CHAPTER 9

C4 Olefins and Diolefins-Based Chemicals

Professor Bassam El Ali

INTRODUCTION

- The C4 olefins produce fewer chemicals than either ethylene or propylene.
- C4 olefins and diolefins are precursors for some significant big-volume chemicals and polymers such as methyl-ter-butyl ether, adiponitrile, 1,4-butanediol, and polybutadiene.
- Butadiene is not only the most important monomer for synthetic rubber production, but also a chemical intermediate with a high potential for producing useful compounds such as:
  - Sulfolane by reaction with SO_2
  - 1,4-Butanediol by acetoxylation-hydrogenation,
  - Chloroprene by chlorination-dehydrochlorination.

CHEMICALS FROM n-BUTENES

- The three isomers constituting n-butenes are 1-butene, cis-2-butene, and trans-2-butene.
- This gas mixture is usually obtained from the olefinic C4 fraction of catalytic cracking and steam cracking processes after separation of isobutene.
- The mixture may be separated into two streams, one constituted of 1-butene and the other of cis- and trans-2-butene mixture. Each stream produces specific chemicals.
- Approximately 70% of 1-butene is used as a co-monomer with ethylene to produce linear low-density polyethylene (LLDPE).
- Another use of 1-butene is for the synthesis of butylene oxide.
- The rest is used with 2-butenes to produce other chemicals.
- n-Butene could also be isomerized to isobutene.

OXIDATION OF BUTENES

- The mixture of n-butenes (1- and 2-butenes) could be oxidized to different products depending on the reaction conditions and the catalyst.
- The three commercially important oxidation products are acetic acid, malefic anhydride, and methyl ethyl ketone.
- Due to the presence of a terminal double bond in 1-butene, oxidation of this isomer via a chlorohydrination route is similar to that used for propylene.

OXIDATION OF BUTENES
ACETIC ACID (CH_3COOH)

- Currently, the major route for obtaining acetic acid is the carbonylation of methanol.
- It may also be produced by the catalyzed oxidation of n-butane.
- The production of acetic acid from n-butene mixture is a vapor-phase catalytic process.
- The oxidation reaction occurs at approximately 270°C over a titanium vanadate catalyst.
- Yield = 70% in acetic acid. The major by-products are carbon oxides (25%) and maleic anhydride (3%):

$$CH_3CH{=}CHCH_3 + 2\,O_2 \longrightarrow 2CH_3\overset{\overset{\large O}{||}}{C}OH$$

OXIDATION OF BUTENES
ACETIC ACID (CH_3COOH)

- Acetic acid may also be produced by reacting a mixture of n-butenes with acetic acid over an ion exchange resin.
- The formed sec-butyl acetate is then oxidized to yield three moles of acetic acid:

$$CH_3CH{=}CHCH_3 + CH_3CH_2CH{=}CH_2 + 2\,CH_3COOH \longrightarrow 2\,CH_3\overset{\overset{O}{||}}{C}O\overset{\overset{CH_3}{|}}{C}HCH_2CH_3$$

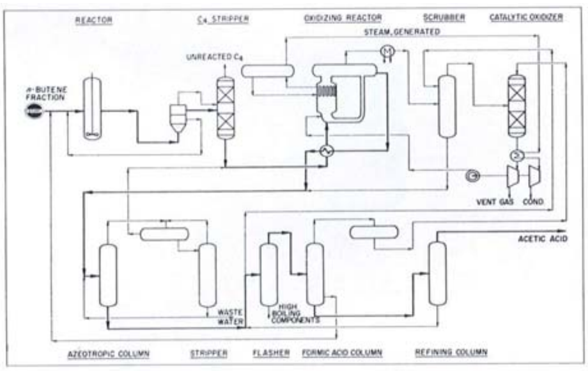
sec-Butyl acetate

$$CH_3\overset{\overset{O}{||}}{C}O\overset{\overset{CH_3}{|}}{C}HCH_2CH_3 + 2\,O_2 \longrightarrow 3\,CH_3COOH$$

OXIDATION OF BUTENES

ACETIC ACID (CH_3COOH)

- The reaction conditions are approximately 100-120°C and 15-25 atm. The oxidation step is non-catalytic and occurs at approximately 200°C and 60 atm.
- An acetic acid yield of 58% could be obtained. By-products are formic acid (6%), higher boiling compounds (3%), and carbon oxides (28%).
- Acetic acid is a versatile reagent. It is an important esterifying agent for the manufacture of cellulose acetate (for acetates.
- Acetic acid is used to produce pharmaceuticals, insecticides, and dyes. It is also a precursor for chloroacetic acid and acetic anhydride.
- The 1994 U.S. production of acetic acid was pproximately 4 billion pounds.



The Bayer AG two-step process for producing acetic acid from n-butenes

OXIDATION OF BUTENES

ACETIC ACID (CH_3COOH)

$$CH_3COOH \longrightarrow \underset{\text{Ketene}}{CH_2{=}C{=}O} + H_2O$$

$$CH_3{=}C{=}O + CH_3\overset{O}{\overset{\|}{C}}OH \longrightarrow CH_3\overset{O}{\overset{\|}{C}}{-}O{-}\overset{O}{\overset{\|}{C}}CH_3$$

- Ketene further reacts with one mole acetic acid, yielding acetic anhydride.
- Acetic anhydride is manly used to make acetic esters and acetyl salicylic acid (aspirin).

