

Aspen plus Simulation Software
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Lecture – 26
Synthesis of Ammonia in Cryogenic Process

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Case Study – Synthesis of NH₃ in cryogenic process

Ammonia has to be synthesized from a mixture of N₂ (24%), H₂ (74%), CH₄ (1%) and Ar (1%). The mixture is flowing at 5000 kmol/h, 50°C and 90 bar. The equilibrium reactor at 50°C and zero pressure drop will be modeled using the concept of minimization of Gibbs energy. The outlet of the reactor will be depressurized at 15 bar using a valve and then flashed at -35°C (with zero pressure drop). Liquid outlet of the flash is the main product line which contains ammonia. The vapour outlet of the flash tank is passed through a membrane separator to separate 90% of mixture of H₂ and N₂ for recycling back to the feed line after appropriate pressure (isotropic compressor with 90% isentropic and 80% mechanical efficiency) and temperature correction. Remaining 10% is purged.

- Employ Ideal, NRTL and Peng Robinson property methods and compare their performance in predicting ammonia production
- The plant is optimized for ammonia production with its quality constraint of 99.8% purity. The operating temperature of flash tank and/or reactor may be used for that purpose.

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In today's lecture, we shall perform a case study on synthesis of ammonia in a cryogenic process. Now, cryogenic process is generally, it is operated around -190°C . But, we do not have to do the simulation at that low temperature because as far as ammonia is concerned at normal condition its boiling point is 33.34°C . So, we shall operate around -35°C .

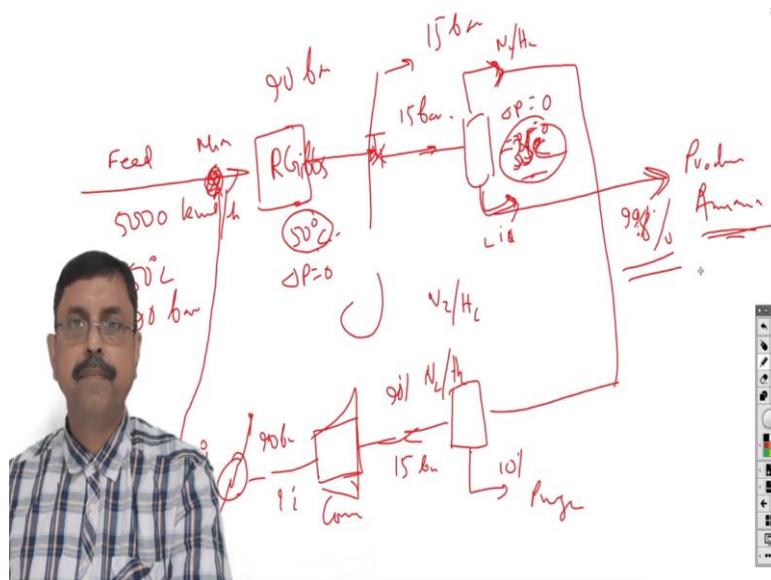
So, let us understand the problem statement first. Ammonia has to be synthesized from a mixture of nitrogen, hydrogen, methane and argon. As we understand that for ammonia production, we need only nitrogen and hydrogen. So, methane and argon will be there as impurities, argon is anyway, it is an inert gas and methane will also not take part in the reaction. So, at normal temperature and pressure nitrogen is mostly inert.

So, in order to have a reaction with nitrogen, we have to have very high temperature and pressure. So, the reactor operates at around 50°C and very high pressure. What is the pressure? As we said mixture is flowing at 5000 kmole/hr 50°C and 90 bar pressure. So, it is 50°C and 90 bar pressure at which the mixture is flowing and the reactor is operating with zero pressure drop.

That means, there will be no pressure drop in the feed line when it enters into the reactor. So, reactor also operates at 90 bar and 50 °C. And what is the type of reactor, it runs on the concept of minimization of Gibbs Energy, as we know that any spontaneous reaction the Gibbs energy will be minimized. So, we will use the block RGibbs. This is a block of aspen plus simulation software this will be used for our simulation.

Now, the outlet of the reactor will be depressurized at 15 bar using a valve and then flashed at -35 °C again with zero pressure drop.

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So, let us understand this properly, we have a feed which is flowing at 5000 kmole/hr 50 °C 90 bar pressure and this is entering into a reactor RGibbs reactor which again will operate at 50 °C and there will be zero pressure drop. And the outlet of this reactor will be depressurized using a valve from 90 bar pressure it will be depressurized to 15 bar and then it will be flashed.

So, 15 bar using a valve then flashed at -35 °C with zero pressure drop. So, we will have -35 °C over here in the flash and zero pressure drop. So, the entire line will have up to this point it will be 90 bar pressure and after that it will be 15 bar pressure and the temperature is -35 °C. So, ammonia will be liquefied and it will go down in the liquid stream.

