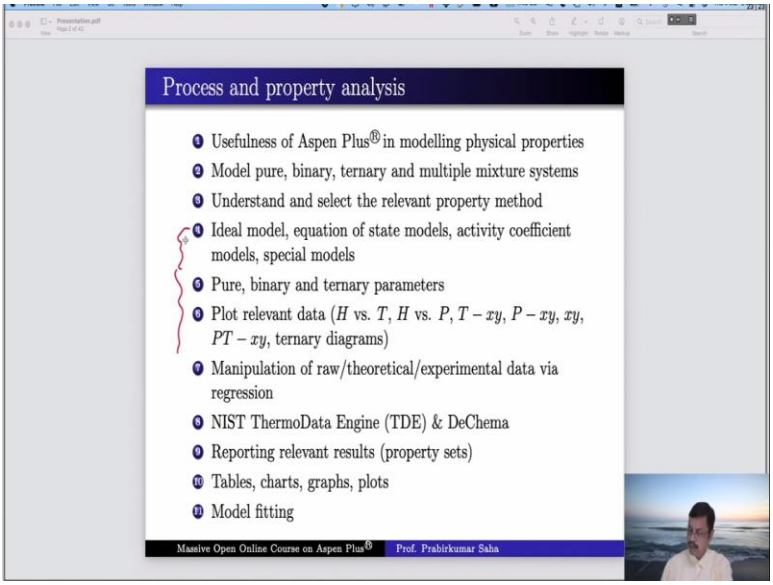
**Aspen Plus Simulation Software: A Basic Course for Beginners**

**Prof. Prabirkumar Saha**
**Department of Chemical Engineering**
**Indian Institute of Technology – Guwahati**

**Lecture – 12**
**Property Methods**

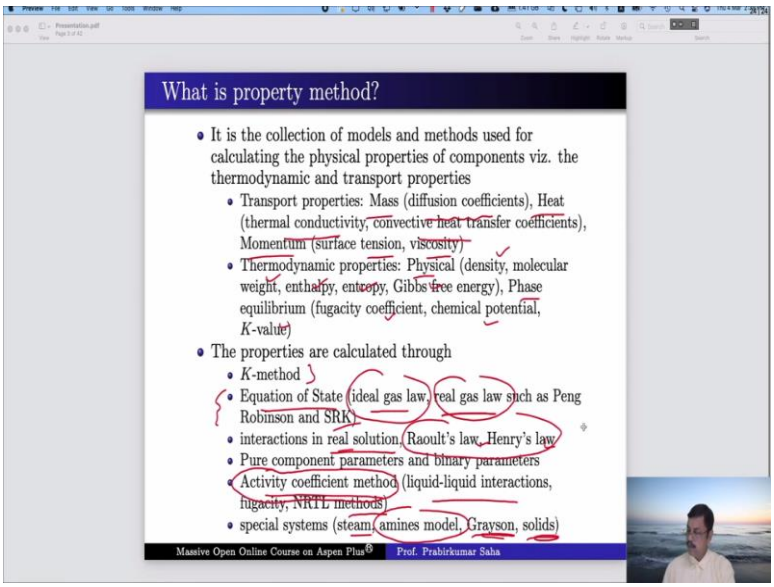
Welcome to the massive open online course on Aspen Plus.

**(Refer Slide Time: 00:39)**




In this week, we are discussing about the process and property analysis. In today's lecture, I am going to discuss about the modeling part, ideal model, equation of state models, activity coefficient and the special models. We will also discuss the pure and binary ternary parameters and how to plot the relevant data. This portion will be covered today.

**(Refer Slide Time: 01:20)**



First, let us understand what is property method? Already we have discussed the property method in a nutshell while we simulated some of the processes in the first three weeks of a lecture series, but we will learn in detail over here. Now the property method is a collection of models and methods used for calculating the physical properties of component namely the thermodynamic and transport properties.

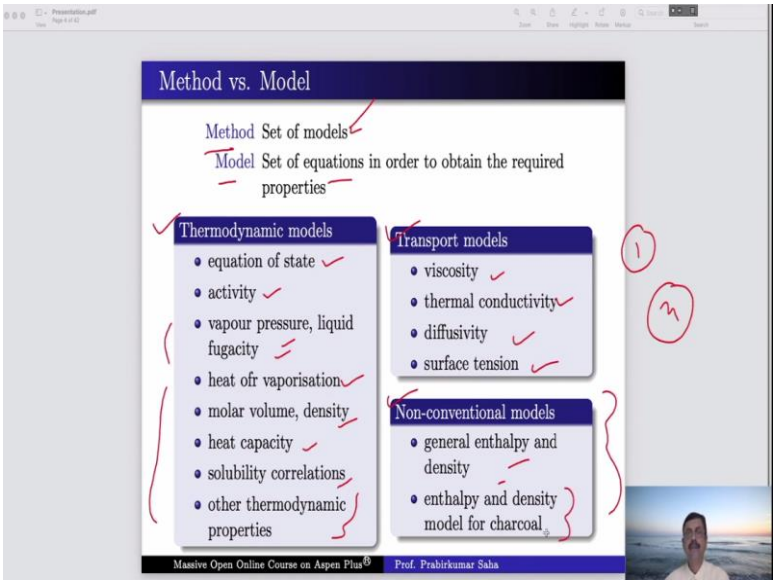
What are the transport properties? We have three types of transport properties related to mass, heat and momentum. For mass we have diffusion coefficients, for heat thermal conductivity, convective heat transfer coefficient and for momentum we have surface tension, viscosity etcetera and what are the thermodynamic properties that we have mainly physical and phase equilibrium properties.

In physical properties we have density, molecular weight, enthalpy, entropy, Gibbs free energy and for phase equilibrium we have fugacity coefficient, chemical potential, K-value etcetera and these properties are calculated through K method. Equation of state that is ideal gas law, real gas law such as Peng Robinson and Redlich-Kwong-Soave that is for vapour phase.

And for liquid phase that is real solution we have Raoult's law, Henry's law or activity coefficient method for liquid-liquid interaction, fugacity, NRTL when we do not have the molecular interaction in the liquid or vapour phase we can use ideal gas or ideal solution laws, but the moment we have liquid-liquid interaction, the molecular interaction between two liquid elements or two gases element in that case it will be real gas law or real solution for that we have to use activity coefficient method for real solutions or real gas law equation of stage.

So, we also have some special systems such as steam which is exclusively for water and steam and for amine model amine package we have amine package for various amine products, Grayson method mainly for petrochemical systems and for solids. We will learn them one by one.

