

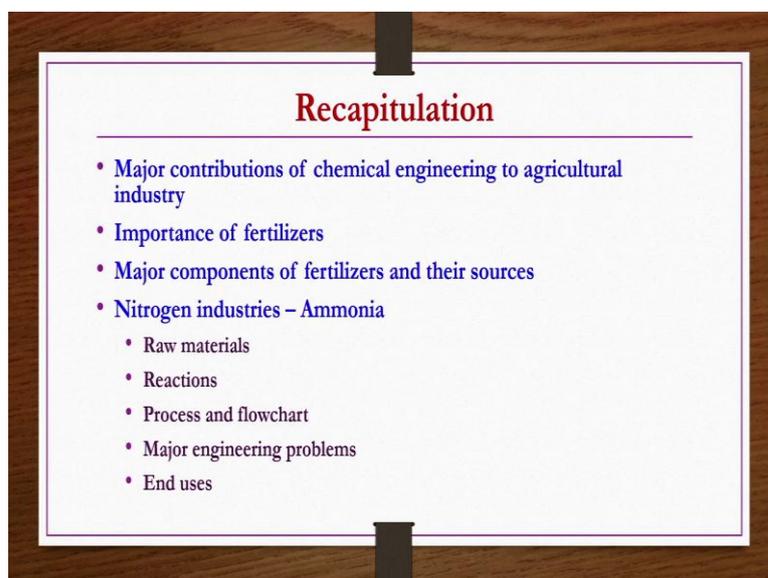
Inorganic Chemical Technology
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Lecture - 15
Nitrogen Industries - Nitric Acid

Welcome to the MOOCs course Inorganic Chemical Technology. The title of today's lecture is Nitrogen Industries - Nitric Acid. We will have a recapitulation of previous class before going into the details of today's class. In the previous lecture we started about fertilizer industries, where we started about nitrogen industries and then discussed about ammonia production.

However, before going into the details of ammonia production what we have done, we have done why are we studying about the fertilizer industries or manufacturing of fertilizers, what are the contributions that chemical engineering is giving to the agriculture industry. So, that the agricultural industry can become productive those kind of things we have seen. So, we started listing a few major contributions of chemical engineering to agriculture industry.

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Where we have seen that fertilizers, pesticides and then several types of unit operations such as drying etcetera are very essential contribution that chemical engineering has given to the agricultural industry. Thus it is very much essential for us, chemical

engineering students to understand about the manufacturing process of different types of fertilizers and pesticides, right.

So, that is the reason we started with the fertilizers. Then we have seen why the fertilizers are important, why not can we expect this you know major components of fertilizers like nitrogen, phosphorus and potassium naturally, what are the reasons etcetera, those things we have seen.

Then we have seen sources of fertilizers, then we started discussing about the nitrogen industries or nitrogenous fertilizers production that is what we started with, we started with ammonia, we started with its raw materials, associated reactions, process and flowchart, major engineering problems and end uses of the ammonia. Those details we have seen in the previous lecture.

In the today's lecture we are going to discuss about the nitric acid. So, before going to the production and then engineering problems of nitric acid production plants etcetera. What we do? We start with its pertinent properties.

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Nitric Acid (HNO₃)

- **Pertinent properties**
 - Mol. Wt.: 63.03
 - Melting point: -42°C
 - Boiling point : 86°C with decomposition
 - Specific gravity: 1.502 at 18°C
 - Solubility: It is completely miscible with water and forms a constant boiling mixture at 110°C and 760 mm which contains 68 wt.% HNO₃
- **Grades:**
 - Concentrated (95%) as technical (USP)
 - Commercial (52 - 68%)
 - Fuming (> 86%)
 - Red fuming (> 95% with 10 - 15% excess dissolved oxides of nitrogen)
 - Nitrating or mixed acid (90% HNO₃ - 15% H₂SO₄ to 50 % HNO₃ - 48% H₂SO₄)

If you see its properties, molecular weight is 63.03, melting point is minus 42 degree centigrade, then boiling point with decomposition is 86 degree centigrade, because it decomposes as the temperature reaches 86 degree centigrade rather completely boiling. Then specific gravity 1.502 at 18 degree centigrade, coming to the solubility it is

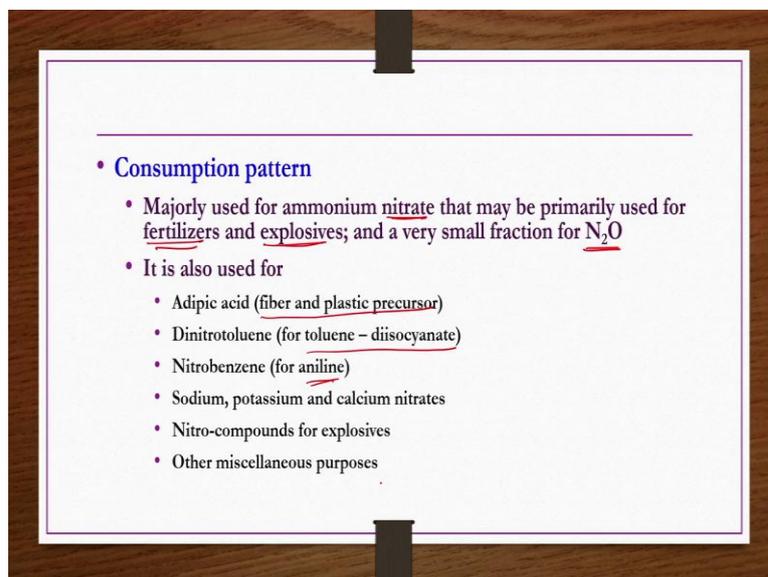
completely miscible with water and forms a constant boiling mixture at 110 degree centigrade and 760 mm, which contains 68 weight percent of nitric acid.

Then coming to the grades, concentrated technical grade or concentrated nitric acid as technical grade as per the United States Pharmacopoeia. If it is 95 percent nitric acid is there, then it is considered as concentrated as well as the technical grade for a pharmaceutical applications. Then commercial grade, if it is having 52 to 68 percent of nitric acid, then it is considered as commercial grade nitric acid.

