

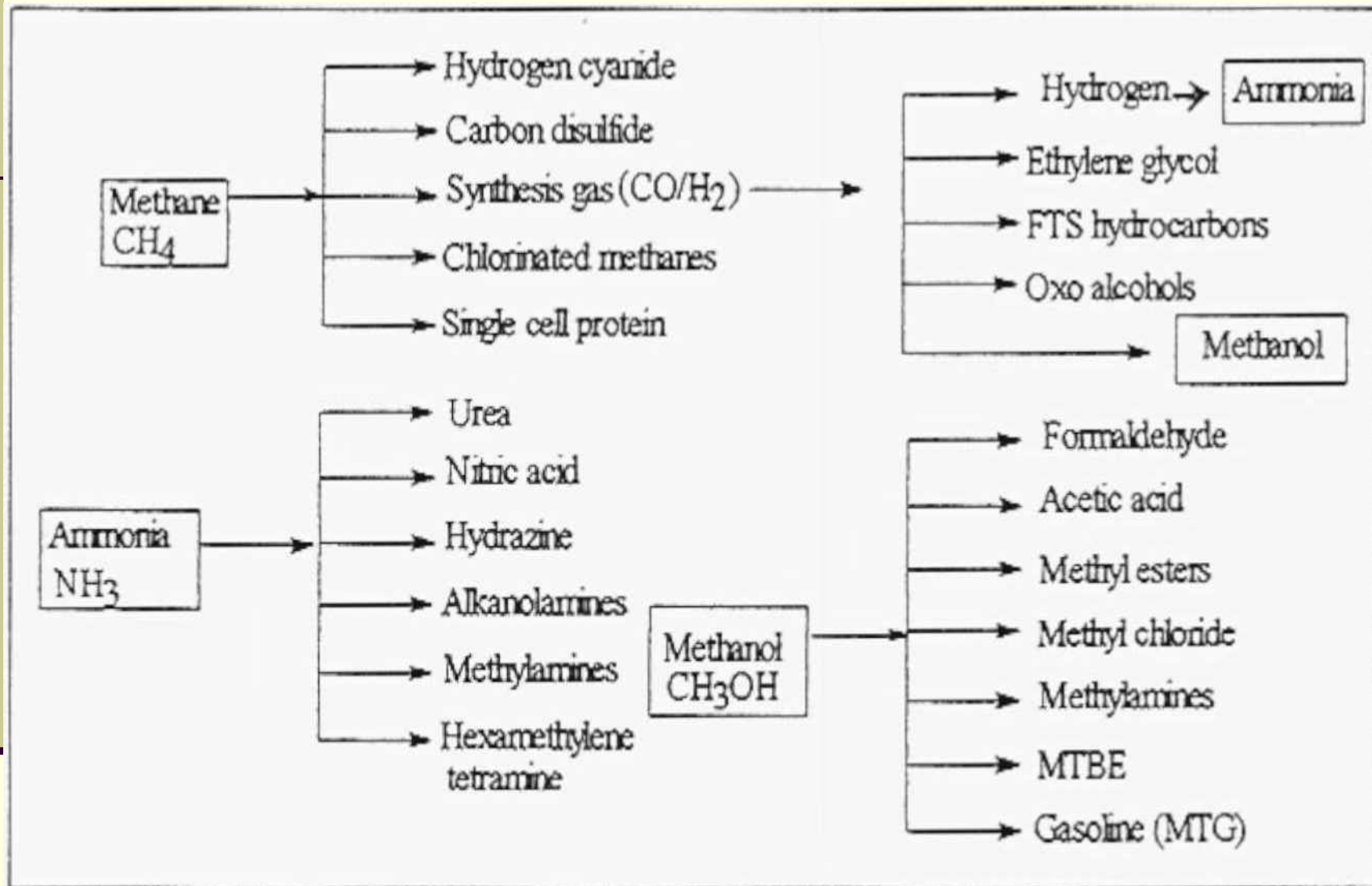
# CHAPTER 5

## CHEMICALS BASED ON METHANE

# INTRODUCTION

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- Methane is a one-carbon paraffinic hydrocarbon that is not very reactive under normal conditions.
- Only a few chemicals can be produced directly from methane under relatively severe conditions.
- Chlorination of methane is only possible by thermal or photochemical initiation.
- Methane can be partially oxidized with a limited amount of oxygen or in presence of steam to a synthesis gas mixture.
- Many chemicals can be produced from methane via the more reactive **synthesis gas** mixture.
- Synthesis gas is the precursor for two major chemicals, ammonia and methanol. Both compounds are the hosts for many important petrochemical products.



**Important chemicals based on methane, synthesis gas, ammonia, and methanol.**

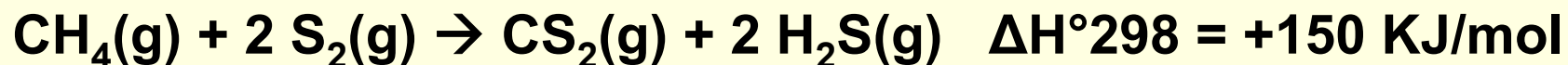
# CHEMICALS BASED ON DIRECT REACTIONS OF METHANE

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- A few chemicals are based on the direct reaction of methane with other reagents.
- These are carbon disulfide, hydrogen cyanide chloromethanes, and synthesis gas mixture.
- Currently, a redox fuel cell based on methane is being developed.

# CARBON DISULFIDE (CS<sub>2</sub>)

- Methane reacts with sulfur at high temperatures to produce carbon disulfide.
- The reaction is endothermic, and an activation energy of approximately 160 KJ is required.
- Activated alumina or clay is used as the catalyst at approximately 675°C and 2 atmospheres.
- The process starts by vaporizing pure sulfur, mixing it with methane, and passing the mixture over the alumina catalyst.



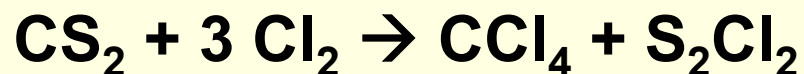
# CARBON DISULFIDE (CS<sub>2</sub>)

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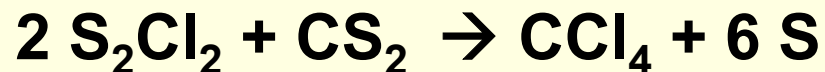
- Hydrogen sulfide, a co-product, is used to recover sulfur by the Claus reaction.
- A CS<sub>2</sub> yield of 85-90% based on methane.
- An alternative route for CS<sub>2</sub> is by the reaction of liquid sulfur with charcoal. However, this method is not used very much.

# USES OF CARBON DISULFIDE (CS<sub>2</sub>)

- Carbon disulfide is primarily used to produce rayon and cellophane (regenerated cellulose).
- CS<sub>2</sub> is also used to produce carbon tetrachloride using iron powder as a catalyst at 30°C.



- Sulfur monochloride is an intermediate that is then reacted with carbon disulfide to produce more carbon tetrachloride and sulfur.



- The net reaction is:



# HYDROGEN CYANIDE (HCN)

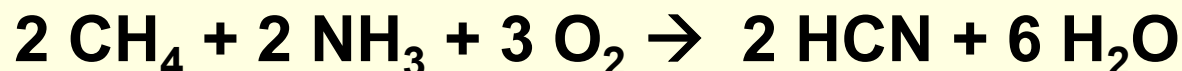
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- Hydrogen cyanide (hydrocyanic acid) is a colorless liquid (b.p. 25.6°C) that is miscible with water, producing a weakly acidic solution.
- It is a highly toxic compound.
- A very useful chemical intermediate with high reactivity.
- It is used in the synthesis of acrylonitrile and adiponitrile, which are important monomers for plastic and synthetic fiber production.



# HYDROGEN CYANIDE (HCN)

- Hydrogen cyanide is produced via the Andrussov process using ammonia and methane in presence of air.
- The reaction is exothermic, and the released heat is used to supplement the required catalyst-bed energy.



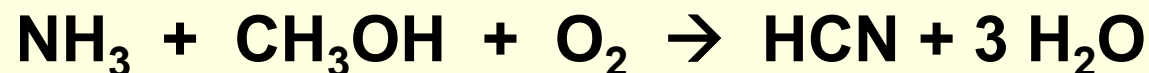
- A platinum-rhodium alloy - a catalyst at 1100°C.
- Approximately equal amounts of ammonia and methane with 75 vol % air are introduced to the preheated reactor.
- The catalyst has several layers of wire gauze with a special mesh size (approximately 100 mesh).

# HYDROGEN CYANIDE (HCN)

- The Degussa process: ammonia reacts with methane in absence of air using a platinum, aluminum-ruthenium alloy as a catalyst at approximately 1200°C.
- The reaction produces hydrogen cyanide and hydrogen. The yield is over 90%. The reaction is endothermic and requires 251 KJ/mol.



- Hydrogen cyanide may also be produced by the reaction of ammonia and methanol in presence of oxygen.



# HYDROGEN CYANIDE (HCN)

- Hydrogen cyanide is a reactant in the production of acrylonitrile, methyl methacrylates (from acetone), adiponitrile, and sodium cyanide.
- It is also used to make oxamide, a long-lived fertilizer that releases nitrogen steadily over the vegetation period.
- Oxamide is produced by the reaction of hydrogen cyanide with water and oxygen using a copper nitrate catalyst at about 70°C and atmospheric pressure.



# CHLOROMETHANES

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- The successive substitution of methane hydrogens with chlorine produces a mixture of four chloromethanes:
  - Monochloromethane (methyl chloride,  $\text{CH}_3\text{Cl}$ )
  - Dichloromethane (methylene chloride,  $\text{CH}_2\text{Cl}_2$ )
  - Trichloromethane (chloroform,  $\text{CHCl}_3$ )
  - Tetrachloromethane (carbon tetrachloride,  $\text{CCl}_4$ )

# PRODUCTION OF CHLOROMETHANES

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- Methane is the most difficult alkane to chlorinate.
- The reaction is initiated by chlorine free radicals obtained via the application of heat (thermal) or light ( $h\nu$ ).
- Thermal chlorination (**more widely used industrially**) occurs at approximately 350-370°C and atmospheric pressure.

# PRODUCTION OF CHLOROMETHANES

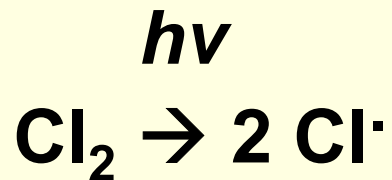
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- A typical product distribution of chloromethanes for a  $\text{CH}_4/\text{Cl}_2$  feed ratio of 1.7 is:
  - mono- (58.7%)
  - di- (29.3%)
  - tri- (9.7%)
  - tetra- (2.3%)

# PRODUCTION OF CHLOROMETHANES

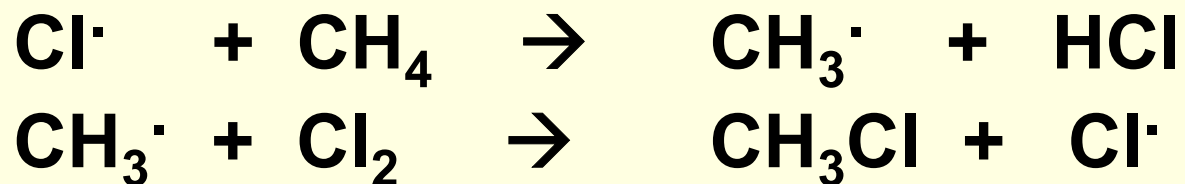
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- The highly exothermic chlorination reaction produces approximately 95 KJ/mol of HCl.
- The first step is the breaking of the Cl-Cl bond (bond energy = + 584.2 KJ), which forms two chlorine free radicals (Cl atoms):



# PRODUCTION OF CHLOROMETHANES

- The Cl atom attacks methane and forms a methyl free radical plus HCl.
- The methyl radical-reacts in a subsequent step with a chlorine molecule, forming methyl chloride and a Cl atom:



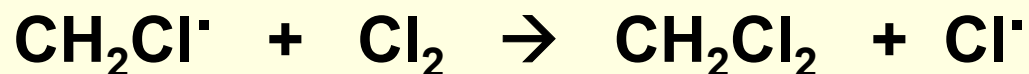


# PRODUCTION OF CHLOROMETHANES

- The new Cl. atom either attacks another methane molecule or reacts with a methyl chloride molecule to form a chloromethyl free radical  $\text{CH}_2\text{Cl}^\cdot$  and HCl.



- The chloromethyl free radical then attacks another chlorine molecule and produces dichloromethane along with a  $\text{Cl}^\cdot$  atom:



- This formation of  $\text{Cl}^\cdot$  free radicals continues until all chlorine is consumed.
- Chloroform ( $\text{CHCl}_3$ ) and carbon tetrachloride ( $\text{CCl}_4$ ) are formed in a similar way by reaction of  $\text{CHCl}_2$  and  $\text{CCl}_3$  free radicals with chlorine.

# PRODUCTION OF CHLOROMETHANES

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- Product distribution among the chloromethanes depends primarily on the mole ratio of the reactants.
- For example, the yield of monochloromethane could be increased to 80% by increasing the  $\text{CH}_4/\text{Cl}_2$  mole ratio to 10:1 at  $450^\circ\text{C}$ .
- If dichloromethane is desired, the  $\text{CH}_4/\text{Cl}_2$  ratio is lowered and the monochloromethane recycled.
- Decreasing the  $\text{CH}_4/\text{Cl}_2$  ratio generally increases polysubstitution and the chloroform and carbon tetrachloride yield.

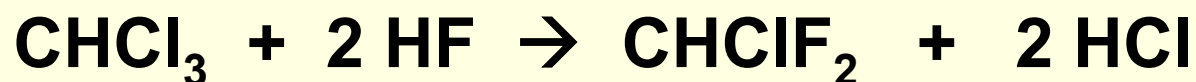
# Uses of Chloromethanes

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- The major use of methyl chloride is to produce silicon polymers.
- Other uses include the synthesis of tetramethyl lead as a gasoline octane booster, a methylating agent in methyl cellulose production, a solvent, and a refrigerant.
- Methylene chloride has a wide variety of markets. One major use is a paint remover. It is also used as a degreasing solvent, a blowing agent for polyurethane foams, and a solvent for cellulose acetate.

