Inorganic Chemical Technology

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Lecture - 16
Nitrogen Industries - Urea

Welcome to the MOOCs course Inorganic Chemical Technology. The title of today's lecture is Nitrogen Industries, Urea. Before going into the details of today's lecture about manufacturing of Urea, what we do? We will have a kind of recapitulation of what we have discussed in last two classes, ok.

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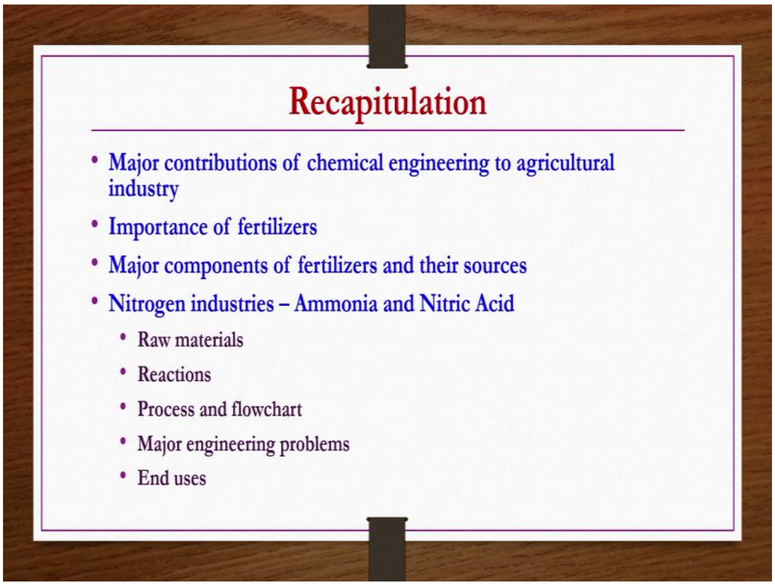

Recapitulation

- Major contributions of chemical engineering to agricultural industry
- Importance of fertilizers
- Major components of fertilizers and their sources
- Nitrogen industries – Ammonia and Nitric Acid
    - Raw materials
    - Reactions
    - Process and flowchart
    - Major engineering problems
    - End uses

We have seen what are the major contributions of chemical engineering to agriculture industry that is what we started in this week. Then we found that chemical engineers has given tremendous contribution to the agricultural industry, especially in terms of production of fertilizers, pesticides and then several unit operations such as freeze drying, etcetera in food industry.

Like that enormous contribution chemical engineers has given to agriculture industry, where we realized that the fertilizers is one of the component, a production of which is not possible without the contribution of chemical engineers. Then we started discussing about the fertilizers. Importance of fertilizers, what are the major components of the fertilizers and their sources we have discussed.

Then we started with a nitrogenous fertilizer industries, that is nitrogen industries we started with where, we started discussion on production of ammonia in one lecture and in another lecture, we discussed the production of nitric acid.

In the nitrogen industries, while discussing about the production of ammonia and nitric acid, what we have started with? We started with the conventional steps of raw materials associated chemical reactions, process and flowchart, followed by major engineering problems and final end uses or economics. In this lecture, we are going to discuss about the urea.

We start with some basics about the urea, why it is important and then what are the applications, etcetera. Then we go to the pertinent properties of the urea followed by the reactions and then process flowchart, major engineering problems. Finally, economics associated with the urea production plants and then urea product ok.

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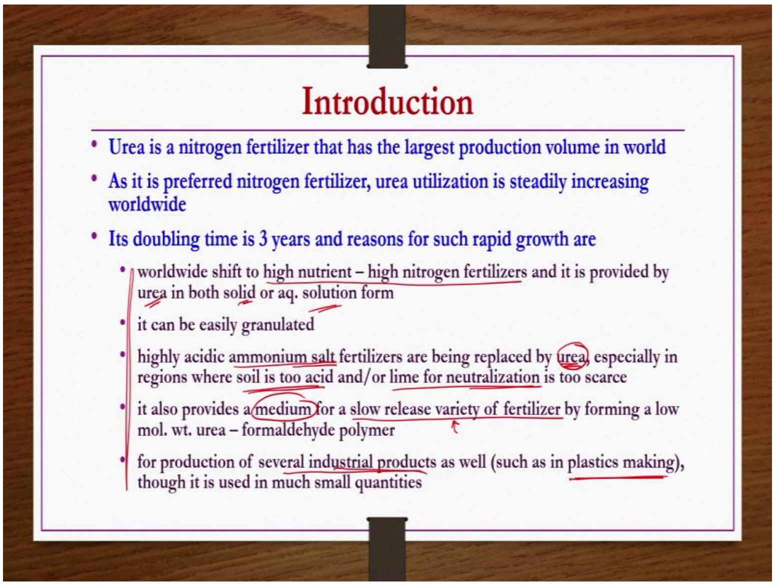

Introduction

- Urea is a nitrogen fertilizer that has the largest production volume in world
- As it is preferred nitrogen fertilizer, urea utilization is steadily increasing worldwide
- Its doubling time is 3 years and reasons for such rapid growth are
  - worldwide shift to high nutrient – high nitrogen fertilizers and it is provided by urea in both solid or aq. solution form
  - it can be easily granulated
  - highly acidic ammonium salt fertilizers are being replaced by urea, especially in regions where soil is too acid and/or lime for neutralization is too scarce
  - it also provides a medium for a slow release variety of fertilizer by forming a low mol. wt. urea – formaldehyde polymer
  - for production of several industrial products as well (such as in plastics making), though it is used in much small quantities

Urea is a nitrogen fertilizer that has the largest production volume in the world. In general, compared to the nitrogen phosphorus and potassium industries individually, if you take, nitrogen is one of the largest one amongst all fertilizer industries within the nitrogen fertilizer industries, urea is a largest producing component. And then that has been used extensively as a fertilizer for a you know agricultural purpose.

So, urea has been extensively used as a fertilizer for the agricultural purpose, because it is preferred nitrogen fertilizer. Its utilization is steadily increasing worldwide. So, that its doubling time is 3 years and there are suitable reasons why the utilization of urea is doubling within a short span of 3 years can be summarized because of the following reasons.

Worldwide shift to high nutrient, high nitrogen fertilizers, agricultural industry mostly, moving towards high nitrogen fertilizers which is having high nutrients that is one reason. And then this requirement of high nutrient and then high nitrogen fertilizer can be fulfilled by urea.

In fact, it is fulfilling very much adequately and it is doing in both solid form as well as the aqueous solution form. In the solid form, it is taken as a urea granule solution form, it is taken as a urea solution, urea in ammonia solution kind of forms. It is utilized as fertilizer in liquid form.

It can easily be granulated and then highly acidic ammonium salt fertilizers, something like ammonium sulfate etcetera, they are you know highly acidic especially when the regions where the soil is too acidic. So, such ammonium salt fertilizers are not good. So, that is the reason such ammonium salt fertilizers are being replaced by the urea that is one reason because this ammonium salt fertilizers are highly acidic.

Even if there is no option alternative option to this ammonium salt fertilizers, then also other problem is that lime required for neutralization is also too scarce in many of the regions. So, in regions where the soil is too acidic and our lime for neutralization is too scarce this urea is replacing ammonium salt fertilizers.

It also provides a medium for a slow release variety of fertilizer by forming a low molecular weight urea formaldehyde polymer. What does it mean by some plants? What does it mean by slow release variety of fertilizers? Some plant required steady supply of fertilizers for a longer duration of time. Slowly it has to be steadily, it has to be given for longer duration of time.

So, for that cases this urea acts as a very good medium alright in the form of a low molecular weight urea formaldehyde polymers and then that slow release of fertilizer requirement whatever is there that is being fulfilled when you use this urea as a medium.