Fuming nitric acid, if it is having more than 86 percent HNO₃; red fuming nitric acid if it is having 95 percent or more HNO₃ with additional 10 to 15 percent excess dissolved oxides of nitrogen such as dinitrogen, tetroxide etcetera. Then nitrating or mixed acid, which is nothing but a mixture of nitric acid and sulfuric acid, its fraction of fraction of nitric acid and then H₂SO₄ varies in general.

It may be rich in HNO₃ as much as 90 percent HNO₃ and then and then it may be having you know as low as 15 percent H₂SO₄. Then it may also have 50 percent HNO₃ and then 48 percent H₂SO₄, wide ranges are possible depending on the applications.

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Consumption pattern, primarily ammonium nitrate production purpose, this nitric acid is used. That ammonium nitrate primarily be used for fertilizers, as well as for explosives ok. It is also used for a production of several chemicals such as adipic acid, which is used

as a fiber and plastic precursor in polymer industries, then dinitrotoluene for preparation of toluene, diisocyanate mixers.

Then nitrobenzene preparations, something like for aniline preparation. Then sodium, potassium and calcium nitrate productions, other nitro compounds for explosive purpose as well. And then so many other miscellaneous purposes also this nitric acid is used.

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Methods of production

- Primarily four methods
- *** (1) Ammonia oxidation process:**
- Up to 90% of HNO_3 produced by this method which include four primary reaction steps as follows
 - NH_3 oxidation to NO
 - NO oxidation to NO_2
 - NO_2 absorption in water
 - Concentration of HNO_3
- Differences in various plants are in
 - pressure levels in oxidation and absorption
 - power recovery
 - methods of dehydrating 60% acid formed by absorption

Now, methods of production, primarily four methods of production are there. The first one is ammonia oxidation process. Whatever the nitric acid that is available in the market, 90 percent of it is coming from this process, it is very essential process. So, we are going to discuss production of nitric acid from this process ok.

It is having four steps, four reaction steps. 1st step is ammonia oxidation to nitric oxide, then oxidation of nitric oxide to nitrogen dioxide, then absorption of nitrogen dioxide in water to get HNO_3 that is nitric acid and then finally concentration of HNO_3 . You may get 57 to 60 percent of HNO_3 something like that in this process that can be further concentrated up to 95 percent HNO_3 .

So, these four steps are primary steps, important steps in this nitric acid production by ammonia oxidation process. Differences in various plants are actually so many plants; modern plants are; in fact, almost all plants are based on ammonia oxidation process as we said that 90 percent of HNO_3 is coming from this process only. So, from one plant to

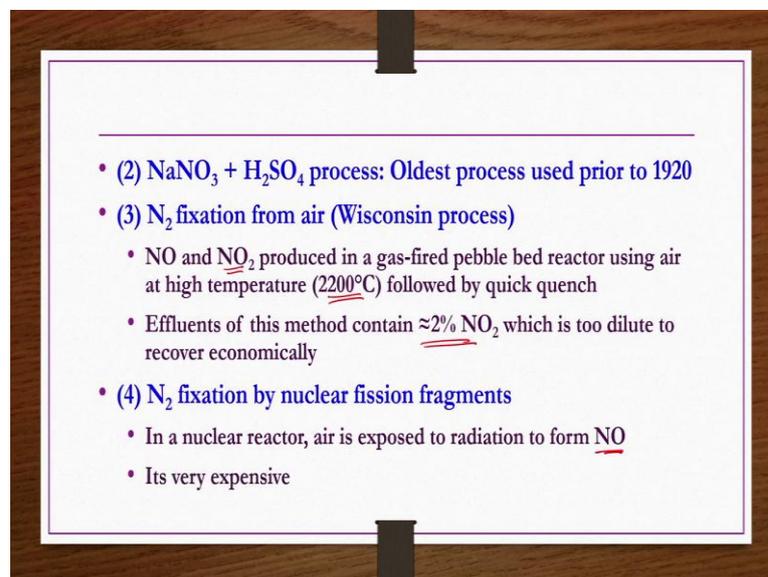
the other plant there may be some variation, some changes in the conditions or designs etcetera.

So, some of the important variations are pressure levels in oxidation and absorption. That is one important difference you may find out from one plant to the other plant. Then power recovery, how the power is being recovered, here in this process there is a source of steam, how it is being collected as a process steam or turbine steam or for the production of you know other purposes etcetera.

Those things you know that comes all under power recovery. How the plant is doing the power recovery and then methods of dehydrating 60 percent acid formed by absorption. By absorption you can get 57 to 60 percent of acid only, if you how are you increasing its concentration up to 95 percent it is possible. So, how are you doing it? So, what are these dehydrating methodologies followed by different plants?

You know these may be a few variations that may be found between different plants producing nitric acid.

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2nd process is the oldest process which was used to prior to 1920, where its production is by the reaction between sulfuric acid and sodium nitrate, but it is no more used nowadays. 3rd process is nitrogen fixation from air which is also; which is also known as Wisconsin process. Here NO and then nitrogen dioxide produced in a gas-fired pebble

bed reactor using air at high temperature as much as like 2200 degree centigrade followed by quick quenching.

But; however, effluents of this method contain only 2 percent of NO₂ which is too dilute to recover economically. Whereas, the fourth method is the nitrogen fixation by nuclear fission fragments. In a nuclear reactor air is exposed to radiation to form NO, however this method is very expensive.

