Industrial Inorganic Chemistry

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Lecture - 34
Nitrogen Fertilizer and Urea

Hello. So, welcome back where we are talking about the molecule urea, and how we can use urea as the typical mineral fertilizers. And from the inorganic chemistry point of view what you should know that whatever we are giving is your nitrogen, carbon, oxygen and hydrogen to the soil.

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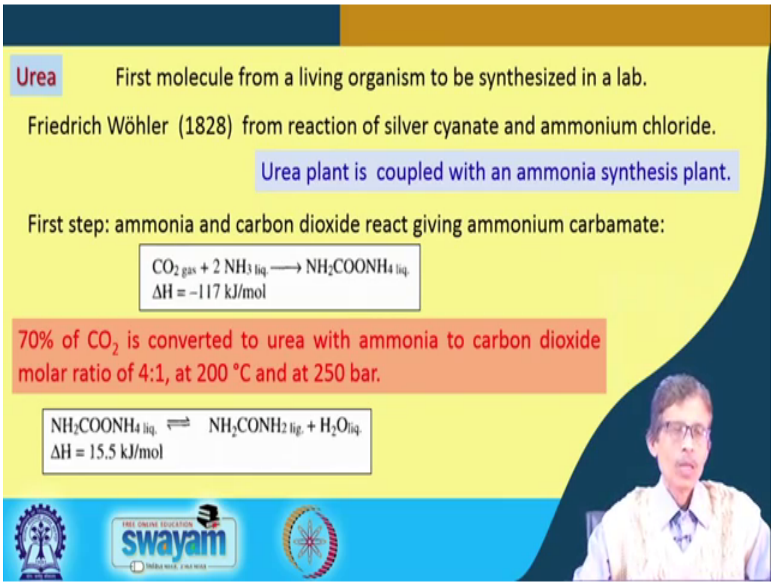

Urea First molecule from a living organism to be synthesized in a lab.

Friedrich Wöhler (1828) from reaction of silver cyanate and ammonium chloride.

Urea plant is coupled with an ammonia synthesis plant.

First step: ammonia and carbon dioxide react giving ammonium carbamate:

$CO_{2\,gas} + 2\,NH_{3\,liq.} \longrightarrow NH_2COONH_{4\,liq.}$
$\Delta H = -117$ kJ/mol

70% of CO_2 is converted to urea with ammonia to carbon dioxide molar ratio of 4:1, at 200 °C and at 250 bar.

$NH_2COONH_{4\,liq.} \rightleftharpoons NH_2CONH_{2\,liq.} + H_2O_{liq.}$
$\Delta H = 15.5$ kJ/mol

So, the molecule urea which is also historically very important, because it is the first molecule from a living organism because urea we know our body is also producing urea through the corresponding consumption of the protein molecule, decomposition of the protein molecule as we all know. The protein is the big (Refer Time: 00:59) molecule out of the small building materials of amino acids.

So, amino acids are nothing but NH 2 CH 2 is the smallest one the glycine, NH 2 CH 2 COH. So, all these you have the nitrogen, hydrogen, carbon and oxygen. So, nitrogen, hydrogen, carbon, oxygen containing molecule, we also produce. So, we also have the urea from our body. So, when people got it as the first molecule what we can have whether we are able to synthesize in the laboratory. So, people are excited that time long back when it was first synthesized in the laboratory which is in 1828. So, it is close to say basically two thousand 200 years.

So, these 200 years of history is going to because is tell us that Friedrich Wohler in Berlin in Germany. So, he was trying to get it basically from a reaction of metathesis. The reaction he was being carried out is one is your silver cyanide, and another is your ammonium chloride.

Why you was doing that particular reaction because his intention was very clear that he knows and the common knowledge or the prevailing knowledge at that time was that that if you try to react silver ion Ag plus with Cl minus we all know that form a saturated level or because the silver chloride form as a low solubility, because your KSP value the solubility product value is also very less. So, silvers from silver cyanide will react with the chloride of ammonium chloride giving a silver chloride precipitate and what else.