# Uses of Chloromethanes

- Chloroform is mainly used to produce chlorodifluoromethane (Fluorocarbon 22) by the reaction with hydrogen fluoride:



- This compound is used as a refrigerant and as an aerosol propellant. It is also used to synthesize tetrafluoroethylene, which is polymerized to a heat resistant polymer (Teflon):



# Uses of Chloromethanes

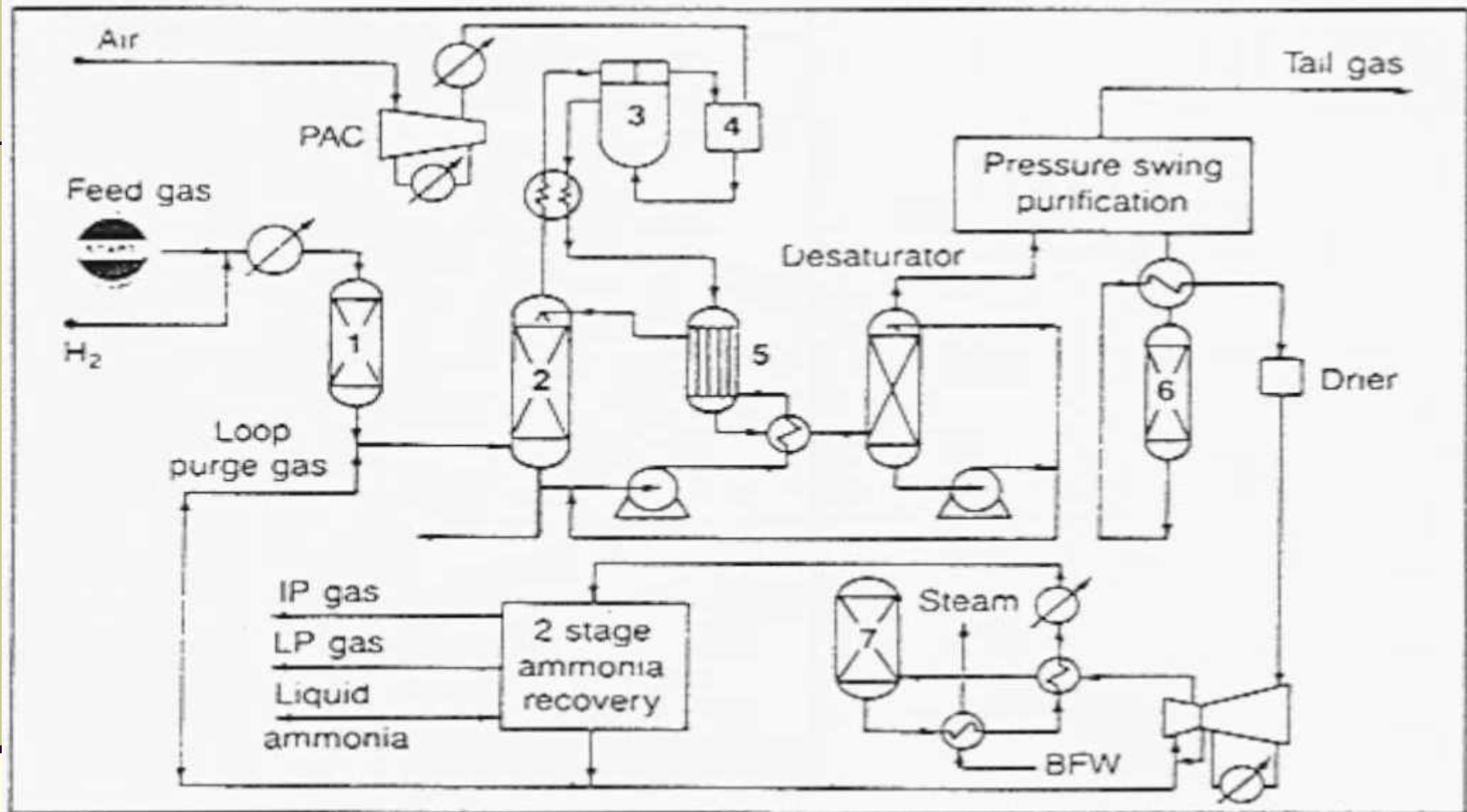
- Carbon tetrachloride is used to produce chlorofluorocarbons by the reaction with hydrogen fluoride using an antimony pentachloride ( $\text{SbCl}_5$ ) catalyst:



- The formed mixture is composed of trichlorofluoromethane (Freon-11) and dichlorodifluoromethane (Freon-12).
- These compounds are used as aerosols and as refrigerants.
- Due to the depleting effect of chlorofluorocarbons (CFCs) on the ozone layer, the production of these compounds may be reduced appreciably.

# Uses of Chloromethanes

- Much research is being conducted to find alternatives to CFCs with little or no effect on the ozone layer.
- Among these are HCFC-123 ( $\text{HCCl}_2\text{CF}_3$ ) to replace Freon-11 and HCFC-22 ( $\text{CHClF}_2$ ) to replace Freon-12 in such uses as air conditioning, refrigeration, aerosol, and foam.
- These compounds have a much lower ozone depletion value compared to Freon-11, which was assigned a value of 1.
- Ozone depletion values for HCFC-123 and HCFC-22 relative to Freon-11 equals 0.02 and 0.055.



The ICI process for producing synthesis gas and ammonia: (1) desulfurization, (2) feed gas saturator, (3) primary reformer, (4) secondary reformer, (5) shift converter, (6) methanator, (7) ammonia reactor

# SYNTHESIS GAS

## (STEAM REFORMING OF NATURAL GAS)

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- Natural gas is the preferred feedstock when it is available from gas fields (non-associated gas) or from oil wells (associated gas).
- The first step in the production of synthesis gas is to treat natural gas to remove hydrogen sulfide.
- The purified gas is then mixed with steam and introduced to the first reactor (**primary reformer**).
- The reactor is constructed from vertical stainless steel tubes lined in a refractory furnace.
- The **steam to natural gas ratio** varies from **4-5** depending on natural gas composition (natural gas may contain ethane and heavier hydrocarbons) and the pressure used.



# SYNTHESIS GAS

## (STEAM REFORMING OF NATURAL GAS)

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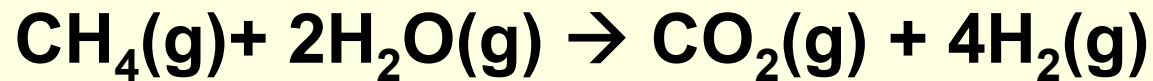
- A promoted nickel type catalyst contained in the reactor tubes is used at temperature and pressure ranges of 700-800°C and 30-50 atmospheres.
- The reforming reaction is equilibrium limited. It is favored at high temperatures, low pressures, and a high steam to carbon ratio.
- These conditions minimize methane slip at the reformer outlet and yield an equilibrium mixture that is rich in hydrogen.
- The product gas from the primary reformer is a mixture of H<sub>2</sub>, CO, CO<sub>2</sub>, unreacted CH<sub>4</sub>, and steam.

# SYNTHESIS GAS

## (STEAM REFORMING OF NATURAL GAS)

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- The main steam reforming reactions are:



- For the production of methanol, this mixture could be used directly with no further treatment except adjusting the  $\text{H}_2/(\text{CO} + \text{CO}_2)$  ratio to approximately 2:1.

# SYNTHESIS GAS

## (STEAM REFORMING OF NATURAL GAS)

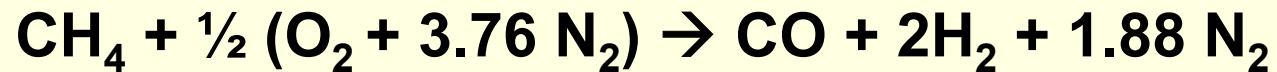
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- For producing hydrogen for ammonia synthesis, further treatment steps are needed.
- First, the required amount of nitrogen for ammonia must be obtained from atmospheric air.
- This is done by partially oxidizing unreacted methane in the exit gas mixture from the first reactor in another reactor (secondary reforming).
- The main reaction occurring in the secondary reformer is the partial oxidation of methane with a limited amount of air.

# SYNTHESIS GAS

## (STEAM REFORMING OF NATURAL GAS)

- The product is a mixture of hydrogen, carbon dioxide, carbon monoxide, plus nitrogen, which does not react under these conditions.



$$\Delta H^\circ = -32.1 \text{ KJ}$$

- The reactor temperature can reach over 900°C in the secondary reformer due to the exothermic reaction heat.
- The second step after secondary reforming is removing carbon monoxide, which poisons the catalyst used for ammonia synthesis.
- This is done in three further steps, shift conversion, carbon dioxide removal, and methanation of the remaining CO and CO<sub>2</sub>.

# SYNTHESIS GAS (STEAM REFORMING OF NATURAL GAS)

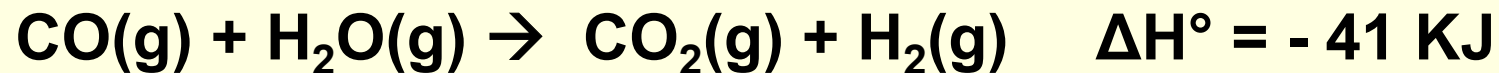
**Table 5-1**  
**Typical analysis of effluent from primary and secondary reformers**

<b>Constituent</b>	<b>Primary reformer</b>	<b>Secondary reformer</b>
<b>H<sub>2</sub></b>	<b>47</b>	<b>39.0</b>
<b>CO</b>	<b>10.2</b>	<b>12.2</b>
<b>CO<sub>2</sub></b>	<b>6.3</b>	<b>4.2</b>
<b>CH<sub>4</sub></b>	<b>7.0</b>	<b>0.6</b>
<b>H<sub>2</sub>O</b>	<b>29.4</b>	<b>27.0</b>
<b>N<sub>2</sub></b>	<b>0.02</b>	<b>17.0</b>

# SYNTHESIS GAS

## Shift Conversion

- The product gas mixture from the secondary reformer is cooled then subjected to shift conversion.
- In the shift converter, carbon monoxide is reacted with steam to give carbon dioxide and hydrogen.
- The reaction is exothermic and independent of pressure:



- The feed to the shift converter contains large amounts of carbon monoxide which should be oxidized.
- An **iron catalyst promoted with chromium oxide** is used at a temperature range of 425-500°C to enhance the oxidation.

# SYNTHESIS GAS

## Shift Conversion

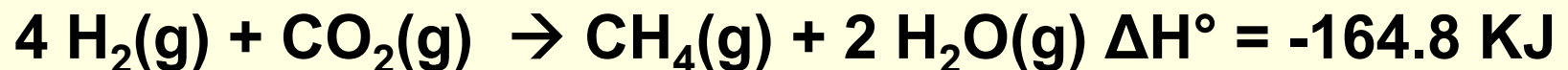
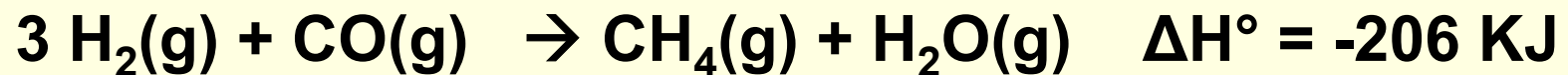
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- Exit gases from the shift conversion are treated to remove carbon dioxide.
- This may be done by absorbing carbon dioxide in a physical or chemical absorption solvent or by adsorbing it using a special type of molecular sieves.
- Carbon dioxide, recovered from the treatment agent as a by-product, is mainly used with ammonia to produce urea.
- The product is a pure hydrogen gas containing small amounts of carbon monoxide and carbon dioxide, which are further removed by methanation.

# SYNTHESIS GAS

## Methanation

- Catalytic methanation is the reverse of the steam reforming reaction.
- Hydrogen reacts with carbon monoxide and carbon dioxide, converting them to methane.
- Methanation reactions are exothermic, and methane yield is favored at lower temperatures:





# SYNTHESIS GAS

## Methanation

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- The forward reactions are also favored at higher pressures.
- However, the space velocity becomes high with increased pressures, and contact time becomes shorter, decreasing the yield.
- The actual process conditions of pressure, temperature, and space velocity are practically a compromise of several factors.
- **Rany Nickel** is the preferred catalyst. Typical methanation reactor operating conditions are 200-300°C and approximately 10 atmospheres.
- The product is a gas mixture of hydrogen and nitrogen having an approximate ratio of 3:1 for ammonia production.

# CHEMICALS BASED ON SYNTHESIS GAS

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- Many chemicals are produced from synthesis gas.
- Synthesis gas is also important for the production of aldehydes from olefins.
- The catalytic hydroformylation reaction (Oxo reaction) is used with many olefins to produce aldehydes and alcohols of commercial importance.

# CHEMICALS BASED ON SYNTHESIS GAS

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- The two major chemicals based on synthesis gas are ammonia and methanol.
- Each compound is a precursor for many other chemicals.
- From ammonia, urea, nitric acid, hydrazine, acrylonitrile, methylamines and many other minor chemicals are produced.
- Each of these chemicals is also a precursor of more chemicals.

# CHEMICALS BASED ON SYNTHESIS GAS

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- Methanol, the second major product from synthesis gas, is a unique compound of high chemical reactivity as well as good fuel properties.
- It is a building block for many reactive compounds such as formaldehyde, acetic acid, and methylamine.
- It also offers an alternative way to produce hydrocarbons in the gasoline range (Mobil to gasoline MTG process).
- It may prove to be a competitive source for producing light olefins in the future.

# AMMONIA (NH<sub>3</sub>)

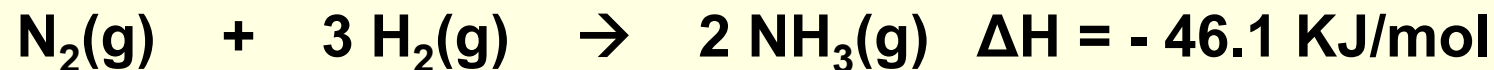
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- Ammonia is one of the most important inorganic chemicals, exceeded only by sulfuric acid and lime.
- This colorless gas has an irritating odor, and is very soluble in water, forming a weakly basic solution.
- Ammonia could be easily liquefied under pressure (liquid ammonia), and it is an important refrigerant.
- Anhydrous ammonia is a fertilizer by direct application to the soil.
- Ammonia is obtained by the reaction of hydrogen and atmospheric nitrogen, the synthesis gas for ammonia.
- The 1994 U.S. ammonia production was approximately 40 billion pounds (sixth highest volume chemical).

# Ammonia Production (Haber Process)

- The production of ammonia is of historical interest because it represents the first important application of thermodynamics to an industrial process.

- The ammonia synthesis reaction:



- Increasing the temperature increases the reaction rate, but decreases the equilibrium ( $K_c @ 500^\circ\text{C} = 0.08$ ).
- Iron oxide promoted with other oxides such as potassium and aluminum oxides is currently used to produce ammonia in good yield at relatively low temperatures.