And unreacted nitrogen and hydrogen this will go through the vapour string here you will be having nitrogen and hydrogen. To continue we have, the liquid outlet of the flash is the main product line which contains ammonia and the vapour outlet of the flash tank is passed

through a membrane separator to separate 90% of the mixture of hydrogen, nitrogen for recycling back to the feed line after appropriate pressure and temperature correction.

That means, this line will be passed through a membrane separator. So, this membrane separator will have 90% of nitrogen and hydrogen 10% will be purged and this will be passed through a compressor because it was at 15 bar pressure. So, it will be compressed to 90 bar and we do not know what will be the temperature after compression. So, we will have an appropriate heater or cooler and at this end, we will have 50 °C outlet.

So, this will be fed into the feed line through a mixer. So, this is a mixer. So, this is the recycle line and this is the product line which will have mostly ammonia. Now, what we are supposed to do? We have to employ ideal property method, NRTL property method and Peng Robinson property method and compare their performance in predicting the ammonia production.

Now, we all know that all 3 cannot perform equally well because ideal is anywhere ideal property method, NRTL is based on the activity coefficient, Peng Robinson it is on equation of state model. So, now, we should check which one is best for this ammonia production process. To the best of our knowledge so far we have learned aspen plus, Peng Robinson should be the most effective because it is equation of state model and the entire operation will be vapour faced.

So, equation of state model is the most appropriate property method for this system but we have to check with proper analysis. So, that is our first job and the second job is the plant has to be optimized for ammonia production with its quality constant of 99.8% purity. So, that we have to ensure that this product line where ammonia is coming out it should have 99.8% of ammonia.

The operating temperature of flash tank and the reactor may be used for that purpose. So, we are free to change the temperature 35 °C the flash tank and the temperature of the reactor 50 °C. So, these 2 temperatures we are free to change in order to attain 99.8% purity in the product line. So, we have to employ the optimization technique over here. So, this is the total task. So, in order to do that let us go to the aspen plus window.

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So, let us enter the components, we have hydrogen, nitrogen, ammonia, methane and argon. All of them are very common components. So, if you write in this fashion the component name will be automatically identified. And press next, we have to enter the method names. So, we are supposed to use ideal method, then NRTL method and Peng Robinson method.

So, these are the 3 methods that we have to use. So, press next, run now, go to the simulation. So, let us first use only up to this portion at this point there is no point in adding any mixer let us take a reactor which is RGibbs, this is the material stream and this is the product stream. So, renew it, reactor this is the feed line and this is the R out. Press next, it will ask for the feed composition.

It is 50 °C 90 bar pressure 5000 kmole/hr and the mole fractions of the composition they are 24% nitrogen, 74% Hydrogen, methane and argon they are 1% each. So, hydrogen is 0.74, nitrogen is 0.24, methane is 0.01 and argon is 0.01. So, total it will be 1. So, this is the feed and the RGibbs the specification of RGibbs reactor, calculate phase and chemical equilibrium, pressure, there is no pressure drop in this slide up to the reactor.

So, we write pressure drop 0. And temperature 50 °C and it is fully defined. Now, let us use the block option with ideal first. So, let us use ideal block option and run the process. So, we have got the stream result. So, this is the stream result we have and we have this stream results. So, this is the feed and after the reaction of 5000 kmole it becomes 2600 kmole.

Hydrogen gets reduced from 3700 to 100. Nitrogen also gets reduced, ammonia production almost 2400 kmole as expected the methane and argon they remain without any change so, they are inert in this case. The mole fraction of ammonia is 0.9228. So, this is the ideal case let us cut this portion for our later comparison. So, just keep it over here. Now, we shall use NRTL property method and run the system once again.

And here we have got a new set of values because this is the set we have got using NRTL. Earlier it was ideal case this is NRTL. So, again we cut this portion and keep it for later use. And finally, we take the block option of Peng Robinson and read on the system go back to the stream result. Now, you can see the mole fraction has increased from 9 to 28 to 9 to 30 and the mole flows also earlier it was 2600 point something now, it is complete 2600.

So, again we cut this portion for comparison purpose. Now, let us compare as we have seen, this is the case of ideal property method this is the case of NRTL and finally, this one is with Peng Robinson. Now, first to comparable, because ideal and NRTL, none of them represent the system properly but the third one Peng Robinson, you just check this one the mass flow for ideal case 4.36 kg/hr of nitrogen is unused and the same amount of nitrogen remains unreacted, if you use NRTL.