So, he was trying to make basically the synthesis of ammonium cyanide, ammonium is the cationic part of ammonium chloride, and cyanide is the anionic part of silver cyanide. So, he was basically looking to make, he was trying to make ammonium cyanide. So, if he was able to make ammonium cyanide, but to his outer surprised he found that is not a typical ammonium cyanide molecule, but it is something else that gave the birth of urea. So, some transformation will take place. And if that particular time the person or the laboratory available material or is perception basically tells that, that it is not a cyanide molecule, something or some rearrangement has occurred.

And the character of the typical cyanide because cyanide the silver cyanide can be obtained from sodium cyanide is known the character of this thing is known. And the character of the ammonium part of the ammonium chloride was also known that time. So, that particular compound what is obtained in their hand is not having ammonium part as well as cyanide parts. So, it has lost its character in terms of its ammonium part or its cyanide part. So, it is something the rearrange part what is obtained is nothing but your urea. so that is the discovery of urea.

So, urea plant basically nowadays large number of urea plants we have throughout all the different types of advanced countries, even in our country also. So, what we should have because we now know that it is the corresponding ingredient is your ammonia. So, ammonia synthesis will be largely dependent on your urea plant. So, if the industry is interested to plant or industrially produce ammonia, they will have the urea also.

So, side by side they can have two plants where ammonia is being produced, and another part this ammonia is being consumed for urea production. So, what should be the first step following that Wohler's technique or the Wohler's reaction in test tube basically in laboratory what he has done if you go for a little bit of higher scale, we go beyond test tube to your round bottom flask, round bottom flask of different size starting from 50 to 525 litres. So, the first step of that particular exploration is that ammonia and carbon dioxide is reacting so not that through that silver process. So, direct ammonia and carbon dioxide is reacting giving you ammonium carbamate.

So, it is basically simply the carbamate formation the way we know that it confirm the different types of carbamates of organic molecules also. So, CO 2 as a gas, NH 3 as a like ammonia or liquid form giving you a NH 2 COONH 4 that means the ammonium salt of a NH 2 CO and the corresponding exothermicity of the reaction is known the amount of heat liberated from that particular reaction is known.

So, when we do this reaction, so how much we can convert from left to right, because all these reactions are reversible in nature so, the reaction what we take it 70 percent of the carbon dioxide because that is also very useful technique where you can reduce the amount of carbon dioxide from the environment, because this is also a headache, it is a greenhouse gas, carbon dioxide is a greenhouse gas.

So, it is required for our temperature rise of the globe, and also it is not helpful to increase the carbon dioxide in the atmosphere. So, if we are able to consume more and more of carbon dioxide, it is always be helpful for the environment. So, directly that CO 2 will be converted to urea, and ammonia is only the starting material or the required material for its conversion. And this particular one that the ratio of ammonia to carbon dioxide ratio, molar ratio is 4 is to 1.

So, more amount of ammonia will be required. So, you see that the reactions stoichiometry is 2 is to 1, but we are adding a are going for a reaction which is 4 is to 1. So, excess amount of ammonia should be there. And that excess amount of ammonia should be recycled; we should not lose that amount of NH 3. So, the mass action basically will tell you that if we are able to increase the corresponding ammonia concentration or the pressure of the ammonia, because that is the only index of increasing the concentration of ammonia at a high temperature of 200 degree centigrade, pressure is also higher which is 250 bar.

So, at high pressure and high temperature reaction, this reaction is forming that we all know that how we make the ammonia through another very difficult process which is the (Refer Time: 08:00) process of ammonia synthesis from the elemental thing that means, the nitrogen or the hydrogen that we have already seen earlier. So, this particular process we can have. So, this particular reaction basically that give you that corresponding decomposition, it is a reversible one. So, once you make this ammonium carbamate, so ammonium carbamate in the liquid form basically. So, this is also a liquid urea, urea in the liquid form this is q. So, this will be the liquid form, and water is also again in the liquid form. And this is little bit of endothermic reaction of 15.5 kilo joule mole inverse.

So, now this gives us the whole story that how ammonium carbamate is reorganized or decomposition. So, basically we are following a decomposition reaction of ammonium carbamate with the liberation of water molecule. So, water you have to take out.

So, one molecule of water if you are able to take out from that particular inorganic salt, you are happy to get a compound which is your urea and that urea basically if I demand it, it should be a inorganic compound. It can be the origin from the living organisms, but it is basically inorganic compound, because it is produced from a particular inorganic salt and its all other implications are similar to that of your ammonia or carbon dioxide.