# Ammonia Production (Haber Process)

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- In a commercial process, a mixture of hydrogen and nitrogen (exit gas from the methanator) in a ratio of 3:1 is compressed to the desired pressure (150-1,000 atmospheres).
- The compressed mixture is then preheated by heat exchange with the product stream before entering the ammonia reactor.
- The reaction occurs over the catalyst bed at about 450°C.
- The exit gas containing ammonia is passed through a cooling chamber where ammonia is condensed to a liquid, while unreacted hydrogen and nitrogen are recycled.
- Usually, a conversion of approximately 15% per pass is obtained under these conditions.

# Uses of Ammonia

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- The major end use of ammonia is the fertilizer field for the production of urea, ammonium nitrate and ammonium phosphate, and sulfate.
- Anhydrous ammonia could be directly applied to the soil as a fertilizer. Urea is gaining wide acceptance as a slow-acting fertilizer.
- Ammonia is the precursor for many other chemicals such as nitric acid, hydrazine, acrylonitrile, and hexamethylenediamine.
- Anhydrous liquid ammonia **may be used** as a clean fuel for the automotive industry.



# Uses of Ammonia

- Compared with hydrogen, anhydrous ammonia is more manageable.
- It is stored in iron or steel containers and could be transported commercially via pipeline, railroad tanker cars, and highway tanker trucks.
- The oxidation reaction produces only nitrogen and water. However, many factors must be considered such as the co-production of nitrogen oxides.



# Production of Urea

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- The highest fixed nitrogen-containing fertilizer 46.7 wt %, urea is a white solid that is soluble in water and alcohol.
- It is usually sold in the form of crystals, prills, flakes, or granules.
- Urea is an active compound that reacts with many reagents.
- By reacting with formaldehyde, it produces an important commercial polymer (urea formaldehyde resins) that is used as glue for particle board and plywood.

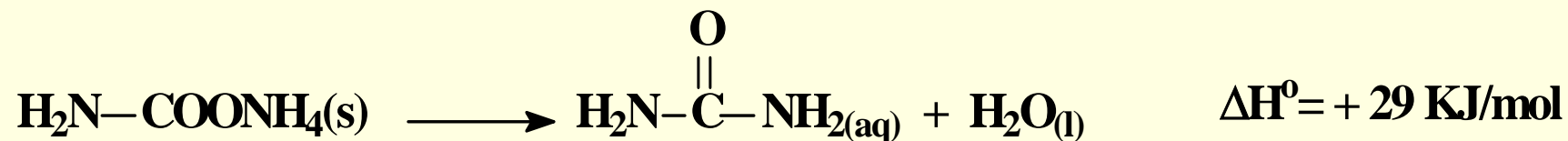
# Production of Urea

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- The technical production of urea is based on the reaction of ammonia with carbon dioxide.
- The reaction occurs in two steps: ammonium carbamate is formed first, followed by a decomposition step of the carbamate to urea and water.
- The first reaction is exothermic, and the equilibrium is favored at lower temperatures and higher pressures.
- Higher operating pressures are also desirable for the separation absorption step that results in a higher carbamate solution concentration.
- A higher ammonia ratio than stoichiometric is used to compensate for the ammonia that dissolves in the melt.

# Production of Urea

- The reactor temperature ranges between 170-220°C at a pressure of about 200 atm.

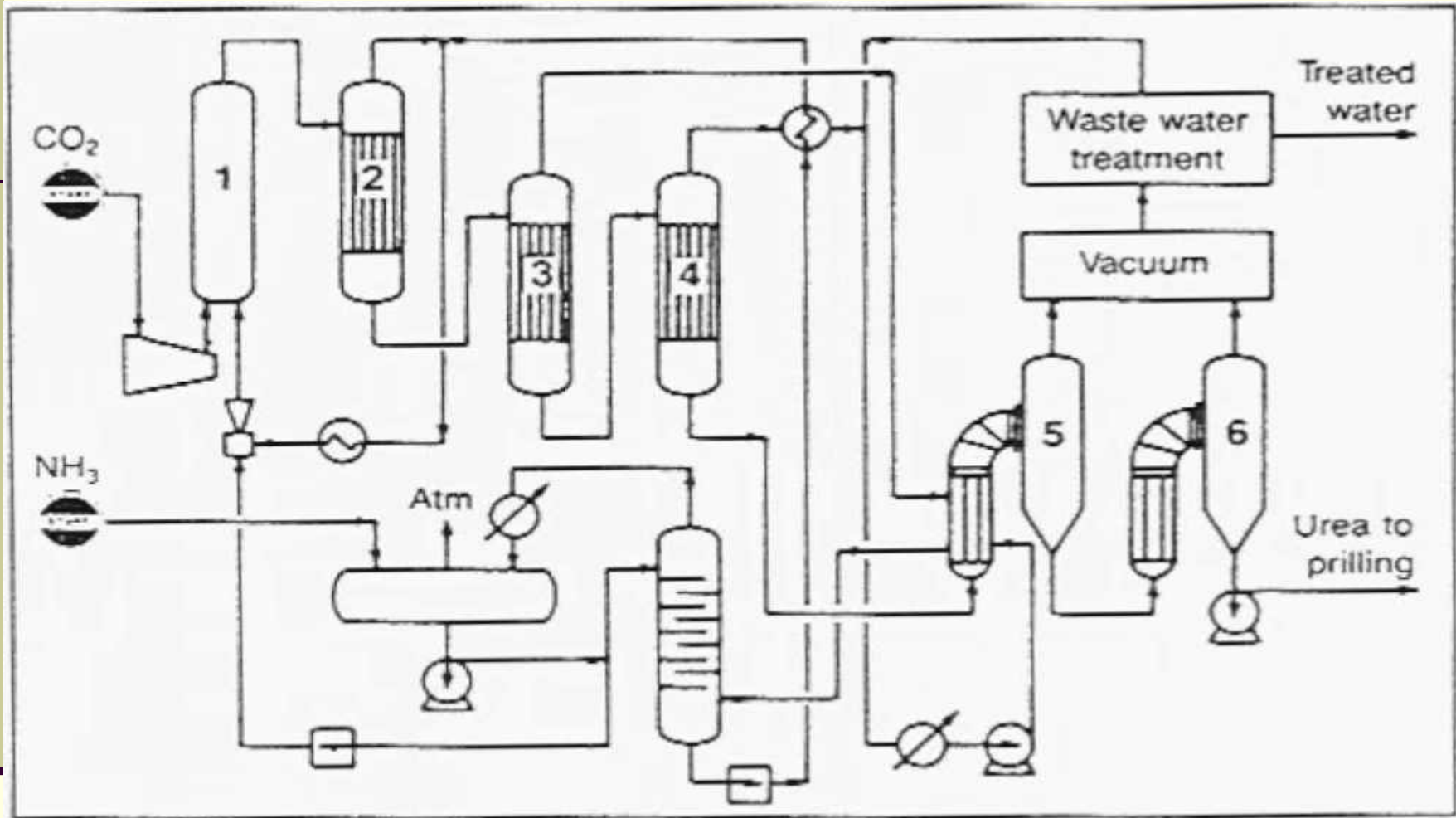


- The second reaction represents the decomposition of the carbamate.

# Production of Urea

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- The reaction conditions are 200°C and 30 atm.
- Decomposition in presence of excess ammonia limits corrosion problems and inhibits the decomposition of the carbamate to ammonia and carbon dioxide.
- The urea solution leaving the carbamate decomposer is expanded by heating at low pressures and ammonia recycled.
- The resultant solution is further concentrated to a melt, which is then prilled by passing it through special sprays in an air stream.



The Snamprogetti process for producing urea. (1) reactor, (2,3,4) carbonate decomposers, (5,6) crystallizing and prilling.

# Uses of Urea

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- The major use of urea is the fertilizer field, which accounts for approximately 80% of its production.
- About 10% of urea is used for the production of adhesives and plastics (urea formaldehyde and melamine formaldehyde resins).
- Animal feed accounts for about 5% of the urea produced.
- Urea possesses a unique property of forming adducts with n-paraffins. This is used in separating  $C_{12}$ - $C_{14}$  n-paraffins from kerosene for detergent production.

# Nitric Acid ( $\text{HNO}_3$ ) from Ammonia

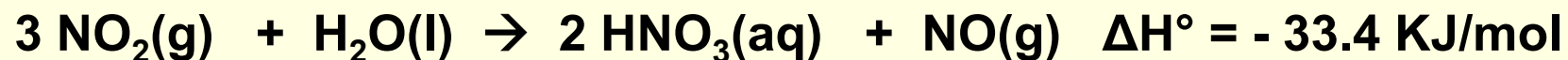
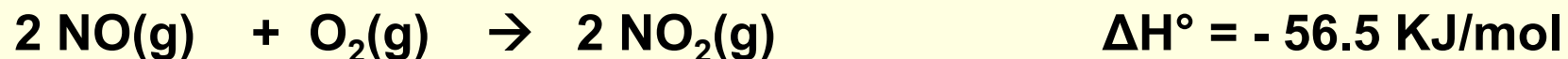
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- Nitric acid is one of the most used chemicals. It is a colorless to a yellow liquid, which is very corrosive.
- It is a strong oxidizing acid that can attack almost any metal.
- The most important use of nitric acid is to produce ammonium nitrate fertilizer.
- Nitric acid is commercially produced by oxidizing ammonia with air over a platinum-rhodium wire gauze.



# Nitric Acid (HNO<sub>3</sub>) from Ammonia

- The following sequence represents the reactions occurring over the heterogeneous catalyst:



- The three reactions are exothermic, and the equilibrium constants for the first two reactions fall rapidly with increase of temperature.

# Nitric Acid ( $\text{HNO}_3$ ) from Ammonia

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- Increasing pressure favors the second reaction but adversely affects the first reaction.
- Space velocity should be high to avoid the reaction of ammonia with oxygen on the reactor walls, which produces nitrogen and water, and results in lower conversions.
- The concentration of ammonia must be kept below the inflammability limit of the feed gas mixture to avoid explosion.
- Optimum nitric acid production was found to be obtained at approximately  $900^\circ\text{C}$  and atmospheric pressure.

# Uses of Nitric Acid ( $\text{HNO}_3$ )

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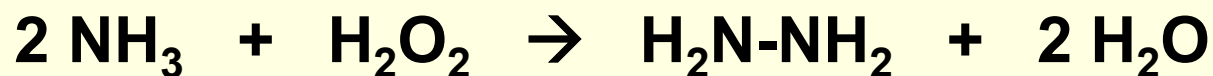
- The primary use of nitric acid is for the production of ammonium nitrate for fertilizers.
- A second major use of nitric acid is in the field of explosives.
- It is also a nitrating agent for aromatic and paraffinic compounds, which are useful intermediates in the dye and explosive industries.
- It is also used in steel refining and in uranium extraction.

# Production of Hydrazine (H<sub>2</sub>N-NH<sub>2</sub>) From Ammonia

- A colorless, fuming liquid miscible with water, hydrazine (diazine is a weak base but a strong reducing agent).
- Hydrazine is used as a rocket fuel because its combustion is highly exothermic and produce 620 KJ/mol:  
**H<sub>2</sub>N-NH<sub>2</sub> + O<sub>2</sub> → N<sub>2</sub> + 2 H<sub>2</sub>O + 620 KJ**
- Hydrazine is produced by the oxidation of ammonia using the Raschig process.
- Sodium hypochlorite is the oxidizing agent and yields chloramine NH<sub>2</sub>Cl as an intermediate.
- Chloramine further reacts with ammonia producing hydrazine:  
**2NH<sub>3</sub> + NaOCl → H<sub>2</sub>N-NH<sub>2</sub> + NaCl + H<sub>2</sub>O**
- Hydrazine is then evaporated from the sodium chloride solution.

# Production and Uses of Hydrazine (H<sub>2</sub>N-NH<sub>2</sub>)

- Hydrazine can also be produced by the Puck process. The oxidizing agent is hydrogen peroxide:



- Rocket fuel.
- As blowing agent and in the pharmaceutical and fertilizer industries.
- Due to the weak N-N bond, it is used as a polymerization initiator.
- As a reducing agent, hydrazine is used as an oxygen scavenger for steam boilers. It is also a selective reducing agent for nitro compounds.
- Hydrazine is a good building block for many chemicals, especially agricultural products, which dominates its use.

# METHYL ALCOHOL (CH<sub>3</sub>OH)

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- Methyl alcohol (methanol) is the first member of the aliphatic alcohol family.
- It ranks among the top twenty organic chemicals consumed in the U.S.
- Methanol was originally produced by the destructive distillation of wood (wood alcohol) for charcoal production.
- Currently, it is mainly produced from synthesis gas.
- As a chemical compound, methanol is highly polar, and hydrogen bonding is evidenced by its relatively high boiling temperature (65°C), its high heat of vaporization, and its low volatility.

# METHYL ALCOHOL (CH<sub>3</sub>OH)

- Due to the high oxygen content of methanol (50 wt%), it is being considered as a gasoline blending compound to reduce carbon monoxide and hydrocarbon emissions in automobile exhaust gases.
- It was also tested for blending with gasolines due to its high octane (RON = 112).
- Possible use of pure (straight) methanol as an alternative fuel for gasoline cars.
- Several problems encountered: the cold engine startability due to its high vaporization heat (heat of vaporization is 3.7 times that for gasoline), its lower heating value, which is approximately half that of gasoline, and its corrosive properties.
- Methanol is a potential fuel for gas turbines because it burns smoothly and has exceptionally low nitrogen oxide emission levels.

# METHYL ALCOHOL (CH<sub>3</sub>OH)

- Due to the high reactivity of methanol, many chemicals could be derived from it. It could be:
  - oxidized to formaldehyde, an important chemical building block.
  - carbonylated to acetic acid, and
  - dehydrated and polymerized to hydrocarbons in the gasoline range (MTG process).
- Methanol reacts almost quantitatively with isobutene and isoamylenes, producing methyl t-butylether (MTBE) and tertiary amyl methyl ether (TAME).
- Both are important gasoline additives for raising the octane number and reducing carbon monoxide and hydrocarbon exhaust emissions.
- Additionally, much of the current work is centered on the use of shape-selective catalysts to convert methanol to light olefins as a possible future source of ethylene and propylene.