But Peng Robinson it correctly calculates the unreacted nitrogen and this is different from other 2. And Peng Robinson is the correct one, because it is based on equation of state model. So, for subsequent analysis, we will use Peng Robinson property method. So, we have covered this portion. Now, we continue this point onwards. So, the outlet of the reactor will be depressurized at 15 bar using a valve and then flashed at -35°C .

So, first let us take valve over here and then a flash tank. This one will enter over here, this one will enter over here, this is the ammonia line, this is the flash tank, this is the valve out and one more line over here this is flash out. This will be depressurized at 15 bar that is why it is said 15 bar and flash will operate with 0 pressure drop and -35°C . So, I think everything has been set. So, we can just run the process, done.

The stream results are available; you see the stream result this is the valve out. This is ammonia, this is flash out at the vapour phase temperature and pressures are given. Let us see, mole flow rate. So, we have in the ammonia line 2386.8 kmole/hr of ammonia is being produced. Whereas, 99.4785 kmole/hr of hydrogen remains unreacted. The unreacted nitrogen is very small, if you obviously compared with feed, I think the entire nitrogen has been used up.

So, check the mole fraction. So, in the ammonia line we have the mole fraction or the quality of ammonia is 99.09% but we have to achieve 99.8%. So, we are not happy with this figure we have to optimize. What else information do we have? We have the F out that is coming out as vapour phase through the flash top it is having 52% of hydrogen, almost no nitrogen, very few amounts of ammonia and obviously this methane and argon anyway it will be there.

So, we really cannot throw this much of hydrogen, we have to use them up. So, for that reason we have to recycle it. So, let us recycle. So, for recycling, we know it is said liquid outlet of the flash is the main product that contains ammonia, the vapour outlet of the flash tank is passed through a membrane separator to separate 90% of the mixture of hydrogen and nitrogen.

So, we will have a membrane separator and then it has to be undergone pressure and temperature correction. So, we have to increase the pressure from 15 bar to 90 bar and we have to use an isotropic compressor for that with 90% isotropic and 80% mechanical efficiency. So, let us first use a separator over here and then we will have a compressor and then one exchanger and finally, we will have mixer.

So, this one will go into this way and this one let us flip it, so, this one will go to this. This one will enter over here and this one will reconnect the destination at this point this one will reconnect the destination at this point and we have the product line. So, another material out line will be here, this is the purge. So, first we rename them, this is membrane separator. Then we have a compressor then we have a heater or cooler.

Whatever it may be, mostly cooler because compressor will raise the temperature to a very high extent. And this will be a mixer, this will be purge this will be separated out, this will be compressor out, this will be recycle, this you can write combined flow. So, first we have to define separator, separate has outlet stream that will have 90% of hydrogen and nitrogen it is said 90% of the mixture of hydrogen and nitrogen will be separated through membrane separator.

So, we write over here 0.9 and 0.9. Membrane separator is defined, compressor it will compress using and the discharge pressure will be 90 bar because compression has to meet the pressure requirement with the feed otherwise this flow will not meet this line and what else the efficiencies. Efficiencies are 90% isentropic and 80% mechanical. So, 90% isentropic, 80% mechanical efficiencies and finally heater there will be no pressure drop but the temperature will be 50 °C.

So, it is ready to run the system. So, it is raw now, you can just tick this and check the temperature and pressure in the lines, vapour fraction, molar flow rate, quite a lot information

we are asking for. And you can zoom out; no, so much of zooming is not good. Zoom to fit. We will keep it over here and then we will say zoom to fit. This is good. So, you can check the feed line.

So, initially we have 5000 kmole/hr and we are getting 892 kmole/hr in the recycle line. So, the total is going out so, being reacted and renewed mole account is 3492 kmole/hr, out of which 2329 kmole is going out as ammonia and the rest is going out. 10% of that is being flashed and the remaining is being compressed and recycled back. Vapour fraction, here 100% vapour.

This is 92% vapour. This is total liquid, total vapour and this is 100% vapour, because we are separating only hydrogen and nitrogen not others, others are going over here 77% vapour. Even after completion it remains as vapour and meets the feed line. Temperature 50 °C all throughout after the valve the temperature reduces, because we have depressurized.

In the flash it is -35, it continues up to the compressor and when you are compressing from 15 bar to 90 bar, the pressure is increased from -35 to 144. And this should not be a heater, this is a cooler actually which will cool down the temperature from 144 to 50 °C. So, that the temperature and pressure condition of feed and recycled line, they are same and they can meet over here.

And finally, the pressure it is 90 bar, 90 bar, 90 bar, up to this point, where it becomes 15 bar it is depressurized and the remains 15 bar, 15 bar, 15 bar, 15 bar and then again compressed to 90 bar. So, this portion is 15 bar, this portion it is 90 bar.