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HNO₃ production by ammonia oxidation

- **Chemical reactions:**
- **Major reactions – ammonia oxidation**
 - (a) $\underline{NH_3} + \frac{5}{4} \underline{O_2} \leftrightarrow \underline{NO} + \frac{3}{4} \underline{H_2O} (g); \Delta H^\circ = -54.0 \text{ kcal}$ (HNO₃)
 - (b) $\underline{2NO} + \underline{O_2} \leftrightarrow \underline{2NO_2}; \Delta H^\circ = -27.2 \text{ kcal}$
- **Side reactions – ammonia oxidation**
 - (c) $\underline{NH_3} + \frac{3}{4} \underline{O_2} \leftrightarrow \frac{1}{2} \underline{N_2} + \frac{3}{2} \underline{H_2O} (g); \Delta H^\circ = -75.7 \text{ kcal}$
 - (d) $\underline{NH_3} \leftrightarrow \frac{1}{2} \underline{N_2} + \frac{3}{2} \underline{H_2}; \Delta H^\circ = -11.0 \text{ kcal}$
 - (e) $\underline{NH_3} + \underline{O_2} \leftrightarrow \frac{1}{2} \underline{N_2O} + \frac{3}{2} \underline{H_2O} (g)$
 - (f) $\underline{NH_3} + \frac{3}{2} \underline{NO} \leftrightarrow \frac{5}{4} \underline{N_2} + \frac{3}{2} \underline{H_2O} (g); \Delta H^\circ = -107.9 \text{ kcal}$

Am NH₃
 + compressed air
 ↓
 HNO₃
 ↓
 10-12% (NO) (HNO₃)

So, the best option is to produce nitric acid by ammonia oxidation process. Before going into the details of this process, we have to list out what are these reactions. We have just seen that four important reactions are there in this process. So, we have to see all these reactions and then we go to the flow chart followed by process description and then major engineering problems of this process followed by end uses.

Chemical reactions, major reactions of ammonia oxidation, when ammonia is oxidized it will give NO and then water. 2 moles of NO further oxidized to give 2 moles of nitrogen dioxide, which can be absorbed in an absorption tower to get HNO₃. Side reactions, ammonia oxidation, here ammonia can also be oxidized to give nitrogen and water that depends on the how many moles required those things are there.

So, insufficient oxygen is there, so then it is possible that it is giving nitrogen and then water. Then ammonia may be decomposed to its basic elements nitrogen and hydrogen

ok. Then ammonia oxidation may also take place to give NO and then water, whereas the ammonia may be reacting with the NO to give nitrogen and then water.

So, now these reactions first reactions A and B we are calling major reactions because here NO₂ is forming that NO₂ may be absorbed in water to get a HNO₃, Right. So, that is what the process that actually HNO₃ production is the purpose of this process, right. So, these are major reaction and important reaction also. But during the process where you have the anhydrous ammonia and then compressed air actually you take as raw material or feed material to react and then give HNO₃.

So, in between, so many steps are there and then from this reaction. So, many gases are forming because of the either of the; major reactions or side reactions because their conditions of formation may be closely related, right. Actually when anhydrous ammonia reacts with the compressed air you get only 10 to 12 percent of NO only. This further NO has to be oxidized to get NO₂ that is taking place in absorption in absorption tower, right. In absorption tower this is taking place ok.

So, where it increases its yield increases further, so that's a different thing. But when you see these reactions are occurring between ammonia and compressed air you are getting gaseous mixture where only 10 to 12 percent of NO is there. Remaining may be so many other things like you know nitrogen, hydrogen and then water vapours etcetera all those things may be there.

So, all these reactions are detrimental to the process, these have to be as minimum as possible, you cannot avoid completely ok. But as minimum as possible such a way that you have to do the design and then such a way you have to maintain the operating conditions ok.

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• **Nitric oxide oxidation and absorption**

- (g) $2NO + O_2 \leftrightarrow 2NO_2$; $\Delta H^\circ = -27.2 \text{ kcal}$
- (h) $3NO_2(g) + H_2O(l) \leftrightarrow 2HNO_3(aq) + NO(g)$; $\Delta H^\circ = -32.2 \text{ kcal}$
- (i) $2NO_2 \leftrightarrow N_2O_4$; $\Delta H^\circ = -11.46 \text{ kcal}$
- (j) $2NO_2(g) + H_2O(l) \leftrightarrow HNO_3(aq) + HNO_2$
- (k) $2HNO_2 \leftrightarrow H_2O + NO + NO_2$

• **Raw materials**

- Ammonia from synthetic ammonia process ←
- Clean and filtered air
- Platinum-rhodium make-up catalyst

There are few more reactions that is nitric oxide oxidation and absorption here 2NO reacting with oxygen O₂ to give 2NO₂ that is nitrogen dioxide. This nitrogen dioxide 3 moles of nitrogen dioxide reacts with 1 mole of water that is in absorption then you get 2 moles of HNO₃ nitric acid and then 1 mole of NO ok.

However this nitrogen dioxide may also be forming dinitrogen tetroxide, which is not required or the absorption between nitrogen dioxide and water may take place such a way that you have 2 moles of nitrogen dioxide only, then you get 1 mole nitric acid and then 1 mole nitrous acid. So, here in this reaction h you are getting 2 moles of nitric acid whereas, here you are getting only 1 mole.

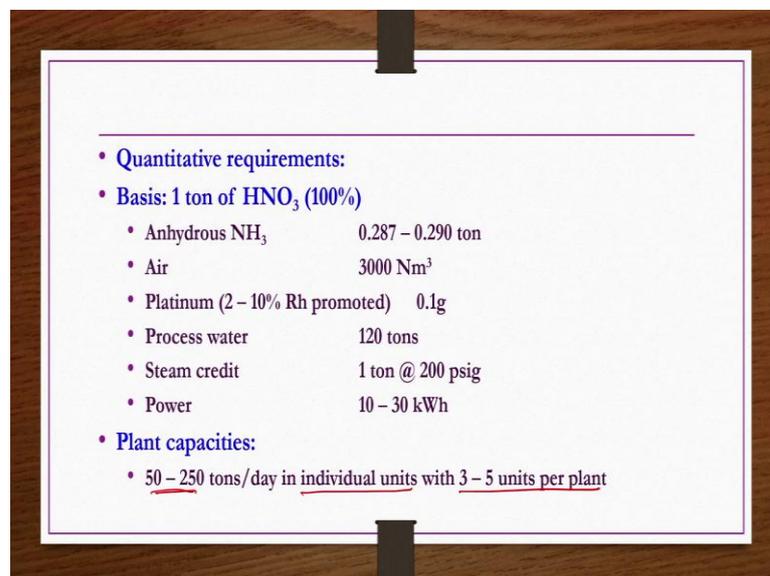
Whereas, the additional 1 mole you are getting nitrous acid. Here in this reaction H you are getting 2 moles of nitric acid, whereas in reaction j you are getting only 1 mole of nitric acid. That only we change is what, here you are get you are using 3 moles of a nitrogen dioxide, whereas here in this reaction you are getting only 2 moles of a nitrogen dioxide.