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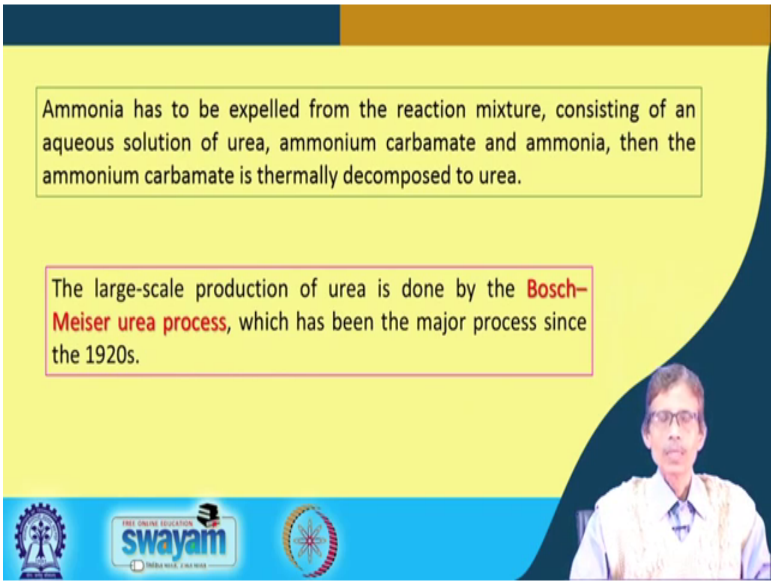

Ammonia has to be expelled from the reaction mixture, consisting of an aqueous solution of urea, ammonium carbamate and ammonia, then the ammonium carbamate is thermally decomposed to urea.

The large-scale production of urea is done by the Bosch–Meiser urea process, which has been the major process since the 1920s.

So, making this thing is also from the reaction mixture. So, the excess amount of ammonia what is happening there. So, since the mole ratio is high or the molar ratio of 4 is to 1 is giving you a reaction where you have extra ammonia there. So, the excess ammonia has to be removed from the reaction medium, and you can have a aqueous solution of urea, ammonium carbamate as well as ammonia. So, all these are there and selectively you have to crystallize urea from that medium.

And whatever ammonium carbamate is produced which will undergo thermal decomposition. So, simply heating of that ammonium carbamate will give you urea. So, the heating process will also be responsible for your basically the thermal gravimetric degradation product of urea that because it is losing one of the water molecule.

So, nowadays if experiment is given to the students in the laboratory that you go for a thermal gravimetric estimation or gravimetric estimation of urea, what will you do, we will just simply go for is corresponding thermal degradation of ammonium carbamate will find a very distinct loss due to the removal of a water molecule at a particular temperature where water is removed which will be beyond 100 degree centigrade is not that of water of crystallization or the water kept in the material.

So, we can have huge amount of production or large scale production basically because the most of the country are producing huge amount of urea because urea has a huge demand in different industrial sectors. So, one of the particular process is the Bosch-

Meiser urea process. Bosch is the name will immediately tell you it is from the German origin. So, the people you see that it was first prepared in Berlin Friedrich Wohler did it in 1828. But you see it took around 92 years to produce industrially the large amount of urea by this particular process, and it was the major process basically since 1920s for urea production through this particular process.

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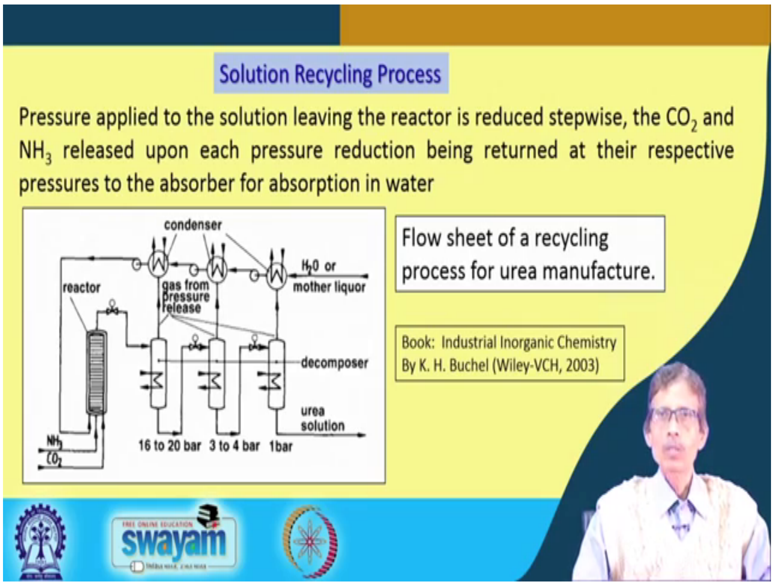

