

ACCURACY REQUIREMENTS FOR PHYSICAL PROPERTIES: A CASE STUDY

Georges Heyen, Boris Kalitventzeff

Department of Chemical Engineering, Université de Liège, Allée de la Chimie, 4000 Liège, Belgium
Belsim s.a., Rue de Bruxelles 174k, 4340 Awans, Belgium

The quality of any engineering design depends on the reliability of basic data used to characterize materials handled in the process. There have been instances where the calculated behavior has been sufficiently erroneous to cause the physical layout of a process to be incorrect. In this article, we will present and discuss the origin of errors, and their potential consequences on plant design. To illustrate the importance of proper selection of the physical property estimation method, a computer calculation of a distillation column fitted with a vapor recompression system is presented. Physical properties obtained from the reference data bank available in a simulation programme are compared to experimental data. Some pure component properties and binary interaction coefficients in Soave-Redlich-Kwong equation of state are adjusted. Sensitivity of the model response with respect to variation in the physical property values is discussed. The case study illustrates the sources and consequences of uncertainties:

- inaccurate laboratory measurements;
- inadequate thermodynamic models;
- approximations in the plant model.

1. PROPERTIES AND PROCESS MODELING IN EQUIPMENT DESIGN

Contemporary design methods rely heavily on the detailed modeling of chemical and physical phenomena occurring in chemical processes. This approach can only be adopted if physical and thermodynamic properties are available for all mixtures handled. An enormous number of substances and their mixtures have to be addressed: as a metric of the problem complexity, we can recognize that over 56 million organic and inorganic substances are now described in the CAS registry (CAS, 2011). One cannot expect that properties have been measured for the huge number of mixtures that could be prepared from those components, thus models are needed either to correlate and interpolate the available measurements, or to predict mixture properties from pure component information.

Equipment models incorporate several types of equations. Balance equations are based on fundamental conservation laws, and must be enforced rigorously. Energy balance equations involve measurable quantities, such as pressure, temperature, composition and flows, from which models are used to estimate conceptual properties, like enthalpy or entropy (O'Connell et al, 2009). Unit operation models also involve additional constitutive equations to define the rate of transformations occurring in the equipment; these make use of additional physical properties, like viscosity, thermal conductivity or diffusion coefficients, that must be estimated using specific models.

The quality and reliability of any design is thus clearly dependent on the accuracy of constitutive models, and particularly to the physical property values. The properties or model parameter values can be provided from many sources, which are, cited in increasing order time and resource requirements:

- Primary literature, compilations and databases;
- Estimation from correlations, prediction using empirical models;
- Computation from molecular simulation;
- New laboratory measurements.

Literature search provides a wealth of information, but this can also be a time consuming adventure. The bulk of available data is for pure components: mixture data are usually limited to two or three component systems over limited range of temperature and pressure. Experimental procedures are not always completely described, and this excludes any estimation of the data reliability. Some experimental procedures are out-dated, and measurements obtained from them should be handled with caution. Progress in the sample purification techniques can also explain why proposed values for some physical properties have drifted with time.

Access to computerized data banks can also give easy access to large amount of information. Caution should be exercised when comparing measurements from different data sources, since estimates of measurement reliability are seldom reported. Even if the development of such a data bank systems represents a considerable effort, it still is far from being able to provide answers to all problems. Nature complexity is of another order of magnitude. Most basic data needed for process design have never been measured (and probably will never be). Thus good estimation tools must also be available.

Direct measurements must be reduced to model equations, e.g. using least squares fitting to obtain parameters of empirical correlations. This procedure may also introduce uncertainty in the physical property model. Relatively few experimental data exist for mixtures, and thus their properties have to be estimated. Since models are always based on simplifying assumptions, they cannot achieve excellent reliability for all properties. For instance, assuming that an equation of state that predicts accurately the liquid saturation pressure will also provide good estimates of density or residual enthalpy may lead to serious errors.

2. RELIABILITY OF EXPERIMENTAL DATA

Laboratory measurements are the ultimate basis for any design procedure, since any model contains adjustable parameters that must be tuned using experimental data. Whenever possible, experimental data obtained by trained personnel using good laboratory equipment and well prepared samples should be preferred as the basic data source for important design problems. However this attitude cannot always be accepted, due to the high cost of good measurement and the time needed to carry the experimental work.