Methyl Ethyl Ketone $CH_3\overset{\displaystyle O}{\overset{\|}{C}}CH_2CH_3$

- Methyl Ethyl Ketone MEK (2-butanone) is a colorless liquid similar to acetone, but its boiling point is higher (79.5°C).
- The production of MEK from n-butenes is a liquid-phase oxidation process similar to that used to produce acetaldehyde from ethylene using a Wacker-type catalyst ($PdCl_2/CuCl_2$).
- The reaction conditions are similar to those for ethylene. The yield of MEK is approximately 88%.

$$CH_2{=}CHCH_2CH_3 + {}^1/_2\,O_2 \longrightarrow CH_3\overset{\displaystyle O}{\overset{\|}{C}}CH_2CH_3$$

Methyl Ethyl Ketone $CH_3\overset{\displaystyle O}{\overset{\|}{C}}CH_2CH_3$

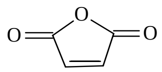
- Methyl Ethyl Ketone may also be produced by the catalyzed dehydrogenation of sec-butanol over zinc oxide or brass at about 500°C.
- The yield from this process is approximately 95%.
- MEK is used mainly as a solvent in vinyl and acrylic coatings, in nitrocellulose lacquers, and in adhesives.
- It is a selective solvent in dewaxing lubricating oils where it dissolves the oil and leaves out the wax.

Methyl Ethyl Ketone $CH_3\overset{\displaystyle O}{\overset{\|}{C}}CH_2CH_3$

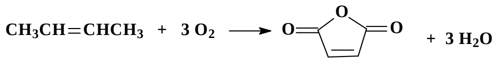
- MEK is also used to synthesize various compounds such as methyl ethyl ketone peroxide, a polymerization catalyst used to form acrylic and polyester polymers and methyl pentynol by reacting with acetylene.
- Methyl pentynol is a solvent for polyamides, a corrosion inhibitor, and an ingredient in the synthesis of hypnotics

$$CH_3\overset{\displaystyle O}{\overset{\|}{C}}CH_2CH_3 + HC{\equiv}CH \longrightarrow CH_3CH_2\underset{\displaystyle OH}{\overset{\displaystyle CH_3}{C}}{-}C{\equiv}CH$$

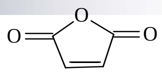
Maleic Anhydride



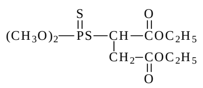
- Maleic anhydride, a solid compound that melts at 53ºC, is soluble in water, alcohol, and acetone, but insoluble in hydrocarbon solvents.
- The production of maleic anhydride from n-butenes is a catalyzed reaction occurring at approximately 400-440oC and 2-4 atm.
- A special catalyst, constituted of an oxide mixture of molybdenum, vanadium, and phosphorous, may be used.
- Approximately 45% yield of maleic anhydride could be obtained from their route.



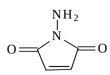
Maleic Anhydride



- Maleic anhydride polymerizes with other monomers while retaining the double bond, as in unsaturated polyester resins.
- These resins, which represent the largest end use of maleic anhydride, are employed primarily in fiber-reinforced plastics for the construction, marine, and transportation industries.
- Maleic anhydride can also modify drying oils such as linseed and sunflower.
- As an intermediate, maleic anhydride is used to produce malathion, an important insecticide, and maleic hydrazide, a plant growth regulator.

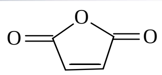


Malathion

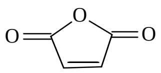


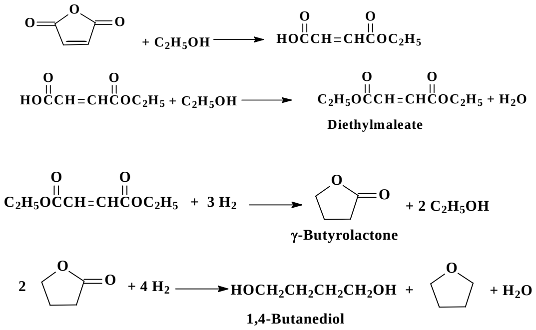
Maleic hydrazide

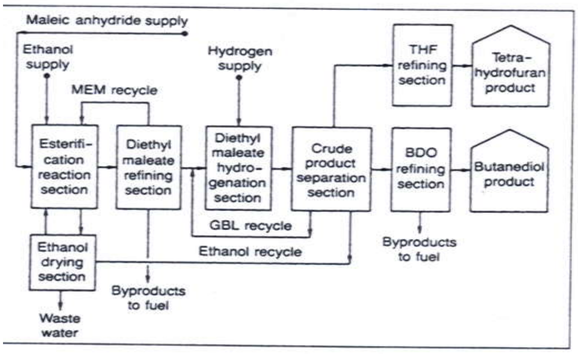
Maleic Anhydride



- Maleic anhydride is also a precursor for 1,4-butanediol through an etherification route followed by hydrogenation.
- In this process, excess ethyl alcohol esterifies maleic anhydride to monoethyl maleate.
- In a second step. The monoester catalytically esterifies to the diester. Excess ethanol and water are then removed by distillation. The ethanol-water mixture is distilled to recover ethanol which is recycled.
- Hydrogenation of diethylmaleate in the vapor phase over a nonprecious metal catalyst produces diethyl succinate. Successive hydrogenation produces γ-butyrolactone, 1,4-butanediol and tetrahydrofuran.
- Selectivity into the co-products is high, but the ratios of the co-products may be controlled with appropriate reactor operating conditions.