That means if insufficient nitrogen dioxide is formed in the NO oxidation process that is occurring in absorption tower, then you get insufficient HNO₃ or acid strength may not be sufficient enough. In addition to that you may also get nitrous acid. This nitrous acid may be decomposed to form NO and then NO₂ that is nitrogen dioxide and then water vapor acid, right.

So, now these reactions all these reactions occurring in this NO oxidation and absorption process as well as the side reaction and then a main reaction that we have seen in the previous slide all of them are reversible. So, whenever you have the reversible reaction the thermodynamics and then kinetics of corresponding equations become very complicated and then they become important factor in the design as well as the operation of the process or the plant ok.

Next if you see the raw materials, obviously here raw materials ammonia from synthetic ammonia process that we have seen in the previous lecture. And then clean and filtered air ok. Catalyst makeup catalyst is required which is a platinum rhodium alloy catalyst.

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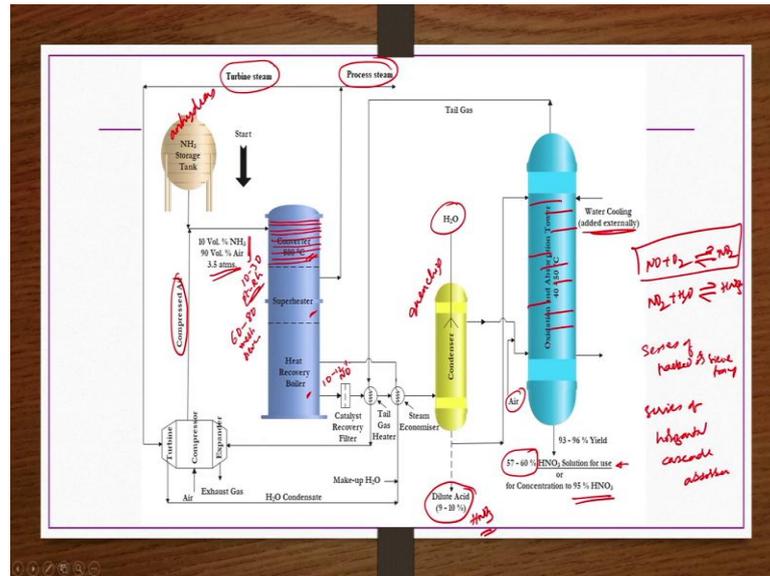


Quantitative requirements:	
Basis: 1 ton of HNO₃ (100%)	
• Anhydrous NH ₃	0.287 – 0.290 ton
• Air	3000 Nm ³
• Platinum (2 – 10% Rh promoted)	0.1g
• Process water	120 tons
• Steam credit	1 ton @ 200 psig
• Power	10 – 30 kWh
Plant capacities:	
• <u>50 – 250 tons/day in individual units with 3 – 5 units per plant</u>	

Quantitative requirements, if you see to produce 1 ton of a 100 percent nitric acid, you need anhydrous ammonia 0.287 to 0.290 tons, air 3000 normal cubic meters, platinum with 2 to 10 percent rhodium promoted only 0.1 grams, process water 120 tons in this reaction. So, much of heat is evolved, so then cooling is required. ah.

You know then you; need you need so much of process water, about to get one ton of a nitric acid you need 120 tons of process water because absorption is also involved here not only absorption, cooling of the system is also required in order to recover the energy etcetera. Steam credit 1 ton at 200 psig, power 10 to 30 kilowatt hours and in plant capacities between 50 to 250 tons in individual units with 3 to 5 units per plant. In a plant you may be having 3 to 5 units producing nitric acid ok.

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Now, we see flow chart for the nitric acid production from ammonia oxidation process ok. Here what we, have we have anhydrous ammonia and then we have compressed air. These are mixed together at what volume ratios, they mixed at 10 volume percent of ammonia and then 90 volume percent air at 3.5 atmosphere for the mixing this is the pressure requirement that is taken to a shell and tube kind of reactor, which is having 3 section converter section where the catalytic reactions are taking place superheater and then heat recovery boiler section.

This mixture of anhydrous ammonia and then compressed air come to the reactor at the top where you have converter section which is having maybe 10 to 30 platinum rhodium sheets like you know maybe they; may be seen as a 60 to 80 mesh sieves kind of things made up of these material. So, they are arranged as a kind of stake here and then this gases pass through these catalytic sheets, platinum rhodium sheets, right.

So, then the reaction takes place and then when this reaction takes place 800 degree centigrade the gases, whatever are coming out there may be a very high temperature like as much as 800 degree centigrade. So, they are passed through superheater and then heat recovery boiler to collect some steam, this collected steam is either used as a process steam or it is taken to the turbine as a turbine steam, right.

So, the gases here after this whatever gases are having they are having only 10 to 12 percent of NO only and then remaining are either NO₂ or you know N₂O₄ or N₂O₂

or N_2O etcetera. This kind of so many gases may also be present and then when this reaction occurs and then these gases are flowing down the it is possible this gases may also be carrying some amount of catalyst because you know this catalyst are formed as a kind of mesh, as a kind of sieves ok.

So, this catalyst recovery is done, then they is passed through a tail gas heater and then steam economizer and then it's sent to a quenching system, right. Where the cooling of this gases takes place using the spray water you know suddenly high temperature gases are cooled to low temperature by spraying with cold temp cold water, right. Here so whatever little amount of NO_2 is there that would be absorbed by H_2O and then dilute acid 9 to 10 percent HNO_3 acid would be formed that is collected at the bottom.

But majority of that is not absorbed because only a little amount of NO_2 is there and then 10 to 12 percent of NO is only there. So, these gases after cooling what is done, they are mixed with air and then sent to oxidation and then absorption tower right, which is at 40 to 50 degree centigrade. Here in this section only this NO oxidation to NO_2 is taking place and then NO_2 absorption in water to HNO_3 is also taking place and then we have seen other possible reactions also in this one.