It is also used for production of several industrial products though in small quantities. Some products like such as plastic making etcetera for this purpose or you know some other chemicals that we are going to see in the end uses anyway.

So, because of these many reasons its utilization is increasing. So, demand is increasing that is the reason because of that these things the doubling time is decreasing, doubling time is less than 3 years in general.

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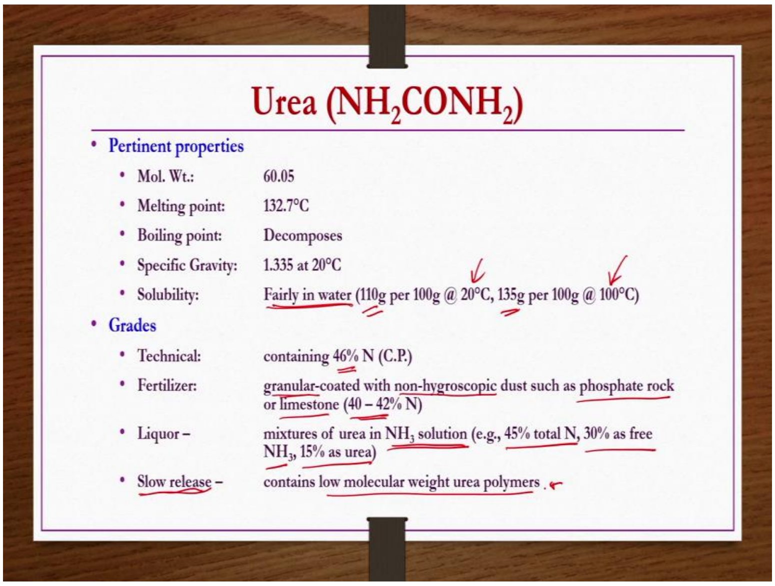

Urea (NH_2CONH_2)

- Pertinent properties
  - Mol. Wt.: 60.05
  - Melting point: 132.7°C
  - Boiling point: Decomposes
  - Specific Gravity: 1.335 at 20°C
  - Solubility: Fairly in water (110g per 100g @ 20°C, 135g per 100g @ 100°C)
- Grades
  - Technical: containing 46% N (C.P.)
  - Fertilizer: granular-coated with non-hygroscopic dust such as phosphate rock or limestone (40 – 42% N)
  - Liquor – mixtures of urea in NH_3 solution (e.g., 45% total N, 30% as free NH_3, 15% as urea)
  - Slow release – contains low molecular weight urea polymers

Now, we start discussing about urea which is nothing but NH 2 CONH 2. Its pertinent property is if you see molecular weight is 60.05, melting point is 132.7 degree centigrade and then it decomposes; that means, it does not have any boiling point. Specific gravity is 1.335 at 20 degree centigrade and about the solubility it is soluble fairly in water and its solubility increases with increasing the temperature of solution forming.

That is at 20 degree centigrade 110 grams of urea soluble per 100 grams of water whereas, at 100 degree centigrade 135 grams of urea is soluble in 100 grams of water. Coming to the grades it is available in different grades. The first one is the technical grade where the purity is usually high.

Technical grade urea contains 46 percent N whereas, the fertilizer if you take in granular form granular coated with non-hygroscopic dust such as phosphate rock or limestone it contains 40 to 42 percent N. It also available in a liquor grade, liquor grade it is usually a mixture of urea in ammonia solution such as example for example, 45 percent total N 30 percent as free ammonia and 15 percent as urea.

It also acts as a slow release medium that also we have seen. So, slow release grade it contains slow molecular weight urea polymers such as urea formaldehyde polymers. So, these urea polymers such as urea formaldehyde etcetera are good if you wanted to supply the nutrients and then nitrogen fertilizers to plants in a slow manner for a longer period. That is what it means by slow release.

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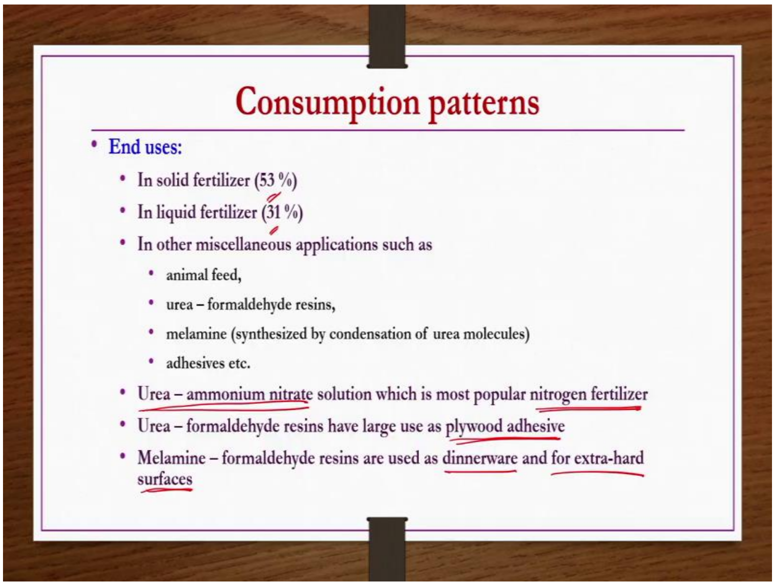

Consumption patterns

- End uses:
  - In solid fertilizer (53 %)
  - In liquid fertilizer (31 %)
  - In other miscellaneous applications such as
    - animal feed,
    - urea – formaldehyde resins,
    - melamine (synthesized by condensation of urea molecules)
    - adhesives etc.
  - Urea – ammonium nitrate solution which is most popular nitrogen fertilizer
  - Urea – formaldehyde resins have large use as plywood adhesive
  - Melamine – formaldehyde resins are used as dinnerware and for extra-hard surfaces

Consumption patterns if you see end uses in solid fertilizer form 53 percentage is used in general in liquid fertilizer 31 percent it is used. In other miscellaneous applications also it is used such as animal feed. Most of the cattle’s and sheep’s they are able to digest our urea and then they required high amount of proteins. So, 40 percent of their proteins can be fulfilled by feeding them this urea because they are having the digestive system such as that they can digest urea also.

And the remaining protein requirements of those sheep’s and cattle’s may be supplied by the low cost other nutrients ok. So, but this is true in countries where urea is available in excessive, but it is not possible in India because we are having shortage of fertilizers even today. Urea formaldehyde resins other application then melamine which is synthesized by the condensation of the urea molecules.

Then adhesives etcetera then urea ammonium nitrate solution which is most popular nitrogen fertilizers. Actually chemical fertilizers mixed fertilizers etcetera are also there. So, we are going to discuss one by one urea ammonium nitrate solution whatever is there.

So, ammonium nitrate is another nitrogen fertilizer that we are going to discuss in the next lecture. So, their solution of urea and ammonium nitrate is most popular amongst the nitrogen fertilizer. So, it is also used that way. Urea formaldehyde resins have large use as plywood adhesives whereas, the melamine which obtained by the condensation of urea molecules.

So, melamine formaldehyde resins are used as dinnerware and for extra hot surfaces if you wanted to have. So, these are used. Now, we start the production of urea. So, what are the processes available? All the processes, all the plants that are existing they are based on the ammonium carbamate decomposition method, ok.

