Lecture 10. Technology of organic substances. Organic synthesis industry, its value, raw material base. Syntheses based on carbon monoxide. Production of methyl alcohol. Physico-chemical basis of the process. Technological scheme. The catalysts of the process.

The most important productions of the main organic synthesis on a basis:

- Synthesis gas (methanol, formaldehyde);
- Alkanes (the highest acids and alcohols, butadiene and isoprene)
- Alkenes (ethanol and изопропанол);
- Acetylene (ethyl aldehyde, ukssny acid and its anhydride);
- Aromatic hydrocarbons (ethyl benzene and styrene, phenol);
- Naftenov (caprolactam)

Synthesis on the basis carbon oxide

Organic synthesis on the basis carbon oxide are widely used in industry. Aliphatic hydrocarbons, alcohols, aldehydes, carboxylic acids and their derivatives, other are obtained from carbon oxide.

1. Hydrocarbons's synthesis (Fisher F, Tropsh G., 1928-1935)

$$nCO + (2n + 1)H_2 \xrightarrow{CO} C_nH_{2n+2} + nH_2O \text{ или}$$

$$2nCO + (n + 1)H_2 \xrightarrow{Fe} C_nH_{2n+2} + nCO_2$$

2. **Ox process or hydroformylation (Reln O. 1938)**

$$CH_2{=}CH_2 + CO + H_2 \rightarrow CH_3{-}CH_2{-}CHO \xrightarrow{H_2} CH_3{-}CH_2{-}CH_2OH$$

$$CH_3{-}CH_2{-}CHO \xrightarrow{O_2} CH_3{-}CH_2{-}COOH$$

$$R{-}CH{=}CH_2 + CO + H_2 \rightarrow R{-}CH_2{-}CH_2{-}CHO \xrightarrow{H_2} R{-}CH_2{-}CH_2{-}CH_2OH,$$

где $R = C_8{-}C_{16}$

3) Synthesis of carboxylic acids and their derivatives (Reppe V. 1949)

$$CH_2{=}CH_2 + CO + H_2O \rightarrow CH_3{-}CH_2{-}COOH$$

$$CH{\equiv}CH + CO + ROH \rightarrow CH_2{=}CH{-}COOR$$

$$ROH + CO \rightarrow RCOOH$$

4) Synthesis of primary alcohols (Patar 1924)

$$nCO + (n+1)H_2 \rightarrow C_nH_{2n+1}OH$$

- **Methanol** is a new future alternative fuels and it also widely uses as a raw material for MTBE and other materials (ρ=796 kg/m3). T boiling point = 64,7 ºC, freezing point= - 95 ºC.

- Until 1934 methanol obtained by dry distillation of wood. At present the main method of obtaining it is the synthesis of methanol from carbon monoxide and hydrogen.

Physical and chemical bases of synthesis CH_3OH

$$CO + 2H_2 \rightleftarrows CH_3OH - \Delta H_1 \qquad \Delta H_1 = 90{,}7 \text{ кДж}$$

$$CO + 3H_2 \rightleftarrows CH_4 + H_2O - \Delta H_2 \qquad \Delta H_2 = 209 \text{ кДж}$$

$$2CO + 2H_2 \rightleftarrows CH_4 + CO_2 - \Delta H_3 \qquad \Delta H_3 = 252 \text{ кДж}$$

$$CO + H_2 \rightleftarrows CH_2O - \Delta H_4 \qquad \Delta H_4 = 8{,}4 \text{ кДж}$$

$$CO_2 + 3H_2 \rightleftarrows CH_3OH + H_2O - \Delta H_5 \qquad \Delta H_5 = 49{,}5 \text{ кДж}$$