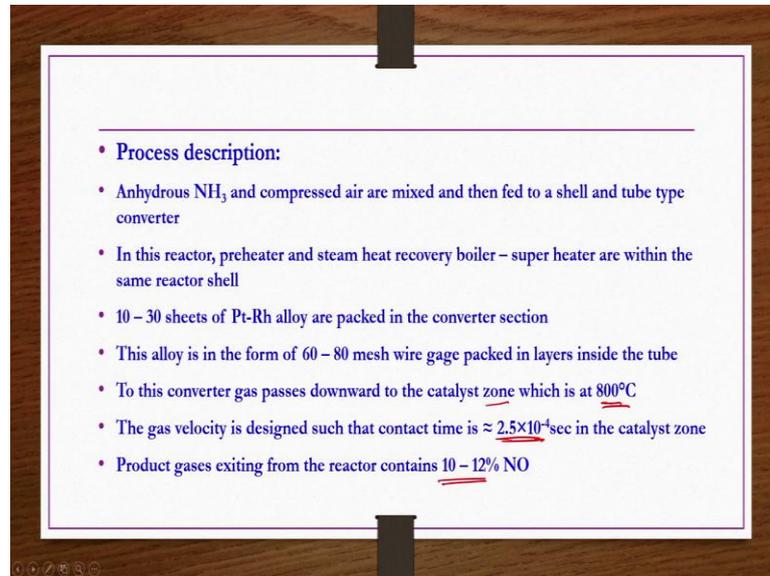
And then this 40 to 50 degree centigrade is best suitable temperature because equilibrium constants are not very high in this particular reaction where this oxidation of nitrous oxide is taking place to produce nitrogen dioxide, right. So, now here water cooling is provided from the top which is added externally. So, that whatever the NO_2 is formed that would be absorbed and then you get 57 to 60 percent of HNO_3 solution for use as it is.

If that acid strength is sufficient or if you need higher concentration acid then you have to do concentration of this HNO_3 to get 95 percent HNO_3 . Whereas tail gases which are not being absorbed they will be sent back to the expander by passing through a tail gas heater and then this process continues like this ok. So, now here, so many factors engineering; factors would be there. So, we are going to see one by one after having seen after seeing the steps of the process ok.

So, in this process further it is important to understand, what is the tower made up of especially this oxidation and absorption tower there are different possibilities are there. So, this absorption tower or oxidation and absorption tower is in general made up of

series of packed or sieved trays which are arranged to vertical manner like this or you have a series of horizontal cascade absorber, which may be arranged like in a horizontal manner like this in a cascade manner like this ok.

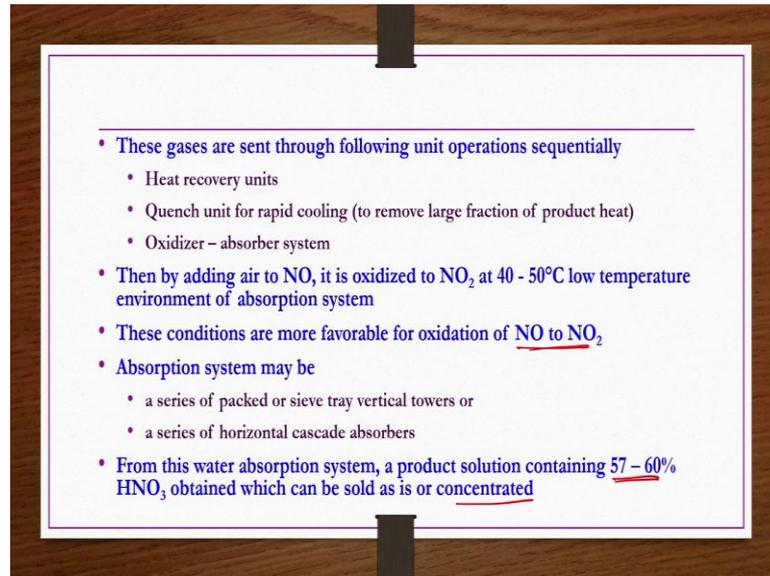
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Now, process description, anhydrous ammonia and compressed air are mixed and then fed to shell and tube type converter, in this reactor preheater and then steam heat recovery boiler superheater are within the same reactor shell 10 to 30 sheets of platinum, rhodium alloy are packed in the converter section.

This alloy is in the form of 60 to 80 mesh wire packed in layers inside the tube, to this converter gas passes down to the catalyst zone which is at 800 degree centigrade. The gas velocity is designed such a way that contact time is very less or ruff and puff minus 4 seconds in the catalyst zone. Product gases exiting from the reactor contains only 10 to 12 percent of NO.

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These gases are sent through following unit operations sequentially like heat recovery units, quench unit for rapid cooling to remove large fraction of product heat, oxidizer absorber system, then by adding air to the NO it is oxidized to NO₂ at 40 to 50 degree centigrade low temperature of absorption system.

These conditions are more favourable for oxidation of NO to form NO₂. Absorption system may be a series of packed or sieve tray vertical towers or a series of horizontal cascade absorbers. From this water absorption system a product solution containing 57 to 60 percent HNO₃ obtained, which can be sold as it is or concentrated as per the requirement up to 95 percent HNO₃.

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Nitric acid concentration (up to 95%) by two approaches:

- **(1) Concentration by H_2SO_4 :**
 - In silicon – iron or stoneware towers, rectification of HNO_3 by 93% H_2SO_4 (66° Be) produces concentrated nitric acid and 70% H_2SO_4
 - This 70% H_2SO_4 can be re-evaporated to 93% or used elsewhere in the plant
- **(2) Concentration by $Mg(NO_3)_2$:**
 - Dilute HNO_3 from absorption system along with 70 – 75% $Mg(NO_3)_2$ solution fed to dehydrating tray tower
 - In this process magnesium nitrate solution acts as extractive distillation agent that removes water at 100°C or higher; and allows rectification without azeotrope formation
 - Finally the dilute $Mg(NO_3)_2$ solution can be re-concentrated by evaporation for reuse purpose
- **Advantages of $Mg(NO_3)_2$ process:**
 - Operating costs are approximately about half of those encountered with H_2SO_4 concentration
 - Capital requirements are only 70% as great; acid quality and yield are improved

So, now we see how to increase the concentration of nitric acid from 60 percent to 90, 95 percent HNO_3 etcetera as per the requirement. There are two approaches are there. 1st approach is concentration by H_2SO_4 . In this process what happens? Silicon, iron or stoneware towers are used where rectification of HNO_3 by 93 percent H_2SO_4 produces concentrated nitric acid. Whereas, sulfuric acid concentration decreased to 70 percent. This 70 percent H_2SO_4 may be re evaporated to 93 percent or used elsewhere in the plant as it is.

