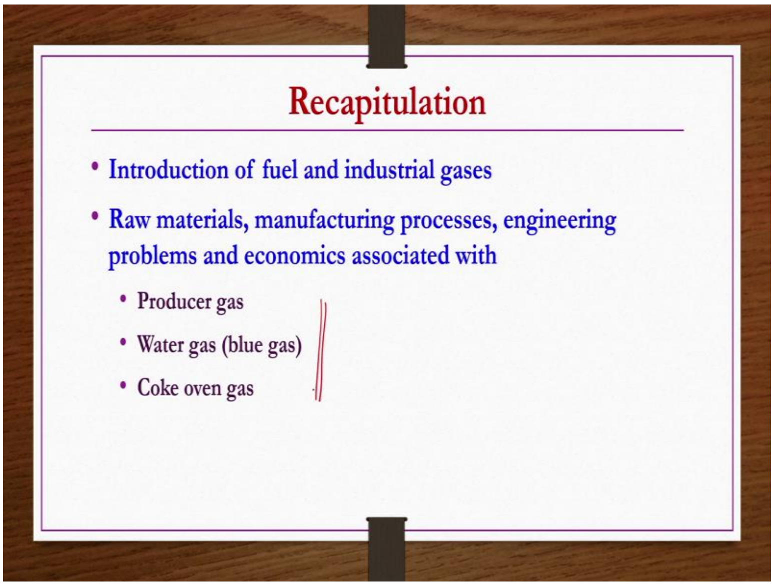
Inorganic Chemical Technology
Prof. Nanda Kishore
Department of Chemical Engineering
Indian Institute of Technology, Guwahati

Lecture - 06
Natural Gas, LPG and Syngas

Welcome to the MOOCs course Inorganic Chemical Technology, the title of today's lecture is Natural Gas, LPG and Syngas. Before going into the details of production of natural gas liquefied petroleum gas and syngas what we are going to do now? We are going to have a kind of recapitulation of what we have seen in the previous lecture.

(Refer Slide Time: 00:53)

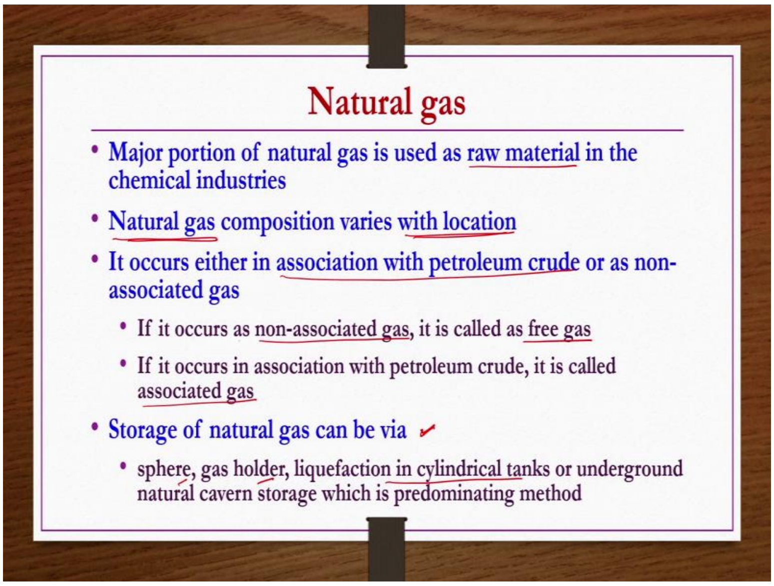


Recapitulation

- Introduction of fuel and industrial gases
- Raw materials, manufacturing processes, engineering problems and economics associated with
  - Producer gas
  - Water gas (blue gas)
  - Coke oven gas

In the previous lecture we have seen introduction of fuel and industrial gases. Then again we have seen a few details of like raw materials, manufacturing processes, engineering problems and economics associated with the production of three different type of gases like producer gas, water gas or blue gas which is also known as blue gas it is known as blue gas because of the flame color when it is burnt right and then coke oven gas the production process of these three gases that we have seen in the previous lecture.

(Refer Slide Time: 01:30)



Natural gas

- Major portion of natural gas is used as raw material in the chemical industries
- Natural gas composition varies with location
- It occurs either in association with petroleum crude or as non-associated gas
  - If it occurs as non-associated gas, it is called as free gas
  - If it occurs in association with petroleum crude, it is called associated gas
- Storage of natural gas can be via ✓
  - sphere, gas holder, liquefaction in cylindrical tanks or underground natural cavern storage which is predominating method

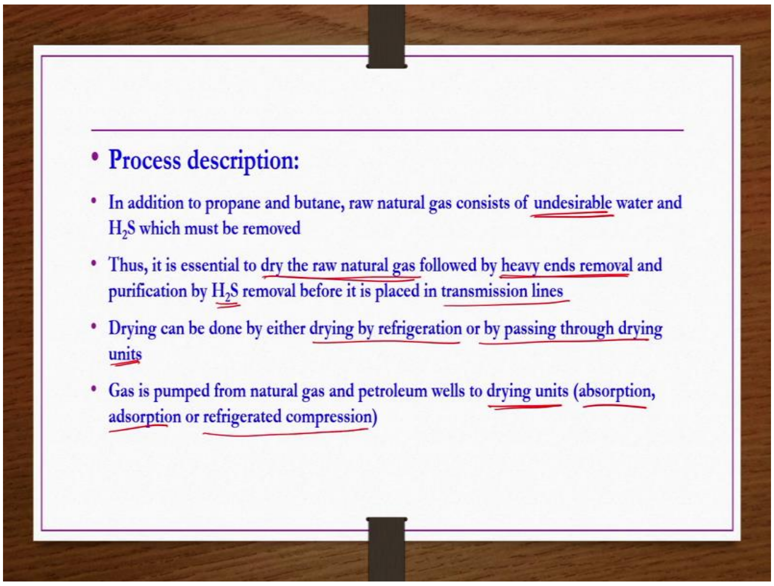
Now, in this lecture we will be starting with production of natural gas. Natural gas; major portion of natural gas is used as raw material in the chemical industries. Natural gas composition varies with location actually you know this natural gas consist of primarily methane, but some traces of or some fraction of ethane, propane, butane etcetera would also be there in addition to the moisture and then some sulphides.

So, the moisture may be there in terms of like you know or the gas may be wet because of this moisture. So, before using it natural gas for the required heating purpose etcetera and what you have to do? You have to dry it properly and then remove any heavy end products are there and then you should also remove H2S and then make it purify as much as possible, then only you should use it for the heating purpose ok.

It occurs either in association with petroleum crude or as non associated gas. If it occurs as non associated gas it is called as free gas. If it occurs in association with petroleum crude it is called as associated gas ok, from the wells mostly you get the natural gas as a free gas if it is a natural gas well, if it is a petroleum crude well then you get this natural gas along with the petroleum crude.

So, then under such conditions if it is coming from the petroleum well in association with the petroleum crude then it is known as the associated gas. Storage of natural gas can be done by several methods those things like you know we have already seen several unit operations in the 1st week of the lecture. So, for the storage of natural gas often we use sphere, gas holders, liquefaction in cylindrical tanks or underground natural carbon storage etcetera are predominant methods for the storage of natural gas ok.