When vapor-liquid equilibrium data are required to perform distillation design, the accuracy of available data has always to be questioned. Experimental uncertainty may arise from physical limits in the measuring devices (sensitivity of sensor, for instance), from uncertainty in calibration or in reference sample preparation. Sample purification is also a source of error: even small amount of impurities can modify significantly the value of some physical properties. Observation and transcription errors tend to decrease in computer controlled measuring devices, but may still exist.

As an example to illustrate the range of deviations that can be expected, we can examine data reported for Benzene in the NIST Webbook (NIST 2011): 183 measured values are reported, some dating back to 1884. Measured values range from 351,15 to 354,80K. Measurement uncertainty can be as high as 2 K. Recommended value is 353,3 \pm 0.1 K. When no experimental value of boiling point is available, estimation using empirical correlation can be applied. However inaccuracies from 2 to 3 °C can be expected even with the best methods. Errors larger than 10°C are not uncommon (Poling et al, 2001)

Vapor pressure measurements whose accuracy is better than 0,2% can be obtained with the best experimental techniques. However, relying on published values can lead to larger errors. We conducted a survey on 38 pure chlorofluorocarbons where discrepancies as large as 5% were found between values reported in technical documents. 50% of reported values were within 1% of average values, and 75% within 2%.

Composition measurements have also a limit in precision. Chromatography provides composition analysis with a typical error of 2%; uncertainty can grow much larger (8 to 10%) for trace components. The accuracy of the best refractometers is 0,2% for liquid samples, and 0,4% for vapor samples; errors from 1 to 3% are not uncommon in routine measurements.

From the previous discussion, we can conclude that estimates of relative volatilities α can be affected by errors ranging from 0,3% for very good measurements, up to 5 or 10% when published values of uncertain quality are relied upon. Thus uncertainty on $(\frac{\Delta\alpha}{\alpha})$ ranges typically from 1 to 2%.

3. CAPABILITIES OF EMPIRICAL PROPERTY MODELS

Experimental values are seldom used directly in the plant design procedures. Laboratory data are usually presented in tables, and can not be directly processed in computer calculations: tables have to be reduced to equations, e.g. using least-squares fitting to obtain parameters of empirical correlations for temperature dependent properties in some reference state. Fitted property values include such items as heat capacity curves, transport properties, or vapor pressure. This procedure has also the benefit to smooth out experimental noise. Empirical correlations proposed to fit those experimental data are numerous. They might also introduce some inaccuracy in the calculation procedure, if they were not able to fit measured data within experimental uncertainty. More details about those models can be found in thermodynamics textbooks, or in compilations such as Poling et al (2001).

Numerous equations of state have been proposed to allow prediction of PVT diagrams, and calculation of departure functions (namely the difference between a thermodynamic function of a real species or mixture, and the same property for the ideal gas). Calculation of physical properties of a complex fluid based on fundamental principles is within the reach of present day computers. Paralleling the development of molecular theory has been the development of empirical correlation able to fit measured values or even to estimate some physical properties which have not been measured and which cannot be practically calculated from theory: they rely on observed trends for property values among component families to provide suitable estimates of unmeasured quantities. However those tools will never supersede the need for good quality experimental work, since empirical correlations can only be based on accurate measurements.

Cubic equations of state are successful for almost ideal systems, such as hydrocarbons (Soave 1972, Peng and Robinson 1976)), and in some non-ideal cases (Schmidt 1980, Harmens 1980, Heyen 1982, Wong 1992). They handle both sub- and supercritical components in a homogeneous way. We conducted an extensive comparison on the capabilities of several cubic equations of state to predict pure component vapor pressure and saturated liquid volume. 1190 data points for 100 components were used in the comparison.

The results are summarized in Table 1. It shows that most models reproduce vapor pressure within 2% of experimental values. A closer look at the results revealed that most discrepancies appear in the low-pressure range (below the boiling point temperature). One may thus expect accuracy of the same level when multicomponent vapor-liquid equilibrium calculations are conducted.

Liquid volume predictions are usually of poorer accuracy: simple models, such as cubic equations of state, have been optimized to predict vapor pressure, in order to be used in VLE calculation. Other properties, such as liquid density or enthalpy, cannot be reproduced simultaneously with the same level of accuracy by the same equations.

