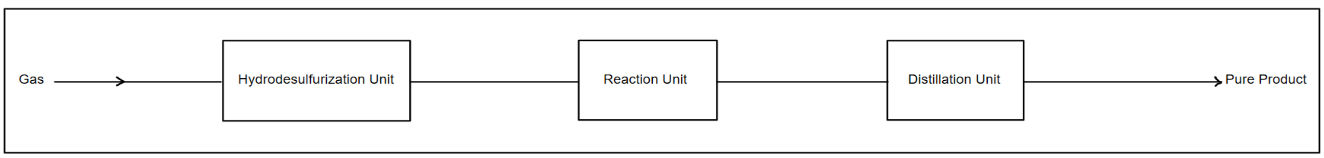
Process Plant Design

Session 4

Methanol plants components

- Hydrodesulfurization unit: In order to protect downstream catalysts against sulfur poisoning or de-activation we need to have a unit in which sulfur components are removed by means of reactor.
- Reaction Unit: where all reactions take place and intermediate and then final products are produced.
- Purification Unit: The products produced need purification. We can sell only pure products. In this regard, we need a distillation column to do increase the purity of the products.

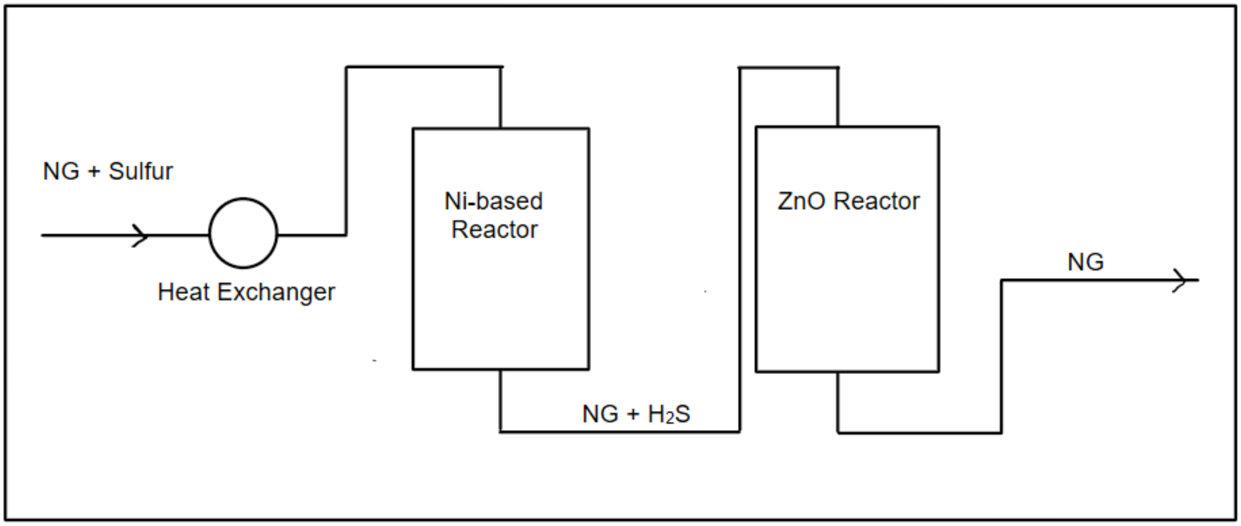
So, the first version of PFD becomes like this:



Now Let's detail it.

1.Hydrodesulfurization unit:

- Based on numerous articles, the best way to remove sulfur compounds is to remove them via catalysts. Based on research, the best procedure to remove the sulfur is that at first the hydrogen stream is added to gas containing sulfur and then they pass through reactor containing Ni-based catalysts, which results in all conversion of sulfur compound to H_2S.
- Now the gas containing H_2S passes through second reactor which contain absorber catalysts. The absorber is ZnO which is typical in all desulfurization reactor and absorbs the H_2S like this: $H_2S + ZnO = ZnS + H_2O$.
- To make sure that the H_2S is absorbed, it is normal practice to add another ZnO Reactor as a guard.
- Based on research, the operating condition should be above 300 C and pressure around 48barg. As a result, we need a heat exchanger to increase NG temperature from atmospheric temperature to a temperature above 300C.



