Inorganic Chemical Technology
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Lecture - 14
Nitrogen Industries - Ammonia

Welcome to the MOOCs course Inorganic Chemical Technology. The title of today's lecture is Nitrogen Industries - Ammonia. From this lecture onwards for couple of weeks what we will be doing, we will be discussing about fertilizer industries, different types of fertilizers industries like you know nitrogen fertilizers, phosphorus fertilizers and then potassium fertilizers and then different types of fertilizers production that we are going to discuss, right.

So, before going into the details of a production of some fertilizers, what we will do? We will have a kind of a few basic introduction about the agricultural industries and then requirement of fertilizers etcetera.

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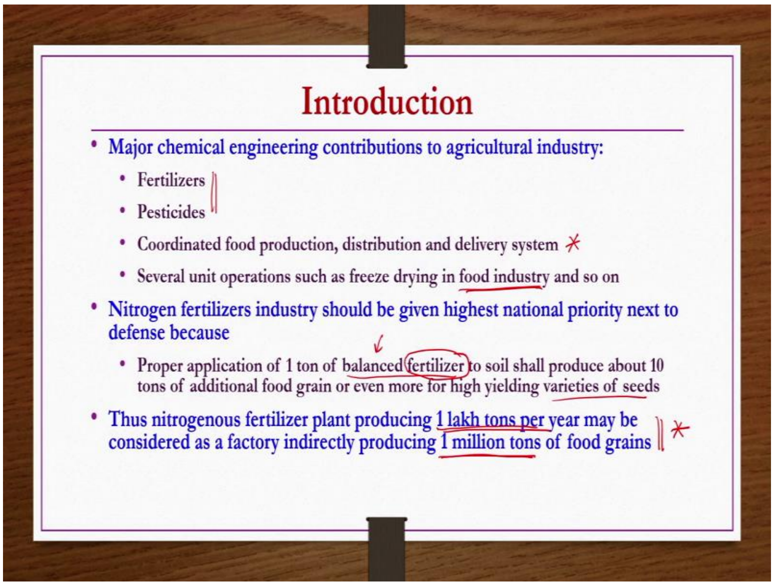

Introduction

- Major chemical engineering contributions to agricultural industry:
  - Fertilizers
  - Pesticides
  - Coordinated food production, distribution and delivery system *
  - Several unit operations such as freeze drying in food industry and so on
- Nitrogen fertilizers industry should be given highest national priority next to defense because
  - Proper application of 1 ton of balanced fertilizer to soil shall produce about 10 tons of additional food grain or even more for high yielding varieties of seeds
- Thus nitrogenous fertilizer plant producing 1 lakh tons per year may be considered as a factory indirectly producing 1 million tons of food grains *

Now, before going into the details of these fertilizers industries, it is very essential to know as a chemical engineering graduates why is it required to study about the fertilizer industries or agricultural industries, you know that is what it is very essential to see.

So, that we can understand from you know contributions point of view, if you see the contributions of chemical engineering to agricultural industry then you can realize how much important is chemical engineering for the growth of agricultural industry that is what you can realize.

For example, major chemical engineering contribution to agricultural industry are fertilizers, pesticides. All these things are manufactured and then processed by only chemical engineers only. Without chemical engineers, fertilizer industries and pesticides industries cannot run and then also coordinated food production distribution and delivery system not only fertilizers, but regarding to the food also its production distribution and delivery system also huge lot of contribution is there from the chemical engineering discipline.

And then several unit operations such as freeze drying etcetera, in food industry are very much contributions of chemical engineering discipline. So, like that if you keep on listing so almost all components of agricultural industry or fertilizer industry, you know you need to have a contribution of chemical engineering or chemical engineering contribution is going to be the most important one, ok.

So, nitrogen fertilizer industries should be given highest national priority next to the defense. Because for example, if you do proper application of one ton of balanced fertilizers to soil shall produce about 10 tons of additional food grains or even more for high yielding varieties of seeds. What do you mean by balanced fertilizers?

Fertilizers you know we are going to see, but balanced fertilizer in the sense for the growth of plants you need a few basic important growth elements like nitrogen, phosphorus and potassium, right. You cannot give or you know you cannot supply excessive or nitrogen or low of potassium like that they should be a kind of balanced supply of fertilizer is required.

So, that is the reason balanced fertilizers if you supply 1 ton to a soil then you may produce about 10 tons of additional food grains or even more if your seeds are having high yielding capacity, right. So, that means, indirectly if you have a fertilizer industry and you are producing 1 lakh tons per year of nitrogen fertilizers then; that means, indirectly you are producing 1 million tons or 10 lakh tons of food grains such is the importance of a fertilizer industries, right.

Not only this one, but also there are some additional reasons then you can understand that why the nitrogen fertilizer industry should be given highest priority next to the defense for any country which is mostly dependent on agricultural industry.

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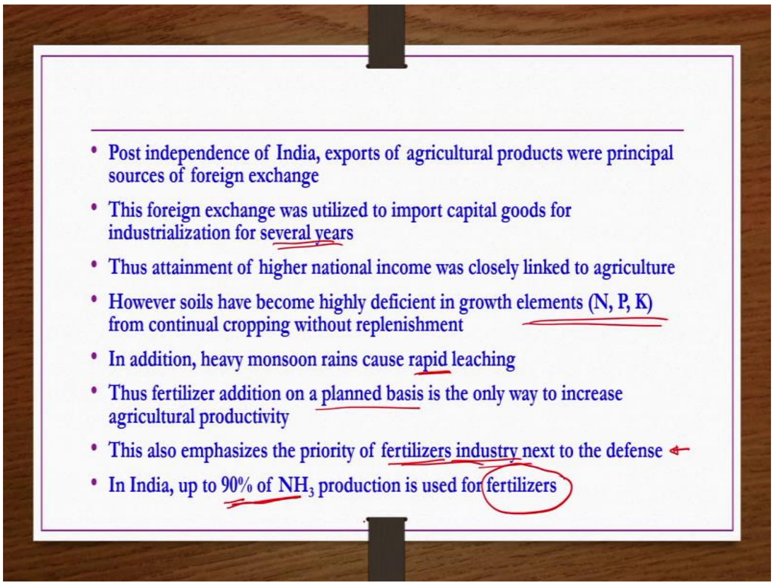

- Post independence of India, exports of agricultural products were principal sources of foreign exchange
- This foreign exchange was utilized to import capital goods for industrialization for several years
- Thus attainment of higher national income was closely linked to agriculture
- However soils have become highly deficient in growth elements (N, P, K) from continual cropping without replenishment
- In addition, heavy monsoon rains cause rapid leaching
- Thus fertilizer addition on a planned basis is the only way to increase agricultural productivity
- This also emphasizes the priority of fertilizers industry next to the defense
- In India, up to 90% of NH_3 production is used for fertilizers

For example, if you take India post independence of India exports of agricultural products were principal sources of foreign exchange and this foreign exchange was used or utilized for the import of capital goods for the industrialization for several years. This continued for several years, ok.

So, that what does it mean? For attainment of higher national income agricultural resources or agriculture industry is playing very much important role, right. Attainment of higher national income was closely linked to agriculture for so many years post independence of India, right.

However, soils have become highly deficient in growth elements like nitrogen phosphorous and potassium because of a continual cropping without replenishment in addition to that one. Heavy monsoon rains also cause rapid leaching of these elements you know growth elements from the soils.

So, once these elements are gone from the soil or reduced or in deficient then obviously, the growth of plant and then production of roots, vegetable, grains etcetera is also going to be you know affected. So, obviously, external sources of fertilizer has to be supplied in a balanced manner or in a proper manner.

Thus, fertilizer addition on a planned basis is the only way to increase agricultural productivity. Because of this also you can say that priority of fertilizers industry is very much high next to the defense. Or next to the defense if any industry if you wanted to prioritize you have to prioritize agricultural industry thereby fertilizer industry.

In India up to 90 percent of ammonia produced is used for the fertilizer productions. This lecture and coming few lectures we are going to see production of ammonia and then from ammonia what other kind of a nitrogenous fertilizers you can produce those things that we are going to see in today's and then next couple of lectures.

So, now with this little introduction of contribution of chemical engineering to the agriculture industry and then importance of fertilizer to the agriculture industry you know what we start? We start with you know discussing about the important components of a fertilizers.