Maleic Anhydride 





A block diagram for producing 1,4-butanediol from maleic anhydride

Butylene Oxide ($CH_3CH_2\overset{O}{CH-CH_2}$)

- Butylenes oxide, like propylene oxide, is produced by the chlorohydrination of 1-butene with HOCl followed by epoxidation.
- The reaction conditions are similar to those used for propylene.
- Butylenes oxide may be hydrolyzed to butylenes glycol, which is used to make plasticizers.
- 1,2-Butylene oxide is a stabilizer for chlorinated solvents and also an intermediate in organic synthesis such as in surfactants and pharmaceuticals.

$$CH_3CH_2CH=CH_2 + HOCl \longrightarrow \underset{\text{Butylene chlorohydrin}}{CH_3CH_2CHOHCH_2Cl}$$

$$2\,CH_3CH_2CHOHCH_2Cl + Ca(OH)_2 \longrightarrow 2\,CH_3CH_2\overset{O}{CH-CH_2} + 2\,H_2O$$

Hydration of n-Butenes
(sec-Butanol [$CH_3CHOHCH_2CH_3$])

- Sec-butanol (2-butanol, sec butyl alcohol), a liquid, has a strong characteristic odor. Its normal boiling point is 99.5oC, which is near water's.
- The alcohol is soluble in water but less so than isopropyl and ethyl alcohols.
- sec-Butanol is produced by a reaction of sulfuric acid with a mixture of n-butenes followed by hydrolysis.
- Both 1-butene and cis- and trans-2-butenes yield the same carbocation intermediate, which further reacts with the HSO_4^{1-} ions, producing a sulfate mixture.

Hydration of n-Butenes
(sec-Butanol [$CH_3CHOHCH_2CH_3$])

$$\begin{matrix} CH_2{=}CH{-}CH_2CH_3 \\ \text{or} \\ CH_3{-}CH{=}CH{-}CH_3 \end{matrix} \quad + H^+ \longrightarrow [CH_3\overset{+}{C}H{-}CH_2CH_3]$$

- The sulfation reaction occurs in the liquid phase at approx. 35^oC. An 85 wt% alcohol yield could be realized.
- The reaction is similar to the sulfation of ethylene or propylene and results in a mixture of sec-butyl hydrogen sulfate and di-sec-butyl sulfate.
- The mixture is further hydrolyzed to sec-butanol and sulfuric acid.

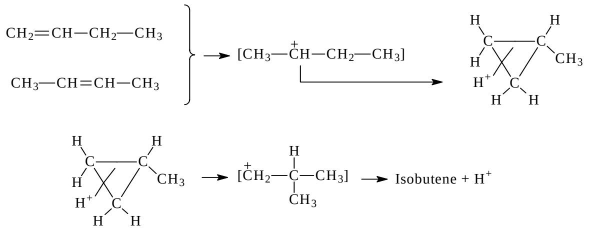
$$3\,CH_3CH_2CH{=}CH_2 + 2\,H_2SO_4 \longrightarrow CH_3CH_2\underset{}{\overset{CH_3}{\overset{|}{C}}}HOSO_3H + (CH_3CH_2\overset{CH_3}{\overset{|}{C}}H)_2OSO_3$$

$$\xrightarrow{+\,3\,H_2O} 3CH_3CH_2CHOHCH_3 + 2H_2SO_4$$

Isomerization of n-Butenes

- n-Butene could be isomerized to isobutene using Shell FER catalyst which is active and selective.
- n-Butene mixture from steam cracker or FCC after removal of C_5 olefins via selective hydrogenation step passes to the isomerization unit.
- It has been proposed that after the formation of a butyl carbocation, a cyclopropyl carbocation is formed which gives a primary carbenium ion that produces isobutene.

Isomerization of n-Butenes



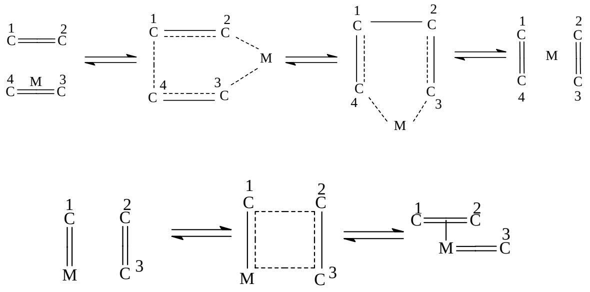
Dr. Bassam El Ali_CHEM 453

METATHESIS OF OLEFINS

- Metathesis is catalyzed reaction that converts two olefin molecules into two different olefins.
- It is an important reaction for which many mechanistic approaches have been proposed by scientists working in the fields of homogenous catalysis and polymerization.
- One approach is the formation of a fluxional five-membered metallocycle.
- The intermediate can give back the starting material or the metathetic products via a concerted mechanism.
- Another approach is a stepwise mechanism that involves the initial formation of a metal carbine followed by the formation of a four-membered metallocycle species.

Dr. Bassam El Ali_CHEM 453

METATHESIS OF OLEFINS



Dr. Bassam El Ali_CHEM 453

METATHESIS OF OLEFINS

- Olefin metatheses are equilibrium reactions among the two-reactant and two-product olefin molecules.
- If chemists design the reaction so that one product is ethylene, for example, they can shift the equilibrium by removing it from the reaction medium.
- Because of the statistical nature of the metathesis reaction, the equilibrium is essentially a function of the ratio of the reactants and the temperature.