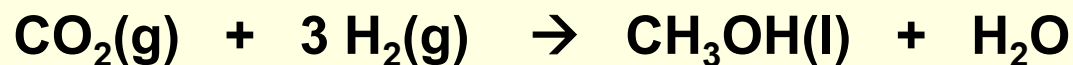
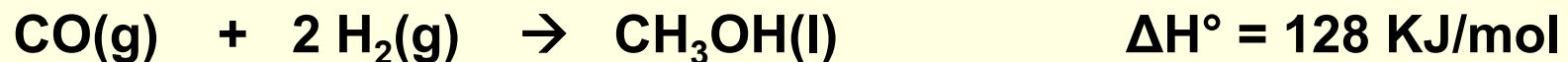
# PRODCUTION OF METHANOL (CH<sub>3</sub>OH)

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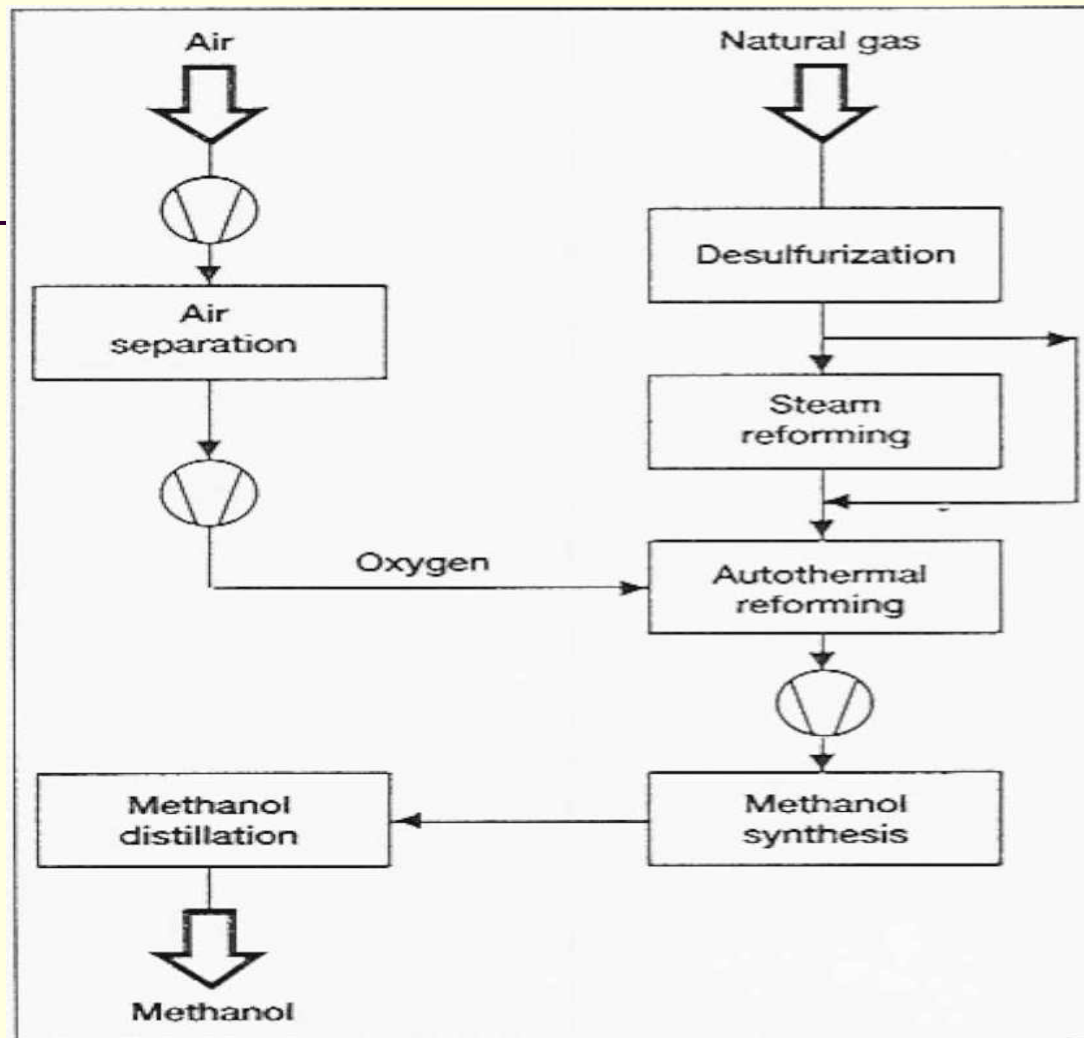
- Methanol is produced by the catalytic reaction of carbon monoxide and hydrogen (synthesis gas).
- Because the ratio of CO:H<sub>2</sub> in synthesis gas from natural gas is approximately 1:3, and the stoichiometric ratio required for methanol synthesis is 1:2, **carbon dioxide is added** to reduce the surplus hydrogen.
- An energy-efficient alternative to adjusting the CO:H<sub>2</sub> ratio is to combine the steam reforming process with autothermal reforming (combined reforming) so that the amount of natural gas fed is that required to produce a synthesis gas with a stoichiometric ratio of approximately 1:2.05.

# PRODCUTION OF METHANOL (CH<sub>3</sub>OH)

- If an autothermal reforming step is added, pure oxygen should be used. (This is a major difference between secondary reforming in case of ammonia production, where air is used to supply the needed nitrogen).
- An added advantage of combined reforming is the decrease in NO<sub>x</sub> emission.
- However, a capital cost increase (for air separation unit) of roughly 15% is anticipated when using combined reforming in comparison to plants using a single train steam reformer.



- Old processes use a zinc-chromium oxide catalyst at a high-pressure range of approximately 270-420 atmospheres for methanol production.

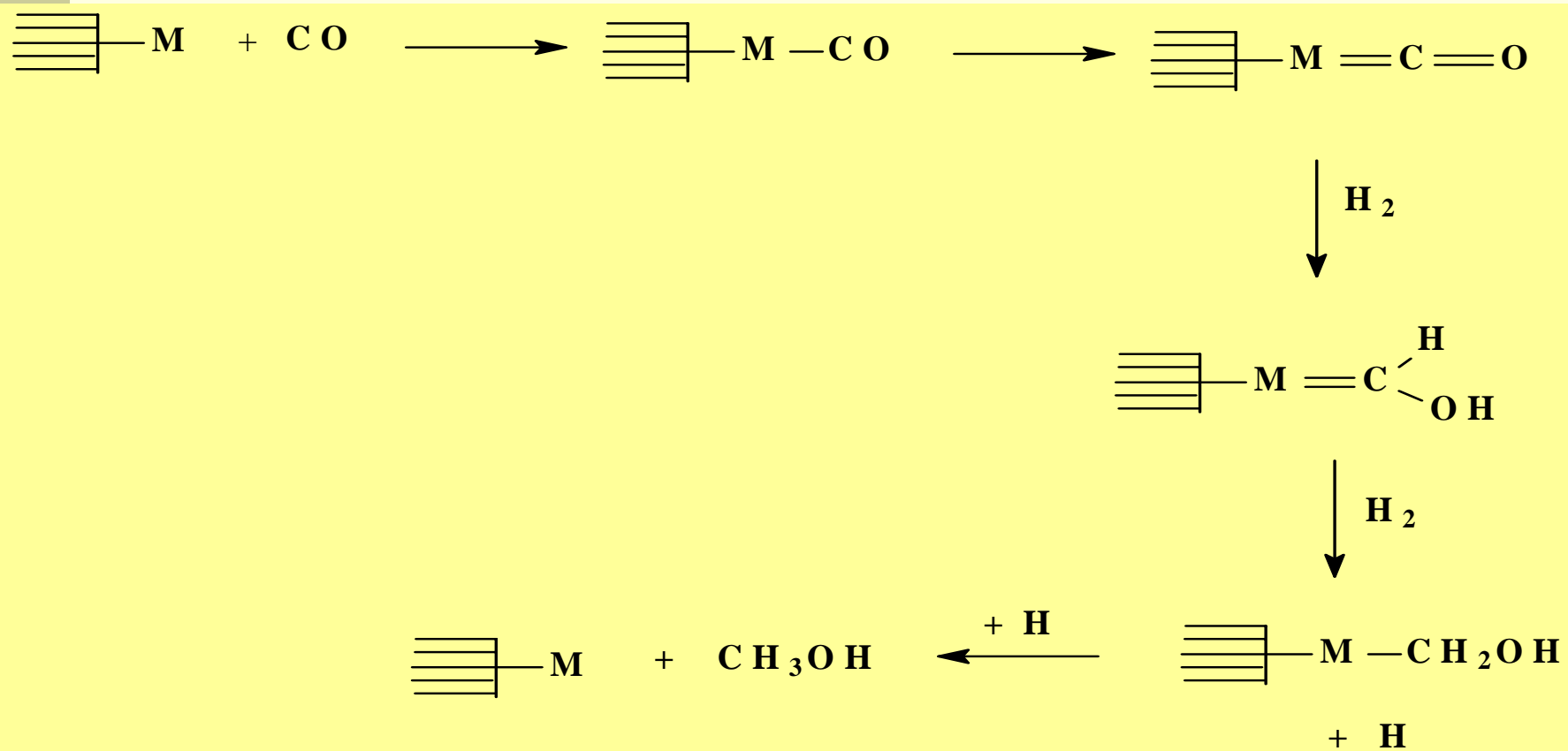


**A block flow diagram showing the combined reforming for methanol synthesis**

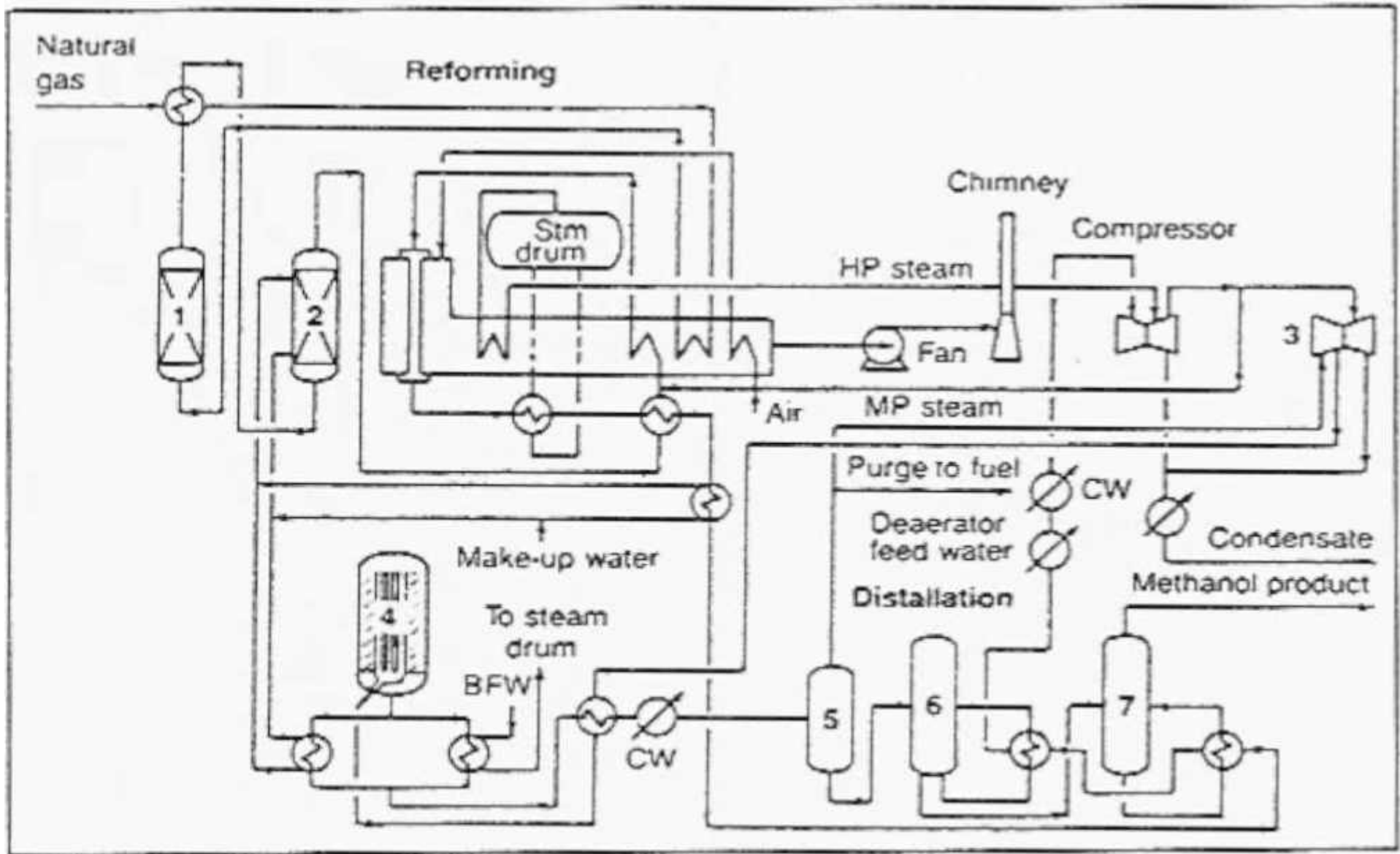
# PRODUCTION OF METHANOL (CH<sub>3</sub>OH)

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- A low-pressure process has been developed by ICI operating at about 50 atm. (700 psi) using a new active copper-based catalyst at 240°C.
- The synthesis reaction occurs over a bed of heterogeneous catalyst arranged in either sequential adiabatic beds or placed within heat transfer tubes.
- The reaction is limited by equilibrium, and methanol concentration at the converter's exit rarely exceeds 7%.
- The converter effluent is cooled to 40°C to condense product methanol, and the unreacted gases are recycled.
- Crude methanol from the separator contains water and low levels of by-products, which are removed using a two-column distillation system.
- Methanol synthesis over the heterogeneous catalyst is thought to occur by a successive hydrogenation of chemisorbed carbon monoxide.



## Mechanism of the reaction of production of methanol



The ICI low-pressure process for producing methanol: (1) desulfurization, (2) saturator (for producing process steam), (3) synthesis loop circulator, (4) reactor, (5) heat exchanger and separator, (6) column for light ends recovery, (7) column for water removal

# USES OF METHYL ALCOHOL (CH<sub>3</sub>OH)

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- Approximately 50% of methanol production is oxidized to formaldehyde.
- As a methylating agent, it is used with many organic acids to produce the methyl esters such as methyl acrylate, methylmethacrylate, methyl acetate, and methyl terephthalate.
- Methanol is also used to produce dimethyl carbonate and methyl-t-butyl ether, an important gasoline additive.
- It is also used to produce synthetic gasoline using a shape selective catalyst (MTG process).