Table 1: Average relative error (%) for predicting vapor pressure and saturated liquid volume

Class	n-Alkanes		Hydrocarbons		Non polar		Polar		All comp.	
Data points	250		216		311		413		1190	
Equation	Pv	Vl	Pv	Vl	Pv	Vl	Pv	Vl	Pv	Vl
Soave	2,51	18,07	1,93	17,54	1,64	11,23	3,23	25,35	2,43	18,71
Peng-Robinson	2,07	8,24	1,34	6,45	1,60	6,36	2,68	13,85	2,03	9,37
Harmens-Knapp	2,18	4,90	1,33	5,53	1,59	5,92	4,13	10,86	2,55	7,35
Schmidt-Wenzell	2,88	4,62	1,19	6,93	1,45	6,38	7,23	14,96	3,71	9,09
Heyen	2,06	1,27	1,22	2,08	1,79	3,45	3,66	9,83	2,39	4,96

When physical properties are only required in a small temperature range, accuracy can be improved by refitting the equation of state constant in order to match experimental data in a smaller domain.

Activity coefficient models, such as NRTL or UNIQUAC, can be selected to model highly non-ideal liquids. They also require tuning of binary coefficients to represent experimental phase equilibrium data. When measured phase equilibrium data are not available, the UNIFAC group contribution method could be applied with caution, since larger discrepancies can be observed for some systems.

The evaluation of thermodynamic properties (enthalpy, entropy, free energy) is based on ideal gas heat capacity C_p° . Usually, C_p° values are fitted with 2nd to 4th order polynomials. This achieves better than 1% accuracy on large temperature ranges. However polynomials should be used with caution when extrapolation is attempted.

An extensive review of correlation methods for transport properties can be found in Poling et al (2001).

Good predictive methods have been proposed to estimate vapor phase viscosity. They are able to reproduce experimental data both for pure components and mixtures. Predictions are usually within 5% accuracy.

No general theory is available to predict accurately the viscosity or liquid mixtures. Errors in the range from 20 to 30% are not uncommon, especially at high temperature. Viscosity of liquid mixtures can hardly be estimated when pure component viscosities are not known precisely. The errors to be expected from the best correlations range from a few per cent for non-polar mixtures to 10 per cent or more for polar mixtures.

Predictive methods have been proposed to estimate vapor phase thermal conductivity. Errors vary, but should not exceed 5 to 8 % for nonpolar compounds at low pressure. No present method can be generally recommended for polar mixtures, where the composition dependence of thermal conductivity can be highly non linear. All estimation techniques for thermal conductivity of liquids are empirical. Errors are usually less than 10% for pure liquids. Similar accuracy can be expected for mixtures, when pure component experimental data is available.

4. CASE STUDY: CALCULATION OF A PROPENE PURIFICATION COLUMN

The goal is to model a 150-stage distillation column, designed to produce polymerisation grade propene (99.6% purity) from chemical grade propene (93% propene, 7% propane). As shown in figure 1, the saturated liquid feed (0,085 kmol/s) enters stage 110 (1 being the top). Stage efficiency is 75%. Column pressure is 1.0 MPa at the top, 1.1 MPa at the bottom.

Reflux is produced by mechanical vapor recompression: top vapor is compressed to 1.55 MPa, desuperheated in exchanger E2, condensed in E3 shell. Condensed propene is recycled as reflux after being subcooled in E1 by exchange with top

Table 2: Basic properties for pure components

	Propene	Propane
T_C (K)	364,90	369,82
P_C (MPa)	4.6204	4.2496
V_C (m ³ /kmol)	0,181	0,203
ω original	0,1477	0,1454
ω optimized	0,1547	0,1616

