Chapter 3. 에틸렌으로부터 화학 제품과 고분자

- 에틸렌 생성의 약 80%는 polyethylene등 열가소성 고분자 (thermoplastic polymer) 생산의 원료고 사용됨
- Ethylene 을 이용하여 제조 가능한 고분자는 :

  (1) Low density PE (LDPE) - 저밀도 폴리에틸렌

  (2) High density PE(HDPE) – 고밀도 폴리에틸렌

  (3) Linear low density PE(LLDPE) – 중밀도 폴리에틸렌

  (4) Ethylene oligomer

  (5) Poly (vinyl chloride), (PVC)

  (6) Poly (vinyl acetate), (PVAc)

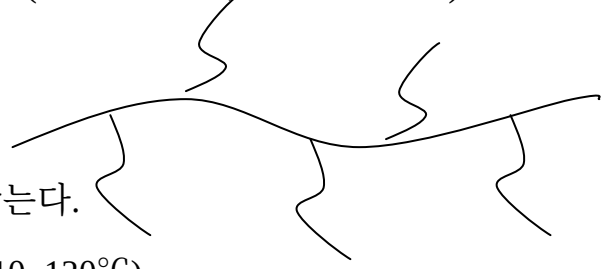
  (7) Polystyrene, (PS)

  (8) Poly (ethylene glycol), (PEG) 등

P. 101

3.1.2 저밀도 폴리에틸렌

- 1932년 영국 ICI 에서 합성. (온도 200 ℃, 1300-2600 bar)
- 밀도 : 0.915 (g/cm3)
- 필름 제조에 이용.
- 구조는 branched 구조를 갖는다.



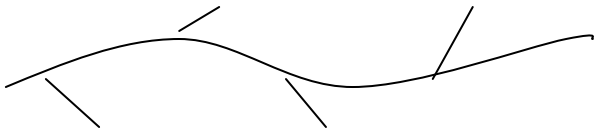
- 결정화도는 약 55% (Tm=110~120℃)
- 개시제로 organic peroxide 이용

3.1.3 고밀도 폴리에틸렌

- 1954년 Ziegler 촉매 [TiCl4 (사염화 티타늄촉매) / Al(C2H5)3 (트리에틸 알루미늄)의 조합으로 이루어져 있음] 개발로 실용화 함.
- 밀도 : 0.965 (g/cm3)
- 사출 성형이나 blow molding 등에 있는 linear 구조를 갖는다.
- 결정화도는 약 85~95% (Tm=130~136℃)

3.1.4 선형 저밀도 폴리에틸렌 (LLDPE)

- LDPE 와 HDPE 중간 정도의 물서을 갖는다.
- 밀도는 0.915 ~ 0.925 (g/cm3)
- Linear with short branch 구조



- 결정화도는 55 ~60%
- comonomer로서 1-butene, 1-hexene or 1-octene 사용
- LDPE 보다 높은 인장강도를 나타낸다. (Tensile strength)
- 낮은 gauge films 생산가능

3.1.5 고분자량 polyethylene

- 밀도가 0.941(g/cm3) 이상인 고분자량 PE는 공정의 어려움, 따라서 많이 쓰이지는 않음.

- 주로 rope 제조에 이용.
- 고강도 PE 섬유 제조에 이용.
- Gel spinning 하여 (wax 또는 dichloromethane 이용) 잘 배향된 섬유제조, 높은 인장강도를 나타냄.

◆ Petrochemicals from ethylene.

. 국내 Ethylene 생산

- 1990년, 125만 톤
- 1995년, 355만 톤
- 1995년(미국) 2,200만 톤
- 2000년(미국) 2,600만 톤

. Ethylene 은

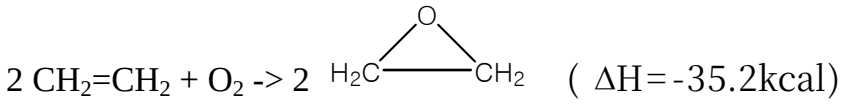
- readily available
- low cost
- high purity이므로 petrochemical industry에서 prime raw material 이라고 함.

