

Lecture Nine

METHYLALCOHOL (CH₃OH)

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. The current world demand for methanol is approximately 25.5 million tons/year (1998) and is expected to reach 30 million tons by the year 2002. The 1994 U.S. production was 10.8 billion pounds.

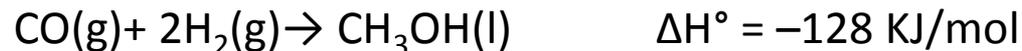
Methanol was originally produced by the destructive distillation of wood (wood alcohol) for charcoal production. Currently, it is mainly produced from synthesis gas.

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. 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). During the late seventies and early eighties, many experiments tested the possible use of pure (straight) methanol as an alternative fuel for gasoline cars. Several problems were encountered, however, in its use as a fuel, such as 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.

Production of Methanol

Methanol is produced by the catalytic reaction of carbon monoxide and hydrogen (synthesis gas). Because the ratio of CO:H₂ 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:H₂ 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. Figure 5-4 is a combined reforming diagram. If an autothermal reforming step is added, pure oxygen should be used.

An added advantage of combined reforming is the decrease in NO 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. The process scheme is viable and is commercially proven. The following reactions are representative for methanol synthesis.



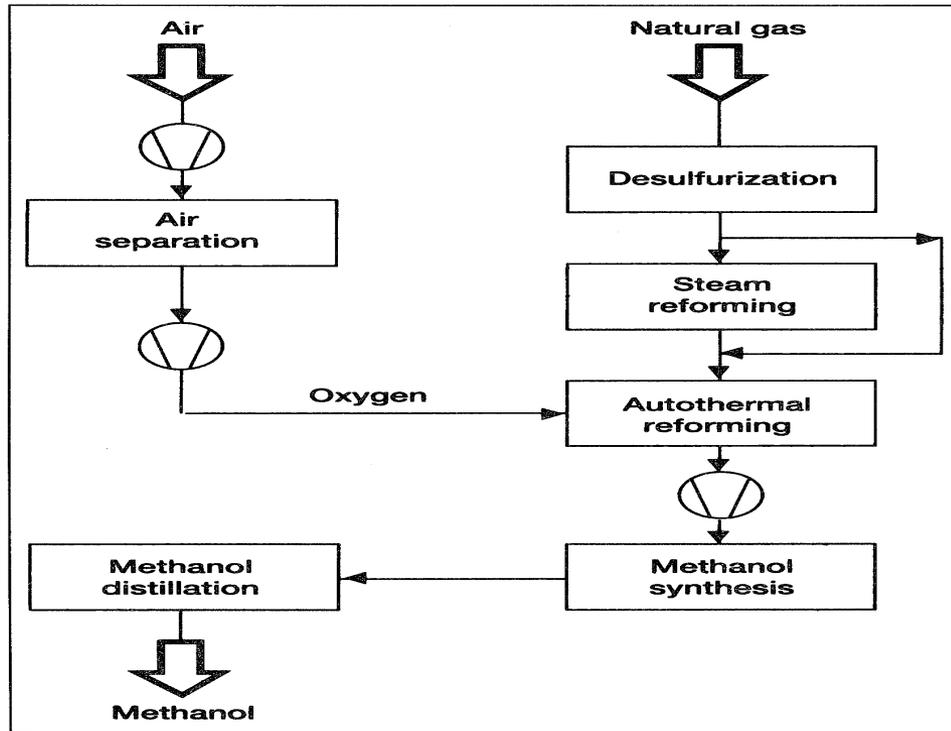


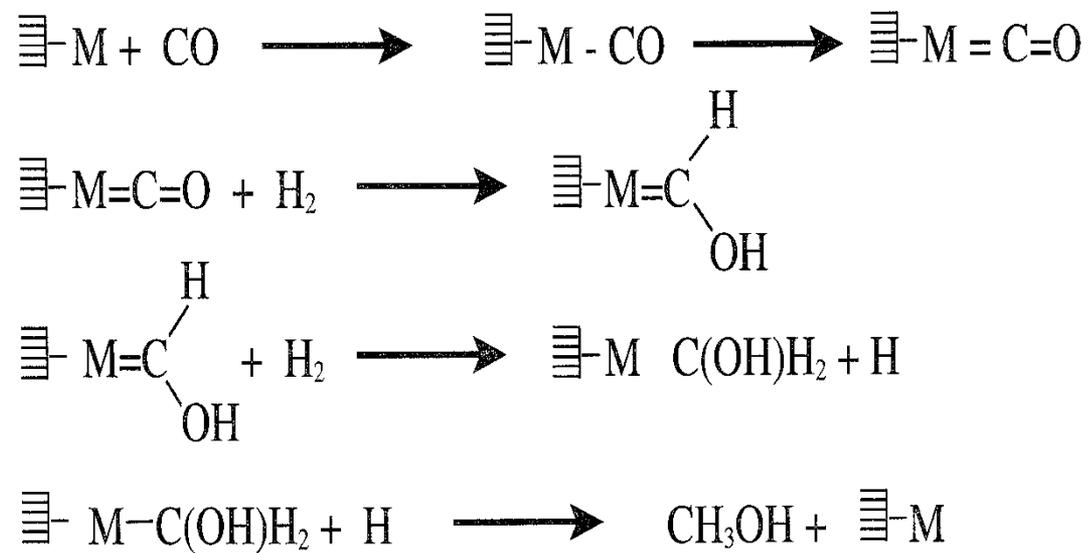
Figure 5-4. A block flow diagram showing the combined reforming for methanol synthesis.