**(Refer Slide Time: 04:22)**

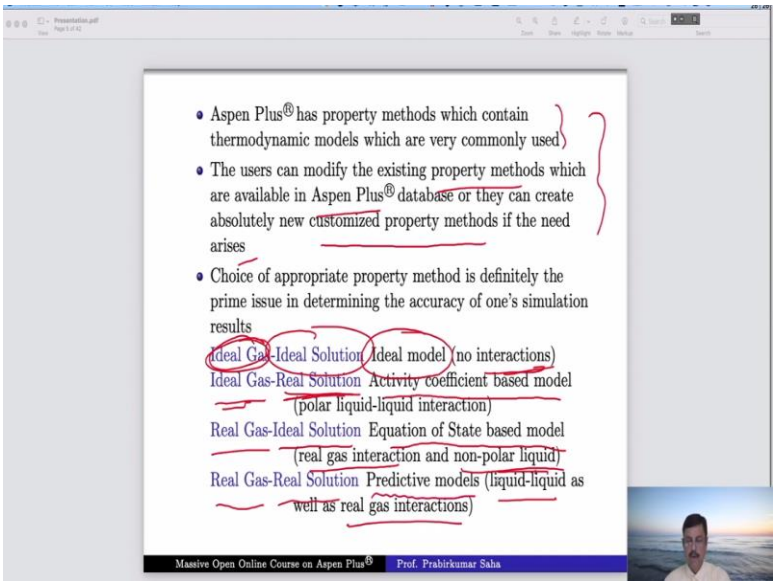



Next, we will learn about method versus model. Now many a times we use the word method and model interchangeably. Sometimes we say method sometimes we say model, but there is a slight difference between them. Method is actually a set of models which are used for calculating or computing the process parameters or physical property parameters and model is a set of mathematical equations in order to obtain that required properties.

So, model may have only a single equation or it may have multiple equations and method may contain only one model or it can be a set of models working together. So, among the set of models we have three types of models thermodynamic model, transport model and non-conventional models. So as we have already discussed before that model is basically a set of mathematical equations, mathematical models.

So, those mathematical models are there for these items. In thermodynamic case we have equation of state, activity, vapour pressure, liquid fugacity, heat of vaporization, molar volume, density, heat capacity, solubility correlation and other thermodynamic properties whereas in transport models we have viscosity, thermal conductivity, diffusivity, surface tension, etcetera. And there are certain non-conventional models which will calculate general enthalpy and density or say enthalpy and density model for charcoal these are special models that we have.

**(Refer Slide Time: 06:29)**




Aspen Plus has property methods which contain this thermodynamic models which are very commonly used and users can modify the existing property method which are available in Aspen plus database or they can create absolutely new customize property methods if the need arises. We will discuss them after a few slides. Now the choice of appropriate property method is definitely the prime issue in determining the accuracy of one's simulation results.

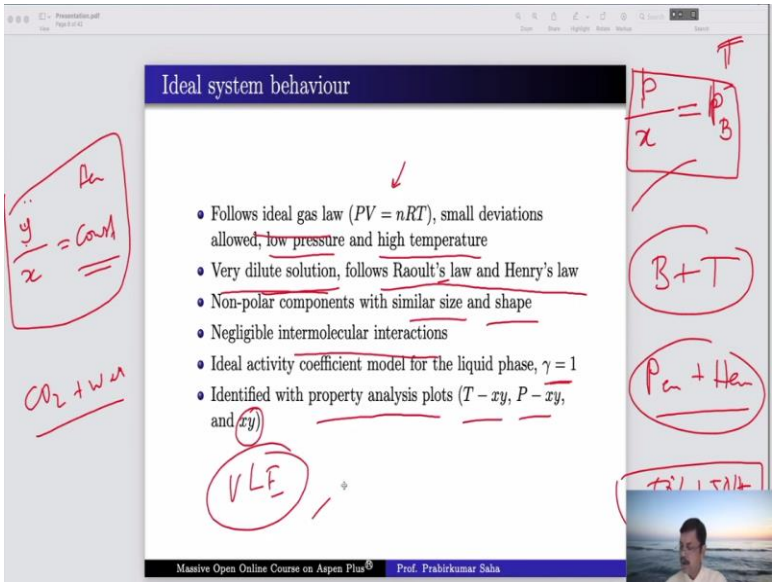
As I said that there can be various combinations of vapour phase and liquid phase. It may be ideal gas I mean ideal liquid solution or ideal gas this combination that means when there is no intermolecular interaction in that case we can use ideal model property method, but the moment there is some interaction between two liquids especially for say real solution that means when some polar components are present in the solution then definitely there will be some liquid-liquid interaction.

In that case it will no longer be ideal solution it will be a real solution, but the gas phase maybe ideal. In such situation we have to use activity coefficient based model. On the other hand, if there is no intermolecular interaction in the liquid phase that means the liquid phase is ideal whereas there are intermolecular interaction in gas phase that is real gas it is no longer the ideal gas.

In such situation we will use equation of state based model where you will have real gas interaction and non-polar liquid. If the liquid has non polar components then there will be no interaction among the liquid-liquid molecules, but the moment polar components come in the

liquid we will have some interaction and the fourth combination maybe real gas and real solution where there will be liquid-liquid as well as real gas interaction. In such situation we will use some predictive kind of model.

**(Refer Slide Time: 09:06)**




Now let us understand what is ideal system behavior? Now as I said that ideal system behavior means there will be no liquid-liquid or vapour-vapour interaction there will be no molecular interaction between them. In such situation say ideal gas it will follow the ideal gas law that is PV = nRT. There will be small deviation it is allowed, but large deviation is not allowed from PV = nRT.

And this will be valid only in the low pressure region and high temperature region. Similarly, in the liquid case the ideal solution should be very dilute solution and it will follow the Raoult's law and Henry's law. Now already yesterday we have discussed what is Henry's law we know that for very dilute solution if the mole fraction of a component in the vapour phase is y and the mole fraction of the same component in liquid phase is x.

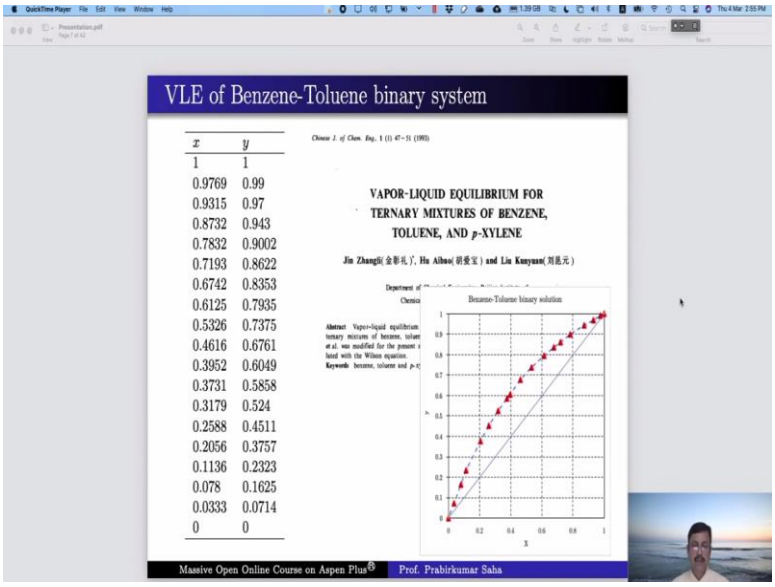
Then for a dilute solution y / x is constant and this constant is called the Henry's constant and this is a Henry's law whichever the component that follows this law is called Henry's component and we have given certain examples like $CO_2$ in water it follows Henry's law. Raoult's law as you know that the dilute solution that this condition is not required for Raoult's law it is the entire concentration range between two components will be valid.