. Ethylene 의 용도

- Polyethylene : 44%
- Ethylene oxide : 16%
- Vinyl chloride : 13%
- Ethyl benzene : 8%

- Others : 19%

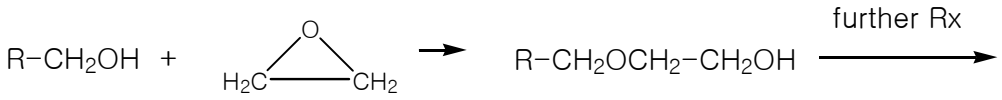
(1) Ethylene Oxide (EO)

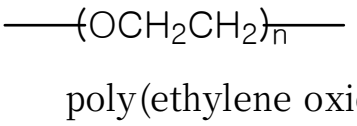


- Produced by air or O_2 oxidaton.
- Silver 촉매

(용도)

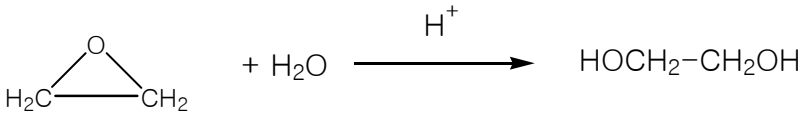
- Poly(ethylene oxide) (PEO) 생산





(2) Ethylene Glycol : CH_2OH-CH_2OH (EG)

(a) produced by hydration of ethylene oxide,



(b) produced directly from ethylene, acetoxylation,

$2\ CH_2=CH_2 + 2H_2O + O_2 \rightarrow 2\ HOCH_2\text{-}CH_2OH$

(c) from formaldehyde and carbon monoxide

$HCHO + CO + 2H_2 \rightarrow HOCH_2CH_2OH$

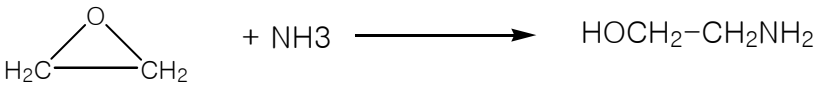
(d) from syn gas

$2\ H_2 + CO \rightarrow CH_3OH$

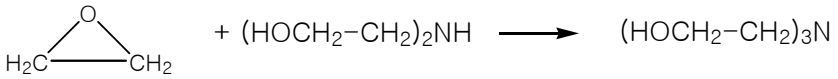
$CH_3OH \rightarrow HCHO + H_2$

(3) Ethanolamine

(반응)



(monoethanol amine)



diethanolamine triethanolamine

(용도)

- sweetening of acid gases
- detergent(세제) 생산

$RCOOH + HOCH_2CH_2NH_2 \rightarrow RCONH + CH_2CH_2OH + H_2O$

- for the production of ethanolamide detergents from fatty acids.

(4) Vinyl chloride, $CH_2=CHCl$

- 92% of the vinyl chloride monomer (VCM) is produced by the “balancedoxychlorination process”.

(반응)

(ⅰ) First step (direct chlorination) :