(Refer Slide Time: 03:20)



- **Process description:**
  - In addition to propane and butane, raw natural gas consists of undesirable water and H_2S which must be removed
  - Thus, it is essential to dry the raw natural gas followed by heavy ends removal and purification by H_2S removal before it is placed in transmission lines
  - Drying can be done by either drying by refrigeration or by passing through drying units
  - Gas is pumped from natural gas and petroleum wells to drying units (absorption, adsorption or refrigerated compression)

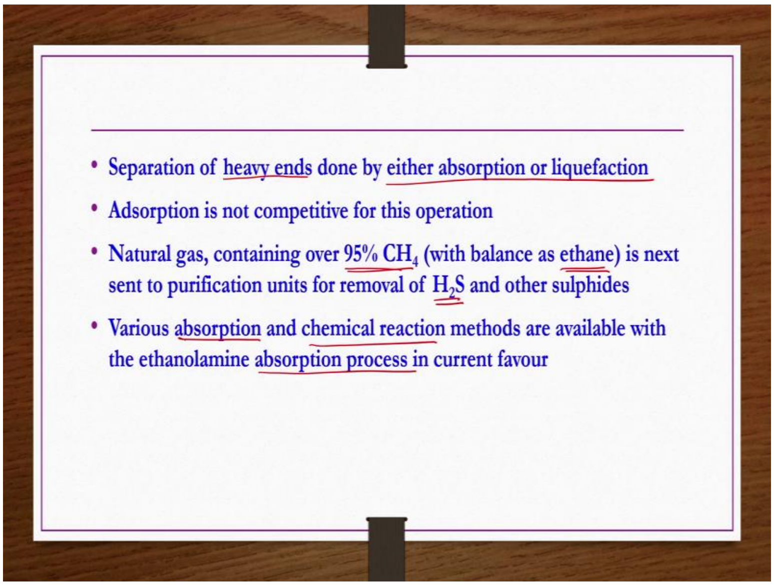
Now, we will be seeing the process description of natural gas production. In this natural gas production there are three primary steps; one is the drying of the raw natural gas that we are getting from the natural gas wells or petroleum crude wells. Then after drying then there may be some heavy end products may be there. So, those heavy end products should be removed and then after that further purification should be done by removing the sulphide etcetera.

So, these three stages are very essential in producing as much pure natural gas as possible ok. So, in addition to propane and butane raw natural gas consist of undesirable water in the form of moisture or the gas may be wet and H2S which must be removed ok. So, how to remove?

So, in order to remove this one it is essential to dry the raw natural gas, so that to remove the moisture etcetera followed by removing of the heavy ends by absorption kind of techniques and then followed by purification of H2S removal again by absorption kind of techniques before we are putting it in transmission lines from which the gas is supplied to the required points ok.

So, drying can be done either drying by refrigeration or by passing through drying units. So, what are those units? Gas is pumped from natural gas and petroleum wells to drying units such as like absorption, adsorption or refrigerated compression ok.

(Refer Slide Time: 04:55)

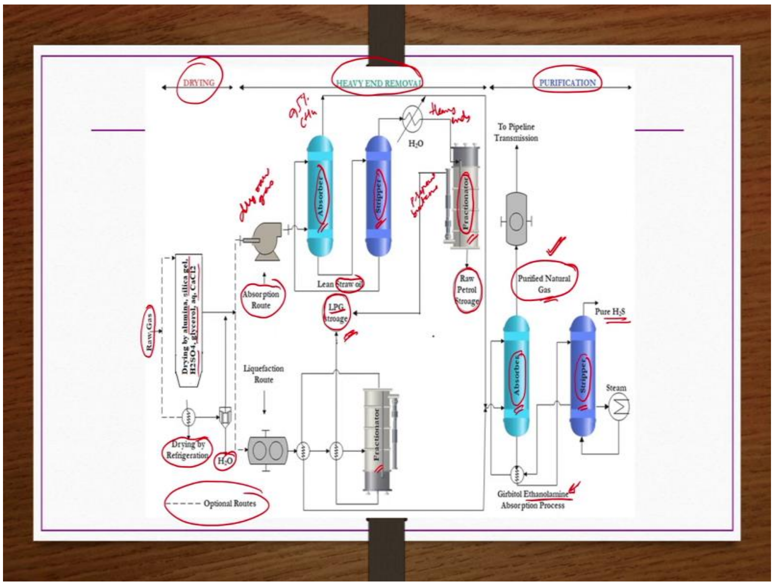


- Separation of heavy ends done by either absorption or liquefaction
- Adsorption is not competitive for this operation
- Natural gas, containing over 95% CH_4 (with balance as ethane) is next sent to purification units for removal of H_2S and other sulphides
- Various absorption and chemical reaction methods are available with the ethanolamine absorption process in current favour

Then after that separation of heavy ends done by either absorption or liquefaction two options are there. Adsorption can also be done, but adsorption has not found economic or it is not found competitive for this purpose of producing the natural gas pure natural gas. Natural gas containing over 95 percent of methane with balance of ethane is next sent to purification units for removal of H2S and other types of sulphides if at all present ok.

Various absorption and chemical reaction methods are available with the ethanol amine absorption processes in current favour right. This whatever the process that I explained that same thing we are going to see by a simplified you know flow sheet. So, that is what we are having here.

(Refer Slide Time: 05:44)



So, as I mentioned getting purified natural gas is having three stages; one is the drying stage then another one is heavy end removal stage, another one is the purification stage which is a last stage ok. So, the raw natural gas whether it is associated gas or free gas that you get from the wells right, it is associated gas if you get it from the petrol crude wells, it is a free gas if you get from the natural gas wells right.

So, that gas should be dried first. Drying can be done by 2 ways; one is drying by refrigeration right another one is drying by passing through this gas through different media like alumina, silica gel or passing through H2SO 4 solution glycerols or aqueous calcium chloride solution etcetera right.

So, once you do this drying what are you doing? You are doing nothing but removing the moisture which is in the form of water you are removing. So, once you remove the moisture from the raw natural gas, then you will be having a dry gas which is still raw which is not purified then after that there are two options are there. So, the dotted lines in flow sheets often represent options optional routes.

Let us say start with the simplified one. So, if you wanted to produce liquefied petroleum gas also through the same process in fact, actually LPG is a by product from the natural gas production plant or from petroleum crude refining plants ok. So, now, let us say this dry raw gas if you pass through a fractionator after passing through some units like steam turbines etcetera. So, then in the fractionator what you can do? You can do a fractionation of the components whatever the components are present.

So, let us say whatever the propane and butane components are there those things you separate in the fractionator and then take them to the LPG storage right. So, that is what happens, right. So, now, this like you know in the same natural gas production section we are getting LPG also right. So, this is one optional route right.

So, that you can produce LPG also in the natural gas production plant itself right. Now, other route is absorption route where you pass the dry gas through absorber through an absorber for which straw oil you will be using as a kind of solution for absorbing the heavy ends because this dry raw gas whatever is there it is free from moisture only rest all things are still there. So, then high ends you have to remove right.

So, how do you remove them? By using straw oil. What is straw oil? Straw oil is nothing but the high boiling point fractions, high boiling point distillates coming out from the petroleum crude fractionator right; that means, you know some kind of a heavy products from the petroleum crude whatever you get. So, actually they can also be cracked further and then get some kind of products because petroleum crude is kind of one resource each and every fraction is having market value from chemical plant view ok.

So, those heavy ends you have to remove by using the straw oil which is again coming from the petroleum industry ok. So, now, since you know that petroleum industry each and every fraction is important one you cannot leave it. So, after removing the heavy ends whatever the lean or spent straw oil is there that you pass through a stripper section, right.

From the stripper what you can do? You remove whatever the water etcetera or whatever the heavy ends that you absorb in the solution they can be stripped off in the stripped section and then further you remove water from those section. So, then those heavy ends; those heavy ends you can take in a fractionator in a fractionator, ok.

Whereas, the dry natural gas after removing the heavy ends whatever are there that is after passing the absorber you believe that the heavy ends are completely removed not believe. In fact, your operating conditions in the absorber etcetera should be maintain such a way that there should not be any heavy ends right.

After removing these heavy ends, so then whatever the gas is there natural gas is there that is almost 95 percent pure methane with some amount of ethane etcetera would be there. So, this gases after removing the heavy ends you will be having 95 percent pure methane with some amount of ethane and then some sulphide. So, that gas you have to take to a another absorber section right where you can remove the H2S; where you can remove the H2S from the gas.

So, then you get purified natural gas that purified natural gas you can take to the storage section and then from there to pipeline transmission you can do it right. Here whatever the solution that we are using in this absorber column is ethanol amine solution, right which is also having some market value.