# USES OF METHYL ALCOHOL (CH<sub>3</sub>OH)

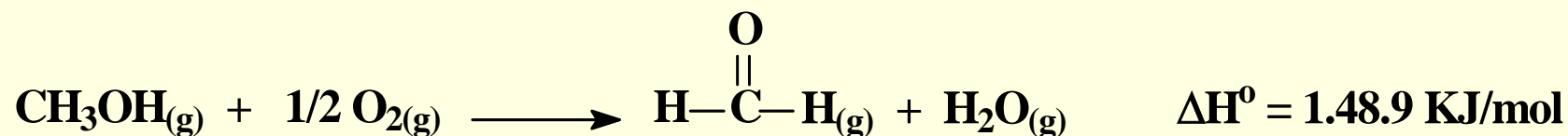
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- Olefins from methanol may be a future route for ethylene and propylene in competition with steam cracking of hydrocarbons.
- The use of methanol in fuel cells is being investigated.
- Fuel cells are theoretically capable of converting the free energy of oxidation of a fuel into electrical work.
- In one type of fuel cells, the cathode is made of vanadium which catalyzes the reduction of oxygen, while the anode is iron (III) which oxidizes methane to CO<sub>2</sub> and iron (II) is formed in aqueous H<sub>2</sub>SO<sub>4</sub>.

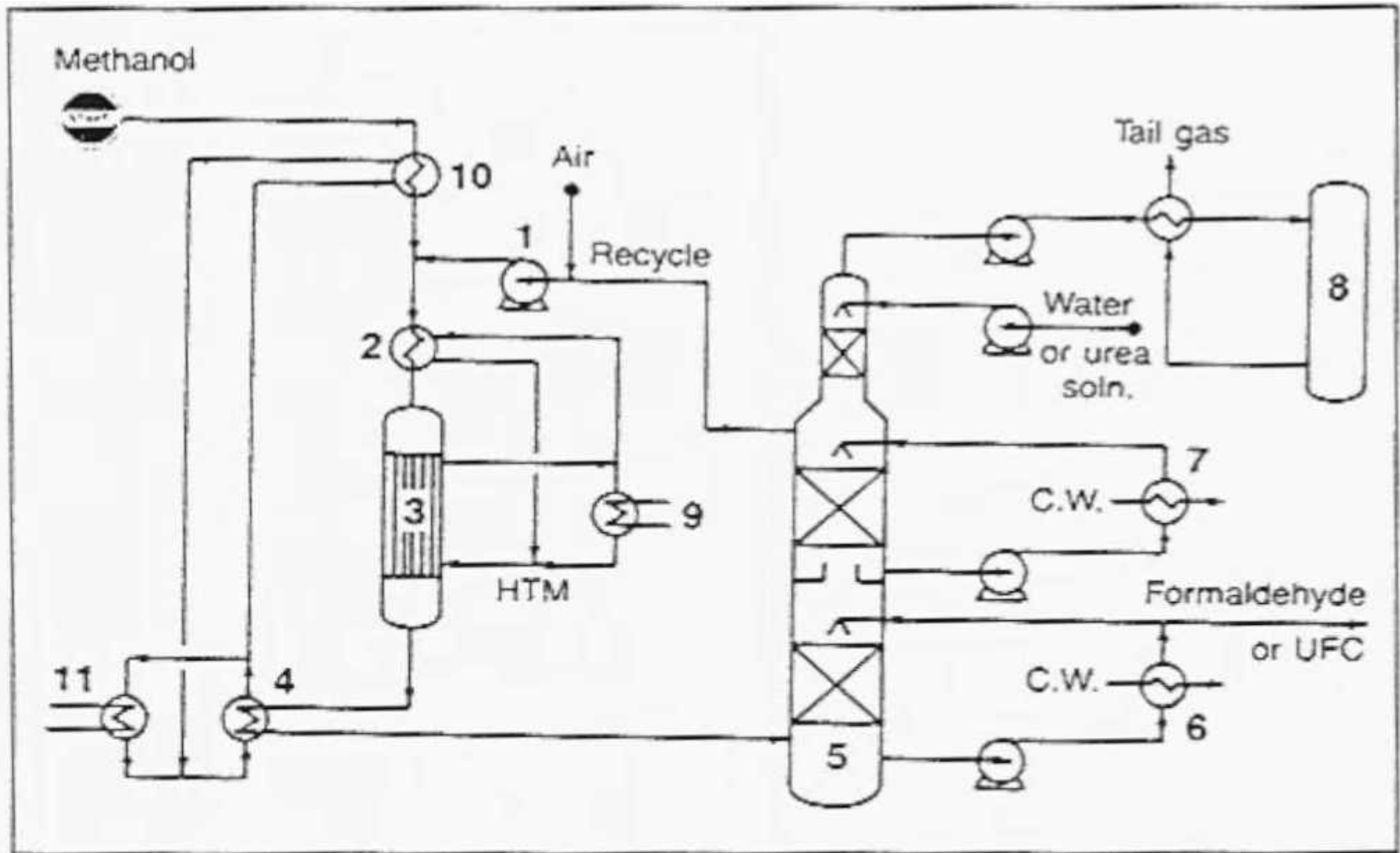


# FORMALDEHYDE FROM METHYL ALCOHOL (CH<sub>3</sub>OH)

- The main industrial route for producing formaldehyde is the catalyzed air oxidation of methanol.



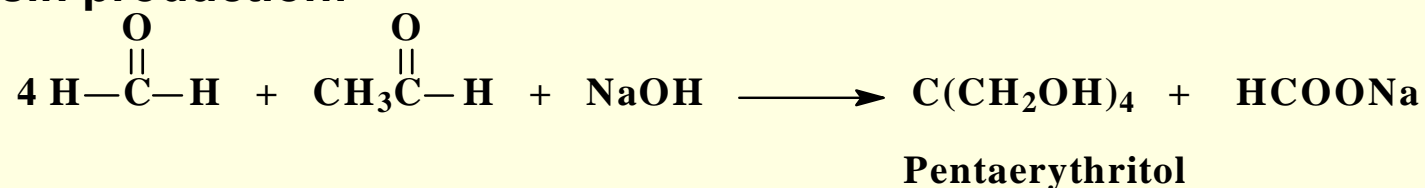
- A silver-gauze catalyst is still used in some older processes (at about 500°C).
- New processes use an iron-molybdenum oxide catalyst. Chromium or cobalt oxides are sometimes used to dope the catalyst.
- The oxidation reaction is exothermic and occurs at ≈ 400-425°C and 1 atm. Excess air is used to keep the methanol air ratio below the explosion limits.



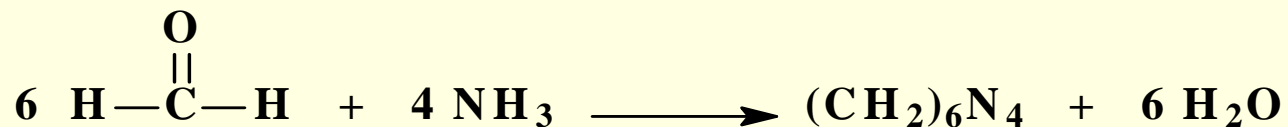
The haldor Topsøe and Nippon Kasei process for producing formaldehyde: (1) blower, (2) heat exchanger, (3) reactor, (4) steam boiler, (5) absorber, (6,7) coolers, (8) incinerator, (9) heat recovery, (10) methanol evaporator, (11) boiler feed water.

# USES OF FORMALDEHYDE

- Condensation polymerization of formaldehyde with phenol, urea, or melamine produces phenol-formaldehyde, urea formaldehyde, and melamine formaldehyde resins.
- These are important glues used in producing particle board and plywood.
- Condensation of formaldehyde with acetaldehyde in presence of a strong alkali produces pentaerythritol, a polyhydric alcohol for alkyd resin production:



- Formaldehyde reacts with ammonia and produces hexamethylenetetramine (hexamine):



# USES OF FORMALDEHYDE

- Methyl chloride is produced by the vapor phase reaction:  
 **$\text{CH}_3\text{OH} + \text{HCl} \rightarrow \text{CH}_3\text{Cl} + \text{H}_2\text{O}$**
- Many catalysts are used such as zinc chloride on pumice, cuprous chloride, and ignited alumina gel. The reaction conditions are 350°C at nearly atmospheric pressure. The yield is approximately 95%.
- Zinc chloride is also a catalyst for a liquid-phase process using concentrated hydrochloric acid at 100-150°C. Hydrochloric acid may be generated in situ by reacting sodium chloride with sulfuric acid.
- Methyl chloride from methanol may be further chlorinated to produce dichloromethane, chloroform, and carbon tetrachloride.

# ACETIC ACID FROM METHYL ALCOHOL (CH<sub>3</sub>OH)

- The carbonylation of methanol is currently one of the major routes for acetic acid production.
- The basic liquid-phase process developed by BASF uses a cobalt catalyst at 250°C and a high pressure of about 70 atmospheres.
- The newer process uses a rhodium complex catalyst in presence of CH<sub>3</sub>I, which acts as a promoter.
- The reaction occurs at 150°C and atmospheric pressure. A 99% selectivity is claimed with this catalyst:



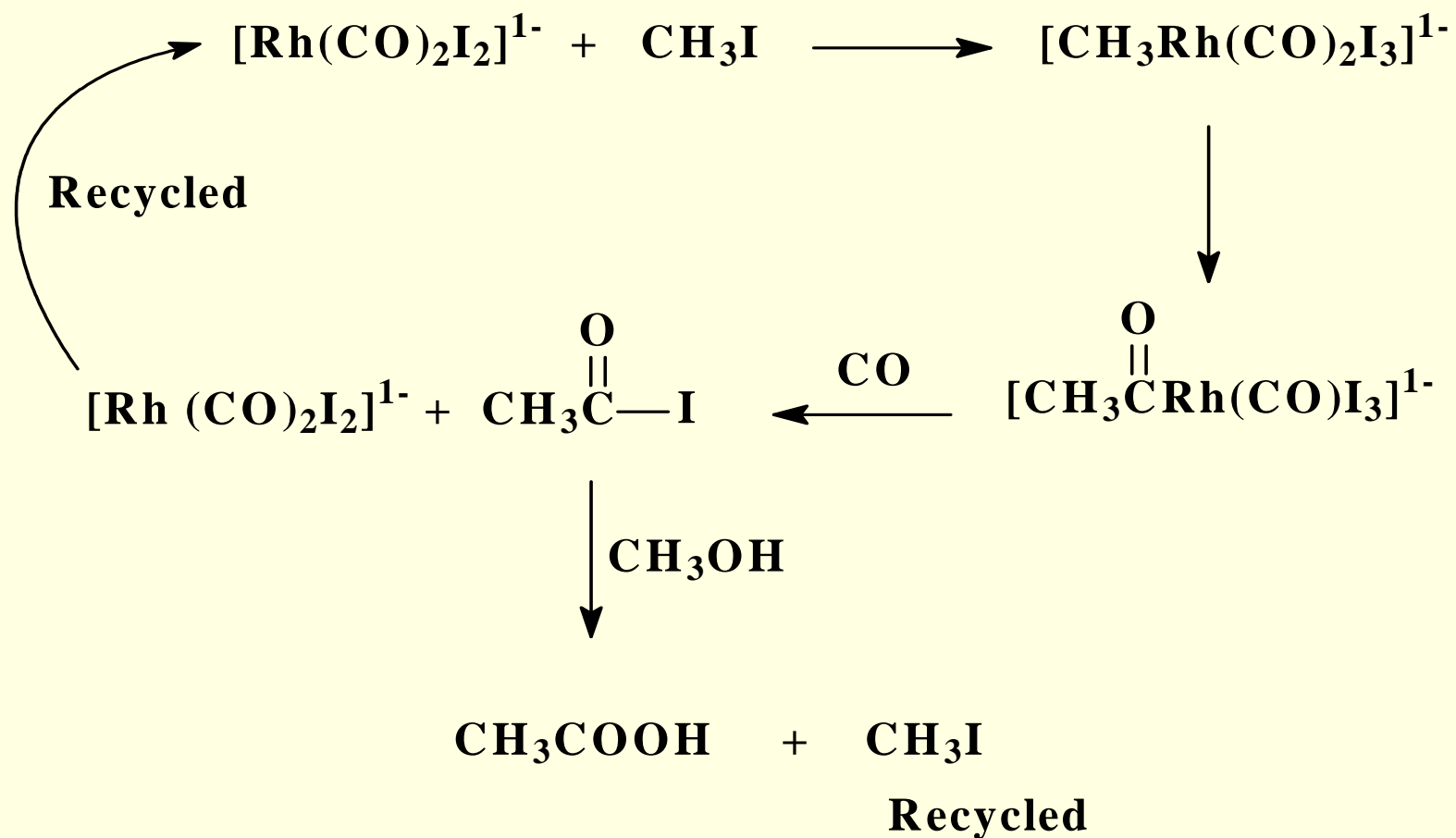
- Acetic acid is also produced by the oxidation of acetaldehyde and the oxidation of n-butane, but acetic acid from the carbonylation route has an advantage over the other commercial processes.