And it is between non-polar components for similar size and shape. For instance, if it is benzene plus toluene or say pentene and hexane they follow the ideal solution behavior. In such cases they will follow Raoult's law that means for the entire range of this concentration even for 50% benzene and 50% toluene case when the solution is not dilute even for this case this kind of logic or this kind of relationship holds.

In such situation the partial pressure of the component in question if we are discussing about benzene toluene system they will say partial pressure of benzene in the vapour phase by the mole fraction of benzene in the liquid phase that ratio is equal to the vapour pressure of benzene for that particular temperature obviously this relationship with change Temperature. So, this is called the Raoult's law.

And ideal solution follows Raoult's law and then will have negligible intermolecular interaction. Ideal activity coefficient model for the liquid phase we will have activity coefficient to be one and it can be identified with the property analysis plot that is temperature versus the mole fraction xy or pressure versus mole fraction xy or xy that is the vapour liquid equilibrium diagram. So, ideal system behavior can be identified with all of them.

**(Refer Slide Time: 13:12)**

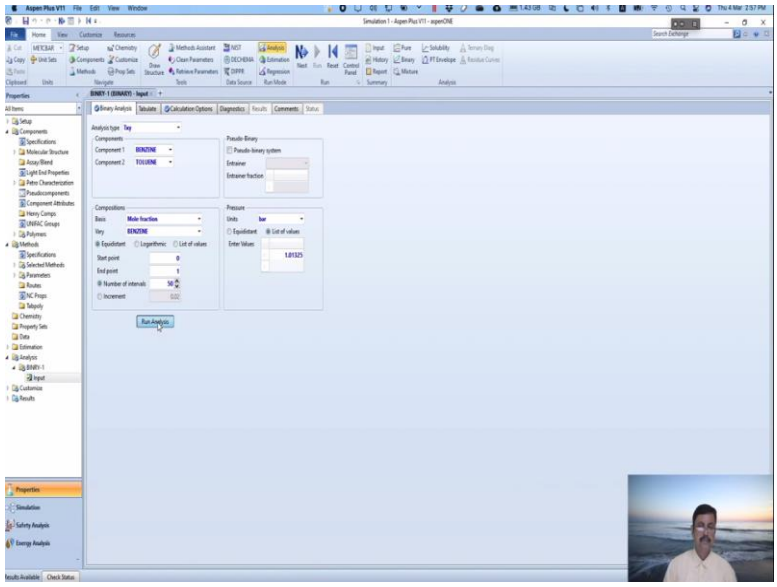



Now we come to the next section it is an example that is vapour liquid equilibrium of benzene, toluene\, binary system that we were discussing a few minutes back. Now this vapour liquid equilibrium for benzene toluene binary system has been taken from this

particular journal. It is Chinese journal of chemical engineering volume 1 published in 1993 they demonstrated some experimental study.

And the result that I have tabulated over here that is obtained from this particular journal paper and I have plotted this over here. So, you can see you will have some kind of plot. Now let us see whether benzene toluene binary system follows ideal behavior for that we have to go to the Aspen Plus simulation window.

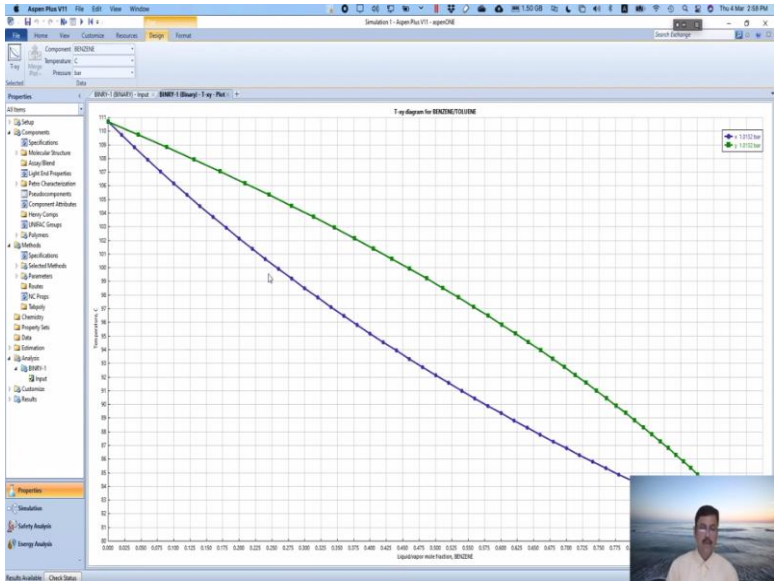
**(Refer Slide Time: 14:33)**



Let us go to Aspen plus simulation window and so benzene and toluene are added. Press next and we will use ideal method so let us run. Now you can observe over here analysis this binary analysis. So, here you can generate Txy, Pxy, Gibbs free energy mixing curves for binary system. So, we will try to find out the vapour liquid equilibrium for benzene toluene binary system.

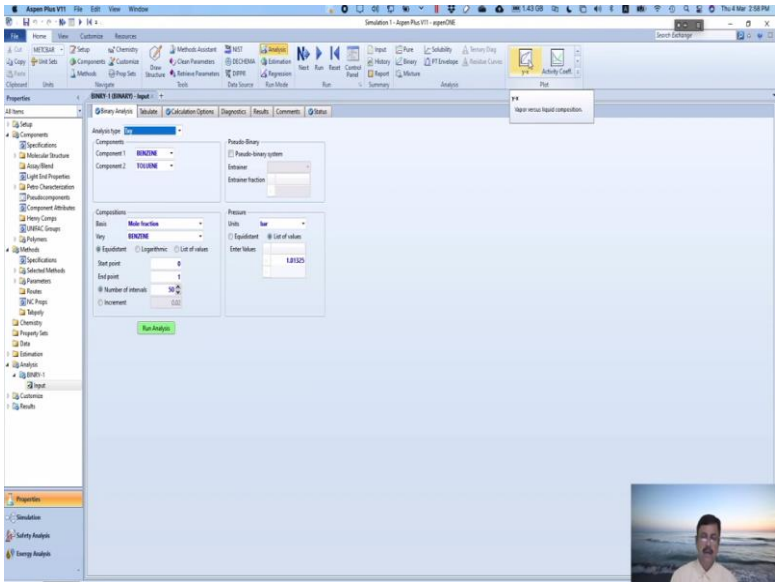
So, let us click over here. So, this is the analysis type Txy benzene, toluene basis is mole fraction for benzene and we have starting point 0, ending point 1 that is the mole fraction 0 to 1 for benzene and we have number of intervals 50 and the pressure is one atmosphere. So, let us run analysis.