So, after when you use it for absorption of H2S and other sulphide, so now it is contaminated. So, once it is contaminated rather throwing it what you can do? You can send it through the stripping section because these ethanol amine solutions are also expensive you cannot you know afford to throw litres of tons of such kind of solutions, ok.

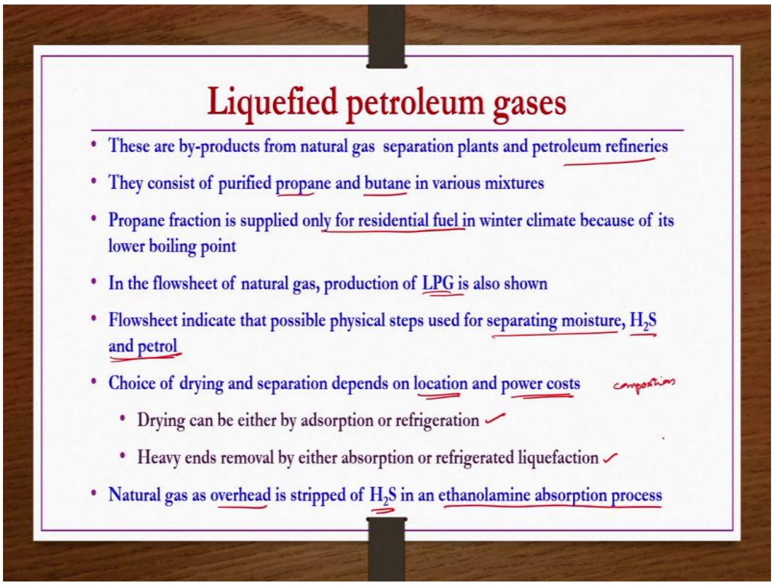
So, then what you do? The spin solution whatever is that you take to the stripping section and from the dilute solution or spent solution whatever spent ethanol amine solution whatever is there from there you separate out H2S. So, that you can get the pure ethanol ammine again and that you can send back to the absorption column again ok.

So, the heavy ends also you can what you can do? You can take them to the fractionator from there what you can do? You can take out whatever the propane and then butane fractions are there. So, they can separate out by fractionation you can separate out those fractions by fractionator and then you take them to the LPG storage. So, this is how this plant from the natural gas plant itself you can get the liquefied petroleum gas as well ok.

So, now what you see here? So, the absorption stripping here and then fractionation that is nothing but distillation, then again absorption stripping these kind of operations are there fractionation these kind of operations are there all these operations absorption stripping and then distillation you study in mass transfer operations course and then you can understand how much important are those concepts that you have learnt in mass transfer course or you are going to learn in your mass transfer course, right.

So, the bottoms that you get from the fractionator while processing the heavy ends they are nothing but you can take them to the raw petroleum storage and then these are further can be processed to get more products from it. So, now, you can see from the natural gas whatever we have whether it is associated with free gas, then so many products you are getting not only purified natural gas and LPG, but also you are getting some raw petrol that can be further processed to get more products from it ok.

(Refer Slide Time: 13:15)



Liquefied petroleum gases

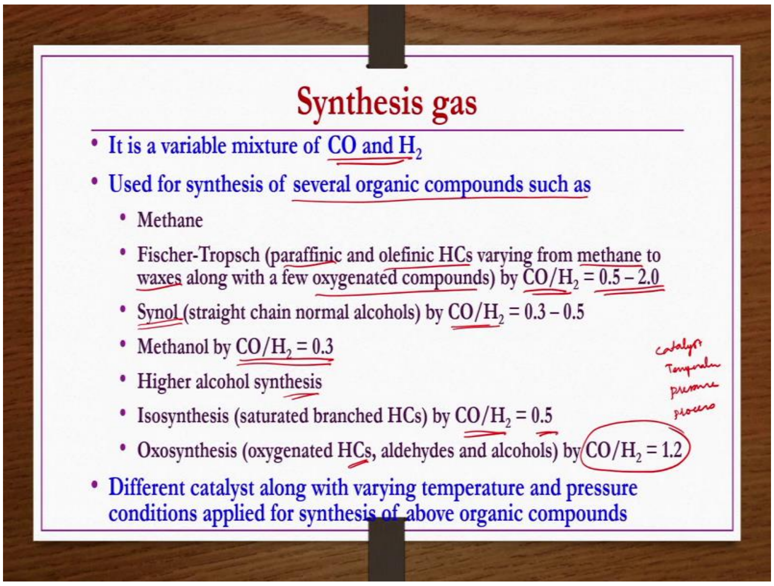
- These are by-products from natural gas separation plants and petroleum refineries
- They consist of purified propane and butane in various mixtures
- Propane fraction is supplied only for residential fuel in winter climate because of its lower boiling point
- In the flowsheet of natural gas, production of LPG is also shown
- Flowsheet indicate that possible physical steps used for separating moisture, H_2S and petrol
- Choice of drying and separation depends on location and power costs composition
    - Drying can be either by adsorption or refrigeration ✓
    - Heavy ends removal by either absorption or refrigerated liquefaction ✓
- Natural gas as overhead is stripped of H_2S in an ethanolamine absorption process

So, now next is liquefied petroleum gases that we have already seen anyway; however, these are by products from natural gas separation plants and petroleum refineries. They consist of purified propane and butane in various mixtures. Propane fraction is supplied only for residential fuel in winter climate because of its low or lower boiling point and in the flow sheet of natural gas production of LPG is also shown that we have already discussed.

In the flow sheet what we have seen that possible physical steps such as separating moisture by drying and then H2S and then petrol that is raw petrol, storage whatever is there that is nothing but petrol right. Choice of drying and separation depends on location and power cost. Location as well as the power cost and also composition also what is the composition of a raw natural gas that you are having.

So, based on that one also these things are you know are going to change. So, drying can be done either by adsorption or refrigeration, heavy ends removal by absorption or refrigerated liquefaction also possible, then natural gas as overhead is stripped of H2S in an ethanol amine absorption process right.

(Refer Slide Time: 14:41)



Synthesis gas

- It is a variable mixture of CO and H_2
- Used for synthesis of several organic compounds such as
  - Methane
  - Fischer-Tropsch (paraffinic and olefinic HCs varying from methane to waxes along with a few oxygenated compounds) by $CO/H_2 = 0.5 – 2.0$
  - Synol (straight chain normal alcohols) by $CO/H_2 = 0.3 – 0.5$
  - Methanol by $CO/H_2 = 0.3$
  - Higher alcohol synthesis
  - Isosynthesis (saturated branched HCs) by $CO/H_2 = 0.5$
  - Oxosynthesis (oxygenated HCs, aldehydes and alcohols) by $\boxed{CO/H_2 = 1.2}$
- Different catalyst along with varying temperature and pressure conditions applied for synthesis of above organic compounds

catalyst
Temperature
pressure
process

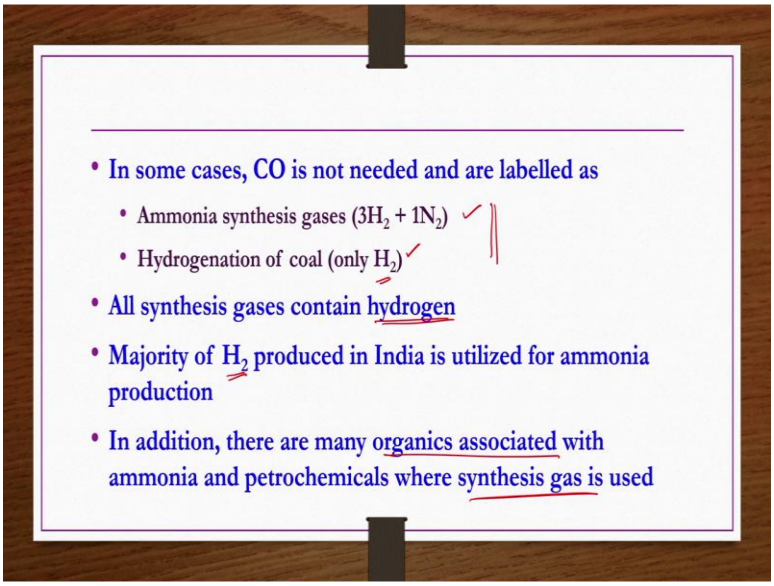
So, the flow sheet is the same flow sheet that we have seen ok. Now, we are going to see few basics of synthesis gas and then how to produce synthesis gas by different approaches that is what we are going to discuss. Synthesis gas it is a variable mixture of CO and H2.