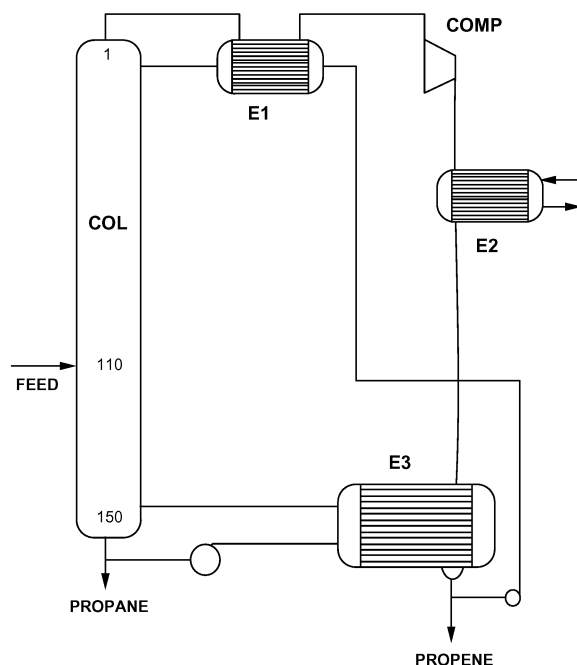


Figure 1: Propene purification

vapor. Stripping vapor in the column is obtained by circulating a large flow of bottom liquid in E3 tubes. Good heat transfer coefficient can be obtained by forced convection; liquid is only partially vaporized in the exchanger, and flashes when recycled in the column.

Soave (1972) equation of state has been selected to estimate vapor-liquid equilibrium constants and vapor phase volume. Lee-Kesler-Plöcker equation provides departure enthalpy for both vapor and liquid phases. Gunn-Yamada correlation is used to estimate liquid density. Pure component parameters have been retrieved in the databases linked to BELSIM (2011) simulation programme. Properties predicted using the default physical property models have been compared to experimental data available in Hancock (1973).

For liquid propene, thermal conductivity is overestimated by 9%. Discrepancy on specific heat is lower than 2%. Average error on viscosity is 5%.

For propene vapor, average error on viscosity is below 2%; thermal conductivity is underestimated by 2 to 10%. Discrepancy on ideal gas heat capacity is below 0,2%.

The coefficients of equations of state used to estimate thermodynamic properties in the present study are calculated from critical point coordinates and Pitzer's acentric factor. Default values of those parameters are given in Table 2. Tuning the model for accurate phase equilibrium calculations was the next step.

Hancock (1973) reports 59 experimental sets of vapor-liquid equilibrium data for the propene-propane system, at pressures ranging from 0.3 to 4.2 MPa. We used this information to adjust the binary interaction coefficient δ_{12} of Soave equation of state, in order to reproduce as well as possible the experimental information.

Temperature and liquid composition were selected as independent variables, and assumed to be error-free; errors on pressure measurements were assumed to follow a Gaussian distribution, with zero mean and a standard distribution equal to 1% of the measured value. For vapor molar fractions, a standard deviation of 0.01 was assumed.

The first computer run revealed that one experimental data point was suspect ($T=360.95$ K, $P=4.0236$ MPa, $x_{\text{propane}}=0.4312$, $y_{\text{propane}}=0.4420$); the departure between experimental and predicted propane mole fraction in vapor phase was larger than 0.02, compared to an average residual equal to 0.005. This results obviously from a misprint in the table: propane, being the heavier component, should be present in lesser amount in vapor phase. The outlier point was deleted from the data set.

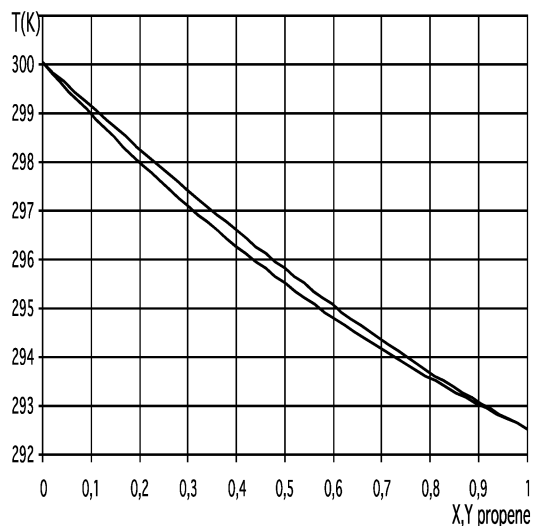


Figure 2: Isobaric vapor-liquid equilibrium
Propene-Propane, Soave equation, $P=1.0$ MPa

