Industrial Processes and Scale-up

PRO II Numerical practice: Liquid-vapor equilibrium of the system Benzene-CycloHexane

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- Benzene Teb=80,13°C
- Cyclohexane Teb=80,64°C

In order to evaluate the liquid-vapor equilibrum of this mixture, we need to calculate the vapor pressure of the two pure compounds at different temperatures.

By using PRO II software we can make this calculation, thanks to the rich software database.

1) We calculate the vapor pressure of benzene and cyclohexane in a temperature range between 50-100°C, using 100 calculation points;
2) We calculate the vapor-liquid equilibrium in this T range, with the hypothesis that this mixture is not an azeotropic one.

It is possible to calculate the relative volatility of the mixture benezene/cyclohexane by considering it as ideal, case 1 of this table:

	Gas behavior	Gas phase mixture behavior	Liquid phase mixture behavior	Note
1	Perfect	Ideal	Ideal	Low pressure;
2	Perfect	Ideal	Non ideal	Low pressure
3	Real	Ideal	Ideal	High pressure
4	Real	Ideal	Non ideal	High pressure
5	Real	Non ideal	Non ideal	High pressure

LV Equilibrium in case #1 (Law and Dalton Law)

$$y_i P = x_i p_i^{\circ}(T)$$

Equilibrium constant: $k_i = \frac{y_i}{x_i}$

Relative volatility: $\alpha_{i,j} = \frac{k_i}{k_j}$ $\alpha_{i,j} = \frac{\frac{y_i}{x_i}}{\frac{y_j}{x_j}} = \frac{y_i x_j}{y_j x_j}$

