Lecture №11

Production of ethanol.
Physical-chemical basis of the process.
Conditions and process flow scheme

Uses of ethanol

- as a solvent in the manufacture of varnishes and perfumes;
- in the preparation of essences and flavorings;
- in many medicines and drugs;
- as a disinfectant and in tinctures ;
- as a fuel (E85, a mixture of 85% ethanol and 15% gasoline) and gasoline additive.

C_2H_5OH melts at –114.1°C, boils at 78.5°C, and has a density of 0.789 g/mL at 20°C.

Manufacture of Ethanol

1. I**ndirect hydration** by addition of H_2SO_4 and subsequent saponification of the sulfuric acid ester.

2. D**irect catalytic hydration**.

Alcohol production by indirect hydration

I. Absorption is carried out by absorbing ethylene with sulphuric acid.

- $CH_2{=}CH_2 + H_2SO_4 \rightarrow CH_3CH_2OSO_3H$

- $2CH_2{=}CH_2 + H_2SO_4 \rightarrow (CH_3CH_2)2SO_4$

In absorption tower

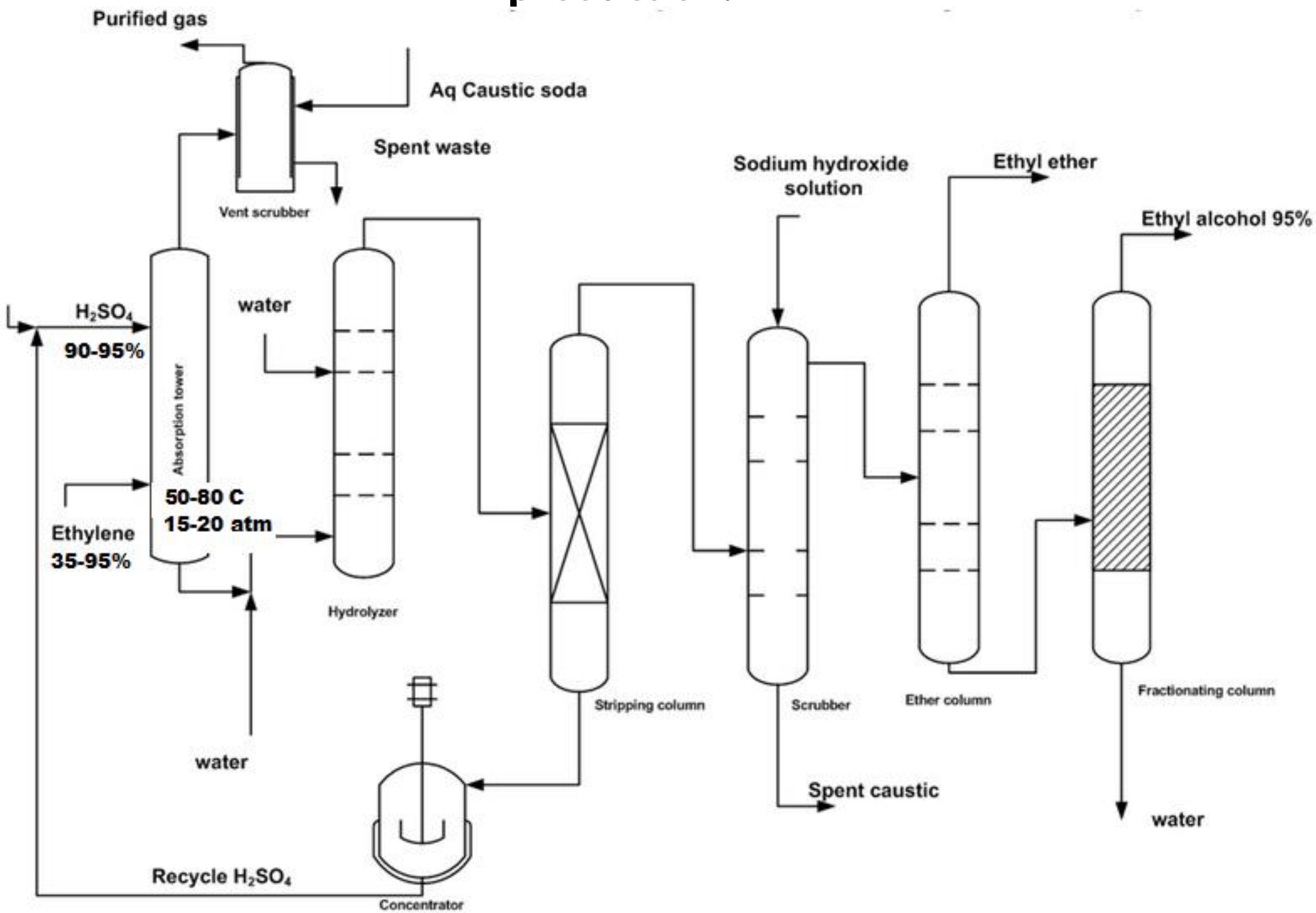
P = 15-20 atm

$C(CH_2{=}CH_2)$=35-95 %

$C(H_2SO_4)$=90-95%

T=50-80 ^{o}C.