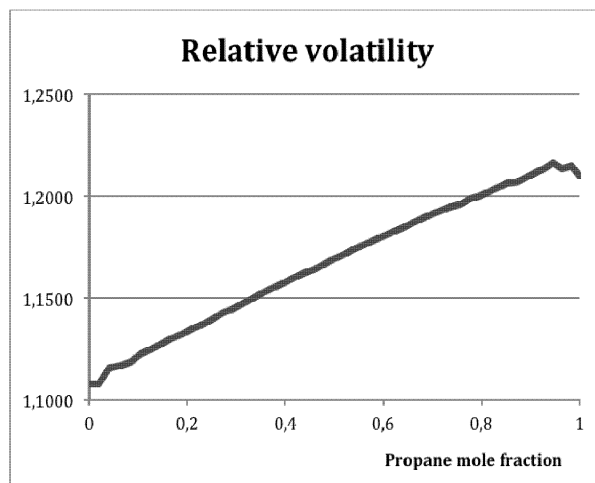


Figure 3: relative volatility $K_{\text{propene}} / K_{\text{propane}}$
Soave equation of state with optimal binary coefficient

The second run of the parameter fitting program leads to following results:

Average relative residual on P:	0.82%	Average absolute residual on y_{propane} :	0.0045
Optimal δ_{12} :	0.00330	Standard deviation for δ_{12} :	0.00079

However pure component vapor pressure was not perfectly reproduced. Since the operating pressure of the plant to be designed is in the 1.0 to 1.5 MPa range, we decided to adjust acentric factors to reproduce exactly the 1.0 MPa boiling point for both pure components, leading to the results shown in Table 2.

A last run of the parameter fitting programme, with the modified ω leads to following results:

Average relative residual on P:	1.20%	Average absolute residual on y_{propane} :	0.0014
Optimal δ_{12} :	0.00760	Standard deviation for δ_{12} :	0.0014

Average discrepancy on vapor phase composition has been markedly decreased. Goodness of fit for pressure is slightly worse when all experimental data (from 0.3 to 4.0 MPa) are taken into account; however some improvement is observed on pressure predictions in the 1.0 MPa range.

The calculated phase diagram of propene-propane system at 1.0 MPa is reproduced in figure 2 and the predicted relative volatility is illustrated in figure 3. Since relative volatility is close to 1, separation by distillation is difficult and requires a large number of stages.

4.1 Preliminary calculation

In the design of distillation columns, limiting operating conditions should be examined. The minimum number of plates needed to achieve the desired separation at total reflux is identified, as well as the minimum reflux ratio allowable with an infinite number of plates. Short cut design methods based on those limiting conditions can be used to get order of magnitude estimates of the column size and the quality of separation. They are useful as initial values for more detailed calculations, based on iterative solution of the complete set of mass, energy and equilibrium equations.

A short cut calculation is first performed, based on Fenske, Underwood and Gilliland equations. The propene top recovery fraction is specified at 98%, while 95 % of incoming propane is recovered in the bottom stream. Condenser is total, and mechanical vapor recompression is not considered.

The short cut model estimates that the minimum number of theoretical plates at total reflux is 49, while minimum reflux ratio R_{\min} should be 6.82. Assuming R/R_{\min} to be 1.5, the model predicts the actual reflux ratio to be 10.23, with a required number of equilibrium stages equal to 73 (thus roughly 100 trays would be needed if efficiency is 0.75). The optimal feed stage should be number 32. Both condenser and reboiler duties are equal to 12.6 MW. Distillate flow rate is 0.077766 kmol/s, with propene mole fraction equal to 99,618%. Residual flow rate is 0.007233 kmol/s, with a propene mole fraction of 21,86%.

The predicted size appears too low, compared to what is described in literature (150 to 200 stages).

In order to explain this discrepancy, a sensitivity analysis is carried out for the short cut design models, in order to assess error propagation arising from erroneous volatility ratios.

Fenske equation allows to calculate the minimum number of plates needed to achieve a given separation into distillate D and bottom B between two key components i and r at total reflux:

$$N_m = \frac{\ln\left(\frac{x_i}{x_r}\right)_D - \ln\left(\frac{x_i}{x_r}\right)_B}{\ln \alpha_{i-r}} \quad (1)$$

When average relative volatility α_{i-r} is close to one, its logarithm can be approximated by a „Taylor series development limited to first order, and the minimum number of plates is proportional to the inverse of $(\alpha-1)$:

$$\ln \alpha_{i-r} \approx \alpha_{i-r} - 1 \quad (2)$$

$$N_m \propto \frac{1}{\alpha_{i-r} - 1} \quad (3)$$

Underwood's equation allows estimating the minimum reflux ratio R_m needed to achieve a specified separation from a given feed F with an infinite number of plates.