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Case Study – Synthesis of NH₃ in cryogenic process

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So, our job is not over we have to continue our operation the plant is optimized for the ammonia production with its quality constraint of 99.8% purity. What does it mean? It means that ammonia production has to be maximized. So, we have to produce as much ammonia as possible from the system but with a rider included. We cannot compromise with the quality of the ammonia. So, our ammonia quality has to be 99.8%.

So, this is our constraint. So, not only we have to maintain the maximum productivity of ammonia but we have to ensure 99.8% purity of ammonia. We cannot compromise with that and we are free to change the operating temperature of the flash tank and the reactor for this purpose. So, for that let us do the simulation once again. Now, one thing you should remember that we have not checked the purity and flow rate of ammonia, after we have connected the recycle loop that we have not checked.

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So, let us check that, if you check the stream result of flash tank, you will see the molar flow rate of ammonia 2323.52 kmole/hr and here it is 99.78% purity. Now, it is almost 99.8 but it is still less but 2323.52, I believe this has reduced you compare with your previous result. So, this is your previous result when you are getting 99.0899.

So, this is without recycling you are getting much less purity but your production of ammonia was higher it was 2386. But now, you are getting 2323. So, it has reduced. Now, one thing is

sure that, if you want to increase the ammonia production then the best way is to reduce the temperature from 35 °C below. Maybe -40, -50 or so, then more and more amount of ammonia will come from this line to this line.

So, it will increase from 2323 to something else it may be 2400 whatever. But in the bargain, you will lose the quality of ammonia. So, through the optimization routine, you have to ensure the product rate, as well as the product quality. So, let us do the optimization. For that go to model analysis tool and optimization, press new, here you have to add a new variable, name it ammonia flow, this unit to maximize.

Ammonia flow which is a molar flow type so, molar flow in the ammonia line the component is ammonia. Objective you have to maximize ammonia flow but you have a constraint that purity cannot be compromised. So, you have this constraint. What is the constraint? Constraint name is Ammpur. And what is ammpur? It is the mole fraction. So, this is mole fraction of stream ammonia, then component ammonia and we fix the spec of ammpur which should be greater than or equal to 0.998.

And we have to give a tolerance also because, no simulation can reach exact value. So, even if it is 0.9979 you should be able to accept that. Go to input, vary. What will you vary? You can vary; first let us vary the temperature of the flash. So, it is a block variable. Which block? The flash tanks. What is the variable? Since temperature and we give a range. Now, it is operating at -35.

So, give it say -40 and upper limit give 0. Let us see within 0 to -40 or -50 you can say. So, within this upper and lower limit, let us find out for which temperature flash we get highest amount of ammonia production without compromising the quality. So, run it; it is converged. So, let us see the results. So, it says the final value has reduced earlier it was 2323 right now, it is showing 2124.63 but the constraint it is 0.9979.

So, earlier it was 0.9978 now, it has reached 0.9979. And we had given the tolerance value of point 0001. So, it had met the tolerance but, in the bar, again we have reduced from 2323 to 2124.63. So, we have reduced around 200 kmole/hr of ammonia, just to increase this much of purity. But let us not get disheartened, we have another variable that we can vary.

Because it is said in the problem that operating temperature of flash tank and or reactor, so, we can vary the flash tank temperature and also, we can vary the reactor temperature as well. So, let us change the reactor temperature and see. So, for that go to input, plus reset and vary another variable and that variable is block variable. Which block the reactor and what is the variable? It is temperature.

So, we can vary both reactor temperature and the flash tank temperature. At this point, what is the reactor temperature? It is 50 °C. So, let us give the lower range 0 and higher range 60. Let us check whether it can meet within this. So, run it once again and check it is converged. Go to the result. Now, the final value has reached to 0.998 exact. Now, it is not 0.7997999, nothing like that it has reached 0.998.

But, in the bargain we probably have lost much of the ammonia, let us see. So, molar flow it is 2123. So, from 2323 to 2123, so, 200 kmole/hr of ammonia has been lost but we could achieve 99.8% of purity. So, that is how we can significantly optimize our process and arrive at the desired production level. But one thing before using modeling analysis tool you have to remember every time you use the modeling analysis tool.

You have to use this one, this is purge simulation results. Because in optimization or sensitivity analysis or for that matter any kind of model analysis tool it does not have iteration. And all those iteration values are there in the memory. And aspen plus begins from where it ended. But that might take you in some other direction of the optimization routine.

So, every time you use the model analysis tool you have to purge all the previous results by pressing this. So, it is just kind of rewind, rewind the simulation and from there you can rerun your model analysis tool and I believe we will get to the exact result

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With that we finish our case study as well as this lecture. And we shall bring in another interesting case study in our next lecture. Till then, thank you and goodbye.