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

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. Figure 5-5 shows the ICI methanol synthesis process.

Methanol synthesis over the heterogeneous catalyst is thought to occur by a successive hydrogenation of chemisorbed carbon monoxide.



Other mechanisms have been also proposed.

Uses of Methanol

Methanol has many important uses as a chemical, a fuel, and a building block. 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). Olefins from methanol may be a future route for ethylene and propylene in competition with steamcracking 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_2 and iron (II) is formed in aqueous H_2SO_4 . The benefits of low emission may be offset by the high cost. The following describes the major chemicals based on methanol.

Acetic Acid (CH₃COOH)

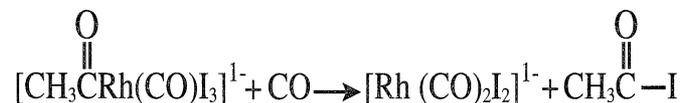
The carbonylation of methanol is currently one of the major routes for acetic acid production. The basic liquid-phase process uses a cobalt catalyst at 250°C and a high pressure of about 70 atmospheres. The newer process uses a rhodium complex catalyst in presence of CH₃I, which acts as a promoter. The reaction occurs at 150°C and atmospheric pressure. A 99% selectivity is claimed with this catalyst:



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 cisinsertion 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:



Figure 5-7 is a flow diagram showing the Monsanto carbonylation process.

Acetic acid is also produced by the oxidation of acetaldehyde and the oxidation of n-butane. However, acetic acid from the carbonylation route has an advantage over the other commercial processes because both methanol and carbon monoxide come from synthesis gas, and the process conditions are quite mild.

Uses of Acetic Acid.

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.

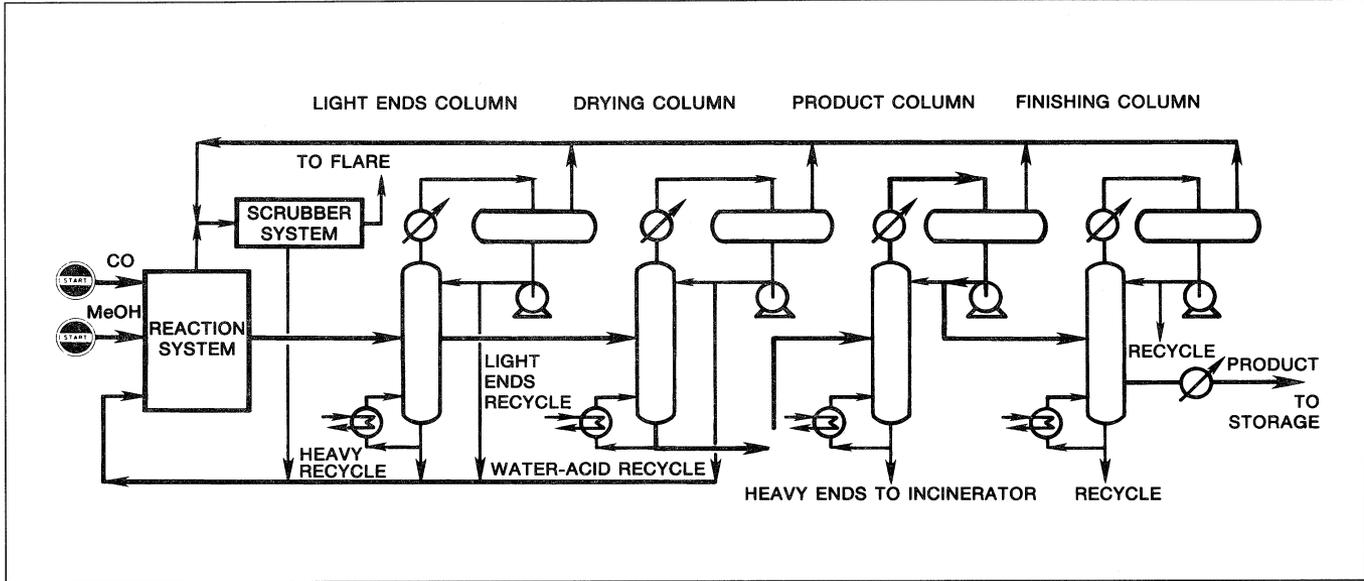


Figure 5-7. The Monsanto methanol carbonylation process for producing acetic acid.