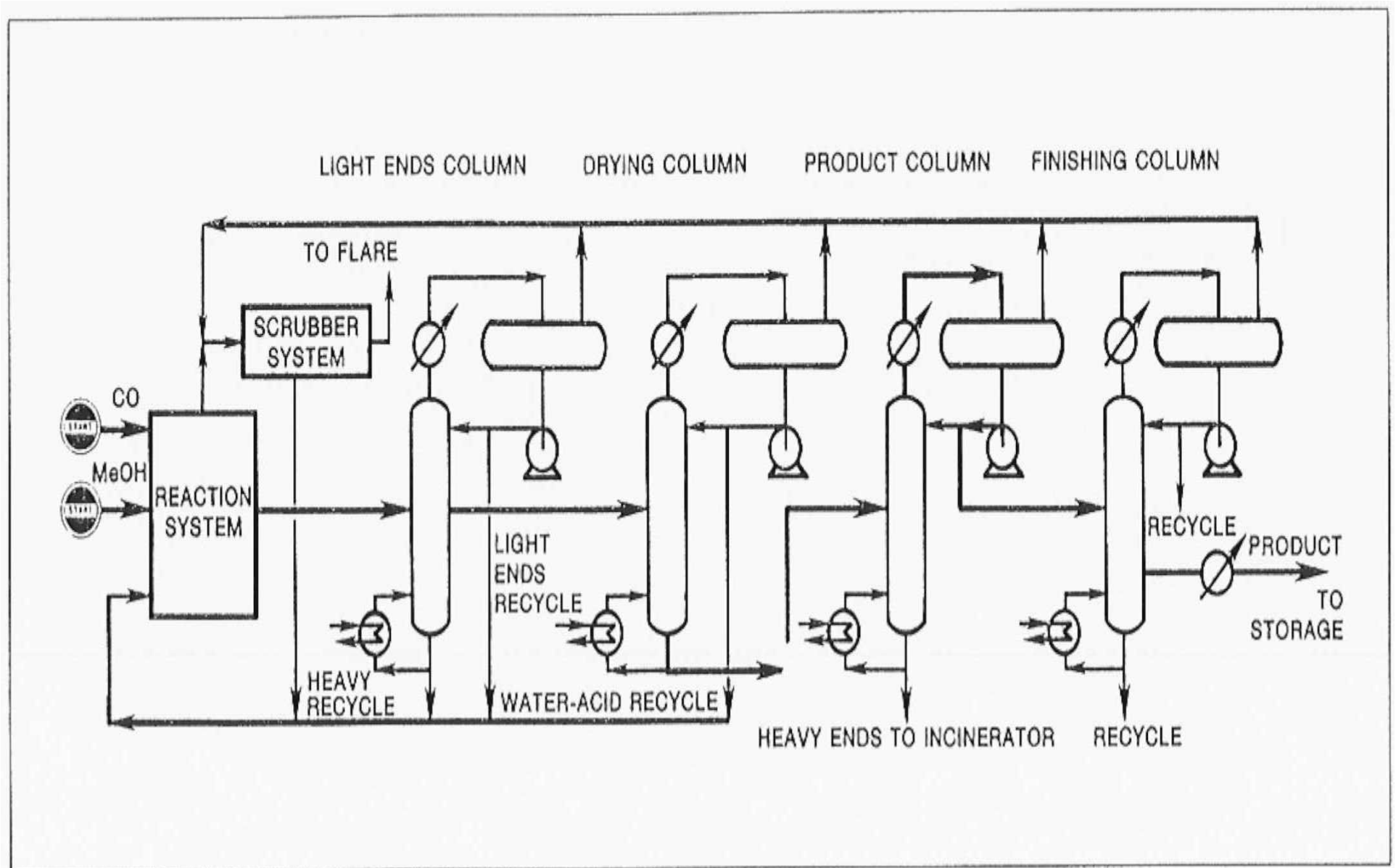
# ACETIC ACID FROM METHYL ALCOHOL (CH<sub>3</sub>OH)

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- The mechanism of the carbonylation reaction is thought to involve a first-step oxidative addition of the methyl iodide promoter to the Rh(I) complex, followed by a carbonyl cis insertion step.
- Carbonylation followed by reductive elimination produces back the Rh(I) catalyst.
- The final step is the reaction between acetyl iodide and methyl alcohol, yielding acetic acid and the promoter.

# ACETIC ACID FROM METHYL ALCOHOL (CH<sub>3</sub>OH)





The Monsanto methanol carbonylation process for producing acetic acid



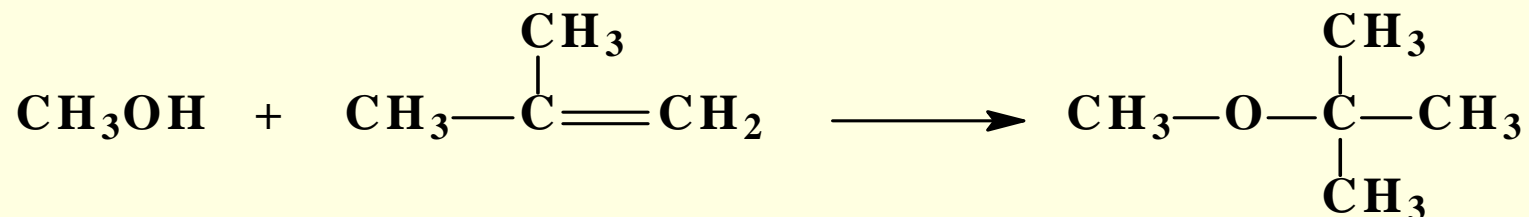
# USES OF ACETIC ACID

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- The main use of acetic acid is to produce vinyl acetate (44%), followed by acetic acid esters (13%) and acetic anhydride (12%).
- Vinyl acetate is used for the production of adhesives, film, paper and textiles. Terephthalic acid consumes 12% of acetic acid demand.
- Acetic acid is also used to produce pharmaceuticals, dyes, and insecticides.
- Chloroacetic acid (from acetic acid) is a reactive intermediate used to manufacture many chemicals such as glycine and carboxymethyl cellulose.

# METHYL TERTIARY BUTYL ETHER FROM METHYL ALCOHOL (CH<sub>3</sub>OH)

- MTBE is produced by the reaction of methanol and isobutene:

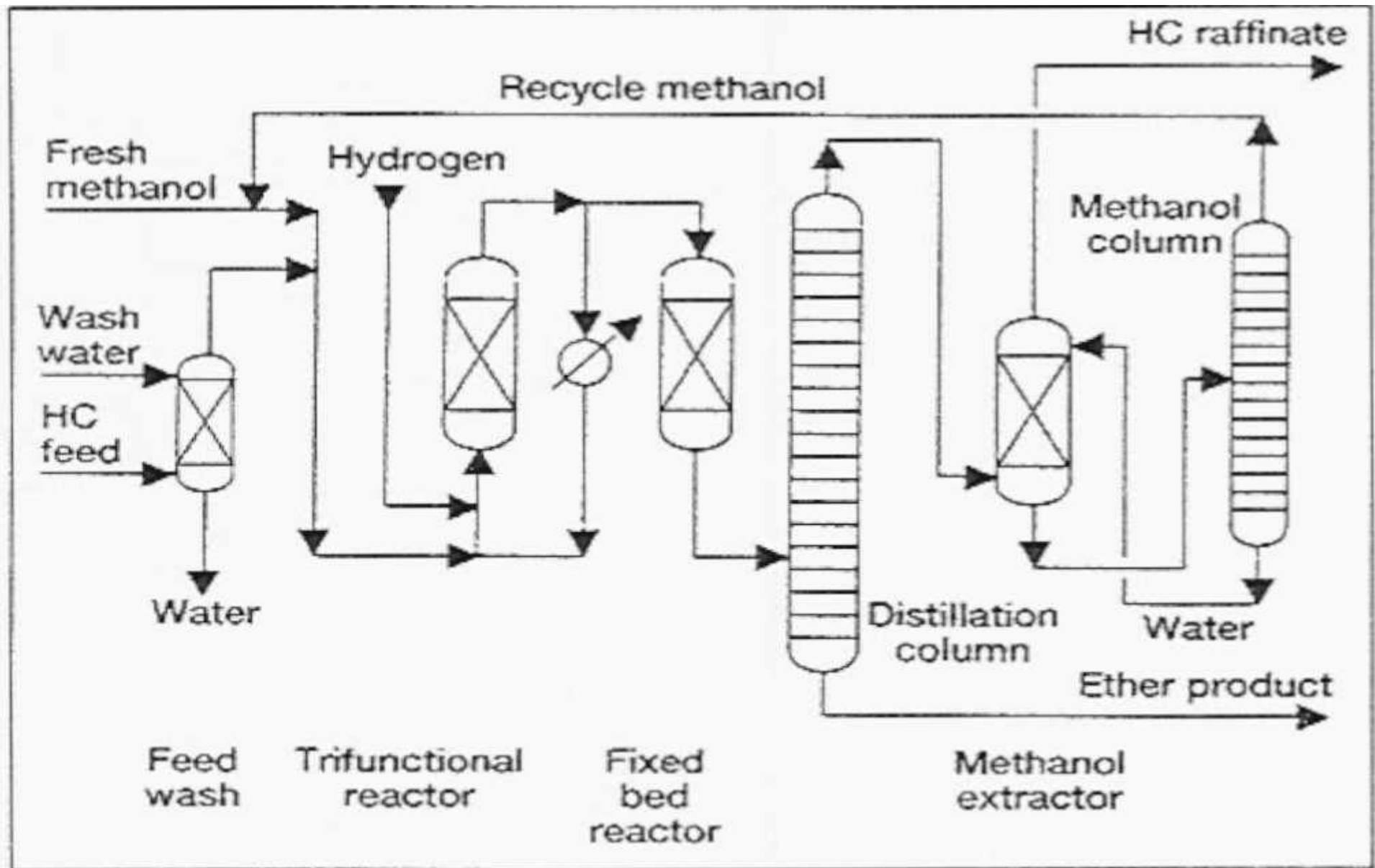


- The reaction occurs in the liquid phase at relatively low temperatures (about 50°C) in the presence of a solid acid catalyst.
- Few side reactions occur such as the hydration of isobutene to tertiary butyl alcohol, and methanol dehydration and formation of dimethyl ether and water.
- However, only small amounts of these compounds are produced.

# METHYL TERTIARY BUTYL ETHER FROM METHYL ALCOHOL (CH<sub>3</sub>OH)

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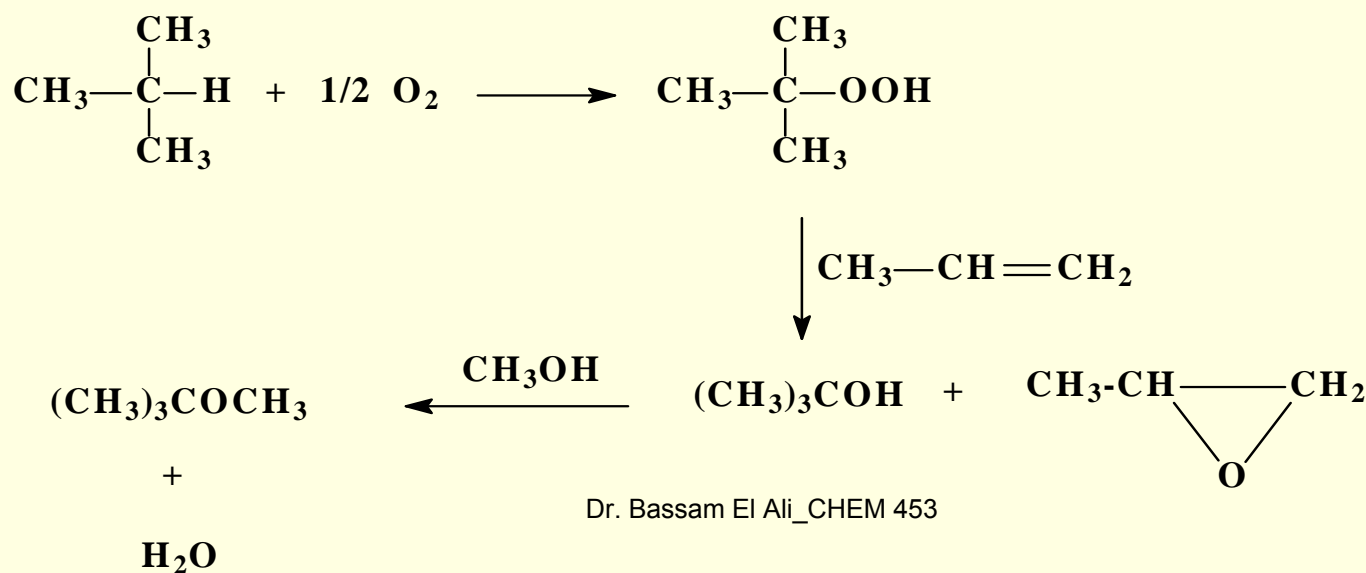
- The MTBE reaction is equilibrium limited.
- Higher temperatures increase the reaction rate, but the conversion level is lower.
- Lower temperatures shift the equilibrium toward ether production, but more catalyst inventory is required.
- Therefore, conventional MTBE units are designed with two reactors in series. Most of the etherification reaction is achieved at an elevated temperature in the first reactor and then finished at a thermodynamically favorable lower temperature in the second reactor.



Simplified flow diagram of the British Petroleum Etherol process

# METHYL TERTIARY BUTYL ETHER FROM METHYL ALCOHOL (CH<sub>3</sub>OH)

- An alternative way for the production of MTBE is by using isobutane, propene, and methanol. This process coproduces propylene oxide.
- In this process, isobutane reacts with oxygen giving t-butyl hydroperoxide. The epoxide reacts with propene yielding t-butyl alcohol and propylene oxide.
- t-Butyl alcohol loses water giving isobutene which reacts with methanol yielding MTBE.



# METHYL TERTIARY BUTYL ETHER

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- MTBE is an important gasoline additive because of its high octane rating.
- It reduces carbon monoxide and hydrocarbon exhaust emissions probably (the exact means is not known) by reducing the aromatics in gasolines.
- In the past few years, many arguments existed regarding the use of MTBE as a gasoline additive.
- It was found that leakage from old gasoline storage tanks pollutes underground water.
- Compared to other constituents of gasoline, MTBE is up to 10 times more soluble in water. It also has little affinity for soil, and unlike other gasoline components, it passes through the soil and is carried by the water.

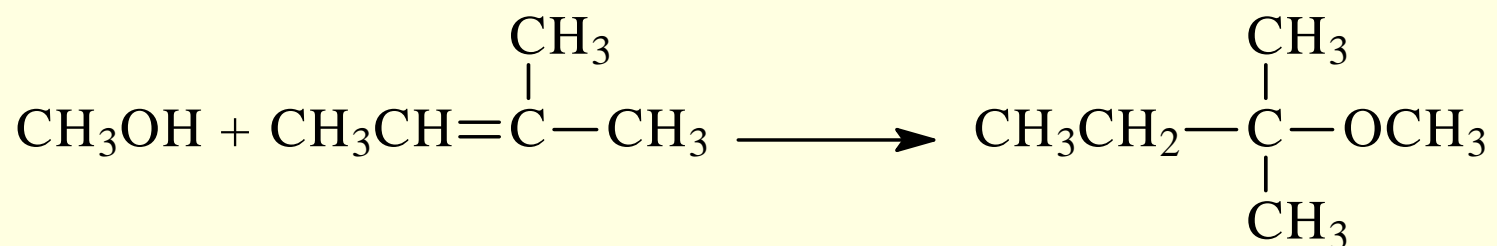
# METHYL TERTIARY BUTYL ETHER

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- Many recommendations are being thought to reduce pollution effects of MTBE.
- One way is to use alternative oxygenates which are not as soluble in water as MTBE.
- Another way is by phasing out the 2% oxygen by weight required in reformulated gasoline. These changes will affect the future demand for MTBE. Currently, the worldwide consumption of MTBE reached 6.6 billion gallons of which 65% is consumed in the U.S.

# TERTIARY AMYL METHYL ETHER FROM METHYL ALCOHOL (CH<sub>3</sub>OH)

- TAME can also be produced by the reaction of methanol with isoamylenes. The reaction conditions are similar to those used with MTBE, except the temperature is a little higher:



- Similar to MTBE, TAME is used as gasoline additive for its high octane rating and its ability to reduce carbon monoxide and hydrocarbon exhaust emissions.