**(Refer Slide Time: 16:29)**



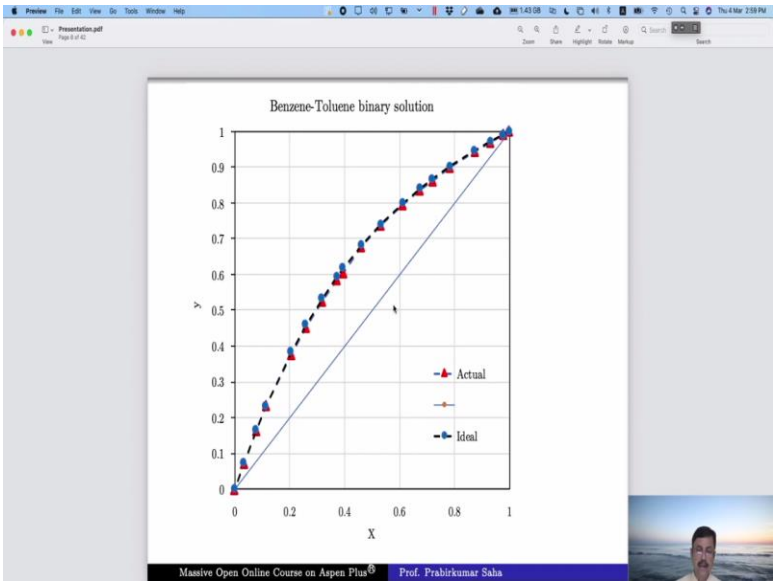
So, this is the Txy diagram for benzene toluene system at one atmosphere. So, at different temperature the values of x and y will differ. So, this is the x diagram and this is the y diagram. So, this is the bubble point curve and this is the dew point curve.

**(Refer Slide Time: 16:56)**



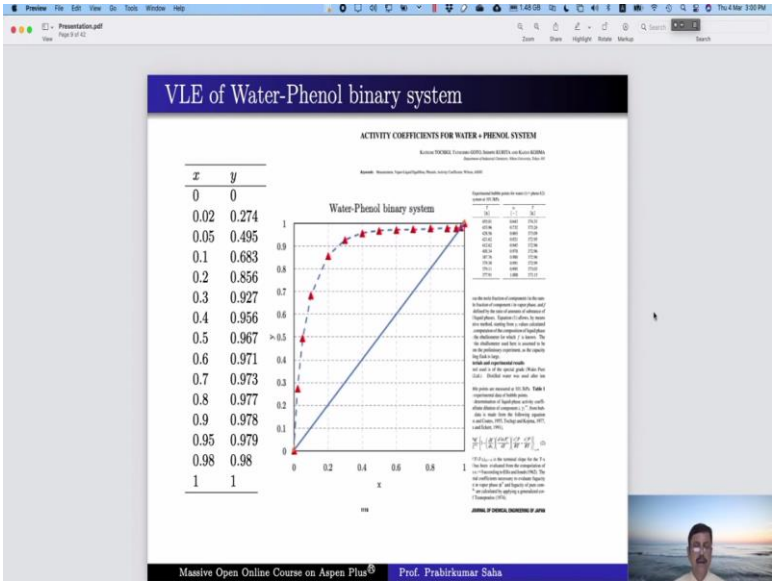
Now go to the plot and plot yx because this is the vapour liquid equilibrium curve and check this is the vapour liquid equilibrium curve for benzene toluene system using ideal model or ideal system behavior. Now, let us compare it with this one. So, this is the experimental result and this is the model result. Let us see how close they are.

**(Refer Slide Time: 17:35)**




And this is the closeness, this is the actual and this is the ideal behavior. So, you can understand that the experimental result and the ideal model behavior they almost superimpose on each other. So, we can say that benzene, toluene binary system it demonstrates ideal behavior.

**(Refer Slide Time: 18:10)**

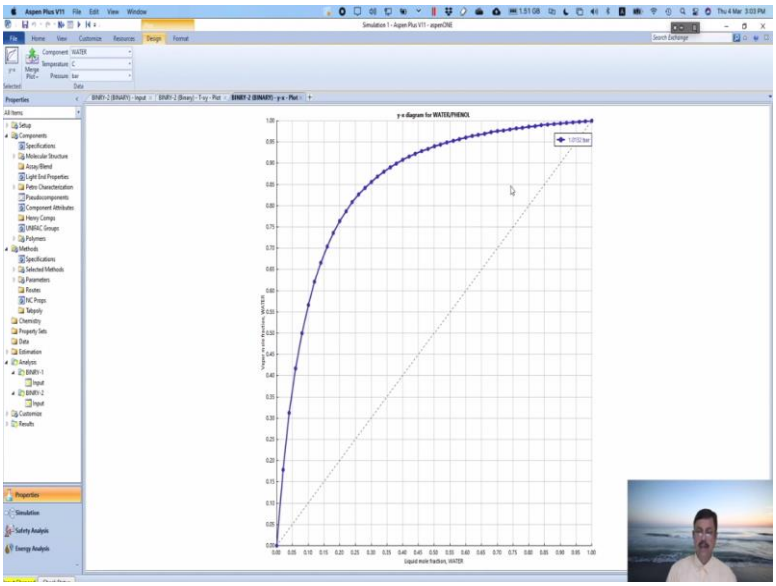



| x | y |
|---|---|
| 0 | 0 |
| 0.02 | 0.274 |
| 0.05 | 0.495 |
| 0.1 | 0.683 |
| 0.2 | 0.856 |
| 0.3 | 0.927 |
| 0.4 | 0.956 |
| 0.5 | 0.967 |
| 0.6 | 0.971 |
| 0.7 | 0.973 |
| 0.8 | 0.977 |
| 0.9 | 0.978 |
| 0.95 | 0.979 |
| 0.98 | 0.98 |
| 1 | 1 |

But is it true for water phenol binary system let us try. We have got the data from this particular journal paper. Journal of chemical engineering of Japan they have published some paper and I have taken the data from there and this is the xy data and I have plotted over here. This is the experimental data. Now let us try to see whether the ideal model behavior works for it for that let us go back to component water and phenol water and phenol so write water and phenol.

Now the model is there run now again you take this binary over here, second binary unit comes up press water and then phenol, mole fraction of water from 0 to 1 with 50 intervals pressure remain same run analysis. Again you can find this is the bubble point curve and this is the dew point curve.