$$\alpha_{i,j} = \frac{p_i^{\circ}(T)}{p_j^{\circ}(T)}$$

$$y_1 = \frac{\alpha_{1,2} x_1}{1 + (\alpha_{1,2} - 1) x_1}$$

For $\alpha_{1,2} = 1$ $y_1 = x_1$

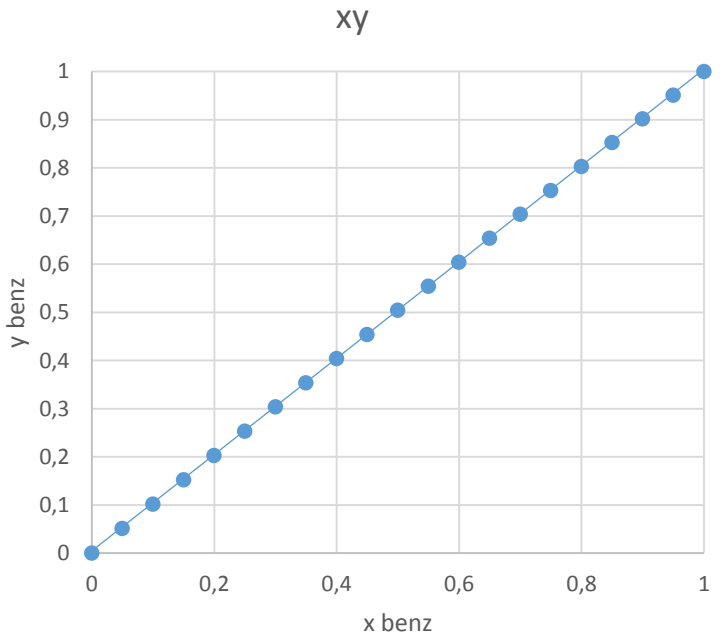
For $\alpha_{1,2} > 1$ $y_1 > x_1$

For $\alpha_{1,2} < 1$ $y_1 < x_1$

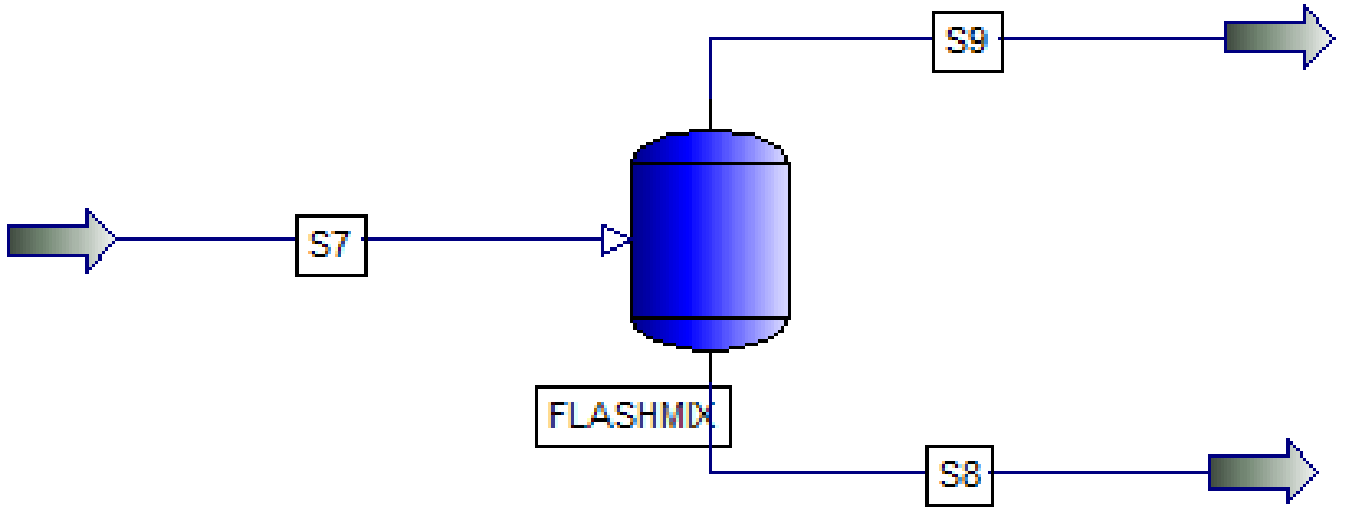
From the data of the pressure vapore calculated with PRO II it is possible to calculate the relative volatility.
In the range of boiling of the mixture, it is possible to calculate a mean relative volatility, using the equation:

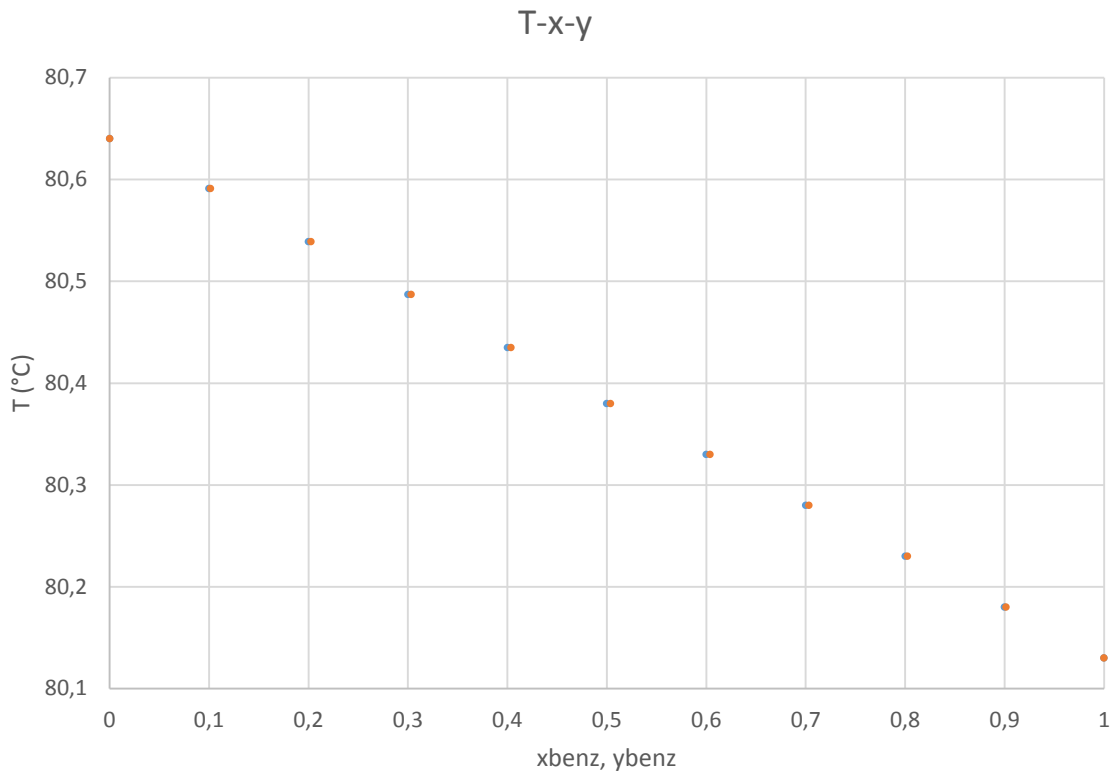
$$y_1 = \frac{\alpha_{1,2} x_1}{1 + (\alpha_{1,2} - 1) x_1}$$