# DIMETHYL CARBONATE

## FROM METHYL ALCOHOL (CH<sub>3</sub>OH)

- Dimethyl carbonate (DMC) is a colorless liquid with a pleasant odor. It is soluble in most organic solvents but insoluble in water.
- The classical synthesis of DMC is the reaction of methanol with phosgene.
- Because phosgene is toxic, a non-phosgene-route may be preferred. The new route reacts methanol with urea over a tin catalyst. However, the yield is low.
- Using electron donor solvents such as trimethylene glycol dimethyl ether increases the yield.
- Dimethyl carbonate is used as a specialty solvent. It could be used as an oxygenate to replace MTBE. It has almost three times the oxygen content as MTBE.



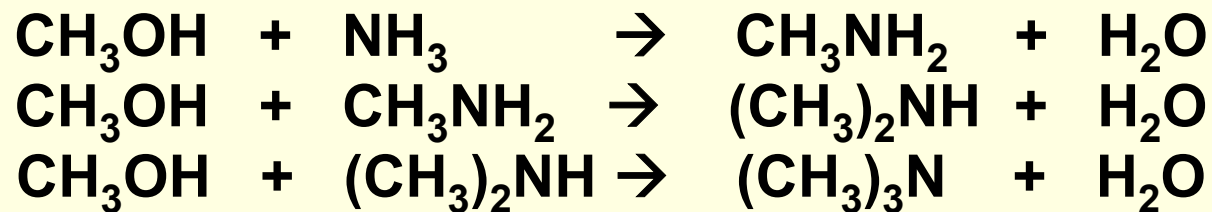
Property	MTBE	ETBE	TAME
Blending octane (R + M/2)	110	111	105
Blending octane (RON)	112–130	120	105–115
Blending octane (MON)	97–115	102	95–105
Reid vapor pressure (psi)	7.8	4.0	2.5
Boiling point (°C)	55	72	88
(°F)	131	161	187
Density (kg/l)	.742	.743	.788
(lb/gal)	6.19	6.20	8.41
Energy density (kcal/l)	89.3	92.5	98.0
(kBtu/gal)	93.5	96.9	100.8
Heat of vaporization (kcal/l)	0.82	0.79	0.86
(kBtu/gal) @ nbp	0.86	0.83	0.90
Oxygenate requirement (vol% @ 2.7 wt% ox.)	15.0	17.2	16.7
Solubility in water (wt%)	4.3	1.2	1.2
Water pickup (wt%)	1.4	0.5	0.6
Heat of reaction (kcal/mol)	9.4	6.6	11
(kBtu/lb mol)	17	12	20

## Properties of oxygenates (MTBE, TAME, and ETBE)

# METHYLAMINES

## FROM METHYL ALCOHOL (CH<sub>3</sub>OH)

- Methylamines can be synthesized by alkylating ammonia with methyl halides or with methyl alcohol.
- The reaction with methanol usually occurs at approximately 500°C and 20 atmospheres in the presence of an aluminum silicate or phosphate catalyst.
- The alkylation does not stop at the monomethylamine stage, because the produced amine is a better nucleophile than ammonia.
- The product distribution at equilibrium is monomethylamine MMA (43%), dimethylamine DMA (24%), and trimethylamine TMA (33%):



# USES OF METHYLAMINES

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- Dimethylamine is the most widely used of the three amines.
- Excess methanol and recycling monomethylamine increases the yield of dimethylamine.
- The main use of dimethylamine is the synthesis of dimethylformamide and dimethylacetamide, which are solvents for acrylic and polyurethane fibers.
- Monoethylamine is used in the synthesis of Sevin, an important insecticide.
- Trimethylamine has only one major use, the synthesis of choline, a high-energy additive for poultry feed.

# Hydrocarbons from Methanol

## (Methanol to Gasoline MTG Process)

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- Methanol may have a more important role as a basic building block in the future because of the multisources of synthesis gas.
- In 1975, a Mobil research group discovered that methanol could be converted to hydrocarbons in the gasoline range with a special type of zeolite (ZSM-5) catalyst.
- The reaction of methanol over a ZSM-5 catalyst could be considered as dehydration-oligomerization reaction. It may be simply represented as:



- where  $(\text{CH}_2)_n$  represents the hydrocarbons (paraffins + olefins + aromatics).
- The hydrocarbons obtained are in the gasoline range.

# Hydrocarbons from Methanol (Methanol to Gasoline MTG Process)

**Table 5-3**  
**Analysis of gasoline from MTG process**

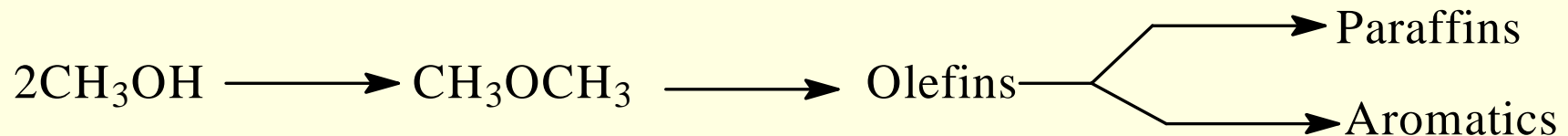
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Components,		wt%
Butanes		3.2
Alkylates	28.6	
C5 gasoline	<u>68.2</u>	
		100.0

Components,		wt%
Paraffins		56
Olefins		7
Naphthenes	4	
Aromatics	<u>33</u>	
		100

# Hydrocarbons from Methanol (Methanol to Gasoline MTG Process)

- The MTG process has been operating in New Zealand since 1985.
- Converting methanol to hydrocarbons is not as simple as it looks from the previous equation.
- Many reaction mechanisms have been proposed, and most of them are centered around the intermediate formation of dimethyl ether followed by olefin formation.
- Olefins are thought to be the precursors for paraffins and aromatics:



# Hydrocarbons from Methanol (Methanol to Gasoline MTG Process)

	Hydrocarbon distribution (wt%) in				
	Erionite	ZSM-5	ZSM-11	ZSM-4	Mordenite
C <sub>1</sub>	5.5	1.0	0.1	8.5	4.5
C <sub>2</sub>	0.4	0.6	0.1	1.8	0.3
C <sub>2</sub> <sup>2-</sup>	36.3	0.5	0.4	11.2	11.0
C <sub>3</sub>	1.8	16.2	6.0	19.1	5.9
C <sub>3</sub> <sup>2-</sup>	39.1	1.0	2.4	8.7	15.7
C <sub>4</sub>	5.7	24.2	25.0	8.8	13.8
C <sub>4</sub> <sup>2-</sup>	9.0	1.3	5.0	3.2	9.8
C <sub>5</sub> <sup>+</sup> aliphatic	2.2	14.0	32.7	4.8	18.6
A <sub>6</sub>	–	1.7	0.8	0.1	0.4
A <sub>7</sub>	–	10.5	5.3	0.5	0.9
A <sub>8</sub>	–	18.0	12.4	1.3	1.0
A <sub>9</sub>	–	7.5	8.4	2.2	1.0
A <sub>10</sub>	–	3.3	1.5	3.2	2.0
A <sub>11</sub> <sup>+</sup>	–	0.2	–	26.6	15.1

Methanol conversion to hydrocarbons over various zeolites (370°C, 1 atm, 1 LHSV)



# OXO ALDEHYDES AND ALCOHOLS (Hydroformylation Reaction)

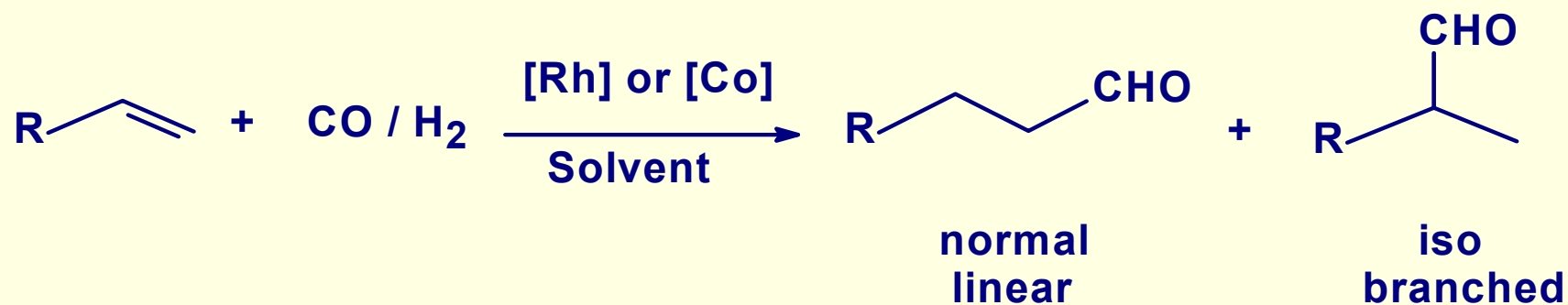
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- Hydroformylation of olefins (Oxo reaction) produces aldehydes with one more carbon than the reacting olefin. For example, when ethylene is used, propionaldehyde is produced.
- This reaction is especially important for the production of **higher aldehydes** that are further hydrogenated to the corresponding **alcohols**.
- The reaction is catalyzed with **cobalt or rhodium complexes**.
- Olefins with terminal double bonds are more reactive and produce aldehydes which are hydrogenated to the corresponding primary alcohols.
- With olefins other than ethylene, the hydroformylation reaction mainly produces a straight chain aldehyde with variable amounts of branched chain aldehydes.

# *Hydroformylation Catalysis*

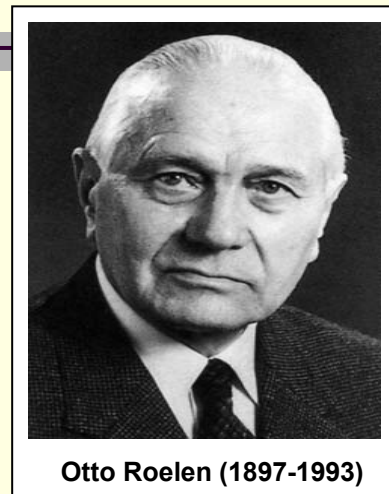
## *(Oxo Process)*

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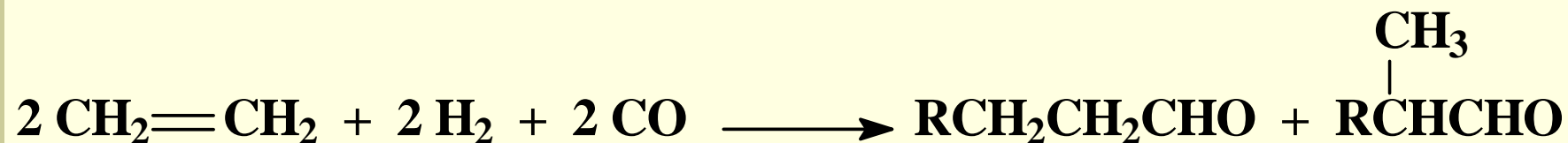
# *Hydroformylation Catalysis (Oxo Process)*

- *discovered by Otto Roelen in 1938*
- *Largest homogeneous catalytic process*
- *> 10 million tones of aldehydes (alcohols) per year*
- *Commercial catalysts are complexes of Co or Rh*
- *Selectivity to linear (normal) or branched (iso) products is important*



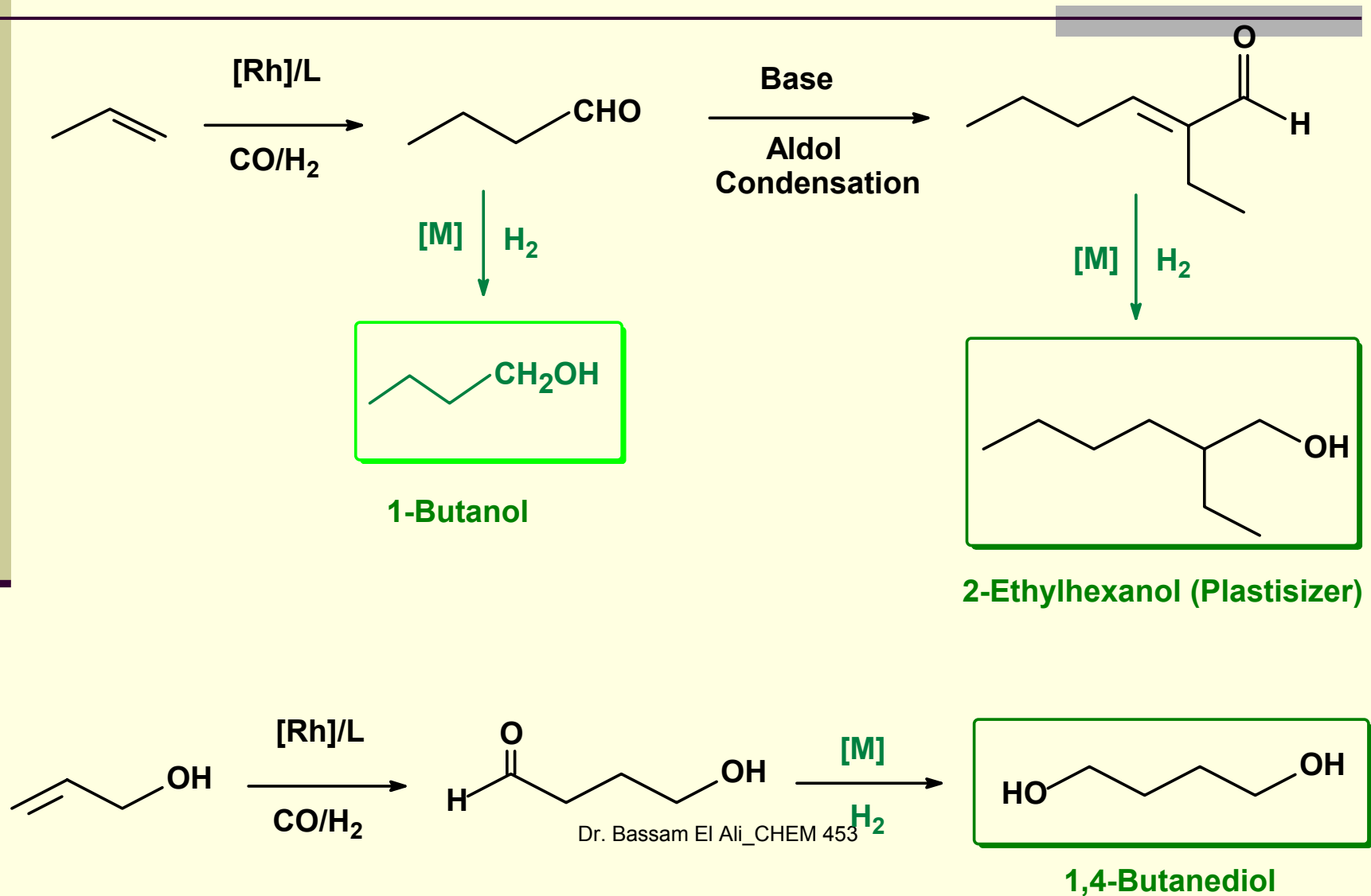
Otto Roelen (1897-1993)

# OXO ALDEHYDES AND ALCOHOLS (Hydroformylation Reaction)



- The largest commercial process is the hydroformylation of propene which yields n-butyraldehyde and isobutyraldehyde.
- n-Butyraldehyd (n-butanal) is either hydrogenated to n-butanol or transformed to 2-ethyl-hexanol via aldol condensation and subsequent hydrogenation. 2 Ethylhexanol is an important plasticizer for polyvinyl chloride.
- Other olefins applied in the hydroformylation process with subsequent hydrogenation are propylene trimer and tetramer for the production of decyl and tridecyl alcohols.