secondary conversion of CH_3OH

$$2CH_3OH \rightleftarrows CH_3\text{–}O\text{–}CH_3 + H_2O$$

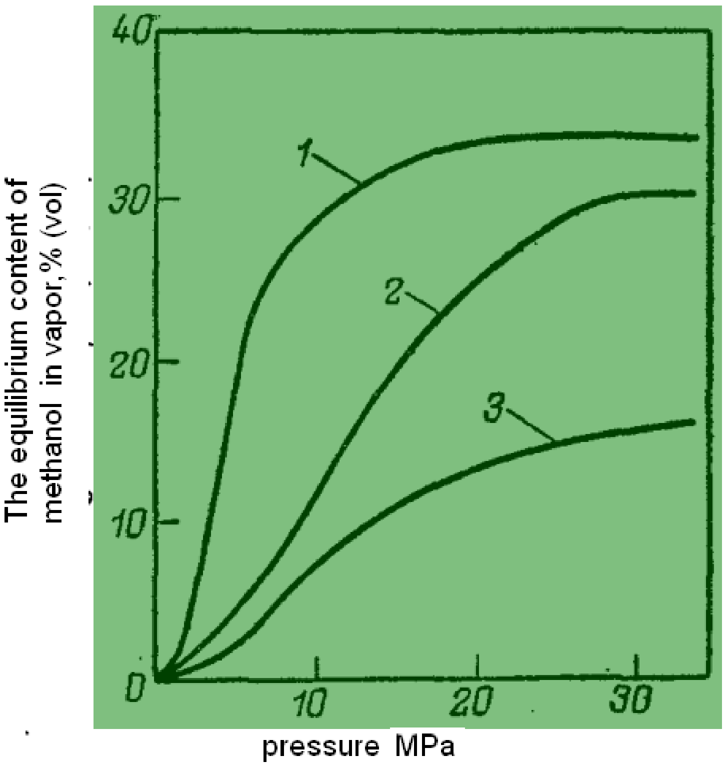
$$CH_3OH + nCO + 2nH_2 \rightleftarrows CH_3(CH_2)_n\text{-}OH$$

$$CH_3OH + H_2 \rightleftarrows CH_4 + H_2O$$

The original catalysts (ZnO-CrO) were only active at high temperature. Therefore, the pressure has to be high (250-350 bar) to reach acceptable conversions. The catalysts that active at low temperature were not resistance to impurities.

The catalysts (CU/Zno/AlO) is very selective. In modern plants, the catalysts are active at low temperature which led to "low-pressure plants". The reaction temperature is critical. A low temperature is favorable from thermodynamic point of view, but the rate of reaction is also low at lower temperature. The pressure for modern plant is usually in the range of 50-100 bar.

Formation of methanol proceeds with heat's release and with decreasing of volume. We should carry on the process at high pressure and low temperature to increase the yield of methanol. Moreover, composition of gas strongly influences on equilibrium yield of methanol , i.e. ratio H_2:CO



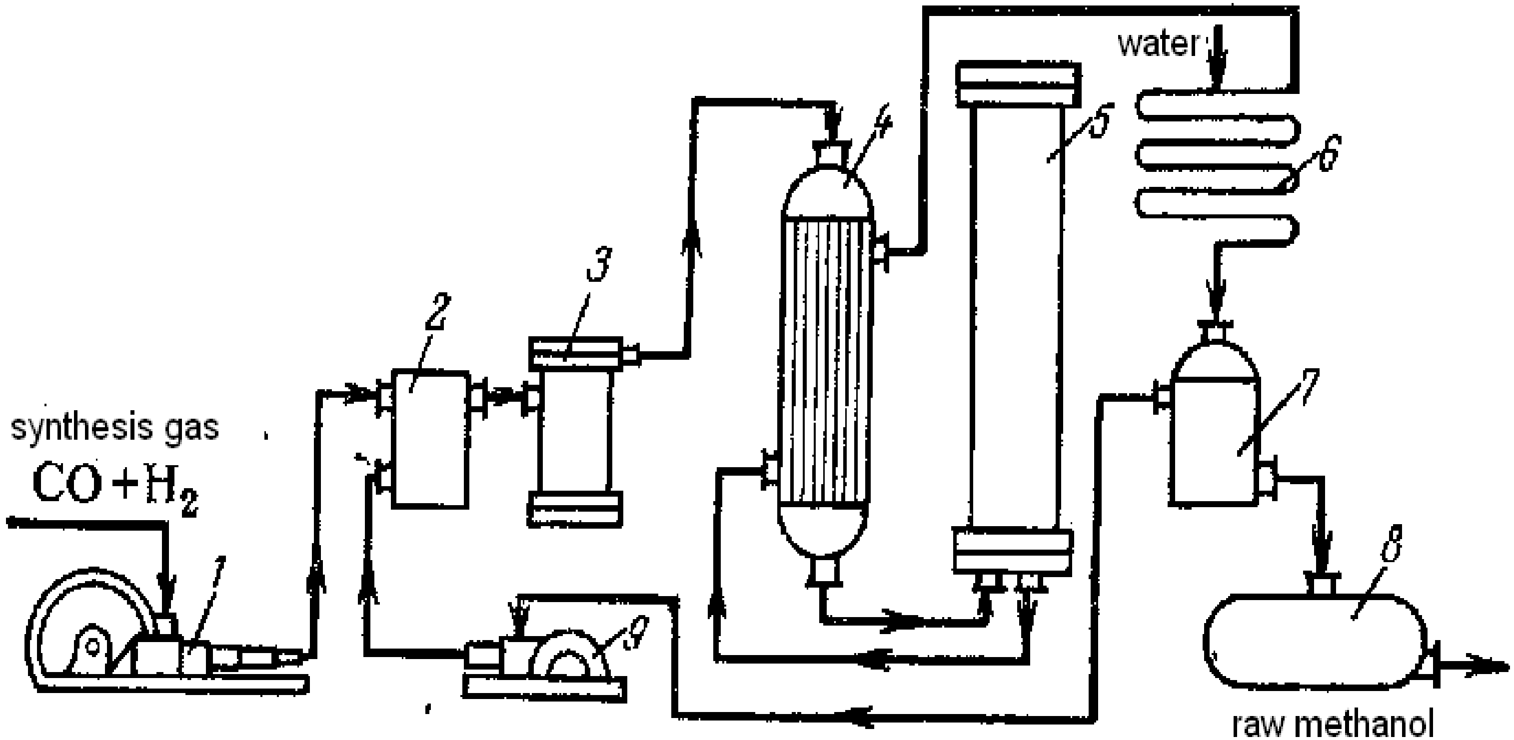
Dependence of the equilibrium methanol content in the gas mixture on pressure and temperature (H_2:CO=4:1)
1 – 240^{0}C; 2 – 340^{0}C; 3 – 400^{0}C