And then it is used for synthesis of several organic components such as methane and then Fischer Tropsch that is paraffinic and olefinic hydrocarbons varying from methane to waxes along with few oxygenated components also by taking different CO to H2 ratio varying between 0.5 to 2. It can also be used for the production of synol which is straight chain normal alcohols by taking CO to H2 ratio between 0.3 to 0.5.

Then methanol can also be produced by synthesis gas if you take CO to H2 ratio 0.3 then higher alcohol synthesis is also possible isosynthesis that is saturated branched hydrocarbons production is also possible by taking CO to H2 ratio 0.5. And then oxosynthesis that is oxygenated hydrocarbons aldehydes and alcohol something like that can also be produced by taking synthesis gas having CO divided by H2 ratio 1.2.

Then obviously, all these process require different catalyst different temperature, different pressure conditions and then different process right. So, it is not possible to get all of them by single process alright using by a small narrow range of temperature or pressure or using a single catalyst it is not possible, right. So, different catalyst along with varying temperature and pressure conditions applied for synthesis of these organic components using synthesis gas, ok.

(Refer Slide Time: 16:38)

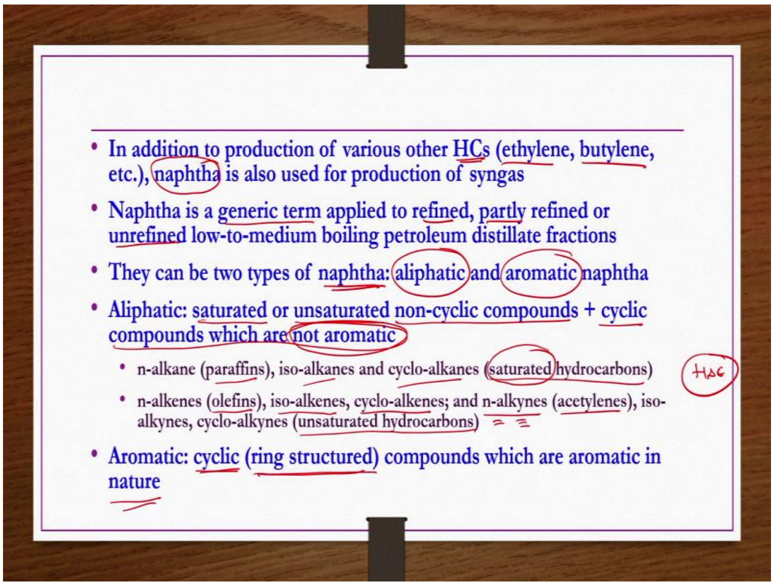


- In some cases, CO is not needed and are labelled as
  - Ammonia synthesis gases ($3H_2 + 1N_2$) ✓
  - Hydrogenation of coal (only H_2)✓
- All synthesis gases contain hydrogen
- Majority of H_2 produced in India is utilized for ammonia production
- In addition, there are many organics associated with ammonia and petrochemicals where synthesis gas is used

In some cases carbon monoxide is not needed and are labelled as ammonia synthesis gases having hydrogen and nitrogen or hydrogenation of coal only having H2. Since we are talking about synthesis gas all synthesis gases contain H2 hydrogen right whether it is ammonia synthesis gas or proper synthesis gas or water gas or coke oven gas.

You can see that now all of these are used for different synthesis purposes and then their H2 would definitely be there ok. Majority of H2 produced in India is utilized for ammonia production in addition there are many organics associated with ammonia and petrochemicals where synthesis gas is used. So, n number of fused number of applications are there.

(Refer Slide Time: 17:27)



- In addition to production of various other HCs (ethylene, butylene, etc.), naphtha is also used for production of syngas
- Naphtha is a generic term applied to refined, partly refined or unrefined low-to-medium boiling petroleum distillate fractions
- They can be two types of naphtha: aliphatic and aromatic naphtha
- Aliphatic: saturated or unsaturated non-cyclic compounds + cyclic compounds which are not aromatic
  - n-alkane (paraffins), iso-alkanes and cyclo-alkanes (saturated hydrocarbons)
  - n-alkenes (olefins), iso-alkenes, cyclo-alkenes; and n-alkynes (acetylenes), iso-alkynes, cyclo-alkynes (unsaturated hydrocarbons)
- Aromatic: cyclic (ring structured) compounds which are aromatic in nature

So, in addition to production of various other hydrocarbons like ethylene, butylene etcetera naphtha is also used for production of syngas. Since we are going to use naphtha for production of syngas we will have a few basics of a naphtha, what it is? Naphtha is generic term applied to refined or partly refined or unrefined low to medium boiling petroleum distillate fractions.

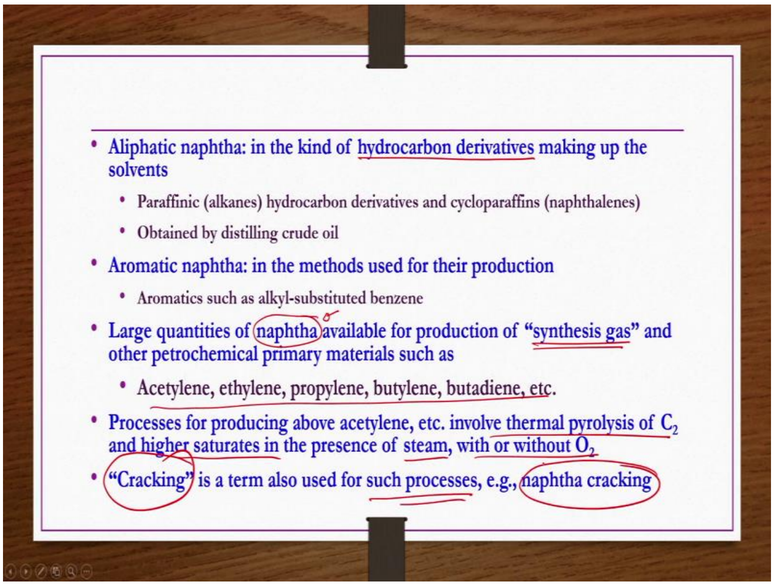
They can be two types; aliphatic naphtha and then aromatic naphtha, then what does mean by aliphatic and aromatic? Aliphatic means saturated or unsaturated non cyclic compounds plus there may be a few cyclic compounds which are not aromatic which are not aromatic.

Something like n alkenes which are also known as paraffins, iso-alkanes, cycloalkanes all of them are saturated hydrocarbons, saturated in the sense you have the single bonds ok. Whatever the bonds between CH etcetera are there all of them are single bonds then we call them saturated hydrocarbons. In fact, hydrocarbons in the sense hydrogen and carbons are there in addition to this there may be some other components like O, N etcetera.

So, if the all the bonds are single bonds then we call them saturated hydrocarbons. n-alkenes which are also known as olefins, iso alkanes, cycloalkanes and alkynes which are also known as acetylenes, iso alkenes, cycloalkanes etcetera, which are known as unsaturated hydrocarbons. If you have double bond or triple bonds in the molecular structure of a component, then you can call them unsaturated hydrocarbon.

Aromatics in the sense cyclic compounds which are nothing but ring structured, but having aromatic in nature, so then we call them aromatic. In fact, entire organic components category may be grouped as two groups; one is the aliphatic group another one is the aromatic group ok.