# APPLICATIONS OF HYDROFORMYLATION (OXO) PROCESS



## Companies using Rh/PR<sub>3</sub> Hydroformylation Technology to Produce Alcohols

Company	Location	Country	kT/year
BASF	Ludwigshafen	Germany	470
Huels	Marl	Germany	330
Union Carbide	Texas City, TX	USA	320
Celanese-Ruhrchemie	Oberhausen	Germany	320
Union Carbide	Taft, LA	USA	~300
Mitsubishi	Mizushima	Japan	220
Texas Eastman	Longview, TX	USA	190
Oxo Chemie	Lavera	France	175
Kyowa	Yokkaichi	Japan	175
Beroxo	Stenungsund	Sweden	125
Celanese	Bay City, TX	USA	110
BASF	Freeport, TX	USA	100
Lucky Ltd	Naja	S. Korea	70
Chisso	Chiba	Japan	65
Ciquine	Camacari	Brazil	60
BASF	Tarragona	Spain	50
TSK	Kawasaki	Japan	40

# *Flexible Plastics:* Products made from **OXO ALCOHOLS**



# OXO ALDEHYDES AND ALCOHOLS (Hydroformylation Reaction)

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- Several commercial processes are currently operative. Some use a rhodium catalyst complex incorporating phosphine ligands  $\text{HRhCO}(\text{PPh}_3)$  at relatively lower temperatures and pressures and produce **less branched aldehydes**.
- Older processes use a cobalt carbonyl complex  $\text{HCo}(\text{CO})_4$  at higher pressures and temperatures and produce a higher ratio of the branched aldehydes.



# OXO ALDEHYDES AND ALCOHOLS (Hydroformylation Reaction)

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- The hydroformylation reaction using **phosphine ligands** occurs in an aqueous medium. Selectivity is also higher. Having more than one phase allows for complete separation of the catalyst and the products.
- In order to make the catalysts soluble in water, ionic ligands are attached to the catalyst. The Rhurchemie/Rhone-Poulenc process for the production of butyraldehyde from propylene is based on this technology.

# OXO ALDEHYDES AND ALCOHOLS (Hydroformylation Reaction)

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- Hydroformylation of higher olefins is possible when polyethylene glycol is used as a solvent. Higher olefins have greater affinity for ethylene glycol than for water, therefore allowing greater reaction rates. To facilitate the separation of the products, pentane is added to the system.
- The reaction takes place at 120°C and 70 KPa. When 1-hexene is used, the ratio of n-heptanal to the iso- was 0.73-3.75.

# OXO ALDEHYDES AND ALCOHOLS (Hydroformylation Reaction)

**Catalysts used in some commercial oxo processes and approximate conditions for propylene hydroformylation**

<b>Process</b>	<b>Catalyst</b>	<b>Conditions</b>	<b>% Normal</b>
Ruhrchemie	$\text{Co}^{2+}$ , $\text{Co}^{\circ}$	150°C, 300 atm.	70
BASF	$\text{HCo}(\text{CO})_4$	150°C, 30 MPa	70
ICI	$\text{Co}^{2+}$	high pressure	70
Shell	$\text{Co}/\text{PR}_3$	180, 50 atm	88
UCC	$\text{HRh}(\text{CO})(\text{PPh}_3)_3$	100, 30 atm	94

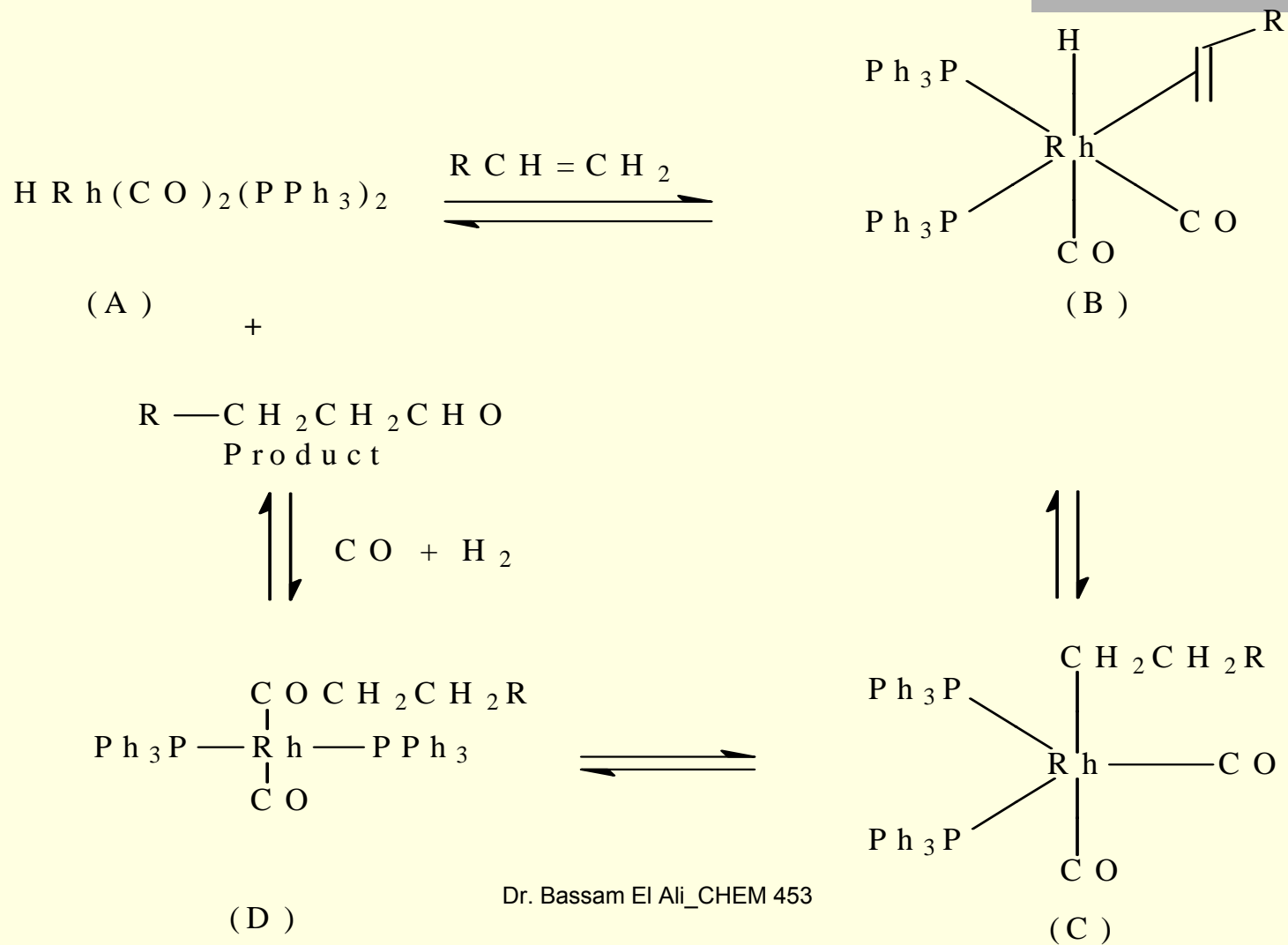
# Hydroformylation Reaction

## Mechanism

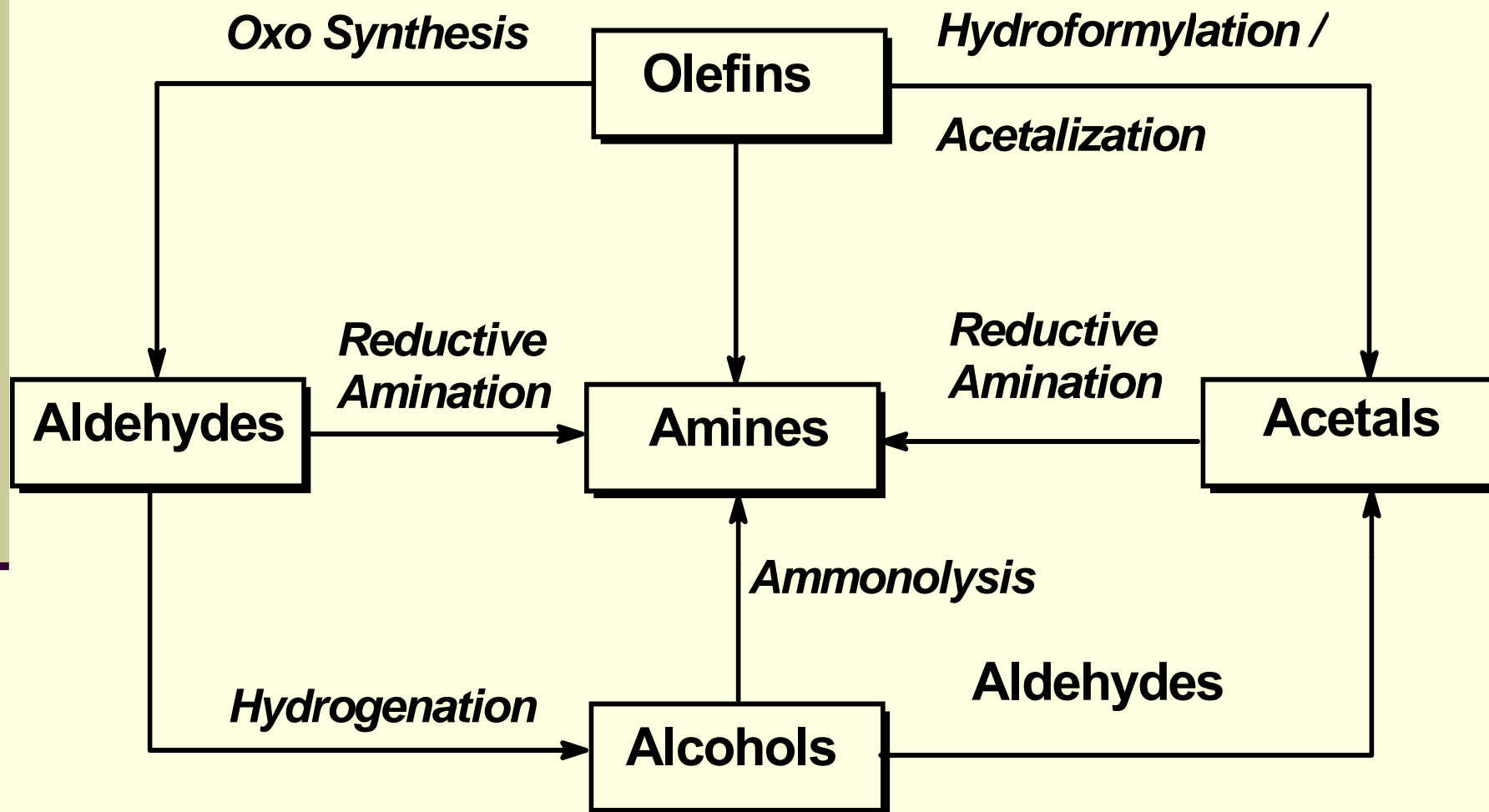
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- A simplified mechanism for the hydroformylation reaction using the rhodium complex starts by the addition of the olefin to the catalyst (A) to form complex (B).
- The complex (B) rearranges, probably through a fourcentered intermediate, to the alkyl complex (C).
- A carbon monoxide insertion gives the square-planar complex (D).
- Successive  $\text{H}_2$ , and CO addition produces the original catalyst and the product ( $\text{PPh}_3$  is triphenyl phosphine):

# Hydroformylation Reaction Mechanism



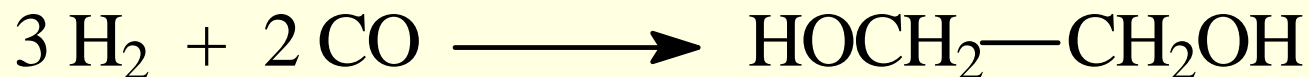
# Synthesis pathways to aldehydes, amines and acetals



# ETHYLENE GLYCOL FROM SYNGAS

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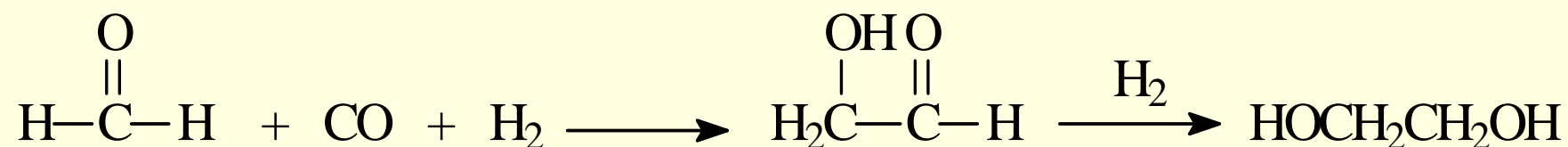
- Ethylene glycol could be produced directly from synthesis gas using an Rh catalyst at 230°C at very high pressure (3,400 atm).
- In theory, five moles synthesis gas mixture are needed to produce one mole ethylene glycol:



- Other routes have been tried starting from formaldehyde or paraformaldehyde.

# ETHYLENE GLYCOL FROM SYNGAS

- One process reacts formaldehyde with carbon monoxide and H<sub>2</sub> (hydroformylation) at ~ 4,000 psi and 110°C
- The process is using a rhodium triphenyl phosphine catalyst with the intermediate formation of glycolaldehyde.
- Glycolaldehyde is then reduced to ethylene glycol:





# ETHYLENE GLYCOL FROM SYNGAS

- The DuPont process (the oldest syngas process to produce ethylene glycol) reacts formaldehyde with CO in the presence of a strong mineral acid.
- The intermediate is glycolic acid, which is esterified with methanol.
- The ester is then hydrogenated to ethylene glycol and methanol, which is recovered.