And then to obtain the L-V equilibrium curve. We are in the hypothesis that the mixture is ideal (case 1)

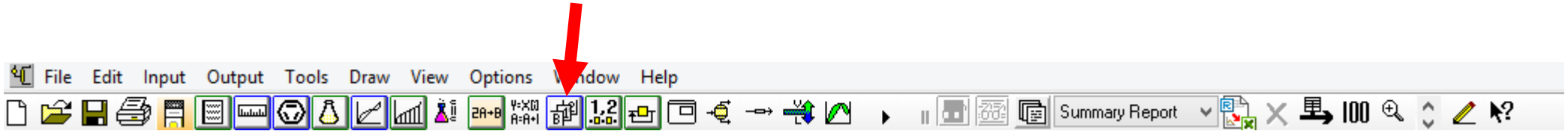


It is now possible to calculate the boiling temperature of several mixtures benzene/cyclohexane having different compositions. We can make it by the FLASH tool in PRO II. Falsh are contiunuos distillation column single-stage that operate at the boiling temperature of the fed mixture. This temperature obviously is dependent from the pressure set in the Flash.

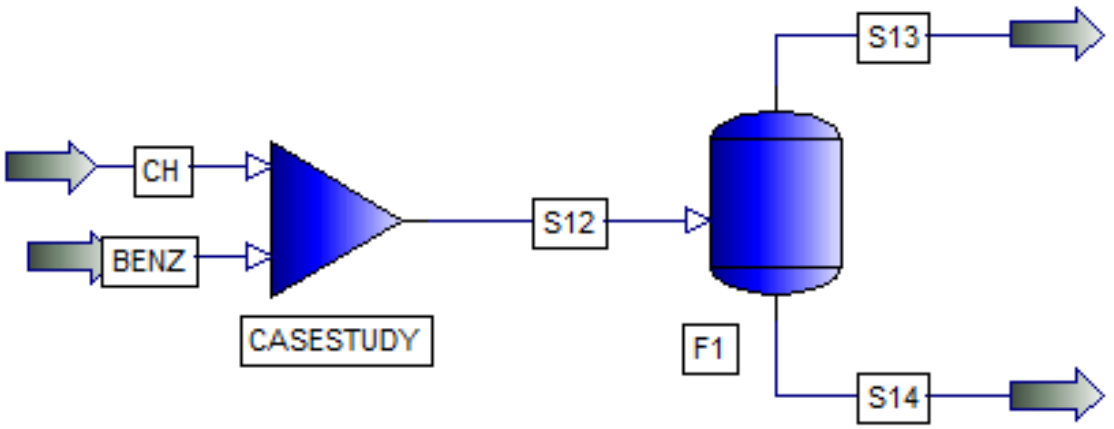




In similar calculations , where the same kind of operation is made by changing one variable of the process, it is convenient to use «CASE STUDY» options of PRO II.



Example of application of Case Study



We can use the flow of stream «Benz» to change, by the mixer, the composition of the mixture fed in the Flash.

The system benzene/cyclohexane is absolutely not ideal.

We can observe by using PRO II the difference in the L-V equilibrium if we consider the non-ideality of the mixture. We can use for this scope different thermodynamics models for the non-ideality evaluation:

- Ideal mixture (already discussed, as reference)
- Van Laar Model
- NRTL Model
- UNIQUAC Model
- UNIFAC Model (Previsional)

I coefficienti di attività dipendono da temperatura, pressione e composizione. Mentre la dipendenza dalla pressione è solitamente debole, quella dalla temperatura e dalla composizione è molto più marcata.

The activity coefficient are dependent from temperature, pressure and composition. The dependence from composition and temperature is very high.

The equation and the meaning of these models will be discussed in a dedicated lesson.