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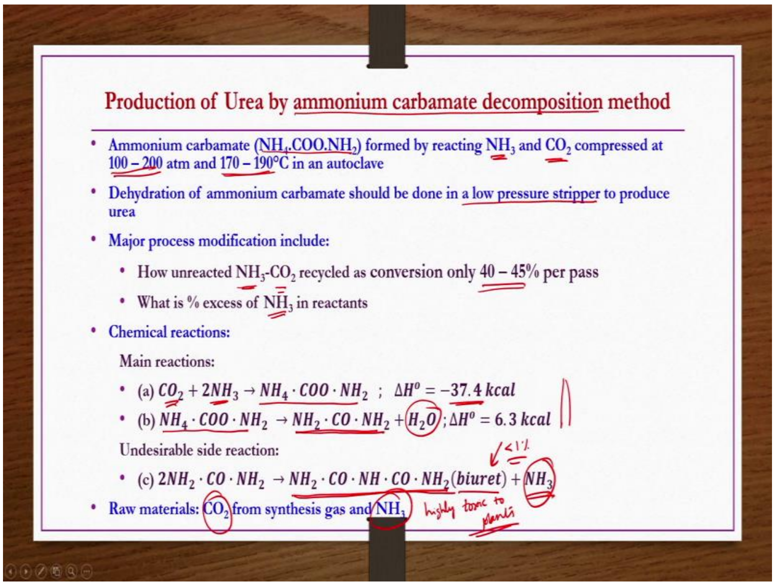

Production of Urea by ammonium carbamate decomposition method

- Ammonium carbamate ($NH_4.COO.NH_2$) formed by reacting NH_3 and CO_2 compressed at 100 – 200 atm and 170 – 190°C in an autoclave
- Dehydration of ammonium carbamate should be done in a low pressure stripper to produce urea
- Major process modification include:
  - How unreacted NH_3-CO_2 recycled as conversion only 40 – 45% per pass
  - What is % excess of NH_3 in reactants
- Chemical reactions:

  Main reactions:
  - (a) $CO_2 + 2NH_3 \rightarrow NH_4 \cdot COO \cdot NH_2$; $\Delta H^o = -37.4\ kcal$
  - (b) $NH_4 \cdot COO \cdot NH_2 \rightarrow NH_2 \cdot CO \cdot NH_2 + H_2O$; $\Delta H^o = 6.3\ kcal$

  Undesirable side reaction:
  - (c) $2NH_2 \cdot CO \cdot NH_2 \rightarrow NH_2 \cdot CO \cdot NH \cdot CO \cdot NH_2 (biuret) + NH_3$
- Raw materials: CO_2 from synthesis gas and NH_3

Whatever the urea production that is possible today is based on the ammonium carbamate decomposition method only. What is ammonium carbamate? If you take a reaction between ammonia and then carbon dioxide at high pressures and low temperatures then this ammonium carbamate will form and then if you do the dehydration of this ammonium carbamate then you will get urea ok.

So, that is the basic process. But from one plant to the other plant there would be definitely some variations. Those variations are in terms of a unreacted ammonia and then CO 2 recycling. Because, we are soon you are going to realize that the conversion of ammonium CO 2 to urea is approximately 40 to 45 percent only if you do the single pass process.

So, remaining ammonia and then CO 2 you have to appropriately used are you have to recycle ok. So, based on how are you doing the recycling that is the one reason possible for changes in plants from one plant to the other plant. Other possible way is that this reaction whatever that is there between ammonia and then carbon dioxide is highly exothermic.

So, then whatever the heat liberated how are you handling? One way is by giving the excess ammonia reactant. So, how are you giving excess ammonia reactant to the process? So, that way another you know alternative is possible. But basic process if you take is the same reaction between ammonia and then carbon dioxide at high pressure and moderately high temperatures ok.

So, details we are going to see anyway now. Ammonium carbamate formed by reacting ammonia and then CO 2 compressed at 100 to 200 atmosphere and 170 to 190 degrees centigrade in an autoclave. It does not mean that whether you use 100 atmosphere or 200 atmosphere you are getting the same conversion.

Obviously not, if you use higher pressure then; obviously, the conversion is going to be higher. But you know when you go for higher pressure. So, then capital cost and then compression cost etcetera all that increases. Temperature also you cannot go more than this one. Because, in this up to this range urea production rate increases, but beyond 185 190 degrees centigrade it is sharply false. Such kind of reasons are there.

So, then under these conditions these range conditions only you have to operate in our as per your requirements, ok. So, if you do the dehydration of ammonium carbamate that is this molecule from this molecule if you take out the water then what you get NH 2 CO NH 2 that is nothing but urea ok. But this is done in a low pressure stripper only. So, flowsheet anyway we are going to discuss. Now, we see process modifications.

Because we have been seeing that for production of some chemicals that we have already discussed more than one method is available in general right. More than one method available. So, but here we have only one process, but only modifications are possible from one plant to the other plant.

So, they are based on the how unreacted ammonia CO 2 are recycled because purpose you are getting 40 to 45 percent conversion only that is one option for modification and then what is the excess of ammonia in the reactants? Why excess of ammonia in the reactants is required?

Because the reaction between ammonia and then CO 2 is highly exothermic so, whatever the heat liberated. So, in order to pick up the sensible heat of the reaction you have to supply the additional reactant and then that ammonia you are supplying that is the other option possible.

Chemical reactions: So, this ammonia and then CO 2 reacting right to give ammonium carbamate its exothermic reaction. Then dehydration of this ammonium carbamate is taking place to give urea plus water right. So, these are the main reaction, but there is a danger of site reaction also.

What is that two moles of auto molecules of urea react together to give biuret that is NH 2 CO NH CO NH 2 plus ammonia. So, you want ammonia to be consumed not to be liberated that is one way it is undesirable reaction. Other way this component whatever is there this is highly toxic to plants; actually we are supplying these fertilizers to produce to provide required nutrients for the growth of the plant.

But if such kind of highly toxic molecules or components present in the fertilizers. So, that is not going to be helpful to the plants indeed that is going to be dangerous to the plants. So, that is the reason this should not be present in the urea or final product even if it is present it should be less than 1 percent ok raw materials; obviously, CO 2 from synthesis gas and ammonia.

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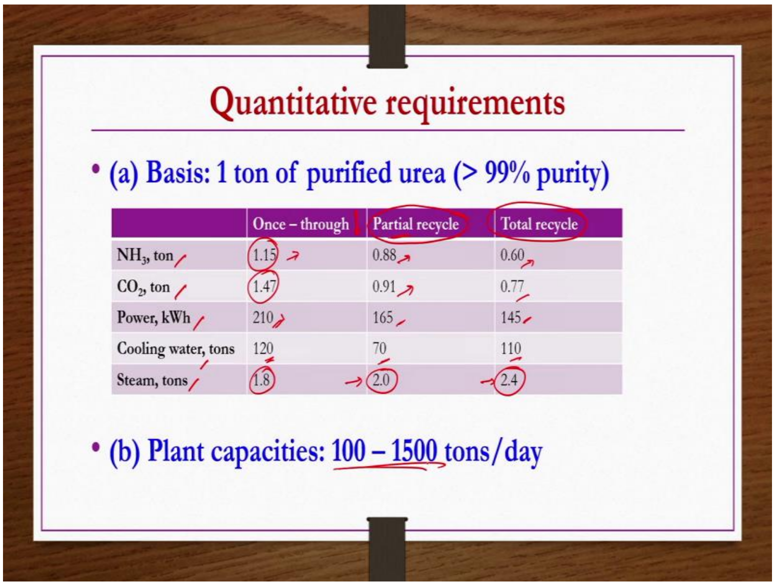

Quantitative requirements

- (a) Basis: 1 ton of purified urea (> 99% purity)

	Once – through	Partial recycle	Total recycle
NH_3, ton	1.15	0.88	0.60
CO_2, ton	1.47	0.91	0.77
Power, kWh	210	165	145
Cooling water, tons	120	70	110
Steam, tons	1.8	2.0	2.4

- (b) Plant capacities: 100 – 1500 tons/day

Now, the quantitative requirements. Let us say if you wanted to produce 1 ton of purified urea that is more than 99 percent purity then you required ammonia CO 2 power cooling water and then steam. So, but the quantity is varies. How does it varies? Are you doing it once through process? Are you doing partial recycle or total recycle? That way the quantity is changing.