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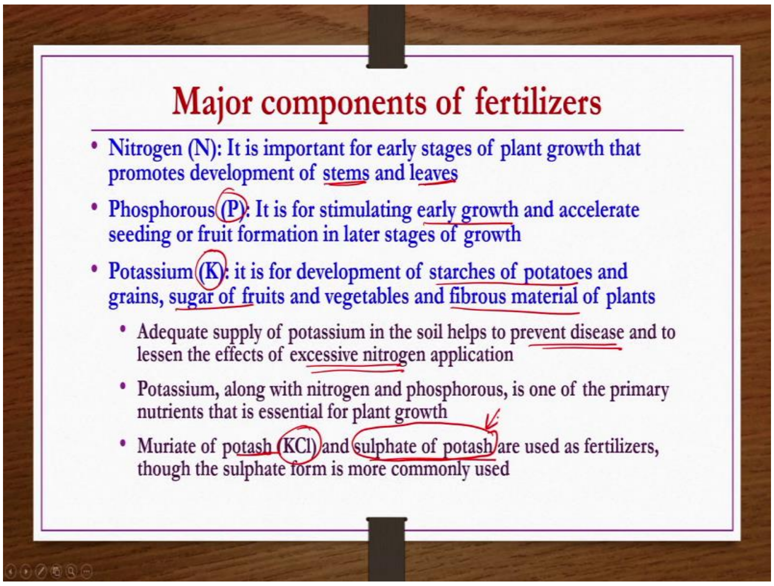

Major components of fertilizers

- Nitrogen (N): It is important for early stages of plant growth that promotes development of stems and leaves
- Phosphorous (P): It is for stimulating early growth and accelerate seeding or fruit formation in later stages of growth
- Potassium (K): it is for development of starches of potatoes and grains, sugar of fruits and vegetables and fibrous material of plants
    - Adequate supply of potassium in the soil helps to prevent disease and to lessen the effects of excessive nitrogen application
    - Potassium, along with nitrogen and phosphorous, is one of the primary nutrients that is essential for plant growth
    - Muriate of potash (KCl) and sulphate of potash are used as fertilizers, though the sulphate form is more commonly used

So, now we are going to discuss major components of fertilizers which are essential at early stages and then fruit formation stages or grain formation stages or you know cellulose formation in potatoes and another grains etcetera different stages are there. So, at what stage what component is essential that is what we are going to see.

For example, you have nitrogen it is very much important for early stages of plant growth that promotes development of stems and leaves. It is very much essential at the early stages. But for stimulating the early growth and accelerate seeding or fruit formation in later stages of the growth then you need phosphorus, ok.

Whereas, for development of starches of potatoes and grains and sugars of fruits and vegetables and fibrous materials of plants then you need potassium, ok. Potassium is very much essential for example, if adequate supply of potassium in the soil is done then it prevents disease not only disease it lessen the effect of excessive nitrogen application.

Sometimes you know at the early stage you may be supplying the more amount of nitrogen as fertilizers and then that may be causing some kind of a side effects to the plant growth or to the fruit formation or other kind of stages like you know cellulose or for the development of fibrous materials etcetera.

So, those effects whatever are there because of the excessive nitrogen they can be balanced or lessened by the adequate supply of the potassium. Potassium along with nitrogen and phosphorus is one of the primary nutrients that is essential for plant growth. Muriate of potash that is potassium chloride and sulphate of potash are used as fertilizers directly whereas; the sulphates of potash are more commonly used as fertilizers directly.

Now, having seen the major components of the fertilizers their requirement how do you decide how much N how much P how much K should be provided for a given plant growth and then fruit formation etcetera?

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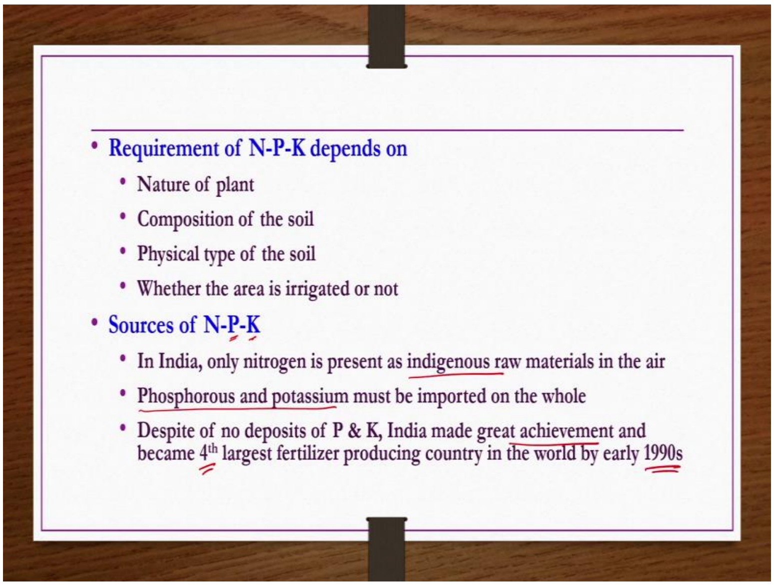

- Requirement of N-P-K depends on
  - Nature of plant
  - Composition of the soil
  - Physical type of the soil
  - Whether the area is irrigated or not
- Sources of N-P-K
  - In India, only nitrogen is present as indigenous raw materials in the air
  - Phosphorous and potassium must be imported on the whole
  - Despite of no deposits of P & K, India made great achievement and became 4th largest fertilizer producing country in the world by early 1990s

That depends on several factors like nature of plant, composition of the soil and then physical type of the soil, whether the area is irrigated or not like that. So, many parameters may be there right. So, all these parameters should be considered and accordingly N-P-K fraction has to be decided.

Sources of N-P-K right sources of nitrogen. Nitrogen is available as indigenous raw material in the air for any country, but; however, phosphorus and potassium are not available in majority of the countries as a exploitable sources. For example, for India these are not available, exploitable sources of potassium and phosphorus are not available in India. So, we are completely depending on imports.

Despite of that despite we do not have a proper phosphorous and potassium sources India made great achievement and became 4th largest fertilizer producing country in the world by early 90s whereas, now India is second largest fertilizer producing country in the world.

So, now we understand that nitrogen is available as indigenous raw material from the air, but potassium and phosphorus you know what are the ancient sources if you wanted to see? We understand that for growth of any plant this N-P-K are essential and then some of them may be there in the soil some of them may be in the grown plants it may be there.

Let us say in olden days after collecting the all agricultural products whatever the agricultural wastages were there they used to be burnt on the field itself because people know that this potassium and then phosphorus sources are present in the plant. So, then on burning those agricultural waste in the agricultural field itself then what happens? The ashes would be form and then those ashes would be a kind of sources of this potassium.

Probably that is the reason in ancient days people or farmers used to burn the agricultural wastages after collecting the products in the agricultural field itself, right.

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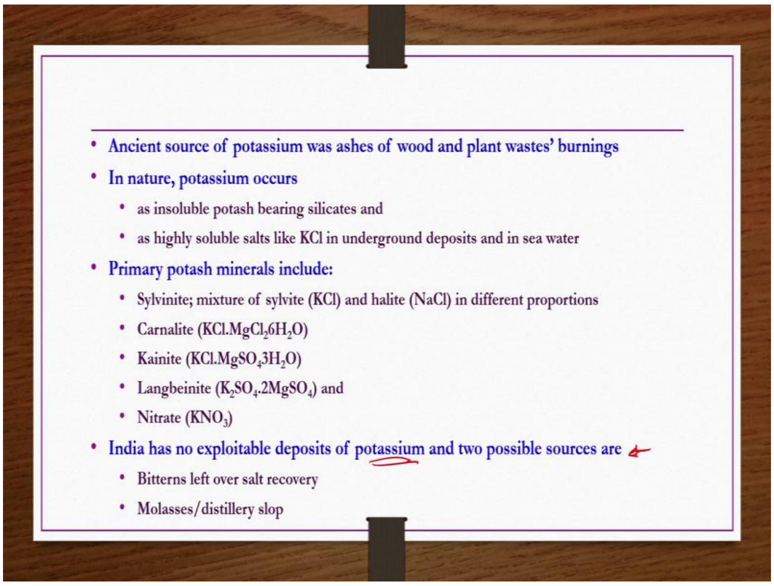

- Ancient source of potassium was ashes of wood and plant wastes' burnings
- In nature, potassium occurs
  - as insoluble potash bearing silicates and
  - as highly soluble salts like KCl in underground deposits and in sea water
- Primary potash minerals include:
  - Sylvinite; mixture of sylvite (KCl) and halite (NaCl) in different proportions
  - Carnalite ($KCl.MgCl_2 6H_2O$)
  - Kainite ($KCl.MgSO_4 3H_2O$)
  - Langbeinite ($K_2SO_4.2MgSO_4$) and
  - Nitrate (KNO_3)
- India has no exploitable deposits of potassium and two possible sources are
  - Bitterns left over salt recovery
  - Molasses/distillery slop

In nature potassium occurs in two different forms. As insoluble potash bearing silicates and as highly soluble salts like potassium chloride in underground deposits and in sea water. Primary potash minerals include sylvinite which is a mixture of sylvite that is KCl and halite that is NaCl in different proportions. Potassium chloride and sodium chloride in different proportions if you take that is nothing but sylvinite.