(Refer Slide Time: 19:34)



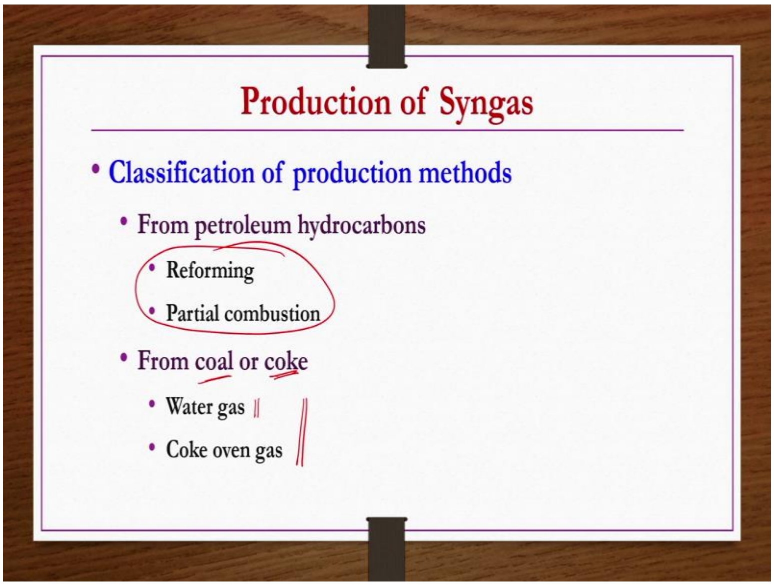
- Aliphatic naphtha: in the kind of hydrocarbon derivatives making up the solvents
  - Paraffinic (alkanes) hydrocarbon derivatives and cycloparaffins (naphthalenes)
  - Obtained by distilling crude oil
- Aromatic naphtha: in the methods used for their production
  - Aromatics such as alkyl-substituted benzene
- Large quantities of naphtha available for production of “synthesis gas” and other petrochemical primary materials such as
  - Acetylene, ethylene, propylene, butylene, butadiene, etc.
- Processes for producing above acetylene, etc. involve thermal pyrolysis of C_2 and higher saturates in the presence of steam, with or without O_2
- “Cracking” is a term also used for such processes, e.g., naphtha cracking

So, aliphatic naphtha is in the kind of hydrocarbon derivatives making up the solvents example like paraffinic hydrocarbon derivatives and then cycloparaffins like naphthalenes etcetera these are obtained by distilling the crude, then aromatic naphtha in the sense in the methods used for their production etcetera. Aromatics such as alkyl substituted benzene etcetera.

So, the large quantities of naphtha is available for production of synthesis gas not only synthesis gas in fact, synthesis gas is a very small minor component because naphtha is a very generic term so, but this naphtha is also used for production of other petrochemical primary materials such as acetylene, ethylene, propylene, butylenes, butadiene etcetera and so and so.

And then processes for producing above chemicals like this involve thermal pyrolysis of C2 and then higher saturates in the presence of steam with or without oxygen. Cracking is also another term used for such processes example naphtha cracking, right.

(Refer Slide Time: 20:42)



Production of Syngas

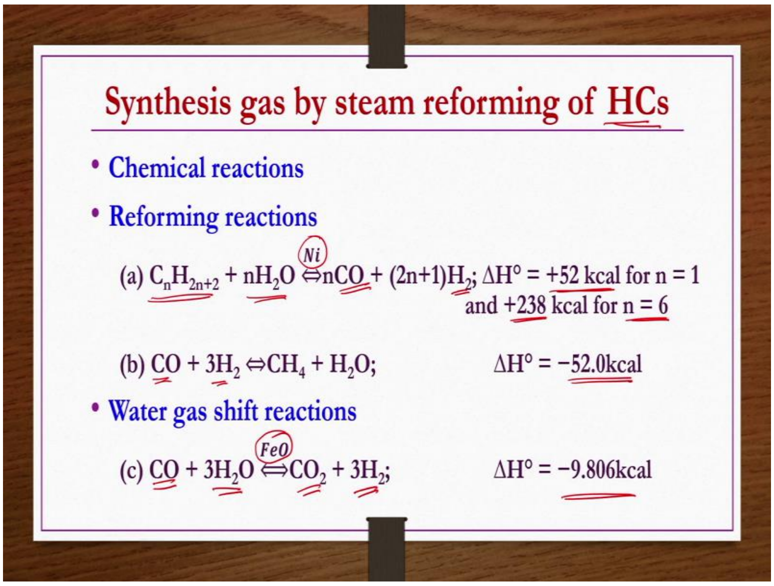
- Classification of production methods
  - From petroleum hydrocarbons
    - Reforming
    - Partial combustion
  - From coal or coke
    - Water gas
    - Coke oven gas

Next is production of syngas, we will see how many methods are available for production of the syngas, Classification of production methods; one is from petroleum hydrocarbons another one is from coal and coke. From petroleum hydrocarbons you can produce syngas by reforming or partial combustion of hydrocarbons right. From coal or coke what we can have? We can have water gas and coke oven gas.

In fact, this water gas, syngas also if you see only CO and H2 are there sometimes in syngas CO2 may also be present right, but in water gas only CO and H2 would be there. If the CO and H2 is produced from the coal and coke, then they are called as water gas, but if the same CO and H2 gas mixture is produced from the hydrocarbons or naphtha then we call them you know syngas that is a minor difference one should understand between syngas and water gas.

So, since these things we have already seen in the previous class what we are going to see? We are going to see syngas production from hydrocarbons by reforming and partial combustion methods.

(Refer Slide Time: 21:51)



Synthesis gas by steam reforming of HCs

- Chemical reactions
- Reforming reactions

(a) $C_nH_{2n+2} + nH_2O \overset{Ni}{\Leftrightarrow} nCO + (2n+1)H_2$; $\Delta H^\circ = +52$ kcal for n = 1 and +238 kcal for n = 6

(b) $CO + 3H_2 \Leftrightarrow CH_4 + H_2O$; $\Delta H^\circ = -52.0$kcal

- Water gas shift reactions

(c) $CO + 3H_2O \overset{FeO}{\Leftrightarrow} CO_2 + 3H_2$; $\Delta H^\circ = -9.806$kcal

Syngas or synthesis gas by steam reforming of hydrocarbons we will see now, we start with. So, the chemical reactions that are involved in this process are provided here, there are two types of reactions occurring here in this process; reforming reactions and water gas shift reaction.

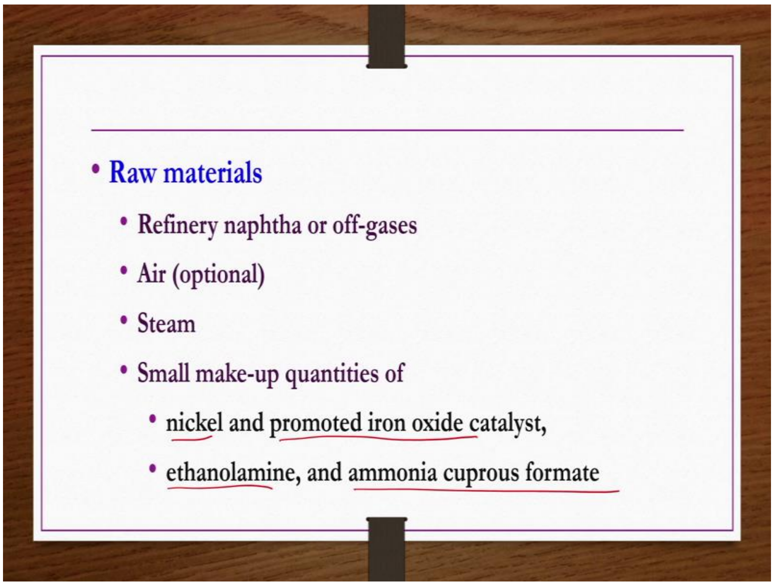
In the reforming reactions what we have? We have alkanes and then it reacts with the steam in the presence of nickel catalyst, then what you get? You get carbon monoxide and a hydrogen right. CnH2n+2 is generic formula for the alkenes, if n is equals to 1 then it is methane. Let us say if you have n is equals to 1, then delta H naught for this reaction is plus 52 kilo calories.