What you can see why partial recycle or total recycles are required? Because we have already seen the conversion in single pass is 40 to 45 percent only. You have to make sure as much NH 3 and CO 2 being consumed to form urea. So, that way you know in order to increase the conversion you have to do this recycling.

So, what you can see compared to the ones through the requirement of ammonia in partial recycle is decreasing and it is further decreasing in the case of total recycle. That means, if you wanted to produce 1 ton of purified urea by total recycling then you need to have only 0.6 tons of ammonia.

Whereas, the same purity urea of 1 ton you wanted to produce then if you do the process only once through then you need 1.15 tons of ammonia. You can see the difference is almost half like compared to the ones through total recycle ammonia requirement is half. Same is true with CO 2.

CO 2 once through if you do 1.47 tons required it decreases to 0.91 tons if you do the partial recycle and then it decreases further to 0.77 tons if you do the total recycle. What do you mean by partial recycle? You should not see is as a kind of percentage of recycle the process that we are going to see flow sheet there I will explain. So, what it is mean by difference between these two terminologies ok.

Power requirements also you can see if you do once through 210 kilowatt hour power is required to produce 1 ton of purified urea and then partial recycling if you do you required only 165 kilowatt hours it further decrease to 145 kilowatt hours if you do total recycle.

Cooling water requirements is a slightly fluctuating, but steam requirement you can see it is increasing. Most steam is required if you do the total recycling ok. Anyway these are the process variable modifications to the process that we are going to see anyway. How are you going to use unused ammonia? That is because ammonia is very expensive from very expensive ammonia you are producing urea.

So, you must try to convert completely ammonia and then get urea as much as possible right. So, if you are not able to do. So, how are you going to use it? Probably you can use it for a chemical fertilizers production like ammonium, nitrate, ammonium sulfate etcetera. Plant capacities in general is between 100 to 1500 tons per day.

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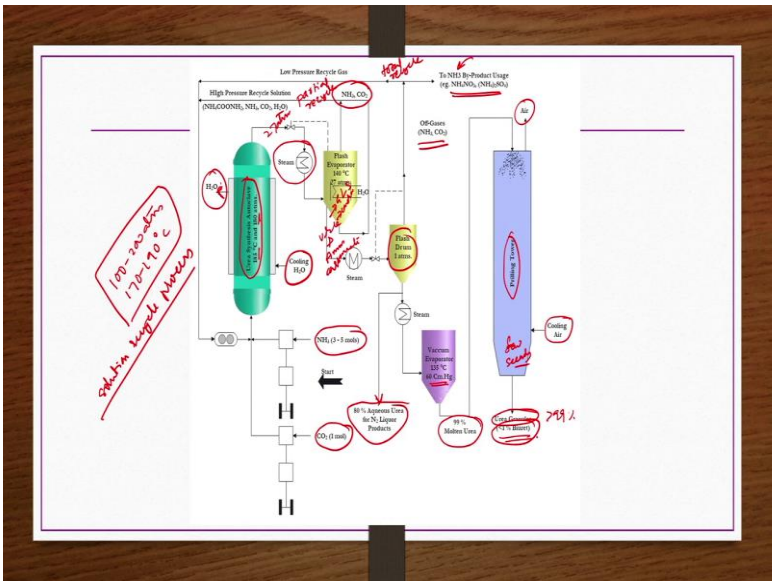

Process flow sheet if you take 1 mole of CO 2 and then 3 to 5 moles of ammonia they are individually compressed. They are individually compressed to the required pressure of the reaction and then sent to urea synthesis autoclave. Here the temperature is 185 degree centigrade and pressure is 180 atmosphere is mentioned. Though process may occur reaction may occur between 100 to 200 atmospheres and then temperature 170 to 190 degree centigrade right.

But specifically we have written because this method is also known as the solution recycle process. So, specific to this process these are the conditions to be specified ok. So, individually compressed to CO 2 and then ammonia are sent to the autoclave reactor where 185 degrees centigrade temperature and 180 atmosphere are being maintained.

So, here the reaction takes place and ammonium carbonate forms. There would be unreacted NH 3 CO 2 as well because we know that conversion is less here less than 50 percent. And then there is a water formation also there ok. All these gases are forming here. So, they are in you know when this reaction takes place what happens? Lot of heat is being liberated because of exothermic nature of the reaction.

Thus, water cooling is being maintained for this autoclave reactor. You circulate cooling water so that the you know temperature does not shoot up. You do not want temperature to go beyond 190 or 185 degrees centigrade because, we are going to see the process as per the researchers other you know experimental observations.

When the temperatures crosses beyond 180, 190 degree centigrade the urea production rate sharply falls down that you do not want. That is the reason temperature must be properly controlled in this process ok. So, whatever these components that are formed because of the this reaction that is ammonium carbonate unreacted NH 3, unreacted CO 2 and then water etcetera.

Their pressure is reduced to the 27 atmosphere and then sent to a flash evaporator. Actually they are at 180 atmosphere. So, then when you reduce the pressure to 27 atmosphere there is a possibility of a steam requirement ok that is given here fine. So, these liquid solutions including ammonium carbonate, ammonia, CO 2, water that liquid solution whatever is there that is sent to the flash evaporator which is having a gas liquid separator.

This is having gas liquid separator as well as a condenser provision in this one right. So, this ammonium then CO 2 solution will be collected from the flash evaporator and then recycled at high pressure as partial recycle option as partial recycle option. This is what terminology partial recycle that we are used in the quantitative requirements right. So, whatever the urea along with the ammonium carbamate is there urea and ammonium carbamate solution are there.

That we take to the flash drum in which further decomposition of ammonium carbamate takes place right and then you get approximately 80 percent of aqueous urea. So, that you can take as it is as a product and then whatever the off gases unreacted NH 3 CO 2 gases are there they will be taken as a low pressure recycle gas which is known as the total recycle option as per the terminology that we have taken or what you can do this ammonia you can take.

And then use for the chemical fertilizer production such as ammonium nitrate, ammonium sulfate production for that purpose you can use it. Let us say aqueous urea solution whatever you got 80 percent if that is not of your requirement sufficient purity is not there you further purify it then what you do you can take this one to vacuum evaporator at 135 degrees centigrade and 600 mmHg at this vacuum pressure and then 135 degree centigrade. The purity increases to 99 percent molten urea right.

99 percent pure molten urea is taken here, if you want in molten form you can collect it as otherwise if you want in granular form you can take this to prilling tower right; where this molten urea is spread from the top as a droplets and then from the bottom cooling air is provided. So, this drops of molten urea and then cooling air contact each other in a counter current manner and they form urea granules that collected from the bottom whether the clean air is going from the top.

So, this urea is having more than 99 percent purity and then less than 1 percent biuret. Because this has to be very less. Otherwise it is going to be toxic to the plants ok. How you make sure this one? So, whatever this process that is occurring that has to occur just about the melting point of a urea and then the contact term has to be few seconds few seconds only. Then only production of a biuret can be reduced.