METATHESIS OF OLEFINS

- For an equimolar mixture of ethylene and 2-butene at 350°C, the maximum conversion to propylene is 63%.
- Higher conversions require recycling unreacted butanes after fractionation.
- This reaction was first used to produce 2-butene and ethylene from propylene. .
- The reverse reaction is used to prepare polymer-grade propylene form 2-butene and ethylene.

$$CH_3CH{=}CHCH_3 + CH_2{=}CH_2 \rightleftharpoons 2\,CH_3CH{=}CH_2$$

METATHESIS OF OLEFINS

- The metathetic reaction occurs in the gas phase at relatively high temperatures (150-350°C) with molybdenum or tungsten supported catalysts or at low temperature (≈50°C) with rhenium-based catalyst in either liquid or gas-phase.
- The liquid-phase process gives a better conversion. Equilibrium conversion in the range of 55-65% could be realized, depending on the reaction temperature.

METATHESIS OF OLEFINS

- The process has been jointly developed by Institute Français du Pétrole and Chinese Petroleum Corp.
- The C4 feed is mainly composed of 2-butene (1-butene does not favor this reaction but reacts differently with olefins, producing metathetic by-products).
- The reaction between 1-butene and 2-butene, for example, produces 2-pentene and propylene.
- The amount of 2-butene depend on the ratio of 1-butene in the feedstock.
- 3-Hexene is also a by-product from the reaction of two butane molecules (ethylene is also formed during this reaction).

METATHESIS OF OLEFINS

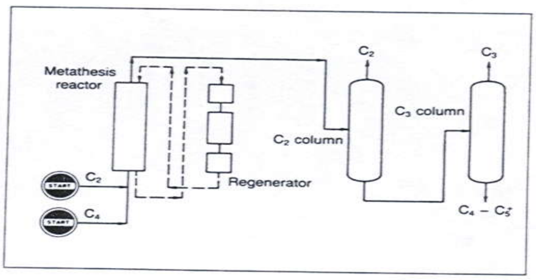
Properties of feed to the metathesis process

Composition	Wt%
n-Butane	2.8
Butane-1	7.2
Butene-2	90.0

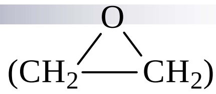
Results of metathesis of 2-butene at two conversion levels

Item	Case 1	Case 2
Ethylene feed, kg/h	8.1	8.1
Total C_4 feed, kg/h	14.3	13.4
C_4 recycle, kg/h	4.4	9.6
Butene-2 conversion		
% per pass	62.3	59.6
% overall	87.8	94.6
Propylene product		
% selectivity	93.8	96.6
% yield from butane-2	82.4	91.3

METATHESIS OF OLEFINS

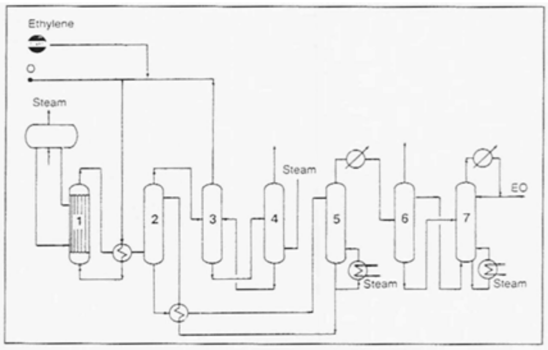


A flow diagram showing the metathesis process for producing polymer grade propylene from ethylene and 2-butene.

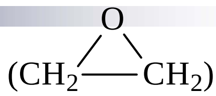
Ethylene Oxide 

Production

- Epoxidation reaction occurs at approximately 200-300°C with a short residence time of one second.
- A selectivity of 70-75% can be reached for the oxygen based process.
- Selectivity is the ratio of moles of ethylene oxide produced per mole of ethylene reacted.
- Ethylene oxide selectivity can be improved when the reaction temperature is lowered and the conversion of ethylene is decreased (higher recycle of unreacted gases).



The Scientific Design Co. Ethylene Oxide process: (1) reactor, (2) scrubber, (3,4) CO_2 removal, (5) stripper, (6,7) fractionators.

Ethylene Oxide 

Derivatives of Ethylene Oxide

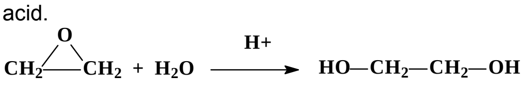
- Ethylene oxide is a highly active intermediate.
- It reacts with all compounds that have a labile hydrogen such as water, alcohols, organic acids, and amines.
- The epoxide ring opens, and a new compound with a hydroxyethyl group is produced.
- The addition of a hydroxyethyl group increases the water solubility of the resulting compound.
- Further reaction of ethylene oxide produces polyethylene oxide derivatives with increased water solubility.