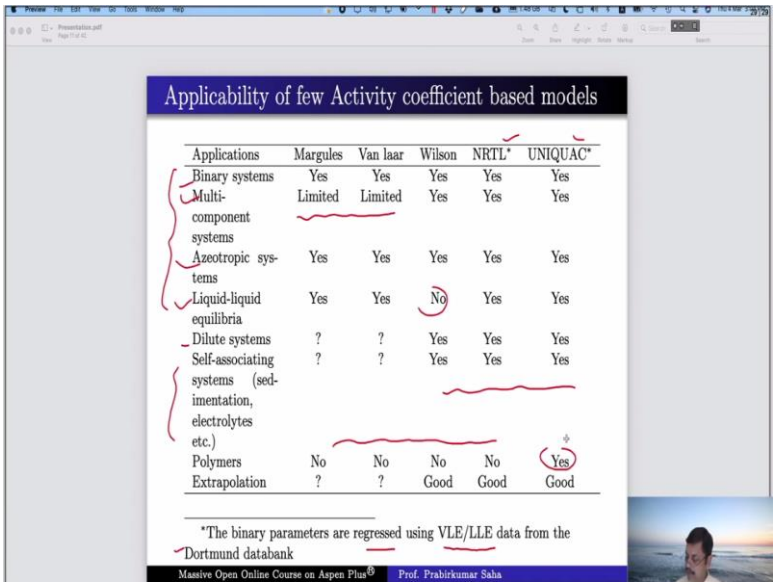
**(Refer Slide Time: 19:56)**



Now bring in the yx diagram. So, you have got the yx diagram for water and phenol system at one atmosphere pressure. Now can you compare this with this yes we have done and this is the comparison. This is the actual curve the red triangle and the ideal curve is the blue circles surely they do not match with each other. Now we have tried Wilson also Wilson is another activity coefficient model that also we have tried and that also do not match with the experimental data.

So, we have to find some other property method for water phenol binary system, but definitely it is not an ideal behavior. So, it is a non-ideal solution we can certainly say that water phenol binary system is a non-ideal binary system definitely because water is a polar compound it is not non-polar. So, because it is a polar compound there will be some intermolecular interaction.

**(Refer Slide Time: 21:31)**

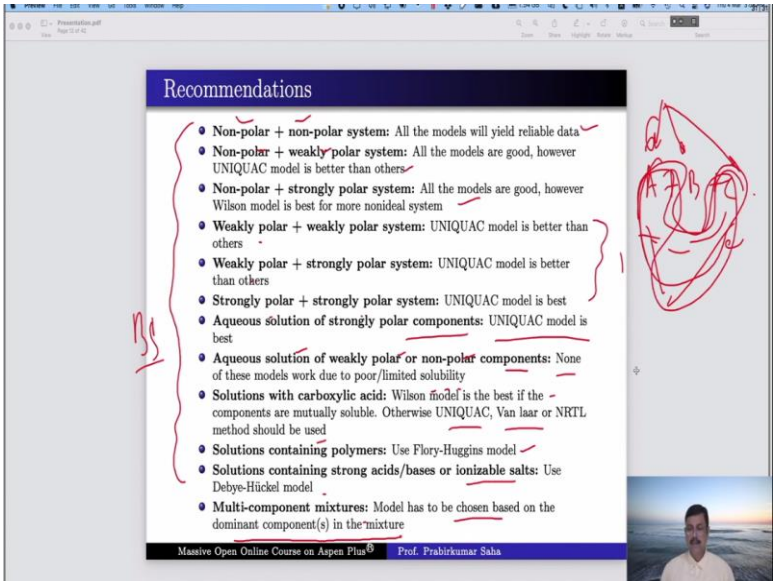



Now here we have got some activity coefficient based model they are Margules Van Laar, Wilson, NRTL and UNIQUAC. Now the binary parameters of NRTL and UNIQUAC they have been regressed using vapour liquid equilibrium or liquid-liquid equilibrium data from the Dortmund databank. Now we see that for binary systems, multi component systems, Azeotropic systems and liquid-liquid equilibrium for four of them almost all the activity coefficient based model they work except Wilson model does not work for liquid-liquid equilibrium.

And Margules and Van Laar model they have limited applicability on multi component system, but this Margules and Van Laar module they do not work for dilute system and self associating system such as sedimentation and electrolyte, but Wilson, NRTL and UNIQUAR they work for this kind of system. The polymer systems only UNIQUAC model works none of these Margules, Van Laar, Wilson, NRTL they work for polymer system.

And for extrapolation kind of work we cannot use Margules and Van Laar we have to use Wilson, NRTL or UNIQUAR activity based coefficient model.

**(Refer Slide Time: 23:26)**




Now we have certain recommendations for mainly binary system. The last one will be for multicomponent mixture here for binary system we have two components if both of them are non-polar then all the models will yield reliable data, but if one of them is non-polar and other one is weakly polar then all the models are good however UNIQUAC model is better than others.

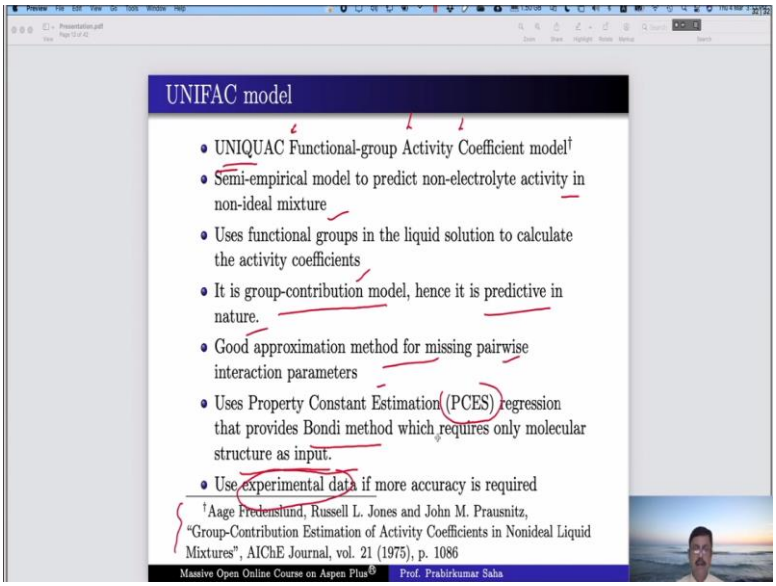
And if there is a non-polar strongly polar combination in such situation all the models are good however Wilson model is the best for such non-ideal system and when we have a combination such as weakly polar or weakly polar, weakly polar and strongly polar, strongly polar and strongly polar for this kind of system UNIQUAC model is better than others. Again for aqueous solution of strongly polar component that means one of the component is water.

The other component is strongly polar component then UNIQUAC model is the best and aqueous solution of weakly polar or non-polar components none of these model was due to poor or limited solubility because water is a polar solvent and if the component is non polar or weakly polar then it will not be dissolved in water. So, none of this models work. Solutions with carboxylic acid.