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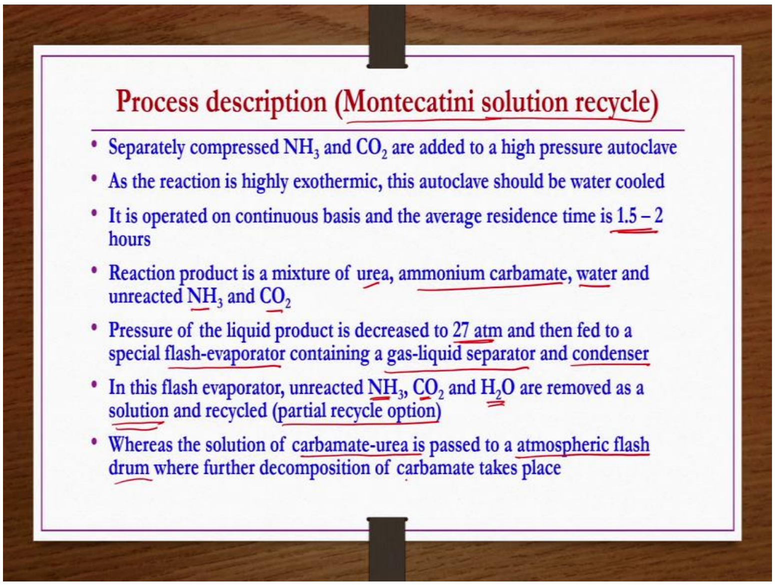

Process description (Montecatini solution recycle)

- Separately compressed NH_3 and CO_2 are added to a high pressure autoclave
- As the reaction is highly exothermic, this autoclave should be water cooled
- It is operated on continuous basis and the average residence time is 1.5 – 2 hours
- Reaction product is a mixture of urea, ammonium carbamate, water and unreacted NH_3 and CO_2
- Pressure of the liquid product is decreased to 27 atm and then fed to a special flash-evaporator containing a gas-liquid separator and condenser
- In this flash evaporator, unreacted NH_3, CO_2 and H_2O are removed as a solution and recycled (partial recycle option)
- Whereas the solution of carbamate-urea is passed to a atmospheric flash drum where further decomposition of carbamate takes place

So, this is about the flowchart. The same thing is described here as I mentioned this is known as the solution recycle process which is also known as the Montecatini solution recycle process. Separately compressed ammonium CO 2 are added to a high pressure autoclave. As the reaction is highly exothermic this autoclave should be water cooled.

It is operated at continuous basis and average residence time within the autoclave is 1.5 to 2 hours. Reaction product is a mixture of urea, ammonium carbamate, water and unreacted ammonium CO 2. Pressure of the liquid product is decreased to 27 atmosphere and then fed to a special flash evaporator which is also containing gas liquid separator and a condenser.

In this flash evaporator, unreacted ammonia CO 2 and then water are removed as a solution and recycle which is a partial recycle option. Whereas the solution of carbamate and urea is passed to a atmospheric flash drum where further decomposition of carbamate takes place.

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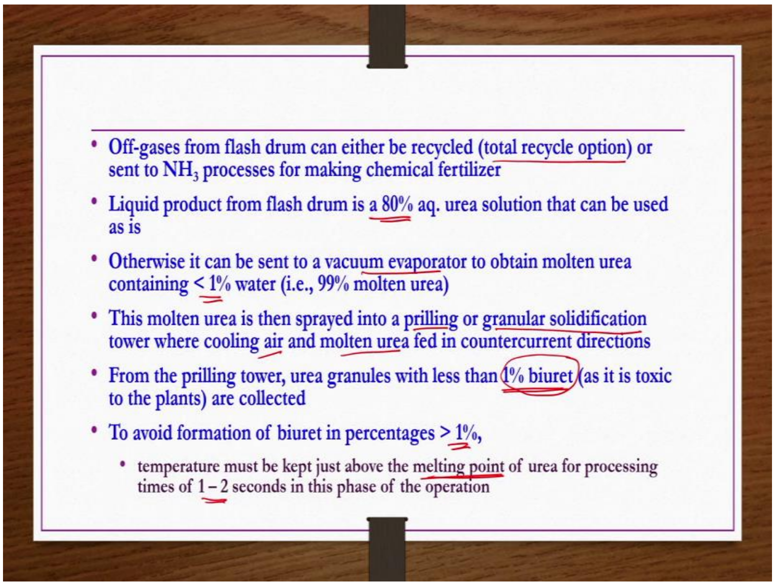

- Off-gases from flash drum can either be recycled (total recycle option) or sent to NH_3 processes for making chemical fertilizer
- Liquid product from flash drum is a 80% aq. urea solution that can be used as is
- Otherwise it can be sent to a vacuum evaporator to obtain molten urea containing < 1% water (i.e., 99% molten urea)
- This molten urea is then sprayed into a prilling or granular solidification tower where cooling air and molten urea fed in countercurrent directions
- From the prilling tower, urea granules with less than 1% biuret (as it is toxic to the plants) are collected
- To avoid formation of biuret in percentages > 1%,
  - temperature must be kept just above the melting point of urea for processing times of 1 – 2 seconds in this phase of the operation

And off gases from the flash drum can either be recycled as total recycle option or sent to ammonia processes for making chemical fertilizers like ammonium sulphate, ammonium nitrate etcetera. Liquid product from flash drum is 80 percent aqueous urea solution that can be used as it is or it can be sent to a vacuum evaporator to obtain molten urea containing less than 1 percent water that is 99 percent molten urea.

This molten urea is then sprayed into a prilling or granular solidification tower where cooling air and molten urea fed in a counter current directions. From the prilling tower urea granules with less than 1 percent biuret are collected. Because this is nothing but when two molecules of ammonia joining together then only it is forming.

So, whatever this formation is there that is possible in the prilling tower only ok. So, in order to avoid the formation of biuret in percentages of more than 1 percent, temperature must be kept just above the melting point of urea for processing times of 1, 2, 2 seconds only in this phase of the operation.

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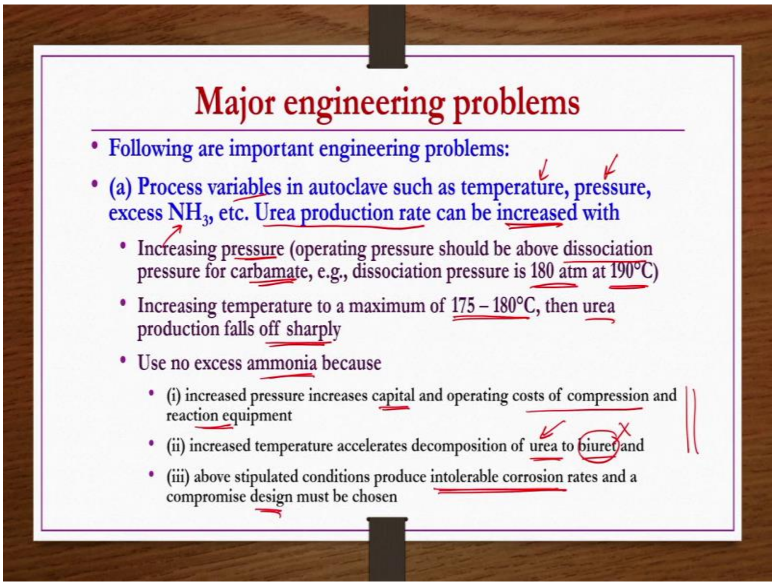

Major engineering problems

- Following are important engineering problems:
- (a) Process variables in autoclave such as temperature, pressure, excess NH_3, etc. Urea production rate can be increased with
  - Increasing pressure (operating pressure should be above dissociation pressure for carbamate, e.g., dissociation pressure is 180 atm at 190°C)
  - Increasing temperature to a maximum of 175 – 180°C, then urea production falls off sharply
  - Use no excess ammonia because
    - (i) increased pressure increases capital and operating costs of compression and reaction equipment
    - (ii) increased temperature accelerates decomposition of urea to biuret and
    - (iii) above stipulated conditions produce intolerable corrosion rates and a compromise design must be chosen

If you see the major engineering problems, there are several engineering problems. Actually, engineering problems in the sense options are you know different kind of situations how to handle? What are the alternative those things we are going to discuss. Following our important engineering problems: The first one is process variables in autoclave such as temperature, pressure and then excess ammonia.