Then carnalite is one other primary potash mineral and then kainite and then langbeinite and nitrates form. So, in this different form the potash mineral is available in general. India has no exploitable deposits of potassium and two possible sources are: first one is the bitterns left over salt recovery. From the sea water when you do the salt production when you recover all the salt you know what happens highly concentrated salty solution would be remaining that is known as the bitterns left over salt recovery.

That bitterns is a source of several minerals not only potassium, but several other minerals also since potassium would be this. So, that can be taken as a one of the source for the potassium. Then molasses or distillery slops etcetera are also having some minerals including potassium.

Now, having seen a few basic introductory information about the agricultural industry major components of fertilizers etcetera. We start with our main topic of nitrogenous fertilizers or nitrogen industry that is what we are going to discuss.

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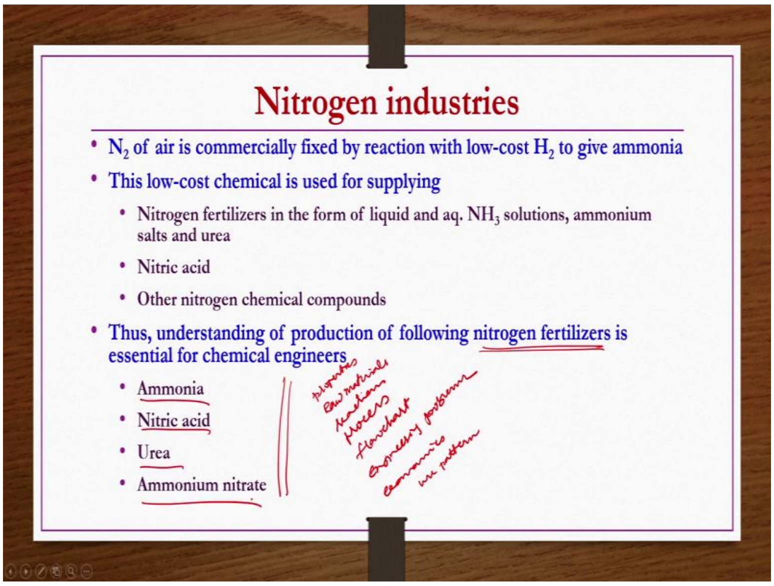

Nitrogen industries

- N_2 of air is commercially fixed by reaction with low-cost H_2 to give ammonia
- This low-cost chemical is used for supplying
  - Nitrogen fertilizers in the form of liquid and aq. NH_3 solutions, ammonium salts and urea
  - Nitric acid
  - Other nitrogen chemical compounds
- Thus, understanding of production of following nitrogen fertilizers is essential for chemical engineers
  - Ammonia
  - Nitric acid
  - Urea
  - Ammonium nitrate

properties
Raw materials
reactions
process
flowchart
Engineering problems
economics
use pattern

Nitrogen of air is commercially fixed by reaction with low cost hydrogen to give ammonia. This is what how are we going to produce ammonia from nitrogen and hydrogen that is what we are going to see in this lecture, right. So, this low cost chemical is used for supplying nitrogen fertilizers in the form of liquid and aqueous ammonia solutions, ammonium salts and urea, nitric acid and other nitrogen chemical compounds, right.

So, thus understanding of production of following nitrogen fertilizers is essential for chemical engineers. So, what are the first one is ammonia which is we are going to discuss today in this lecture. Then nitric acid we will be discussing tomorrow in the next lecture then urea, then ammonium nitrate.

So, there may be others also there, but we are going to discuss primarily these four nitrogenous fertilizers how to produce. We start with the; obviously, raw materials properties, pertinent reactions if any and then process, flowchart, engineering problems that one has to be careful about in the plants and then economics or use pattern etcetera. These details we are going to see for each of these nitrogenous fertilizer component.

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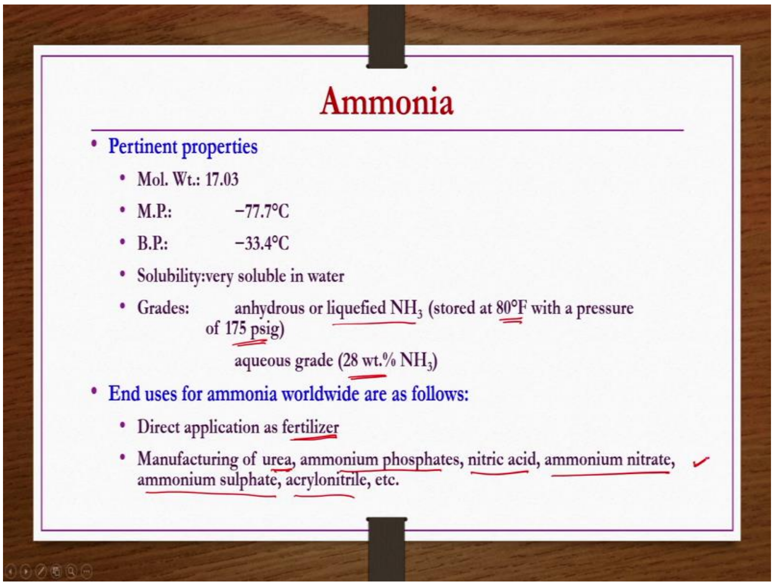

Ammonia

- Pertinent properties
  - Mol. Wt.: 17.03
  - M.P.: −77.7°C
  - B.P.: −33.4°C
  - Solubility:very soluble in water
  - Grades: anhydrous or liquefied NH_3 (stored at 80°F with a pressure of 175 psig)
    aqueous grade (28 wt.% NH_3)
- End uses for ammonia worldwide are as follows:
  - Direct application as fertilizer
  - Manufacturing of urea, ammonium phosphates, nitric acid, ammonium nitrate, ✓ ammonium sulphate, acrylonitrile, etc.

So, let us start with ammonia. If you see the pertinent properties molecular weight is 17.03 melting point is minus 77.7 degree centigrade, boiling point is minus 33.4 degree centigrade, solubility very much soluble in water. Grades anhydrous or liquefied ammonia stored at 80 degrees Fahrenheit with a pressure of 175 psig is one particular grade.

Other grade is aqueous grade where you have 28 percent ammonia. End uses for ammonia worldwide are you know if you wanted to list primarily it can be used directly as a fertilizer. But in addition to its use as fertilizer it can also be used for production of different other types of fertilizers as well as the chemicals like manufacturing of urea, ammonium phosphate, nitric acid, ammonium nitrate, ammonium sulfate, acrylonitrile etcetera.

So, except this acrylonitrile rest whatever highlighted ones are there presented ones are one or other kind of fertilizer only.