Ethylene Glycol ($HOCH_2CH_2OH$)

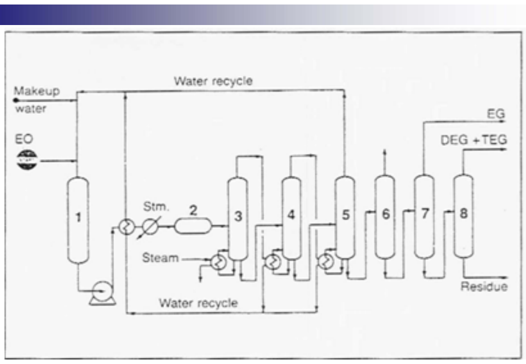
- Ethylene glycol (EG) is colorless syrupy liquid, and is very soluble in water.
- Current world production of ethylene glycol is approximately 15 billion pounds.
- Most of that is used for producing polyethylene terephthalate (PET) resins (for fiber, film, bottles), antifreeze, and other products.
- Approximately 50% of the world EG was consumed in the manufacture of polyester fibers and another 25% went into the antifreeze.

Ethylene Glycol ($HOCH_2CH_2OH$)

- The main route for producing ethylene glycol is the hydration of ethylene oxide in presence of dilute sulfuric acid.



- The hydrolysis reaction occurs at a temperature range of 50-100°C. Contact time is approximately 30 minutes.
- Di - and triethylene glycols are co-products with the monoglycol.
- Increasing the water/ethylene oxide ratio and decreasing the contact time decreases the formation of higher glycols.

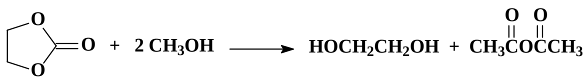


The Scientific Design Co. process for producing ethylene glycols from ethylene oxide: (1) feed tank, (2) reactor, (3,4,5) multiple stage evaporators, # 4 operates at lower pressure than # 3, while # 5 operates under vacuum, evaporated water is recycled to feed tank, (6) light ends stripper, (7,8) vacuum distillation columns.

Ethylene Glycol ($HOCH_2CH_2OH$)

- A water/ethylene oxide ratio of 10 is normally used to get approximately 90% yield of the monoglycol. However, the di- and the triglycols are not an economic burden, because of their commercial uses.
- A new route to ethylene glycol from ethylene oxide via the intermediate formation of ethylene carbonate has recently been developed by Texaco.
- Ethylene carbonate may be formed by the reaction of carbon monoxide, ethylene oxide, and oxygen.
- Ethylene carbonate is a reactive chemical. It reacts smoothly with methanol and produces ethylene glycol in addition to dimethyl carbonate

Ethylene Glycol ($HOCH_2CH_2OH$)



- The reaction occurs at approximately 80-130°C using the proper catalyst.
- Many catalysts have been tried for this reaction, and there is an indication that the best catalyst types are those of the tertiary amine and quaternary ammonium functionalized resins.
- This route produces ethylene glycol of a high purity and avoids selectivity problems associated with the hydrolysis of ethylene oxide.

Alternative Routes to Producing Ethylene Glycol ($HOCH_2CH_2OH$)

- Ethylene glycol could also be obtained directly from ethylene by two methods: the Oxirane acetoxylation and the Teijin oxychlorination processes.
- The production of ethylene glycol from formaldehyde and carbon monoxide (Chapter 5).
- In the Oxirane process, ethylene is reacted in the liquid phase with acetic acid in the presence of a TeO_2 catalyst at approximately 160° and 28 atmospheres.
- The product is a mixture of mono- and diacetates of ethylene glycol.

Alternative Routes to Producing Ethylene Glycol ($HOCH_2CH_2OH$)

$$2\,CH_2{=}CH_2 + 3\,CH_3COOH + O_2 \longrightarrow CH_3\overset{O}{\overset{\|}{C}}OCH_2CH_2OH + CH_3\overset{O}{\overset{\|}{C}}OCH_2CH_2O\overset{O}{\overset{\|}{C}}CH_3 + H_2O$$

- The acetates are then hydrolyzed to ethylene glycol and acetic acid.
- The hydrolysis reaction occurs at approximately 107-130°C and 1.2 atmospheres. Acetic acid is then recovered for further use.

Alternative Routes to Producing Ethylene Glycol ($HOCH_2CH_2OH$)

- The solubility of the product ethoxylates can be varied according to the number of ethylene oxide units in the molecule.
- The solubility is also a function of the chain-length of the alkyl group in the alcohol or in the phenol. Longer-chain alkyl groups reduce water solubility.
- In practice, the number of ethylene oxide units and the chain-length of the alkyl group are varied to either produce water-soluble or oil-soluble surface active agents.

Alternative Routes to Producing Ethylene Glycol ($HOCH_2CH_2OH$)

- Linear alcohols used for the production of ethoxylates are produced by the oligomerization of ethylene using Ziegler catalysts or by the Oxo reaction using alpha olefins.
- Similarly, esters of fatty acids and polyethylene glycols are produced by the reaction of long-chain fatty acids and ethylene oxide.

$$R\overset{O}{\overset{\|}{C}}OH + n\,CH_2\overset{O}{\frown}CH_2 \longrightarrow RCO(CH_2O)_{n-1}H$$

- The C_{12}-C_{18} fatty acids such as oleic, palmitic, and stearic are usually ethoxylated with EO for the production of nonionic detergents and emulsifiers.

Production of Ethanolamines from Ethylene Glycol ($HOCH_2CH_2OH$)

- A mixture of mono-, di-, and triethanolamines is obtained by the reaction between ethylene oxide (EO) and aqueous ammonia.
- The reaction conditions are approximately 30-40°C and atmospheric pressure.

$$6\ \overset{O}{CH_2{-}CH_2} + 3\ NH_3 \longrightarrow H_2NCH_2CH_2OH + NH(CH_2CH_2OH)_2 + N(CH_2CH_2OH)_3$$

- The relative ratios of the ethanolamines produced depend principally on the ethylene oxide/ammonia ratio. A low EO/NH3 ratio increases monoethanolamine yield. Increasing this ratio increases the yield of di-and triethanolamines.