Wilson model is the best if the components are mutually soluble otherwise UNIQUAC, Van Laar or NRTL model should be used. If the solution contains polymers then you have to use Flory Huggins model, if the solutions contains strong acid or bases or ionizable salts then you have to use Deybe Huckel model.

So, these are for binary systems and for multi component mixtures the model has to be chosen based on the dominant component in this mixture. So, suppose we have a combination of A + B + C then we have to see what are the dominant component in this mixture whether it is A and B or B and C or it is A and C. So, the dominant components will decide what should be the binary system and you have to plan your property method.

**(Refer Slide Time: 26:29)**



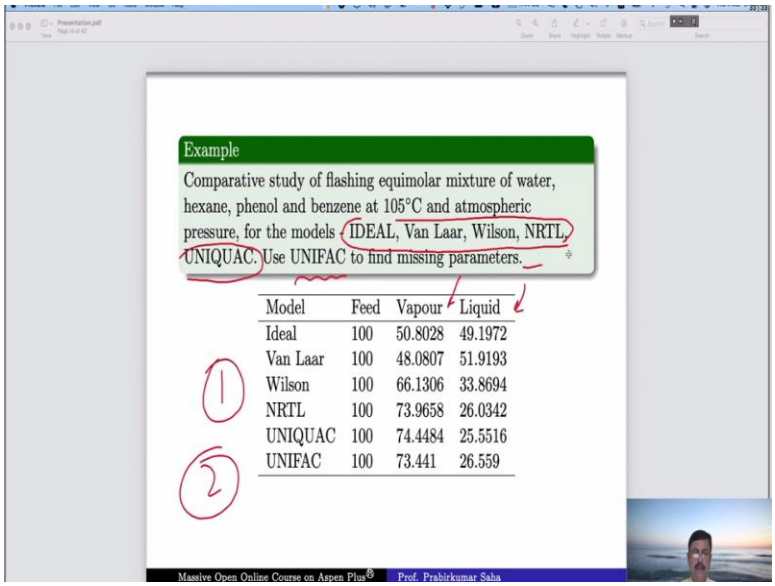

Now, we have heard of UNIFAC model, but we have never used it till now. The question is what is UNIFAC model. UNIFAC models means it is the short form of UNIQUAC functional group, activity coefficient is FAC. So, UNIFAC it is UNIFAC model that way. So that has been developed by Fredenslund and Jones and Prausnitz in 1975 it has been published in AIChE Journal.

So, interested people can go and refer this particular Journal paper to understand more of UNIFAC model. It is semi empirical model to predict the non electrolyte activity in non-ideal mixture. It uses the functional groups in ideal solution to calculate the activity coefficient and it is a group contribution model hence it is predictive in nature. So, in many combinations the direct interaction is not available.

In such situation UNIFAC model predicts the interaction beautifully. So, it is a good approximation method for missing pairwise interaction parameters and it uses the property constant estimation PCES regression that provides Bondi method which requires only the

molecular structure as input and if more accuracy is needed then you have to use experimental data rather than the UNIFAC model. We shall learn it better by using an example.

**(Refer Slide Time: 28:34)**




So, this is the example it says comparative study of flashing equimolar mixture of water, hexane, phenol and benzene at 105 degree centigrade and atmospheric pressure for the models ideal, Van Laar, Wilson, NRTL, UNIQUAC and use UNIFAC to find the missing parameters. So, let us see what it does. Now this particular example does two things. One is it shows how the choice of different property method is different result that is the number one.

And number two lesson that we find is use of UNIFAC method to find missing parameter. Now let us go to the Aspen Plus example.

**(Video Starts: 29:42)**

Now in the components we have to have water, hexane, phenol and benzene. So, water, phenol and benzene is there we have to use hexane and we will use first ideal model. So, ideal model is already there what are the models we have Van-Laar, Wilson, NRTL, UNIQUAC.

So, Van Laar, Wilson, UNIQUAC and NRTL so, press next so this is done. Next is NRTL this is also done then UNIQUAC this is done and finally Wilson. Now for the time being let us use ideal method. Property methods I have fixed now we have to go to the simulation

chamber. So go to flash bring in flash over here, materials so this is feed, this is vapour and this is liquid.

So just rename them this is feed, this is vapour and this is liquid press next. We have 105 degree centigrade and atmospheric pressure so 105 and atmospheric pressure and we have equimolar mixture of water, hexane, phenol, benzene. So, equimolar of four things. So, we say it is 25 should be 25, 25, 25 and 25 remember there would not be any toluene and total it will be 100 moles so it will be equimolar all of them have same number of moles.

Press next we have to give the flash option let us say heat duty is zero and the flash pressure again it is one atmosphere. Now all the block parameters are set run it. Now the stream results are available. See what is the stream result? The molar flow feed is 100, vapour 50.808 and liquid 49.1972. So, vapour is 50.8028 and liquid 49.1972. Now let us run this with Van Laar model.

So, for that we can go to the block option we do not have to go back to properties here only we can change the block option from ideal to Van Laar. So, we have got the stream results. So, the molar flow rate vapour is 48.0805. So, this is using Van Laar liquid is 51.91. So, using Van Laar it has reduced from 50 to 48. Now, if you use UNIQUAC then you are expected to have 74 just check go to block option and go to UNIQUAC and run.

See the stream result, it is 74.4484. So, you can understand how by changing the property method our simulation results change that is why it is very, very important to choose a proper property method so that the results simulate the experimental data as close as possible otherwise it will give a wrong result altogether if we do not use the proper property method.

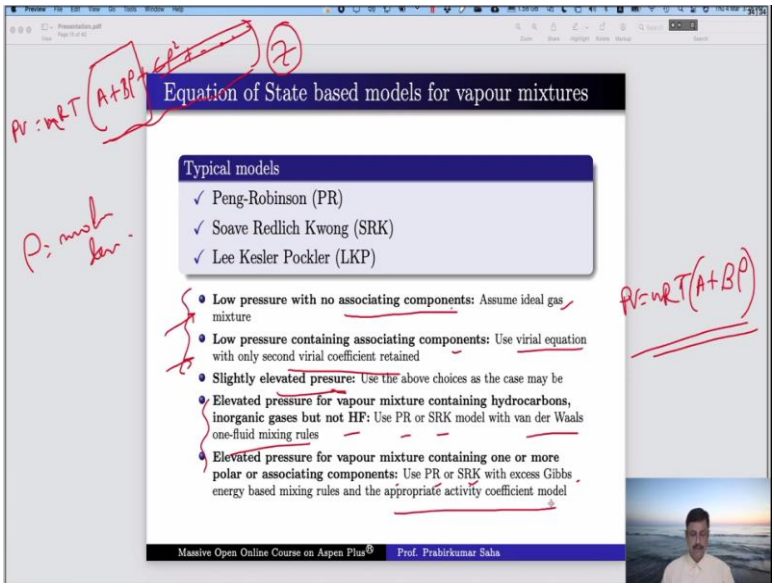
Now the second task we have to use UNIFAC to find missing parameter. So, what are the missing parameter? You go back to property method and see the binary interaction between all the components for instance go to Wilson method. Now, here we have the temperature dependent binary parameter with water and phenol combination, but do we have water hexane combination we do not.