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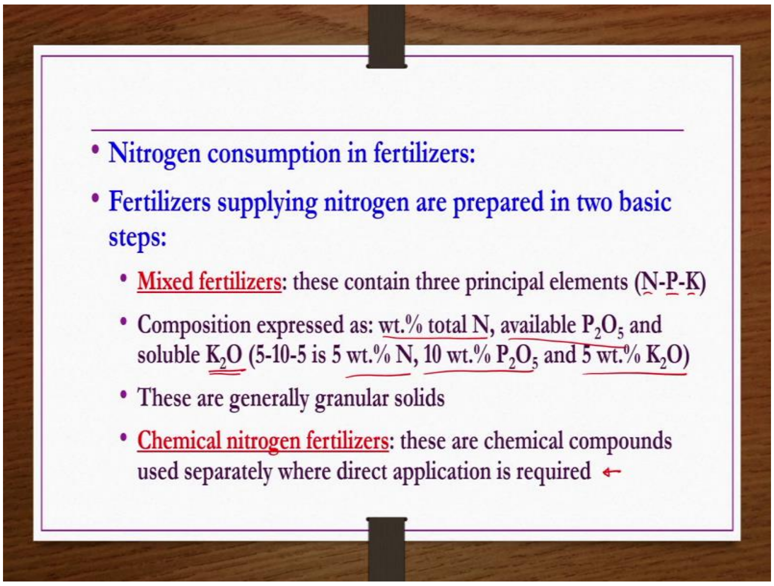

- Nitrogen consumption in fertilizers:
- Fertilizers supplying nitrogen are prepared in two basic steps:
  - Mixed fertilizers: these contain three principal elements (N-P-K)
  - Composition expressed as: wt.% total N, available P_2O_5 and soluble K_2O (5-10-5 is 5 wt.% N, 10 wt.% P_2O_5 and 5 wt.% K_2O)
  - These are generally granular solids
  - Chemical nitrogen fertilizers: these are chemical compounds used separately where direct application is required ←

Nitrogen consumption in fertilizers if you see fertilizers supplying nitrogen are prepared in two basic steps. One is the mixed fertilizers these contain three principal elements N-P-K because they are all three are mixed that is the reason these are known as the mixed fertilizers. This N-P-K indicate let us say for example, composition expressed as weight percent total N, available phosphorus pentoxide and potassium oxide.

Let us say 5-10-5 fertilizer; that means, 5, weight percent of N, 10 weight percent of P 2 O 5 and 5 weight percent of K 2 O are present in the fertilizer that is what it mean by, ok. These are generally in granular solid form. Then chemical nitrogen fertilizers these are chemical compounds used separately where direct application is required, ok. Like ammonia nitrogenous fertilizer directly you can apply as it is. So, these are the chemical nitrogen fertilizers.

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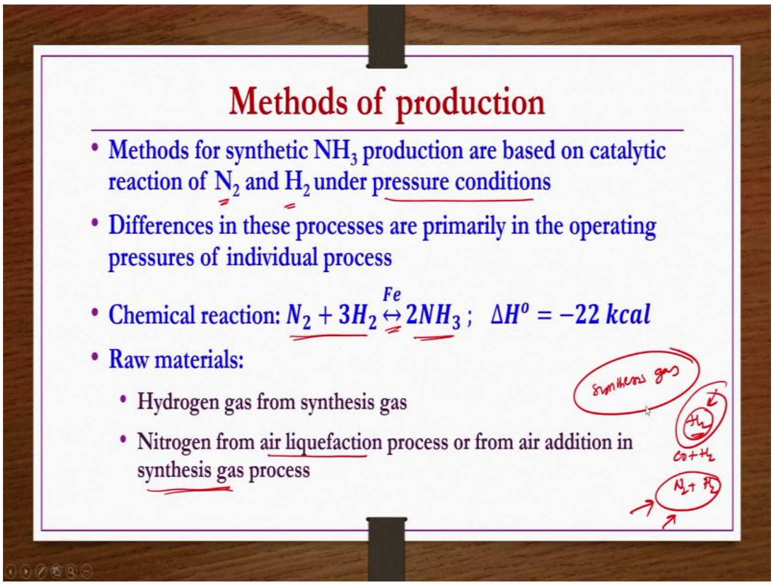

Methods of production

- Methods for synthetic NH_3 production are based on catalytic reaction of N_2 and H_2 under pressure conditions
- Differences in these processes are primarily in the operating pressures of individual process
- Chemical reaction: $N_2 + 3H_2 \overset{Fe}{\leftrightarrow} 2NH_3$; $\Delta H^o = -22\ kcal$
- Raw materials:
  - Hydrogen gas from synthesis gas
  - Nitrogen from air liquefaction process or from air addition in synthesis gas process

Methods of production of ammonia if you see methods for synthetic ammonia production are based on catalytic reaction of nitrogen and then hydrogen under pressure conditions. In fact, all methods are. In fact, if you take any N number of plant from one plant to the other plant if you go the synthetic ammonia production process what you see the difference primarily is operating pressure under what pressure the catalytic reaction is taking place between N 2 and H 2 that is the primary difference.

There may be some minor differences from one plant to the other plant of synthetic ammonia. But however, primarily at what pressure this reaction is taking place. Based on the pressure you know the conversion is going to be changed, right. The pressure applied here in this reactions in general varies between 100 atmospheres to 1000 atmosphere pressure.

Differences in these processes are primarily in the operating pressures of individual processes. It has a chemical reaction 1 mole of N 2, 3 moles of H 2 reacts together at high pressure in the presence of iron catalyst you get 2 moles of ammonia and this reaction is reversible, ok. Raw materials obviously, one is the nitrogen from the air and then hydrogen from the synthesis gas.

Nitrogen not only from the air liquefaction process, but also air addition in synthesis gas process also we have seen that you know nitrogen is available. In fact, when we were discussing about synthesis gas few lectures before in the production of synthesis gas there were different sources H 2 source after the conversion of the reactor gases mixture is there. So, that gases mixture is having you know several components CO H 2 N 2 and then H 2 S etcetera.

So, when you do the proper purification steps as per your requirement you can get H 2, you can get C O plus H 2, you can get N 2 plus H 2 like this you can get. So, directly H 2 you can get from synthesis gas or N 2 plus H 2 can also be you know obtained by addition of air. So, this is nothing but ammonia synthesis gas this is nothing but hydrogen synthesis gas, ok.

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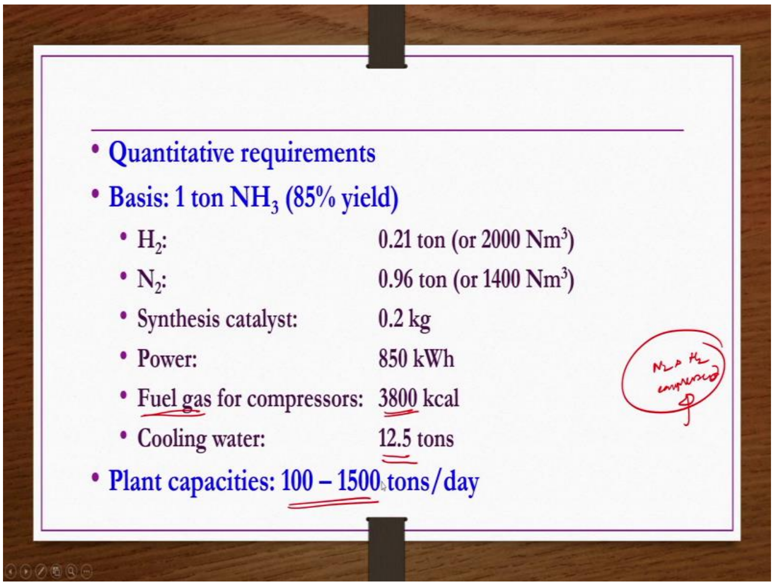

- Quantitative requirements
- Basis: 1 ton NH_3 (85% yield)
  - H_2: 0.21 ton (or 2000 Nm^3)
  - N_2: 0.96 ton (or 1400 Nm^3)
  - Synthesis catalyst: 0.2 kg
  - Power: 850 kWh
  - Fuel gas for compressors: 3800 kcal
  - Cooling water: 12.5 tons
- Plant capacities: 100 – 1500 tons/day

N_2 & H_2 compressed

P

Quantitative requirements basis if you take as one ton of ammonia 85 percent yield then how much hydrogen is required? 0.21 tons or 2000 normal cubic meters, nitrogen 0.96 tons or 1400 normal cubic meters. Synthesis catalyst only 0.2 kgs for production of 1 ton ammonia and then power 850 kilowatt hours then fuel gas for compressors 3800 kilocalories.