$$R_m + 1 = \sum_i \frac{\alpha_i x_{i,D}}{\alpha_i - \theta} \quad (4)$$

where θ is obtained by solving:

$$1 - q = \sum_i \frac{\alpha_i x_{i,F}}{\alpha_i - \theta} \quad (5)$$

If we restrict the analysis to a binary system, with saturated liquid feed ($q=1$), the solution is:

$$R_m + 1 = \frac{(x_{1,F} + \alpha x_{2,F})(x_{1,F} - x_{1,D})}{x_{1,F} x_{2,F} (\alpha - 1)} \quad (6)$$

We notice that the minimum reflux ratio is also roughly proportional to the inverse of $(\alpha-1)$ when the relative volatility α is close to unity.

The previous analysis allows to infer how any imprecision on the relative volatility value will influence the estimate of the number of plates:

$$\frac{\Delta N_m}{N_m} \propto \frac{\Delta \alpha_{i-r}}{\alpha_{i-r} - 1} \quad (7)$$

as well as the estimation of the minimum reflux ratio:

$$\frac{\Delta R_m}{R_m} = \frac{1}{1 + \frac{\Delta \alpha}{\alpha - 1}} - 1 \quad (8)$$

Uncertainty will increase markedly when relative volatility gets closer to unity. The actual reflux ratio needed to achieve a given separation is proportional to the minimum reflux ratio. Usual safety coefficients applied when designing equipment (column body and internals, pumps, heat exchangers) will normally allow recovering errors up to 10%. As indicated in the analysis of uncertainties on relative volatility, a 2% error should not be exceptional.

Application of sensitivity equations (7) and (8) shows that a 2% uncertainty in α leads to an error larger than 10% in the minimum number of plates when α is lower than 1,25. Similarly a 10% error in reflux ratio estimation may be expected when α is lower than 1,28.

Larger safety factors should be selected if the uncertainty on physical property models cannot be reduced below that margin by carrying out extra measurements.

4.2 Detailed model

Distillation column is modelled as a set of equilibrium stages. The model implies solving simultaneously all mass, energy and equilibrium equations, supplemented by a proper set of specifications. The distillate flow rate is set to the value obtained from short cut calculation, namely 0.077766 kmol/s. We assume that the condensate is not subcooled in E2. The reflux flow rate is set to 1 kmol/s. Temperature is set to 305 K at E1 gas outlet. Outlet temperature of compressor after cooler is set to 311 K.

When mass and energy balance have been solved for all the equipment, a more detailed simulation is carried out for the heat exchangers. The simulation takes into account the internal geometry of the equipment (number and size of tubes, number of passes). Heat transfer coefficients are estimated from standard correlations requiring the use of physical properties, like density, viscosity and thermal conductivity. Compressor is calculated assuming a fixed isentropic efficiency.

The condenser-reboiler duty predicted by the rigorous model is 14.9 MW. Propene mole fraction in distillate is 99,614%. Residual flow rate is 0.007233 kmol/s, with a propene mole fraction of 21,89%. The predicted purities are thus quite similar to those specified in the short cut model. But the number of plates is 50% larger, and the

Figure 4: Calculated temperature and composition profile in column

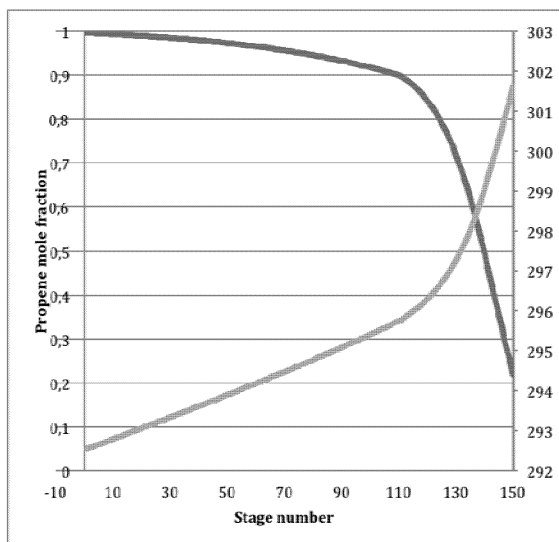
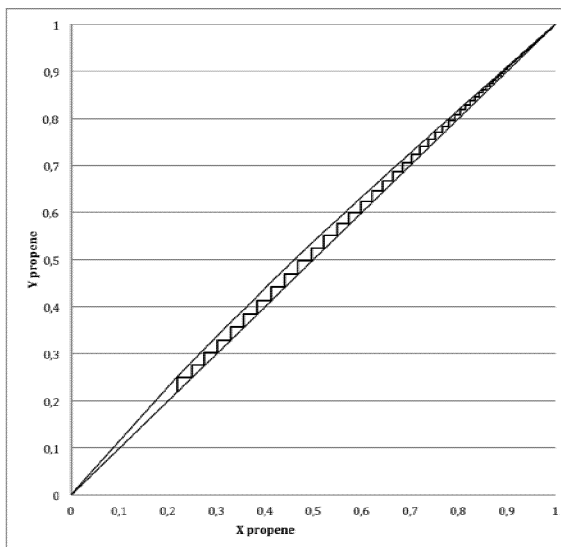