How should it be? Should they be is it better if you increase or decrease those kind of details we are going to see. So, urea production rate can be increased by increasing the pressure. Operating pressure should be above the dissociation pressure of carbamate. Because dissociation pressure depends on the temperature at which temperature are you doing the dissociation.

Let us say if you do the dissociation at 190 degrees centigrade corresponding dissociation pressure is 180 atmosphere ok. So, if your operating temperature is 190 degree centigrade pressure should be more than 180 atmosphere. Increasing temperature to a maximum of 175 to 180 degree centigrade; otherwise, beyond this temperature is urea production falls off sharply. You cannot go beyond this temperature.

Use no excess ammonia because excess ammonia people often use in order to pick up the sensible heat of the reaction because the reaction is exothermic in the autoclave. So, for that purpose in general ammonia is used in excess, but; however, it is not recommended if you are using high pressure and then high temperature. Why? Because, increased pressure increases capital cost as well as the operating cost of compression and then reaction equipment right.

Let us say if you wanted to do this reaction at let us say 180 degrees centigrade, but the atmospheric pressure is there. So, then you can use SS316 kind of material which are not expensive at all. But the same reaction at the same temperature, but pressure is higher something like you know 100 atmospheric pressure or something like that then the construction of material that is to be used for autoclave has to be inconel.

So, that is a expensive material. Inconel material is 4 to 5 times costlier than the SS316. But here in the pressure is in the range of 180 to 200 atmosphere in such case even expensive materials may be required right. So, cost of the reaction equipment also increases. Increased temperature acts rate decomposition of urea to biuret.

So, at the higher temperature what happens 2 molecules of urea joined together to form this one; which is not good for the plants. Despite of this problem if you do not worry about the equipment cost etcetera, then if you maintain higher temperature and higher pressure what happens? You know corrosion intolerable corrosion may takes place that is the problem. So, you have to compromise on the design. There is no other option ok.

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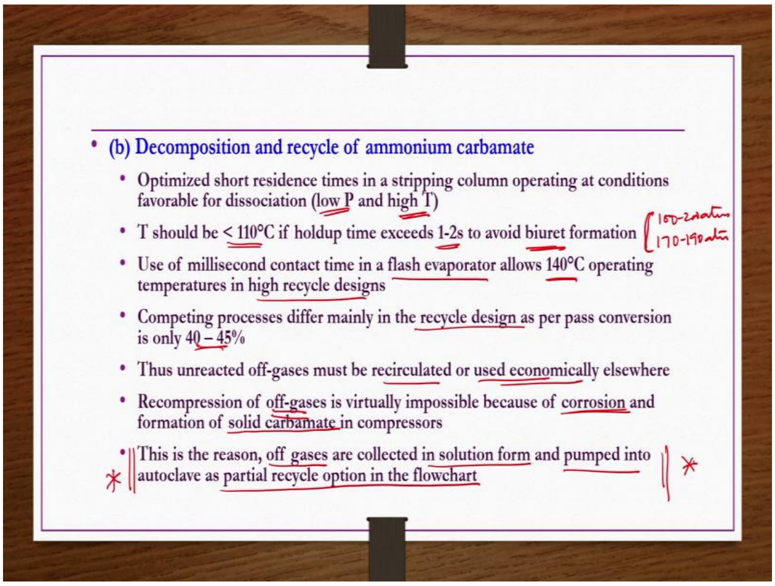

- (b) Decomposition and recycle of ammonium carbamate
  - Optimized short residence times in a stripping column operating at conditions favorable for dissociation (low P and high T)
  - T should be $\leq$ 110°C if holdup time exceeds 1-2s to avoid biuret formation
  - Use of millisecond contact time in a flash evaporator allows 140°C operating temperatures in high recycle designs
  - Competing processes differ mainly in the recycle design as per pass conversion is only 40 – 45%
  - Thus unreacted off-gases must be recirculated or used economically elsewhere
  - Recompression of off-gases is virtually impossible because of corrosion and formation of solid carbamate in compressors
  - This is the reason, off gases are collected in solution form and pumped into autoclave as partial recycle option in the flowchart

100-200 atm
170-190 atm

Next one is decomposition and recycle of ammonium carbamate. How the dehydration of ammonium carbamate taking place? How the unreacted ammonium CO 2 are being recycled? These are very important parameters in urea production plant. If you are able to handle this thing efficiently so that to make sure that entire or almost all ammonia is being consumed for the urea production so, then that plant is going to be very effective ok.

So, optimized short residence times in stripping column operating at conditions favorable for dissociation for dissociation, low pressure and then high temperatures are favorable. So, at such conditions you have to operate. Let us say if your hold up time exceeds 1 to 2 seconds then temperature should be less than 110 degree centigrade.

You cannot even imagine of 170 because in the flow sheet we have seen or in general, if the pressure is between 100 to 200 atmosphere reaction may occur between 170 to 190 atmosphere. So but in such conditions your contact time has to be very less if the hold-up time is very high then temperature you have to reduce to 110 degree centigrade. Otherwise this will form which is very toxic to the plants.

Use of millisecond contact time in flash evaporator allows temperature up to 140 degree centigrades in high recycle designs or total recycle designs. Competing process differ mainly in the recycle design as we know that per pass conversion is only 40 to 45 percent.

Thus, unreacted off gases must be recirculated or used economically. If you cannot recycle then you have to use economically. How you use? You have to neutralize this one or you have to go for production of ammonium sulphate, ammonium nitrate, kind of chemical fertilizer productions.

Why? Because, recompression of off gases is virtually not possible because of corrosion and then formation of solid carbamate in compressors actually, this carbamate has to undergo dehydration. If it is already solidified, so then dehydration may not be easy for it to produce urea. And then also if you do the re compression then corrosion is a big problem. At higher pressure corrosion is very big problem in such kind of plants. That is also one of the engineering problem that we are going to see.

So, this is the reason off gases are collected in solution form and pumped into autoclave as partial recycle option in the flow chart that we have seen. So, we are going to see in the subsequent slides there are n number of options are there. But, however, we discussed this solution recycle method because of this reason. It is a best option actually.

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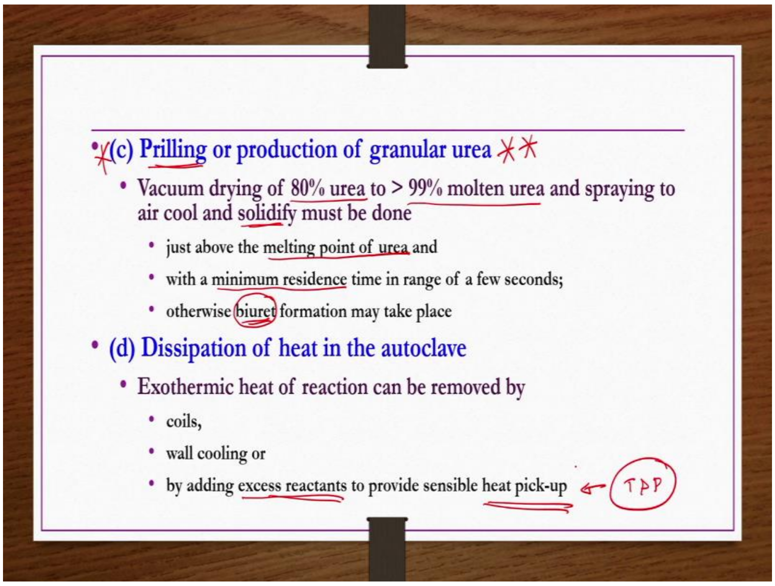

- (c) Prilling or production of granular urea **
  - Vacuum drying of 80% urea to > 99% molten urea and spraying to air cool and solidify must be done
    - just above the melting point of urea and
    - with a minimum residence time in range of a few seconds;
    - otherwise biuret formation may take place
- (d) Dissipation of heat in the autoclave
  - Exothermic heat of reaction can be removed by
    - coils,
    - wall cooling or
    - by adding excess reactants to provide sensible heat pick-up ← TPP

Another important engineering problem is prilling or production of granular urea. Vacuum drying of 80 percent urea to 99 percent or more purer molten urea and spraying to air cool and solidifying must be done. And then how it can be done? It should be done just about the melting point of urea in the prilling tower and then with a minimum residence time few seconds or fractions of seconds only in general. Otherwise, biuret formation may take place.