This fuel gases are very much essential. Because now in the previous slide we have seen this N 2 and H 2 are compressed our reaction is taking place at high pressure conditions. If you are doing compression to the high pressure obviously, efficient compressors are required for those compressors fuel oils in general used. So, those fuel oils you know having some energy like 3800 kilocalories is very much essential.

Then cooling water because these reactions are exothermic as well as the high temperature reactions high pressure reactions are there. So, then maintaining proper or required temperature and pressure is required. So, then accordingly cooling water requirement would also be there here 12.5 tons. Plan capacities 100 to 1500 tons per day.

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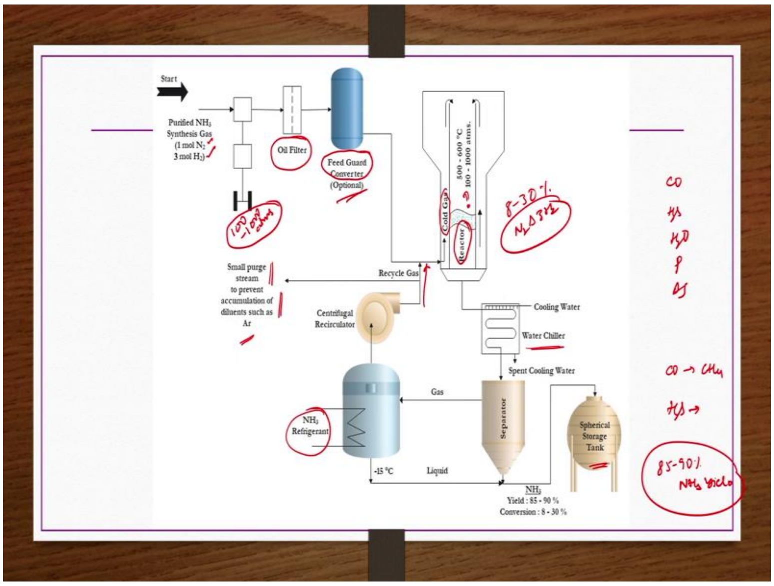

Now, the process we are going to see schematically how to get ammonia from its synthesis gas. Ammonia synthesis gas is nothing but 1 mole of N 2 and 3 moles of H 2, purified ammonia synthesis gas is compressed between 100 to 1000 atmospheric pressures, right. So, when you are compressing to such high pressures obviously, you need high efficient compressors and then these compressors are run by the fuel oils.

So, in this process while compressing it is possible some of the oil may also be going along with the compressed synthesis gas. So, that oil has to be removed by oil filter. Sometimes these gases may also include some impurities like CO etcetera H 2 S and then H 2 O, phosphorous, arsenic etcetera may also be there, right.

So, then if it is not pure these kind of impurities are there. So, then you can have feed Guard converter which is a common terminology, but it is a kind of setup where you can do the catalytic reaction where you can do absorption like that. Let us say CO, methanation reaction can be done to get the methane, if H 2 S is there so then it can work as a absorber by using ethanol amine solution and then absorb the H 2 S etcetera it is the optional. It depends on the purity of synthesis gas.

If the ammonia synthesis gas is pure then you do not need this setup. So, then compressed ammonia synthesis gas purified synthesis gas which is compressed to pressure of 100 to 1000 atmosphere depending on the conversion that you want, depending on the yield that you want. After oil filtering sent to a reactor. This reactor is provided with the cold gases because inside the temperature and pressure are high.

So, then proper maintaining the temperature as per the requirement is good and then whatever the synthesis compressed gas is there that is sent to a tubular reactor system. This reactor is enclosed with the shell kind of shapes in which cold gas is going. This reactor is having something like packed bed kind of a structure where catalytic particles are packed and then heated to required temperature of 500 to 600 degree centigrade.

To this reactor where the catalyst particles are already heated to this temperature hot gases which are compressed or preheated gases which are compressed to 100 to 1000 atmosphere are sent in, right. So, now depending on what atmospheric pressure are you maintaining 100 or 500 or 1000 depending on that one conversion 8 to 30 percent conversion of this N 2 and then 3 H 2 mixture takes place.

So, whatever the ammonia synthesis gas forming the ammonia gas. So, that ammonia gas is passed through a water chiller to reduce the temperature then followed by a separator. In the separator if you have any undesired you know or unreacted N 2, H 2 etcetera are coming they are separated and then sent to a NH 3 refrigerator where ammonia is liquefied then stored in a spherical storage tank, ok.

Whatever the unreacted N 2 and 3 H 2 are there they are feedback to the reactor in order to increase the yield or in order to increase the conversion of the N 2 and 3 H 2. By this method 85 to 90 percent of ammonia yield is possible in this method depending on the pressure that you are operating.

From the reactor whatever the unreacted gases are there they are being sent here again to the reactor like this and then as well as the this cooling gases also sent here after the centrifugal recirculator, ok. Some amount of small purge stream is also there to prevent accumulation of diluents such as organics etcetera if at all they are present, ok.

This is what you know simple process looks very simple. And then in fact it is simple only thing that the reactor has to be designed such a way that it should be capable of holding a reaction high pressure reaction at temperature of 500 to 600 degree centigrade.

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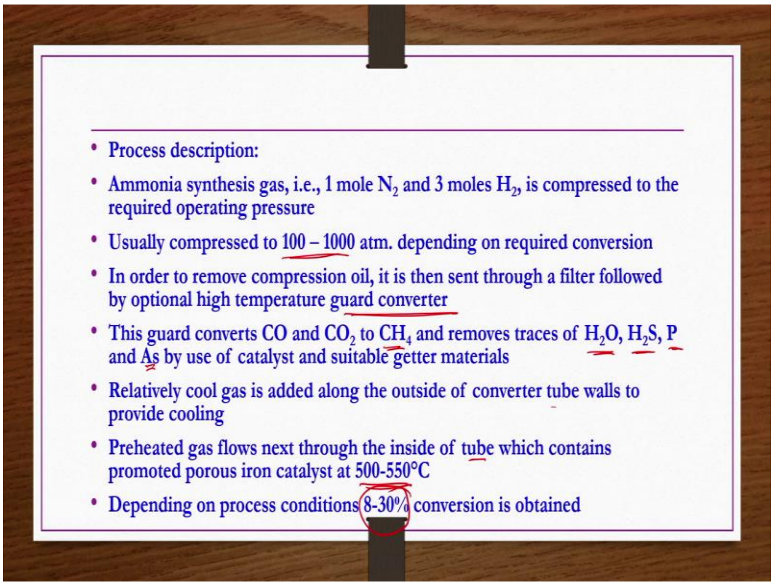

- Process description:
- Ammonia synthesis gas, i.e., 1 mole N_2 and 3 moles H_2, is compressed to the required operating pressure
- Usually compressed to 100 – 1000 atm. depending on required conversion
- In order to remove compression oil, it is then sent through a filter followed by optional high temperature guard converter
- This guard converts CO and CO_2 to CH_4 and removes traces of H_2O, H_2S, P and As by use of catalyst and suitable getter materials
- Relatively cool gas is added along the outside of converter tube walls to provide cooling
- Preheated gas flows next through the inside of tube which contains promoted porous iron catalyst at 500-550°C
- Depending on process conditions 8-30% conversion is obtained

The process steps if you see ammonia synthesis gas that is 1 mole of nitrogen and 3 moles of hydrogen is compressed to required operating pressure. Usually it is compressed to 100 to 1000 atmospheric pressure depending on the required conversion. In order to remove compression oil it is then sent through a filter followed by optional high temperature guard converter.

This guard converts CO and C O 2 to methane and remove traces of H 2 O, H 2 S, phosphorus and arsenic if at all they are present by use of catalyst and suitable getter materials. Getter materials in the sense let us say if you wanted to absorb the H 2 S then ethanolamine solution may be available there like that for example, like that. But if your synthesis gas pure enough these things are not there. So, then this the guard converter is completely optional.

Relatively cool gas is added along the outside of converter tube walls to provide the cooling. Preheated gas flows next through the inside of the tube which contains promoted porous iron catalyst at 500 to 550 degree centigrades. Depending on process contribution 8 to 30 percent of conversion takes place in this process.