If you have n is equals to 6, then delta H naught is plus 238 kilo calories; that means, as n increasing delta H naught is increasing in the positive side. More and more endothermic it is becoming right. That means, as you move towards to the higher alkanes what happen? Production of a syngas from higher alkanes becomes more and more tougher; that means, you have to give more energy why?

Because delta H naught is increasing; that means, you know the enthalpy of the reactants is much smaller compared to the enthalpy of the products. So, then you have to give more and more energy ok. Other possible reaction is that that CO and then H2 whatever are there. So, that may be reversibly forming methane and then water with delta H naught as minus 52.0 kilo calories. Water gas shift reaction the CO react with the water reversibly in the presence of iron oxide catalyst to produce CO2 plus 3H2 with delta H naught minus 9.806 kilo calories right.

So, now, all these reactions are possible. So, then conditions reaction conditions and then design of the reactor etcetera one has to be very carefully do. So, that desired product forms more rather than the other products or desired reaction progresses much better compared to the other reactions.

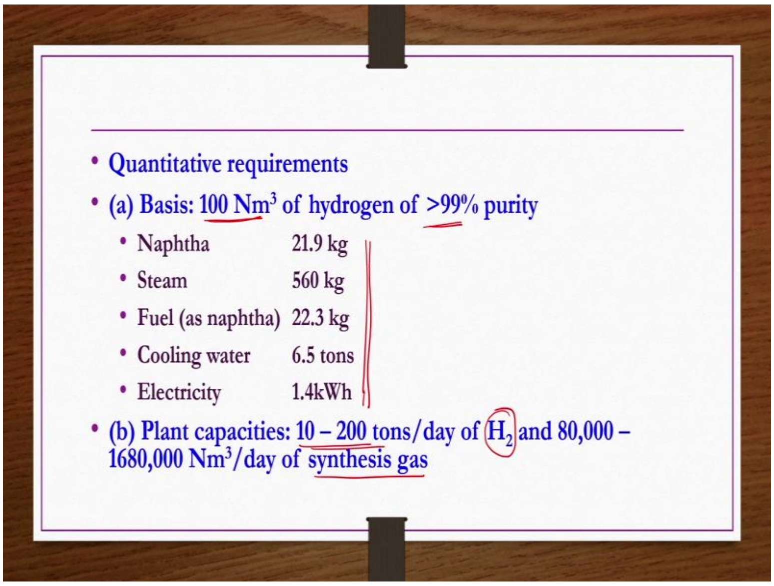
(Refer Slide Time: 24:05)



- Raw materials
  - Refinery naphtha or off-gases
  - Air (optional)
  - Steam
  - Small make-up quantities of
    - nickel and promoted iron oxide catalyst,
    - ethanolamine, and ammonia cuprous formate

So, raw materials required as we are discussing the production of a syngas from the naphtha. So, then; obviously, one of the raw materials is the refinery naphtha or off gases, air is optional then steam, then small makeup quantities of nickel and promoted iron oxide catalyst in addition to that some solution for absorption like ethanol amine and ammonia cuprous formates solutions right. So, these are the raw materials if you have these raw materials we can produce syngas, but how much quantity of these things are required that depends on the basis, right.

(Refer Slide Time: 24:44)



- Quantitative requirements
- (a) Basis: 100 Nm^3 of hydrogen of >99% purity

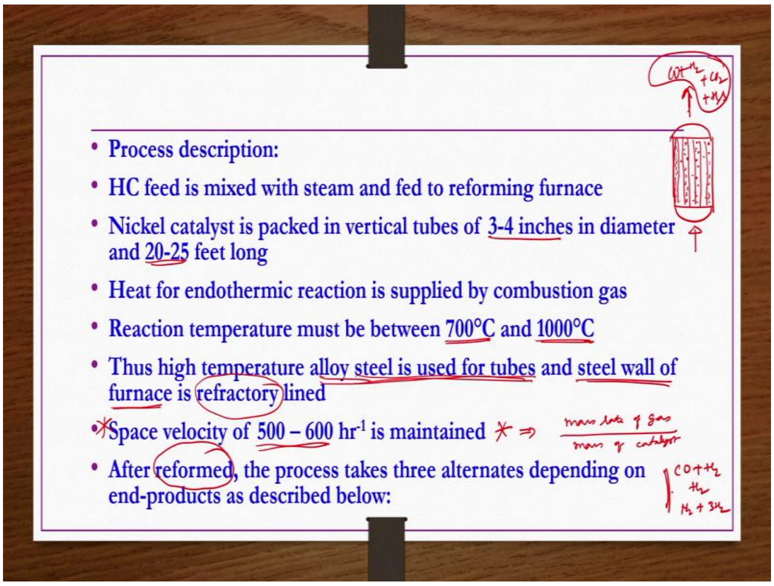
Naphtha	21.9 kg
Steam	560 kg
Fuel (as naphtha)	22.3 kg
Cooling water	6.5 tons
Electricity	1.4kWh

- (b) Plant capacities: 10 – 200 tons/day of H_2 and 80,000 – 1680,000 Nm^3/day of synthesis gas

So, quantitative requirements basis let us say if you wanted to produce 100 normal cubic meters of hydrogen which is having more than 99 percent purity, then you need to have 21.9 kgs of naphtha, steam 560 kgs, fuel as naphtha 22.3 kgs, cooling water 6.5 tons, electricity 1.4 kilo watt hour. All these things are obtained by doing the proper material and energy balance for the plant flow sheet that we are going to discuss further in the few coming slides ok.

They are not you know rough values they are based on the proper material and energy balance calculation for the production process flow sheet that we are going to discuss ok. Plant capacities if you wanted to produce only H2, then 10 to 200 tons per day is possible, if you wanted to produce synthesis gas that is CO plus H2 more than 80,000 normal meter cube per day of synthesis gas one can produce such big plants are available.

(Refer Slide Time: 25:48)



- Process description:
- HC feed is mixed with steam and fed to reforming furnace
- Nickel catalyst is packed in vertical tubes of 3-4 inches in diameter and 20-25 feet long
- Heat for endothermic reaction is supplied by combustion gas
- Reaction temperature must be between 700°C and 1000°C
- Thus high temperature alloy steel is used for tubes and steel wall of furnace is refractory lined
- *Space velocity of 500 – 600 hr^{-1} is maintained * ⇒ $\frac{\text{mass rate of gas}}{\text{mass of catalyst}}$
- After reformed, the process takes three alternates depending on end-products as described below:

$CO+H_2$
H_2
N_2+3H_2

Process description first we see and then we will go to the flow sheets. So, hydrocarbon feed is mixed with steam and fed to reforming furnace. Nickel catalyst is placed in vertical tubes of 3 to 4 inches in diameter and 20 to 25 feet long. So, in the reactor the tubics like let us say if you have the reactor like this right you are allowing the gas to pass through actually right so then catalytic bed is required so in order to make bed, so why are you not having you know just pouring in this catalytic particles in this one like a packed bed something like that? That may be question right.

So, that can be done, but the reaction temperature here is very high 1000 degree centigrade or something like that approximately 700 to 1000 degree centigrade. So, at such high temperature if the catalyst are you know mixed with sand etcetera because these beds catalytic beds are not made of purely catalyst they are also mixed with some kind of a inorganic materials like sands etcetera. So, at that temperature, so other components may be interfering right.

So, if any impurities are there in, so they may be interfering with the process and then purity of the products may substantially decrease or separating the further impurities because of the sand other kind of material is going to be very tough and then economically not feasible. For that reason what you can have? You can have a column, you can have tubes, you can have a n number of tubes like this of let us say 3 to 4 inches in diameter and 20 to 25 feet long and then in these tubes you put this catalyst particles like this.