So, this is very important, very very essential. This is equivalent to like autoclave option. If you wanted to produce urea granules so, reaction taking place autoclave how much are they important? How much is partial recycle important? How much is total recycle option is important? Equally or even more important is this prilling or production of urea. Because, if you are not doing it effectively this will form and then that is not going to be good for the plant.

Though it is having other chemical applications a number of chemical applications and then accordingly you can use it. But however, as long as your target is urea so then this is very much important point that you should be worried about then dissipation of heat in the autoclave. We know that the reaction is exothermic and then that heat has to be removed. Why the heat has to be removed?

Because if the temperature within the reactor autoclave raises beyond the 185 190 degree centigrade what happens, the urea production falls down sharply right. So, this removal of heat can be done by coils, by wall cooling or by adding excess reactants to provide sensible heat pickup. So, if you are going for this option then you have to compromise on the temperature and pressure of reaction that you have to maintain in the autoclave.

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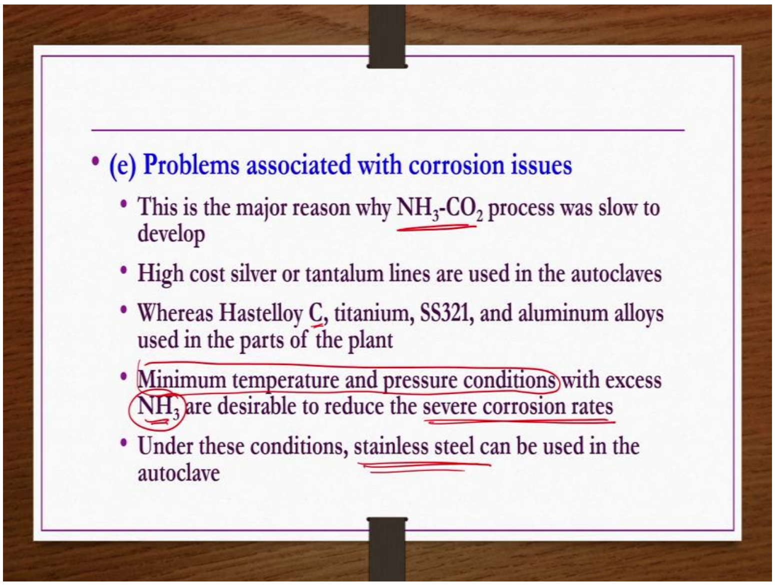

- (e) Problems associated with corrosion issues
  - This is the major reason why NH_3-CO_2 process was slow to develop
  - High cost silver or tantalum lines are used in the autoclaves
  - Whereas Hastelloy C, titanium, SS321, and aluminum alloys used in the parts of the plant
  - Minimum temperature and pressure conditions with excess NH_3 are desirable to reduce the severe corrosion rates
  - Under these conditions, stainless steel can be used in the autoclave

Problems associated with the corrosion issues. This is the major reason why NH 3 CO 2 process was slow to develop. Because, high cost silver or tantalum lines are used in the autoclaves. Whereas the Hastelloys carbon, titanium, SS321 and aluminum alloys used in the other parts of the plant. Minimum temperature and pressure conditions with excess ammonia are desirable to reduce the severe corrosion rates.

So, if your temperature pressure you are decreasing so then again your production rate is falling down right. So, again you have to take all these problems accordingly you have to optimize the condition and then operate under such optimized conditions. Under these conditions stainless steel can be used. As long as if you are using minimum temperature and pressure with excess ammonia then probably you can make autoclave using the stainless steel.

But when you use such minimum temperature and pressure conditions conversion is going to be decreasing as per one of the engineering problems that we have already discussed. So, if you cannot go for a material of construction which is of high cost as per the pressures of 100 to 200 atmospheres required in the autoclave. You can go for the stainless steel, but your temperature pressure has to be minimum and then if the temperature pressure are minimum then you have to give the excess ammonia.

So, the excess ammonia cost is increasing and then when you compromise on temperature and pressure then conversion or production rate of urea is going to decrease. So, production rate of urea is decreasing so then you have to do more number of times of you know recycle etcetera. So, again you have to take all these points into the concentration before coming to the final conclusion.

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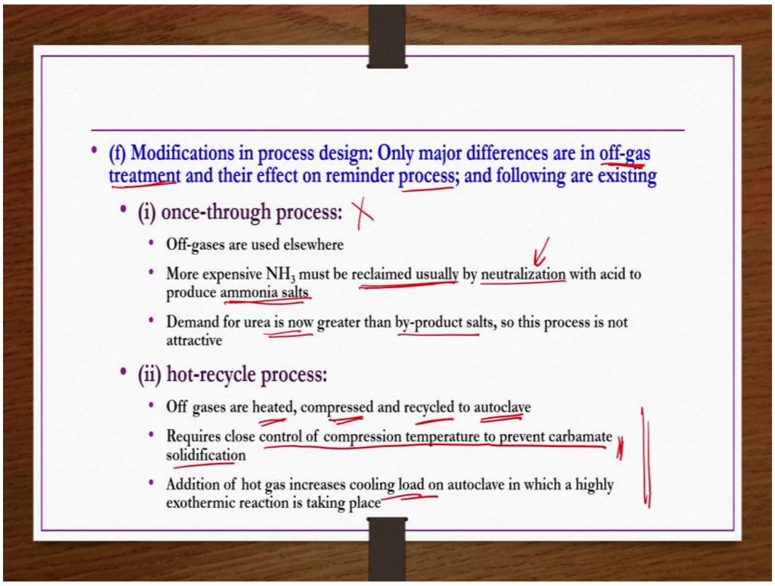

- (f) Modifications in process design: Only major differences are in off-gas treatment and their effect on reminder process; and following are existing
  - (i) once-through process:
    - Off-gases are used elsewhere
    - More expensive NH_3 must be reclaimed usually by neutralization with acid to produce ammonia salts
    - Demand for urea is now greater than by-product salts, so this process is not attractive
  - (ii) hot-recycle process:
    - Off gases are heated, compressed and recycled to autoclave
    - Requires close control of compression temperature to prevent carbamate solidification
    - Addition of hot gas increases cooling load on autoclave in which a highly exothermic reaction is taking place

Then modifications in process design. As we already discussed only major differences are in off-gas treatment how are you doing this off-gas treatment and their effect on reminder process and then following are the options. Once through process, if you do once through process only 40 to 45 percent that is less than 50 percent conversion is taking place remaining of ammonia you have to use carefully; economically you have to use ok.

Off gases are used elsewhere like in ammonium sulphate, ammonium nitrate production. But however, soon we are going to see that demand of urea is increasing because of these ammonium salts are you know very acidic they are not good for the soils. Especially where the neutralization is a problem, especially soil is itself is acidic. So, using the off gases for the production of ammonium salts etcetera is not good anyway as per the present market.

In the present market urea demand is more compared to the ammonium salts like ammonium nitrate and ammonium sulphate. So, one has to be careful about that one. More expensive ammonia because ammonia itself is one of the reactant, important reactant and it is very expensive if you are not using properly so, then your process is not going to be economically feasible.