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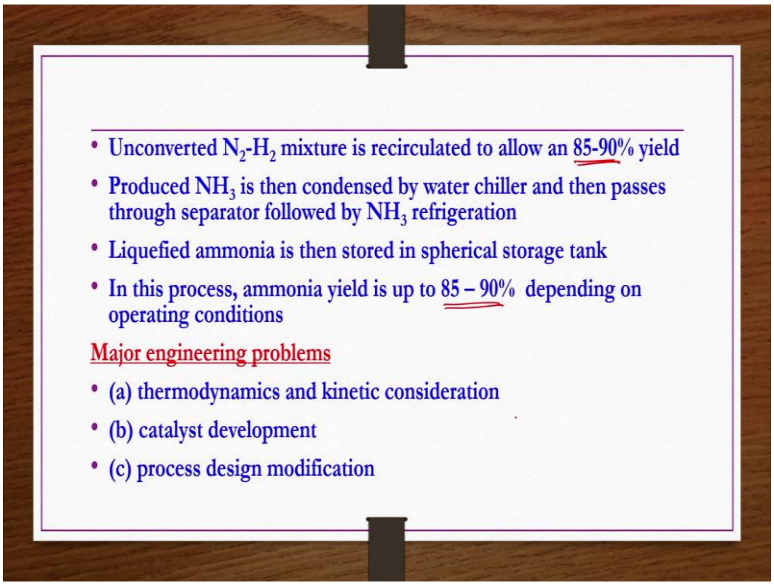

- Unconverted N_2-H_2 mixture is recirculated to allow an 85-90% yield
- Produced NH_3 is then condensed by water chiller and then passes through separator followed by NH_3 refrigeration
- Liquefied ammonia is then stored in spherical storage tank
- In this process, ammonia yield is up to 85 – 90% depending on operating conditions

Major engineering problems

- (a) thermodynamics and kinetic consideration
- (b) catalyst development
- (c) process design modification

Unconverted N 2 and then H 2 mixture is recirculated to allow 85 to 90 percent yield. Otherwise in one single run without recirculation you can get only approximately 8 to 11 percent of yield only 8 to 10 percent yield of ammonia only you get it. So, recirculation is one of the important parameter to make sure efficiently it is recirculating the unreacted N 2 and H 2 to the reactor.

Produce ammonia is then condensed by water chiller and then passes through a separator followed by ammonia refrigeration. Liquid ammonia is then stored in spherical storage tank. In this process ammonia yield is up to 85 to 90 percent depending on operating conditions. This is all about the process how to get ammonia from the ammonia synthesis gas using a high pressure catalytic reactor, right.

So, now, what we see what are the possible engineering problem that one should be careful about. So, whenever there is a reversible reaction then thermodynamics and kinetics place essential role and then if the catalytic reaction is there then catalyst is the other important. So, these are the engineering parameter then one should be careful.

So, major engineering problems thermodynamics and kinetic consideration, catalyst development and process design modifications based on these two considerations.

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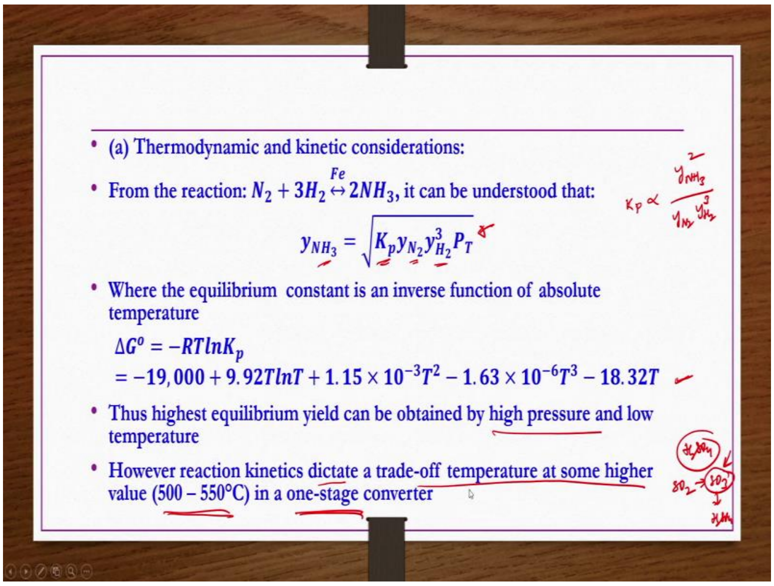

- (a) Thermodynamic and kinetic considerations:
- From the reaction: $N_2 + 3H_2 \overset{Fe}{\leftrightarrow} 2NH_3$, it can be understood that:

$$y_{NH_3} = \sqrt{K_p y_{N_2} y_{H_2}^3 P_T}$$

$$K_p \propto \frac{y_{NH_3}^2}{y_{N_2} y_{H_2}^3}$$

- Where the equilibrium constant is an inverse function of absolute temperature

$$\Delta G^o = -RTlnK_p$$
$$= -19,000 + 9.92TlnT + 1.15 \times 10^{-3}T^2 - 1.63 \times 10^{-6}T^3 - 18.32T$$

- Thus highest equilibrium yield can be obtained by high pressure and low temperature
- However reaction kinetics dictate a trade-off temperature at some higher value (500 – 550°C) in a one-stage converter

H_2SO_4

$SO_2 \rightarrow SO_3 \rightarrow H_2SO_4$

So, now we see individually one after other first starts with thermodynamics and kinetic considerations. Now, from the reactions N 2 plus 3, H 2 reversibly giving rise to 2NH 3 in the presence of iron catalyst what you can understand the equilibrium constant whatever is there that is proportional to y NH 3 that is fraction of you know ammonia square divided by y N 2 and then y H 2 cube, right.

This is what you can understand there may be other parameters etcetera. So, from here what you can write y NH 3 is equals to square root of K p y N 2 y H 2 cube P T. So, y N 2 is nothing but the mole fraction of N 2, Y H 2 is nothing but the mole fraction of H 2, y NH 3 is nothing but the mole fraction of NH 3, P T is the total pressure and then K p is the equilibrium constant.

This equilibrium constant is inverse function of absolute temperature and then if it is related to the Gibbs free energy then you have delta G naught is equals to minus RTlnK p which is further equal to minus 19000 plus 9.92 TlnT plus 1.15 multiplied by 10 power minus 3 T square minus 1.63 multiplied by 10 power minus 6 T cube minus 18.32 T.

So, from here what we can understand if you wanted to have higher you know y NH 3 in exit gas then P T has to be very high since K p is inversely proportional to the temperature then temperature has to be low, ok. So, high pressure low temperature provides highest possible equilibrium yield as per this equation that we have seen here, right.

However, reaction kinetics dictate a trade off temperature at some higher value 500 to 550 degree centigrade in a one-stage converter is essential. 500 to 550 degree centigrade is not a low temperature. But however considering the pressure having the pressure almost up to 1000 atmospheric pressure if you wanted to have the higher conversion of these reactants.

So, compared to that one this is a low temperature only, ok. Now, you may be thinking that like you know in the H 2 SO 4 production in previous lectures that we have seen where SO 2 is oxidized to SO 3 which is a reversible reaction and then from this SO 3 or getting H 2 SO 4 this is what we have seen.

So, but SO 2 to SO 3 conversion oxidation whatever is there this can be done in conventionally if it is a conventional plant two-stage converters are there high temperature stage low temperature stage whereas, the modern plants are even having 3 to 4 stages also. So, you may be thinking why cannot we have such kind of converters here.