Figure 6: Calculated McCabe and Thiele diagram



reflux ratio (12.86) is 25% higher. This can be explained by examining Figure 4. Most composition variations occur in the stripping section, and the temperature evolution in the rectification section (plates 1 to 110) reflect mainly the influence of pressure drops on the equilibrium temperature. Mac Cabe and Thiele diagram (Figure 5) shows that most of the stages operate with a high propene mole fraction, and the operating line is very close to the equilibrium curve. In this composition domain, relative volatility is close to 1.10.

The average volatility, calculated as a plate average, is 1.11: it differs significantly from the average volatility estimated by the short cut model, namely 1.15, being the geometric average between top and bottom values. Using the correct average volatility would raise the estimation of minimum number of plates from 49 to 65, and the minimum reflux ratio from 6.8 to 9.15. Thus the failure of the shortcut model is not due to modelling equations (1-5) being wrong, but to an inappropriate evaluation of the average volatility. This example illustrates dramatically the limitations of short cut models, even for a binary separation where non-ideality is moderate.

Additional equipment has also been designed besides the columns. Compressor power is 1556 kW, assuming 80% isentropic efficiency. This is required to raise the vapor pressure from 0.97 MPa to 1.65 MPa. Compressor exhaust temperature is 333.4 K.

The three heat exchangers (compressed vapor desuperheater, boiler-condenser and reflux subcooler) have been sized using standard procedures for shell and tube equipment. The compressor aftercooler (unit E2) has to cool the distillate vapor down to 312.2 K (dew point is 311.4 K). Cooling water requirement is 90.0 kg/s.

In the reboiler, the flow of liquid circulated through the tubes is 20 times larger than the required boilup rate of the column. This enhances the forced convection heat transfer coefficient. Only 3.76% of the liquid is evaporated in the tubes. The required amount for boilup is flashed in the column bottom.

4.3 Sensitivity analysis

The simulation program has been modified to add known perturbations to the values returned by the physical property estimation package. Starting with the base case simulation described above, we repeat calculations of the distillation column with modified values of several thermodynamic properties, in order to assess their influence on the predicted plant behaviour. All specifications are held constant.

First the logarithm of propene fugacity coefficient has been increased by 0.01. This corresponds closely to a 1% increase in relative volatility. All design specifications, and particularly the reflux flow rate, have been kept constant. The most significant consequence is a drop of propene purity in the distillate. It is reduced from

99.61% to 99.29%, and would not meet any more the commercial specifications for polymerisation grade products.

The calculation has been repeated by allowing the reflux rate to increase, in order to recover the original purity. Reflux rate has to grow from 1 kmol/s to 1.205 kmol/s. Such an increase would probably exceed the spare capacity of the compression system and the heat exchangers. In practice, the production capacity would be decreased to 83% of its nominal value. Thus a rather small variation of a physical property can lead to severe perturbations on the plant performance.

As a second perturbation, the heat capacity of pure propene has been artificially raised by 1 J/mol/K. This represents approximately a 1% perturbation, since saturated liquid C_p is 107.8 J/mol/K and saturated vapor C_p is 77.6 J/mol/K at 1.0 MPa. This has almost no effect on the simulated results. Propene purity is not modified. The heat load of exchanger E1 increases by 1.2%. The reboiler heat load decreases by 0.03%. All these effects are within normal design margins and could be recovered in the real plant by some adjustment of operating conditions.