$CH_2=CH_2 + Cl_2 \rightarrow ClCH_2CH_2Cl$

-to produce ethylene dichloride

(ⅱ) $ClCH_2$-CH_2Cl -> CH_2=$CHCl$ + HCl

- second step is pyrolysis

(iii) third step is oxychlorination,

$$2\ CH_2{=}CH_2 + 4\ HCl + O_2 \rightarrow 2\ CH_2Cl\text{-}CH_2Cl + H_2O$$

recycled

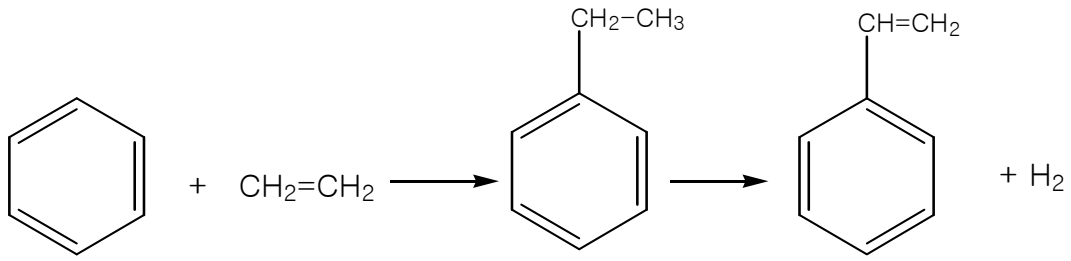
(ⅳ) overall reaction

$$4\ CH_2{=}CH_2 + 2\ Cl_2 + O_2 \rightarrow 4\ CH_2{=}CHCl + 2H_2O$$

(용도)

① PVE생산 – pipe, films, coatings, moldings

(5) Ethylbenzene



styrene

(6) Ethanol, ethyl alcohol, CH_3CH_2OH

(반응)

(ⅰ) Fermentation is the process used.

(ⅱ) Synthetic process : indirect hydration of ethylene.

(a) $3CH_2=CH_2 + 2\ H_2SO_4 \rightarrow CH_3CH_2OSO_3H + (CH_3\text{-}CH_2O)_2SO_2$

monoethyl sulfate diethyl sulfate

(b) $CH_3CH_2OSO_3H + (CH_3CH_2O)_2SO_2 + 3\ H_2O \rightarrow 3\ CH_3CH_2OH + 2\ H_2SO_4$

(iii) direct hydration of ethylene

$$CH_2=CH_2 + H_2O \rightarrow CH_3CH_2OH$$

(용도)

- 용제(solvents)
- 유기합성 용, 중간체 (intermediate)로 작용. 즉, ethyl chloride, ethyl ether, glycol ethyl ethers 등 제조에 이용.

(7) Acetaldehyde : CH3CHO

(반응)

(ⅰ) by the silver catalyzed oxidation of ethanol

$$2\ CH_3CH_2OH + O_2 \rightarrow 2\ CH_3CHO + 2\ H_2O$$

(ii) by the dehydrogenation of ethanol

$$CH_3CH_2OH \rightarrow CH_3CHO + H_2$$

(iii) produced directly from ethylene

촉매 : liquid phase homogeneous catalysts : $CuCl_2$, $PdCl_2$

(iv) produced by the vapor, phase catalytic oxidation of ethylene,

$$CH_2=CH_2 + O_2 + H_2O \rightarrow CH_3CHO + CH_3COOH$$

(v) produced by the noncatalyzed oxidation of propane

(용도)

acetic acid 생산, n-butanol 합성에 이용.

- by the liquid phase oxidation of acetaldehyde,

$$2\ CH_3CHO + O_2 \rightarrow 2\ CH_3COOH$$

(8) Vinyl acetate :

- produced from ethylene and acetic acid

(ⅰ) gas phase 촉매 산화 반응

$$2\ CH_2{=}CH_2 + 2\ CH_3COOH + O_2 \rightarrow 2\ CH_2{=}CHOCOCH_3 + 2\ H_2O$$

(most economical, 많이 사용되는 반응임.)

(용도)

polyvinyl acetate생산, vinyl acetate copolymer, polyvinyl alcohol 생산(more details in Chap. 12)

(9) Acrylic acid : $CH_2{=}CHCOOH$

- by oxidative carbonylation with carbon monoxide and oxygen with a palladium/copper 촉매

$$2\ CH_2{+}CH_2 + 2\ CO + O_2 \rightarrow 2\ CH_2{=}CHCOOH$$

(용도)

아크릴 섬유, plastics

(10) Propionaldehyde : CH_3CH_2CHO

- Produced by the hydroformylation of ethylene,

$$CH_2{=}CH_2 + CO + H_2 \rightarrow CH_3\text{-}CH_2CHO$$

(용도) (ⅰ) Propanol 생산

$$CH_3CH_2CHO + H_2 \rightarrow CH_3CH_2CH_2OH$$

- solvents for coatings에 이용.