So, that there is no issue of impurities because of the foreign material etcetera all those kind of things ok. So, that is one reason. So, one has to be careful while selection you know otherwise unnecessarily you are increasing the steel tube cost, if there are no reason why should you increase and then these are not small you know small diameter reactors they are large diameter reactors. And then if you have 3 to 4 inch diameter tube, so how many tubes you need and all those things you have to calculate. So, there should be a proper reason for the selection.

So, here in this region why the nickel catalyst is not placed as a bed along with sand particles is because of this region. So, now, you can have steel tubes in the in that one you can put this nickel catalyst. Heat for endothermic reaction is supplied by combustion gas and then reaction temperature must be between 700 degree centigrade to 1000 degree centigrades.

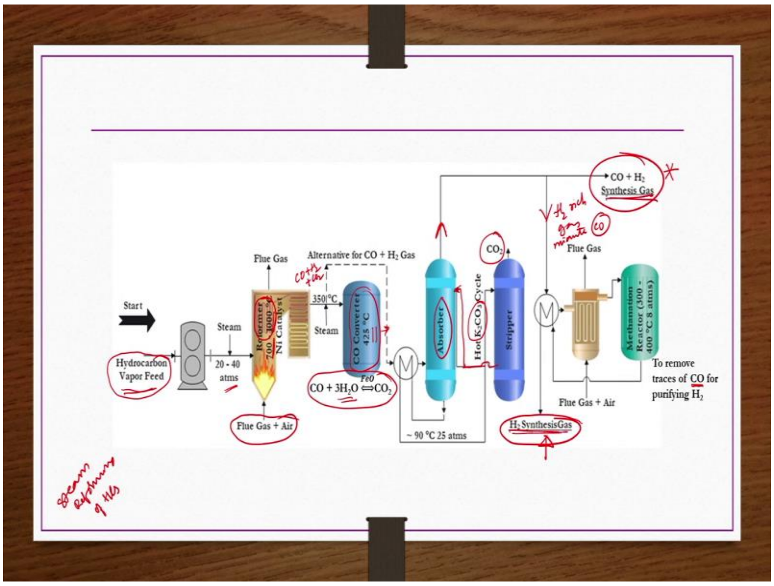
Thus high temperature alloy steel is used for the tubes for the tubes that these tubes are made of high temperature alloy steel whereas, the steel wall of furnace because this furnace is made up of the steel again. So, that furnace wall whatever is there that is also refractory lined ok.

Space velocity should be maintained between 500 to 600 hour inverse which is very high. Space velocity is nothing but what mass rate of gas that is entering the furnace or the reactor per mass of catalyst. So, this space velocity calculation that we have seen in the first week, so that much you have to maintain.

So, this is another very important design parameter space velocity. So, after reforming has been done that is whatever the reforming reaction that we have seen in previous slides. So, when you allow these gases whatever the hydrocarbons in the gases form let us say you pass through the furnace which is having catalyst at 700 to 1000 degree centigrades.

So, then you know what happens? The several gases not only CO plus H2, but also CO2 etcetera may be there may be some impurities H2 etcetera also there. So, these gases now these whatever the effluent gases are there so they can be processed in three different ways depending on the what is your end product; end product is CO plus H2 or it is only H2 or it is ammonia synthesis gas. So, based on that one three different approaches are there, so those things we are going to see now.

(Refer Slide Time: 30:19)



So, now this is the flow sheet for the you know steam reforming process; steam reforming of hydrocarbons in order to get synthesis gas ok. So, what happens? There is another product also here if you want to get hydrogen synthesis gas, subsequents flow sheet we are going to see how to get ammonia synthesis gas from the same thing.

So, whatever the hydrocarbon feed is there that is taken in the vapor form and then it is mixed with the steam at 20 to 40 atmospheres and then that is fed to the reforming reactor. Reforming reactor here it is having vertical tubes with nickel catalyst filled in and then this furnace is operating at 700 to 1000 degree centigrade and then fuel for this furnace that is because it has to burn. So, then there should be source how to burn how to generate the energy for that one that is done by using flue gases plus air.

So, when this mixture of hydrocarbons and steam enters this reactor at such high temperature because the furnace or the reactor is at high temperatures. And then there is also catalyst immediately those hydrocarbons will be producing different types of gases including CO H2, CO2, H2S etcetera depending on the impurities.

So, now those gases are you know further processed depending on what is your product. Let us say your product is synthesis gas because these gases are primarily having a CO plus H2 plus CO2 only there is no H2S because the hydrocarbon feed you are taking such a way that there is no sulphur in that one, right.

So, this mixture what you can do? If you wanted to produce only synthesis gas having CO plus H2, then you can pass through an absorption column by taking this alternative approach right. In the absorption column you can use potassium carbonate solution for the absorption purpose you can have this solution right.

So, when you use this solution from the top and then you feed the gases from the bottom at approximately 90 degree centigrade and 25 atmosphere whatever CO 2 etcetera is there CO2 gas is there that will be absorbed; that will be absorbed by the solution and then almost pure CO and H2 Synthesis gas is collected from the top right.

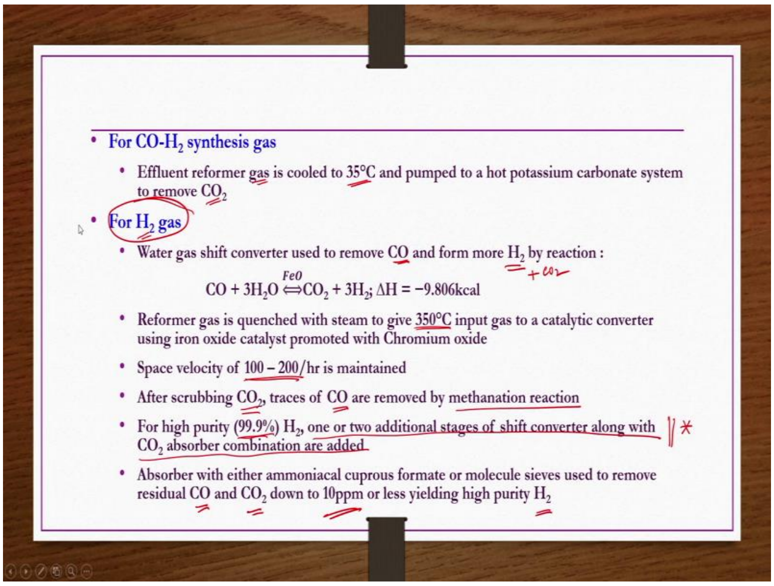
So, now, this potassium chromate solution has become diluted, now you cannot throw it as it is. So, what you can do? You can take that solution to the stripper section and then strip off the CO2 and then whatever the pure potassium coordinate solution is there that you can take back to the absorption column again. So, that you can do the recycling of the same amount of the solution for the absorption the process would be economic ok.

Now, let us say that is what that is about the production of a synthesis gas. Let us say if you wanted to produce hydrogen, so then what you do? These gases whatever are there that you take to CO converter chamber which is operating at 425 degree centigrade which is nothing but combustion chamber let us say right. So, here when you take these gases whatever the CO that is present in the effluent gases that, will be reacting with the steam because steam is also allowed to this reactor at 350 degree centigrades.

So, the CO will reactor with the steam in the presence of a iron oxide catalyst to give CO2. Once we have this CO2, then the process is same then again you take this one the effluent follow the same process of taking them to the absorption column right absorb the CO2 etcetera. So, then after that mostly you have H2 rich gas 95 percent or 99 percent etcetera. If at all some amount of with minor minute amount of CO is there, so that you wanted to remove.

So, what you can do? That gas you take to the methanation reactor which is operating at 300 to 400 degree centigrade and 8 atmospheric conditions. So, here because of the methanation you can remove the CO and then H2 would be further purified and then that H2 you can collect as a H2 Synthesis gas ok. So, out of three alternative roots after the reforming reaction two we have discussed; one is the production of synthesis gas another one is the production of hydrogen synthesis gas, right.