Viscosity and thermal conductivity estimations are not used in the distillation column simulation, but are needed in the calculation of heat exchangers. We repeated the simulation of the heat exchangers and compressor train by keeping constant the flowrate, temperature and pressure of all streams originating from the column.

Gas and liquid thermal conductivity and viscosity were increased alternatively by 10%. Propene heat capacity was increased by 1 J/mol/K. Table 6 reflects the main results of this analysis.

We note that rather large perturbations of transport property values have a moderate effect on the predicted behavior of the heat exchangers. This effect would even be smaller if fouling resistance had been taken into account, since fouling accounts for a significant part of transfer resistance in well-designed equipment.

Table 6: Influence of 10% increase of some physical property values on selected process variables.

Process variable		Conductivity Gas (+10%)	Conductivity Liquid (+10%)	Viscosity Gas (+10%)	Viscosity Liquid (+10%)	C_p propene (+1 J/mol/K)
E1	Duty	2,10%	0,45%	-0,69%	-0,33%	1,18%
Comp.	Work	0,15%	0,03%	0,05%	-0,03%	-0,10%
E2	Duty	4,67%	0,45%	-1,38%	-0,33%	0,27%
E2	ΔP gas	-3,30%	-0,01%	1,69%	0,00%	-0,08%
E2	ΔP water	-0,02%	0,01%	0,01%	1,25%	0,00%
E3	Duty	-0,67%	0,43%	-0,61%	-1,27%	-0,59%

5. CONCLUSIONS

Process design engineers should always identify the sensitive part in the plant under study, and if their accuracy requirements are beyond the limit of existing correlations, they should accept there is no substitute for accurate experimental data.

Some guidelines for design can be proposed:

- statistical error distribution, product allowances and flexibility in the process design may help compensate for design errors ("*Mother Nature forgives engineers!*"); however one should not rely on this statement without a careful and thorough sensitivity analysis;
- distillation columns with high purity requirements (superfractionators) require high quality K-values (0.2% accuracy);
- error compensation should not be assumed in the design of those columns;
- 10% tolerance on heat exchanger surface can usually be achieved with lower accuracy K-values;
- many properties need to be known within $\pm 30\%$ to be able to calculate kinetic and design parameters like pressure drops or heat transfer coefficients within $\pm 10\%$.

Thus the right question to formulate when performing equipment design is not "*are measurements needed?*" but "*what is the minimum amount of experiments that will avoid major mistakes?*".

6. REFERENCES

- BELSIM (2011), <http://www.belsim.com/>, accessed February 14, 2011
- E.G. Hancock, ed. (1973), Propylene and its industrial derivatives, Ernest Benn Ltd, London
- Harmens A., Knapp H. (1980), Three-Parameter cubic Equation of State for normal Substances, Ind. Eng. Chem. Fund. 19, 291
- Heyen G. (1982), A cubic equation of state with extended range of application. in "Chemical Engineering Thermodynamics", S.A.Newman ed, Ann Arbor Science Publishers
- NIST Webbook 2011, <http://webbook.nist.gov/cgi/cbook.cgi?ID=C71432&Units=SI&Type=TBOIL>, accessed February 14, 2011
- O'Connell J.P., Gani R., Mathias P.M., Maurer G., Olson J.D., Crafts P. A., 2009, Thermodynamic Property Modeling for Chemical Process and Product Engineering: Some Perspectives, Ind. Eng. Chem. Res. 48, 4619–4637
- Peng D.Y., Robinson D.B. (1976), A new Two-Constant Equation of State, Ind. Eng. Chem. Fund, 15,59-64
- Poling B.E., Prausnitz J.M., O'Connell J.P. (2001), The Properties of Gases and Liquids (5th ed), McGraw-Hill
- Schmidt G., Wenzel H. (1980), A modified Van der Waals Type Equation of State, Chem Eng Sci. 35, 1503
- Soave G. (1972), Equilibrium Constants from a modified Redlich-Kwong Equation of State, Chem. Eng. Sci., 27, 1197-1203
- Wong D.S.H., Sandler S.I. (1992), A Theoretically Correct Mixing Rule for Cubic Equations of State, AIChE J. 38, 671
- Zudkevitch, D., 1980; Forensic thermodynamics - Erroneous decisions on thermodynamic data can cause plant failures; EFCE Publication Series; Taylor & Francis: U.K., Issue 11, pp 885-905.