- for ink used in painting on food containers.

(ii) Propionic acid 생산

$$2\ CH_3CH_2CHO + O_2 \rightarrow 2\ CH_3CH_2COOH$$

- used as a 곡식 방부제

(11) Linear Alcohols :

- produced from ethylene from a four-step process

(용도)

생 분해성임. C_{12-16} range are used to make detergents.

C_{10-12} : 가소제 생산에 이용 (plasticizers)

C_{16-18} : modifiers for was-and-wear resins.

C_{20-26} : lubricants and mold-release agents.

Production of Olefins

. 3가지 중요한 Olefin
- Ethylene
- Propylene
- Butadiene

⑴ Ethylene

- ethylene을 생산하는 중요한 원료로서 다음의 4가지가 이용된다.

① Naphtha (67%) ② Gas oil (20%)

③ LPG (9%) ④ Ethane (4%)

(see Fig. 7.3)

. Gas oil - A liquid petroleum distillate with viscosity and boiling range between kerosine and lubricating oil. Boiling range between 230℃ and 430℃.

⑵ Propylene - the second most important olefin.

- 63%가 ethylene 의 coproduct

⑶ Butadiene - 세 번째로 중요한 Olefin

- Ethylene의 coproduct
- Produced by butane and butene dehydrogenation.

(Ⅰ) Olefin Feedstocks 의 일반적인 사항.

- heavier feeds는 ethane 보다 비싸나 propylene, butadiene 그

리고 BTX 등과 같은 byproducts를 더 많이 생산함.

- Paraffin hydrocarbons, alkanes easiest to crack
- n-alkanes 는 ethylene yield가 좋음.
- Isobutane과 isopentene과 같은 branched chain alkanes(isoparaffins)은 propylene을 생산 yield가 좋음.
- Naphthens 과 cycloparaffins 은 cracking 하기가 쉽지 않은데, 이는 the ring must be opened first.
- Ethane cracking 시 온도는 약 800℃
- Naphtha 또는 gas oil cracking 시 온도는 약 675~700℃.

(Ⅱ) Gas Feedstocks

- the gaseous feedstock for ethylene production

(ⅰ) Ethane (ⅱ) Propane

(ⅲ) n-Butane (ⅳ) various mixture of these

(ⅰ) Ethane : High ethylene yield

C_2H_6 -> C_2H_4 (Temp. = 약 800℃)

Yield : wt%

ⓐ Ethylene	80.9%
ⓑ Hydrogen and Methane	12.9%
ⓒ Propylene	1.8%
ⓓ Butadiene	1.9%
ⓔ Others	2.5%

. Ethane feedstock의 성분

ⓐ Ethane 94.2% ⓑ Propylene 3.0 wt%

ⓒAcetylene 1.9 wt% ⓓ Propane 0.9 wt%

(ii) Propane :

- Propane gives a lower ethylene yield and a longer quantity of coproduct

- Yield : wt% (see Table 7.1)

(a) Ethylene 44.0% (b) Propylene 15.6%

(c) Butadiene 3.4% (d) BTX 2.8

(e) Others 34.2

(iii) Ethanepropane mixture

- cocracking으로 인한 효과 (see Table 7.3)

(iv) n-Butane

- is a minor source of ethylene.
- n-butane is cracked at the highest conversion level because any unconverted butane will be contained in the C^4_4 products. This makes recovery of the butadiene and butanes more difficult and expensive.

(III) Liquid Feedstocks

(i) Naphtha - gas feedstock 보다 다양한 coproducts를 얻을

수 있음.

- Cracking의 severity에 따라서 ethylene, propylene, butadiene 등의 yield % 가 달라짐.

(ii) Reformer Raffinate

- Produce relatively less ethylene and more propylene than virgin (straight run) naphtha.

. Raffinate - the portion of an oil that is not dissolved in solvent refining of lubricating oil.