OXIDATION OF n-BUTANE (Acetic Acid and Acetaldehyde)

The oxidation of n-butane represents a good example illustrating the effect of a catalyst on the selectivity for a certain product. The noncatalytic oxidation of n-butane is nonselective and produces a mixture of oxygenated compounds including formaldehyde, acetic acid, acetone, and alcohols. Typical weight % yields when n-butane is oxidized in the vapor phase at a temperature range of 360–450°C and approximately 7 atmospheres are: formaldehyde 33%, acetaldehyde 31%, methanol 20%, acetone 4%, and mixed solvents 12%.

On the other hand, the catalytic oxidation of a n-butane, using either cobalt or manganese acetate, produces acetic acid at 75–80% yield. Byproducts of commercial value are obtained in variable amounts. In the Celanese process, the oxidation reaction is performed at a temperature range of 150–225°C and a pressure of approximately 55 atmospheres.



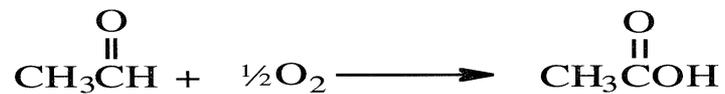
The main by-products are formic acid, ethanol, methanol, acetaldehyde, acetone, and methylethyl ketone (MEK). When manganese acetate is used as a catalyst, more formic acid ($\approx 25\%$) is obtained at the expense of acetic acid.

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.

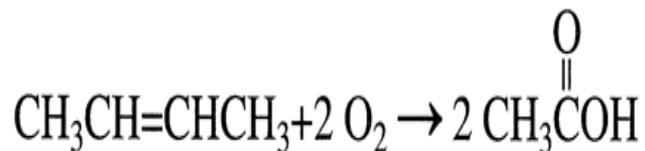
It is also produced by the catalyzed oxidation of acetaldehyde:



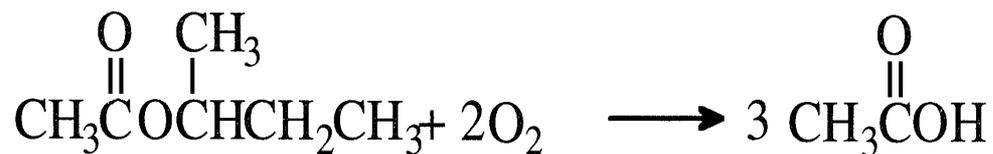
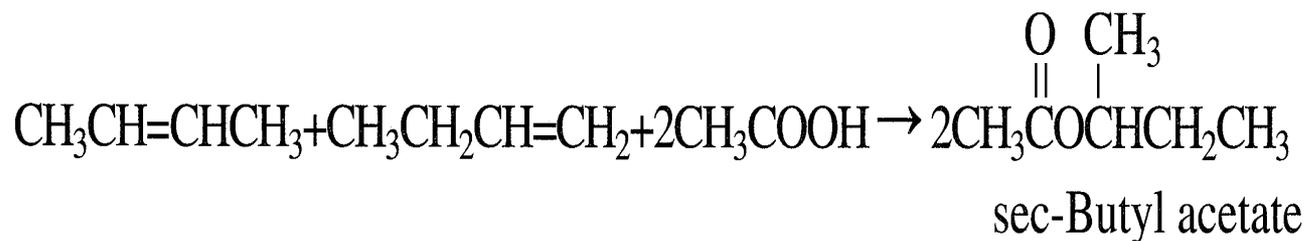
The reaction occurs in the liquid phase at approximately 65°C using manganese acetate as a catalyst.

Currently, the major route for obtaining acetic acid (ethanoic 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. A 70% acetic acid yield has been reported. The major by-products are carbon oxides (25%) and maleic anhydride (3%):



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:



The reaction conditions are approximately 100–120°C and 15–25 atmospheres. The oxidation step is noncatalytic and occurs at approximately 200°C and 60 atmospheres. An acetic acid yield of 58% could be obtained. By-products are formic acid (6%), higher boiling compounds (3%), and carbon oxides (28%). Figure 9-1 shows the Bayer AG two-step process for producing acetic acid from n-butenes.