2.Reaction unit

- Each reaction units as its name suggests has some reactors by which products are produced. Some reactions are exothermic and some reactions are endothermic. So it means that we need some reactors, to which sometimes we have to give energy and from which sometimes we can energy.
- In methanol plants, methanol is produced when a mixture of H_2 + CO + CO_2 passes over a reactor filled with Cu-based catalysts. The mixture which is called Syngas is produced when natural gas passes through a reactor filled with Ni-based catalysts. The reactor is called fired heater.
- In fired heater the structure is like this that we have a number of vertical tubes and inside the tubes there are catalysts. The gas passes through the catalytic tubes and alongside the tubes the mixture of H_2 + CO + CO_2 is produced. The reaction is endothermic which means it requires heat, which is supplied by burners inside the fired heaters.
- The burners stream which provides heat to catalytic tubes has a high temperature even after heat exchange with catalyst tubes. So, it sounds we can use that energy as a means of optimization.
- Notice that it is right that the gas reacts with steam over the catalyst and receive heat from the burners and as a result

yield syngas but for the reaction to take place, the inlet temperature should be above 500C.

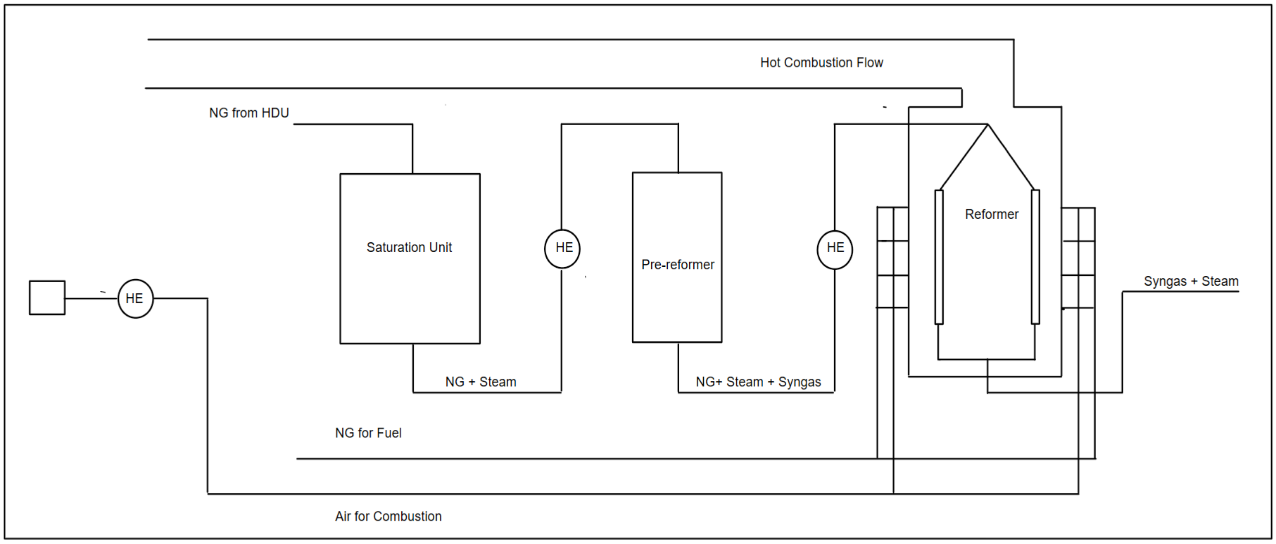
$$CH_4 + H_2O = Syngas$$

Note that burners are not sth difficult. It is simple chemistry. What do I mean? In burners we have combustion and in order for combustion to take place we know that we need hydrocarbons and air. It means that we have to connect two pipes to burners, one for hydrocarbons and one for air. We can't use air with atmospheric temperature for combustion since it is not efficient. Thus, we need a heat exchanger.