(iii) Gas Oil

- a liquid petroleum distillate with viscosity and boiling range between kerosene and lubricating oil. Boiling range between 230~430℃
- not as desirable as naphtha

(ethylene 생산에 있어서 naphta 만큼 좋지 않음)

- naphtha 보다 density가 높으며, a lower hydrogen content, a higher sulfur content 그리고 높은 aromatic compounds 를 포함하고 있음.

(iv) Crude oil

- ethylene, BTX 그리고 acetylene의 yield는 naphtha 나 gas oil을 cracking 하는 것 보다 crude oil을 direct cracking 하는 것이 높음.
- 2가지 process가 있음..

① The crude oil is sprayed directly into 2,000℃

superheated steam inside the reactor.

② Direct cracking by a fluidized bed reactor.

(IV) Other processes

- ethylene, other olefins 그리고 BTX를 생산하기 위해 더 나은 process를 개발하는 노력은 끊임없이 진행되고 있다. 그 노력의 결과로서

(ⅰ) Hydropyrolysis - a cracking process characterized by operating in the presence of hydrogen under pressure.

-특징 -

(a) absence of a catalyst

(b) higher operating temp.

(c) shorter processing time

-반응조건 -

(a) 온도 : 800~900℃

(b) 촉매 : none

(c) 압력 : 10~30 atm

(d) 반응시간 : less than 0.1 sec

- Yield

. Vary with feedstock and recycling

- Feed stock 이 Naphtha일 경우

(a) Ethylene 44~45%

(b) Methane 34%

(c) Aromatic gasoline 20%

- Feedstock이 gas oil일 경우

(a) Ethylene 35%

(b) Methane 25~30%

(c) Heavy fuel 13%

(ii) Millisecond pyrolysis

- Millisecond furance의 개발로 인한 olefin pyrolysis의 새로운 breakthrough가 가능해짐
- 반응시간 : 0.03~0.1s
- 온도 : 870℃ (moderate severity)
  925℃ (high severity)
- 위의 조건에서 ethylene yield가 10~20% 증가

(iii) Thermal Regenerative Cracking (TRC)

- a new process : Cost를 20% 감소하여 어떤 feedstock 으로부터 ethylene 생산

(iv) Cracking oil by steam and molton salts (COSMOS)

- cosmos process는 일반적인 naphtha cracking에 이용될 수 있는externally heated tubular furnace를 사용함.

(v) Coproduct Treatment

- Ethylene demand governs the amount of coproduct propylene, butadiene and BTX
- Heavier feedstocks will increase C4 production.

. Acetylene ($HC{\equiv}CH$)

- ethylene 생산 시 coproduct로 얻어짐.

. Other source of ethylene

(Ⅴ) Diolefin으로서 Butadiene과 Isoprene

(ⅰ) Butadiene - (CH_2=CH-CH=CH_2)

- raw material for the most widely used synthetic rubber.
- SBR(styrenebutadiene-rubber)
- polybutadiene
- 대부분의 Butadiene은 ethylene 생산 시 by-product로 얻어짐.
- the dehydrogenation of butane to butanes to butadiene is currently the most important "on purpose" source of butadiene.

(반응)

CH_3-CH_2-CH_2-CH_3 -> mixture of butanes -> CH_3=CH-$CHCH_3$

(ⅱ) Other methods for the production of butadiene.

(a) From ethyl alcohol

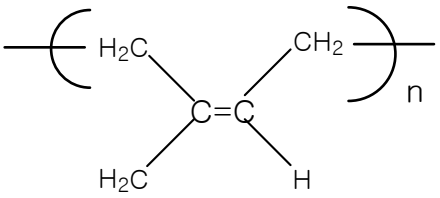
(b) The hydration of acetylene

(c) from acetylene and formaldehyde

(ⅲ) Isoprene

CH_2=C-CH=CH_2, 2-methyl1,3-butadiene

- an important elastomer raw material
- cis-polyisoprene is similar in its structure to natural rubber.



cis -1,4 -polyisoprene

- 대부분의 isoprene은 cis -polyisoprene 생산에 이용됨.