Process flow diagram of indirect hydration of ethylene for industrial alcohol production:



Finally, a fractionating column produces industrial alcohol with **95% ethanol** and **5% water** that is also called as rectified spirit.

II. Hydrolysis of sulfuric esters to ethanol:

$$CH_3CH_2OSO_3H + (CH_3CH_2)2SO_4 + 3\ H_2O \rightarrow 3\ CH_3CH_2OH + 2\ H_2SO_4$$

or

$$CH_3CH_2OSO_3H + H_2O \rightarrow CH_3CH_2OH + H_2SO_4$$

$$(CH_3CH_2)2SO_4 + 2H_2O \rightarrow 2CH_3CH_2OH + H_2SO_4$$

The mixture is allowed for 4 hours space time to complete the reaction at 70 ^oC. So formed esters can be converted to ethanol with less diethyl ether formation.

In any case, 5-10% of diethyl ether is formed by the side reaction.

$$2C_2H_5OH \rightarrow C_2H_5OC_2H_5 + H_2O$$

A perfectly designed process for producing ethanol from ethylene would be the catalytic hydration method developed based on direct hydration technology. This method has very less bottleneck factors when compared to other methods like indirect hydration technology. Direct catalytic hydration method posses optimized energy consumption and material balance. Equipments used in catalytic hydration are lesser than old process in practice.

Petrochemical industry that has high source of ethylene stock prefer to select this method. Ethylene with 95% concentration is the best raw material quality that this process can handle. Designing a plant that handles catalytic hydration has high scope in modern continuous processes. Project of ethanol production has much more important in most petrochemical industries due to its growing demand in the international market. Engineers who can improve the existing process and bring out high performance by rectifying the problems are in demand for a process industry.

Direct catalytic hydration of ethylene

Catalyst: H_3PO_4 /SiO_2

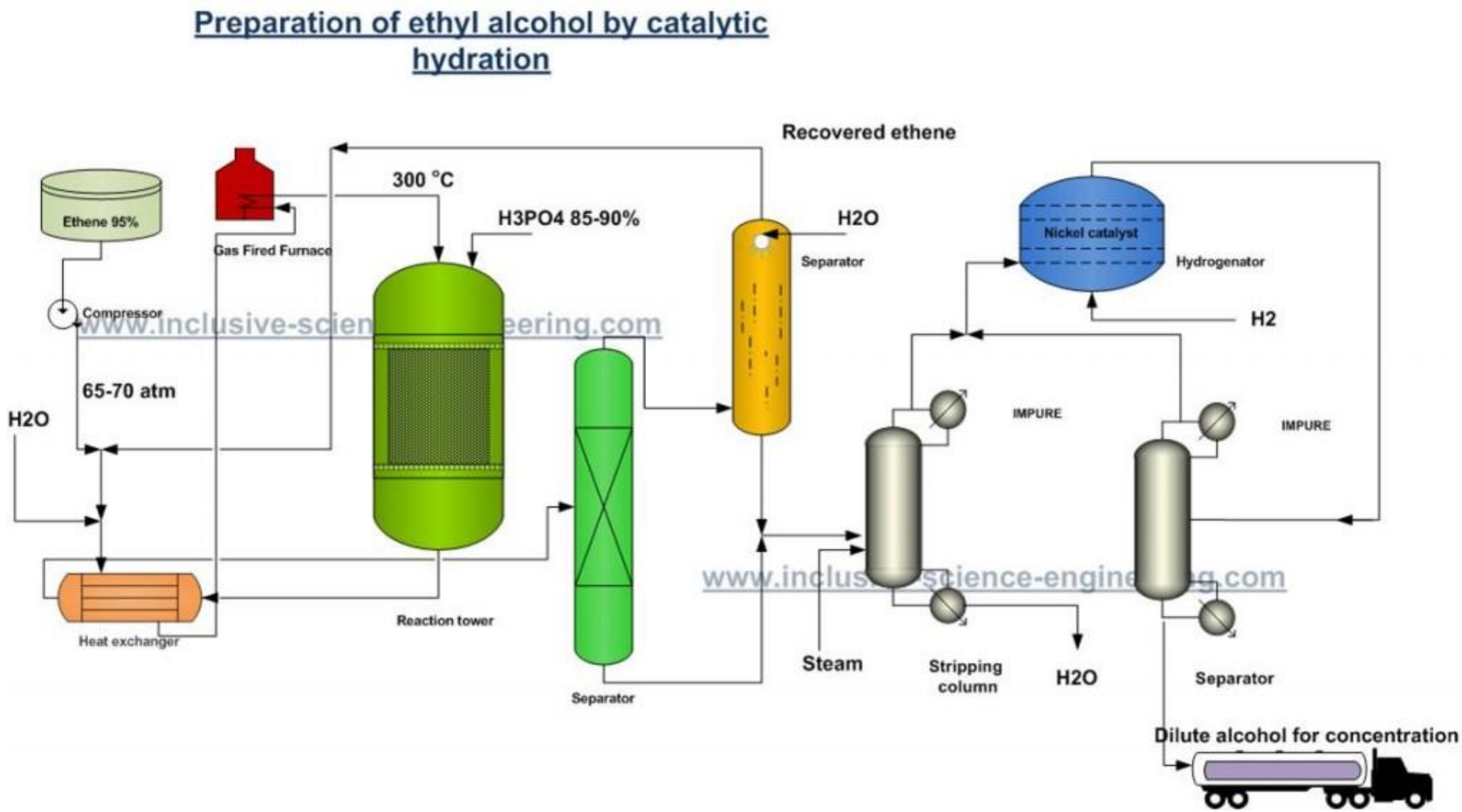
$C(H_3PO_4)$= 85-90%.
P=65-70 atm
T=300 °C.