Other method is concentration by magnesium nitrate solution. Here magnesium nitrate solution and then dilute acid from the absorption tower are fed to dehydrating tray tower. In this process magnesium nitrate solution acts as extractive distillation agent that removes water at 100 degree centigrade or higher and allows rectification without azeotrope formation, right.

Finally whatever dilute magnesium nitrate solution is there, that can be re-concentrated by evaporation for reuse purpose. Out of these two method magnesium nitrate method is you know advantages. One is the clearly you can see the H_2SO_4 is more expensive than the magnesium nitrate ok. So, not only that one the cost wise operating cost wise, operating costs are approximately about half of those encountered with H_2SO_4 concentration process.

In addition capital requirements are only 70 percent as great and acid quality yield are also improved by this magnesium nitrate process ok.

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Major engineering problems:

- Primarily two issues: (a) Thermodynamics and kinetics and (b) Process design modification
- (a) Thermodynamics and kinetic considerations:
 - In this process, reactions are reversible and exothermic in the forward direction
 - One-step high-temperature converter design may be used for ammonia conversion as $NH_3 + \frac{3}{4}O_2 \leftrightarrow NO + \frac{3}{4}H_2O (g)$ has an extremely favorable equilibrium constant
 - In addition, slight advantage of equilibrium is also possible on operating at low pressure (1 atm)
 - This advantage is more than offset by increased capacity in a given reactor volume with subsequent catalyst and reactor savings when operating at high pressure (3-8 atm)
 - $2NO + O_2 \leftrightarrow 2NO_2$ (NO oxidation) do not have as large as equilibrium constant ← at low T
 - Thus it predominates in cooling and absorption system of process operating at 40-50°C
 - All of NO which is liberated on absorption of NO₂ must also be re-oxidized in the absorption tower

Now, we see major engineering problems primarily two issues are there. One is the thermodynamics and kinetics, which will always be there if you have a many reversible reactions and in process design modifications. First start with thermodynamics and kinetic considerations. In this process reactions are reversible and the exothermic in the forward direction all reactions are reversible. All reactions are reversible and then all reactions are exothermic in the forward direction.

One step high temperature converter design may be used for ammonia conversion as ammonia oxidizes to give NO, which is having extremely favourable equilibrium constant. In addition a slight advantage of equilibrium is also possible on operating at low pressures like 1 atmosphere. This advantage is more than offset by increased capacity in a given reactor volume with subsequent catalyst and reactor savings when operating at high pressures 3 to 8 atmosphere.

In this case operating at 3 to 8 atmosphere itself is a high pressure. Then further NO oxidation do not have as large as equilibrium constant. So, then this occurs at low temperatures low temperature of 40 to 50 degree centigrade itself is sufficient. Thus it predominates in cooling and absorption system of process operating at 40 to 50 degree

centigrade. So, in this process more than the catalytic converter this absorption tower whatever is there you know oxidation and absorption tower that is very important.

Because here the conditions you need only low temperature conditions 40 to 50 degree centigrade and then input gas that is coming here is only having 10 to 12 percent NO, whereas you are getting from this one acid having up to 60 percent HNO₃. Such important is this process, but however, the converter the shell and tube reactor or converter system whatever is there that is unavoidable because after that step only it is happening.

There in that process having multi stage reaction etcetera is not going to be useful because NO oxidation is not taking place much in that section. NO oxidation is favourable at low temperature. So, do the oxidation of ammonia at high temperature to get NO in the converter in the catalytic converter and then whatever the gases are there that after quenching you take it to the oxidation absorption tower, which is operating at low temperature of 40 to 50 degree centigrade.

So, that you get majority of NO is being converted to the NO₂ and then majority of NO₂ is being absorbed in water to get HNO₃. All of NO which is liberated on absorption of NO₂ must also be re-oxidized in the absorption tower ok. So, that recycling can also be done, recirculation of this NO gas, unreacted NO gas may also be done, again by sending it to the absorption or oxidation absorption tower itself.

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Summary of reaction kinetics of NH₃ oxidation stage:

- $NH_3 + \frac{5}{4}O_2 \leftrightarrow NO + \frac{3}{4}H_2O$ is favored to form NO by increasing temperature until an optimum is reached which increases with higher gas velocities
- Advantage of this is that back diffusion of NO into the higher NH₃ concentration region is prevented
- Under such case, reaction $NH_3 + \frac{3}{2}NO \leftrightarrow \frac{5}{4}N_2 + \frac{3}{2}H_2O(g)$ is quite possible and thus, it should be avoided for high NO yield
- At given set of conditions, alloying platinum with rhodium improves yield
- Diffusional transport of NH₃ molecules to the catalyst surface and rate of NO formation can be very nearly corresponded to each other
- Rate of ammonia oxidation reaction is directly proportional to the system pressure

Handwritten notes on the slide include: "High T 850-900", "10-30%", "10-20%", "10-15%", "NH₃", "NO", and "gamma".

Summary of reaction kinetics of ammonia oxidation stage, if you see ammonia oxidation to give NO is favoured by increasing temperature until an optimum is reached which increases with high or higher gas velocities. That means this reaction will happen at high temperature. How much high approximately at 800 degree centigrade is found to be optimum one?

See all these things when you do, if you take the kinetics and thermodynamics of individual reactions and do, so much of thermodynamics and then chemical reaction analysis, kinetic analysis then you can understand these things. But you know this course is not dedicated on the thermodynamics or kinetics, we are taking a summary of you know those studies, right.

Studies have found that ammonia oxidation to give NO is possible when the temperature is high, as much as 800 degree centigrade. If you operate at low temperature like 500 or 400 degree centigrade, NO may not form or rather forming NO it may be decomposing to N₂ and H₂ and then forming other kind of components as well N₂ and water something like that, as we have seen in the side reactions.