Since there is the problem of cocking when hydrocarbons receive heat, we have to add steam alongside the gas. In order to do so, we need a saturation unit to saturate the gas with steam.

Before going to create the new PFD, just notice that the composition is mostly methane for Ammonia, Methanol and Hydrogen plants but sometimes it contains small amount of ethane. Of course, we can convert ethane to Syngas via catalysts inside tubes of the reformer, but it is risky since it reduces lifetime of the catalyst. To overcome the problem, we put another reactor. In methanol terminology we call fired heater "Reformer" since it reforms the methane to Syngas and call the new reactor Pre-reformer.

Since the nature of this reaction is the same as the reaction in fired heater, it requires heat. To tackle the problem, we need a heat exchanger to increase the inlet temperature to around 500C and a good catalyst so that no burner is needed.



Now, let's improve the process and make it more optimized:

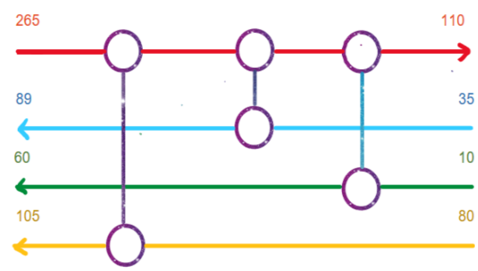
1.Syngas production

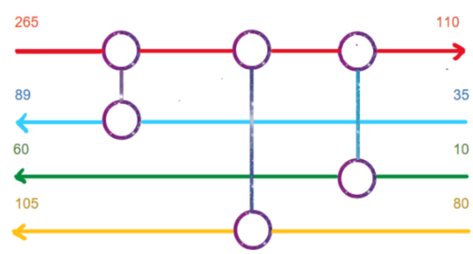
- In old technologies, reformers were the only means to produce Syngas. After years of research, they added ATR or Auto Thermal Reactor. The reactor catalytic reactions are exactly the same as those in the reformer but this time instead of having large fired heater as the reformer, we design the reactor in a way that in its top part oxygen reacts with excess NG and as a result, produces heat like what happens in burners and in its lower part we put catalysts, over which the reactions take place. The heat required for the reaction comes from the reaction between oxygen and NG.
- We know from day 2 that oxygen is extremely dangerous and extreme care should be given to its transfer. We learned from the example that we need filter to remove particles, we are supposed to use orifice transmitter for flow measurement, a globe control valve-FV- to regulate its flow. Finally, we need a shell and tube heat exchanger to preheat the oxygen to 230C before it enters the ATR.

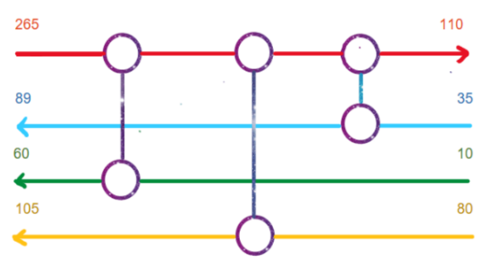
2.Heat exchanger network design

- After the preliminary design of plant and then simulation of that in Aspen Hysys or Plus, we get more info about the streams and can decide better.
- After this stage we should try to optimize our design. One of sections which is always the center of research and attention, is energy- Energy Optimization.
- One of the sources which can impact the energy consumption drastically is heat exchanger network. In a simple way, it means how heat exchangers are put together and mapped. Some call it also Pinch Analysis of the unit.
- After the preliminary simulation in Aspen Hysys we activate energy analysis feature and export the data to Aspen Energy Analyzer to get the optimized one.

Which one?