Acetic acid is a versatile reagent. It is an important esterifying agent for the manufacture of cellulose acetate (for acetate fibers and lacquers), vinyl acetate monomer, and ethyl and butyl 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 approximately 4 billion pounds.

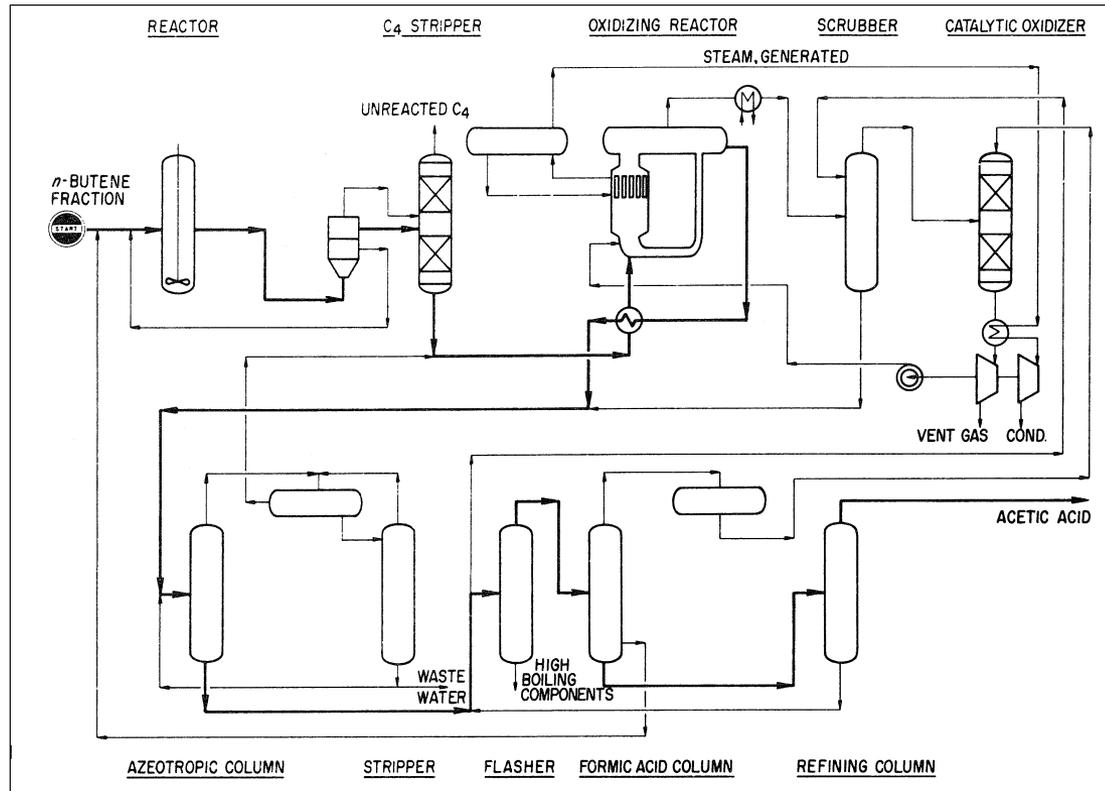


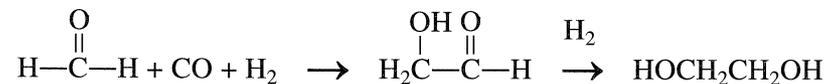
Figure 9-1. The Bayer AG two-step process for producing acetic acid from n-butenes.

ETHYLENE GLYCOL(CH₂OHCH₂OH)

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:

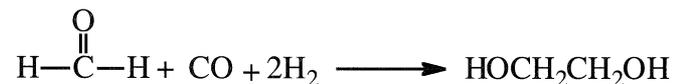


Other routes have been tried starting from formaldehyde or paraformaldehyde. One process reacts formaldehyde with carbon monoxide and H₂(hydroformylation) at approximately 4,000 psi and 110°C using a rhodium triphenyl phosphine catalyst with the intermediate formation of glycolaldehyde. Glycolaldehyde is then reduced to ethylene glycol:



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. The net reaction from either process could be represented as:



Ethylene glycol (EG) is colorless syrupy liquid, and is very soluble in water. The boiling and the freezing points of ethylene glycol are 197.2° and -13.2°C, respectively.

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.

EG consumption in the US was nearly 1/3 of the world's. The use pattern, however, is different; about 50% of EG is consumed in antifreeze.

The US production of ethylene glycol was 5.55 billion pounds in 1994, the 30th largest volume chemical.

The main route for producing ethylene glycol is the hydration of ethylene oxide in presence of dilute sulfuric acid (Figure 7-4):