So, if the main reaction to occur, the temperature has to be as much high as possible like up to 800 degree centigrade in the catalytic reactor zone. Advantage of this is that back diffusion of NO into the higher ammonia concentration region is prevented. In such kind of catalytic reactors, this catalytic zone whatever we have seen in the shell and tube section the top section, what we are having? We are having 10 to 30 sheets of a platinum rhodium alloy, which are like you know are in the wire forms.

Within that small region 10 to 30 sheets are there. So, when the; so many sheets are there. So, whatever gases input gases of anhydrous ammonia and then air are there? So, moment they come here, there some NO may be forming, right. So, when this NO this form and then there is no sufficient space to move it quickly to the next level, what will happen?.

It may back diffuse to ammonia higher ammonia concentration region, which are usually at the top because from the top anhydrous ammonia along with the compressed air are coming ok. So, what is the advantage? If you do a reaction at high temperature quickly it oxidized ammonia oxidized to NO. So, ammonia concentration decreases gradually and more NO is forming.

So, back diffusion of NO into the ammonia is not possible or can be prevented. Under such case reaction between ammonia and then nitric oxide may also take place to give nitrogen and water vapours which is quite possible, but it should be avoided ok because we do not want N_2 or H_2O , but we want NO from NO we can get NO_2 and then from there we can get HNO_3 .

At given set of conditions alloying platinum with rhodium improves yield and then diffusional transport of ammonia molecules to the catalyst surface at what rate ammonia is diffusing onto the catalyst surface that is formed as a 60 to 80 mesh wire, mesh size wire. So, then at what rate, diffusion of this ammonia is taking place onto the catalyst surface and then moment it comes and then diffuses. So, let us say we have the catalyst particle like this bigger one we have taken ok.

For example, this is here and then we are just taking it here. So, from the bulk of ammonia that is input coming. So, when it comes and then diffused by diffusion it reaches here. It reach moment it reaches the catalyst surface, immediately it is forming NO right because its high temperature reaction the catalytic surface is at the high temperature at approximately 800 degree centigrade.

This NO is forming, right. So, this at what rate NH_3 is diffusing to the surface of catalyst and then at what rate, NO is forming on the catalyst surface when this oxidation of ammonia is taking place on the catalyst surface these two rates are very nearly corresponded to each other and then that makes easy process calculations like you know subsequent process or you know formation you know the rate.

If the NH_3 coming at one rate and then NO is going out at a slower rate, so then NO may be accumulated on the catalyst surface which is not good, right. If both of them are at this almost similar rate, so then whatever rate ammonia is reaching the catalyst surface at the same rate NO may be forming and then leaving out to the bulk of NO region.

So, then it is going to be another advantage. Then rate of ammonia oxidation reaction is directly proportional to the system pressure. So, higher pressure conditions may be better for the oxidation of ammonia. How much pressure is higher pressure that is again the question here?

You cannot have like 1000 it depends on the process to process, right. This reaction actually can be taken place at a one atmospheric pressure as well and then intermediate 3 to 4 atmospheric pressure also, but if you are going a pressure as like 6 to 8 atmosphere or something like that. So, that pressure in this case is considered as a high pressure.

However rate of ammonia oxidation reaction is directly proportional to the system pressure that we understand from the reversible reaction between ammonia and then air oxidizing to give NO.

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Design criteria based on absorption of nitrogen oxides by chemical reaction with water

- For absorber operation efficiency, lower temperature is preferable
- Physical absorption rates favored by increasing pressure that shifts chemical equilibrium to produce higher acid strengths
- In the gas phase, the rate of absorption is dependent on concentration of NO₂
- If the concentration of NO₂ > 5%, then controlling reaction is solution of N₂O₄ accompanied by hydrolysis to HNO₃ and HNO₂

Handwritten notes on the slide:

$$\text{NH}_3 \rightleftharpoons \text{NO}$$

$$\text{NO} + \text{H}_2\text{O} \rightleftharpoons \text{HNO}_2$$

Design criteria based on absorption of nitrogen oxides by chemical reaction with water for absorber operation efficiency lower temperature is preferable because equilibrium constants of this NO₂ absorption into water are NO oxidizing into NO₂ both of them are actually reversible. So, then these rates you know not very high equilibrium constants are not very high.

So, then if the equilibrium constants are not very high, so you do not need to unnecessarily use the high temperature high pressure conditions because that is not going to improve anyway for this reaction, the reaction kinetics are like that. So, then you can operate at low temperature. Physical absorption rates favoured by increasing pressure that shifts the chemical equilibrium to produce higher acid strength.

So, whatever this reaction let us say is there, forming HNO₃, if you are doing physical absorption in order to accelerate the absorption process, if you increase the pressure you know it is good. So, when you increase the pressure more HNO₃ is forming and then as you keep on moving it the equilibrium shifts, equilibrium shifts to produce higher acid strength that is possible.

Higher amount of if you keep on forming HNO₃ and then recovering from the bottom, more HNO₃ is forming and then its acid strength may be increasing that is the possibility and then that you can have by physical absorption and then physical absorption rates may be increased by increasing the pressure.

Then in the gas phase the rate of absorption is dependent on concentration of NO₂ right, if more NO₂ is present in the gases mixture. So, then higher absorption of NO₂ may takes place to give higher acid concentrations ok. If the concentration of NO₂ is more than 5 percent, then controlling reaction is the solution of dinitrogen tetroxide accompanied by hydrolysis to give HNO₃ and then HNO₂.

This reaction if the acid strength is more, then you know controlling reaction this forming a component by the hydrolysis to these nitric acid and then nitrous acid are going to be the controlling reactions.

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(b) Process design modifications

- Large no. of plants use either of following operating pressure options
 - Intermediate (3–4 atm) or high pressures (8 atm) rather than complete atmospheric pressure conditions or
 - A combination of 1 atm pressure oxidation and high pressure absorption
- Because of high cost of high pressure vessels, high pressure operations are limited
- Advantages of elevated pressure processes :
 - High reaction rates and lower volumes in both oxidation and absorption equipment
 - Higher acid strength and lower investment costs
- Disadvantages of higher pressure processes:
 - Lower oxidation yields
 - Higher catalyst losses unless good filtering procedures are used
 - High power requirements if power recovery units are not specified

Now, we see process design modifications, these are also based on the experience of different plants we are not going into the details because our understanding our scope of the course is understanding the process how it is occurring in a plant ok. Large number of plants use either of the following operating pressure options such as intermediate that is 3 to 4 atmosphere or higher pressure, 8 atmosphere rather than completely atmospheric pressure conditions.