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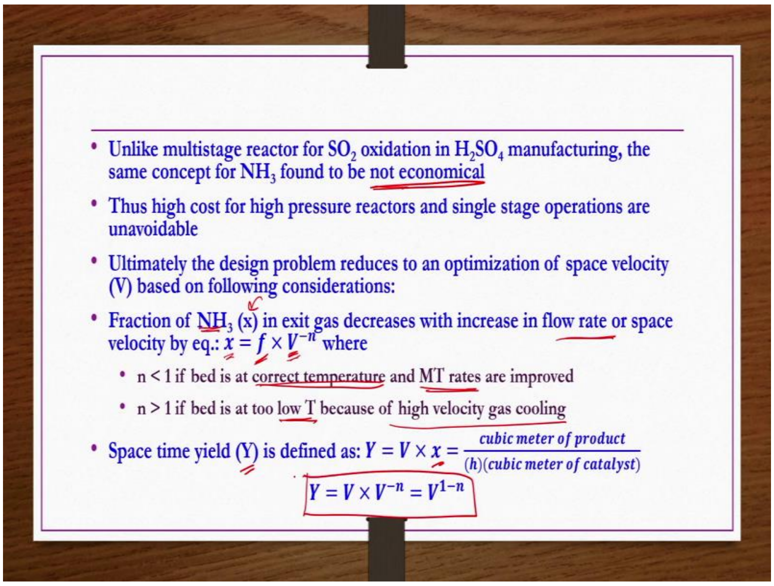

- Unlike multistage reactor for SO_2 oxidation in H_2SO_4 manufacturing, the same concept for NH_3 found to be not economical
- Thus high cost for high pressure reactors and single stage operations are unavoidable
- Ultimately the design problem reduces to an optimization of space velocity (V) based on following considerations:
- Fraction of NH_3 (x) in exit gas decreases with increase in flow rate or space velocity by eq.: $x = f \times V^{-n}$ where
  - n < 1 if bed is at correct temperature and MT rates are improved
  - n > 1 if bed is at too low T because of high velocity gas cooling
- Space time yield (Y) is defined as: $Y = V \times x = \frac{cubic\ meter\ of\ product}{(h)(cubic\ meter\ of\ catalyst)}$

$$\boxed{Y = V \times V^{-n} = V^{1-n}}$$

So, if people have already tried indeed, but they found such approach in the case of ammonia synthesis is not economical. So, it is of no use here in this case. So, ultimately what happens you have to have high pressure equipment high pressure equipments are very costly very very costly.

So, then this high cost for high pressure reactors and single stage operations are unavoidable in ammonia synthesis. Then obviously, in this cases you know what you have the process parameters like temperature, pressure and then catalyst and then flow rate at which the gases are coming to the reactor etcetera these are the primary factors.

So, catalyst is keep aside temperature pressures we have already seen low temperature and then high pressures are good for equilibrium yield, right. So, then remaining parameter is only the space velocity, right. So, ultimately design problem reduces to an optimization of space velocity based on following consideration. Fraction of ammonia that is x in exit gas decreases with increase in flow rate or space velocity, right. Increasing flow rate; that means, increasing the space velocity.

Space velocity may be put as mass rate of the gases coming into the catalytic reactor divided by the weight of the catalyst or mass of the catalyst that is how you can see. So, if the mass rate is increasing; that means, space velocity is also increasing. Now, here what we understand x in the exit gas decreases with increase in flow rate or space velocity.

So, that means, x is inversely proportional to the space velocity V and then it is having some power n, ok. And there are mass transfer heat transfer and so many other things are may be there. So, then other parameters may also be there like temperature, pressure etcetera their effects are all put together and then included as f because we are seeing now only effect of V space velocity as a region.

So, that means, if the bed is at correct temperature and then mass transfer rates are improved then n has to be less than 1 and then if the bed is at 2 low temperature something like 200, 300 degree centigrade then n has to be greater than 1 because of high velocity gas cooling, ok.

Now, space time yield if you define it is nothing but fraction of ammonia in the exit gas multiplied by the space velocity that you can put it as cubic meter of product per hour per cubic meter of catalyst. So, x if you substitute here this one so, then there is a relation between Y and V. So, Y is equals to V power 1 minus n you can get.

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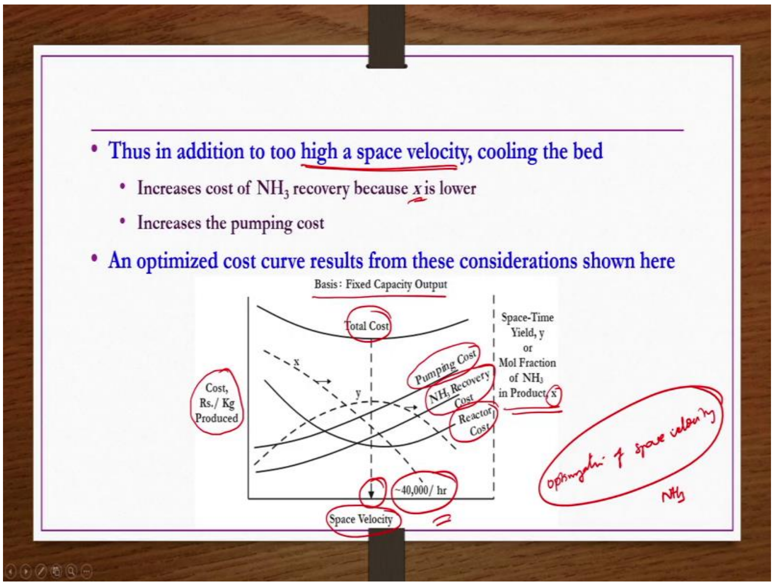

- Thus in addition to too high a space velocity, cooling the bed
  - Increases cost of NH_3 recovery because x is lower
  - Increases the pumping cost
- An optimized cost curve results from these considerations shown here

So, now what you understand? In addition to too high space velocity cooling the bed will increase the cost of ammonia recovery because x is lower here and then it also increases the pumping cost. If you are increasing the velocity space flow rate you are increasing that means, you are increasing the space velocity high space velocity that means, high flow rates has to be given and then if you have high flow rates then pumping cost would be high that will increase the pumping cost that is what it mean by.

So, an optimized cost curve results from these considerations are shown here. If you take a fixed capacity output as basis and then you plot cost of production cost rupees per kg of produced versus space velocity. So, as space velocity increases the pumping cost increases because when this space velocity increases the flow rate increases in order to have the high flow rate high efficiency pumping is required so, then pumping cost goes increases.

Similarly, ammonia recovery cost decreases because ammonia is present in small fractions only in the exit gas. We have seen in a single pass up to 8 percent conversion is taking place 8 to 10 percent conversion is taking place or even less. So, in order to if you increase the space velocity its recovery cost would also be increasing, right. Reactor cost if you do with respect to the space velocity it decreases and then further increases with respect to increasing the space velocity.

So, when you add these together and then have the total cost this total cost is found to decrease with the space velocity up to certain point up to certain value of the space velocity then it increases again. So, for the conventional plants it has been found that space velocity approximately 40,000 hour inverse, space velocity is having time inverse units because it is a mass rate of the gases per mass of the catalyst.

So, it is inverse of kg per hour divided by kg is you know hour inverse that is what you are having. So, for the most of the conventional plants as per the basis whatever we have discussed approximately 40,000 hour inverse space velocity is found to be optimum one. Now, mole fraction of ammonia in product if you plot that is x versus space velocity x has found to be decreasing with increasing this space velocity just now previous slide we have seen and then space time yield y what happens it increases and then it decreases, ok.

So, based on this consideration you have to take both you know you have to consider all not only temperature, pressure also you should consider pumping cost, ammonia recovery cost and then reactor cost etcetera everything you have to include and then accordingly you have to choose the optimized space velocity. So, this is the optimization of space velocity for the production of ammonia from the ammonia synthesis gases at varying pressures.