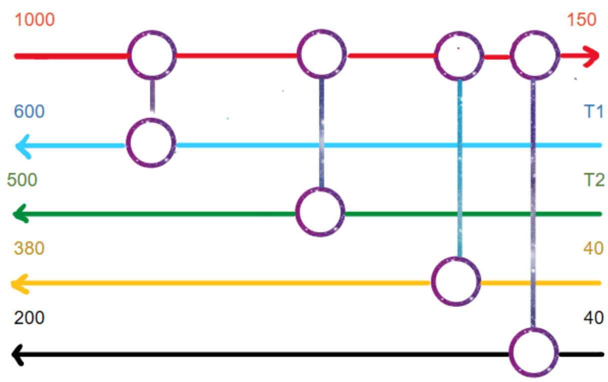




Now let's put together what we have:

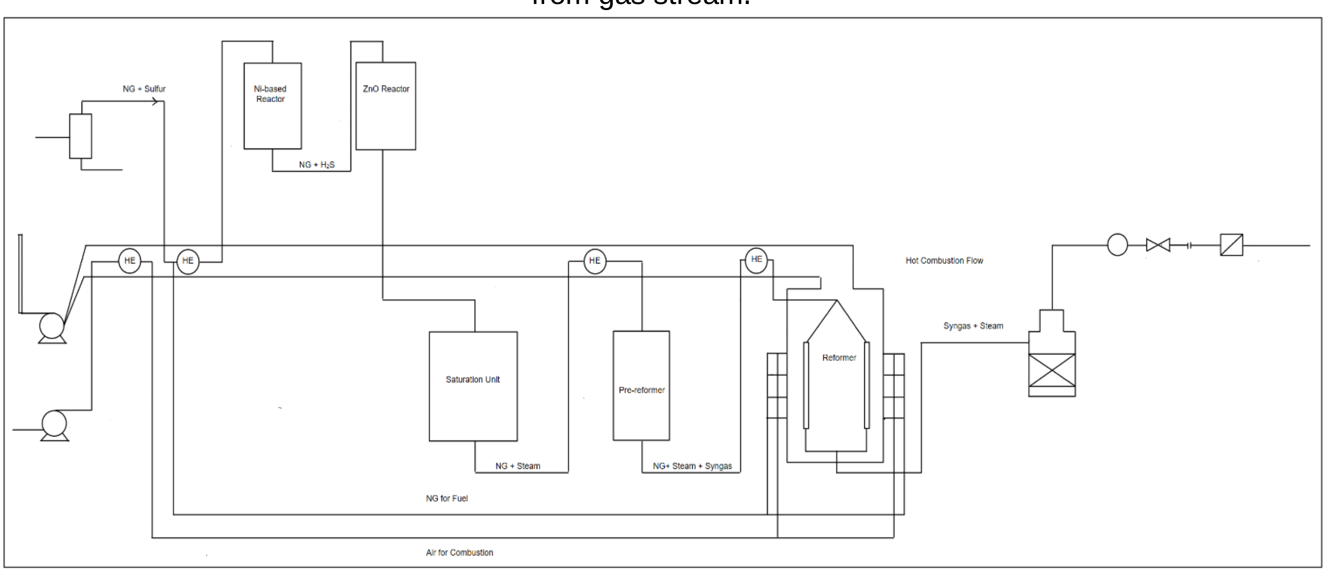
Stream	Temperature	Type
Combustion Stream	1000 C	Hot
Reformer Inlet	600C	Cold
Pre-reformer Inlet	500C	Cold
Sulfur Reactor Inlet	380C	Cold
Air Pre-heater	200C	Cold

So, it becomes like this:



3.Miscallanious — Most fired heaters has a forced fan to push the air and induced fan to take out the combustion stream.

At the inlet of plants, it is a normal practice to put K.O. drum at the inlet of plants to separate the condensate from gas stream.



Methanol production happens in a shell and tube reactor with Cu-based catalyst inside tubes. The operating pressure and temperature are 70-90 barg and 210-240C respectively. The feed composition to the reactor inlet contains H_2 + CO + CO_2. So the outlet of ATR might be good match but it has some problems which should be addressed to make it more suitable for methanol reactors.

1.Operating pressure — The operating pressure for ATR gas stream is 24barg, while the demanded pressure should be above 70 barg. It means we need a compressor to increase the pressure from 24 barg to 70 barg and that should be centrifugal type since the flowrate is high.