Non ideality mixture

$$y_i P = \gamma_i x_i p_i^{\circ}(T)$$

$$\frac{y_i}{x_i} = \frac{\gamma_i p_i^{\circ}(T)}{P} \qquad \frac{y_j}{x_j} = \frac{\gamma_j p_j^{\circ}(T)}{P}$$

$$\alpha_{i,j} = \frac{k_i}{k_j}$$

$$\alpha_{i,j} = \frac{\frac{y_i}{x_i}}{\frac{y_j}{x_j}} = \frac{\gamma_i p_i^{\circ}(T)}{P} \cdot \frac{P}{\gamma_j p_j^{\circ}(T)} = \frac{p_i^{\circ}(T)}{p_j^{\circ}(T)} \cdot \frac{\gamma_i}{\gamma_j}$$

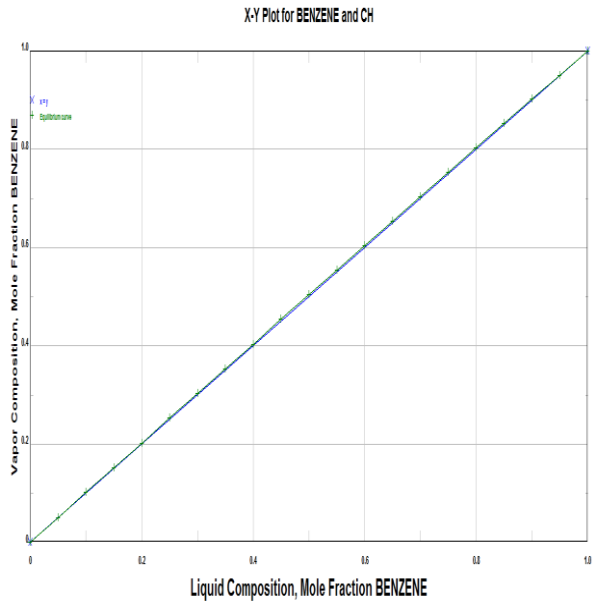
Contribution of the RATIO of the vapor pressure

Contribution of the RARIO of the activity coefficients

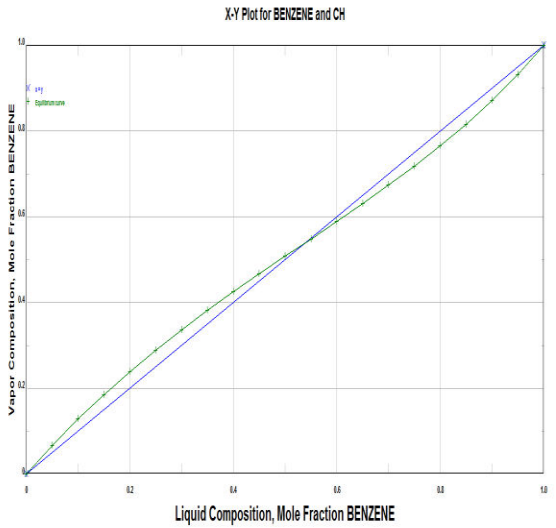
For each composition of the mixture!