Dr. Bassam El Ali_CHEM 453

Production of Ethanolamines from Ethylene Glycol

Weight ratios of ethanolamines as a function of the mole ratios of the reactants

	Moles of ethylene oxide / moles of ammonia		
	0.1	0.5	1.0
Monoethanolamine	75-61	25-31	12-15
Diethanolamine	21-27	28-32	23-26
Triethanolamine	4-12	37	65-69

Dr. Bassam El Ali_CHEM 453

Production of Ethanolamines from Ethylene Glycol ($HOCH_2CH_2OH$)

- Ethanolamines are important absorbents of acid gases in natural gas treatment processes.
- Another major use of ethanolamines is the production of surfactants.
- The reaction between ethanolamines and fatty acids produces ethanolamides.
- For example, when lauric acid and monoethanolamine are used, N-(2-hydroxyethyl)-lauramide is obtained.

$$CH_3(CH_2)_{10}\overset{\overset{O}{\|}}{C}OH + HOCH_2CH_2NH_2 \longrightarrow CH_3(CH_2)_{10}CONH(CH_2)_2OH + H_2O$$

Dr. Bassam El Ali_CHEM 453

Production of Ethanolamines from Ethylene Glycol ($HOCH_2CH_2OH$)

- Ethanolamines are important absorbents of acid gases in natural gas treatment processes.
- Another major use of ethanolamines is the production of surfactants.
- The reaction between ethanolamines and fatty acids produces ethanolamides.
- For example, when lauric acid and monoethanolamine are used, N-(2-hydroxyethyl)-lauramide is obtained.
- Monoethanolamides are used primarily in heavy-duty powder detergents as foam stabilizers and rinse improvers.

$$CH_3(CH_2)_{10}\overset{\overset{O}{||}}{C}OH + HOCH_2CH_2NH_2 \longrightarrow CH_3(CH_2)_{10}CONH(CH_2)_2OH + H_2O$$

Production of 1,3-Propanediol from Ethylene Glycol

- 1,3-Propanediol is a colorless liquid that boils at 210-211°C. It is soluble in water, alcohol, and ether.
- It is an intermediate for polyester production.
- It could be produced via the hydroformylation of ethylene oxide which yields 3-hydroxypropionaldehyde. Hydrogenation of the product produces 1,3-propanediol.
- The catalyst is a cobalt carbonyl that is prepared in situ from cobaltous hydroxide, and nonylpyridine is the promotor.
- Oxidation of the aldehyde produces 3-hydroxypropionic acid. 1,3-Propanediol and 3-hydroxypropionic acid could also be produced from acrolein.

$$CH_2\overset{O}{\frown}CH_2 + CO + H_2 \longrightarrow HO—(C_2H_4)CHO$$

$$HO\text{-}(C_2H_4)CHO + H_2 \longrightarrow \underset{OH}{CH_2}—CH_2—\underset{OH}{CH_2}$$

Production of ACETALDEHYDE from Ethylene

- Acetaldehyde is a colorless liquid with a pungent odor.
- It is a reactive compound with no direct use except for the synthesis of other compounds.
- For example, it is oxidized to acetic acid and acetic anhydride. It is a reactant in the production of 2-ethylhexanol for the synthesis of plasticizers.
- There are many ways to produce acetaldehyde.
- Historically, it was produced either by the silver-catalyzed oxidation or by the chromium activated copper-catalyzed dehydrogenation of ethanol.
- Currently, acetaldehyde is obtained from ethylene by using a homogeneous catalyst (**Wacker catalyst**).

Production of ACETALDEHYDE from Ethylene

- Acetaldehyde is a colorless liquid with a pungent odor.
- It is a reactive compound with no direct use except for the synthesis of other compounds.
- For example, it is oxidized to acetic acid and acetic anhydride. It is a reactant in the production of 2-ethylhexanol for the synthesis of plasticizers.
- There are many ways to produce acetaldehyde.
- Historically, it was produced either by the silver-catalyzed oxidation or by the chromium activated copper-catalyzed dehydrogenation of ethanol.
- Currently, acetaldehyde is obtained from ethylene by using a homogeneous catalyst (**Wacker catalyst**).

The Wacker Process

- It is an industrial process for the manufacture of ethanol by oxidizing ethene. Commercially it gives 95% yield of acetaldehyde which is converted to the ethanol.
- The favorable economics of the process is due to the abundance of ethylene.
- The reaction is catalyzed by $PdCl_2$ -$CuCl_2$.
- During the reaction palladium forms a complex with ethylene, is reduced to Pd(0), and is then reoxidized by Cu(II).
- The process is run in one vessel at 50-130 ^oC and at pressures of 3-10 atm.