Solution Recycling Process

Pressure applied to the solution leaving the reactor is reduced stepwise, the CO_2 and NH_3 released upon each pressure reduction being returned at their respective pressures to the absorber for absorption in water

Flow sheet of a recycling process for urea manufacture.

Book: Industrial Inorganic Chemistry By K. H. Buchel (Wiley-VCH, 2003)

So, what we can have now that if you go for a technique where you have the solution technique. So, solution process, the reactors and everything is handling in solution. And the excess amount of one of the reactant is your NH 3, NH 3 is a gas. So, gas is coming out from the solution medium, and that we have to recycle. So, it should be known as the solution recycling process. The solution recycling process will now tell us how the corresponding excess amount of ammonia can be utilized since the reaction is a high temperature high pressure reaction. So, you have the pressure which we are applying on the solution, and the pressure applied to the solution living the reactor is reduced stepwise.

So, you have the pressure inside the reactor, but when it is leaving the reactor you have less pressure because the, it is released from the particular reactor. So, the carbon dioxide and ammonia released from that particular reactor if some unreacted carbon dioxide basically, and more amount of ammonia because NH 3 we are giving or you are using more. So, upon each pressure reduction steps, so you several pressure reduction step. If we are starting from say 100 bar or 50 bar of pressure, we just step wise we are reducing one after another, and returned at their respective places to the absorber for absorption in water.

So, ammonia can be observed in water or CO 2 can also be absorbed in the water, after you have reduce the pressure sufficiently. So, the flow chart or the diagram what we can the basically a line diagram or the line drawing what you can consider because you just have the orientations basically because you must have a little bit of this thing in your mind that where you can have your handling a (Refer Time: 13:51) difficult thing of industry people are mostly handling all three together because they always expect also the solid product, but they are also using handling the gas they can have the industrial gas production also.

We are having huge number of industrial sectors the government sectors also those who are handling gases starting from your natural gases to any another specialty gases also we have GAIL, we have Gas Authority of India Limited in our country.

So, all these things, so what we can have since ammonia and carbon dioxide now you can have compared to our several previous techniques what we have seen making of ammonium sulphate, and all these thing that is this acid you are putting from the top and gas from the bottom. But here we are putting both NH 3 and CO 2 from the bottom of the reactor because both of them are of gaseous origin.

So, during the reactions where this is basically the valve, you have the meter, the corresponding flow meter, And you know the internal pressure of the gas because all you should monitor the that particular chamber, the reaction chamber, the internal pressure the pressure should not build up such that you there can be explosion. So, that is you have and then it is going from. So, you can get it that one.

So, these two arrows basically these two arrow heads basically pointing out that introduction of NH 3 and CO 2 to this particular reactor, and then it is going to the three other chambers of three different places one is form 16 to 20 bar pressure within the chamber, another is 3 to 4 bar, and last is only 1 bar. So, all these things are moving and that moment basically going through this arrowhead, then this, then to this, then this, this, this, this, and then it goes basically because all these three (Refer Time: 15:46) basically the corresponding decomposer for the decomposition of your ammonium carbamate.

So, we are having now the corresponding urea solution. So, this particular solution when it is leaving this particular chamber, you have water externally you can put more mother liquor, and the ammonia as well as the carbon dioxide which is then again condensed because you release the pressure that will be aerifiction the dilute gases is there. So, it is again be compressed. So, as you are reducing the pressure in this three chambers, you can have also three different compresses. So, condensers we call. So, condensers, so this basically can give us directly from this particular heads; that means, the from the top then this will also release gas this will also release gas, and this is also release the gas from the pressure release.