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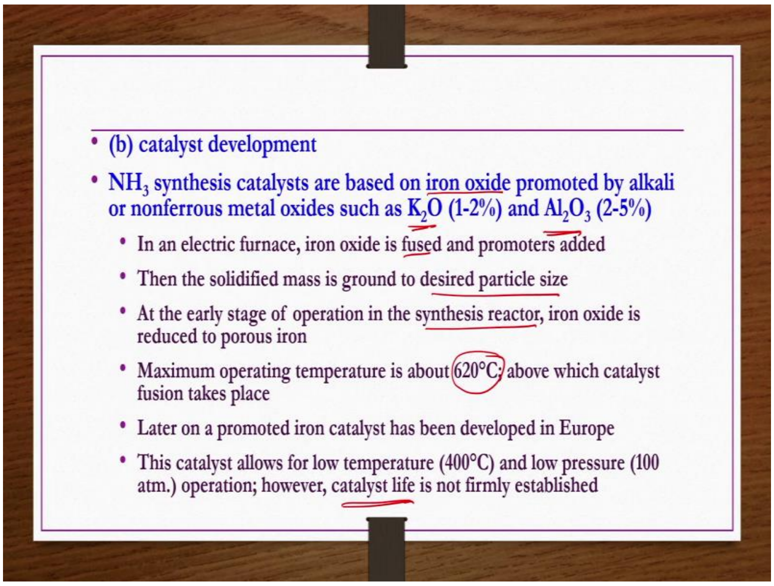

- (b) catalyst development
- NH_3 synthesis catalysts are based on iron oxide promoted by alkali or nonferrous metal oxides such as K_2O (1-2%) and Al_2O_3 (2-5%)
  - In an electric furnace, iron oxide is fused and promoters added
  - Then the solidified mass is ground to desired particle size
  - At the early stage of operation in the synthesis reactor, iron oxide is reduced to porous iron
  - Maximum operating temperature is about 620°C; above which catalyst fusion takes place
  - Later on a promoted iron catalyst has been developed in Europe
  - This catalyst allows for low temperature (400°C) and low pressure (100 atm.) operation; however, catalyst life is not firmly established

Next one is the catalyst development. Actually ammonia synthesis catalyst are based on iron oxide which are promoted by alkali or non ferrous metal oxide such as potassium oxide and alumina, ok. Iron oxides are you know catalyst you know very much famous for the ammonia synthesis. How do you produce them? In electric furnace iron oxide is fused and promoters are added then solidified mass is ground to desired particle size.

At the early stage of operation in the synthesis reactor iron oxide is reduced to porous iron and then maximum operating temperature is about 620 degree centigrade because beyond that if you operate the reactor the catalyst fusion may take place, ok. Later on promoted iron catalyst has been developed in Europe which is found to be good to operate at low temperature and low pressure, but; however, catalyst life has not been established it properly.

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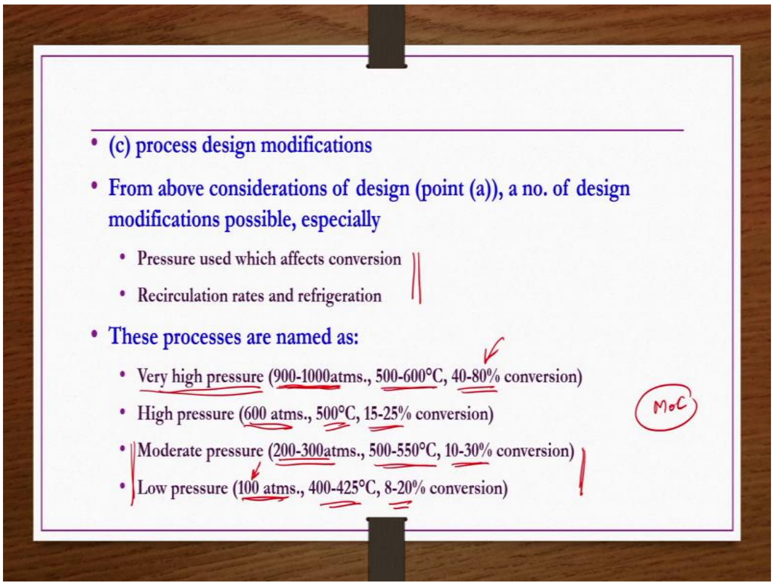

- (c) process design modifications
- From above considerations of design (point (a)), a no. of design modifications possible, especially
  - Pressure used which affects conversion
  - Recirculation rates and refrigeration
- These processes are named as:
  - Very high pressure (900-1000atms., 500-600°C, 40-80% conversion)
  - High pressure (600 atms., 500°C, 15-25% conversion)
  - Moderate pressure (200-300atms., 500-550°C, 10-30% conversion)
  - Low pressure (100 atms., 400-425°C, 8-20% conversion)

MoC

So, now process design modifications. Now from above consideration of design that is you know thermodynamics and kinetics basis we have found that you know high pressure and low temperature is better and then based on that one only space velocity has to be optimized that also we have done.

Based on those consideration a number of design modifications are possible especially pressure used which affects the conversion, lower pressure gives the lower conversion, higher pressure gives the higher conversion, ok. Then another one is the recirculation rates and refrigeration we have seen per single pass only 8 to 10 percent of a N 2 and 3 H

2 conversion has been taken place to give yield of ammonia and then rest is all unreacted.

So, if you do not properly recirculate it to the reactor you know it is not going to be efficient. So, these two are the very much essential points in having different types of processes, right. So, these processes are named as high pressure where 900 to 1000 atmospheric pressure is maintained temperature is around 500 to 600 degree centigrade and then you can see conversions 40 to 80 percents.

Now, 40 to 80 percent is very broad picture, right. So, but this again depends on the recirculation rates and other factors also. If those things are also optimized. So, then you may be having 70 to 80 percent conversion because such high pressures are very good for the higher equilibrium yield.

Then high pressures first one is very high pressure processes second one is the high pressure where the pressure is 600 atmosphere temperature is 500 degree centigrade, but the conversion is only 15 to 25 percent. See when the pressure is reduced from 1000 to 600 conversion has fallen from 80 percent to 25 percent such important is the pressure in this ammonia synthesis.

Then moderate pressure where 200 to 300 atmospheres are applied. Temperature is still in the same range of 500 to 550 degree centigrade, but conversion you see only 10 to 30 percent conversion. And then low pressure approximately 100 atmospheres and then 400 to 425 degree centigrade this temperature range, but the conversion is only 8 to 20 percent.

Actually 100 atmospheres is not a low pressure, but considering the upper limit and the process that is 1000 atmosphere the lower limit of 100 atmosphere is a very low pressure, ok. Now, temperature variations are not much when you change pressure from low to high, ok. So, that means, this temperature trade off temperature of 500 to 550 degree centigrade to whatever we have discussed is based on the experience though theoretically it says that low temperature is good for higher equilibrium yield, ok.

So, now what you understand temperature is not playing much role if it is between 450 to 550 degree centigrade, but the pressure is playing very important role, ok. But construction material of construction for high pressure vessels are very expensive. And then high pressure reactor designs are also very tough to get you have to make sure that there is no leakage and all that.

So, all the cost and the design point of view if you have the issues then it is better to go for low or moderate pressure conversion processes. So, because of the cost of material of construction and then as well as the designing of high pressure reactor is very tough that is the reason it is many plants are you know usually operates at moderate or high pressure conditions only they very few plants are having you know operating at very high pressures.

Though the conversion is very high. Because safety is also important not only the conversion and then production. Because working in high pressure reactors nearby reactors is always dangerous any small leakage may lead to disastrous effects. So, that is the reason it is better to select the pressure according to requirements from the safety point of view as well.

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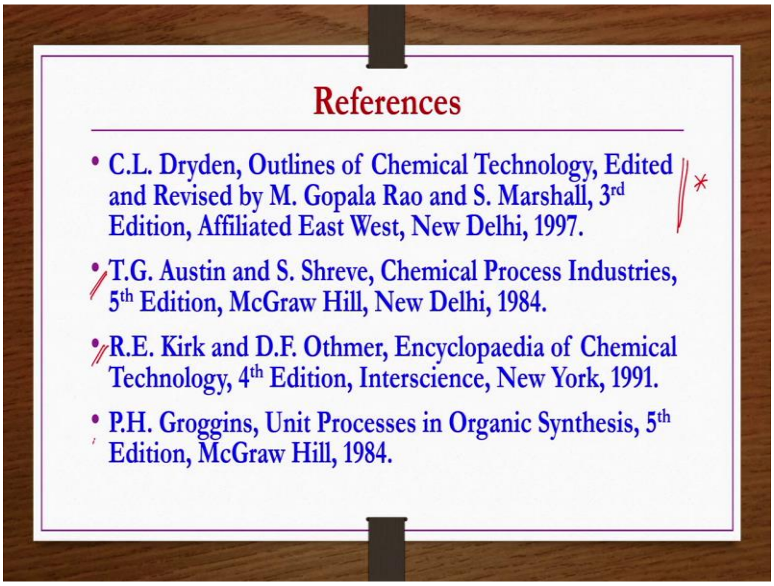

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References for this lecture are provided here. But however, most of the details may be obtained from this book a few other additional details may be found from the remaining reference books as well.

Thank you.