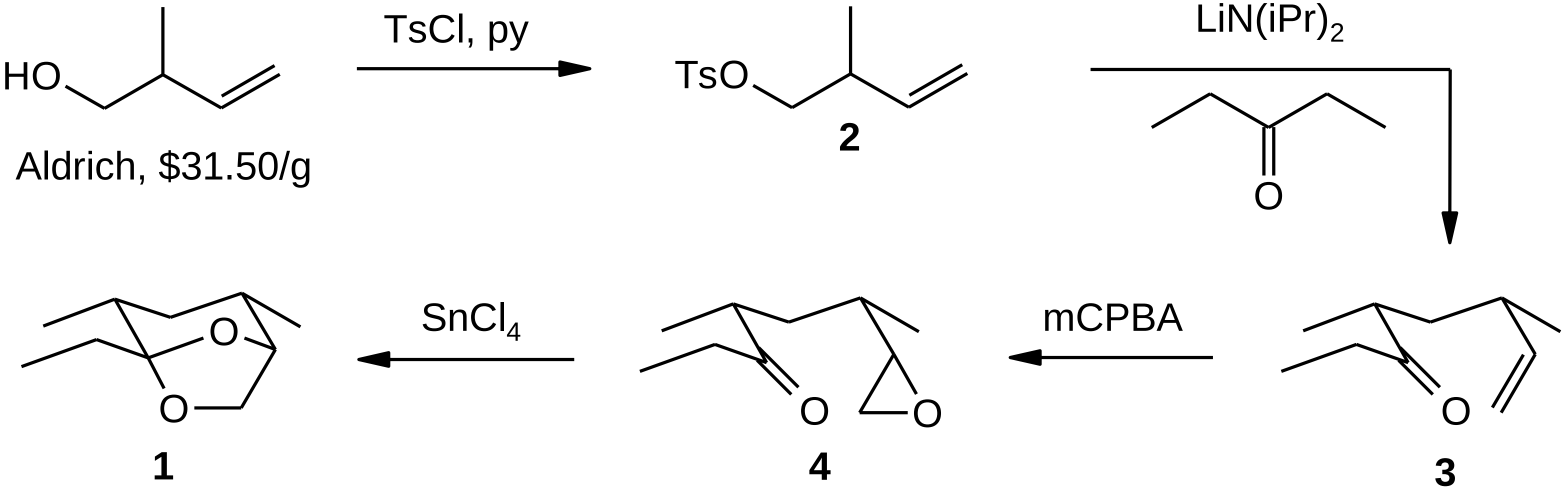
OsO$_4$

oxidation

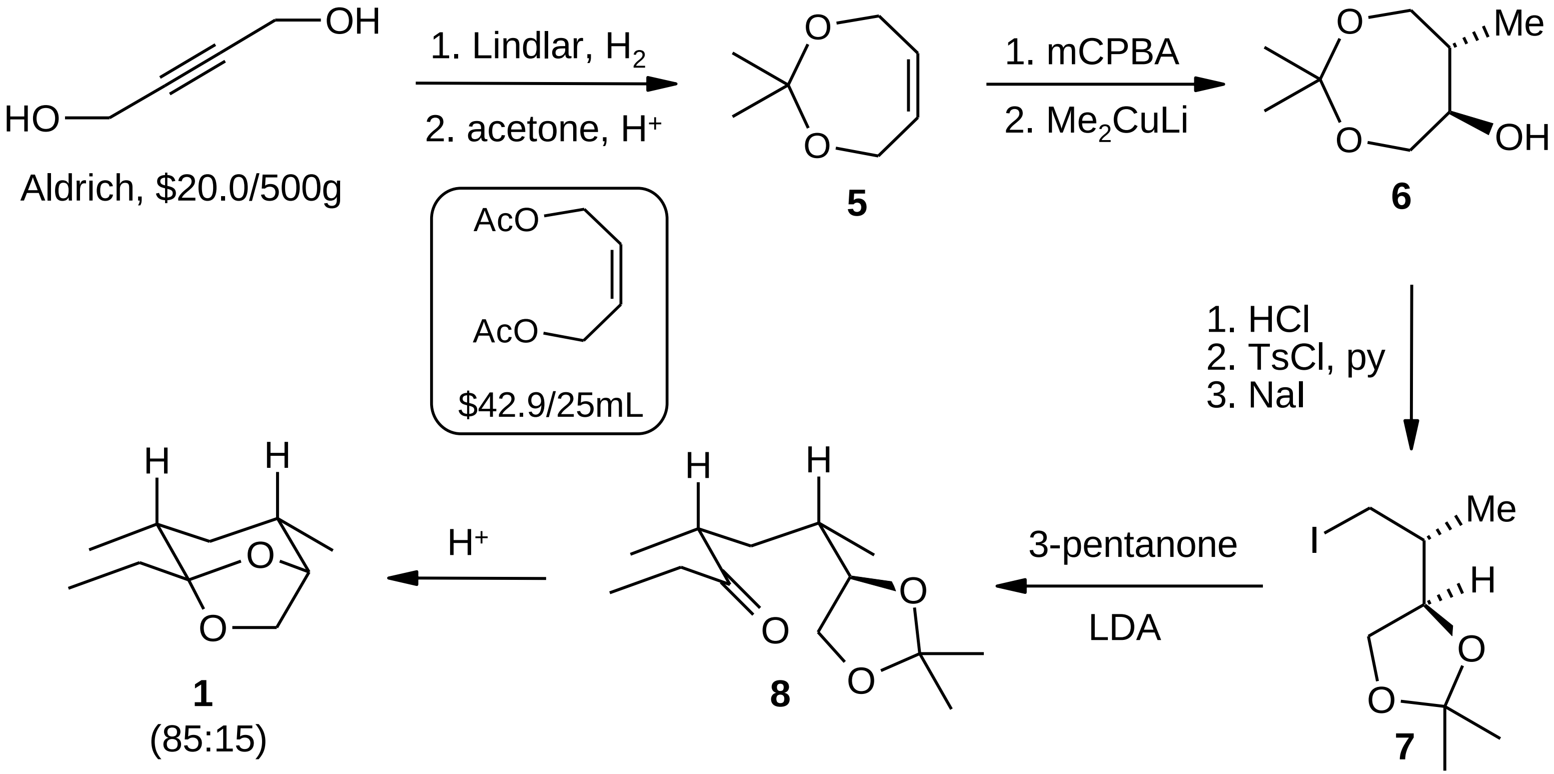
multistriatin: a pheromone
of the elm bark beetle

?

A Stereorandom Synthesis of Multistriatin



Industrial Production :
Stereoselective Synthesis of Multistriatin



Aldrich, \$20.0/500g

1. Lindlar, H_2
2. acetone, H^+

\$42.9/25mL

5

1. mCPBA
2. Me_2CuLi

6

1. HCl
2. TsCl, py
3. NaI

7

3-pentanone
LDA

8

H^+

1
(85:15)

Design and Synthesis

- Retro synthetic Analysis
    1. recognize the FGs in TM
    2. disconnect by known methods and reliable reactions
    3. repeat 1 and 2 until the readily available SMs are obtained
    4. design as many alternative retrosynthetic routes as possible
- Synthesis
    1. write down the synthetic schemes containing the detailed reaction conditions according to the analyses
    2. compare the pros and cons between the syntheses designed; the number of steps, availability of reagents/starting materials, selectivity (chemo-/regio-/stereo-), economy, process, etc
    3. modify the selected synthetic plan whenever unexpected problems are encountered