So, since we are reducing the pressure compared to the original chamber, so pressure release will give take out that particular gas in this particular port, and this one, this one are solved three together can condense the gas molecules, and then again it can be inserted again to the reaction chamber. So, that is the typical recycling process. So, that is why the process is known as solution recycling process.

So, only thing that you should keep in your mind that how the whole procedure is following, and how that particular process is falling for a recycling process. And if we can have a recycling process, we will be not losing any amount of those material that material loss is minimized. So, your production cost would be less, and so we can have huge profit out of this particular industrial procedure. So, that chart or the diagram what is given is nothing but your flow sheet for a recycling process for urea manufacture.

When you go for urea manufacturing is should be able to identify the flowchart also if the flowchart is only given to you, you should be able to identify it in terms of that it is the recycling process for urea manufacture. So, if the diagram is given, we will be given four options for a multiple choice type of questions that we can always considered, otherwise we do not have any other options or you can draw it, we can write it, level it all these diagrams, this flow chart.

So, remember that nicely in that you should able to identify or name the corresponding procedure for your urea manufacturing process. And everything what we following the entire course as been designed basically on this particular single book, so basically it is the Industrial Inorganic Chemistry again from Wiley-VCH and again from the German origin, because that is the only country which is most important from the discovery to the industrial production of the chemicals particularly the inorganic chemicals.

So, that is the country. So, most of the time we are simply follow this particular book, we are taking we are in dated to that particular book also, because all the diagrams are also taken from that particular book. So, if we have this particular book also you can also follow nicely the thing what I am being taught here for in a stepwise manner.

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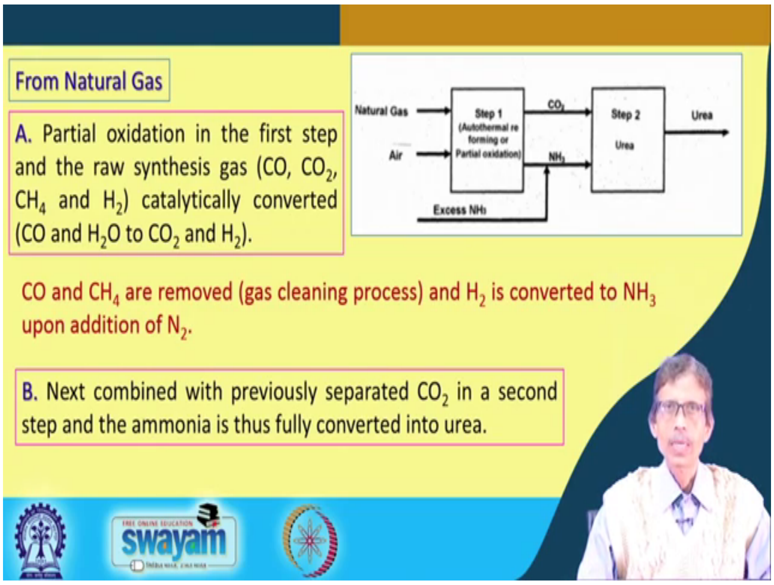
From Natural Gas

A. Partial oxidation in the first step and the raw synthesis gas (CO, CO_2, CH_4 and H_2) catalytically converted (CO and H_2O to CO_2 and H_2).

CO and CH_4 are removed (gas cleaning process) and H_2 is converted to NH_3 upon addition of N_2.

B. Next combined with previously separated CO_2 in a second step and the ammonia is thus fully converted into urea.

So, urea now will just go for from natural gas sources. So, the natural gases which we all know that is basically the methane. And liquefied natural gases are we have which is known as LNG not LPG, it is LNG because this part of the country the eastern part of the country do not have that much source of natural gases compared to the western part of our country, where you have the Bombay-high, the Bombay offshore, they are producing huge amount of natural gases, but they are now put processing.

And all these things now they are bringing all these natural gases in the port of this eastern side by different companies, they are also bringing for our domestic use for automobile use, and lastly for the manufacture of this important compound like the fertilizer like urea, because this natural gas of the methane can also be a source from the shell gas. So, shell gas if the cell gas activity by the geology start increasing, so shell gas production is also increasing because smaller small companies from western part is coming to this eastern part of our country is also devoted to that particular shell gas for the manufacture of urea or any other nitrogen base fertilizer.