Non ideal ELV from PRO II

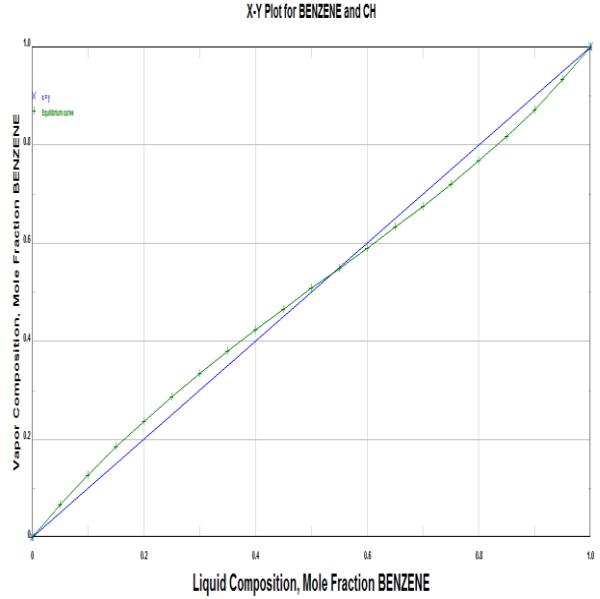
Ideal



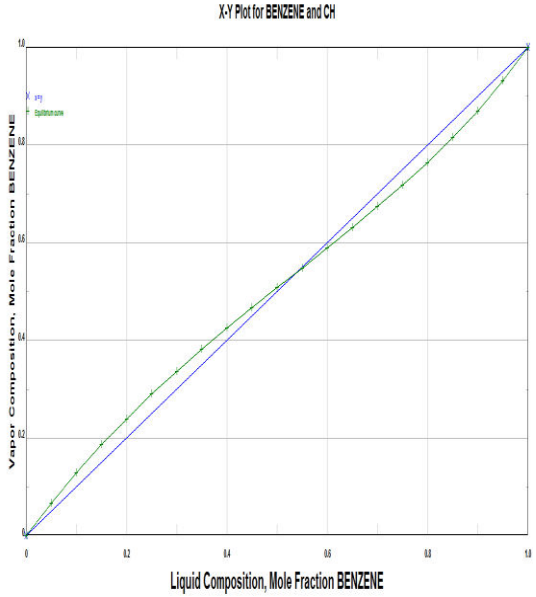
Van Laar



NRTL

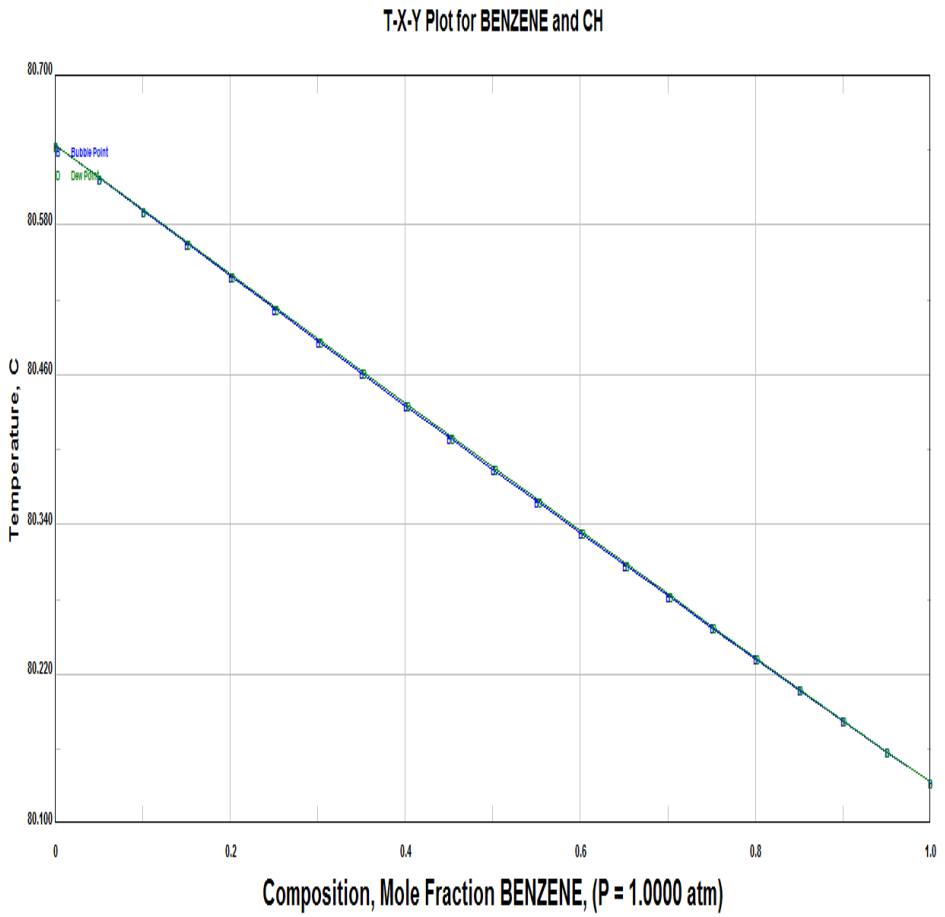


UNIFAC

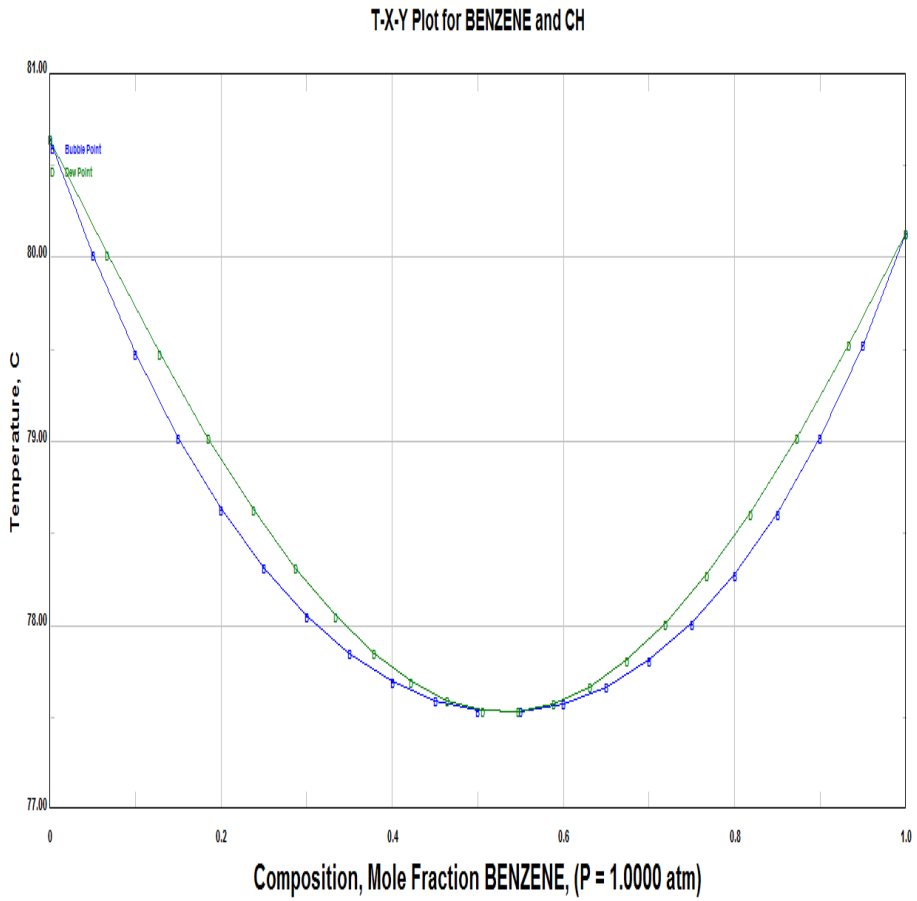


Non ideal ELV from PRO II

Ideal



NON Ideal



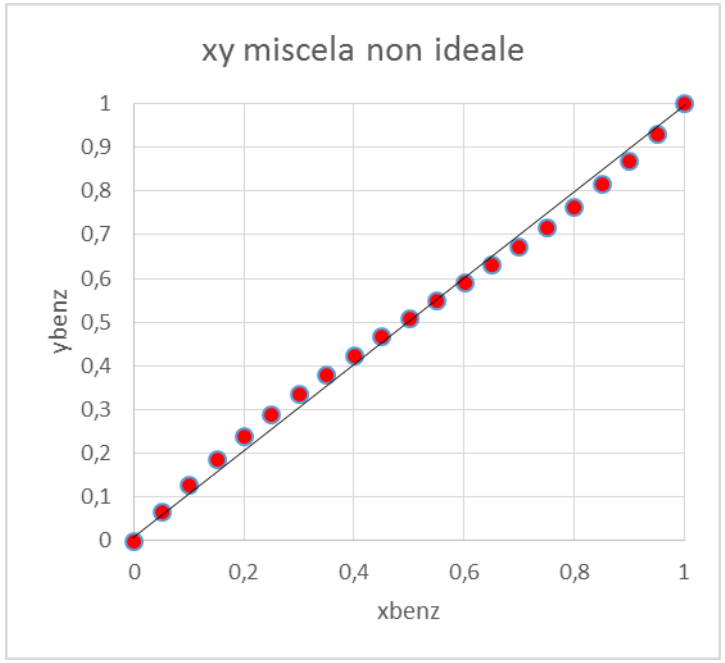
We can verify these calculations!

1) We calculate the different activity coefficients with PRO II with the different modelsper il calcolo dei coefficienti di attività usando i vari modelli
2) We can use the previous equations for the validation of these diagrams

For simplicity it is convenient to consider constant the ratio between the vapor pressures of cyclohexane and benzene, and to multiply this number for the ratio between the activity coefficients (different for each composition).

In this way, it is possible to calculate the relative volatility for each point of composition of the mixture and with this to calculate the molar fraction (y) with the previous equation:

$$y_1 = \frac{\alpha_{1,2} x_1}{1 + (\alpha_{1,2} - 1) x_1}$$



Calculation of the boiling temperature of a mixture

$$\sum_{i=1}^{n} y_i = \sum_{i=1}^{n} \frac{x_i p_i^{\circ}(T)}{P} = 1$$

IDEAL MIXTURES

$$\sum_{i=1}^{n} y_i = \sum_{i=1}^{n} \frac{\gamma_i x_i p_i^{\circ}(T)}{P} = 1$$

NON IDEAL MIXTURE