Do we have water toluene combination? No, we do not. Water benzene combination we do not have. So, we have water phenol combination only. So, other temperature dependent

binary parameters in Wilson method we do not have at all, but we have the option to estimate the missing parameter by ticking this one estimate missing binary parameters using UNIFAC or other methods.

So, just tick it and then run. The moment you run all the missing parameters will come. Water phenol was the last one so we got water benzene, water toluene, water hexane and phenol hexane was also absent it was not there, but phenol hexane has been calculated. So, all of them have been calculated using RPCES that we have got from here the regression using PCES. **(Video Ends: 38:50)**

**(Refer Slide Time: 38:53)**




Now we will learn equation of state based models for vapour mixtures and we have three typical models Peng Robinson, Redlich-Kwong-Soave and Lee-Kesler Pockler this models. Now we have certain recommendations if we have low pressure with no associating components then we can safely use ideal gas mixture, but if we have low pressure with some associating components then we have to use virial equation with only second virial coefficient written.

What is the virial equation? For ideal gas law we know it is PV = nRT and virial equation is NRT into A + B into rho + C into rho square plus

$$PV = nRT *(A + B\rho + C\rho^2 + D\rho^3 + ……..)$$

$\rho$=Molar density

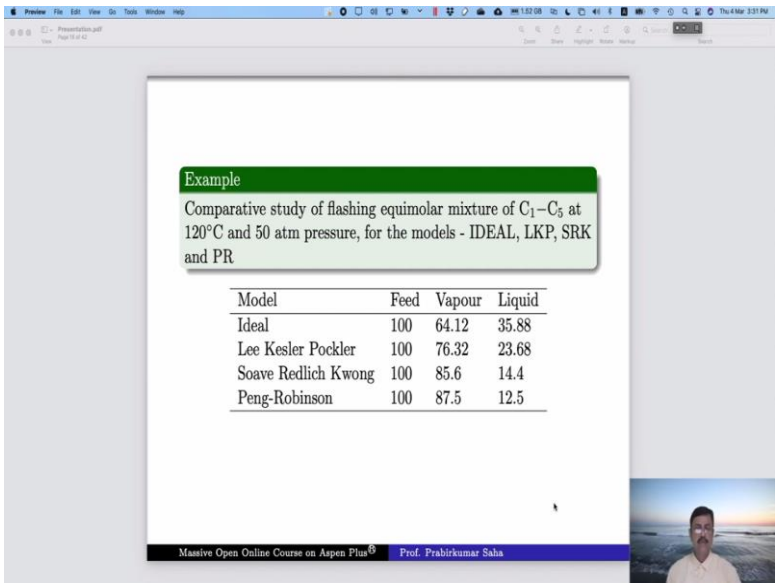
and so on and this one rho is equal to molar density. Actually this is nothing, but the compressibility factor J and here it is said that only second virial coefficient written. So, all of them will be cut only this much is written. So, actually it should be PV = nRT into A + B rho.

$$PV = nRT *(A + B\rho)$$

So, this kind of virial equation can be used for this system and if you have slightly elevated pressure then you can easily associate with either low pressure with associating components or low pressure containing associate component. So, you can choose the cases as it maybe and if you have elevated pressure then you have two choices for vapour mixture containing hydrocarbons inorganic gases, but not hydrogen chloride.

Then you can use Peng Robinson or Redlich-Kwong-Soave model with van der Waals one fluid mixing rules, but if you have vapour mixture containing one or more polar or associating components then you have to use Peng Robinson or Redlich-Kwong-Soave model with excess Gibbs energy based mixing rule and the appropriate activity coefficient based model.

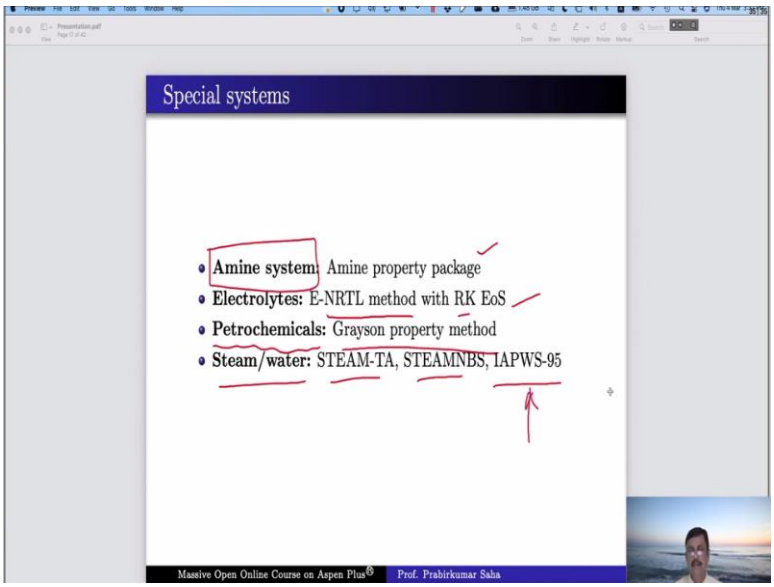
**(Refer Slide Time: 41:56)**




Now this is another example of similar nature that we had done a few minutes back. The same kind of example is given. So, comparative study of flashing equimolar mixture of C1 to C5 that is methane, ethane, propane, butane and pentane. So, instead of water, hexane, phenol, benzene we are using C1 to C5 at 120 centigrade and 50 atmosphere pressure for the models ideal LKP, SRK and PR.

That is ideal model, Lee Kesler Pockler model, Redlich-Kwong-Soave model and Peng Robinson and this will be equimolar mixture. So, earlier for this case we took 25 moles of water, 25 hexane, 25 phenol and 25 benzene because we had four components, in this case we are having five components. So, we have to take 20, 20 each. So, the same thing we have to do and check whether we get this figures for vapour and liquid. So, I would not do it here on the Aspen domain I give it as a task for you to practice.