The Wacker Process

- Developed simultaneously by Wacker-Chemie.
- It involves the reaction of ethylene with palladium(I) chloride in water (reaction 1).
- Palladium is thereby reduced to palladium black.
- To make the reaction catalytic, palladium is reoxidized by reaction with copper(II) chloride and oxygen (reactions 2 and 3).

$$C_2H_4 + PdCl_4^{2-} + 3H_2O \longrightarrow CH_3CHO + Pd^0 + 2H_3O + 4Cl^- \quad (1)$$

$$Pd^0 + 2CuCl_2 + 2Cl^- \longrightarrow PdCl_4^{2-} + 2CuCl \quad (2)$$

$$CuCl + 4H_3O^+ + 4Cl^- + O_2 \longrightarrow 4CuCl_2 + 6H_2O \quad (3)$$

Major Features

- First, ethylene coordinates to palladium, replacing a chloride ion.

$$C_2H_4 + PdCl_4^{2-} + 3H_2O \longrightarrow CH_3CHO + Pd^0 + 2H_3O + 4Cl^-$$

- Then, addition of hydroxyl to the ethylene takes place to form a hydroxyethyl ligand.

$$Pd^0 + 2CuCl_2 + 2Cl^- \longrightarrow PdCl_4^{2-} + 2CuCl$$

- Successively, a series of hydrogen migrations takes place to form acetaldehyde.

$$CuCl + 4H_3O^+ + 4Cl^- + O_2 \longrightarrow 4CuCl_2 + 6H_2O$$

Important Chemicals from Acetaldehyde
Acetic Acid

- Acetic acid is obtained from different sources.
  - Carbonylation of methanol is currently the major route.
  - Oxidation of butanes and butenes is an important source of acetic acid, especially in the U.S.
  - It is also produced by the catalyzed oxidation of acetaldehyde.
  - The reaction occurs in the liquid phase at approximately 65°C using manganese acetate as a catalyst.

$$CH_3\overset{O}{\overset{\|}{C}}H + 1/2O_2 \longrightarrow CH_3\overset{O}{\overset{\|}{C}}OH$$

Important Chemicals from Acetaldehyde
n-Butanol

- n-Butanol is normally produced from propylene by the Oxo reaction.
- It may also be obtained from the aldol condensation of acetaldehyde in presence of a base.

$$2\ CH_3\overset{O}{\overset{\|}{C}}H \xrightarrow{OH^-} CH_3CHOHCH_2\overset{O}{\overset{\|}{C}}H$$

Important Chemicals from Acetaldehyde
n-Butanol

- The formed 3-hydroxybutanal eliminates one mole of water in the presence of an acid producing crotonaldehyde.
- Hydrogenation of crotonaldehyde produces n-butanol.

$$CH_3CHOHCH_2\overset{\overset{\large O}{||}}{C}H \xrightarrow{H^+} \underset{\text{Crotonaldehyde}}{CH_3CH{=}CH\overset{\overset{\large O}{||}}{C}H} + H_2O$$

$$CH_3CH{=}CH\overset{\overset{\large O}{||}}{C}H + H_2 \longrightarrow \underset{\text{n-Butanol}}{CH_3CH_2CH_2CH_2OH}$$

Important Chemicals from Acetaldehyde
Vinyl Acetate ($CH_2{=}CHO\overset{\overset{O}{||}}{C}CH_3$)

- Vinyl acetate is a reactive colorless liquid that polymerizes easily if not stabilized.
- Important monomer for the production of polyvinyl acetate, polyvinyl alcohol, and vinyl acetate copolymers.
- The U.S. production of vinyl acetate, the 40th highest-volume chemical, was approximately 3 billion pounds in 1994.

Important Chemicals from Acetaldehyde
Vinyl Acetate ($CH_2{=}CHO\overset{\overset{O}{||}}{C}CH_3$)

- Vinyl acetate was originally produced by the reaction of acetylene and acetic acid in the presence of mercury(II) acetate.
- Currently, it is produced by the catalytic oxidation of ethylene with oxygen, with acetic acid as a reactant and palladium as the catalyst.

$$CH_2{=}CH_2 + CH_3\overset{\overset{O}{||}}{C}OH + 1/2O_2 \longrightarrow CH_2{=}CHO\overset{\overset{O}{||}}{C}CH_3 + H_2O$$

Important Chemicals from Acetaldehyde

Vinyl Acetate ($CH_2{=}CHO\overset{\overset{\Large O}{||}}{C}CH_3$)

- The process is similar to the catalytic liquid-phase oxidation of ethylene to acetaldehyde (Wacker Process).
- The difference between the two processes is the presence of acetic acid.
- Acetaldehyde is a major co-product. The mole ratio of acetaldehyde to vinyl acetate can be varied from 0.3:1 to 2.5:1.
- The liquid-phase process is not used extensively due to corrosion problems and the formation of a fairly wide variety of by-products.

Important Chemicals from Acetaldehyde

Vinyl Acetate ($CH_2{=}CHO\overset{\overset{\Large O}{||}}{C}CH_3$)

- In the vapor-phase process, oxyacylation of ethylene is carried out in a tubular reactor at approximately 117°C and 5 atmospheres.
- The palladium acetate is supported on carriers resistant to attack by acetic acid.
- Conversions of about 10-15% based on ethylene are normally used to operate safely outside the explosion limits (approximately 10% O_2).
- Selectivities of 91-94% based on ethylene are attainable.