So, what basically we can have because the challenge you should think of from academic point of view because basically first you consider from this academic point of view the feasibility of the reaction, then the process development, the industrial challenges and all these things will come afterwards. So, the first thing what we can do is that you have the natural gas. So, natural gas is mostly the hydrocarbon based on methane. So, we go for partial oxidation. So, if you have a hydrocarbon containing carbon and hydrogen, and you try to oxidize it, what can happen.

So, originally you can have methane. So, CH_4 will be there. So, we get basically raw is not a very pure form. So, is a raw synthesis gas will obtain through that particular partial oxidation, and its mixture of the original compound of this gas that means, the methane along with carbon monoxide and carbon dioxide, and some amount of hydrogen also, some amount of hydrogen will also be there, because we all know that the oxidation of water as another source of getting the synthesis gas will also give you a mixture of this hydrogen and oxygen and all other things like that carbon, when it is dropping on the coke that will giving a carbon dioxide and carbon monoxide.

But what we can do that synthesis gas will be treated catalytically now, and we try to get the conversion of the whole thing that means, what we do not want; that means, the water. As I told you that the reduction of water or the breaking down of water on the heated coke giving you hydrogen and oxygen and that oxygen can be consumed for giving you carbon monoxide and carbon dioxide if the carbon is available for in the form of a red heat coke, but in this particular case your carbon is available in the form of two oxides that means carbon monoxide and carbon dioxide.

So, that carbon monoxide and carbon dioxide whatever available, still they are, but we go for the oxidation of carbon monoxide to carbon dioxide, and at the same time H_2O will be converted to H_2. So, that is the most important part of all these reactions that you have to have methane then CO_2 and H_2O in that particular thing. So, like a block diagram, block flowchart, you have two boxes only instead of drawing in a full form of the reactors.

So, we will feed this particular chamber with natural gas along with water because this sorry air, because this air, why we are feeding air over there because the air will be given for your oxidation because here we are using this particular one for oxidation. So, the step one is nothing but is auto thermal reforming or partial oxidation we call it as a partial oxidation you see here witness partial oxidation, because we are not going for exhaustive oxidation which is also known as auto thermal reforming of the gases you have there. So, we get CO 2 as well as ammonia because ammonia will be feeding over there. So, ammonia we have to bring from somewhere else.

So, this chamber will only give us carbon dioxide and hydrogen if it is available, because this hydrogen will be the most useful one if we are able to get it from natural gas source, the shell gas source or any other source of it, because that hydrogen will be combined with the nitrogen of the atmosphere. So, atmospheric nitrogen will now react because this are the raw material for the production of NH 3 through have a process. Two gases nitrogen and hydrogen will combined to give you the ammonia.

So, the excess amount of ammonia which is being introduced over here. So, these two again we have again two gaseous thing that means the way we get ammonia from the combination of nitrogen and hydrogen. One is very cheaply available from atmosphere, and another only you have to bring hydrogen is giving you the corresponding ammonia production, and that ammonia production again through the use of carbon dioxide which is again the source of atmosphere. So, atmosphere can give us amount carbon dioxide, but that carbon dioxide is not highly concentrated, so that is why you have rely on synthesis gas.

This two will give you for your step 2 that means step 2 already we have seen the reactor thing and all these things. So, we will couple this for the step 2 parts. So, the previous flow chart for the diagram the flow sheet will be attached over here to make you more and more amount of urea. Thing is that you have starting material of the starting thing is your natural gas.

So, the feed basically in this particular point the CO and CH 4 which are there. So, already you have CO and CH 4, so can be removed because we do not need this two for your urea production. So, we have a step what is known now as the gas cleaning process or gas cleaning step we are cleaning some part of the gas. So, those gases the carbon monoxide and methane are driven away only hydrogen is taken care of. So, hydrogen is now converted to ammonia upon addition of dinitrogen. So, N 2 will be the reused for your useful production of NH 3, so that useful production of NH 3 will now take you to that step 2 which is your step number 2 which is this step. So, this step will then you have very simple one we combine with previous is separated CO 2 because CO 2 was separated earlier. So, there is no need to bring CO 2 because CO 2 was already there in your natural gas in your synthesis gas.