$$\mathbf{H_2O + CH_2{=}CH_2 \rightarrow {}^{H_3PO_4} \rightarrow CH_3CH_2OH}$$

The side reaction:

$$C_2H_2 + H_2O \rightarrow CH_3CHO \text{ (acetaldehyde)}$$

$$CH_3CHO + H_2O \rightarrow {}^{Ni}\!\rightarrow CH_3CH_2OH$$



Finally, C_2H_5OH is produced at different concentration as per the requirement in separators with a yield of 95-97% ethanol.

Physical-chemical basis of the process

$$CH_2{=}CH_{2(g)} + H_2O_{(g)} \rightleftharpoons CH_3CH_2OH_{(g)} \quad \Delta H = -45\ kJ\ mol^{-1}$$

- The reaction is reversible, and the formation of the ethanol is exothermic.
- Only 5% of the ethene is converted into ethanol at each pass through the reactor. By removing the ethanol from the equilibrium mixture and recycling the ethene, it is possible to achieve an overall 95% conversion.

The proportions of ethene and steam

- The equation shows that the ethene and steam react 1 : 1.
- Because water is cheap, it would seem sensible to use an excess of steam in order to move the position of equilibrium to the right according to Le Chatelier's Principle. In practice, an excess of ethene is used.
- This is very surprising at first sight. Even if the reaction was one-way, you couldn't possibly convert all the ethene into ethanol. There isn't enough steam to react with it.
- The reason for this oddity lies with the nature of the catalyst. The catalyst is phosphoric acid coated onto a solid silicon dioxide support. If you use too much steam, it dilutes the catalyst and can even wash it off the support, making it useless.

The temperature

- According to Le Chatelier's Principle, this will be favoured if you lower the temperature.
- In order to get as much ethanol as possible in the equilibrium mixture, you need as low a temperature as possible. However, 300°C isn't particularly low.
- The lower the temperature you use, the slower the reaction becomes.
- 300°C is a compromise temperature producing an acceptable proportion of ethanol in the equilibrium mixture, but in a very short time. Under these conditions, about 5% of the ethene reacts to give ethanol at each pass over the catalyst.

The pressure

- According to Le Chatelier's Principle, if you increase the pressure the system will respond by favouring the reaction which produces fewer molecules. That will cause the pressure to fall again.
- High pressures also increase the rate of the reaction.

- ***Problems with high pressures***
- There are two quite separate problems in this case:
- High pressures are expensive. It costs more to build the original plant because you need extremely strong pipes and containment vessels. It also needs a lot of energy to produce the high pressures. That can make the ethanol uneconomic to produce.
- At high pressures, the ethene polymerises to make poly(ethene). Apart from wasting ethene, this could also clog up the plant.

The catalyst

- The catalyst has no effect whatsoever on the position of the equilibrium. Its only function is to speed up the reaction.

- In the absence of a catalyst the reaction is so slow that virtually no reaction happens in any sensible time.