You may not get the desired profit ok. It must be reclaimed by neutralization with acid to produce ammonium salts. You are neutralizing. So, again additional cost is there right and then ammonium salts their demand is less ok. So, it is again not going to work. Demand for urea is now greater than byproducts salts. So, this process is not attractive. So, people are not following this once through process.

Then, hot recycle process. Off gases are heated compressed and recycled to autoclave in general. Some people, some plants they do. But there are again issues with because in the autoclave exothermic reaction is taking place and then to that one if you are sending the hot off gases as a recycle then cooling load will increase. Such kind of problems would be there.

So, it requires close control of compression temperature to prevent carbamate solidification. This is also one problem; not only cooling load you know what happens if compression temperature increases? So, what happens you know carbamate solidification may take place that you do not want. Addition of hot gas increases cooling load on autoclave in which a highly exothermic reaction is already taking place. So, this is also not a viable approach anyway.

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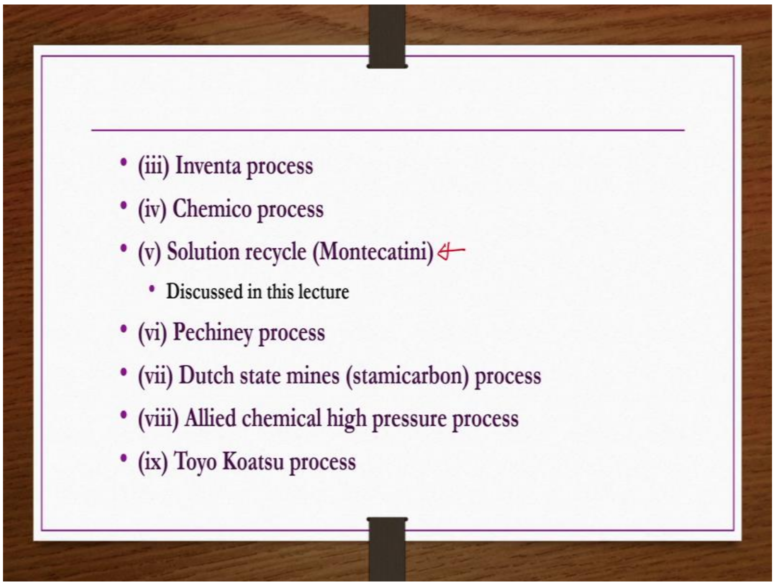

- (iii) Inventa process
- (iv) Chemico process
- (v) Solution recycle (Montecatini)
  - Discussed in this lecture
- (vi) Pechiney process
- (vii) Dutch state mines (stamicarbon) process
- (viii) Allied chemical high pressure process
- (ix) Toyo Koatsu process

Other processes like commercial processes like we are not going to discuss in general like inventa process, chemico process, solution, recycle or Montecatini process this we have already discussed. The process that today we have discussed is this one which is the best one. Pechiney process, Dutch state mines process or stamicarbon process, Allied chemical high pressure process and then Toyo Koatsu process. All these are commercial process. These are commercial names in general ok.

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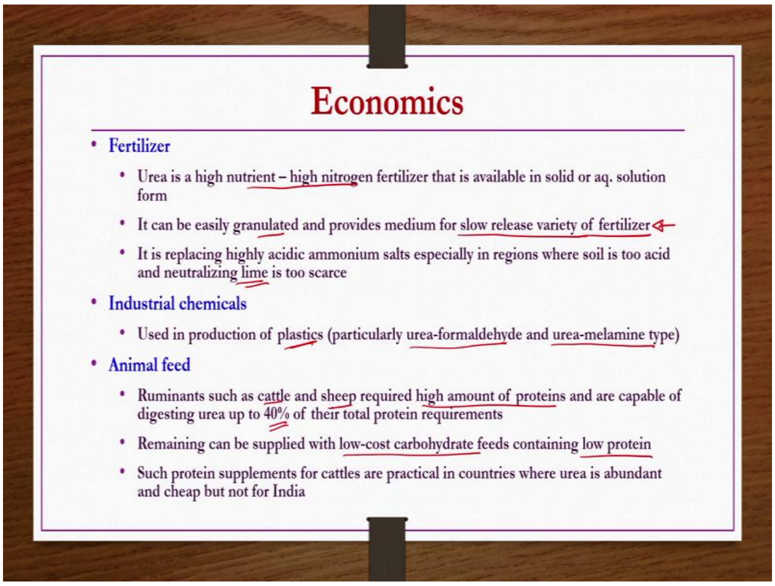

Economics

- Fertilizer
  - Urea is a high nutrient – high nitrogen fertilizer that is available in solid or aq. solution form
  - It can be easily granulated and provides medium for slow release variety of fertilizer
  - It is replacing highly acidic ammonium salts especially in regions where soil is too acid and neutralizing lime is too scarce
- Industrial chemicals
  - Used in production of plastics (particularly urea-formaldehyde and urea-melamine type)
- Animal feed
  - Ruminants such as cattle and sheep required high amount of proteins and are capable of digesting urea up to 40% of their total protein requirements
  - Remaining can be supplied with low-cost carbohydrate feeds containing low protein
  - Such protein supplements for cattles are practical in countries where urea is abundant and cheap but not for India

So, we are not going to discuss them anyway. Economics; fertilizer it is used as a fertilizer. Urea is a high nutrient, high nitrogen fertilizer that is available in solid or aqueous solution form right. It can be easily granulated and provides medium for slow release variety of fertilizer because some plants required. Its steady slow rate for longer duration fertilizer has to be supplied for that case it is really urea is a good medium. It is replacing highly acidic ammonium salts.

Especially in regions where soil is too acidic and neutralizing lime is also too scarce. Industrial chemicals production also it is used not only as a fertilizer. So, what are they used in production of plastics such as urea formaldehyde and urea melamine type etcetera. It is also used as a feed as I already mentioned. Ruminants such as cattle and sheep they have ability to digest this urea and they require high amounts of proteins.

So, 40 percent of their protein requirement can be fulfilled by feeding urea to the animals and then remaining requirement can be fulfilled by low cost carbohydrate feeds containing low proteins. However, this is good for countries where urea is abundantly available, but it is not the case for India.

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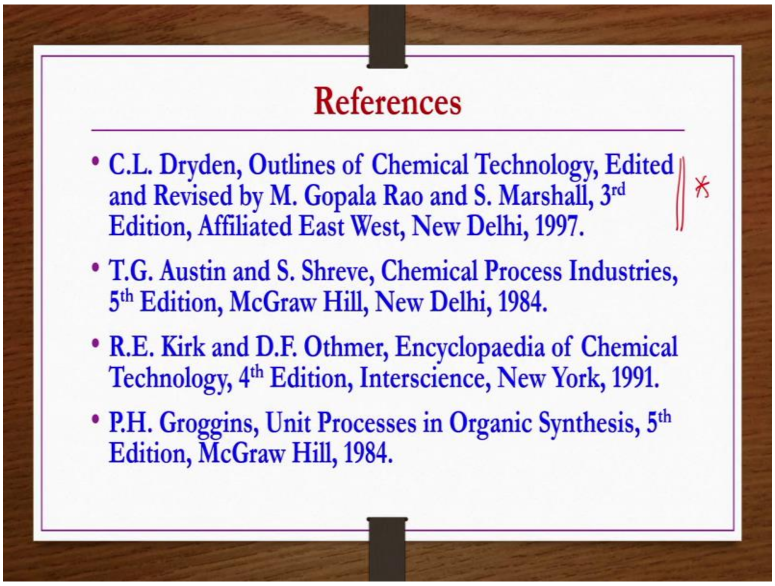

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References are provided here. This lecture is prepared from this particular reference completely.

Thank you.