So, only thing that your separation of CO 2 earlier solves that this CO 2 should not go out along with your carbon monoxide, it should be preserved or it should be kept for only reaction with NH 3, so that only reaction with NH 3 will tell us that the use of that particular CO 2, what was originally available should be consumed for your urea production.

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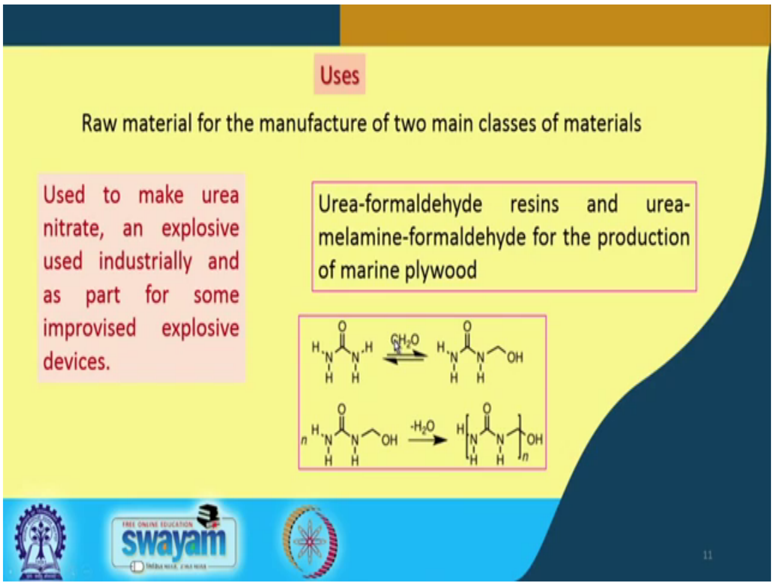

Uses

Raw material for the manufacture of two main classes of materials

Used to make urea nitrate, an explosive used industrially and as part for some improvised explosive devices.

Urea-formaldehyde resins and urea-melamine-formaldehyde for the production of marine plywood

Then we will see we will just quickly see how these are very important areas of application of urea. So, raw material it is basically a raw material for the production and manufacture of two main classes of material one is nothing but it is very simple compound which we call as urea nitrate. So, urea we have 3 NH 2 and like your ammonia, ammonia is giving you the ammonium type of thing addition of one more proton on the nitrogen. Similarly, urea can take up extra hydrogen to make it urea. So, cation so di cationic form so which can take off the nitrate as your corresponding explosive like your ammonium nitrate.

So, this can also be utilized for some improvised explosive devices for blast making some expedition physiological expedition in all these things we require all is research and development quality explosives the RDX as so we all know. So, regular improvement of all these RDX are there. So, urea can one of the component in terms of your urea nitrate. Then the urea formaldehyde resin and the urea melamine formaldehyde resins are also there for the production of plywood which is used for the marine water or the sea water. So, is a marine type of plywood, so which will also resistant to the material what is present in your sea water, but it is much more corrosive than that of pure water system.

So, urea is taken out with formaldehyde for the polymerization resin making urea is one of the component. Then you can have along with your melamine, melamine is again a nitrogen base cyclic molecule. So, melamine along with formaldehyde, so it is a three component resin have some improved quality, so that improve quality of that urea melamine formaldehyde is utilized for making this. So, how this particular one is reacting, so the urea formaldehyde structure you should know little bit of this particular structure.

So, again in the next class, we will start from here basically. So, we will not follow the other part. So, the other part will follow with complete over here these particular things. So, the formation of these urea and with that of your formaldehyde giving you the corresponding one this NH 2 will be convert it to NH CH 2, so that is the most useful reaction of any nitrogen based compound, any phenol based compound with that of your formaldehyde.

So, once you get this particular introduction of your alcohol part along with your NH part, so this will be a very highly reactive parts, so is this a this amine alcohol. So, the amine alcohol part starting from this is very reactive one. So, n number of such amine alcohol part will be then polymerized to give you the corresponding resin part which is after curing give you a very solid product and that solid product is also chemically resistant.

And there are lots of application because the resin application will follow after wards and will just categorize this in terms of the resin use, and resin making of all this things and that is concentrated on resin making only. But here we are talking in terms of only the use of urea. So, next day we will complete the urea use other part, and will follow that one ok.

So, thank you very much.