OXIDATIVE CARBONYLATION OF ETHYLENE

Acrylic acid: $CH_2{=}CH\overset{\overset{O}{||}}{C}OH$

- The liquid phase reaction of ethylene with carbon monoxide and oxygen over a Pd^{2+}/Cu^{2+} catalyst system produces acrylic acid.
- The yield based on ethylene is about 85%.
- Reaction conditions are approximately 140°C and 75 atmospheres.
- The catalyst is similar to that of the Wacker reaction for ethylene oxidation to acetaldehyde, however, this reaction occurs in presence of carbon monoxide.

$$CH_2{=}CH_2 + CO + 1/2O_2 \longrightarrow CH_2{=}CH\overset{\overset{O}{||}}{C}OH$$

CHLORINATION OF ETHYLENE

- The direct addition of chlorine to ethylene produces ethylene dichloride (1,2-dichloroethane).
- Ethylene dichloride is the main precursor for vinyl chloride, which is an important monomer for polyvinyl chloride plastics and resins.
- Other uses of ethylene dichloride include its formulation with tetraethyl and tetramethyl lead solutions as a lead scavenger, as a degreasing agent, and as an intermediate in the synthesis of many ethylene derivatives.

CHLORINATION OF ETHYLENE

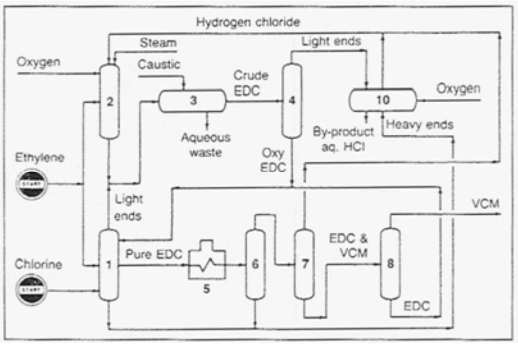
- The reaction of ethylene with hydrogen chloride, on the other hand, produces ethyl chloride. This compound is a small-volume chemical with diversified uses (alkylating agent, refrigerant, solvent,…).
- Ethylene reacts also with hypochlorous acid, yielding ethylene chlorohydrin.
- Ethylene chlorohydrin via this route was previously used for producing ethylene oxide through an epoxidation step.
- Ethylene chlorohydrin is a useful agent for introducing the ethylhydroxy group. It is also used as a solvent for cellulose acetate

$$CH_2{=}CH_2 + HOCl \rightarrow ClCH_2CH_2OH$$

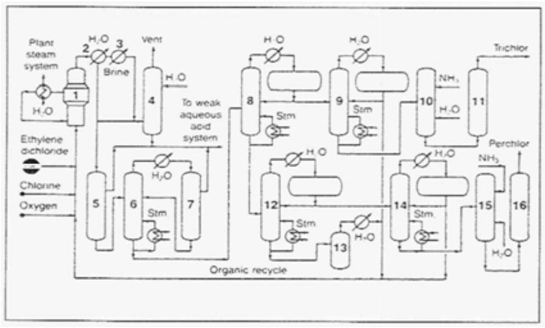
CHLORINATION OF ETHYLENE
Vinyl Chloride ($CH_2{=}CH\text{-}Cl$)

- Vinyl chloride is the most important vinyl monomer in the polymer industry.
- Vinyl chloride monomer (VCM) was originally produced by the reaction of hydrochloric acid and acetylene in the presence of $HgCl_2$ catalyst.
- The reaction is straightforward and proceeds with high conversion (96% on acetylene.

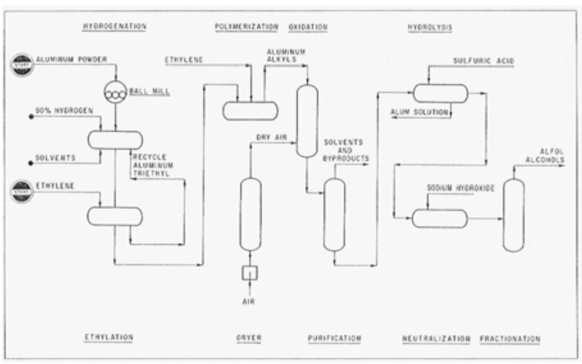
$$H\text{-}C{\equiv}CH \quad + \quad HCl \longrightarrow CH_2{=}CH{-}Cl$$



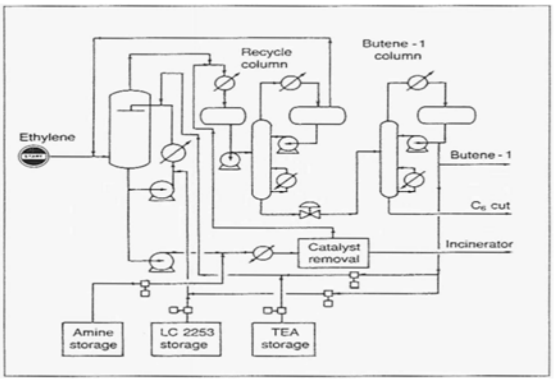
The European Vinyls Corporation process for producing vinyl chloride: (1) chlorination section, (2) oxychlorination reactor, (3) steam stripping and caustic treatment of water effluent, (4) EDC distillation, (5) pyrolysis furnace, (6,7,8) VCM and EDC separation, (10) by-product reactor.



The PPG Industries Inc. Chloroethylene process for producing perchloro and trichloroethylene: (1) reactor, (2)graphite exchanger, (3) refrigerated condenser, (4) scrubber, (5) phase separation of perchlor from trichlor, (6,7) azeotropic distillation, (8) distillation train, (9-11) crude trichlor separation – purification, (10-16) crude perchlor separation – purification.



The alfol process for making even numbered straight chain alpha alcohols



A flow diagram of the institute Français du Pétrole process for producing 1-butene from ethylene