Some systems have a mixed kind of things, that you know at atmospheric pressure oxidation can takes place and at high pressure absorption can takes place. We have seen from the kinetics and in thermodynamics consideration oxidation is favourable at 40 to 50 degree centigrade only or we have seen NO oxidation to NO₂ is not having very high equilibrium constant. So, you know increasing temperature pressure is not going to help in any way.

So, then you can do this reaction at 1 atmosphere and then whatever this NO₂ is forming, it has to be absorbed in water to give HNO₃, of course which is also a reversible reaction. So, this we have seen absorption is usually can be enhanced absorption can easily be enhanced by increasing the pressure, right. So, you can do the absorption at higher pressure, whereas oxidation at the lower pressure that is also possible.

So, people do a combination of both; that means, whatever the oxidation and absorption tower is there, the designing is such a way that wherever the; whichever the region oxidation is taking place the pressure is maintained low like atmospheric pressure. And then wherever the region where the absorption of NO₂ in water is taking place the pressure is maintained that is high pressure something like 8 atmosphere is maintained.

Because of high cost of high pressure vessels, high pressure operations are limited because actually let us say even in the laboratory scales in general if you have a 1 reactor of 100 ml, if it is reaction if you wanted to do the reaction at 1 atmospheric pressure then material of construction is not you know SS316 kind of materials may be used and then that may not be very expensive.

But for the same volume reactor, if you wanted to do a reaction at high pressures like you know 100 bars or 200 bars you need to go for different material of construction like Inconel etcetera which may be expensive, right. So; obviously, if you go for high

pressure reactors or high pressure systems, then you know cost of material of construction whatever is there that cost increases and then overall that unit construction cost also increases, whether it is unit operation or unit process.

So, because of high cost of high pressure vessels, high pressure operations are; obviously limited. If you have option to do a process or operation at low pressures it is better to go for the low pressure because of such cost issues. If you do not have any option, the reaction has to go or the process has to go only at the high pressure. So, then you do not have any option for that, you have to go for a expensive high pressure vessels.

But if you have option, then you can go for the low pressure or you know vessels, if the pressure is not a big reason for the success of any operations or operation or process. Advantages of elevated pressures, high reaction rates and then lower volumes in both oxidation and absorption equipment and then higher acid strength and lower investment cost.

Disadvantages of higher pressure processes, lower oxidation yields and then higher catalyst losses, unless good filtering processes are used and then higher power requirements if power recovery units are not specified.

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Economics

- Mostly used in fertilizer industry as
 - An acidulant for phosphate rock to produce nitro-phosphate for mixed fertilizers
 - In production of NH₄NO₃ (synthetic nitrogen fertilizer containing 35% N)
- Due to population growth and increased standard of living, HNO₃ consumption in fertilizer industry is expected to increase
- In the form of ammonium nitrate-oil mixtures which is a cheap open-pit explosive for quarrying, mining and constructions purpose
- Its use in the form of explosives is almost stable with very little growth
- Rocket propellant compositions provides a small but increasing market for such products as
 - Fuming red nitric acid (conc. HNO₃ with N₂O₄ solubilized), N₂O₄ and monopropellants such as tetra-nitromethane

HNO₃

Now, we see economics of nitric acid that is end use of a nitric acid, where we can use it. Majorly it is used in fertilizer industry as an acidulant for phosphate rock to produce

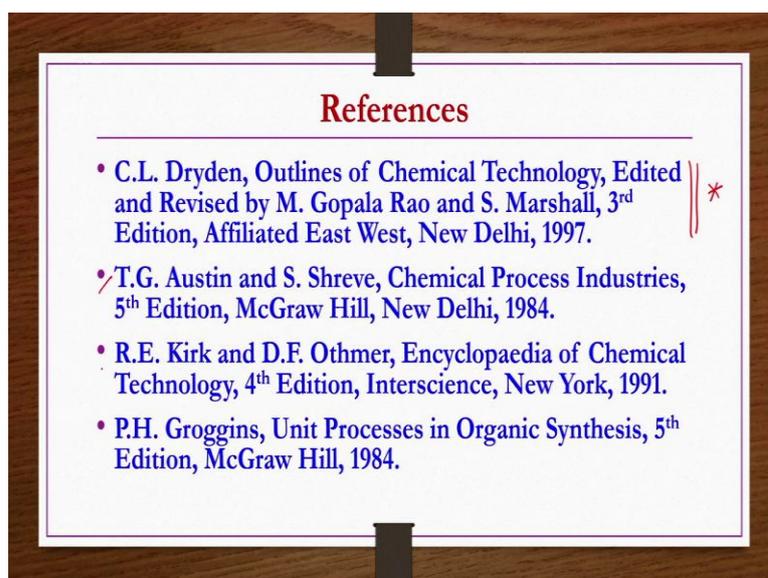
nitro phosphate for mixed fertilizers mixed fertilizers we are going to discuss you know later on in the subsequent course after couple of weeks.

In production of ammonium nitrate which is a synthetic nitrogen fertilizer containing 35 percent end due to population growth and increased standard of living this HNO₃ consumption. In fertilizer industry is expected to increase anyway. In the form of ammonium nitrate oil mixers which is a cheap open pit explosive for quarrying mining and constructions purpose for mining purpose some construction purpose you may often require to use some explosives.

So, this ammonium nitrate and oil mixers are you know economical explosive sources. It's used in the form of explosives is almost stable with very little growth because almost like you know saturation has come. Rocket propellant compositions provides a small, but increasing market for such products as fuming grade nitric acid that is concentrated HNO₃ having more than 86 percent HNO₃ with N₂O₄ solubilized.

And N₂O₄ and non-propellant such as tetra nitromethane, these are also used as rocket propellant and then in order to manufacture these things also you need to have this nitric acid.

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Now, the references for today's lecture are provided here. But the entire lecture is prepared from this reference book. Whereas, additional details you may find from these books as well.

Thank you.