The figure shows, that when temperature increases the equilibrium concentration of methanol increases. In order to increase equilibrium concentration of methanol it is necessary to increase pressure. However, when ratio H_2:CO increases and pressure increase equilibrium concentration of methanol sharply decreases, so optimal process conditions are to achieve the maximum possible yield of methanol.

Pressure of the process - 20-30 MPa, Temperature of the process - 370-420 C.

- The plants production process that can be divided into four main stages:
  - Feed Purification.
  - Reforming.
  - Methanol Synthesis.
  - Methanol Purification.

Methanol synthesis scheme



1 - compressor, 2 - mixer, 3 – filter, 4 - heat exchanger, 5 - synthesis column, 6 - condensing apparatus, 7 – separator, 8 - collecting tank, 9 – circulation compressor

The picture shows scheme of methanol's synthesis mixture H_2 and CO in ratio 4:1 compressed till 25 MPa in compressor 1 and it is mixed with unreacted gas circulation in mixer 2 by injection compressor and is arrived in filter 3, where it is claned from oil. Then mixture heated till 200^0C in heat exchanger and it is directed to column of methanol's synthesis. Then mixture arrived to interpipe space of heat exchanger and cooled heating gas mixture arriving to synthesis. Such organization of process allows to proceed process avtothermals.

The gas mixture containing vapor of methanol from heat exchanger arrived in water comdensator 6, then in separator 7, where liquid methanol separated from unreacted gas. The unreacted gas returned in mixer by circulation compressor. Methyl alcohol-raw merged in collecting tank from separator and it is directed on rectification for cleaning from any organic substance.

The yield of pure methanol-raw after rectification amounted 84-87%

Uses of the methanol

- Fuel internal combustion engines, flammable as gasoline.
- As a solvent and as an antifreeze in pipelines.
- About 40% of methanol is converted to formaldehyde, and from there into products as diverse as plastics, plywood, paints, explosives, and permanent press textiles.
- In the 1990s, large amounts of methanol were used in the United States to produce the gasoline additive methyl tert-butyl ether (MTBE).
- Other chemical derivatives of methanol include dimethyl ether, which has replaced chlorofluorocarbons as the propellant in aerosol sprays, and acetic acid.

Synthesis on the basis paraffin hydrocarbon

Paraffin hydrocarbon are the raw materials for the synthesis of most organic products. A wide variety of products is produced from paraffins by oxidation, halogenation and sulfonation and et al.

When oxidation of hydrocarbons depending on the process conditions get alcohol, aldehyde, acid, CO, H_2 et al.