(Refer Slide Time: 34:59)



- For CO-H_2 synthesis gas
  - Effluent reformer gas is cooled to 35°C and pumped to a hot potassium carbonate system to remove CO_2
- For H_2 gas
  - Water gas shift converter used to remove CO and form more H_2 by reaction :

    + CO_2

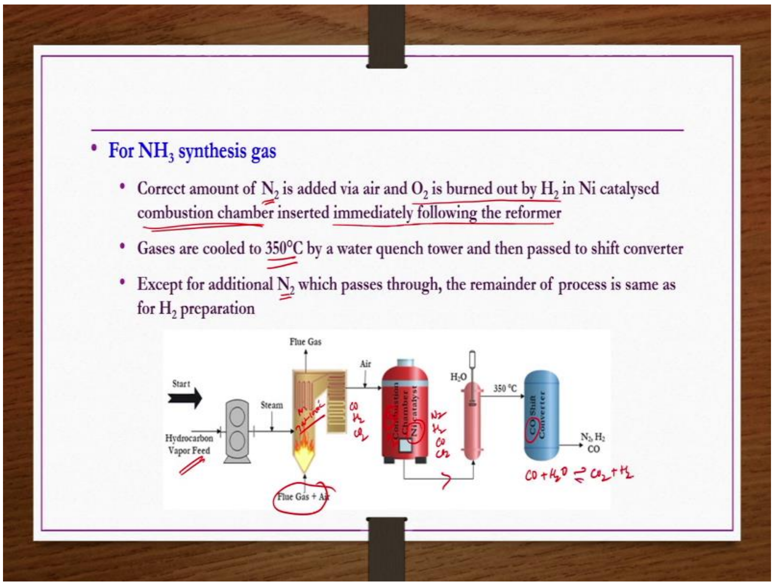
    $$CO + 3H_2O \overset{FeO}{\Leftrightarrow} CO_2 + 3H_2; \Delta H = -9.806 kcal$$
  - Reformer gas is quenched with steam to give 350°C input gas to a catalytic converter using iron oxide catalyst promoted with Chromium oxide
  - Space velocity of 100 – 200/hr is maintained
  - After scrubbing CO_2, traces of CO are removed by methanation reaction
  - For high purity (99.9%) H_2, one or two additional stages of shift converter along with CO_2 absorber combination are added || *
  - Absorber with either ammoniacal cuprous formate or molecule sieves used to remove residual CO and CO_2 down to 10ppm or less yielding high purity H_2

Next one is we will be discussing ammonia synthesis gas, But whatever we have seen in the previous slide same thing is presented here as a description. For CO H2 Synthesis gas the effluent reformer gas is cool to 35 degree centigrade and pump out to a hot potassium carbonate system to remove CO2 simply. For H2 gas what we have done? Water gas shift converter used to remove CO by reacting CO with water or steam, so that to get CO2.

So, then the effluence from there would be having more H2 and then plus CO2 ok with less CO almost negligible CO, so by this reaction ok. So, what happens? Whatever the CO is there that is unreacted CO ok. So, reformer gas is quenched with steam to give 350 degree centigrade input gas to catalytic converter using iron oxide catalyst promoted with the chromium oxide for this reaction. Then space velocity is this much is maintained. After scrubbing CO2 traces of CO if at all present they are removed by the methanation reaction ok.

For high purity almost that is 99.9 percentage H2 one or two additional stages of shift converter along with the CO2 absorber combination are added. Absorber with either ammoniacal cuprous formate or molecule sieves used to remove residual CO and CO2 down to 10 ppm or less yielding high purity H2 this is what if you wanted to get the pure H2. So, this is the second alternative.

(Refer Slide Time: 36:44)



- For NH_3 synthesis gas
  - Correct amount of N_2 is added via air and O_2 is burned out by H_2 in Ni catalysed combustion chamber inserted immediately following the reformer
  - Gases are cooled to 350°C by a water quench tower and then passed to shift converter
  - Except for additional N_2 which passes through, the remainder of process is same as for H_2 preparation

$CO + H_2O \rightleftharpoons CO_2 + H_2$

Third alternative is for ammonia synthesis gas. Correct amount of nitrogen is added via air and oxygen is burned out by H2 in nickel catalysed combustion chamber inserted immediately following the reformer; immediately after following the reformer. Whatever the previous main flow sheet that we have seen in the previous section where we produced CO plus H2 as one product and then H2 as another product depending on the option what you want there after the furnace chamber whatever section is there immediately you put one combustion chamber, right.

So, that you can burn out whatever the oxygen that is present in the air and then you get the nitrogen alone then that nitrogen further purified along with the hydrogen in a similar way to get the nitrogen and ammonium in the required fractions for synthesis of the ammonia.

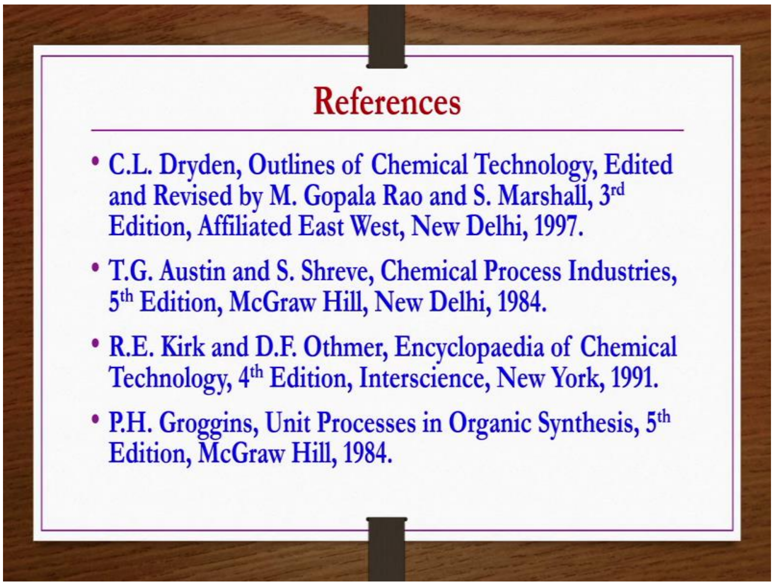
Gases are cooled to 35 degree centigrade by water quench tower and then passed to shift converter. Except for N2 additional N2 which passes through the remainder of process is same as H2 preparation that we have seen. So, that is if you redraw it once again, so whatever the hydrocarbon in vapor form are there they are mixed with steam and then fed to the reformer reactor. So, this is the reformer reactor this reactor is having nickel catalyst and then operating at 700 to 1000 degree centigrades.

For this reactor flu gas and air are supplied in order to have the required energy and then whatever the effluents that are coming from the reformer are having CO, H2, CO2 etcetera. So, now, here what you do? You allow the air and then pass it through the combustion chamber which is again having the nickel catalyst.

So, then whatever O2 is there from the air that will be that O2 will be burned out by the H2 ok, then you will be having only H2, N2, CO and then CO2 only. So, then what you do? You can pass through this quenching these gases because the gases coming out of this combustion chamber would be at high temperature.

So, these gases you have to scrub with the water or cool down using the quenching water tower ok like this. Then after cooling this one you reduce the temperature to 350 degree centigrade those gases are sent to CO shift converter. Now here CO shift converter when you use whatever the CO is there that will react with the water and then it will give CO2 plus H2.

(Refer Slide Time: 39:26)



References

- C.L. Dryden, Outlines of Chemical Technology, Edited and Revised by M. Gopala Rao and S. Marshall, 3rd Edition, Affiliated East West, New Delhi, 1997.
- T.G. Austin and S. Shreve, Chemical Process Industries, 5th Edition, McGraw Hill, New Delhi, 1984.
- R.E. Kirk and D.F. Othmer, Encyclopaedia of Chemical Technology, 4th Edition, Interscience, New York, 1991.
- P.H. Groggins, Unit Processes in Organic Synthesis, 5th Edition, McGraw Hill, 1984.

The references for this lecture are provided here.

Thank you.