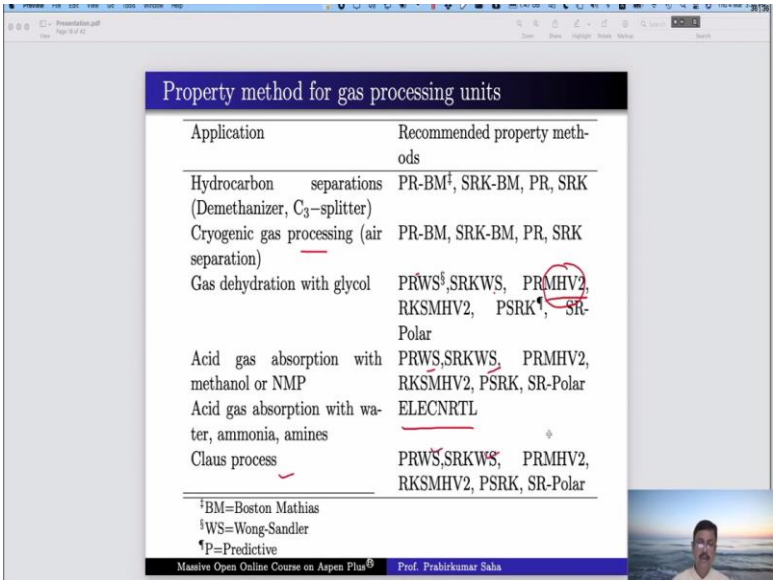
**(Refer Slide Time: 43:28)**




So, Aspen Plus has some special system packages also. They are mostly amine property package for amine system that means the system where we have lot of different kind of amines if they are in the system we can use amine package and amine systems are popularly used for carbon dioxide sequestration. For electrolyte we have special version of NRTL method that is called E-NRTL or ELECNRTL package.

And that is with Redlich-Kwong model equation of state. We have Grayson property package for petrochemical products and for steam and water we have steam table and steam NBS and more recently and more popular it is IAPWS-95 package that is exclusively for steam and water.

**(Refer Slide Time: 44:38)**

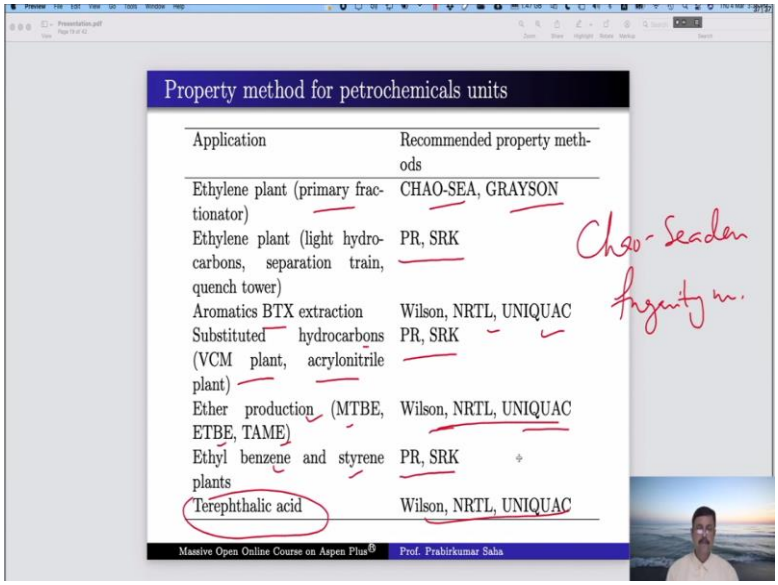



And there is some more property method for gas processing units. We have several applications and the corresponding recommended property method. So, we have hydrocarbon separation such as Demethanizer or C3 splitter for that we can use PR-BM that is Peng Robinson Boston Mathias property method or Soave-Redlich-Kwong Boston Mathias property method.

The same kind of property methods can be used for cryogenic gas processing for air separation. If you have gas hydrogen with glycol application, then you can use Peng Robinson Wong-Sandler method or Soave-Redlich-Kwong Wong-Sandler method. You can also use Peng Robinson MHV2 where MHV2 property package is used along with Peng Robinson method.

For acid gas absorption with methanol or NMP we can again use Peng Robinson Wong Sandler or SRK Wong-Sandler. For acid gas absorption with water, ammonia or amines you can safely use NRTL method ELECNRTL and for Claus process you can again use Peng Robinson Wong-Sandler or SRK Wong-Sandler method.

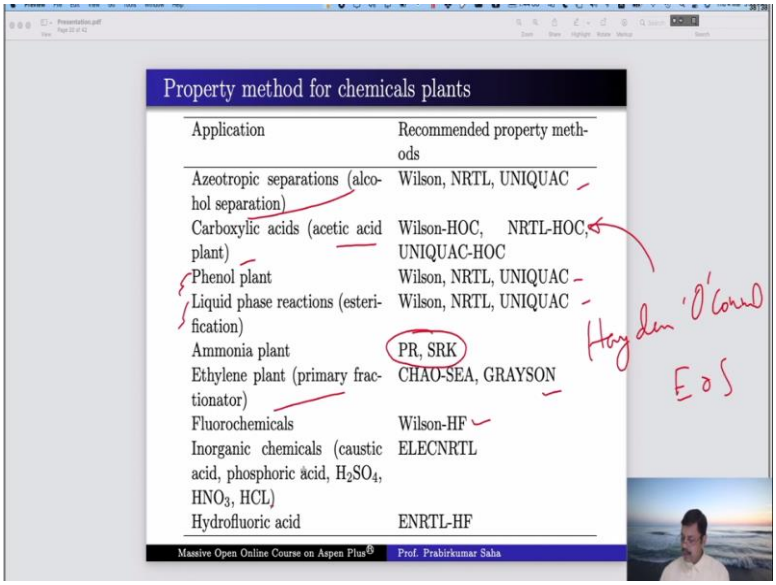
**(Refer Slide Time: 46:40)**




To continue with the suggestions and recommendation we have the property method suggestion for petrochemical unit, several applications are suggested like for ethylene plant primary fractionators we can use CHAO SEA and GRAYSON package, CHAO-SEA means CHAO Seader fugacity model. If we have ethylene plant with light hydrocarbon and separation train, quench tower then we can use Peng Robinson or Redlich-Kwong Soave model.

For aromatics benzene toluene xylene extraction, we can use Wilson, NRTL, UNIQUAC model for substituted hydrocarbons like VCM plant, acrylonitrile plant we can again use Peng Robinson and SRK. For Ether production like methyl tert-butyl ether or ETBE or TAME we can use Wilson, NRTL, UNIQUAC. The same models can be used for Terephthalic acid and for ethyl benzene and styrene plants you can use Peng Robinson and Redlich-Kwong Soave method.

**(Refer Slide Time: 48:09)**




And for property method for chemical plants we have recommended property methods like Wilson, NRTL, UNIQUAC for Azeotropic separation like alcohol separation, Phenol plant, liquid phase reactions like Esterification and if you have carboxylic acid for a acidic acid plant we have to use Hayden O'Connell equation of state method to add with Wilson, NRTL or UNIQUAC.

For Ammonia plant you can use Peng Robinson or SRK method for flurorochemical you can use Wilson and HF, ethylene plant, primary fractionators again you can use CHAO-SEA and Grayson, inorganic chemicals like caustic acid, phosphoric acid, sulfuric acid, $HNO_3$, HCL you can use ELECNRTL and hydrofluoric acid you can use E-NRTL HF package. So, we end our lecture at this point today. Thank you.