2.Operating temperature — The operating temperature of ATR gas stream is approximately 1000 C, which is not suitable for the reactor which demands a temperature around 210C. It means we have to decrease the temperature which is indeed a good opportunity for us to use its heat and optimize the energy.

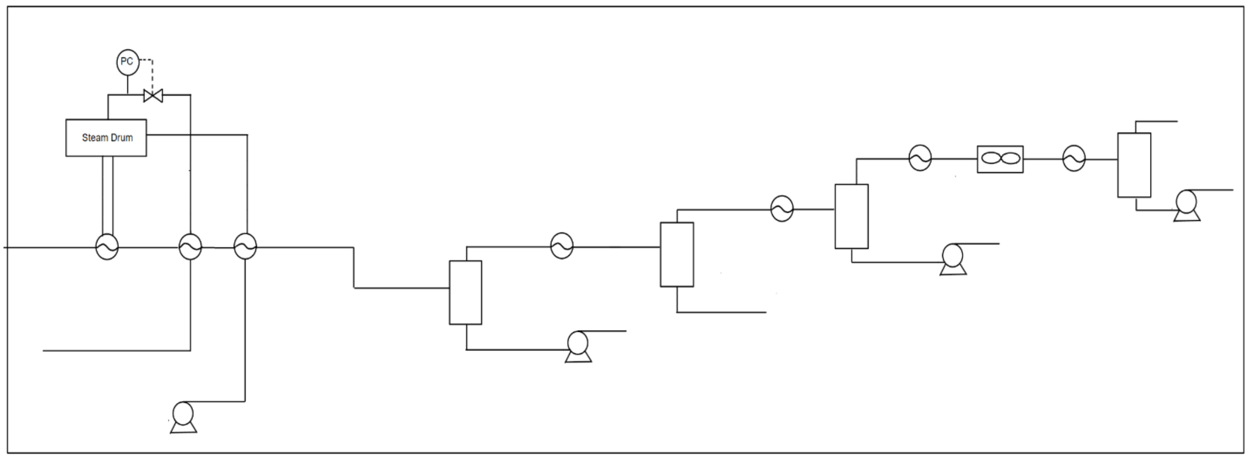
But how much decrease? On the surface one might think that the temperature should be decreased to 210C. But if we take all parameters into account, then we find out that it should be decreased to atmospheric temperature such as 48C since we have a large centrifugal compressor and if we want to construct the compressor for such high temperature, the cost of material would be extremely high. Moreover, the failure rate of material used at such high temperature and pressure is high.

3.Pinch analysis — Now let's check how we can get the best out of its energy. In last session we talked about shell and tube heat exchangers which act as steam generator which requires a great deal of energy. Then we had superheaters and BFW preheaters which required also a great deal of energy. So, for their mapping, the location after steam generator seems the best option. Due to its high flow and temperature, it still has prodigious amount of energy. We can use the energy to warm-up reboilers in distillation column and also heat the DMW before entrance to deaerator.

4.Design note — Whenever the temperature is in range of 65-150, it is a normal practice to consider an air-cooled heat exchanger and then water-cooled heat exchanger in our design. The outlet temperature of air-cooled heat exchanger is always 65C.

5.Miscelanious — Since the stream has some amount of steam, with by passing through different heat exchangers, the steam gives away its energy and starts becoming condensate. So, we have to consider separator in our design.

By incorporating all above notes, then the design becomes like this:



Now let's go through the production:

1. Reactor

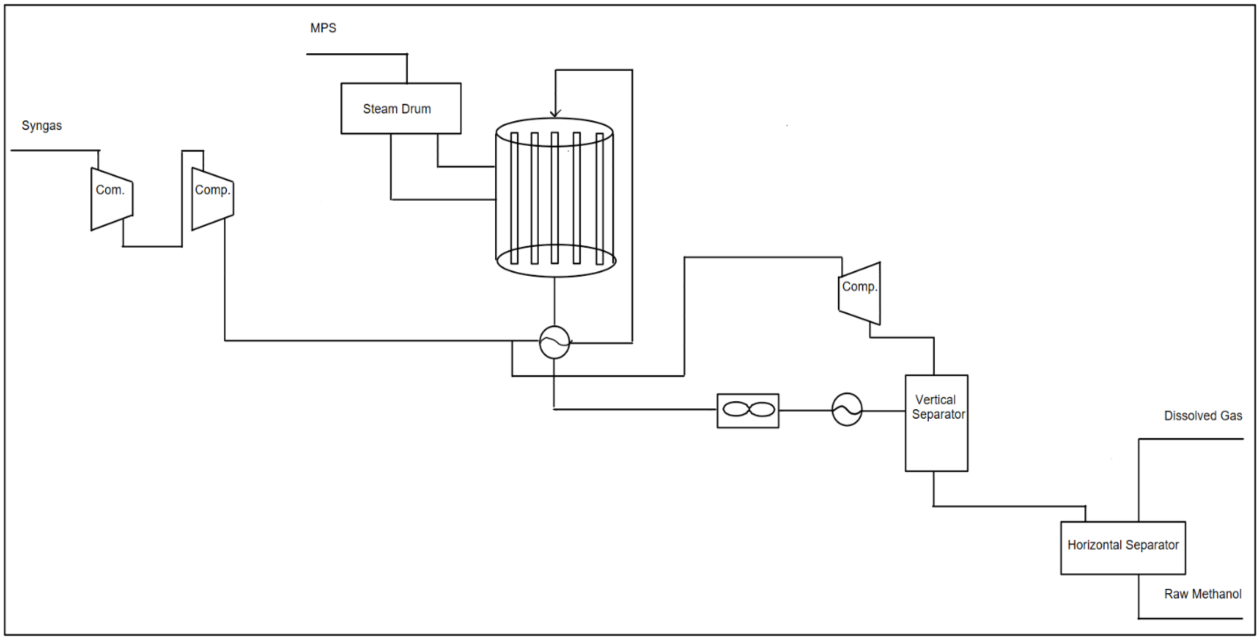
- As stated above, the best operating pressure and temperature are 70-90 barg and 210 C. So, we need a compressor to increase the pressure and a heat exchanger to increase the temperature.
- The reactor type is a shell and tube heat exchanger. Inside the tubes is the catalyst, over which Syngas passes and methanol is produced over the length. Inside the shell there is BFW which absorbs the heat from the tube side, since the reaction is exothermic. The vaporized BFW now goes to a steam drum and exits as MPS.

2.Heat exchanger network

- The mixture which contains methanol and unreacted Syngas even after heat exchange with BFW, still has good temperature to be used. So we can use it to increase the temperature of the inlet that we needed to increase. So we need a heat exchanger here.
- Based on simple simulation in Aspen Hysys, the outlet temperature is about 260C and after the heat exchange with the inlet gas, its temperature reaches in range of 100-150, so based on design note, at this point we are supposed to use a air-cooled heat exchanger and then water-cooled heat exchanger.

3.Separators

- Since we have unreacted Syngas, then the best thing to do is to have a separator, from lower part of which the impurified methanol is separated and from upper part of which the unreacted gas is separated and sent back to the reactor but we need a recirculating compressor to increase the pressure again to 70-90 barg.
- The methanol which is separated from lower part contains some amount of dissolved gas [CO+CO_2+H_2]. They should be removed and can be re-used. To do so we use a separator.
- Simple rule in separator design:
  1.If gas flowrate to liquid flowrate is high or otherwise it is gas dominant, then we use vertical separator.
- 2.If liquid flowrate to gas flowrate is high or otherwise it is liquid dominant, then we use horizontal separator.
- Based on above rule the configuration of the first separator which is gas dominant is vertical and the configuration of the second separator which is liquid dominant is horizontal. Its being horizontal gives also the opportunity for the dissolved gas to easily be separated from the liquid volume.


MPS
Steam Drum
Syngas
Com.
Comp.
Comp.
Vertical Separator
Dissolved Gas
Horizontal Separator
Raw Methanol